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Air Quality Criteria for Oxides of Nitrogen

Volume II of III

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PREFACE

The U S Environmental Protection Agency (EPA) promulgates the National Ambient Air Quality Standards (NAAQS) on the basis of scientific information contained in criteria documents. In 1971, the first air quality criteria document for nitrogen oxides (NO_x) was issued by the National Air Pollution Control Administration, a predecessor of EPA. On the basis of scientific information contained in that document, NAAQS were promulgated for nitrogen dioxide (NO_2) at levels of 0.053 ppm ($100 \mu\text{g}/\text{m}^3$), averaged over 1 year. The last full-scale NO_x criteria document revision was completed by EPA in 1982, leading to an Agency decision in 1985 to reaffirm the annual average NO_2 NAAQS of 0.053 ppm. The present, revised criteria document, Air Quality Criteria for Oxides of Nitrogen, assesses the current scientific basis for periodic reevaluation of the NO_2 NAAQS in accordance with the provisions identified in Sections 108 and 109 of the Clean Air Act.

Key chapters in this document evaluate the latest scientific data on (a) health effects of NO_x measured in laboratory animals and exposed human populations and (b) effects of NO_x on agricultural crops, forests, and ecosystems, as well as (c) NO_x effects on visibility and nonbiological materials. Other chapters describe the nature, sources, distribution, measurement, and concentrations of NO_x in the environment. These chapters were prepared and peer reviewed by experts from various state and Federal government offices, academia, and private industry for use by EPA to support decision making regarding potential risks to public health and the environment. Although the document is not intended to be an exhaustive literature review, it is intended to cover all the pertinent literature through early 1993.

The Environmental Criteria and Assessment Office of EPA's Office of Health and Environmental Assessment acknowledges with appreciation the contributions provided by the authors and reviewers and the diligence of its staff and contractors in the preparation of this document at the request of EPA's Office of Air Quality Planning and Standards.

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AUTHORS

Chapter 9 Effects of Nitrogen Oxides on Vegetation

Dr J H B Garner
Environmental Criteria and Assessment Office
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Dr Beverley A Hale
Department of Horticultural Science
University of Guelph
Guelph, Ontario, Canada N1G 2W1

Dr Robert Heath
Department of Botany and Plant Sciences
University of California
Riverside, CA 92507

Dr Delbert C McCune
Boyce Thompson Institute for Plant Research
at Cornell University
Tower Road
Ithaca, NY 14853

Dr David C MacLean
Boyce Thompson Institute for Plant Research
at Cornell University
Tower Road
Ithaca, NY 14853

Dr David T Tingey
Environmental Research Laboratory
U.S Environmental Protection Agency
200 SW 35th Street
Corvallis, OR 97333

Dr A R Wellburn
Department of Biochemistry
Biological Science Building
University of Lancaster, LA1 4YQ
United Kingdom

Chapter 10 The Effects of Nitrogen Oxides on Natural Ecosystems and Their Components

Dr J H B Garner
Environmental Criteria and Assessment Office
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Dr Paul J. Hanson
Environmental Sciences Division
Oak Ridge National Laboratory
Automated Sciences Group
Oak Ridge, TN 37831

Dr Dale W Johnson
Biological Sciences Division
Desert Research Institute
P O Box 60220
Reno, Nevada 89509

Dr James T Morris
Department of Biology
University of South Carolina
Columbia, SC 29208

Dr John Stoddard
Environmental Research Laboratory
Watershed Branch
U S Environmental Protection Agency
200 SW 35th Street
Corvallis, OR 97333

Dr David T Tingey
Environmental Research Laboratory
U S Environmental Protection Agency
200 SW 35th Street
Corvallis, OR 97333

AUTHORS (cont'd)

Chapter 11 Effects of Nitrogen Oxides on Visibility

Ms. Lauraine G Chestnut
R.C.G /Hagler Bailly & Company
1881 Ninth Street
Suite 201
Boulder, CO 80302

Mr Douglas A Latimer
Latimer & Associates
2769 Iris Avenue
Suite 117
Boulder, CO 80304

Chapter 12 Effects of Nitrogen Oxides on Materials

Mr Douglas R Murray
TRC Environmental Consultants
800 Connecticut Boulevard
East Hartford, CT 06108

CONTRIBUTORS AND REVIEWERS

Chapters 9 and 10

Dr Dennis Baldocchi
Atmospheric Turbulence & Diffusion Division
NOAA
P O Box 2456
Oak Ridge, TN 37831

Dr Michael Berry
Environmental Criteria and Assessment Office
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Dr William B Bowden
Department of Forest Resources
James Hall
University of New Hampshire
Durham, NH 03824

Prof Dr Robert Guderian
Universitat Gesamthochschule Essen
Postfach 103 764 4300
Essen 1 Germany

Walter W Heck
USDA/ARS
North Carolina State University
1509 Varsity Drive
Raleigh, NC 27606

Dr George Hendry
Environmental Biotechnology Division
Building 318
Brookhaven National Laboratories
Upton, NY 11973

Dr Allen Legge
Alberta Research Council
Environmental Research and Engineering
Department, 3rd Floor
6815 8th Street N E
Calgary, Alberta T2E 7H7
Canada

Dr William McFee
Department of Agronomy
Lilly Hall
Purdue University
West Lafayette, IN 47609

Dr David McKee
Office Air Quality Planning and Standards
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Dr Joseph Miller
AIR Programs
North Carolina State University
1509 Varsity Drive
Raleigh, NC 27606

Dr Eva Pell
Department of Plant Pathology
211 Buckhout Laboratory
Pennsylvania State University
University Park, PA 16802

Dr Richard Reinert
AIR Programs
North Carolina State University
1509 Varsity Drive
Raleigh, NC 27606

Dr Paul Ringold
U S Environmental Protection Agency
401 M Street, SW
Washington, DC 20406

Ms Rosalina Rodriguez
Office of Air Quality Planning and
Standards
U S Environmental Protection Agency
Research Triangle Park, NC 27711

CONTRIBUTORS AND REVIEWERS (cont'd)

Mr. Kenneth Stolte
National Park Service
Air Quality Division
12795 W Alameda Parkway
Lakewood, CO 80255

Dr. R A Skeffington
National Power Technology and Environmental
Center
Kelvin Avenue
Leatherhead, Surrey KT22 7SE
United Kingdom

Dr John Skelly
Department of Plant Pathology
212a Buckhout Laboratory
Pennsylvania State University
University Park, PA 16802

Dr Timothy C Strickland
Corvallis Environmental Research Laboratory
Watershed Branch
U S Environmental Protection Agency
Corvallis, OR 97333

Dr George E Taylor, Jr
Biological Sciences Center
Desert Research Institute
P O Box 60220
Reno, NV 89506-0220

Dr C Ray Thompson
2032 Fairview Avenue
Riverside, CA 92506

Dr Gary Whiting
3 Holiday Drive
Hampton, VA 23669

Chapter 11

Mr Allen C Basala
Air Quality Management Division
Office of Air Quality Planning and Standards
U S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dr Michael Berry
Environmental Criteria and Assessment Office
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Ms F. Vandiver Bradow
Environmental Criteria and Assessment Office
U S. Environmental Protection Agency
Research Triangle Park, NC 27711

Ms Darcy Campbell
Radian Corporation
Research Triangle Park, NC 27709
(Formerly with U S Environmental Protection
Agency)

Dr Leland B Deck
Air Quality Management Division
Office of Air Quality Planning and Standards
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Dr Thomas G Dzubay
Atmospheric Research and Exposure
Assessment Laboratory
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Dr Thomas G Ellestad
Atmospheric Research and Exposure
Assessment Laboratory
U S Environmental Protection Agency
Research Triangle Park, NC 27711

CONTRIBUTORS AND REVIEWERS (cont'd)

Dr Charles W Lewis
Atmospheric Research and Exposure Assessment
Laboratory
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Ms Beverly E Tilton
Environmental Criteria and Assessment Office
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Mr Robert K Stevens
Atmospheric Research and Exposure Assessment
Laboratory
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Chapter 12

Dr Michael Berry
Environmental Criteria and Assessment Office
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Mr Fred H Haynie
Private Consultant
300 Oakridge Road
Cary, NC 27511

Ms F Vandiver Bradow
Environmental Criteria and Assessment Office
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Dr Frederick Lipfert
Private Consultant
23 Carll Court
Northport, NY 11768

Ms Darcy Campbell
Radian Corporation
Research Triangle Park, NC 27709
(Formerly with U S Environmental Protection
Agency)

Mr John W Spence
Atmospheric Research and Exposure
Assessment Laboratory
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Dr Thomas Graedel
AT&T Laboratories
600 Mountain Avenue
Murray Hill, NJ 07974-2070

Ms Beverly E Tilton
Environmental Criteria and Assessment Office
U S Environmental Protection Agency
Research Triangle Park, NC 27711

U S ENVIRONMENTAL PROTECTION AGENCY
SCIENCE ADVISORY BOARD
CLEAN AIR SCIENTIFIC ADVISORY COMMITTEE

Oxides of Nitrogen Review

Former Chairman

Dr Roger O McClellan
Chemical Industry Institute of Toxicology
P O Box 12137
Research Triangle Park, NC 27709

Chairman

Dr George T Wolff
General Motors Research Laboratories
Environmental Science Department
Warren, MI 48090

Members

Dr Glen R Cass
Environmental Engineering Science
Department
Mail Code 138-78
California Institute of Technology
Pasadena, CA 91125

Dr Jean Ford, Medical Director
Harlem Hospital Center
506 Lenox Avenue
New York, NY 10037

Dr Benjamin Liu
University of Minnesota
125 Mechanical Engineering
111 Church Street, S E
Minneapolis, MN 55455-0111

Dr Joseph Mauderly
Inhalation Toxicology Research Institute
P O Box 5890
Albuquerque, NM 87185

Dr Marc B Schenker
Division of Occupational and Environmental
Medicine
I E H R Building
University of California
Davis, CA 95616

Dr Mark J Utell
Pulmonary Disease Unit
Box 692
University of Rochester Medical Center
601 Elmwood Avenue
Rochester, NY 14642

Consultants

Dr William C Adams
Human Performance Laboratory
Department of Physical Education
University of California
Davis, CA 95616

Dr John Balmes
San Francisco General Hospital
Occupational Health Clinic
Building 9, Room 109
San Francisco, CA 94110

CLEAN AIR SCIENTIFIC ADVISORY COMMITTEE (cont'd)

Consultants (cont'd)

Dr Douglas Dockery
Harvard School of Public Health
Department of Environmental Science and
Physiology
665 Huntington Avenue
Boston, MA 02115

Dr James Fenters
IIT Research Institute
10 West 35th Street
Chicago, IL 60616

Dr Gareth Green
Harvard School of Public Health
677 Huntington Avenue
Boston, MA 02115

Dr. Robert Mercer
Center for Extrapolation Modeling
Box 3177
Duke University Medical Center
Department of Medicine
Durham, NC 27710

Dr John Skelly
Department of Plant Pathology
212A Buckhout Laboratory
Pennsylvania State University
University Park, PA 16802

Dr Michael J Symons
School of Public Health
Room 3104D
McGavran Greenberg Hall
University of North Carolina at Chapel Hill
Chapel Hill, NC 27599

Dr Warren White
8840 Waterman Avenue
St Louis, MO 63130

Designated Federal Official

Mr Randall C. Bond
U S Environmental Protection Agency
Science Advisory Board (A-101F)
401 M Street, S W
Washington, DC 20460

Staff Secretary

Ms Janice Jones
U S Environmental Protection Agency
Science Advisory Board (A-101F)
401 M Street, S W
Washington, DC 20460

**PROJECT TEAM FOR DEVELOPMENT OF
AIR QUALITY CRITERIA FOR OXIDES OF NITROGEN**

Scientific Staff

**Dr Dennis J Kotchmar, Project Manager
Environmental Criteria and Assessment Office
(MD-52)
U S Environmental Protection Agency
Research Triangle Park, NC 27711**

**Ms Beverly Comfort
Environmental Criteria and Assessment Office
(MD-52)
U S Environmental Protection Agency
Research Triangle Park, NC 27711**

**Dr Robert W Elias
Environmental Criteria and Assessment Office
(MD-52)
U S Environmental Protection Agency
Research Triangle Park, NC 27711**

**Mr William G Ewald
Environmental Criteria and Assessment Office
(MD-52)
U S Environmental Protection Agency
Research Triangle Park, NC 27711**

**Dr J H B Garner
Environmental Criteria and Assessment Office
(MD-52)
U S Environmental Protection Agency
Research Triangle Park, NC 27711**

**Mr Thomas B McMullen
Environmental Criteria and Assessment Office
(MD-52)
U S Environmental Protection Agency
Research Triangle Park, NC 27711**

**Ms Ellie R Speh, Office Manager
Environmental Criteria and Assessment Office
(MD-52)
U S Environmental Protection Agency
Research Triangle Park, NC 27711**

**Ms Beverly Tilton
Environmental Criteria and Assessment Office
(MD-52)
U S Environmental Protection Agency
Research Triangle Park, NC 27711**

Technical Support Staff

**Mr Douglas B Fennell, Technical
Information Specialist
Environmental Criteria and Assessment Office
(MD-52)
U S Environmental Protection Agency
Research Triangle Park, NC 27711**

**Mr Allen G Hoyt, Technical Editor and
Graphic Artist
Environmental Criteria and Assessment Office
(MD-52)
U S Environmental Protection Agency
Research Triangle Park, NC 27711**

**Ms Diane H Ray, Technical Information
Manager (Public Comments)
Environmental Criteria and Assessment Office
(MD-52)
U S Environmental Protection Agency
Research Triangle Park, NC 27711**

**Mr Richard N Wilson, Clerk
Environmental Criteria and Assessment Office
(MD-52)
U S Environmental Protection Agency
Research Triangle Park, NC 27711**

PROJECT TEAM FOR DEVELOPMENT OF
AIR QUALITY CRITERIA FOR OXIDES OF NITROGEN (cont'd)

Document Production Staff

Ms. Marianne Barrier, Graphic Artist
ManTech Environmental Technology, Inc
P.O. Box 12313
Research Triangle Park, NC 27709

Ms. Wendy B. Lloyd, Word Processor
ManTech Environmental Technology, Inc
P.O. Box 12313
Research Triangle Park, NC 27709

Mr. John R. Barton, Document Production
Coordinator
ManTech Environmental Technology, Inc
P.O. Box 12313
Research Triangle Park, NC 27709

Mr. J. Derrick Stout, Graphic Artist
ManTech Environmental Technology, Inc
P.O. Box 12313
Research Triangle Park, NC 27709

Ms. Lynette D. Cradle, Lead Word
Processor
ManTech Environmental Technology, Inc
P.O. Box 12313
Research Triangle Park, NC 27709

Mr. Peter J. Winz, Technical Editor
ManTech Environmental Technology, Inc
P.O. Box 12313
Research Triangle Park, NC 27709

Ms. Jorja R. Followill, Word Processor
ManTech Environmental Technology, Inc
P.O. Box 12313
Research Triangle Park, NC 27709

Technical Reference Staff

Mr. John A. Bennett, Bibliographic Editor
ManTech Environmental Technology, Inc
P.O. Box 12313
Research Triangle Park, NC 27709

Ms. Deborah L. Staves, Bibliographic
Editor
Research Information Organizers
P.O. Box 13135
Research Triangle Park, NC 27709

Ms. Susan L. McDonald, Bibliographic
Editor
Research Information Organizers
P.O. Box 13135
Research Triangle Park, NC 27709

Ms. Patricia R. Tierney, Bibliographic
Editor
ManTech Environmental Technology, Inc
P.O. Box 12313
Research Triangle Park, NC 27709

Ms. Blythe Hatcher, Bibliographic Editor
Research Information Organizers
P.O. Box 13135
Research Triangle Park, NC 27709

9. EFFECTS OF NITROGEN OXIDES ON VEGETATION

9.1 INTRODUCTION

Of the various nitrogen oxides (NO_x) in the ambient air (Chapter 7), only nitric oxide (NO) and nitrogen dioxide (NO_2) have been considered important phytotoxics, however, there is growing concern that nitric acid (HNO_3) may also impact vegetation. The effects of NO_x on terrestrial vegetation can range from the molecular to the organismal, and then to the ecosystem level. The occurrence and magnitude of the vegetational effects depend on the concentration of the pollutant, the duration of the exposure, the length of time between exposures, and the various environmental and biological factors that influence the response. Some of the earliest observable physiological effects include changes in carbon dioxide fixation (photosynthesis), alterations in specific enzymes, changes in metabolite pools, and alterations in the translocation of photosynthate. Biochemical changes within the plants can be expressed as visible foliar injury, premature senescence, increased leaf abscission, and altered plant growth and yield. These changes at the individual plant level may lead to altered reproduction, changes in competitive ability, or reduction of plant vigor. The linkages among altered biochemical processes, foliar injury, and reduced plant yield are not well understood. Likewise, no clear relationship exists between foliar injury and reduced plant yield for species in which the foliage is not part of the yield. Foliar injury from NO_2 is rarely found in the field. However, when found, the injury is usually associated with and confined to areas near specific industrial sources. For example, NO_2 -induced vegetation injury has been observed near HNO_3 factories and arsenals, but there are no published reports of NO -induced injury under field conditions.

In this chapter, the general methodologies used in studies of air pollution effects are discussed first, to provide a basis for understanding the methods, approaches, and experimental designs used in the studies presented later. In addition, the direct effects of NO_x on vegetation are reviewed, with emphasis on studies relating effects to known exposure concentrations and durations of NO and NO_2 . Because, of the two pollutants, most available data pertained to NO_2 , this pollutant receives the most attention. Factors that influence plant

response to NO_x are also included. Because of the possibility that the pollutant mixtures may exert effects at combinations lower than either gas alone, effects of NO_2 in combination with other pollutants are evaluated. Effects of nitrogen deposition, critical loads, and effects on ecosystem processes are reviewed in Chapter 10. Nitrogen oxides are intimately involved in the formation of ozone (O_3) and other photochemical oxidants. Their role in O_3 formation is discussed in Chapter 5. The effects of these chemicals on plants are reviewed in *Air Quality Criteria for Ozone and Other Photochemical Oxidants* (U S Environmental Protection Agency, 1986).

Information from the previous NO_x criteria document (U S Environmental Protection Agency, 1982) considered of fundamental importance is discussed and related to more recent studies. All data that relate exposure-response information to yield loss or crop loss were drawn directly from primary references, regardless of their citation in the previous criteria document. Generally, only published materials that have undergone scientific review have been cited. Data used in the development of this chapter were derived from a range of diverse studies that were conducted to determine the effects of NO_x on various plant species and to characterize plant responses. The studies cited were generally conducted to test specific biological hypotheses or to produce specific biological data rather than to develop air quality criteria.

9.2 METHODOLOGIES USED IN VEGETATION EFFECTS RESEARCH

In vegetation effects research, the choice of methodologies (study design and data analysis procedures, chamber type, field vs laboratory) is crucial to the interpretation and subsequent applicability of experimental results. This section provides reference information for better understanding the studies discussed in the remainder of the chapter. Prior to initiation of a study, the desired outcome should be carefully evaluated. Is the goal to develop pollutant-exposure/plant-response models that may be applied to vegetation growing outdoors or rather to develop models describing mechanisms of action at the cellular level? Is the study to provide some information on a large number of species or cultivars or rather a great deal of information on a few? Are factors that may modify plant response to pollutant

exposure under investigation? The answers to these and other questions provide the framework for choosing the appropriate chamber type, exposure concentration, duration, and frequency, plant species and developmental stage, response variables, and replication and blocking plans, as well as statistical treatment of the data. This section discusses the various methods used to determine plant response to NO_x, including experimental design and data analyses, exposure systems, pollutant climatology and chemistry, and terminology.

9.2.1 Experimental Design and Statistical Analyses

The selection of an appropriate experimental design for specific objectives is a critical step in determining the success of a study and the application of the results. The number and kind of factors controlled, the patterns of randomization, and the number of replicates used in an experiment determine what treatment comparisons may be made, whether trends can be plotted and curves fitted, the precision of estimates, and the range of conditions over which inferences may be made. An experimental design focuses an experiment on its specific objectives, but in doing so, limits the application of the results. No experimental design has universal application.

In pollution studies, the toxic and diffusive nature of the gases means that in the vast majority of experiments, containment chambers must be used to separate treatments. Depending on the number of chambers available at any one time, randomized complete or incomplete block designs (RCBDs, RIBDs) are most commonly used, frequently blocked over time. Completely randomized designs (CRDs, in which all replications of all treatments are carried out at the same time) are relatively uncommon due to the high cost of chamber installation. In experiments where factors in addition to concentration of NO₂ are being investigated, the number of treatments increases and study design becomes more complicated. A multifactor experiment may be conducted as a full (all combinations of factor levels) or partial (some combinations of factor levels) factorial. Treatment factors that can easily be confined to a potted plant (such as comparisons of species, or soil nitrogen or water status) are often included as a split-plot factor in a full factorial design, thus increasing the efficiency of data collection. Treatment factors that are not so easily contained, such as other pollutant gases, air temperature, or radiation levels can be investigated in combination

with NO₂ concentration in partial factorial designs, although this approach seems largely confined to O₃/sulfur dioxide (SO₂) mixture studies (Ormrod et al , 1984)

The simpler experimental plans described above (RCBD, CRD) are easily analyzed by traditional analysis of variance (ANOVA) techniques, where the total sum of squares is partitioned among experimental factors, replicates or blocks (known collectively as sources of variation), and residual or error. If the ANOVA is generated by a computer statistical package, each of these sources of variation is compared to the error mean square by an F test to determine the probability (p value) that there is a difference among treatments. If the p value for any experimental factor is less than 5% (this threshold can be as high as 10% or as low as 1%, depending on the importance of making Type I or Type II errors), then the treatment means for the factor(s) may be further analyzed, using suitable techniques.

An excellent discussion of treatment means comparison has been prepared by Chappelka and Chevone (1989). The choice of suitable analysis depends mainly on whether the levels of the factor(s) are quantitative or qualitative. If they are qualitative (for example, comparison of cultivars in their response to NO₂), then an unplanned comparison technique such as multiple range (Duncan new, Sheffe, or Student-Newman-Keul) or least significant difference test (Steel and Torrie, 1980) would be appropriate. Many of these tests have safeguards that reduce the danger of detecting significant treatment-related effects when none, in fact, exist. These tests are not appropriate for qualitative treatments (for example, multiple concentrations of NO₂ or other environmental quality parameters such as light level, temperature, or humidity), although they are often misused in that way. Much less commonly utilized for qualitative factors are preplanned comparisons, which may be either orthogonal (mutually independent) or nonorthogonal. This approach is suitable when treatments can be grouped in various ways to generate biologically meaningful comparisons, and is particularly applicable to studies of pollutant mixtures. A good example of this approach is given by Chappelka and Chevone (1989), where the effects of SO₂ and O₃ on tulip poplar (*Liriodendron tulipifera* L.) were investigated. When considering pollutant mixtures, it is important to determine whether the joint action of the pollutants is less than additive, additive, or greater than additive. The authors developed three orthogonal tests (1) [(O₃ - control) + (SO₂ - control)] = [(O₃ + SO₂) - control], (2) O₃ + SO₂ = control, (3) O₃ = SO₂. Contrast 1 tests the additivity of O₃ in combination with SO₂.

In Contrast 2, O_3 in combination with SO_2 has a significant deleterious effect on stem, root, and leaf dry matter production in tulip poplar. In Contrast 3, the effects of O_3 alone did not differ from those of SO_2 . Despite the considerable statistical power associated with these contrasts, they are rarely used in air pollution studies.

For quantitative treatments, some kind of regression analysis is usually indicated. This may take the form of orthogonal polynomials, where X evenly spaced treatments are partitioned into $X - 1$ single degree of freedom polynomial contrasts (linear, quadratic, and perhaps cubic). This gives the investigator a good idea of the shape of the response (i.e., whether the plant response per unit of NO_2 is similar over the range of concentrations [linear] or changes [quadratic and cubic]). Alternatively, polynomial regression is useful for treatments that are not evenly spaced. Rather than generating contrasts, a single dose-response function can contain linear, quadratic (and possibly cubic), and interaction terms. Each of the coefficients will have an error term and P value for the probability that it is different. Although it is rarely included, a confidence interval can be calculated for the entire regression equation to illustrate the likely range of values for the response variable. A nonlinear regression model may also be used to derive exposure-response functions.

9.2.2 Exposure Systems

9.2.2.1 Supply

The chambers in which plants are exposed to pollutant gases are an "open" system—that is, they are continuously supplied with "fresh" air (i.e., air that has not previously been through the chambers), which is then exhausted from the exposure system. This open system prevents depletion of carbon dioxide (CO_2) by photosynthesis and also provides the means by which the pollutant gases are delivered in constant concentration to the plant material. In artificial exposure experiments, NO_2 is usually supplied to the chambers from pressurized cylinders equipped with a two-stage regulator. The NO_2 cylinder contains the gas in dilute form (usually less than 5,000 ppm in nitrogen) and must be further diluted by being metered into an air stream before the gas is introduced into the plant chamber. This dilution and mixing of NO_2 into the air supply of the chamber very often occurs in a prechamber or mixing plenum so that the experimental material is exposed to a uniform atmosphere (Marie and Ormrod, 1984). Cylinders of greater concentration are generally not used (although they

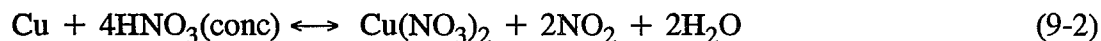
would last longer, reducing handling costs) due to the greater danger to personnel from leaks or accidental releases

Nitrogen dioxide for plant exposure can also be generated in the laboratory by any one of several methods. Some studies have produced NO₂ from liquid dinitrogen tetroxide (N₂O₄), provided that the container of N₂O₄ is kept at or above 25 °C, which vaporizes N₂O₄ to NO₂. The NO₂ is then delivered to the air supply to the exposure chambers through flow meters or needle valves (Fuhrer and Erismann, 1980, MacLean et al, 1968, Spierings, 1971). Chemical reactions can produce NO₂ in the laboratory for the purposes of plant exposure, but they are instantaneous reactions, and so are difficult to maintain for the purpose of metering into plant chambers for a long period of time. Nitrogen dioxide may be produced by the following reactions (Sinn et al, 1984)

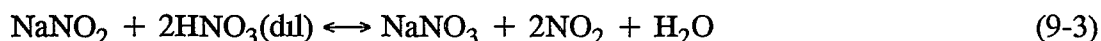
- (1) heating lead nitrate



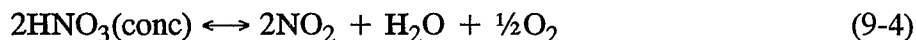
- (2) combining nitric acid and copper chips



- (3) combining nitric acid and sodium nitrate



Nitrogen dioxide can also be generated by bubbling air through concentrated hot (83 °C) HNO₃ (Oleksyn, 1984)



The advantage of these methods of NO₂ production is that they cost much less than pressurized cylinders, so are useful to laboratories that are less well equipped. There is a disadvantage in these methods, however, in that the production of NO₂ is highly variable, making good replication of experiments difficult.

Fumigation studies using NO_x usually employ activated charcoal to remove atmospheric SO₂, NO₂, O₃, and hydrocarbons from the incoming air before it is directed towards the clean-air grown plants (controls) or prior to the addition of specific amounts of NO_x into the

air stream diverted towards treatment plants. Unfortunately, activated charcoal is a very variable commodity. Different efficiencies of various types of activated charcoal may be traced to the original source of wood from which it was made. In an attempt to achieve uniformity, the source of the wood used in manufacture is often specified, the most usual being coconut-shells heated to 600 °C for 1 h before packaging. Nevertheless, the efficiency with which each batch of activated charcoal removes atmospheric contaminants varies, not just with respect to different atmospheric contaminants but also with age, humidity, degree of activation, and temperature (American Society for Testing and Materials, 1982).

Furthermore, charcoal filters can desorb as well as adsorb—a fact often recorded by monitors early in the morning as the filter units start to warm up in the sun. Most, if not all, NO₂ is normally removed by fresh activated charcoal, but such a filter has no capacity to adsorb NO (Commission of the European Communities, 1986, see also Table 9-1). Studies of NO_x effects must therefore employ an additional stage of air purification to avoid this problem. Purafil™ (Purafil Inc., Atlanta, GA), which consists of alumina pellets impregnated with potassium permanganate, is commonly used in this additional filtration. This oxidizes any incoming NO to NO₂, which can then be trapped by activated charcoal.

However, there is an additional complication with O₃ fumigations of plants because inadvertent exposures to NO_x may also occur. Electrical discharge ozonizers are frequently used in O₃ fumigations of plants, but some investigators have not heeded warnings given several years ago (Harris et al., 1982) that such ozonizers supplied with ultrapure air will also form HNO₃ and dinitrogen pentoxide (N₂O₅). For example, an air-fed ozonizer producing 8,650 ppm O₃ also forms 57 ppm HNO₃ and 94 ppm N₂O₅. Production of N₂O₅ can be prevented by the use of pure oxygen instead of air, but the formation of HNO₃ is not entirely prevented. An alternative, safer procedure is to use an air-fed ozonizer and bubble the O₃-enriched air through ultrapure water that is changed regularly. Recently, Brown and Roberts (1988) have drawn renewed attention to errors of interpretation that may occur if plants are supplied with additional nitrogen during experimental fumigations with O₃. Some studies of air pollution effects on trees have led to reports that increased nitrate leaching can occur when O₃ is the sole pollutant (Krause et al., 1985, Skeffington and Roberts, 1985a,b, Krause, 1988). In some of these cases, Purafil™ as well as activated charcoal had been used to clean the air before it was enriched with O₃, and hence no deposition of nitrate from the

TABLE 9-1. ADSORPTION CAPACITIES OF ACTIVATED CHARCOAL AT ONE-FIFTH OF THE U.S. OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION (OSHA)^c PERMISSIBLE EXPOSURE LIMITS^a SET FOR PEOPLE

| Contaminant | Permissible Exposure Limits | Adsorptive Capacity (wt %) ^b |
|-------------------|-----------------------------|---|
| Ammonia | 50 | 4×10^{-5} |
| Carbon monoxide | 50 | 1×10^{-8} |
| Hydrogen chloride | 5 | 1×10^{-8} |
| Hydrogen fluoride | 3 | 1×10^{-8} |
| Hydrogen sulfide | 20 | 2×10^{-5} |
| Nitric oxide | 25 | 1×10^{-8} |
| Nitrogen dioxide | 5 | 2×10^{-2} |
| Nitrous oxide | 54 | 4×10^{-4} |
| Sulfur dioxide | 5 | 3×10^{-5} |

^aAs defined by the 29CER 1910 OSHA Standard dated April 22, 1986

^bData provided by Westates Carbon Inc , Los Angeles for activated charcoal types G201, G204, G210, and G216 made from coconut-shells

air would have been expected. In experiments that are interpreted in this way, it is very important to have an assurance that the air is purified to remove all NO_x, and also that no NO_x entered the fumigation chamber along with the O₃.

9.2.2.2 Chambers

Because NO₂ is both toxic and diffusive in nature, laboratory studies of its phytotoxicity must be conducted in chambers with controlled entry and exit of air. The most common chamber now in use for gaseous pollutant studies in general is the continuous stirred tank reactor (CSTR) (Heck et al , 1978). This chamber design is typified by the use of Teflon® on all surfaces that come in contact with the pollutant gases (thus minimizing gas uptake by the system) as well as a fan for vigorous mixing of the chamber air, thus minimizing the leaf boundary layer and maximizing pollutant uptake by the foliage (Rogers et al , 1977). The CSTR is particularly well designed for determination of absorption and

adsorption of pollutants on a per unit area of foliage basis, and has been so used in studies of NO₂ phytotoxicity (Elkley et al , 1982) Other chamber designs have been used for exposing plants to NO₂, these generally differ from CSTRs in that the chamber walls are usually rigid transparent (non-Teflon®) material and they may or may not have fans (Heck et al , 1968, Srivastava and Ormrod, 1984)

There are some limitations to the use of laboratory chambers for estimating field plant response to NO₂ temperature and humidity in the chamber tend to be very stable over time, unlike those conditions experienced by plants in the field, light levels are generally lower in chambers than in the field, and boundary-layer resistance is generally much lower in the chambers (due to the mixing fan) than in the field These differences may modify both the uptake of pollutants by plants and the ability of plants to detoxify or repair damage, potentially altering the amount of injury expressed by the plant Field investigations have been conducted using open-top chambers that allow plant exposure under atmospheric conditions more similar to ambient (U S Environmental Protection Agency, 1986) The disadvantage of field exposure systems are loss of tight control of pollutant concentration around the vegetation, confounding of replication over time by climatic differences among growing seasons, and possible modification of plant response by interaction of climatic conditions specific to any one year Although chamberless methods for exposing plants are in use (Zonal Air Pollution System, for example), most data from these exposure systems describe plant response to SO₂ (Lee and Lewis, 1978, Muller et al , 1979)

9.2.2.3 Monitoring

The amount of NO₂/NO_x/NO in air is now most commonly detected by chemiluminescent analyzers, which are available from manufacturers such as Monitor Labs and Thermo-Electron Regardless of the instrument source, the principle of operation is the same when NO and O₃ react in the gaseous phase, NO₂ is produced ($\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 + h\nu$) The NO₂ molecules generated by this process are electronically excited, and their decay to a lower energy state results in the emission of light The intensity of this emission is linearly proportional to the concentration of NO₂ produced in the reaction Prior to the reaction with O₃, the NO₂ in the air sample must be converted to NO, which is usually accomplished using a catalyst, such as molybdenum (Mo), and heat $3\text{NO}_2 + \text{Mo} \rightarrow 3\text{NO} +$

MoO₃. Because most sources of air to be analyzed contain a mixture of NO and NO₂, the determination of NO₂ concentration is by necessity a two-step process. First the amount of NO in the air is determined by bypassing the NO₂ to NO converter. Then the air is passed through the converter to determine NO_x, which is the original NO plus the NO₂ that has been converted to NO. The difference between these two readings determines NO₂. $NO_2 = NO_x - NO$. Most NO_x analyzers have a mode selection feature that allows any one of these parameters to be displayed and recorded although both NO_x and NO are alternately measured.

Calibration of the analyzers is a key to gathering high quality pollutant dose-plant response data. The principle of calibration requires a gas source of known concentrations of NO, as well as a source of zero air. The source of NO is usually a pressurized cylinder containing between 50 and 100 ppm NO in nitrogen and should be traceable to a National Bureau of Standards NO in N₂ Reference Material. Zero air is defined as air that is free of any contaminants that will cause a detectable response in any mode of the analyzer (NO, NO₂, or NO_x) or react with NO, NO₂, or O₃ in the gas phase (ThermoElectron Corp, n.d.).

Concentration of NO_x in an air sample can be determined by its colorimetric reactions (Saltzman, 1954) or by its ability to oxidize a chemical mixture. This latter process is the basis of the Mast NO₂ Meter (Mast Co., OH). The air sample is percolated through a chemical mixture, the resulting redox potential of which is measured by a potentiometer. However, these chemical means are rarely used today for determination of NO₂ because the chemiluminescent methods are capable of measuring the various NO_x species, and do so with greater accuracy and sensitivity. Concentration refers to the amount of pollutant in the air expressed either on a v/v (parts per million [ppm], microliters per liter [μ L/L]) or w/v (micrograms per cubic meter [μ g/m³]) basis, the v/v basis is usually preferred, as it remains constant over air temperature, whereas w/v varies with air temperature.

9.2.3 Pollutant Climatology

Approximately 80 to 90% of the NO₂ in the atmosphere is the result of oxidative reactions, with the remaining 10 to 20% emitted from anthropogenic activities. Consequently, as a secondary pollutant, its concentration is closely linked to meteorological conditions. The conversion of NO₂ to NO and the consequent production of O₃ is related to

sunlight and air temperature, so that the appearance and disappearance of NO_2 , NO , and O_3 in an artificial environment are closely linked (Figure 9-1)

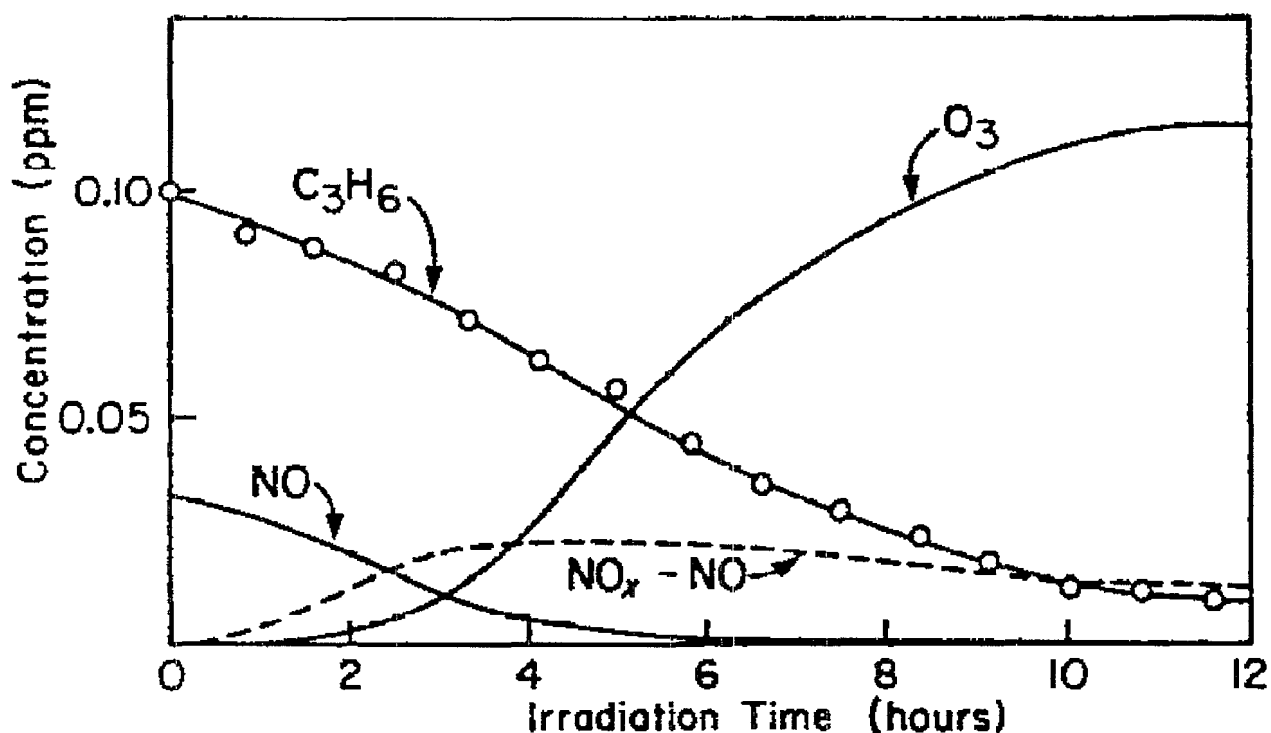


Figure 9-1. Propylene and nitric oxide oxidation under artificial illumination. Nitric oxide is oxidized to nitrogen dioxide and other oxides of nitrogen. Ozone concentrations build up after the ratio of nitrogen dioxide to nitric oxide increases.

Source Stern (1986)

9.2.4 Pollutant Chemistry

Oxides of nitrogen are produced from both natural and anthropogenic processes forest fires and electric storms (NO , NO_2), soil processes (NO , nitrous oxide [N_2O]), and oceans (N_2O) are some of the natural sources, whereas combustion of oil and coal (NO , NO_2 , N_2O) and gas (NO , NO_2) are the main anthropogenic sources (Stern, 1986) Once emitted into the atmosphere, these compounds undergo transformation as part of the photochemical smog

cycle (Figure 9-2) The reactive cycle centers around photolysis of NO_2 into NO and atomic oxygen (O); O is then available to combine with molecular oxygen (O_2) to form O_3 , and NO is available to react either with O_3 for the production of NO_2 and O_2 , or with hydroperoxyl to form NO_2 and hydroxyl

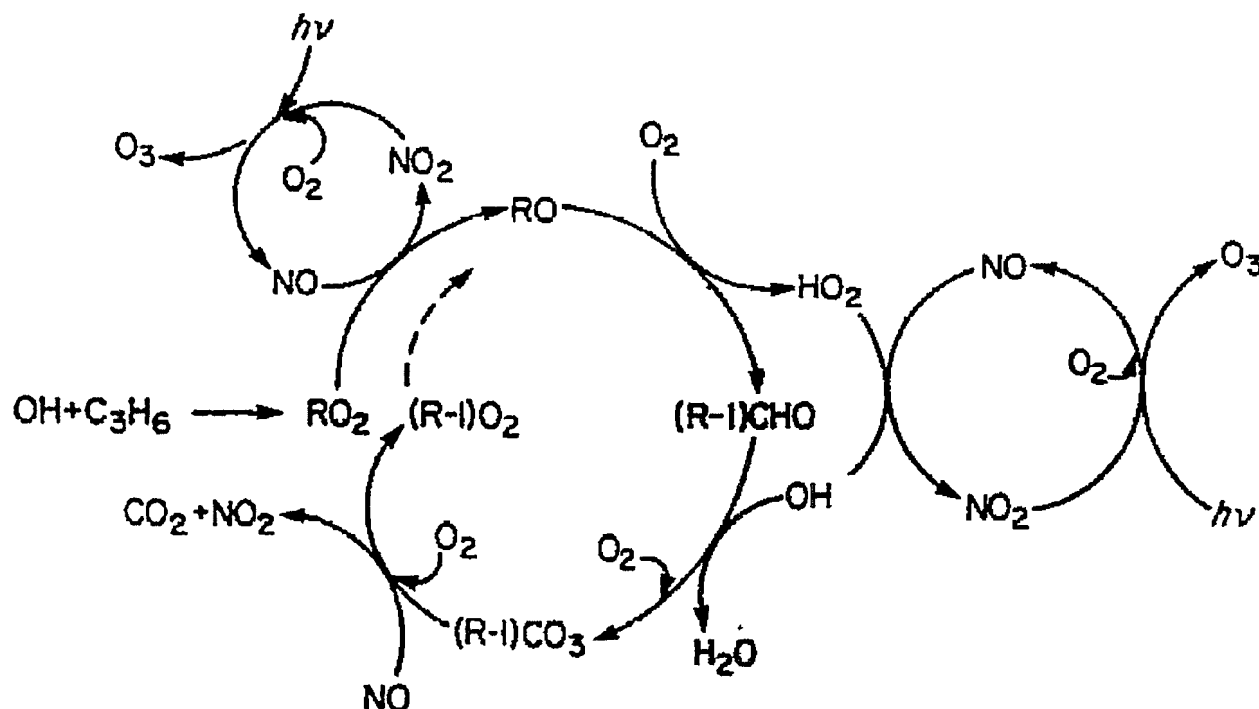


Figure 9-2. The cyclic interaction of free radicals, hydrocarbons, nitric oxide, nitrogen dioxide, and ultraviolet radiation in photochemical smog. In this example, hydroxyl radical reacts with propylene at the left side of the diagram, forming RO_2 . This cycle interacts with nitric oxide and molecular oxygen. The inorganic nitrogen oxides-ozone cycle is shown on the right side of the diagram, with photolysis of nitrogen dioxide eventually forming ozone.

Source Stern (1986)



This cycle describes the primary relationship among NO_2 , NO , and O_3 and is known as the inorganic nitrogen cycle (Stern, 1986). These pollutants can then be deposited to sinks by any of a number of processes—wet or dry deposition in either original or modified form. The individual processes of the deposition/transformation cycle have been well described (Figure 9-3). Once the pollutants have been deposited to vegetation or soil, they become available to the biosphere.

9.3 MODE OF ACTION

9.3.1 Gas Uptake

9.3.1.1 External Nitrogen Oxides Ratios Around Leaves

In order to understand the uptake of NO_x by plants, several considerations have to be taken into account. First, the composition of the atmosphere around leaves with respect to all pollutants (not just NO_x) has to be determined regularly. Second, all routes of entry of NO_x into a plant have to be defined and assessed. Even now, it is not certain that all possible routes of access are known, especially those that may involve nonaqueous processes prior to entry into cells (see Section 9.3.1.5). Finally, controlled exposures with NO_x should be done in such a way that inadvertent confusions with the effects of other pollutants such as O_3 are eliminated, and that the exact form of the nitrogen-containing gaseous pollutants (i.e., NO_2 or NO , or the ratio of the two) as well as their concentrations are defined (see Section 9.2.2.2).

During combustion, the primary NO_x species produced is nitrogen monoxide or NO (Figure 9-4), only a little of which comes from nitrogen in the fuel. The majority of the NO is generated from the direct combination of atmospheric oxygen and nitrogen within flames (Palmer and Seery, 1973). All ignition reactions involve or produce free radicals (i.e., chemicals that are capable of independent existence and that have one or more unpaired electrons in their outer electronic orbitals) such as O and atomic nitrogen. Nitric oxide is also a free radical ($\text{N}=\text{O}$), which, like others, will react so as to lose or gain an electron.

Oxidation of NO by O_3 occurs rapidly ($k = 1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$), even at very low concentrations (Willix, 1976). Altshuler (1956) has calculated that a 50% conversion of NO by 0.1 ppm O_3 would take less than 1 min at an NO concentration of 0.1 ppm.

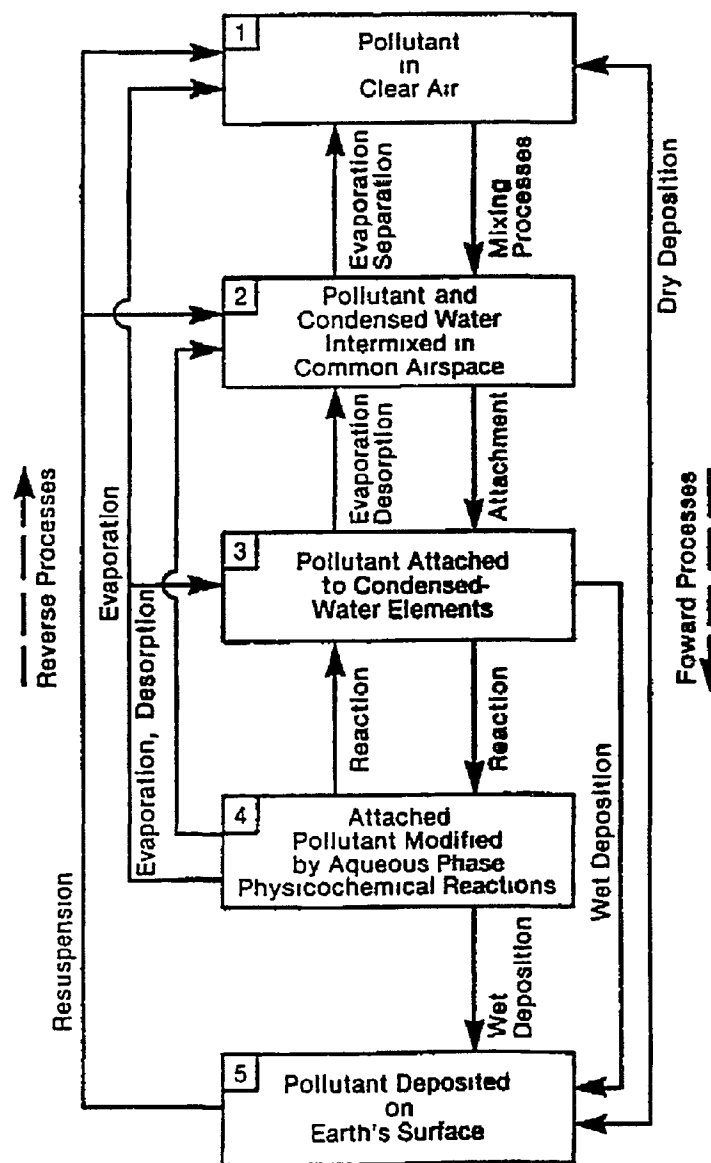


Figure 9-3. Phase interaction diagram for pollutant scavenging processes. Initially, the pollutant may be in the gas phase (Box 1). The presence of water vapor in the atmosphere provides for the intermixing of gaseous pollutants with aqueous droplets in the same space (i.e., in a cloud [Box 2]). The pollutant gases can become attached to the water droplets (i.e., be absorbed [Box 3]), and undergo chemical reaction (Box 4). The gaseous and aqueous pollutants return to the earth's surface (Box 5). Some of these processes have reversible pathways, and others are unidirectional.

Source: National Research Council (1983), in Stern (1986)

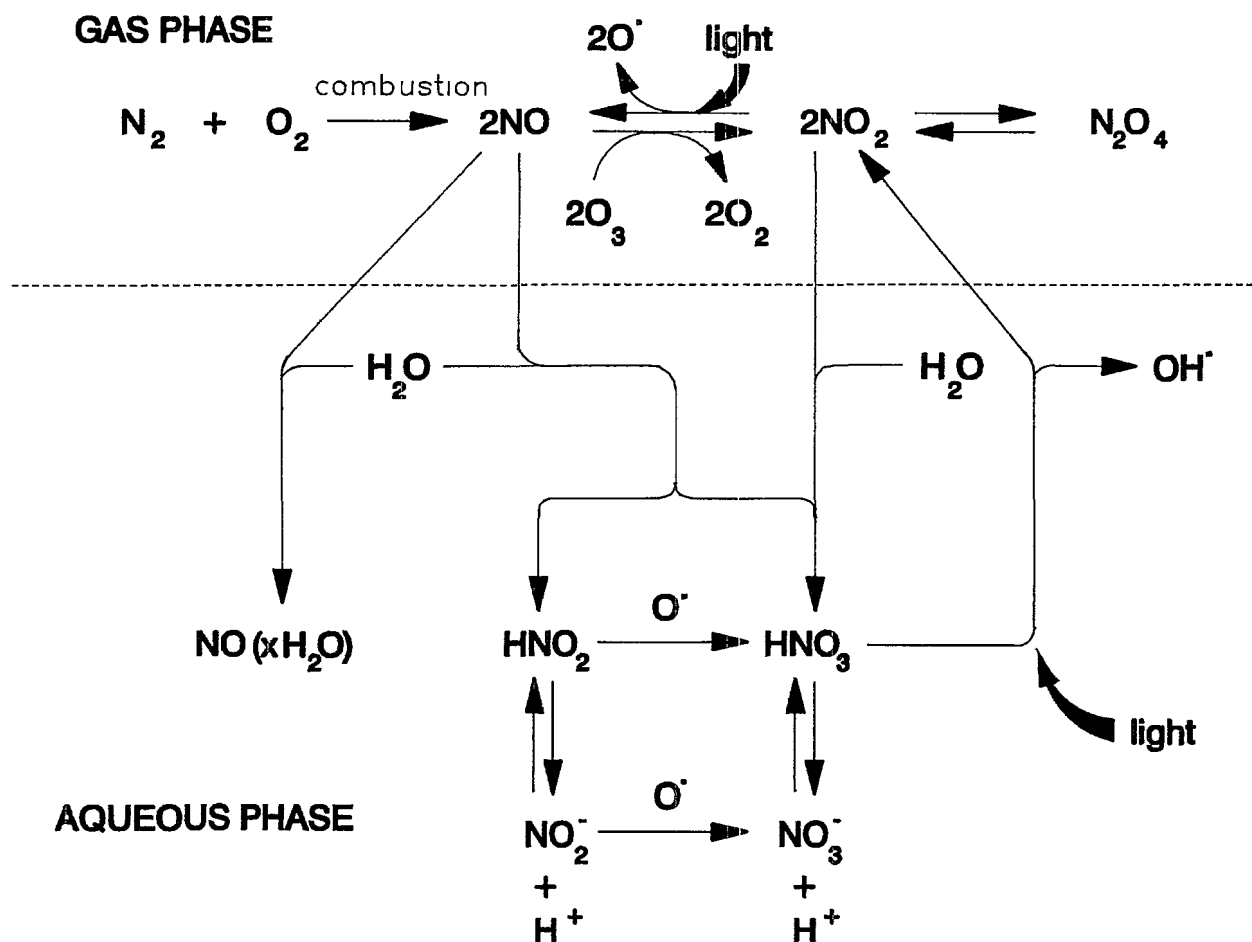


Figure 9-4. Important interconversions of the different forms of nitrogen oxides after combustion in the atmosphere and in aqueous solutions in contact with atmospheres containing nitrogen oxides.

Source Rowland et al (1985)

Consequently, this reaction is regarded as the most important mechanism forming NO_2 in the atmosphere. Other pollutants, such as hydrocarbons and SO_2 , can also react with NO_x , but the importance of these reactions is dependent upon the environmental conditions (Demerjian et al, 1974, Willix, 1976)

Concentrations of NO_2 in the atmosphere are due to a balance between two sets of reactions—those that form the pollutant (already described) and those that cause its breakdown. Production of NO and O from NO_2 is the major reverse reaction (Holmes and Daniels, 1934, Ford and Endow, 1957), which is catalyzed by wavelengths of light less than

440 nm. As a consequence of these forward and back reactions, a wide range of atmospheric NO-to-NO₂ ratios around plants are possible (Fowler and Cape, 1982), depending on levels of light and O₃

Because the concentration of CO₂ in the atmosphere limits rates of photosynthesis, enrichment of atmospheres with CO₂ (to 1,000 ppm) is a frequent practice in the greenhouse industry (Hand, 1982), but effects of NO_x pollution on horticultural crops grown in CO₂-enriched atmospheres have been observed. For example, Capron and Mansfield (1975), Ashenden et al (1977), and Law and Mansfield (1982) detected large amounts of NO (up to 0.45 ppm) in greenhouses equipped with hydrocarbon burners to provide heat and/or CO₂ to crops. Although the ratio of NO to NO₂ can vary with burner design and method of heating, this ratio is much higher inside (four parts NO to one of NO₂) than outside greenhouses. There are two explanations for this observation, even though the glass cut-off effect prevents the light-induced back conversion of NO₂ to NO. First, because the pollutants are monitored close to their source, little time is available for oxidation of NO to NO₂, and second, the air inside modern greenhouses contains little O₃ from outside because the ventilation rates are often below one air change per hour (Hurd and Sheard, 1981).

9.3.1.2 Solution Properties of Nitrogen Oxides

The use of nitrogen-15 (¹⁵N)-radiolabeled NO₂ (¹⁵NO₂) has established that plants can remove NO_x from the air (see Section 9.3.1.4). However, for a gaseous pollutant to enter an internal mesophyll cell, its molecules must pass through the extracellular water covering the plant cell (Mansfield and Freer-Smith, 1981). Consequently, solubility of a gas in an aqueous medium is an important factor in determining the rate at which it is taken up. The gaseous form of NO is only slightly soluble in pure water, but the presence of contaminants such as substituted phenols can alter apparent solubilities (Nash, 1970). In water alone, however, the real limitation for NO₂ entering the cell appears to be the rate of its solubilization in water (Lee and Schwartz, 1981, Lee and Tang, 1988). Pfafflin and Ziegler (1981) have studied the reactions that operate in a mixed aqueous/gas phase.

Nitrogen dioxide differs markedly from NO because it reacts with water and this feature significantly increases the apparent solubility of NO₂ relative to NO. Reaction of NO₂ with water is not just a simple hydration producing HNO₃. Based on results from

conductivity experiments, Lee and Schwartz (1981) concluded that NO_2 undergoes a comparatively slow heterogeneous reaction with water to form a dissolved NO_2 species that then reacts with itself to give both HNO_3 and nitrous acid (HNO_2 , see Figure 9-4). The extent and relative importance of this dissolution has been questioned (Dasgupta, 1982), but, over pH ranges that are biologically important, any HNO_3 (pK_a of -1.4) that forms will completely ionize to nitrate. Similarly, HNO_2 will form nitrite, but the equilibrium governing this ionization has a pK_a of 3.3 , which means some undissociated HNO_2 will exist below pH 6 , especially near cell walls where pH values as low as 4 can occur.

Although the solubility of NO in water has been measured (47.1 mL of gas/L of water at 20°C and 1 atm), the chemical form of the gas in solution is less certain (Schwartz and White, 1981). Some studies have suggested that NO reacts with water to form a compound similar to hydroxylamic acid (Beattie, 1967), but the gas is now considered to be relatively unreactive with water (Bonner, 1970). However, isotopic exchange between gaseous ^{15}NO and solutions of N^{18}O_2 has been detected (Bonner and Jordan, 1973, Jordan and Bonner, 1973). In the case of extracellular water in a plant, this would suggest that NO may form both nitrate and nitrite ions, just like NO_2 (see Figure 9-4), but at much slower rates.

Solubility of NO in aqueous media varies with temperature, and like many other gases, NO is more soluble at lower temperatures than at higher temperatures. Stephen and Stephen (1963) found, for example, that 73.8 mL/L of NO was taken up at 0°C , as compared to 40 mL/L at 30°C . This reduction in solubility of NO as temperature rises has implications for plants growing at low temperatures, especially as rates of conversion of NO to NO_2 are reduced at lower temperatures. As a result, more NO as a proportion of total NO_x may persist in colder atmospheres and more NO may dissolve in aqueous layers in contact with this colder air.

The chemistry of the two acids (HNO_3 and HNO_2) produced by NO and NO_2 is markedly different. As already stated, HNO_3 is a strong acid, whereas HNO_2 is regarded as much weaker (pK_a of 3.3). Over the probable pH range (5.5 to 7) of extracellular water (White et al., 1981, Hartung et al., 1988), HNO_3 ionizes fully to form both nitrate ions and protons (see Figure 9-4). By contrast, HNO_2 will be present mainly as nitrite ions and protons along with very small amounts of undissociated acid. Consequently, for the plant to metabolize the products of the two gases NO_2 and NO , it must mainly deal with nitrate,

nitrite, and protons—all of which can pass through cell membranes (Schloemer and Garrett, 1974; Heber and Purczeld, 1978, Gutknecht and Walter, 1981), but only two of which (nitrate and protons) are normally present in appreciable quantities inside cells

Atmospheric NO_2 also exists in equilibrium with its dimer, N_2O_4 , which could complicate the gas-liquid transfers still further. Fortunately, at low ambient concentrations, this equilibrium is very much in favor of NO_2 (Altshuller, 1956, Lee and Schwartz, 1981). A similar preference exists for NO and NO_2 rather than another higher oxide, N_2O_5 , which is produced, for example, by some O_3 generators using air (see Section 9.2.2.1)

9.3.1.3 Foliar Uptake of Nitrate

Wet and dry deposition of NO_x are important processes in the redistribution of nitrogen throughout the environment (Varhelyi, 1980) and the processes involved in the deposition of various forms of NO_x onto plants are covered elsewhere (Section 9.4). However, little information exists to confirm or refute the possibility that nitrate (or ammonium) in water droplets on the outside cuticles of leaves or needles may gain access to the internal cells without falling off, entering the soil, and being taken up by the roots. Foliar feeding of nodulated legumes with ^{15}N -labeled nitrate ions ($^{15}\text{NO}_3^-$) produced a similar distribution of ^{15}N (Oghoghorie and Pate, 1972) to that found in experiments using $^{15}\text{NO}_2$ (see Section 9.3.1.4), but it required 14 days for 60% of the labeled nitrate to be imported into the mesophyll from the leaf surface. Afterwards, the majority of ^{15}N was detected in an ethanol-insoluble fraction, which indicates that the nitrate had been reduced to ammonia (NH_3), incorporated into amino acids, and subsequently incorporated into proteins. Unfortunately, the site of reduction in these studies was not determined. Later experimentation using $^{15}\text{NO}_3^-$ in different acid rain treatments (pH 4.0, 3.4, 2.7) of green beans (*Phaseolus vulgaris* L. cv. University of Idaho) showed that the amount of nitrogen absorbed by foliage decreased as the rainfall pH was reduced (Evans et al., 1986). Amounts of nitrogen accumulated directly into the leaves from the rain droplets on the leaves was found to be only a small percentage of that present in simulated rain when compared with the amounts of nitrogen already present in the leaves. Ammonium and nitrate labeled with ^{15}N have also been used to estimate the amount of foliar uptake of nitrogen by red spruce (*Picea rubens* Sarg.) from simulated cloud water applied over a period of 50 h.

(Bowden et al , 1989) Accumulation rates of ^{15}N were found to be very low Less than 1.5% of the nitrogen required for new growth was found to come from ammonium and nitrate in the cloud water These conclusions agree with those obtained by Wolfenden and Wellburn (1986) using high performance ion chromatographic (HPIC) analyses of nonaqueously prepared chloroplasts from barley given different acid rain treatments (pH 5.6, 4.0, 3.0) Sulfate in dried-down rain droplets on leaf surfaces significantly increases the levels of sulfate inside chloroplasts but nitrate in the same droplets had no corresponding effect

Response of plant cells to acidity provided by gaseous pollutants such as NO_x has been described elsewhere (Nieboer et al , 1984), but there is one important effect of nitrate upon the tonoplast membrane that is relevant to detrimental effects of both wet and dry nitrogen deposition on plants Both cell and tonoplast membranes contain energy (ATP)-dependent hydrogen ion (H^+) pumps, and the tonoplast pump is strongly inhibited by nitrate (Hager and Biber, 1984) Consequently, plants that deposit extra protons in their vacuoles when they experience additional acidity and nitrate at the same time will have extra difficulty in maintaining cellular control

9.3.1.4 Evidence of Nitrogen Uptake Using Nitrogen-15 Labeled Gases

Fumigation experiments using $^{15}\text{NO}_2$ have demonstrated that plants take up this gas, that it is converted to nitrite and nitrate, and that only natural modes of nitrogen metabolism are involved (Rogers et al , 1979a, Yoneyama and Sasakawa, 1979, Kaji et al , 1980) Soon after fumigation, most of the ^{15}N is in soluble form, but as time passes, more becomes insoluble (Yoneyama et al , 1980a) Kaji et al (1980) showed that after only 20 min of exposure, glutamine and alanine were strongly labeled, and Yoneyama and Sasakawa (1979) and Okano et al (1984) showed that the bulk of the label passed to glutamate and asparagine as well About 5% of the ^{15}N label that enters a leaf then moves on to other leaves or to the roots (Rogers et al , 1979a)

In the past, ^{15}N -labeled nitrogen molecule dilution has been a successful technique to estimate the amount of nitrogen fixation by leguminous crops (Fried and Middleboe, 1977) and the same methodology has been adapted to measure the contribution of $^{15}\text{NO}_2$ to total nitrogen metabolism within a plant (Okano et al , 1986) Testing eight herbaceous plants

(sunflower, *Helianthus annuus* L , radish, *Raphanus sativus* L , tomato, *Lycopersicon esculentum* Mill, tobacco, *Nicotiana tabacum* L , cucumber, *Cucumis sativus* L , kidney bean, *Phaseolus vulgaris* L , maize, *Zea mays* L , and sorghum, *Sorghum vulgare* L) with this method, Okano et al (1988) showed that sunflowers exposed to NO₂ (0.5 ppm for 14 days) show absorption rates of 0.57 mg nitrogen/dm²/day —four times those of *Sorghum* spp (0.16 mg nitrogen/dm²/day) Other species have intermediate values in the order shown in Table 9-2 They suggested that the total amount of NO₂-derived nitrogen depended primarily upon the unit area presented by different plant species and that this may explain the larger reductions in growth of sunflower and radish (both C₃ plants) to NO₂ and the relative tolerance of sorghum and maize (both C₄ plants) Their measurements of stomatal conductances also showed high values for sunflower and low rates for sorghum (see Table 9-2), which would seemingly also account for these differences When regression analysis is applied to the rates of NO₂ uptake and stomatal conductances, a linear relationship ($r = 0.984$) is obtained that does not pass through the origin From this, Okano et al (1988) concluded that a portion of the NO₂ does not enter the leaf through the stomata

TABLE 9-2. RATES OF NITROGEN DIOXIDE ABSORBED AND STOMATAL CONDUCTANCES IN EIGHT HERBACEOUS SPECIES

| Species | Rate (mg nitrogen/dm ² /day) | Conductance (cm/s) |
|-------------|---|--------------------|
| Sunflower | 0.57 | 2.07 |
| Radish | 0.44 | 1.69 |
| Tomato | 0.35 | 0.91 |
| Tobacco | 0.33 | 0.85 |
| Cucumber | 0.27 | 0.72 |
| Kidney bean | 0.24 | 0.58 |
| Maize | 0.21 | 0.16 |
| Sorghum | 0.16 | 0.20 |

Source Okano et al (1988)

9.3.1.5 Access of Nitrogen Oxides into Leaves

Both deposition velocities of atmospheric nitrogen-containing compounds and stomatal conductances of plants exposed to NO_x show large variation (see also Section 9.9), but one feature of such measurements relating to NO and NO_2 is quite clear. Stomata have to be open for major uptake of these atmospheric pollutants to occur. Gaseous uptake of NO_2 is much reduced when stomata are closed (Saxe, 1986b, Hanson et al., 1989) or when conifers are dormant (Skarby et al., 1981, Johansson, 1987).

Until now, the main avenue of entry of NO_x has always been thought to be wholly through the stomata (see Figure 9-5) in a similar manner to that of CO_2 . However, Lenzian and Kerstiens (1988) suggest that not only is the cuticle a very large reservoir with respect to adsorbed NO_2 (to the extent of increasing its own weight by up to 20%), but that the two gases NO and NO_2 may cross isolated cuticles more readily (two- to sixfold more readily) than other air pollutants like SO_2 and hydrogen fluoride (HF). This is especially the case with cuticles isolated from conifers or citrus trees. They have also shown that specific sites for NO_2 exist in plant cuticles and that irreversible binding takes place so that cuticles become completely "nitrated" during their lifetime. Only after total nitrogen saturation has been achieved does the water permanence increase two- to fivefold, although the barrier towards other gases is unaffected. Uptake of NO_2 and NO into cuticles has also been demonstrated by labeling studies using $^{15}\text{NO}_2$ and ^{15}NO (Kisser-Priesack et al., 1987). Despite this, it is still difficult to evaluate from these studies using isolated cuticles how much or to what extent NO_x can cross undetached cuticles and gain access to epidermal cells. Calculations, based on results obtained from *Abies* cuticles exposed to 0.052 ppm NO_2 , show that the flux through the cuticle would be of the order of $2 \mu\text{g}/\text{m}^2/\text{h}$, a rate of deposition 1 to 2 orders of magnitude less than stomatal deposition at similar concentrations of NO_2 .

Behavior, frequency, and distribution of stomata are important factors in determining the amount of air pollutants entering a plant (Pande, 1985). As already mentioned, closed stomata are not a complete barrier to NO_x because a portion penetrates the cuticle. Nevertheless, the consistent trend from all gas-exchange studies (Darrall, 1989) is that there is less response of a plant to NO_x under conditions that cause stomatal closure. These include stresses such as low light, humidity, or nitrogen status (Srivastava et al., 1975a, Law and Mansfield, 1982, Kaji et al., 1980, Yoneyama et al., 1980c). Atmospheric NO_x can

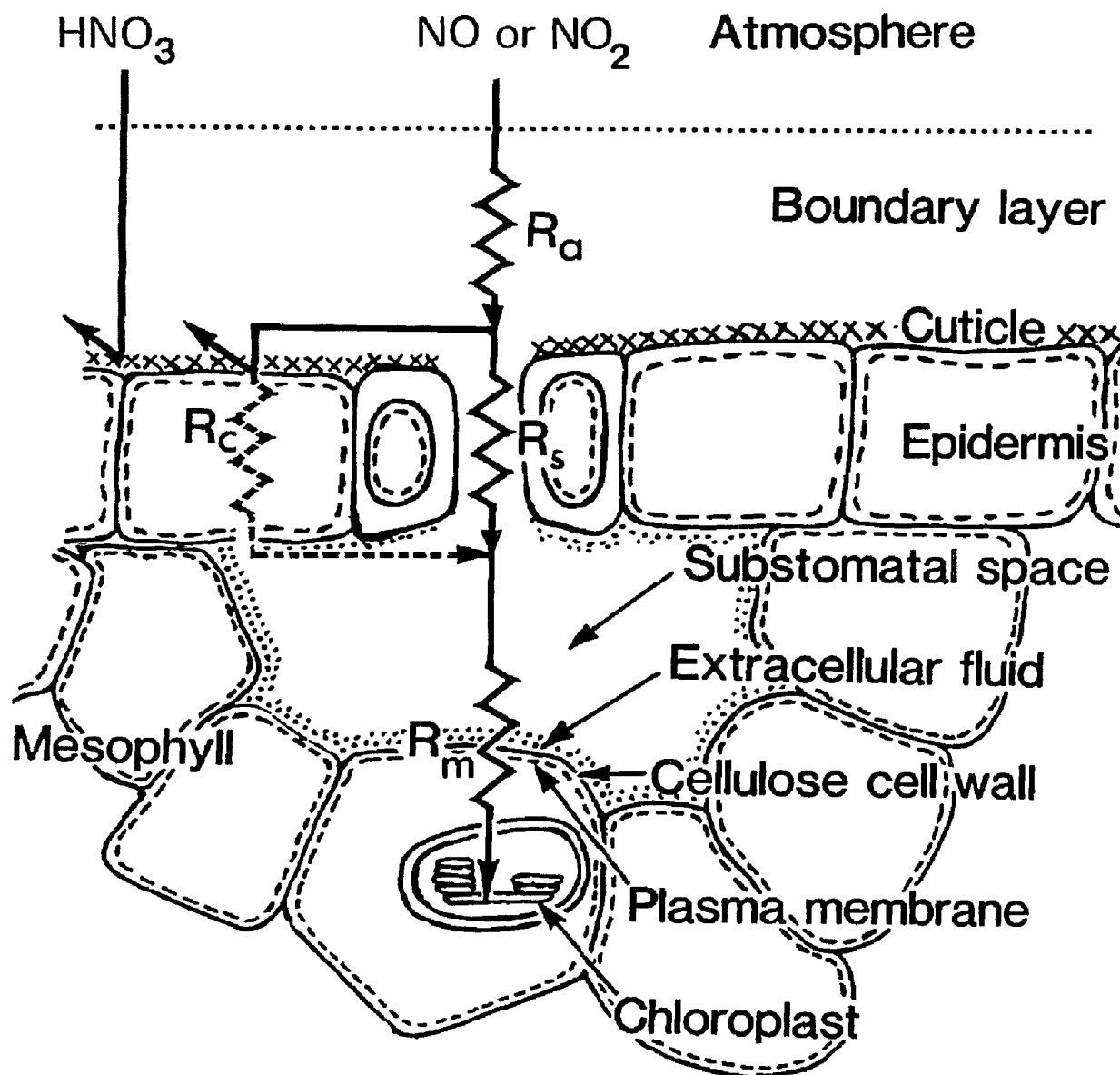


Figure 9-5. Likely access routes for nitrogen oxides into a plant leaf. The layer of still air or boundary layer imposes a resistance (R_a) that depends on a number of factors including wind speed. Access is then limited by the degree of stomatal opening (R_s) or to a much lesser extent by penetration through the cuticle of epidermal layers (R_c). The mesophyll resistance (R_m) consists of a number of different components before the major sites of reaction are encountered.

Source Wellburn (1988)

also cause direct reductions in stomatal conductance (Carlson, 1983), which are then reflected in decreases in transpiration and photosynthesis (see Section 9 3 3 2)

In conclusion, the stomatal aperture plays the major role in determining the extent of the effects of NO_x on plants by limiting access to intercellular air spaces

9.3.1.6 Access of the Products of Nitrogen Oxides into Cells

Zeevaart (1976) was the first to suggest that any NO_2 entering a leaf dissolves in the extracellular water of the substomatal cavity to form both HNO_2 and HNO_3 , which then dissociate to form nitrate, nitrite, and protons (see Figure 9-4 and Section 9 3 1 2) Large air spaces exist in a leaf, which amount to 50 to 80% of the leaf by volume (Nobel, 1974), and from this, it follows that the inner leaf cells provide a large surface area for the absorption of NO_x Solubilities of NO and NO_2 in the extracellular water are affected by pH and the presence of other substances that may determine, in part, the rates of uptake of NO_x (Soderlund, 1981) Anderson and Mansfield (1979), for example, found that NO was more soluble in xylem sap than in distilled water, presumably because of much higher ionic strengths Because xylem sap is continuous with the extracellular water in a leaf, an enhanced solubility of NO in the latter may be expected over that predicted by the water solubility figures alone (see Section 9 3 1 2)

Mesophyll resistance is a collective term that describes all those parameters involved in gaseous uptake between the stomata and the final site of reaction of an incoming gas It includes components such as solubility, dissolution, penetration of the cell wall or membranes, and the intervening cellular metabolism The ability of this resistance (see Figure 9-5) to regulate pollutant uptake has received little attention, partly because the factors involved in mesophyll resistance are difficult to measure (Capron and Mansfield, 1977) By deduction, Srivastava et al (1975a,b) implicated mesophyll resistance to the flux of NO_2 into *Phaseolus vulgaris* L as being responsible for increased leaf tolerance to this pollutant gas with time This possibility also may account for differences in tolerance shown by different sweet pepper and tomato cultivars exposed to NO or NO_2 (Murray and Wellburn, 1985, see Sections 9 3 2 1 and 9 3 2 2)

Cellular biochemical mechanisms are components of the mesophyll resistance (see Section 9 3 2) The effectiveness of plant metabolism to assimilate or transform the products

of NO_x in aqueous solution (see Section 9.3.3) may alter the uptake of NO_x . Bennett et al (1975), for example, found that NO_x was absorbed most efficiently by foliage near the top of plant canopies where both light intensities and metabolic rates are highest.

9.3.1.7 Levels of the Products of Nitrogen Oxides in Cells

Nitrite is a normal intermediate in the sequential reduction of nitrate to NH_3 prior to synthesis of amino acids within plants (see Figure 9-6). Relative contributions of root and shoot tissue to the assimilation of nitrate, and its subsequent reduction, differ widely between species as well as being dependent upon the nitrate concentration around the roots (Kato et al, 1974; Lee and Stewart, 1978). Even nitrate metabolism by ecotypes and cultivars of the same species may vary (Rajagopal et al, 1976, Harris and Whittington, 1983). Use of $^{15}\text{NO}_2$ has also shown that, once inside a plant, ^{15}N can be transferred to all parts of the plant except mature leaves (Yoneyama et al, 1980a, Okano et al, 1984b). This process is extremely rapid. For example, radioactive label from atmospheric nitrogen-13 labeled NO_2 (half-life = 10 min) surrounding single barley leaves was detected in all the remaining parts of the seedlings, including the roots, within minutes (Rowland, 1985), although the vast bulk of the label remained in the exposed leaves.

Many of the concentrations used in studies cited below exceed those usually found in the ambient air. (For ambient concentrations see Chapter 7). In general, when bean plants (*Phaseolus vulgaris* L. cv. Kinghorn Wax) are exposed to NO_x (0.02 ppm NO_2 for 5 days), nitrite levels rarely rise (Srivastava and Ormrod, 1984, 1986). However, Zeevaart (1976) did report a large increase of nitrite rather than nitrate when peas were exposed to exceptionally high levels of NO_2 (8.4 ppm) for 1 to 2 h. Similarly, when Yu et al (1988) fumigated both spinach (*Spinacia oleracea* L. cv. New Asia) and kidney beans (*Phaseolus vulgaris* L. cv. Shun Endogawa) in the dark, elevated levels of nitrite only occurred with high levels of NO_2 (3.5 ppm). Even at levels of 8 ppm NO_2 in the light, only spinach showed accumulations of nitrite, but both species had very large accumulations of NH_3 . At much lower levels of NO_2 (0.25 ppm), Spierings (1971) detected a slight decrease in the nitrate content of tomato (cv. Moneymaker) leaves after exposure to NO_2 for 4 mo, but could detect no nitrite in the juice from compressed fresh tissues. Likewise, Taylor and Eaton (1966)

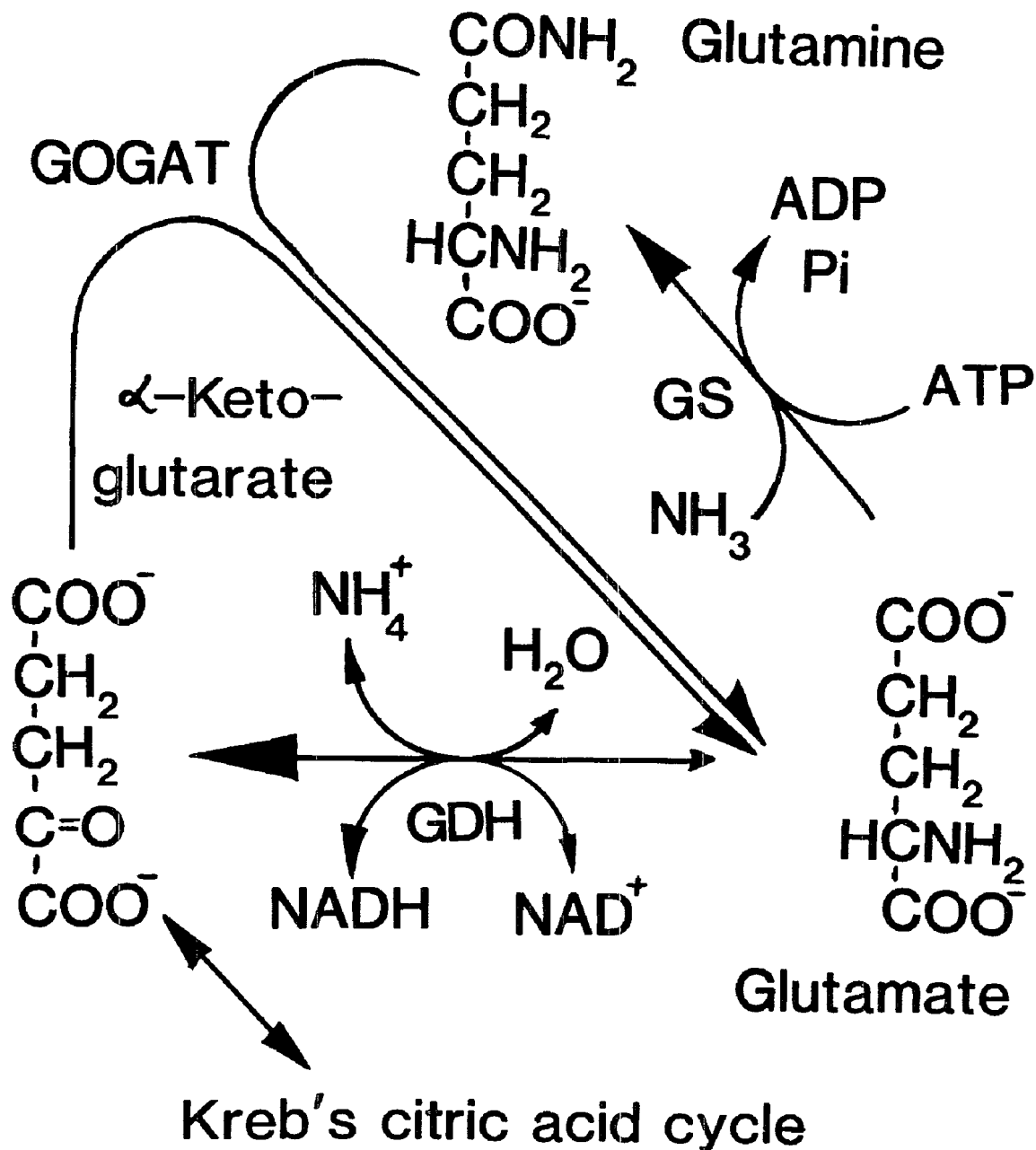


Figure 9-6. Uptake and metabolic pathways involved in the uptake of nitrogen oxides into plant leaf tissue from the atmosphere. The enzymes involved include nitrate reductase, nitrite reductase, glutamine synthetase (GS), glutamate synthase (GOGAT), and glutamate dehydrogenase (GDH).

Source Wellburn (1988)

reported a slight decrease (1.8 mequiv nitrogen/g fresh wt) in nitrate content from leaves of tomato after 19 days of exposure to NO₂ (0.42 to 0.54 ppm)

Recent work has shown that changes in levels of total nitrate in response to NO₂ depend upon the amounts of nitrogen supplied as nitrate to the roots of plants at the time of exposure (Srivastava and Ormrod, 1984, 1986, 1989, Okano and Totsuka, 1986, Rowland et al., 1987, Rowland-Bamford and Drew, 1988). Hydroponically grown barley (0.1 mM nitrate) accumulate 85% more nitrate than controls when exposed to 0.3 ppm NO₂ for 9 days, but similarly polluted seedlings grown with 10 mM nitrate have even 25% less nitrate than controls (Rowland et al., 1987). This difference in nitrate content was not significant in bean (cv Kinghorn Wax) shoots exposed to 0.5 ppm NO₂ for 14 days (6 h/day) when grown with high levels of nitrate (20 mM), but levels of nitrate in the roots of the same plants were very different (Srivastava and Ormrod, 1986). Those grown in clean air had only 40% of the root nitrate found in polluted plants.

By contrast, concentrations of total nitrogen (as opposed to nitrate content) within plant shoots usually decline following exposure to NO₂. Elkley and Ormrod (1981d), for example, found a significant decrease in the total nitrogen content of three cultivars of petunia exposed intermittently to 0.8 ppm NO₂ over 4 days, and similar decreases in shoot total nitrogen were found in bean (cv Kinghorn Wax) and soybean (*Glycine max* Merr. cv Williams) with increasing NO₂ concentrations (Srivastava and Ormrod, 1986, Sabaratnam et al., 1988a). The reasons why shoot nitrogen levels may decline after exposure to NO_x remain unclear, but translocation of additional nitrogen from shoots to roots appears to offer a partial explanation. This reallocation of NO₂-derived nitrogen to the roots was shown to be highly significant using barley (*Hordeum vulgare* L. cv Patty) grown hydroponically at both medium (1 mM) and low (0.01 mM) levels of unlabeled nitrate and exposed to ¹⁴NO₂ (0.5 ppm) for 8 days, followed by ¹⁵NO₂ (0.5 ppm) for 3 h, and then back to unlabeled NO₂ for 1 more day (Rowland et al., 1987).

Nitrate and nitrite concentrations in isolated chloroplasts from barley (cv Patty) exposed to atmospheric NO₂ (0.28 ppm for 1 to 3 days) have been measured using HPIC (Wellburn, 1985). Concentrations of nitrate decline significantly to a low point on the second day of fumigation before rising back to control levels. Levels of nitrite show the converse, rising to a maximum on the second day before falling back. These changes may

be explained by imbalances in the relative speeds of induction of the two enzymes, nitrate reductase (NaR) and nitrite reductase (NiR) (see Sections 9 3 2 1 and 9 3 2 2) The first enzyme is induced faster than the second, so initially more nitrate is converted to nitrite and, when the second enzyme catches up, nitrite declines again

9.3.1.8 Cycling, Partitioning, and Elimination of Nitrogen Dioxide Derived Nitrogen

As Section 9 3 1 4 has already mentioned, uptake studies with $^{15}\text{NO}_2$ have shown incorporation of label in leaves into glutamine, asparagine, glutamate, and alanine Although several groups have also demonstrated transfer of this label into roots, Okano et al (1984b) showed that this relocation was biphasic—an initial afflux of soluble metabolites from the leaves followed by a slower redistribution as label moved out of the leaf protein fraction Closer examination of the ^{15}N label in the various components of both roots and shoots of snapbeans (*Phaseolus vulgaris* L cv Blue Bush Lake 290) after just 3 h of exposure also reveals differences (Rogers et al , 1979a) In the leaves, 63% of the label was found to be associated with the protein/nucleic acid fraction, 33% with the amino acid/amide fraction, and very little with nitrate (5%) In roots, however, the balance between the first two fractions was approximately equal (47 and 41%, respectively)

Using $^{15}\text{NO}_3^-$, Rowland et al (1987) have shown that nitrate uptake by roots is unaffected by exposure of barley (cv Patty) leaves to atmospheric NO_2 (0.3 ppm for 9 days), but such a fumigation does affect the ability of the roots to respond to changes in root nitrate supply The allocation of label from $^{15}\text{NO}_3^-$ remaining in the roots was found to be reduced by fumigation with NO_2 , especially in those barley seedlings grown at low levels of nitrogen supply A pronounced effect of atmospheric NO_2 was also found in the xylem of similar plants growing on low levels of nitrate in the form of raised amounts of serine, asparagine, and glutamine In barley seedlings well supplied with nitrate, the main effect of atmospheric NO_2 was to increase the amount of reduced nitrogen in the roots (Rowland et al , 1987) This was thought to be due to a decrease in the transport of organic nitrogen from the roots to the shoots in the xylem stream

Consequently, the responses of plants to atmospheric NO_2 are very different if the nitrogen supply is either limiting or adequate (see also Section 9 3 1 7) If there is sufficient

nitrogen, there is less redistribution of nitrogen and less influence on roots by nitrogen derived from NO_2 taken in by the leaves

Law and Mansfield (1982) calculated that the input of nitrogen as NO from a 66 kW kerosene burner into a greenhouse with a floor area of 0.05 ha may amount to over 100 kg/ha in a growing season of 100 days. Theoretically, such a burner could fulfill virtually all the nitrogen requirement of a tomato crop. In practice, greenhouse crops seem to have a limited capacity to utilize nitrogen from NO because a supply of NO cannot compensate for the reduction in yield due to a deficiency of soil nitrogen (Mansfield and Murray, 1984). This is not true in the case of foliar uptake of NO_2 . Faller (1972), for example, fumigated nitrogen-deficient sunflowers (*Helianthus annuus* L.) with NO_2 (0.8 to 3.1 ppm for 21 days) and found a reduction in the symptoms of nitrogen deficiency, 6 to 28% more growth in the primary leaves, but not in the roots, and increases of 70 to 116% in leaf nitrogen and 19 to 70% in root nitrogen.

Once pollutant-derived nitrogen has been reduced, the form in which it is stored varies (see Section 9.3.1.4). Most, if not all, of the common protein amino acids can accumulate ^{15}N derived from $^{15}\text{NO}_2$ (Durmishidze and Nutsubidze, 1976; Yoneyama et al., 1980d). However, the extent of ^{15}N accumulation is not only species dependent, but is also time dependent. As rates of processes involved in uptake and utilization of nitrogen vary over 24 h, it is not surprising to find that effects of NO_x also differ over the same period. In spinach and sunflowers, exposure to $^{15}\text{NO}_2$ during the night causes enrichments in ^{15}N of different amino acids compared to those labeled during conventional daytime fumigations (Yoneyama et al., 1980d), but the mechanism by which this occurs is unknown.

Time-course studies have also shown that the content of glutamine in the first trifoliate leaf of *Phaseolus vulgaris* increases rapidly after exposure to 4.0 ppm NO_2 (Ito et al., 1984b), but levels reach a plateau after only 4 h of fumigation. Because the plants received NO_2 throughout the whole of this 8-h experiment, this suggests that the controls on the rates of nitrogen metabolism in these plants responded to the pollutant by establishing a new steady-state level and that nitrogen was passed from glutamine to another compound for storage. Ito et al. (1986) have suggested asparagine, ureides, or glutathione as such possibilities.

So far, all of the studies discussed above indicate a participation of the normal pathway of nitrate reduction followed by synthesis of amino acids and proteins as a means by which plants detoxify NO_x (see Figure 9-6 and Section 9.3.2). However, it is possible that other natural metabolic processes could detoxify the products of atmospheric NO_x . One obvious pathway is polyamine production. In the case of uptake of NO_x , this possibility appears not to have been investigated, although significant effects of other air pollutants such as SO_2 on polyamine production are known (Priebe et al., 1978).

Other means of detoxification, such as the release of other nitrogen-containing gases, may also be important. Natural emissions of N_2 , NO , and NH_3 from plant tissue and canopies have been reported (Vanecko and Varner, 1955; Hill, 1971; Farquhar et al., 1979), but no fumigation studies using NO_x have detected emissions of NH_3 . Where an association has been detected between NO_2 uptake and NO release, the amount of the latter may amount to 70% of the NO_2 absorbed or adsorbed (Nishimura et al., 1986) and emissions of NO are strongly dependent upon humidity. Release of NO after treatment of plant tissue with certain herbicides (Klepper, 1979) or during the *in vivo* assays of NaR activity (Harper, 1981) are both known to be associated with accumulations of nitrite ions, and both enzymic (Nelson et al., 1983) and non-enzymic (Klepper, 1979; Nishimura et al., 1986) mechanisms of release have been proposed.

9.3.2 Cellular Sites of Biological Interaction

9.3.2.1 Role of Oxides of Nitrogen in Metabolism

The hydration products as NO_2 is converted into nitrite (NO_2^-) and nitrate (NO_3^-) ions through interaction with water are normal anions within the plant, and as such, can be incorporated into normal metabolic pathways, up to certain maximum rates, dependent upon nitrogen supply from the roots and type of plant. Where both NO and NO_2 are present, NO seems also to be converted into nitrite and nitrate. Metabolic incorporation leads to detoxification of most of the species of NO_x , making the potentially toxic compounds not only harmless to the plant but important to its normal growth. Naturally, the incorporation alters the nitrogen level within the plant and so alters the "normal" state of the plant, where normal is defined as that state before its fumigation by NO_2 . In addition, under high levels of NO_2 flux into the plant, incorporation could overwhelm the nitrogen metabolism and cause

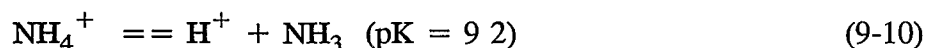
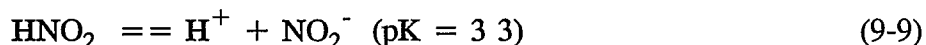
the plant to deviate so far from its normally balanced state that the plant is unable to return to its previous homeostatic state after fumigation

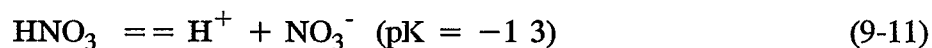
In order to discuss these concepts more completely, two areas must be well defined (1) what types of metabolic pathways are available to NO_x compounds and (2) what is meant by the normal state and how far can plants deviate from that state without permanent injury to the plant

9.3.2.2 Metabolic Pathways

Plants require reduced nitrogen compounds to form proteins, nucleic acids, and many secondary products in order to survive and grow Under most circumstances, nitrogen enters the plant through the roots in three modes (1) absorption of NH_3 (and ammonium), (2) absorption of nitrate (and nitrite), and (3) nitrogen fixation by symbiotic organisms Thus, any pollutant that can be converted chemically or biologically into nitrate, nitrite, or NH_3 can be used by the plant Nitrogen oxides that fall upon the soil have the potential of being easily converted by microbial or chemical action and, therefore, can be readily adsorbed by the roots Ground deposited NO_x can enter the metabolic pathway readily through the soil/root interface, however, deposition can overload the soil/plant systems (see Chapter 10) Gaseous NO_x that enters through the leaf can likewise be converted through enzyme systems that can handle the derived compounds

The chemical species that will be dealt with in the following sections are HNO_2 , ammonium ion (NH_4^+), and HNO_3 The first two are a weak acid and weak base, respectively (see Equations 9-9 and 9-10 below), and, therefore, their actual chemical forms are dependent on pH. These forms govern the manner in which these chemicals can move throughout the plant At normal biological pH, both species (acid and salt) of each compound can exist within an organelle or tissue On the other hand, HNO_3 is such a strong acid that it exists predominantly as NO_3^- under all biological conditions





Although plants can use both ammonium and nitrate, nitrate seems to be less toxic, even in high concentrations, for the plant and, thus, is classed as a "relatively innocuous" compound (Mifflin, 1980). Nitrite and ammonium seem to be compounds whose concentration is highly regulated and is maintained at low levels within the plant. To prevent high NH_3 levels from occurring, the plant will convert ammonium to amino groups as rapidly as possible.

Nitrate is converted first to nitrite via the enzyme NaR , with the resulting nitrite being converted to ammonia by another enzyme, Nir . The full conversion of nitrate into NH_3 requires eight electrons, or the equivalent of four molecules of (NAD(P)H) per molecule of NO_3^- . Because NAD(P)H has a free energy content of about 28 kcal/mole, converting one mole of NO_3^- to NH_4^+ requires about 115 kcal of energy, or about the equivalent of 18% of a glucose molecule (see Schubert and Wolk, 1982). Another manner in which to express the energy requirement for nitrogen conversion is to express it as carbon lost per nitrogen gained. Thus, 1 mole of nitrogen converted as described above is equivalent to a minimum carbon loss of 1.1 mole. Yet Amthor (1989) states that if growth and maintenance respiration did not change during measurements, the value of carbon respired to nitrogen assimilated was as high as 2 to 3.5 moles/mole. For the most part, energy as reducing equivalents come from carbohydrate or organic acids oxidation (glycolysis, tricarboxylic acid cycle, or photosynthesis). Thus, NH_3 fertilizer is energetically "cheaper" for the plant to use but can be more toxic, if not well regulated. Nitrate requires more energy, thus, it would appear that there is less for the total plant productivity. Yet it is hard to demonstrate the lowering of plant productivity by concurrent nitrogen reduction (Robinson, 1988).

More recently, detailed flux and pool balance sheets in nitrogen metabolism have been prepared. For example, Magalhaes et al. (1990) have shown that NH_4^+ can move into corn roots at a rate of $1.75 \mu\text{mole nitrogen/g fresh weight of plant material (FW)/h}$ and then move into the shoots at a rate of $1.25 \mu\text{mole nitrogen/g FW/h}$. The NH_4^+ pools were 3.85 and $0.45 \mu\text{mole/g FW}$ for the root and shoot, respectively (corresponding approximately to 4 and 0.5 mM for a soil NH_4^+ level of 50 mM). On the other hand, cow pea cultured cells will maintain an internal NH_4^+ level of only $0.1 \mu\text{mole/g FW}$ with an external NH_4^+ level of

88 mM (Mayer et al , 1990) Rates of NaR have been measured to be 4 to 6 and 2 to 3 $\mu\text{mole/g FW/h}$ for barley and corn roots, respectively (Siddiqi et al , 1990) Wellburn (1984) measured NaR and NiR activities in tomato (resistant to NO_2 exposures) as 3.6 to 5.4 $\mu\text{mole/g FW/h}$, respectively Woodin et al (1985) measured NaR as 0.4 $\mu\text{mole/g FW/h}$, yet upon NO_3^- fertilization, that value rose fivefold in less than a day to 2 $\mu\text{mole/g FW/h}$ Thus, it seems that the rate of nitrogen reduction can range from 0.4 to 5 $\mu\text{mole/g FW/h}$, depending on the species and soil fertilizer concentration

Although the emphasis of this chapter is on how the movement of gaseous NO_x affects plant growth, it is important to understand total nitrogen metabolism at the root level The two nitrogen sources can strongly interact with each other First, NO_x and dry deposited nitrogen (acids of nitrogen compounds) can fall upon the ground and be incorporated into the soil where they can be absorbed by the roots With cultivated crops, this is trivial because much more nitrogen is added by the grower as fertilizer In natural regions (e.g., rangelands and forests), soil nitrogen levels are much lower, generally too low to support vigorous growth. Second, soil nitrogen can directly alter the amount of nitrogen metabolism within the shoot and leaves

The absorption of nitrogen from the soil is not strictly proportional to the amount of nitrogen present, but is hyperbolic with amount (Figure 9-7, also see Penning de Vries, 1982) More nitrogen in the soil is not mirrored directly by more nitrogen uptake, except at low levels (see also Chapter 10) Transport, in general, is by carriers or is active, and so its rate can be saturated (see Glass et al , 1990, Siddiqi et al , 1990) Space does not permit a complete discussion, however, detailed reports are given in Durzan and Steward (1983), Haynes (1986), and Goh and Haynes (1986) Many of the past experiments performed on the competition of soil nitrogen and NO_x -derived nitrogen have not made full use of these facts. The soil level is often much too high and the added NO_x causes only small changes in growth or total nitrogen For example, few changes were obtained in bean growth experiments with soil nitrate levels of 10 to 20 mM (Srivastava and Ormrod, 1986)

9.3.2.3 Transport of Nitrogen Species

Weak acids move into cells or organelles by anion transporters or by diffusion of the uncharged acid form through the membrane Weak bases move by the same general

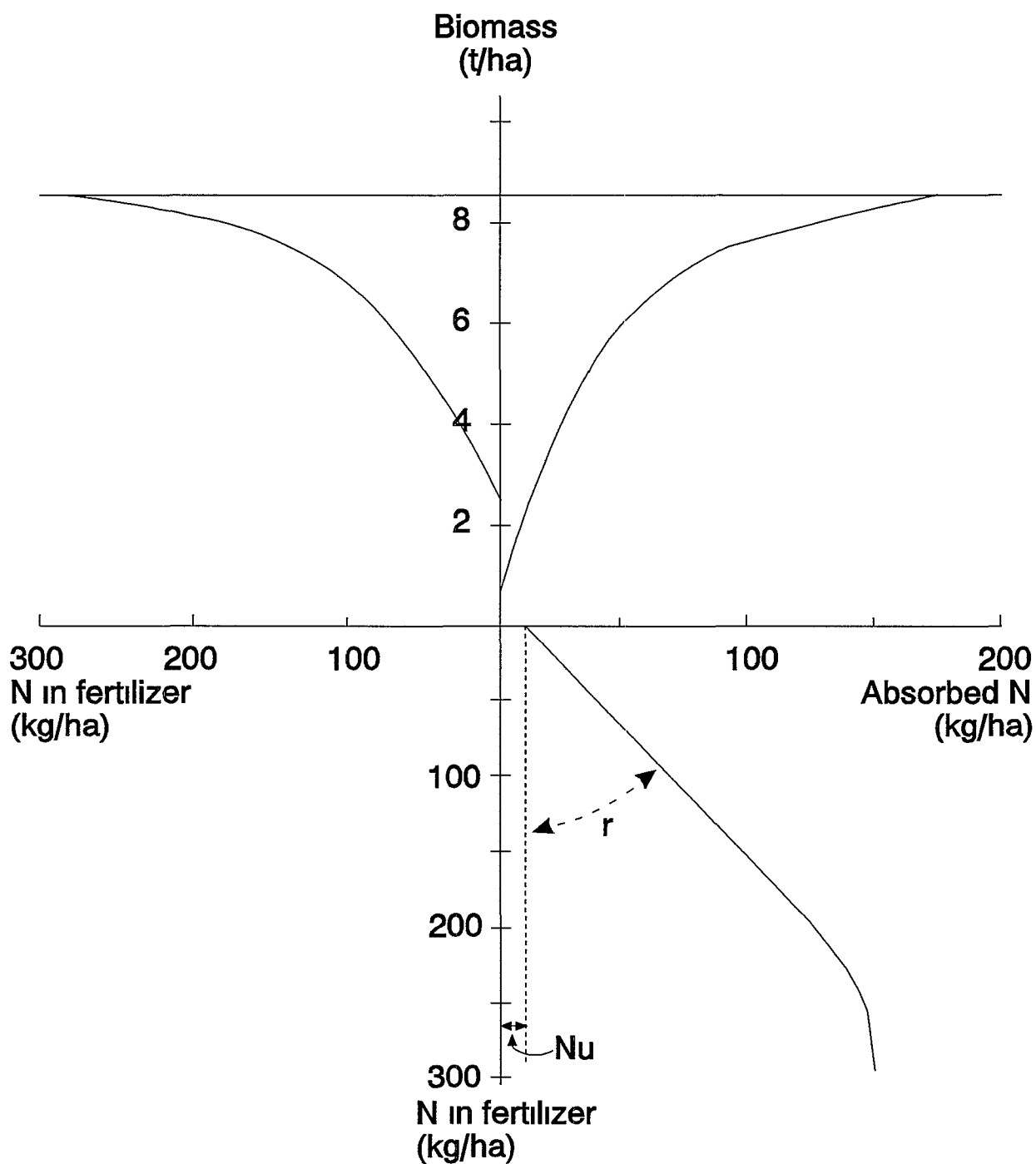


Figure 9-7. The relationship between applied nitrogen, soil nitrogen, and biomass production for a C_4 grass. N_u is the nitrogen absorbed from the unfertilized soil and r is the recovery fraction of the fertilizer nitrogen.

Source Penning de Vries (1982)

mechanisms, using cation transporters or diffusion of the uncharged base form (Figure 9-8) The carrier/transporters use energy to move the ions by either using the ionic gradients of the same-charge species (counter-transport) or the reverse-charge species (co-transport), or using the energy contained in a high-energy phosphate bond (e g , via H^+ -specific ATPase, see Briskin et al , 1987) Uncharged species diffusion is generally less rapid than an energy-driven transport process Under certain pH gradients, however, or if the transporter is lacking, it can be very effective, for example, the uncoupling of chloroplast photophosphorylation by NH_3 (Walker and Crofts, 1970)

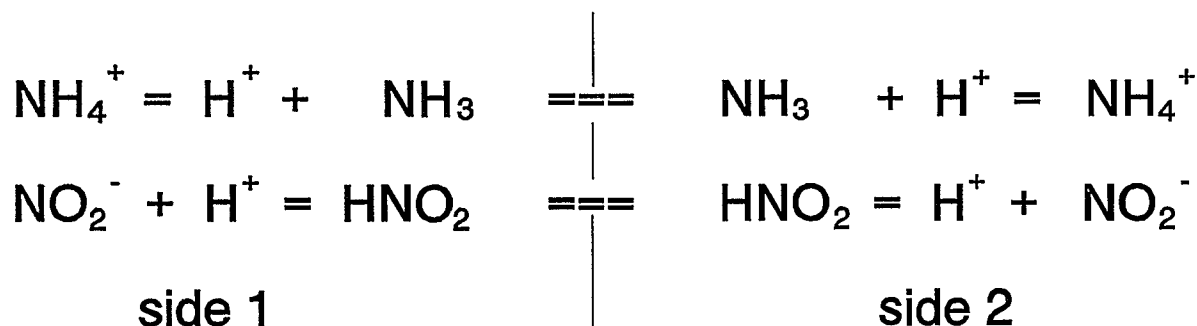


Figure 9-8. Schematic of the distribution of a weak base or acid across a biological membrane. The two sides are indicated across the membrane, represented as a vertical line. The concentration of the uncharged species is the same on both sides. In other words, the diffusion of uncharged species is fast enough to maintain a chemical potential equilibrium.

Source Walker and Crofts (1970)

The formulation of how pH will affect the accumulation of the species has been previously given (Heath and Leech, 1978), but will be repeated here in abbreviated form For the weak acid HNO_2 , the equilibrium condition, $K_a = [H^+][NO_2^-] / [HNO_2]$, exists on both sides of the membrane (sides 1 and 2) The concentration of HNO_2 is the same on both

sides because it is uncharged and can diffuse rapidly through the membrane. Thus, equilibrium means

$$[\text{H}^+]_1 [\text{NO}_2^-]_1 = [\text{H}^+]_2 [\text{NO}_2^-]_2 \quad (9-12)$$

For the weak base NH_3 , the equilibrium condition of $K_b = [\text{H}^+] [\text{NH}_3] / [\text{NH}_4^+]$ likewise holds on both sides of the membrane. Here the concentration of NH_3 is the same on both sides because it is uncharged and can diffuse rapidly (Crofts, 1967). The equilibrium condition then gives rise to

$$[\text{NH}_4^+]_1 [\text{NH}_4^+]_2 = [\text{H}^+]_1 [\text{H}^+]_2 \quad (9-13)$$

For example, the plasma membrane separates a wall region, which is estimated to be at a pH of about 4.3, from the cytoplasm, which is maintained at a pH of about 7. From the above formulas, we can estimate that if the total concentration of $\text{HNO}_2 + \text{NO}_2^-$ within the wall is 1 mM, the concentration of HNO_2 is 91 μM . In the cytoplasm, the concentration of HNO_2 is still only 91 μM (the same as in the wall region). However, in the cytoplasm, the concentration of nitrite will be about 46 mM (500 times larger) due to the unequal pH. The total concentration of nitrite will thus be high, even in the absence of a nitrite carrier.

The same argument can be used for a weak base, however, between the wall/cytoplasm membrane there is no accumulation, but rather an exclusion, of the base. Because the K_a for NH_3 is very basic, little NH_3 exists in the wall region (actually about 5 nM). With the same 1 mM total ammonium species outside in the wall, the concentration of NH_4^+ within the cytoplasm becomes only 5 μM , and so the total is slightly above 5 μM (compared with 1 mM outside). However, as the total ammonium inside rises, the ammonium outside would rise even more rapidly (for 0.5 mM inside, the outside would be nearly 0.5 M), leading to a path for rapid loss of ammonium from the cells.

There seems to exist in the roots a transporter for NH_3 that ensures a steady supply of NH_4^+ internally so that uncharged-species diffusion plays only a small role. This is not the case for chloroplasts, where the NH_3 can easily be accumulated in the grana space, which is

quite acidic relative to the stroma space, there, the high concentration of NH_3 can function as an uncoupler (Walker and Crofts, 1970)

9.3.2.4 Role of Cellular Hydrogen Ion Concentration

The above arguments are critical for understanding how nitrogen species can move through biological organisms. Ammonium can accumulate in spaces of low pH and nitrite can accumulate in spaces of high pH (compared with neighboring spaces). This is not true for strong acids such as HNO_3 , which is completely dissociated to nitrate in biological organisms. Both nitrogen compounds are acids, and their formation can distort normal internal pH if they are present in high concentrations (see Raven, 1988). The actual change in pH depends on their concentration and the buffering capacity of the organelle or tissue space.

For example, NO_x could form about 0.05 N H^+ upon its conversion to nitrate and nitrite at an atmospheric concentration of 0.1 ppm (see above). In a wall of about $0.5 \mu\text{m}$ thickness, this would be $2.5 \times 10^{-9} \text{ equ/cm}^2$ wall. Morvan et al. (1979) measured only about $7.5 \times 10^{10} \text{ equ/cm}^2$ wall H^+ -buffering sites. These unbuffered, accumulated acids would then lower the pH of the wall region. This acidification would tend to loosen the wall and allow the cell to expand in a manner not controlled by the cell (Taiz, 1984, Luethen et al., 1990). Once these acids are inside the cell, their metabolism and conversion to NH_4^+ seems to be a different story.

A largely unproven hypothesis is that the accumulation of NO_2 from the atmosphere with a concurrent conversion into HNO_2 and HNO_3 would change the acidity of the leaf. Raven (1988) has theoretically examined the accumulation of nitrogen from several sources, including ammonium and nitrate from the roots, and ammonium nitrate (dry deposition) and NO_x from the atmosphere into the leaves. He concluded that pH balance by the cell is difficult under many conditions, but that NO_x accumulation leads to an excess in H^+ of only 0.22 mol/mol nitrogen. He argues that uptake of phosphate and sulfur with conversion of ammonium into amino acids interacts to keep this number small. This is not true for NH_3 uptake, which is able to produce a large number of excess H^+ .

Okano and Totsuka (1986) have shown that at 2 ppm NO_2 , the amount of nitrogen accumulated from NO_2 in sunflowers is roughly $7.2 \times 10^{-10} \text{ mol nitrogen/g FW/s}$

Using Raven's number from above, there is about 2.4×10^{-7} N H⁺ produced per second due to the uptake of NO₂. The concentration of organic acids within the vacuole is about 250 mM (Lin et al, 1977), with a buffer capacity of about 140 (change in salt concentration per change in pH [Bull, 1964]). Within the vacuole at pH 4, the rate of H⁺ produced due to the above uptake of NO₂ would have to be maintained constantly for over 1.5 h in order to lower the pH by only 0.3 pH units. This is such a slight disturbance because the nitrogen source is so weak. More research needs to be done with nitrogen-deficient soils and plants to more precisely measure these pH effects. It remains true, however, that any shift in pH in the cytoplasm could alter the rate of formation of several metabolites because many enzymatic reactions are highly sensitive to pH.

9.3.2.5 Reductases

Once formed, nitrate will feed into the general nitrate pool in the leaf, which is derived from the root by transport via the xylem water stream. This xylem water stream, in turn, is driven largely by transpiration through the stomata and, therefore, the stomatal apertures can partially control the movement of nitrate. Nitrate from the xylem is contained within the cell wall and must move into the cytoplasm to be converted to NO₂⁻ by NaR. This enzyme can be rapidly induced to high activity upon exposure to nitrate (Woodin et al, 1985). Typical enzymatic parameters of this reductase are listed in Table 9-3. The reduction of nitrate to nitrite within the cytoplasm is driven by NADH from respiration (and glycolysis). Thus, rapid nitrate reduction would be expected to induce higher respiration rates, which are measured under some circumstances (Aslam et al, 1987, Bloom et al, 1989).

Both atmosphere-derived nitrite and nitrite from the roots add to the cytoplasmic pool, from which nitrite moves into the chloroplast by a presumed carrier molecule. Nitrite would not be expected to move passively into the chloroplast because the internal pH of the chloroplast stroma is higher than that of the cytoplasm (at about pH 8 to 8.5 when the leaf is illuminated, see arguments above). Normally, nitrite is reduced by a six-electron process via photosynthesis. Although the evidence is somewhat contradictory (see Robinson, 1988, Kaiser and Foerster, 1989), the demand for these electrons does not seem to inhibit or slow CO₂ fixation except at high levels of light or low CO₂ levels, where the CO₂ fixation process is nearly saturated (Pace et al, 1990). Typical enzymatic parameters of this reductase are

**TABLE 9-3. ENZYME PARAMETERS FOR CRITICAL ENZYMATIC STEPS
IN PLANT USE OF NITROGEN COMPOUNDS**

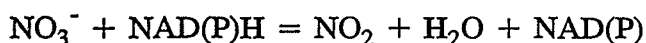
K_m and V_{max} are the Michaelis-Menten parameters for each enzyme system, even though some enzyme systems listed here do not strictly behave according to these kinetics

- A. Nitrate Transporter in Root Membranes.** Kinetic parameters of the enzyme located on the plasma membrane of root cells to transport nitrate ions (NO_3^-) inward (Siddiqi et al , 1990).

$$V_{max} \quad 0.3 \text{ to } 3 \text{ } \mu\text{mol/g FW/h}$$

$$K_m \quad 60 \text{ to } 100 \text{ } \mu\text{M}$$

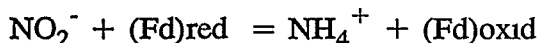
- B. Nitrate Reductase** Molybdenum protein associated with electron transport chain (Hageman and Hucklesby, 1971)



$$V_{max} \quad 3 \text{ to } 5 \text{ } \mu\text{mol/g FW/h}$$

| | $K_m (\mu\text{M})$ |
|-----------------|---------------------|
| NO_3^- | 4,500 |
| NADPH | 15 |
| NADH | 9 |

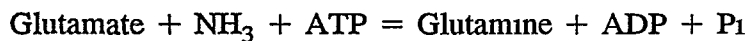
- C. Nitrite Reductase.** Enzyme associated with ferredoxin (Fd) within the photosynthetic electron transport chain (Losada and Paneque, 1971, Wellburn, 1990)



$$V_{max} \quad 3 \text{ to } 5 \text{ } \mu\text{mol/g FW/h}$$

| | $K_m (\mu\text{M})$ |
|-----------------|---------------------|
| Fd | 10 |
| NO_2^- | 100 |

- D. Glutamine Synthetase** Enzyme within plant tissue (Durzan and Steward, 1983)



$$V_{max}: \quad 5.4 \text{ to } 9.9 \text{ } \mu\text{mol/g FW/h}$$

| | $K_m (\mu\text{M})$ |
|---------------|---------------------|
| Glutamate | 3,000-12,000 |
| NH_3 | 10-20 |
| ATP | 100-1,000 |

TABLE 9-3 (cont'd). ENZYME PARAMETERS FOR CRITICAL ENZYMATIC STEPS IN PLANT USE OF NITROGEN COMPOUNDS

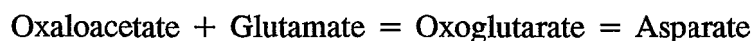
E. Glutamate Synthetase. Mitochondrial enzyme (Durzan and Steward, 1983)



V_{\max} 18 to 36 $\mu\text{mol/g FW/h}$

| | $K_m(\mu\text{M})$ |
|--------------|--------------------|
| Glutamine | 300-1,500 |
| Oxoglutarate | 40-600 |
| NAD(P)H | 7-30 |

F. Amino Transferase. Enzyme system occurring in several organelles of the cell



K_m (acids) = 1 to 40 mM

G. Asparagine Synthetase.



| | $K_m(\text{mM})$ |
|-------------------|------------------|
| Asparate | 0.7-2 |
| Glutamine | 0.1-1 |
| (NH_3) | 2.0-9 |

H. Chloroplast Amino Acid/Organic Acid Transporter. Enzyme located on chloroplast envelope to exchange amino acids and organic acids (Woo et al , 1987)

V_{\max} 80 to 100 $\mu\text{mole/g FW/h}$

also listed in Table 9-3 In darkness, nitrite cannot be reduced and so its concentration can rise to high levels if the rate of nitrate reduction is maintained Taylor (1973) suggested that this was the reason for the production of large amounts of visible injury by NO_x in low light or darkness

Nitrite seems to be regulated to remain at a low level within cells At high levels, nitrite is toxic and could alter the photosynthetic process by altering the pH of the stroma of the chloroplast and so inhibiting normal CO_2 fixation (Brunswick and Cresswell, 1988a,b)

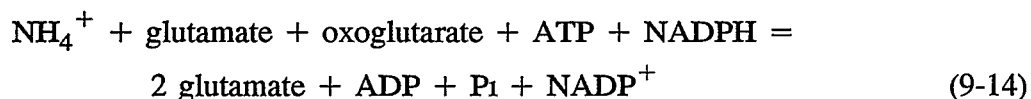
High concentrations of NH_3 are also toxic. Ammonia acts as an uncoupler of photophosphorylation. Thus, a critical limit in concentration must exist for both molecules for normal cells. Although Table 9-3 can give an estimate of what that limit may be by using the K_m of each enzyme system, more experimentation on actual concentrations is needed. For example, the decline in both growth and photosynthesis (nearly 50%) in radish occurs when the level of ammonium within the plant rises above a certain amount after the use of NH_3 as a fertilizer (2,000 ppm, 0.2% of the dry weight, Goyal et al., 1982). Nitrate fertilizer does not cause such a rise in ammonium (200 ppm), nor does it cause a decline in photosynthesis and growth, metabolites derived from nitrate seem to be well regulated under most circumstances.

If nitrate is added to the NH_3 fertilizer (at 10% of ammonium), the level of NH_3 within the plant remains low (200 to 600 ppm), again, nitrate metabolites aid in the regulation of NH_3 levels (Goyal et al., 1982). Under these conditions, the internal concentration of nitrate remains low—at about 500 ppm—for NH_3 fertilizer. However, the internal concentration rises to 14,500 ppm with nitrate fertilizer alone. These numbers reflect the level of nitrate and ammonium within the radish plants best defined as "normal". The internal nitrate level can rise without problems if the ammonium concentration is held low, whereas a rise of the ammonium level induces toxic effects, such as a decline in photosynthesis. These interactions may help to link the apparent toxic effects caused by NO_x exposure to excess accumulation of partially reduced forms of NO_x (see later sections).

9.3.2.6 Amine Metabolism

The metabolic pathway of nitrogen in the chloroplast is summarized in Figure 9-9. Three major sections of the metabolism are apparent: (1) reduction of the oxidized forms of NO_x to ammonium (previously discussed), (2) conversion of free ammonium into an amino group of an amino acid, and (3) movement of that amino acid into proteins or the nitrogen groups of other metabolites (such as polyamines).

The photosynthetic process generates NH_3 that is, as has been noted, closely regulated by the cell (Rhodes et al., 1976). The conversion of ammonium into an amino group keeps the concentration of NH_3 low and is carried out by the glutamate cycle. Coupling the equations shown under D and E in Table 9-3 yields Equation 9-14.



The reducing power comes from photosynthetically produced NADPH. The amine nitrogen on glutamate of this system can be coupled to the conversion of pyruvate to alanine and glycoxylate to glycine (Chapman and Leech, 1979). These amino acids and organic acids can be transported into and out of the chloroplast by specific transporters located on the chloroplast envelope (Woo et al., 1987). The rate of transport seems to be fast enough to move the carbon and nitrogen metabolites into and out of the cytoplasm with little problem, but is limited in its absolute speed. Once in the cytoplasm, the amino group can be used in many ways to form other secondary products and proteins. For a detailed discussion see Pate (1983) and Durzan and Steward (1983).

For the most part, these amine interconversions (Table 9-3) can move the amine group rapidly between the metabolites. There is the possibility, however, of the formation of "bottlenecks" in that movement if the system becomes overloaded with nitrogen (Ito et al., 1984b). The concentrations of metabolites due to any overload should indicate at what point the concentration of external NO_x would become toxic to the plant. Under those conditions, the excess nitrogen supplied by NO_x cannot be incorporated into metabolism without biochemical disruptions.

9.3.3 Chemical and Biochemical Responses

9.3.3.1 Nitrate Reductase Activities

Reduction of nitrate and incorporation of reduced nitrogen into a wide range of compounds is found in nearly all higher plants (Runge, 1983). Because it is substrate induced, the levels of activity of NaR (or NAD(P)H nitrate oxidoreductase, Enzyme Commission number [EC] 1.6.6.2), which catalyses the reduction of nitrate to nitrite (see Figure 9-6), are determined by the supply of nitrate (Beevers and Hageman, 1969). Current evidence favors the concept that the activity of NaR in higher plants is regulated by changes in turnover of enzyme involving fresh synthesis and breakdown (Remmler and Campbell, 1986) rather than activation-inactivation of the original protein. Increases in nitrate supply

cause an increase in the level of NaR mRNA, which correlates with the induction of NaR protein (Cheng et al , 1986, Crawford et al , 1986)

Because NO₂ dissolves in aqueous media, such as the extracellular fluid and cytoplasm, to form both nitrate and nitrite (see Section 9 3 1 above), this gas has often been thought of as a potential source of substrate for NaR. Consequently, effects of NO_x on the levels of activity of NaR have been much studied. Induction of NaR activities by atmospheric NO₂ was first demonstrated by Zeevaart (1974) in peas (*Pisum sativum* L. cv. Rondo) grown only on an ammonium-based medium so that they were initially devoid of NaR activity. When exposed to very high levels of NO₂ (12 ppm) for up to 1 h, rapid induction of NaR activities took place and the first signs of enhanced activity were observed within 10 min from the start of fumigation. In studies of lack of growth of horticultural crops growing in CO₂-enriched greenhouses, where levels of atmospheric NO_x can be very high (see Section 9 3 1 1), Murray and Wellburn (1985) could only find a significant increase in shoot NaR activity in one cultivar (Ailsa Craig) of tomato (*Lycopersicon esculentum* Mill.), but not in another (Eurocross BB) or in two pepper varieties (*Capsicum annum* L. cvs. Bell Boy and Rhumba) exposed to 1.5 ppm NO₂ for 18 h. In these cultivars, no change in any of the shoot NaR levels occurred with 1.5 ppm NO nor did any change occur in the levels of root NaR activities with either gas.

Srivastava and Ormrod (1984) showed that the large increases in shoot NaR activities in *Phaseolus vulgaris* (cv. Kinghorn Wax) were associated with increases in root nitrate supply. These were accentuated by NO₂ fumigation (0.5 ppm for 5 days), but only when the supply of nitrogen to the roots was low (<1 mM). At similar levels of NO₂ (0.3 ppm for 9 days), Rowland et al. (1987) found that barley (*Hordeum vulgare* L. cv. Patty), grown hydroponically with both low (0.01 mM) and adequate (0.1 mM) levels of nitrate in the nutrient solution, also showed significant increases in levels of shoot, but not root, NaR activities. Therefore, between- and within-species differences, as well as the availability of nutrients and developmental age of the tissues involved, determine if NaR levels of activity are significantly affected by atmospheric NO₂.

Rates of entry of NO₂ into leaves, however, depend primarily on the stomatal aperture rather than induced changes in the levels of NaR activity. Using the same hydroponic system as before, Rowland-Bamford et al. (1989) exposed various barley mutants, known to

show deficiencies in their ability to induce NaR activities, to NO_2 (0.3 ppm for 9 days). Fluxes of NO_2 into leaves, net water vapor loss, and stomatal conductances were very similar in both wild-type controls and the mutants, even though the levels of NaR activities in the latter were much reduced in both shoots and roots relative to those in the wild type (cv. Steptoe). Levels of NaR activity in the shoots of this cultivar (Steptoe) behaved differently than those found in the barley cultivar (Patty) used in previous studies (Rowland et al., 1987). When grown on nitrate and exposed to NO_2 , levels of shoot NaR activities in the cultivar Steptoe were reduced (Rowland-Bamford et al., 1989), as were those in the mutants that already had low levels of NaR activity. Only when grown on ammonium did Steptoe behave like Patty (i.e., show enhanced levels of NaR in the presence of NO_2), but root levels of NaR activity were much reduced when either Steptoe or the mutant seedling shoots were exposed to atmospheric NO_2 , irrespective of the source of nitrogen in the hydroponic medium.

Induction of NaR may be abolished by fumigation of squash cotyledons with high levels of NO_2 (Hisamatsu et al., 1988). This effect has been ascribed to an inhibition caused by the accumulation of large amounts of ammonium and certain amino acids known to take place in squash cotyledons during NO_2 fumigation (Takeuchi et al., 1985).

Alteration of nitrogen supply to the roots of many nonwoody plant species is known to change shoot NaR activities (Steer, 1982), but the relative importance of root, as opposed to shoot, reduction of nitrate in conifers may differ from that in angiosperms. Amundson and MacLean (1982) have suggested that several woody species may be particularly sensitive to injury by NO_2 because some species only reduce nitrate in their roots. However, Wingsle et al. (1987), using Scots pine (*Pinus sylvestris* L.) seedlings, have shown a significant increase (15 to 400 μmol nitrite formed/g FW/h) in shoot NaR activities after 7 days of fumigation with 85 ppb NO_2 , but were unable to alter and increase such activities in control seedlings by increasing the amount of nitrate supplied to the roots. Similarly, Norby et al. (1989) were able to detect a threefold increase in shoot NaR activities in 1-year-old red spruce (*Picea rubens* Sarg.) exposed to either NO_2 (75 ppb) or HNO_3 vapor (75 ppb) for just 1 day. Elevated levels of NaR activity persisted for longer after the HNO_3 vapor treatment and older seedlings were slower to react, but spraying the seedlings with acid mist containing nitrate (pH 3.5 and pH 5) had no effect on shoot NaR activities.

9.3.3.2 Nitrite Reductase

Although NaR is located in the cytosol, probably near the cell or plasma membrane, NiR (EC 1.6.6.4) activities in higher plants are confined to plastids (Dalling et al., 1972, Wallsgrove et al., 1979), even in root tissues (Emes and Fowler, 1979). Reduction of nitrite by light to form NH_3 in chloroplasts (see Figure 9-6) is dependent upon six electrons arriving via ferredoxin from the photosynthetic electron transport chain spanning the thylakoids (see Figure 9-6; Losada et al., 1965, Beevers and Hageman, 1969, 1980). When levels of extractable NiR and NaR in pea seedlings subjected to different light, shade, drought, and nitrate treatments are followed, activities of both rise in response to increased nitrate supply (Gupta and Beevers, 1983). However, when plants are exposed to drought or are transferred to darkness, NaR activities decline more rapidly than those of NiR, even though the initial induction by nitrate of NiR is 30 to 40 times higher than that of NaR (Ingle et al., 1966, Joy, 1969). Rao et al. (1981) have suggested that the light-dependent component of this NaR induction is mediated by phytochrome and that induction of NiR by nitrate is an independent process from that of NaR.

This double induction of both NaR and NiR is important when alternative sources of nitrogen, such as nitrite or NO_x pollution, are concerned. Back conversion of nitrite to nitrate in plant tissues has been demonstrated (Aslam et al., 1987), but induction of NaR does not occur until nitrate can be detected in the leaves. Only nitrate can induce NaR, but definitive studies to prove that nitrate alone may induce NiR activities have not been done. Nitric oxide produces both NO_2^- and NO_3^- in aqueous fluids (see Section 9.3.1.2), but the initial rate of appearance of nitrate may be quite slow by comparison to that of nitrite. Thus plants exposed to high proportions of NO could be at risk from elevated nitrite concentrations if additional NiR is not induced in the chloroplasts fast enough, especially if there are ample supplies of nitrate (the accepted inducer) coming from the roots that preset the level of shoot NiR with respect to nitrate.

During CO_2 -enrichment in greenhouses (see Section 9.3.1.1), NO fumigations of different cultivars of tomato (0.4 ppm for 3 h) or lettuce (cv. Pascal, 0.3 ppm for 8 days) induced significant additional levels of NiR activity (Wellburn et al., 1980, Besford and Hand, 1989). In lettuce, the doubling of NiR activity may be accounted for by a significant increase in amount of a 62 kD protein, which reacts with antibodies to NiR (Besford and

Hand, 1989) Nevertheless, there was a considerable difference in the responses of tomato (cv Ailsa Craig) to fumigation with NO (1.5 ppm for 18 h) when the two enzymes NaR and NiR were compared (Murray and Wellburn, 1985) No induction of NaR activities occurred, but those of NiR were more than doubled This has the implication that additional NiR activity may be induced by nitrite rather than nitrate in certain circumstances The pollutant NO, however, has no effect on the basal level of NiR activity in another tomato cultivar, Sonato.

Sweet peppers (*Capsicum annum* L.) respond to NO_x (1.5 ppm of either NO or NO₂ for 18 h) quite differently Levels of activity of NiR in both Bell Boy and Rhumba cultivars of sweet pepper are severely decreased by exposure to either NO or NO₂ and, unlike some cultivars of tomato, levels of NaR activities in pepper are unaffected by NO_x (Murray and Wellburn, 1985) Tomato and pepper also differ in the manner by which their metabolism of nitrogen is regulated (Wallace and Steer, 1983) Such varietal differences are particularly interesting in view of a growth study conducted by Anderson and Mansfield (1979) that demonstrated that NO can affect the growth of different cultivars of tomato to various extents The tomato cultivar most affected by NO (Ailsa Craig) in terms of growth was also the one in which the respective activities of NaR and NiR were affected by fumigations with either NO₂ or NO (Wellburn et al., 1980)

From fumigation studies of spinach and kidney beans with high levels of NO₂ (3.5 to 8 ppm), Yu et al. (1988) concluded that the relative tolerance of spinach over kidney beans was not due to enhanced levels of NiR activity, but to its enhanced ability to metabolize nitrite using existing levels of NiR They ascribed the growth reduction that did occur with spinach when exposed to NO₂ in the light as being mainly due to an accumulation of NH₃ rather than of nitrite

When Yoneyama et al. (1979a) exposed kidney bean (cv Shin Edogawa), sunflower (cv. Russian Mammoth), and maize (cv Dento) plants to 4 ppm NO₂ either during the day or at night for up to 6 h, levels of NiR activity were increased in all cases, but the rate of stimulation varied between species Although enzyme activities from sunflower leaves reacted rapidly to the presence of the gas, enzyme activity in maize increased slowly and to a lesser extent overall Darkness accentuated these differences Unfortunately, no allowance was made for possible natural diurnal rhythms of enzymic activity, which occurs, for

example, with levels of NaR activities (Deng et al , 1990) This is an important consideration and many studies using NO_x fumigation neglect this natural phenomenon It is highly likely that sensitivity of plants to atmospheric pollutants like NO_x shows a diurnal rhythmicity—a possibility never investigated and often ignored

9.3.3.3 Glutamate Formation and Conversion

In higher plants, NH₃ released by NiR is incorporated into glutamate by means of the glutamine synthetase (GS, EC 6 3 1 2)/glutamine oxoglutarate aminotransferase or glutamate synthase (GOGAT, EC 2 6 1 53) cycle (see Figures 9-6 and 9-10) rather than by amination achieved using glutamate dehydrogenase (GDH, EC 1 4 1 3, Lea and Mifflin, 1974, Mifflin and Lea, 1976) Activities of both enzymes of the GS/GOGAT cycle have been detected in chloroplasts, but GS activity also occurs in the cytosol (Emes and Fowler, 1979) Activity of GDH, by contrast, is confined to mitochondria (Mifflin, 1970)

Kidney beans (cv Kinghorn Wax) exposed to 0.02 to 0.5 ppm NO₂ for 5 days show increased levels of GOGAT activity (Srivastava and Ormrod, 1984), and levels of related transaminase activities were raised in a sensitive tomato cultivar (Ailsa Craig) when exposed for 14 days to 0.2 to 0.5 ppm NO (Wellburn et al , 1980) Levels of GDH were also increased by this treatment, but the higher constitutive levels of GS were unaffected Peas (*Pisum sativum* L cv Feltham First), by contrast, showed no changes in levels of GDH activities when exposed to 0.1 to 0.5 ppm NO₂ for 6 days, although this enzyme is strongly affected by similar SO₂, NH₃, SO₂ + NH₃, and SO₂ + NO₂ fumigations (Wellburn et al , 1976)

It is presumed that GDH operates in a deaminative mode during periods of excess reduced nitrogen formation after exposure to atmospheric NO_x, whereas the GS/GOGAT cycle (Figure 9-10) remains responsible for glutamate formation under these conditions One way to follow such changes is to measure the ratios of GDH to GS activities because this removes the bases of expression When studying the effects of lower levels of atmospheric NO₂ (0.25 ppm for 63 days) on several clones and cultivars of the grass *Lolium perenne* L using this method, a significant increase in GDH activities occurred, even though the measured GS activities were still approximately fifty times those of GDH (Wellburn et al , 1981) In other words, the noninduced conversion of NH₃ to glutamate by GS (and

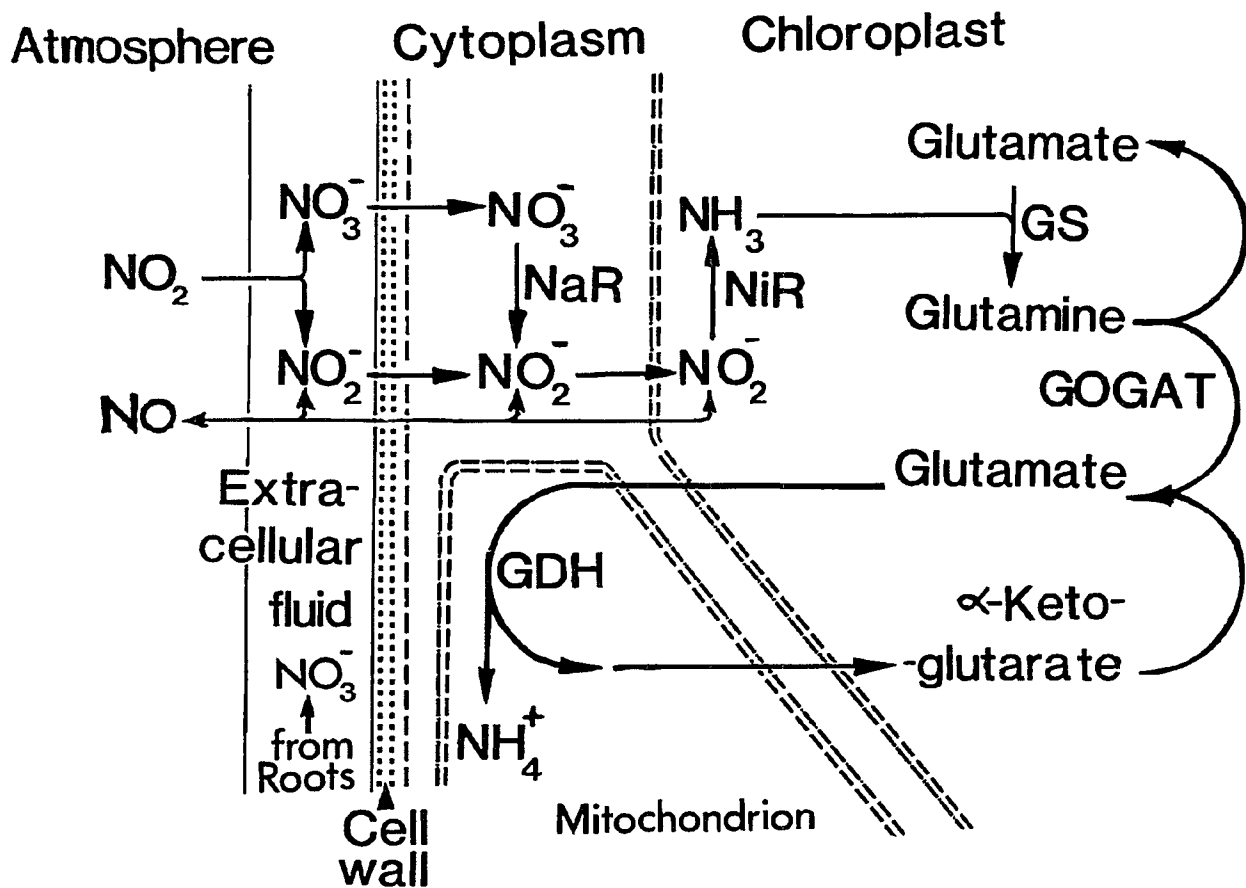


Figure 9-10. The possible interconversions between glutamate, glutamine, and α -ketoglutarate that involve the uptake and release of ammonia in plants. The mitochondrial enzyme glutamate dehydrogenase is much more likely to catalyze the deamination of glutamate in the light.

Source Wellburn (1988)

GOGAT) in the plastids always predominates, but a pathway catalyzed by GDH to remove excess glutamate from NO_x -treated tissues appears in the cytoplasm of exposed cells

When crude extracts from spinach (cv New Asia) were treated with nitrite (5 mM), either in the light or in the dark, levels of GS and GOGAT activities were reduced by 26 and 55%, respectively (Yu et al , 1988) However, at levels of 25 mM nitrite, GS and GOGAT activities were inhibited by 87% in the light and 57% in the dark Yu et al (1988) concluded that part of the toxicity ascribed to nitrite in these circumstances could be due to a

failure of the GS/GOGAT cycle to remove NH_3 fast enough. This then permits uncoupling reactions to take place (see Section 9.3.2.6), which then impairs ATP formation.

9.3.3.4 Fluxes of Amino Acids

A frequent response of plants to NO_x is an increase in leaf amino acid content (Prasad and Rao, 1980, Ito et al., 1984b, 1986, Takeuchi et al., 1985, Rowland, 1986). Even increases in root amino acid content due to NO_2 fumigations have been detected (Rowland, 1986). Nevertheless, increased amino acid content is only a reflection of many interrelated processes—protein or amino acid biosynthesis and degradation, enhanced nitrate assimilation, or reduced elimination of organic nitrogen.

Reports of changes in individual amino acids due to NO_x exposure are contradictory. Takeuchi et al. (1985), for example, reported increases of glutamate in squash, whereas Ito et al. (1986), using beans (*Phaseolus vulgaris* L. cv. Shin Edogawa), detected the reverse. Similar examples can be quoted for both aspartate and arginine. In angiosperms, however, there does appear to be agreement over increases of asparagine and glutamine in response to NO_x (e.g., Prasad and Rao, 1980, Ito et al., 1984b, 1986).

Studies on conifers show the reverse. Levels of glutamine and arginine, an important nitrogen storage compound for species like Scots pine, are much reduced by NO_2 fumigation (85 ppb for 10 days, Wingsle et al., 1987). These reductions mainly account for the marked reduction in total amino acids in these trees—another disparity with the angiosperm literature.

9.3.3.5 Effects of Ammonia

Localized sources of NH_3 , such as animal stockyards and ammonium nitrate fertilizer plants, may have adverse effects on crops and conifers, but other emissions from livestock, such as higher amines or hydrogen sulfide, can add to the effect (Van der Eerden, 1982). Ammonia-affected conifers are usually prone to frost injury (see Section 10.4.4), but reductions in crop growth are not always accompanied by visible injury. Symptoms of injury are necrosis on older leaves or needles and are often specific. For example, black spots occur on the backs of cauliflower and Brussels sprout leaves (Van der Eerden, 1982).

Little research has been done to identify the specific biochemical and physiological consequences to plants of external sources of NH_3 , which produce extra NH_4^+ inside a

plant. The inhibitory effects of NH_4^+ acting as an uncoupler of phosphorylation in both mitochondria and chloroplasts have long been known. In chloroplasts, this effect of NH_3 is highly dependent on both light and pH (Walker and Crofts, 1970). Losada and Arnon (1963) used ammonium levels of 1 mM, equivalent to a dry weight content of $150 \mu\text{g/g}$, to inhibit photophosphorylation. Such levels are frequently found in NH_3 -damaged plant tissues. Moreover, tomato plants (cv. Moneymaker) exposed to 2.86 ppm NH_3 are only injured in the dark when large amounts of ammonium ($200 \mu\text{g/g d wt}$) accumulate in the plants (Van der Eerden, 1982). In the light, however, this injury does not occur because NH_3 is immediately converted to glutamine and asparagine, levels of which rise sharply if temperatures and carbohydrate contents are not limiting. This fact could explain the extreme sensitivity of conifers to NH_3 during the winter.

9.3.4 Physiological Responses

Although the sections below concentrate on the effects of NO_x alone, a recent review (Darrall, 1989) has already considered many of the important physiological interactions between NO_x and other common air pollutants (see Section 9.6). In terms of stomatal responses and changes to root:shoot ratios, almost all the relevant studies have been done with mixtures of NO_x , SO_2 , and/or O_3 rather than NO_x alone.

9.3.4.1 Dark Respiration

Srivastava et al. (1975a,b) showed that dark respiration in kidney beans (cv. Pure Gold Wax) was more depressed by high levels of NO_2 (1 to 7 ppm for 4 to 8 h) than photosynthesis at certain stages of the growth. Moreover, this apparent inhibition could not be reversed quickly by removing NO_2 from the fumigation stream, which implies product buildup. However, exposure of Scots pine to atmospheric NO_2 (0.5 ppm) for 2 days (Oleksyn, 1984) or fumigation of various mature ornamental pot plants in CO_2 -enriched atmospheres containing NO_x (1 ppm NO or NO_2) for 4 days (Saxe, 1986a,b) failed to show any inhibitory effects on dark respiration. In the latter studies, NO_2 fumigations even showed slight stimulatory effects. Carlson (1983), however, did find an inhibition of dark respiration in soybean, but only at the highest levels of NO_2 employed (0.6 ppm for 2 to 3 h). By contrast, Sabaratnam et al. (1988b), also using soybeans (cv. Williams), found that

treatment with 0.2 ppm NO₂ for 7 h/day for 5 days increased dark respiration by 13% immediately and by 46% after the fumigation had been stopped. Similarly, exposure of black turtle beans (*Phaseolus vulgaris* L. cv. Domino) to 0.1 ppm NO₂ (7 h/day for 15 days) enhanced dark respiration during fumigation, but this effect disappeared after the exposure ended (Sandhu and Gupta, 1989).

On balance, therefore, it must be concluded that it is unlikely that NO_x pollution at realistic levels has a primary effect on dark respiration. Nevertheless, secondary effects elicited by altered amino acid patterns or changes in levels of ammonium, nitrite, etc. may well take place and have an effect on mitochondrial enzymes and levels of ATP (Matsumoto et al., 1971; Matsumoto and Wakiuchi, 1974).

9.3.4.2 Effects on Photosynthesis

Two types of experiment have been used to investigate the effects of atmospheric NO_x on photosynthetic reactions: those using techniques capable of monitoring these reactions *in vivo* using intact plants and those performed *in vitro* with extracts of plant tissue. The latter usually involve isolated chloroplasts or thylakoid membranes and examine the effects of the products of atmospheric NO_x, such as nitrate and nitrite, on these suspensions.

A good example of the *in vivo* approach, and probably the most important and informative, has been to follow changes in the rates of uptake and release of CO₂ using infrared gas analysis (IRGA) in the light and in the dark in order to provide estimates of net photosynthesis. Using IRGA, Hill and Bennett (1970) showed that both NO and NO₂ (up to 10 ppm for 2 h) inhibited net photosynthesis in intact leaves of oats (*Avena sativa* L. cv. Park) and alfalfa (*Medicago sativa* L. cv. Ranger). During 90-min fumigations, they found that the minimum concentrations to produce inhibition were 0.6 ppm for each of these two gases, which are well below those required to produce visible injury in each. Furthermore, they found that inhibition was faster with NO than with NO₂ and was reversible. Mixed fumigations with both NO and NO₂ were found to produce the same amount of inhibition as the sum of that produced by each pollutant alone (Hill and Bennett, 1970), but in subsequent studies, the same group (White et al., 1974) failed to observe a depression of net photosynthesis in alfalfa from exposures to mixtures of NO_x (0.25 to 0.4 ppm NO₂ and 0.1 to 0.15 ppm NO for 1 to 2 h).

During their various studies of the rapidity by which various pollutants inhibit photosynthesis, Bennett and Hill (1973) concluded that NO caused the fastest response, followed in turn by NO₂, SO₂, O₃, and HF. However, after a 2-h exposure in each case, this order was reversed if the overall depressions of net photosynthesis were compared.

Subsequent reports using IRGA are also contradictory. Srivastava et al (1975a,b), for example, concluded that their observed decrease in net photosynthesis was related to NO₂ concentration and length of exposure, even though they used high concentrations of NO₂ (1 to 7 ppm for up to 5 h) on beans (*Phaseolus vulgaris* L. cv. Pure Gold Wax). Meanwhile, Bull and Mansfield (1974) had found a similar effect of NO₂ on peas (*Pisum sativum* L. cv. Feltham First), but at much lower concentrations (0.05 to 0.25 ppm) for longer exposures (28 days). Subsequently, Capron and Mansfield (1976) exposed tomato plants (*Lycopersicon esculentum* Mill. cv. Moneymaker) to mixtures of NO and NO₂ (0.10 to 0.50 ppm each for 20 h) and found an additive effect of the two gases on the inhibition of net photosynthesis. Similarly, Bruggink et al (1988) found a 38% reduction in net photosynthesis of tomato (cv. Abunda) exposed to 1 ppm NO at 350 ppm CO₂ on the third day of exposure, but rather less (24% reduction) at 1,000 ppm CO₂. Both these reductions in photosynthesis could not be explained by increases in stomatal resistance.

By contrast, Carlson (1983) fumigated soybeans (*Glycine max* Merr.) with NO₂ (0.2 to 0.6 ppm for 2 to 3 h) and was less convinced that NO₂ had a significant effect on net photosynthesis measured by IRGA, although he did find evidence for a reduction in photorespiration with increasing NO₂ concentrations. Likewise, Oleksyn (1984) did not find any effect of NO₂ (0.5 to 1 ppm) on net photosynthesis during a 2-day exposure of Scots pine seedlings. Saxe (1986a), however, showed that reductions in net photosynthesis in eight cultivars of five genera (*Ficus*, *Hedera*, *Hibiscus*, *Dieffenbachia*, and *Nephrolepis*) took place at a lower dose of NO (1 ppm for 12 h) than those required to reduce transpiration (4 ppm for 5 h). He also showed that the toxicity of NO towards net photosynthesis was 22 times that of NO₂. Like Hill and Bennett (1970) and Srivastava et al (1975a,b), he concludes that the main effects of NO_x are on mesophyll cells rather than guard cells. He also maintained that only a proportion of the NO effect could be attributed to the stomata and that the mechanism of NO toxicity is different from that of NO₂.

It is now evident that different levels of NO₂ can bring about both increases and decreases in net photosynthesis within the same species. Sabaratnam et al (1988a) found that low levels of NO₂ (0.2 ppm, 7 h/day for 5 days) increased net photosynthesis in soybean (*Glycine max* Merr cv Williams) at the onset of fumigation and 24 h after fumigation ceased. However, reductions in net photosynthesis are observed at higher levels of NO₂ (0.5 ppm) under the same exposure conditions. These researchers also used the techniques of growth analysis on the same experimental material. They found that the increase in leaf area ratio (LAR) of 42% brought about by exposure to 0.5 ppm NO₂ was insufficient to compensate for the large decrease (51%) in the net assimilation ratio (NAR), which caused a decline in relative growth rate (RGR). These observations are similar to those made by Okano et al (1985b) after they fumigated sunflowers (cv Russian Mammoth) and maize (cv Dento) with a range of NO₂ concentrations (up to 1 ppm) for 14 days. At levels of 0.2 ppm, NAR was significantly raised (10%), but at 0.5 ppm NO₂, NAR was reduced to a similar extent. These changes in NAR could be accounted for by changes in LAR. The NAR and RGR also increased when black turtle beans (cv Domino) were exposed to 0.1 ppm NO₂ (7 h/day) for 15 days (Sandhu and Gupta, 1989), but the LAR was unaffected.

Assimilation rates of carbon-13 (¹³C)-labeled CO₂ (¹³CO₂) determined by ¹³C-nuclear magnetic resonance spectroscopy are not in accord with the majority of IRGA studies of the effects of NO₂ on net photosynthesis. This is partly explained by the fact that this technique measures only unidirectional uptake of CO₂, whereas IRGA measures bidirectional flow of CO₂. Exposure of kidney beans (cv Shin Edogawa) to 2 ppm NO₂ for 4 days enhanced ¹³CO₂ fixation by 18% in the primary leaves and 39% in the first trifoliate leaves (Okano et al, 1985a). However, shorter exposures (10 min) of similar plants to equivalent levels of NO₂ had no effect on ¹³CO₂ uptake, but there was a significant increase in the pool sizes of sucrose and fructose (Ito et al, 1985a), which indicates changes in translocation. Meanwhile, large differences were noted in the fluxes of label between amino acids such as glycine and serine, which are key metabolites during photorespiration, demonstrating that recycling of label was taking place.

Studies of the effects of NO₂ alone on carbon allocation are rare. Amounts of soluble sugars, especially glucose, in kidney beans (cv Shin Edogawa) exposed to high levels of NO₂ (2 to 4 ppm for 7 days) were significantly decreased in the roots by 4 ppm NO₂,

implying reduced translocation, but soluble sugar content in leaves fluctuated markedly with no clear trend (Ito et al , 1985b) In these studies, reductions in root sugar content correlated with reduced root dry weight It might be expected that decreased sugar content might account for reductions in root respiration Ito et al (1985b) did find decreased root respiration, but it required the full 7 days of exposure at 2 ppm NO₂ for this to occur

Another noninvasive technique that is able to determine rates of photosynthesis exploits relative changes in chlorophyll fluorescence When a dark-adapted plant is illuminated, chlorophyll molecules fluoresce *in vivo*, and the intensity of this prompt fluorescence varies with time in a characteristic manner Consequently, effects of environmental stress on photosynthetic reactions have been studied *in vivo* by monitoring the change in fluorescence with time. Changes in the patterns of *in vivo* fluorescence in response to chilling injury (Melcarek and Brown, 1977), O₃ (Schreiber et al , 1978), and heavy metals (Arndt, 1974, Homer et al , 1980) have all been reported

Exposure of tomato or sweet pepper to 1.5 ppm NO₂ for up to 4 days had virtually no effect on either the pattern of induction or the peak values of emitted fluorescence (Murray, 1984a). However, Shimazaki (1988) has been able to demonstrate an effect of NO₂ on chlorophyll fluorescence induction using radish plants, but only using high levels of pollutant (4 ppm) while fumigating in the dark When chloroplasts were subsequently isolated from these plants, no effects on their photochemical activities could be detected By contrast, exposure to both nitrite and nitrate can affect the fluorescence yield from algal cells (Kessler and Zumft, 1973, Serrano et al , 1981), but prior treatment of such cells using sonication or Triton X is required before any effect may be detected with nitrate (Serrano et al , 1981) Nitrite treatments, however, do not need this denaturation before showing such an effect Moreover, the effect of nitrite under these circumstances is concentration dependent

Discrepancies between individual *in vivo* studies of NO_x effects on net photosynthesis and on dark respiration (Section 9.3.4.1) lead to the general conclusion that, in many instances, investigators have been dealing with different exposure conditions and with situations where different levels of NO₂ can produce opposing effects It is now clear that many studies claiming to have fumigated just with NO₂ may have also contained NO, but, worse than that, many control treatments that have used activated charcoal to clean the air may have still left significant levels of NO (see Section 9.2.2.1) In many instances, when

the levels of NO_2 used were relatively high, little or no comment has been made on the parallel levels of NO . Where NO has been specifically identified, the inhibitory effects described are more pronounced. For example, fumigation of lettuce (*Lactuca sativa* L cv Ambassador) growing at high CO_2 (950 ppm) with 2 ppm NO and 0.5 ppm NO_2 reduced net photosynthesis by 15 to 20% within 30 min (Caporn, 1989).

As discussed elsewhere (Section 9.3.1.2), the major product of NO_2 in solution is nitrate, which rises quite markedly within cells with little consequence. However, both NO and NO_2 produce nitrite in solution, which may be highly toxic. Consequently, any explanations of *in vivo* changes, using experimental evidence derived from parallel *in vitro* studies involving separated systems, concentrate on the specific effects of nitrite rather than nitrate within chloroplasts, especially as the plastids are also the sites of N₂R activity (see Section 9.3.3.2).

Nitrite uptake into plastids is profoundly affected by darkness, temperature, and the level of nitrate ions (Brunswick and Cresswell, 1988a), as well as the stromal pH, the rate of nitrite reduction, and the internal levels of plastidic nitrite. It now appears that there is a specific protein carrier system on the inner chloroplast envelope to allow uptake of nitrite, which is distinct from that of the phosphate or sulfate translocators (Brunswick and Cresswell, 1988b). Consequently, nitrite can enter chloroplasts and act as an indirect proton pump across the plastid envelopes (Heber and Purczeld, 1978). This inward movement of acidity has an effect on both stromal pH levels and trans-thylakoid proton gradients. A reduction in stromal pH, for example, may affect the reactions of the Calvin cycle because the activity of enzymes like ribulose-1,5-bis-phosphate carboxylase/oxygenase is pH-dependent (Heldt et al., 1986). Purczeld et al. (1978) have shown that adding nitrite to a suspension of spinach chloroplasts causes a reduction of the stromal pH, which then inhibits the fixation of CO_2 .

Unlike NH_4^+ (see Section 9.3.3.5), nitrite has no inhibitory effect on *in vitro* determinations of the rates of phosphorylation (Asada et al., 1968), which implies that both nitrite and NH_3 levels are tightly controlled if the influx of nitrogen is slow enough. However, a possible site of action for nitrite within thylakoid membranes has been demonstrated. Using ESR spectroscopy to monitor the release of manganese from the water-splitting complex in a preparation of pepper chloroplast thylakoids before and after the

addition of 2.0 mmoles of nitrite (0.02 mM final concentration), Wellburn (1984) found that nitrite enhanced the release of bound manganese from thylakoids and suggested the involvement of free radical events in this response similar to those predicted by Mudd (1982).

As mentioned elsewhere (Section 9.3.1.2), acidification processes are also thought to be important factors in the toxicity of nitrite. Robinson and Wellburn (1983), using red-light-induced quenching of 9-amino-acridine (9-AA) fluorescence, have shown that high concentrations of nitrite around 0.5 mM can reduce the pH gradient across the thylakoid membranes of oats (*Avena sativa* L. cv. Pinto). The mechanism of this effect is still uncertain, but it is probable that a free radical mechanism is involved because there are many similarities between the effects of O₃ alone and the combined effects of nitrite and sulfite (Robinson and Wellburn, 1983), which could arise from mixed exposures to SO₂ and NO_x (see Section 9.6).

This similarity in response between O₃ alone and mixtures of SO₂ and NO_x has been known for some time (Reinert et al., 1975). Furthermore, mixed fumigations of peas (cv. Waverex) with either O₃ alone (0.15 ppm) or with SO₂ + NO₂ + O₃ (0.05 ppm each) for 21 days enhanced the levels of activity of ascorbate peroxidase and glutathione reductase (Mehlhorn et al., 1987), both of which are involved in free radical scavenging. Similarly, when wheat (*Triticum aestivum* L. cv. RR21) was grown for 80 days in atmospheres containing NO₂ (1 ppm, 2 h/day), significant reductions (17%) in ascorbate levels were detected (Prasad and Rao, 1980).

Wellburn (1985) fumigated barley (cv. Patty) seedlings for 1 to 3 days with NO₂ (0.28 ppm) and measured the levels of nitrite and nitrate inside the chloroplasts using HPIC. Levels of nitrate inside the plastids actually fell by 45% (to 1.2 mM) on the second day before rising back to the clean-air control levels, while levels of nitrite rose from 0.1 mM to 0.15 mM before falling back over the same period. Unfortunately, similar experiments have not been conducted using NO as a fumigant gas. In response to increases of 0.5 mM nitrite, Robinson and Wellburn (1983) detected reductions of trans-thylakoid proton gradients of about a whole pH unit using preparations of oat chloroplasts. This would imply severely impaired abilities of the photosynthetic membranes to sustain ATP formation. Reductions in stromal pH and changes in levels of NADPH, ATP, triose phosphates, and orthophosphate

are well known to reduce carbon fixation (Bassham, 1971, Heldt et al , 1986) In a wider context, therefore, reduced availability of ATP for synthesis of starch, amino acids, protein, etc will also limit growth, repair, and other physiological processes

Another implication of elevated nitrite levels inside chloroplasts is the possibility that reduction of nitrite may take preference over the reduction of NADP⁺ and fixation of CO₂ (Thomas et al , 1976, Larsson et al , 1985) At levels of 0.5 mM nitrite, CO₂ fixation is reduced by as much as 50% because NADP⁺ fails to compete with nitrite for electrons coming through the photosynthetic electron transport chain from water (Magalhaes et al , 1974) Robinson (1986, 1988), however, claims that CO₂ and nitrite do not compete for reductant at saturating light intensities In an attempt to resolve these inconsistencies, Pearson and Elliott (1988) have examined the effect of bicarbonate on the nitrite utilization/concentration interrelationships at the whole plant level They conclude that, although there are differences between species, fixation of CO₂ and reduction of nitrite only compete at low light levels and high nitrite concentrations But these are the very conditions that may prevail in plants exposed to atmospheric NO_x in northern latitudes Consequently, this competition for reductant may be a very important component in any physiological explanation of lack of growth caused by NO_x

9.3.4.3 Root Physiology

Conditions around the root may also be involved in determining the response of a plant to NO_x (Anderson and Mansfield, 1979, Mansfield and Murray, 1984) Normally, roots provide all the nitrogen requirements of the shoots and any changes in the metabolism of nitrate by roots in response to NO_x is likely to determine the overall nitrogen balance of plants More than one possible pathway exists in leaves for the absorption of nitrogen from NO₂ (see Section 9.3.1.5)

Amounts entering through the roots by an air-soil-root pathway, although small, are not insignificant Tracer experiments using ¹⁵NO₂ have shown uptake by roots after NO₂ has been absorbed into the soil, as well as direct incorporation through the leaves (Yoneyama et al , 1980a,b, see also Section 9.3.1.4) Any atmospheric NO₂ absorbed by the soil is likely to be converted to nitrate and nitrite by soil microorganisms (see Section 10.1.3) Yoneyama et al (1979b) found that although nitrite only accumulates in the upper soil layer,

increases in NH_3 also occur in soils exposed to NO_2 . It appears that soil water content is an important factor in determining the presence of these ions. Spierings (1971) found increases in nitrate concentration in soil that had been fumigated with 0.25 ppm NO_2 for 45 days. Some nitrogen derived from NO_2 can therefore be taken up by roots and metabolized into plant constituents, but this process takes longer.

At high concentrations of $^{15}\text{NO}_2$ (4.8 ppm), amounts of ^{15}N taken up by roots via the soil are insignificant when compared to direct incorporation through the leaves over periods of an hour (Yoneyama et al., 1980a,d). However, over a week after the $^{15}\text{NO}_2$ fumigation had been terminated, up to 54% of the labeled NO_2 eventually entered through the roots. Therefore, the soil route may only be important under long-term exposures. Similarly, investigations involving solution culture of plants have shown that an indirect route via the roots under these conditions could involve a very substantial input of nitrogen derived from NO_2 . As might have been expected, there was a dramatic increase in nitrate concentration in a recirculating hydroponic system over 24 h due to exposure of the solutions to 0.3 ppm NO_2 (Rowland, 1985). There may be similar implications for irrigated crops.

Only one study has been made of the effect of NO_2 on the nodulation of legumes. Srivastava and Ormrod (1986) exposed 8-day-old kidney beans (cv. Kinghorn Wax) seedlings to various levels of NO_2 (0.02 to 0.5 ppm, 6 h/day for 15 days). They found exposure to atmospheric NO_2 increased the levels of nitrogen in the roots, but decreased nodule weight and levels of nitrogenase activity. This is what would have been predicted if more nitrogen, as a proportion of total nitrogen, is taken up by the leaves as NO_x because high root nitrogen inhibits nodulation.

9.3.5 Tissue and Organ Responses

9.3.5.1 Lipid and Membrane Effects

Plants exposed to high concentrations of NO_2 usually show a characteristic water-soaked appearance before necrosis takes place (see Van Haut and Stratmann, 1967). From similar observations, Berge (1963) concluded that NO_2 causes cellular plasmolysis due to the breakdown of lipids in membranes. Unsaturated lipids in monolayers readily bind molecules like NO_2 (Felmeister et al., 1970), and direct peroxidation of fatty acids as a consequence of this attached NO_2 has been studied extensively (Estefan et al., 1970, Roehm

et al , 1971a, Rowlands and Gause, 1971, Pryor and Lightsey, 1981) Two types of reactions take place within fatty acids Attachment of the NO₂ to a double bond may cause a *cis* to *trans* isomerization or it may cause the removal of hydrogen from methylene groups Both processes may initiate lipid peroxidation, as well as changes in the surface properties of monolayers The question then arises Could similar detrimental changes take place in membranes of plants exposed to realistic levels of NO₂? Mudd et al (1984) concluded that the ambient levels of NO₂ are much too low to have such effects

Ambient levels of O₃, rather than those of NO₂, are far more likely to initiate peroxidation of lipids within membrane systems (Roehm et al , 1971b) but it is not certain if the proteins or lipids of membranes are oxidized preferentially Mudd et al (1984) discussed both possibilities and cited studies involving proteins that favored the idea that attack by O₃ occurs more readily on proteins Clearly, this whole field should be reexamined and such studies should include mixed effects of NO₂, NO, and O₃ upon membranes because a photodynamic equilibrium exists naturally in the atmosphere (Section 9 3 1 1) and some previous O₃ exposures may have inadvertently included various mixtures of NO and NO₂ (Section 9 2 2)

There are strong indications that atmospheric NO₂ inhibits lipid biosynthesis rather than causing damage to existing lipids in membranes Fumigation of jack pine (*Pinus banksiana* LAM) seedlings with 2 ppm for 2 days inhibited the biosynthesis of phospholipids and galactolipids (Malhotra and Khan, 1984), and high levels of nitrite (25 mM) exert a similar effect in *Chlorella pyrenoidosa* (Yung and Mudd, 1966) Inhibition of the latter is greater in the dark than in the light, possibly because adequate amounts of NADPH are not available at night

9.3.5.2 Changes Inside Cells and Tissues

The amount of damage suffered by a plant varies in its severity according to various factors, such as concentration and length of exposure, plant age, edaphic factors, light, humidity, etc Symptoms are often divided into "invisible" (or hidden) injury and "visible" (obvious) injury In the former, there is an overall reduction in growth, but no obvious symptom of visible injury It is often associated with decreases in transpiration and

photosynthesis (see Section 9.3.4.2) but a variety of ultrastructural changes have also been associated with invisible air pollution injury (Huttunen and Soikkeli, 1984, Fink, 1988)

In a specific ultrastructural study of atmospheric NO_x on plants, Lopata and Ullrich (1975) found tubular protrusions from the plastid envelope closely associated with mitochondria. This ultrastructural feature can also be induced by imperfect fixation (Wellburn, 1982a). So, like many other aspects of these studies of cellular pathology, not a great deal of useful information on the specific effects of atmospheric NO_x , or any other type of air pollutant, can be gained from the use of the conventional transmission electron microscope.

Most plants appear able to tolerate an accumulation of nitrate, even though this may be undesirable if they subsequently form a part of the human diet (Roberts et al., 1983). An accumulation of nitrites, however, can have serious toxic effects on plants. As already described (Section 9.3.1.7), an accumulation of nitrite is sometimes detected when plants are exposed to NO_2 (Zeevaart, 1976, Yoneyama et al., 1979a), but not always (Spierings, 1971). No direct evidence exists to prove that the nitrite ion itself is toxic to plants (Heber and Purczeld, 1978; Lee, 1978), but a number of investigators have concluded that it is the acidification that accompanies the accumulation of nitrite that accounts for the toxicity (Bingham et al., 1954, Zeevaart, 1976, Lee, 1978). Nitrite ions are reduced inside the chloroplast (Section 9.3.3.2) and, therefore, all pollutant-derived nitrogen is likely to enter the chloroplast eventually. Although possible reactions between nitrite and cellular constituents during the passage of the ion into the chloroplast must not be overlooked, interest in the toxic reactions of high levels of NO_x has concentrated upon the chloroplast and especially on the photosynthetic reactions. Some of these have been discussed already (Section 9.3.4.2).

Zeevaart (1976) concluded that acidification will only damage plants at high concentrations of NO_2 because NiR requires six protons from the stroma for every NO_2^- reduced. The pH will only change if the number of protons entering the chloroplast exceeds the amount removed by the reduction of nitrite. However, he was unable to explain the effects of NO_2 (5 ppm for 1 h) on *Nicotiana glutinosa* in the light by assuming acidification, although the injury did seem to be linked to condition of the thiol groups. Interestingly, nitrite is known to affect thiol-containing proteins (Hewitt, 1975, see also Section 9.3.3.2),

which are important, for example, in the regulation of fructose-1,6-bis-phosphatase activity (Buchanan et al , 1979)

9.3.6 Secondary Metabolic Responses

One of the most obvious effects of NO_x on plants in the short term is that frequently they are a deeper green color than those grown in clean air. This was clearly evident, for example, when Horsman and Wellburn (1975) reported a 10% increase in chlorophyll content of peas (cv Feltham First) exposed to 1 ppm NO_2 for 6 days. After longer periods, this effect disappears, and NO_2 has an inhibitory effect on pigment biosynthesis thereafter (Zeevaart, 1976). More recently, Sandhu and Gupta (1989) found large increases in both chlorophyll a (130%) and chlorophyll b (193%) immediately after exposing black turtle beans (*Phaseolus vulgaris* L cv Domino) to 0.1 ppm NO_2 (7 h/day) for 15 days but, at maturity, levels of both had fallen overall by 14%. Similarly, Sabaratnam et al (1988a) found that exposure of soybean (cv Williams) to NO_2 (0.2 ppm, 7 h/day for 5 days) had a stimulatory effect on chlorophyll a and total chlorophyll content, whereas 0.3 ppm had no effect and 0.5 ppm reduced all chlorophyll levels by 45%.

Unlike O_3 (Pell and Pearson, 1984), NO_2 does not have an effect on glycoalkaloid content (Sinn and Pell, 1984) and there are no reports of NO_2 -induced changes in levels of polyamines. However, Mehlhorn and Wellburn (1987) detected threefold increases in emissions of stress ethylene from peas (cv Feltham First) exposed to either NO or NO_2 (0.15 ppm each), even though no visible injury occurred. When combinations of either NO or NO_2 (50 to 150 ppb each for 7 h) were given along with 50 ppb O_3 , ethane as well as ethylene also evolved, but more significantly, extensive visible injury did occur. Mehlhorn and Wellburn (1987) concluded from these observations that, although stress ethylene formation determines plant sensitivity to O_3 , other air pollutants like NO or NO_2 may enhance O_3 -mediated injury by initiating stress ethylene formation.

9.4 EXPOSURE-RESPONSE RELATIONSHIPS

9.4.1 Foliar Injury and Loss in Aesthetic Value

Foliar injuries (defined as "any change in the appearance and/or function of a plant that is detrimental to the plant " American Phytopathological Society, 1974) from NO₂ are rarely observed at the ambient concentrations that occur in North America (see Chapter 7), but acute exposures from accidental spills or releases can induce foliar symptoms in sensitive plant species. A symptom is usually considered to be a change from the normal appearance in some part of the plant, most often in its foliage, that is observable by the unaided eye or through a lens of low magnification. Generally, these changes involve discoloration (yellowing), pigment changes, necrosis, and/or premature senescence of foliar tissues.

Foliar symptoms have a practical significance in two ways. First, they constitute a diminution of the aesthetic or economic value of the plant when this depends on the appearance of its foliage. Second, they offer one diagnostic means for assessing the occurrence of NO₂-induced effects in vicinities of some sources (Taylor and MacLean, 1970, Donagi and Goren, 1979).

9.4.1.1 Characteristics of Foliar Symptoms

There is no single type of symptom that is distinctive for NO₂-induced foliar injury (National Research Council, 1977), and the types induced by NO₂ are similar to those induced by other air pollutants, such as SO₂, HF, or O₃ (Matsushima, 1977). The kind of lesion produced and its location on the leaf depend upon concentration of NO₂, morphology of leaf, and species of plant. Consequently, diagnoses must evaluate the kind, size, and distribution of lesions on a leaf, as well as the pattern of their occurrence among leaves on the same plant and among different species of plants in the same location. Nitrogen dioxide-induced foliar symptoms have been illustrated in color plates (Van Haut and Stratmann, 1967; Lacasse and Treshow, 1976, Malhotra and Blauel, 1980, Taylor and MacLean, 1970) and described synoptically (Lacasse and Treshow, 1976, National Research Council, 1977) or with reference to individual species of plants (Czech and Nothdurft, 1952, Van Haut and Stratmann, 1967).

Descriptions of symptoms (and defoliation) resulting from acute exposures to NO₂ under experimental conditions are summarized below for several broad groupings of plants

(Van Haut and Stratmann, 1967, Taylor and MacLean, 1970, Lacasse and Treshow, 1976, MacLean et al , 1968)

Broad-leaved (dicotyledonous) plants Injury to leaves of broad-leaved plants from an acute exposure to NO₂ is usually characterized by the rapid appearance of irregularly-shaped intercostal lesions. The earliest indications of injury are gray-green water-soaked areas located on the upper surface of the leaf. Tissues in these areas collapse, become dry and bleached, turn white-to-tan, and extend through the leaf from its upper to lower surface. The resulting necrotic lesions are usually indistinguishable from those produced by SO₂. On most broad-leaved plants, NO₂-induced lesions are distributed between the veins over the entire leaf surface and eventually may fall from the leaf, leaving irregular holes with darkened margins. Occasionally, the lesions may increase in size, coalesce, and form necrotic strips between the veins. In some species of plants, NO₂-induced injury tends to occur more frequently along the margins of the leaf. For example, necrosis on maple and oak leaves often begins at the margins or the tips of the lobes and extends into the mid-portions of the leaves. In species with finely dissected compound leaves, such as carrot and parsley, NO₂-induced injury is usually confined to the tips and margins of the leaflets.

Narrow-leaved (monocotyledonous) plants Acute exposures to NO₂ of narrow-leaved plants most frequently result in a yellow-to-ivory-to-white necrosis that begins at or just below the tips of leaf blades. Necrotic margins and striped necrotic lesions between the veins also occur. In most grains and grasses, injury from acute exposure affects the entire width of the leaf blade, and area of the affected portion varies with the magnitude of the exposure. Grains also develop longitudinal necrotic strips between the veins, and these can coalesce to form large necrotic areas on the leaf surface. The awns (beards) of rye and barley spikes are also susceptible to injury from NO₂, bleached necrosis begins at the tips and progresses towards the base.

Coniferous plants Injury to leaves of conifers from acute exposures to NO₂ usually begins at the tips of the needles and progresses towards the base. In the initial stages of injury, the tips of needles take on a dull, gray-green color that becomes light brown and then dark brown or red-brown. The boundary between healthy and injured tissues is sharply delineated by a brown or red-brown band. Young, emerging needles develop NO₂-induced

injury at their tips, whereas older needles may occasionally develop necrosis in the medial or basal portions of the needle

Most of the foliar lesions described above are produced by an irreversible necrosis, chlorosis, or bronzing of the affected tissue, but there are foliar symptoms that can take other forms. For example, some symptoms are characterized by the appearance of a deeper green coloration of the leaf, which is often accompanied by a distortion of the leaf. In addition, the foliar chlorosis that results from extended or recurrent exposures to relatively low concentrations of NO_2 can often be a transitory change, and young leaves recover and become green again after exposure has ceased.

The abscission of the leaf itself can also be symptomatic of exposure to NO_2 under two general circumstances. With acute exposures, defoliation of young leaves occurs without the concomitant development of foliar lesions in citrus exposed to very high NO_2 (150 ppm for 4 h or 250 ppm for 1 h) (MacLean et al, 1968). Injured needles of conifers may drop prematurely, spruce needles drop shortly after injury develops, injured larch and fir needles may not fall for several months, and injured pine needles can remain on the tree for more than a year. However, if injury is severe, with necrosis covering more than half of the needle surface, defoliation usually occurs within a month. With chronic exposures, defoliation is the sequel to accelerated aging and premature senescence with chlorosis and death (Thompson et al, 1971, Spierings, 1971, Thompson et al, 1970, Sinn and Pell, 1984). Foliar injury, a measurable change in plant structure or function at either the organ, cellular or molecular level, may or may not lead to damage. Damage results in loss of intended use or role (e.g., agricultural yield, landscaping aesthetics, wildlife habitat) of a plant.

9.4.1.2 Exposure-Effect Relationships

Three important characteristics of foliar injury with respect to its relationship to exposure are (1) there is a zero baseline, that is, lesions produced by other agents are absent or clearly distinguishable from those induced by NO_2 (at least under experimental conditions), (2) a threshold exposure must be exceeded for the production of injury, and (3) measures of its occurrence are monotonic functions of concentration of NO_2 or duration of exposure. Measures of effect are usually based on the incidence and severity of foliar

injury Incidence is usually represented with reference to number of leaves per plant or number of plants per sample with lesions, and severity with reference to the area of a leaf or total amount of foliar tissue of a plant that is affected by these lesions

Exposures are the product of concentration and duration, the units of which are ppm/h or ppm/day, for a static exposure (constant concentration for the entire duration) the simple mathematic product is used, whereas for variable or dynamic exposures, the integral of pollutant concentration over time is used Duration refers to the length of time during which the plant is exposed to pollutants experimentally or in the ambient air Duration is usually measured in hours/day for episodic exposures or in days/week or days/growing season for chronic exposure An ambient exposure is similar to that which plants experience when growing in their natural habitat or as crops in the field It usually implies that the pollutant concentration is "dynamic" (i.e., changes during the exposure period occur in a pattern that, when used experimentally, (simulates the ambient atmosphere) Ambient exposures are usually episodic Peak gas concentrations are intermittent

Short-Term Exposures

Neither incidence nor severity of foliar injury have been expressed as explicit functions of the variables of concentration (C) and duration of exposure (T) for exposures to NO₂ Nevertheless, a relationship between the concentration of NO₂ (C_I) required to produce a certain percentage of foliar injury (I) and the duration of exposure (T) was tested in short-term (≤ 8 h) exposures with eleven species of plants (Heck and Tingey, 1979) and is given in Equation 9-15

$$C_I = a_0 + a_1 I + a_2 T^{-1}, \quad (9-15)$$

This represents a development of the O'Gara-Thomas form, which was derived for the effects of SO₂ (Thomas and Hill, 1935) and is expressed in Equation 9-16 with the substitution of the terms c_I for a₀ + a₁ I and k_I for a₂

$$C_I = c_I + k_I T^{-1} \text{ for } C_I \geq c_I \quad (9-16)$$

The parameter c_I expresses an asymptotic value for concentration, that is, one that would produce foliar injury no greater than I if applied indefinitely. The two forms are equivalent in expressing the relationship between concentration and duration for the threshold ($I = 0$).

Alternatives to the O'Gara-Thomas equation have been proposed for the threshold for SO₂-induced foliar injury (Guderian et al., 1960, Zahn, 1963, Guderian, 1977), and a simple approximation to these forms is given by the inclusion of the parameter b in Equation 9-17

$$C_I = c_0 + k_0 T^{-b} \text{ for } C_I \geq c_0, I \geq b > 0 \quad (9-17)$$

For the defoliation of citrus by acute exposures to NO₂, it was proposed that b was about equal to 1 (MacLean et al., 1968), for the threshold of a particular chlorotic symptom on leaves of pea (Zeevaart, 1976), b would have a value of about 0.5, and for the threshold for foliar injury in alfalfa with duration in the range of 2 to 200 h and concentration of NO₂ from 1 to 7 ppm (Zahn, 1975), b would have a value of about 0.8.

Another approach, which was based upon the assumption that the tolerance of elements of foliar tissue to injury follows a log-normal distribution, was developed and tested for the effects of SO₂ and O₃ (Larsen and Heck, 1976). This is expressed by Equation 9-18,

$$C_I = c_m T^{-b} s^z \text{ with } I = \Phi(z), \quad (9-18)$$

where C_I is the concentration that produces a specified amount of injury, c_m is the concentration required to produce injury on 50% of the foliar tissue on a plant of median tolerance in a 1-h exposure, T is the duration of exposure in hours, b is an exponent whose value varies with species exposed and concentration and duration of exposure, s is the geometric standard deviation of the tolerance distribution, z is a standard normal variate (i.e., normally distributed with mean equal to zero and variance equal to unity), I is the fraction of foliar area injured, and Φ is the integral of the normal distribution function. Although this has not been tested with NO₂, it could be applicable.

These relationships are consistent with what is known about the mechanisms of action of NO₂ (Section 9.3). For example, it can be assumed that the rate of uptake of NO₂ is to

be proportional to its atmospheric concentration and that injury results when the rate of uptake of NO_2 exceeds a certain value over a given period of time. This differential in rates would presumably be expressed by the term $C - c_0$ (Equation 9-17), which could also be taken to represent the difference between the rates of influx and metabolic removal of toxic products within the foliar tissue. Accordingly, an NO_2 -induced increase in the rate of change in the levels of NaR and NiR could increase the threshold (c_0), an NO_2 -induced increase in stomatal resistance could decrease uptake (C), and a change in the differential between rates of influx and detoxification during exposure could be represented by the parameter b .

When the concentration of NO_2 fluctuates during an exposure, the dynamics of response comprise those of the recovery processes, and a continuous exposure can be more effective than intermittent exposures of the same cumulative duration. For example, a continuous exposure of 60 min produced about 50% more injury than did three 20-min exposures separated by intervals of 10 min (Matsushima, 1971). Similarly, a series of seven 30-min exposures declined in effectiveness with an increase in the length of the period between exposures from 10 to 45 min (Zahn, 1975).

Based on experimentally derived estimates for the parameters in Equation 9-15, the concentrations of NO_2 required to produce 5% foliar injury for different durations of exposure are given in Figure 9-11 for three categories of plants—sensitive, intermediate, and tolerant (Heck and Tingey, 1979). It should be noted that for sensitive plants, the concentrations range from 6 ppm for 0.5 h to 2 ppm for 8 h. These concentrations are, respectively, from 120- to 40-fold greater than the National Ambient Air Quality Standard (NAAQS) primary standard of 0.05 ppm, and it has been observed that the ratio of a 1-h maximum concentration to the annual arithmetic mean concentration rarely exceeds the value of 12 (Chapter 8, U.S. Environmental Protection Agency, 1982).

Long-Term Exposures

The derivation of an exposure-effect or exposure-response relationship for foliar injury is inherently more problematic for a long-term exposure than for a short-term exposure because it involves the aggregation of a series of lower-level episodes. In addition to the problem posed by the dynamics of response and recovery during and following a single

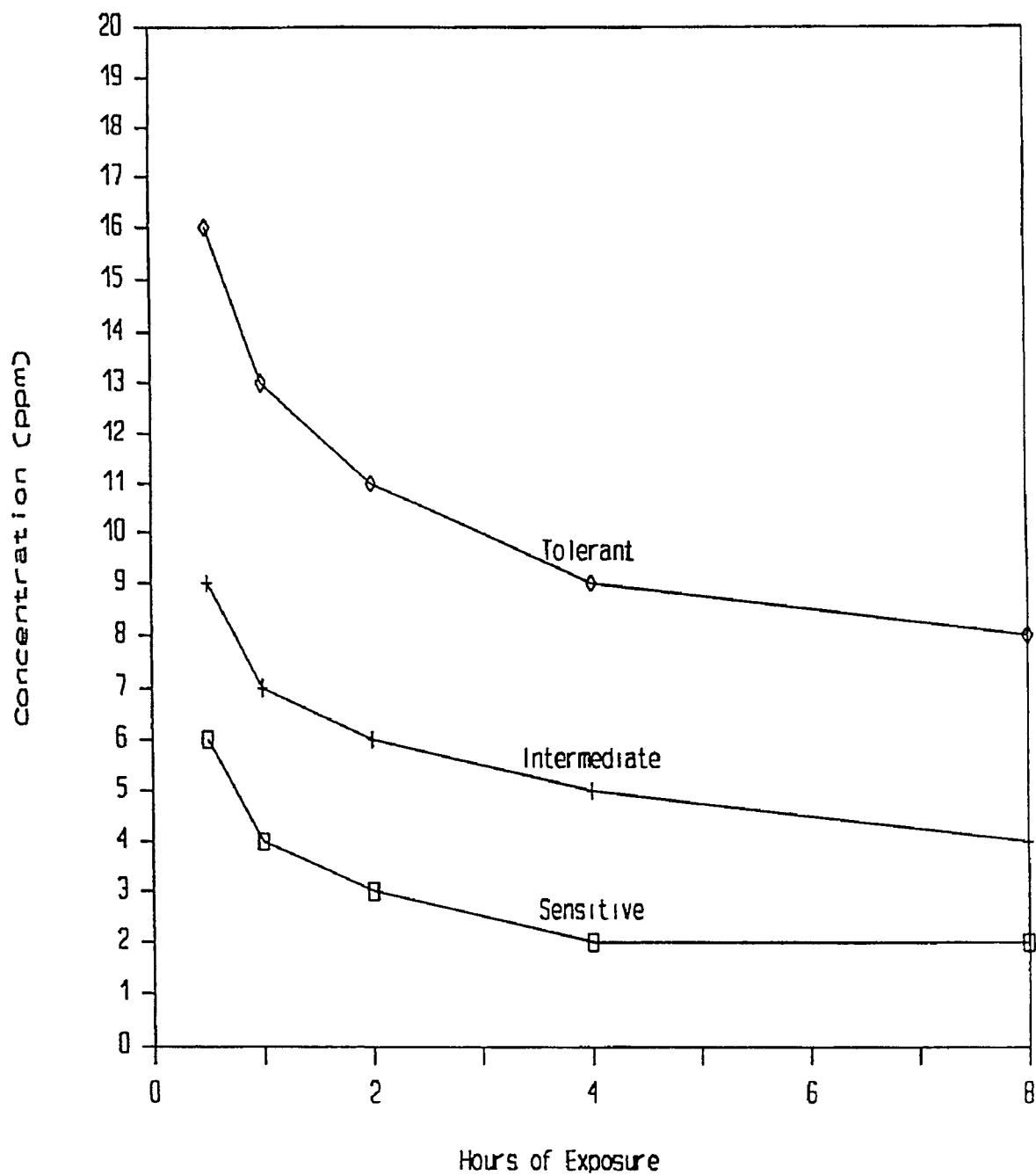


Figure 9-11. Minimum exposures to nitrogen dioxide required to produce 5% foliar injury on sensitive, intermediate, and tolerant categories of plants.

Source Heck and Tingey (1979)

exposure, there is the problem of the degree to which the concentration of NO_x and duration in one exposure can act to sensitize or desensitize the plant to the effect of NO_x in an ensuing exposure

Experimental investigations have used two kinds of regimes one has been a uniform concentration applied continuously for a period of several days to several weeks, the other comprised a series rectangular pulses of uniform concentration and duration applied with more or less regular frequency (Long-term, continuous exposures could also be regarded as a series of day/night episodes because of the substantial influence of light on the plant's uptake and response to NO_x [see Section 9.6.2.1]) A compilation of the results of experimental, long-term exposures with respect to the occurrence of foliar symptoms is given in Table 9-4 (The species of plants used, with scientific names, are listed in Appendix A, Table 9A)

These results are also summarized in Figure 9-12 with respect to the duration of exposure and the concentration of NO_x employed That is, duration is expressed as the cumulative time during which NO_x was present and not the total length of the experimental period, and concentration is expressed as that of NO_x when present and not the arithmetic mean for the entire experimental period Also present in Figure 9-12 is a series of reference points representing 0.05 ppm as an annual mean and other maxima that could be associated with it (cf Chapter 8, U.S. Environmental Protection Agency, 1982) 0.10 ppm for 876 h (twofold the annual mean for 10% of the hours), 0.15 ppm for 87 h (threefold the annual mean for 1% of the hours), 0.25 ppm for 24 h, and 0.6 ppm (12-fold the annual mean) as a maximum 1-h concentration

With three exceptions, foliar injury was not produced by exposures in the concentration-duration plane area below this reference line Two of these occurred with exposures to 0.10 ppm NO_2 exposures for 4 h/day for 35 days (total of 140 h) produced chlorotic lesions on one-third of the clones of eastern white pine (Yang et al., 1982, 1983a,b), and exposures for 6 h/day for 28 days (total of 168 h) produced no injury to loblolly pine, Virginia pine, white ash, or willow oak, but induced a chlorosis on green ash and sweetgum (Kress and Skelly, 1982) The third occurrence of injury was with increased leaf drop in bearing navel orange trees exposed to 0.0625, 0.125, or 0.25 ppm NO_2

**TABLE 9-4. COMPILATION OF OCCURRENCE OF FOLIAR SYMPTOMS IN
LONG-TERM OR INTERMITTENT EXPOSURES TO NITROGEN OXIDES IN
EXPERIMENTAL INVESTIGATIONS^a**

| NO _x (ppm) | Exposure Duration | Effect (Occurrence of Foliar Lesions) |
|--------------------------|-------------------------------------|--|
| 0.02 | 24 h/day, 5 days | No injury to bean (Srivastava and Ormrod, 1984) |
| 0.02 | 6 h/day, 14 days | No injury to bean (Srivastava and Ormrod, 1986) |
| 0.037 | 24 h/day, 260 days | Increased loss of foliage in navel orange (Thompson et al , 1971) |
| 0.05 | 4 h/day, 35 days | No injury to eastern white pine (Yang et al , 1982, 1983b) |
| 0.0625 | 24 h/day, 290 days | Increased leaf drop in navel orange (Thompson et al , 1970) |
| 0.075 | 24 h/day, 260 days | Increased loss of foliage in navel orange (Thompson et al , 1971) |
| 0.08 | 3 h/day, 38 days | No injury to wheat (Runeckles and Palmer, 1987) |
| 0.08 | 3 h/day, 40 days | No injury to radish or bean (Runeckles and Palmer, 1987) |
| 0.08 | 3 h/day, 56 days | No injury to mint (Runeckles and Palmer, 1987) |
| 0.10 | 4 h/day, 35 days | Chlorotic lesions on one-third of the clones of eastern white pine (Yang et al , 1982, 1983a,b) |
| 0.10 | 6 h/day, 14 days | No injury to bean (Srivastava and Ormrod, 1986) |
| 0.10 | 6 h/day, 28 days | No injury to loblolly pine, Virginia pine, white ash, willow oak, chlorosis on green ash and sweetgum (Kress and Skelly, 1982) |
| 0.10 | 24 h/day, 5 days | No injury to bean (Srivastava and Ormrod, 1984) |
| 0.10 | 24 h/day, 6 days | No injury to pea (Wellburn et al , 1976) |
| 0.10 | 24 h/day, 15 days | No injury to potato, corn, pea, or tobacco (Elkiey et al , 1988) |
| 0.10 | 24 h/day, 19 days | No injury to tomato (Capron and Mansfield, 1977) |
| 0.10 | 24 h/day, 21 days | No injury to tomato (Wellburn et al , 1976) |
| 0.10 | 104 h/week, 56 weeks | No injury to European white birch or downy birch (Wright, 1987) |
| 0.10 | 3 h/day, 15 days, 1 every 2 days | No injury to soybean (Klarer et al , 1984) |
| 0.11 | 24 h/day, 7 days | No injury to potato, intumescences developed on one of four cultivars (Petitte and Ormrod, 1986) |
| 0.11 | 24 h/day, 14 days | No injury to tomato (Marie and Ormrod, 1984), no injury to potato (Petitte and Ormrod, 1984), but yellowing of lower leaves in one of two cultivars of potato (Petitte and Ormrod, 1988) |
| 0.11 | 104 h/week, 8 weeks | No injury to orchard grass or Kentucky bluegrass (Ashenden, 1979b) |

TABLE 9-4 (cont'd). COMPILATION OF OCCURRENCE OF FOLIAR SYMPTOMS IN LONG-TERM OR INTERMITTENT EXPOSURES TO NITROGEN OXIDES IN EXPERIMENTAL INVESTIGATIONS^a

| NO _x (ppm) | Exposure Duration | Effect (Occurrence of Foliar Lesions) |
|--------------------------|-------------------------------------|--|
| 0 11 | 104 h/week, 20 weeks | No injury to timothy or Italian ryegrass (Ashenden and Williams, 1980), no injury, but darker green color on orchard grass and Kentucky bluegrass (Ashenden, 1979b), no lesions on timothy, perennial ryegrass, or orchard grass, frequently greener than controls (Wellburn et al , 1981) |
| 0 125 | 24 h/day, 290 days | Increased leaf drop in navel orange (Thompson et al , 1970) |
| 0 15 | 24 h/day, 10 days | No injury (but darker green foliage) in red top, creeping bentgrass, colonial bentgrass, red fescue, perennial ryegrass, lesions on 2 of 12 cultivars of Kentucky bluegrass (Elkiey and Ormrod, 1980), moderate to no injury to Kentucky bluegrass (Elkiey and Ormrod, 1981a) |
| 0 20 | 3 h/day, 15 days, 1 every 2 days | No injury to soybean (Klarer et al , 1984) |
| 0 20 | 5 h/day, 2 days/week, 12 weeks | No lesions, but premature senescence and defoliation in potato (Sinn and Pell, 1984) |
| 0 20 | 5 h/day, 2 days/week, 16 weeks | No lesions, but premature senescence and defoliation in potato (Sinn and Pell, 1984) |
| 0 20 | 4 h/day, 35 days | Injury to two of three clones of eastern white pine (Yang et al , 1983a) |
| 0 20 | 6 h/day, 10 days | Injury to Murray red gum (Elkiey and Ormrod, 1987) |
| 0 20 | 24 h/day, 6 days | No injury to pea (Wellburn et al , 1976) |
| 0 20 | 24 h/day, 14 days | No injury to corn or sunflower (Okano et al , 1985b) |
| 0 20 | 24 h/day, 77 days | No injury (reduced senescence) on orchard grass and perennial ryegrass (Taylor and Bell, 1988) |
| 0 21 | 24 h/day, 20 days | No injury to radish (Godzik et al , 1985) |
| 0 25 | 80 h | No injury to tomato (Troiano and Leone, 1977) |
| 0 25 | 3 h/day, 6 days/4 weeks | No injury to azalea (Sanders and Reinert, 1982a) |
| 0 25 | 9 h/day, 3 days | No injury to petunia (de Cormis and Luttringer, 1977) |
| 0 25 | 24 h/day, 37 days | Epinasty and chlorosis in older leaves of tomato (Spierings, 1971) |
| 0 25 | 24 h/day, 63 days | No lesions on timothy, perennial ryegrass, or orchard grass, frequently greener than controls (Wellburn et al , 1981) |
| 0 25 | 24 h/day, 128 days | Loss of leaves in lower portion of the canopy of tomato (Spierings, 1971) |
| 0 25 | 24 h/day, 290 days | Increased leaf drop in navel orange (Thompson et al , 1970) |
| 0 30 | 3 h/day, 3 days, 1 apart | No injury to radish (Sanders and Reinert, 1982b) |
| 0 30 | 3 h/day, 3 days/week, 3 weeks | No injury to radish (Reinert and Sanders, 1982) |

TABLE 9-4 (cont'd). COMPILATION OF OCCURRENCE OF FOLIAR SYMPTOMS IN LONG-TERM OR INTERMITTENT EXPOSURES TO NITROGEN OXIDES IN EXPERIMENTAL INVESTIGATIONS^a

| NO _x (ppm) | Exposure Duration | Effect (Occurrence of Foliar Lesions) |
|--------------------------|--------------------------------|--|
| 0 30 | 4 h/day, 35 days | Injury to two of three clones of eastern white pine (Yang et al , 1983a) |
| 0 30 | 6 h/day, 3 days, 1 apart | No injury to marigold (Sanders and Reinert, 1982b) |
| 0 30 | 6 h/day, 3 days/week, 3 weeks | No injury to marigold (Reinert and Sanders, 1982) |
| 0 30 | 10 h/day, 14 days | No injury to sunflower, corn, bean, cucumber, tomato, or Swiss chard (Yoneyama et al , 1980c) |
| 0 30 | 24 h/day, 7 days | Crinkling and darker green coloration on sunflower (Okano and Totsuka, 1986) |
| 0 30 | 24 h/day, 9 days | Injury to buckwheat (Fujiwara, 1973, Ishikawa, 1976) |
| 0 30 | 24 h/day, 19 days | Injury to tomato (Ishikawa, 1976) |
| 0 30 | 24 h/day, 20 days | No injury to taro, injury to eggplant (Ishikawa, 1976) |
| 0.30 | 24 h/day, 27 days | No injury to soybean (Ishikawa, 1976) |
| 0 30 | 24 h/day, 30 days | No injury or premature abscission on poplar hybrids, Japanese zelkova, shira oak, sweet viburnum, camphor tree, or oleander (Okano et al , 1989) |
| 0 30 | 24 h/day, 55 days | No injury to grape (Ishikawa, 1976) |
| 0 33 | 5 h/day, 5 days/week, 16 weeks | No injury to creosote bush, desert willow, or brittle bush (Thompson et al , 1980) |
| 0 33 | 5 h/day, 5 days/week, 32 weeks | No injury to creosote bush, saltbush, brittle bush, or desert willow (Thompson et al , 1980) |
| 0.39 | 164 h | No injury to tomato (Troiano and Leone, 1977) |
| 0 40 | 2 8 h, 10 events in 2 mo | No symptoms or senescence on soybean (Irving et al , 1982) |
| 0 40 | 6 h/day, 10 days | |
| 0 40 | 9 h/day, 5 days | No injury to geranium (de Cormis and Luttringer, 1977) |
| 0 40 ^b | 24 h/day, 21 days | No injury to tomato (Wellburn et al , 1976) |
| 0.40 ^b | 24 h/day, 35 days | Injury to tomato (Anderson and Mansfield, 1979) |
| 0.49 | 9 h/day, 5 days | No injury to petunia, tomato, or geranium (de Cormis and Luttringer, 1976) |
| 0 50 | 6 h/day, 14 days | Injury present occasionally on bean, depended upon nitrate level supplied (Srivastava and Ormrod, 1986) |
| 0 50 | 9 h/day, 5 days | No injury to tomato (de Cormis and Luttringer, 1977) |
| 0.50 | 24 h/day, 3 days | No injury to Kentucky bluegrass (Elkiey and Ormrod, 1981b) |
| 0.50 | 24 h/day, 5 days | Injury to bean (Srivastava and Ormrod, 1984) |
| 0.50 | 24 h/day, 10 days | Epinasty in tomato (Spierings, 1971) |

TABLE 9-4 (cont'd). COMPILATION OF OCCURRENCE OF FOLIAR SYMPTOMS IN LONG-TERM OR INTERMITTENT EXPOSURES TO NITROGEN OXIDES IN EXPERIMENTAL INVESTIGATIONS^a

| NO _x (ppm) | Exposure Duration | Effect (Occurrence of Foliar Lesions) |
|--------------------------|-------------------------------------|--|
| 0 50 | 24 h/day, 13 days | No lesions to timothy, perennial ryegrass, or orchard grass, plants were frequently greener than controls (Wellburn et al , 1981) |
| 0 50 | 24 h/day, 14 days | No injury to sunflower, radish, tomato, tobacco, cucumber, bean, corn, or sorghum, darker green color in sunflower and radish (Okano et al , 1988), no injury to corn and younger leaves of sunflower were crinkled and darker green (Okano et al , 1985b) |
| 0 50 | 24 h/day, 19 days | Injury to tomato (Capron and Mansfield, 1977) |
| 0 50 | 24 h/day, 21 days | No injury to tomato (Wellburn et al , 1976) |
| 0 50 | 24 h/day, 35 days | Chlorosis and heavy defoliation on citrus (Thompson et al , 1970) |
| 0 6 | 24 h/day, 35 days | No injury to turnip or lettuce (Ishikawa, 1976) |
| 0 6 | 24 h/day, 41 days | No injury to pimento or spinach (Ishikawa, 1976) |
| 0 6 | 24 h/day, 51 days | No injury to rice (Fujiwara, 1973, Ishikawa, 1976) |
| 0 7 ^c | 24 h/day, 21 days | No injury to four cultivars of tomato (Mortensen, 1985b) |
| 0 7 ^c | 24 h/day, 28 days | Injury to three of four cultivars of tomato (Mortensen, 1985b) |
| 0 85 ^d | 24 h/day, 18 days | No injury to cucumber (Mortensen, 1985a) |
| 0 85 ^d | 24 h/day, 22 days | No injury to tomato (Mortensen, 1985a) |
| 0 85 ^d | 24 h/day, 35 days | No injury to chrysanthemum (Mortensen, 1985a) |
| 0 85 ^d | 24 h/day, 43 days | No injury to rose or baby's tears (Mortensen, 1985a) |
| 0 85 ^d | 24 h/day, 55 days | No injury to English ivy (Mortensen, 1985a) |
| 0 85 ^d | 24 h/day, 77 days | No injury to English ivy or Boston fern (Mortensen, 1985a) |
| 0 85 ^d | 24 h/day, 104 days | No injury to African violet (Mortensen, 1985a) |
| 0 85 ^d | 24 h/day, 121 days | No injury to African violet (Mortensen, 1985a) |
| 1 0 | 27 h | Injury to endive (Zahn, 1975) |
| 1 0 | 10 h/day, 28 days | Injury to barley (Zahn, 1975) |
| 1 0 ^b | 10 h/day, 139 days | No injury to English or Algerian ivy, rubber tree, benjamin tree, hibiscus, Boston fern, scorching on <i>Dieffenbachia</i> (Saxe and Christensen, 1984,1985) |
| 1 0 | 537 h in 67 days, 1 event/day | No injury to European larch (Zahn, 1975) |
| 1 0 | 639 h in 57 days, 1 event/day | Slight chlorosis on bean (Zahn 1975) |
| 1 0 | 1,900 h in 161 days, 1 event/day | No injury to Norway spruce (Zahn, 1975) |
| 1 0 | 24 h/day, 2 days | Slight injury to cotton, bean, and endive (Heck, 1964) |

TABLE 9-4 (cont'd). COMPILATION OF OCCURRENCE OF FOLIAR SYMPTOMS IN LONG-TERM OR INTERMITTENT EXPOSURES TO NITROGEN OXIDES IN EXPERIMENTAL INVESTIGATIONS^a

| NO _x (ppm) | Exposure Duration | Effect (Occurrence of Foliar Lesions) |
|--------------------------|--------------------------------|--|
| 1 0 ^b | 24 h/day, 5 days | No injury to tomato (Bruggink et al , 1988) |
| 1 0 | 24 h/day, 6 days | No injury to pea (Wellburn et al , 1976), epinasty and darker green coloration were present on pea seedlings (Horsman and Wellburn, 1975) |
| 1 0 | 24 h/day, 14 days | No injury to corn or sunflower (Okano et al , 1985b), younger leaves of sunflower were crinkled and darker green (Okano and Totsuka, 1986) |
| 1.0 | 24 h/day, 35 days | Chlorosis and heavy defoliation on navel orange (Thompson et al , 1970) |
| 1.0 | 5 h/day, 5 days/week, 12 weeks | No injury to alfilaria (Thompson et al , 1980) |
| 1 0 | 5 h/day, 5 days/week, 16 weeks | No injury to <i>Chaenactis carphoclina</i> , saltbush, or burro weed, injury to creosote bush, desert willow, brittle bush (Thompson et al , 1980) |
| 1.0 | 5 h/day, 5 days/week, 17 weeks | No injury to scorpion weed (Thompson et al , 1980) |
| 1 0 | 5 h/day, 5 days/week, 32 weeks | No injury to burro weed, injury to brittle bush, creosote bush, desert willow, saltbush (Thompson et al , 1980) |
| 1 2 | 30 h | |
| 1.5 ^c | 24 h/day, 25 days | |
| 2 0 | 24 h/day, 4 days | No injury to bean (Okano et al , 1984b), but darker green foliage in bean (Okano et al , 1985a, Ito et al , 1984a, 1985a) |
| 2 0 | 24 h/day, 7 days | No injury but darker green color in bean (Ito et al , 1985b) |
| 2 1 | 357 h in 51 days, 1 event/day | No injury to rose, slight chlorosis on carrot (Zahn, 1975) |
| 2 6 | 24 h/day, 4 days | No injury to tobacco (Taylor and Eaton, 1966) |
| 3.0 | 8 h/day, 8 days | No injury to Japanese zelkova (Matsushima et al , 1977) |
| 3.1 | 9 h/day, 3 days | No injury to rape (day) (Zahn, 1975) |
| 4 0 | 24 h/day, 2 days | Injury to bean (Ito et al , 1984a, 1985b) |
| 7 3 | 7 h/day, 3 days | Injury to rape (Zahn, 1975) |
| 12 | 3 h/day, 2 days | Injury to taro (Matsushima, 1977) |
| 12 | 3 h/day, 5 days | No injury to Citrus unshu (Matsushima, 1977) |
| 12 | 3 h/day, 6 days | No injury to ginkgo (Matsushima, 1977) |
| 12 | 3 h/day, 7 days | No injury to common camellia, Japanese aucuba, Japanese black pine, hinoki cypress, fragrant olive (Matsushima, 1977) |

^aNO_x = Nitrogen oxides

NO = Nitric oxide

NO₂ = Nitrogen dioxide

^bNO

^c20% NO₂ + 80% NO

^d0 15 ppm NO₂ + 0 70 ppm NO

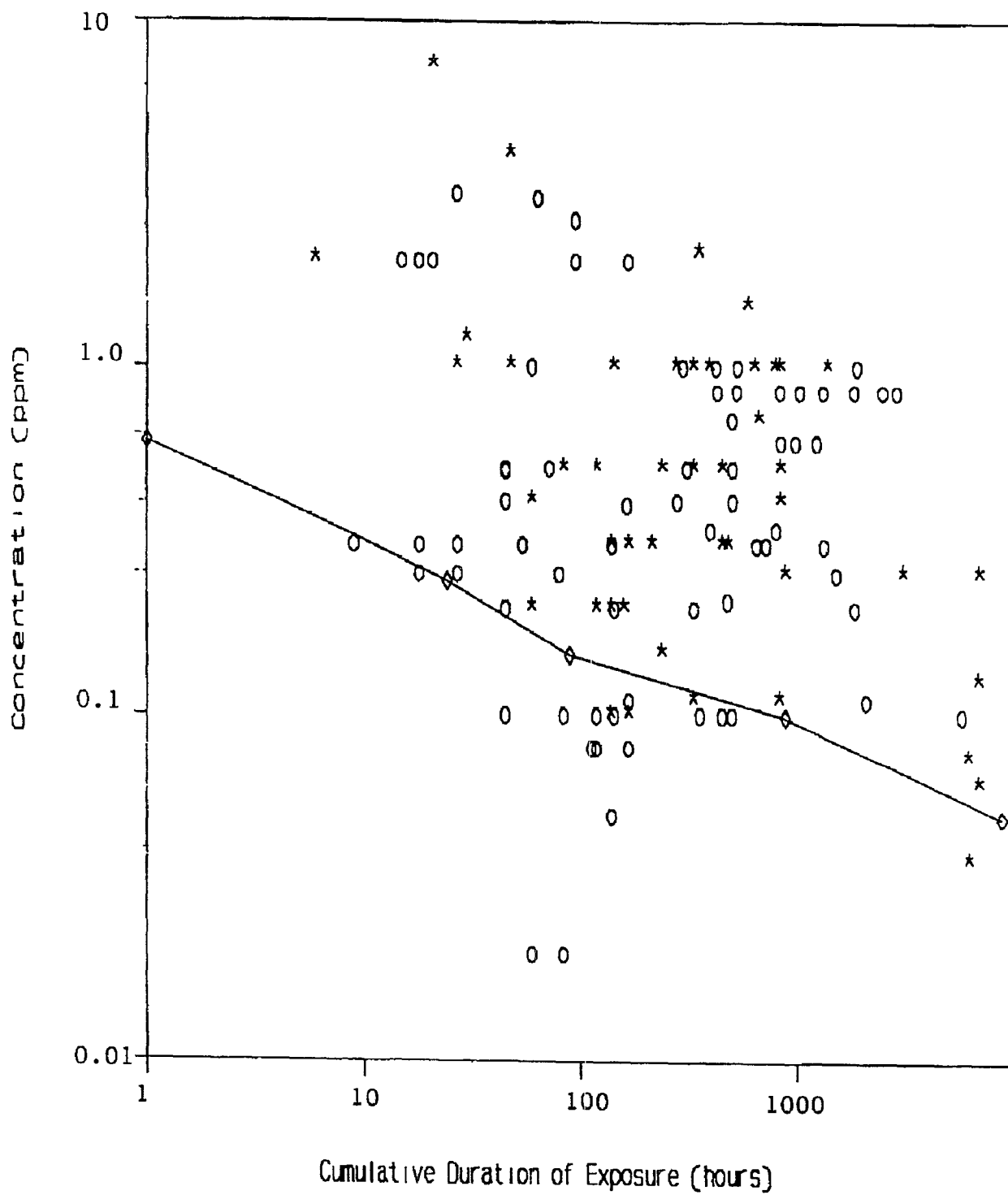


Figure 9-12. Occurrence (*) or absence (o) of foliar injury from nitrogen oxides in long-term experimental exposures.

continuously for 8 mo (Thompson et al , 1970) The mass of leaves dropped tended to increase with the concentration of NO₂, but neither the trend nor the effect of NO₂ at the lowest concentration were judged to be statistically significant and a significant effect was found only when the effects of all three concentrations were pooled

The degree to which foliar injury can be used as a surrogate measure for other kinds of effects, such as reduced growth or yield, has been a persistent and still unresolved problem The yield of fruit of navel orange (Thompson et al , 1970, 1971) or tomato (Spierings, 1971) and of tubers in potato (Sinn and Pell, 1984) appeared to be related to the degree of NO₂-induced premature senescence and abscission of foliage

9.4.2 Loss in Growth and Yield

The effect of NO_x on the growth, development, or reproduction of plants has occupied the position of greatest practical and continuing concern in research Because these kinds of effects have been studied primarily in the context of agriculture, they can include changes that may occur in the quality and marketability, as well as in the quantity, of product Nevertheless, most of the information on productivity of commercial plants could be of substantial relevance to an understanding of effects in natural systems

A compilation of the effects of exposures to NO_x on the growth, development, or reproduction of plants is provided in Appendix 9B These results are organized with reference to general use and species of plant, concentration of NO_x, conditions of exposure, nature of effect, and experimental methods The concentrations and durations of exposure employed to produce these results are also summarized in Figure 9-13 with reference to what could be considered an upper boundary of exposures consistent with some characteristics of ambient exposures in the United States (See Chapter 7)

The latter illustrates a major problem in the evaluation of experimentally produced effects, namely, the extent to which the characteristics of experimental exposures are comparable to those that are operationally significant in ambient situations For example, over the range of concentrations employed, those greater than 0.5 to 0.6 ppm for durations greater than 1 h would not be consistent with 1-h maxima observed in ambient monitoring or with the ratios of 1-h maxima to annual mean (none greater than 14, and 70% in the range of 5 to 8) in the United States (Chapter 8, U S Environmental Protection Agency, 1982)

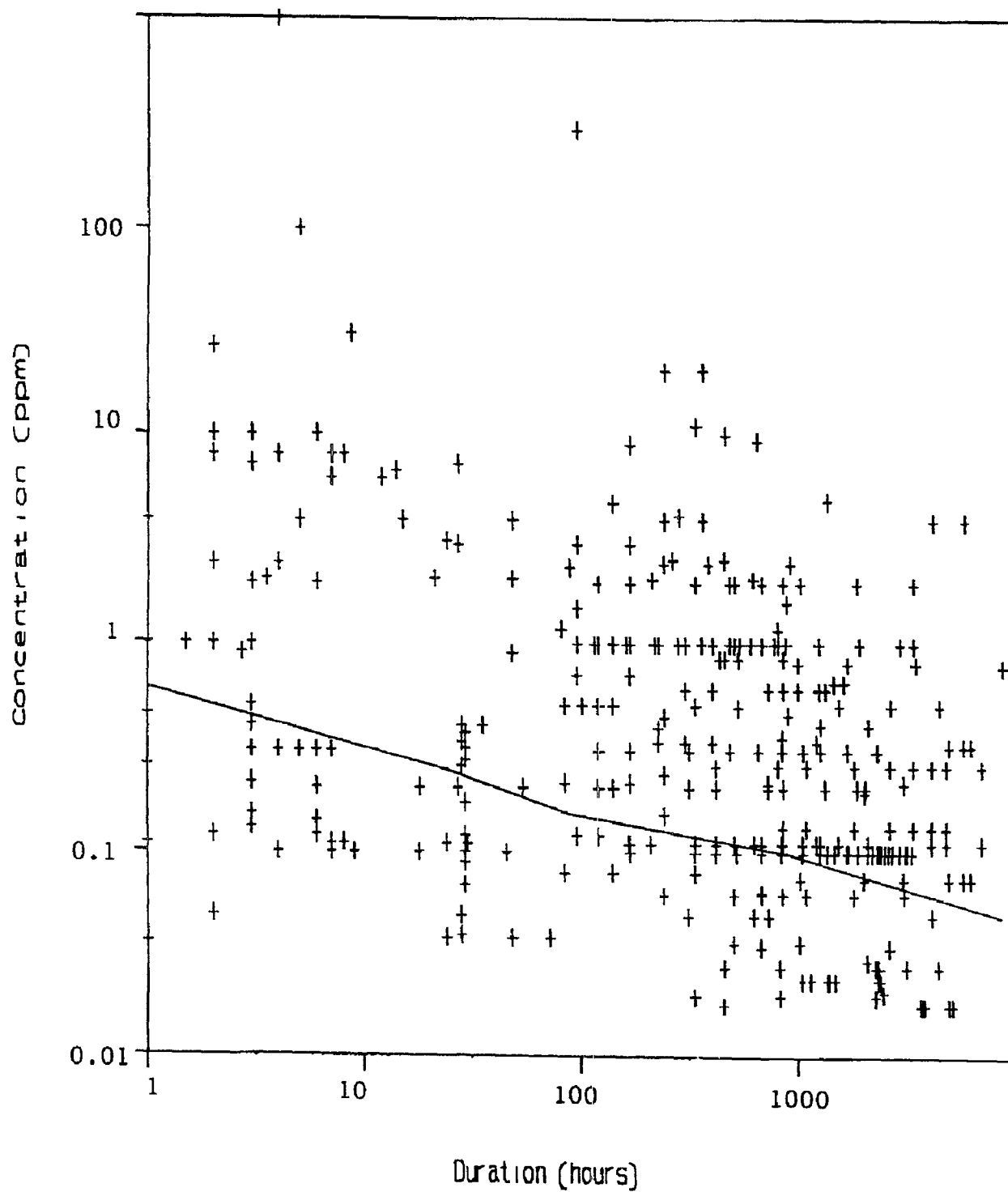


Figure 9-13. Exposures employed in experimental investigations on the effect of nitrogen oxides on growth and yield of plants.

Similarly, a mean concentration of greater than 0.2 ppm for a period of 24 h or more would not be consistent with ambient exposures. Other order statistics indicate that over the longer term, 90% of the monitored values were no greater than about twice the median and 99% were no greater than about three times the median concentration. Accordingly, long-term exposures employing constant concentrations continuously for one week to several months do not reflect the intermittent exposures expected in the United States (see Chapter 7). Unlike the situation with single acute exposures, no formal expression has been offered for the relative effectiveness of a given concentration of NO_x as a function of duration and frequency of exposure.

A summarization of experimental results that fall within or somewhat above the upper envelope of what would be consistent with ambient exposures in the United States is given in Table 9-5. Some of the problems associated with determining the relationship between effects on growth and yield and exposure to NO_x can be illustrated with reference to two of the most widely studied crops: tomato (Figure 9-14) and green bean (Figure 9-15). In both species, there is no clear demarcation between those exposures that result in reduced growth and those that do not. One reason for this is the intervention of biological factors and environmental conditions (Section 9.5), which can determine whether growth is increased, reduced, or affected at all. Another reason is that several measures of growth and yield (depending upon the species of plant) have been used to study the effects of NO_x : mass of the plant; number or mass of leaves, stems, roots, tubers, flowers, fruit, or seeds; foliar area; and length of stem or foliar elements. Not all measures are affected equally or indeed in the same way by an exposure to NO_x in the same species (i.e., the growth of one organ can be reduced while that of another can be increased).

Increased growth has been noted in other species. In rooted cuttings of European white birch, NO_2 at 0.04 ppm for 9 weeks significantly increased the mass of stem by 54%, mass of leaves by 45%, stem height by 50%, and internode length by 38% (depending on photoperiod and light intensity), but had no significant effect at 0.05 ppm for 4 weeks in seedlings (Freer-Smith, 1985). In garden pea, NO_2 at 0.039 ppm for 2 h/day, 1 day/week, for 3 weeks (Edelbauer and Maier, 1988) or at 0.1 ppm for 15 days (Elkley et al., 1988) had no effect on growth, but at 0.12 ppm (2 h/day, 1 day/week, 3 weeks), it significantly

TABLE 9-5. SOME EFFECTS OF NITROGEN OXIDES ON THE GROWTH AND YIELD OF PLANTS WITH RESPECT TO CONCENTRATIONS AND EXPOSURES USED IN EXPERIMENTAL INVESTIGATIONS^a

| NO _x (ppm) | Exposure Duration | Effect (Occurrence of Foliar Lesions) |
|--------------------------|-------------------------------|---|
| 0 018 | to 187 days | No effect on mass of shoots, but significantly increased mass of dead leaves and decreased number of flowering shoots in perennial ryegrass, significantly decreased mass of shoots by 131 days, and mass of dead leaves and number of flowering shoots by 183 days in common timothy (NO ₂ at 0 006 ppm + NO at 0 012 ppm) (Lane and Bell, 1984b) |
| 0 02 | 5 days | Increase in plant height and decrease in mass and area of leaf depended on level of nitrate supplied in 12-day-old green bean seedlings (Srivastava and Ormrod, 1984) |
| 0 02 | 6 h/day, 14 days | Decreases in masses of shoot or root and increases in number of nodules depended on level of nitrate in 23-day-old green bean seedlings (Srivastava and Ormrod, 1986) |
| 0 024 | to 215 days | Significantly increased mass of shoots after 156, but not after 207 days of exposure, and decreased number of flowering shoots after 207 days in perennial ryegrass, significantly increased mass of shoot after 97, but not after 215 days of exposure in common timothy, no effect on percent dead leaf mass or mass of shoots after 153 days in orchard grass (control was NO ₂ at 0 009 ppm, background SO ₂ at 0 003 ppm) (Lane and Bell, 1984b) |
| 0 025 | 7 h/day, 5 days/week, 3 weeks | Significantly increased the mass of seeds in 57-day-old green bean plants (Sandhu and Gupta, 1989) |
| 0 028 | to 187 days | Significantly decreased the mass of shoots and number of flowering shoots, but increased the mass of dead leaves in perennial ryegrass, increased mass of shoots by 131 days, decreased mass of dead leaves, but increased the number of flowering shoots after 183 days in common timothy (NO ₂ at 0 021 ppm + NO at 0 007 ppm) (Lane and Bell, 1984b) |
| 0 03 | 8 weeks | Did not significantly affect mass of plant, but advanced bud-break in 6-mo-old seedlings of Sitka spruce exposed during dormancy (Freer-Smith and Mansfield, 1987) |
| 0 039 | 2 h/day, 1 day/week, 3 weeks | No effect on mass of plant or leaf area (added to continuous exposure of 0 0094 ppm) of 5-week-old green pea plants (Edelbauer and Maier, 1988) |
| 0 04 | 9 weeks | Significantly increased mass and height of stem, mass of leaves, and internode length (depending upon photoperiod and light intensity) in rooted cuttings of European white birch (Freer-Smith, 1985) |
| 0 05 | 7 h/day, 5 days/week, 3 weeks | Significantly increased masses of shoot, roots, and seeds in 57-day-old green bean plants (Sandhu and Gupta, 1989) |
| 0 05 | 4 h/day, 35 days | No significant effect on length of needles in 2-year-old ramets of eastern white pine (Yang et al , 1983b) |
| 0 05 | 4 weeks | No significant effect on mass of roots, stem, or leaves in 1-mo-old seedlings of European white birch (Freer-Smith, 1985) |

TABLE 9-5 (cont'd). SOME EFFECTS OF NITROGEN OXIDES ON THE GROWTH AND YIELD OF PLANTS WITH RESPECT TO CONCENTRATIONS AND EXPOSURES USED IN EXPERIMENTAL INVESTIGATIONS^a

| NO _x (ppm) | Exposure Duration | Effect (Occurrence of Foliar Lesions) |
|--------------------------|-------------------------------|--|
| 0.08 | 3 h/day, 56 days | No effect on mass of plant or roots in rooted cuttings of mint or 38-day-old wheat plants, increased mass of plant and hypocotyl in 40-day-old radish plants, increased mass of 40-day-old green bean plants (Runeckles and Palmer, 1987) |
| 0.1 | 3 h every 2 days, 4 weeks | No effect on mass of leaves, stem, roots, or nodules or on number of nodules in 7-week-old soybean plants (Klarer et al , 1984) |
| 0.1 | 7 h/day, 5 days | No effect on relative growth rate of 5-week-old soybean plants (Sabaratnam and Gupta, 1988) |
| 0.1 | 7 h/day, 5 days/week, 3 weeks | Significantly increased masses of shoot and roots, numbers of pods and seeds, and mass of seeds in green bean plants (Sandhu and Gupta, 1989) |
| 0.1 | 6 h/day, 14 days | Significantly decreased mass of shoot and roots, but increased number of nodules, depending on level of nitrate, in 23-day-old green bean seedlings (Srivastava and Ormrod, 1986) |
| 0.1 | 6 h/day, 28 days | No significant effect on height, mass of shoot, or mass of roots in 6- to 8-week-old seedlings of pitch pine, Virginia pine, willow oak, or green ash, decreased root mass in white ash and sweetgum, decreased height (depending on clone) in loblolly pine (Kress and Skelly, 1982) No significant effect on height in 2- to 3-week-old seedlings of American sycamore (Kress et al , 1982a) |
| 0.1 | 4 h/day, 35 days | Significantly reduced length and mass of needles, depending on the clone, in 2-year-old ramets of eastern white pine (Yang et al , 1983b) |
| 0.1 | 5 days | Significantly increased plant height, but decreased mass and area of leaf, depending upon level of nitrate, in 12-day-old green bean seedlings (Srivastava and Ormrod, 1984) |
| 0.1 | 10 days | No effect on growth in green bean or common sunflower (Totsuka et al , 1978) |
| 0.1 | 15 days | No effect on mass of plant in garden pea, green bean, potato, or tobacco, but increased mass of plant and leaf area in maize seedlings (Elkiey et al , 1988), changes in leaf area and masses of leaves, stem, roots, or flowers and fruit were of unstated significance in green bean and common sunflower (Totsuka et al , 1978) |
| 0.1 | 19 days | No effect on leaf area, mass of leaves, shoot, or roots in tomato plants (Capron and Mansfield, 1977) |
| 0.1 | 20 days | No effect on number of tillers or leaves, leaf area, or mass of leaves or roots in barley seedlings (Pande and Mansfield, 1985) |
| 0.1 | 104 h/week, 8 weeks | Significantly reduced mass of plant (but not numbers of leaves or tillers), depending upon cultivar, in Kentucky bluegrass seedlings (Whitmore and Mansfield, 1983, Whitmore et al , 1982) No effect on height of downy birch (Wright, 1987) |

TABLE 9-5 (cont'd). SOME EFFECTS OF NITROGEN OXIDES ON THE GROWTH AND YIELD OF PLANTS WITH RESPECT TO CONCENTRATIONS AND EXPOSURES USED IN EXPERIMENTAL INVESTIGATIONS^a

| NO _x (ppm) | Exposure Duration | Effect (Occurrence of Foliar Lesions) |
|--------------------------|--------------------------------|---|
| 0 1 | 104 h/week, 21 weeks | No effect on mass of Kentucky bluegrass seedlings exposed from emergence (Whitmore and Mansfield, 1983, Whitmore et al , 1982) |
| 0 1 | 104 h/week, 22 weeks | No significant effect on stem height, leaf area, or mass of shoot in second-year cuttings of black poplar, downy birch, or common apple, increased stem height in European white birch and white alder and leaf area and mass of shoot in small-leaved European linden (Freer-Smith, 1984, Whitmore and Freer-Smith, 1982) |
| 0 1 | 104 h/week, 28 weeks | No effect on orchard grass, significantly decreased mass of shoot—depending upon cultivar and stage of development in common timothy, perennial ryegrass (Whitmore and Mansfield, 1983), and Kentucky bluegrass (Whitmore and Mansfield, 1983, Whitmore et al , 1982) |
| 0 1 | 104 h/week, 33 weeks | Significantly reduced mass of shoot and number of culms in Kentucky bluegrass grown as swards (Whitmore and Mansfield, 1983, Whitmore et al , 1982) |
| 0 1 | 104 h/week, 60 weeks | No significant effect on stem height or mass of shoot in second-year cuttings of black poplar, downy birch, common apple, or small-leaved European linden, increased mass of shoot in European white birch, increased stem height and mass of shoot in white alder (Freer-Smith, 1984, Whitmore and Freer-Smith, 1982) No effect on height, stem diameter, and mass of shoot or roots in European white birch or downy birch (Wright, 1987) |
| 0 11 | 7 or 14 days | No effect on leaf area or mass of leaves, stem, or roots in 20- or 24-day-old potato plants from sprouts or rooted cuttings (Petitte and Ormrod, 1984,1988) |
| 0 11 | 4 weeks | No effect on leaf area or mass of leaves, stem, or roots in tomato plants (Marie and Ormrod, 1984) |
| 0 11 | 5 h/day, 5 days/week, 12 weeks | No effect on height or mass of plant or on number of inflorescences in <i>Chaenactis carphoclina</i> (Thompson et al , 1980) |
| 0 11 | 5 h/day, 5 days/week, 17 weeks | No significant effect on height or mass of plant or on number of inflorescences in alfilaria, desert marigold, or scorpion weed, or on mass of plant in <i>Plantago insularis</i> (Thompson et al , 1980) |
| 0 11 | 5 h/day, 5 days/week, 16 weeks | No significant effect on linear growth or mass of shoot in brittle bush, burro weed, creosote bush, or desert willow, linear growth was not affected, but mass of shoot was increased in four-wing saltbush (Thompson et al , 1980) |
| 0 11 | 5 h/day, 5 days/week, 32 weeks | No significant effect on linear growth or mass of shoot in brittle bush, burro weed, creosote bush, desert willow, or four-wing saltbush, reduced mass of seed in burro weed and number of inflorescences in brittle bush (Thompson et al , 1980) |

TABLE 9-5 (cont'd). SOME EFFECTS OF NITROGEN OXIDES ON THE GROWTH AND YIELD OF PLANTS WITH RESPECT TO CONCENTRATIONS AND EXPOSURES USED IN EXPERIMENTAL INVESTIGATIONS^a

| NO _x (ppm) | Exposure Duration | Effect (Occurrence of Foliar Lesions) |
|--------------------------|------------------------------|--|
| 0.11 | 104 h/week, 4 weeks | No effect on mass of green leaves, dead leaves and stubble, or roots, leaf area, number of leaves, or number of tillers in common timothy, Italian ryegrass, (Ashenden and Williams, 1980, Ashenden and Mansfield, 1978) or orchard grass (Ashenden, 1979b) Mass of roots reduced in Kentucky bluegrass (Ashenden, 1979b) |
| 0.11 | 104 h/week, 8 weeks | No effect on mass of green leaves, dead leaves and stubble, or roots, leaf area, number of leaves, or number of tillers in common timothy, Italian ryegrass (Ashenden and Williams, 1980, Ashenden and Mansfield, 1978) Decreased mass of green leaves and leaf area in orchard grass, and decreased mass of green leaves, dead leaves and stubble, or roots, leaf area, and number of leaves in Kentucky bluegrass (Ashenden, 1979b) No effect on growth in mass of leaves, stem, or roots, but significantly decreased number of leaves and increased area per leaf in 1-year black poplar cuttings (Freer-Smith, 1984, Whitmore et al , 1982) |
| 0.11 | 104 h/week, 10 weeks | No effect on mass of leaves, stem, or roots in black poplar during winter (Freer-Smith, 1984, Whitmore et al , 1982) |
| 0.11 | 104 h/week, 12 weeks | Significantly decreased mass of green leaves in orchard grass (Ashenden, 1979b), mass of dead leaves and stubble and of roots in Italian ryegrass (Ashenden and Williams, 1980, Ashenden and Mansfield, 1978), mass of roots in common timothy (Ashenden and Williams, 1980, Ashenden and Mansfield, 1978), and mass of green leaves, dead leaves and stubble, and roots, and leaf area and number of leaves in Kentucky ryegrass (Ashenden, 1979b) |
| 0.11 | 104 h/week, 16 weeks | No effect on mass of green leaves, dead leaves and stubble, or roots, leaf area, and number of leaves or tillers in orchard grass (Ashenden, 1979b) or in Italian ryegrass (Ashenden and Williams, 1980, Ashenden and Mansfield, 1978) Significantly decreased mass of roots in common timothy (Ashenden and Williams, 1980, Ashenden and Mansfield, 1978) and mass of green leaves, dead leaves and stubble, or roots, and leaf area in Kentucky bluegrass (Ashenden, 1979b) |
| 0.11 | 104 h/week, 20 weeks | No effect on mass of green leaves, dead leaves and stubble, or roots, leaf area, and number of leaves or of tillers in common timothy or Italian ryegrass (Ashenden and Williams, 1980, Ashenden and Mansfield, 1978) Significantly decreased mass of dead leaves and stubble in orchard grass (Ashenden, 1979b) and mass of green leaves, dead leaves and stubble, and roots in Kentucky bluegrass (Ashenden, 1979b) |
| 0.11 | 104 h/week, 22 weeks | No effect on growth in mass of stem or roots in 1-year black poplar cuttings (Freer-Smith, 1984, Whitmore et al , 1982) |
| 0.12 | 2 h/day, 1 day/week, 3 weeks | Significantly increased mass of plant and leaf area after 3 weeks, but no effect after 2 weeks in garden pea (added to continuous exposure of 0.029 ppm) (Edelbauer and Maier, 1988) |

TABLE 9-5 (cont'd). SOME EFFECTS OF NITROGEN OXIDES ON THE GROWTH AND YIELD OF PLANTS WITH RESPECT TO CONCENTRATIONS AND EXPOSURES USED IN EXPERIMENTAL INVESTIGATIONS^a

| NO _x (ppm) | Exposure Duration | Effect (Occurrence of Foliar Lesions) |
|--------------------------|-----------------------------------|--|
| 0 15 | 10 days | No effect on area of third youngest leaf of 48-day-old plants (at start) in redtop, creeping bentgrass, colonial bentgrass, red fescue, or perennial ryegrass, significant reduction in 1 out of 12 cultivars of Kentucky bluegrass (Elkiey and Ormrod, 1980) No effect on fresh mass, but both decreased and increased leaf area in Kentucky bluegrass, depending upon cultivar and environmental conditions (Elkiey and Ormrod, 1981a) |
| 0 16 | to 22 days | Significantly decreased mass of leaf after 10 days and both mass and area of leaf after 22 days in tomato (Taylor and Eaton, 1966) |
| 0 2 | 3 or 6 h | No effect on mass of leaves or root in radish plants (Reinert and Gray, 1981) |
| 0 2 | 7 h/day, 5 days | No effect on relative growth rate of 5-week-old soybean plants (Sabaratnam and Gupta, 1988) |
| 0 2 | 3 h/day, once/2 days, 4 weeks | No effect on mass of leaves, stem, roots, or nodules or on number of nodules in 7-week-old soybean plants (Klarer et al , 1984) |
| 0 2 | 14 days | Significantly decreased leaf area, but did not affect mass of leaves, stem, or roots in 28-day-old sunflower plants, no effect in maize (Okano et al , 1985a) |
| 0 2 | 38 days | No effect on leaf area (+11) in common sunflower (Natori and Totsuka, 1980) |
| 0 2 | 50 days | Significantly increased mass of plant and leaf area depending on fertilizer in soil in tomato (NO) (Anderson and Mansfield, 1979) |
| 0 2 | 60-67 days | No effect on leaf area in tomato or cucumber (Natori and Totsuka, 1980) |
| 0 2 | 11 weeks | Significantly increased mass of roots and shoots and number of tillers in two populations of perennial ryegrass (Taylor and Bell, 1988) |
| 0 2 | 5 h/day, 2 days/week, 12-16 weeks | Significantly decreased number and mass of tubers and accelerated senescence and abscission of foliage in potato (Sinn and Pell, 1984) |
| 0 21 | 1 h | No effect on leaf area, height, or fresh mass of leaves or stems in tomato (Goodyear and Ormrod, 1988) |
| 0 21 | 1 h/day, 15 days | No effect on mass of plant in green bean or tobacco (Elkiey et al , 1988) |
| 0 21 | 20 days | No effect on mass of leaves or root (0 to +20) in six cultivars of radish (Godzik et al , 1985) |
| 0 25 | 3 h/day, 6 days in 4 weeks | Significantly decreased masses of stems and leaves and length of shoot in two out of eight cultivars of 1-year-old azalea plants (Sanders and Reinert, 1982b) |
| 0 3 | 7 h/day, 5 days | No effect on relative growth rate of 5-week-old soybean plants (Sabaratnam and Gupta, 1988) |

TABLE 9-5 (cont'd). SOME EFFECTS OF NITROGEN OXIDES ON THE GROWTH AND YIELD OF PLANTS WITH RESPECT TO CONCENTRATIONS AND EXPOSURES USED IN EXPERIMENTAL INVESTIGATIONS^a

| NO _x (ppm) | Exposure Duration | Effect (Occurrence of Foliar Lesions) |
|--------------------------|----------------------------|--|
| 0.3 | 3 h/day, 3 days in 1 week | No effect in 30-day-old radish plants (Sanders and Reinert, 1982a) |
| | 6 h/day, 3 days in 1 week | No effect on masses of shoot or flowers, but significantly increased mass of roots in 58-day-old French marigold plants (Sanders and Reinert, 1982a) |
| | 3 h/day, 9 days in 4 weeks | No effect in 30-day-old radish plants (Reinert and Sanders, 1982) |
| | 6 h/day, 9 days in 4 weeks | No effect in 58-day-old French marigold plants (Reinert and Sanders, 1982) |
| 0.3 | 10 h/day, 14 days | Significantly decreased leaf area and mass of leaf sheath in maize. Had no effect on leaf area or mass of leaf, stem, or roots in tomato or Swiss chard. Significantly increased the leaf area and mass of leaves, stem, and roots in cucumber, the leaf area and mass of leaves and stem in common sunflower, and the leaf area and masses of stem and roots in green bean (Yoneyama et al., 1980c) |
| 0.37 | 2.5 h/event, 10 events | No effect on yield of soybean plants grown in field plots (Irving et al., 1982) |
| 0.4 | 3 or 6 h | No effect on mass of leaves or root in 25-day-old radish plants (Reinert and Gray, 1981) |
| 0.4 | 2.9 h/event, 10 events | No effect on yield of soybean plants grown in field plots (Irving et al., 1982) |
| 0.5 | 1 h | No effect on height or number of leaves, but significantly increased leaf area, mass of leaves, and mass of stem in rooted cuttings of black poplar, significantly increased leaf area in Carolina poplar (Eastham and Ormrod, 1986) |
| 0.5 | 7 h | Significantly decreased number of pods and seeds and mass of seeds in soybean (Gupta and Sabaratnam, 1988) |
| 0.5 | 7 h/day, 5 days | Significantly decreased relative growth rate of 5-week-old soybean plants (Sabaratnam and Gupta, 1988) |
| 0.5 | 6 h/day, 14 days | Significantly decreased mass of shoot and roots, but increased or decreased number of nodules, depending on level of nitrate, in 23-day-old green bean seedlings (Srivastava and Ormrod, 1986) |

^aNO_x = Nitrogen oxides
NO₂ = Nitrogen dioxide
NO = Nitric oxide
SO₂ = Sulfur dioxide

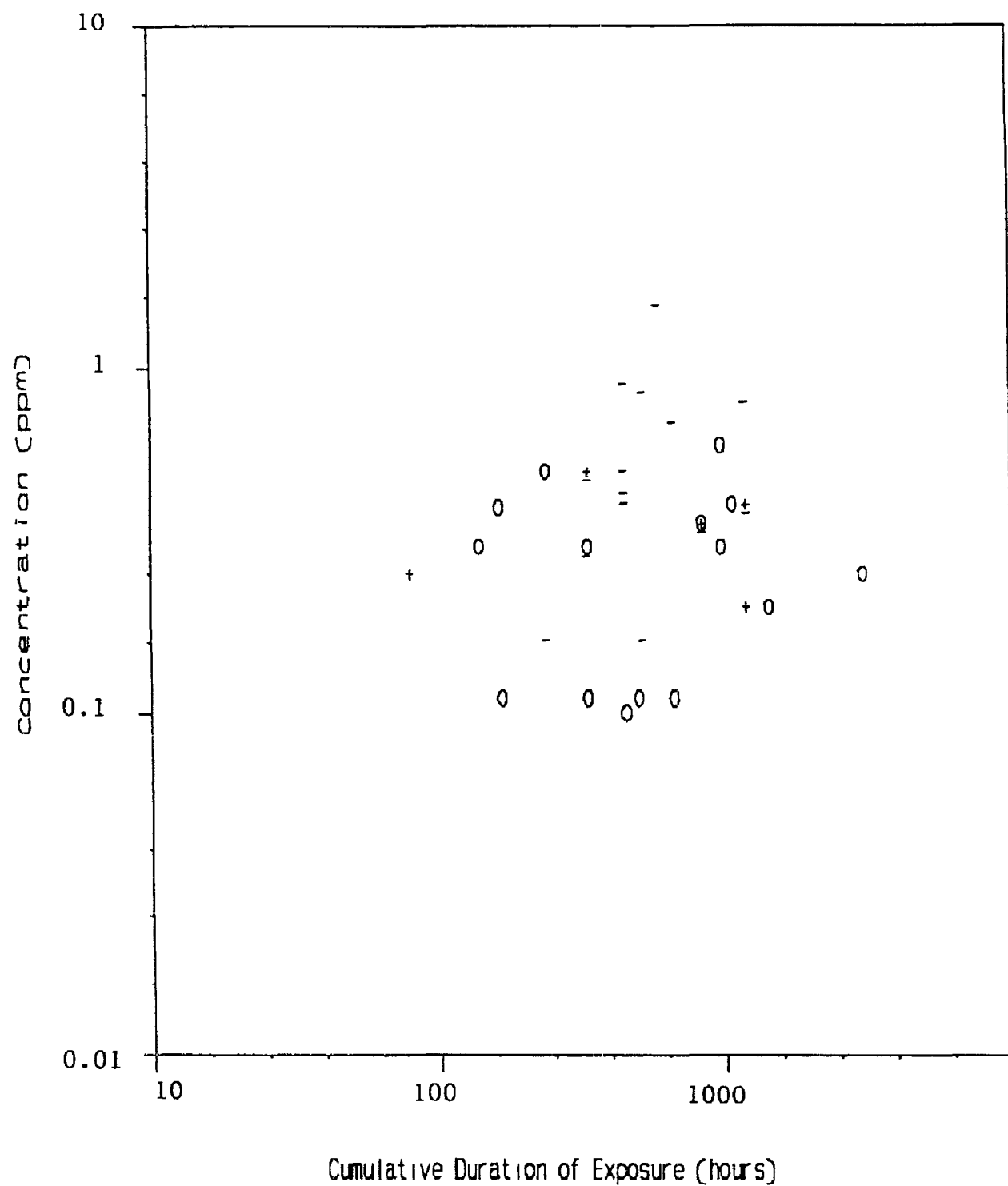


Figure 9-14. Experimental exposures to nitrogen oxides resulting in the occurrence of increased (+), decreased (-), or unaffected (o) growth or yield in tomato.

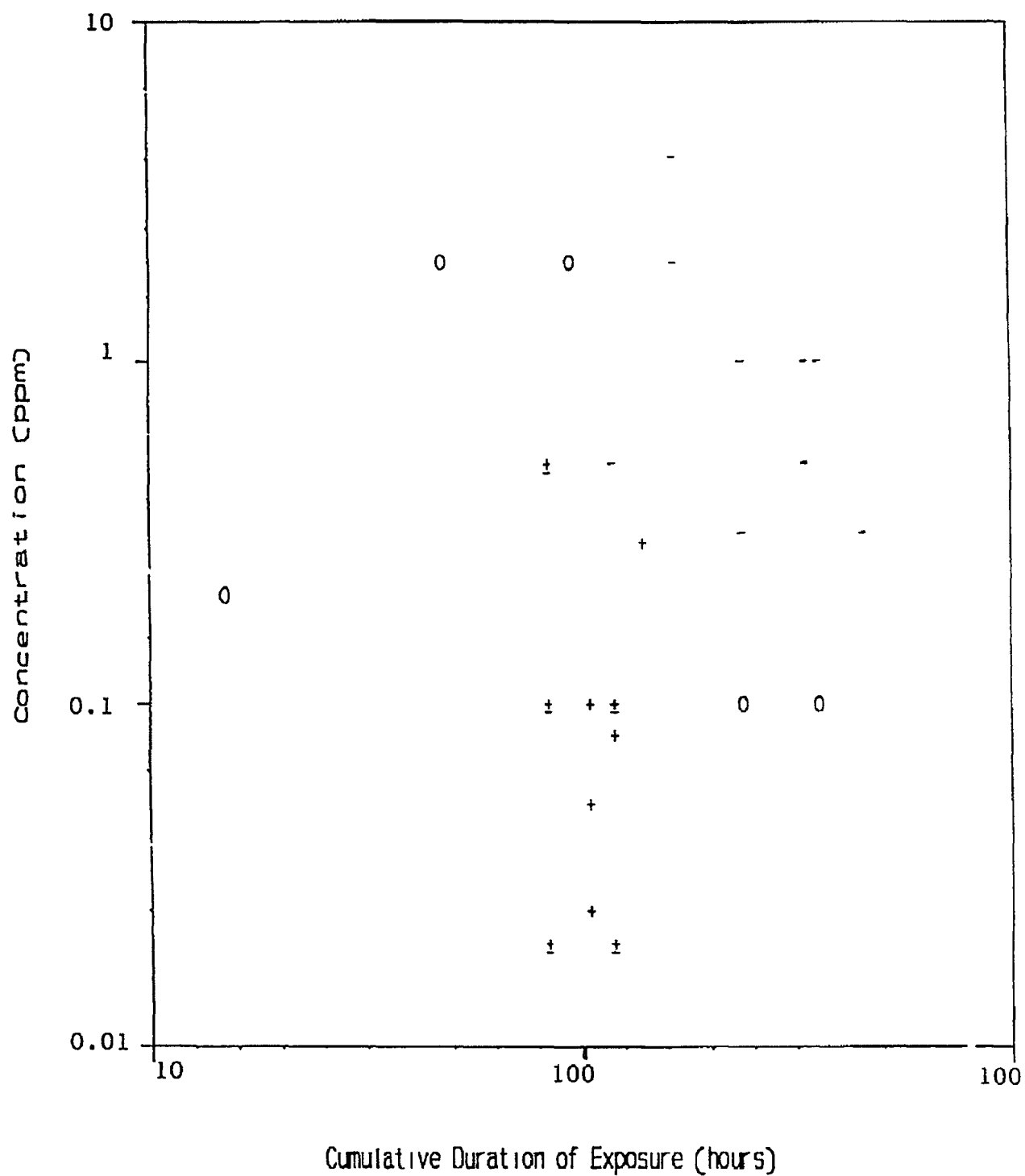


Figure 9-15. Experimental exposures to nitrogen oxides resulting in increased (+), decreased (-), or unaffected (o) growth or yield in green bean.

increased the mass of plant by 20% and leaf area by 31% after 3 weeks of exposure, but not after 2 weeks (Edelbauer and Maier, 1988)

In several species, stimulations of growth occurred at lower concentrations of NO_x than did inhibitions. For example, a 1-h exposure to NO_2 at 0.5 ppm significantly increased leaf area, mass of leaves, and mass of stem in rooted cuttings of black poplar and increased leaf area in Carolina poplar, whereas NO_2 at 1.0 ppm significantly decreased mass of stem in black poplar and decreased height in Carolina poplar (Eastham and Ormrod, 1986)

In radish, exposure to NO_2 at 0.08 ppm, for 3 h/day for 40 days substantially increased mass of plant (93%) and hypocotyl (215%) (Runeckles and Palmer, 1987), whereas continuous or intermittent exposures ranging from several hours to 3 weeks to NO_2 in the range of 0.2 to 0.4 ppm had no significant effect on growth of leaves or root (Reinert and Gray, 1981, Godzik et al., 1985, Sanders and Reinert, 1982a, Reinert and Sanders, 1982), and reductions in mass of plant (33%) and leaf area (29%) occurred with a continuous exposure to NO_2 at 0.5 ppm for 14 days (Okano et al., 1988). Similarly, with cucumber, exposures to NO_2 at 0.2 ppm (Natori and Totsuka, 1980) or 0.3 ppm increased leaf area and the masses of leaves, stems, and roots (Yoneyama et al., 1980c), whereas exposure to NO_2 at 0.5 ppm for 14 days decreased the mass of plant and the leaf-weight ratio (Okano et al., 1988)

Because the exposure-effect relationship for growth is not monotonic, it is difficult to determine whether an exposure that produces no effect is one below the threshold for any effect at all, or is in the range of exposures between those that increase growth and those that decrease it.

In some studies, measures of growth are evaluated once, at maturity or some other defined time. In others, changes in these variables over time have been used to determine the effects of NO_x not only on rate of growth but also on certain stages of vegetative or reproductive development. Consequently, another problem in the interpretation of experimentally produced effects is the relationship of changes occurring in young plants or with short-term exposures to those effects on growth and yield that would eventually be manifest in mature plants or with long-term exposures.

When potato plants were subjected to NO_2 at 0.2 ppm for 5 h/day, 2 days/week, for 12 to 16 weeks in field exposure chambers, both the number and mass of tubers were reduced (by up to 38% and 51%, respectively, depending on cultivar), and reductions in

yield were associated with an accelerated senescence and abscission of foliage (Sinn and Pell, 1984) Shorter term (7-, 14-, or 15-day) exposures to lower concentrations (0.10 or 0.11 ppm NO₂) had no effect on the growth of younger (20-, 24-, or 30-day-old) plants (Petitte and Ormrod, 1984, 1988, Elkley et al , 1988)

There was no significant effect on yield of soybeans grown in field plots and exposed (by a zonal air pollution system) 10 times during the growing season to concentrations of NO₂ ranging from 0.12 to 0.37 ppm for an average of 2.5 h per event in one year or concentrations from 0.07 to 0.4 ppm for an average of 2.9 h per event in another year (Irving et al., 1982) No significant effect on the growth of 7-week-old soybean plants occurred in exposures of 3 h/day, once every 2 days, for 15 events to NO₂ at 0.1 or 0.2 ppm, although the number of nodules was decreased by 4% at the lower concentration and by 15% at the higher (Klarer et al , 1984) The absence of effects on growth by NO₂ concentrations at or less than 0.4 ppm is consistent with the lack of an effect on the relative growth rate of 5-week-old soybean plants by exposures of 7 h/day for 5 days at concentrations less than or equal to 0.3 ppm and a reduction when the concentration was 0.5 ppm (Sabaratnam and Gupta, 1988) However, a single exposure to 0.5 or 1.0 ppm for 7 h, when plants were 1 mo old, was reported to decrease yield of pods and seeds when plants were harvested 80 days later (Gupta and Sabaratnam, 1988)

Two series of long-term, continuous exposures with bearing navel orange trees utilized the addition of NO₂ to charcoal-filtered ambient air No significant effects of NO₂ with an 8-mo exposure (May through December) were found with respect to number or mass of fruit per tree when levels were one or two times that of ambient (based upon hourly means of the preceding day) in the Los Angeles Basin (range of 0 to 0.18 ppm) (Thompson et al , 1971) With a series of defined levels (1.0, 0.5, 0.25, 0.125, or 0.0625 ppm) for 290 days, the number and mass of fruit per tree were significantly reduced by more than 70% at the two highest concentrations (0.5 and 1.0 ppm) Although yield of trees subjected to the lowest concentration (0.0625 ppm) of NO₂ was not significantly different from those receiving filtered air, pooled values for the three lower concentrations (0.0625, 0.125, and 0.25 ppm, mean = 0.1458 ppm) gave a significant reduction in number of fruit (51% reduction) and mass of fruit (45% reduction) (Thompson et al , 1970)

Five species each of desert annuals and shrubs were subjected to intermittent exposures (5 h/day for 5 days/week) to NO₂ at 0.11, 0.33, or 1.0 ppm under greenhouse conditions for periods ranging from 9 to 32 weeks (depending on species). At the lowest concentration of NO₂, there was no significant effect on height or mass of plant or on number of inflorescences in *Chaenactis carphoclinia*, Gray after 12 weeks, on mass of plant in *Plantago insularis*, Easter after 17 weeks, nor on height or mass of plant or number of inflorescences in alfilaria, desert marigold, or scorpion weed after 17 weeks. With exposures of 16 weeks, there was no significant effect on linear growth or mass of shoot in brittle bush, burro weed, creosote bush, or desert willow, and linear growth was not affected, but mass of shoot was increased, in four-wing saltbush. With exposures of 32 weeks, there was no significant effect on linear growth or mass of shoot in brittle bush, burro weed, creosote bush, desert willow, or four-wing saltbush, but there was a reduction in the mass of seed in burro weed and the number of inflorescences in brittle bush (Thompson et al., 1980).

A general form for the relationship between exposure to NO_x and an effect on growth or yield is suggested by common features of many studies, and it would have the following characteristics: (1) a threshold exposure that must be exceeded for an effect (i.e., a deviation from the unexposed state) to occur, (2) an increase in growth or yield at exposures above the threshold but below those that produce a decrease, (3) an increasingly greater reduction in growth or yield with increasing concentration of NO_x or duration or frequency of exposure (greater than those that produce an increase in growth), yielding a nonmonotonic but unimodal relationship, and (4) within the same species, the exposure-effect relationship can be different for reproductive and vegetative development and it can vary among different organs of the same plant (e.g., an effect on the growth of roots could occur at a lesser or greater exposure than what would produce the same degree of effect in the growth of stems or leaves).

Experimental investigations have not provided a clear demarcation between exposures to NO_x that adversely affect the growth, development, or reproduction of plants and those that do not. Nevertheless, single exposures of 24 h or less that could produce adverse effects are at concentrations of NO₂ greater than what have been shown to occur in ambient exposures in the United States. In periods of 2 weeks or greater duration with intermittent exposures of several hours per day, adverse effects on growth or yield start to appear when the

concentration of NO_x reaches the range of 0.1 to 0.5 ppm, depending on the species of plant, nature of effect, and conditions of exposure

9.5 FACTORS AFFECTING PLANT RESPONSE TO NITROGEN OXIDES

9.5.1 Characteristics of the Plant

Those characteristics of a plant that are known to affect its response to NO_x can be arranged into three general categories (1) genetic, which includes species, race, cultivar, or clone; (2) phenologic, such as the stage of development of a plant or temporal changes in the states of its organs, and (3) phenotypic, which results from the interaction of the inherent genetic factors of the plant with the conditions of its environment (The last category will be considered in a discussion of the influence of environmental conditions, Section 9.5.2)

9.5.1.1 Species of Plant

More than 250 species have been used in investigations of NO_x (Appendix 9A). The bulk of research has been devoted to herbaceous species, and most of these represent plants that are grown commercially. The woody species preponderantly represent trees and shrubs that both are cultivated as ornamentals and occur as components of natural plant communities in temperate climatic zones. Species of plant determines the exposure-response relationship in several ways.

First, species determines sensitivity (or tolerance) to NO_x and thereby the magnitude of the effect or risk associated with a given exposure. Variations in sensitivity to NO_x occur among the species of plants, and the results of several comparative studies (Czech and Nothdurft, 1952, Benedict and Breen, 1955, MacLean et al., 1968, Van Haut and Stratmann, 1967) have been compiled, with species placed in the three general categories of high, moderate, or low sensitivity (National Research Council, 1977). More recent studies have provided additional information on certain commercial plants (Taylor et al., 1975, Matsushima, 1977), desert species (Thompson et al., 1980), and several species of ornamental, greenhouse crops, with reference to their sensitivity to NO₂-induced effects on

commercial value (Mortensen, 1985a, Saxe, 1986a, Saxe and Christensen, 1985) The results of several of these studies are summarized in Table 9-6

Classifications of different species according to their sensitivity have relied on two operationally distinct methods One measured relative sensitivity as the magnitude of exposure required to achieve a certain effect (Czech and Nothdurft, 1952, Van Haut and Stratmann, 1967) The other used the degree of effect produced by a certain exposure (Benedict and Breen, 1955, Kress and Skelly, 1982, Mortensen, 1985a) A combination of both methods was also used (MacLean et al , 1968, Thompson et al , 1980, Taylor et al , 1975, Zahn, 1975, Matsushima, 1977) All such classifications are subject to the caveat that relative sensitivity depends upon stage of development, environmental conditions, and kind of effect that is observed (Van Haut and Stratmann, 1967)

Some interspecific differences in response have been associated with differences in the uptake of NO_x (see Sections 9 3 1 and 9 6), which in turn have been investigated in relation to other characteristics, such as growth rate, stomatal density, or unit of effective leaf area (Okano et al , 1988) Nevertheless, the inherent factors determining response are numerous and complex, and no single factor or set of them has yet been advanced to provide a consistent explanation of interspecific differences

It has been shown that the kind and magnitude of the effect of NO_x depends on the processes (e g , growth or reproduction) and organ (e g , leaves, stems, or roots) considered (see Section 9 5 2 and Appendix 9A) Consequently, a second way in which species enters into the exposure-response relationship is that it determines the function of the plant, and thereby, which of the various effects that may be produced by NO_x will be of greatest practical significance For example, the effect of paramount importance would be yield of seed in cereals, fruit in tomato, tubers in potato, appearance and rate of development in floricultural crops, and wood volume in forest trees It has also been shown that species (as well as other taxa) can determine the kind of foliar symptom that is produced by exposure to NO_x (Section 9 4 1)

To the extent that species governs the type of life cycle followed by the plant in the habitat it occupies, species may also determine what temporal characteristics of exposure and what sets and ranges of environmental conditions should be considered in estimations or predictions of the plant's response to NO_x

TABLE 9-6. RELATIVE SENSITIVITIES OF PLANTS TO NITROGEN DIOXIDE^a

| Sensitive | Intermediate | Tolerant |
|--|--|---|
| Conifers | | |
| European larch | Colorado blue spruce Nikko fir White fir White spruce | Austrian pine English yew Hinoki cypress Japanese black pine Loblolly pine Pitch pine Virginia pine |
| Trees and Shrubs | | |
| European white birch | Japanese maple Japanese zelkova Little-leaf linden Norway maple | Beech Black locust Black poplar Elder English oak European hornbeam Ginkgo (Maidenhair tree) Green ash Scotch elm Sweetgum White ash White oak |
| Field Crops and Grasses | | |
| Alfalfa (lucerne) Barley Oats Red clover Spring clover Spring vetch Tobacco | Annual bluegrass Potato Rye Sweet corn Wheat | Kentucky bluegrass |
| Fruit Trees and Shrubs | | |
| Apple (wild) Pear (wild) | Crabapple Grapefruit Japanese pear Orange Tangelo | |
| Garden Crops | | |
| Carrot ^b Celery ^b Leek Lettuce Parsley Pea Pinto bean Rhubarb | Bush bean ^b Celery ^b Tomato | Asparagus Bush bean ^b Cabbage Carrot ^b Kohlrabi Onion |

**TABLE 9-6 (cont'd). RELATIVE SENSITIVITIES OF PLANTS TO
NITROGEN DIOXIDE^a**

| Sensitive | Intermediate | Tolerant |
|--------------------------------------|----------------------|-------------------------|
| Ornamental Shrubs and Flowers | | |
| Azalea | Cape jasmine | Carissa |
| Bougainvillea | Catawba rhododendron | Croton |
| Chinese hibiscus | Common zinnia | Daisy |
| Common petunia | Dahlia | Gladiolus |
| Oleander | Flossflower | Japanese morning glory |
| Pyraecantha | Fuchsia | Lily-of-the-valley |
| Rose ^b | Gardenia | Plantain lily |
| Snapdragon | Ixora | Rose ^b |
| Sweet pea | Japanese pittosporum | Shore juniper |
| Tuberous begonia | Ligustrum | Spring heath |
| | Oleander | |
| | Paperbark tree | |
| | Petunia | |
| Weeds | | |
| Common mugwort | Cheeseweed | Lamb's-quarters |
| Common plantain | Chickweed | Nettle-leaved goosefoot |
| Horseweed | Common chickweed | Pigweed |
| Mustard | Dandelion | Red root |
| Sunflower | | |
| Desert Species | | |
| Creosote bush | Brittle bush | Alfilaria |
| | Desert willow | Burro weed |
| | | Chaenactis (CN) |
| | | Desert marigold |
| | | Four-wing saltbush |
| | | Scorpion weed |

^aCompiled from Benedict and Breen (1955), Czech and Nothdurft (1952), Kress and Skelly (1982), MacLean et al (1968), Matsushima (1977), Taylor and MacLean (1970), Thompson et al (1980), Van Haut and Stratmann (1967)

^bDifferent investigators reported different susceptibilities

9.5.1.2 Intraspecific Variation

Differences among cultivars, races, families, or clones within several species have demonstrated that intraspecific variation in sensitivity to NO_x can occur (Table 9-7). However, no analyses have been made of the genetic factors that may determine it in crops, nor have analyses been made of the statistics that could describe its distribution in natural populations.

**TABLE 9-7. INTRASPECIFIC DIFFERENCES IN THE RESPONSES OF
PLANTS TO NITROGEN OXIDES^a**

Tomato

Exposure to NO at 0.4 ppm increased growth in two cultivars (Sonato and Eurocross BB, to a greater degree in the former) and decreased growth in two others (Extase and Adagio, to a greater degree in the latter) (Anderson and Mansfield, 1979)

Two cultivars (Ailsa Craig and Sonato) differed in response to NO-induced increases in the level of nitrate reductase in leaves (Wellburn et al., 1980)

Two cultivars (Ailsa Craig and Eurocross BB) differed with respect to effects of exposure to NO or to NO₂ at 1.5 ppm on the levels of nitrate or nitrite reductase in leaves and content of nitrate or amines (Murray and Wellburn, 1985)

Eight cultivars were compared in an exposure to NO_x at 0.7 ppm in enriched (1,000 ppm) CO₂. Foliar lesions and the greatest reductions in growth occurred in three cultivars (Rianto, Dombito, and Virosa), significant reductions in growth occurred in three other cultivars (Marathon, Abunda, and Ida), and no effects on growth were produced in two cultivars (Sonatine and Dombello) (Mortensen, 1985b)

Potato

Two cultivars (Kennebec and Atlantic) were exposed to NO₂ at 0.2 ppm, but there were no differences between them in rate of senescence of leaves or in reductions in number or mass of tubers (Sinn and Pell, 1984)

Four cultivars (Superior, Norchip, Kennebec, and Russet Burbank) were exposed to NO₂ at 0.11 ppm, stem fresh weight was reduced in Kennebec, and it was postulated that varietal differences in response may be related to maturity class (Petitte and Ormrod, 1984). When Kennebec and Russet Burbank were exposed to NO₂ at 0.11 ppm as rooted cuttings, fresh mass of roots was decreased in Kennebec (Petitte and Ormrod, 1988). NO₂-induced intumescences of the leaf occurred in Kennebec and Russet Burbank, but not in the other two cultivars (Petitte and Ormrod, 1986)

Pepper

Activity of nitrate reductase in leaves of two cultivars (Bell Boy and Rumba) was not affected by exposure to NO₂ at 1.5 ppm, but activity of nitrite reductase was reduced in Bell Boy, this cultivar also had a greater increase in content of amines in foliage (Murray and Wellburn, 1985)

Radish

Six cultivars were exposed to NO₂, but no conclusions are possible as to the influence of genetic factors because no foliar lesions were produced and there was no effect on dry mass of leaves or roots (Godzik et al., 1985)

Lettuce

Six cultivars were exposed to NO₂, but no conclusions are possible as to the influence of genetic factors because there was no effect on dry mass of leaves or growth rate (Mortensen, 1985b)

TABLE 9-7 (cont'd). INTRASPECIFIC DIFFERENCES IN THE RESPONSES OF PLANTS TO NITROGEN OXIDES^a

Barley

There was a significant association between increased mass of straw and ambient NO₂ in two cultivars (Aramir and Claret), but not in two others (Dram and Golden Promise), a significant association between increased number of tillers and NO₂ occurred with Golden Promise, but not with the other cultivars (Ashmore et al , 1988)

The degree to which exposure to NO₂ at 0.3 ppm altered the level of nitrate reductase varied among mutants deficient in the enzyme, genotype did not affect uptake of NO₂ (Rowland-Bamford et al , 1989)

Oats

Three cultivars (Clintland 64, 329-80, and Pendek) were classified as susceptible to NO₂-induced foliar injury in a concentration-duration factorial design, based on statistics for the dose-response function, about a 48% range in threshold dose for 1 h (Heck and Tingey, 1979)

Corn

Both cultivars (Pioneer 509-W and Golden Cross) were judged tolerant to NO₂-induced foliar injury (Heck and Tingey, 1979)

Cotton

In a concentration times duration factorial design, two cultivars (Paymaster and Acala 4-42) were classed as intermediate in susceptibility to foliar injury, but there appeared to be a difference in statistics describing the dose-response function (equivalent to a 40% difference in threshold dose for 1 h) (Heck and Tingey, 1979)

Tobacco

In a concentration times duration factorial design, three cultivars (Bel B, Bel W3, and White Gold) were classed as intermediate in susceptibility to foliar injury and one (Burley 21) was classed as tolerant (Heck and Tingey, 1979)

Timothy

Two cultivars (Eskimo and S48) differed in growth response to NO₂ at 0.062 ppm when exposed at later stages of development (Whitmore and Mansfield, 1983)

Red fescue

The growth of two cultivars (Highlight and Pennlawn) was not affected by NO₂ at 0.15 ppm for 10 days, but foliar injury occurred in Pennlawn (Elkiey and Ormrod, 1980)

Red clover

In three cultivars (Astra, Deben, and S123), but not in a fourth (Altaswede), there was a significant association between reduced growth of roots and ambient NO₂ (Ashmore et al , 1988)

TABLE 9-7 (cont'd). INTRASPECIFIC DIFFERENCES IN THE RESPONSES OF PLANTS TO NITROGEN OXIDES^a

Orchard grass

Two populations (Rainham and S26) differed in susceptibility to foliar injury from NO₂ at 4.8 ppm (Taylor and Bell, 1988)

Perennial ryegrass

Two clones (Rainham and S23) differed with respect to growth under exposure to NO₂ at 0.2 ppm and soil-nitrogen (Taylor and Bell, 1988)

Two cultivars (S23 and S24) differed as to the influence of stage of development on the growth reduction produced by NO₂ at 0.062 ppm (Whitmore and Mansfield, 1983)

Effects of NO₂ on levels of nitrite reductase and bioenergetic functions varied among different clones (Wellburn et al., 1981; Wellburn, 1982b)

Kentucky bluegrass

In twelve cultivars, NO₂ at 0.15 ppm for 10 days produced a significant reduction in leaf area in one (Baron) and foliar injury in two others (Cheri and Skoftu) (Elkiey and Ormrod, 1980)

Exposure to NO₂ at 0.15 ppm increased the growth of one cultivar (Merion), but not of two others (Cheri and Touchdown) that had foliar injury (Elkiey and Ormrod, 1981a)

Exposure to NO₂ at 0.062 ppm decreased growth in one cultivar (Monopoly), but not in another (Arima) (Whitmore and Mansfield, 1983)

Among nine cultivars, rates of uptake of NO₂ in light and dark varied over a three- to twofold range (Elkiey and Ormrod, 1981b)

Petunia

A comparison of 15 cultivars with respect to foliar injury induced by 1-h exposures to NO₂ at 8, 16, or 32 ppm indicated a range of tolerance (ED₅₀) of about threefold. White Cascade was judged the most susceptible (Feder et al., 1969)

Nitrogen content in leaves of three cultivars (Capri, White Magic, and White Cascade) was reduced by exposure to NO₂ at 0.8 ppm (Elkiey and Ormrod, 1981d). Rate of absorption of NO₂ was less in Capri than in the other two cultivars (Elkiey and Ormrod, 1981c)

Japanese morning glory

Four cultivars (Heavenly Blue, Hamano Yosoo1, Scarlet O'Hara, and Murasaki Jishi) had foliar injury ranging from severe to slight after a 1-h exposure to NO₂ at 0.12 ppm (Matsushima, 1977)

African violet

With two cultivars (Lena and Rosa Roccoco) under CO₂ enrichment, NO_x at 0.85 ppm reduced growth in Lena. A delay in flowering and decrease in number of flowers occurred in both cultivars, but were greater in Lena (Mortensen, 1985a)

TABLE 9-7 (cont'd). INTRASPECIFIC DIFFERENCES IN THE RESPONSES OF PLANTS TO NITROGEN OXIDES^a

English ivy

Two cultivars (Gloire de Marengo and Harald) were exposed to NO_x at 0.85 ppm under CO₂ enrichment, the growth of neither was affected (Mortensen, 1985a)

Chrysanthemum

Two cultivars (Refour and Horim) were exposed to NO_x at 0.85 ppm under CO₂ enrichment, the growth of neither was affected (Mortensen, 1985a)

Hibiscus

Two cultivars (Red and Moesiana) differed in some ways with respect to the effects of NO or NO₂ on photosynthesis, respiration, or transpiration (Saxe, 1986a)

Under CO₂ enrichment, NO at 1 ppm affected neither cultivar with respect to mass, height, number of shoots, or production time (Saxe and Christensen, 1984, 1985)

Azalea

Eight cultivars from five hybrid groupings had no foliar injury from NO₂ at 0.25 ppm, however, two cultivars (one a Kurume, the other an Indian hybrid) had reduced shoot length (Sanders and Reinert, 1982b)

Orange

Five varieties of orange showed different sensitivities to defoliation by acute exposures to NO₂ (greater than 25 ppm) (MacLean et al., 1968)

European white birch

Two clones tended to differ with respect to effects of NO₂ at 0.062 ppm on growth (Wright, 1987)

The relative standard deviation for growth during exposure to a mixture of SO₂ and NO₂, each at 0.05 ppm, was about threefold greater in seedlings than in clonal cuttings (Whitmore and Freer-Smith, 1982)

Poplar

Three clones of poplar (two from one hybrid cross and one from another) differed in the degree to which exposure to NO₂ at 0.3 ppm increased foliar mass and area (Okano et al., 1989)

Sycamore

No difference occurred between two half-sib families with respect to increased growth following exposure to NO₂ at 0.1 ppm (Kress et al., 1982a)

TABLE 9-7 (cont'd). INTRASPECIFIC DIFFERENCES IN THE RESPONSES OF PLANTS TO NITROGEN OXIDES^a

Eastern white pine

Eight clones differed with respect to the relationship between concentration of NO₂ (0.1 to 0.3 ppm) and the induction of symptoms and the decreased growth in mass and length of needles (Yang et al., 1982, 1983a,b)

Loblolly pine

Two collections of seed were exposed to NO₂ at 0.1 ppm, but no conclusions are possible as to the influence of genetic factors because there was no effect of NO₂ on height or dry masses of top or root of seedlings (Kress and Skelly, 1982)

| | | |
|------------------------------------|-----------------------------------|--|
| ^a NO = Nitric oxide | NO _x = Nitrogen oxides | ED ₅₀ = Median effective dose |
| NO ₂ = Nitrogen dioxide | CO ₂ = Carbon dioxide | SO ₂ = Sulfur dioxide |

Some intraspecific differences in response have been determined over a range of exposures to NO_x, thereby allowing quantitative estimates to be made as to the influence of this factor on exposure-response relationships. In a concentration-duration factorial design, statistics for the exposure-response function for foliar injury yielded about a 48% difference in the threshold exposure for 1 h between cultivars of oat and about a 40% difference between cultivars of cotton. This approach was also used to classify two cultivars of corn and one cultivar of tobacco as tolerant and three cultivars of tobacco as intermediate in sensitivity to foliar injury (Heck and Tingey, 1979). The same kind of experiment found different sensitivities to defoliation by acute exposures to NO₂ among five varieties of orange (MacLean et al., 1968). A comparison of 15 cultivars of petunia at three concentrations of NO₂ yielded a range of tolerance to foliar injury of about threefold (Feder et al., 1969).

Usually, comparisons have been made with respect to magnitude of effect produced within the same exposure, which means that the exposure-response relationship must be at hand to transform differences in response to differences in exposure required to produce equivalent effects. The preponderance of evidence has been obtained from agriculturally important species. Although many different cultivars of several species of crops have been used, the number of investigations in which two or more were employed under the same regime at the same time is limited.

The effects of NO_x on growth have been shown to vary with cultivar in barley (mass of straw and number of tillers) (Ashmore et al , 1988), tomato (increases as well as decreases occurred) (Anderson and Mansfield, 1979), timothy at later stages of development (Whitmore and Mansfield, 1983), and in clover (Ashmore et al , 1988), and with clone as well as cultivar in perennial ryegrass with respect to the influence of soil nitrogen (Taylor and Bell, 1988) or the stage of development (Whitmore and Mansfield, 1983) In Kentucky bluegrass, the occurrence of foliar injury as well as effects of NO_2 on growth varied with cultivar (Elkley and Ormrod, 1980, 1981a, Whitmore and Mansfield, 1983)

Differences occurred among cultivars of potato with respect to NO_2 -induced effects on growth of roots or stem, and it was postulated that varietal differences in response might be related to maturity class (Petitte and Ormrod, 1984, 1988) However, there were no differences between two cultivars of different maturities with respect to effect of NO_2 on rate of senescence of leaves or in reductions in number or mass of tubers (Sinn and Pell, 1984)

When plants were exposed to NO or NO_2 under CO_2 enrichment, differences occurred among eight cultivars of tomato with respect to severity of foliar lesions and reductions in growth (Mortensen, 1985b) Between-cultivar differences were also found in effects on growth of African violet (Mortensen, 1985a) and in physiological response (Saxe, 1986a), but not in growth of hibiscus (Saxe and Christensen, 1984, 1985) No differences occurred in English ivy or Chrysanthemum (Mortensen, 1985a)

Intraspecific differences with respect to the effects of NO_2 on growth also occurred in woody species (e g , among eight cultivars of azalea [Sanders and Reinert, 1982a], two clones of European white birch [Wright, 1987], three clones of poplar [Okano et al , 1989], and eight clones of eastern white pine [Yang et al , 1983a,b]) On the other hand, no differences were found between two half-sib families of sycamore (Kress et al , 1982a) or between two collections of seed of loblolly pine (Kress and Skelly, 1982)

Intraspecific variation in the metabolic responses of plants to NO or to NO_2 (see Section 9 4 2) has been demonstrated among cultivars of tomato (Murray and Wellburn, 1985, Wellburn et al , 1980) and pepper (Murray and Wellburn, 1985) with respect to the levels of NaR or NiR in leaves and foliar content of nitrate or amines In addition, the effect of NO_2 on NiR varied among different clones of perennial ryegrass (Wellburn et al , 1981,

Wellburn, 1982b), and the effect of NO₂ on NaR varied among barley mutants deficient in the enzyme (genotype did not affect uptake of NO₂) (Rowland-Bamford et al , 1989)

Cultivar of petunia affected the nitrogen content of leaves after exposure to NO₂ (Elkiey and Ormrod, 1981d) and the rate of uptake of NO₂ by the leaves (Elkiey and Ormrod 1981c) Among nine cultivars of Kentucky bluegrass, rates of uptake of NO₂ in the dark (adsorption) varied over a twofold range, and rates of uptake in the light above those in the dark (absorption) varied over a threefold range (Elkiey and Ormrod, 1981b) The joint-distribution of estimates for rates of absorption and adsorption among these cultivars (Figure 9-16) shows that caution must be exercised in the drawing of conclusions as to the causes of intraspecific variation in response when only two or three cultivars are used

9.5.1.3 Stage of Development

The "critical periods of development" (Van Haut and Stratmann, 1967) are one or more periods in the life of a plant during which an exposure to NO₂ could produce the greatest adverse effect on yield Which stages of development correspond to these periods depends upon the species of plant for oats, the critical period is during flowering, for radish and mangels, during early tuber formation and at the cotyledonary leaf stages, and for bean, during the transition from vegetative to reproductive growth and during fruit development (Van Haut and Stratmann, 1967).

The inhibitory effect of NO₂ at 0.068 ppm on the growth of Kentucky bluegrass appeared to be greater during periods of slower growth in fall and winter than during periods of more rapid growth in spring (Ashenden, 1979b, Whitmore et al , 1982) With four species of grasses exposed for 7 mo to NO₂ at 0.062 ppm, Kentucky bluegrass and one cultivar of timothy (but not another) showed a greater reduction of growth by NO₂ when exposed from emergence than when exposures started 6 weeks later, one cultivar of perennial ryegrass (but not another) showed no effect when exposed from emergence, but showed reduced growth when exposures started 6 weeks later, and there was no effect of stage of development or of NO₂ on growth in orchard grass (Whitmore and Mansfield, 1983)

In marigold plants at three ages (7 weeks apart), stage of development did not alter the effect of NO₂ at 0.3 ppm on growth—an increase in mass of roots (Sanders and Reinert, 1982a) The effect of stage of development was not discernible in radish exposed at three

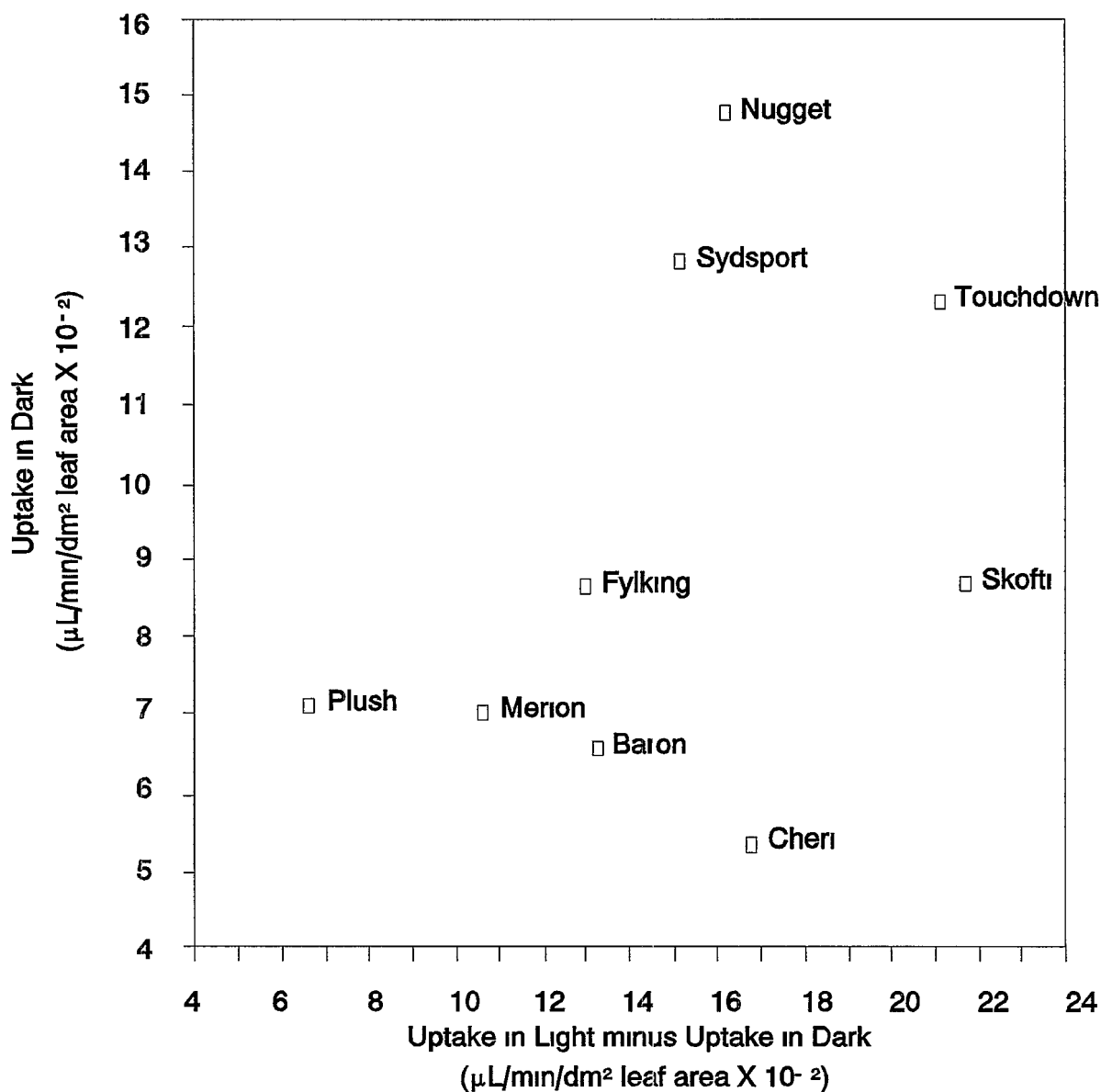


Figure 9-16. Relation between uptake of nitrogen dioxide in the dark and in the light for nine cultivars of Kentucky bluegrass.

Source Elkley and Ormrod (1981b)

ages to 0.3 ppm (Sanders and Reinert, 1982b) or in tomato at two ages exposed to 0.2 ppm (Goodyear and Ormrod, 1988) because there were no NO_2 -induced effects on growth.

Each leaf of a plant also passes through progressive changes in sensitivity to NO_2 during its development, which also depends upon the species of plant. In broadleaved plants,

sensitivity is low in young leaves in their early developmental stages, increases with expansion, reaches a maximum with full growth, and then declines. Consequently, the location of foliar tissue with greatest sensitivity moves from the outer leaves toward the center with development of rosette plants, and from the base to the apex of shoot as it develops in caulescent plants. In woody plants, a secondary flush of growth during the summer is less sensitive than the first flush in the spring. In conifers, the most sensitive foliage of spruce and fir is that of the current year when it becomes fully developed in late spring or early summer, the most sensitive foliage of larch is the needles of the spur shoots in the first week of emergence, and needles of pine are most sensitive when they emerge in the spring (Van Haut and Stratmann, 1967)

9.5.2 Environmental Conditions

Environment at its most inclusive denotes the aggregate of all external conditions and influences affecting a plant as well as the medium surrounding it. Clarity is better served by reserving the term "environment" for the medium and using the term "environmental conditions" to denote its state variables and other properties that govern the exchange of mass, energy, heat, or momentum between a plant and its environment. In experimental work, environmental conditions have usually been treated as individual factors that are monitored and controlled at certain levels during experimental periods.

These factors are commonly placed in two general classes: (1) biotic, such as pests and pathogens of the plant, and (2) abiotic, such as physical and chemical properties of the air or soil. Nothing is known of the influence of biotic factors on the plant's sensitivity to NO_x . Because abiotic factors can substantially influence the plant's response to NO_x , the association between temporal and spatial variations in environmental conditions and the occurrence and dispersion of NO_x must enter into estimations or predictions of possible effects.

Studies of abiotic factors have been almost evenly divided between an interest in their effects on sensitivity to NO_x and their use as manipulable variables to explore the mechanisms of action of NO_x . The results of both kinds of investigations indicate that environmental conditions exert their influence by altering processes controlling (1) entrance of the pollutant into the leaf, (2) detoxification of the pollutant within the foliar tissue, and

(3) sensitivity of metabolic systems to the pollutant (see Section 9.4) There has also been some distinction as to whether changes in the levels of one or more environmental factors are to be evaluated as affecting the system before, during, or after exposure to NO_x . Consequently, some results may be interpreted as an environmental condition affecting sensitivity of the plant to NO_x , whereas others may be seen as NO_x affecting the plant's response to an environmental stress. These same considerations are also important in evaluating other air pollutants as environmental factors with respect to their joint action with NO_x (see Section 9.7).

9.5.2.1 Climatic Factors

Climatic factors act on a plant directly from the atmosphere, and among those known to affect the response of a plant to NO_x are light intensity, photoperiod (length of the daylight period during a 24-h cycle), temperature, precipitation, RH, and the gases CO_2 , NH_3 , SO_2 , O_3 , and HF. (The joint-action of SO_2 , O_3 , or HF with NO_x is assessed with respect to the effects of mixtures of pollutants in Section 9.6.)

Except in greenhouse operations, climatic factors can be considered to be unmanaged variables, they pose a problem in the assessment of effects because their temporal variations may be coherent with changes in the concentration of NO_x at any site and because variation in one factor is usually accompanied by variations in the others.

Light

The influence of light on the response of plants to NO_x may be generally viewed as occurring in three domains. First, there are the changes in intensity of light that may occur during exposures in daylight. Second, there is the presence or absence of light that differentiates exposures during day from those during the night. Third, there are the seasonal variations in day length, which indirectly affect the response of plants to NO_x through an extended effect on growth and development.

Generally, susceptibility to foliar injury from NO_x is greater in the dark than in the light for most species of plants. In bean, foliar injury was much more severe in the dark than in the light with short-term exposures (10 h or less) over a wide range of concentrations (e.g., 10,000 ppm [Dolzmann and Ullrich, 1966], 16 ppm [Kato et al., 1974], 7 ppm

[Anderson and Mansfield, 1979], or 3.5 ppm [Yu et al., 1988]) In pea, spinach, radish, dock, jimson weed, and two species of tobacco (Anderson and Mansfield, 1979), as well as with rose and rape (Zahn, 1975), the incidence or severity of foliar injury was greater with exposures in the dark than with exposures in the light. Nevertheless, the difference in sensitivity between light and dark was not so great in barley (Zahn, 1975), and the sensitivity of wild tobacco was greater in the light than in the dark (Anderson and Mansfield, 1979). In sugar beet, the concentration of NO_2 required to induce foliar injury was about 10-fold greater in darkness than in light (Czech and Nothdurft, 1952). With tomato maintained at 1,000 ppm CO_2 , foliar injury decreased in severity with an increase in photon flux density (30, 95, 175, or 250 $\mu\text{mol}/\text{m}^2/\text{s}$) during exposure to 1.5 ppm NO_x (20% NO_2 + 80% NO) for 25 days (Mortensen, 1986). In sunflower, nitrogen-deficient plants were more susceptible in the dark, but those supplied with nitrogen as nitrite or ammonium were more susceptible in the light (Yoneyama et al., 1979a).

Light is probably the predominate environmental factor known to affect the uptake of NO_x , and the rate of uptake of NO_x generally follows the same form of light-saturation curve as do photosynthetic CO_2 uptake and transpiration (Rogers et al., 1979b; Hill, 1971). However, the effects of light on foliar sensitivity to injury as well as other lines of evidence indicate that light intensity can also affect mesophyll resistance to NO_2 and that this could be related to the occurrence of NO_2 -induced lesions. One of these is a discrepancy between changes in the rate of transpiration and uptake of NO_x , which could indicate that stomatal resistance increases while mesophyll resistance decreases during exposure. A stable uptake of NO_2 over a 5-h period was accompanied by an 11% decrease in rate of transpiration for corn and soybean (Rogers et al., 1979b), in potato, uptake was not entirely explained by a first-order rate constant for NO_2 (Sinn et al., 1984). Uptake of NO_2 was related linearly to photosynthetic flux density and doubled over the range of 0.2 to 420 $\mu\text{E}/\text{m}^2/\text{s}$ in a tomato mutant (*flacca*) that does not have stomatal closure in the dark (Murray, 1984).

The presence of light can influence not only sensitivity, but also the form and development of foliar lesions. In bean, chlorosis occurred only with exposures in the light, whereas exposure in the dark produced wilting and the occurrence of water-soaked areas, which then became necrotic but remained green. Transferral to the light after exposure in the dark accelerated the rate of development of lesions and produced bleached necrotic areas.

(Yu et al , 1988) In very young leaves of pea, alfalfa, vetch, and clover (but not of other legumes), an interveinal chlorosis was produced only by exposure in light and not in darkness or when exposure in the dark was followed by a period of light Nevertheless, the leaves became green again in the postexposure period if subjected to light of sufficiently high intensity Exposures in the dark or of older leaves produced only necrotic lesions (Anderson and Mansfield, 1979) There was no effect of light intensity after exposure on the development of NO₂-induced symptoms in lettuce (Czech and Nothdurft, 1952)

Besides the intensity or presence of light, periodic variations in sensitivity within the quotidian cycle may also contribute to differences in response between night and day exposures Alfalfa was more sensitive to NO₂-induced foliar injury in the morning than in the afternoon (Zahn, 1975) When subjected to 2-h exposures to NO₂ in controlled-environment chambers, oat seedlings showed a peak in sensitivity about 12 to 16 h after the beginning of the light period, rye seedlings showed the same behavior in the light and another peak in sensitivity, higher than that in the light, in the dark about 2 to 4 h after the end of the light period (Figure 9-17) (Van Haut and Stratmann, 1967, Van Haut, 1975) There is also some evidence from exposures of bean and sunflower to NO₂ at 4 ppm in light and darkness that a quotidian cycle could be a component of temporal changes observed in the foliar levels of nitrite and NiR (Yoneyama et al , 1979a) The degree to which light entrains the phase or frequency of these cycles of foliar sensitivity to NO_x is unknown

The evidence is too sparse and contradictory to support any general conclusion as to whether NO_x is more effective in dark or in light with respect to its inhibition or promotion of growth except that such effects may be determined by species of plant In tomato grown with CO₂ enrichment (at 1,000 ppm), exposure to 1.5 ppm NO_x (20% NO₂ + 80% NO) for 25 days decreased mass of shoots at all photon flux densities (30, 95, 175, or 250 $\mu\text{mol}/\text{m}^2/\text{s}$), but decreased number of leaves and length of stem only at the two lower levels of light intensity (Mortensen, 1986) Daytime exposures to NO₂ at 0.3 ppm, 10 h/day for 2 weeks had no effect on the growth of corn, sunflower, or bean seedlings, but nighttime exposures produced the following a decreased growth of leaves (but not roots) of corn, an increased growth of leaf and stem (but not root) in sunflower, and an increased growth of stem and root (but not leaf) in bean In cucumber under the same regimes, both daytime and

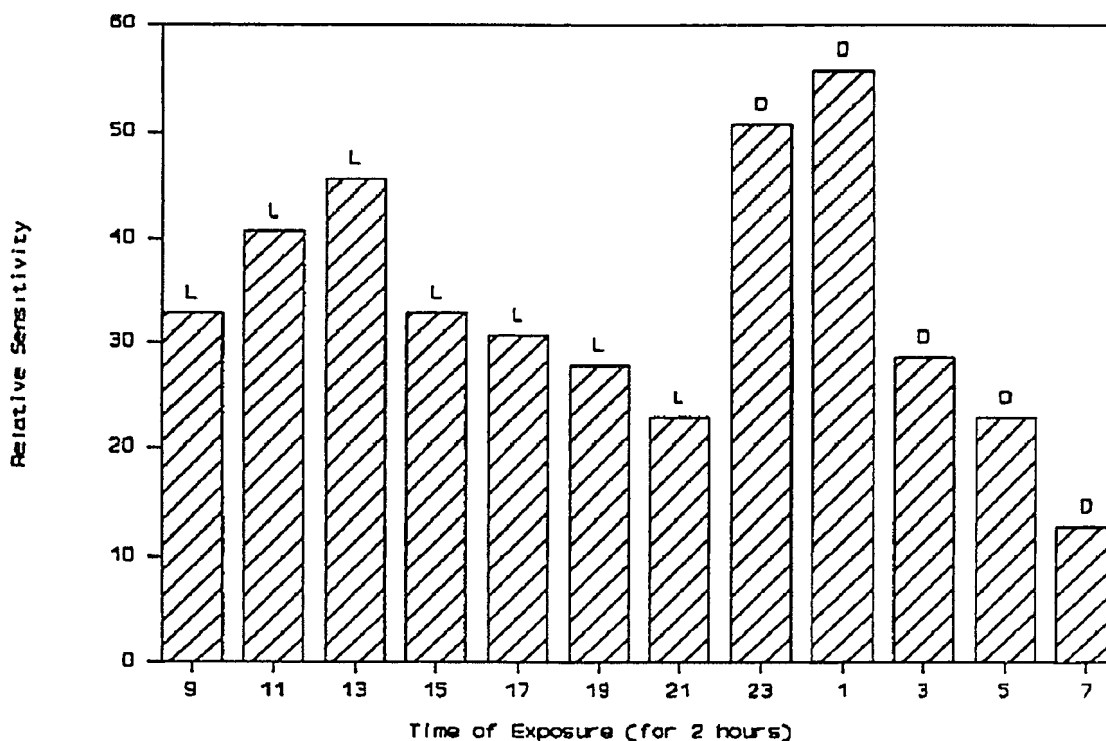


Figure 9-17. Variations in sensitivity of oat seedlings to foliar injury from nitrogen dioxide with hour of the day in light (L) and darkness (D).

Source Van Haut and Stratmann (1967)

nighttime exposures increased the masses of leaf, stem, and root, but the increases were relatively greater with daytime exposures (Yoneyama et al , 1980c) Growth of roots, but not of stem or leaves, appeared to be greater with a nighttime than with a daytime exposure during the week following a 1-h exposure to NO_2 at 2 ppm in 2-week-old sunflower seedlings, no effects were apparent in 4-week-old sunflower or in 2- or 4-week-old corn seedlings (Yoneyama et al , 1980d)

Exposure of European white birch to NO_2 at 0.04 ppm for 9 weeks had no effect on growth under a photoenvironment with a photoperiod of 16 h and photon flux density of $280 \mu\text{mol}/\text{m}^2/\text{s}$; however, NO_2 increased the masses of stem and leaves as well as leaf area, stem height, and length of internodes with a photoperiod of 12 h and a photon flux density of $100 \mu\text{mol}/\text{m}^2/\text{s}$, which was close to the photosynthetic compensation point (Freer-Smith, 1985) The influence of light intensity is not separable from that of photoperiod or temperature on seasonal changes in the effect NO_2 on the growth of grasses (Whitmore,

1985), broadleaved trees (Freer-Smith, 1984), or conifers (Freer-Smith and Mansfield, 1987)

Temperature

The inhibitory effect of NO₂ on photosynthetic CO₂ uptake in bean leaves was greatest (around 30%) at the optimum temperature for photosynthesis (around 30 °C), and lesser degrees of inhibition occurred above (about 22% at 35 °C) or below (about 14% at 15 °C) this point. The inhibitory effect of NO₂ on dark respiration increased with an increase in temperature (from 39% at 15 °C to 51% at 35 °C). Uptake of NO₂ at 3 ppm by bean leaves increased with increases in temperature over the range of 15 to 35 °C (about a twofold difference between the lowest and highest temperatures) in the light, however, uptake increased about 75% from 15 to 25 °C, but not above 25 °C, in the dark. The inhibition of transpiration in the light by NO₂ was 7% at 15 °C and 15% at 35 °C (Srivastava et al , 1975b)

The effect of temperature was not distinguishable from that of several other factors that could have affected the development and response of grasses (Whitmore and Mansfield, 1983, Lane and Bell, 1984b) or trees (Freer-Smith, 1984) to NO₂. The imposition of low temperatures (less than 0 °C) during a series of exposures to NO₂ could be regarded as a test for changes in cold-tolerance rather than an effect of temperature on the plant's response to NO₂ (Freer-Smith and Mansfield, 1987)

With air temperatures in the range of -6 to 3 °C, there was no measurable uptake of NO or NO₂ by spruce or pine, and the deposition rate was estimated to be less than 4% of that during the day with ambient summer temperatures (Granat and Johansson, 1983)

Mist and Relative Humidity

The misting of plants during exposure was without apparent effect on bean, but tended to increase the rate of development of foliar lesions on spinach and young plants of barley and rye (Czech and Nothdurft, 1952), it also increased the severity of NO₂-induced foliar injury in Kentucky bluegrass (Elkiey and Ormrod, 1981a). Although NO₂ at 0.15 ppm in continuous 10-day exposures had no effect on growth (foliar area) of Kentucky bluegrass when mist was present, NO₂ increased growth in the absence of mist, depending upon

cultivar and whether plants were grown with adequate or deficient levels of sulfur or nitrogen in the soil (Elkiey and Ormrod, 1981a) In the earlier study, mist was applied (total deposition of 0.67 mm) throughout a 1-h exposure (Czech and Nothdurft, 1952) In the latter investigation, mist was applied for two 5-min periods, 4 h apart, each day during the photoperiod, and stomatal aperture increased for 2 to 3 h after each application (Elkiey and Ormrod, 1981b). Mist may be viewed as effectively acting as an increase in humidity and thereby increasing or delaying a decrease in stomatal conductance

Uptake of NO_2 at 3 ppm by bean leaves was 47% greater at 80% RH than at 45 or 20% RH after 2 h of exposure and about 19% greater after 5 h of exposure The inhibition of photosynthesis of bean leaves by NO_2 at 3 ppm tended to be greater at 80 and 45% RH (22 and 33%, respectively) than at 20% RH (16%), and inhibition of transpiration by NO_2 was greater at 45 or 80% RH (7 and 6%, respectively) than at 20% RH (1%) at 25 °C (Srivastava et al., 1975b).

Carbon Dioxide

The joint action of carbon dioxide and NO_x has received attention for the practical reason that both gases are generated in the combustion of fossil fuels, particularly in the greenhouse culture of plants when burners are used to enrich the atmosphere with carbon dioxide and NO_x species arise as byproducts

In general, it appears that when NO_x inhibited growth at normal levels of CO_2 , an increase in the level of CO_2 resulted in a net increase in growth, although there was still an inhibitory effect of NO_x In tomato, exposure to 0.35 ppm NO for 35 days at normal levels of CO_2 resulted in decreases in leaf area, mass of plant and shoot, and relative growth rate, with CO_2 at 1,000 ppm, NO increased leaf area and was without effect on the other variates (Anderson and Mansfield, 1979)

The same general pattern also occurred with the effect of NO_x on apparent photosynthesis (uptake of CO_2 in the light) an increase in the level of CO_2 resulted in a net increase in uptake, although there was still an inhibitory effect of NO_x In bean plants, NO_2 at 3 ppm decreased apparent photosynthesis by a constant amount at concentrations of CO_2 from 100 to 600 ppm and at 2,000 ppm Because apparent photosynthesis increased with an increase in CO_2 concentration, the relative effect of NO_2 decreased with an increase in CO_2

(Srivastava et al , 1975b) Photosynthesis was decreased by NO at 1 ppm, but the inhibitory effect of NO at 1,000 ppm CO₂ was greater than, equal to, or less than that at normal CO₂ levels, depending on the species of plant (Saxe, 1986a)

Ammonia

Atmospheric NH₃ reduced the severity of foliar symptoms produced by NO₂, but this effect depended on light intensity and species of plant In the dark, NH₃ in the range of 2 to 7 ppm reduced foliar injury from a 1-h exposure to NO₂ at 6.4 to 90 ppm in pea, wild tobacco, celery, and bean (concentrations were different for each species) In the light, the same kind of effect occurred in pea, but not in wild tobacco The action of NH₃ was attributed to its neutralization of the HNO₂ or HNO₃ produced in the foliar tissue by NO₂ (Zeevaart, 1976) (see Sections 9.3.2.5 and 9.3.4.2)

9.5.2.2 Edaphic Factors

Edaphic factors act on the plant directly from the soil, and those affecting the plant's response to NO_x include soil moisture tension (and salinity) and mineral nutrition (level and form of sources of nitrogen or sulfur) These may also be viewed as manipulated variables in managed systems, through irrigation or fertilization Although temporal variations may occur in edaphic factors, their rates of change will be less rapid than with the climatic factors or concentration of NO_x Nevertheless, their spatial variations may be associated with the pattern of dispersion of NO_x in a locality

Soil Moisture and Salinity

The sensitivity of plants to NO_x decreases as water becomes less available in the soil The severity of NO₂-induced foliar lesions in 10 species of weeds exposed to 20 or 50 ppm for 4 h was greater for plants in soil at about field capacity than for those near incipient wilting (Benedict and Breen, 1955) Although stomatal conductance was not measured, it can be presumed that this was decreased by water stress and resulted in a decreased uptake of NO₂

Increases in the salinity of solution bathing the roots of bean seedlings (by the addition of sodium chloride to give concentrations of 20 to 80 mM) resulted in decreases in stomatal

conductance, uptake of NO_2 , and level of nitrite in foliage exposed to NO_2 at 0.31 ppm for 2 h (Fuhrer and Erismann, 1980)

Soil Sulfur

A level of sulfur in soil, which was low enough to produce foliar symptoms of deficiency, decreased the severity of NO_2 -induced foliar symptoms in Kentucky bluegrass (NO_2 at 0.15 ppm in 10-day exposures). Sulfur-deficiency also altered the effect of NO_2 on growth (foliar area), depending upon cultivar. In one cultivar, NO_2 increased the growth of plants given complete nutrient, but not that of sulfur-deficient plants; in another, NO_2 had no effect on plants given complete nutrient, but decreased the growth of sulfur-deficient plants (Elkley and Ormrod, 1981a).

Soil Nitrogen

The availability of inorganic nitrogen in soil appears to affect the plant's response to NO_x in several ways, such as the marginal value of NO_x as an additional source of nitrogen, the capacity of the foliar tissue to reduce and assimilate NO_x , and other changes in the physiological state of the plant that can influence its response to NO_x . These effects of nitrogen in the soil depend on concentration of NO_x , species of plant, effect measured, degree of nitrogen deficiency induced, and form of inorganic nitrogen supplied. The incidence or severity of NO_x -induced foliar injury can be affected by the level of nitrogen in the soil or nutrient solution supplied to the roots, but the evidence is contradictory as to the effect of nitrogen deficiency on the sensitivity of the plant to NO_x .

Some data show that NO_x -induced foliar injury *increases* with an increase in nitrogen deficiency. (1) a doubling of the level of nitrogen in soil decreased the severity of foliar injury in rape and barley exposed to NO_2 , and further increases in nitrogen (above that adequate for normal growth) decreased injury in rape but not in barley (Zahn, 1975), (2) foliar injury in sunflower exposed to NO_2 at 2 ppm did not occur with nitrate supplied at 15 or 5 mM, but did when nitrate was absent (Okano and Totsuka, 1986), (3) with exposures to NO_2 at 4 ppm for 3 h, injury occurred in sunflower (in the dark) without nitrate, but not when nitrate was provided at 10 or 100 ppm, and injury occurred in bean (older leaves in the light) provided with nitrate at 10 ppm, but not at 100 ppm (Yoneyama et al., 1979a),

(4) severity of NO_2 -induced foliar injury decreased with increases of nitrate from 0 to 2 and 5 mM and did not occur at 10, 25, or 50 mM in bean exposed to 3 ppm for 5 h (Srivastava et al , 1975c), (5) in short-term (3-h) exposures to NO_2 at 2 ppm, injury that developed during the postexposure period of 2 days became less severe with increasing levels of nitrate (Srivastava and Ormrod, 1984), and (6) foliar injury was more severe in bean grown with deficient nitrogen under acute exposure to 17.2 ppm for 1 h (Kato et al , 1974)

Other data show that NO_x -induced foliar injury *decreases* with an increase in nitrogen deficiency (1) two out of three cultivars of Kentucky bluegrass had less severe foliar injury when grown under nitrogen-deficient conditions and exposed to NO_2 at 0.15 ppm continuously for 10 days (Elkley and Ormrod, 1981a), (2) foliar injury of bean was more apparent when nitrate was supplied at 10 mM during exposure to NO_2 at 0.5 ppm for 24 h in plants previously grown under deficient conditions (Srivastava and Ormrod, 1989), (3) foliar injury of bean occurred when nitrate was supplied at 20 mM, but not at lower concentrations, during exposure to NO_2 at 0.5 ppm for 5 days in plants previously grown under deficient conditions (Srivastava and Ormrod, 1984), and (4) foliar injury occurred infrequently in bean exposed to NO_2 for 6 h/day over 14 days, and it tended to be greater in incidence in plants grown in 10 or 20 mM nitrate but not in 0, 1, or 5 mM in Hoagland's solution (Srivastava and Ormrod, 1986)

It should be noted that the form of nitrogen can also be important (1) in cucumber subjected to acute exposure to NO_2 , injury did not occur with nitrate, but did with ammonium salts as the source of nitrogen (Kato et al , 1974), and (2) injury developed in sunflower supplied with ammonium or nitrite, but not in deficient plants or those supplied with nitrate (Yoneyama et al , 1979a)

Although NO_x can be a supplemental source of nitrogen for plants in nitrogen-deficient soils, the boundary between inhibition and promotion of growth by NO_x is obscured by many factors, but tends to occur at levels of soil nitrogen that are substantially limiting to growth. The interactive effects of NO_x and soil nitrogen on growth have been studied most extensively in the following groups of plants

| | |
|---------|--|
| Grasses | In Kentucky bluegrass, the effect of nitrogen deficiency on growth (foliar area) depended on cultivar. NO_2 increased growth in plants grown on complete nutrient, but had no effect on nitrogen-deficient plants in one cultivar, whereas NO_2 increased growth in nitrogen-deficient plants, but had no effect in complete |
|---------|--|

nutrient in two other cultivars (Elkley and Ormrod, 1981a) With perennial ryegrass, there was no significant interaction of NO_2 at 0.2 ppm for 11 weeks with level of nitrate on growth of shoots and roots, although NO_2 reduced senescence and mass of dead shoots at the higher level of nitrate more effectively in one population than in another (Taylor and Bell, 1988)

Cereals: With corn, NO_2 at 0.3 ppm for 2 weeks increased the dry mass of roots by 46% at a medium level of soil nitrogen and decreased root mass by 29% at low soil nitrogen with a 5% or less effect on the mass of shoots (Matsumaru et al, 1979) With barley, NO_2 at 0.3 ppm for 9 days increased root mass with no nitrate and increased shoot mass at 10 mM nitrate, with no significant effects at higher levels of nitrate (Rowland et al, 1987)

Sunflower The increased growth produced by NO_2 in nitrogen-deficient plants occurred predominantly in the youngest leaves, with about a 180% increase in mass, whereas other tissues of the shoot were increased about 25% (Faller, 1972) At 0.3 ppm in 7-day exposures, NO_2 partially reversed depressed growth of leaves and stems, with no effect on roots, and symptoms of nitrogen deficiency in sunflower grown on artificial soil receiving nutrient solution containing 0, 5, or 15 mM potassium nitrate with other nutrients at full strength (Okano and Totsuka, 1986) In exposures for 2 weeks, 0.3 ppm NO_2 reduced the masses of leaves, stem, and roots by 11 to 17% at high levels of soil nitrogen, produced a slightly greater inhibition of leaves and stem, but a 45% reduction in root mass at medium soil nitrogen, and had negligible effects on roots or stem, but increased shoot mass by 17% at low soil nitrogen (Matsumaru et al, 1979)

Tomato Exposures to NO_x at about 2 ppm (in a CO_2 -enriched atmosphere) had negligible effects (less than 5%) on fruit production (over 4 mo) in plants supplied with 33 or 85 ppm nitrogen in soil but reduced production by 13% in plants supplied with 170 ppm nitrogen (Law and Mansfield, 1982) Exposure to NO_2 at 0.25 or 0.39 ppm did not affect growth (mass of leaves or stem) with a nitrate level of 28 mg/L in solution supplied to the roots (which produced stunted plants), but growth was increased by NO_2 with a fivefold increase in the level of nitrate (Troiano and Leone, 1977) On the other hand, the mass of tomato shoots and roots was decreased in soils of high fertility by exposures to NO at 0.2, 0.4, or 0.8 ppm, but increased and then decreased with increasing concentration of NO in soils with medium or low levels of fertility (Anderson and Mansfield, 1979) These effects on tomato with NO_2 (Troiano and Leone, 1977) or NO (Anderson and Mansfield, 1979) could be viewed as changes in size as there were no differential effects on growth of leaves, stem, or roots Nevertheless, exposure to NO_2 at 0.3 ppm for two weeks at three levels of soil-nitrogen produced no effect on mass of roots, but a decreased mass of stem and leaves of about 20% at the lowest level, a decreased mass of leaves of 18%, stem of 24%, and roots of 31% at the medium level, and a slight effect on leaves, but decreased mass of stem or roots of 15 to 20% at the highest level (Matsumaru et al, 1979)

Bean The complexity of the interaction of concentration of NO_2 , level of nitrate supplied, and nature of effect is illustrated in Figure 9-18 for bean seedlings grown at five levels of nitrate (0, 1, 5, 10, or 20 mM) and exposed to four levels of NO_2 (0, 0.02, 0.1, or 0.5 ppm). When exposed to NO_2 for 6 h/day over a period of 14 days, increases in concentration of NO_2 produced decreases in the mass of shoot with relatively slight decreases in mass of roots at the three lower levels of nitrate and relatively greater decreases in mass of roots and then decreases in mass of shoot at the two higher levels of nitrate (Srivastava and Ormrod, 1986). When exposed to NO_2 continuously for 5 days, increases in the concentration of NO_2 produced an increase and then a decrease in stem length with no effect on foliar mass with no added nitrate and decreases in foliar mass with slight effects on stem length at the three higher levels of nitrate (Srivastava and Ormrod, 1984).

9.6 EFFECTS OF POLLUTANT MIXTURES

A publication by Menser and Heggstad (1966) provided the initial impetus for extensive research into the effects of pollutant combinations on plants. They showed that tobacco (Bel W3) exposed to low concentrations of either O_3 or SO_2 was uninjured, but substantial foliar injury occurred when the plants were exposed to both pollutants simultaneously. The authors called this response a synergistic effect. Subsequent studies have confirmed this report and extended the observations to show that pollutant combinations can influence not only foliar injury responses, but other plant processes as well.

Typically it is assumed that the major effect of NO_x at ambient concentrations on plants is through its participation in the photochemical formation of oxidants such as O_3 , recognizing that the phytotoxicity of NO_x is quite low relative to O_3 . Given the broad variety of pollutant sources in the United States, it is possible that NO_x could co-occur with other compounds, on either a local or a regional scale. Consequently, in a natural environment, plants may be exposed to varying combinations and concentrations of NO_x , O_3 , and SO_2 . Oxides of nitrogen in combination with compounds other than these is also possible, but will not be considered here due to a lack of studies addressing these combinations.

The exposure regime is an important consideration in evaluating studies in which plants are exposed to mixtures. The evaluation must consider not only the reported biological impact, but also must determine if the pollutant concentrations and their individual and joint

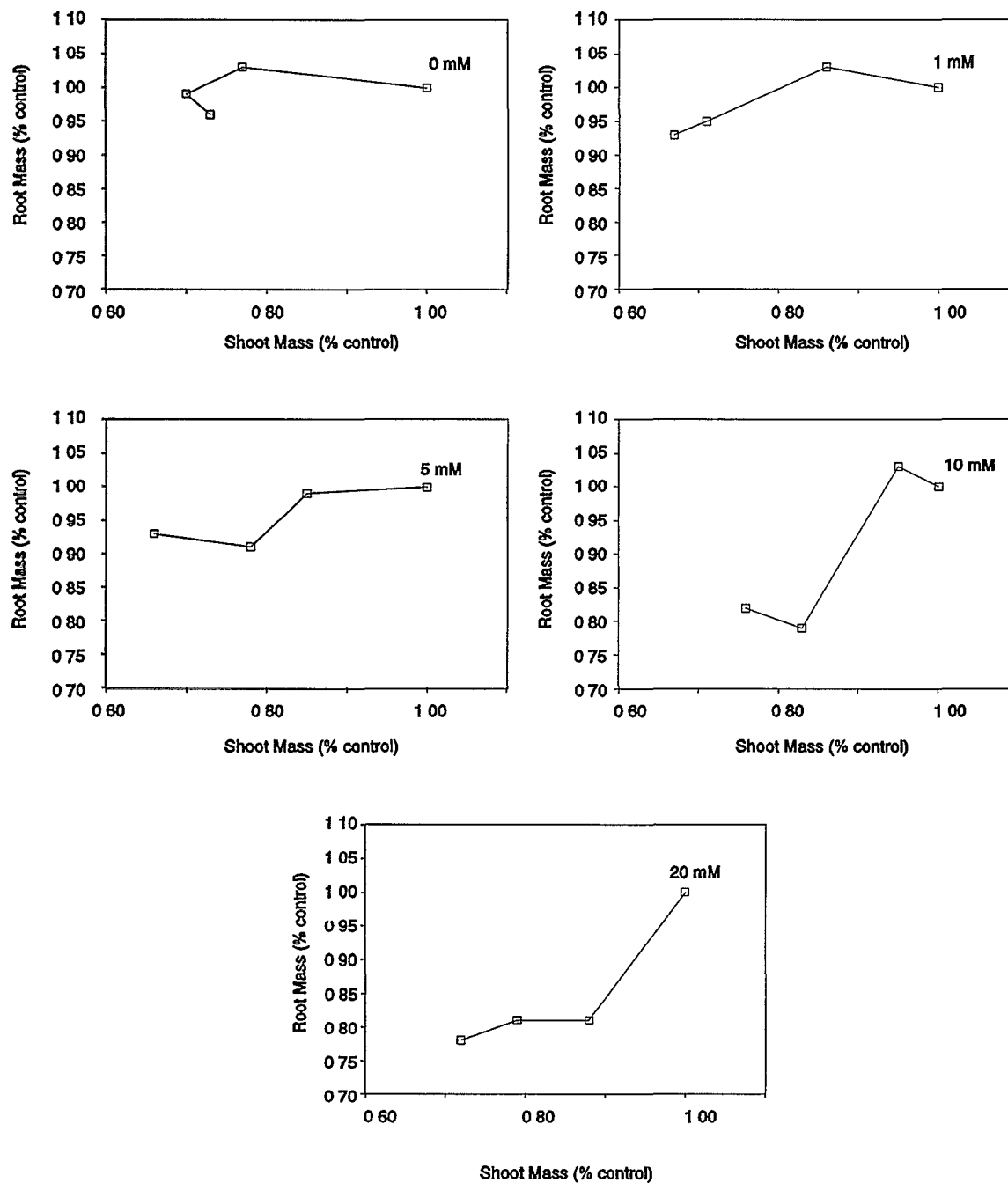


Figure 9-18. Effects of exposure to 0, 0.02, 0.1, or 0.5 ppm nitrogen dioxide on the dry weight of roots and shoots of bean seedlings grown in solutions containing 0, 1, 5, 10, or 20 mM nitrate.

Source: Srivastava and Ormrod (1986)

occurrences were reasonable in relation to concentrations and frequency of occurrence monitored in the ambient air. Analyses of ambient-air monitoring data have studied the frequency of pollutant (NO_2/SO_2 and NO_2/O_3) co-occurrence (Lefohn and Tingey, 1984, Lane and Bell, 1984a, Jacobson and McManus, 1985, Lefohn et al., 1987a). In general, the studies have concluded that (1) the co-occurrence of two-pollutant mixtures lasted only a few hours per episode, (2) the time between episodes is generally large (weeks, sometimes months), and (3) the periods of co-occurrence represent a very small portion of the potential plant growing period. At this time, it appears that most of the experiments have used longer exposure durations and higher frequencies at co-occurrences than are typically measured in the ambient air.

When studying the potential impact of pollutant combinations on vegetation, the important question is: does the presence of a second pollutant cause a greater impact on vegetation than the presence of the individual pollutants? If a second pollutant increases the impact on vegetation, then this fact must be considered in establishing criteria to protect plants, in their various functions, from pollutant effects.

9.6.1 Mode of Action

9.6.1.1 Mode of Action of Pollutant Mixtures

Underlying biochemical changes that may explain some of the detrimental effects on plant growth caused by combinations of SO_2 and NO_2 (see Section 9.3.3) have been studied (see also Roberts et al., 1983). No changes in the *in vitro* rates of photosynthetic electron flow were detected in chloroplasts isolated from grasses (*Lolium*, *Dactylis*, *Phleum*, and *Poa*) treated with low levels of SO_2 or NO_2 (0.068 ppm each for 140 days) singly or in combinations of $\text{SO}_2 + \text{NO}_2$ (Wellburn et al., 1981). By contrast, ratios of $\text{NAD(P)H}/\text{NAD(P)}^+$ and rates of ATP formation were much reduced by SO_2 and $\text{SO}_2 + \text{NO}_2$ fumigations. Furthermore, levels of certain enzymes such as GDH (but not GS) were stimulated in a more than additive manner in SO_2 -sensitive perennial rye grass (*Lolium perenne* L.) (cv. Aberystwyth S23) and in mutant material that was derived from S23 known to be tolerant of SO_2 (S23 Bell resistant) when fumigated with $\text{SO}_2 + \text{NO}_2$. However, no effects were detected in another *Lolium* clone (Helmshore) collected from a highly polluted area around Manchester, UK.

Ammonia formed by the concerted action of the enzymes NaR and NiR is normally assimilated into amino acids by the GS/GOGAT pathway within plastids, whereas GDH is probably involved in the breakdown of amino acids (see Section 9.3.3). Why low level fumigation with either SO₂ alone or SO₂ + NO₂ should significantly enhance GDH activity but not affect GS activity is not known. High levels of GDH activities may be indicative of secondary metabolic events, related to the removal of amino acids such as glutamate, which occur in plant tissues as a consequence of exposure to mixtures of pollutants.

The possibility of changes in the levels of NiR activity due to SO₂, NO₂, or SO₂ + NO₂ have also been investigated using plastid preparations from fumigated tillers of the SO₂-sensitive perennial rye grass (*Lolium perenne* L. cv. Aberystwyth S23) (Wellburn et al., 1981). Sulfur dioxide has no direct effect upon the levels of NiR activity, even at a relatively high concentration (1 ppm), but NO₂ alone induces a significant increase in NiR after 9 days at 0.25 ppm or after 7 days at 0.5 ppm. This feature was also shown by the SO₂-resistant Helmsshore clone after 13 days of fumigation. Most important of all are the combined effects of SO₂ + NO₂. In such circumstances, the presence of SO₂ completely prevents the rise in NiR activity normally induced by NO₂ alone.

Inhibition of a potential means of detoxification of the products of NO₂ in plants was also shown by all clones of *Lolium* and other grass species (Wellburn et al., 1981). After 20 weeks of fumigation, levels of NiR activity in plants grown in NO₂-polluted air (0.068 ppm) were approximately double those in plants growing in clean air. By contrast, the SO₂ + NO₂ treatment failed to increase the levels of NiR normally found in treatments with NO₂ in all grasses. Indeed, with the exception of the S23 Bell SO₂-resistant *Lolium* clone, all levels of NiR activity were significantly depressed below clean-air control levels. The additional presence of SO₂, therefore, prevents the induction of additional NiR activity normally associated with NO₂ fumigation. Consequently, these plants are then open to damage by the products of both pollutants (sulfite and nitrite) in a number of ways at the same time.

Until recently, little progress has been made with exposures to mixtures containing O₃ + NO₂ or SO₂ + O₃ + NO₂ at the biochemical level. In a preliminary experiment, which unfortunately did not include simultaneous exposures of 4-year-old Norway spruce (*Picea abies* L.) clones to NO₂ alone, Klumpp et al. (1989b) showed that NaR activities were

enhanced by $O_3 + NO_2$ and $SO_2 + O_3 + NO_2$ treatments in current-year needles, but were reduced in 1-year-old needles. However, responses to the fumigation mixtures were highly dependent upon the availability of calcium (Ca) and magnesium (Mg) to the seedlings. For example, inhibition of NaR activities by mixtures of $SO_2 + NO_2$ in current-year needles only occurred when Ca and Mg levels were very low. In the same series of experiments, treatments with $SO_2 + NO_2$, $O_3 + NO_2$, or $SO_2 + O_3 + NO_2$ increased superoxide dismutase activities in younger needles, but peroxidase levels only rose in treatments containing SO_2 (Klumpp et al, 1989a). This time, levels of both enzymes were enhanced by deficiencies in the supply of Ca and Mg to the plants, which indicates that both pollutant mixtures and mineral deficiencies elicit free-radical-induced injury.

Symptoms of injury caused by mixtures of SO_2 and NO_2 often resemble those due to O_3 alone (Reinert et al, 1975). For this reason, evidence for more fundamental damage induced by free radicals, as well as changes in levels of enzyme activity associated with free radical scavenging, has been sought. Generally, O_3 damage is characterized by membrane-associated injury and, as a consequence, gradients of protons or other ions are not maintained (Mudd, 1982). An effective and sensitive probe of proton gradients across membranes is obtained by following changes in the light-dependent fluorescence quenching of an added amine like 9-AA. This can be applied to a number of systems, including the generation of a pH gradient across isolated thylakoid membranes, which is generated by photosynthetic electron flow and then harnessed by coupling factors to form ATP.

Changes in light-induced quenching of 9-AA fluorescence by detached thylakoid membranes obtained from lysed oat (*Avena sativa* L. cv Pinto) chloroplasts have been studied in the presence of various concentrations of O_3 , sulfite, sulfate, nitrite, and/or nitrate (Robinson and Wellburn, 1983). The ability of the photosynthetic membranes to create and maintain effective proton gradients in these different conditions was then determined. Relatively high concentrations of sulfate, nitrate, sulfite, or nitrite were required to affect the redistribution of the 9-AA probe in the light. Pulses of O_3 , by contrast, were highly effective in creating significant reductions in the light-induced quenching of 9-AA fluorescence, even at very low levels (5 nmol O_3). This damage by O_3 to the effectiveness of thylakoids to generate proton gradients was aggravated by light. However, a few seconds later, an additional repair mechanism was also detected, but this appeared to occur only in

the dark. Similarly, mixtures of sulfite and nitrite were also found to be a highly disruptive—detrimental effects being detected at concentrations as low as 0.1 mM of each. This type of membrane damage could explain the known sensitivity of plant growth to O_3 alone or to $SO_2 + NO_2$ mixed fumigations (see Section 9.3.5). Moreover, the destructive influence of combinations of sulfite and nitrite indicate that, under certain conditions, the two together are capable of initiating free-radical reactions within membranes (similar to those of O_3 alone), which cause a breakdown in the mechanisms involved in the creation of proton gradients across thylakoid membranes. Nash (1979), during chemical studies of mixtures of SO_2 and NO_2 , concluded that together, these gases in solution produce sulfite radicals that exist long enough to seek out sensitive disulfide bonds in proteins. Related events may also occur on other membranes, such as the inner envelope membranes of mitochondria or plastids, or the plasma membrane, which are all involved in similar proton-dependent activities.

Many investigations have shown that mixtures of air pollutants can have a detrimental effect on growth (Bennett and Hill, 1975; Mansfield and Freer-Smith, 1981), but not many have linked interaction between pollutants to changes in physiological processes. Bull and Mansfield (1974) showed significant depressions of net photosynthesis in peas (cv. Feltham First) due to $SO_2 + NO_2$ at levels of 0.05 to 0.25 ppm, but detected no interaction between the two gases. By contrast, White et al. (1974) were able to find a more than additive effect of the two gases on net photosynthesis in alfalfa (cv. Ranger) at concentrations around 0.15 ppm of each, but not at higher levels. Later work from the same laboratory (Hou et al., 1977) confirmed this result and demonstrated that doubling the CO_2 concentration reduced the inhibition of net photosynthesis by the mixture. This effect was attributed to stomatal closure in response to the high CO_2 levels. Mixtures of NO_2 (2.0 ppm) + O_3 (0.3 ppm) inhibited photosynthesis and altered the translocation of assimilates in kidney bean to a greater degree than expected from responses to NO_2 or O_3 alone (Okano et al., 1985a). Root and lower stem of plants exposed to $O_3 + NO_2$ received far less photoassimilate relative to control plants. Ozone is well known for reducing photosynthesis; the authors speculate that the reduction of nitrite was inhibited by O_3 and amplified by the presence of NO_2 , leading to the photosynthesis and translocation effects.

Mixtures of SO_2 and NO_2 can also reduce stomatal conductance and transpiration (Darrall, 1989). For example, more than additive reductions in stomatal conductance of

three soybean varieties (Hark, Beeson and Amsoy) due to SO₂ (2 ppm) + NO₂ (0.5 ppm) were detected in less than 5 h (Amundson and Weinstein, 1981). In this case, NO₂ alone had no effect. Levels of over 1 ppm NO or 2 ppm NO₂ are usually required for this to occur (Darrall, 1989, Saxe and Murali, 1989). Carlson (1983), working in the short term (2 to 24 h) with soybean (*Glycine max* L.) and up to 0.6 ppm of SO₂, NO₂, or of both, however, found reductions in stomatal conductance for both gases separately and in combination. He also observed reductions in net photosynthesis and residual conductance as a result of the SO₂ and the SO₂ + NO₂ treatments.

Rates of inhibition of net photosynthesis in sunflowers (*Helianthus annuus* L. cv Russian Mammoth) induced by NO₂ + O₃ mixtures differ from those induced by SO₂ + NO₂ or SO₂ + NO₂ + O₃ mixtures (Furukawa and Totsuka, 1979). Mixtures of NO₂ (1 ppm) + O₃ (0.2 ppm) decreased rates of net photosynthesis steadily throughout the exposure period (2 h), whereas mixtures with SO₂ induced an abrupt change to lower steady levels within 30 min. Only in the SO₂ + NO₂ treatment is the extent of the inhibition determined by the levels of NO₂.

Stomatal conductances can also increase at low levels (<0.1 ppm) of SO₂ (Darrall, 1989) and enhance transpiration rates. Levels of either SO₂ or NO₂ (both 0.1 ppm), for example, cause short-term increases in transpiration by beans (cv Canadian Wonder) during the first 3 days of exposure (Ashenden, 1979a). By contrast, exposures to SO₂ + NO₂ cause a short-term decrease in transpiration, but over the longer term, this effect may be reversed. Exposure of clonal birch (*Betula pendula* Roth) to SO₂, NO₂, or SO₂ + NO₂ (0.02 to 0.06 ppm each) for 20 to 30 days resulted in significant rates of water loss from the leaves (Neighbour et al., 1988) due to all gaseous treatments.

Rates of dark respiration and net photorespiration in the experiments of Carlson (1983) on soybean were also reduced by mixtures of SO₂ + NO₂, as well as by NO₂. Effects of NO_x alone on dark respiration have been discussed elsewhere (Section 9.3.4.1), but various combinations of SO₂ + NO₂ + O₃ can also stimulate dark respiration of current year needles of Norway spruce (Klumpp and Guderian, 1989). Using 11 different provenances of Norway spruce, Saxe and Murali (1989) have shown that both night transpiration and dark respiration are stimulated by various mixtures of NO + NO₂ (2.5 to 9 ppm of each). However, the most sensitive population (Westerhof) showed 6.6 times less net photosynthesis

and 5.5 times more transpiration than tolerant "Rachovo" spruce. However, at lower levels of NO₂ (1 to 1.15 ppm), no effects on net photosynthesis or transpiration were detected.

There are no reports of any changes in carbohydrate allocation in response to fumigations with NO₂ alone at concentrations between 0.04 and 0.4 ppm (Darrall, 1989). Nevertheless, adverse interactions between SO₂ and NO₂ on root:shoot ratios (81% of controls) have been detected in barley (*Hordeum vulgare* L. cv. Patty) fumigated for 20 days with 0.1 ppm of each (Pande and Mansfield, 1985). In radishes (*Raphanus sativus* L. cv. Cherry Belle), however, Reinert and Gray (1981) could only detect additive effects of SO₂, NO₂, or O₃ (0.4 ppm each for 7 days). Darrall (1989) has summarized the details of other mixed fumigations in the literature that are known to cause changes in root:shoot ratios. The mechanisms by which mixtures of pollutants bring about fundamental changes in the apportionment of material between roots and shoots are not known, but critical changes in phloem loading and transport could be responsible.

9.6.2 Exposure Response Data for Pollutant Mixtures

9.6.2.1 Description of Foliar Injury

Of the three major atmospheric pollutants (O₃, NO₂, and SO₂), NO₂ is the least likely to cause visible injury because of both its relatively low phytotoxicity and its low ambient concentration. In combination with other pollutants, however, NO₂ has the potential to modify the injury associated with the other gases. Most of the descriptions of injury arise from controlled environment studies. Because of the generally greater sensitivity of plants to pollutant exposure under controlled environment conditions, it is possible that the exposure conditions that led to the injury symptoms in these studies would not result in similar injury under field conditions. Several key early studies clearly described the injury symptoms from NO_x mixtures and established the potential for enhancement of NO_x injury by SO₂.

A survey of the sensitivity of six species to SO₂/NO₂ mixtures in 4-h exposures found that neither 2.0 ppm NO₂ nor 0.5 ppm SO₂ alone caused foliar injury (Tingey et al., 1971). However, a mixture of 0.10 ppm NO₂ and 0.10 ppm SO₂ administered for 4 h caused foliar injury to pinto bean, radish, soybean, tomato, oat, and tobacco. Exposure to 0.15 ppm NO₂ in combination with 0.1 ppm SO₂ for 4 h caused greater foliar injury than did lower concentrations. Traces of foliar injury were observed at 0.05 ppm NO₂ and 0.05 ppm SO₂,

no single gas exposures were performed. In these species, upper leaf surface injury most often occurred as discrete interveinal necrotic flecking, except for pinto bean and soybean, which developed a dark, reddish-brown pigment in the cells on the upper leaf surface (Tingey et al., 1971). The authors noted that with those exceptions, upper leaf surface injury was similar to that caused by O_3 in most species. Lower leaf injury in the two bean species was similar to the upper leaf surface injury, whereas in radish and tobacco, lower surface injury was noted as silvering of the interveinal areas (Table 9-8). Fujiwara et al. (1973) found greater-than-additive effects when peas were exposed to 0.1 ppm NO_2 in combination with 0.1 ppm SO_2 . When NO_2 and SO_2 (0.2 ppm of each gas) were used, the effect was only additive (data not in Table 9-8).

The effect of all three gases (NO_2 , SO_2 , O_3) on visible injury of shore juniper (*Juniperus conferta*) was assessed after a single 4-h exposure to O_3 (0.3 ppm), SO_2 (0.15 ppm), and NO_2 (0.15 ppm), the effects on visible injury were additive (Fravel et al., 1984). The injury resembled small, elongated, tan foliar lesions in response to O_3 and NO_2 , and was similar in appearance to the injury noted after O_3 alone (Table 9-8).

Bennett et al. (1975) studied the effects of NO_2 and SO_2 mixtures on radish, Swiss chard, oat, and pea. Treatments consisted of 1- and 3-h fumigations with the pollutants separately and with SO_2 and NO_2 (1:1) mixtures in concentrations ranging from 0.125 to 1.0 ppm. No visible injury occurred on experimental plants treated with NO_2 alone or from exposures to SO_2 concentrations of less than or equal to 0.5 ppm. The minimum exposure doses that caused visible injury to radish leaves were 1-h exposures to a mixture of NO_2 and SO_2 (0.5 ppm of each gas) or to 0.75 ppm of SO_2 alone. The data indicated that SO_2 and NO_2 in combination may enhance the phytotoxicity of these pollutants, but relatively high doses were required to cause injury. The remaining studies described in Table 9-8 do not detail the appearance of visible injury, but rather concentrate on whether or not its occurrence was enhanced by SO_2 and/or O_3 . These studies, which mainly focused on NO_x/SO_2 mixtures, mostly demonstrated that the likelihood of visible injury response to NO_x increases with concentration of the other gas, and with the addition of O_3 .

Very few studies have addressed the occurrence of NO_x mixture injury in field-situated plants (Table 9-9). A broad survey of native U.S. species' sensitivity to SO_2/NO_2 indicated

**TABLE 9-8. VISIBLE INJURY IN CONTROLLED
EXPOSURES TO NITROGEN OXIDE MIXTURES^a**

| Species | Gas Mixture | Exposure | Effect ^b | Reference |
|-----------------|--|-----------------|---------------------|------------------------------------|
| Tobacco | NO ₂ + SO ₂ | Low episode | 0 | Tingey et al (1971) |
| | | Medium episode | - | |
| | | High episode | - | |
| Bean | NO ₂ + SO ₂ | Low episode | 0 | Tingey et al (1971) |
| | | Medium episode | 0/- | |
| | | High episode | 0/- | |
| Tomato | NO ₂ + SO ₂ | Low episode | 0 | Tingey et al (1971) |
| | | Medium episode | 0/- | |
| | | High episode | 0 | |
| Radish | NO ₂ + SO ₂ | Low episode | 0 | Tingey et al (1971) |
| | | Medium episode | 0/- | |
| | | High episode | - | |
| Oat | NO ₂ + SO ₂ | Low episode | 0 | Tingey et al (1971) |
| | | Medium episode | 0/- | |
| | | High episode | 0/- | |
| Soybean | NO ₂ + SO ₂ | Low episode | 0/- | Tingey et al (1971) |
| | | Medium episode | 0/- | |
| | | High episode | 0/- | |
| Radish | NO ₂ + SO ₂ | Medium episode | - | Sanders and Reinert (1982b) |
| | NO ₂ + O ₃ | Medium episode | - | |
| | NO ₂ + SO ₂ + O ₃ | Medium episode | - | |
| | NO ₂ + SO ₂ | Medium seasonal | - | Reinert and Sanders (1982) |
| | NO ₂ + O ₃ | Medium seasonal | - | |
| | NO ₂ + SO ₂ + O ₃ | Medium seasonal | - | |
| Marigold | NO ₂ + SO ₂ | Medium episode | ? | Sanders and Reinert (1982b) |
| | NO ₂ + O ₃ | Medium episode | - | |
| | NO ₂ + SO ₂ + O ₃ | Medium episode | - | |
| | NO ₂ + SO ₂ | Medium seasonal | - | Reinert and Sanders (1982) |
| | NO ₂ + O ₃ | Medium seasonal | - | |
| | NO ₂ + SO ₂ + O ₃ | Medium seasonal | - | |
| Rhododendron | NO ₂ + SO ₂ | Medium seasonal | 0 | Sanders and Reinert (1982a) |
| | NO ₂ + O ₃ | Medium seasonal | - | |
| | NO ₂ + SO ₂ + O ₃ | Medium seasonal | - | |
| Potato | NO ₂ + SO ₂ | Low seasonal | - | Petitte and Ormrod (1984, 1988) |
| Kidney bean | NO ₂ + SO ₂ | High episode | 0/- | Ito et al (1984a) |
| Carolina poplar | NO ₂ + SO ₂ | High episode | - | Eastham and Ormrod (1986) |
| Black poplar | | Medium episode | 0 | |
| | | High episode | - | |
| Oat | NO ₂ + SO ₂ | Medium episode | 0 | Bennett et al (1975) |
| Beet | | | 0 | |
| Radish | | | - | |
| Pea | | | 0 | |
| Shore juniper | | | 0 | |
| | NO ₂ + SO ₂ | Low episode | 0 | Fravel et al (1984) |
| | NO ₂ + SO ₂ + O ₃ | Medium episode | - | |
| | | Medium episode | - | |

**TABLE 9-8 (cont'd). VISIBLE INJURY IN CONTROLLED
EXPOSURES TO NITROGEN OXIDE MIXTURES^a**

| Species | Gas Mixture | Exposure | Effect ^b | Reference |
|--------------------|--|-----------------|---------------------|----------------------------------|
| White pine | NO ₂ + SO ₂ | Low episode | - | Yang et al (1982) |
| | NO ₂ + O ₃ | Low episode | - | |
| | NO ₂ + SO ₂ + O ₃ | Low episode | - | |
| European birch | NO ₂ + SO ₂ | Low seasonal | - | Neighbour et al (1988) |
| Downy birch | ? | ? | ? | |
| Sitka spruce | NO ₂ + SO ₂ | Low seasonal | - | Freer-Smith and Mansfield (1987) |
| Radish | NO ₂ + SO ₂ | Medium seasonal | - | Godzik et al (1985) |
| Black poplar | NO ₂ + SO ₂ | Low seasonal | 0/- | Freer-Smith (1984) |
| Little-leaf linden | | | 0 | |
| Apple | | | 0 | |
| European birch | | | - | |
| Speckled alder | | | - | |
| Loblolly pine | NO ₂ + O ₃ | Low seasonal | - | Kress and Skelly (1982) |
| Pitch pine | | | - | |
| Scrub pine | | | - | |
| Sweet-gum | | | - | |
| White ash | | | - | |
| Red ash | | | - | |
| Willow oak | | | 0 | |
| Loblolly pine | NO ₂ + O ₃ | Low seasonal | 0 | Kress et al (1982b) |
| | NO ₂ + SO ₂ + O ₃ | | - | |
| Kidney bean | NO ₂ + O ₃ | High episode | - | Okano et al (1985a) |

^aNO₂ = Nitrogen dioxide

SO₂ = Sulfur dioxide

O₃ = Ozone

^bThe following codes are used to indicate the exposure effect

+ = Less effect of mixture than single gases

0 = No different effect of mixture than single gases

- = Greater effect of mixture than single gases

? = Not recorded

**TABLE 9-9. VISIBLE INJURY IN FIELD CHAMBER AND
FIELD EXPOSURES TO NITROGEN OXIDE MIXTURES^a**

| Species | Gas Mixture | Exposure | Effect ^b | Reference |
|-------------------|-----------------------------------|-----------------|---------------------|-----------------------|
| Desert ecosystems | NO ₂ + SO ₂ | High episode | 0 | Hill et al (1974) |
| Creosote bush | NO ₂ + SO ₂ | Medium seasonal | - | Thompson et al (1980) |
| Burro weed | | High seasonal | - | |

^aNO₂ = Nitrogen dioxide

SO₂ = Sulfur dioxide

^bThe following codes are used to indicate the exposure effect

+ = Less effect of mixture than single gases

0 = No different effect of mixture than single gases

- = Greater effect of mixture than single gases

that the addition of NO₂ to SO₂ (in a 1 0 0 28 proportion) did not cause more injury than did the SO₂ alone (Hill et al , 1974) In addition, the injury from the mixtures resembled that from SO₂ alone—varying with species, appeared as regions of discolored (tan, grey-brown, yellow-brown, rusty brown) patches of interveinal necrotic tissue

The studies described in this section make several points The first is that NO₂ in combination with other pollutant gases frequently can result in more injury than is associated with the individual gases, particularly as exposure concentration increases or O₃ is added However, the occurrence of injury arises only from mixture concentrations that are much higher than those observed in the ambient environment The second is that the addition of NO₂ to other gases does not result in unique injury symptoms—the combination usually causes symptoms that resemble those resulting from the other pollutant, or may resemble those from a pollutant not included in the mix For example, shore juniper injury from NO₂/O₃ resembled O₃ injury and desert native species injury from NO₂/SO₂ resembled SO₂ injury, so that if NO_x mixture injury did occur in plants, it would be difficult to positively identify the causal agents

9.6.3 Losses in Growth and Yield

When evaluating the available literature to determine the risk to vegetation from pollutant mixtures, it is important to consider the experimental exposure regime used to

induce the response. For example, were the pollutant concentrations and durations similar to what would be expected to occur in the ambient environment? Was the frequency of exposure similar to what occurs in the field?

An analysis of ambient air quality data from the United States showed that the frequency of pollutant co-occurrence (at concentrations equal to or greater than 0.05 ppm for both pollutants) was low, with most sites experiencing fewer than 10 h of pollutant co-occurrence during the growing season (Lefohn and Tingey, 1984). The report also indicated that the frequency of pollutant co-occurrence used in most experimental studies of vegetation effects was much greater than the frequency of occurrence in the ambient air. A recent study in an area of the Ohio River Valley (United States), containing several coal-fired power plants, found that the simultaneous occurrence of NO₂ and SO₂ was rare (Jacobson and McManus, 1985). Using minimum concentrations of 0.03 and 0.05 ppm for NO₂ and SO₂, respectively, the authors showed that these gaseous concentrations co-occurred for less than 1 % of the total hours monitored. Air monitoring data from central London, England, also support the conclusion that the joint occurrence of NO₂ and SO₂ is small (Lane and Bell, 1984a). The authors characterized 3 mo (January through March) and found that the joint occurrence of the two gases accounted for less than 1 % of the monitoring time, using minimum concentrations of 0.05 ppm for each gas.

Lefohn et al. (1987a) conducted additional analyses of pollutant co-occurrence. In the study, co-occurrence was defined as elevated concentrations (using a threshold concentration of ≥ 0.03 ppm) for at least 1 h any time during the day (24 h). The pollutant monitoring data (based on 110 site-years of data for NO₂ and SO₂ and 71 site-years for NO₂ and O₃) were obtained from comonitoring sites located in both urban and rural areas. The analyses found that the co-occurrences at most rural sites (5-mo summer period) were infrequent, less than 12 % of the days. The infrequent co-occurrence is not surprising because most sites experienced only a few hours per year when the concentrations of NO₂ or SO₂ were ≥ 0.03 ppm.

To conduct experiments that are relevant to field conditions, it is important that the pollutant exposure regimes utilize concentration distributions and temporal sequences of exposure that reflect the area for which inferences are being made. Unless this is done, it is difficult to extrapolate to field conditions using data from more intense experimental

exposures. For example, in a study on the effects of power plant emissions (NO_2 and SO_2) on native desert plants, the authors qualified their results with the statement that the pollutant concentrations, exposure duration, and frequency of exposures were much higher than would be expected to occur around power plants in the area of interest (Thompson et al , 1980) In a study on the effects of air pollutants, singly and in combination, on poplars, Mooi (1984) attempted to simulate the long-term mean concentrations of O_3 , NO_2 , and SO_2 that occurred in Holland Lane and Bell (1984a) analyzed 3 mo (January through March) of air quality data from central London to design experimental plant exposures that simulated the distributions of SO_2 and NO_2 Lefohn et al (1987b) have developed a procedure to construct exposure regimes that simulate pollutant co-occurrence Additional studies that simulate ambient air quality, including the joint frequency distributions of the gases, will provide much-needed information to properly assess the potential environmental impact from pollutant mixtures on plants and ecosystems

9.6.3.1 Laboratory and Greenhouse Studies—Sequential Exposures

Several newer studies are important because they assess plant response to NO_2 in combination with other pollutants in temporal patterns of exposure that are more similar to those observed under ambient conditions Although they may not reproduce actual exposure regimes, they explore modification of plant response to NO_x by pre- or postexposure to other gases (Table 9-10) This concept was explored much earlier by Matsushima (1971), who observed more leaf injury on several plant species from a mixture of NO_2 and SO_2 than that caused by each pollutant alone He also tested different sequences of exposure When NO_2 exposure preceded SO_2 , the degree of injury was similar to that resulting from individual exposures to either gas But when SO_2 exposure was followed by NO_2 , the degree of leaf injury increased as would be typical of simultaneous exposures to both pollutants.

Spinach was exposed to SO_2 and/or NO_2 in various concurrent or sequential patterns within a 24-h period (Hogsett et al , 1984) During the day, plants were exposed to 0.8 ppm of each gas simultaneously for 2 h, or sequentially to SO_2 followed by NO_2 (each for 2 h) or NO_2 followed by SO_2 (each for 2 h), or, during the night, plants were exposed to either both gases at 0.8 or 1.5 ppm concurrently for 2 h Each of the five treatments was repeated

TABLE 9-10. GROWTH/YIELD IN CONTROLLED EXPOSURES TO NITROGEN OXIDE MIXTURES^a

| Species | Gas Mixture | Exposure | Effect ^b | Reference |
|-----------------|--|-----------------|---------------------|-----------------------------|
| Radish | NO ₂ + SO ₂ | Medium episode | 0 | Sanders and Reinert (1982b) |
| | NO ₂ + O ₃ | Medium episode | - | |
| | NO ₂ + SO ₂ + O ₃ | Medium episode | - | |
| Marigold | NO ₂ + SO ₂ | Medium seasonal | 0 | Reinert and Sanders (1982) |
| | NO ₂ + O ₃ | Medium seasonal | - | |
| | NO ₂ + SO ₂ + O ₃ | Medium seasonal | - | |
| | NO ₂ + SO ₂ | Medium episode | 0 | Sanders and Reinert (1982b) |
| | NO ₂ + O ₃ | Medium episode | 0 | |
| | NO ₂ + SO ₂ + O ₃ | Medium episode | 0 | |
| | NO ₂ + SO ₂ | Medium seasonal | 0 | Reinert and Sanders (1982) |
| | NO ₂ + O ₃ | Medium seasonal | 0 | |
| | NO ₂ + SO ₂ + O ₃ | Medium seasonal | 0 | |
| Rhododendron | NO ₂ + SO ₂ | Medium seasonal | 0 | Sanders and Reinert (1982a) |
| | NO ₂ + O ₃ | Medium seasonal | 0 | |
| | NO ₂ + SO ₂ + O ₃ | Medium seasonal | 0 | |
| Tomato | NO ₂ + SO ₂ | Low seasonal | 0/- | Marie and Ormrod (1984) |
| Potato | NO ₂ + SO ₂ | Low seasonal | - | Petitte and Ormrod (1988) |
| Tobacco | NO ₂ + SO ₂ | Low seasonal | 0 | Elkley et al (1988) |
| Corn | | | - | |
| Kidney bean | | | 0 | |
| Pea | | | 0 | Elkley et al (1988) |
| Potato | | | - | |
| Tobacco | NO ₂ + SO ₂ | Low episode | 0/- | |
| Kidney bean | | | 0/- | Goodyear and Ormrod (1988) |
| Tomato | NO ₂ + O ₃ | Medium episode | 0/- | |
| Kidney bean | NO ₂ + O ₃ | High seasonal | - | |
| Carolina poplar | NO ₂ + SO ₂ | Medium episode | 0 | Eastham and Ormrod (1986) |
| | | High episode | 0 | |
| Black poplar | | Medium episode | - | |
| | | High episode | 0 | |
| White pine | NO ₂ + O ₃ | Low seasonal | - | Yang et al (1982) |
| | NO ₂ + SO ₂ | Low seasonal | - | |
| | NO ₂ + SO ₂ + O ₃ | Low seasonal | - | |
| European birch | NO ₂ + SO ₂ | Low seasonal | - | Wright (1987) |
| Downy birch | | | - | |
| European birch | NO ₂ + SO ₂ | Low seasonal | 0/- | Freer-Smith (1985) |

**TABLE 9-10 (cont'd). GROWTH/YIELD IN CONTROLLED
EXPOSURES TO NITROGEN OXIDE MIXTURES^a**

| Species | Gas Mixture | Exposure | Effect ^b | Reference |
|---------------------|--|-----------------|---------------------|----------------------------------|
| Kentucky bluegrass | NO ₂ + SO ₂ | Low seasonal | - | Whitmore and Mansfield (1983) |
| Perennial rye grass | | | 0 | |
| Timothy | | | 0 | |
| Orchard grass | | | 0 | |
| Sitka spruce | NO ₂ + SO ₂ | Low seasonal | - | Freer-Smith and Mansfield (1987) |
| Radish | NO ₂ + SO ₂ | Medium seasonal | - | Godzik et al (1985) |
| Black poplar | NO ₂ + SO ₂ | Low seasonal | - | Freer-Smith (1984) |
| Little-leaf linden | | | - | |
| Apple | | | - | |
| European birch | | | - | |
| Speckled adler | | | - | |
| Loblolly pine | NO ₂ + O ₃ | Low seasonal | 0 | Kress and Skelly (1982) |
| Pitch pine | | | 0 | |
| Scrub pine | | | 0 | |
| Sweetgum | | | - | |
| White ash | | | - | |
| Red ash | | | - | |
| Willow oak | | | 0 | |
| American plane tree | NO ₂ + O ₃ | Low seasonal | + | |
| Loblolly pine | | | 0 | |
| American plane tree | NO ₂ + O ₃ + SO ₂ | Low seasonal | - | Kress et al (1982a) |
| Loblolly pine | | | + | Kress et al (1982b) |
| Kidney bean | NO ₂ + O ₃ | High episode | - | Okano et al (1985a) |

^aNO₂ = Nitrogen dioxide

SO₂ = Sulfur dioxide

O₃ = Ozone

^bThe following codes are used to indicate the exposure effect

+ = Less effect of mixture than single gases

0 = No different effect of mixture than single gases

- = Greater effect of mixture than single gases

weekly for 5 weeks. Two plants from each treatment were harvested each week during the exposure period. Concurrent exposure during the day resulted in a slightly depressed growth rate at the beginning of the exposure period (Days 14 to 28), but by the end of the exposure period, market yield parameters were unchanged from control values. Sequential daytime exposures had no effect on plant growth. The nighttime concurrent exposures did reduce plant growth, starting with the first exposures. By the end of the exposure period, both concurrent exposures had reduced total, leaf, and root dry weights in comparison to control plants, and 1.5 ppm had reduced leaf area and fresh weight. A lack of physiological or metabolic data make it difficult to speculate on the mechanism by which this effect takes place. However, this study suggested that concurrent exposure to SO_2 and NO_2 likely has more potential for reduction of plant growth than sequential exposure, and that plants exposed to darkness are less able to detoxify or repair NO_2/SO_2 stress.

A similar study of tomato response to NO_2 and O_3 contrasted daytime sequential versus concurrent exposures, and day/night sequential versus day or night exposures (Goodyear and Ormrod, 1988). In the first experiment, plants at the 4-to-6 or 9-to-11 leaf stage were exposed once for 1 h to 0.08 ppm O_3 and 0.21 ppm NO_2 . Leaf and stem fresh weights of 4-to-6 leaf plants were smaller after exposure to the concurrent gases than in control plants. In the second experiment, plants at the 4-to-6 leaf stage were exposed once to 0.08 ppm O_3 and 0.21 ppm NO_2 either concurrently for 1 h or in either sequence, each gas for 1 h. NO_2 then O_3 , or O_3 then NO_2 . In contrast to the first experiment, concurrent exposure no longer reduced plant growth, but O_3 followed by NO_2 resulted in plants that were generally smaller (suggesting reduction in vigour) than those from either control, concurrent, or NO_2 followed by O_3 treatments. The lack of consistency in the effect of NO_2 plus O_3 between experiments was hypothesized to be due to the difference in the time of day at which exposure to the gases took place, the suggested mechanism was that stomatal conductance varies during the day, leading to differences in internal dose of the gases. The exposure of plants to NO_2 at night followed by O_3 during the day had no effect on growth.

These two studies (Goodyear and Ormrod, 1988, Hogsett et al., 1984) clearly indicate that NO_2 has little potential for reduction of plant growth when it occurs as a single gas in a sequential exposure. Because this type of exposure is more common in the ambient

environment (see introduction), NO₂ mixtures with other ambient pollutants such as SO₂ or O₃ are likely to cause little plant injury

9.6.3.2 Laboratory and Greenhouse Studies—Concurrent Exposure

A large number of studies on the interaction between NO₂ and SO₂ have been carried out using plants grown under artificial conditions and exposed to concurrent pollutant regimes that are less likely to occur under most ambient situations, but that may occur in the vicinity of a source, such as SO₂/NO₂ near a power plant. These studies may be useful in establishing relative species sensitivities, or identifying modifying factors of plant/pollutant interaction (Table 9-10)

Ten species native to the Mojave/Eastern Mojave-Colorado desert were exposed to high, medium, or low concentrations of SO₂ and NO₂ for 25 h/week for a period of 9 to 32 weeks, depending on the species and year of experimentation (Thompson et al., 1980). In the first year of the study, only the highest concentration mixture (1.0 ppm NO₂ plus 2.0 ppm SO₂) reduced growth and/or dry weight of some perennial species (*Larrea divericata*, *Chilopsis linearis*, *Ambrosia dumosa*, and *Atriplex canescens*). The most extreme response was a 60% reduction in growth of *L. divericata*. These results were fairly consistent with the second year of experimentation, except that the growth of some of the species (*L. divericata*, *A. dumosa*) was reduced by medium (0.33 ppm NO₂ and 0.67 ppm SO₂) and low (0.11 ppm NO₂ and 0.22 ppm SO₂) concentration gas mixtures. In contrast, growth of *Encelia farinosa* was increased by high and medium concentration mixtures (101% and 51%, respectively). Of great importance was the observation that seed and flower production of two perennials (*A. dumosa* and *E. farinosa*) were severely inhibited by all mixtures of the gases. Because these two species contrast in their growth response to the gas mixture, reduction of flowering in *Ambrosia* may have resulted from generally depressed plant vigor, whereas flowering in *Encelia* may have been directly inhibited by the gas mixture, allowing more photoassimilate to be partitioned to shoot growth—perhaps NO₂ was acting as a fertilizing source of nitrogen. This suggests that the survival of perennials, of either the same plant from season to season or the germination of new individuals, may be threatened by mixtures of SO₂ and NO₂, but only if the ambient seasonal exposure increases significantly in comparison to current levels. Like the perennials, the growth of several

annual species was inhibited by the high or medium concentration mixtures (*Baileya pleniradiata*, *Phacelia crenulata*, *Plantago insularis*, and *Erodium cicutarium*) between 40 and 80% compared to control. The flowering success of several of these species was also reduced by the mixtures of SO₂ and NO₂. This study demonstrated that a high concentration mixture caused visible injury in a significant number of species. It also demonstrated that response to the mixtures is species specific. Response to the low concentration mixture stimulated growth in several species. It is likely that this study optimized plant sensitivity to gases, as soil water was maintained at nonstress levels, and RH was high, ensuring that the rate of gas exchange was high. The authors noted that SO₂ did not change plant response to NO₂, so that the mixture posed no greater threat than that from either of the single gases.

The exposure of tomato to continuous SO₂ and NO₂ reduces growth (Marie and Ormrod, 1984). After 14 days in 0.11 ppm SO₂ plus 0.11 ppm NO₂, tomato (cv. Fireball) leaf area and fresh weight were about 50% of control plants. After 28 days, root growth (fresh weight) was reduced by 65%. An examination of the data indicates that root size was decreased similarly at 7 and 14 days, but this decrease was not statistically significant ($p > 0.05$). The same growth trends were seen in plants exposed for the same periods to SO₂ and NO₂ at 0.05 ppm, however, these differences were also not statistically significant ($p > 0.05$).

Potato (*Solanum tuberosum*) growth is reduced by exposure to concurrent SO₂ and NO₂ at 0.11 ppm. After 7 days, root fresh weight in Kennebec and shoot and root fresh weights in Russet Burbank were reduced to about 60% of control values (Petitte and Ormrod, 1988). After 14 days, the growth reduction included stems. Although both shoot and root size of Russet Burbank were reduced by pollutant exposure, roots were more severely impacted than stems or leaves, as indicated by the increase in leaf/root dry weight ratio and the decrease in leaf/stem dry weight ratio at 7 and 14 days. Stems of this cultivar seemed to be the strongest sink for photoassimilates. A similar study of four potato cultivars exposed to SO₂ and NO₂ at 0.11 ppm for 7 or 14 days indicated that cultivars with a late maturity classification (Russet Burbank and Kennebec) tended to be more sensitive than those of an earlier maturity classification (Superior and Norchip) (Petitte and Ormrod, 1984). The growth reduction of the two cultivars was similar to that reported in Petitte and Ormrod (1988). These three

studies indicate that plant growth may be inhibited by combined exposures of NO_2 + SO_2 that have concentrations of NO_2 that are noninjurious by themselves

The exposure of potato, corn, pea, tobacco, and pinto bean to SO_2 (0.15 ppm) and NO_2 (0.10 ppm) continuously for 15 days resulted in little effect on growth (Elkney et al., 1988). Only potato (cv. Kennebec) had smaller shoot fresh and dry weights in comparison to control. Tobacco and bean were then exposed to various combinations of the two gases, every day for 15 days, and the growth responses were mixed. Tobacco leaf area was reduced by 0.11 ppm of both gases when delivered continuously, or when 0.11 ppm NO_2 was combined with 0.34 ppm SO_2 for 1 h/day. Bean leaf area was also reduced by exposure to continuous regime, as well as by 0.05 ppm SO_2 combined with 0.1 ppm NO_2 on a continuous basis. Bean shoot dry weight was reduced by exposure to 0.11 ppm NO_2 continuously combined with 0.34 ppm SO_2 for 1 h. Kidney bean (cv. Shin-edogawa) was exposed to NO_2 (2.0 or 4.0 ppm) and O_3 (0.1, 0.2, or 0.4 ppm) continuously for 2, 4, or 7 days (Ito et al., 1984a). In general, mixture effects were similar to effects of O_3 alone, indicating that NO_2 did not increase injury from other pollutants. After 4 and 7 days, plant dry weight from the gas mixture was smaller than control, and after 7 days, the root/shoot ratio in plants exposed to the gas mixture appeared to be smaller. This change in relative mass of the roots was likely due to alteration in photoassimilate transport from the shoot to the root, as the reduction in root mass was accompanied by apparently lower concentrations of soluble sugars (see "Mode of Action", Section 9.6.1 for further discussion).

Exposure of Kentucky Blue Grass to SO_2 and NO_2 , both at either 0.4, 0.7, or 1.0 ppm, continuously for 20, 34, or 38 days resulted in a decrease in growth at 38 days that appeared to be linearly related to concentration of the pair of gases (Whitmore, 1985). The treatments were not replicated, but polynomial regression would have been a valid approach to analysis, and it seems likely that the linear component would have been significant. In a second, replicated experiment, the dose (parts per million-days) was related to growth as percent of control, the dose-response relationship indicated growth stimulation at low concentrations, followed by growth inhibition that related less to dose as dose increased. Because single-gas treatments were not included, it is difficult to comment on the effect of NO_2 on the phytotoxicity of the other gases. As well, parts per million-day as a unit of dose is not in widespread use, making it difficult to compare this study with others. The sensitivity of

grasses to SO₂/NO₂ mixtures is of particular importance in Great Britain where these gases may co-occur, albeit at relatively low concentrations. A number of studies have examined growth responses of various grass species to long term exposure to SO₂/NO₂ mixtures (Ashenden and Mansfield, 1978, Ashenden, 1979b, Ashenden and Williams, 1980). Although each of the studies is nonreplicated, they are very similar in methodology, and will be considered together. Each of these studies exposed various pasture grasses (*Poa*, *Phleum*, *Dactylis*, and *Lolium*) to 0.11 ppm SO₂ and/or NO₂, 5 days/week for 20 weeks. All three studies reported reduced growth of shoot portions of the plants in response to the gas mixture, and the degree of reduction was greater than that expected from the response of the plants to the single gases.

The response of *Populus nigra* to a single 1-h exposure to 0.5 ppm SO₂ was modified by the presence of 0.5 ppm NO₂ (Eastham and Ormrod, 1986). Leaf and stem mass tended to be greater than the control in the presence of NO₂, and intermediate in the presence of both gases. For leaf area, leaf fresh and dry weights, and stem dry weight, the two gases at 0.5 ppm were antagonistic in their effect, in that the presence of one gas reduced the effect of the other. However, when the concentration of each gas was increased to 1.0 ppm, there was no main effect of the pollutants on growth, and no interaction between the gases for either *P. nigra* or *Populus canadensis*. However, all of the *P. nigra* and some of the *P. canadensis* plants were visibly injured by the gas mixture. The latter pollutant regime may have been too severe for a positive effect on leaf area and stem mass (in contrast to the first regime), but not severe enough for a negative effect on growth.

The interaction of O₃, NO₂, and SO₂ has been investigated less frequently than two-gas interactions, probably due to the large number of treatments required to expose plants to all possible combinations of the three gases. Nitrogen dioxide did not modify plant response to SO₂ and O₃ for radish (*Raphanus sativus*) and marigold (*Tagetes patula*) when plants were exposed to 0.3 ppm of all gases three times for 3 or 6 h, respectively (Sanders and Reinert, 1982b). Nitrogen dioxide also did not modify response to SO₂ or O₃ except for a reduction in root and total plant dry weights of marigold exposed to SO₂. A similar study of radish and marigold exposed to 0.3 ppm for 3 or 6 h, respectively, nine times within 3 weeks indicated that visible injury on radish appeared to be less than additive compared to the single pollutants for NO₂/O₃ and NO₂/O₃/SO₂, whereas NO₂/SO₂ appeared to be greater.

than additive (Reinert and Sanders, 1982) The effect of NO_2/SO_2 and $\text{NO}_2/\text{SO}_2/\text{O}_3$ on marigold was less than additive, but the effect of NO_2/O_3 was greater than additive Marigold root dry weight in response to NO_2/SO_2 was smaller than control This study demonstrates that the presence of other gases can increase or reduce the effect of NO_x on root growth, depending on the plant species and the identity of the other gas

A similar study exposing 16-day-old radish (*Raphanus sativus*) to all three gases at 0.1, 0.2, or 0.4 ppm once for 3 h resulted in no interaction among the three gases, and an $\text{NO}_2 \times \text{O}_3$ interaction only resulted in a reduction of root fresh and dry weight (Reinert et al., 1982). Increasing SO_2 concentration to 1.6 ppm in a second experiment resulted in an interaction between NO_2 and SO_2 in reducing root fresh and dry weights

A study of azalea (*Rhododendron* spp.) indicated that there was no interaction among the pollutants, although NO_2 combined with SO_2 caused injury on some of the cultivars (Sanders and Reinert, 1982a) The plants were exposed to all combinations of the three gases at 0.25 ppm six times during a 4-week period

Growth studies of yellow poplar (*Liriodendron tulipifera*) in response to various combinations of O_3 (0.07 ppm), SO_2 (0.06 ppm), and NO_2 (0.01 ppm) for 6 h/day for 35 consecutive days indicated that the treatments differentiate after 2 weeks of exposure (Mahoney et al., 1984) At this time, the single-gas treatments (SO_2 or O_3) had no effect in comparison to control, and the plants grew taller than those exposed to $\text{SO}_2 + \text{NO}_2$, $\text{SO}_2 + \text{O}_3$, or $\text{O}_3 + \text{SO}_2 + \text{NO}_2$ (there was no difference among these mixture treatments) Although NO_2 alone was not one of the treatments, it is clear that the addition of NO_2 did not further decrease growth in response to $\text{SO}_2 + \text{O}_3$, but its addition did decrease growth in response to SO_2 alone A pair of studies on the effects of $\text{SO}_2/\text{NO}_2/\text{O}_3$ mixtures on a variety of tree species demonstrated that the addition of NO_2 to $\text{O}_3 + \text{SO}_2$ could suppress growth in sycamore (Kress et al., 1982a) or slightly stimulate growth in loblolly pine (Kress et al., 1982b).

9.6.4 Field Chamber and Field Studies

Long-term field study of the impact of SO_2 on the effect of NO_2 on plant productivity is a less common approach to gas mixture studies, likely due to the significant effort required to conduct such a large study (Table 9-11) Soybean (*Glycine max* L. cv Northrup King,

**TABLE 9-11. GROWTH/YIELD IN FIELD CHAMBER AND
FIELD EXPOSURES TO NITROGEN OXIDE MIXTURES^a**

| Species | Gas Mixture | Exposure | Effect ^b | Reference |
|---------------------------|-----------------------------------|-----------------|---------------------|-------------------------------|
| Creosote bush | NO ₂ + SO ₂ | High seasonal | - | Thompson et al (1980) |
| | | Medium seasonal | - | |
| | | Low seasonal | 0 | |
| Desert willow | NO ₂ + SO ₂ | High seasonal | 0 | Thompson et al (1980) |
| | | Medium seasonal | 0 | |
| | | Low seasonal | 0 | |
| Brittle bush | NO ₂ + SO ₂ | High seasonal | 0 | Thompson et al (1980) |
| | | Medium seasonal | 0 | |
| | | Low seasonal | 0 | |
| Burro weed | NO ₂ + SO ₂ | High seasonal | + | Thompson et al (1980) |
| | | Medium seasonal | + | |
| | | Low seasonal | 0 | |
| Four-wing saltbush | NO ₂ + SO ₂ | High seasonal | 0 | Thompson et al (1980) |
| | | Medium seasonal | 0 | |
| | | Low seasonal | 0 | |
| Desert marigold | NO ₂ + SO ₂ | High seasonal | - | Thompson et al (1980) |
| | | Medium seasonal | 0 | |
| | | Low seasonal | 0 | |
| <i>Plantago insularis</i> | NO ₂ + SO ₂ | High seasonal | 0 | Thompson et al (1980) |
| | | Medium seasonal | 0 | |
| | | Low seasonal | 0 | |
| <i>Phacelia crenulata</i> | NO ₂ + SO ₂ | High seasonal | - | Thompson et al (1980) |
| | | Medium seasonal | - | |
| | | Low seasonal | 0 | |
| <i>Alfilaria</i> | NO ₂ + SO ₂ | High seasonal | - | Thompson et al (1980) |
| | | Medium seasonal | - | |
| | | Low seasonal | 0 | |
| Crunch-weed | NO ₂ + SO ₂ | High seasonal | - | Thompson et al (1980) |
| | | Medium seasonal | - | |
| | | Low seasonal | 0 | |
| White pine | Arsenal emissions | Lifetime | - | Stone and Skelly (1974) |
| Yellow poplar | NO ₂ + SO ₂ | Low seasonal | - | Ashenden and Williams (1980) |
| Italian ryegrass | | | - | |
| Orchard grass | | Low seasonal | - | |
| Italian ryegrass | NO ₂ + SO ₂ | | - | Ashenden and Mansfield (1978) |
| Timothy | | | - | |
| Kentucky bluegrass | | | 0/- | |
| Orchard grass | NO ₂ + SO ₂ | Low seasonal | 0/- | Ashenden (1979b) |
| Kentucky bluegrass | | | 0/- | |
| Soybean | NO ₂ + SO ₂ | Low seasonal | - | Irving et al (1982) |

^aNO₂ = Nitrogen dioxide

SO₂ = Sulfur dioxide

^bThe following codes are used to indicate the exposure effect

+ = Less effect of mixture than single gases

0 = No different effect of mixture than single gases

- = Greater effect of mixture than single gases

1492) was exposed to NO₂ and SO₂ in the presence of ambient O₃ in a field situation equipped with a Zonal Air Pollutant (delivery) System (Irving et al , 1982) In both years (replications), the plants received 10 fumigations, the concentrations of the individual gases ranged from 0.13 to 0.42 ppm for SO₂ and 0.06 to 0.40 ppm for NO₂ Nitrogen dioxide exposures had no effect on seed yield in either year, whereas SO₂ had no effect the first year and reduced yield by 6% the second The combined pollutant exposures reduced yield 9 to 25%, depending on the specific concentrations of pollutants Premature leaf senescence was observed both years in the plots exposed to both pollutants The authors concluded that soybean exposed to mixtures of SO₂ and NO₂, at concentrations that do not exceed the NAAQS, may display reduced growth and marketable yield Although the frequency of pollutant exposure (10 events/60 days) was not unusually high, the average concentrations and their frequency of occurrence, however, was much higher than typically measured in the ambient air at most rural sites The reduced yield may have been related to the measured decrease in chlorophyll in the concurrent plots (13 to 44%) versus the control plots This reduction in chlorophyll content can be indicative of a premature senescence of the plants, leading to incomplete yield expression

The sensitivity of eastern white pine (*Pinus strobus* L) to SO₂, O₃, and NO₂ at either 0.05 or 0.1 ppm for 4 h/day, for 35 consecutive days was clone specific (Yang et al , 1982) Pollutant combinations that included O₃ were more injurious than SO₂ + NO₂, although some clones were insensitive (as measured by reduction in needle dry weight) to all combinations. The sensitivity of the clones (as measured by reduction in needle length) was dependent on the gas combination and the concentration (only one clone was sensitive to 0.05 ppm). A comparison of needle dry weight and length response to the pollutants indicated that needle dry weight was a more sensitive indicator of pollutant stress in one of the clones

9.6.5 Factors Affecting Response

Although the modification of plant response to air pollutants by various biological, chemical, and physical factors has been quite widely examined for single-gas exposures, the same modifying factors have not been extensively examined for gas mixtures Many of the

studies that address modification of gas-mixture response by external factors have not included single-gas treatments, making it difficult to conclude whether the NO₂ is more harmful in combination than alone

9.6.5.1 Physical Factors

Light and temperature are the most common physical factors examined for their role in modification of plant response to gas mixtures. In the fumigation of *Betula pendula* continuously for up to 12 weeks with 0.04 or 0.05 ppm each of NO₂ and SO₂ in low and medium light intensities, leaf area from trees exposed to the gas mixture at the higher light intensity was similar to that from SO₂ alone (Freer-Smith, 1984). At the lower light intensity, leaf area response to the gas mixture was lower than that observed in the SO₂ treatment.

The response of grass species to SO₂/NO₂ mixtures as modified by light demonstrates that, as in birch, conditions that are optimal for growth tend to reduce the effect of the gas mixture on plant growth. A 46-day exposure of *Poa pratensis* to 0.40 ppm SO₂ and NO₂ under light and temperature regimes that promoted either fast or slow growth indicated that plant growth was reduced by the pollutant mixture more under slow-growth conditions than under fast-growth conditions (Whitmore, 1985). A 4-week continuous exposure of winter wheat (*Triticum aestivum*) to 80 to 100 ppb SO₂ and NO₂ at different light intensities suggested that the mixture caused an increase in the shoot-root ratio as compared to the control, and that lower light intensity further increased the shoot-root ratio (Gould and Mansfield, 1988).

Although these studies as individuals are poorly replicated, they demonstrate a clear trend when considered as a group: lower light intensity enhances the reduction of growth by SO₂/NO₂ mixtures. The mechanism for this modification may relate to the role of light in detoxification of either gas, or reduction in vigour (and consequent energy for repair) of the plants.

9.7 DISCUSSION AND SUMMARY

9.7.1 Introduction

In this chapter, the biochemistry and physiology of individual plants and agricultural crops have been discussed in relation to the types of injury induced by exposures to NO_x and in relation to protection of the plant in part, either by exclusion or detoxification of NO_x .

The discussion in this section is organized to follow movement of gases from the atmosphere into the sites of action within the leaf. Plant response at the action sites determines the amount and type of injury induced by the exposure. Metabolic incorporation of nitrogen from the atmosphere increases the amount of nitrogen present in the plant prior to exposure. The amount of gaseous nitrogen entering the plant is determined by the concentration and duration of the exposure. The capability of plants to handle the added nitrogen determines whether the exposure results in an increase or decrease in growth or only foliar injury. Climatic and edaphic factors also influence plant response. A model can be constructed that summarizes and explains the material presented in the chapter. A portion of that model is shown in Figure 9-19. Seven major processes will be discussed in sequence, leading from entry of atmospheric gases into the plant to plant injury.

- Process 1. Gaseous diffusion through the boundary layer, stomate, and substomal cavity
- Process 2. Reactions of the gases at the cell's surface upon passing into a water phase within the wall region of the cell
- Process 3. Movement of reaction product(s) into the cell
- Process 4. Enzymatic or chemical transformations within the cell
- Process 5. Disturbance of normal metabolism within the cells
- Process 6. Transformation of biochemical and physiological disruption into loss of plant productivity
- Process 7. Transformation of nitrogen in the chloroplast

Processes 1 and 2 are, for the most part, dependent upon physical and chemical interactions and reactions between gases and surfaces. The concentration and species of gases within the atmosphere are critical for these events. Processes 3 and 4 are normal physiological processes and can be investigated by standard biochemical methods. Much that is described here is derived from a fundamental understanding of the biochemistry and physiology of normal events within the plant and from basic research. Processes 5 and 6 are

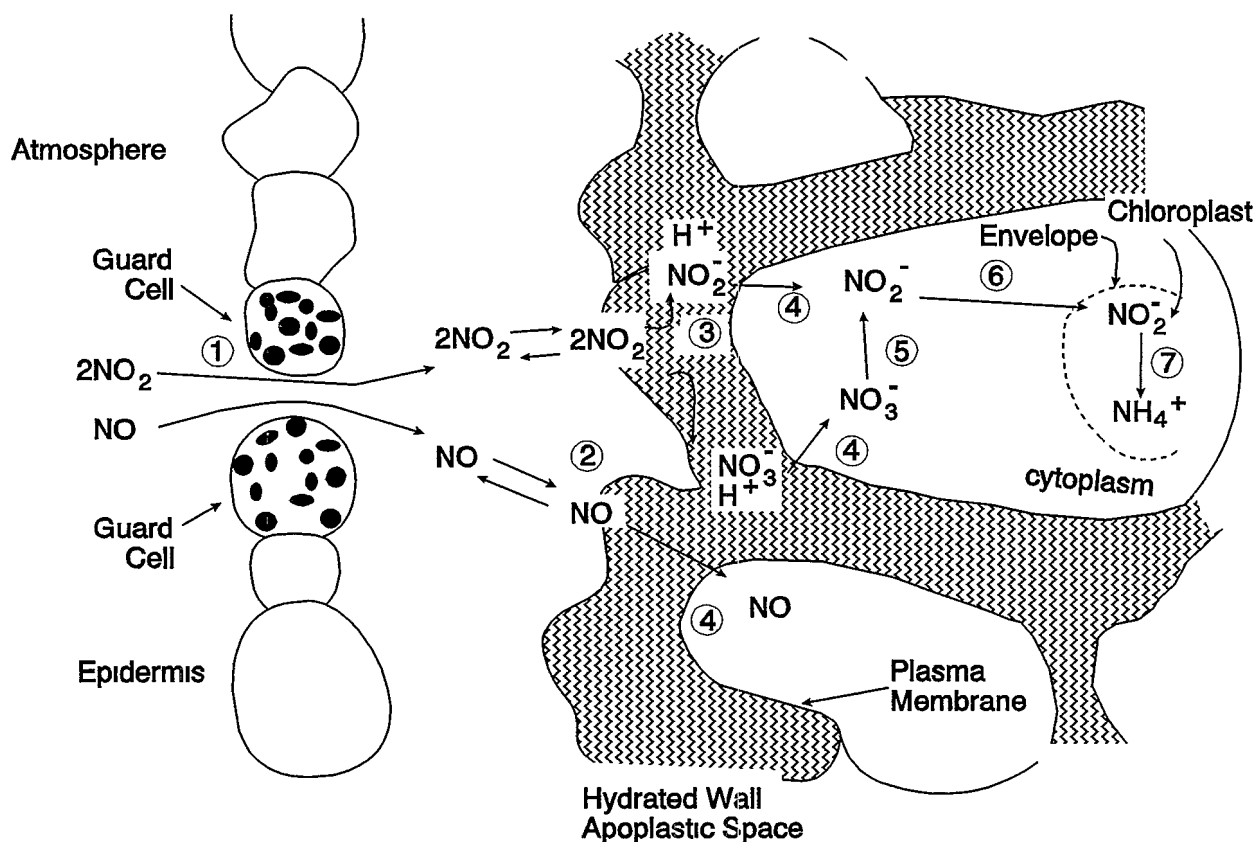


Figure 9-19. A schematic of the movement of gaseous oxides of nitrogen into the mesophyll cells of plant leaves. The diagram has been copied from an electron micrograph and gives approximately the correct relationships. The actual dimensions are very dependent upon the species and growing conditions of the plant. The numbers represent the processes listed in the text.

pathological processes that disrupt normal cell homeostasis, or metabolic balance

Homeostasis is largely governed by the genetic makeup of the plant and the environment in which the plant is located. Process 6 is the culmination of preceding events, which tend to lower plant productivity generally by interfering with orderly energy or carbon transformations or by lowering the efficiency of those transformations.

Several new findings emerge from the recent data compared with the data summarized in the last criteria document (U.S. Environmental Protection Agency, 1982). One is that NO and NO_2 interact differently within the plant. Thus, the effects of NO_x must be categorized according to NO_x species. Nitrogen dioxide is water soluble and can be incorporated into

normal plant nitrogen metabolism, up to a certain concentration. Nitric oxide is a water insoluble compound and induces free-radical reactions. Although the exact sequence of reactions is still unknown, it is clear that NO behaves differently than NO₂. The third category contains the remainder of NO_x species, which are not well defined and whose reactions are poorly understood. For certain gases, some processes function similarly, whereas for others, these processes function quite differently. Some of these differences will become better defined as the two major components of NO_x (NO and NO₂) are discussed.

Another new finding is that the cell can incorporate NO₂ into normal metabolism, after NO₂ is hydrated to HNO₃ and HNO₂ that exist in ionic form in the aqueous milieu of the cell. Despite the fact that NO₂⁻ and NO₃⁻ are normal anions in the plant, too much nitrogen can be toxic. The conversion of the biochemical species can overwhelm the stepped metabolic process so that the concentration can rise to detrimental levels.

The rest of this discussion will be organized into five subsections: (1) atmospheric concentrations and composition of NO_x, (2) entry and exclusion of gases, (3) initial cellular sites of biological interactions and pools of nitrogen compounds, (4) regulatory maintenance of reduced nitrogen compounds and possible detoxification, and (5) toxic reactions within the tissues.

9.7.2 Atmospheric Concentrations and Composition

As summarized in Chapter 3, there are many different species of NO_x with different oxidation states (Table 9-12). Ambient air concentrations, trends, and exposure patterns are discussed in Chapter 7. Although the concentrations and reactions of many of them have been investigated, little is known about possible reactions with biological organisms for many of these compounds. For plants, the two major oxidized species (NO and NO₂) with their hydrated acidic species (HONO₂ and HONO) have been reasonably well investigated. Research on the effects of other species of NO_x on plants, including the higher homologues such as N₂O₄, is rare. Yet it is necessary to be aware of these other species and possible reactions with other oxidizing agents in order to understand the reactions that might occur within the plant under single or multiple exposures. For example, hydrogen peroxide is present not only within the atmosphere, but also within the cell wall (but outside the membrane) and within the cell itself, even if at low levels. The possibility exists for many

TABLE 9-12. TYPES OF OXIDES OF NITROGEN IN THE GASEOUS PHASE OF AN ATMOSPHERE ^a

| Formula | Name | Oxidation State |
|-------------------------------|----------------------|-----------------|
| NO ₂ | Nitrogen dioxide | (+4) |
| NO | Nitric oxide | (+2) |
| HONO ₂ | Nitric acid | (+5) |
| N ₂ O ₅ | Dinitrogen pentoxide | (+5) |
| HONO | Nitrous acid | (+3) |
| N ₂ O ₄ | Dinitrogen tetroxide | (+4) |
| NO ₃ | Nitrate radical | (+5) |
| N ₂ O ₃ | Dinitrogen trioxide | (+3) |
| NO ⁺ | Nitrosonium ion | (+3) |

^aSpecies are arranged from the highest to lowest concentrations in general urban atmospheres (see Chapter 3)

further reactions of NO_x species with this compound in the atmosphere and in the cell. Also, compounds such as O₃ will give rise to other oxidative compounds, such as O₂⁻ and HO•, when dissolved in water. These multiple products and reactions set the stage for an even more complex series of reactions under pollutant exposures involving several types of pollutants (e.g., SO₂ and O₃ with NO_x).

A dynamic equilibrium will be established between O₃, NO₂, and NO in the presence of sunlight (see Chapters 3 through 5). Further reactions and transformations that affect NO_x will occur in the atmosphere. The amount of each compound in ambient air is not constant during the day, but each will be present in varying concentrations and must be individually metabolized by the plant. As the components enter the plant tissue through the stomates, they will dissolve within the extracellular water and, to a rough approximation, their solution concentrations will be governed by their solubility, as calculated by Henry's Law. For example, at 0.1 ppm of each gas, the concentrations of NO and NO₂ within the cell will be 2.0×10^{-10} M and 1.2×10^{-9} M, respectively. (The solubility of NO can be easily measured because it is unreactive with water [Schwartz and White, 1981] at 1.93×10^{-3} M/atm. The solubility of the other NO_x species are more difficult to measure because they react with water. On the basis of equilibrium arguments, Schwartz and White [1981] have given the following solubility coefficients: NO₂⁻, 1.2×10^{-2} M/atm, HNO₃, 2.5×10^5 M/atm, HNO₂, 1×10^5 M/atm). Although these concentrations are small by metabolic

standards, they could be quite phytotoxic at a protein level. On the other hand, although the gaseous acids (HNO_2 and HNO_3) within the atmosphere are low in concentration, the solubility coefficients of these acids are so high that the corresponding concentrations of each acid in the cell can become relatively large (e.g., the concentrations of HNO_2 and HNO_3 can be as high as 2 to 5 mM).

For the purposes of this summary, it is assumed that NO_2 and NO can form HNO_3 and HNO_2 , which are able to ionize to form nitrate and nitrite. A few of the possible reactions and their kinetic constants are given in Table 9-13 (from Troiano and Leone, 1977, Schwartz and White, 1981, Section 9.3). There are many more possible reactions but their rate constants are unknown because individual concentrations of all reactants are not known. It is also not clear which of these reactions can occur within a leaf; few measurements have been made under biological conditions.

TABLE 9-13. POSSIBLE REACTIONS BETWEEN NITROGEN DIOXIDE AND NITRIC OXIDE, AND WATER

| Reaction | K_{eq} |
|---|-----------------------|
| 1. $2\text{NO}_2(\text{g}) = 2\text{H}^+(\text{a}) + \text{NO}_2^-(\text{a}) + \text{NO}_3^-(\text{a})$ | 2.44×10^2 |
| 2. $\text{NO}(\text{g}) + \text{NO}_2(\text{g}) = 2\text{H}^+(\text{a}) + 2\text{NO}_2^-(\text{a})$ | 3.28×10^{-5} |
| 3. $3\text{NO}_2(\text{g}) = 2\text{H}^+(\text{a}) + 2\text{NO}_3^-(\text{a}) + \text{NO}(\text{g})$ | 1.81×10^{-9} |

The reactions are shown as those that operate in a mixed, aqueous (a)/gaseous (g) phase (Pfafflin and Ziegler, 1981). Equilibrium constants at 25 °C taken from Schwartz and White (1981). Units are in molar and atmospheres for the liquid and gaseous species respectively.

9.7.2.1 Foreign Compounds in Plants

Plants can deal with foreign chemicals by several methods. Gaseous compounds can be excluded from the tissues or cells either because stomatal closure prevents entry into the leaf or the impermeability of the membrane prevents entry from the cell spaces. When not excluded, the plant can either tolerate (to a certain level) or detoxify the compounds. Tolerance can occur by storage in a different tissue or organelle. Detoxification can occur through chemical modification followed by movement of the newly formed compound out of the cell, or through conversion into a compound that can enter the normal metabolic pathways. For NO_x , several of these methods could operate.

Exclusion A compound such as NO does not easily penetrate the cell because its solubility in water is low. Yet its free radical nature seems to be too reactive to exist for a long enough time to move through a membrane (however, see later sections)

Tolerance Nitrogen dioxide seems to be hydrated rapidly and its hydrated acid forms move easily through water. Once in the aqueous phase, its products can enter the usual metabolic pathways. A reductive form of NO_x , nitrite, however, can build up to higher than normal levels within the cell and so ultimately becomes toxic.

In order to understand the level at which these compounds become toxic, the entrance of nitrate and nitrite into the cells and their cellular metabolism must be understood, as must be the biochemical events that are initiated when concentrations of those compounds become too high for the cell to tolerate. The remainder of this section will be devoted to these processes.

9.7.3 Entry and Exclusion of Gases

In order to trace the ultimate fates of gaseous species and to determine the levels that can overwhelm the plant's mechanisms for utilizing or detoxifying a gas, it is necessary to understand two major physiological processes: the penetration of the gas into the leaf and the solubilization of the gas within the leaf.

The general movement of gases into a leaf is along a well defined path (Farquhar and Sharkey, 1982), which gives rise to a linear flux law of

$$J = g (C_o - C_i) \quad (9-19)$$

where the flux (J) into the internal space of a leaf (in units of moles per square meter per second) is linearly related to the gradient of concentrations from the outside (C_o) inwards (to C_i) (in units of moles per cubic meter) by a proportionality constant called the conductance (g). This conductance is a measure of what resistances exist to gas flow, g is inversely proportional to that resistance.

Yet two points must be noted. Not all gases follow the same path. Water evaporates on surfaces near the stomates so that the epidermal and only some mesophyll cells lose water.

to the transpirational stream. Carbon dioxide, on the other hand, moves to where CO_2 fixation occurs, generally in the mesophyll cells. In addition, Cowan and Farquhar (1977) have redefined the parameters of Equation 9-9 such that g is measured in moles per square meter per second and C_o/C_i are measured as partial pressures of the gas. Although this may be useful for water vapor, it does not follow the general definitions of flux and permeability (Troshin, 1966). Also we can speak of an internal concentration fraction of the external concentration ($f = C_i / C_o$). Equation 9-19 then becomes $J = g C_o (1-f)$.

9.7.3.1 Internal Concentration of the Gases

As described above for a given external concentration and a fixed conductance, the rate of movement of NO_x will be dependent on the internal concentration. Furthermore, the internal concentration is critical for reactions that will occur at the cell surfaces, reactions that depend upon the local concentration and the rate at which the gas is delivered to the site. Many of the calculations regarding the amount of NO_x that enters the leaf are based on an internal concentration of NO_x of zero, the simplest assumption upon which to base the calculations. Thus, the flux of nitrogen into the plant from NO_2 is given as the stomatal conductance (for water vapor but corrected for the diffusion coefficient of NO_2 relative to water) times the external concentration. In water, however, the real limitation for NO_2 entering the cell seems to be the rate of its solubilization in water (see later and Lee and Schwartz, 1981; Lee and Tang, 1988). Although the reactivity of NO_2 with cell components may reduce its concentration in water, one should not assume that the internal concentration of NO_2 is zero. If it is not zero, the use of a zero value for the internal concentration of NO_2 will give the maximum rate of flux through the stomates, but not the true rate.

Obviously, one method for determining the flux would be to directly measure the accumulation of nitrogen from NO_2 . Some measurements have been made, but nitrogen accumulation from the air cannot easily be distinguished from the nitrogen accumulation derived from soil fertilizers (e.g., nitrate). As an illustration of how experiments can eliminate this ambiguity, Okano et al. (1986, 1988) have used a stable isotope of nitrogen to investigate the interactions of these two sources of nitrogen. Furthermore, their data (from sunflowers) allow the calculation of the internal concentration of NO_2 . Their calculations show that the internal concentration of NO_2 is about 68 and 83% of the external

concentration at 0.3 and 2 ppm NO_2 (7 days, 24 h/day), respectively, under all soil nitrate conditions reported. The internal NO_2 (based on a percentage) is lower at the lower concentration of external NO_2 than that at the higher concentration, indicating a rate-limiting reaction at the cell surface at the higher concentration. It should be noted that, not surprisingly, 2 ppm NO_2 lowered conductances and leaves of exposed plants showed some visible injury (Okano et al., 1988).

The reactions that are critical for the cell surface are (1) diffusion and adsorption of NO_2 into the water phase, (2) conversion of NO_2 into nitrate and nitrite (see Equation 1 in Table 9-13), and (3) the diffusion to and reaction with their enzymes to convert them into needed biochemicals (NaR and NiR). The rates for diffusion and conversion are important because the ability of the reductases to convert the oxides to reduced ammonia is strictly limited. Unfortunately, no information regarding reductase activities was given in these experiments by Okano et al. (1986, 1988).

In a later paper, Okano et al. (1988) showed clearly that the amount of nitrogen accumulated from atmospheric NO_2 was directly proportional to stomatal conductance for several plant species, low conductance led to low accumulation. The highest conductances led to visible injury in radish and sunflower. Some NO_2 accumulation occurred when the conductance was zero, but the authors suggested that this could be due to entry of adsorbed NO_2 through the cuticle. Other data (Wellburn, 1990) indicate that this is not possible (but see Rowland-Bamford and Drew, 1988, for a counter-example). Also, NO_2 entering the soil might contribute to the apparent nitrogen absorption by the roots, thus yielding a false accumulation. However, the measurements of Okano et al. (1988) suggested that this particular pathway was very small. Two important points must be made here: (1) as in the case of all gaseous pollutants, if the stomates are closed, no gas can enter and no reactions are possible, and (2) depending upon the chemical species involved, penetration of pollutants through the nearly impermeable cuticle is always possible, but the rate will be small and will lead to contradictory evidence.

The solubilization of NO_2 in water is a critical factor in determining the rate at which NO_2 can enter the cell, but present data on that process are not very useful due to uncertainties in how additions to the water affect the solubilization. Lee and Tang (1988) found that the mixing of gaseous NO_2 into an aqueous solution depended on the average

speed of the molecules in the gas phase and an accommodation coefficient, which was the fraction of gas molecules colliding with the water surface that dissolved within the aqueous phase. That accommodation coefficient was dependent on the chemical additions to water and ranged from 10^{-7} for pure water to 6.3×10^{-4} for water containing quinone. The high value can be translated into an effective "conductance" of 0.0585 m/s at normal temperatures. Under these somewhat specialized conditions, the internal concentration of NO_2 ($[\text{NO}_2]_i$) can be then calculated when the flux through the stomates is balanced by the accommodation "flux". This balance occurs when the accommodation coefficient (R_a) times $[\text{NO}_2]_i$ times the average speed of the molecules (which depends on the gas temperature) equals the real gas conductance (g) times the difference between the external and internal gas concentration. If the internal concentration is defined as $f \times [\text{NO}_2]$ where $[\text{NO}_2]$ is the external concentration, then $f = g/(R_a + g)$. For a stomatal conductance of 0.4 cm/s, the internal concentration fraction of the external concentration (f) is only 7%.

This value of internal concentration is similar to values calculated from the data of Omasa et al. (1980a,b), showing internal concentrations that were 11 and 16% of external. On the other hand, Saxe (1986b) studied eight different species as to their ability to remove NO_2 from an atmosphere with their transpiration rate and calculated that the internal concentration fraction was very near zero. The uncertainty of how much NO_2 was removed from the atmosphere by the soil, pots and foliage (surface reactions only) made it difficult to be more precise, yet Saxe's data suggest that f was extremely low.

Rowland-Bamford and Drew (1988) also attempted to determine the internal level of NO_2 . Their experiments on barley at low light levels (20 to 25% of the level of full sunlight) indicated that the level of internal NO_2 was, at best, only about 5 to 10% that of the external level (at 0.3 ppm). That level was lowest in the morning and rose significantly in the afternoon. Interestingly, at the lowest light intensity, the net flux rate (per unit of light) was quite low, whereas at higher light levels, the flux rate became nearly a thousandfold higher. Incident light can stimulate total NO_2 incorporation and so reduce the internal level of NO_2 . As will be discussed later, this dependence of NO_2 incorporation on light is due to NiR activity, which is dependent upon photosynthetic electron transport. Light energy builds reducing power, which causes a more rapid conversion of the acidic forms of hydrated NO_2 into NH_4^+ .

The rate of entry of the NO_2 into the leaf is only one step in the process of nitrogen accumulation. The rate at which its hydrated products can be incorporated into the normal metabolism of the leaf also plays an important role in determining possible limitations to the use of the nitrogen of NO_2 in the cell. These interrelationships can determine how fast NO_2 can enter the plant tissue and increase the total nitrogen load upon the plant.

9.7.3.2 Interfacial Movement of the Gases into the Water Phase

The movement of NO into the leaf is an entirely different question due principally to its chemical structure. Although some authors believe that NO can be converted into soluble compounds, chemical investigations (Wellburn, 1990, Equation 2 of Table 9-13) suggest that NO is relatively insoluble and, by itself, nonreactive with water. Thus only a small amount of NO will enter the water phase unless it encounters a reactive aqueous species (usually a free radical, Wellburn, 1990). Because unbounded free radicals are relatively rare in biological systems, the path of diffusion will be long and the rate of reaction will be slow. Therefore, the internal concentration of NO should be similar to the external concentration, and the stomates will exert only a small effect on the rate of NO reactions.

On the other hand, it is clear from the equilibrium relations that NO and NO_2 together can be reactive (see Equations 2 and 3 in Table 9-13). At concentrations of 0.1 ppm, the amount of NO_2^- that can be formed from both NO and NO_2 would be $2.3 \times 10^{-8}/[\text{H}^+]$ M, where the $[\text{H}^+]$ is the local concentration. If the combined reaction between NO and NO_2 occurred within the acidic cell wall ($[\text{H}^+] \approx 3 \times 10^{-4}$ N), then the concentration of NO_2^- formed within the wall could be nearly 100 μM at equilibrium. It is doubtful that, under natural conditions, NO can occur without some NO_2 being present (Lefohn et al., 1991). Unfortunately, measurements in the field and in the laboratory have rarely measured each species independently, making it difficult to find which nitrogen species places the plants at risk.

The calculated internal concentrations are slightly different, if one assumes that NO_2 occurs alone and that the level of internal NO_2 (equal to $f \times [\text{NO}_2]_o$, where $f < 1$) is lower than the external value. The assumption must be made that these reactions are in equilibrium with the aqueous environment of the cell wall (at a pH of 4.3). The amounts of nitrate and nitrite in equilibrium with that internal NO_2 level (as ppm), is given as

$$[\text{NO}_2^-][\text{NO}_3^-] = 2.44 \times 10^2 [\text{NO}_2]^2 f^2 / [\text{H}^+]^2 \quad (9-20)$$

For $[\text{NO}_2] = 0.1$ ppm, this becomes

$$[\text{NO}_2^-][\text{NO}_3^-] = 2.44 \times 10^{-4} f^2 \quad (9-21)$$

As will be seen later, a reasonable guess for the cellular concentration of nitrate and nitrite, based upon enzyme activity, would be 4.5 mM and 100 μM , respectively. Thus, $[\text{NO}_2^-][\text{NO}_3^-] = 10^{-4} \times 5 \times 10^{-3} = 5 \times 10^{-7} \text{ M}^2$. Thus either f is equal to 2 to 3% and the level of internal NO_2 is very much reduced, as suggested earlier, or the level of both nitrite and nitrate will be much larger than the above reasonable guesses.

9.7.4 Initial Cellular Sites of Biological Interaction and Pools of Nitrogen Compound

9.7.4.1 Role of Oxides of Nitrogen in Metabolism

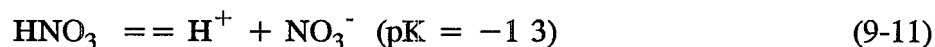
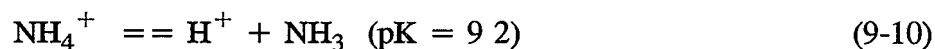
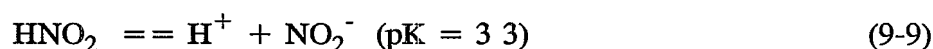
The hydration products as NO_2 is converted into NO_2^- and NO_3^- through interaction with water are normal anions within the plant, and as such, can be incorporated into normal metabolic pathways, up to certain maximum rates, dependent on nitrogen supply from the roots and on type of plant. Where both NO and NO_2 are present, NO seems also to be converted into nitrite and nitrate. Metabolic incorporation leads to detoxification of most of the species of NO_x , making the potentially toxic compounds not only harmless to the plant, but important to its normal growth. Naturally the incorporation alters the nitrogen level within the plant and so alters the "normal" state of the plant, where normal is defined as that state before its fumigation by NO_2 . In addition, under high levels of NO_2 flux into the plant, incorporation could overwhelm the nitrogen metabolism and cause the plant to deviate so far from its normally balanced state that the plant is unable to return to its previous homeostatic state after fumigation.

In order to discuss these concepts more completely, two areas must be well defined (1) what types of metabolic pathways are available to NO_x compounds and (2) what is meant by the normal state and how far can plants deviate from that state without permanent injury to the plant?

9.7.4.2 Metabolic Pathways

Plants require reduced nitrogen compounds to form proteins, nucleic acids, and many secondary products in order to survive and grow. Under most circumstances, nitrogen enters the plant through the roots in three modes: (1) absorption of NH_3 (and ammonium), (2) absorption of nitrate (and nitrite), and (3) nitrogen fixation by symbiotic organisms. Thus, any pollutant that can be converted chemically or biologically into nitrate, nitrite, or NH_3 can be used by the plant. Nitrogen oxides that fall upon the soil have the potential of being easily converted by microbial or chemical action and, therefore, can be readily adsorbed by the roots. Ground-deposited NO_x can enter the metabolic pathway readily through the soil/root interface, however, deposition can overload the soil/plant systems (see Chapter 10). Gaseous NO_x that enters through the leaf can likewise be converted through enzyme systems that can handle the derived compounds.

The chemical species that will be dealt with in the following sections are HNO_2 , NH_4^+ , and HNO_3 . The first two are a weak acid and weak base, respectively (see Equations 9-9 and 9-10 below), and, therefore, their actual chemical forms are dependent on pH. These forms govern the manner in which these chemicals can move throughout the plant. At normal biological pH, both species (acid and salt) of each compound can exist within an organelle or tissue. On the other hand, HNO_3 is such a strong acid that it exists predominantly as NO_3^- a nitrate ion under all biological conditions.



Although plants can use both ammonium and nitrate, nitrate seems to be less toxic, even in high concentrations, for the plant and, thus, is classed as a "relatively innocuous" compound (Mifflin, 1980). Nitrite and ammonium seem to be compounds whose concentrations are highly regulated and maintained at low levels within the plant. The

biological protocol to prevent high NH_3 levels is to convert, as rapidly as possible, ammonium to amino groups

Nitrate is converted first to nitrite via the enzyme NaR with the resulting nitrite being converted to NH_3 by another enzyme, NiR. The full conversion of nitrate into NH_3 requires eight electrons, or the equivalent of four molecules of NAD(P)H per molecule of NO_3^- . Because each NAD(P)H has a free energy content of about 28 kcal/mole, converting one mole of NO_3^- to NH_4^+ requires about 115 kcal of energy, or about the equivalent of 18% of a glucose molecule (see Schubert and Wolk, 1982). Another manner in which to express the energy requirement for nitrogen conversion is to express it as carbon lost per nitrogen gained. Thus, one nitrogen converted as above is equivalent to a minimum carbon loss of 1.1 (mole/mole). Yet Amthor (1989) states that if growth and maintenance respiration did not change during measurements, the value of carbon respired to nitrogen assimilated was as high as 2 to 3.5. For the most part, energy as reducing equivalents come from carbohydrate or organic acids oxidation (glycolysis, tricarboxylic acid cycle, or photosynthesis). Thus, NH_3 fertilizer is energetically "cheaper" for the plant to use but can be more toxic, if not well regulated. Nitrate requires more energy, thus, it would appear that there is less for the total plant productivity. Yet it is hard to demonstrate the lowering of plant productivity by concurrent nitrogen reduction (Robinson, 1988).

More recently, detailed flux and pool balance sheets in nitrogen metabolism have been prepared. For example, Magalhaes et al. (1990) have shown that NH_4^+ can move into corn roots at a rate of $1.75 \mu\text{mole N/g FW/h}$ and then move into the shoots at a rate of $1.25 \mu\text{mole N/g FW/h}$. The NH_4^+ pools were 3.85 and $0.45 \mu\text{mole/g FW}$ for the root and shoot, respectively (corresponding approximately to 4 and 0.5 mM for a soil NH_4^+ level of 50 mM). On the other hand, cow pea cultured cells will maintain an internal NH_4^+ level of only $0.1 \mu\text{mole/g FW}$ with an external NH_4^+ level of 88 mM (Mayer et al., 1990). Rates of NaR have been measured to be 4 to 6 and 2 to $3 \mu\text{mole/g FW/h}$ for barley and corn roots, respectively (Siddiqi et al., 1990). Wellburn (1984) measured NaR and NiR activities in tomato (resistant to NO_2 exposures) as 3.6 and $5.4 \mu\text{mole/g FW/h}$, respectively. Woodin et al. (1985) measured NaR as $0.4 \mu\text{mole/g FW/h}$, yet upon NO_3^- fertilization, that value rose fivefold in less than a day to $2 \mu\text{mole/g FW/h}$. Thus, it seems that the rate of nitrogen

reduction can range from 0.4 to 5 $\mu\text{mole/g FW/h}$, depending on the species and soil fertilizer concentration

Although the emphasis of this chapter is on how the movement of gaseous NO_x affects plant growth, it is important to understand total nitrogen metabolism at the root level. The two nitrogen sources can strongly interact with each other. First, NO_x and dry deposited nitrogen (acids of nitrogen compounds) can fall upon the ground and be incorporated into the soil, where they can be absorbed by the roots. With cultivated crops, this is trivial because much more nitrogen is added by the grower as fertilizer. In natural regions (e.g., rangelands and forests), soil nitrogen levels are much lower, generally too low to support vigorous growth. Second, soil nitrogen can directly alter the amount of nitrogen metabolism within the shoot and leaves.

The absorption of nitrogen from the soil is not strictly proportional to the amount of nitrogen present. The rate of absorption is hyperbolic with amount (Figure 9-7), also see Penning de Vries, 1982). More nitrogen in the soil is not mirrored directly by more nitrogen uptake, except at low levels (see also Chapter 10). Transport, in general, is by carriers or is active, and so its rate can be saturated (see Glass et al., 1990, Siddiqi et al., 1990). Space does not permit a complete discussion, however, detailed reports are given in Durzan and Steward (1983), Haynes (1986), and Goh and Haynes (1986). Many of the past experiments performed on the competition of soil nitrogen and NO_x -derived nitrogen have not made full use of these facts. The soil level is often much too high and the added NO_x causes only small changes in growth or total nitrogen. For example, few changes were obtained in bean growth experiments with soil nitrate levels of 10 to 20 mM (Srivastava and Ormrod, 1986).

9.7.4.3 Transport of Nitrogen Species

Weak acids move into cells or organelles by anion transporters or by diffusion of the uncharged acid form through the membrane. Weak bases move by the same general mechanisms, using cation transporters or diffusion of the uncharged base form (Figure 9-8). The carrier/transporters use energy to move the ions by either using the ionic gradients of the same-charge species (counter-transport) or the reverse-charge species (cotransport), or using the energy contained in a high-energy phosphate bond (e.g., via H^+ -specific ATPase, see

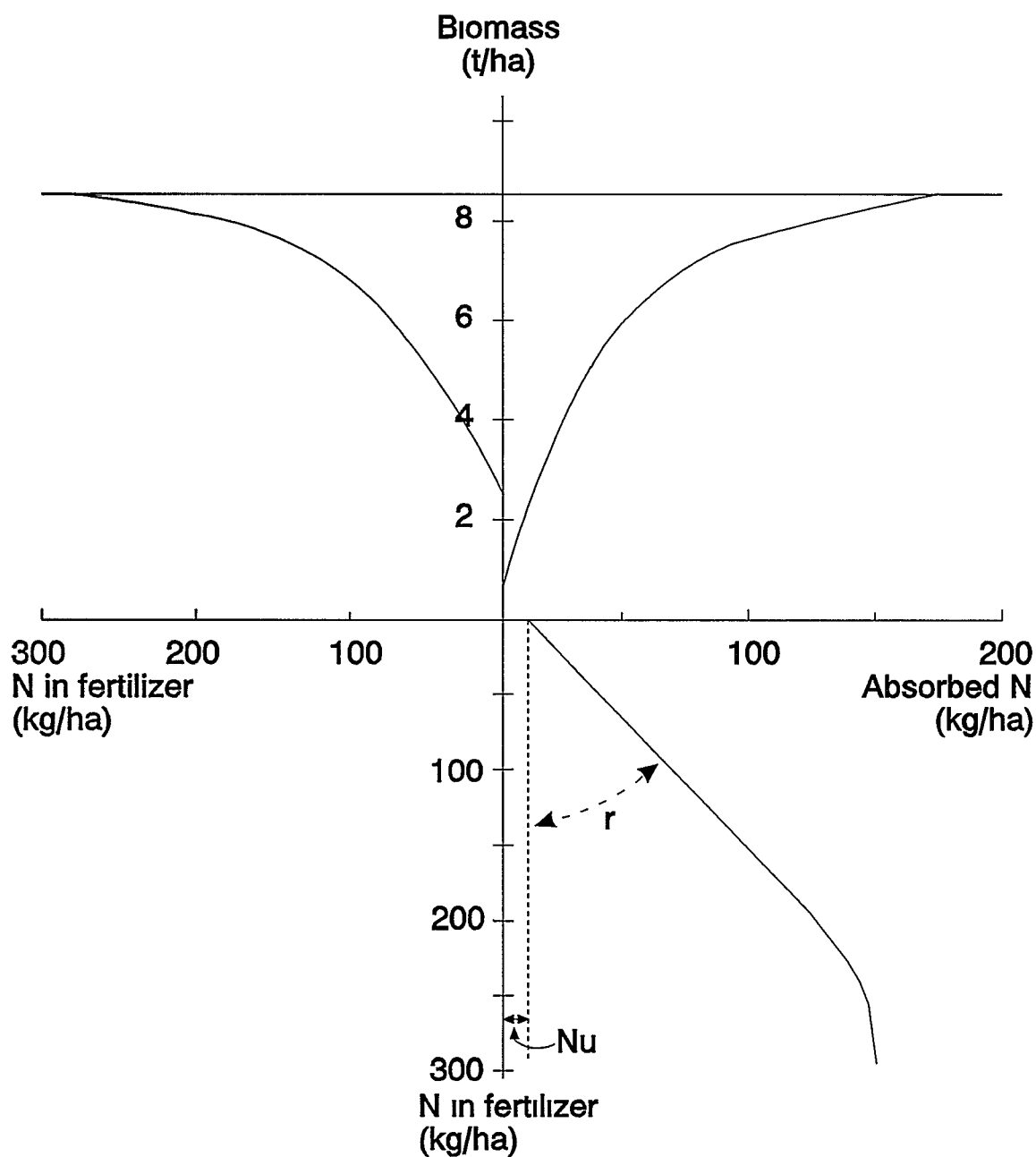


Figure 9-7. The relationship between applied nitrogen, soil nitrogen, and biomass production for a C_4 grass. N_u is the nitrogen absorbed from the unfertilized soil and r is the recovery fraction of the fertilizer nitrogen.

Source Penning de Vries (1982)

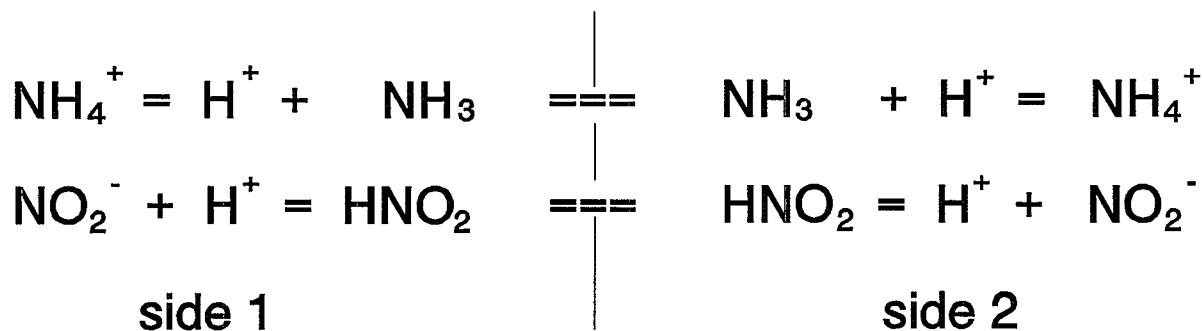


Figure 9-8. Schematic of the distribution of a weak base or acid across a biological membrane. The two sides are indicated across the membrane, represented as a vertical line. The concentration of the uncharged species is the same on both sides. In other words, the diffusion of uncharged species is fast enough to maintain a chemical potential equilibrium.

Source Walker and Crofts (1970)

Briskin et al , 1987) Uncharged species diffusion is generally less rapid than an energy-driven transport process Under certain pH gradients, however, or if the transporter is lacking, it can be very effective, for example, the uncoupling of chloroplast photophosphorylation by NH_3 (Walker and Crofts, 1970)

The formulation of how pH will affect the accumulation of the species has been previously given (Heath and Leech, 1978), but will be repeated here in abbreviated form For the weak acid HNO_2 , the equilibrium condition, $K_a = [\text{H}^+][\text{NO}_2^-] / [\text{HNO}_2]$, exists on both sides of the membrane (sides 1 and 2) The concentration of HNO_2 is the same on both sides because it is uncharged and can diffuse rapidly through the membrane Thus, equilibrium means

$$[\text{H}^+]_1 [\text{NO}_2^-]_1 = [\text{H}^+]_2 [\text{NO}_2^-]_2 \quad (9-12)$$

For the weak base NH_3 , the equilibrium condition of $K_b = [\text{H}^+] [\text{NH}_3] / [\text{NH}_4^+]$ likewise holds on both sides of the membrane Here the concentration of NH_3 is the same on both sides because it is uncharged and can diffuse rapidly (Crofts, 1967) The equilibrium condition then gives rise to

$$[\text{NH}_4^+]_1 [\text{NH}_4^+]_2 = [\text{H}^+]_1 [\text{H}^+]_2 \quad (9-13)$$

For example, the plasma membrane separates a wall region, which is estimated to be at a pH of about 4.3, from the cytoplasm, which is maintained at a pH of about 7. From the above formulas, we can estimate that if the total concentration of $\text{HNO}_2 + \text{NO}_2^-$ within the wall is 1 mM, the concentration of HNO_2 is 91 μM . In the cytoplasm, the concentration of HNO_2 is still only 91 μM (the same as in the wall region). However, in the cytoplasm, the concentration of nitrite will be about 46 mM (500 times larger) due to the unequal pH. The total concentration of nitrite will thus be high, even in the absence of a nitrite carrier.

The same argument can be used for a weak base, however, between the wall/cytoplasm membrane there is no accumulation, but rather an exclusion, of the base. Because the K_a for NH_3 is very basic, little NH_3 exists in the wall region (actually about 5 nM). With the same 1 mM total ammonium species outside in the wall, the concentration of NH_4^+ within the cytoplasm becomes only 5 μM , and so the total is slightly above 5 μM (compared with 1 mM outside). However, as the total ammonium inside rises, the ammonium outside would rise even more rapidly (for 0.5 mM inside, the outside would be nearly 0.5 M), leading to a path for rapid loss of ammonium from the cells.

There seems to exist in the roots a transporter for NH_3 that ensures a steady supply of NH_4^+ internally so that uncharged-species diffusion plays only a small role. This is not the case for chloroplasts, where the NH_3 can easily be accumulated in the grana space, which is quite acidic relative to the stroma space; there, the high concentration of NH_3 can function as an uncoupler (Walker and Crofts, 1970).

9.7.4.4 Role of Cellular Hydrogen Ion Concentration

The above arguments are critical for understanding how nitrogen species can move through biological organisms. Ammonium can accumulate in spaces of low pH and nitrite can accumulate in spaces of high pH (compared with neighboring spaces). This is not true for strong acids such as HNO_3 , which is completely dissociated to nitrate in biological organisms. Both nitrogen compounds are acids, and their formation can distort normal internal pH if they are present in high concentrations (see Raven, 1988). The actual change

in pH depends on their concentration and the buffering capacity of the organelle or tissue space

For example, NO_x could form about 0.05 N H^+ upon its conversion to nitrate and nitrite at an atmospheric concentration of 0.1 ppm (see above). In a wall of about $0.5 \mu\text{m}$ thickness, this would be $2.5 \times 10^{-9} \text{ equ/cm}^2$ wall. Morvan et al (1979) measured only about $7.5 \times 10^{10} \text{ equ/cm}^2$ wall H^+ -buffering sites. These unbuffered, accumulated acids would then lower the pH of the wall region. This acidification would tend to loosen the wall and allow the cell to expand in a manner not controlled by the cell (Taiz, 1984, Luethen et al, 1990). Once these acids are inside the cell, their metabolism and conversion to NH_4^+ seems to be a different story.

A largely unproven hypothesis is that the accumulation of NO_2 from the atmosphere with a concurrent conversion into HNO_2 and HNO_3 would change the acidity of the leaf. Raven (1988) has theoretically examined the accumulation of nitrogen from several sources, including ammonium and nitrate from the roots, and ammonium nitrate (dry deposition) and NO_x from the atmosphere into the leaves. He concluded that pH balance by the cell is difficult under many conditions, but that NO_x accumulation leads to an excess of H^+ of only 0.22 mol/mol nitrogen. He argues that uptake of phosphate and sulfur with conversion of NH_3 into amino acids interact to keep this number small. This is not true for NH_3 uptake, which is able to produce a large number of excess H^+ .

Okano and Totsuka (1986) have shown that at 2 ppm NO_2 , the amount of nitrogen accumulated from NO_2 in sunflowers is roughly $7.2 \times 10^{-10} \text{ mol nitrogen/g FW/s}$. Using Raven's number from above, there is about $2.4 \times 10^{-7} \text{ N H}^+$ produced per second due to the uptake of NO_2 . The concentration of organic acids within the vacuole is about 250 mM (Lin et al, 1977), with a buffer capacity of about 140 (change in salt concentration per change in pH [Bull, 1964]). Within the vacuole at pH 4, the rate of H^+ produced due to the above uptake of NO_2 would have to be maintained constantly for over 1.5 h in order to lower the pH by only 0.3 pH units. This is such a slight disturbance because the nitrogen source is so weak. More research needs to be done with nitrogen-deficient soils and plants to measure more precisely these pH effects. It remains true, however, that any shift in pH in the cytoplasm could alter the rate of formation of several metabolites because many enzymatic reactions are highly sensitive to pH.

9.7.4.5 Reductases

Once formed, nitrate will feed into the general nitrate pool in the leaf, which is derived from the root by transport via the xylem water stream. This xylem water stream, in turn, is driven largely by transpiration through the stomata and, therefore, the stomatal apertures can partially control the movement of nitrate. Nitrate from the xylem is contained within the wall and must move into the cytoplasm to be converted to NO_2^- by NaR. This enzyme can be rapidly induced to high activity upon exposure to nitrate (Woodin et al., 1985). Typical enzymatic parameters of this reductase are listed in Table 9-3. The reduction of nitrate to nitrite within the cytoplasm is driven by NADH from respiration (and glycolysis). Thus, rapid nitrate reduction would be expected to induce higher respiration rates, which are measured under some circumstances (Aslam et al., 1987, Bloom et al., 1989).

Both atmosphere-derived nitrite and nitrite from the roots add to the cytoplasmic pool, from which nitrite moves into the chloroplast by a presumed carrier molecule. Nitrite would not be expected to move passively into the chloroplast because the internal pH of the chloroplast stroma is higher than that of the cytoplasm (at about pH 8 to 8.5 when the leaf is illuminated, see arguments above). Normally, nitrite is reduced by a six-electron process via photosynthesis. Although the evidence is somewhat contradictory (see Robinson, 1988, Kaiser and Foerster, 1989), the demand for these electrons does not seem to inhibit or slow CO_2 fixation except at high levels of light or low CO_2 levels, where the CO_2 fixation process is nearly saturated (Pace et al., 1990). Typical enzymatic parameters of this reductase are also listed in Table 9-3. In darkness, nitrite cannot be reduced and so its concentration can rise to high levels if the rate of nitrate reduction is maintained. Taylor (1973) suggested that this was the reason for the production of large amounts of visible injury by NO_x in low light or darkness.

Nitrite seems to be regulated to remain at a low level within cells. At high levels, nitrite is toxic and could alter the photosynthetic process by altering the pH of the stroma of the chloroplast and so inhibiting normal CO_2 fixation (Brunswick and Cresswell, 1988a,b). High concentrations of NH_3 are also toxic. Ammonia acts as an uncoupler of photophosphorylation. Thus, a critical limit in concentration must exist for both molecules for normal cells. Although Table 9-3 can give an estimate of what that limit may be by using the K_m of each enzyme system, more experimentation on actual concentrations is

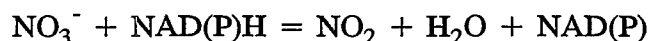
**TABLE 9-3. ENZYME PARAMETERS FOR CRITICAL ENZYMATIC STEPS
IN PLANT USE OF NITROGEN COMPOUNDS**

K_m and V_{max} are the Michaelis-Menten parameters for each enzyme system, even though some enzyme systems listed here do not strictly behave according to these kinetics

- A. Nitrate Transporter in Root Membranes.** Kinetic parameters of the enzyme located on the plasma membrane of root cells to transport nitrate ions (NO_3^-) inward (Siddiqi et al , 1990)

$$\begin{array}{l} V_{max} \quad 0.3 \text{ to } 3 \text{ } \mu\text{mol/g FW/h} \\ K_m \quad 60 \text{ to } 100 \text{ } \mu\text{M} \end{array}$$

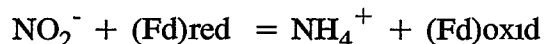
- B. Nitrate Reductase** Molybdenum protein associated with electron transport chain (Hageman and Hucklesby, 1971)



$$V_{max} \quad 3 \text{ to } 5 \text{ } \mu\text{mol/g FW/h}$$

| | $K_m (\mu\text{M})$ |
|-----------------|---------------------|
| NO_3^- | 4,500 |
| NADPH | 15 |
| NADH | 9 |

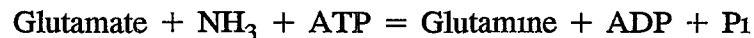
- C. Nitrite Reductase.** Enzyme associated with ferredoxin (Fd) within the photosynthetic electron transport chain (Losada and Paneque, 1971, Wellburn, 1990)



$$V_{max} \quad 3 \text{ to } 5 \text{ } \mu\text{mol/g FW/h}$$

| | $K_m (\mu\text{M})$ |
|-----------------|---------------------|
| Fd | 10 |
| NO_2^- | 100 |

- D. Glutamine Synthetase** Enzyme within plant tissue (Durzan and Steward, 1983)



$$V_{max} \quad 5.4 \text{ to } 9.9 \text{ } \mu\text{mol/g FW/h}$$

| | $K_m (\mu\text{M})$ |
|---------------|---------------------|
| Glutamate | 3,000-12,000 |
| NH_3 | 10-20 |
| ATP | 100-1,000 |

TABLE 9-3 (cont'd). ENZYME PARAMETERS FOR CRITICAL ENZYMATIC STEPS IN PLANT USE OF NITROGEN COMPOUNDS

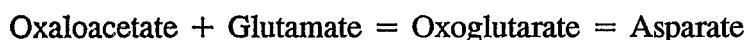
E. Glutamate Synthetase. Mitochondrial enzyme (Durzan and Steward, 1983)



V_{\max} 1.8 to 3.6 $\mu\text{mol/g FW/h}$

| | $K_m (\mu\text{M})$ |
|--------------|---------------------|
| Glutamine | 300-1,500 |
| Oxoglutarate | 40-600 |
| NAD(P)H | 7-30 |

F. Amino Transferase. Enzyme system occurring in several organelles of the cell



K_m (acids) = 1 to 40 mM

G. Asparagine Synthetase.



| | $K_m (\text{mM})$ |
|-------------------|-------------------|
| Aspartate | 0.7-2 |
| Glutamine | 0.1-1 |
| (NH_3) | 2.0-9 |

H. Chloroplast Amino Acid/Organic Acid Transporter. Enzyme located on chloroplast envelope to exchange amino acids and organic acids (Woo et al, 1987)

V_{\max} 80 to 100 $\mu\text{mole/g FW/h}$

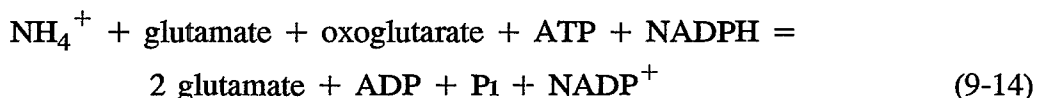
needed. For example, the decline in both growth and photosynthesis (nearly 50%) in radish occurs when the level of ammonium within the plant rises above a certain amount upon the use of NH_3 as a fertilizer (2,000 ppm, 0.2% of the dry weight, Goyal et al, 1982). Nitrate fertilizer does not cause such a rise in NH_3 (200 ppm), nor does it cause a decline in photosynthesis and growth, metabolites derived from nitrate seem to be well regulated under most circumstances.

If nitrate is added to the NH_3 fertilizer (at 10% of ammonium), the level of NH_3 within the plant remains low (200 to 600 ppm), again, nitrate metabolites aid in the regulation of NH_3 levels (Goyal et al , 1982) Under these conditions, the internal concentration of nitrate remains low—at about 500 ppm—for NH_3 fertilizer However, the internal concentration rises to 14,500 ppm with nitrate fertilizer alone These numbers reflect the level of nitrate and ammonium within the radish plants best defined as "normal" The internal nitrate level can rise without problems if the ammonium concentration is held low, whereas a rise of the ammonium level induces toxic effects, such as a decline in photosynthesis These interactions may help to link the apparent toxic effects caused by NO_x exposure to excess accumulation of partially reduced forms of NO_x (see later sections)

9.7.4.6 Amine Metabolism

The metabolic pathway of nitrogen in the chloroplast is summarized in Figure 9-9 Three major sections of the metabolism are apparent (1) reduction of the oxidized forms of NO_x to ammonium (previously discussed), (2) conversion of free ammonium into an amino group of an amino acid, and (3) movement of that amino acid into proteins or the nitrogen groups of other metabolites (such as polyamines)

The photosynthetic process generates NH_3 that is, as has been noted, closely regulated by the cell (Rhodes et al , 1976) The conversion of ammonium into an amino group keeps the concentration of NH_3 low and is carried out by the glutamate cycle Coupling the equations shown under D and E in Table 9-3 yields



The reducing power comes from photosynthetically produced NADPH The amine nitrogen on glutamate of this system can be coupled to the conversion of pyruvate to alanine and glycoxylate to glycine (Chapman and Leech, 1979) These amino acids and organic acids can be transported into and out of the chloroplast by specific transporters located on the chloroplast envelope (Woo et al , 1987) The rate of transport seems to be fast enough to move the carbon and nitrogen metabolites into and out of the cytoplasm with little problem,

but is limited in its absolute speed. Once in the cytoplasm, the amino group can be used in many ways to form other secondary products and proteins and will not be further discussed (see Pate, 1983, Durzan and Steward, 1983)

For the most part, these amine interconversions (Table 9-3) can move the amine group rapidly between the metabolites. There is the possibility, however, of the formation of "bottlenecks" in that movement if the system becomes overloaded with nitrogen (Ito et al., 1984b). The concentrations of metabolites due to any overload should indicate at what point the concentration of external NO_x would become toxic to the plant. Under those conditions, the excess nitrogen supplied by NO_x cannot be incorporated into metabolism without biochemical disruptions.

9.7.5 Regulatory Maintenance of Reduced Nitrogen Compounds (Detoxification)

As summarized above, NO_x exposure can overload the nitrogen metabolism pathways, as seen in Figure 9-19, in which key features in the changes in normal plant growth occurring upon exposure to NO_x are noted. Unfortunately, most of the studies made on plants exposed to NO_x have not traced the inhibition or stimulation of these pathways, but rather have looked for visible injury or change in gross productivity (measured by several possible methods). A summary of such investigations was made in the previous NO_x criteria document (U.S. Environmental Protection Agency, 1982) and is reproduced in Figure 9-20. The curves in the figure represent envelopes of the studies where either (A) metabolic and growth effects or (B) visible injury patterns (threshold for foliar lesions) were noted for a given duration of NO_2 exposure (abscissa) at a given concentration (ordinate). The lowest curve on the plot indicates where major alterations in plant metabolism occur (largely undefined, but most studies used an inhibition of photosynthesis as the marker). The region of the figure below this curve is where NO_2 does not affect plant metabolism. A second region in the figure exists between this curve and the next higher curve, in which disturbances in metabolism and growth occur (the plant is not normal) but tissue death is not observed. Exposures at levels and duration in a third region above this curve ("threshold for foliar lesion") results in cell or tissue death (foliar lesions). At very short durations and very high exposure concentration, plant death occurs. Although not shown on this curve,

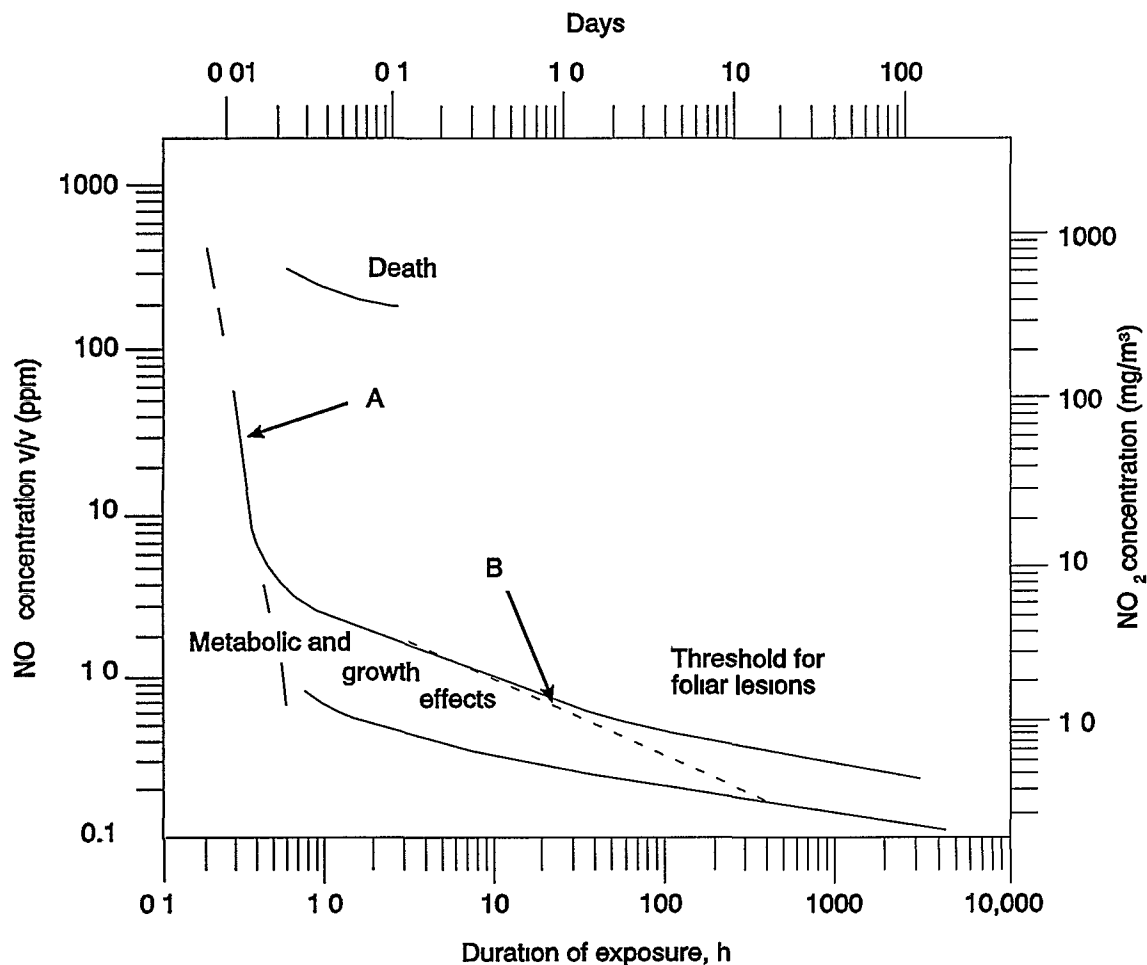


Figure 9-20. The relationship between the onset of either foliar lesions or metabolic and growth effects and the effective dose of nitrogen dioxide. The curves contain data points of plant exposures above which effects were observed.

Source U S Environmental Protection Agency (1982), Heck and Tingey (1979)

there is a poorly-defined region where growth stimulation can occur with NO_2 exposure for some plants under some conditions (see next section) It is important to note that the NO_2 concentration necessary to induce any changes is nonlinearly dependent on the duration of exposure

Under some stresses, such as radiation, the exposure (concentration multiplied by time) defines injury levels For a given exposure (high concentration for a short time or a low concentration for a long time), the injury is the same On Figure 9-20 that curve would be a

straight line of unity slope on the graph. Clearly, this exposure concept is not useful here. The boundaries between the regions are curved. No explanation for these curved boundaries is known. Understanding of the metabolic events surrounding NO_x conversion into metabolically active amines may help in discovering an explanation.

9.7.5.1 Nitrogen Oxides Incorporation with Nontoxic Effects

If the flow of nitrate from the roots is limiting initially (and hence the plant's growth rate was low), then the nitrate from NO_x will be beneficial. That nitrate nitrogen will stimulate both NH_4^+ and amino acid production (Koch et al., 1988). Higher levels of amino acids will stimulate protein formation and thus growth. However, if the level of nitrate from the roots is adequate at the beginning, the added NO_x will shift normal relationships away from the optimum. In either case, the normal state of the plant will have been disturbed (Van Keulen et al., 1989).

It is useful to return to Figure 9-20 to examine in more detail the relationships between concentration and duration of exposure and the formation of toxic effects such as altered metabolism and foliar injury. The curves can easily be broken into two sections in which the relation between duration and concentration is nearly linear. Only the curve that marks the beginning of threshold foliar injury will be examined. The first section (Section A) extends from about 0.13 to 0.78 h (8 to 47 min) and has a very steep slope. The second section (Section B) extends from about 3 h to 14 days and has a relatively shallow slope.

Following the discussion in the main body of the chapter, these two sections can be separately fitted to a power-law relationship such as

$$C^n \times T = D_o \quad (9-22)$$

where C is the external concentration in parts per million, n is a constant, T is the time in hours, and D_o is a constant. This formula is fitted to the curves, and the following values for each section for the constants are found

| <u>Section</u> | <u>Time Region</u> | <u>n (power)</u> | <u>D_o</u> |
|----------------|--------------------|-------------------------------|-------------------------|
| A | 15 to 50 min | 0.30 | 1.6 |
| B | 3 h to 14 days | 2.90 | 55.4 |

Section A represents very high levels of NO_2 , which occur infrequently in nature. Although it may be interesting to discuss that section, such an endeavor will not foster an understanding of the problems that occur under natural levels of NO_2 . At very high levels of NO_2 , the rate at which the NO_2 can enter the tissue water and be converted into nitrate/nitrite is very limited. In Section A, then, the concentration of internal NO_x would be expected to be very near that of the outside. In other words, the stomates are probably not limiting the reaction rates unless they are closed. However, for both sections of the curve, the flux rate and the amount of nitrogen that enters the plant could be determined with proper measurements.

For the longer time periods at concentrations that may occur within the environment (Section B), the flow of NO_x into the cells is high enough to lower the internal NO_x concentrations (relative to the external value). Under these conditions, the external levels would not match the observed reactions well, the internal levels may be very low and stomatal aperture would influence reactions greatly. The ability of the plant to utilize the nitrite and NH_3 formed would be the governing mechanism of detoxification within this time scale of days to weeks.

For time periods of an hour or greater, the flow through the stomate and pools of metabolites should have stabilized to a nearly steady-state level, and also the activity of inducible reductase enzymes should have begun to rise. The major question then becomes whether the plant can handle the total increased flow of nitrogen. Calculations of existing data show that the flow of nitrogen from NO_x is near that of the highest flow of nitrogen that can be used by the plant, especially if it has a source of nitrogen from the roots. One of the more critical steps is the flow rate of nitrogen into and out of the NH_3 pool. If the flow of nitrogen into that pool exceeds the flow out, many metabolites, including NH_3 , will increase and so force the cell to near its toxic point.

For much lower exposures and longer durations, however, the question of limitations becomes whether the plant can find some method to use the accumulated nitrogen (now converted to amino acids and proteins). That problem reduces to how fast the plant can grow. A typical value of nitrogen within a plant is about 1% of the dry weight (levels of 2 to 3% are at the high end of the scale). Therefore, injury at low levels of NO_x over many days of exposure would be predicted to be observed only when the plant simply cannot grow fast enough to use all of the excess accumulated nitrogen (Van Keulen et al., 1989).

The above arguments give a rationale for the shape of the curve in Figure 9-20. However, the exact shape will depend greatly upon the species, growing conditions, gas exchange, and enzymological parameters. The above hypothesis should aid in understanding critical sites within the plant for study and for setting standards. Different parts of the plant's growth cycle are important through these different exposure time scales. The plant should be able to tolerate different concentrations and flow rates at different developmental times.

9.7.6 Toxic Reactions in the Tissues

The most obvious sign that NO_x exposure is exceeding the ability of the plant to assimilate the extra nitrogen is the appearance of visible injury on the leaf surface. Unfortunately, each air pollutant does not induce a specific, characteristic, visible signature. For the most part, visible injury patterns consist of localized chlorotic spots, which in the presence of light and with time, develop into a necrotic section between the veins. Tip and margin injury is more extensive than injury across the leaf. These injured regions are where the maximum air flow occurs and the boundary layer resistance to flow is much smaller. Higher air exchange would increase the pollutant dose. The tissue next to the larger veins remains apparently untouched until much of the leaf is destroyed, perhaps due to the plant's ability to export the excess nitrogen through the veins to other portions. Other evidence of injury is early senescence or leaf drop, as if the aging processes within the leaf have been accelerated. Little is known about these processes. Under conditions where nitrogen is limiting to the plant, the initial coloration pattern may be just the opposite—an increase in greening. In monocotyledonous plants, the blade possesses different developmental ages along its length, but the transport vessels extend longitudinally. Thus, specific regions of

injury along the blade would not be uncommon if the export of nitrogen near an individual transport vessel is made critical. Also, cells that have just completed their development are most sensitive; again, these are the cells in which nitrogen metabolism is most strained. Excess nitrogen could push the cells into nitrogen toxicity through an excess of nitrite or NH_3 .

9.7.6.1 Concept of Exposure Index

Data presented previously (in Figure 9-20) clearly show that the concept of dose (concentration \times exposure time) is not valid, as the effects of NO_2 are decidedly nonlinear. Most of the exposure data presented in Table 9-4 have been discussed in Section 9.4. It would be useful to update the data in Figure 9-20 using all of the observations from Table 9-4. Yet, there is so much narrative in the table that to summarize the effects easily is difficult. The majority of the observed effects, however, fall into three categories: (1) no change or effect, (2) slight increase in mass of the plant or portions of the plant, and (3) decrease in mass of the plant or portions of the plant. Those plants for which no effects are noted must be tolerant of the excess nitrogen from NO_x or must be able to exclude NO_x . Those plants that increase in mass are often those that are suffering from a nitrogen deficiency and so, not surprisingly, they grow better under conditions closer to their nitrogen optimum. The more important category is that in which productivity is lowered. Productivity loss is generally due to a loss of carbon fixation if the other nutrients are present in correct abundances (Sinn and Pell, 1984). There is little evidence that NO_x exposure causes nutrient shifts for other than nitrogen, however, few investigations have addressed that issue. Nitrogen toxicity has been linked to calcium- and potassium-ion imbalances (Goh and Haynes, 1986, Touraine et al., 1988). Future research should be focused upon that area.

A simplistic, but useful, approach to determine what type of exposure index (a combination of duration and concentration) could be used is to transform the narrative in Table 9-4 (Section 9.4.1.2) into a gross quantitative measure of (1) no effect, (2) decrease, or (3) increase in some measure of productivity, without regard to the actual type of measurement. Similarly, the duration can be classed as number of days of exposure, without regard to the fine details of hours per day or number of days per week. Naturally, this approach loses information, but it has the benefit of allowing a tabulation of effects to

determine whether there are definite levels of exposure that will lead to toxic injury. It must be noted that even if the details are examined in the table, there are too many variables mentioned or determined, such as humidity, light intensity, soil water potential, and tissue or soil nitrogen, to allow a coherent detailed understanding of the conditions leading to toxicity. Furthermore, an examination of the data will indicate that some plants were exposed under higher than normal levels of CO_2 . Again, these parameters will alter the production of toxic symptoms, but the attempt to obtain a broader picture of exposure eliminates any focus on the details.

Diagrams of such tabulations are presented in Figure 9-21, along the lines of Figure 9-20, as $\log(\text{concentration})$ versus $\log(\text{duration})$. The data indicating a decline in some measures of productivity are shown in Figure 9-21A, as a "scattergram". There are several points of interest. The data seem to indicate that as the duration of exposure lengthens, the concentration required to cause some decrease in productivity declines. Hence, exposure for a day to 1 ppm is somewhat equivalent to 0.1 ppm for a month. The figure also shows a linear fit to the data with a slope of 1.7 ± 0.2 , again, indicating a nonlinear dependence of dose ($\text{time} \times \text{concentration}$). Furthermore, the line below the axis label shows the lowest measured concentration within the varied time intervals for which a decline in productivity was noted. For durations of a day or longer a decline is noted for concentrations of 0.02 to 0.1 ppm.

Data for which no observed effect was noted are given in Figure 9-21B and show less dependence on concentration. Again, the data can be fitted to a line with a slope of 2.7 ± 0.6 . Here, the maximum concentration for which there was no effect is shown below the x-axis. For durations of exposure above a day, concentrations as high as 2.1 ppm have been used without an effect being observed.

Data for which a stimulation of some measure of productivity exist are presented in Figure 9-21C. There are fewer examples from the literature, but fitting the data to a line gives a slope above unity of 2.1 ± 0.4 . The minimum values here indicate that exposures to 0.1 ppm NO_x for 1 day to 2 weeks can cause an increase, whereas for longer exposures (greater than 1 mo), increases can be induced by as low as 0.024 ppm.

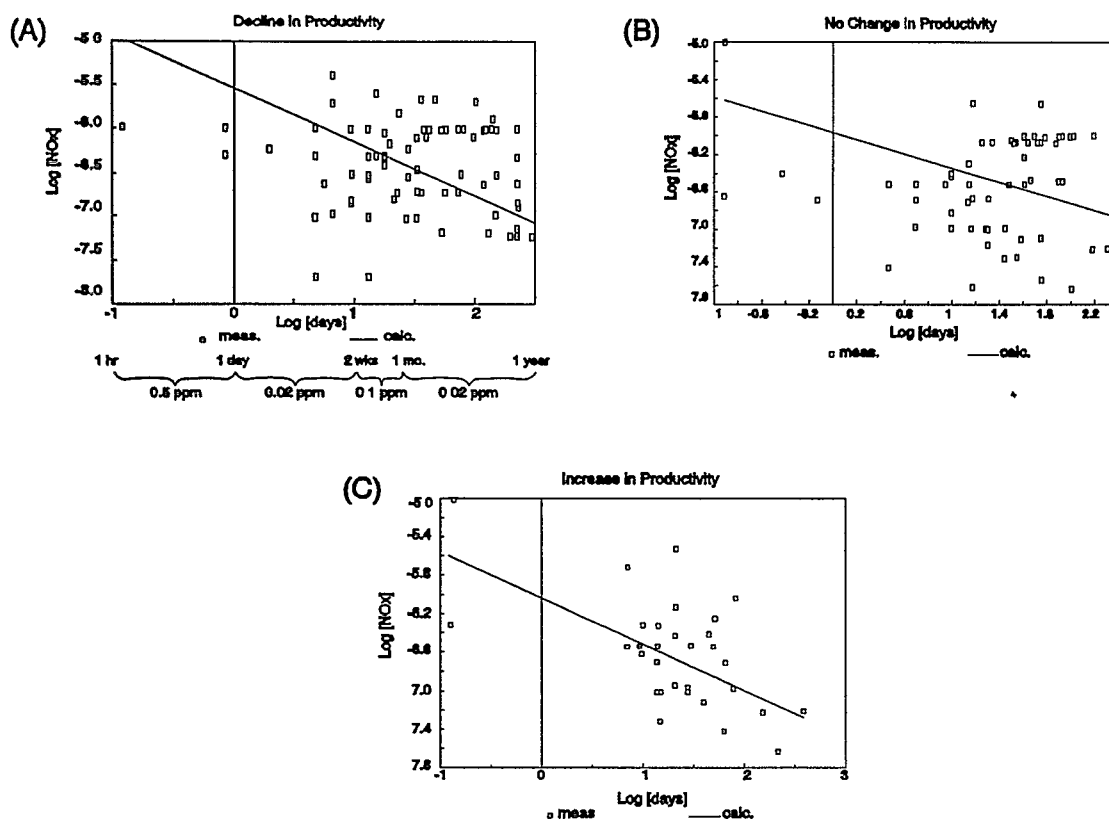


Figure 9-21. Diagram of studies of nitrogen oxides effects on plant productivity. This figure is similar to Figure 9-20; however, separate experiments are shown by individual symbols as a function of log (concentration of nitrogen dioxide) and log (duration of exposure). The data are from Table 9-4. All the data in each subfigure were fitted to a linear curve by least squares. Numbers below the curve are minimum values of concentrations reported in the indicated time interval. The three separate figures are for (A) decline in productivity (exponent = 2.7 ± 0.2 , $r^2 = 0.200$, $n = 87$), (B) no observed effect upon productivity (exponent = 1.7 ± 0.2 , $r^2 = 0.200$, $n = 87$), and (C) increase in productivity (exponent = 2.1 ± 0.4 , $r^2 = 0.200$, $n = 87$). The measure of productivity ranged from leaf and root growth and early senescence to flower/seed production.

Unfortunately, there are still no clear conclusions available from the data regarding exposure indices. There are, however, a few tentative concepts that can be stated from these data sets.

- (1) Although there are no absolute limits, for the most part, a lower concentration will cause some shift in productivity (higher or lower) with longer periods of exposure
- (2) The concept of a strict dose (concentration \times time) does not work. The effects are decidedly nonlinear, the slopes of the Figures 9-20 and 9-21 suggest that it may be a power of 2 to 3 (see Equation 9-22)
- (3) Under varied circumstances within the range of NO₂ exposure given in Figure 9-21, a given species will be either affected or not affected by NO₂. Not enough is known to determine precisely when a plant will be altered by the exposure
- (4) The majority of the data in Figure 9-21A and 9-21B suggest that concentrations below 0.1 ppm for days to a month have little effect on productivity. The data are less clear for very long exposures, it may be that very low concentrations over a year of exposure may be enough to cause ecological problems. The lack of data make any conclusion premature

9.7.6.2 Inhibited Processes

As previously stated, excess nitrate causes little injury to the plant, however, excess nitrite and NH₃ can alter photosynthesis. Therefore, one area of toxicity may be in the buildup of these compounds and their inhibition of photosynthetic processes. Nitrate is routinely used to poison the H⁺-ATPase on the tonoplast, but at a level of about 40 mM (O'Neill et al, 1983, K_i = 10 mM), whereas NH₃ in a concentration of tens of micromolar can uncouple photophosphorylation (Walker and Crofts, 1970). Although nitrate can build to high levels, this may be an indication of the limitation on nitrate metabolism.

Nitrite also appears to alter the ability for a pH gradient to develop properly within the chloroplast (via light-driven electron transport, Heath and Leech, 1978), and without the pH gradient, the ATP production and normal carbon fixation are severely limited, thus inhibiting photosynthesis. Under high light or saturating CO₂, nitrite can intercept electrons and so

inhibit NADPH used for CO₂ fixation Under most conditions some believe that nitrogen reduction does not directly compete for reducing equivalences and so would not slow CO₂ fixation One of the best hypotheses for nitrite-induced injury is the alteration of normal pH within varied organelles of the cell, however, this area has not received much study, although the hypothesis seems to be a reasonable one

Excess NH₃ is injurious to living cells, and plants attempt to regulate its level metabolically When regulation fails, tissue "burn" is common and may also be traced to pH imbalance. Here, again, the linkage between tissue NH₃ and NO_x exposure has not been established by research

Nitrogen dioxide appears not to cause injury directly because of its conversion into the salts of oxidized nitrogen There is little information regarding the actual speed of these reactions in water solutions and how biochemical ions and compounds could alter that speed Furthermore, these reactions most probably are occurring within the cell wall area and, therefore, surface effects that are largely unknown at the present time are expected to play a major role. Most of the chemical studies that indicate that NO₂ can react with double bonds of fatty acids are done in organic or nonpolar solutions The majority of these highly reactive compounds behave differently in polar solvents

Nitric oxide is an even more enigmatic species Its solubility indicates that it does not react rapidly with water to form nitrite There is apparently no good measurement of internal NO, but it is presumed to be nearly that of the external value Most of the chemical studies of NO that indicate that it reacts rapidly with free radicals have been conducted in nonpolar solvents and are, therefore, suspect To be sure, there are many biochemical reactions that occur via free radicals and so NO could easily react with free radicals and alter normal metabolism Yet under most conditions, these critical free radical reactions are heavily protected or tightly bound within enzymes It may be that only at high levels is there enough free NO present to initiate these damaging reactions It is hard to calculate what the level of NO would have to be in the atmosphere to build reactive conditions of NO within the cell water because there are so many unknowns

Like nitrite, NO can alter photosynthesis The inhibition of photosynthesis by NO seems to require time to build In one study (Bruggink et al , 1988), no effect of NO on photosynthesis was observed until after 2 days of exposure for 8 h/day at 1 ppm NO

Interestingly, the inhibition was only seen in the afternoon at first, when levels of sugars are high and the level of photosynthesis in the control was declining. Also of interest is the apparent increase in stomatal conductance induced initially by NO (1 ppm increases the conductance by about 15 to 30%). Because the internal NO level is estimated to be high, this small amount of increase would not greatly change the nitrite within the tissues. However, the decline in photosynthesis is not linked to lower conductance. A rise in conductance is sometimes observed with SO₂ exposure and has been linked to altered guard cell metabolism, possibly through a reaction with the membranes, which in turn would alter the normal relationship between the guard and epidermal cells (Mansfield and McCune, 1988). Yet an increase in transpiration is not commonly observed with NO_x fumigations. An increase in transpiration may be only transitory, and under most cases, NO_x alters the ionic relationships between the epidermis and guard cells to the extent that the stomate closes. Certainly, at high levels of NO_x exposure, transpiration declines.

It has been argued that only low concentrations of NO_x should be used in air quality research. Unfortunately, under this scenario, the mechanisms of toxicity cannot be well investigated and so exactly what may be happening at other levels of NO_x is difficult to understand. Past studies indicate that the sugar levels within leaf tissues are being altered (Ito et al., 1985a). In some cases, the levels decline, indicating that photosynthesis has been inhibited. In the cases where the sugar levels rise, translocation to other portions of the plant may have been inhibited to a greater degree than photosynthesis, leading to a buildup of the soluble sugar pools. Once translocation into the root is limited, the growth of the root is inhibited. This uneven allocation of nutrients, in turn, alters root/shoot ratios. It has been observed that a lowered level of sugar within the root leads to a demise of nitrogen-fixing nodules (Srivastava and Ormrod, 1986).

Chemical evidence favors lipid damage by NO_x. If direct lipid alteration occurred within the membranes, the membrane function would drastically decline. Ions and metabolites would leak out and metabolism would be altered detrimentally. Changes in the osmotic relation between the varied cell types may be a consequence of these reactions. Little direct evidence has been observed for NO_x, however, lipid synthesis has been observed to be inhibited by high levels of NO_x (Malhotra and Khan, 1984). This may be, however, due to lowered metabolism in general.

Histologically, cells exposed to large amounts of NO_x exhibit disruption of organelles that appears to be ionically or osmotically induced. If the pH of these organelles is greatly altered by NO_2^- or NH_3 , ion pumping will be changed and the balance of these ions will be greatly altered. Certainly there is no real evidence that disruption of some ionic concentrations occurs (Wellburn, 1985), but further understanding of the ionic balances is needed.

In general, most of the observations can be explained by a buildup of nitrite or NH_3 beyond normal levels. The weak acid and base could then alter the normal pH within each organelle, leading to an inhibition of the metabolism of that organelle. Under this concept, photosynthesis is inhibited by the loss of the pH gradient and the ability to produce ATP. In addition, having the wrong stomatal pH lowers the enzymic rate of carbon and thus inhibits CO_2 fixation. If translocation is inhibited to a larger degree by the altered pH, the levels of soluble sugars could decline. If translocation is inhibited more than photosynthesis, the levels of sugars rise because they cannot be exported. With a decline in available export carbohydrates, growth and fruit and seed productivity decline and root metabolism is lowered. If energy becomes a problem within the roots, ion transport is inhibited and so nutrients could also be ultimately limited (Touraine et al, 1988).

9.7.6.3 Pollutants in Combination

The data collected for pollutants in combination do not give a coherent picture. The experiments have been conducted under a very wide range of conditions, using relatively high concentrations for the most part. Mechanistically, it is difficult to understand what is happening. There are two major sources of interactions that are poorly understood: (1) the gaseous phase in which the pollutants can chemically alter one another to the extent that new combinations are made and (2) the metabolic pathways in which activity in one particular pathway can lower the carbon and energy abilities for another. The gas-phase chemistry must take into account the humidity both externally and within the leaf, especially at the wall surface. Little is known of the possible interactions there.

The metabolic pathways can interact in ways that depend on the nature of the pollutant and its interaction with the normal physiology. For example, O_3 is known to alter membrane permeability, which in turn lowers the net metabolism of the cell (Heath, 1980, 1988). The

loss of ions and energy alters the ability of the cell to respond to changes in pH due to nitrogen transformations and reduced nitrogen forms through NADH/NADPH processes. Metabolism of sulfur from SO_2 requires both energy and carbon skeletons. The processing of sulfur into amino acids is linked directly to the formation of those compounds from nitrogen. One expects interactions, but how they will develop is difficult to predict presently because the interrelationships are many and are currently difficult to model.

In any event, studies of co-occurrence of NO_2/SO_2 and NO_2/O_3 (Lefohn and Tingey, 1984, Lane and Bell, 1984a, Jacobson and McManus, 1985, Lefohn et al., 1987a) concluded that (1) the co-occurrence of two-pollutant mixtures lasted only a few hours per episode, (2) the time between episodes is generally large (weeks, sometimes months), and (3) the periods of co-occurrence represent a very small portion of the potential plant growing period.

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APPENDIX 9A

**TABLE 9A. SPECIES OF PLANTS USED IN EXPERIMENTAL
STUDIES ON THE EFFECTS OF OXIDES OF NITROGEN**

| Common Name ^a | Scientific Name |
|-------------------------------|--|
| Herbaceous Species: | |
| <u>Vegetable Crops</u> | |
| Onion | <i>Allium cepa</i> L |
| Leek | <i>Allium ampeloprasum</i> L |
| Tampala | <i>Amaranthus tricolor</i> L |
| Celeriac | <i>Apium graveolens</i> L var <i>rapaceum</i> (Mill) Gaud -Beaupr |
| Beet | <i>Beta vulgaris</i> L |
| Swiss chard | <i>Beta vulgaris</i> L |
| Kale | <i>Brassica oleraceae</i> L var <i>acephala</i> DC |
| Broccoli | <i>Brassica oleraceae</i> L var <i>botrytis</i> L |
| Cabbage | <i>Brassica oleraceae</i> L var <i>capitata</i> |
| Kohlrabi | <i>Brassica oleraceae</i> L var <i>gongylodes</i> |
| Turnip | <i>Brassica rapa</i> L |
| Green pepper | <i>Capsicum annuum</i> L var <i>annuum</i> |
| Chick pea | <i>Cicer arietinum</i> L |
| Endive | <i>Cichorium endivia</i> L |
| Taro | <i>Colocasia esculenta</i> (L) Schott var <i>antiquorum</i> (Schott) F J Hubb and Rehd |
| Cucumber | <i>Cucumis sativus</i> L |
| Squash | <i>Cucurbita maxima</i> Duch |
| Carrot | <i>Daucus carota</i> L var <i>sativus</i> Hoffm |
| Strawberry | <i>Fragaria chiloensis</i> (L) Duchesne |
| Woodland strawberry | <i>Fragaria vesca</i> L |
| Sweet potato | <i>Ipomea batatas</i> (L) Lam |
| Garden lettuce | <i>Lactuca sativa</i> L |
| Tomato | <i>Lycopersicon lycopersicum</i> (L) Karst ex Farw |
| Currant tomato | <i>Lycopersicon pimpinellifolium</i> (Jusl) Mill |
| Parsnip | <i>Pastinaca sativa</i> L |
| Parsley | <i>Petroselinum crispum</i> (Mill) Nyman ex A W Hill |

**TABLE 9A (cont'd). SPECIES OF PLANTS USED IN EXPERIMENTAL
STUDIES ON THE EFFECTS OF OXIDES OF NITROGEN**

| Common Name ^a | Scientific Name |
|------------------------------|--|
| Green bean | <i>Phaseolus vulgaris</i> L |
| Garden pea | <i>Pisum sativum</i> L |
| Radish | <i>Raphanus sativus</i> L |
| Rhubarb | <i>Rheum rhabarbarum</i> L |
| Black salsify | <i>Scorzonera hispanica</i> L |
| Eggplant | <i>Solanum melongena</i> L |
| Potato | <i>Solanum tuberosum</i> L |
| Spinach | <i>Spinacia oleracea</i> L |
| Broad bean | <i>Vicia faba</i> L |
| Watermelon | <i>Citrullus lanatus</i> (Thunb) Matsum and Nakai |
| <u>Field crops</u> | |
| Oats | <i>Avena sativa</i> L |
| Sugar beet | <i>Beta vulgaris</i> L |
| Rape | <i>Brassica napus</i> L |
| Buckwheat | <i>Fagopyrum esculentum</i> Moench |
| Soybean | <i>Glycine max</i> (L) Merrill |
| Upland cotton | <i>Gossypium hirsutum</i> L |
| Common sunflower | <i>Helianthus annuus</i> L |
| Barley | <i>Hordeum vulgare</i> L |
| Tobacco | <i>Nicotiana tabacum</i> L |
| Paddy rice | <i>Oryza sativa</i> L |
| Castor bean | <i>Ricinus communis</i> L |
| Common rye | <i>Secale cereale</i> L |
| Sesame | <i>Sesamum indicum</i> L |
| Sorghum | <i>Sorghum bicolor</i> (L) Moench |
| Common wheat | <i>Triticum aestivum</i> L |
| Durum wheat | <i>Triticum turgidum</i> L |
| Maize | <i>Zea mays</i> L |
| <u>Forage, Pasture, Turf</u> | |
| Bentgrass | <i>Agrostis capillaris</i> L |

TABLE 9A (cont'd). SPECIES OF PLANTS USED IN EXPERIMENTAL STUDIES ON THE EFFECTS OF OXIDES OF NITROGEN

| Common Name ^a | Scientific Name |
|--------------------------|---|
| Redtop | <i>Agrostis gigantea</i> Roth |
| Creeping bentgrass | <i>Agrostis stolonifera</i> L var <i>palustris</i> (Huds) Farw |
| Colonial bentgrass | <i>Agrostis tenuis</i> Sibth |
| Smooth brome | <i>Bromus inermis</i> Leyss |
| Orchard grass | <i>Dactylis glomerata</i> L |
| Red fescue | <i>Festuca rubra</i> L |
| Italian ryegrass | <i>Lolium multiflorum</i> Lam |
| Perennial ryegrass | <i>Lolium perenne</i> L |
| Alfalfa | <i>Medicago sativa</i> L |
| Mat-grass | <i>Nardus stricta</i> L |
| Common timothy | <i>Phleum pratense</i> L |
| Annual bluegrass | <i>Poa annua</i> L |
| Kentucky bluegrass | <i>Poa pratensis</i> L |
| Red clover | <i>Trifolium pratense</i> L |
| Crimson clover | <i>Trifolium incarnatum</i> L |
| Spring vetch | <i>Vicia sativa</i> L |
| Hedge vetch | <i>Vicia sepium</i> |
| <u>Floricultural</u> | |
| Flossflower | <i>Ageratum houstonianum</i> Mill |
| Common snapdragon | <i>Antirrhinum majus</i> L |
| Sprenger asparagus | <i>Asparagus densiflorus</i> (Knuth) Jessop Cv <i>Sprengeri</i> |
| Begonia | <i>Begonia</i> sp |
| Hollyhock begonia | <i>Begonia gracilis</i> HBK |
| Begonia | <i>Begonia multiflora</i> Benth |
| King begonia | <i>Begonia rex</i> Putz |
| China aster | <i>Callistephus chinensis</i> (L) Nees |
| Oxeye daisy | <i>Chrysanthemum leucanthemum</i> L |
| Florist's chrysanthemum | <i>Chrysanthemum X morifolium</i> Ramat |
| Painted leaf | <i>Coleus shirensis</i> Gurke |
| Lily-of-the-valley | <i>Convallaria majalis</i> L |
| Dahlia | <i>Dahlia pinnata</i> Cav |

**TABLE 9A (cont'd). SPECIES OF PLANTS USED IN EXPERIMENTAL
STUDIES ON THE EFFECTS OF OXIDES OF NITROGEN**

| Common Name ^a | Scientific Name |
|--------------------------|--|
| Dumb cane | <i>Dieffenbachia maculata</i> (Lodd) G Don |
| Golden pothos | <i>Epipremnum aureum</i> (Linden and Andre) Bunt |
| Spring heather | <i>Erica carnea</i> L |
| Summer hyacinth | <i>Galtonia candicans</i> (Bak) Decne |
| Garden gladiolus | <i>Gladiolus X hortulanus</i> L H Bailey |
| Plantain lily | <i>Hosta</i> sp |
| Patience plant | <i>Impatiens wallerana</i> Hook f |
| Japanese morning-glory | <i>Ipomoea nil</i> (L) Roth |
| Palm-Beach-bells | <i>Kalanchoe blossfeldiana</i> Poelln |
| Sweet pea | <i>Lathyrus odoratus</i> L |
| Daffodil | <i>Narcissus pseudonarcissus</i> L |
| Boston fern | <i>Nephrolepis exaltata</i> (L) Schott |
| Garden geranium | <i>Pelargonium X hortorum</i> L H Bailey |
| Geranium | <i>Pelargonium zonale</i> (L) L'Her ex Ait |
| Common garden petunia | <i>Petunia X hybrida</i> Hort Vilm -Andr |
| Fairy primrose | <i>Primula malacoides</i> Franch |
| German primrose | <i>Primula obconica</i> Hance |
| Common African violet | <i>Saintpaulia ionantha</i> H Wendl |
| Common salvia | <i>Salvia officinalis</i> L |
| Baby's-tears | <i>Soleirolia soleirolu</i> (Req) Dandy |
| French marigold | <i>Tagetes patula</i> L |
| Tulip | <i>Tulipa gesnerana</i> L |
| Periwinkle | <i>Vinca</i> sp |
| Common periwinkle | <i>Vinca minor</i> L |
| Common zinnia | <i>Zinnia elegans</i> Jacq |
| <u>Weeds and Native</u> | |
| Bear's garlic | <i>Allium ursinum</i> L |
| Redroot | <i>Amaranthus retroflexus</i> L |
| Adam-and-Eve | <i>Arum maculatum</i> L |
| Common mugwort | <i>Artemisia vulgaris</i> L |

**TABLE 9A (cont'd). SPECIES OF PLANTS USED IN EXPERIMENTAL
STUDIES ON THE EFFECTS OF OXIDES OF NITROGEN**

| Common Name ^a | Scientific Name |
|--------------------------|---|
| Desert marigold | <i>Baileya pleniradiata</i> Harv and Gray |
| Beggar-tick | <i>Bidens frondosa</i> L |
| White mustard | <i>Brassica hirta</i> Moench |
| Crunch-weed | <i>Brassica kaber</i> (DC) L C Wheeler var <i>pinnatifida</i> (Stokes) L C Wheeler |
| | <i>Chaenactis carphoclinia</i> Gray |
| Lamb's-quarters | <i>Chenopodium album</i> L |
| Goosefoot | <i>Chenopodium murale</i> L |
| Canada thistle | <i>Cirsium arvense</i> (L) Scop |
| Jimsonweed | <i>Datura stramonium</i> L |
| Crabgrass | <i>Digitaria</i> sp |
| Horseweed | <i>Erigeron canadensis</i> L |
| Alfilaria | <i>Erodium cicutarium</i> (L) L'Her |
| Japanese clover | <i>Lepedeza striata</i> (Thunb ex J Murr) Hook and Arn |
| Lupine | <i>Lupinus angustifolius</i> L |
| Mallow | <i>Malva parviflora</i> L |
| Wood melic | <i>Melica uniflora</i> Retz |
| Mint | <i>Mentha piperita</i> L |
| Millet grass | <i>Milium effusum</i> L |
| Sensitive plant | <i>Mimosa pudica</i> L |
| Tobacco | <i>Nicotiana glutinosa</i> |
| Wild tobacco | <i>Nicotiana rustica</i> L |
| European wood sorrel | <i>Oxalis acetosella</i> L |
| Scorpion weed | <i>Phacelia crenulata</i> Torr ex S Wats |
| | <i>Plantago insularis</i> Eastw |
| Common plantain | <i>Plantago major</i> L |
| Dock | <i>Rumex ambiguous</i> |
| Broad-leaved dock | <i>Rumex obtusifolius</i> L |
| Bladder campion | <i>Silene vulgaris</i> (Moench) Garcke |
| Common chickweed | <i>Stellaria media</i> (L) Cyrillo |
| Common dandelion | <i>Taraxicum officinale</i> Weber |

TABLE 9A (cont'd). SPECIES OF PLANTS USED IN EXPERIMENTAL STUDIES ON THE EFFECTS OF OXIDES OF NITROGEN

| Common Name ^a | Scientific Name |
|--------------------------|--|
| Wood dog violet | <i>Viola reichenbachiana</i> Jord ex Boreau |
| Devil's tongue | |
| Trees and Shrubs | |
| <u>Fruits</u> | |
| | <i>Citrus aurantium</i> L |
| | <i>Citrus natsudaoidai</i> |
| Grapefruit | <i>Citrus X paradisi</i> Macfady |
| Sweet orange | <i>Citrus sinensis</i> (L) Osbeck |
| Mandarin orange | <i>Citrus reticulata</i> Blanco var <i>unshu</i> |
| Japanese persimmon | <i>Diospyros kaki</i> L f |
| Common apple | <i>Malus pumila</i> Mill |
| Peach | <i>Prunus persica</i> (L) Batsch |
| Wild pear | <i>Pyrus communis</i> L |
| Currant | <i>Ribes</i> sp |
| Grape (American hybrids) | <i>Vitis vinifera</i> |
| Fox grape | <i>Vitis labrusca</i> L |
| <u>Ornamentals</u> | |
| Japanese aucuba | <i>Aucuba japonica</i> Thunb |
| Bougainvillea | <i>Bougainvillea spectabilis</i> Willd |
| Boxwood | <i>Buxus microphylla</i> Siebold and Zucc |
| Common camellia | <i>Camellia japonica</i> L |
| Karanda | <i>Carissa carandas</i> L |
| Croton | <i>Codiaeum variegatum</i> (L) Blume |
| Algerian ivy | <i>Hedera canariensis</i> Willd |
| English ivy | <i>Hedera helix</i> L |
| Benjamin tree | <i>Ficus benamina</i> L |
| Rubber plant | <i>Ficus elastica</i> Roxb ex Hornem |
| Hybrid fuchsia | <i>Fuchsia X hybrida</i> Hort ex Vilm |
| Common gardenia | <i>Gardenia jasminoides</i> Ellis |
| Chinese hibiscus | <i>Hibiscus rosa-sinensis</i> L |
| Hortensia | <i>Hydrangea macrophylla</i> (Thunb) Ser subsp <i>macrophylla</i> |

**TABLE 9A (cont'd). SPECIES OF PLANTS USED IN EXPERIMENTAL
STUDIES ON THE EFFECTS OF OXIDES OF NITROGEN**

| Common Name ^a | Scientific Name |
|--------------------------|---|
| Flame-of-the-woods | <i>Ixora coccinea</i> L |
| Glossy privet | <i>Ligustrum lucidum</i> Ait |
| Paperbark tree | <i>Melaleuca quinquenervia</i> (Cav) S T Blake |
| Common oleander | <i>Nerium oleander</i> L |
| Fragrant olive | <i>Osmanthus fragrans</i> (Thunb) Lour |
| Japanese pittosporum | <i>Pittosporum tobira</i> (Thunb) Ait |
| Firethorn | <i>Pyracantha coccinea</i> M J Roem |
| Azalea | <i>Rhododendron canescens</i> |
| Catawba rhododendron | <i>Rhododendron catawbiense</i> Michx |
| Cultivated rose | <i>Rosa</i> sp |
| <u>Natural</u> | |
| Hedge maple | <i>Acer campestre</i> L |
| Box elder | <i>Acer negundo</i> L |
| Japanese maple | <i>Acer palmatum</i> Thunb |
| Norway maple | <i>Acer platanoides</i> L |
| Red maple | <i>Acer rubrum</i> L |
| Black alder | <i>Alnus glutinosa</i> (L) Gaertn |
| White alder | <i>Alnus incana</i> (L) Moench |
| Burro weed | <i>Ambrosia dumosa</i> (Gray) Payne |
| Four-wing saltbush | <i>Atriplex canescens</i> (Pursh) Mutt |
| European white birch | <i>Betula pendula</i> Roth |
| Downy birch | <i>Betula pubescens</i> J F Ehrh |
| European hornbeam | <i>Carpinus betulus</i> L |
| Hornbeam | <i>Carpinus caucasica</i> Gros |
| Australian pine | <i>Casuarina cunninghamiana</i> Miq |
| Desert willow | <i>Chilopsis linearis</i> Cav |
| Camphor tree | <i>Cinnamomum camphora</i> (L) J Presl |
| | <i>Corylus betulus</i> |
| Russian olive | <i>Elaeagnus angustifolia</i> L |
| Brittle bush | <i>Encelia farinosa</i> Gray ex Torr |

**TABLE 9A (cont'd). SPECIES OF PLANTS USED IN EXPERIMENTAL
STUDIES ON THE EFFECTS OF OXIDES OF NITROGEN**

| Common Name ^a | Scientific Name |
|--------------------------|---|
| Murray red gum | <i>Eucalyptus camadulensis</i> Dehnh |
| Spindle tree | <i>Euonymus japonica</i> Thunb |
| European beech | <i>Fagus silvatica</i> L |
| White ash | <i>Fraxinus americana</i> L |
| European ash | <i>Fraxinus excelsior</i> L |
| Green ash | <i>Fraxinus pennsylvanica</i> Marsh |
| Maidenhair tree | <i>Gingko biloba</i> L |
| Honeylocust | <i>Gleditsia triacanthos</i> L |
| English walnut | <i>Juglans regia</i> L |
| Creosote bush | <i>Larrea divaricata</i> Cav |
| Sweetgum | <i>Liquidambar styraciflua</i> L |
| Yellow poplar | <i>Liriodendron tulipifera</i> L |
| Toringo crab apple | <i>Malus Sieboldi</i> (Regel) Rehd |
| American sycamore | <i>Platanus occidentalis</i> L |
| Carolina poplar | <i>Populus canadensis</i> Moench |
| Black poplar | <i>Populus nigra</i> L |
| Hybrid poplar | <i>Populus nigra</i> x <i>P. maximowiczii</i> |
| Hybrid poplar | <i>Populus maximowiczii</i> x <i>P. plantereensis</i> |
| Sargent cherry | <i>Prunus sargentii</i> Rehd |
| Japanese pear | <i>Pyrus pyrifolia</i> (Burm f) Nakai |
| White oak | <i>Quercus alba</i> L |
| Oak | <i>Quercus iberica</i> Stev |
| Oak | <i>Quercus imberber</i> Stev |
| Shira oak | <i>Quercus myrsinaefolia</i> Blume |
| English oak | <i>Quercus robur</i> L |
| Pin oak | <i>Quercus palustris</i> Muenchh |
| Willow oak | <i>Quercus phellos</i> L |
| Black locust | <i>Robinia pseudoacacia</i> L |
| European elderberry | <i>Sambucus nigra</i> L |
| White beam | <i>Sorbus aria</i> (L) Crantz |

**TABLE 9A (cont'd). SPECIES OF PLANTS USED IN EXPERIMENTAL
STUDIES ON THE EFFECTS OF OXIDES OF NITROGEN**

| Common Name ^a | Scientific Name |
|------------------------------|--|
| Common lilac | <i>Syringa vulgaris</i> L |
| Small-leaved European linden | <i>Tilia cordata</i> Mill |
| Large-leaved lime | <i>Tilia platyphyllos</i> Scop |
| American elm | <i>Ulmus americana</i> L |
| Scotch elm | <i>Ulmus glabra</i> Huds |
| Sweet viburnum | <i>Viburnum odoratissima</i> Ker-Gawl var <i>awabuki</i> (C Koch) Zab |
| Summer grape | <i>Vitis aestivalis</i> Michx |
| Japanese zelkova | <i>Zelkova serrata</i> (Thunb) Mak |
| <u>Conifers:</u> | |
| Silver fir | <i>Abies alba</i> Mill |
| White fir | <i>Abies concolor</i> (Gord) Lindl ex Hildebr |
| Nikko fir | <i>Abies homolepis</i> Siebold and Zucc |
| Caucasian fir | <i>Abies nordmanniana</i> (Steven) Spach |
| Deodar cedar | <i>Cedrus deodara</i> (D Don) G Don |
| Port-Orford-cedar | <i>Chamaecyparis lawsoniana</i> (A Murr) Parl |
| Hinoki cypress | <i>Chamaecyparis obtusa</i> (Siebold and Zucc) Endl |
| Japanese cedar | <i>Cryptomeria</i> spp |
| Shore juniper | <i>Juniperus conferta</i> Parl |
| European larch | <i>Larix decidua</i> Mill |
| Japanese larch | <i>Larix kaempferi</i> (Lamb) Carriere |
| Norway spruce | <i>Picea abies</i> (L) Karst |
| White spruce | <i>Picea glauca</i> (Moench) Voss |
| Blue spruce | <i>Picea pungens</i> Engelm |
| Red spruce | <i>Picea rubens</i> Sarg |
| Sitka spruce | <i>Picea sitchensis</i> (Bong) Carr |
| Japanese red pine | <i>Pinus densiflora</i> Sieb and Zucc |
| Shortleaf pine | <i>Pinus echinata</i> Mill |
| Pine | <i>Pinus elodarica</i> Medw |
| Mountain pine | <i>Pinus mugo</i> Turra |
| Austrian pine | <i>Pinus nigra</i> Arnold |

**TABLE 9A (cont'd). SPECIES OF PLANTS USED IN EXPERIMENTAL
STUDIES ON THE EFFECTS OF OXIDES OF NITROGEN**

| Common Name ^a | Scientific Name |
|--------------------------|---|
| Cluster pine | <i>Pinus pinaster</i> Ait |
| Pitch pine | <i>Pinus rigida</i> Mill |
| Eastern white pine | <i>Pinus strobus</i> L |
| Scots pine | <i>Pinus sylvestris</i> L |
| Loblolly pine | <i>Pinus taeda</i> L |
| Japanese black pine | <i>Pinus thunbergiana</i> Franco |
| Virginia pine | <i>Pinus virginiana</i> Mill |
| Douglas-fir | <i>Pseudotsuga menziesii</i> (Mirb) Franco |
| English yew | <i>Taxus baccata</i> L |
| Lichens | <i>Anaptychia neoleucomelanena</i> <i>Lecanora chrysoleuca</i> <i>Parmelia praesignis</i> <i>Usnea cavernosa</i> |

^aCommon and scientific names given below conform with those in Hortus Third and may differ from those used in the original publications

APPENDIX 9B

APPENDIX 9B. TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a

| Species or Crop | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|--|--------------------------|--|--|-----------------------|----------------------|
| Vegetable crops: | | | | | |
| Swiss chard (<i>Beta vulgaris</i> L) | | | | | |
| 0 3 | 10 h/day, 14 days | Leaf area (-5 or -3), mass of shoot (+9 or +2), mass of root (+19 or +15), daytime or nighttime exposure, 30-day-old plants (Yoneyama et al , 1980c) | | CE/GH | ChLum |
| Endive (<i>Chicorium endivia</i> L) | | | | | |
| 1 0 | 620 h over 1 mo | Yield (-37), owing to reduced growth of foliage ^e (Zahn, 1975) | | GH/FE | G-S |
| Garden lettuce (<i>Lactuca sativa</i> L) | | | | | |
| 0 5 ^f | 16 days | Mass of plant (-11*), 30 days old, CO ₂ at 1,200 ppm (Caporn, 1989) | | GH | ChLum |
| 0 85 ^g | 33 days | Mass of plant (0), seedlings, CO ₂ at 1,000 ppm (Mortensen, 1985a) | | CE | ? |
| 0 9 ^h | 32 days | Mass of plant (-14 to +7), depended on cultivar, 3-week-old plants, CO ₂ at 1,000 ppm (Mortensen, 1985b) | | CE | ChLum |
| 2 5 ^h | 16 days | Mass of plant (-18*), 30 days old, CO ₂ at 1,200 ppm (Caporn, 1989) | | GH | ChLum |
| | 22 days | Mass of plant (-32*), 36 days old, CO ₂ at 1,200 ppm (Caporn, 1989) | | | |
| Green pepper (<i>Capsicum annuum</i> L var <i>annuum</i>) | | | | | |
| 2 0 ⁱ | over 110 days | Mass of plant (-20), yield of fruit (-17), delayed fruiting (10 days), CO ₂ at 2,000 ppm ^e (Law and Mansfield, 1982) | | GH | ? |
| Tomato (<i>Lycopersicon lycopersicum</i> [L] Karst ex Farw) | | | | | |
| 0 1 | 19 days | Leaf area (+6), mass of leaves (+14), mass of shoot (-15), mass of roots (+21), 35-day-old plants (Capron and Mansfield, 1977) | | CE | L-G-S |
| 0 11 | 1 week | Leaf area (-2), mass of leaves (+4), mass of stem (-1), mass of roots (+5), 4-week-old plants (Marie and Ormrod, 1984) | | CE | B942 |
| | 2 weeks | Leaf area (-9), mass of leaves (-2), mass of stem (-3), mass of roots (+7), 5-week-old plants (Marie and Ormrod, 1984) | | CE | B942 |
| | 3 weeks | Leaf area (-16), mass of leaves (+11), mass of stem (+19), mass of roots (+11), 6-week-old plants (Marie and Ormrod, 1984) | | CE | B942 |
| | 4 weeks | Leaf area (-9), mass of leaves (+6), mass of stem (+10), mass of roots (+9), 7-week-old plants (Marie and Ormrod, 1984) | | | |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | | Effect | | |
|--------------------------|----------------------|--|-----------------------|----------------------|
| NO _x (ppm) | Exposure Duration | (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
| 0 16 | 10 days | Mass of fifth leaf (-33*), exposures started when third or fourth true leaf appeared (Taylor and Eaton, 1966) | CE | B942 |
| | 22 days | Mass (-20**) and area (-19**) of fifth leaf, exposures started when third or fourth true leaf appeared (Taylor and Eaton, 1966) | CE | Saltzman |
| 0 2 | 60 days | Leaf area (-31) ^e (Natori and Totsuka, 1980) | | |
| 0 2 ^j | 50 days | Mass of plant (+96*, +2, or -7), leaf area (+120*, +4, or -5), 0, 1 ×, or 2 × additions of fertilizer to soil, plants 9 to 10 weeks old (Anderson and Mansfield, 1979) | CE | Saltzman |
| 0 21 | 1 h | Leaf area (+3), height (+2), fresh mass of leaves (+1) or stems (-1), plants at 4- to 6-leaf stage (Goodyear and Ormrod, 1988) | CE | ChLum |
| | | | GH | ChLum |
| 0 25 | 80 h | Mass of leaves (-6 or +17**), mass of stem (0 or +26), nitrogen-nutrient level at 28 or 140 mg/L, 5-week-old plants (Troiano and Leone, 1977) | CSTR/GH | B952 |
| | 125 h | Number of fruit (-11), mass per fruit (-13), mass of plant (-41), increased senescence and abscission of foliage ^e (Spierings, 1971) | CE/GH | MastTM |
| 0 28 | 14 days | Fresh mass (-18*) or dry mass (-6) of fifth leaf, exposures started when third or fourth true leaf appeared (Taylor and Eaton, 1966) | GH, CE | Saltzman |
| 0 3 | 10 h/day, 14 days | Leaf area (-8 or -8), mass of leaf (-1 or -2), mass of stem (0 or -4), mass of roots (-13 or +8), daytime or nighttime exposure, 30-day-old plants (Yoneyama et al , 1980c) | CE | Saltzman |
| | 14 days | Mass of leaves (-19, -17, or -7), mass of stem (-23, -24, or -15), mass of roots (+6, -31, or -20), plants grown at 26, 105, or 260 ppm nitrogen nutrient, 5-week-old plants ^e (Matsumaru et al , 1979) | CE/GH | ChLum |
| | 41 days | No effect on growth ^e (Ishikawa, 1976) | CE/GH GH, CE | ChLum Saltzman |
| 0 35 ^j | 35 days | Mass of shoot (-27 to +89), leaf area (-28 to +48), depended upon cultivar (Anderson and Mansfield, 1979) | GH | ChLum |
| | | Mass of plant (-21* or -1), leaf area (-21* or +24*), absence or presence of CO ₂ at 1,000 ppm, plants 7 to 8 weeks old (Anderson and Mansfield, 1979) | GH | ChLum |
| 0 39 | 164 h | Mass of leaves (-8 or +14), mass of stem (0 or +16), nitrogen-nutrient level at 28 or 140 mg/L, 5-week-old plants (Troiano and Leone, 1977) | CE/GH | MastTM |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|-----------------|--------------------------|----------------------|--|-----------------------|----------------------|
| 9B-4 | 0 4 ^j | 19 days | Leaf area (-25*), mass of leaves (-30*), mass of shoot (-42*), mass of roots (-12*), 35-day-old plants (Capron and Mansfield, 1977) | CE | L-G-S |
| | | 45 days | Length of shoot (+12) ^e (Spierings, 1971) | GG, CE | Saltzman |
| | | 50 days | Mass of plant (+38*, -24*, or -44*), leaf area (+21*, -28*, or -44*), 0, 1 ×, or 2 × additions of fertilizer to soil, plants 9 to 10 weeks old (Anderson and Mansfield, 1979) | GH | ChLum |
| | 0 43 | 19 days | Fresh mass (-18*) or dry mass (-37**) of fifth leaf, exposures started when third or fourth true leaf appeared (Taylor and Eaton, 1966) | CE | Saltzman |
| | 0 5 | 10 days | Length of shoot (+11), mass of leaves (-22) ^e (Spierings, 1971) | 6GH, CE | Saltzman |
| | | 14 days | Mass of plant (+8*), leaf area (+7*), leaf-weight ratio (-6**), 6-week-old plants (Okano et al, 1988) | CE | ChLum |
| | | 19 days | Leaf area (-44*), mass of leaves (-44*), mass of shoot (-62*), mass of roots (-32*), 35-day-old plants (Capron and Mansfield, 1977) | CE | L-G-S |
| | 0 5 ^h | 19 days | Leaf area (-24*), mass of leaves (-29*), mass of shoot (-32*), mass of roots (-32*), 35-day-old plants (Capron and Mansfield, 1977) | CE | L-G-S |
| | 0 6 | 41 days | No effect on growth ^e (Ishikawa, 1976) | | |
| | 0 7 ^h | 21 or 28 days | Relative growth rate for mass of plant (-19* to -9* to -5), depended on cultivar, 6- to 7-week-old plants, CO ₂ at 1,000 ppm (Mortensen, 1985b) | GH, CE | Saltzman |
| | | | | CE | ChLum |
| | 0 8 ^j | 50 days | Mass of plant (-6, -17*, or -31*), leaf area (-11, -7, or -31*), 0, 1 ×, or 2 × additions of fertilizer to soil, plants 9 to 10 weeks old (Anderson and Mansfield, 1979) | GH | ChLum |
| | 0 85 ^g | 22 days | Leaf area (-23*), mass of plant (-29*), number of leaves (-6), height (-13*), seedlings, CO ₂ at 1,000 ppm (Mortensen, 1985a) | CE | ? |
| | 0 9 ^k | 19 days | Leaf area (-79*), mass of leaves (-59*), mass of shoot (-64*), mass of roots (-21*), 35-day-old plants (Capron and Mansfield, 1977) | CE | L-G-S |
| | 1 5 ^h | 25 days | Number of leaves (-26*, -8*, -2, or +4), mass of shoot (-65*, -33*, -15*, or -25*), length of shoot (-60*, -19*, +7, or -6), photon flux densities of 30, 95, 175, or 250, 6-week-old plants, CO ₂ at 1,000 ppm (Mortensen, 1986) | CE | ChLum |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|---|--------------------------|-------------------------------|---|-----------------------|----------------------|
| Eggplant (<i>Solanum melongena</i> L.) | | | | | |
| | 0 3 | 30 days | Height of plant (-2), number of leaves (-4), mass of stem and leaves (-8), number of flowers and fruit (-50), fresh mass of fruit (+16), some defoliation ^e (Fujiwara, 1973, Ishikawa, 1976) | GH, CE | Saltzman |
| | 0 6 | 30 days | Height of plant (-2), number of leaves (-4), mass of stem and leaves (-32), number of flowers and fruit (-50), fresh mass of fruit (+41), some defoliation ^e (Ishikawa, 1976) | | |
| Greenbean (<i>Phaseolus vulgaris</i> L.) | | | | | |
| | 0 02 | 5 days | Plant height (+23*, +16*, +6*, +4, +8*), mass of leaf (+7, 0, -8*, -12*, -5*), area of leaf (+3, 0, 0, -9, -9*), unifoliate leaf, depended on level of nitrate (0, 1, 5, 10, 20 mM), 12-day-old seedlings (Srivastava and Ormrod, 1984) | CE | ChLum |
| | | 6 h/day, 14 days | Mass of shoot (-23*, -14, -15, -5, -12), mass of root (+3, +3, -1, +3, -19*), number of nodules (+34*, +17, +85*, -13, -4), depended on level of nitrate (0, 1, 5, 10, 20 mM), 23-day-old seedlings (Srivastava and Ormrod, 1986) | CE | ChLum |
| | 0 025 | 7 h/day, 5 days/week, 3 weeks | Mass of shoot (-7), mass of roots (+9), number of pods (+21), number of seeds (+5), mass of seeds (+23*), 57-day-old plants (Sandhu and Gupta, 1989) | GH | CSI |
| | 0 05 | 7 h/day, 5 days/week, 3 weeks | Mass of shoot (+51*), mass of roots (+84*), number of pods (+43), number of seeds (+11), mass of seeds (+31*), 57-day-old plants (Sandhu and Gupta, 1989) | GH | CSI |
| | 0 08 | 3 h/day, 40 days | Mass of plant (+25*), mass of roots (+1), 40-day-old plants (Runeckles and Palmer, 1987) | GH | Mast |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | | Effect | Facility ^c | Monitor ^d |
|--------------------------|-------------------------------|---|-----------------------|----------------------|
| NO _x (ppm) | Exposure Duration | (% deviation from treatment without NO _x) ^b | | |
| 0 1 | 5 days | Plant height (+9*, +9*, +4, +2, +2), mass of leaf (-3, -11*, -27*, -13*, -23*), area of leaf (+8, -8, -8, -8, -11*), unifoliate leaf, depended on level of nitrate (0, 1, 5, 10, 20 mM), 12-day-old seedlings (Srivastava and Ormrod, 1984) | CE | ChLum |
| | 10 days | Growth in leaf area (-2), mass of leaves (+9), mass of stems (+6), mass of roots (0), mass of flowers (-4) ° (Totsuka et al , 1978) | CE | ChLum |
| | 15 days | Growth in leaf area (-6), mass of leaves (-4), mass of stems (-1), mass of roots (+14), mass of flowers and fruit (-13) ° (Totsuka et al , 1978) | CE | ChLum |
| | 15 days | Mass of plant (-3 to +11), (depended on experiment) exposed at 4- to 6-leaf stage (Elkley et al , 1988) | CE | B952 |
| | 7 h/day, 5 days/week, 3 weeks | Mass of shoot (+98*), mass of roots (+178*), number of pods (+86*), number of seeds (+29*), mass of seeds (+46*), 57-day-old plants (Sandhu and Gupta, 1989) | GH | CSI |
| | 6 h/day, 14 days | Mass of shoot (-30*, -29*, -22, -17*, -21), mass of roots (-1, -5, -9, -21*, -19*), number of nodules (+2, +2, +67*, -26, -7), depended on level of nitrate (0, 1, 5, 10, 20 mM), 23-day-old seedlings (Srivastava and Ormrod, 1986) | CE | ChLum |
| 0 21 | 1 h/day, 15 days | Mass of plant (-3), exposed at 4- to 6-leaf stage (Elkley et al , 1988) | | |
| 0 3 | 10 h/day, 14 days | Leaf area (+2 or +23**), mass of leaves (+6 or +9), mass of stem (-12 or +19**), mass of roots (-9 or +26**), daytime or nighttime exposure, 4-week-old plants (Yoneyama et al , 1980c) | CE | B952 |
| 0 32 | 10 days | Fresh mass (-27* or -15*) or dry mass (-22* or -6) of plant, depending on experiment, started with 6-day-old seedling (Taylor and Eaton, 1966) | CE/GH | ChLum |
| | 19 days | Fresh mass (-15*) or dry mass (-10*) of plant, started with 6-day-old seedling (Taylor and Eaton, 1966) | CE | Saltzman |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|-----------------|---------------------------------------|---------------------------------------|------------------------------------|--|-----------------------|----------------------|
| 9B-7 | Cucumber (<i>Cucumis sativus</i> L.) | 0 5 | 6 h/day, 14 days | Mass of shoot (-27*, -33*, -34*, -24*, -28*), mass of roots (-4, -7, -7, -18*, -22*), number of nodules (+8, +11, +40*, -57*, -2), depended on level of nitrate (0, 1, 5, 10, 20 mM), 23-day-old seedlings (Srivastava and Ormrod, 1986) | CE | Saltzman |
| | | | 5 days | Plant height (+6*, -3, -7*, +2, +4), mass of leaf (0, -9*, -33*, -31*, -33*), area of leaf (+3, -12, -24*, -22*, -21*), unifoliate leaf, depended on level of nitrate (0, 1, 5, 10, 20 mM), 12-day-old seedlings (Srivastava and Ormrod, 1984) | CE | ChLum |
| | | | 14 days | Mass of plant (-7), leaf area (-14*), leaf-weight ratio (+4), 4-week-old plants (Okano et al, 1988) | | |
| | | 1 0 | 10 days | Growth in leaf area (-36), mass of leaves (-11), mass of stem (-23), mass of roots (-36), mass of flowers (-39) ^e (Totsuka et al, 1978) | CE | ChLum |
| | | | 14 days | Growth depression ^e (cited in Taylor et al, 1975) | | |
| | | | 15 days | Growth in leaf area (-25), mass of leaves (+5), mass of stem (-13), mass of roots (-53), mass of flowers and fruit (-82) ^e (Totsuka et al, 1978) | CE | ChLum |
| | | | 639 h over 2 mo | Yield (-27) with number of fruit (-19) and mass per fruit (-10) ^e (Zahn, 1975) | | |
| | | 2 0 | 7 days | Mass of plant (0, -7, or -19*), after 2, 4, or 7 days of exposure, plants 10 days old at start (Ito et al, 1984a, 1985b) | CE | ChLum |
| | | 4 0 | 7 days | Mass of plant (-32*, -29*, or -40*), after 2, 4, or 7 days of exposure, plants 10 days old at start (Ito et al, 1984a, 1985b) | GH/FE CE | G-S ChLum |
| | | 0 1 | 15 days | Mass of plant (-3), exposed at 4- to 6-leaf stage (Elkley et al, 1988) | GH CE | ChLum B952 |
| | | 0 12 | 2 h/day, 1 day/week, 3 weeks | Mass of plant (+20*), leaf area (+31*), after 3 weeks, but no effect after 2 weeks, (added to continuous exposure of 0 029 ppm), 5-week-old plants (Edelbauer and Mauer, 1988) | GH | ChLum |
| | | Cucumber (<i>Cucumis sativus</i> L.) | | | | |
| | | 0 2 | 67 days | Leaf area (+17) ^e (Natori and Totsuka, 1980) | CE | ChLum |
| | | 0 3 | 10 h/day, 14 days | Leaf area (+24** or +14*), leaf mass (+24** or +6*), stem mass (+47** or +25*), root mass (+13** or +9*), exposed in light or dark, 4-week-old seedlings (Yoneyama et al, 1980a) | CE/GH | ChLum |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|--|--------------------------|----------------------------------|---|-----------------------|----------------------|
| | 0 5 | 14 days | Mass of plant (-9*), leaf area (+5), leaf-weight ratio (-5**), 4-week-old plants (Okano et al , 1988) | | |
| | 0 85 ^g | 18 days | Mass of plant (-9), seedlings, CO ₂ at 1,000 ppm (Mortensen, 1985a) | CE | ChLum |
| Woodland strawberry (<i>Fragaria vesca</i> L) | | | | | |
| | 1 0 | 213 h over 7 weeks | No significant effect on yield ^e (Zahn, 1975) | CE | ? |
| Carrot (<i>Daucus carota</i> L var <i>sativus</i> Hoffm) | | | | | |
| | 2 1 | 357 h over 50 days | Yield of roots (-30) ^e (Zahn, 1975) | GH/FE | G-S |
| Radish (<i>Raphanus sativus</i> L) | | | | | |
| | 0 08 | 3 h/day, 40 days | Mass of plant (+93*), mass of hypocotyl (+215*), 40-day-old plants (Runeckles and Palmer, 1987) | GH/FE | G-S |
| | 0 2 | 3 or 6 h | Mass of leaves (+1), mass of root (-7), 25-day-old plants (Godzik et al , 1985) | | |
| | 0 21 | 20 days | Mass of leaves (0 to + 11), mass of root (0 to +20) six cultivars, 26-day-old plants (Godzik et al , 1985) | GH | Mast |
| | 0 3 | 3 h/day, 3 days/week, 3 weeks | Mass of leaves (+1), mass of root (-4), fresh mass of root (-5), 30-day-old plants (Sanders and Reinert, 1982b) | CSTR/GH | ChLum |
| | | 3 h/day, 3 days/week, 3 weeks | Mass of leaves (+17), mass of root (-5), 30-day-old plants (Reinert and Sanders, 1982) | GH | B852 |
| | 0 4 | 3 or 6 h | Mass of leaves (+1), mass of root (-7), 25-day-old plants (Reinert and Gray, 1981) | | |
| | 0 5 | 14 days | Mass of plant (-33*), leaf area (-29*), leaf-weight ratio (+25), 4-week-old plants (Okano et al , 1988) | CSTR/GH | ChLum |
| | 2 1 | 278 h over 38 days | Mass of root (-13) and mass of plant (-27) ^e (Zahn, 1975) | CSTR/GH | ChLum |
| Field crops | | | | | |
| Oats (<i>Avena sativa</i> L) | | | | | |
| | 30 | 1 h | No effect on growth, 3-mo-old plants ^e (Czech and Nothdurft, 1952) | CE | ChLum |
| Barley (<i>Hordeum vulgare</i> L) | | | | | |
| | 0 1 | 20 days | Number of tillers (0), number of leaves (+5), leaf area (+2), mass of leaves (-1), mass of roots (+18), 22-day-old seedlings (Pande and Mansfield, 1985) | GH/FE | G-S |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|-----------------|--------------------------------------|--|--------------------------|---|----------------------------------|------------------------------------|
| 9B-9 | Paddy rice (<i>Oryza sativa</i> L) | 0.3 | 9 days | Mass of shoot (+11, +24*, and -3 to +9), mass of roots (+17*, -7, and -12 to +10), grown at 0, 0.01, and 0.1 to 10 mM nitrate, 17-day-old seedlings (Rowland, 1986, Rowland et al , 1987) | FE, GH | ? |
| | | 1.0 | Exposures totaling 660 h | Length of leaf (+27) ^e (Zahn, 1975) | | |
| | | 100 | 1 h | Adverse effect on grain development ^e (Czech and Nothdurft, 1952) | CE | ChLum |
| | | 0.3 | 51 days | Number of ears (+18), mass of grain (+1), mass of straw (0) ^e (Fujiwara, 1973, Ishikawa, 1976) | CE | ChLum |
| | | 0.6 | 51 days | Number of ears (+29), mass of grain (+36), mass of straw (+5) ^e (Fujiwara, 1973) | | |
| | | Common rye (<i>Secale cereale</i> L) | | | | |
| | | 100 | 1 h | Adverse effect on grain development ^e (Czech and Nothdurft, 1952) | GH/FE FE, GH | G-S ? |
| | | Sorghum (<i>Sorghum bicolor</i> [L.] Moench) | | | | |
| | | 0.5 | 14 days | Mass of plant (-8), leaf area (-17), leaf-weight ratio (+5), 4-week-old plants (Okano et al , 1988) | GH, CE GH, CE FE, GH CE | Saltzman Saltzman ? ChLum |
| | | Common wheat (<i>Triticum aestivum</i> L) | | | | |
| | | 0.08 | 3 h/day, 38 days | Mass of plant (+6), mass of roots (-18), 38-day-old plants (Runeckles and Palmer, 1987) | GH | Mast |
| | | 1.0 | 334 h in 40 days | No significant effect on yield, mass per grain (+10), stalk growth (-12) ^e (Zahn, 1975) | GH/FE | G-S |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|---|--|--------------------------|--|----------------------------------|------------------------------------|
| | | | | | |
| 9B-10 Paddy rice (<i>Oryza sativa</i> L) | 0.3 | 9 days | Mass of shoot (+11, +24*, and -3 to +9), mass of roots (+17*, -7, and -12 to +10), grown at 0, 0.01, and 0.1 to 10 mM nitrate, 17-day-old seedlings (Rowland, 1986, Rowland et al, 1987) | FE, GH | ? |
| | 1.0 | Exposures totaling 660 h | Length of leaf (+27) ^e (Zahn, 1975) | | |
| | 100 | 1 h | Adverse effect on grain development ^e (Czech and Nothdurft, 1952) | CE | ChLum |
| | 0.3 | 51 days | Number of ears (+18), mass of grain (+1), mass of straw (0) ^e (Fujiwara, 1973, Ishikawa, 1976) | CE | ChLum |
| | 0.6 | 51 days | Number of ears (+29), mass of grain (+36), mass of straw (+5) ^e (Fujiwara, 1973, Ishikawa, 1976) | | |
| | Common rye (<i>Secale cereale</i> L) | | | | |
| | 100 | 1 h | Adverse effect on grain development ^e (Czech and Nothdurft, 1952) | GH/FE FE, GH | G-S ? |
| | Sorghum (<i>Sorghum bicolor</i> [L.] Moench) | | | | |
| | 0.5 | 14 days | Mass of plant (-8), leaf area (-17), leaf-weight ratio (+5), 4-week-old plants (Okano et al, 1988) | GH, CE GH, CE FE, GH CE | Saltzman Saltzman ? ChLum |
| | Common wheat (<i>Triticum aestivum</i> L) | | | | |
| | 0.08 | 3 h/day, 38 days | Mass of plant (+6), mass of roots (-18), 38-day-old plants (Runeckles and Palmer, 1987) | GH | Mast |
| | 1.0 | 334 h in 40 days | No significant effect on yield, mass per grain (+10), stalk growth (-12) ^e (Zahn, 1975) | GH/FE | G-S |
| | 30 | 1 h | No effect on yield ^e (Czech and Nothdurft, 1952) | FE, GH | ? |
| | 100 | 1 h | Decreased filling of head ^e (Czech and Nothdurft, 1952) | FE, GH | ? |
| | 300 | 1 h | Decreased mass of grains ^e (Czech and Nothdurft, 1952) | FE, GH | ? |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|---|-------------------------------------|--------------------------|----------------------|--|-----------------------|----------------------|
| Maize (<i>Zea mays</i> L.) | | | | | | |
| 0 1 | 15 days | | | Increased mass of plant (+13) and leaf area, 15-day-old seedlings ^e (Elkley et al , 1988) | CE | B952 |
| 0 2 | 14 days | | | Leaf area (-10), mass of leaves (-10), mass of stem (-3), mass of roots (3), 28-day-old plants (Okano et al , 1985a) | CE | ChLum |
| 0 3 | 10 h/day, 14 days | | | Leaf area (-2 or -16*), mass of leaf blade (-5 or -18), mass of leaf sheath (-16 or -24*), mass of roots (-4 or -7), daytime or nighttime exposure, 4-week-old plants (Yoneyama et al , 1980c) | CE/GH | ChLum |
| | 14 days | | | Mass of shoot (-3 or -3), mass of roots (-29 or +46), plants grown at 26 or 105 ppm nitrogen nutrient, 4-week-old plants ^e (Matsumaru et al , 1979) | CE/GH | ChLum |
| 0 5 | 14 days | | | Leaf area (+6), mass of leaves (+1), mass of stem (-10*), mass of roots (-1), 28-day-old plants (Okano et al , 1985a) | CE | ChLum |
| | 14 days | | | Mass of plant (-4), leaf area (+6), leaf-weight ratio (-8**), 4-week-old plants (Okano et al , 1988) | | |
| 0 6 | 6 h/day, 4-5 days/week, 4 weeks (?) | | | Mass of leaves (-3), mass of stem (+8), seedlings 24 days old at start (Amundson et al , 1982) | CE | ChLum |
| 1 2 | 6 h/day, 4-5 days/week, 4 weeks (?) | | | Mass of leaves (+5), mass of stem (+9), seedlings 20 days old at start (Amundson et al , 1982) | | |
| 1 0 | 14 days | | | Leaf area (+2), mass of leaves (-3), mass of stem (-13), mass of roots (-3), 28-day-old plants (Okano et al , 1985a) | CE | ChLum |
| Buckwheat (<i>Fagopyrum esculentum</i> Moench) | | | | | | |
| 0 3 | 30 days | | | Height (-3), number of leaves (+22), leaf mass (-33), stem mass (-43) ^e (Fujiwara, 1973, Ishikawa, 1976) | CE | ChLum |
| 0 6 | 30 days | | | Height (-11), number of leaves (+23), leaf mass (-33), stem mass (-36) ^e (Fujiwara, 1973, Ishikawa, 1976) | | |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|--|---|--------------------------|-------------------------------------|---|-----------------------|----------------------|
| Soybean (<i>Glycine max</i> [L.] Merrill) | | | | | | |
| 9B-12 | 0 1 | | 7 h/day, 5 days | Relative growth rate of plant (+4), 5-week-old plants (Sabaratnam and Gupta, 1988) | GH, CE | Saltzman |
| | | | 3 h/day, once/2 days, 4 weeks | Mass of leaves (+5), mass of stem (0), mass of roots (+6), mass of nodules (-1), number of nodules (-4*), 7-week-old plants (Klarer et al., 1984) | GH, CE | Saltzman |
| | 0 2 | | 7 h/day, 5 days | Relative growth rate of plant (+3), 5-week-old plants (Sabaratnam and Gupta, 1988) | CE | CSI |
| | | | 3 h/day, once/2 days, 4 weeks | Mass of leaves (+9), mass of stem (+5), mass of roots (+2), mass of nodules (+2), number of nodules (-15*), 7-week-old plants (Klarer et al., 1984) | CSTR | ChLum |
| | 0 3 | | 7 h/day, 5 days | Relative growth rate of plant (+1), 5-week-old plants (Sabaratnam and Gupta, 1988) | CE | CSI |
| | 0 37 | | 2 5 h/event, 10 events | Yield (-6 to +8), plants grown in field plots (Irving et al., 1982) | CE | CSI |
| | 0 4 | | 2 9 h/event, 10 events | Yield (-6 to +5), plants grown in field plots (Irving et al., 1982) | CSTR/GH | ChLum |
| | 0 5 | | 7 h/day, 5 days 7 h | Relative growth rate of plant (-47*), 5-week-old plants (Sabaratnam and Gupta, 1988) Number of pods (-32*), number of seeds (-13*), mass of seeds (-34*), exposed when 1 mo old, harvested 80 days later (Gupta and Sabaratnam, 1988) | CE ZAPS | CSI ChLum |
| | Common sunflower (<i>Helianthus annuus</i> L.) | | | | | |
| | 0 1 | | 10 days | Growth in leaf area (-11), mass of leaves (-3), mass of stems (-16), mass of roots (-26) ^e (Totsuka et al., 1978) | CE | ChLum |
| | | | 15 days | Growth in leaf area (+26), mass of leaves (+27), mass of stems (+9), mass of roots (+37), mass of flowers (-24) ^e (Totsuka et al., 1978) | CE | ChLum |
| | 0 2 | | 14 days | Leaf area (-4*), mass of leaves (+2), mass of stems (+8), mass of roots (+16), 28-day-old plants (Okano et al., 1985a) | CE | ChLum |
| | | | 38 days | Leaf area (+11) ^e (Natori and Totsuka, 1980) | CE | ChLum |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | NO _x (ppm) | Exposure Duration | Effect | Facility ^c | Monitor ^d |
|---------------------------------------|--------------------------|-------------------|---|-----------------------|----------------------|
| | | | (% deviation from treatment without NO _x) ^b | | |
| 9B-13 | 1 0 | 7 h | Number of pods (-64*), number of seeds (-46*), mass of seeds (-58*), exposed when 1 mo old, harvested 80 days later (Gupta and Sabaratnam, 1988) | ZAPS CE | ChLum CSI |
| | 0 3 | 7 days | Leaf area (+13, +6, or +10), mass of leaves (+23**, +6, or +14), mass of stems (+20*, +2, or +18), mass of roots (+19, +16, or -2), grown at nitrate levels of 0, 5, or 15mM, 4-week-old plants (Okano and Totsuka, 1986) | CE | ChLum |
| | | 10 h/day, 14 days | Leaf area (+3 or +31**), mass of leaf (-1 or +11*), mass of stems (-10 or +19*), mass of roots (-3 or +4), daytime or nighttime exposure, 4-week-old plants (Yoneyama et al , 1980c) | CE/GH | ChLum |
| | | 14 days | Mass of leaves (+17, -14, or -11), mass of stems (-5, -22, or -14), mass of roots (-7, -45, or -11), plants grown at 26, 105, or 260 ppm nitrogen nutrient, 4-week-old plants ^e (Matsumaru et al , 1979) | CE/GH | ChLum |
| | 0 5 | 14 days | Mass of plant (-12*), leaf area (-6), leaf-weight ratio (+11**), 4-week-old plants (Okano et al , 1988) | CE/GH | ChLum |
| | | 14 days | Leaf area (-6), mass of leaves (0), mass of stems (-22**), mass of roots (-11), 28-day-old plants (Okano et al , 1985a) | CE | ChLum |
| | 0 78 | 8 h/day, 21 days | Height (+6), mass of plants (+8), nitrogen-deficient plants ^e (Faller, 1972) | CE | ChLum |
| | 1 0 | 10 days | Growth in leaf area (-30), mass of leaves (+1), mass of stems (-32), mass of roots (-44) ^e (Totsuka et al , 1978) | CE | ChLum |
| | | 15 days | Growth in leaf area (+6), mass of leaves (+16), mass of stems (-26), mass of roots (-23), mass of flowers (-74) ^e (Totsuka et al , 1978) | GH | ? |
| | | 14 days | Leaf area (-12**), mass of leaves (+2), mass of stems (-34**), mass of roots (-37**), 28-day-old plants (Okano et al , 1985a) | CE | ChLum |
| | 2 0 | 7 days | Leaf area (+35**, -6, -18**), mass of leaves (+42**, +17**, or -4), mass of stems (-18**, -21**, or -19*), mass of roots (-14, -22**, or -12*), grown at nitrate levels of 0, 5, or 15mM, 4-week-old plants (Okano and Totsuka, 1986) | CE | ChLum |
| | 3 1 | 8 h/day, 21 days | Height (+16), mass of plants (+10), nitrogen-deficient plants ^e (Faller, 1972) | CE | ChLum |
| Sugar beet (<i>Beta vulgaris</i> L) | | | | | |
| | 10 | 1 h | No effect ^e (Czech and Nothdurft, 1952) | CE | ChLum |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|--|--------------------------|---|--|-----------------------|----------------------|
| | | | | | |
| | 30 | 1 h | No effect. ^e (Czech and Nothdurft, 1952) | CE | ChLum |
| | 100 | 1 h | Decreased growth ^e (Czech and Nothdurft, 1952) | CE | ChLum |
| Potato (<i>Solanum tuberosum</i> L.) | | | | | |
| | 0 1 | 15 days | Mass of plant (+13), 30-day-old plants (Elkley et al, 1988) | GH | ? |
| | 0 11 | 7 days | Leaf area (-17 to +2), mass of leaves (-16 to +16), mass of stems (-19 to +4), (depending on cultivar) in 20-day-old plants from sprouts (Petitte and Ormrod, 1984) | FE, GH | ? |
| | | | Leaf area (-45 or 0), mass of leaves (-33 or -3), mass of stems (-38 or +6), mass of roots (-18 or -4), (depending on cultivar) in 24-day-old plants from rooted cuttings (Petitte and Ormrod, 1988) | FE, GH | ? |
| | 0 11 | 14 days | Leaf area (-15 to -7), mass of leaves (-9 to -3), mass of stems (-21 to +10), (depending on cultivar) in 20-day-old plants from sprouts (Petitte and Ormrod, 1984) | CE | B952 |
| | | | Leaf area (-7), mass of leaves (-3), mass of stems (+1), mass of roots (+4), in 24-day-old plants from rooted cuttings (Petitte and Ormrod, 1988) | CE | B952 |
| | 0 2 | 5 h/day, 2 days/week, 12-16 weeks | Number of tubers (-38* or -21*), mass of tubers (-51* or -43*), depending on cultivar), accelerated senescence and abscission of foliage (Sinn and Pell, 1984) | GH, CE | ? |
| | 10 | 1 h | No effect ^e (Czech and Nothdurft, 1952) | FE, GH | ? |
| | 30 | 1 h | No effect ^e (Czech and Nothdurft, 1952) | FE, GH | ? |
| | 300 | 1 h | Inhibited tuber formation ^e (Czech and Nothdurft, 1952) | FE, GH | ? |
| Tobacco (<i>Nicotiana tabacum</i> L.) | | | | | |
| | 0 10 | 15 days | Mass of plant (-2 to +4), leaf area increased, (depended on experiment), exposed at 4- to 6-leaf stage ^e (Elkley et al, 1988) | CE | B952 |
| | 0 21 | 1 h/day, 15 days | Mass of plant (-2), exposed at 4- to 6-leaf stage (Elkley et al, 1988) | CE | B952 |
| | 0 5 | 14 days | Mass of plant (-4), leaf area (-9*), leaf-weight ratio (-6**), 6-week-old plants (Okano et al, 1988) | CE | ChLum |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | | Effect | | Facility ^c | Monitor ^d |
|--|------------------------|---|--|-----------------------|----------------------|
| NO _x (ppm) | Exposure Duration | (% deviation from treatment without NO _x) ^b | | | |
| Grasses | | | | | |
| Redtop (<i>Agrostis gigantea</i> Roth) | | | | | |
| 0 15 | 10 days | Area of third youngest leaf (-12), 48 days old at start (Elkiey and Ormrod, 1980) | | CE | B942 |
| Creeping bentgrass (<i>Agrostis stolonifera</i> L) | | | | | |
| 0 15 | 10 days | Area of third youngest leaf (-8), 48 days old at start (Elkiey and Ormrod, 1980) | | CE | B942 |
| Colonial bentgrass (<i>Agrostis tenuis</i> Sibth) | | | | | |
| 0 15 | 10 days | Area of third youngest leaf (-13), 48 days old at start (Elkiey and Ormrod, 1980) | | CE | B942 |
| Orchard grass (<i>Dactylis glomerata</i> L) | | | | | |
| 0 024 ¹ | to 153 days | Percent dead leaf mass (-10), mass of shoots (+4), plants 183 days old (Lane and Bell, 1984b) | | FE | TM |
| 0 1 | 104 h/week, 7 mo | Mass of shoot (-5 or -14), exposed from emergence or 6 weeks later (Whitmore and Mansfield, 1983) | | FE | B952 |
| 0 11 | 104 h/week, 4 weeks | Mass of green leaves (-25), mass of dead leaves and stubble (-29), mass of roots (-13), leaf area (-24), number of leaves (-18), numbers of tillers (-9), seedlings 6 weeks old at start (Ashenden, 1979a) | | GH | ? |
| | 8 weeks | Mass of green leaves (-31**), mass of dead leaves and stubble (-20), mass of roots (-20), leaf area (-24*), number of leaves (-7), number of tillers (-5), seedlings 6 weeks old at start (Ashenden, 1979a) | | GH | ChLum |
| | 12 weeks | Mass of green leaves (-30*), mass of dead leaves and stubble (-24), mass of roots (-12), leaf area (-25), number of leaves (-20), number of tillers (-17), seedlings 6 weeks old at start (Ashenden, 1979a) | | GH | ChLum |
| | 16 weeks | Mass of green leaves (-3), mass of dead leaves and stubble (-19), mass of roots (-18), leaf area (+6), number of leaves (-5), number of tillers (-5), seedlings 6 weeks old at start (Ashenden, 1979a) | | GH | ChLum |
| | 20 weeks | Mass of green leaves (-7), mass of dead leaves and stubble (-46**), mass of roots (-11), leaf area (-21), number of leaves (-33), number of tillers (-1), seedlings 6 weeks old at start (Ashenden, 1979a) | | GH | ChLum |
| Red fescue (<i>Festuca rubra</i> L) | | | | | |
| 0 15 | 10 days | Area of third youngest leaf (-1 to +4), two cultivars, 48 days old at start (Elkiey and Ormrod, 1980) | | GH | ChLum |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|--|--------------------------|------------------------|--|-----------------------|----------------------|
| Italian ryegrass (<i>Lolium multiflorum</i> Lam) | | | | | |
| | 0 11 | 104 h/week, 4 weeks | Mass of green leaves (-3), mass of dead leaves and stubble (-6), mass of roots (-14), leaf area (-14), number of leaves (-11), number of tillers (-21), seedlings 5 weeks old at start (Ashenden and Williams, 1980, Ashenden and Mansfield, 1978) | CE | B942 |
| | | 8 weeks | Mass of green leaves (-13), mass of dead leaves and stubble (0), mass of roots (+5), leaf area (-12), number of leaves (+4), number of tillers (+6), seedlings 5 weeks old at start (Ashenden and Mansfield, 1978) | GH | ChLum |
| | | 12 weeks | Mass of green leaves (-14), mass of dead leaves and stubble (-23*), mass of roots (-47**), leaf area (-27), number of leaves (+24), number of tillers (+10), seedlings 5 weeks old at start (Ashenden and Mansfield, 1978) | GH | ChLum |
| | | 16 weeks | Mass of green leaves (-13), mass of dead leaves and stubble (-13), mass of roots (-17), leaf area (-9), number of leaves (+20), number of tillers (-3), seedlings 5 weeks old at start (Ashenden and Mansfield, 1978) | GH | ChLum |
| | | 20 weeks | Mass of green leaves (-10), mass of dead leaves and stubble (-5), mass of roots (+35), leaf area (+1), number of leaves (-18), number of tillers (-17), seedlings 5 weeks old at start (Ashenden and Mansfield, 1978) | GH | ChLum |
| Perennial ryegrass (<i>Lolium perenne</i> L) | | | | | |
| | 0 018 ^m | 187 days | Mass of shoots (-4), mass of dead leaves (+29*), number of flowering shoots (-35*), plants 52 days old at start (Lane and Bell, 1984b) | FE | TM |
| | 0 028 ⁿ | 187 days | Mass of shoots (-9*), mass of dead leaves (+47*), number of flowering shoots (-42*), plants 52 days old at start (Lane and Bell, 1984b) | FE | TM |
| | 0 024 ^l | 207 days | Mass of shoots (+25* or +3) after 156 or 207 days of exposure, number of flowering shoots (-20*) after 207 days, plants 6 days old at start (Lane and Bell, 1984b) | FE | B952 |
| | 0 1 | 104 h/week, 7 mo | Mass of shoot (-31* or -36**) and (+5 or -19**), exposed from emergence or 6 weeks later, two cultivars (Whitmore and Mansfield, 1983) | GH | ? |
| | 0 15 | 10 days | Area of third youngest leaf (-2), 48 days old at start (Elkiey and Ormrod, 1980) | CE | B942 |
| | 0 2 | 11 weeks | Mass of roots (+69* or +85*), mass of shoots (+30* or +48*), number of tillers (+10* or +21*), depended upon high or low nitrogen level in soil, two populations (Taylor and Bell, 1988) | | |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | | Effect | Facility ^c | Monitor ^d |
|---|------------------------|--|-----------------------|----------------------|
| NO _x (ppm) | Exposure Duration | (% deviation from treatment without NO _x) ^b | | |
| Common timothy (<i>Phleum pratense</i> L.) | | | | |
| 0 018 ^m | to 183 days | Mass of shoots (-9*) by 131 days, mass of dead leaves (-32*), number of flowering shoots (-47*), plants 52 days old at start (Lane and Bell, 1984a) | FE | TM |
| 0 028 ⁿ | to 183 days | Mass of shoots (+11*) by 131 days, mass of dead leaves (-63*), number of flowering shoots (+47*), plants 52 days old at start (Lane and Bell, 1984a) | FE | TM |
| 0 024 ^l | 215 days | Mass of shoot (+26* or +12) after 97 or 215 days of exposure, number of flowering shoots (+5), plants 6 days old at start (Lane and Bell, 1984a) | FE | B952 |
| 0 1 | 104 h/week, 7 mo | Mass of shoot (-31** or -7) and (-21* or -26**), exposed from emergence or 6 weeks later, two cultivars (Whitmore and Mansfield, 1983) | GH | ? |
| 0 11 | 104 h/week, 4 weeks | Mass of green leaves (-25), mass of dead leaves and stubble (-19), mass of roots (-25), leaf area (-26), number of leaves (-8), number of tillers (-3), seedlings 5 weeks old at start (Ashenden and Williams, 1980, Ashenden and Mansfield, 1978) | GH | ChLum |
| | 8 weeks | Mass of green leaves (+1), mass of dead leaves and stubble (+15), mass of roots (+12), leaf area (+13), number of leaves (+5), number of tillers (+2), seedlings 5 weeks old at start (Ashenden and Mansfield, 1978) | GH | ChLum |
| | 12 weeks | Mass of green leaves (-25), mass of dead leaves and stubble (-29), mass of roots (-30*), leaf area (-20), number of leaves (-19), number of tillers (-17), seedlings 5 weeks old at start (Ashenden and Mansfield, 1978) | GH | ChLum |
| | 16 weeks | Mass of green leaves (-12), mass of dead leaves and stubble (-2), mass of roots (-25*), leaf area (-16), number of leaves (+12), number of tillers (+11), seedlings 5 weeks old at start (Ashenden and Mansfield, 1978) | GH | ChLum |
| | 20 weeks | Mass of green leaves (+14), mass of dead leaves and stubble (-12), mass of roots (+1), leaf area (+30), number of leaves (+10), number of tillers (-6), seedlings 5 weeks old at start (Ashenden and Mansfield, 1978) | GH | ChLum |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|---|--------------------------|------------------------|--|-----------------------|----------------------|
| Kentucky bluegrass (<i>Poa pratensis</i> L.) | | | | | |
| 9B-18 | 0 1 | 104 h/week, 8 weeks | Mass of plant (-36* or -5), number of leaves (0 or +2), number of tillers (+7 or +2), two cultivars, seedlings exposed from emergence. (Whitmore and Mansfield, 1983, Whitmore et al , 1982) | GH/FE | ? |
| | | 18 weeks | Mass of plants (0), seedlings exposed from emergence (Whitmore et al , 1982) | GH/FE | ? |
| | | 21 weeks | Mass of plants (-59), seedlings exposed from emergence (Whitmore et al , 1982) | GH/FE | ? |
| | | 7 mo | Mass of shoot (-45** or -24**), exposed from emergence or 6 weeks later (Whitmore et al , 1982) | GH/FE | ? |
| | | 33 weeks | Mass of shoot (-40*), number of tillers (+6), number of culms (-38*), grown as swards (Whitmore et al , 1982) | GH/FE | ? |
| | 0 11 | 104 h/week, 4 weeks | Mass of green leaves (-18), mass of dead leaves and stubble (-7), mass of roots (-33**), leaf area _l (-10), number of leaves (-24), number of tillers (0), seedlings 6 weeks old at start (Ashenden, 1979a) | GH | ChLum |
| | | 8 weeks | Mass of green leaves (-30**), mass of dead leaves and stubble (-27*), mass of roots (-23*), leaf area (-29*), number of leaves (-23*), number of tillers (-13), seedlings 6 weeks old at start (Ashenden, 1979a) | GH | ChLum |
| | | 12 weeks | Mass of green leaves (-33**), mass of dead leaves and stubble (-20*), mass of roots (-37**), leaf area (-34**), number of leaves (-36**), number of tillers (-15), seedlings 6 weeks old at start (Ashenden, 1979a) | GH | ChLum |
| | | 16 weeks | Mass of green leaves (-34**), mass dead leaves and stubble (-25*), mass of roots (-42**), leaf area (-29**), number of leaves (-14), number of tillers (-19), seedlings 6 weeks old at start (Ashenden, 1979a) | GH | ChLum |
| | | 20 weeks | Mass of green leaves (-29**), mass of dead leaves and stubble (-27*), mass of roots (-47**), leaf area (-17), number of leaves (-12), number of tillers (-9), seedlings 6 weeks old at start (Ashenden, 1979a) | GH | ChLum |
| | 0 15 | 10 days | Area of third youngest leaf (-20 to +8), significant (-18*) in 1 out of 12 cultivars, 48 days old at start (Elkiey and Ormrod, 1980) | GH | ChLum |
| | | 10 days | Fresh mass of leaves (-17 to +16), leaf area (-10* to +22*), depended on cultivar and environmental conditions, 45-day-old seedlings (Elkiey and Ormrod, 1981a) | GH | ChLum |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|--|--------------------------|----------------------|--|-----------------------|----------------------|
| Fruits: | | | | | |
| Navel orange (<i>Citrus sinensis</i> [L.] Osbeck) | | | | | |
| 1 × ambient ^o for 8 mo | | | Number of fruit (+11) or mass of fruit (+13) per tree, number of leaves dropped (+57), 15-year-old trees (Thompson et al., 1971) | CE | B942 |
| 2 × ambient ^o for 8 mo | | | Number of fruit (-15) or mass of fruit (-22) per tree, number of leaves dropped (+113), 15-year-old trees (Thompson et al., 1971) | CE | B942 |
| 0.063 | 290 days | | Number of fruit (-61**), mass of fruit (-57**), percentage of fruit dropped (+22*), mass of leaves dropped (+11*), 14-year-old trees (Thompson et al., 1970) | FE | Atlas |
| 0.13 | 290 days | | Number of fruit (-37**), mass of fruit (-32**), percentage of fruit dropped (+14*), mass of leaves dropped (+20*), 14-year-old trees (Thompson et al., 1970) | FE | Atlas |
| 0.25 | 290 days | | Number of fruit (-55**), mass of fruit (-47**), percentage of fruit dropped (+18*), mass of leaves dropped (+31*), 14-year-old trees (Thompson et al., 1970) | FE | Saltzman |
| 0.5 | 290 days | | Number of fruit (-81**), mass of fruit (-80**), percentage of fruit dropped (+30*), increased the mass of leaves dropped within 35 days, 14-year-old trees (Thompson et al., 1970) | FE | Saltzman |
| 1.0 | 290 days | | Number of fruit (-73**), mass of fruit (-70**), percentage of fruit dropped (+25*), increased the mass of leaves dropped within 35 days, 14-year-old trees (Thompson et al., 1970) | FE | Saltzman |
| Common apple (<i>Malus pumila</i> Mill.) | | | | | |
| 0.1 | 104 h/week, 22 weeks | | Stem height (+1), leaf area (-9), mass of shoot (-14), second-year cuttings (Freer-Smith, 1984, Whitmore and Freer-Smith, 1982) | FE | Saltzman |
| | 60 weeks | | Stem height (-2), mass of shoot (-5), second-year cuttings (Whitmore and Freer-Smith, 1982) | FE | Saltzman |
| Currant (<i>Ribes</i> sp.) | | | | | |
| 1.0 | 213 h over 8 weeks | | Yield (-12) ^e (Zahn, 1975) | FE | ? |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|---|--------------------------|-------------------|---|-----------------------|----------------------|
| Floricultural crops: | | | | | |
| Florist's chrysanthemum (<i>Chrysanthemum X morifolium</i> Ramat) | | | | | |
| | 0 85 ^g | 35 days | Mass of plant (-7 or +1), young plants of two cultivars, CO ₂ at 1,000 ppm (Mortensen, 1985a) | FE | ? |
| Dumb cane (<i>Dieffenbachia maculata</i> [Lodd] G Don) | | | | | |
| | 1 0 ^j | 139 days | Mass of plant (-27*), height (+8*), number of lateral shoots (-23*), CO ₂ at 1,000 ppm (Saxe and Christensen, 1984, 1985) | GH | ChLum |
| Benjamin tree (<i>Ficus benamina</i> L) | | | | | |
| | 1 0 ^j | 147 days | Mass of plant (-25*), height (-7), CO ₂ at 1,000 ppm (Saxe and Christensen, 1984, 1985) | GH | ChLum |
| Rubber plant (<i>Ficus elastica</i> Roxb ex Hornem) | | | | | |
| | 1 0 ^j | 128 to 136 days | Mass of plant (-28*), height of plant (-21*), total leaf area (-18), CO ₂ at 1,000 ppm (Saxe and Christensen, 1984, 1985) | GH | ChLum |
| Algerian ivy (<i>Hedera canariensis</i> Willd) | | | | | |
| | 1 0 ^j | 101 days | Mass of plant (-1), length of shoots (0), CO ₂ at 1,000 ppm (Saxe and Christensen, 1984, 1985) | GH | ChLum |
| English ivy (<i>Hedera helix</i> L) | | | | | |
| | 0 85 ^g | 55 or 77 days | Mass of plants (-10 or 0), young plants of two cultivars, CO ₂ at 1,000 ppm (Mortensen, 1985a) | GH | ChLum |
| | 1 0 ^j | 85 or 105 days | Mass of plant (-17*), length of shoots (-13*), number of leaves (-7), CO ₂ at 1,000 ppm (Saxe and Christensen, 1984, 1985) | CE | ? |
| Chinese hibiscus (<i>Hibiscus rosa-sinensis</i> L) | | | | | |
| | 1 0 ^j | 112 or 133 days | Mass of plant (±1), height of plant (+1), number of shoots (0), CO ₂ at 1,000 ppm (Saxe and Christensen, 1984, 1985) | GH | ChLum |
| Palm-Beach-bells (<i>Kalanchoe blossfeldiana</i> Poelln) | | | | | |
| | 0 85 ^g | 54 days | Mass of plant (+8), young plants, CO ₂ at 1,000 ppm (Mortensen, 1985a) | GH | ChLum |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|---|--------------------------|--------------------------------------|--|-----------------------|----------------------|
| Boston fern (<i>Nephrolepis exaltata</i> [L] Schott) | | | | | |
| | 0 85 ^g | 76 days | Mass of plant (-7), young plants, CO ₂ at 1,000 ppm (Mortensen, 1985a) | CE | ? |
| | 1 0 ^j | 112 or 135 days | Mass of plant (+3), number of leaves (-4), CO ₂ at 1,000 ppm (Saxe and Christensen, 1984,1985) | CE | ? |
| Azalea (<i>Rhododendron canescens</i>) | | | | | |
| | 0 25 | 3 h/day, 6 days over 4 weeks | Mass of stems (-10*), mass of leaves (-7*), shoot length (-18*) in two out of eight cultivars, 1-year-old plants (Sanders and Reinert, 1982a) | GH | ChLum |
| Cultivated rose (<i>Rosa</i> sp) | | | | | |
| | 0 85 ^g | 42 days | Mass of plant (-32*), reduced shoot length, young plants, CO ₂ at 1,000 ppm (Mortensen, 1985a) | CSTR/GH | ChLum |
| | 2 1 | 357 h over 8 weeks | No effect ^e (Zahn, 1975) | FE | ? |
| African violet (<i>Saintpaulia ionantha</i> H Wendl) | | | | | |
| | 0 85 ^g | 104 or 121 days | Mass of plant (-18* or -10), number of flowers and buds (-49* or -22*), young plants of two cultivars, CO ₂ at 1,000 ppm (Mortensen, 1985a) | CE | ? |
| Baby's Tears (<i>Soleirolia soleirolu</i> [Req] Dandy) | | | | | |
| | 0 85 ^g | 43 days | Mass of plant (+2), young plants, CO ₂ at 1,000 ppm (Mortensen, 1985a) | GH/FE | G-S |
| French marigold (<i>Tagetes patula</i> L) | | | | | |
| | 0 3 | 6 h/day, 9 days in 4 weeks | Mass of shoot (-3), mass of roots (+4), mass of flowers (+25), 58-day-old plants (Reinert and Sanders, 1982) | CE | ? |
| | | 6 h/day, 3 days | Mass of shoot (+5), mass of flowers (-1), mass of roots (+13**), 58-day-old-plants (Sanders and Reinert, 1982b) | CE | ? |
| Other herbaceous plants | | | | | |
| Desert marigold (<i>Baileyia pleniradiata</i> Harv and Gray) | | | | | |
| | 0 11 | 5 h/day, 5 days/week, 17 weeks | Height (-4), mass of plant (+6), number of inflorescences (+10) (Thompson et al , 1980) | CSTR/GH | ChLum |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|-----------------|--|--------------------------|-----------------------------------|--|-----------------------|----------------------|
| 9B-22 | <i>(Chaenactis carphoclina</i> Gray) | 0 33 | 5 h/day, 5 days/week, 17 weeks | Height (+6), mass of plant (+30), number of inflorescences (+61*) (Thompson et al , 1980) | CSTR/GH | ChLum |
| | | 1 0 | 5 h/day, 5 days/week, 17 weeks | Height (0), mass of plant (+26), number of inflorescences (+65*) (Thompson et al , 1980) | CSTR/GH | ChLum |
| | | 0 11 | 5 h/day, 5 days/week, 12 weeks | Height (-23), mass of plant (+56), number of inflorescences (+40) ^e (Thompson et al , 1980) | GH | ChLum |
| | <i>Alfilaria (Erodium cicutarium</i> [L] L'Her) | 0 33 | 5 h/day, 5 days/week, 12 weeks | Height (-2), mass of plant (+49), number of inflorescences (-6) ^e (Thompson et al , 1980) | GH | ChLum |
| | | 1 0 | 5 h/day, 5 days/week, 12 weeks | Height (-3), mass of plant (+26), number of inflorescences (+35) ^e (Thompson et al , 1980) | GH | ChLum |
| | | 0 11 | 5 h/day, 5 days/week, 16 weeks | Height (-9), mass of plant (-5), number of inflorescences (-16) (Thompson et al , 1980) | GH | ChLum |
| | Mint (<i>Mentha piperita</i> L) | 0 33 | 5 h/day, 5 days/week, 16 weeks | Height (+28*), mass of plant (+24), number of inflorescences (-2) (Thompson et al , 1980) | GH | ChLum |
| | | 1 0 | 5 h/day, 5 days/week, 16 weeks | Height (+8), mass of plant (0), number of inflorescences (-17) (Thompson et al , 1980) | GH | ChLum |
| | | 0 08 | 3 h/day, 56 days | Mass of plant (+4), mass of roots (-6), rooted cuttings (Runeckles and Palmer, 1987) | GH | Mast |
| | Scorpion weed (<i>Phacelia crenulata</i> Torr ex S Wats) | 0 11 | 5 h/day, 5 days/week, 17 weeks | Height (+9), mass of plant (-10), number of inflorescences (-5) (Thompson et al , 1980) | GH | ChLum |
| | | 0 33 | 5 h/day, 5 days/week, 17 weeks | Height (+3), mass of plant (+2), number of inflorescences (+2) (Thompson et al , 1980) | GH | ChLum |
| | | 1 0 | 5 h/day, 5 days/week, 17 weeks | Height (+20), mass of plant (+12), number of inflorescences (+4) (Thompson et al , 1980) | GH | ChLum |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | | Effect | Facility ^c | Monitor ^d |
|--|--------------------------------|--|-----------------------|----------------------|
| NO _x (ppm) | Exposure Duration | (% deviation from treatment without NO _x) ^b | | |
| <i>(Plantago insularis</i> Eastw) | | | | |
| 0 11 | 5 h/day, 5 days/week, 9 weeks | Height (-8), mass of plant (-26), number of inflorescences (-27) (Thompson et al , 1980) | GH | ChLum |
| | 17 weeks | Mass of plant (-36) (Thompson et al , 1980) | GH | ChLum |
| 0 33 | 5 h/day, 5 days/week, 9 weeks | Height (-8), mass of plant (-18), number of inflorescences (-8) (Thompson et al , 1980) | GH | ChLum |
| | 17 weeks | Mass of plant (-33) (Thompson et al , 1980) | GH | ChLum |
| 1 0 | 5 h/day, 5 days/week, 9 weeks | Height (-18*), mass of plant (-18), number of inflorescences (-19) (Thompson et al , 1980) | GH | ChLum |
| | 17 weeks | Mass of plant (-52*) (Thompson et al , 1980) | GH | ChLum |
| Broadleaved trees and shrubs | | | | |
| <i>White alder (Alnus incana</i> [L] Moench) | | | | |
| 0 1 | 104 h/week, 22 weeks | Stem height (+43*), leaf area (+38), mass of shoot (+24), second-year cuttings (Freer-Smith, 1984, Whitmore and Freer-Smith, 1982) | FE | ? |
| | 60 weeks | Stem height (+53**), mass of shoot (+65*), second-year cuttings (Whitmore and Freer-Smith, 1982) | FE | ? |
| <i>Burro weed (Ambrosia dumosa</i> [Gray] Payne) | | | | |
| 0 11 | 5 h/day, 5 days/week, 16 weeks | Linear growth (-15), mass of shoot (+1) (Thompson et al , 1980) | GH | ChLum |
| | 32 weeks | Linear growth (-3), mass of shoot (-5), mass of seed (-29*) (Thompson et al , 1980) | GH | ChLum |
| 0 33 | 5 h/day, 5 days/week, 16 weeks | Linear growth (-11), mass of shoot (+5) (Thompson et al , 1980) | GH | ChLum |
| | 32 weeks | Linear growth (-5), mass of shoot (-6), mass of seed (-59*) (Thompson et al , 1980) | GH | ChLum |
| 1 0 | 5 h/day, 5 days/week, 16 weeks | Linear growth (+10), mass of shoot (+10) (Thompson et al , 1980) | GH | ChLum |
| | 32 weeks | Linear growth (+3), mass of shoot (-6), mass of seed (-46*) (Thompson et al , 1980) | GH | ChLum |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|---|--------------------------|--------------------------------|--|-----------------------|----------------------|
| Four-wing saltbush (<i>Atriplex canescens</i> [Pursh] Mutt) | | | | | |
| | 0 11 | 5 h/day, 5 days/week, 16 weeks | Linear growth (+4), mass of shoot (+18*) (Thompson et al , 1980) | GH | ChLum |
| | | 32 weeks | Linear growth (+4), mass of shoot (+18) (Thompson et al , 1980) | GH | ChLum |
| | 0 33 | 5 h/day, 5 days/week, 16 weeks | Linear growth (+12), mass of shoot (+9) (Thompson et al , 1980) | GH | ChLum |
| | | 32 weeks | Linear growth (+12), mass of shoot (+19) (Thompson et al , 1980) | GH | ChLum |
| | 1 0 | 5 h/day, 5 days/week, 16 weeks | Linear growth (-6), mass of shoot (-1) (Thompson et al , 1980) | GH | ChLum |
| | | 32 weeks | Linear growth (-6), mass of shoot (+11) (Thompson et al , 1980) | GH | ChLum |
| European white birch (<i>Betula pendula</i> Roth) | | | | | |
| | 0 04 | 9 weeks | Mass of roots (+55 or +18), mass of stem (+54** or +11), mass of leaves (+45* or +9), stem height (+50** or +7), internode length (+38** or -1), effect depended upon photoperiod and light intensity, rooted cuttings (Freer-Smith, 1985) | CE | ? |
| | 0 05 | 4 weeks | Mass of roots (+43), mass of stem (+14), mass of leaves (+13), 1-mo-old seedlings (Freer-Smith, 1985) | CE | ? |
| | 0 1 | 104 h/week, 22 weeks | Stem height (+5*), leaf area (+17), mass of shoot (+15), second-year cuttings (Freer-Smith, 1984, Whitmore and Freer-Smith, 1982) | FE | ? |
| | | 60 weeks | Stem height (+4), mass of shoot (+15*), second-year cuttings (Whitmore and Freer-Smith, 1982) | FE | ? |
| | | 104 h/week, 10 mo | Mass of shoot (-11), mass of roots (-23) (Wright, 1987) | FE | ? |
| | | 13 mo | Height (0), stem diameter (+5), mass of shoot (+16), mass of roots (+14), different clone from above (Wright, 1987) | FE | ? |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|---|-----------------------------------|---|--|-----------------------|----------------------|
| Downy birch (<i>Betula pubescens</i> J F Ehrh) | | | | | |
| 0 1 | 104 h/week, 22 weeks | Stem height (-2), leaf area (+10), mass of shoot (+8), second-year cuttings (Freer-Smith, 1984, Whitmore and Freer-Smith, 1982) | FE | ? | |
| | 60 weeks | Stem height (+1), mass of shoot (-5), second-year cuttings (Whitmore and Freer-Smith, 1982) | FE | ? | |
| | 104 h/week, 2 mo | Height (-22) (Wright, 1987) | GH | ? | |
| | 13 mo | Height (-3), stem diameter (0), mass of shoot (+5), mass of roots (0) (Wright, 1987) | GH | ? | |
| Desert willow (<i>Chilopsis linearis</i> Cav) | | | | | |
| 0 11 | 5 h/day, 5 days/week, 16 weeks | Linear growth (-7), mass of shoot (-11) (Thompson et al , 1980) | GH | ChLum | |
| | 32 weeks | Linear growth (+10), mass of shoot (-17) (Thompson et al , 1980) | GH | ChLum | |
| 0 33 | 5 h/day, 5 days/week, 16 weeks | Linear growth (+8), mass of shoot (-9) (Thompson et al , 1980) | GH | ChLum | |
| | 32 weeks | Linear growth (-14) mass of shoot (-17) (Thompson et al , 1980) | GH | ChLum | |
| 1 0 | 5 h/day, 5 days/week, 16 weeks | Linear growth (-4), mass of shoot (-21) (Thompson et al , 1980) | GH | ChLum | |
| | 32 weeks | Linear growth (+19), mass of shoot (-33*) (Thompson et al , 1980) | GH | ChLum | |
| Camphor tree (<i>Cinnamomum camphora</i> 4[L] J Presl) | | | | | |
| 0 3 | 30 days | Mass of plant (+10), leaf area (+2), 1- to 2-year-old plants (Okano et al , 1989) | CE | ChLum | |
| Brittle bush (<i>Encelia farinosa</i> Gray ex Torr) | | | | | |
| 0 11 | 5 h/day, 5 days/week, 16 weeks | Linear growth (+9), mass of shoot (0) (Thompson et al , 1980) | GH | ChLum | |
| | 32 weeks | Linear growth (+23), mass of shoot (+3), inflorescences (-50*), number of leaves produced (+9) and abscized (+15) (Thompson et al , 1980) | GH | ChLum | |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | | Effect | Facility ^c | Monitor ^d |
|---|-----------------------------------|--|-----------------------|----------------------|
| NO _x (ppm) | Exposure Duration | (% deviation from treatment without NO _x) ^b | | |
| 0.33 | 5 h/day, 5 days/week, 16 weeks | Linear growth (+7), mass of shoot (-2) (Thompson et al , 1980) | GH | ChLum |
| | 32 weeks | Linear growth (+7), mass of shoot (+3), inflorescences (-31), number of leaves produced (+26*) and abscized (+50) (Thompson et al , 1980) | GH | ChLum |
| 1 0 | 5 h/day, 5 days/week, 16 weeks | Linear growth (+7), mass of shoot (+7) (Thompson et al , 1980) | GH | ChLum |
| | 32 weeks | Linear growth (+20), mass of shoot (+9), inflorescences (-83*), number of leaves produced (+28*) and abscized (+75*) (Thompson et al , 1980) | GH | ChLum |
| Spindle tree (<i>Euonymus japonica</i> Thunb) | | | | |
| 0 3 | 30 days | Mass of plant (+10), leaf area (-3), 1- to 2-year-old plants (Okano et al , 1989) | CE | ChLum |
| White ash (<i>Fraxinus americana</i> L) | | | | |
| 0 1 | 6 h/day, 28 days | Height (+5), shoot mass (-1), root mass (-27*), 6- to 8-week-old seedlings (Kress and Skelly, 1982) | CSTR/GH | ChLum |
| Green ash (<i>Fraxinus pennsylvanica</i> Marsh) | | | | |
| 0 1 | 6 h/day, 28 days | Height (+1), shoot mass (-10), root mass (-18), 6- to 8-week-old seedlings (Kress and Skelly, 1982) | CSTR/GH | ChLum |
| Creosote bush (<i>Larrea divaricata</i> Cav) | | | | |
| 0 11 | 5 h/day, 5 days/week, 16 weeks | Linear growth (+8) (Thompson et al , 1980) | GH | ChLum |
| | 32 weeks | Linear growth (+5), mass of shoot (+15) (Thompson et al , 1980) | GH | ChLum |
| 0 33 | 5 h/day, 5 days/week, 16 weeks | Linear growth (-11) (Thompson et al , 1980) | GH | ChLum |
| | 32 weeks | Linear growth (-4), mass of shoot (-2) (Thompson et al , 1980) | GH | ChLum |
| 1 0 | 5 h/day, 5 days/week, 16 weeks | Linear growth (-22) (Thompson et al , 1980) | GH | ChLum |
| | 32 weeks | Linear growth (-15), mass of shoot (-17) (Thompson et al , 1980) | GH | ChLum |
| Sweetgum (<i>Liquidambar styraciflua</i> L) | | | | |
| 0 1 | 6 h/day, 28 days | Height (-32), shoot mass (-25), root mass (-27*), 6- to 8-week-old seedlings (Kress and Skelly, 1982) | CSTR/GH | ChLum |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|---|--------------------------|--|---|-----------------------|----------------------|
| | | | | | |
| Common oleander (<i>Nerium oleander</i> L) | 0 3 | 30 days | Mass of plant (+17*), leaf area (+3), 1- to 2-year-old plants (Okano et al , 1989) | CE | ChLum |
| American sycamore (<i>Platanus occidentalis</i> L) | 0 1 | 6 h/day, 28 days | Height at end of exposure (+9 or -4) and two weeks later (+24 or +25), depended on family, 2- to 3-week-old seedlings (Kress et al , 1982b) | CE | ChLum |
| Carolina poplar (<i>Populus canadensis</i> Moench) | 0 5 | 1 h | Height (+9), number of leaves (+3), leaf area (+40*), mass of leaves (+34), mass of stem (+39), rooted cuttings, harvested 3 weeks later (Eastham and Ormrod, 1986) | CE | B952 |
| | 1 0 | 1 h | Height (-1*), number of leaves (-3), leaf area (+7), mass of leaves (-2), mass of stem (-4), rooted cuttings, harvested 3 weeks later (Eastam and Ormrod, 1986) | CE | B952 |
| Hybrid poplar (<i>Populus maximowiczii</i> x <i>Populus</i> sp) | 0 3 | 30 days | Mass of plant (+30**, +35**, or +29*), leaf area (+6, +19**, or +13), depended on clone, 1- to 2-year-old plants (Okano et al , 1989) | CE | ChLum |
| Black poplar (<i>Populus nigra</i> L) | 0 1 | 104 h/week, 22 weeks 60 weeks | Stem height (+3), leaf area (+15), mass of shoot (+18), second-year cuttings (Freer-Smith, 1984, Whitmore and Freer-Smith, 1982) Stem height (0), mass of shoot (-13), second-year cuttings (Whitmore and Freer-Smith, 1982) | FE FE | ? ? |
| | 0 11 | 104 h/week, 8 weeks 10 weeks 22 weeks | Growth in mass of leaves (-22), mass of stems (-14), mass of roots (-16), number of leaves (-43**), area per leaf (+45*), one-year cuttings (Freer-Smith, 1984, Whitmore et al , 1982) Mass of leaves (-27), mass of stems (-20), mass of roots (-21), during winter (Whitmore and Freer-Smith, 1982) Growth in mass of stem (-25), mass of roots (-38), one-year cuttings (Whitmore and Freer-Smith, 1982) | FE FE FE | ? ? ? |
| | 0 5 | 1 h | Height (+11), number of leaves (+7), leaf area (+38*), mass of leaves (+35*), mass of stem (+30*), rooted cuttings (Eastham and Ormrod, 1986) | CE | B952 |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|--|--------------------------|-------------------------|---|-----------------------|----------------------|
| | | | | | |
| | 1 0 | 1 h | Height (-6), number of leaves (-6), leaf area (+1), mass of leaves (-4), mass of stem (-7*), rooted cuttings (Eastham and Ormrod, 1986) | CE | B952 |
| Shira oak (<i>Quercus mysinaefolia</i> Blume) | | | | | |
| | 0 3 | 30 days | Mass of plant (+22), leaf area (-7), 1- to 2-year-old plant (Okano et al , 1989) | CE | ChLum |
| Willow oak (<i>Quercus phellos</i> L) | | | | | |
| | 0 1 | 6 h/day, 28 days | Height (-10), shoot mass (-24), root mass (-14), 6- to 8-week-old seedlings (Kress and Skelly, 1982) | CSTR/GH | ChLum |
| Small-leaved European linden (<i>Tilia cordata</i> Mill) | | | | | |
| | 0 1 | 104 h/week, 22 weeks | Stem height (+6), leaf area (+45*), mass of shoot (+42*), second-year seedlings (Freer-Smith, 1984, Whitmore and Freer-Smith, 1982) | FE | ? |
| | | 60 weeks | Stem height (+3), mass of shoot (-1), second-year cuttings (Whitmore and Freer-Smith, 1982) | FE | ? |
| Sweet birch (<i>Betula odoratissima</i> Ker-Gawl var <i>awabuki</i>) | | | | | |
| | 0 3 | 30 days | Mass of plant (+20), leaf area (-5), 1- to 2-year-old plants (Okano et al , 1989) | CE | ChLum |
| Japanese zelkova (<i>Zelkova serrata</i> [Thunb] Mak) | | | | | |
| | 0 3 | 30 days | Mass of plant (-6), leaf area (+1), 1- to 2-year-old plants (Okano et al , 1989) | CE | ChLum |
| Conifers | | | | | |
| European larch (<i>Larix decidua</i> L) | | | | | |
| | 1 0 | 537 h over 2 mo | No effect ^e (Zahn, 1975) | GH/FE | G-S |
| Norway spruce (<i>Picea abies</i> [L] Karst) | | | | | |
| | 1 3 | 1,900 h over 5 mo | Linear growth of current year (-7), linear growth of following year (-17) ^e (Zahn, 1975) | GH/FE | G-S |
| Sitka spruce (<i>Picea sitchensis</i> [Bong] Carr) | | | | | |
| | 0 03 | 8 weeks | Mass of plant (-5 to +18), advanced bud-break (*), 6-mo-old seedlings exposed during dormancy, harvested 6 weeks after exposure (Freer-Smith and Mansfield, 1987) | CE | ? |

**APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NITROGEN OXIDES ON GROWTH, REPRODUCTION,
AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS^a**

| Species or Crop | NO _x (ppm) | Exposure Duration | Effect (% deviation from treatment without NO _x) ^b | Facility ^c | Monitor ^d |
|--|--------------------------|----------------------|---|-----------------------|----------------------|
| Pitch pine (<i>Pinus rigida</i> Mill) | 0 1 | 6 h/day, 28 days | Height (-16), mass of shoot (-20), mass of roots (-11), 6- to 8-week-old seedlings (Kress and Skelly, 1982) | CSTR/GH | ChLum |
| Eastern white pine (<i>Pinus strobus</i> L) | 0 05 | 4 h/day, 35 days | Length of needles (<-10), 2-year-old ramets (Yang et al , 1982,1983b) | CSTR/GH | ChLum |
| | 0 1 | 4 h/day, 35 days | Length of needles (-13* to +17), mass of needles (-3*, -3, or 0), depended on clone, 2-year-old ramets (Yang et al , 1982,1983b) | CSTR/GH | ChLum |
| | 0 1-0 3 | 4 h/day, 35 days | Changes in length of needle (**) and in mass per unit length of needle (**), effects depended on clones (**), 2-year-old ramets (Yang et al , 1983a) | CSTR/GH | ChLum |
| Loblolly pine (<i>Pinus taeda</i> L) | 0 1 | 6 h/day, 35 days | Height (-11 or -15*), mass of shoot (-10 or -22), mass of roots (-14 or -17), depending on clone, 6- to 8-week-old seedlings (Kress and Skelly, 1982) | CSTR/GH | ChLum |
| Virginia pine (<i>Pinus virginiana</i> Mill) | 0 1 | 6 h/day, 28 days | Height (-13), mass of shoot (-1), mass of roots (-7), 6- to 8-week-old seedlings (Kress and Skelly, 1982) | | |

^aNO_x = Oxides of nitrogen

CO₂ = Carbon dioxide

^bStatistical significance of the effect, as provided in the source, is indicated by

* for 0 01 < α ≤ 0 05 and by ** for α ≤ 0 01

^cExperimental facilities are denoted by the following CE, controlled environment chamber, GH, greenhouse, FE, field exposure chamber, CSTR/GH, continuous-flow stirred-tank reactor in a greenhouse, ZAPS, zonal air pollution system in open field

^dMonitoring methods for NO_x are denoted by the following ChLum, gas-phase chemiluminescent devices, G-S, Griess-Saltzman method, L-G-S, Lyshkow-modified Griess-Saltzman method, B852, B942, or B952, Beckman 852, 942A, or 952A monitors, Saltzman, impingement in Saltzman reagent, Mast TM, Mast meter by triethanolamine method, CSI, Columbia Scientific, Model 1600 Monitor, Mast, Mast meter, TM, triethanolamine method, Atlas, Atlas meter

^eStatistical information not provided

^fNO (with NO₂ at 0 15 ppm)

^gNO₂ at 0 15 + NO at 0 7 ppm

^h20% NO₂ and 80% NO

ⁱNO (with NO₂ at 0 05 ppm)

^jNO

^kNO₂ at 0 5 + NO at 0 4 ppm

^lControl was NO₂ at 0 009 ppm, background SO₂ at 0 003 ppm

^mNO₂ at 0 006 + NO at 0 012 ppm

ⁿNO₂ at 0 021 + NO at 0 007 ppm

^oRange of 0 to 0 2 ppm

10. THE EFFECTS OF NITROGEN OXIDES ON NATURAL ECOSYSTEMS AND THEIR COMPONENTS

10.1 INTRODUCTION

The previous chapter discusses the responses of individual plants exposed to nitrogen oxides (NO_x), which refers to nitric oxide (NO) plus nitrogen dioxide (NO_2). This chapter explains the known effects of nitrogen compounds (e.g., NO_x , nitrate, nitric acid [HNO_3]) on terrestrial and aquatic communities. Because the various ecosystem components are chemically interrelated, stresses placed on the individual components, such as those caused by nitrogen loading, can produce perturbations that are not readily reversed and will significantly alter an ecosystem.

It is known that in many areas of the United States, the deposition of atmospheric nitrogen compounds is significant (U.S. Environmental Protection Agency, 1982), and, since the mid-1980s, the view has emerged that the atmospheric deposition of inorganic nitrogen has impacted both aquatic and terrestrial ecosystems, however, the impacts are generally unknown. Although the evidence linking nitrogen deposition with ecological impacts is tenuous, there has been a growing concern (Skeffington and Wilson, 1988) that the continuous deposition of atmospheric nitrogen compounds (particularly HNO_3 and nitrate ions [NO_3^-]) in North America and most European countries has led to ecosystems formerly limited by nitrogen becoming nitrogen saturated. Though the trend for the composite United States annual average atmospheric NO_2 concentration is downward, it is the deposited nitrate that determines ecosystem response. The above concern has led to attempts in Europe to develop "critical loads" of nitrogen for various ecosystems. A critical load is defined as "a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge" (Nilsson and Grennfelt, 1988).

The above concerns and the known effects of nitrogen compounds are addressed as follows: (1) overview and description and responses of ecosystems to impairment of functions, (2) a generalized description of the nitrogen cycle, (3) deposition of nitrogen into ecosystems, (4) terrestrial ecosystem effects, specifically the response of soil and vegetation.

to nitrogen deposition, (5) effects of nitrogen loading on wetlands and bogs, and (6) discussion of the effects of nitrogen loading on aquatic ecosystems

10.2 ECOSYSTEMS

Ecosystems are composed of populations of "self-supporting" and "self-maintaining" living plants, animals, and microorganisms interacting among themselves and with the nonliving chemical and physical environment within which they exist (Odum, 1989, Billings, 1978; Smith, 1980) Ecosystems usually have definable limits and may be large or small (e.g , fallen logs, forests, grasslands, cultivated or uncultivated fields, ponds, lakes, rivers, estuaries, oceans, the earth) (Odum, 1971, Smith, 1980, Barbour et al , 1980) The environmental conditions of a particular area or region determine the boundaries of the ecosystem as well as the organisms that can live there (Smith, 1980) Together, the environment, the organisms, and the physiological processes resulting from their interactions form the life-support systems that are essential to the existence of any species on earth, including man (Odum, 1989)

Human welfare is dependent on ecological systems and processes Natural ecosystems are traditionally spoken of in terms of their structure and functions Ecosystem structure includes the species (richness and abundance) and their mass and arrangement in an ecosystem. This is termed an ecosystem's standing stock—nature's free "goods" (Westman, 1977) Society reaps two kinds of benefits from the structural aspects of an ecosystem (1) products with market value such as fish, minerals, forest products and pharmaceuticals, and genetic resources of valuable species (e g , plants for crops and timber and animals for domestication), and (2) the use and appreciation of ecosystems for recreation, aesthetic enjoyment, and study (Westman, 1977)

More difficult to comprehend, but no less vital, are the functional aspects of an ecosystem. They are the dynamics of ecosystems and impart to society a variety of benefits, nature's free "services" Ecosystem functions encompass the interactions of the ecosystem components and their environment and maintain clean air, pure water, a green earth, and a balance of creatures, the functions that enable humans to obtain the food, fiber, energy, and other material needs for survival (Westman, 1977)

10.2.1 Characteristics of Ecosystems

Ecosystems have both structure and function. Structure within ecosystems involves several levels of organization. The most visible are (1) the individual and its environment, (2) the population and its environment, and (3) the biological community and its environment, the ecosystem (Billings, 1978). The responses of the constituent organisms to environmental changes or perturbations determine the response of the ecosystem. Populations of plants, animals, and microorganisms (producers, consumers, and decomposers) within an ecosystem live together and interact as communities. Communities, due to the interaction of their populations and of the individuals that constitute them, respond to pollutant stresses differently from individuals. Organisms vary in their ability to withstand environmental changes. The range of variation within which individual organisms can exist and function determines the ability of a population of organisms to survive.

Intense competition among plants for light, water, nutrients, and space, along with recurrent natural climatic (temperature) and biological (herbivory, disease) stresses, can alter the species composition of communities by eliminating those individuals sensitive to specific stresses. Those organisms able to cope with the stresses survive and reproduce. Competition among plants of the same species does not influence species succession (community change over time). Competition among different species, however, results in succession and ultimately produces ecosystems composed of populations of plant species that have a capacity to tolerate the competition stresses (Kozłowski, 1980). Pollutant stresses are superimposed upon the naturally occurring competition stresses mentioned above. Air pollutants are known to alter the diversity and structure of plant communities (Guderian et al., 1985). The primary effect of air pollutants is on the more susceptible members of the plant community in that they can no longer compete effectively for essential nutrients, water, light, space, etc. As a consequence of altered competitive conditions in the community, there is a decline in the sensitive species, permitting the enhanced growth of more tolerant species. The extent of change that may occur in a community depends on the condition and type of community as well as the pollutant exposure.

10.2.2 Ecosystem Functions

Ecosystem function refers to the suite of processes and interactions among the ecosystem components and their environment that involve movement of nutrients and energy through a community as organic matter. The more nutrients are available, the more energy flows. Hydrological, gaseous, and sedimentary cycles are involved. Water is the medium by which nutrients make their never-ending odyssey through an ecosystem (Smith, 1980). In gaseous cycles, which include carbon, oxygen, and nitrogen, the atmosphere is the primary reservoir, and in sedimentary cycles, phosphorus, sulfur, calcium, magnesium, and potassium move from the land to the sea and back.

Vegetation, through the process of photosynthesis, plays a very important role in energy and nutrient transfer. Plants accumulate, use, and store carbon, the basic building blocks of large organic molecules, to maintain physiological processes and to form their structure. During photosynthesis, plants utilize energy from sunlight to convert carbon dioxide (CO₂) from the atmosphere and water from the soil into carbohydrates. Carbohydrates serve as the raw material for further biochemical synthesis (Waring and Schlesinger, 1985).

The energy accumulated and stored by vegetation also is available to other organisms such as herbivores, carnivores, and decomposers. Energy and nutrients move from organism to organism in food chains or food webs that become more complex as ecosystem diversity increases (Odum, 1989). Energy flow through the biological food chains is unidirectional. Ultimately, it is dissipated into the atmosphere as heat and must be replaced (Barbour et al., 1980; Billings, 1978; Odum, 1989). Nutrients and water can be recycled, fed back into the system, and used over and over again (Barbour et al., 1980; Odum, 1989). The plant processes of photosynthesis, nutrient uptake, respiration, translocation, carbon allocation, and biosynthesis are directly related to the ecosystem functions of energy flow and nutrient cycling. Reduction in diversity and structure in ecosystems shortens the food chains, reduces the total nutrient inventory, and returns the ecosystem to a simpler successional stage (Woodwell, 1970).

10.2.3 Ecosystem Response: Impairment of Functions, Changes in Structure

Ecosystems respond to stresses through their constituent organisms. In plant communities, individual species differ appreciably in their sensitivity to stresses, the changes that occur within plant communities reflect such differences. The response of plant populations or species to environmental perturbation depends on their genetic constitution (genotype), their life cycles, and the microhabitats in which the plants are growing. Stresses such as changes in the physical or chemical environment of plant populations apply new selection pressures on individual organisms (Treshow, 1980). A common response in a community under stress is the elimination of the more sensitive populations and an increase in abundance of species that tolerate or are favored by the stress (Woodwell, 1970, Guderian et al., 1985).

Factors that influence the rate or amount of energy flow or of nutrient cycling alter the relationships that exist between organisms and their nonliving environment. Air pollutants, for example, that limit carbon fixation will shift allocation to new leaves, whereas factors that limit the availability of nitrogen or water will shift allocation to the roots (Winner and Atkinson, 1986). Such subtle and indirect effects of pollutant exposures, by inhibiting or altering plant physiological processes, decrease the ability of organisms to compete. Increasing pollutant stresses provide selective forces that favor some genotypes, suppress others, and eliminate those species that lack sufficient genetic diversity to survive. Removal of these organisms from an ecosystem can impair ecosystem functions and set the stage for changes in community structure that possibly may have irreversible consequences (Guderian and Kueppers, 1980).

Abundant evidence exists to show that plant communities undergo structural changes that reduce biological variation when resistant species become dominant (Miller, 1973, Smith, 1980, Treshow, 1980, Woodwell, 1970). In forest communities, the selective removal of the larger overstory plants in favor of plants of small stature results in a shift from a complex forest community to the less complex hardy shrub and herb communities (Woodwell, 1970, Miller, 1973). Thus, there is a change in the occurrence, size, and distribution of plants, in species interactions, and in community composition, and the

processes of energy flow and nutrient cycling are altered. Ultimately, the basic structure of the ecosystem is also changed.

Predicting the effects of nitrogen compounds from anthropogenic sources on natural ecosystems involves uncertainties because (1) it is difficult to accurately determine the atmospheric nitrogen deposition, (2) less is known concerning the response of nonagricultural plant communities to increased supplies of fixed nitrogen than for agricultural crops, and finally, (3) the effects of nitrogen saturation have been studied for only a short time.

The next section outlines the nitrogen cycle and mentions changes in the cycle that may result from the increasing additions of nitrogen. The subsequent sections discuss the observed effects of increased nitrogen deposition on terrestrial, wetland, and aquatic ecosystems and the changes in the nitrogen cycle that have, thus far, been demonstrated.

10.3 THE NITROGEN CYCLE

Nitrogen, one of the main constituents of the protein molecules essential to all life, is recycled within ecosystems. Most organisms cannot use the molecular nitrogen found in the earth's atmosphere. It must be transformed by specific terrestrial and aquatic microorganisms into a form usable by other organisms. The transformations of nitrogen as it moves through an ecosystem is referred to as the nitrogen cycle (National Research Council, 1978). Mature natural ecosystems are essentially self-sufficient and independent of external additions. Modern technology, by either adding or removing nitrogen from an ecosystem, can upset the relationships that exist among the various components and, thus, change its structure and functioning.

Nitrogen usually enters plants through the roots by (1) absorption of ammonia and ammonium, (2) absorption of nitrate (and nitrite), and (3) nitrogen fixation by symbiotic organisms. Therefore, any nitrogen deposited onto the soil that can be converted chemically or biologically into ammonia, nitrate, or nitrite can be used by plants. Nitrogen oxides that fall upon soil have the potential for conversion and adsorption by microbial or chemical action and can enter plants easily through the soil/root interface. Soil-deposited nitrogen, however, can overload the soil/plant system (see below). Gaseous NO_x that enters through

the leaves can also be converted for plant use because most leaves have enzyme systems that can handle the compounds derived from NO_x (see Chapter 9)

The term nitrogen cycle (Figure 10-1) is used to refer to the transformations of nitrogen as it moves through the environment. In general outline, the nitrogen cycle is identical in terrestrial, freshwater, and oceanic habitats, only the microorganisms that mediate the various transformations are different (Alexander, 1977). In terrestrial and aquatic ecosystems, the major nonbiological processes of the nitrogen cycle involve phase transformations rather than chemical reactions. These transformations include (1) volatilization of gaseous nitrogen forms (e.g., ammonia $[\text{NH}_3]$), (2) sedimentation of particulate forms of inorganic nitrogen, and (3) sorption (e.g., of ammonium ions $[\text{NH}_4^+]$ by clays) (National Research Council, 1978). In general, the steps in the nitrogen cycle are as follows: (1) nitrogen fixation, (2) assimilation, (3) ammonification, (4) nitrification, and (5) denitrification. These biological transformations involved in the nitrogen cycle will be discussed below.

Under natural conditions, nitrogen is added to ecosystems by fixation of atmospheric nitrogen, deposition in rain, from windblown aerosols containing both organic and inorganic nitrogen, and from the absorption of atmospheric NH_3 by plants and soil (Smith, 1980). Nitrogen fixation, the conversion of molecular nitrogen into a biologically available form, is mediated almost entirely by microorganisms in both terrestrial and aquatic habitats (Alexander, 1977).

Plants vary greatly in their ability to absorb ammonium and nitrate, however, they can utilize nitrogen in either form with equal efficiency and either form can be converted into amino acids, protein, and nucleic acids. The organic nitrogen in plants is transferred to herbivores when they eat plants. Herbivores may in turn be eaten and the nitrogen utilized by their predators. The urea and excreta of animals and the organic remains of dead plants and animals are eventually decomposed by microorganisms and transformed into NH_3 . Ammonia gas may be (1) volatilized into the atmosphere, (2) converted into nitrates by bacteria, (3) absorbed by plants, or (4) leached into streams, lakes, or eventually the ocean, where it is available for use in aquatic ecosystems.

Modern technology is perturbing the cycle by altering the amounts and fluxes of nitrogen in the various portions of the cycle. For example, increased NO_x emissions from

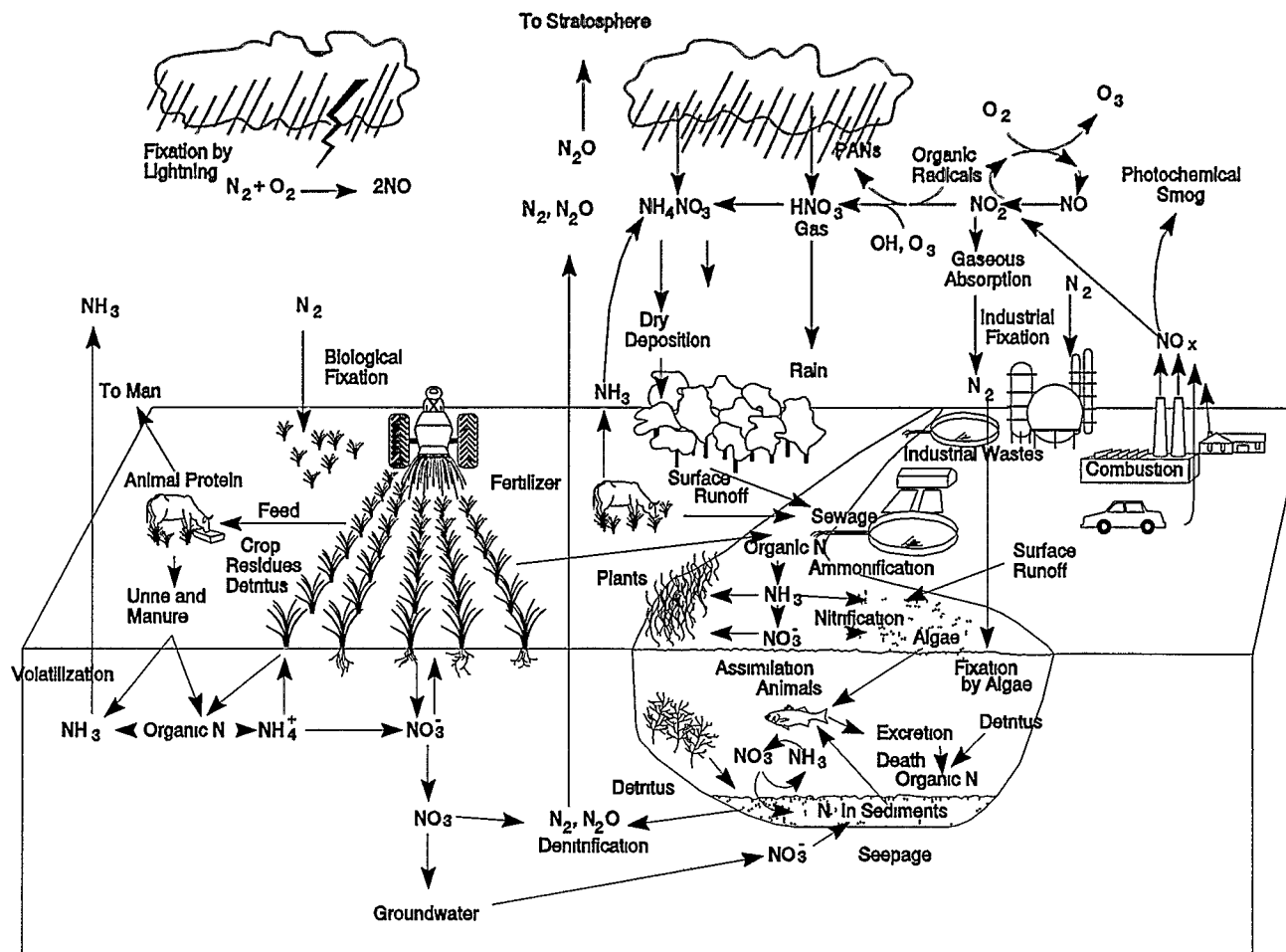


Figure 10-1. Schematic representation of the nitrogen cycle, emphasizing human activities that affect fluxes of nitrogen. The figure depicts possible sources of nitrogen fluxes. Transformations are qualitative, not quantitative.

Source Modified from National Research Council (1978)

transportation and stationary fossil-fuel burning sources over the past 50 years have increased the wet and dry deposition of nitrates and the amount of nitrogen moving through terrestrial and aquatic nitrogen cycles. The recent annual average atmospheric NO_2 concentration trend has been downward, however, the response of the nitrogen cycles is to deposited nitrogen. Crops can utilize only a proportion of the nitrogen fertilizers (containing nitrates, ammonium salts, anhydrous or liquid NH_3 , or urea) added to the agricultural soils, leaching and runoff results (Sprenst, 1987). Also, NH_3 emissions from livestock feedlots have increased the nitrogen moving through the nitrogen cycle. Harvesting of crops, on the other hand, removes nitrogen from agroecosystems and makes them dependent on the addition of inorganic nitrogen fertilizers (Bolin and Arrhenius, 1977). Timber harvesting also removes nitrogen and disrupts the soil-plant-microorganism relationships. Forest clear-cutting increases the loss of nitrates in soil water (Bowden and Bormann, 1986). Burning of the residues left after timber removal may lead to further nitrogen loss (Vitousek, 1981).

10.3.1 Biological Nitrogen Fixation

Nitrogen fixation, the conversion of molecular nitrogen gas (N_2) to NH_4^+ , is accomplished by a limited number of free-living and symbiotic (living in the roots of plants) bacteria and by a number of blue-green algae. Blue-green algae are widely distributed in nature in terrestrial, freshwater, and marine habitats. A number form the algal component of lichens, a few algae are symbiotic living with liverworts, ferns, and cycads, and others, as symbionts, fix nitrogen in the roots of plants. The NH_3 formed is available to plants and other microorganisms. Nitrogen fixation is essential in the maintenance of soil fertility in terrestrial, aquatic, and agricultural ecosystems.

10.3.2 Assimilation

Plants assimilate inorganic nitrogen from the soil and convert it into organic nitrogen. All plants, except certain bog and wetland species, are able to assimilate inorganic nitrogen as either ammonium or nitrate and to convert them into organic molecules such as amino acids, proteins, and nucleic acids. Bacteria are also important assimilators of inorganic nitrogen in the soil, whereas algae are the predominant assimilators of inorganic nitrogen in aquatic habitats. Most plants utilize ammonium more readily than nitrate, however, if no

other factors limit microbial growth, microorganisms will scavenge the available ammonium, making it unavailable. Under these circumstances, nitrate becomes the most important source of nitrogen for plants (Rosswall, 1981).

10.3.3 Ammonification (Mineralization)

Bacteria and fungi form ammonium during the decomposition of dead plants and animals. Proteins in dead plants and animals, as well as the excretion products of animals, are decomposed to amino acids. The nitrogen in amino acids in turn is converted into ammonium. The ammonium may be (1) assimilated by terrestrial or aquatic plants and microorganisms, (2) bound by clay particles in the soil, or (3) converted into nitrates by microorganisms during nitrification. Ammonification is important in renewing the limited supply of inorganic nitrogen utilizable by plants.

During ammonification, gaseous NH_3 may escape into the atmosphere during the process. Its volatilization is a purely physical process whereby NH_3 , in equilibrium with NH_4^+ in solution, is lost as a gas. Gaseous losses are significant if pH is below 7.5 (Reddy and Patrick, 1984). Ammonia volatilization can be mediated by biological activity to the extent that organisms can alter the pH of their environment. Ammonia losses from wetlands are normally significant because submerged and wetland soils generally have pH values between 5.0 and 7.2 (Ponnanperuma, 1972).

10.3.4 Nitrification

Nitrification is the two-step process during which microorganisms first convert NH_4^+ to nitrite ions (NO_2^-) and then to NO_3^- . In the first step, several genera of bacteria (including the genus *Nitrosomonas*) reduce ammonium to nitrite. The second step is accomplished by several genera of bacteria (including *Nitrobacter*) that reduce nitrite to nitrate (Reddy and Patrick, 1984, Atlas and Bartha, 1981). Nitrification is strictly an aerobic process and only oxygen can serve as the electron acceptor. Nitrification can occur in manure piles, during sewage processing, in soil, and in marine environments in the oxygenated water column above the anaerobic sediments or within the surface of oxidized layers of sediments. Recent studies suggest that nitrous oxide (N_2O) is produced during

nitrification Bowden (1986) points out, however, that in the field, N_2O production via nitrification is controlled by the oxidation status of the soil.

Other than atmospheric transformations of NO_x to nitrates, nitrification is the sole natural source of nitrate in the biosphere (National Research Council, 1978) Nitrate is the predominant nitrogenous ion in precipitation (U S Environmental Protection Agency, 1982) It is at this stage that the nitrogen cycle has been most influenced through agricultural practices (Delwiche, 1977, Bolin and Arrhenius, 1977) Natural processes are unable to produce sufficient nitrogen to grow the crops needed to feed humanity This has led to the development and increasing use of industrially made fertilizers In 1970, Delwiche (1970) estimated that the amount of nitrogen fixed annually since 1950 for the production of fertilizer equaled the amount that was fixed by all terrestrial ecosystems before the advent of modern agriculture

Nitrates, whether added to the soil (1) as fertilizers, (2) by nitrification, or (3) from atmospheric deposition, may

- be utilized by microorganisms,
- be taken up by plants,
- be lost through surface runoff into streams, rivers, lakes, wetlands, or oceans,
- percolate into groundwater, or
- escape as gas to the atmosphere (Buckman and Brady, 1969)

10.3.5 Denitrification

Denitrification is an anaerobic bacterial process during which nitrates are converted into atmospheric nitrogen gas Nitrates are converted into nitrites, then gaseous N_2O , and finally into N_2 , which escapes into the atmosphere Under acidic conditions in the soil, nitrites rarely accumulate, but are spontaneously decomposed into NO Under alkaline conditions, they are biologically converted into N_2O and N_2 (Alexander, 1977)

Through denitrification, nitrogen becomes unavailable to most plants and microorganisms because it enters the large atmospheric reservoir, where its residence time may be as long as 10^7 years (Delwiche, 1977) Nitrous oxide has a much shorter residence time (150 years) The photochemical decomposition of N_2O is the main stratospheric source of NO_x (Delwiche, 1977)

Nitrogen resides in five major reservoirs (1) primary rocks, (2) sedimentary rocks, (3) deep-sea sediment, (4) the atmosphere, and (5) the soil-water pool. The web of pathways and fluxes by which oxides of nitrogen are produced, transformed, transported, and stored in the principal nitrogen reservoirs are commonly referred to as the nitrogen cycle and are outlined above. An understanding of the nitrogen cycle is important in placing in perspective human intervention as discussed in other sections of this chapter.

10.4 DRY DEPOSITION RATES OF REACTIVE NITROGEN FORMS

Deposition processes result in the removal of reactive nitrogen compounds from the atmosphere, and their subsequent deposition onto landscape surfaces (e.g., foliage, bark, soil). The fate of dry deposited compounds can be either adsorption to surfaces or absorption (i.e., uptake or incorporation) by surfaces. By quantifying the link between atmospheric processes and deposition of pollutants to plants, deposition measurements provide valuable input data for models of atmospheric chemistry and biogeochemical cycling, and may help explain how pollutants affect plants (Baldocchi et al., 1987, 1988, Hosker and Lindberg, 1982; Taylor et al., 1988). The following discussion is based on Hanson and Lindberg (1991).

Dry deposition characteristics of NO_2 , NO , HNO_3 vapor, NH_3 , and particle forms (NO_3^- and NH_4^+) have been reported in the literature and are discussed in the following sections. Ammonia is not an oxide of nitrogen, but when present at high concentrations in the atmosphere, it contributes to the total amount of nitrogen deposited on landscape surfaces, and by dissolving in aerosols, NH_3 may enhance HNO_3 removal in wet precipitation (Erisman et al., 1988). Therefore, NH_3 deposition data are included here. The dry deposition velocity of HNO_3 is greater than that of ammonium nitrate (NH_4NO_3) and is scavenged by precipitation more efficiently than NH_4NO_3 . Deposition data are unavailable for other potentially important reactive forms of nitrogen: nitrous acid, dinitrogen pentoxide, and the gaseous nitrate radical (NO_3). Peroxynitrate species, such as peroxyacetyl nitrate (PAN), will not be discussed because they are described in another Air Quality Criteria Document (U.S. Environmental Protection Agency, 1986). Nitrous oxide, the most abundant

oxide of nitrogen, will not be discussed because it is virtually inert in the troposphere and shows no tendency for deposition (Singh, 1987)

Garner et al (1989) summarized available information on ambient air concentrations for NO_x and made the following conclusions

- 1 Nitrogen oxides are rarely if ever found in concentrations sufficient to cause visible injury to vegetation
- 2 In high elevation forests typically away from urban sources of pollution, concentrations of NO_x are usually below or at the detection limits of available monitoring equipment (concentrations range from <0.003 ppm to occasional peaks of 0.05 ppm)
- 3 In near-urban or rural forests, concentrations seldom exceed 0.010 ppm (overall range from <0.005 to 0.3 ppm)
- 4 In urban areas of eastern North America, annual average NO_x concentrations are around 0.02 ppm, with values ranging from <0.005 to 0.06 ppm

A number of recent studies in remote areas have shown that air concentrations of NO, NO₂, and HNO₃ are commonly less than 0.005 ppm, with HNO₃ concentrations typically being lower (Cadle et al , 1982, Fahey et al , 1986, Kelly et al , 1984, Lefohn and Tingey, 1984) In rural areas closer to sources of urban pollution, NO₂ and HNO₃ concentrations have been measured in the 0.010- to 0.030-ppm and 0.001- to 0.003-ppm ranges, respectively (Bytnerowicz et al , 1987a, Kelly et al , 1989, Lefohn and Tingey, 1984) A detailed summary of current information on the air chemistry and concentrations of reactive nitrogen compounds can be found in Chapters 5 and 7 of this document

There are several general review articles for additional information on the deposition of nitrogen forms to vegetation and other landscape surfaces Hosker and Lindberg (1982) discuss factors controlling pollutant deposition and capabilities for predicting interactions between atmospheric substances and vegetation McMahon and Denison (1979) provide a more extensive summary of particle deposition Sehmel (1980) summarizes particle and gas dry deposition for a wide range of depositing materials Taylor et al (1988) review pollutant deposition to individual leaves and plant canopies with particular emphasis on physiological sites of regulation The World Health Organization (1987) also provides an extended

discussion of deposition of nitrogen forms important to the establishment of air quality guidelines.

10.4.1 Types of Measurements

Dry deposition measurements have been conducted in the field at the forest canopy level or in chambers using individual plant leaves (Van Aalst and Diederer, 1985). Canopy level measurements are based on the assumption that deposition is a vertical flux from the atmosphere to a defined landscape area restricted by a series of pathway resistances. Leaf-level measurements in chambers, which ignore the atmospheric transport process by inducing turbulent mixing above the surface of leaves, also assume a series of resistances to pollutant gas deposition. Leaf-level and canopy measurements are normalized to leaf and ground areas, respectively.

Canopy measurements typically employ either the eddy correlation or the flux gradient micrometeorological techniques. Both techniques require that measurements be conducted under ideal conditions (e.g., flat, homogeneous, and extensive landscape area), but some progress in applying these techniques to more complex terrain has been made (McMillen, 1988; Hicks et al., 1984). The eddy correlation technique measures vertical, turbulent flux directly from calculations of the mean covariance between wind velocity and pollutant concentration (Wesely et al., 1982). The flux gradient or "profile" technique estimates vertical flux from a concentration profile and eddy exchange coefficients (Erisman et al., 1988; Huebert et al., 1988). One of the most difficult problems with dry deposition estimates of nitrogen species, based on micrometeorological methods, stems from the inability to measure the appropriate atmospheric concentrations. Homogeneous gas phase reactions and gas/particle interactions of HNO_3 and NH_3 (Appel and Tokiwa, 1981), and interferences of HNO_3 with some NO_x sensors (Van Aalst and Diederer, 1985) are two examples of the problems often encountered. Many nitrogen species are so reactive in the canopy air space that their concentrations change significantly during the course of micrometeorological measurements, resulting in misleading flux data (Hicks et al., 1989). Businger (1986) and Baldocchi (1988) provide more extensive discussions of the benefits and/or pitfalls of the canopy measurement techniques.

Comparisons between throughfall or precipitation NO_3^- and NH_4^+ concentrations have also been used to calculate particulate nitrogen deposition to forest canopies (Gravenhorst et al , 1983, Lovett and Lindberg, 1984) However, the reactivity of trace nitrogen gases, their absorption by foliar surfaces (Norby et al , 1989, Garten and Hanson, 1990), and the technique's inability to distinguish gaseous from particle forms (e g , NO_3^- versus HNO_3) may lead to large errors

Three techniques have been used for leaf-level measurements The most common approach is based on mass-balance principles in which the leaf surface is enclosed in an environmentally controlled chamber and pollutant concentrations are compared at the inlet and outlet (Jarvis et al , 1971) The mass-balance technique can be applied to individual leaves and branches (Rogers et al , 1977, Rowland-Bamford and Drew, 1988) or to enclosed crop canopies (Bennett and Hill, 1973, Hill, 1971) Less commonly, isotopic labeling of the exposure gas with nitrogen-15 (^{15}N) has been used to evaluate rates of deposition (Okano et al , 1988, Vose and Swank, 1990) Leaf-washing techniques compare extracts from leaves exposed to pollutants and appropriate controls The difference in ion concentrations between treated and control wash solutions is used to calculate rates of deposition (John et al , 1985, Dasch, 1987) Leaf-wash techniques may underestimate deposition because absorption or translocation processes remove pollutants from the leaf surface (Taylor et al , 1988, Garten and Hanson, 1990) Further, the leaf-wash method can not distinguish various sources of nitrate deposited as HNO_3 , NO_3 , or particulate NO_3^- (Dasch, 1987)

10.4.2 Expressions of Deposition

Rates of pollutant deposition determined from canopy or leaf level measurements can be expressed with similar equations The rate of deposition of pollutant gases to a canopy surface has been defined as

$$F_c = V_d * (C_z - C_o), \quad (10-1)$$

where F_c is flux to the canopy (in nanomoles per square meter per second), V_d is the overall deposition velocity (in meters per second), C_z is the concentration at the height of the measurement (in nanomoles per cubic meter), and C_o is the concentration at receptor sites in

the canopy (in nanomoles per cubic meter) The V_d is the reciprocal of the total canopy resistance to flux An analogous equation can be derived for leaf-level, chamber measurements.

$$F_1 = K_1 * (C_a - C_l), \quad (10-2)$$

where F_1 is flux to leaves, K_1 is the conductance of the leaf to pollutant gas transfer, C_a is the concentration of pollutant in the air around the leaf, and C_l is the concentration of pollutant in or on the leaf (often equal to 0)

Both V_d and K_1 represent concentration corrected deposition rates, and they are the standard variables used to compare deposition characteristics of pollutant gases and receptor surfaces Although V_d and K_1 have the same units, they are based on different receptor areas and characterize processes at different scales of resolution Therefore, the following conversion has been suggested as a first approximation for scaling between canopy and leaf measurements of pollutant deposition so that data obtained with either technique can be compared.

$$V_d = K_1 * LAI, \quad (10-3)$$

where LAI is the leaf area index of the canopy appropriate to the V_d variable (Dasch, 1987, Dolske, 1988; Hanson et al , 1989, Hicks et al , 1987, Jarvis, 1971, O'Dell et al , 1977) For a given plant material and defined exposure, V_d should always be larger than K_1 when canopy leaf area index is greater than one This first-order conversion is admittedly crude, but useful. Complex models are required to rigorously scale measured K_1 data to application at the canopy level of resolution (Baldocchi, 1988, Baldocchi et al , 1987, Hicks et al , 1987; Kramm, 1989) because nonlinear processes are involved and driving variables change with depth in the canopy

10.4.3 Processes Governing Deposition of Gases and Particles

Dry deposition of gases and particles to foliar and nonfoliar surfaces refers to the transfer of nitrogen species between the free atmosphere and landscape surfaces Dry deposition processes need to be understood because they represent the first step in the

transfer of pollutants to physiological sites of action in the leaf interior (Taylor et al , 1988) that are responsible for most deleterious effects on plants Detailed discussions of the factors influencing dry deposition of gases and particles have been published (Hosker and Lindberg, 1982, Sehmel, 1980, Taylor et al , 1988) The reader is also directed to Section 10 4 4 for additional discussion of reactive nitrogen gas deposition to leaves and leaf interior spaces

Pollutant gas deposition to plant surfaces is controlled by atmospheric turbulence, physical and/or chemical properties of gases, the presence of a chemical potential gradient between the atmosphere and receptor sites, and the nature and activity of plant surfaces (Table 10-1) Hosker and Lindberg (1982) divided gaseous pollutant compounds into three groups, based on the processes governing their deposition, and assigned reactive nitrogen compounds to each group as shown below

- (1) Compounds able to adsorb readily to all surfaces (HNO_3 , NH_3)
- (2) Compounds that interact with leaves primarily after diffusion through stomata into interior leaf air spaces (NO_2 , and to some extent, NH_3)
- (3) Compounds that exchange slowly with plants independent of the pathway for deposition (NO , N_2O)

Recent data (Kisser-Priesack et al , 1987) suggest that NO_2 and NO are also deposited onto and through the cuticle, a feature appropriate to Hosker and Lindberg's Category #1 compounds

The theory of particle deposition has been described and discussed in depth in several recent papers (Davidson and Wu, 1990, McMahon and Denison, 1979, Nicholson, 1988, Sehmel, 1980) These authors propose three characteristic features of dry particle deposition

- (1) particles greater than $10\text{ }\mu\text{m}$ exhibit a variable V_d between 5 and 110 mm/s dependent on frictional velocities, whereas a minimum particle V_d has been shown for particles in the size range 0.1 to 1.0 μm (Figure 10-2),

**TABLE 10-1. FACTORS INFLUENCING DRY DEPOSITION
OF REACTIVE NITROGEN COMPOUNDS**

| Micrometeorological Variables | Chemical Properties of Depositing Material | | Receptor |
|-------------------------------|--|------------------------------|-------------------------|
| | Particles | Gases | Surface Variables |
| Aerodynamic resistance | Particle size | Partial | <u>Abiotic features</u> |
| -mass transfer | -diameter | Pressure | |
| -heat | -density | -solubility | Accommodation |
| -momentum | - | - | -dew |
| -1/deposition velocity | agglomeration | concentration | -exudates |
| | | Chemical activity/ reactions | -wax |
| | | | -pubescence |
| Diffusion effect of | Diffusion | Diffusion | Reactive sites |
| -canopy structure | -Brownian | -molecular | -area |
| -extent of fetch | -eddy | | -prior loading |
| | Impaction | | -adsorption |
| | | | -absorption |
| Friction velocity | Gravitational settling | | |
| Surface roughness length | | | |
| Zero plane displacement | | | |
| Wind velocity | Electrostatic effects | | |
| Turbulence | | | |
| Temperature | | | <u>Biotic features</u> |
| | | | Stomatal |
| | | | -conductance |
| | | | -diurnal pattern |
| Relative humidity | | | Plant metabolic rate |
| | | | -assimilation |
| | | | -cell pH |
| Precipitation | | | |
| Solar radiation | | | |

Source: Sehmel (1980)

- (2) deposition velocity of particles (V_d) is approximately a linear function of friction velocity, and
- (3) deposition of particles between the atmosphere and a forest canopy is from 2 to 16 times greater than deposition in adjacent open terrain (i.e., grasslands or other vegetation of low stature)

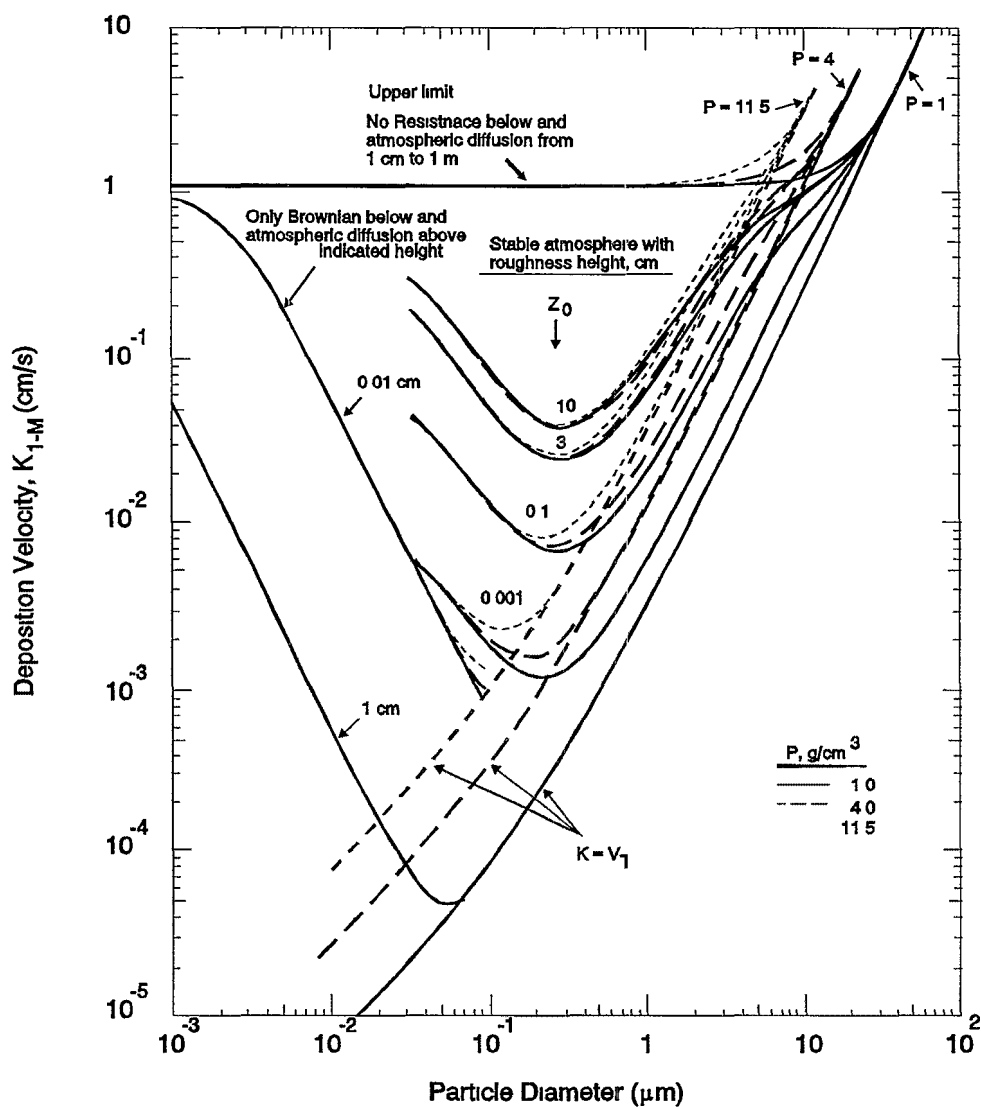


Figure 10-2. Predicted deposition velocities at 1 m for a friction velocity of 30 cm/s and particle densities of 1, 4, and 11.5 g/cm.

Source: Sehmel (1980)

Theoretically based models for predicting particle deposition velocities have recently been published by Bache (1979a,b), Davidson and Wu (1990), and Noll and Fang (1989). Dolske (1988) claims that dry deposition, whether in the form of gases or particles, has from 3 to 20 times the potential of wet deposition to modify the chemical microenvironment of foliar surfaces. This claim was made based on the "cyclic reactivation" of dry deposition by dew and rain, which appears to dissolve and mobilize, but not necessarily remove, the pollutants from the foliar surface.

Independent of the site of deposition of gases or particles (internal versus cuticular), the concentration of the pollutant in ambient air is representative of the driving force responsible for direct and indirect effects on plant physiological processes. However, because the chemical nature of all pollutants are not the same, a single time-averaged concentration (e.g., 24 h versus daylight means) might not be appropriate in all cases. For example, a 24-h mean concentration is appropriate for the largely cuticular deposition observed for aerosol particles and HNO_3 , but a daylight mean would be better for those pollutant gases whose deposition is tightly controlled by stomatal aperture limitations to diffusion (e.g., NO , NO_2).

10.4.4 Deposition of Various Forms of Nitrogen to Foliar Surfaces

Reported deposition velocities or conductances for NO_2 , NO , HNO_3 , NH_3 , and particulate nitrogen forms are presented in Tables 10-2 through 10-10. Each table is organized by plant species or deposition surface and, unless noted otherwise, the listed deposition velocities correspond to daytime conditions. Actual V_d values are highly variable, reaching maximum and minimum values during midday and night periods, respectively. Two types of tables are used to present the data for each of the four gases: tables covering leaf-level or canopy-level measurements. If a cited paper lumped data for NO and NO_2 together as NO_x , those data are presented in Table 10-2 along with the information on NO_2 , but they are indicated as being for NO_x . If the original authors did not calculate K_1 or V_d , concentration and flux data from the original papers were used in Equations 10-1 or 10-2 to generate the values reported in the following tables.

**TABLE 10-2. CONDUCTANCE OF NITROGEN DIOXIDE
TO LEAF SURFACES**

| Species | Concentration (ppmv [$\mu\text{g}/\text{m}^3$]) ^a | Conductance (mm/s) ^{b,c} | Method ^d | Reference |
|--|---|--------------------------------------|---------------------|---------------------------------|
| Austrian pine (<i>Pinus nigra</i>) | 0 400 | 0 3 ^e | Chamber | Elkley et al (1982) |
| Barley (<i>Hordeum vulgare</i>) | 0 3 | 0 5 | Chamber | Rowland-Bamford and Drew (1988) |
| | 0 3 | 0 5 | ¹⁵ N | Rowland-Bamford and Drew (1988) |
| Bean (<i>Phaseolus vulgaris</i>) | 0 04 | 0 7 | Chamber | Fuhrer and Erismann (1980) |
| $g_s = 0.26$ | 0 16 | 0 1 | Chamber | Fuhrer and Erismann (1980) |
| $g_s = 0.05$ | 0 5 | 1 0 | ¹⁵ N | Okano et al (1988) |
| | 1 0 | 0 8 | Chamber | Srivastava et al (1975) |
| | 3 0 | 0 85 | Chamber | Srivastava et al (1975) |
| | 7 0 | 0 63 | Chamber | Srivastava et al (1975) |
| Chinese hibiscus | 1 0 | 0 69 | Chamber | Saxe (1986) |
| (<i>Hibiscus rosa-sinensis</i>) | 1 0 | 0 79 | Chamber | Saxe (1986) |
| | 4 0 | 0 54 | Chamber | Saxe (1986) |
| | 4 0 | 0 65 | Chamber | Saxe (1986) |
| Cucumber (<i>Cucumis sativus</i>) | 0 500 | 1 1 | ¹⁵ N | Okano et al (1988) |
| <i>Diffenbachia maculata</i> | 1 0 | 0 49 | Chamber | Saxe (1986) |
| | 4 0 | 0 31 | Chamber | Saxe (1986) |
| Douglas fir (<i>Pseudotsuga mensiesii</i>) [Mirb] Franco | 0 400 | 0 2 ^e | Chamber | Elkley et al (1982) |
| English ivy (<i>Hedera helix</i>) | 1 0 | 0 56 | Chamber | Saxe (1986) |
| | 4 0 | 0 29 | Chamber | Saxe (1986) |
| European White Birch (<i>Betula pendula</i>) | <0 06 | 3 2 | NA | Freer-Smith (1983) |
| | 0 400 | 0 2 | Chamber | Elkley et al (1982) |
| <i>Ficus benamina</i> | 0 400 | 0 1 | Chamber | Elkley et al (1982) |
| | 1 0 | 0 47 | Chamber | Saxe (1986) |
| | 4 0 | 0 19 | Chamber | Saxe (1986) |
| <i>Hedera canariensis</i> | 1 0 | 0 62 | Chamber | Saxe (1986) |
| | 4 0 | 0 35 | Chamber | Saxe (1986) |
| Honey locust (<i>Gleditsia triacanthos</i>) | 0 400 | 0 2 | Chamber | Elkley et al (1982) |
| Indian rubber (<i>Ficus elastica</i>) | 1 0 | 0 86 | Chamber | Saxe (1986) |
| | 4 0 | 0 69 | Chamber | Saxe (1986) |
| Loblolly pine (<i>Pinus taeda</i>) | 0 020 | 0 6 | Chamber | Hanson et al (1989) |

**TABLE 10-2 (cont'd). CONDUCTANCE OF NITROGEN DIOXIDE
TO LEAF SURFACES**

| Species | Concentration (ppmv [$\mu\text{g}/\text{m}^3$]) ^a | Conductance (mm/s) ^{b,c} | Method ^d | Reference |
|---|---|--------------------------------------|---------------------|-----------------------------|
| Lombardy poplar (<i>Populus nigra</i>) | <0.06 | 2.9 | NA | Freer-Smith (1983) |
| Maize (<i>Zea mays</i>) | 0.2 | 0.6 | ¹⁵ N | Okano et al (1986) |
| | 0.5 | 0.8 | ¹⁵ N | Okano et al (1986) |
| | 0.5 | 0.9 | ¹⁵ N | Okano et al (1986) |
| | 1.0 | 0.7 | ¹⁵ N | Okano et al (1986) |
| Mountain ash (<i>Sorbus aria</i>) | 0.400 | 0.2 | Chamber | Elkley et al (1982) |
| <i>Nephrolepis exaltata</i> | 1.0 | 0.48 | Chamber | Saxe (1986) |
| | 4.0 | 0.22 | Chamber | Saxe (1986) |
| Norway spruce (<i>Picea abies</i>) | 0.400 | 0.2 ^e | Chamber | Elkley et al (1982) |
| Petunia (<i>Petunia hybrida</i>) | 0.400 | 0.6 | Chamber | Elkley and Ormrod (1981) |
| <i>Prunus sargentii</i> | 0.400 | 0.1 | Chamber | Elkley et al (1982) |
| Radish (<i>Raphanus sativus</i>) | 0.500 | 1.9 | ¹⁵ N | Okano et al (1988) |
| Red maple (<i>Acer rubrum</i>) | 0.020 | 1.8 | Chamber | Hanson et al (1989) |
| Red spruce (<i>Picea rubens</i>) | 0.020 | 0.4 | Chamber | Hanson et al (1989) |
| Spruce (<i>Picea sp.</i>) dormant | 0.006-0.03 | <<0.3 | Chamber | Granat and Johansson (1983) |
| Scots pine (<i>Pinus sylvestris</i>) | | | | |
| current shoot | | | | |
| day | NA | 2.2-7.9 | Chamber | Grennfelt et al (1983) |
| night | NA | 0.6-6.0 | Chamber | Grennfelt et al (1983) |
| 1-year shoot | | | | |
| day | NA | 10 | Chamber | Grennfelt et al (1983) |
| night | NA | 3.8 | Chamber | Grennfelt et al (1983) |
| 2-year shoot | | | | |
| day | 0.093 (175) | 10.6 | Chamber | Grennfelt et al (1983) |
| night | 0.093 (175) | 5.8 | Chamber | Grennfelt et al (1983) |
| branches | 0.001 | -1.1-2.1 ^f | Chamber | Johansson (1987) |
| branches | 0.005-0.01 | 0.9-1.7 | Chamber | Johansson (1987) |
| branches | 0.02-0.03 | 1.2-3.5 | Chamber | Johansson (1987) |
| dormant | 0.106 (200) | <1.0 | Chamber | Grennfelt et al (1983) |
| dormant (field) | 0.026 (50) | 0.8 | Chamber | Skarby et al (1981) |
| dormant (field) | 0.066 (125) | 0.6 | Chamber | Skarby et al (1981) |
| dormant (field) | 0.119 (225) | 0.6 | Chamber | Skarby et al (1981) |
| dormant (lab) | 0.053 (100) | 0.2 | Chamber | Skarby et al (1981) |
| dormant (lab) | 0.159 (300) | 0.2 | Chamber | Skarby et al (1981) |
| dormant (lab) | 0.265 (500) | 0.2 | Chamber | Skarby et al (1981) |

**TABLE 10-2 (cont'd). CONDUCTANCE OF NITROGEN DIOXIDE
TO LEAF SURFACES**

| Species | Concentration (ppmv [$\mu\text{g}/\text{m}^3$]) ^a | Conductance (mm/s) ^{b,c} | Method ^d | Reference |
|---|---|--|--|--|
| Sunflower (<i>Helianthus annuus</i>) | 0.2 0.3 0.5 0.5 1.0 2.0 | 1.1 3.0 2.3 2.2 2.1 3.4 | ¹⁵ N ¹⁵ N ¹⁵ N ¹⁵ N ¹⁵ N ¹⁵ N | Okano et al (1986) Okano and Totsuka (1986) Okano et al (1986) Okano et al (1986) Okano et al (1986) Okano and Totsuka (1986) |
| Sweet pepper (<i>Capsicum annuum</i>) | 1.5 NA | 0.02-1.6 1.3 | Chamber NA | Rowland et al (1985) Law and Mansfield (1982) |
| Sycamore maple (<i>A. platanoides</i>) | 0.400 | 0.1 | Chamber | Elkley et al (1982) |
| Sycamore (<i>Platanus occidentalis</i>) | 0.020 | 4.1 | Chamber | Hanson et al (1989) |
| Sorghum (<i>Sorghum vulgare</i>) | 0.500 | 0.6 | ¹⁵ N | Okano et al (1988) |
| Tobacco (<i>Nicotiana tabacum</i>) | 0.500 | 1.3 | ¹⁵ N | Okano et al (1988) |
| Tomato (<i>Lycopersicon esculentum</i>) | 0.500 | 1.5 | ¹⁵ N | Okano et al (1988) |
| light | 1.5 | 2.0-2.8 | Chamber | Murray (1984) |
| dark | 1.5 | 1.1-1.6 | Chamber | Murray (1984) |
| White ash (<i>Fraxinus americana</i>) | 0.020 | 0.7 | Chamber | Hanson et al (1989) |
| White oak (<i>Quercus alba</i>) | 0.020 | 1.3 | Chamber | Hanson et al (1989) |
| White fir (<i>Abies concolor</i>) | 0.400 | 0.3 ^e | Chamber | Elkley et al (1982) |
| White pine (<i>Pinus strobus</i>) | 0.020 | 0.4 | Chamber | Hanson et al (1989) |
| Yellow-Poplar (<i>Liriodendron tulipifera</i>) | 0.020 | 1.5 | Chamber | Hanson et al (1989) |

^aFor nitrogen dioxide (NO₂) at 25 °C, 1 $\mu\text{g}/\text{m}^3$ = 0.000531 ppmv

^bData are presented as a range or the mean of reported values

^cData for broadleaved plants and conifers are presented on a one-sided and total leaf area basis, respectively

^d¹⁵N = nitrogen-15, NA = not available

^eBased on a one-sided leaf area

^fNegative values represent evolution of NO₂ from leaves

**TABLE 10-3. DEPOSITION VELOCITY OF NITROGEN DIOXIDE
TO PLANT CANOPY SURFACES**

| Species | Concentration (ppmv [$\mu\text{g}/\text{m}^3$]) ^a | Velocity (mm/s) ^{b,c} | Method | Reference |
|---|---|-----------------------------------|-----------|-------------------------|
| Alfalfa (<i>Medicago sativa</i>) | | | | |
| | 0 05 | 19 0 | Chamber | Hill (1971) |
| | 0 1 | 20 0 | Chamber | Bennett and Hill (1973) |
| Day | 0 24 | 10 4 | Chamber | Tingey (1968) |
| Night | 0 16 | 4 1 | Chamber | Tingey (1968) |
| Grass | | | | |
| Lawn (NO _x) ^d | 0 017 (32 4) | 1 0-3 0 | Flux grad | Delany and Davies |
| Pasture (NO _x) ^d | NA ^e | -26 0-15 0 | Flux grad | (1983) |
| | | | | Duyzer et al (1983) |
| Oats (<i>Avena sativa</i>) | | | | |
| | 0 08 | 12 5 | Chamber | Hill (1971) |
| Day | 0 08 | 12 5 | Chamber | Tingey (1968) |
| Night | 0 08 | 4 2 | Chamber | Tingey (1968) |
| Soybean (<i>Glycine max</i> [L] Merr.) | | | | |
| Day | 0 008-0 12 | 3 6 | Eddy Corr | Wesely et al (1982) |
| Night | 0 008-0 12 | 0 7 | Eddy Corr | Wesely et al (1982) |
| Spruce (<i>Picea</i> sp.) (NO_x)^d | | | | |
| | 0 018 | 28 0 | Gradient | Enders and Teichmann |
| | 0 029 | 20 0 | Gradient | (1986) |
| | | | | Enders and Teichmann |
| | | | | (1986) |

^aFor nitrogen dioxide at 25 °C, 1 $\mu\text{g}/\text{m}^3$ = 0 000531 ppmv

^bData are presented as a range or the mean of reported values

^cData are based on ground area under the canopy

^dData for nitric oxide and nitrogen dioxide were lumped together as nitrogen oxides

^eNA = Not available

10.4.4.1 Nitrogen Dioxide

Direct measurements of NO₂ deposition to crop species are widely reported (e g , Bennett and Hill, 1973, Okano and Totsuka, 1986, Rogers et al , 1979b, Sinn et al , 1984, Wesely et al , 1982), but fewer observations are available for woody plant species (Elkley et al., 1982; Grennfelt et al , 1983, Rogers et al , 1979b) and fewer still are available for woody plants using near-ambient concentrations of NO₂ (Hanson et al , 1989, Johansson, 1987; Skarby et al , 1981) Tables 10-2 and 10-3 provide a comprehensive listing, by plant

species, of current data on the deposition of NO₂ to leaf and canopy surfaces, respectively. Data are also available for potato plants (Sinn et al , 1984), but conversion of that data to standard units was not possible from the information supplied.

Nitrogen dioxide is deposited on plants over a range of concentrations from as little as 0.005 ppmv (Johansson, 1987) to those as great as 4 to 7 ppmv (Saxe, 1986, Srivastava et al , 1975). The rate of deposition increases in proportion to rising ambient NO₂ concentrations (Sinn et al , 1984, Srivastava et al , 1975, Skarby et al , 1981). At low concentrations of NO₂ (0.0013 ppmv [$2.4 \mu\text{g}/\text{m}^3$]), Johansson (1987) observed no deposition in Scots pine. Johansson suggested that his data indicated a "compensation point" at which rates of NO₂ deposition and evolution balance out. The compensation point was reported in the 0.001 to 0.003 ppmv range. If this compensation point is a general phenomenon, it would indicate little potential for NO₂ deposition at concentrations common across many nonurban areas of the United States (i.e., areas of NO₂ concentration < 0.005 ppmv). However, more recent observations have shown that sunflower (*Helianthus annuus*) does not exhibit an NO₂ compensation point (Foerstel et al , 1989). Additional discussion of the deposition of NO₂ into leaves can be found in Section 9.4.1.

Numerous studies have confirmed the control of stomatal aperture on NO₂ deposition using a variety of techniques (Hanson et al , 1989, Rogers et al , 1977, Rogers et al , 1979a,b, Saxe, 1986, Wesely et al , 1982, see also Section 9.4.1). In addition, Murray (1984), using a tomato mutant whose stomata did not close in the dark, claimed to have found a direct relationship between light and NO₂ deposition.

Until recently, it was assumed that cuticular deposition of NO₂ was negligible. Recent studies by Lenzian and Kerstiens (1988) and Kisser-Priesack et al (1987) clearly demonstrate cuticular deposition rates (see the discussion in Section 9.4.1). However, cuticular deposition rates are one to two orders of magnitude less than representative stomatal uptake rates for tree foliage. Because cuticle deposition is low, it should be considered of minor importance, but not ignored when calculations of total nitrogen deposition to landscapes are attempted.

Whole-canopy measurements of NO₂ deposition conducted in laboratory or field situations (Table 10-3) yield daytime overall deposition velocities (V_d) between 1 and 28 mm/s. Duyzer et al (1983) and Van Aalst and Diederer (1985) cautioned that field

measurements of NO_2 deposition may have been in error because NO_2 analyzers are also sensitive to HNO_3 vapor. Nitric acid vapor has a higher deposition velocity than NO_2 (Section 10.4.4.3) and if monitored simultaneously with NO_2 , could have resulted in an overestimate of deposition (e.g., Hill, 1971). Chemical reactions resulting from photochemical reactions between NO , NO_2 , and ozone (O_3) can also lead to errors in whole-canopy V_d measurements based on micrometeorological techniques (Hicks et al., 1989). Delany et al. (1986) reported that eddy correlation measurements conducted over a grassland were not appropriate for measurements of the fluxes of NO_x . Their data showed that deposition of NO_x predominated in the morning hours, whereas emissions of NO_x were observed in the afternoon. However, their results, which include both NO and NO_2 , were confounded by photochemical reactions with O_3 , resulting in the bimodal pattern of diurnal deposition. Hicks and Matt (1988) also measured apparent bidirectional fluxes of NO_2 from forest canopies, but they could not conclude that such fluxes were a consequence of natural NO_2 emissions (i.e., anthropogenic sources of NO_2 and/or in-canopy transformations of NO_2 to NO could have been responsible for the observed data). Fitzjarrald and Lenschow (1983) conclude that the deposition velocity (V_d) concept is invalid for circumstances when chemical reaction time is less than or comparable to the time required for turbulent diffusion. It appears that this may often be the case for micrometeorologically based measurements of canopy NO_2 deposition.

The leaf-level measurements of NO_2 deposition presented in Table 10-2 encompass a large number and several types of plant species. A simple average of the species-specific data in Table 10-2 for *nondormant* plants indicates the following trend for deposition of NO_2 : broadleaf trees = crop plants > conifer trees = house plants. Mean leaf conductance to NO_2 (K_l) for broadleaf trees and crop plants was approximately 1.3 mm/s, and for conifers and house plants, the mean leaf conductance was between 0.5 and 1.0 mm/s. Hanson et al. (1989) documented a similar pattern. Elkley et al. (1982) reported data on the foliar sorption of NO_2 to 10 ornamental woody plants using an NO_2 concentration of 400 nL/L. Based on one-sided leaf areas for conifers, they observed higher NO_2 deposition to conifers than to hardwoods. Had they used total area to normalize their conifer data, it would have shown the opposite pattern. Okano et al. (1988) reported a positive correlation between NO_2 deposition and stomatal conductance for eight different crops that followed a trend associated

with stomatal densities of the foliage Grennfelt et al (1983) also found a strong relationship between NO_2 deposition and stomatal conductance for Scots pine

10.4.4.2 Nitric Oxide

A comparison of tree and crop data between Tables 10-2 and 10-4, or between Tables 10-3 and 10-5, shows that the K_1 and V_d of NO are considerably less than for NO_2 . Lower conductance and deposition velocities indicate a reduced potential for the deposition of NO by leaves as compared to NO_2 . The lower rate of deposition for NO is expected because of NO's lower aqueous solubility. Deposition data for several species of "house plants" reported by Saxe (1986) indicated the same trend. The deposition of NO to foliar surfaces increased in a linear manner with respect to ambient concentrations (Skarby et al, 1981), and stomatal control over NO deposition has been documented by Saxe (1986). Kisser-Priesack et al (1987) also documented the capacity of Norway spruce and tomato cuticles to absorb gaseous NO labeled with ^{15}N , and concluded that a cuticular pathway for foliar deposition should not be ignored.

As for NO_2 , a compensation point for NO deposition to leaves has been indicated. Nitric oxide concentrations greater than 0.05 ppmv routinely lead to deposition onto plant canopies (Tables 10-4 and 10-5), but NO has also been observed to be evolved from foliage (Farquhar et al, 1983). Klepper (1979) measured NO evolution from soybean plants stressed with herbicides, and an enzyme system responsible for the conversion of nitrite to NO_x has been described by Dean and Harper (1988). Nitric oxide emissions from plants are not widespread, and have only been documented completely for a specific set of plants in the bean family (*Leguminosae*) (Dean and Harper, 1986).

Although more research is needed, two alfalfa studies suggest low deposition velocities for NO to plant canopies (Table 10-5). Given NO's potentially greater phytotoxicity (see Section 9.4.3), deposition data from a broader array of plant species is needed.

10.4.4.3 Nitric Acid Vapor

The dry deposition characteristics of HNO_3 vapor suggest substantially higher deposition for HNO_3 than for other oxides of nitrogen. Micrometeorological measurement of the overall deposition velocity of HNO_3 to pasture grass (see papers by various authors in

TABLE 10-4. CONDUCTANCE OF NITRIC OXIDE TO LEAF SURFACES

| Species | Concentration (ppmv [$\mu\text{g}/\text{m}^3$]) ^a | Conductance (mm/s) ^{b,c} | Method | Reference |
|---|---|--------------------------------------|---------|--------------------------------|
| Chinese hibiscus (<i>Hibiscus rosa-sinensis</i>) | 4 0 | 0 22 | Chamber | Saxe (1986) |
| <i>Diffenbachia maculata</i> | 4 0 | 0 34 | Chamber | Saxe (1986) |
| English ivy (<i>Hedera helix</i>) | 4 0 | 0 10 | Chamber | Saxe (1986) |
| <i>Ficus benjamina</i> | 4 0 | 0 10 | Chamber | Saxe (1986) |
| <i>Hedera canariensis</i> | 4 0 | 0 13 | Chamber | Saxe (1986) |
| Indian rubber (<i>Ficus elastica</i>) | 4 0 | 0 34 | Chamber | Saxe (1986) |
| <i>Nephrolepis exaltata</i> | 4 0 | 0 22 | Chamber | Saxe (1986) |
| Pine/spruce dormant | 0 0005-0 002 | \ll 0 3 | Chamber | Granat and Johansson (1983) |
| Scots pine (<i>Pinus sylvestris</i>) | variable | \ll 0 1 | Chamber | Johansson (1987) |
| dormant (field) | 0 122 (150) | 0 04 | Chamber | Skarby et al (1981) |
| dormant (lab) | 0 244 (300) | 0 04 | Chamber | Skarby et al (1981) |
| | 0 407 (500) | 0 05 | Chamber | Skarby et al (1981) |

^aFor nitric oxide at 25 °C, $1 \mu\text{g}/\text{m}^3 = 0.000814 \text{ ppmv}$

^bData are presented as a mean or range of reported values

^cData for broadleaved plants and conifers are presented on a one-sided and total leaf area basis, respectively

**TABLE 10-5. DEPOSITION VELOCITY OF NITRIC OXIDE
TO PLANT CANOPY SURFACES**

| Species | Concentration (ppmv [$\mu\text{g}/\text{m}^3$]) ^a | Velocity (mm/s) ^{b,c} | Method | Reference |
|----------------------------|---|-----------------------------------|---------|----------------------------|
| Alfalfa | 0 100 | 1 7 | Chamber | Bennett and Hill (1973) |
| (<i>Medicago sativa</i>) | 0 050 | 1 0 | Chamber | Hill (1971) |

^aFor nitric oxide at 25 °C, $1 \mu\text{g}/\text{m}^3 = 0.000814 \text{ ppmv}$

^bData are the mean or a range of reported values

^cData are based on ground area under the canopy

Table 10-6) showed an average V_d for HNO_3 of 29 mm/s. Other studies on crop canopies showed V_d values for HNO_3 over a range from 4 to 260 mm/s. Using throughfall nitrate and ambient HNO_3 concentrations, Dasch (1987) calculated the V_d for an Austrian pine (*Pinus nigra*) (Table 10-7) stand to be 67 mm/s at the stand perimeter and 17 mm/s at interior stand locations. Dollard et al (1987) reported V_d values as high as 260 mm/s for wheat canopies, but recent modeling efforts (Bennett, 1988, Meyers and Hicks, 1988, Meyers et al, 1989) indicate that such high V_d levels may not be possible. Fowler et al (1989a) assumed HNO_3 and hydrochloric acid deposition to vegetation landscapes to be similar and concluded that V_d values for low stature vegetation and crops would range from 5 to 50 mm/s, depending on wind speeds (Table 10-6). Forest landscapes also showed a range of V_d from 40 to 100 mm/s for low and high wind speeds, respectively.

A computer model and ambient HNO_3 concentrations were employed by Hicks et al (1985) to predict the V_d of HNO_3 to broadleaf and high elevation red spruce forests. Their analysis predicted a V_d between 20 and 50 mm/s for the low elevation broadleaf forests, and a V_d between 60 and 120 mm/s for red spruce forests at high elevations. However, a more recent simulation for crop canopies (Meyers and Hicks, 1988) projected that HNO_3 deposition rates are mainly limited by the atmosphere-canopy turbulent exchange mechanisms (wind), and predicted V_d values between 5 and 20 mm/s for slow and fast wind speeds, respectively. Fowler (1984) calculated that the atmospheric resistance to deposition of pollutants would increase from two- to fourfold, depending on the nature of the landscape vegetation, with a change in windspeed from 1 to 4 m/s. Flux gradient simulations based on weekly mean filter pack HNO_3 concentration measurements for a deciduous forest canopy (Meyers et al, 1989) showed 35 mm/s to be an appropriate mean V_d with a range between 20 and 60 mm/s.

Only a few studies have attempted to measure HNO_3 deposition to individual leaves. Dasch (1989) used a mass balance approach to measure HNO_3 deposition to tree foliage (Table 10-7) and found a mean K_1 for two hardwoods to be 8.2 mm/s and a K_1 for *Pinus nigra* to be 2 mm/s. Marshall and Cadle (1989) also used a mass balance approach to measure HNO_3 dry deposition to dormant pine shoots and found much lower K_1 values, ranging from 0.4 to 0.8 mm/s. Hanson et al (1992) measured HNO_3 conductances to foliage of four tree species under low humidity conditions and found a K_1 ranging from

**TABLE 10-6. DEPOSITION VELOCITY OF NITRIC ACID
TO CANOPY SURFACES**

| Species | Concentration (ppmv [$\mu\text{g}/\text{m}^3$]) ^a | Velocity (mm/s) ^{b,c} | Method | Reference |
|---------------------------|---|-----------------------------------|-----------------|--|
| Barley (<i>Hordeum</i>) | NA ^d | 77 | Flux grad | Harrison et al (1989) |
| Beets (<i>Beta</i>) | NA ^d | 14 | Flux grad | Harrison et al (1989) |
| Crop canopies | 0 0001-0 0005 | 5-20 | Model | Meyers and Hicks (1988) |
| wind = 1 m/s | NA ^d | 14 | NA ^d | Fowler et al (1989a) |
| wind = 4 m/s | NA ^d | 50 | NA ^d | Fowler et al (1989a) |
| Forest | 0 001-0 002 | 22-50 | Flux grad | Meyers et al (1989) |
| | NA ^d | 20-50 | Model | Hicks et al (1985) |
| | NA ^d | 20-60 | Model | Hicks and Meyers (1988) |
| wind = 1 m/s | NA ^d | 40 | NA ^d | Fowler et al (1989a) |
| wind = 4 m/s | NA ^d | 100 | NA ^d | Fowler et al (1989a) |
| Grass (pasture) | <0 001 (2 0) | 40 | Flux grad | Erisman et al (1988) |
| | <0 002 (2 6-4 3) | 17-49 | Flux grad | Huebert (1983) |
| | <0 002 (3 2) | 25 | Flux grad | Huebert and Robert (1985) |
| | <0 003 | 6 | Eddy flux | Huebert et al (1988) |
| | NA ^d | 3-18 | Flux grad | Van Aalst and Diederer (1985) |
| | NA ^d | 7-37 | Flux grad | (1985) |
| wind = 1 m/s | NA ^d | 5 | NA ^d | Harrison et al (1989) |
| wind = 4 m/s | NA ^d | 23 | NA ^d | Fowler et al (1989a) Fowler et al (1989a) |
| Pine (<i>Pinus</i>) | 0 001 | 20-70 | Leaf Wash | Dasch (1987) |
| Potato (<i>Solanum</i>) | NA ^d | 4 | Flux grad | Harrison et al (1989) |
| Spruce (<i>Picea</i>) | NA ^d | 60-120 | Model | Hicks et al (1985) |
| Wheat (<i>Triticum</i>) | NA ^d | 50-260 | Flux grad | Dollard et al (1987) |

^aFor nitric acid at 25 °C, 1 $\mu\text{g}/\text{m}^3$ = 0 000388 ppmv

^bData are means or a range of the reported values

^cData are based on ground area under the canopy

^dNA = Not available

1 to 3.3 mm/s Because low humidity caused stomatal closure, their measurements did not include deposition to leaf internal spaces Vose and Swank (1990) used a ¹⁵N-labeling technique to assess HNO₃ deposition to white pine foliage and found rates of "nonextractable" HNO₃ absorption between 5 and 53 nmol/g/s These data were not included in Table 10-7 because the surface adsorbed HNO₃ was removed in a water rinse prior to assaying nonextractable ¹⁵N-labeled HNO₃ Taylor et al (1988) compared foliar deposition characteristics of HNO₃ vapor to those of other pollutant gases and suggested that

TABLE 10-7. CONDUCTANCE OF NITRIC ACID TO LEAF SURFACES

| Species | Concentration (ppmv [$\mu\text{g}/\text{m}^3$]) ^a | Conductance (mm/s) ^{b,c} | Method | Reference |
|---|---|--------------------------------------|---------|---------------------------|
| American elm (<i>Ulmus americana</i>) | 1.2 - 0.012 | 12.0 | Chamber | Dasch (1989) |
| Austrian pine (<i>Pinus nigra</i>) | 0.012-1.2 | 2.0 | Chamber | Dasch (1989) |
| Pin oak (<i>Quercus palustris</i>) | 0.012-1.2 | 4.4 | Chamber | Dasch (1989) |
| Red maple (<i>Acer rubrum</i>) | 0.02-0.03 | 3.3 | Chamber | Hanson et al (1992) |
| Red spruce (<i>Picea rubens</i>) | 0.058-0.067 | 2.6 | Chamber | Hanson et al (1992) |
| Sycamore (<i>Platanus occidentalis</i>) | 0.02-0.07 | 1.1 | Chamber | Hanson et al (1992) |
| White oak (<i>Quercus alba</i>) | 0.04-0.07 | 2.2 | Chamber | Hanson et al (1992) |
| White pine (<i>Pinus strobus</i>) | 37.0-500.0 (95.0-1,288.0) | 0.4-0.8 | Chamber | Marshall and Cadle (1989) |

^aFor nitric acid at 25 °C, $1 \mu\text{g}/\text{m}^3 = 0.000388 \text{ ppmv}$

^bData for broadleaved plants and conifers are presented on a one-sided and total leaf area basis, respectively

^cThe data from Hanson et al (1992) represent cuticular deposition only

HNO_3 deposition might be predominantly to the cuticle. This contrasts with patterns for NO and NO_2 , which show most deposition to leaf interiors. Hanson and Taylor (1990) modeled dry deposition of four pollutant gases to a hypothetical leaf surface, and predicted that HNO_3 vapor deposition through plant cuticles would be greater than cuticular deposition of NO , O_3 , and sulfur dioxide (SO_2). Vose and Swank (1990) conducted a study of HNO_3 deposition to foliar surfaces using ^{15}N -labeled HNO_3 that has confirmed the cuticular pathway for HNO_3 deposition.

10.4.4.4 Ammonia

Ammonia deposition data are limited primarily to crop plants. The average deposition variables for all crop species included in Tables 10-8 and 10-9 are a K_1 for leaves of 5.6 mm/s and a V_d for canopies of 7.4 mm/s. Rates of NH_3 deposition at concentrations above 0.01 ppmv are linearly related to ambient concentration levels (Van Hove et al, 1987, Porter et al, 1972). However, Farquhar et al (1980) observed a temperature-dependent evolution of NH_3 from bean plants resulting in no net exchange of NH_3 at ambient

TABLE 10-8. CONDUCTANCE OF AMMONIA TO LEAF SURFACES

| Species | Concentration (ppmv [$\mu\text{g}/\text{m}^3$]) ^a | Conductance (mm/s) ^{b,c} | Method | Reference |
|--|---|--------------------------------------|-----------|------------------------------|
| Bean (<i>Phaseolus vulgaris</i>) | | | | |
| 26.6 °C | 0.002 | 0 | Chamber | Farquhar et al (1980) |
| | 0.0035 | 2 | Chamber | Farquhar et al (1980) |
| | 0.005 | 3-11 | Chamber | Farquhar et al (1980) |
| 33.4 °C | 0.005 | 0 | Chamber | Farquhar et al (1980) |
| | 0.008 | 6-32 | Chamber | Farquhar et al (1980) |
| | 0.14 | 13 | Chamber | Rogers and Aneja (1980) |
| | 0.071 (50) | 2-5 | Chamber | Van Hove et al (1987) |
| | 0.144 (100) | 2-6 | Chamber | Van Hove et al (1987) |
| | 0.288 (200) | 2.5-6 | Chamber | Van Hove et al (1987) |
| | 0.502 (350) | 2-6 | Chamber | Van Hove et al (1987) |
| Cotton (<i>Gossypium hirsutum</i>) | 0.063 (44) | 2 | Chamber | Hutchinson et al (1972) |
| | 0.331 | 7 | Chamber | Rogers and Aneja (1980) |
| Fescue | 0.341 | 15 | Chamber | Rogers and Aneja (1980) |
| Heather/purple moor grass (<i>Calluna/Molina</i>) | NA ^d | 4 | Estimated | Duyzer et al (1987) |
| Italian rygrass (<i>Lolium multiflorum</i>) | 22.6 (16.0) | 3 | Chamber | Lockyer and Whitehead (1986) |
| | 735.0 (520.0) | 28 | Chamber | Lockyer and Whitehead (1986) |
| Maize (<i>Zea mays</i>) | 0.034 (24.0) | 6.5 | Chamber | Hutchinson et al (1972) |
| | 0.320 | 4 | Chamber | Rogers and Aneja (1980) |
| Oats (<i>Avena</i>) | 0.200 | 13 | Chamber | Rogers and Aneja (1980) |
| Orchard grass | 0.283 | 10 | Chamber | Rogers and Aneja (1980) |
| <i>Populus euramericana</i> | 0.072 | 0.5-5 | Chamber | Van Hove et al (1989a) |
| | 0.143 | 0.5-9 | Chamber | Van Hove et al (1989a) |
| Soybean (<i>Glycine max</i>) | 0.037 (26.0) | 4 | Chamber | Hutchinson et al (1972) |
| | 0.170 | 11 | Chamber | Rogers and Aneja (1980) |
| Sunflower (<i>Helianthus annuus</i>) | 0.045 (31.0) | 4 | Chamber | Hutchinson et al (1972) |
| Tomato (<i>Lycopersicon esculentum</i>) | 0.148 | 10 | Chamber | Rogers and Aneja (1980) |
| Tobacco (<i>Nicotiana tabacum</i>) | 0.173 | 6 | Chamber | Rogers and Aneja (1980) |
| Wheat (<i>Triticum</i>) | 0.277 | 15 | Chamber | Rogers and Aneja (1980) |

^aFor ammonia at 25 °C, $1 \mu\text{g}/\text{m}^3 = 0.00143 \text{ ppmv}$

^bData are the mean or a range of reported values

^cConductance is based on a one-sided leaf area

^dNA = Not available

**TABLE 10-9. DEPOSITION VELOCITY OF AMMONIA
TO PLANT CANOPY SURFACES**

(Data showing net efflux of ammonia from fertilized crop landscapes are not included in this table)

| Species | Concentration (ppmv [$\mu\text{g}/\text{m}^3$]) ^a | Velocity (mm/s) ^{b,c} | Method | Reference |
|--|---|-----------------------------------|-----------|---------------------|
| Bean (<i>Phaseolus vulgaris</i>) | 0 100 | 4 | Chamber | Aneja et al (1986) |
| Fescue (<i>Festuca arundinacea</i>) | 0 603 | 12 | Chamber | Aneja et al (1986) |
| Heather/purple moor grass (<i>Calluna/Molina</i>) | NA ^d | 19 | Flux grad | Duyzer et al (1987) |
| Maize (<i>Zea mays</i>) | 0 250 | 3 | Chamber | Aneja et al (1986) |
| Oats (<i>Avena sativa</i>) | 0 200 | 10 | Chamber | Aneja et al (1986) |
| Orchard grass (<i>Dactylis glomerata</i>) | 0 576 | 10 | Chamber | Aneja et al (1986) |
| Pine (<i>Pinus</i> sp) | NA ^d | 18-26 | Flux grad | Duyzer et al (1987) |
| Soybean (<i>Glycine max</i> [L] Merr) | 0 075 | 6 | Chamber | Aneja et al (1986) |

^aFor ammonia at 25 °C, $1 \mu\text{g}/\text{m}^3 = 0.00143 \text{ ppmv}$

^bData are means or a range of reported values

^cData are based on ground area under the canopy

^dNA = Not available

concentrations between 0.003 and 0.005 ppmv. For ambient concentrations below that "compensation point", NH_3 evolution was observed, and above that concentration, NH_3 was deposited in proportion to ambient NH_3 concentrations. Lemon and Van Houtte (1980) used micrometeorological techniques to reach similar conclusions (i.e., net NH_3 deposition is concentration dependent).

Limited data for forest species show a similar range of K_1 and V_d values. Duyzer et al (1987) have reported V_d for NH_3 to heather-purple moor grass (*Calluna Molina* sp.) canopies to be 19 mm/s, and V_d to Corsican pine (*Pinus nigra var. maritima*) canopies ranged between 18 and 26 mm/s. These values are somewhat greater than those predicted for crop plants. Van Hove et al (1989a) found that NH_3 deposition to *Phaseolus vulgaris* and *Populus euramericana* cuticles decreased with decreasing relative humidity. Furthermore, the cuticle deposition sites exhibited saturation given sufficient exposure time,

little of the adsorbed NH_3 appeared to pass through the cuticle. However, cuticular deposition of NH_3 represents only about 3% of the amount taken up via the stomata (Van Hove et al., 1989a). Van Hove et al. (1989b) reported additional K_1 data for internal and external surfaces of *P. euramericana* leaves ranging from 0.5 to 9 mm/s, depending on stomatal conductance. Van Hove et al. (1990) concluded that calculation of NH_3 deposition to leaves using only stomatal conductance data could result in a serious underestimation of the flux for conditions of low temperature and high relative humidity.

Diurnal patterns of NH_3 deposition follow similar patterns as for plant CO_2 uptake (Hutchinson et al., 1972). Other studies have related NH_3 deposition to diurnal patterns of stomatal opening (Aneja et al., 1986; Rogers and Aneja, 1980). A net deposition of 21 and 86 $\mu\text{mol/g}$ fresh weight/h at 30 and 300 ppmv, respectively, was measured in sunflower leaves using high concentrations of ^{15}N -labeled NH_3 (Berger et al., 1986). Ammonia labeled with ^{15}N was incorporated into corn seedlings (Porter et al., 1972). Numerous other papers encompassing a range of plant species indicate that NH_3 exchange between crop canopies and the atmosphere is a dynamic process, and concentration gradients between the atmosphere and the landscape determine whether net influx or efflux of NH_3 will take place (alfalfa—Dabney and Bouldin, 1985; grazed pasture—Denmead et al., 1974; maize—Farquhar et al., 1979; wheat—Harper et al., 1983, 1987; Parton et al., 1988). All of these studies involved some type of fertilization regime, and it remains unclear to what extent "nutrient poor" natural ecosystems might exhibit NH_3 efflux.

Modeling simulations have come to similar conclusions. A modeled "canopy-level" V_d for ryegrass (*Lolium perenne* L.) was reported to be 3 to 14 mm/s (Cwiling and Lockyer, 1981). Sinclair and Van Houtte (1982) simulated the deposition of NH_3 to a soybean canopy and determined that significant foliar deposition would occur at ambient concentrations as low as 1 $\mu\text{g/m}^3$. However, net deposition of NH_3 by the combined soil-vegetation landscape was predicted to occur routinely only at NH_3 concentrations in the range from 40 to 70 $\mu\text{g/m}^3$.

Denmead et al. (1976) found that ungrazed pasture was capable of absorbing most NH_3 released from the ground, whereas grazed pasture lost NH_3 to the atmosphere. Their observations, although not quantitative, suggest that foliage of an ungrazed grass-clover

pasture is an effective sink for soil-generated NH_3 . Denmead et al (1978) demonstrated that a corn field (*Zea mays*) exhibited net absorption of NH_3 only when soil surfaces were dry

10.4.4.5 Particles (Nitrate and Ammonium)

Direct measurements of aerosol-associated nitrogen deposition to foliar and inert surfaces have been based on surface extractions and extrapolations of throughfall information. Unfortunately, these types of observations are of limited value due to the inability to separate aerosol NO_3^- and NH_4^+ deposition from deposition due to HNO_3 , NO_2 , and NH_3 that display the same ionic forms once deposited to landscape surfaces (Bytnerowicz et al, 1987a, Dasch, 1987, Lindberg and Lovett, 1985, Van Aalst and Diederer, 1985). The average V_d for nitrate and ammonium (Table 10-10) was greater if determined from throughfall measurements (12 and 10 mm/s) than if determined from individual leaf washing experiments (6 and 2 mm/s). However, these differences in V_d between measurement techniques are primarily a function of scale. The leaf-wash measurements extract adsorbed ions from a defined leaf area, but throughfall measurements extract ions from all layers of the canopy (an undefined area) and relate it only to the ground area of the stand (see also discussion in Section 10.4.3). Lindberg and Lovett (1985) estimated dry deposition of nitrate to deciduous forest leaves to be $5.7 \mu\text{g}/\text{m}^2/\text{h}$, but declined to calculate a deposition velocity because of difficulties in (1) obtaining accurate particulate NO_3^- air concentrations (Appel and Tokiwa, 1981) and (2) separating the contribution of HNO_3 dry deposition to NO_3^- on the foliage surface from that of aerosol NO_3^- . Dolske (1988) reported V_d values for NO_3^- deposition to soybean to range from 30.8 down to 0.4 mm/s with a mean of 2.4 mm/s. However, because Dolske's leaf-wash measurements included a component of HNO_3 vapor, the V_d values may represent more than deposition due to aerosol nitrate alone.

Only one published paper has used micrometeorological methods to determine the aerosol nitrate and ammonium deposition to landscape surfaces. The V_d information from Duyzer et al (1987) for aerosol NH_4^+ deposition to heathlands (1.8 mm/s, Table 10-10) was determined using flux gradient analysis of NH_4^+ particles trapped in filtered air leaving denuder tubes.

**TABLE 10-10. MEASURED DEPOSITION VELOCITIES OF
NITRATE AND AMMONIUM**

| Species | Deposition Velocity ^a | | Method | Reference |
|---|--|--|-------------|--------------------------------|
| | NO ₃ ⁻ (mm/s) | NH ₄ ⁺ (mm/s) | | |
| American elm (<i>Ulmus americana</i>) | 11 | NA | Leaf wash | Dasch (1987) |
| Austrian pine (<i>Pinus nigra</i>) | 5-13 | 0 1-0 6 | Leaf wash | Dasch (1987) |
| Beech (<i>Fagus silvatica</i>) | 13 | 10 | Throughfall | Hoefken and Gravenhorst (1982) |
| | 7-17 | 6-13 | Throughfall | Gravenhorst et al (1983) |
| winter | 6-16 | 2-8 | Throughfall | Gravenhorst et al (1983) |
| (<i>Ceanothus crassifolius</i>) | 4 1 ^b | 4 4 | Leaf wash | Bytnerowicz et al (1987b) |
| Chestnut oak (<i>Quercus prinus</i>) | 5 5 | NA | Throughfall | Lovett and Lindberg (1984) |
| dormant | 7 1 | NA | Throughfall | Lovett and Lindberg (1984) |
| Heather/moor grass (<i>Calluna/Molina</i>) | NA | 1 8 | Flux grad | Duyzer et al (1987) |
| Laurel (<i>Kalmia latifolia</i>) | NA | 0 3-1 4 | Leaf wash | Tjepkema et al (1981) |
| Norway spruce (<i>Picea abies</i>) | 11-37 | 7-21 | Throughfall | Gravenhorst et al (1983) |
| winter | 13-32 | 6-16 | Throughfall | Gravenhorst et al (1983) |
| Pasture land | 7-8 | NA | Gradient | Huebert et al (1988) |
| Pin oak (<i>Quercus palustris</i>) | 7-11 | NA | Leaf wash | Dasch (1987) |
| Privet (<i>Ligustrum japonicum</i>) | 2 2-5 4 | NA | Leaf wash | John et al (1985) |
| (<i>Ligustrum ovalifolium</i>) | 1 0-2 1 | NA | Leaf wash | John et al (1985) |
| Soybean (<i>Glycine max</i>) | 2 4 | NA | Leaf wash | Dolske (1988) |
| White pine (<i>Pinus strobus</i>) | NA | 0 3-1 4 | Leaf wash | Tjepkema et al (1981) |

^aNO₃⁻ = Nitrate ion, NH₄⁺ = ammonium ion, NA = not available

^bParticle NO₃⁻ deposition data typically includes some NO₃⁻ from nitric acid vapor

10.4.4.6 Summary

Deposition velocities or conductances for NO_2 , NO , HNO_3 , NH_3 , and particulate nitrogen forms used in experiments are given in Tables 10-2 through 10-10. The majority of the studies were conducted in chambers using concentrations above those usually encountered in the ambient atmosphere. Response to the exposures to the various nitrogen compounds is dependent on their entering into the plants. Evidence of the entrance of the four gases at toxic concentrations from the ambient atmosphere is not presently available.

10.4.5 Deposition of Various Forms of Nitrogen to Nonfoliar Surfaces

In addition to foliage, deposition of particles and gases has also been measured to bark, soil, and snow-covered surfaces (Table 10-11). Measured deposition of NO_2 to normal or wetted bark of three broadleaf and one conifer tree species was similar among species (Hanson et al., 1989). The conductance of NO_2 to wet bark was almost double that to dry bark (Table 10-11). The conductances (K_1) ranged from 0.44 to 0.84 mm/s and were within a factor of 2 of K_1 values for plant leaf surfaces. Nitric acid vapor conductance to bark was nearly an order of magnitude greater than for NO_2 (Hanson et al., 1992, Table 10-11). No data are available for the deposition of other forms of dry deposited nitrogen to bark.

The deposition velocity of NO_2 to soil exceeds that for NO (Judeikis and Wren, 1978, Table 10-11). When compared to foliage or bark surfaces, deposition to the forest floor and soil surfaces show a disproportionately high rate (compare data from Tables 10-2 and 10-11). A comparison of deposition to the soil and forest showed that soil was the primary receptor site of NO_2 (Hanson et al., 1989). Abeles et al. (1971) measured NO_2 deposition to fresh and autoclaved soil and determined that a biological sink was responsible for approximately 12% of the soil NO_2 deposition. However, Ghiorse and Alexander (1976) found no difference in soil deposition after autoclaving or gamma-irradiation and concluded that microorganisms were responsible, not so much for absorption of NO_2 , but for its conversion into nitrate. Mortland (1965) and Sundaresan et al. (1967) documented mechanisms for NO deposition by soil on adsorption or interaction with soil minerals. Prather et al. (1973) and Prather and Miyamoto (1974) provided data on the deposition of NO_2 and NO to calcareous soils, but these data are not included in Table 10-11 because of the extremely high air concentrations used (0.1 to 1.5% by volume).

**TABLE 10-11. CONDUCTANCE OF NONFOLIAR
SURFACES TO REACTIVE NITROGEN GASES**

| Species | Concentration (ppmv [$\mu\text{g}/\text{m}^3$]) | Conductance (mm/s) ^{a,b} | Method | Reference |
|--------------------------|--|--------------------------------------|-----------------|-----------------------------|
| <u>Nitrogen Dioxide</u> | | | | |
| Forest floor | | | | |
| Hardwood | 0.044 | 4.7 | Chamber | Hanson et al (1989) |
| Conifer | 0.043 | 4.8 | Chamber | Hanson et al (1989) |
| Bark | | | | |
| Dry | 0.066 | 0.47 | Chamber | Hanson et al (1989) |
| Wet | 0.058 | 0.93 | Chamber | Hanson et al (1989) |
| Forest litter | | | | |
| Hardwood | 0.076 | 0.06 | Chamber | Hanson et al (1989) |
| Conifer | 0.074 | -0.05 | Chamber | Hanson et al (1989) |
| Soil | | | | |
| Waltham, MA | 3-100 | 0.2 | Chamber | Abeles et al (1971) |
| Sandy loam | 13-53 | 6.0 | Chamber | Judeikis and Wren (1978) |
| Adobe clay | 13-53 | 7.7 | Chamber | Judeikis and Wren (1978) |
| Oak Ridge, TN | 0.050 | 4.2 | Chamber | Hanson et al (1989) |
| Forest | NA ^c | 3.0 | NA ^c | Van Aalst (1982) |
| Snow | 0.006-0.03 | <<0.3 | Chamber | Granat and Johansson (1983) |
| <u>Nitric Oxide</u> | | | | |
| Soil | | | | |
| Sandy loam | 1-4 | 1.9 | Chamber | Judeikis and Wren (1978) |
| Adobe clay | 1-4 | 1.3 | Chamber | Judeikis and Wren (1978) |
| Forest soil | NA ^c | <0.01 | NA ^c | Van Aalst (1982) |
| Snow | 0.0005-0.002 | <<0.3 | Chamber | Granat and Johansson (1983) |
| <u>Nitric Acid Vapor</u> | | | | |
| Bark | 0.06-0.07 | 7.4 | Chamber | Hanson et al (1992) |
| Snow | | | | |
| -18 °C | 0.014 (36) | <0.2 | Chamber | Johansson and Granat (1986) |
| -8 °C | 0.014 (36) | 0.4 | Chamber | Johansson and Granat (1986) |
| -5 °C | 0.014 (36) | 0.4 | Chamber | Johansson and Granat (1986) |
| -4 °C | 0.014 (36) | 1.2 | Chamber | Johansson and Granat (1986) |
| -3 °C | 0.014 (36) | 1.0 | Chamber | Johansson and Granat (1986) |
| -2 °C | 0.014 (36) | 5.7 | Chamber | Johansson and Granat (1986) |

^aData are presented as the mean of reported values

^bData are based on total area for bark and litter, and ground area for snow, forest floor, and soil

^cNA = Not available

Nitric acid vapor is the only oxide of nitrogen to exhibit significant deposition to snow, but it does so only when temperatures exceed -5 °C (Granat and Johansson, 1983, Johansson and Granat, 1986, Table 10-11). Bennett (1988) modeled the deposition of

reactive gases, such as HNO_3 , to urban environments (i.e., cityscapes) and calculated that V_d would be limited to 2 to 5 mm/s by aerodynamic resistances

10.5 EFFECTS OF NITROGEN DEPOSITION ON SOILS

10.5.1 Introduction

The effects of any nutrient upon biological systems must be viewed from the perspective of the amount of that nutrient in the system, the biological demand for that nutrient, and the amount of input. Thus, if a nutrient is deposited on an ecosystem deficient in that nutrient, a growth increase will occur, and this will generally (but not always) be regarded as a positive effect (the deficiency condition in Figure 10-3). If a nutrient is deposited on an ecosystem with adequate supplies of that nutrient, there may be no effect for a period of time or over a range of input values (the sufficiency condition in Figure 10-3). Inputs of any nutrient greatly in excess of a plant's biological demand will result in negative growth responses, or toxic effects of some sort, as shown in the last segment of the curve in Figure 10-3.

Nitrogen is unique among nutrients in that its retention and loss is regulated almost exclusively by biological processes. Whereas other major nutrients (phosphorus [P], sulfur [S], potassium [K], calcium [Ca], magnesium [Mg], and manganese [Mn]) originate primarily from soil minerals and often accumulate in adsorbed/exchangeable pools in the soil, nitrogen originates from the atmosphere and rarely accumulates for long in exchangeable/adsorbed pools. (Ammonium may accumulate by fixation in the interlayers of 2:1 clays or by chemical reactions with humus, but these pools are largely unavailable to either plants or microbes.) In theory, large soil pools of NH_4^+ could occur, because NH_4^+ strongly adsorbs to cation exchange sites (negatively-charged sites on clays and organic matter in soils). Large soil NH_4^+ pools seldom occur, however, because of the action of nitrifiers (soil organisms that convert NH_4^+ to NO_3^- , a process referred to as nitrification), and, in alkaline soils, purely chemical conversion to NH_3 gas followed by volatilization. In those rare soils where nitrification is inhibited and acidity is too great for volatilization, soil NH_4^+ pools can build up to fairly high levels (e.g., Roelofs et al., 1987; Vitousek et al., 1979), but these cases seem to be the exception rather than the rule. Because NO_3^- is

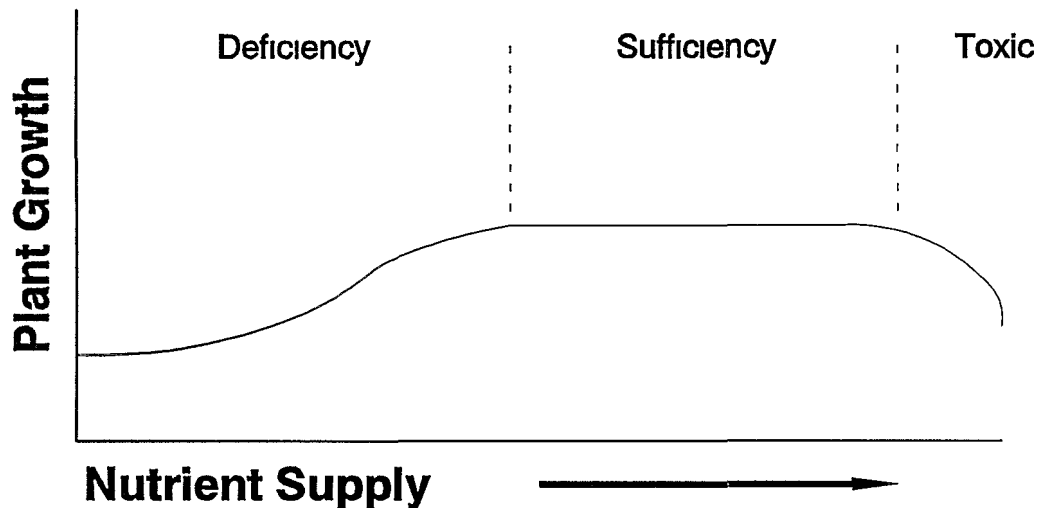


Figure 10-3. Schematic representation of the response of plants to nutrient inputs.

poorly adsorbed to soils (in contrast to sulfate ions $[\text{SO}_4^{2-}]$ and ortho-phosphate, Hingston et al., 1967), nitrification in excess of plant and microbial demand for nitrogen almost always leads to increased NO_3^- leaching (e.g., Van Breemen et al., 1982, Van Miegroet and Cole, 1984; Johnson and Todd, 1988, Foster and Nicolson, 1988). High rates of NO_3^- leaching can be deleterious for two major reasons: (1) the potential acidification of soils and waters and/or mobilization of aluminum ions (Al^{3+}) (as is the case with SO_4^{2-} , Reuss and Johnson, 1986) and (2) the potential contamination of drinking water (the EPA standard for NO_3^- nitrogen being 10 mg nitrogen/L).

Soils are by far the largest nitrogen pool in forest ecosystems, usually exceeding 85% of total ecosystem capital (Cole and Rapp, 1981). Yet most soil nitrogen is inert and unavailable for either uptake or leaching, with only a rather loosely-defined "mineralizable" pool being biologically active (Aber et al., 1989). This "mineralizable pool", the size of which is typically defined either by *in situ* incubation of soils or litter, is that portion of soil nitrogen that heterotrophs (decomposers), autotrophs (plants), and nitrifying bacteria compete for. The processes involved in this competition have been described and modeled, often with a special emphasis on nitrification and nitrate leaching (e.g., Vitousek et al., 1979, Riha et al., 1986). However, a generally applicable and potentially predictive model analogous to, for example, cation exchange and leaching (e.g., Reuss, 1983, Gherini et al., 1985, Cosby et al., 1985) remains elusive. For example, the cessation of nitrate leaching following

harvesting in nitrogen-rich red alder (*Alnus rubra*) forests in Washington (apparently a result of cessation of nitrogen fixation, Bigger and Cole, 1983, Van Miegroet et al , 1990) does not support earlier predictions that nitrate leaching following disturbance is usually greatest in sites with inherently better nitrogen status (e g , Vitousek et al , 1979) Also, the recent discovery of several sites where nitrate leaching is high under undisturbed conditions (Van Miegroet and Cole, 1984, Foster, 1985, Joslin et al , 1987, Johnson et al , 1991) does not support the long-held notion that nitrogen is tightly cycled and conserved in forest ecosystems (e g , Gessel et al , 1973, Cole and Rapp, 1981, Aber et al , 1989)

The following discussion is based on present knowledge and will focus on forest ecosystems, but will include considerations of arid ecosystems as well Arid and semiarid ecosystems are not as susceptible to the soil acidification and groundwater NO_3^- pollution as are forest and agricultural systems in more humid areas because of a lack of water for NO_3^- leaching and because soils are more alkaline There are some important implications of nitrogen deposition on arid and semiarid ecosystems, however, that deserve consideration, namely, vegetation growth increases and increased denitrification Therefore, due consideration of nitrogen cycling in and nitrogen deposition effects on arid ecosystems is given where information is available

Agricultural lands are excluded from this discussion because crops are routinely fertilized with amounts of nitrogen (100 to 300 kg/ha) that far exceed pollutant inputs even in the most heavily polluted areas These high rates of fertilization can lead to groundwater contamination problems and may contribute to the atmospheric N_2O loading as well (e g , Hutchinson and Mosier, 1979), but a discussion of the environmental effects of fertilization are beyond the scope of this section

10.5.2 Pollutant Nitrogen Inputs and Nitrogen Cycling in Natural Ecosystems: A Brief Review

An evaluation of the effects of pollutant nitrogen deposition on terrestrial vegetation and soils must begin with considerations of how these pollutant inputs affect terrestrial nitrogen cycles The general subject of terrestrial nitrogen cycling was reviewed in Section 10 3, only a few of the more germane details are repeated here

Nitrogen, unlike Ca, K, Mg, P, or S, seldom forms large soil inorganic pools that can buffer excessive inputs and provide a readily-available source of nutrient for plants. In theory, large soil pools of NH_4^+ could occur, because NH_4^+ strongly adsorbs to cation exchange sites. Large soil NH_4^+ pools seldom occur, however, because of the action of nitrifiers, and, in alkaline soils, purely chemical conversion to NH_3 gas followed by volatilization. In those rare soils where nitrification is inhibited and pH is too low for volatilization, soil NH_4^+ pools could, in theory, build up to fairly high levels (e.g., Roelofs et al., 1987; Vitousek et al., 1979), but these cases seem to be the exception rather than the rule. The potential for the accumulation of large NH_4^+ pools can also be reduced by purely chemical reactions between ammonium and soil humus (e.g., Foster et al., 1985b). Because NO_3^- is poorly adsorbed to soils, nitrification in excess of plant and microbial demand for nitrogen almost always leads to increased NO_3^- leaching (e.g., Van Breemen et al., 1982, Van Miegroet and Cole, 1984, Johnson and Todd, 1988, Foster and Nicolson, 1988).

Nitrogen can enter forest ecosystems in many forms: (1) wet deposition of NH_4^+ , NO_3^- , and organic nitrogen, (2) dry deposition of these forms plus HNO_3 vapor (Lindberg et al., 1986); and (3) biological fixation of N_2 . Inputs via wet and dry deposition first encounter the forest canopy, where they may be taken up either by trees or by organisms living within the canopy, or the phyllosphere (leaf surface). Deposited nitrogen not taken up within the phyllosphere falls primarily as wet deposition to the forest floor, where plants, decomposers (heterotrophs, which consist of fungi and bacteria), and nitrifying bacteria compete for it (Figure 10-4, top). This competition for nitrogen among heterotrophs, plants, and nitrifying bacteria plays a major role in determining the degree to which a vegetation growth increase will occur and the degree to which incoming nitrogen is retained within the ecosystem. It has been assumed that nitrifiers are poor competitors for nitrogen compared to heterotrophs and plants (Vitousek et al., 1982, Riha et al., 1986, see also review by Davidson et al., 1990). This assumption has recently been challenged by Davidson et al. (1990). Using ^{15}N techniques, these authors found significant nitrification and microbial NO_3^- uptake (12 to 46% of nitrogen mineralization rates) in grassland soils, even when soil NO_3^- pools and NO_3^- leaching rates were very low. They concluded that the small soil NO_3^- pool in this site turned over very rapidly due to nitrification and microbial uptake of NO_3^- and that nitrifiers were quite able competitors for nitrogen. They also point out that NO_3^-

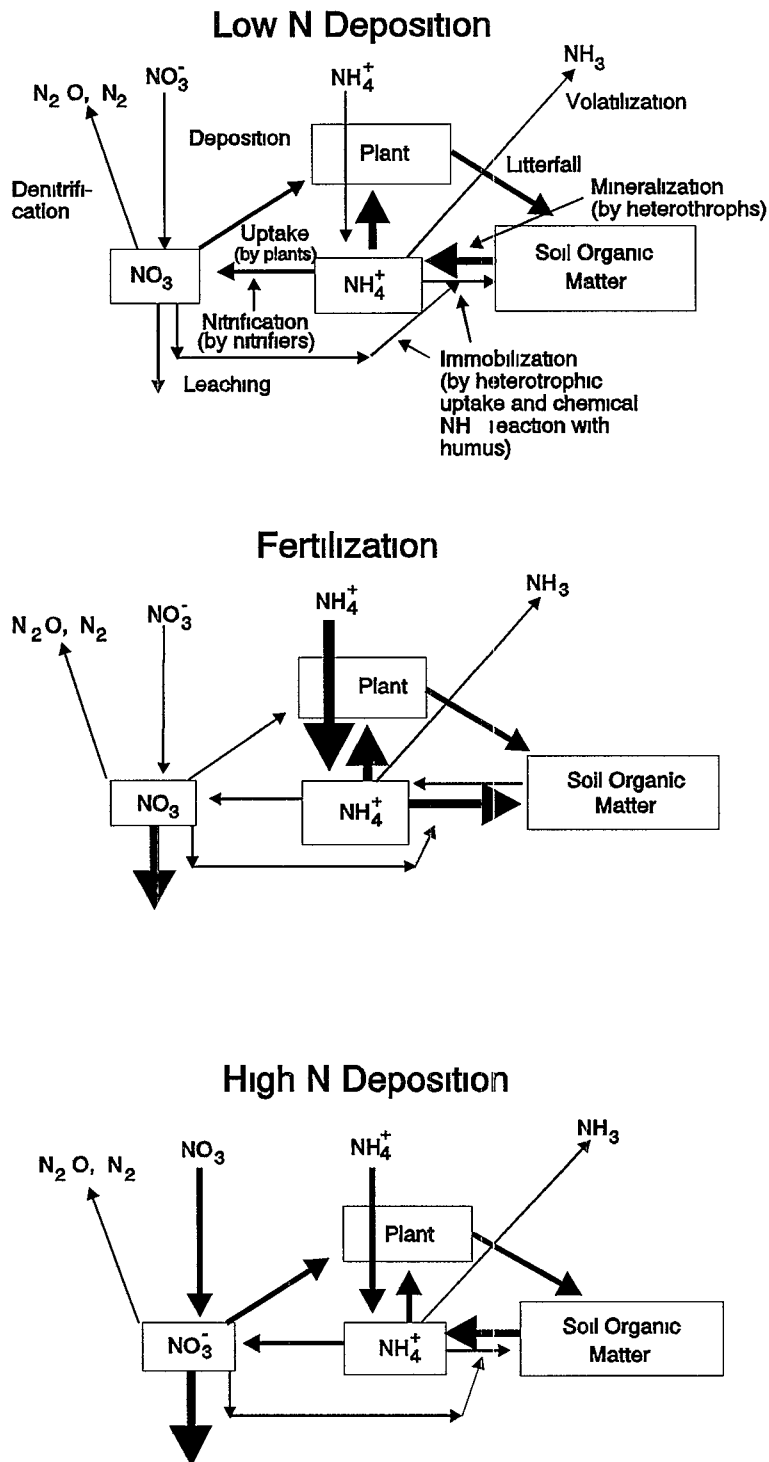


Figure 10-4. Schematic representation of the fate of incoming nitrogen in nitrogen-poor (top), fertilized (center), and high-nitrogen (bottom) input systems.

production during incubation actually represents a net effect of nitrification and microbial NO_3^- uptake, and define this as "net nitrification" The extent to which these results might apply to forest ecosystems is unknown, however, if this pattern proves to be true in general, it will require a substantial redesign of the conceptual model currently used to explain and predict nitrification and NO_3^- leaching

Heterotroph demand for nitrogen (both NH_4^+ and NO_3^-) depends on the supply of labile organic carbon substrates (as well as temperature and moisture conditions) Thus, adding labile organic carbon to a soil should reduce plant uptake and net nitrification by increasing heterotrophic competition for NH_4^+ and increasing microbial NO_3^- uptake Adding labile organic carbon to a soil may also cause increased activity of denitrifying organisms, which also require organic substrates, resulting in reduced nitrate leaching Turner (1977) demonstrated that addition of carbohydrates to a forest soil in Washington caused increased nitrogen deficiency in Douglas fir (*Pseudotsuga menziesii*) trees, presumably by stimulating heterotrophic competition for nitrogen Johnson and Edwards (1979) found that addition of carbohydrate substrate to a forest soil caused an immediate reduction in nitrate leaching and net nitrification production during laboratory incubation of a yellow-poplar forest soil in Tennessee

According to the conceptual model described above, nitrification and NO_3^- leaching will become significant only after heterotroph and plant demand for nitrogen are substantially satisfied, a condition that has been referred to as "nitrogen-saturated" There are various definitions for nitrogen-saturation, many of which are reviewed by Skeffington and Wilson (1988). One definition is "ecosystems where the primary production will not be further increased by an increase in the supply of nitrogen " There are clearly problems with this definition in that ecosystems that are low in nitrogen but limited by another nutrient (such as phosphorus) may not experience an increase in primary production in response to nitrogen input unless phosphorus is added first (e g , Pritchett and Comerford, 1982) Other definitions for nitrogen saturation reviewed by Skeffington and Wilson (1988) include "when external nitrogen input and nitrogen mineralization from the soil exceed the capacity of the ecosystem organisms to absorb more nitrogen," or "an ecosystem which cannot accumulate more N " Aber et al (1989) define nitrogen saturation "as the availability of ammonium and nitrate in excess of total combined plant and microbial nutritional demand "

This definition conveys the same idea as those reviewed by Skeffington and Wilson (1988), but, in its strictest sense, it also is flawed. All ecosystems, even extremely nitrogen-deficient ones, have some small pool of ammonium and nitrate within the soil and litter components. If the definition of Aber et al. (1989) is used in its strictest sense, then all ecosystems are nitrogen saturated to one degree or another. Aber et al. (1989) also state that nitrogen saturation implies limitation on biotic function by some other resource (e.g., phosphorus or water for plants or carbon for microbes). But if this is so, naturally phosphorus-deficient ecosystems (such as those in the southeastern coastal plain) might be considered nitrogen saturated, whereas in reality, these ecosystems are often very low in nitrogen and release virtually no nitrate. Furthermore, as noted above, phosphorus-deficient ecosystems will frequently accumulate substantially more nitrogen once phosphorus limitations are satisfied.

Although the precise definition of nitrogen saturation seems elusive because of various caveats that must be taken into account, the general idea seems to be encompassed in the last and most brief definition reviewed by Skeffington and Wilson (1988): "an ecosystem which cannot accumulate more N." This definition implies that further nitrogen accumulation cannot occur, even though other nutrient limitations are satisfied. This definition will be used in the following discussion.

It is important to note that additional nitrogen inputs to a nitrogen-saturated ecosystem will cause equivalent leaching losses of NO_3^- regardless of the chemical form of the nitrogen entering the system (NH_4^+ , NO_3^- , or organic) to the extent that (1) nitrogen inputs are in biologically available forms, (2) nitrification proceeds uninhibited, and (3) denitrification does not occur (Reuss and Johnson, 1986). There has been an unfortunate tendency among atmospheric deposition researchers to ignore the effects of NH_4^+ and (especially) organic nitrogen on ecosystem acidification and nitrate leaching, an omission that substantially underestimates the acidification potential of atmospheric nitrogen deposition.

The rather simple model depicted in Figure 10-4 does not account for the possibility of nitrification inhibitors. Autotrophic nitrifiers are known to be inhibited by low pH, high soil solution chloride ion (Cl^-) concentrations, and certain organic chemicals, both naturally and synthetically produced (Alexander, 1963; Roseberg et al., 1986). The occurrence and importance of naturally produced nitrification inhibitors has received considerable attention in the ecological literature. An early study by Rice and Pancholy (1972) indicated that

nitrification rates decrease during forest succession due to the presence of chemical nitrification inhibitors (soluble allelopathic compounds produced by plant litter) This somewhat controversial finding stimulated several follow-up investigations in various ecosystems. Some of these investigations supported the contention that nitrification inhibitors were a factor in controlling NO_3^- losses from forest ecosystems (Lodhi, 1978, Olson and Reiners, 1983), but several others found no evidence of them, and concluded that either competition for NH_4^+ or other nutrient limitations controlled nitrification rates (Purchase, 1974, Robertson and Vitousek, 1981, Lamb, 1980, Cooper, 1986)

There is no reason to doubt that inhibitors play a role in some forests, but the extent to which inhibitors occur and the factors leading to their production are unknown Nor is it known how inhibitors might function under conditions of very high, chronic NH_4^+ inputs Roelofs et al. (1987) report little nitrification in Dutch forests subject to very high inputs of NH_4^+ from nearby agricultural activities, but they attribute the lack of nitrification in these forests to low pH The situation reported by Roelofs et al (1987) is unusual, however, there are few cases where these conditions do not lead to high rates of nitrification and NO_3^- leaching. Others have reported high rates of nitrification under very acid soil conditions (Klein et al , 1983, Van Breemen et al , 1982, 1987)

Denitrification (i.e., the microbially mediated conversion of NO_3^- to NO_x and N_2 gases) is thought to be of importance only in forest soils that (1) have elevated NO_3^- inputs and (2) experience anaerobic conditions (e.g., flooded conditions) (Davidson and Swank, 1987). Goodroad and Keeney (1984) provide estimates of denitrification losses from relatively nitrogen-rich forest ecosystems in Wisconsin of 0.2 to 2.1 kg/ha/year, values that are worthy of including in nitrogen budgets, but do not compare to NO_3^- leaching rates that have been shown to occur in some forests (see below) Similarly, Woodmansee (1978) discounts the importance of denitrification in grassland soils, showing that NH_3 volatilization from animal wastes is the major nitrogen loss mechanism Curiously, however, Westerman and Tucker (1978) and Klubek et al (1978) found that denitrification rather than NH_3 volatilization is the major nitrogen loss mechanism from desert soils in the Sonoran and Great Basin desert ecosystems They speculate that microsites with saturated water conditions occur during precipitation events that produce the anaerobic conditions necessary for denitrification to occur Peterjohn and Schlesinger (1990) calculated that 77% of

atmospheric nitrogen inputs to desert ecosystems in the southwestern United States have been lost to the atmosphere since the last glaciation. They stop short of giving values for NO_x and N_2 (denitrification) versus NH_3 (volatilization) losses, but point out that the importance of learning more about the nature of gaseous nitrogen losses from these systems, especially in the case of N_2O , given its importance to the O_3 layer and as a greenhouse gas.

Vegetation demand for nitrogen depends on a number of growth-influencing factors, including temperature, moisture, and the availability of other nutrients. Limitation of moisture in arid ecosystems clearly does not preclude growth responses to nitrogen input, however. Several studies have shown that demonstrated net nitrogen inputs to desert ecosystems produced growth increases despite supposed water limitations (Fisher et al., 1988c, see review by Moorhead et al., 1986). Nitrogen is considered such an important factor in the productivity and function of desert ecosystems that an entire volume has been devoted to the subject (West and Skujins, 1978).

In forest ecosystems, stand age is an important factor determining nitrogen uptake rates. Uptake rates decline as forests mature, especially after the cessation of the buildup of nutrient-rich foliar biomass following crown closure (Switzer and Nelson, 1972, Miller, 1981, Turner, 1981). Thus, one would expect NO_3^- leaching rates to be greater in older forests than in younger forests due to greater NH_4^+ supplies to nitrifiers as well as to lower NO_3^- uptake in older forests. The results of Vitousek and Reiners (1975) support this hypothesis in that they found higher NO_3^- concentrations in streams draining mature spruce-fir forests than in streams draining immature spruce-fir forests in New England.

Processes that cause net nitrogen export from ecosystems, such as fire and harvesting, will naturally push ecosystems toward a state of greater nitrogen demand or even nitrogen deficiency. Frequent fire is normally thought of as an especially effective way of maintaining low ecosystem nitrogen status. However, studies on the effects of fire upon soil nitrogen have produced conflicting results. Some authors have reported total nitrogen contents that were not significantly changed within 1 to 2 years of burning, whereas others have reported significant losses. Jurgensen et al. (1981) found that broadcast burning caused a minor net loss of nitrogen (approximately 100 kg/ha) from a clearcut site in Montana, and concluded that plant reestablishment benefitted from the increased nitrogen availability following this prescribed burn. Wells (1971) noted that although the periodic prescribed

burns have caused significant losses of forest floor material immediately after the burn, there seemed to be a tendency for the system to regain this organic matter over time and approach the control condition. He also found that organic matter and nitrogen were redistributed from the forest floor to the surface mineral soil as a result of burning, the net effect being a redistribution of the organic matter in the profile rather than a reduction. Furthermore, one treatment (annually burned plots) showed significant increases in soil nitrogen (550 to 990 kg/ha), which were attributed to increased activity of nitrogen fixers. In contrast, Grier (1975) noted significant nitrogen losses (855 kg/ha) from an intense fire on the eastern slope of the Cascade Mountains of Washington. It seems that the net effect of fire on ecosystem nitrogen status has a great deal to do with fire intensity.

10.5.3 Fate of Nitrogen in Forest Ecosystems: Contrasts Between Fertilizer and Pollutants

The prospects for forests becoming nitrogen saturated from atmospheric nitrogen inputs have been explored in recent workshops and reviews (Nilsson and Grennfelt, 1988, Schulze et al., 1989, Aber et al., 1989). Critical loads analyses for nitrogen saturation typically consider vegetation uptake and increment as the primary factors controlling forest ecosystem nitrogen retention, and attribute little potential for soil nitrogen accumulation, despite the fact that soils comprise the largest nitrogen pool in virtually all forest ecosystems (Nilsson and Grennfelt, 1988; Schulze et al., 1989). In contrast, numerous forest fertilization studies have shown that litter and soils are major sinks for nitrogen (e.g., Heilman and Gessel, 1963, Mead and Pritchett, 1975, Miller et al., 1976, Melin et al., 1983, Raison et al., 1990). As noted by Aber et al. (1989), it is not surprising that forest ecosystems respond differently to pulse inputs of nitrogen via fertilization versus slow, steady inputs via atmospheric deposition. (The information presented in this section is based on Johnson, 1992)

Fertilization studies differ from pollutant nitrogen deposition in two important respects. Pollutant nitrogen deposition enters the ecosystem at the canopy level, whereas fertilizer is typically (but not always) applied to the soil. Another important difference (as noted by Aber et al., 1989) is that pollutant nitrogen deposition enters the ecosystem as a slow, steady input in rather low concentrations, whereas the fertilizer is typically applied in one to five

large doses Nitrate applications or urea applications to nitrogen-rich sites can result in substantial nitrate leaching losses of fertilizer nitrogen (e g , Overrein, 1969, Matzner et al , 1983, Tschaplinski et al , 1991) However, most studies show minimal loss of fertilizer nitrogen via leaching following single, large applications of ammonium or urea to nitrogen-poor sites (Cole and Gessel, 1965, Overrein, 1969, Cole et al , 1975, Worsnop and Will, 1980) As will be shown later, there are some important differences in the way the nitrogen cycle in soils responds to large, single applications versus slow, steady applications of nitrogen, whether as fertilizer or as atmospheric input There have been cases where fertilizer has been applied in small, frequent doses, and it is useful to briefly review some of those studies here before comparing fertilization with atmospheric nitrogen deposition

10.5.3.1 Case Studies of Forest Fertilization at Differing Intervals

Ingestad (1981) has demonstrated in greenhouse experiments that optimum nitrogen uptake and growth by plants can be achieved by adjusting nitrogen inputs to the rate of plant growth In these experiments, the rate of nitrogen supply (i e , flux density, or nitrogen input per unit area per unit time) was proven to be the critical variable, not necessarily the concentration of nitrogen in the uptake solution Field experiments comparing standard fertilization with simultaneous irrigation and fertilization (IF) have also demonstrated the superior growth response and fertilizer nitrogen recovery by adjusting the flux density of nitrogen input (through the IF treatments) as compared to adding either one or a few large doses of nitrogen as in conventional fertilization (Aronsson and Elowson, 1980, Ingestad, 1981, Landsberg, 1986)

These authors (Aronsson and Elowson, 1980, Ingestad, 1981, Landsberg, 1986) do not report the effects of slow, steady inputs of nitrogen on nitrification and NO_3^- leaching However, multiple or continuous inputs of fertilizer may stimulate a buildup in populations of nitrifying bacteria A fertilizer experiment involving urea-nitrogen applications of 100 kg/ha/year for 3 years in quarterly (25 kg nitrogen/ha/3 mo) and annual (100 kg nitrogen/ha, in March) to young loblolly pine (*Pinus taeda* L) and yellow-poplar (*Liriodendron tulipifera* L) plantations in very nitrogen-poor sites in the Tennessee Valley (Johnson and Todd, 1988) found a buildup in nitrifying bacteria In all cases, the quarterly applications resulted in earlier and more pronounced increases in soil solution nitrate than did

annual applications Figure 10-5 illustrates this pattern for the loblolly pine site Furthermore, only the annual applications resulted in increased growth (Figure 10-6, top) The authors concluded that more frequent fertilization in those particular ecosystems benefited nitrifiers more than trees

In a later study, in a more nitrogen-rich site nearby, exactly the opposite results were obtained in a study comparing a single urea-nitrogen application of 50, 150, and 450 kg nitrogen/ha with multiple (three times at 37.5 kg nitrogen/ha) applications to a young sycamore (*Platanus occidentalis* L.) plantation (Tschaplinski et al., 1991) In this case, the authors found much higher soil solution NO_3^- concentrations in general (including in the control plots), no delay in the onset of nitrate leaching, and the greatest rates of nitrate leaching in the single 450 kg/ha application (Figure 10-7) Tree growth response was also greatest in the 450 kg/ha treatment, but growth responses were also significant in the multiple fertilization treatment (Figure 10-6, bottom) Thus, in this nitrogen-rich site, single fertilization produced the greatest growth response, but at a higher cost in terms of nitrate leaching.

The key to differences in nitrate leaching response observed in these two studies was the initial relative abundance of nitrifiers Aerobic incubations in the laboratory showed that the delay period to the onset of nitrate production was 25 to 30 days in the nitrogen-poor site and 0 to 4 days in the nitrogen-rich site (Johnson and Todd, 1988, Tschaplinski et al., 1991) According to Sabey et al. (1959), the delay period for the onset of nitrate production is closely related to the initial population of nitrifying bacteria These results imply that slow, steady inputs of nitrogen characteristic of pollutant inputs may cause more rapid increases in NO_3^- production in low-nitrogen ecosystems than conventional, single-application fertilization would; however, the opposite would be true in high-nitrogen ecosystems If the initial population of nitrifiers is low, the slow, steady inputs will favor a buildup of their populations more rapidly than single large inputs will and thus cause a relatively early increase in nitrate leaching If the initial population of nitrifiers is high, the rate of nitrate leaching is more likely to be proportional to the input of nitrogen in excess of plant demand regardless of timing and without delays caused by heterotrophic uptake

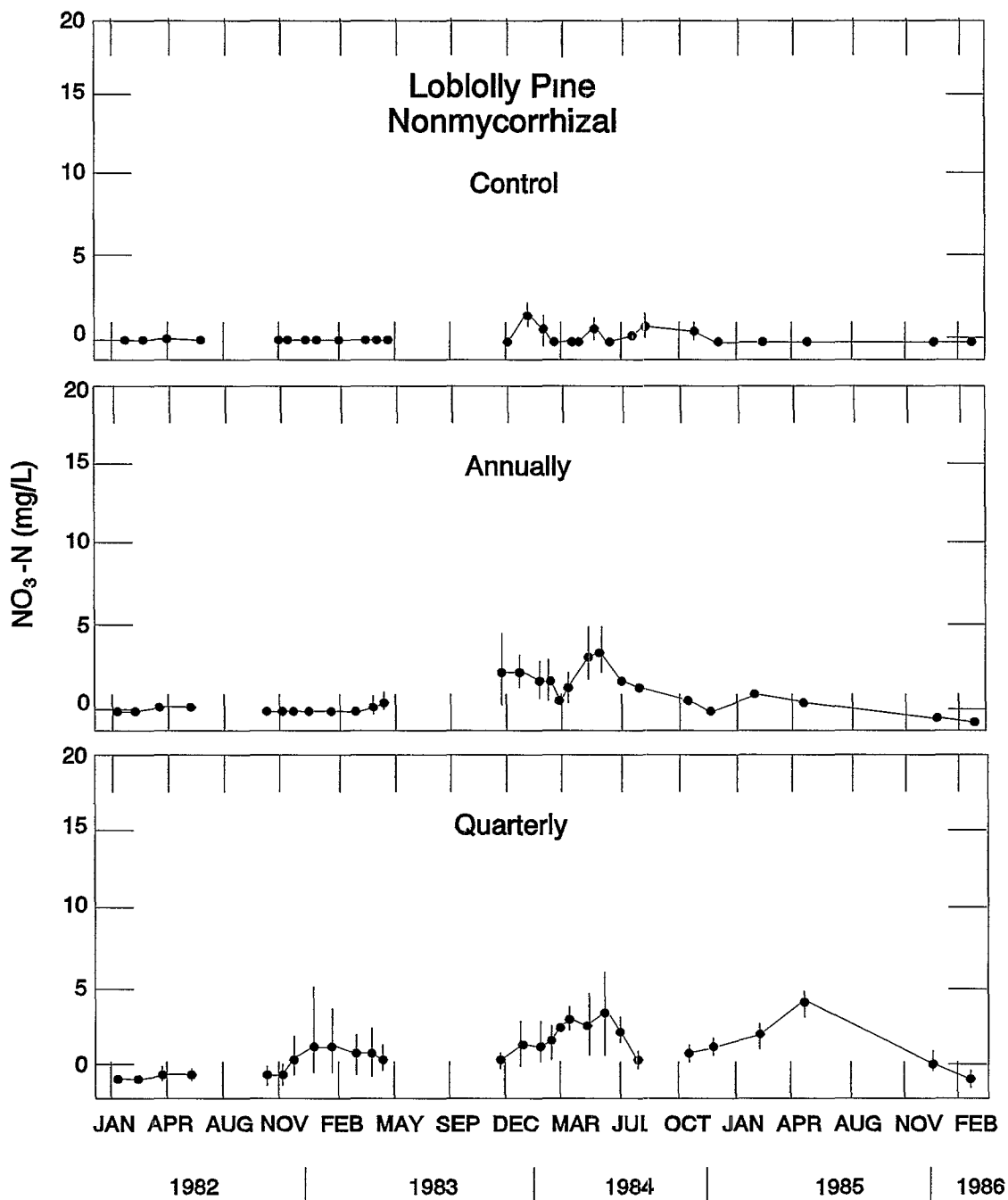


Figure 10-5. Soil solution nitrate concentrations in untreated control (top), annually fertilized (100 kg urea-nitrogen/ha/year, center), and quarterly-fertilized (25 kg urea-nitrogen/ha/3 mo, bottom) loblolly pine plots.

Source Johnson and Todd (1988)

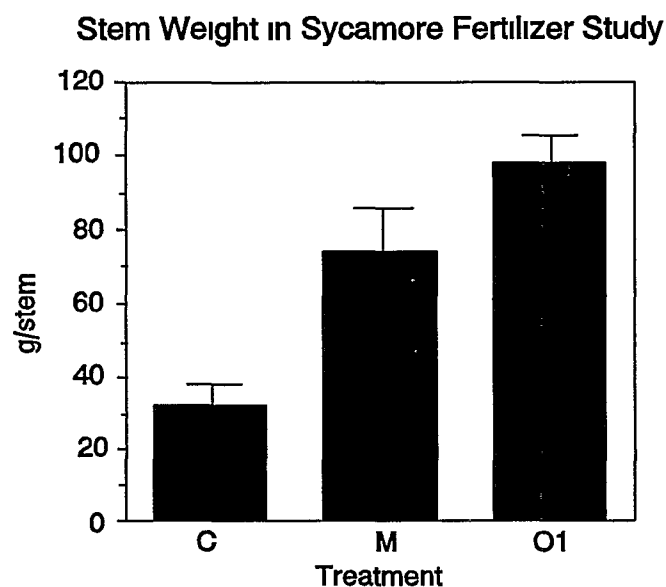
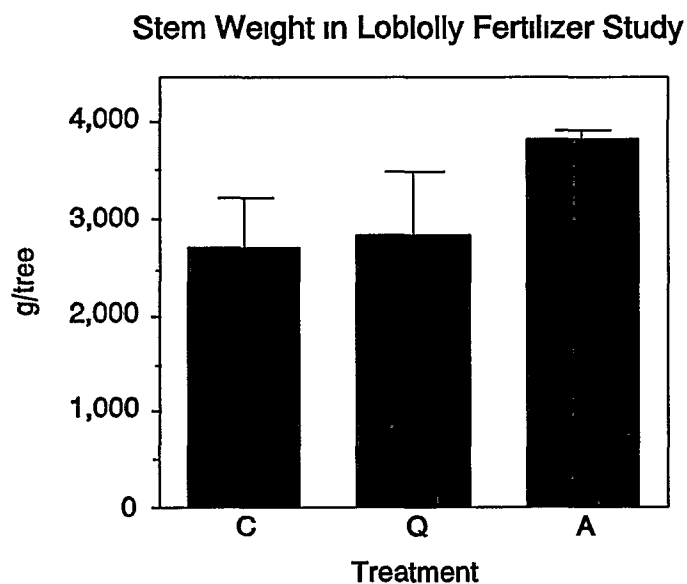


Figure 10-6. Top: Growth of loblolly pine in untreated (C), annual (A) (100 kg urea-nitrogen/ha/year, center), and quarterly (Q) (25 kg urea-nitrogen/ha/3 mo, center) applications of urea-nitrogen. **Bottom:** Growth of American sycamore in untreated C, multiple (m) (37.5 kg urea-nitrogen/ha, three times), and single (O1) (450 kg nitrogen/ha) applications of urea-nitrogen.

Source. Johnson and Todd (1988), Tschaplinski et al (1991)

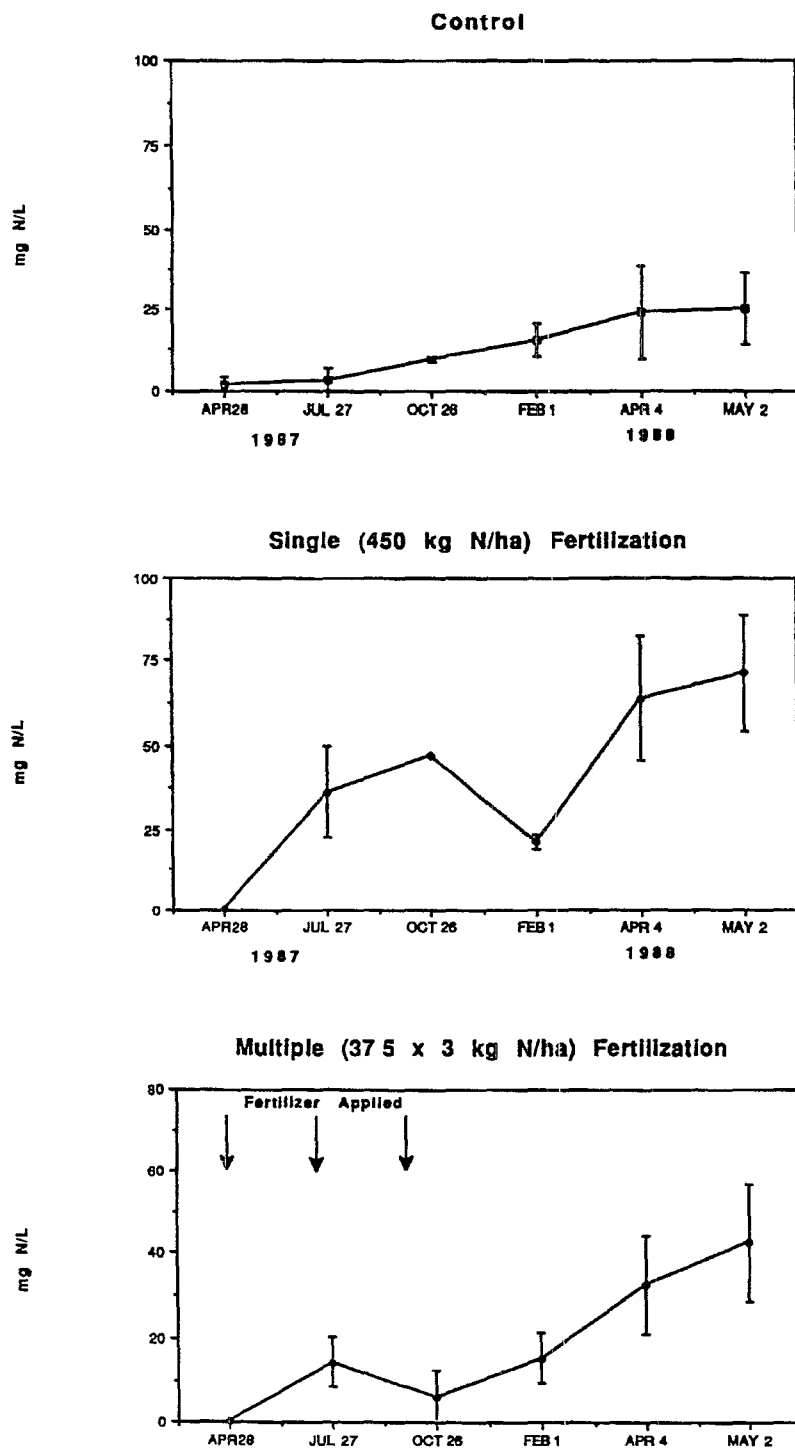


Figure 10-7. Soil solution nitrate concentrations in untreated (top), single (450 kg nitrogen/ha, center), and multiple (37.5 kg urea-nitrogen/ha, three times, bottom) applications of urea-nitrogen.

Source Tschaplinski et al (1991)

10.5.3.2 Fate of Nitrogen from Pulse Fertilization Versus Atmospheric Deposition

In managed forest ecosystems, fertilization has proven quite successful in producing growth increases in nitrogen-deficient forests, even though trees typically recover only 5 to 50% of fertilizer nitrogen in aboveground biomass (the very high tree recovery found by Bockheim et al. [1986], being exceptional, Table 10-12) Increased nitrogen in the soil is not mirrored directly by more nitrogen uptake, except at low levels (see Chapter 9) Fertilizer nitrogen retention in the litter and soil is usually substantial (Table 10-12 and Figure 10-4, center) There are two possible mechanisms for this high litter/soil nitrogen retention: (1) nitrogen uptake by soil heterotrophic organisms, and (2) nonbiological, chemical reactions between NH_3 and soil organic matter (Foster et al , 1985a) The overall result is that the retention of nitrogen on an ecosystem level is usually quite high (averaging 60% of applied nitrogen, Table 10-12) Furthermore, fertilizer recovery in trees, soil, and the total ecosystem increases with the rate of fertilization and shows no sign of leveling off, even at rates of fertilizer nitrogen input of up to 1,500 kg/ha (Figures 10-8 to 10-10)

Table 10-13 gives a summary of nitrogen budgets from the nutrient cycling literature and from the recently completed Integrated Forest Study (IFS, Johnson and Lindberg, 1992) In this summary, atmospheric inputs are compared with outputs via soil solution or stream water (primarily as NO_3^-) and vegetation increment, or the nitrogen necessary to build perennial tissues in biomass (bole, branches) It should be noted that the studies prior to IFS measured nitrogen deposition principally by bulk precipitation, which substantially underestimates nitrogen deposition in many polluted sites (e g , Lindberg et al , 1986) Most of the IFS data include estimates of both wet and dry deposition, and, therefore, nitrogen deposition values reported there are often much greater than those that would have been reported using bulk collectors For that reason, the IFS data are shown separately from previous data in Figures 10-11 to 10-13 It should also be noted that vegetation nitrogen uptake values in each of these systems are much higher than vegetation increment because uptake includes nitrogen taken up and returned annually via litterfall and foliar leaching Vegetation increment was chosen for this analysis because it represents the net nitrogen demand of growing vegetation that must be satisfied from sources external to the nitrogen cycle (atmospheric deposition or soil "mining")

TABLE 10-12. NITROGEN FERTILIZER RECOVERY BY VEGETATION AND SOILS IN VARIOUS STUDIES

| Location | Species and Age (years) | Fertilizer Type and Amount (kg/ha) ^a | Vegetation Recovery (kg/ha and percent) | Soil Recovery (kg/ha and percent) | Reference |
|-------------|-------------------------------|--|--|--|----------------------------|
| Florida | <i>Pinus eliottii</i> , 11 | AS,56 | 6 (11%) | 17 (30%) | Mead and Pritchett (1975) |
| Florida | <i>Pinus eliottii</i> , 11 | AS,224 | 24 (11%) | 40 (18%) | Mead and Pritchett (1975) |
| Mississippi | <i>Pinus taeda</i> , 5 | AN,112 | 16 (14%) | - | Baker et al (1974) |
| Mississippi | <i>Pinus taeda</i> , 6 | AN,224 | 31 (28%) | - | Baker et al (1974) |
| Mississippi | <i>Pinus taeda</i> , 5 | AN,224 | 31 (14%) | - | Baker et al (1974) |
| Mississippi | <i>Pinus taeda</i> , 6 | AN,224 | 146 (65%) | - | Baker et al (1974) |
| New Zealand | <i>Pinus radiata</i> , 14 | NS,960 | 120 (13%) | 488 (51%) | Baker et al (1986) |
| New Zealand | <i>Pinus radiata</i> , 13 | U,224 | 80 (40%) | 120 (60%) | Worsnop and Will (1980) |
| Ontario | <i>Pinus banksiana</i> , 45 | U,300 | 76 (25%) | 79 (26%) | Morrison and Foster (1977) |
| Scotland | <i>Pinus nigra</i> , 36 | AS,252 | 136 (54%) | 176 (67%) | Miller et al (1976) |
| Scotland | <i>Pinus nigra</i> , 36 | AS,504 | 228 (45%) | 78 (15%) | Miller et al (1976) |
| Scotland | <i>Pinus nigra</i> , 36 | AS,1008 | 366 (36%) | 303 (30%) | Miller et al (1976) |
| Scotland | <i>Pinus nigra</i> , 36 | AS,1512 | 495 (32%) | 229 (15%) | Miller et al (1976) |
| Sweden | <i>Pinus sylvestris</i> , 130 | AN,224 | 19 (19%) | 46 (46%) | Melin et al (1983) |
| Sweden | <i>Pinus sylvestris</i> , 120 | U,150 | 12 (8%) | 74 (49%) | Nommik and Moller (1981) |
| Sweden | <i>Pinus sylvestris</i> , 120 | U,300 | 21 (7%) | 87 (29%) | Nommik and Moller (1981) |
| Sweden | <i>Pinus sylvestris</i> , 120 | U,600 | 36 (6%) | 102 (17%) | Nommik and Moller (1981) |

TABLE 10-12 (cont'd). NITROGEN FERTILIZER RECOVERY BY VEGETATION AND SOILS IN VARIOUS STUDIES

| Location | Species and Age (years) | Fertilizer Type and Amount (kg/ha) ^a | Vegetation Recovery (kg/ha and percent) | Soil Recovery (kg/ha and percent) | Reference |
|--------------------|-----------------------------------|--|--|--|---------------------------|
| Sweden | <i>Pinus sylvestris</i> , 120 | AN,150 | 29 (19%) | 32 (21%) | Nommik and Moller (1981) |
| Sweden | <i>Pinus sylvestris</i> , 120 | AN,300 | 60 (20%) | 48 (16%) | Nommik and Moller (1981) |
| Sweden | <i>Pinus sylvestris</i> , 120 | AN,600 | 90 (12%) | 72 (12%) | Nommik and Moller (1981) |
| Tennessee | <i>Pinus taeda</i> , 4 | U,300 | 25 (8%) | - | Johnson and Todd (1988) |
| Western Washington | <i>Pseudotsuga menziesii</i> , 52 | NS,224 | 94 (42%) | 124 (55%) | Heilman and Gessel (1963) |
| Western Washington | <i>Pseudotsuga menziesii</i> , 38 | NS,224 | 204 (50%) | 206 (51%) | Heilman and Gessel (1963) |
| Western Washington | <i>Pseudotsuga menziesii</i> , 30 | NS,400 | 72 (13%) | 284 (51%) | Heilman and Gessel (1963) |
| Western Washington | <i>Pseudotsuga menziesii</i> , 32 | NS,560 | 75 (13%) | 687 (123%) | Heilman and Gessel (1963) |
| Western Washington | <i>Pseudotsuga menziesii</i> , 38 | NS,560 | 149 (20%) | 337 (46%) | Heilman and Gessel (1963) |
| Wisconsin | <i>Pinus resinosa</i> , 37 | AN,100 | 125 (125%) | - | Bockheim et al (1986) |

^aAS = Ammonium sulfate, AN = Ammonium nitrate, NS = Not specified, U = Urea

Source Johnson (1992)

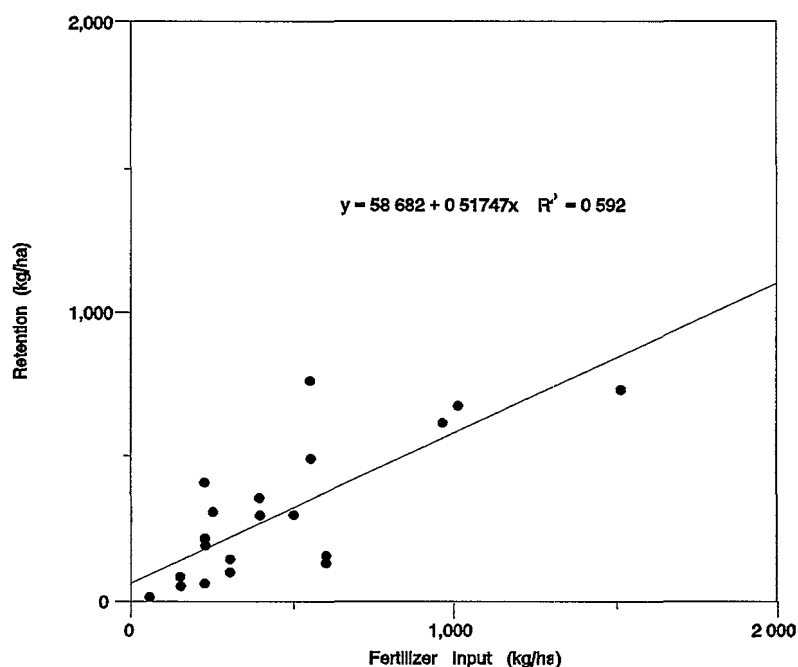


Figure 10-8. Ecosystem recovery of fertilizer nitrogen as a function of fertilizer nitrogen input.

Source Johnson (1992)

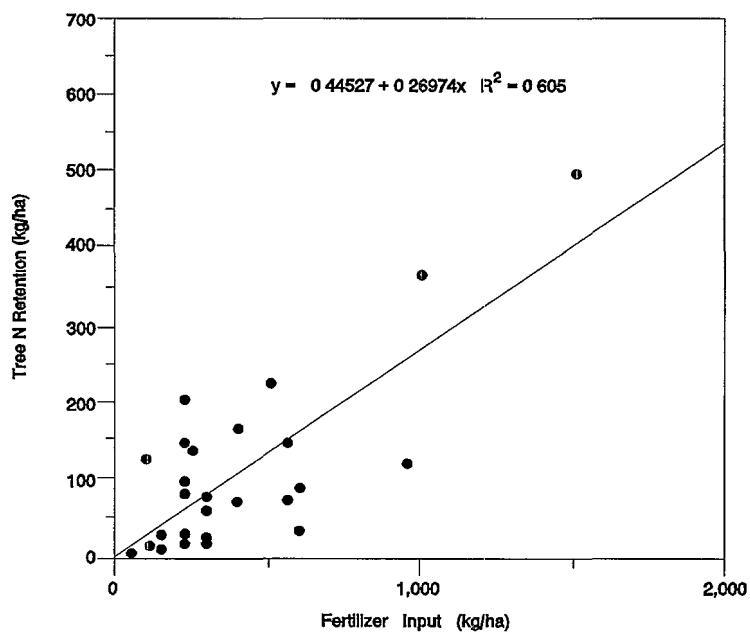


Figure 10-9. Tree recovery of fertilizer nitrogen as a function of fertilizer nitrogen input.

Source Johnson (1992)

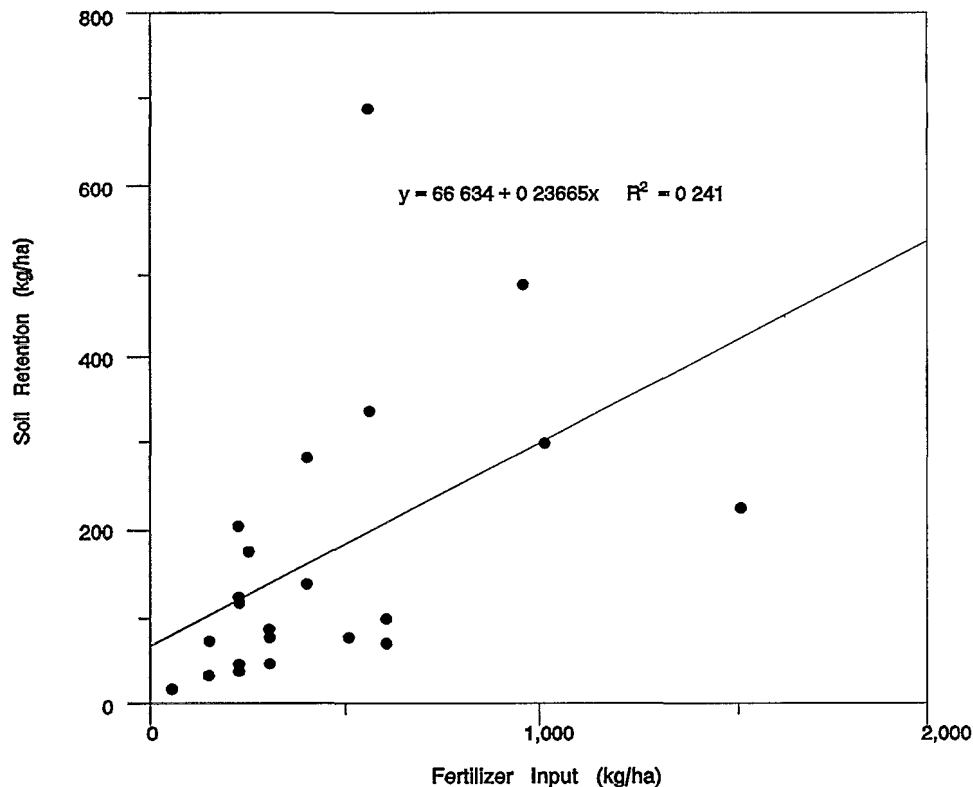


Figure 10-10. Soil recovery of fertilizer nitrogen as a function of fertilizer nitrogen input.

Source Johnson (1992)

The data in Table 10-13 and Figures 10-11 to 10-13 reveal some interesting contrasts between ecosystem retention of fertilizer versus atmospherically deposited nitrogen. First, total ecosystem retention of atmospherically deposited nitrogen ranges from over 99% to -266%, with no apparent relationship to atmospheric input (Figure 10-11). Second, vegetation nitrogen increment accounts for nearly all ecosystem nitrogen retention in most (19 of 24) cases, and calculated soil nitrogen retention is low and frequently negative (14 of 23 cases) (Table 10-13, Figures 10-13 and 10-14). There is no relationship between atmospheric nitrogen deposition and either tree increment or calculated soil retention (Figures 10-12 and 10-13).

The pattern of calculated soil nitrogen versus deposition in Figure 10-13 suggests that heterotrophs are very poor competitors for nitrogen, even at very low nitrogen input levels.

**TABLE 10-13. NITROGEN INPUTS, OUTPUTS, AND VEGETATION INCREMENTS
IN VARIOUS FOREST ECOSYSTEMS**

| Location | Species | Input (kg/ha/year) | Leaching (kg/ha/year) | Net Retention (kg/ha/year) ^a | Vegetation Increment (kg/ha/year) | Calc Soil Retention (kg/ha/year) ^b | Reference |
|----------------|--|-----------------------|--------------------------|---|---|---|---|
| New Hampshire | Northern hardwood | 6.5 | 4.0 | 2.5 (38%) | 9.0 (138%) | -6.5 (-100%) | Bormann et al (1977) |
| Washington | <i>Pseudotsuga menziesii</i> | 1.7 | 0.6 | 1.1 (65%) | 10.0 (588%) | -8.9 (-523%) | Cole and Rapp (1981) |
| Germany | <i>Fagus sylvatica</i> | 21.8 | 4.4 | 17.4 (80%) | 4.1 (19%) | 13.3 (61%) | Cole and Rapp (1981) |
| Germany | <i>Picea abies</i> | 21.8 | 14.9 | 6.9 (32%) | 2.2 (56%) | 4.7 (22%) | Cole and Rapp (1981) |
| U S S R | <i>Picea abies</i> | 1.1 | 0.9 | 0.2 (18%) | 9.0 (818%) | -8.8 (-800%) | Cole and Rapp (1981) |
| Tennessee | <i>Liriodendron tulipifera</i> | 7.7 | 3.5 | 4.2 (55%) | 7.1 (93%) | -2.9 (-60%) | Cole and Rapp (1981) |
| Washington | <i>Abies amabilis</i> | 1.3 | 2.7 | -1.4 (-108%) | | | Turner and Singer (1976) |
| Wisconsin | Aspen-mixed hardwood | 5.6 | 0.05 | 5.5 (99%) | 26.0 (464%) | -20.5 (-364%) | Pastor and Bockheim (1984) |
| Oregon | <i>Pseudotsuga menziesii</i> | 2.0 | 1.5 | 0.5 (25%) | -2.8 (-140%) | 2.3 (115%) | Sollins et al (1980) |
| Washington | <i>Alnus rubra</i> | 70.0 ^c | 71.0 | - | 7.1 | | Van Miegroet and Cole (1984) |
| Holland | <i>Quercus robur</i> , <i>Betula pendula</i> | 54.5 | 78.5 | -24.0 (44%) | 6.0 (11%) | -30.0 (-55%) | Van Breemen et al (1987) |
| Holland | <i>Quercus robur</i> | 56.2 | 28.1 | 28.2 (50%) | 24.0 (43%) | 4.2 (7%) | Van Breemen et al (1987) |
| Holland | <i>Quercus robur</i> | 44.6 | 22.5 | 22.1 (50%) | 17.0 (38%) | 5.1 (11%) | Van Breemen et al (1987) |
| Holland | Mixed deciduous | 62.8 | 87.6 | 24.8 (39%) | | | Van Breemen et al (1987) |
| Tennessee | Mixed deciduous | 13.0 | 3.1 | 9.9 (76%) | 13.5 (104%) | -3.6 (-2.7%) | Henderson and Harris (1975) |
| Ontario | <i>Acer saccharum</i> | 7.8 | 18.2 | -10.4 (-133%) | | | Foster and Nicholson (1988) |
| North Carolina | Mixed deciduous | 7.0 | 0.3 | 6.7 (96%) | 7.1 (101%) | -0.4 (5%) | Swank in Johnson and Lindberg (1992) ^d |
| Washington | <i>Abies amabilis</i> | 2.5 | 1.3 | 1.2 (48%) | 3.6 (144%) | -2.4 (-96%) | Cole and Van Miegroet in Johnson and Lindberg (1992) ^d |
| North Carolina | <i>Picea rubens</i> | 5.9 | 21.6 | -15.7 (-266%) | 0.5 (8%) | -16.2 (-275%) | Johnson et al (1991) |
| North Carolina | <i>Picea rubens</i> | 26.0 ^a | 20.5 | 5.5 (21%) | 1.8 (7%) | 3.7 (14%) | Johnson et al (1991) |
| North Carolina | <i>Pinus strobus</i> | 7.1 ^a | 0.3 | 6.8 (96%) | 6.6 (93%) | -0.2 (-3%) | Swank in Johnson and Lindberg (1992) ^d |

**TABLE 10-13 (con't). NITROGEN INPUTS, OUTPUTS, AND VEGETATION INCREMENTS
IN VARIOUS FOREST ECOSYSTEMS**

| Location | Species | Input (kg/ha/year) | Leaching (kg/ha/year) | Net Retention (kg/ha/year) ^a | Vegetation Increment (kg/ha/year) | Calc. Soil Retention (kg/ha/year) ^b | Reference |
|----------------|------------------------------|-----------------------|--------------------------|---|---|--|---|
| Maine | <i>Picea rubens</i> | 7 6 | 0 3 | 7 3 (96%) | - | - | Fernandez in Johnson and Lindberg (1992) ^d |
| Tennessee | <i>Pinus taeda</i> | 9 7 ^a | 0 6 | 9 1 (94%) | 6 6 (18%) | 2 5 (25%) | Johnson and Lindberg in Johnson and Lindberg (1992) ^d |
| Georgia | <i>Pinus taeda</i> | 9 0 ^a | 0 2 | 8 8 (98%) | - | - | Ragsdale in Johnson and Lindberg (1992) ^d |
| Ontario | Northern hardwood | 7 5 | 23 0 | -15 5 (-207%) | 1 3 (17%) | -16 8 (-224%) | Foster in Johnson and Lindberg (1992) ^d |
| New York | Spruce-fir | 16 0 ^a | 2 8 | 13 2 (83%) | 10 8 (180%) | 2 4 (15%) | Friedland in Johnson and Lindberg (1992) ^d |
| Florida | <i>Pinus eliotii</i> | 6 0 ^a | 0 2 | 5 8 (97%) | 1 8 (30%) | 4 0 (67%) | Gholz in Johnson and Lindberg (1992) ^d |
| North Carolina | <i>Pinus taeda</i> | 14 0 ^a | 2 4 | 11 6 (83%) | 70 1 (500%) | -58 5 (418%) | Binkley and Knoerr in Johnson and Lindberg (1992) ^d |
| Norway | <i>Picea abies</i> | 10 8 ^a | 0 6 | 10 2 (96%) | 9 7 (91%) | 0 5 (5%) | Stuanes in Johnson and Lindberg (1992) ^d |
| Washington | <i>Pseudotsuga menziesii</i> | 4 8 | 0 4 | 4 4 (2%) | 5 4 (113%) | -1 0 (13%) | Cole and Van Miegroet in Johnson and Lindberg (1992) ^d |
| New York | Northern hardwood | 9 5 ^a | 1 5 | 8 0 (84%) | 1 1 (12%) | 6 9 (73%) | Mitchell and Sheppard in Johnson and Lindberg (1992) ^d |

^aInput — Leaching

^bInput — Leaching — Vegetation Increment

^cEstimated input by fixation

^dRefers to principal investigators for the specific data set summarized in Johnson and Lindberg (1992)

Source Johnson (1992)

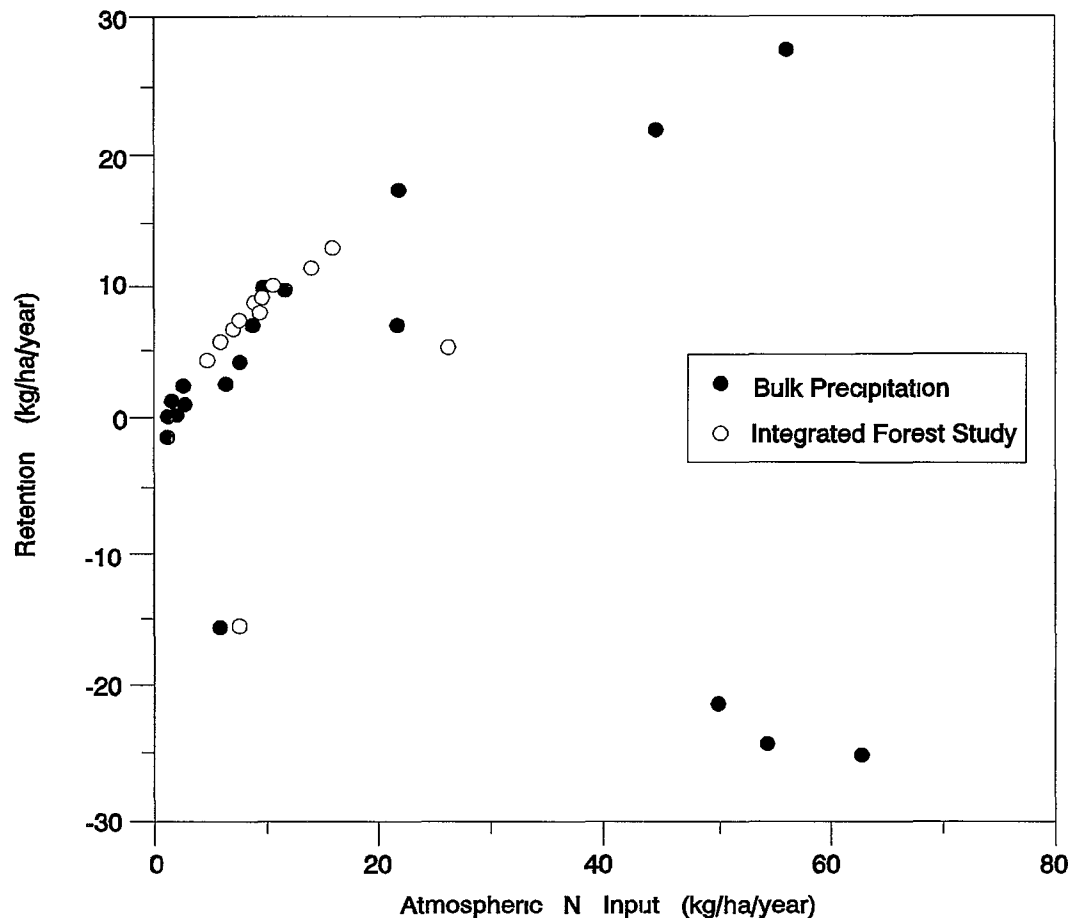


Figure 10-11. Ecosystem nitrogen retention as a function of atmospheric nitrogen input.

Source Johnson (1992)

Indeed, it appears as if the soil is being "mined" for the nitrogen necessary to supply vegetation increment systems with very low atmospheric nitrogen inputs. This is readily apparent when nitrogen output is plotted as a function of input minus vegetation increment (Figure 10-14). Input minus increment can be thought of as nitrogen that is available for either (1) soil heterotroph uptake or (2) nitrate leaching. A negative value for input-increment implies that either the soil is being "mined" for nitrogen to supply tree needs or that there is an unmeasured nitrogen input contributing to tree nitrogen needs. In either case, the data suggest that, contrary to views expressed in the literature (see review above), trees are actually more effective competitors for nitrogen than soil heterotrophs under

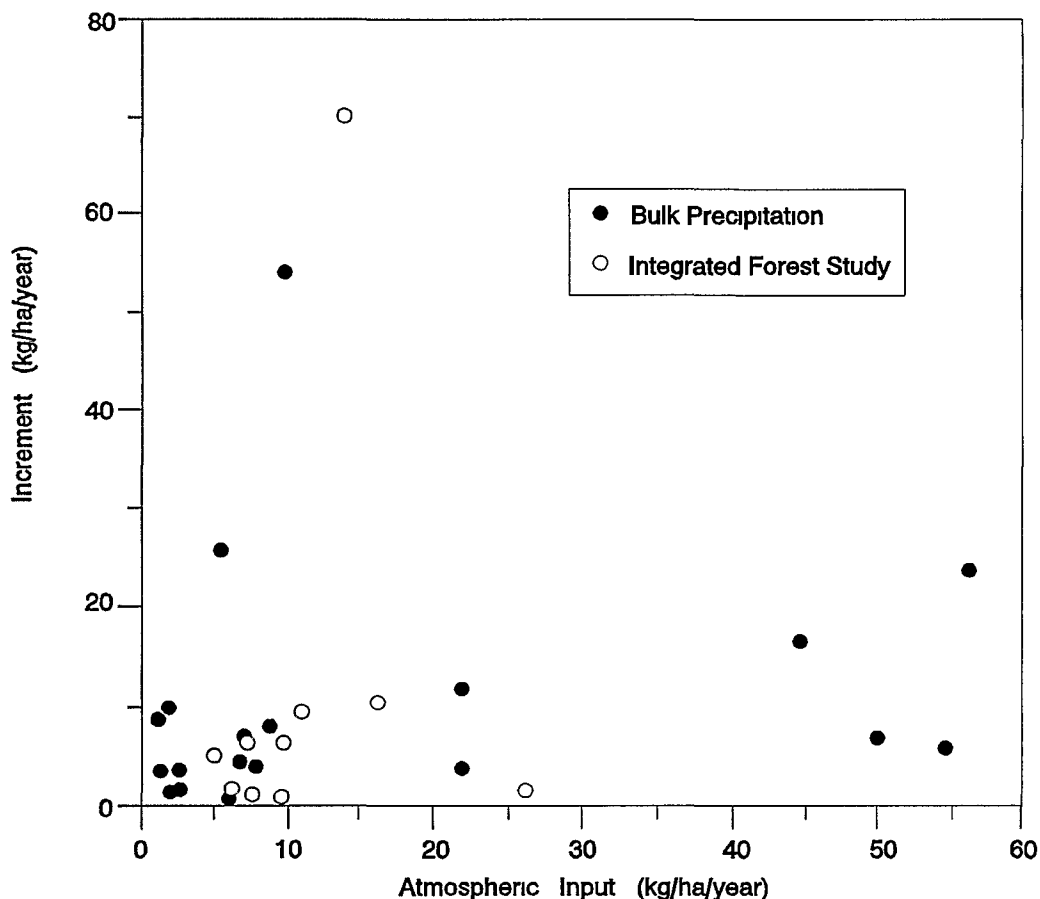


Figure 10-12. Tree nitrogen increment as a function of atmospheric nitrogen input.

Source Johnson (1992)

nitrogen-deficient conditions. Also, the nearly 1:1 relationship between nitrogen output and input-increment after the latter exceeds zero ($r^2 = 0.84$) indicates that nitrogen deposited in excess of vegetation needs is not taken up by heterotrophs, but rather is subject to nitrification and nitrate leaching, perhaps because heterotrophs in these systems are limited by organic substrates or other nutrients.

There are several possible explanations for the rather striking differences in soil nitrogen retention and loss patterns between fertilizer and nutrient cycling/air pollution studies. First, heterotrophic demand for nitrogen in fertilized sites is likely to be greater than in sites subjected to chronically elevated atmospheric nitrogen inputs. Fertilizer

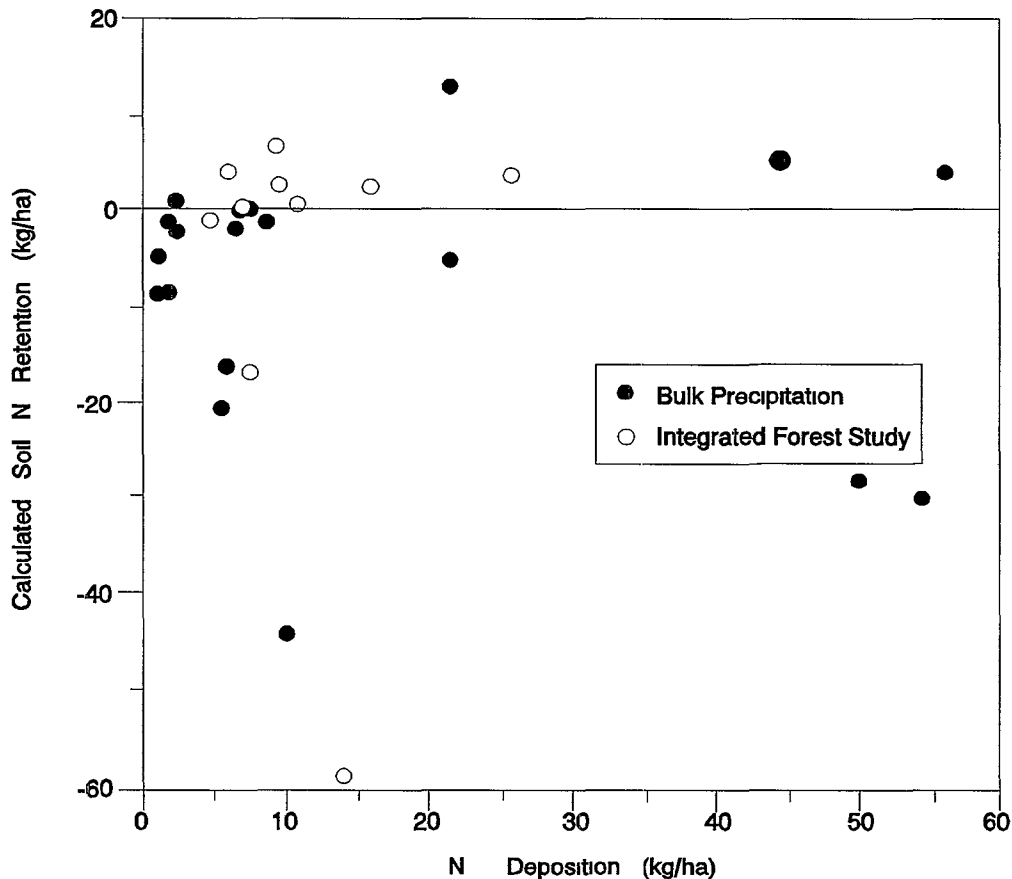


Figure 10-13. Calculated soil nitrogen retention (input-increment-leaching) as a function of atmospheric nitrogen input.

Source Johnson (1992)

nitrogen is typically applied to nitrogen-deficient ecosystems, where nitrogen demand by soil heterotrophs is likely to be high, whereas heterotrophic demand for nitrogen may have been substantially satisfied in sites with chronically high atmospheric nitrogen inputs

Heterotrophic activity in fertilized sites is also likely to be stimulated by mobilization of soil organic carbon, which typically occurs after fertilization (especially with urea, Ogner, 1972, Foster et al , 1985a) Second, as noted above, the slow, steady inputs of nitrogen via air pollution, like slow, steady inputs of fertilizer nitrogen, probably favor nitrification Third, nonbiological retention of nitrogen is likely to be greater with fertilization than atmospheric deposition Ammonium and NH_3 fixation in 2:1 clays is likely to be substantially increased

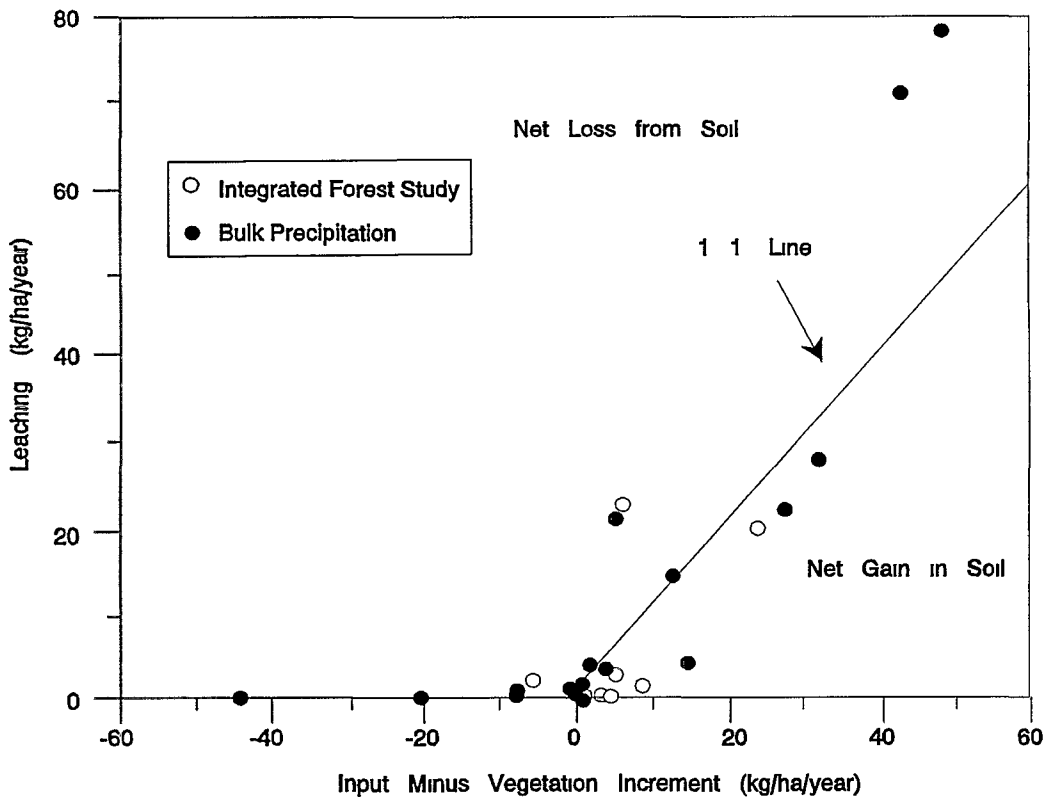


Figure 10-14. Nitrogen leaching as a function of atmospheric nitrogen input minus tree nitrogen increment. Points above the 1:1 line imply net soil loss, and points below the line imply net soil retention.

Source Johnson (1992)

under conditions of high concentrations of one or both following fertilization. It has also been shown that NH_3 can react chemically with soil organic matter to form very stable, nonlabile compounds (Foster et al, 1985b). Conditions following urea fertilization are especially conducive to these reactions in that pH is increased and NH_3 concentrations are high. These conditions would not normally occur in sites subject to chronically high atmospheric nitrogen inputs. In summary, ecosystems retain a greater amount of atmospherically deposited nitrogen than of fertilizer nitrogen, however, no observable relationship exists between atmospherically deposited nitrogen and either tree increment or calculated soil retention. It appears that nitrifiers may not be as poor competitors for nitrogen as was previously suspected, particularly in cases where nitrogen inputs are

increased in small, frequent doses, such as with air pollution. Heterotrophs appear to be the most effective short-term competitors for nitrogen in nitrogen-poor sites, but trees appear to be the most effective competitors for nitrogen over the longer term, as indicated by the apparent mining of nitrogen from soils where atmospheric nitrogen inputs are low and tree nitrogen requirements are high.

10.5.4 Effects of Pollutant Nitrogen Inputs on Soils

10.5.4.1 Soil Biota

The most obvious and immediate effects of pollutant nitrogen inputs on soils are those on the microbial community. An increase in the activity of heterotrophs and nitrifiers associated with an increase in decomposition and nitrification might be expected in response to nitrogen inputs. Studies of microbial responses to nitrogen fertilization have produced mixed results, however. Kelly and Henderson (1978) found increased bacterial activity, but reduced invertebrate populations, 1 year after fairly high levels of urea fertilization (550 and 1,100 kg nitrogen/ha). This change was important because invertebrates play a major role in the initial breakdown of litter. However, the authors found little effect of fertilization on the decomposition of white oak leaf litter. Kowalenko et al. (1978) found that fertilization with NH_4NO_3 and potassium chloride caused a reduction in soil microbial activity (as measured by CO_2 evolution) for at least 3 years. This may have been due to toxic or shock effects due to very large increases in both nitrogen and other ions over a very short time. Weetman and Hill (1973) reviewed the effects of fertilization on soil flora and fauna and concluded that fertilization had a lasting, stimulating effect despite short-term toxic effects of fertilizer components (especially ammonium). Again, we must consider the effects of single, large inputs of nitrogen, typical of fertilization studies, as opposed to the slow, steady inputs of nitrogen at lower concentration typical of pollutant inputs. Aside from the limited information on the effects on nitrifiers, virtually nothing is known regarding the effects of slow, steady inputs of nitrogen on soil microbial communities.

10.5.4.2 Soil Chemistry

The foremost concern about long-term, capacity-controlled effects of excessive nitrogen deposition and NO_3^- leaching is soil acidification and the mobilization of Al^{3+} into

soil solution and surface waters. As a prelude to assessing the effects of excessive nitrogen deposition on soil acidification and Al^{3+} mobilization, a brief review of the components of soil acidity and cation exchange processes is presented.

Soil acidity can be measured in a number of ways, but for the purposes of this discussion, we will refer to base saturation as the primary measure or indicator of soil acidity. Base saturation refers to the degree to which soil cation exchange sites, negatively charged sites to which positively charged ions are adsorbed, are occupied with base cations (calcium ions [Ca^{2+}], magnesium ions [Mg^{2+}], and potassium ions [K^{+}]) as opposed to Al^{3+} and hydrogen ions (H^{+}). Base saturation is a measure of soil acidification, with lower values being more acid. Figure 10-15 shows a soil with 50% base saturation on the left and a soil with 10% base saturation on the right.

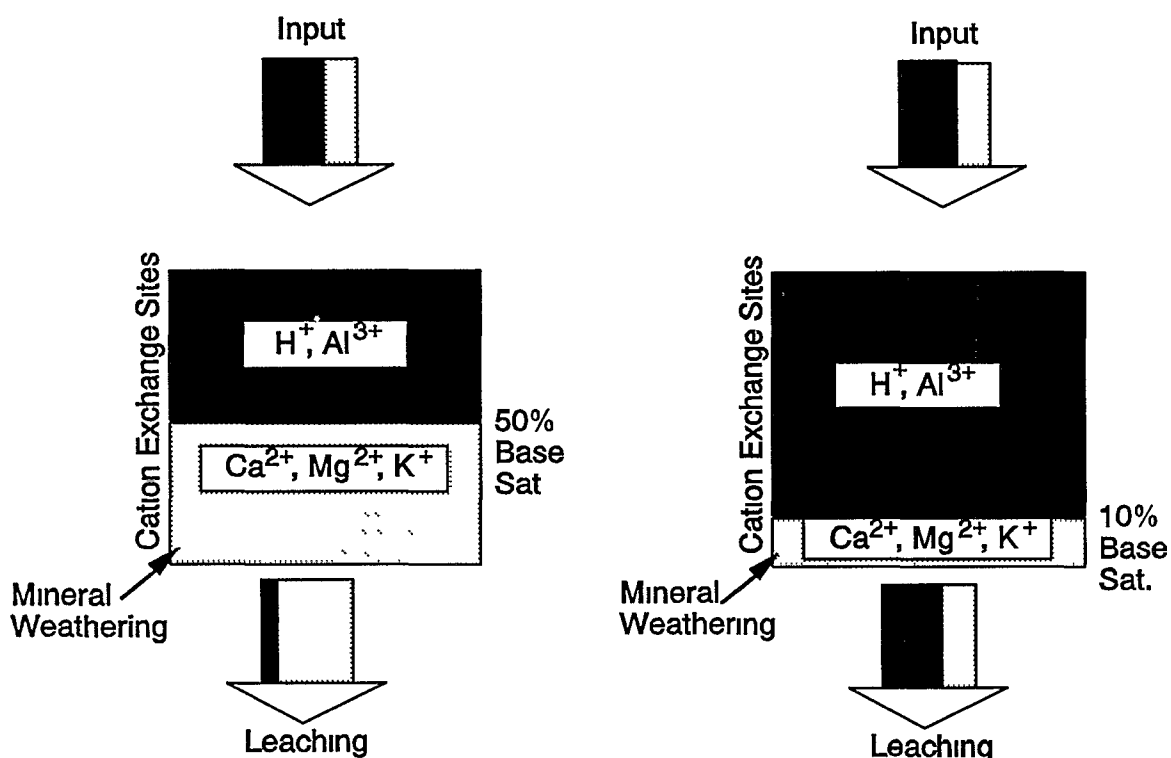


Figure 10-15. Schematic diagram of cation exchange for base cations, aluminum ions, and hydrogen ions in circumneutral (50% base saturation, left) and acid (10% base saturation, right) soils.

Ulrich (1983) describes the various buffering ranges soils go through as they acidify. First is the base cation buffering range, where incoming acid *and* base cations are exchanged primarily for base cations with very little H^+ and Al^{3+} increase (Figure 10-15, left). As soils acidify, exchangeable base cations are replaced by exchangeable Al^{3+} and H^+ , and soils are said to be in the aluminum buffering range (Figure 10-15, right). Incoming cations (acid and base) are exchanged primarily for H^+ and Al^{3+} in soils that are in the aluminum buffering range (Figure 10-15, right).

With the use of a simulation model, Reuss (1983) showed that the transition from the base cation to the aluminum buffering range is very abrupt. His results showed that soil acidification has little effect on the concentration of Al^{3+} in soil solution over a large range of base saturation values above 20%. However, he noted that fairly minor changes in base saturation within the 10 to 20% range can cause quite large increases in soil solution Al^{3+} concentration. This implies that soils with base saturations of 10 to 20% are extremely sensitive to change (although this does not necessarily imply that vegetation will respond to soil change). A series of simple laboratory column studies could tell us much about how far some of our forest soils are from the aluminum buffering range and how much additional acid input might be required to put them into this range.

Once soils are in the aluminum buffering range, the rate of base cation leaching will obviously decrease because Al^{3+} is now a dominant cation in soil solutions. In a soil free of vegetation, continued inputs from the atmospheric deposition, which contains base cations as well as H^+ , will eventually acidify the soil to the point where base cation outputs equal base cation inputs. With forest or other vegetation growing on the soil, however, continued base cation uptake could reduce the base saturation of the soil to the point where export of base cations is less than input by deposition (Figure 10-15, right). Thus, vegetation uptake can, by depleting soil exchangeable base cations, cause the soil to begin accumulating base cations even when the soil is subject to high leaching rates. Of course, this accumulation of base cations is accompanied by substantially increased leaching of Al^{3+} , and the potentially detrimental effects of the latter must be considered.

The same cation exchange principles that will eventually cause a soil to begin accumulating incoming base cations when soils acidify into the aluminum buffering range can also cause an ecosystem to begin accumulating an individual cation (Ca^{2+} , Mg^{2+} , or K^+) if

tree uptake depletes soils of an individual cation (Johnson and Todd, 1987) In this case, the conservation of the individual cation in question need not be accompanied by significant overall soil acidification and increased leaching of Al^{3+} , leaching of the other base cations may be increased instead Johnson et al (1985) noted such a situation with respect to Ca^{2+} in an oak-hickory forest on the Walker Branch watershed in Tennessee In this ecosystem, tree Ca^{2+} is very high, soils are very low in exchangeable Ca^{2+} , and consequently Ca^{2+} leaching is low Thus, the ecosystem shows a net Ca^{2+} gain from atmospheric inputs (accompanied by net losses of Mg^{2+} , K^+ , and sodium ions [Na^+])

The greatest uncertainty in assessing and projecting rates of exchangeable base cation depletion and/or soil acidification is the estimation of primary mineral weathering rates The weathering of primary soil minerals (e g , hornblende, feldspar, plagioclase) represents an input to the exchangeable base cation pool (Figure 10-16) Calculations of the potential rate of soil change from exchangeable pools and input-output budgets (e g , Tomlinson, 1983) represent the worst-case scenario, that is, they assume that weathering is zero A high rate of soil leaching offset by a high rate of weathering results in a high rate of turnover, but not a net depletion of exchangeable cations

Equations and simple models of soil weathering are available for primary to secondary mineral transformations (e.g , Lindsay, 1979) However, these equations are of little value for soils with sizeable nonexchangeable base cation reserves contained in ill-defined minerals (such as amorphous iron [Fe] and aluminum [Al] oxides, Johnson et al , 1985) A further complication arises when mineral weathering is enhanced by organic acids formed in forest litter or exuded by tree roots (Boyle and Voigt, 1973) Thus, at present, there are only empirical approaches to assessing weathering, such as mass balance calculations One mass balance approach involves measuring fluxes and changes in exchangeable cation pools over time and calculating weathering, by difference (Matzner, 1983) A simpler mass balance approach is to estimate the total weathering loss from a soil by the difference in soil element content at present and that of an equivalent amount of primary minerals (i e , element content at the time the soil began to form) and divide by the amount of time the soil has been exposed to weathering (e g , since the last glaciation) (Mazzarino et al , 1983) The latter gives an average weathering rate over geologic time, but it does not represent current weathering rates in the soil The former method gives a better estimate of current

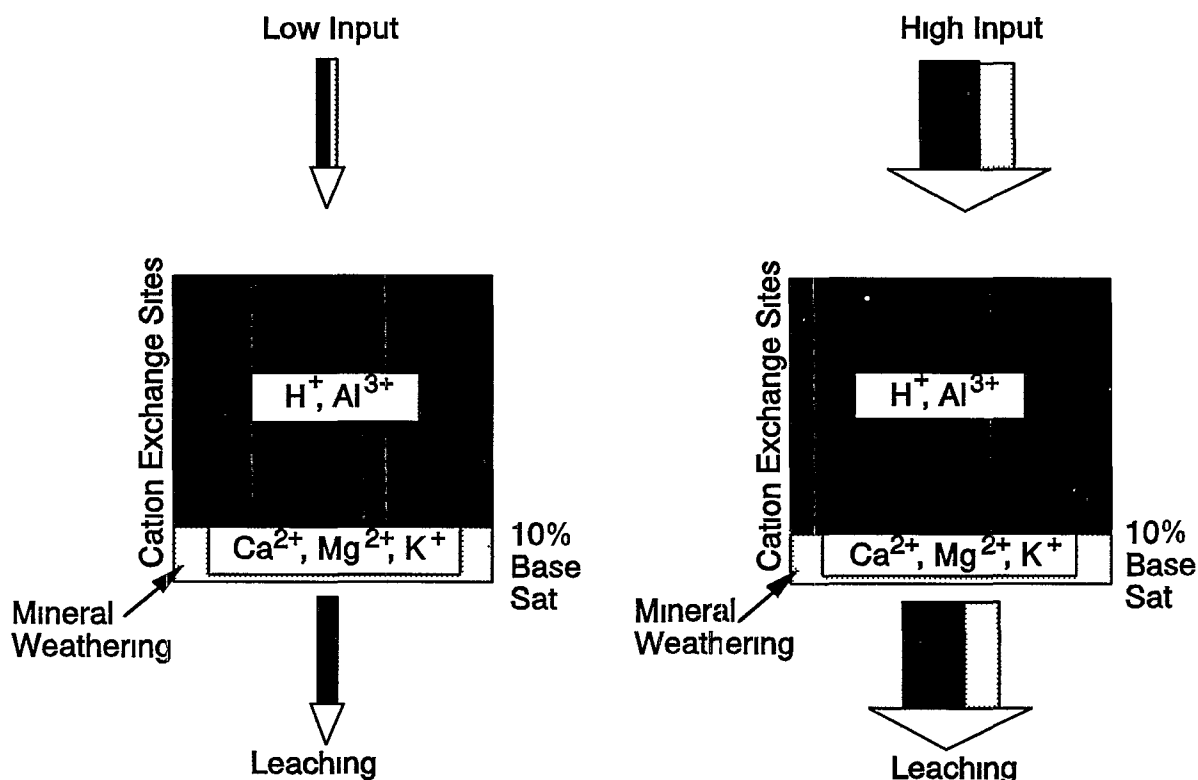


Figure 10-16. Schematic diagram of cation exchange for base cations, aluminum ions, and hydrogen ions in acid soils with low (right) and high (left) atmospheric deposition rates.

weathering rates in the soil, but it is subject to large uncertainties due to errors in each of the estimates used to calculate it. Nonetheless, the plot-scale mass balance method, although imprecise, seems the best for obtaining realistic estimates of current soil weathering rates, especially in systems where leaching has been increased by artificial acid irrigation (Stuanes, 1980).

Because forest soils acidify naturally, it must be true that weathering rates do not keep pace with base cation denudation rates, even under pristine conditions. The relative contribution of acid deposition to the rate of acidification can be assessed by measuring element fluxes (Ulrich, 1980, Matzner, 1983, Johnson et al., 1985), and the actual magnitude of the acidification rate, which equals base cation export minus weathering input, can be estimated by measuring changes in exchangeable base cations and acidity through time.

(taking into account seasonal variations in surface soils, see Haines and Cleveland, 1981) The effects of excess nitrogen and S deposition on the rate of soil acidification cannot be evaluated by simply measuring changes in soils through time, however, because the natural rate of soil acidification (via natural leaching and vegetation uptake) cannot be accounted for by simply measuring changes in soils. If soils do not change during the measurement period, it can be stated that neither acid deposition nor natural processes have caused soil acidification. However, if soils have acidified, measurements of fluxes are necessary to determine the extent to which acid deposition has contributed to the observed rate of acidification.

There are no documented cases in which excessive atmospheric nitrogen deposition has caused soil acidification, however, the potential exists if additions are high enough for a sufficiently long time. Nitrification is an acid-producing process (Alexander, 1963), and thus the potential for soil acidification exists. In practice, however, the levels of nitrogen input necessary to produce measurable soil acidification are quite high. For instance, Tamm and Popovic (1974) report a drop in soil pH from approximately 5 to 4.5 after repeated nitrogen fertilizations totaling 3,900 kg/ha over a period of 10 years. Van Miegroet and Cole (1984) report that 50 years of nitrogen fixation by red alder (*Alnus rubra*) caused the soil beneath that stand to be 0.5 pH units lower (pH 4.6) than that in an adjacent Douglas-fir (*Pseudotsuga menziesii*) stand (pH 5.2). Total nitrogen input rates were not known, but typical rates for red alder range from 50 to 200 kg/ha/year (Van Miegroet and Cole, 1984). Van Breemen et al. (1982, 1987) report high acidification pressure on forests of the Netherlands subject to very high inputs of nitrogen from nearby agricultural activities (often considerably in excess of 50 kg nitrogen/ha/year, Van Breemen et al., 1982, 1987, Nilsson and Grennfelt, 1988). The H^+ budgets for these sites indicate the clear possibility (if not probability) that soils have been acidified, but actual changes in soil acidity over time have not been measured.

Soil acidification is usually thought of as an undesirable effect, but in some cases, the benefits of alleviating nitrogen deficiency may outweigh the detriments of soil acidification. For instance, Van Miegroet and Cole (1984) found that excessive N_2 fixation by red alder caused large increases in NO_3^- leaching and a significant amount of soil acidification relative to adjacent natural Douglas-fir stands, yet Douglas-fir growth is invariably superior on sites

formerly occupied by red alder due to the differences in nitrogen status (Tarrant and Miller, 1963, Binkley, 1983, Van Miegroet et al , 1992)

10.5.5 Effects on Natural Waters

A major recent concern over the effects of soil acidification due to atmospheric deposition of both nitrogen and S is the mobilization of Al^{3+} , which can be toxic to some terrestrial vegetation and might be carried to surface waters where it is toxic to fish. As in the case of soil acidification, a brief review of processes leading to soil solution and surface water acidification will be presented as a prelude to discussions as to the effects of atmospheric nitrogen deposition on these processes.

Increased concentrations of NO_3^- or any other mineral acid anion (e.g., SO_4^{2-} or Cl^-) in soil solution lead to increases in the concentrations of all cations in order to maintain charge balance. Figure 10-16 shows the effects of low (left) and high (right) inputs of cations, which are also accompanied by low and high inputs of anions, respectively, to the fictitious soil with 10% base saturation shown on the right of Figure 10-15. As can readily be seen, the concentrations of H^+ and Al^{3+} in soil solution are determined not only by base saturation, but also by total cation (and anion) input rates. Extremely acid soils are a necessary but not sufficient condition for the mobilization of Al^{3+} ; elevated inputs of cations and anions, whether by atmospheric deposition, fertilization, or natural processes, must also occur.

The composition of the cations in a solution in equilibrium with soil can be described fairly accurately by well-known selectivity equations developed more than 50 years ago (Reuss, 1983). In essence, these equations predict that the concentration of a given cation in soil solution is governed by the proportion of this cation on the soil exchange complex and the total ionic concentration in soil solution.

Reuss (1983) points out one very interesting aspect of these equations with respect to the question of Al^{3+} mobilization. As total ionic concentration increases, the concentration of Al^{3+} increases to the 3/2 power of the increase in the concentrations of ratio Ca^{2+} and Mg^{2+} and to the third power of K^+ , Na^+ , and H^+ . In other words, as total cation and anion concentrations increase, individual cation concentrations increase as follows: $\text{Al}^{3+} > \text{Ca}^{2+}$ and $\text{Mg}^{2+} > \text{K}^+$, Na^+ , and H^+ . Thus, soil solution Al^{3+} concentrations

increase not only as the soil acidifies (i.e., as the proportion of Al^{3+} on the exchange complex increases), but also as the total ionic concentration of soil solution increases (These equations also imply that K^+ , Na^+ , and H^+ will be the least affected by increased NO_3^- leaching.)

There are several studies in which Al^{3+} concentrations in both soil solution and stream waters have been shown to be positively correlated with NO_3^- concentrations. The NO_3^- - Al^{3+} pulses in soil solution have implications for forest nutrition and are invoked in some hypotheses of forest decline discussed in the next section. Researchers on aquatic effects of acid deposition have long noted springtime pulses of NO_3^- , Al^{3+} , and H^+ in acid-affected surface waters of the northeastern United States (Galloway et al., 1980; Driscoll et al., 1989b). In less acid systems, NO_3^- pulses may be associated with base cations rather than Al^{3+} and H^+ . Foster et al. (1989) noted pulses of NO_3^- and base cations in soil solutions and streams at the Turkey Lakes site in Ontario. Driscoll et al. (1989a) reviewed the North American data relevant to the role of nitrogen in the acidification of surface waters and explored relationships between atmospheric nitrogen deposition, soil carbon to nitrogen ratio, and stream water nitrate concentrations. They found no consistent relationships between these factors, and suggested that vegetation uptake, as hypothesized by Vitousek and Reiners (1975) may be one of the most important factors in determining stream water nitrate concentrations.

10.5.6 Effects of Pollutant Nitrogen Deposition on Vegetation Nutrient Status

Because nitrogen is the most commonly limiting nutrient for growth in forest ecosystems in North America (Cole and Rapp, 1981), deposition of nitrogen in any biologically available form to most forest ecosystems is likely to produce increased vegetation growth to some extent. Kauppi et al. (1992) reported that, in stark contrast to earlier claims of forest decline, the biomass of European forests increased over the 1971 to 1990 period. They attribute this growth increase to increases in nitrogen deposition and base their conclusions on the magnitude of the increase in nitrogen deposition and all known responses of European forests to nitrogen fertilizer. It is logical to assume that the same growth increase would occur in many forests in North America (especially western North

America) with increased nitrogen deposition, given known nitrogen deficiencies and responses to nitrogen fertilization (Aber et al , 1989, Gessel et al , 1973) The degree of response will depend on the amount of nitrogen deposited, the nitrogen demand by vegetation, and the competition from soil heterotrophic organisms for this nitrogen, as described above In addition to changes in growth, increased nitrogen deposition can cause significant changes in tree physiological function, can alter susceptibility to insect and disease attack, and can even alter plant community structure (see Section 10 5 6 1) This section briefly reviews plant physiological responses associated with increased nitrogen nutrition (see Section 10 6 for more in-depth coverage), gives a more in-depth review of soil-mediated effects of nitrogen deposition on vegetation, and updates plant community/successional changes that are reported to be occurring in high-deposition areas of Europe

10.5.6.1 Physiological Effects of Excess Nitrogen Inputs

Nitrogen addition can have several impacts on trees in addition to improvement of growth, including susceptibility to other pollutants Nitrogen fertilization has been noted to increase the resistance of eastern white pine (*Pinus strobus* L) to SO₂ injury (Cotrufo and Berry, 1970) Nitrogen fertilization usually depresses mycorrhizal development (Weetman and Hill, 1973, Menge et al , 1977) Because the mycorrhizal association is thought to be an adaption to nutrient deficient conditions, suppression of mycorrhizae by nitrogen inputs might be expected

Several hypotheses posed to explain current forest declines in eastern North America invoke the effects of excess nitrogen deposition on physiological processes These physiological responses generally invoke altered carbohydrate allocation, causing increased sensitivity to drought, frost, or insect attack Friedland et al (1984) posed the hypothesis that excessive nitrogen deposition induced growth later into autumn, which caused susceptibility to frost in red spruce in the northeastern United States Evans (1986) followed up on this, observing that winter injury apparently occurred to first-year twigs and adding the alternative hypothesis that excessive nitrogen deposition could have caused reduced bark formation as well as, or instead of, late growth into the autumn in first-year twigs Waring (1987) poses a hypothesis in which boreal coniferous species are unable to store nitrate taken up from soil solutions, necessitating the formation of amino acids in green leaves, causing

reduced allocation of carbohydrate to roots and increased susceptibility to drought and pathogens.

More recent studies on response of red spruce to nitrogen lend no support to the various hypotheses for nitrogen-induced physiological damage and decline described above. Sheppard et al. (1989) found the evidence for pollutant-induced susceptibility to freezing injury in red spruce to be weak, based on laboratory studies with detached shoots. DeHayes et al. (1989) found that treatment of red spruce seedlings with NH_4NO_3 increased rather than decreased cold tolerance. Thus, the hypothesis that nitrogen causes direct damage to red spruce is not supported by laboratory studies. Climate is thought to play a major role in the severe red spruce decline in the northeastern United States, perhaps with some additional exacerbation due to the direct effects of acid mist on foliage (Johnson et al., 1992). There is some evidence to suggest that indirect effects of nitrogen saturation, namely nitrate and Al leaching, may be contributing factors to red spruce decline in the southern Appalachians, and this literature is reviewed below.

10.5.6.2 Soil-Mediated Effects on Vegetation

Nitrogen inputs in excess of tree and heterotrophic nitrogen demand may cause immobilization of some nutrients (especially P and S) and losses of other cation nutrients due to increased nitrate leaching, as discussed above. In some cases, the benefits of enhanced nitrogen status will greatly outweigh the detrimental effects of decreased availability of other nutrients. For instance, the benefits of nitrogen fixation during a red alder (*Alnus rubra* Boug.) stage to subsequent Douglas-fir (*Pseudotsuga menziesii* [Murb.] Franco) forests in the Pacific Northwest are well documented despite the fact that excessive nitrogen fixation during the red alder stage causes considerable phosphorus immobilization and soil acidification (Van Miegroet and Cole, 1984). In other cases, effects of excessive nitrogen deposition may be clearly deleterious to plant nutrition. For instance, Roelofs et al. (1987) report that K and Mg deficiencies in declining Dutch forests are caused by excessive foliar leaching due to high inputs of NH_4^+ .

Ulrich (1983) hypothesized that these nitrate-induced Al^{3+} pulses during warm dry years caused root damage and were a major contributor to what has been termed "forest injury" observed in Germany during the mid 1980s. This hypothesis is disputed by other

German forest scientists who point out that "forest injury" occurred on base-rich as well as base-poor soils (the base-rich soils are not subject to Al^{3+} pulses) (e.g., Rehfuss, 1987). Mulder et al. (1987) document NO_3^- - Al^{3+} pulses in soil solutions from forest sites in the Netherlands. Aluminum toxicity is one of several nitrogen-related hypotheses posed to explain forest decline in that country. (Other hypotheses are discussed in the following section.) Johnson et al. (1992) found pulses of NO_3^- and total Al in soil solutions during late autumn from red spruce forests in the Great Smoky Mountains of North Carolina. The pulses were attributed to a combination of high rates of nitrogen mineralization and low uptake in these over mature forests. The soils at these sites were very rich in nitrogen, (up to 10,000 kg nitrogen/ha) and atmospheric nitrogen deposition was also quite high (26 kg nitrogen/ha/year), both of which contribute to the high rates of NO_3^- leaching at these sites. The peak total Al concentrations (70 $\mu\text{M/L}$) associated with these NO_3^- pulses were below the concentration for monomeric Al at which injury to red spruce seedlings occurs in laboratory studies (200 $\mu\text{M/L}$, Joslin and Wolfe, 1988), and there was no visible evidence of red spruce decline at these sites. However, the possibility of Al inhibition of Ca and Mg uptake cannot be excluded. Spot checks revealed that 80 to 90% of total Al in these soil solutions was in monomeric form. It is noteworthy that Bondietti et al. (1989) found an inverse correlation between Al and Ca concentrations in tree rings of red spruce in the southern Appalachians.

Shortle and Smith (1988) present a hypothesis for the decline of red spruce in which Al inhibits Ca uptake, Ca deficiency reduces cambial growth (because the demand for Ca per unit of cambium surface is constant), reduced cambial growth causes a reduction in functioning sapwood, and reduced sapwood causes a reduction in leaf area. However, Johnson (1983) finds no support for the Al hypothesis in the seriously declining trees of Camel's Hump, VT. He found that, although the degree of dieback and decline increases with elevation, both Al concentration and Al:Ca ratios in fine roots decrease with elevation. He further points out that high elevation soils where much of the decline occurs are histosols (organic soils) where Al toxicity is unlikely due to the mitigating effects of organics on soil solution Al activity.

Thus, the situation with respect to the Al hypothesis and red spruce decline remains very unclear. There is little support for the Al hypothesis in the northeast, where decline is

very severe Cook and Johnson (1989) concluded from extensive tree ring and climatic analyses that red spruce has been out of equilibrium with its climate for the last 150 years, making it susceptible to injury from a variety of causes, both naturally and anthropogenically induced. Given the soil solution Al levels found in southern Appalachian red spruce forests, the possibility of some Al effect cannot be excluded, yet decline in this region is much more subtle (being evidenced primarily by somewhat controversial tree ring analyses) and no unexpected levels of mortality have yet occurred Binkley et al (1989) report that forests in the South have responded most strongly to additions of nitrogen and phosphorus, probably because growth of most stands in this area have been nitrogen- and phosphorus-limited

10.5.6.3 Ecosystem-Level Responses to Nitrogen Deposition

Growth responses to increased nitrogen inputs may not always be regarded as desirable, especially if they result in changes in species composition For instance, improved growth and vitality due to increased nitrogen deposition may not be deemed desirable in wilderness areas Different genera and species respond differentially to increased nitrogen availability, for instance, deciduous species (angiosperms) generally have a greater demand for nitrogen per unit biomass produced than do coniferous species (gymnosperms) (Cole and Rapp, 1981) Tilman (1987) found marked changes in species composition as a result of experimental nitrogen additions to abandoned old fields in Minnesota Thus, there is a real possibility for changes in ecosystem composition with increased nitrogen loading Changes from heathland to grassland in Holland have been attributed to high rates of nitrogen deposition (Roelofs et al , 1987). Ellenberg (1987) points to further species changes in Central European ecosystems as a likely consequence of elevated nitrogen He states that "more than 50% of the plant species in Central Europe can only compete on stands that are deficient in nitrogen supply."

There may be significant ecosystem-level effects of nitrogen via host-pathogen interactions. Increased nitrogen inputs can affect tree resistance to insect and disease either positively or negatively. Nitrogenous fertilizers are known to reduce the production of phenols in plant tissues, thereby reducing resistance to infection by pathogenic fungi (Shigo, 1973). Hollis et al (1975) noted that additions of phosphorus and nitrogen to sites deficient in these elements increased the incidence of fusiform rust in slash pine On the other hand,

increased nitrogen input will increase resistance to bark beetle and other insect attacks if it improves tree nutrient status (Weetman and Hill, 1973). In addition to changes in tree physiology, increased nitrogen inputs cause changes in stand structure that result in changes in understory composition and microclimate that could either increase or decrease the likelihood of insect or disease attack Brunsting and Heil (1985), addressing the recent changes from heather (*Calluna* sp) to grasses in the Netherlands, noted that nitrogen fertilization (56 kg nitrogen/ha) leads to increased growth of grasses only when *Calluna* stands are opened up by beetle attacks By increasing the nitrogen concentration of heather foliage, high nitrogen input stimulates larval growth and increases body weight of beetles

The effects of increased nitrogen additions on host-pathogen interactions remain largely speculative Most research to date has been conducted in fertilized forest plantations Insufficient research has been done on the responses of the either plantations or natural ecosystems to pathogen attack under conditions of increased atmospheric nitrogen deposition to make any definitive statements Nonetheless, these interactions are potentially very important, given the devastation that pathogens can produce, and further attention should be given to the issue of effects of increased nitrogen deposition, both positive and negative, on host-pathogen interactions

10.5.7 Critical Loads for Atmospheric Nitrogen Deposition

Recently, there have been efforts to set critical loads for nitrogen deposition for natural ecosystems (Nilsson and Grennfelt, 1988, Fox et al , 1989, Schulze et al , 1989) (also see Section 10 4 3) In that the values for these critical loads may take on considerable political importance, it is appropriate to examine the assumptions that have been made in defining them

The Workshop held at Skokloster, Sweden in March 1988 (Nilsson and Grennfelt, 1988) adopted the following definition for a critical load "A quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge " In this document (Nilsson and Grennfelt, 1988) and the subsequent publication synthesizing much of it (Shulze et al , 1989), nitrogen critical loads were aimed "to protect soils from long-term chemical changes with respect to base saturation" (Nilsson and Grennfelt, 1988, Schulze

et al., 1989) The critical loads for nitrogen are estimated from two equations The first equation is posed as a one that must be satisfied in order to maintain a constant exchangeable base cation pool in the soil

$$BC \text{ leaching} \leq BC \text{ weathering} + BC \text{ deposition} - BC \text{ growth}, \quad (10-4)$$

where *BC* represents base cations Equation 10-4 is perhaps best understood by rearranging

$$BC \text{ leaching} + BC \text{ growth} \leq BC \text{ weathering} + BC \text{ deposition} \quad (10-5)$$

Equation 10-5 is simply a statement of mass balance for the soil cation exchange complex and states that removal rates via leaching (*BC leaching*) and plant uptake (*BC growth*) must be equalled or exceeded by inputs via deposition and weathering (the release of base cations from unavailable, mineral forms to ionic states available for plant uptake, leaching, or replenishing cation exchange sites) in order to keep soils from acidifying (keep base saturation constant) This is followed by another equation describing the roles of NO_3^- and SO_4^{2-} in causing soil leaching

$$\text{nitrate leaching} + \text{sulfate leaching} \leq BC \text{ leaching} \quad (10-6)$$

Nilsson and Grennfelt (1988) state that Equation 10-6 assumes that all base cation leaching is caused by nitrate and sulfate, ignoring the potentially substantial cation leaching by naturally produced carbonic and organic acids (e g , Johnson et al , 1977) However, the use of the "less than or equal to" sign in Equation 10-6 does, in fact, allow for leaching by naturally produced carbonic and organic acids Base cation leaching will be less than nitrate plus sulfate leaching if Al^{3+} and H^+ are present to significant extent in soil solutions

Combining Equations 10-4 and 10-6, the authors obtain

$$\begin{aligned} \text{acceptable nitrate leaching} &\leq BC \text{ weathering} + BC \text{ deposition} \\ &\quad - BC \text{ growth} - \text{sulfate leaching} \end{aligned} \quad (10-7)$$

In obtaining Equation 10-7, the authors assumed (without stating so) that only the "equal to" and not the "less than" sign in Equation 10-6 applied, in short, they assumed that all base cation leaching was due to nitrate and sulfate leaching, and that no H^+ and Al^{3+} leaching occurred

To estimate nitrate leaching, the authors use the nitrogen balance equation

$$N \text{ input} \leq N \text{ growth} + N \text{ immobilization} - N \text{ mineralization} + N \text{ denitrification} - N \text{ fixation} + N \text{ leaching}, \quad (10-8)$$

where N represents nitrogen. Again, this equation is best understood by rearranging

$$N \text{ leaching} \geq (N \text{ input} + N \text{ fixation} + N \text{ mineralization}) - (N \text{ growth} + N \text{ immobilization} + N \text{ denitrification}) \quad (10-9)$$

Equation 10-9 can be thought of as a mass balance equation for the soil inorganic nitrogen pool, with the first three terms being inputs to that pool and the second three terms being outputs from that pool other than leaching. The inputs consist of atmospheric deposition ($N \text{ input}$), fixation ($N \text{ fixation}$), and release from soil organic matter during decomposition ($N \text{ mineralization}$). The nonleaching outputs include plant uptake ($N \text{ growth}$), heterotrophic uptake ($N \text{ immobilization}$), and denitrification ($N \text{ denitrification}$). The remainder must be leaching ($N \text{ leaching}$). It is assumed in their analysis that nitrogen denitrification and nitrogen fixation are negligible in forest ecosystems and that nitrogen immobilization minus nitrogen mineralization, which is the net annual nitrogen accumulation in the soil, equals only 1 to 3 kg nitrogen/ha/year. The latter numbers are based on an estimate of the net nitrogen accumulation in soils of Sweden since the last glaciation (obtained by dividing nominal soil nitrogen content values by the number of years since glaciation). Soil nitrogen accumulation rates can be much higher. Jenkinson (1970) documents net annual soil nitrogen accumulations of over 50 kg/ha/year over an 81-year period (from 1883 to 1964) after a former agricultural site (Broadbalk) was allowed to revert to forest at the Rothamsted Experiment Station in England. This high rate of soil nitrogen accumulation was greater than thought possible from atmospheric deposition alone.

and may have been in part due to the action of free-living nitrogen-fixers in the soil. Liming may have played some role in stimulating these high accumulation rates, a nearby site (Geescroft) that had not been limed showed nitrogen accumulations of only 23 kg/ha/year over the same period (Jenkinson, 1970).

Given these equations and estimates of the various parameters within them, the authors calculate critical loads for various forest ecosystems. These values range from a low of 3 to 5 kg nitrogen/ha/year for raised bogs to a high of 5 to 20 kg nitrogen/ha/year for deciduous forests. A critical concentration for nitrate in groundwater (10 mg nitrogen/L) is then calculated based on an assumption of precipitation surplus (precipitation minus evapotranspiration) of 100 to 400 mm/year, giving values of 10 to 40 kg nitrogen/ha/year.

In contrast to the rather quantitative approach taken at the Skokloster Workshop, a far more subjective approach is taken in determining critical nitrogen loads for wilderness areas in the U.S. Forest Service-sponsored workshop held at Cary Arboretum in Millbrook, NY, in May 1988. In this case, rather than attempting to come up with specific critical loads, the workshop participants were asked to establish "green" and "red" lines, the former being values below which deleterious effects are very unlikely to occur, and the latter being values above which deleterious effects will very likely occur. The "rationale used in selecting nitrogen values" for terrestrial ecosystem critical loads consists of a brief overview of the nitrogen cycle and some educated guesswork, in view of the fact that "data on nitrogen cycling in wilderness areas is quite scarce at best, and in many areas completely lacking." Despite the lack of nitrogen cycling data, the authors provide guesses at green- and red-line values for specific wilderness areas ranging from 3 to 10 kg nitrogen/ha/year for green values and 10 to 15 kg/ha/year for red values. These values were quantitatively similar to those obtained in the Skokloster workshop, and actually show very little spread between green and red lines.

10.5.8 An Evaluation of Critical Loads Calculations for Nitrogen Deposition

There are a number of points that need to be emphasized before the Skokloster critical load values are used for assessment or policy-making. First, the assumption that soils can accumulate only 1 to 3 kg nitrogen/ha/year is certainly not valid over the short term in most

forest ecosystems, as shown amply by a number of forest fertilization studies described in Section 10.5.3. Having stated that, however, it should also be noted that both heterotroph and ecosystem-level recovery of atmospherically deposited nitrogen seems to be lower than that of fertilizer nitrogen, as also noted in Section 10.5.3. The authors of the critical load document (Nilsson and Grennfelt, 1988) recognize that nitrogen retention in the soil can be quite high on a temporary basis, but they assume that only net increment in trees is significant over the longer term (i.e., harvest rotation lengths of 50 to 100 years). Nonetheless, even "temporary" retention of atmospherically deposited nitrogen could be significant. If nitrogen-deficient systems can retain as much as 600 kg nitrogen/ha in the soil by heterotrophs (see Table 10-13), an atmospheric nitrogen input of 25 kg/ha/year could be retained for 24 years. Recall that Jenkinson (1970) found an average annual nitrogen accumulation of about 25 kg/ha/year in soils at the Rothamsted Experiment Station in England over a 74-year period (1888-1962). This accumulation, which was calculated by differences in measured soil nitrogen content over time, is of special interest in that it actually *exceeded* estimated atmospheric nitrogen deposition over that period. It seems clear that estimates of atmospheric nitrogen inputs to these sites are low, due either to underestimates of dry deposition or nitrogen fixation.

A critical unknown in soil heterotrophic nitrogen retention is the change (if any) in the relative competitiveness of trees, heterotrophs, and nitrifiers, as noted earlier. There is some evidence to suggest that nitrifiers become more competitive with slow, steady inputs (Johnson and Todd, 1988). Also, it is clear that tree nitrogen from the irrigation and fertilizer experiments noted above (Aronsson and Elowson, 1980; Ingestad, 1981; Landsberg, 1986) can increase substantially with increasing nitrogen deposition rate, bringing into question calculations of nitrogen sequestering by trees from areas that are not nitrogen saturated.

Also inherent in at least the final calculations is the assumption that no natural leaching processes are currently contributing to soil acidification. That is, all base cation leaching is attributed to sulfate and nitrate. This assumption is clearly false; carbonic and organic acids are present in all soil systems and contribute to leaching and acidifying processes to varying degrees (Johnson et al., 1977; Richter et al., 1983; Ulrich, 1980). The net result of this assumption, ironically enough, is to underestimate soil acidification (i.e., the acidification by

carbonic and organic acids do not enter into the calculations) and, therefore, set critical loads (as defined in these calculations) too low

The weakest link in this chain of calculations is, as always, base cation weathering. Although the chemical transformations of many weathering reactions are well known (Lindsay, 1979), quantification of weathering rates under field conditions has remained elusive. The weathering numbers used in calculating these critical loads are crude mass balance estimates based on amounts of minerals and cation nutrients left in soils 8,000 to 12,000 years after the last glaciation (when fresh minerals were first exposed). These calculations do not account for changes in weathering rates with time (rates were likely much faster initially with fresh minerals than later during the course of weathering), nor do they account for the possibility of increased weathering rates with increased acidification pressure or with vegetation rooting (e.g., Boyle and Voigt, 1973).

The entire critical loads concept that formed the basis of the Skokloster document is based on preventing soil acidification. Implicit in this goal is the assumption that soils reach and remain in some kind of steady-state, nonacid condition in nature, an assumption that is probably fallacious given the presence of extremely acid soils in pristine, unmanaged forests (e.g., Johnson et al., 1977). Furthermore, it is not at all clear that soil acidification is always harmful. As shown in the red alder/Douglas fir succession example above, the benefits of nitrogen deposition may well outweigh the detriments of soil acidification. It should be kept in mind that forests of the northern hemisphere have historically been nitrogen deficient, and that growth increases brought about by fertilization (often at levels far in excess of critical loads) have been regarded as beneficial, at least in commercial forest lands. Value judgments inevitably come into play in setting critical loads for pollutant deposition of nutrients, especially in the case of nitrogen.

The green and red lines for nitrogen deposition established for wilderness areas in the Cary Arboretum workshop (Fox et al., 1989) were almost totally subjective guesses and are, therefore, open to many criticisms and arguments. Given the fact that wilderness areas, especially those in the western United States, are very likely nitrogen-limited, even the green lines are not a guarantee of having no effect, as is acknowledged by the authors. They state, however, that "in our judgement, the Green Line levels are sufficiently low that perceptible deleterious effects upon plant health, changes in species composition, or degradation of water

quality are unlikely " In view of the very low nitrogen deposition rates in some parts of the western United States, (1 to 2 kg/ha/year, Table 10-13), it seems likely that increases of up to 10 kg/ha/year will result in some increases in plant growth and plant health, and, quite possibly, changes in species composition The judgment that deleterious effects on plant health and water quality are unlikely to occur at these levels seems to be a reasonable one for the short term (i.e., until biological nitrogen demand is satisfied in these slow-growing ecosystems), but remain open to serious question over the long term

10.5.9 Conclusions

There is little doubt that, because of its role in plant growth, nitrogen deposition has had an effect on many, if not most terrestrial ecosystems Because most forest ecosystems in North America are nitrogen deficient, one of the most noticeable initial changes in response to increased nitrogen deposition is likely to be a growth increase (Gessel et al., 1973, Aber et al., 1989) Whether such a growth increase is deemed desirable or undesirable in a particular ecosystem is entirely a matter of management objectives (timber production or species preservation), and, ultimately, a value judgment by society

All current information indicates that "nitrogen-saturated" forests are relatively rare and limited in extent (e.g., Cole and Rapp, 1981), especially in managed forests Forest management practices, especially with respect to harvesting and fire, will have a major effect on the degree to which forests become nitrogen saturated The critical load values given in the Skolster document (Nilsson and Grennfelt, 1988) are unlikely to produce nitrogen saturation in highly productive, intensively managed forests of the timberbelts in the southeastern and northwestern United States that are frequently harvested and/or subjected to control burning Indeed, there is considerable concern that intensive management practices in these forests are causing nitrogen depletion (Boyle and Ek, 1972, Kimmins, 1977, Smith et al., 1986)

Because of the great variation in both natural forest nitrogen uptake rates and management intensity, it is not reasonable to assign one critical load for all forest ecosystems Intensively managed, short-rotation forests might beneficially utilize up to 100 kg nitrogen/ha/year, whereas a value as low as 10 kg nitrogen/ha/year may produce undesired growth increases in very slow-growing virgin forests in wilderness areas

In summary, it is clear that both the assumptions and the mechanics for calculations of critical loads are seriously faulted. Specifically, the assumption that soil acidification should be the primary consideration for setting critical loads is not supported by a substantial body of literature indicating that nitrogen status itself is most often the determinant of forest ecosystem productivity. Also, the assumption that a single or even a series of critical loads can be set for forest ecosystems of widely varying ages and site conditions is certainly not valid. Finally, calculations of critical loads fail to account for natural processes of soil acidification, and implicitly assume that (1) nitrogen fixation is negligible and (2) soils are naturally in a steady-state condition.

10.6 TERRESTRIAL ECOSYSTEM EFFECTS—VEGETATION

Ecosystems respond to environmental stresses through their constituent organisms (see Section 10.2). Plant populations, when exposed to any environmental stress, can exhibit four different reactions: (1) no response—the individuals are resistant to the stress, (2) severe response—mortality of all individuals and local extinction of the extremely sensitive population, (3) physiological accommodation—the growth and reproductive success of individuals are unaffected because the stress is physiologically accommodated, and (4) differential response—members of the population respond differentially, with some individuals exhibiting better growth and reproductive success due to genetically determined traits (Taylor and Pitelka, 1992, Garner, 1992). Differential response results in the progressive elimination over several generations of sensitive individuals and a shift in the genetic structure of the population toward greater resistance (microevolution). Physiological accommodation and microevolution, with only the latter affecting biodiversity, are the most likely responses for exposure to chronic stress (i.e., stresses that are of intermediate-to-low intensity and of prolonged duration) (Taylor and Pitelka, 1992). The primary effect of air pollution on the more susceptible members of the plant community is that they can no longer compete effectively for essential nutrients, water, light, and space, and are eliminated. The extent of change that may occur in a community depends on the condition and type of community, as well as the pollutant exposure (Garner, 1992).

Plant responses are foliar or soil mediated. Subsequent to the dry and wet deposition of nitrogen forms from the atmosphere (Section 10 4), nitrogen-containing compounds can impact the terrestrial ecosystems when they enter plant leaves and alter metabolic processes (Chapter 9) or by modifying the nitrogen cycle and associated soil chemical properties (Section 10 5) Changes in biochemistry that result in reduced vigor and growth and decrease the plant's ability to compete for light, water, space, and nutrients can be manifested as changes in plant populations, communities, and ultimately, ecosystems (Chapter 9, Section 10 2) Interpretation of the effects of wet and dry deposited nitrogen compounds at the ecosystem level is difficult because of the interconversion of nitrogen compounds and the complex interactions that exist between biological, physicochemical, and climatic factors (Sections 10 2 and 10 5, U S Environmental Protection Agency, 1982) Nevertheless, reactive nitrogen compounds have been hypothesized to impact ecosystems through modifications of individual plant physiological processes upon entering plants through the foliage, or through alterations in the nitrogen status of the ecosystem

10.6.1 Foliage-Mediated Vegetation Effects

Reactive nitrogen compounds can have an impact on terrestrial ecosystems through ambient air exposures by entering plants, usually through the leaves, and disturbing "normal" physiological processes However, in the United States, concentrations seldom reach phytotoxic levels (Chapters 7 and 9) Because information on the direct effects of NO and NO₂ alone and in combination with other pollutants have been described in detail in Sections 9 3 through 9 6, they will not be discussed here

Very little information is available on the direct effects of HNO₃ vapor on vegetation, and essentially no information is available on its effects on ecosystems Norby et al (1989) reported that HNO₃ vapor (0 075 ppmv) induced nitrate reductase activity (NRA) in red spruce foliage Because the induction of NRA is a step in the process leading to the formation of organic nitrogen compounds (amino acids), the nitrate from HNO₃ could function as an alternative source of nitrogen for plant growth However, in plants under stress, the reduction of nitrate to amino acids consumes energy needed for alternative metabolic processes, a potentially slight negative impact

The effects of NH_3 , a reduced nitrogen gas, have been summarized by Van der Eerden (1982). However, NH_3 concentrations seldom reach phytotoxic levels in the United States, consequently it will not be extensively discussed here (U S Environmental Protection Agency, 1982). In contrast, high NH_3 concentrations in Europe have been observed (Van Dijk and Roelofs, 1988). Van der Eerden (1982) summarized available information on the response of crop and tree species to NH_3 fumigation and concluded that the following concentrations produced no adverse effects: 0.107 ppmv ($75 \mu\text{g}/\text{m}^3$) yearly average, 0.858 ppmv ($600 \mu\text{g}/\text{m}^3$) daily average, and 14.3 ppmv ($10,000 \mu\text{g}/\text{m}^3$) hourly average.

Submicron, ammonium sulfate aerosols have been shown to affect foliage of *Phaseolus vulgaris* L. (Gmur et al., 1983). At a concentration of $26 \text{ mg}/\text{m}^3$ (37 ppmv), 3 weeks of exposures produced leaf chlorosis, necrosis, and loss of turgor. Gmur et al. (1983) reported that these foliar symptoms were not correlated with changes in shoot or root dry mass, and suggested that no relationship to plant growth was expected. However, the 3-week experiment was not long enough for significant changes in dry matter to be observed. The level of NH_3 producing the leaf effects (37 ppmv) exceeds normal ambient levels for the United States, but it is representative of reported high concentration episodes in Europe (Gmur et al., 1983). Cowling and Lockyer (1981) reported beneficial effects of NH_3 on the growth of *Lolium perenne* L. due to sorption of NH_3 nitrogen through leaves. Van Hove et al. (1989b) studied the effects of 50 and $100 \mu\text{g}/\text{m}^3$ NH_3 on *Populus euramericana* L. over a 6- to 8-week period and found increases in photosynthesis at $100 \mu\text{g}/\text{m}^3$, but no changes in stomatal characteristics up to that level of NH_3 .

10.6.2 Soil-Mediated Vegetation Effects

Effects of dry nitrogen deposition to terrestrial ecosystems result from the addition of nitrogen to ecosystem soils at a rate above that experienced during normal successional processes. (The effects of nitrogen deposition on soils has been discussed in Section 10.5.) Growth responses to added nitrogen would be anticipated in many cases because many natural systems are nitrogen limited (Krause, 1988, National Research Council, 1979, see also Sections 10.5 and 10.7). However, if atmospheric additions of nitrogen exceed the "buffering" capacity of an ecosystem, alterations in soil chemistry are expected to take place (Section 10.5). Inputs of nitrogen to natural ecosystems alleviate deficiencies and allow

increased growth of some plants, but in doing so, also can impact interplant competitive relationships and alter species composition and diversity in sensitive ecosystems (U S Environmental Protection Agency, 1982, Ellenberg, 1987, Kenk and Fischer, 1988) Schulze (1989) also has proposed that excessive additions of nitrogen lead to nutrient deficiencies of other elements (Ca, Mg) Symptoms of Mg deficiency and drought are frequently associated with large amounts of soil nitrate Aber et al (1989) stated that when nitrogen becomes readily available, some other resources (e g , P for plants or C for microorganisms) become limiting

In addition to the potential for increasing plant productivity through fertilization, the deposition of nitrogen from the atmosphere to ecosystems has been hypothesized to alter normal nutrient cycles and physiological processes, resulting in increased susceptibility of forests to other environmental stresses (Sections 10 5 and 10 6, Lindberg et al , 1987, Nihlgard, 1985, McLaughlin, 1985, Schulze, 1989) Physiological imbalances resulting from excessive nitrogen additions are also hypothesized to disrupt the winter hardening process (Nihlgard, 1985, Friedland et al , 1984, Waring, 1987), produce nutrient imbalances (Nihlgard, 1985, Waring, 1987, Schulze, 1989), and alter carbon allocation patterns within plants (Nihlgard, 1985, McLaughlin, 1985) Changes in nitrogen supply can have an impact on an ecosystem's nutrient balance and, as discussed in the previous section, alter many plant and soil processes involved in nitrogen cycling (Aber et al , 1989) Among the processes affected are (1) plant uptake and allocation, (2) litter production, (3) immobilization (includes ammonification [the release of ammonium] and nitrification [the conversion of ammonium to nitrate during the decay of litter and soil organic matter]), (4) NO_3^- leaching, and (5) trace gas emissions (Aber et al , 1989 [Figure 10-17]) Aber et al (1989) have developed an integrated set of hypotheses that portray the progression of changes in major plant and soil processes in northern forest ecosystems in response to chronic nitrogen deposition and conclude that these ecosystems have a limited capacity to accumulate nitrogen Nitrogen fixation is usually inhibited at high levels of available nitrogen (Waring and Schlesinger, 1985)

An increase in the nitrogen litter content and in litter decomposition rates and an alteration in nitrogen cycling have been observed in the more highly polluted areas when compared with moderate- and low-polluted areas of the San Bernardino Mountains of

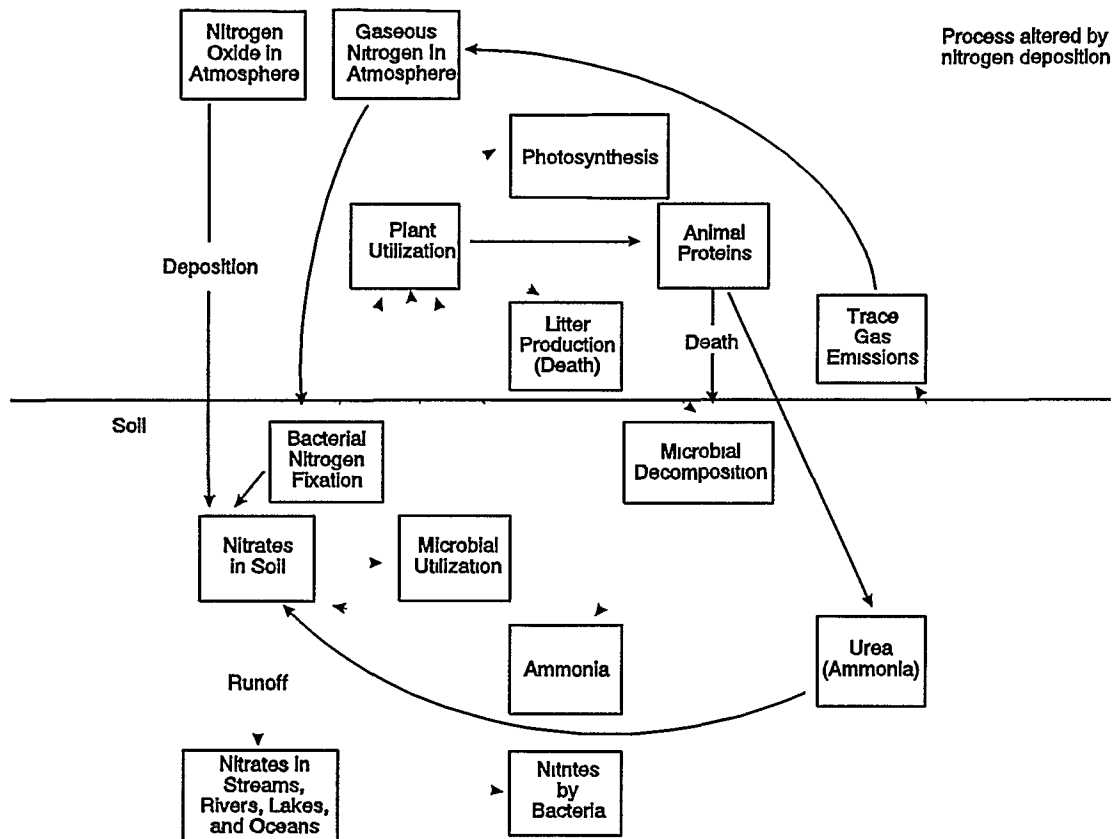


Figure 10-17. Nitrogen cycle (dotted lines indicate processes altered by chronic nitrogen deposition).

Source Garner (1992)

Southern California (Fenn and Dunn, 1989) A pollutant concentration gradient exists with 24-h O_3 concentrations at the high sites in the west averaging 0.1 ppm or higher, moderate sites ranging from 0.06 to 0.08 ppm, and low sites in the east averaging 0.05 ppm or less (Fenn, 1991) Nitrogen and sulfur compounds also occur in the pollutant mixture to which the mountains downwind of the Los Angeles Basin are exposed (See 10.2, Bytnerowicz et al., 1987a,b, Solomon et al., 1992) A nitrogen deposition gradient from west to east parallels the decreasing O_3 gradient Deposition of nitrogen exceeds that of sulfur (Fenn and Bytnerowicz, 1992) Annual average HNO_3 concentrations in 1986 ranged from 1.2 ppb near the Southern California coast to 2.7 ppb in the San Gabriel Mountains (Solomon et al., 1992).

The effects of O₃ exposure and injury to ponderosa (*Pinus ponderosa* Laws) and Jeffrey pine (*P. jeffreyi* Grev & Balf) on a mixed conifer forest in the San Bernardino Mountains, east of Los Angeles, have been studied for many years (Miller, 1973, Miller, 1984, U S Environmental Protection Agency, 1986) The litter layers under trees severely injured by O₃ is deeper than that under trees less severely injured (Fenn and Dunn, 1989) A comparison study of litter decomposition rates of L-layer litter indicates that litter from the more polluted areas in the west decomposed at a significantly ($p = 0.01$) faster rate than litter from moderate to low pollution levels (Fenn and Dunn, 1989, Fenn, 1991) Nitrogen content of litter was greatest at the high pollution sites and was positively correlated with the litter decomposition rate The higher nitrogen and lower Ca content of the litter suggests that litter in the western plots originated from younger needles than at the less polluted sites, possibly due to O₃-induced needle abscission Fungal diversity was also greater in the litter from the western San Bernardino Mountains (Fenn and Dunn, 1989)

When the factors associated with enhanced litter decomposition were investigated, it was found that nitrogen concentrations of soil, foliage, and litter of ponderosa and Jeffrey pine were greater in the plots where pollution concentrations were high than in moderate- or low-pollution sites This was also true for sugar pine (*Pinus lambertiana* Dougl) and for incense cedar (*Calocedrus decurrens* [Torr] Florin), two O₃-tolerant species The rate of litter decomposition for all three pine species was greater at the high-pollution sites Therefore, the increased rate of litter decomposition in the high-pollution plots does not appear to be related to O₃ sensitivity or premature needle abscission, but rather due to higher levels of nitrogen in the soils (Fenn, 1991)

Nitrogen is the mineral nutrient that most frequently limits growth in both agricultural and natural systems (Chapin et al , 1987) The uptake of nitrogen and its allocation is of overriding importance in plant metabolism and governs, to a large extent, the utilization of phosphorus, potassium, and other nutrients, and plant growth As indicated earlier (Section 10.1), plants usually obtain nitrogen by absorbing ammonium (or ammonia) or nitrate (or nitrite) through their roots or through fixation by symbiotic organisms Nitrogen availability via the nitrogen cycle typically controls net primary productivity Normally, the acquisition of nitrogen is a major carbon expense for plants Plants expend a predominant fraction of the total energy available to them in the form of carbohydrates in the acquisition

of nitrogen through the processes of (1) absorption, bringing nitrogen into the plant from the environment, (2) translocation, moving inorganic nitrogen within the plant, and (3) assimilation, conversion of inorganic to organic nitrogen (Chapin et al , 1987)

Absorption of nitrogen from the soil requires constant and extensive root growth to meet the needs of a rapidly growing plant because the soil pools of mineral nitrogen, ammonium, or nitrate in the immediate vicinity of the roots are usually so small that they are quickly depleted (Section 10 5) A crude estimate suggests that the fraction of carbon budget spent on absorption, translocation, and assimilation ranges from 25 to 45 % for ammonium, 20 to 50 % for nitrate, 40 to 45 % nitrogen fixation, and 25 to 50 % for formation of mycorrhizae (Chapin et al., 1987)

Nitrogen uptake influences photosynthesis because in the leaves of plants with C_3 photosynthesis (the pathway used by most of the world's plants), approximately 75 % of the total nitrogen is contained in the chloroplasts and is used during photosynthesis The nitrogen-photosynthesis relationship is, therefore, critical to the growth of trees (Chapin et al , 1987). As a rule, plants allocate resources most efficiently when growth is equally limited by all resources When a specific resource such as nitrogen limits growth, plants adjust by allocating carbohydrates to the organs that acquire the most strongly limiting resources (Figure 10-18)

Among boreal and subalpine conifers, nitrogen added to the soil may not increase growth Depending on the plant species, nitrogen use efficiency above a critical level decreases. All plants do not necessarily benefit from the added nitrogen in the leaves More nitrogen in the soil is not mirrored directly by increased nitrogen uptake except at low levels (Section 10 5) This is particularly true of conifers that are adapted to low-resource environments and tend to have low potential growth rates The photosynthetic capacity of conifer foliage is low and not greatly enhanced by increased nitrogen content (Waring, 1985, Chapin, 1991) High leaf nitrogen content is not always an advantage when other resources, among which are light and water, are limited

Nitrate reductase is the enzyme that catalyses the reduction of nitrate to nitrite Its levels of activity are determined by the supply of nitrate (Section 9 3 2) The nitrate reductase enzyme activity in roots and shoots determines the pattern of nitrate assimilation Increases in root nitrate supply are associated with large increases in the shoot Nitrogen

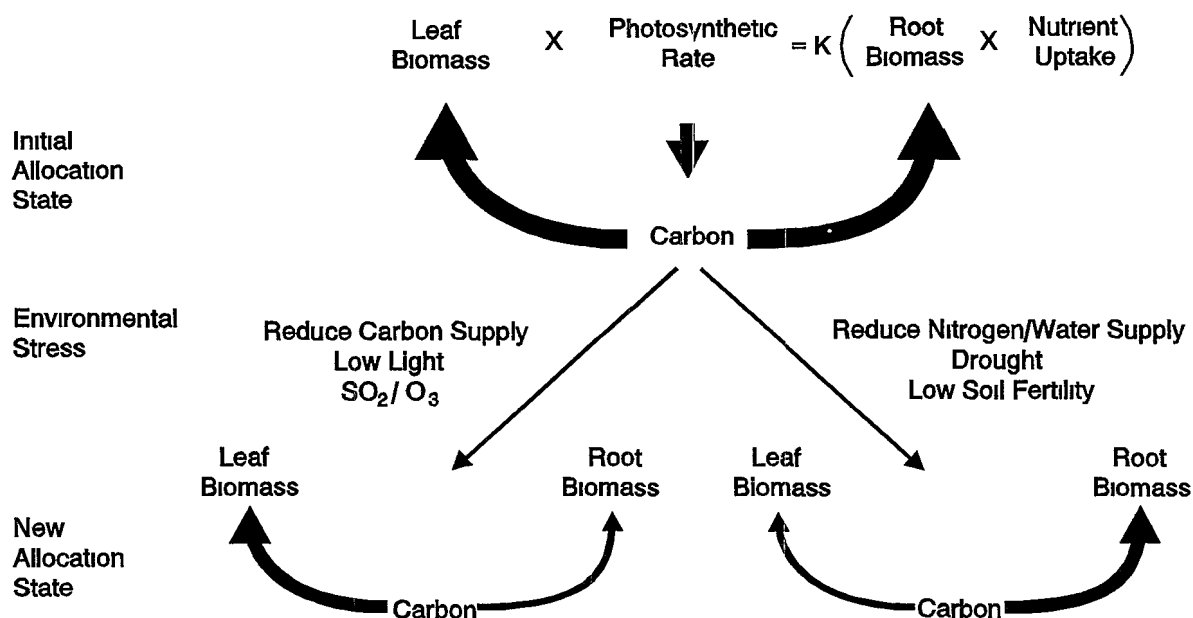


Figure 10-18. Impact of a reduced supply of carbon to the shoot, or water and nitrogen to the roots, on subsequent allocation of carbon.

Source Winner and Atkinson (1986)

source and environmental conditions such as light, temperature, pH, CO₂ and molecular oxygen (O₂) tensions, and water potential, factors that regulate nitrate reductase activity, exert a regulatory effect on the supply of reduced nitrogen to the plant (Haynes, 1986)

Studies indicate that the single most important nitrogenous component limiting photosynthetic capacity is ribulose-1,5-biphosphate carboxylase-oxygenase (RUBISCO), the primary CO₂-fixing enzyme in C₃ and the ultimate CO₂-fixing enzyme in plants with C₄ and CAM photosynthetic pathways (Chapin et al , 1987) In individual leaves, nitrogen availability during growth controls the RUBISCO level The importance of photosynthesis limitation by RUBISCO varies with light and CO₂ availability and with the partitioning of nitrogen among potentially limiting factors Sun plants invest more nitrogen in RUBISCO than shade plants, in low light, increased RUBISCO is not beneficial When photosynthesis is measured at light saturation, leaf nitrogen is closely correlated with photosynthetic capacity But when light is low, photosynthesis increases very little, if at all, with increasing leaf nitrogen (Chapin et al , 1987) In dense conifer forests, lack of sunlight makes the metabolic conversions of nitrate inefficient because photosynthesis (i.e., the production of

large amounts of carbohydrates) and other light-driven reactions become limiting (Zeevaart, 1976). Altered carbohydrate allocation results

Patterns of carbohydrate allocation directly influence growth rate. Excess nitrate alters carbohydrate allocation between shoots and roots (Figure 10-18). It shifts carbohydrate allocation to the shoots, increases production of foliage, and provides nitrogen in a form difficult for the plant to metabolize (Waring, 1987). The capacity of gymnosperms in general, and subalpine and boreal species in particular, to synthesize the enzymes required to reduce the increased nitrate in foliage or roots appears to be limited. Reduced allocation of carbohydrates to the roots, on the other hand, is associated with the accumulation of amino acids in foliage (Waring, 1987). Conifers are plants characteristic of resource-poor environments and tend to have low potential growth rates. When nitrogen is no longer limiting, deficiencies of other nutrients may occur (Aber et al., 1989, Kenk and Fischer, 1988). Competition under the above circumstances favors deciduous tree species, and other plants characteristic of resource-rich environments, rather than conifers (Waring, 1987).

Altered shoot root ratios resulting from different patterns of carbon allocation can lead to increased susceptibility to drought because shoots grow at the expense of roots under high nitrogen availability (Freer-Smith, 1988, Norby et al., 1989, McLaughlin, 1985, Waring, 1987). Changes in carbon nitrogen ratios of tissues resulting from an excessive supply of nitrogen can also result in altered host-pathogen, mycorrhizal, and pest-plant interactions (Chapin et al., 1987, Grennfelt and Hultberg, 1986, Nihlgard, 1985).

Although much has been hypothesized about the impact of excessive inputs of nitrogen into forest ecosystems, direct experimental information to prove or disprove these hypotheses is not widely available. Margolis and Waring (1986) showed that fertilization of Douglas fir with nitrogen could lengthen the growing season to the point where frost damage became a problem. However, Klein and Perkins (1987) presented other evidence that showed no additional winter injury of high elevation conifer forests when fertilized with 40 kg total nitrogen/ha/year. On the other hand, De Temmerman et al. (1988) provided data showing increased fungal outbreaks and frost damage on several pine species exposed to very high NH_3 deposition rates ($> 350 \text{ kg/ha/year}$). Numbers of species and fruiting bodies of fungi have also increased concomitantly with nitrogen deposition in Dutch forests (Van Breemen and Van Dijk, 1988). An increase in total amino acid concentrations in needles known to

take place in response to dry deposition of NO_x (Section 10 4) has also been suggested to favor outbreaks of insect pests (Waring and Pitman, 1985, White, 1984) Schulze (1989) presents a clear progression of evidence that indicates that canopy uptake of nitrogen together with root uptake has caused a nitrogen imbalance in Norway spruce leading to its decline Van Dijk et al (1990) conducted a greenhouse study to determine the impact of ammonium in rainwater on three coniferous trees (Douglas fir, Corsican pine, and Scots pine) and found no sign of deterioration in seedlings receiving nitrogen at the rate of 48 kg/ha/year At the very high rates of application of 480 kg nitrogen/ha/year, increases in shoot root ratio and reductions in fine root and mycorrhizal biomass were observed However, this level of nitrogen addition (i e , simulated deposition) is approximately one order of magnitude greater than most rates of deposition in North America or Europe Kenk and Fischer (1988) summarized fertilization experiments on German forests and found little evidence for growth-limiting effects, but since 1960, some indication of increased growth that could be the result of atmospheric nitrogen deposition was indicated for Norway spruce. Further, they point out that atmospheric deposition has eliminated or diminished the former widespread nitrogen deficiencies Miller and Miller (1988) concluded that fertilizer trials are not appropriate for extrapolation as indicators of forest response to nitrogen deposition (i e , the timing of applications is typically quite different), but nevertheless they also suggested that results of such trials ought to be reconcilable with the "natural" phenomenon

In addition to these indirect soil-mediated effects on individual plants, Ellenberg (1987) has suggested that current balances of interspecific competition in some sensitive ecosystems can be altered by additional sources of nitrogen and result in the displacement of existing species by plants that can utilize the excess nitrogen more efficiently (see Section 10 5 4) Because the competitive equilibrium of plants in any community is finely balanced, the alteration of any one of a number of parameters (e g , increases in nitrogen) can alter ecosystem structure and function (Skeffington and Wilson, 1988) For example, Roelofs et al (1987) proposed that NH_3 /ammonium deposition leads to heathland changes via two modes (1) acidification of the soil and associated loss of cations such as K^+ , Ca^{2+} , and Mg^{2+} , and (2) nitrogen enrichment, which results in "abnormal" plant growth rates and altered competitive relationships

Excessive nitrogen inputs to terrestrial ecosystems can cause differential competitive advantage among plants within a heathland (Heil and Bruggink, 1987, Heil et al , 1988) (see also Section 10.7.4.4). The authors established that the changing nature of unmanaged heathlands in the Netherlands, where *Calluna vulgaris* (L.) Hall is being replaced by grass species, is a result of the eutrophic effect of acidic rainfall and large nitrogen inputs arising from intensive farming practices in the region. Both *Calluna vulgaris* (L.) Hall and *Molinia caerulea* (L.) Moench are stress-tolerant species (Grime, 1979), but they have different growth patterns. *Calluna* is an evergreen, but its long growing season can normally compensate for its slow growth rate, so that it competes successfully with the faster growing *Molinia* under normal nutrient-limiting conditions. A large increase in the nitrogen supply, however, improves the competitive advantage of *Molinia*, increasing its growth rate so that it becomes the dominant species in the heathland.

In support of hypotheses that nitrogen deposition is altering interspecific competition, Roelofs et al (1987) have observed that nitrophilous grasses (*Molinia* and *Deschampsia*) are displacing slower growing plants (*Erica* and *Calluna*) on heathlands in the Netherlands, and the authors suggest that a clear correlation exists between this change and nitrogen loading. Statistical data for the correlation was not provided. These changes in the Netherlands have taken place under nitrogen loadings of between 20 and 60 kg nitrogen/ha/year. Liljelund and Torstensson (1988) have shown clear signs of vegetation changes in response to nitrogen deposition rates of 20 kg/ha/year. Van Breemen and Van Dijk (1988) summarized data for heathlands showing a substantial displacement of heathland plants by grasses from 1980 to 1986. They summarize data showing increases in the presence of nitrophilous plants in the herb layers of forests. It was observed also that the fruiting bodies of mycorrhizal fungi have decreased in number. Ellenberg (1988) has also suggested that long before toxic effects appear on individual plants, ionic inputs (NO_3^- and NH_4^+) have influenced competition between organisms.

10.6.2.1 Foliage and Soil-Mediated Effects—Combined Stress

The environment is seldom optimal in either natural or agricultural communities. It is not unusual, therefore, for plants growing in natural habitats to encounter multiple stresses. Plant responses to multiple stresses depend on resource (carbon and nitrogen) interactions at

levels ranging from the cell to the ecosystem (Chapin et al., 1987) At the present time, data dealing with the response of trees or other vegetation to the combined stresses of O₃ exposure above ground and nitrate deposition through the soil are sparse Tjoelker and Luxmoore (1991), however, have assessed the effects of soil nitrogen availability and chronic O₃ stress on carbon and nutrient economy in 1-year-old seedlings of loblolly pine (*Pinus taeda* L) and yellow poplar (*Liriodendron tulipifera* L) Elevated O₃ concentrations altered biomass partitioning to needles of the current year Ozone concentrations of 0 108 ppm reduced the biomass of current-year needles in loblolly pine seedlings grown at the highest (172 µg/g) nitrogen supply by 20%, but not those grown with a low (59 µg/g) supply of nitrogen The interaction between O₃ and nitrogen suggests that plants grown with a high nitrogen supply are more sensitive to chronic O₃ stress in terms of biomass reduction (Tjoelker and Luxmoore, 1991) Similar results in the growth of domestic radish (*Raphanus sativa* L, cv Cherry Bell) were obtained by Pell et al (1990) Brewer et al (1961) and Harkov and Brennan (1980) observed increased foliar injury when plants were grown with an adequate nitrogen supply

10.6.3 Nitrogen Saturation, Critical Loads, and Current Deposition

Ecosystem nitrogen saturation and the definition of the critical levels of total nitrogen deposition at which changes or negative impacts begin to appear in ecosystems have been the subject of several recent conferences in Europe (Nilsson and Grennfelt, 1988, Brown et al, 1988, Skeffington and Wilson, 1988) Miller and Miller (1988) proposed three definitions for nitrogen-saturated ecosystems (1) no response to additional nitrogen, (2) growth reductions in response to added nitrogen, and (3) added nitrogen leads to increased losses of nitrate in stream water, and concluded that the third was the most reasonable (see also Section 10 3) Brown et al (1988) reported that a recent workshop concluded that nitrogen saturation could be best defined as occurring when nitrogen outputs from ecosystems exceeded inputs This conclusion was based on a model of plant/soil nitrogen saturation put forth by Agren and Bosatta (1988) Aber et al (1989) similarly define nitrogen saturation as the availability of ammonium and nitrate in excess of total combined plant and microbial nutritional demands The concept of nitrogen saturation leads to the possibility of defining a critical nitrogen load (deposition rate) at which no change or

deleterious impacts will occur to an ecosystem (Nilsson and Grennfelt, 1988) It is important to recognize that the magnitude of such a "critical load" will be site- and species-specific, being highly dependent on initial soil chemistries and biological growth potentials (i.e., nitrogen demands)

10.6.3.1 Critical Nitrogen Loads That Have Been Proposed

Skeffington and Wilson (1988) summarized and discussed the following possible criteria as potentially useful for defining appropriate critical nitrogen loads on ecosystems

- prevent nitrate levels in drinking or surface waters from rising above standard levels,
- ensure proton production is less than weathering rate,
- maintenance of a fixed NH_3 -base cation balance,
- maintain nitrogen inputs below nitrogen outputs (the nitrogen saturation approach), and
- minimize accelerations in the rates of ecological succession (vegetation changes due to altered interspecific competition)

De Vries (1988) has also defined criteria for a combined critical load for nitrogen and S for Dutch forest ecosystems based on the following nitrogen contents of foliage, nitrate concentrations in groundwater, NH_4/K ratios, Ca/Al ratios, and Al concentrations in soil solution Based on these criteria, De Vries concluded that current rates of nitrogen and S deposition in the Netherlands exceed acceptable levels

Schulze et al. (1989) have also proposed critical loads for nitrogen deposition based on an ecosystem total anion and cation balance This approach makes the assumption that processes determining ecosystem stability are related to soil acidification and nitrate leaching (see also Section 10.5.6) They concluded that in order to limit the mobilization of aluminum and other heavy metals resulting from acidification and nitrate leaching (a negative result), critical nitrogen deposition rates could not exceed 3 to 14 kg nitrogen/ha/year for silicate soils or 3 to 48 kg nitrogen/ha/year for calcareous-based soils Other critical loads have been proposed at rates of nitrogen deposition ranging from as little as 1 kg to levels near 100 kg nitrogen/ha/year, depending on the impacts considered acceptable and the criteria used to define the critical load

Critical loads less than 20 kg/ha/year have been proposed based on criteria to minimize species changes (Van Breeman and Van Dijk, 1988, Liljelund and Torstensson, 1988)

Vegetational changes from heathland to grassland occurred in the Netherlands when nitrogen deposition was greater than 20 kg/ha/year. Changes in the beech and oak woodlands in two areas of southern Sweden were observed when nitrogen deposition ranged from 20 to 30 kg/ha/year (Liljelund and Torstensson, 1988). Changes in the species composition of softwater pools were noted when NH_4^+ deposition was in the 10- to 20-kg nitrogen/ha/year range. Nitrogen deposition would have to decrease to less than 6 kg/ha/year to return both terrestrial and aquatic vegetation to the flora that was abundant decades ago (Van Breeman and Van Dijk, 1988). Liljelund and Torstensson (1988) point out that establishing critical loads depends on the criteria used. One critical load would be required to prevent species change, whereas another would be required to prevent community change. Using the criteria that ecosystem nitrogen inputs should not exceed outputs, critical loads have been proposed as low as 1 to 5 kg nitrogen/ha/year for poorly productive sites with low productivity or in the range from 5 to 30 kg nitrogen/ha/year for sites having medium quality soils and for common forested systems (Boxman et al., 1988, Rosen, 1988, Skeffington and Wilson, 1988, World Health Organization, 1987).

In their summary of a recent conference on critical nitrogen loading, after discussing various options for setting a critical nitrogen load, Skeffington and Wilson (1988) concluded that "we do not understand ecosystems well enough to set a critical load for nitrogen deposition in a completely objective fashion." Brown et al. (1988) further concluded that there was probably no universal critical load definition that could be applied to all ecosystems, and a combination of scientific, political, and economic considerations would be required for the application of the critical load concept.

The following terrestrial ecosystems have been suggested as being at risk from the deposition of nitrogen-based compounds:

- heathlands with a high proportion of lichen cover,
- low meadow vegetation types used for extensive grazing and haymaking, and
- coniferous forests, especially those at high altitudes (World Health Organization, 1987, Aber et al., 1989)

These oligotrophic ecosystems are considered at risk from atmospheric nitrogen inputs because plant species having high potential growth rates, but normally restricted by low nutrient concentrations, can gain a competitive advantage, and their growth at the expense of existing species changes the "normal" species composition and displaces some species.

entirely (Ellenberg, 1987, Waring, 1987) Sensitive natural ecosystems, unlike highly manipulated agricultural systems, may be prone to damage from exposure to dry-deposited nitrogen compounds because processes of natural selection whereby tolerant individuals survive may not be keeping pace with the current levels of atmospheric nitrogen deposition (World Health Organization, 1987, Waring, 1987)

10.6.3.2 Current Rates of Total Nitrogen Deposition

Application of the concept of critical nitrogen loading has not yet been widely adopted in North America (based on the very limited published data), but a comparison of total nitrogen deposition data for North America and proposed critical loads just discussed should provide a reasonable comparison of the status of terrestrial systems with respect to changes expected from elevated levels of nitrogen deposition Tables 10-14 and 10-15 summarize information regarding the total deposition of nitrogen to a variety of ecosystems/forest types in North America Table 10-14 summarizes information regarding the total deposition of nitrogen to a variety of ecosystems/forest types or regional areas in North America and Europe.

Nitrogen deposition can be divided into four categories, depending on its origin cloud water, precipitation, dry particles, and gaseous forms Figure 10-19 summarizes wet deposited nitrate and ammonium deposition data for various states that were part of the National Acid Deposition Program (NADP) Table 10-15 specifically addresses the issue of relationships between ecosystems' nitrogen inputs and outputs Data in these tables indicate that total deposition of nitrogen in North America, particularly the eastern United States, is comparable to that found for many areas in Europe North American sites would appear to have total nitrogen deposition rates less than 25 kg nitrogen/ha/year It is also obvious from these summary tables that much of our information on nitrogen deposition is limited to information on nitrate and ammonium deposition in rainfall Lindberg et al (1987) concluded that the lack of data on multiple forms of nitrogen deposition limits our ability to accurately determine current levels of nitrogen loading

Olsen (1989) summarized nitrate and ammonium concentration and wet deposition data for the United States and southern Canada for the period from 1979 through 1986 For 1986, the greatest annual rates of ammonium and nitrate deposition were localized in the

**TABLE 10-14. MEASUREMENTS OF VARIOUS FORMS OF
ANNUAL NITROGEN DEPOSITION TO NORTH AMERICAN AND
EUROPEAN ECOSYSTEMS**

| Site Location/ Vegetation | Forms of Nitrogen Deposition (kg/ha) ^a | | | | Total ^b | Reference |
|-------------------------------|---|------|-----------|-------|--------------------|------------------------------|
| | Wet | | Dry | | | |
| | Cloud | Rain | Particles | Gases | | |
| <u>United States</u> | | | | | | |
| California, Chaparral | -- | 8 2 | -- | -- | 23 ^c | Riggan et al (1985) |
| California, Sierra Nevada | -- | -- | -- | -- | (2) | Williams and Melack (1991a) |
| Georgia, Loblolly pine | -- | 3 7 | 1 0 | 4 2 | 9 | Lovett (1992) |
| North Carolina, Loblolly pine | -- | 8 7 | 2 2 | 4 1 | 15 | Lovett (1992) |
| North Carolina, Hardwoods | -- | 4 8 | 0 5 | -- | 5 3 | Swank and Waide (1988) |
| North Carolina, White pine | -- | 3 7 | 0 9 | 2 7 | 7 | Lovett (1992) |
| North Carolina, Red spruce | 8 7 | 6 2 | 3 6 | 8 6 | 27 | Lovett (1992) |
| New Hampshire, Deciduous | -- | 7 0 | -- | -- | (7) | Likens et al (1970) |
| New Hampshire, Deciduous | -- | 9 3 | -- | -- | (9) | Likens (1985) |
| New York, Red spruce | 7 3 | 6 1 | 0 2 | 2 3 | 16 | Lovett (1992) |
| New York, Mixed deciduous | -- | 4 8 | 0 8 | 2 5 | 8 | Lovett (1992) |
| Tennessee, Mixed deciduous | -- | 2 9 | 4 1 | 6 1 | 13 | Kelly and Meagher (1986) |
| Tennessee, Oak forest #1 | -- | 3 2 | 4 4 | 4 0 | 12 | Kelly and Meagher (1986) |
| Tennessee, Oak forest #2 | -- | 2 9 | 4 4 | 4 0 | 11 | Kelly and Meagher (1986) |
| Tennessee, Oak forest #1 | -- | 6 9 | 1 3 | -- | 8 | Kelly (1988) |
| Tennessee, Oak forest #2 | -- | 6 0 | 1 2 | -- | 7 | Kelly (1988) |
| Tennessee, Oak forest | -- | 4 5 | 1 8 | 3 8 | 10 | Lindberg et al (1986) |
| Tennessee, Loblolly pine | -- | 4 3 | 0 6 | 1 4 | 9 | Lovett (1992) |
| Washington, Douglas fir | -- | 2 9 | 1 3 | 0 6 | 5 | Lovett (1992) |
| Washington, Douglas fir | -- | 1 0 | -- | -- | (1) | Henderson and Harris (1975) |
| <u>U S Regions</u> | | | | | | |
| Adirondacks | -- | 6 3 | 4 7 | -- | 11 | Driscoll et al (1989a) |
| Midwest | -- | 4 2 | 2 9 | -- | 7 1 | Driscoll et al (1989a) |
| Northeast | -- | 21 7 | -- | -- | 22 | Munger and Eisenreich (1983) |
| Northwest | -- | 16 6 | -- | -- | 17 | Munger and Eisenreich (1983) |
| Southeast | -- | 20 6 | -- | -- | 21 | Munger and Eisenreich (1983) |
| Southeast Appalachians | -- | 4 2 | 3 1 | -- | 7 3 | Driscoll et al (1989a) |

**TABLE 10-14 (cont'd). MEASUREMENTS OF VARIOUS FORMS OF
ANNUAL NITROGEN DEPOSITION TO NORTH AMERICAN AND
EUROPEAN ECOSYSTEMS**

| Site Location/ Vegetation | Forms of Nitrogen Deposition (kg/ha) ^a | | | | Total ^b | Reference |
|------------------------------------|---|------|-------------------|-------|--------------------|---------------------------------|
| | Wet | | Dry | | | |
| | Cloud | Rain | Particles | Gases | | |
| <u>Canada</u> | | | | | | |
| Alberta (southern) | -- | 7 3 | 12 2 | -- | 19 5 | Peake and Davidson (1990) |
| British Columbia | -- | 5 5 | -- | -- | (5) | Feller (1987) |
| Ontario | -- | 3 7 | -- | -- | (4) | Linsey et al (1987) |
| Ontario (southern) | -- | 2 3 | 1 4 | -- | 3 7 | Ro et al (1988) |
| <u>Federal Republic of Germany</u> | | | | | | |
| Spruce (Southeast slope) | -- | 16 5 | -- | -- | 16 5 | Hantschel et al (1990) |
| Spruce (Southwest slope) | -- | 24 3 | -- | -- | 24 3 | Hantschel et al (1990) |
| <u>Netherlands</u> | | | | | | |
| Oak-birch | -- | -- | -- | -- | 24-56 ^c | Van Breemen and Van Dijk (1988) |
| Deciduous/spruce | -- | -- | -- | -- | 21-42 ^c | Van Breemen and Van Dijk (1988) |
| Scots pine | -- | -- | -- | -- | 17-64 ^c | Van Breemen and Van Dijk (1988) |
| Douglas fir | -- | -- | -- | -- | 17-64 ^c | Van Breemen and Van Dijk (1988) |
| Douglas fir | -- | 19 3 | 95 7 ^d | -- | 115 | Draaijers et al (1989) |
| <u>Norway</u> | | | | | | |
| Spruce | -- | 10 3 | 0 7 | 0 2 | 11 2 | Lovett (1992) |
| | -- | -- | -- | -- | 3-19 ^c | Royal Society (1983) |
| <u>United Kingdom</u> | | | | | | |
| Spruce forest | 1 9 | 8 0 | -- | 13 5 | 23 4 | Fowler et al (1989a) |
| Cotton grass moor | 0 4 | 8 0 | -- | 4 0 | 12 4 | Fowler et al (1989a) |

^a-- Symbolizes data not available or, in the case of cloud deposition, not present

^bMeasurements of total deposition data that do not include both a wet and dry estimate probably underestimate total nitrogen deposition and are enclosed in parentheses

^cTotal nitrogen deposition was based on bulk deposition and throughfall measurements and does include components of wet and dry deposition

^dIncludes deposition from gaseous forms

**TABLE 10-15. NITROGEN INPUT/OUTPUT RELATIONSHIPS
FOR SEVERAL ECOSYSTEMS**

| Site/Vegetation | Inputs (kg/ha/year) | Efflux ^a (kg/ha/year) | Reference |
|------------------------------------|------------------------|-------------------------------------|------------------------------|
| <u>United States</u> | | | |
| Florida, Slash pine | 5 9 ^b | 0 | Van Miegroet et al (1992) |
| Georgia, Loblolly pine | 9 0 ^b | 0 | Van Miegroet et al (1992) |
| Minnesota, Spruce | 7 5 ^b | 0 | Van Miegroet et al (1992) |
| North Carolina, Loblolly pine | 15 0 ^b | 0 | Van Miegroet et al (1992) |
| North Carolina, Oak/hickory | 8 2 ^c | 3 2 | Cole and Rapp (1981) |
| North Carolina, Red spruce | 27 1 ^b | 11 0-20 0 | Van Miegroet et al (1992) |
| North Carolina, White pine | 8 8 ^c | 0 2 | Cole and Rapp (1981) |
| North Carolina, White pine | 7 4 ^b | 0 | Van Miegroet et al (1992) |
| New Hampshire, N hardwood | 6 5 | 4 0 | Bormann et al (1977) |
| New Hampshire, N hardwood | 23 6 | 17 4 | Likens et al (1977) |
| New York, Deciduous | 8 0 ^b | 1 0 | Van Miegroet et al (1992) |
| New York, Red spruce | 15 9 ^b | 3 0 | Van Miegroet et al (1992) |
| Oregon, Douglas fir | 2 0 | 1 5 | Sollins et al (1980) |
| Tennessee, Loblolly pine | 8 7 ^b | 0-2 0 | Van Miegroet et al (1992) |
| Tennessee, Hardwood | 13 2 ^b | 4 4 | Kelly and Meagher (1986) |
| Tennessee, Hardwood | 13 0 | 3 1 | Henderson and Harris (1975) |
| Tennessee, Hardwood | 8 7 | 1 8 | Cole and Rapp (1981) |
| Tennessee, Oak forest | 7 0-8 0 ^d | 1 25 | Kelly (1988) |
| Tennessee, Oak forest | 11 5 ^b | 3 2 | Kelly and Meagher (1986) |
| Tennessee, Shortleaf/pine | 8 7 | 1 8 | Cole and Rapp (1981) |
| Tennessee, Yellow/poplar | 7 7 | 3 5 | Cole and Rapp (1981) |
| Washington, Douglas fir | 1 7 | 0 6 | Cole and Rapp (1981) |
| Washington, Douglas fir | 4 7 ^b | 0 | Van Miegroet et al (1992) |
| Washington, Red alder | 70 0 ^b | 71 0 | Van Miegroet and Cole (1984) |
| Washington, Silver fir | 1 3 | 2 7 | Turner and Singer (1976) |
| Wisconsin, N hardwoods | 5 6 | 0 05 | Pastor and Bockheim (1984) |
| <u>Canada</u> | | | |
| Ontario, Maple | 7 8 | 18 2 | Foster and Nicolson (1988) |
| <u>Federal Republic of Germany</u> | | | |
| Norway spruce | 21 8 | 14 9 | Cole and Rapp (1981) |
| Beech | 21 8 | 4 4 | Cole and Rapp (1981) |
| <u>Netherlands</u> | | | |
| Oak | 45 0 | 22 0 | Van Breemen et al (1987) |
| Oak/birch | 54 0 | 78 0 | Van Breemen et al (1987) |
| Oak | 56 0 | 28 0 | Van Breemen et al (1987) |
| Mixed deciduous | 63 0 | 68 0 | Van Breemen et al (1987) |

**TABLE 10-15 (cont'd). NITROGEN INPUT/OUTPUT RELATIONSHIPS
FOR SEVERAL ECOSYSTEMS**

| Site/Vegetation | Inputs (kg/ha/year) | Efflux ^a (kg/ha/year) | Reference |
|-----------------------|------------------------|-------------------------------------|---------------------------|
| <u>Norway</u> | | | |
| Spruce | 11 2 ^b | 0 | Van Miegroet et al (1992) |
| <u>Sweden</u> | | | |
| Coniferous | 2 1 | 0 6-1 0 | Rosen (1982) |
| <u>United Kingdom</u> | | | |
| Mixed hardwood | 5 8 | 12 6 | Cole and Rapp (1981) |
| <u>U S S R</u> | | | |
| Norway spruce | 1 1 | 0 9 | Cole and Rapp (1981) |

^aAn estimate based on nitrogen losses from the soil profile or from stream flow out of a watershed

^bIncludes precipitation, cloud (where appropriate), particulate, and gaseous forms of nitrogen deposition

^cIncludes nitrogen inputs from precipitation and particulate forms of deposition

^dMean of two oak forests in eastern Tennessee

northeastern United States and southern Canada (Olsen, 1989) Peak values were 5 and 25 kg/ha/year for ammonium and nitrate, respectively Similar wet deposition data for 1987 showed peak deposition rates of 3 5 and 16 kg/ha/year for ammonium and nitrate, respectively (National Atmospheric Deposition Program, 1988) Zemba et al (1988) summarized wet nitrate deposition data from 77 stations located in eastern North America and found that peak nitrate deposition (> 20 kg/ha/year) occurred between Lakes Michigan and Ontario. They also found the temporal pattern of nitrate deposition was quite even throughout the year (Schwartz, 1989) Wet deposition of NH_4^+ in Europe ranges between 3.5 and 17 3 kg NH_4^+ /ha/year (Buijsman and Erisman, 1987, Heil et al , 1987) Boring et al. (1988) have also published an extensive review of the sources, fates, and impacts of nitrogen inputs to terrestrial ecosystems

For an oak-hickory forest in eastern Tennessee, dry deposition made up greater than 80% of the total atmospheric deposition of nitrogen ions (Lindberg et al , 1986) Barrie and Sirois (1986) estimated that dry deposition contributed 21 to 30% of total NO_3^- deposition in eastern Canada Lovett and Lindberg (1986) also concluded that dry deposition of nitrate is the largest form of inorganic nitrogen deposited to oak-hickory forests in eastern Tennessee Significant nitrogen inputs from the deposition of NO_2 have been predicted (Hanson et al ,

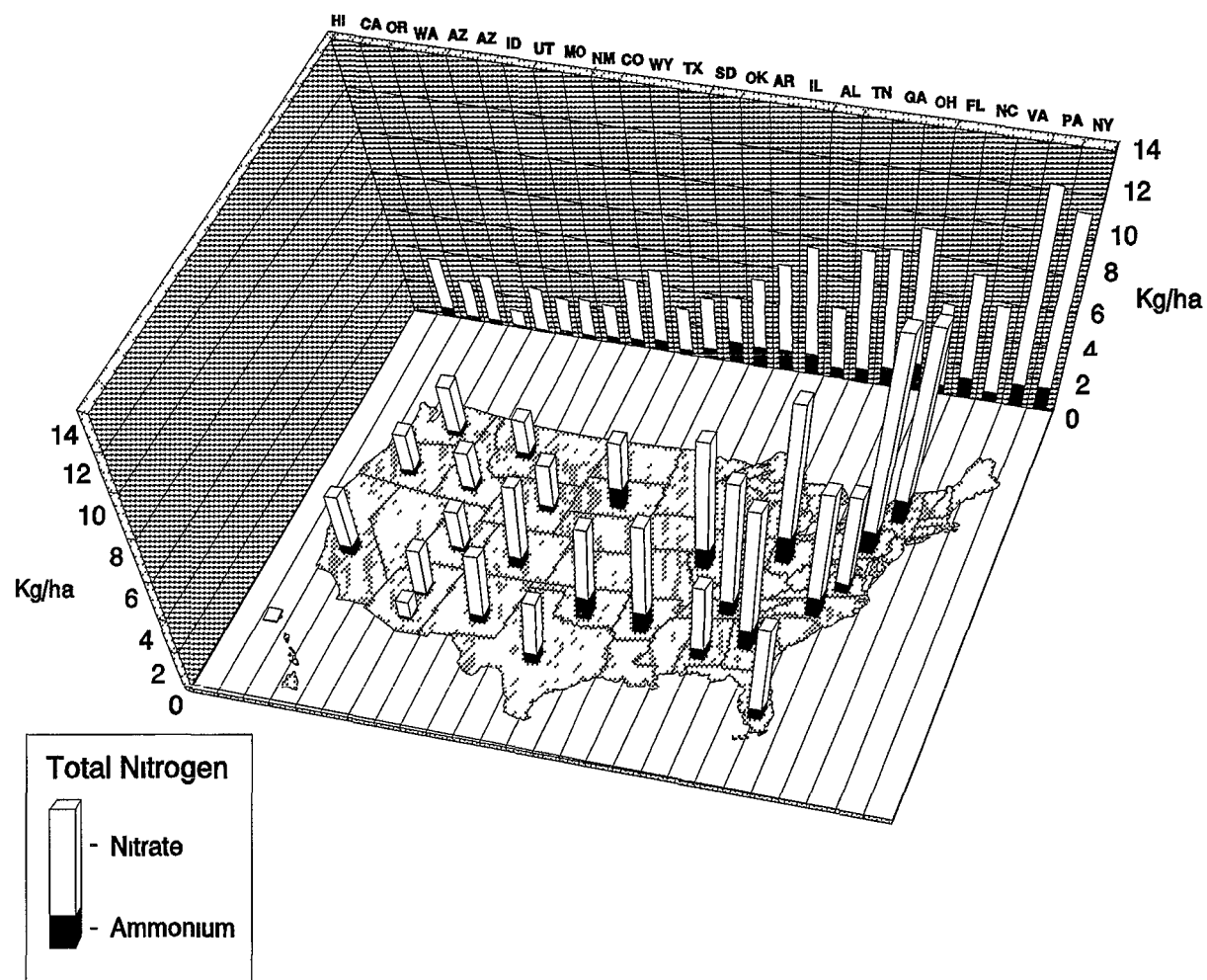


Figure 10-19. Mean annual wet nitrate and ammonium deposition to various states located throughout the United States.

Source Data from the National Atmospheric Deposition Program (1988) are for a single year, and data summarized by Bohm (1991) are for the period 1985 through 1988

1989; Hill, 1971; Kelly and Meagher, 1986) Duyzer et al (1987) has also predicted that dry deposition of NH_3 can reach levels as high as 54 kg/ha/year in areas of high ambient concentration (0.017 ppmv) Typical values of NH_3 deposition in central Europe and Scandinavia range between 20 and 40 kg/ha/year (Grennfelt and Hultberg, 1986)

Based on the current rates of nitrogen deposition (loading) occurring in North America (Tables 10-14 through 10-16), one might conclude that current rates of nitrogen deposition in North America are sufficient to induce at least minor changes in some ecosystems (i.e., rates of deposition in North America exceed some of the critical load levels proposed for Europe) However, because ecosystems have a variable capacity to buffer changes caused by elevated inputs of nitrogen, and because deposition has been taking place for so many years, it is difficult to make general conclusions about the type and extent of change resulting from nitrogen deposition in North America Furthermore, current estimates of total nitrogen deposition to ecosystems and regions of the United States (Tables 10-14 through 10-16) usually do not account for gaseous nitrogen losses from ecosystems (e.g., N_2O and NH_3), therefore, the estimates of net nitrogen deposition may be overestimated (Wetselaar and Farquhar, 1980, Bowden, 1986, Anderson and Levine, 1987, Schimel et al., 1988) Melillo et al (1989) indicate that losses of nitrogen from ecosystems in the form of N_2O are likely to average in the range of 2 to 4 kg nitrogen/ha/year Higher levels of atmospheric nitrogen deposition are also expected to lead to increased rates of N_2O emissions

10.7 ECOSYSTEM EFFECTS—WETLANDS AND BOGS

10.7.1 Introduction

The diverse ecosystems that make up the biosphere interact through the cycling of essential elements and compounds The availability of these essential elements determines the rates of biological processes within a given ecosystem For example, the availability of nitrogen in the form of NO_3^- or NH_4^+ , which cycles through an enormous atmospheric pool of N_2 , is an important determinant of the productivity of ecosystems Ecosystems interact and function in different ways with complex feedback mechanisms, they influence the cycles of essential elements and, to some extent, even the earth's climate

TABLE 10-16. BULK DEPOSITION OF NITROGEN IN NORTH AMERICAN WETLANDS (kg nitrogen/ha/year)^a

| Site | NH ₄ ⁺ | NO ₃ ⁻ | Org-N | Tot-N | Reference |
|---|------------------------------|------------------------------|-------|-----------|-----------------------------|
| Chesapeake Bay, riverine tidal emergent marsh | 2.7 | 4.3 | 4.7 | 11.7 | Jordan et al (1983) |
| Massachusetts, salt marsh | 1.4 | 2.3 | 3.9 | 7.6 | Valiela and Teal (1979) |
| Massachusetts, basin bog | 2.5 | 5.0 | NR | | Hemond (1983) |
| Minnesota, spruce bog | 1.7 | 1.7 | 3.8 | 7.3 | Verry and Timmons (1982) |
| Minnesota, spruce bog | 3.0 | 2.0 | 0.5 | 5.5 | Urban and Eisenreich (1988) |
| Iowa, prairie marsh | 4.0 | 4.0 | NR | | Davis et al (1983) |
| Florida, everglades | 3.0 | 9.6 | NR | | Flora and Rosendahl (1982) |
| Manitoba, emergent marsh | NR | NR | NR | 6.6-12.08 | Kadlec (1986) |
| Ontario, poor fen | NR | 3.1 | NR | | Bayley et al (1987) |

^aNH₄⁺ = Ammonium ion
 NO₃⁻ = Nitrate ion
 Org-N = Organic nitrogen
 Tot-N = Total nitrogen
 NR = Not reported

Wetlands fulfill an important role in these global cycles as net sources and sinks for biogenic gases. They transfer to the atmosphere globally significant quantities of methane (CH₄) (Harriss et al, 1982, 1985) and reduced sulfur gases (Steudler and Peterson, 1984). Elkins et al (1978) discuss the possibility that coastal marshes may function as net sinks for N₂O. Because of the anaerobic nature of their waterlogged soils, decomposition of organic matter in wetland soils is incomplete. Consequently, wetlands function as sinks and long-term storage reservoirs for organic carbon. It has been estimated that wetlands once sequestered a net of 57 to 83 × 10⁶ metric tons of carbon per year worldwide, although recent widespread drainage of wetland soils has shifted the carbon balance (Armentano and Menges, 1986). Although this rate of carbon uptake is small in comparison to other global carbon fluxes, such as the annual release of carbon from combustion of fossil fuel (5 to 6 × 10⁹ metric tons/year, Rotty, 1983) or the net uptake of CO₂-carbon by the ocean (1.6 × 10⁹ metric tons/year, Tans et al, 1990), it is important when the net balance between large fluxes is considered and it is certainly important over geologic time scales (Armentano and Menges, 1986).

These gases (CH_4 , N_2O , and reduced sulfur compounds) modify atmospheric chemistry and global climate. The destruction of O_3 in the upper atmosphere by its reaction with N_2O is one example. Combustion sources are currently raising the atmospheric concentration of N_2O (Hao et al, 1987). The rise in anthropogenic releases of NO_x to the atmosphere also increases the deposition of biologically available forms of nitrogen onto the landscape, with potential effects on productivity (or other aspects of function) and community structure.

Locally, wetlands function as habitats for wildlife, flood control systems, stabilizers and sinks for sediments, storage reservoirs for water, and biological filters that maintain water quality. Studies of riparian forests, for example, generally indicate that they exert a positive influence on the water quality of receiving streams by intercepting and removing nutrients from runoff (Yates and Sheridan, 1983, Brinson et al, 1984, Peterjohn and Correll, 1984, Qualls, 1984). And as sediment traps, salt marshes like those on the Louisiana coast can accumulate annually an impressive 0.76 cm of sediment (DeLaune et al, 1983). These functions are a great monetary value to society (Westman, 1977).

Wetlands also harbor a disproportionate (relative to habitat area) share of flora that are threatened by extinction. Of the 130 plant species from the conterminous United States that are formally listed as endangered or threatened (Code of Federal Regulations, 1987), 18 species (14%) occur principally in wetland habitats. On the national list of plant species that are identified as endangered (Status LE or PE), threatened (Status LT or PT), or potentially threatened (Status 1 or 2), 1,776 species are listed for the conterminous United States (Federal Register, 1985), and 302 (17%) of these occur principally in wetland habitats. The national list of plant species that occur in wetlands includes 6,728 entries (Reed, 1988), and because this list includes plant species found primarily in upland habitats as well as plants from the entire United States and its territories, we can estimate conservatively that the endangered or potentially threatened wetland plant species represent an alarming 4.5% (302/6,728) of this total.

Wetland plants are undoubtedly threatened because of loss of habitat, which in the United States, has been largely a consequence of agricultural development involving drainage (Tiner, 1984). Total wetland area, including intertidal and palustrine areas, in the conterminous United States (Figure 10-20) totaled 437,609 km^2 during the mid-1950s and decreased to 400,567 km^2 , or 5.1% of total land area, by the mid-1970s (Frayer et al,

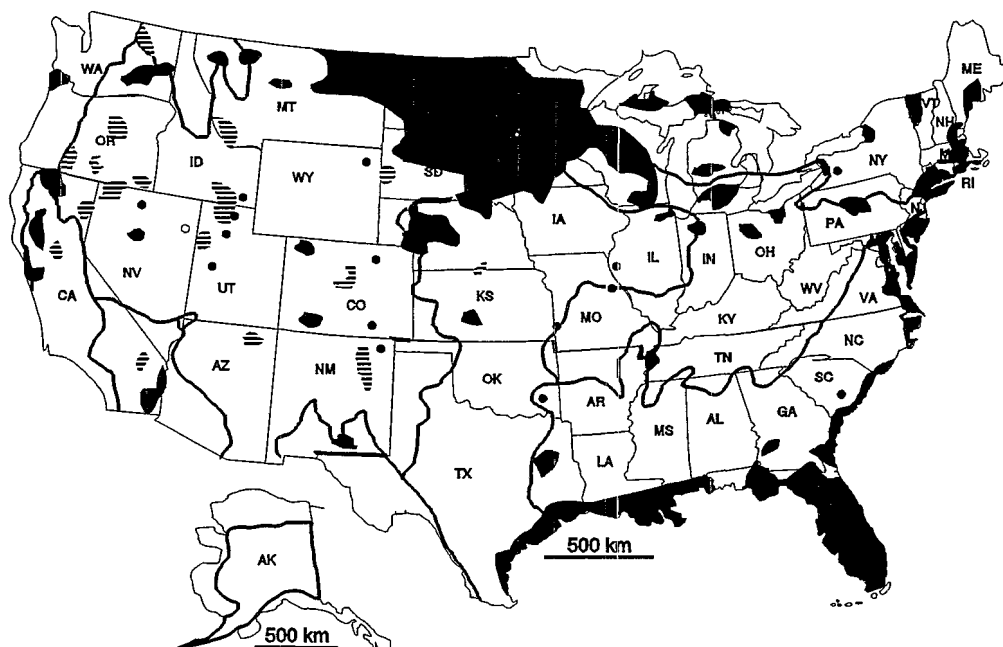


Figure 10-20. Map of the United States showing location of the major groups of inland freshwater marshes. Contours delineate physiographic regions.

Source Hofstetter (1983)

1983) The net loss of wetland habitats during these two decades is equivalent to an annual rate of loss of $1,852 \text{ km}^2/\text{year}$ ($715 \text{ mi}^2/\text{year}$). However, it can also be concluded that current rates of atmospheric nitrogen deposition in parts of Europe, elevated by anthropogenic emissions, alter the competitive relationships among plants and threaten wetland species adapted to infertile habitats. Those data are reviewed here, and on this basis, we can anticipate similar effects of atmospheric nitrogen deposition in the United States.

10.7.2 Atmospheric Nitrogen Inputs

Atmospheric nitrogen inputs occur as both wet and dry deposition. Most studies of atmospheric nitrogen inputs into wetlands focus only on wet deposition or bulk deposition. Accurate measurements of wet deposition are carried out by analyzing nitrogen in precipitation immediately following a precipitation event. Frequently, however, rainfall is

accumulated over some period of time before it is analyzed, and the resulting measurement of deposition rate is usually referred to as bulk deposition. Bulk deposition rates combine wet deposition with some component of dry deposition. Where dry deposition has been carefully measured, it has been concluded that (1) the relative importance of wet and dry deposition varies geographically, (2) that dry deposition can exceed wet deposition (Boring et al., 1988), and (3) that bulk precipitation samplers underestimate the combined dry plus wet deposition rate (Dillon et al., 1988). The available wet surface area of vegetation, onto which nitrogen gases will diffuse, significantly affects the dry deposition rate (Heil et al., 1987). Levy and Moxim (1987) modeled the fate of NO_x emissions to the atmosphere and concluded that dry deposition accounts for greater than one-half of the total NO_x deposition in North America.

The rate of bulk NO_3^- deposition has been shown to be positively correlated with the concentration of NO_2 in the air. Press et al. (1986) measured atmospheric concentrations of NO_2 and bulk deposition of NO_3^- at several sites in northern Britain for 18 mo. Nitrogen dioxide concentrations (2-week averages) ranged from near zero to $25 \mu\text{g}/\text{m}^3$ and were correlated significantly ($p < 0.001$) with concentrations of NO_3^- , collected in bulk samplers, that varied from near zero to about 3 mg nitrogen/L.

A third, and rarely measured, mechanism of deposition that is locally important is the interception or capture of fog or cloud droplets by vegetation. Lovett et al. (1982) estimated that the cloud deposition of NO_3^- in an alpine habitat in New Hampshire was 101.5 kg nitrogen/ha/year, compared to a bulk deposition rate of 23.4 kg nitrogen/ha/year. The same phenomenon was observed by Woodin and Lee (1987), who collected 1.45 times as much water as "throughflow" (collected beneath vegetation) passing through experimental *Sphagnum* mats in the field as from adjacent bulk deposition gauges. Their data also suggest that the deposition of solutes by this mechanism is important, and that bulk precipitation samplers underestimate total deposition.

Table 10-16 summarizes several studies that report wet or bulk deposition rates of nitrogen in North American wetlands. From the data presented, it may be concluded that bulk deposition rates of NH_4^+ , NO_3^- , and organic nitrogen vary geographically and their relative importance varies. In general, however, inputs of NO_3^- , NH_4^+ , and organic nitrogen are all of the same order of magnitude, and their combined rate of deposition varies

from 5.5 to 12.1 kg nitrogen/ha/year. Other studies, however, indicate that wet NO_3^- deposition alone exceeds 15 kg nitrogen/ha/year over most of the midwest and 20 kg nitrogen/ha/year in portions of the northeast United States (Zemba et al., 1988).

Rates of nitrogen deposition, and NH_4^+ deposition in particular, in areas of western Europe are greater than in North America. In areas of Britain, bulk deposition rates of 43 and 46 kg/ha/year have been reported (Press and Lee, 1982, Ferguson et al., 1984). The combination of NO_3^- and NH_4^+ deposition downwind of Manchester and Liverpool is reported to be 32 kg nitrogen/ha/year (Lee et al., 1986). Nitrogen deposition in fens near Utrecht was 21 kg nitrogen/ha/year of inorganic nitrogen and 3 to 5 kg nitrogen/ha/year of organic nitrogen in bulk precipitation and 18 kg nitrogen/ha/year of inorganic nitrogen in dry deposition (Koerselman et al., 1990). Roelofs (1983) reported that wet deposition of nitrogen in the Netherlands averages 15 kg nitrogen/ha/year and is as great as 20 to 60 kg nitrogen/ha/year in areas of intensive stockbreeding, 75 to 90% of this being deposited as NH_4^+ . In Europe, 81% of total NH_3 emissions are from livestock wastes, with the greatest emission densities concentrated in the Netherlands and Belgium (Bujsman, 1987). Annual NH_3 emissions from animal excreta in the Netherlands are reported to be 230 kt/year (Van der Molen et al., 1989) or about 60 kg/ha/year country-wide.

The chemistry of surface runoff from watersheds is probably of greater significance to most wetlands than the chemistry of direct deposition, but the nitrogen load of surface runoff probably increases with nitrogen deposition and with the size of the catchment area. Atmospheric deposition accounts for a large fraction of the total nitrogen entering watersheds (Robertson and Rosswall, 1986). Atmospheric deposition apparently has become a major source of NO_3^- to surface waters in North America, especially in the east and upper midwest (Smith et al., 1987a), and increases in total nitrogen concentration at stream monitoring stations are strongly associated with high levels of atmospheric nitrate deposition (Smith et al., 1987b). However, the direct contribution made by atmospheric deposition to the nitrogen load in surface water because of nitrogen in surface runoff is unknown. Measurements by Buell and Peters (1988) of stream chemistry in Georgia indicated that 93% of the precipitation inputs of NH_4^+ and NO_3^- were retained by the watershed. A study by Correll (1981) of mass nutrient balances of a small watershed of the Rhode River estuary on the Chesapeake Bay showed that total wet nitrogen deposition to 88 ha of tidal marshes and

mudflats was 740 kg nitrogen (8.4 kg/ha) in 13 mo, compared to total nitrogen in runoff from 2,050 ha of watershed of 10,000 kg nitrogen. Only about 7% (740 kg/10,740 kg) of the nitrogen entering the wetland was from direct deposition. However, in as much as nitrogen deposition onto the watershed ($8.4 \text{ kg/ha} \times 2,050 \text{ ha} = 17,220 \text{ kg}$) exceeded total runoff from the watershed to the wetland (10,000 kg), deposition could have contributed the majority of nitrogen entering the wetland indirectly through runoff. But the contributions of other nitrogen sources to runoff, such as fixation, fertilizer, and animal waste, were not given.

10.7.3 The Wetland Nitrogen Cycle

The feature of wetlands that sets them apart from terrestrial ecosystems is the anaerobic (oxygen-free) nature of their waterlogged soils, which alters the relative importance of various microbial transformations of inorganic and organic nitrogen compounds. Generally, the absence of O_2 retards the decomposition of organic matter (Tate, 1979, DeLaune et al., 1981; Van der Valk and Attiwill, 1983, Godshalk and Wetzel, 1978, Clark and Gilmour, 1983). Complex aromatic ring structures are more resistant to microbial attack under anoxic conditions (Tate, 1979), leading to the formation and buildup of peat in wetland environments. Anoxic soils also favor the rapid conversion of NO_3^- to N_2O or N_2 . This process is accomplished by bacteria and is referred to as denitrification or dissimilatory nitrate reduction, and it results in quantitatively important losses of nitrogen from wetland ecosystems. Finally, the hydrology of wetlands favors diffusive exchanges of nitrogen compounds to and from sediments and advective transport (carried by water) of nitrogen compounds between ecosystems. This often results in movements of NH_4^+ from anoxic sediments to the oxidized surface sediment or water column, where nitrification (the oxidation of NH_4^+ to NO_3^- by bacteria) can occur, and the return movement of NO_3^- to the anoxic sediment layers, where denitrification can occur. The nitrogen cycle in wetlands has been reviewed recently by Reddy and Patrick (1984), Savant and De Datta (1982), and Bowden (1987). Important steps in the nitrogen cycle are summarized in Section 10.3.

Table 10-17 presents the nitrogen budgets of wetlands that exhibit a wide range of nitrogen inputs. The two bog sites (Table 10-18) are representative of wetlands that contain

TABLE 10-17. NITROGEN BUDGETS OF SELECTED WETLANDS
(kg nitrogen/ha/year)^a

| Location and Wetland Type | UK Salt Marsh ^b | MA Salt Marsh ^c | Dutch Rech Fen ^d | Dutch Disc Fen ^d | French Heath ^e | MA Bog ^f | MN Bog ^g |
|----------------------------------|----------------------------------|----------------------------------|-----------------------------------|-----------------------------------|------------------------------|------------------------|------------------------|
| INPUTS | | | | | | | |
| Precipitation | NR | 7 9 | 43 7 ^h | 42 0 ^h | 8 1 | 7 5 | 8 6 |
| Fixation | 3 36 | 68 0 | 2 1 | 12 7 | 1 3 | 3 36 | 0 5 |
| Surface, ground or tidal water | 43 4 ⁱ | 668 0 | 7 3 | 20 9 | 0 | 0 | 0 |
| Total | | 743 9 | 53 1 | 75 6 | 9 4 | 1 09 | 0 91 |
| INTERNAL CYCLE | | | | | | | |
| Plant assimilation | 225 4 | 214 0 ^j | 274 0 ^k | 90 0 ^k | 82 0 | 38 0 | 66 0 |
| Mineralization | 194 9 | 193 0 ^j | 244 0 ^l | 79 0 ^l | 74 0 | 26 0 | 50 0 |
| OUTPUTS | | | | | | | |
| Denitrification | 3 78 | 143 0 | 1 4 | 1 1 | NR | 1 0 | 1 8 |
| Ammonia volatilization | NR | 0 35 | NR | NR | NR | Trace | NR |
| Surface or subsurface DIN export | 2 4 ^m | 102 0 | 2 1 | 6 7 | 3 0 | 2 0 | 0 |
| Surface or subsurface ON export | 43 0 ^m | 552 0 | 45 8 ⁿ | 80 4 ⁿ | 3 0 | 1 0 | 2 0 |
| Total | | 797 4 | 49 3 | 88 2 | | 4 0 | 3 8 |

^aUK = United Kingdom

MA = Massachusetts

MN = Minnesota

NR = Not reported

DIN = Dissolved inorganic nitrogen

ON = Dissolved and particulate organic nitrogen

^bAbd Aziz and Nedwell (1986a,b) salt marsh dominated by *Puccinellia maritima* (a grass)

^cValiela and Teal (1979) salt marsh dominated by *Spartina alterniflora*

^dKoerselman et al (1990) Dutch eutrophic recharge and mesotrophic discharge fens, respectively

^eRoze (1988) mesophilous heathland (shrub bog) dominated by *Erica ciliaris* (heath) and *Ulex minor*

^fUrban and Eisenreich (1988) ombrotrophic *Sphagnum* bog forested with black spruce (*Picea mariana*) and with an understory of shrubs and sedges

^gHemond (1983) ombrotrophic bog dominated by *Sphagnum*

^hIncludes bulk plus dry deposition of inorganic and organic nitrogen

ⁱRepresents the net exchange of nitrate ion (the major component) and small particulate organic nitrogen rather than an absolute rate

^jCalculated from Morris et al (1984) and Valiela et al (1984)

^kFrom Verhoeven et al (1988), assuming a root shoot quotient of 1 0

^lFrom Verhoeven et al (1988)

^mRepresents the net exchange of dissolved organic nitrogen (the major component), ammonium ion, and large particulate organic nitrogen rather than an absolute rate

ⁿIncludes primarily hay harvested by mowing

**TABLE 10-18. RESULTS OF NITROGEN FERTILIZATION EXPERIMENTS
IN WETLAND ECOSYSTEMS**

| Salt Marsh Ecosystems | Rate of Nitrogen Application (kg/ha/year) | Length of Study (years) | Control Biomass (g/m ²) ^a | Percent Increase ^b | Nitrogen- Form Applied ^c | Reference |
|------------------------------|--|-------------------------------|--|----------------------------------|---|------------------------------|
| <i>Spartina</i> | 200 | 1 | 1,660 | 16 | NH ₄ ⁺ | Patrick and Delaune (1976) |
| <i>Spartina</i> | 200 | 1 | 816 | 25 | NH ₄ NO ₃ | Gallagher (1975) |
| <i>Spartina</i> | 220 | 3 | 320 | 131 | Sludge | Vahela et al (1975) |
| <i>Spartina</i> | 650 | 3 | 320 | 269 | Urea | Vahela et al (1975) |
| <i>Spartina</i> | 670 | 2 | 250 | 120 | Sludge | Vahela and Teal (1974) |
| <i>Spartina</i> | 1,040 | 1 | 450 | 100 | NH ₄ ⁺ | Haines (1979) |
| <i>Spartina</i> | 3,120 | 2 | 235 | 413 | NH ₄ ⁺ | Morris (1988) |
| <i>Puccinellia</i> | 320 | 2 | 64 | 175 | NH ₄ ⁺ | Cargill and Jefferies (1984) |
| <i>Puccinellia</i> | 320 | 2 | 64 | 73 | NO ₃ ⁻ | Cargill and Jefferies (1984) |
| <i>Carex</i> | 320 | 2 | 65 | 146 | NH ₄ ⁺ | Cargill and Jefferies (1984) |
| <i>Panicum hemitomon</i> | 30 | 1 | 1,320 | 6 | NH ₄ ⁺ | DeLaune et al (1986) |
| <i>Panicum hemitomon</i> | 100 | 1 | 1,320 | 42 | NH ₄ ⁺ | DeLaune et al (1986) |
| <i>Typha glauca</i> | 1,350 | 2 | 1,726 | 36 | NH ₄ NO ₃ | Neely and Davis (1985a) |
| <i>Sparganium eurycarpum</i> | 1,350 | 2 | 637 | 86 | NH ₄ NO ₃ | Neely and Davis (1985a) |
| bog | 300 | 1 | 180 | 25 | Urea | Sanville (1988) |
| bog | 7 | 1 | 200 | 10 | Sludge | Sanville (1988) |
| fen | 450 | 1 | 350 | 57 | Mineral-N | Vermeer (1986) |
| wet grassland | 450 | 1 | 400 | 68 | Mineral-N | Vermeer (1986) |

^aControl biomass is the maximum, nonfertilized aboveground standing crop

^bPercent increase indicates the response of control biomass during the year of fertilization at the indicated rate of application, computed as $100 \times (\text{Experimental}-\text{Control})/\text{Control}$

^cNH₄⁺ = Ammonium ion

NH₄NO₃ = Ammonium nitrate

NO₃⁻ = Nitrate ion

Mineral-N = Mineral nitrogen

plant species that are adapted to low levels of nitrogen. They are examples of ombrotrophic bogs, meaning that they receive nutrients exclusively from precipitation. They develop where precipitation exceeds evapotranspiration and where there is some impediment to drainage of the surplus water (Mitsch and Gosselink, 1986). Bogs are dominated by *Sphagnum* spp. and may be sparsely forested. The *Sphagnum* builds a dense layer of peat,

raised above the elevation of the surrounding land so that they receive neither runoff from uplands nor inputs from groundwater. Peat-forming bog ecosystems are widely distributed throughout the northern hemisphere, but they are most common in formerly glaciated regions. The distribution of peatland area in North America is shown in Figure 10-21. The bog ecosystems represented in Table 10-17 are located in Minnesota (Urban and Eisenreich, 1988) and Massachusetts (Hemond, 1983).

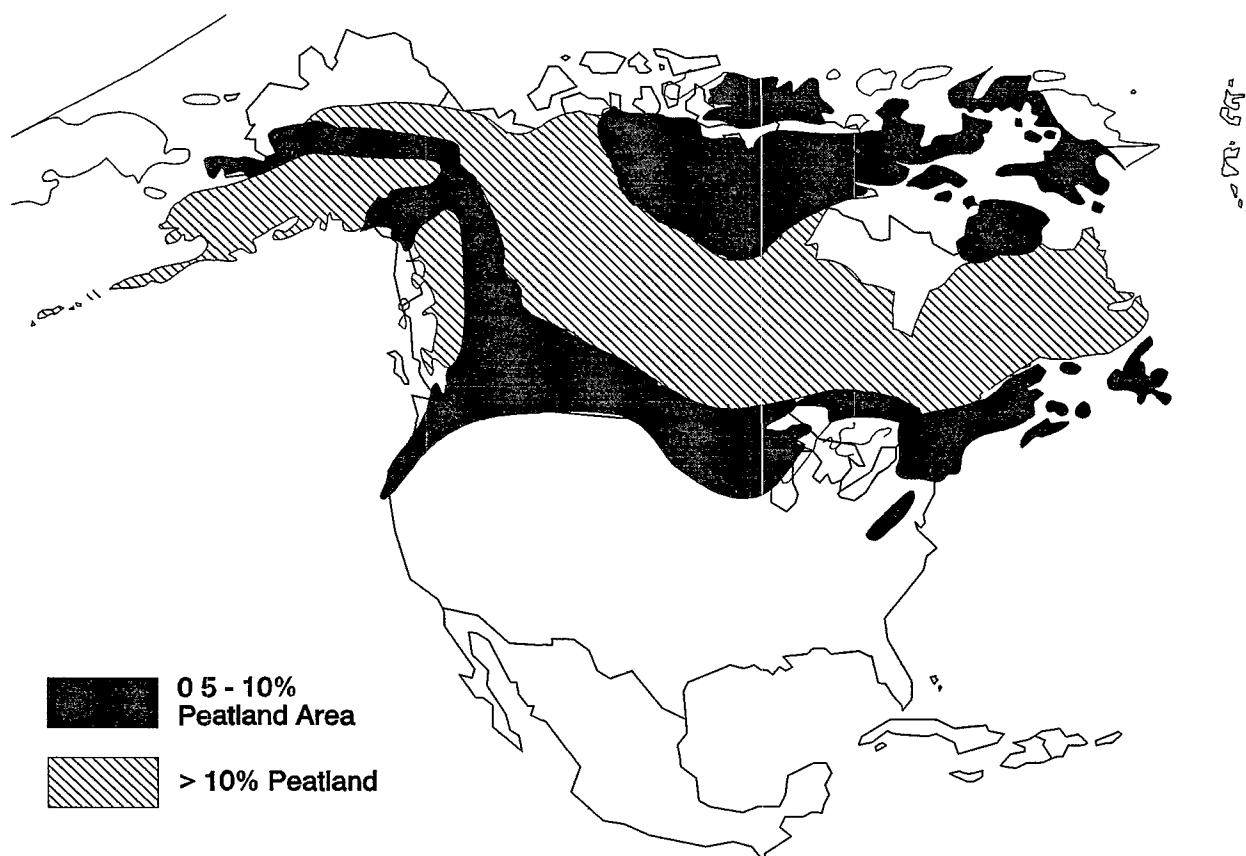


Figure 10-21. Distribution of North American peatlands.

Source: Mitsch and Gosselink (1986)

In bog ecosystems, the most important nitrogen inputs are from wet and dry deposition (see the row labeled "precipitation" in Table 10-17). The total input of nitrogen in these examples is about 10 kg nitrogen/ha/year, and atmospheric deposition accounts for most of this (Urban and Eisenreich, 1988, Hemond, 1983). Also note that the total nitrogen outputs

from the system are approximately 4 kg nitrogen/ha/year. The outputs are accounted for by denitrification (1 to 1.8 kg nitrogen/ha/year) and by export in runoff of dissolved inorganic nitrogen (as NH_4^+) and dissolved organic nitrogen (DON). No export of particulate organic nitrogen was reported; nitrogen accumulated in plant tissues is largely recycled within the bog.

Bog wetlands are representative of one end of a continuum, but there are also other wetlands where atmospheric nitrogen deposition represents a significant fraction of the total input of inorganic nitrogen. For example, wetfall contributed more than 95% of the NH_4^+ and NO_3^- entering the 1,000-km² Shark River Slough, the major fresh water drainage of Everglades National Park (Flora and Rosendahl, 1982). However, the importance of organic nitrogen in the surface inflow may be considerable, depending on how easily or rapidly it is mineralized by the microbial community. In this ecosystem, rainfall is about 84% of total water input, and one can generalize that the significance of atmospheric nitrogen deposition increases in wetlands as rainfall increases as a fraction of the total water budget.

The French heathland or shrub bog (Table 10-17) is another example of a wetland with low nitrogen inputs and outputs, but with an intermediate rate of internal cycling. The moderate size of the internal nitrogen cycle depends on the accumulation of a large quantity of organic nitrogen in the soil humus (Roze, 1988). A fraction of this organic pool mineralizes each year and is assimilated by the plant community. Organic and inorganic nitrogen in the soil is about 91% of total nitrogen in this heathland ecosystem, with the remaining 9% being contained within the plant biomass. A moderate rate of nitrogen mineralization in the soil is balanced by assimilation by the plant community, and nitrogen is largely conserved within the ecosystem.

In the Dutch fens (Table 10-17), the inputs and outputs of nitrogen are intermediate between those of the bogs and salt marshes. Both fens are influenced by their close proximity to heavily fertilized pastures, by atmospheric nitrogen deposition, and by annual mowing and harvest of aboveground vegetation. The fen that occupies a site of groundwater recharge is influenced by water that is diverted from the highly polluted River Vecht during periods of high evapotranspiration, and the discharge fen is influenced by nutrients in groundwater (Verhoeven et al., 1988). However, atmospheric nitrogen deposition in these fens supplies more nitrogen than all other inputs combined (Table 10-17).

The coastal salt marsh ecosystems in Table 10-17 are characteristic of wetlands that are adapted to large nitrogen inputs. Coastal salt marshes have a temperate, worldwide distribution. They exist within the intertidal zone and are alternately flooded and drained daily by the action of the tides. The example from Massachusetts is a salt marsh dominated by the grass *Spartina alterniflora* (Valiela and Teal, 1979). The salt marsh example from the United Kingdom in Essex is dominated by the grass *Puccinellia maritima* (Abd Aziz and Nedwell, 1986b).

In salt marsh ecosystems, the most important nitrogen inputs are from those brought into the marsh in tidal water and, in some cases, groundwater. Input of particulate organic nitrogen from sedimentation and/or NO_3^- is apparently the dominant mechanism by which these ecosystems remove nitrogen from surface water because the diffusion gradients for NH_4^+ and DON normally favor diffusion out of the sediment. These surface and groundwater sources of nitrogen are one to two orders of magnitude greater than inputs from precipitation (Table 10-17). In the Massachusetts salt marsh, groundwater inputs of NO_3^- and DON are important and account for 60 and 56 kg nitrogen/ha/year, respectively, of the total inputs (Valiela and Teal, 1979). In contrast, the Essex, United Kingdom, marsh is not influenced by groundwater (Abd Aziz and Nedwell, 1986b). Both salt marshes have large nitrogen inputs from tidal water, and in the Massachusetts marsh, these are largely as NH_4^+ (54 kg nitrogen/ha/year), DON (337 kg nitrogen/ha/year), and particulate organic nitrogen (139 kg nitrogen/ha/year) (Valiela and Teal, 1979). There are additional inputs and outputs, such as deposition of bird faeces and shellfish harvest, but these are insignificant in comparison to other rates (Valiela and Teal, 1979).

The large inputs of nitrogen in salt marshes are balanced by equally large outputs (Table 10-17), but there are important transformations that take place within the marsh. Denitrification accounts for 17.9% of the total nitrogen loss from the Massachusetts marsh. Because the denitrification rate is greater than the combined inputs of NO_3^- , this implies that rates of nitrification are large. In both marshes, the greatest nitrogen losses occur in tidal water exchange, and in the Massachusetts marsh, there is a net loss of all forms of dissolved nitrogen in tidal water. The Massachusetts marsh exports large amounts of NH_4^+ (73 kg nitrogen/ha/year), NO_3^- (25 kg nitrogen/ha/year), DON (380 kg nitrogen/ha/year), and particulate organic nitrogen (17 kg nitrogen/ha/year) (Valiela and Teal, 1979).

Nitrogen inputs and outputs in tidal water were given as net exchanges of different nitrogen components in the Essex, United Kingdom, study (Abd Aziz and Nedwell, 1986b), rather than as absolute rates. This is the reason for the discrepancy in the rates of tidal-water imports and exports of nitrogen in the Essex and Massachusetts marshes (Table 10-17). However, valid comparisons can be made of the net exchanges. There is a large net export of DON (43 kg nitrogen/ha/year) from the Essex marsh (Abd Aziz and Nedwell, 1986b), and this is consistent with the net DON loss in tidal water of 45 kg nitrogen/ha/year from the Massachusetts marsh (Valiela and Teal, 1979). The marshes differ in the net tidal-water exchanges of other forms of nitrogen.

The rate of internal nitrogen cycling (assimilation and mineralization) within ecosystems is directly proportional to the rate of primary production (e.g., Verhoeven and Arts, 1987), although high rates of productivity can be supported by high external nutrient inputs when conditions are unfavorable for high mineralization rates (Verhoeven et al., 1988). Mineralization rates differ greatly between the wetland types represented in Table 10-17. Nitrogen assimilation by the plant communities varies from 38 to 66 kg nitrogen/ha/year in the bog ecosystems, compared to 225 to 274 kg nitrogen/ha/year in the salt marsh and fen ecosystems, respectively. The nitrogen cycle in the bog and heathland ecosystems is largely closed (Figure 10-22). In contrast, the nitrogen cycle in salt marshes and fens is open, and there is a great exchange of nitrogen with adjacent systems (Figure 10-21). In all these ecosystems, the rate of nitrogen mineralization almost balances plant assimilation in the manner of a closed cycle (Table 10-17). However, it is unlikely that the salt marsh could function as a closed system and maintain its productivity or community structure. Likewise, it is unlikely that the bog ecosystem could maintain its community structure if the nitrogen inputs were greatly increased by some means. In general, as the input rate of nitrogen increases, there are concomitant increases in the output rate and magnitude of the internal cycle (Table 10-17). In ecosystems with closed nutrient cycles and small rates of internal cycling, like bogs, if nitrogen loadings increase significantly, then we can predict that productivity will increase, but as will be discussed later, the increased productivity will be accompanied by changes in species composition to those adapted to an elevated nutrient regime (Figure 10-22).

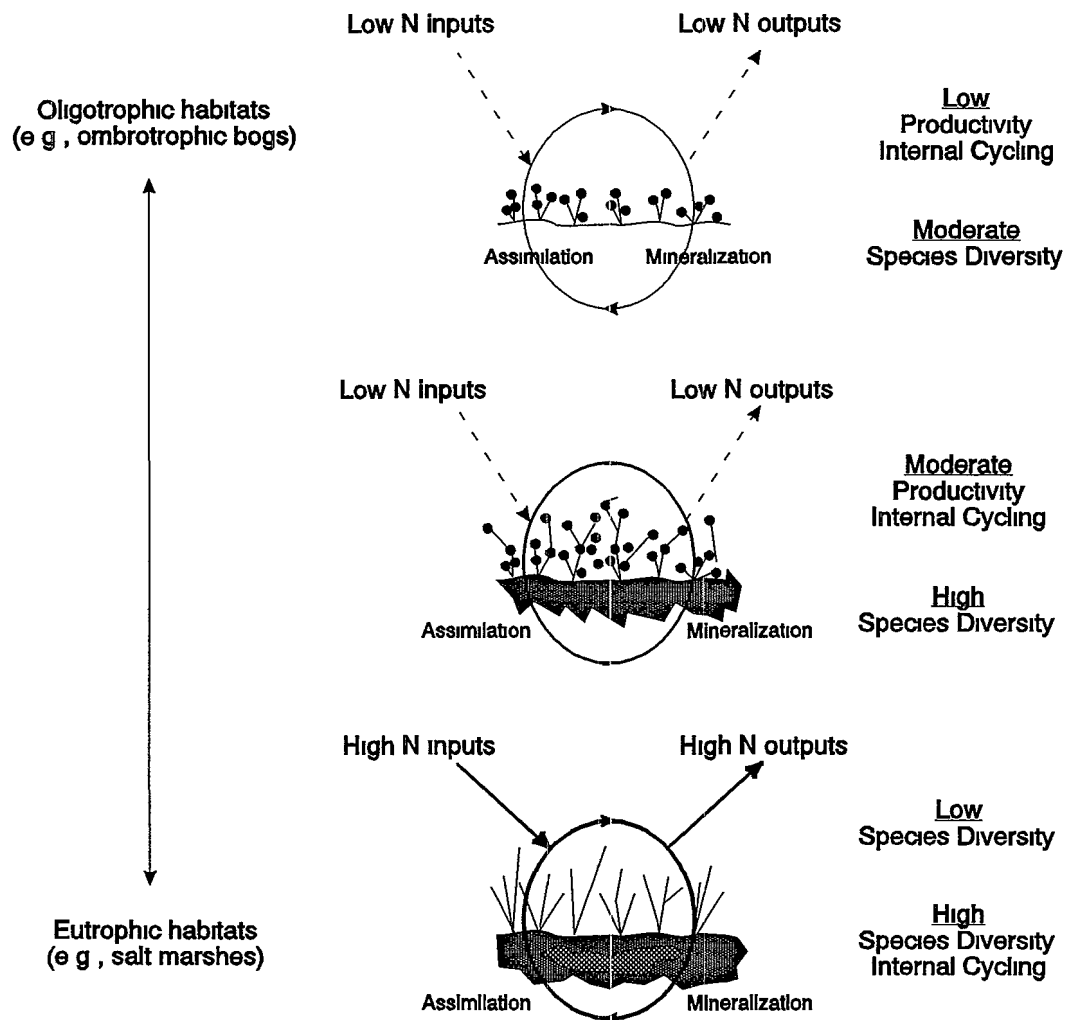


Figure 10-22. Conceptual relationships among trends in nitrogen cycling, productivity, and species diversity along a gradient from oligotrophic (nutrient-poor) to eutrophic (nutrient-rich) habitats.

10.7.4 Effects of Nitrogen Loading on Wetland Plant Communities

10.7.4.1 Effects on Primary Production

Numerous field experiments involving nitrogen fertilization have documented that primary production in wetland ecosystems is commonly limited by the availability of nitrogen. Results of this type of experiment are presented in Table 10-18. In all of the fertilization experiments included in the table, only sewage sludge, urea, or mineral nitrogen in the form of NH_4^+ or NO_3^- were applied. Except in the case of sewage sludge applications, where the numerous elements contained in sludge preclude attributing the results

to any specific element, the stimulation of growth that was observed can be attributed solely to application of nitrogen. Rates of application ranged from 7 to 3,120 kg nitrogen/ha/year (Table 10-18), and in most studies, these have been 1 to 2 orders of magnitude greater than rates of atmospheric deposition (Table 10-16). These applications stimulated increases in standing biomass by 6 to 413 % (Table 10-18).

Several studies have investigated the effects of different nitrogen sources. Cargill and Jefferies (1984) found that applications of NH_4^+ increased production of *Puccinellia phryganodes* (a grass) in a subarctic salt marsh by 175 %, whereas equivalent applications of NO_3^- increased production by only 73 %. Applications of NO_3^- were perhaps less effective than NH_4^+ because of denitrification of NO_3^- by bacteria in the anaerobic marsh sediments. This demonstrates the importance of competition between plants and microbes for specific inorganic nitrogen compounds, with plants being the best competitors for NH_4^+ .

The greatest stimulation of growth is often achieved when nitrogen applications are combined with applications of other nutrients. In the study of Cargill and Jefferies (1984), applications of inorganic phosphate (P_i) combined with NH_4^+ stimulated production to a greater extent than NH_4^+ alone. Sanville (1988) observed that combinations of nitrogen, in the form of urea, and P_i stimulated production in a *Sphagnum* bog to a greater extent than nitrogen applications alone, and that singular additions of P_i had no significant effect on growth. These results demonstrate that other nutrients, P_i in these examples, become secondarily limiting after nitrogen applications reach a threshold.

In one study of a wet heathland in the central Netherlands, total aboveground biomass failed to respond on experimental sites fertilized for 3 years at a rate of 200 kg nitrogen/ha/year, but sites fertilized with 40 kg phosphorus/ha/year did show a significant increase in biomass (Aerts and Berendse, 1988). Thus, wetlands are not universally limited by nitrogen. However, as discussed above (see Section 10.5.2), the Netherlands is an area of extreme high nitrogen deposition, and the threshold for nitrogen limitation is perhaps exceeded by anthropogenic inputs in this area.

Fertilization experiments of salt marshes in Massachusetts by Valiela and Teal (1974) and in Louisiana by Patrick and Delaune (1976) involving singular applications of either nitrogen or P_i demonstrated that primary production was stimulated by nitrogen and not by phosphorus. Vermeer (1986) obtained the same result in freshwater fen and wet grassland

communities in the Netherlands. However, fertilization with nitrogen increased the biomass and dominance of grasses at the expense of other species in fen and wet grassland communities. Some *Equisetum* spp (horsetail) had a smaller biomass contribution upon fertilization. This tendency toward a change in species composition or dominance has also been observed in other fertilization experiments. Jefferies and Perkins (1977) found species-specific changes in stem density at a Norfolk, England, salt marsh after fertilizing monthly with 610 kg NO₃⁻-nitrogen/ha/year or 680 kg NH₄⁺-nitrogen/ha/year over a period of 3 to 4 years.

A final conclusion of the data in Table 10-19 is that the stimulation of primary production by nitrogen applications is not a linear function of the rate of nitrogen application. This can be seen by comparing the results of fertilization studies of *Spartina* (Table 10-18). The greatest increase in standing biomass, both in terms of absolute amount and in terms of the percent increase, was obtained in studies where the control biomass was low. This implies that the in situ nitrogen supply in some wetlands already is near a threshold where other factors become limiting. Ultimately, available light energy, water, and temperature are the limiting factors.

The data included in Table 10-18 pertain to growth of aboveground biomass only. In several of these studies, measurements of belowground biomass were also made (Valiela and Teal, 1974; Hanes, 1979; Valiela et al., 1976; Gallagher, 1975). Results were variable, with some studies showing a small decrease in living belowground biomass (Valiela et al., 1976), and others showing small increases in belowground macroorganic matter (Gallagher, 1975) or no change (Valiela and Teal, 1974). The normal technique of coring sediments to measure belowground production is subject to great error (Singh et al., 1984). However, the evidence from controlled-growth experiments (Morris, 1982; Steen, 1984) clearly shows that the response of leaf growth to increased nitrogen supply is much greater than the response of roots.

It should be emphasized that all of the fertilization studies summarized in Table 10-18 are short-term results in which nitrogen was applied for 3 years or less. We cannot assume that long-term nitrogen applications will yield the same results. Studies of several wetland ecosystems that have been fertilized for long periods by increased atmospheric inputs indicate

**TABLE 10-19. RATES OF NITROGEN DEPOSITION IN SEVERAL
AREAS OF NORTH AMERICA**

| Area | Deposition Rate (kg/ha/year) | | | Source |
|--|---------------------------------|-------------------------------|-------|-----------------------------|
| | NO ₃ ^{-a} | NH ₄ ^{+b} | Total | |
| Alaska ^c (Poker Flat) | 0 10 | 0 06 | 0 16 | Galloway et al (1982) |
| Sierra Nevada, CA ^d (Emerald Lake) | 1 11 | 1 19 | 2 30 | Williams and Melack (1991a) |
| Ontario, Canada ^e (Experimental Lakes Area) | 1 75 | 1 96 | 3 71 | Linsey et al (1987) |
| British Columbia, Canada ^e | 3 64 | 1 82 | 5 46 | Feller (1987) |
| Upper Midwest ^f | 4 20 | 2 94 | 7 14 | Driscoll et al (1989a) |
| Southeastern United States ^g (Walker Branch, TN) | 7 56 | 2 52 | 10 08 | Lindberg et al (1986) |
| New Hampshire ^e | 6 50 | 2 80 | 9 30 | Likens (1985) |
| Catskills ^c | 8 12 | 4 09 | 12 24 | Stoddard and Murdoch (1991) |
| Adirondacks ^f | 8 26 | 2 66 | 10 92 | Driscoll et al (1989a) |

^aNO₃⁻ = Nitrate ion

^bNH₄⁺ = Ammonium ion

^cDry deposition estimated as 35% of total deposition

^dDry deposition sampled as part of snowpack, no correction for dry deposition made

^eBulk precipitation measurements, no correction for dry deposition made

^fValues corrected for dry deposition based on ratios in Hicks (1989)

^gIncludes estimates for dry deposition and gaseous uptake of nitrogen areas, dissolved organic nitrogen can occur in greater concentrations than the inorganic species (Moore and Nuckols, 1984)

that changes in species composition and succession accompany the increases in nitrogen loadings and primary production. These studies are summarized below.

One implication of a long-term increase in leaf growth is that the demand for mineral elements and water from the soil will increase. Howes et al (1986) observed that the rate of evapotranspiration increased from a salt marsh dominated by *Spartina alterniflora* in sites where aboveground biomass was increased by nitrogen fertilization. Increased evapotranspiration can influence the direction of succession of some wetlands by altering the water balance of the soil. The feasibility of this mechanism to alter bog succession was

demonstrated in a model by Logofet and Alexandrov (1984) Their model suggests that nitrogen inputs greater than a threshold of 7 kg nitrogen/ha/year can change the direction of succession from that of an open oligotrophic bog to a mesotrophic bog dominated by trees Furthermore, in flowing water systems, like salt marshes, an increase in aboveground production should lead to an increased export from the system of nutrients that are incorporated in or leached from aboveground biomass Therefore, the long-term ecosystem and community responses to increased inputs of nitrogen can not be predicted from results of short-term field experiments like those summarized in Table 10-19

10.7.4.2 The Fate of Added Mineral Nitrogen

Experiments in the field and laboratory have followed the fate of applied nitrogen by using ^{15}N as a tracer This stable isotope, ^{15}N , comprises 0.37% of naturally occurring nitrogen It can be quantified together with the more common isotope of nitrogen, nitrogen-14, with a mass spectrometer and is used experimentally much like radioactive isotopes, except that ^{15}N is normally used in greater than trace amounts due to the lower sensitivity of the instrumentation used to detect it

Experiments in which different mineral forms of ^{15}N were added to sediments in the absence of plants demonstrate that mineral nitrogen is rapidly used by the microbial community Smith and DeLaune (1985) added the equivalent of 100 kg nitrogen/ha in one application as ^{15}N -labeled NH_4^+ ($^{15}\text{NH}_4^+$) to sediments of a shallow saline lake They found 15 days after the addition, 20% had been converted to organic nitrogen in the sediment, and the fraction in organic matter remained constant at this level for the remaining 337 days of the experiment The amount of $^{15}\text{NH}_4^+$ in the sediment decreased exponentially to a nondetectable level by Day 200 Diffusion of NH_4^+ into the water column and denitrification accounted for a loss of 80% of the $^{15}\text{NH}_4^+$ from the sediment

Lindau et al (1988) made single additions of either ^{15}N -labeled NO_3^- or $^{15}\text{NH}_4^+$, equivalent to 100 kg nitrogen/ha, to the floodwater within chambers containing swamp sediment By Day 27, only 39.6% and 6.2% of the ^{15}N from NH_4^+ and NO_3^- , respectively, remained in the sediment and overlying water column The remaining fractions had been lost from the chambers by denitrification The loss of 60% of the applied $^{15}\text{NH}_4^+$ within 27 days demonstrates that NH_4^+ can be rapidly converted to NO_3^- by nitrifying bacteria in

aerobic parts of the system, and that NO_3^- diffuses into the anaerobic sediments where denitrification occurs. Nitrification was apparently the rate limiting step because the loss of ^{15}N by denitrification was more rapid when it was applied as NO_3^- .

DeBusk and Reddy (1987) made single additions of $^{15}\text{NH}_4^+$ to the floodwater above cores of sediments taken from swamps that had been receiving primary wastewater effluent for 2 and 50 years prior to the experiment. The rate of application was equivalent to 15 kg nitrogen/ha. After 21 days, 0.5 to 2.3% of the added nitrogen was recovered in the floodwater, largely as NO_3^- , and 13.6 to 17.8% was recovered in the sediment, largely as organic matter. The remaining 80% was apparently lost by denitrification, indicating that conversion of NH_4^+ to NO_3^- and diffusion of NO_3^- to anaerobic sites of denitrification is rapid. This result is consistent with that of Lindau et al. (1988). Furthermore, there was no difference in the response of the two sediment types, which demonstrates that the nitrification-denitrification potential of sediments is unchanged in sediment receiving sewage effluent for 50 years. However, the bacteria in the sediments must have a continuous supply of suitable carbon substrates as well as nitrogen to sustain continuous nitrification-denitrification reactions.

Short-term measurements of slurries of marl and peat sediments from the Florida Everglades (Gordon et al., 1986) demonstrated that 10 to 34% of NO_3^- added at levels of 10 and 100 μM (1 μM = 14 μg nitrogen/L) was rapidly denitrified within 24 h. Denitrification rates decreased following this initial burst of activity as the balance of the added NO_3^- was converted to NH_4^+ . This experiment suggests that the process of dissimilatory nitrate reduction to ammonium (reammonification) competes successfully with the denitrification process. However, this experiment was conducted on sediment slurries that were incubated under a nitrogen atmosphere, which prevented nitrification reactions from occurring. Under an oxygen atmosphere, nitrification would have generated a continuous supply of NO_3^- and denitrification would then have consumed a greater fraction of the NO_3^- over time.

The behavior of mineral nitrogen applied to vegetated wetland sediments is quite different from the results described above and indicates that plants successfully compete with microbes for mineral nitrogen. DeLaune et al. (1983) followed the fate of $^{15}\text{NH}_4^+$ placed below the soil surface in a Louisiana salt marsh dominated by *Spartina alterniflora*. The

singular application of $^{15}\text{NH}_4^+$ was equivalent to 72 kg nitrogen/ha. At the end of the first growing season, 93 % of the added nitrogen was recovered in aboveground biomass, roots, and soil. An average of 28 % was in aboveground biomass and 65 % was in soil and belowground biomass. The high rate of recovery of ^{15}N in vegetation and soil is consistent with results of Buresh et al (1981) and Patrick and Delaune (1976). In the study of DeLaune et al (1983), ^{15}N recovered in soil and belowground biomass declined to 50 % by the end of the second growing season and to 43 % by the end of the third growing season. Nitrogen in aboveground biomass decreased to 12 % of original ^{15}N by the end of the third growing season. The annual declines were postulated to have occurred due to the loss of nitrogen from the leaves, either by physical transport of aboveground plant material off the site or by decomposition of leaf material at the sediment surface followed by nitrification-denitrification reactions. Similar results were obtained in a freshwater marsh dominated by *Panicum hemitomon* (maiden cane). DeLaune et al (1986) added 30 kg/ha of $^{15}\text{NH}_4^+$ -nitrogen to sediments and recovered a mean of 80 % in the combined aboveground (18 %) and belowground biomass and soil (62 %) at the end of the first growing season.

Dean and Biesboer (1985) applied $^{15}\text{NH}_4^+$ to the floodwater in cylinders containing sediment only and in cylinders containing *Typha latifolia* (broadleaved cattail). Additions were made biweekly during a single growing season for a total application equivalent to 82 kg nitrogen/ha/season. At the end of the growing season, 3 weeks after the last addition, 75.3 % of added ^{15}N was recovered in the plant-soil system. A total of 53.6 % was contained in the plants, including both above- and belowground biomass, and 21.7 % was contained in the soil. In the sediment-only system, only 34.6 % of the added ^{15}N was recovered, most of this, 33 % of the added ^{15}N , was in the sediment. The remaining 65.4 % was thought to have been lost through nitrification-denitrification reactions.

The experiments discussed above indicate that plant biomass is the major sink for free NH_4^+ , and that in the absence of plants, the major fate is nitrification-denitrification. It should be emphasized that the nitrification-denitrification process can dominate only in environments, like wetlands, that have separate and distinct aerobic and anoxic zones of microbial activity where solutes freely diffuse between them.

10.7.4.3 Effects of Nitrogen Loading on Microbial Processes

Changes in deposition rate and the chemical form of nitrogen in deposition can potentially influence microbial processes and details of the internal nitrogen cycle of wetlands. For instance, the decomposition rate is sensitive to the nitrogen concentration of decomposing tissues and of the surrounding environment. Tissues with elevated nitrogen concentrations normally are observed to decompose at a faster rate than tissues containing low nitrogen concentrations (Marinucci et al., 1983, Neely and Davis, 1985b). The difference in decomposition rates can be impressive. For example, litter from nitrogen-fertilized *Spartina alterniflora* decomposed 50% faster than control litter (Marinucci et al., 1983).

The dynamics of nitrogen within decomposing litter is also sensitive to the litter's nitrogen status. That is, litter of low original nitrogen content often acts as a net nitrogen sink during the first months of decomposition, whereas nitrogen-rich litter is likely to be an exporter rather than an accumulator during decomposition (Neely and Davis, 1985b). There is some controversy about the mechanism of nitrogen immobilization (Bosatta and Staaf, 1982; Aber and Melillo, 1982, Bosatta and Berendse, 1984), but its importance to the wetland nitrogen cycle is recognized (Brinson, 1977, Morris and Lajtha, 1986, Damman, 1988).

Microbial nitrogen transformations are also affected by the nitrogen status of the environment. It is well known that NH_4^+ inhibits the activity of nitrogen-fixing bacteria (diazotrophs) (Buresh et al., 1980). It is thought that NH_4^+ represses synthesis by bacteria of the nitrogenase enzyme (the enzyme in bacteria that accomplishes the transformation). There may be direct inhibition by NH_4^+ of enzyme activity, as suggested by Yoch and Whiting (1986). Kolb and Martin (1988) observed a decrease in nitrogenase activity as well as the proportion of diazotrophs among the heterotrophic bacteria in soil after application of NH_4NO_3 . They suggested that the decrease in proportion of diazotrophs represents a competitive suppression by nondiazotrophs in the presence of combined nitrogen (NH_4^+ or NO_3^-). Dicker and Smith (1980) observed a similar repression of nitrogen fixation in salt marsh sediments amended with either NH_4^+ or NO_3^- .

Acidification, which may be caused by deposition of NO_x or NH_4^+ , can impact the nitrogen cycle. The decomposition rate is decreased by acidification (Leuven and Wolfs,

1988, Hendrickson, 1985), but the degree of inhibition is dependent on the buffering capacity of the litter (Gallagher et al , 1987) Nitrification is also affected by acidification Nitrification was inhibited at pH 4 to 5 in cypress swamps (Dierberg and Brezonik, 1982), and at pH 5.4 to 5.7 in lakes (Rudd et al , 1988) Acidification blocks the nitrogen cycle by inhibiting nitrification and leads to an accumulation of NH_4^+ (Roelofs, 1986, Schuurkes et al , 1986, 1987, Rudd et al , 1988) Also, the ratio of N_2O : N_2 produced by denitrifying bacteria is apparently pH sensitive, with little N_2O being produced under anoxic conditions at pH 7 and almost 100% N_2O being produced at pH 5 (Focht, 1974) This is significant because a shift to N_2O production upon acidification of the environment could have a deleterious effect on stratospheric O_3

Finally, NO_3^- and NH_4^+ have been shown to influence the relative and absolute production of end products of dissimilatory nitrate reduction (Blackmer and Bremner, 1978, Knowles, 1982, Prakasam and Krup, 1982) King and Nedwell (1985) observed approximately equal reduction to either NH_4^+ or N_2O (in the presence of acetylene, the gas added to assay the rate of production of N_2O) in sediment slurries incubated anaerobically with 250 μM NO_3^- As the nitrate concentration was increased up to 2 mM (1 mM = 14 mg nitrogen/L), the proportion of the nitrate that was denitrified to N_2O increased up to 83% High nitrate concentrations have also been shown to favor N_2O production and inhibit N_2 production, perhaps due to the competitive role that exists between NO_3^- and N_2O terminal electron acceptors during anaerobic respiration (Cho and Sakdinar, 1978, Blackmer and Bremner, 1978) Seitzinger et al (1983, 1984) observed higher ratios of $\text{N}_2\text{O}:\text{N}_2$ production and higher absolute rates of N_2O production from eutrophic sediments than from unpolluted sediments of Narragansett Bay, RI Smith and DeLaune (1983) reported that N_2O production from salt marsh and brackish marsh soils increased from 0.22 and 0.04 mg N_2O -nitrogen/ m^2 /day, respectively, to 1.5 and 2.9 mg N_2O -nitrogen/ m^2 /day after amending the sediments with 1.2 to 1.5 g NH_4^+ -nitrogen/ m^2 Others (Betlach and Tiedje, 1981), however, failed to observe an inhibition of N_2O reduction in the presence of NO_3^- Little is known about the significance of this process in general or the potential for NO_3^- or NH_4^+ in deposition to alter natural rates of N_2O production Only a small fraction of depositional nitrogen inputs are likely to be evolved as N_2O For example, Pedrazzini and Moore (1983) recovered only 0.39% of fertilizer nitrogen as N_2O from submerged soils amended with 34 g

NO_3^- -nitrogen/ m^2 and 12 g NH_4^+ -nitrogen/ m^2 in the laboratory. However, on a global basis, even small changes in the production of N_2O are potentially significant considering the role of N_2O in the destruction of stratospheric O_3 (Crutzen, 1970, Hahn and Crutzen, 1982)

10.7.4.4 Effects on Biotic Diversity and Ecosystem Structure

In the introduction, it was pointed out that wetlands harbor about 17% of the total number of plant species formally listed as endangered in the United States. Although it is beyond the scope of this review to survey the physiological ecology of these wetland plants, several species on this list are widely recognized to be adapted to nitrogen-poor or infertile environments. These include the isoetids (Boston, 1986) and the insectivorous plants (Keddy and Wisheu, 1989, Moore et al., 1989, Wisheu and Keddy, 1989), like the endangered green pitcher plant, *Sarracenia oreophila*. In eastern Canadian wetlands, nationally rare species are found principally on infertile sites (Moore et al., 1989, Wisheu and Keddy, 1989). Therefore, management practices should recognize that alterations in competitive relationships between species occur when the fertility of the environment changes.

These assertions are supported by research on floristic changes related to nitrogen deposition in central Europe. Nitrogen supply is a critical factor in plant nutrition in many natural ecosystems and in agriculture and grassland management as well. Ellenberg (1988) surveyed the nitrogen requirements of 1,805 plant species from West Germany and concluded that 50% can compete successfully only in habitats that are deficient in nitrogen supply. Furthermore, of the threatened plants, 75 to 80% are indicator species for habitats poor in nitrogen supply (i.e., they grow only in nitrogen-poor habitats). When stratified by ecosystem type, it is also clear that the trend of rare species occurring with greater frequency in nitrogen-poor habitats is a common phenomenon across many ecosystem types (Figures 10-23 and 10-24).

There is a history in western Europe of changes in wetland community composition that are thought to result from deposition of atmospheric pollutants. *Sphagnum* species are largely absent from ombrotrophic peat bogs in areas of Britain where they were once common (Tallis, 1964, Ferguson et al., 1984, Lee et al., 1986). Ombrotrophic wetlands downwind of the Manchester and Liverpool conurbations have been extensively modified by atmospheric pollution for greater than 200 years, with the virtual elimination of the dominant

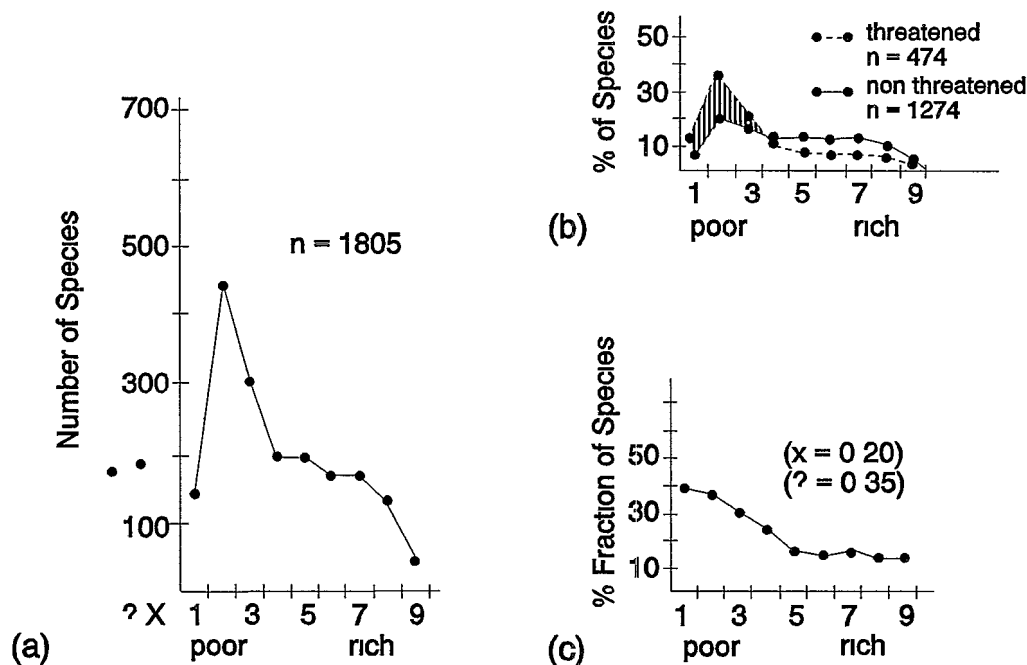


Figure 10-23. Distribution of 2,164 Central European plant species on a nitrogen indicator value gradient from very poor (1), to sufficient (5), to rich (7), to surplus (9), due in part to nitrogen deposition. (a, c) Species with unknown preference are indicated with a "?", and those not influenced by nitrogen supply are indicated with an "x". (b) Most threatened species can compete only on nitrogen-deficient stands. (c) The fraction of threatened species diminishes with increasing nitrogen until sufficiency (5) is reached and then remains constant. In every type of ecosystem, threatened species are concentrated in the poor to very poor portion of the nitrogen gradient.

Source Ellenberg (1988)

peat-forming *Sphagnum* mosses from more than 60,000 ha of bog (Lee et al , 1986) This has led to a loss of water retention and widespread erosion Nitrogen pollutants from atmospheric deposition have been implicated in this process, although studies of this particular area should be interpreted cautiously because of its long history of exposure to multiple pollutants (Lee et al , 1986) The combination of NO_3^- and NH_4^+ deposition, about 32 kg nitrogen/ha/year, is more than double the deposition rates in the Berwyn Mountains in North Wales, which still support healthy *Sphagnum* communities, and contributes

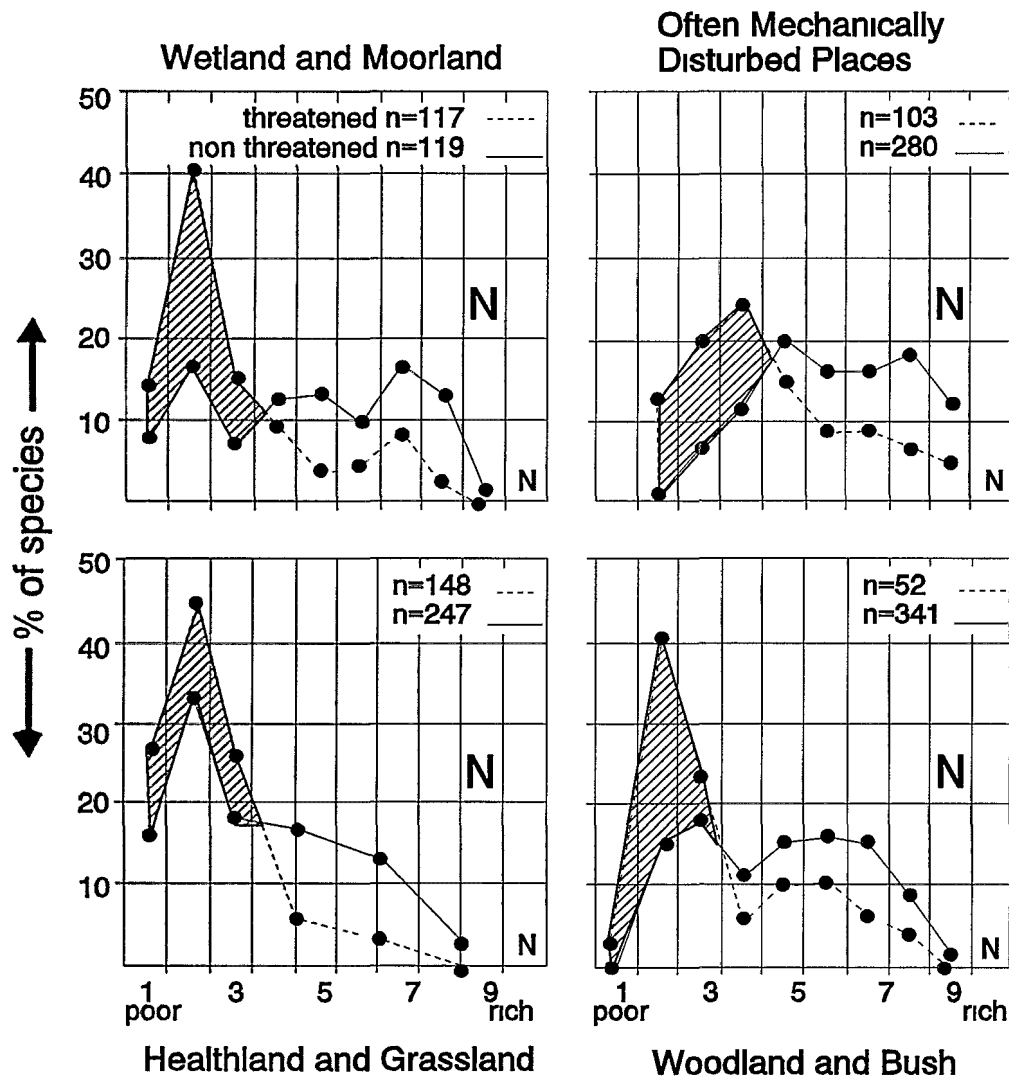


Figure 10-24. Distribution of Central European plant species along a gradient of nitrogen indicator values (see Figure 10-23) across ecosystem types. In every analyzable type of ecosystem, threatened plant species are concentrated in the poor (1) to very poor portion of the gradient.

Source: Ellenberg (1988)

significantly to a supraoptimal nitrogen supply (Lee et al , 1986) In the Netherlands, there has been a great decline during the past three decades in communities dominated by *iosetids* in soft water areas and their conversion to later successional stages dominated by grasslands or by *Juncus bulbosus* (rush) and *Sphagnum* spp (Roelofs, 1983, 1986, Roelofs et al , 1984, Schuurkes et al., 1986)

Vermeer and Berendse (1983) correlated biomass with species numbers and soil chemical characteristics in several fen and grassland communities in the Netherlands. In fens, they found a negative correlation between biomass and NH_4^+ concentration and a positive correlation between biomass and pH. There was also a positive correlation between biomass and number of species. In wet grasslands, a positive correlation was found between biomass and NO_3^- , P_i , and K^+ . In all wetland types investigated, they report that species number was greatest when the standing biomass of the site was in the range of 400 to 500 g/m^2 . They concluded that domination by a few species is associated with eutrophic conditions at the high end of the biomass scale as well as with conditions unfavorable for growth at the low end of the scale. Similarly, in wetlands of eastern Ontario and western Quebec, the greatest diversity of species (3 to 24 per 0.25 m^2) occurs at intermediate standing crops (60 to 500 g/m^2) and the lowest density of species (2 to 5 per 0.25 m^2) at standing crops greater than 1,500 g/m^2 (Moore and Keddy, 1989, Wisheu and Keddy, 1989). In Great Britain, species density in fens was greatest (about 12 per 0.25 m^2) at standing crops less than 1,000 g/m^2 and lowest (3 per 0.25 m^2) when standing crop was 4,000 g/m^2 or greater (Wheeler and Giller, 1982). Exceptions to this trend are found where annual mowing and harvest of wetland vegetation minimize the accumulation of surface litter (Verhoeven et al., 1988), and possibly where intense pressure from grazing animals favors domination by specific plant species (Jensen, 1985, Berendse, 1985).

10.7.4.5 Mechanisms of Nitrogen Control Over Ecosystem Structure

Nitrogen supplied in excess of a plant's nutritional requirements has a direct toxic effect on some species. The concentrations of six elements in the tissues of five *Sphagnum* species have been investigated in relationship to atmospheric deposition in Europe (Ferguson et al., 1984). When *Sphagnum* species were transplanted from a relatively clean-air site to a polluted site, the concentrations of nitrogen, sulfur, lead, Fe, and phosphate increased significantly, but the concentration of potassium did not. The greatest change observed was for nitrogen, which increased by absolute amounts that varied from 17.7 mg/g of tissue in *Sphagnum recurvum* to 5.3 mg/g in *Sphagnum capillifolium* above control levels of about 10 mg/g (1% of dry weight). Because the nitrogen supply originating from the soil probably did not differ, as indicated by the similarity in total nitrogen concentration of the peat from

the polluted and clean sites, it is possible that nitrogen deposition had a direct effect on nitrogen uptake in these species. The authors concluded that the element supply from deposition at the polluted site, where nitrogen deposition is 43 kg nitrogen/ha/year, is supraoptimal for growth of ombrotrophic *Sphagnum* species. They noted the existence of a "good" *Sphagnum* cover at one site where a nitrogen deposition rate of 20 kg nitrogen/ha/year was measured. Similarly, Press et al. (1986) observed tissue nitrogen concentrations as high as 2.5% of dry weight in *Sphagnum cuspidatum* transplanted to a site of high nitrogen deposition in northern Britain and found that this level of nitrogen was associated with decreased growth.

Competitive relationships among species change with the nitrogen status of the environment. In weakly buffered ecosystems, a high deposition of NH_4^+ leads to acidification and nitrogen enrichment of soil. Consequently, plant species characteristic of poorly buffered environments disappear. Among the acid-tolerant species, there will be competition between slow-growing and fast-growing nitrophilous grasses or grass-like species. This process contributes to the observed change from heathlands into grasslands. *Molinia caerulea* (L.) Moench and/or *Deschampsia flexuosa* (L.) Trin (grasses) expand at the expense of *Erica tetralix* or *Calluna vulgaris* (L.) Hall (shrubs) and other heathland species (Berendse and Aerts, 1984, Roelofs et al., 1987, Aerts and Berendse, 1988, 1989). In over 70 heathlands investigated, the shrub bogs dominated by *Erica tetralix* or *Calluna* had dissolved NH_4^+ levels in the soil water of 55 and 84 μM , whereas those dominated by the grasses *Deschampsia* and *Molinia* had average NH_4^+ concentrations of 248 and 429 μM (Roelofs et al., 1987).

Several controlled-growth studies also have been conducted to identify the mechanisms of nitrogen control over species composition. This is a nontrivial task because there are a great number of interactions among biochemical and geochemical processes. There are direct and indirect effects of nitrogen deposition, and cause and effect can be difficult to ascertain. Roelofs (1986), for example, states that acidification, which can result from deposition of NO_x , SO_4^{2-} , or NH_4^+ , can decrease the availability of dissolved CO_2 in water, which leads to the complete elimination of submerged plant species. Deposition of NH_4^+ and its subsequent nitrification or absorption by plants generates acidity. Biochemical conversions of SO_4^{2-} and NO_3^- generate alkalinity. These processes are mediated by

bacteria, macrophytes, and algae (Kelly et al , 1982, Raven, 1985) Atmospheric deposition of nitrogen can significantly affect the nitrogen budget of some wetland ecosystems, their acidity, and their carbon budgets (Roelofs, 1986)

Schuurkes et al (1986) studied effects of acidification and nitrogen supply on growth of several common wetland plants under controlled laboratory conditions All species utilized NH_4^+ and NO_3^- as a nitrogen source, except *Sphagnum flexuosum*, which did not assimilate NO_3^- When NH_4^+ and NO_3^- were offered simultaneously in equal amounts, NO_3^- uptake was the dominant form of nutrition (63 to 73%) in plants that are characteristic of soft waters (low Ca^{2+} and Mg^{2+}), whereas NH_4^+ strongly dominated the nutrition (85 to 90%) in species from acid waters Differences in the site of uptake, either leaves or roots, among species were also found They concluded that high deposition of NH_4^+ and SO_4^{2-} , the most important sources of acidification in the Netherlands, is leading to an expansion of acid-tolerant nitrophilous plants

The nutrition of *Sphagnum* is apparently species specific Although *S flexuosum* did not assimilate NO_3^- (Schuurkes et al , 1986), the activity of nitrate reductase in *S cuspidatum* (Press and Lee, 1982) and in *S fuscum* (Woodin et al , 1985) clearly shows that NO_3^- can be utilized by these species *S magellanicum* was shown to grow best when given the equivalent of 4.1 kg NO_3^- -nitrogen/ha/year plus 19 kg NH_4^+ -nitrogen/ha/year in simulated rain, when given 0.25 times that amount of NO_3^- and 1.5 times (and 4 times) as much NH_4^+ , growth decreased (Rudolph and Voigt, 1986) Bayley et al (1987) reported that the dominant *Sphagnum* spp in a poor fen in Ontario, *S fuscum* and *S magellanicum*, were able to assimilate an NO_3^- input of 4.71 kg nitrogen/ha/year, including 1.6 kg nitrogen/ha/year applied in simulated acid rain, and growth increased at least during the first year after the additional nitrogen was applied Roelofs et al (1984) observed that growth of *S cuspidatum* was greatest in a medium containing 500 μM NH_4^+ , and growth was less at 1,000 or 100 μM NH_4^+ Press et al (1986) observed that the best growth of this same species occurred in nitrogen-free solutions, and that even small additions (10 μM) of either NH_4^+ or NO_3^- reduced growth It is doubtless that some variations in results of nutritional studies are influenced by other variables, like pH

The genus *Sphagnum* is an important group in bogs everywhere, and it is important to understand its nutritional physiology and ecology However, it should be emphasized that

the consequences of nitrogen fertilization in a natural environment, with fluctuating climate and competition among numerous species, can be quite different from what may be predicted from studies of a single species in laboratory culture. For example, Aerts et al (1989) assert that competition for light dictates the outcome of competition between species that differ in growth rate potential and nutrient requirement.

In a 2-year greenhouse experiment designed to differentiate between acid and nitrogen effects, Schuurkes et al (1987) exposed mixtures of different wetland plant species to simulated rain containing various combinations of SO_4^{2-} , NH_4^+ , and NO_3^- . Marked changes were observed in systems receiving rain with 510 and 1,585 μM NH_4^+ , plants typical of nutrient-poor soft waters (like the isoetids *Littorella uniflora* [shoreweed], *Luronium natans* [water plantain], and *Pilularia globulifera*) were adversely affected at this level of nitrogen input, whereas other species (*Juncus bulbosus*, *Sphagnum cuspidatum*, and the grass *Agrostis canina*) expanded. Acidification with none or only a small NH_4^+ addition had no clear effects, although biomass of *Sphagnum* was slightly higher. Within sulfuric acid treatments, only pH 3.5 rain markedly acidified the water. Based on these experiments, Schuurkes et al (1987) recommended that to preserve the remaining oligotrophic wetlands, acid inputs should not exceed 250 mol/ha/year, and that the annual nitrogen deposition should not be greater than 1,380 mol/ha/year or 19.4 kg nitrogen/ha/year ($\text{NO}_3^- + \text{NH}_4^+$), except that the potential acidifying influence of this nitrogen input, if in the form of NH_4^+ , exceeds the allowable acid input. This limit is supported by Liljelund and Torstensson (1988), who concluded from their review that the limit for many species may be well below 20 kg nitrogen/ha/year and for oligotrophic (nutrient-poor) bogs, is probably about 10 kg nitrogen/ha/year. These limits are exceeded currently in the United States, where wet nitrate deposition alone exceeds 15 kg nitrogen/ha/year over most of the Midwest, New York, and New England (Zemba et al, 1988). The effects of the nitrate deposition, however, are yet to be determined.

10.8 AQUATIC EFFECTS OF NITROGEN OXIDES

10.8.1 Introduction

For a variety of reasons, nitrogen deposition has not historically been considered a serious threat to the integrity of aquatic systems. Most terrestrial systems have been assumed to retain nitrogen strongly, leading to a small probability that deposited nitrogen will ever make its way to the surface waters that drain these terrestrial systems. Nitrogen within aquatic ecosystems can arise from a variety of sources, including point-source and non-point-source pollution and biological fixation of gaseous nitrogen, in addition to the deposition of NO_x . In cases where nitrogen is known to be affecting aquatic systems, it has been assumed that some source other than deposition is responsible. The amounts of nitrogen provided to aquatic systems by these other sources often outweigh by a large margin the amount of nitrogen potentially provided by atmospheric deposition. In the past decade, however, our understanding of the transformations that nitrogen undergoes within watersheds has increased greatly, and in areas of the country where nonatmospheric sources of nitrogen are small, we can begin to infer cases where nitrogen deposition is having an impact on aquatic systems.

Estimating the effects of NO_x emissions and nitrogen deposition on aquatic systems is made difficult by the large variety of nitrogen compounds found in air, deposition, watersheds, and surface waters, as well as the myriad of pathways through which nitrogen can be cycled in terrestrial and aquatic ecosystems. These complexities have the effect of decoupling nitrogen deposition from nitrogen effects, and reduce our ability to attribute known aquatic effects to known rates of nitrogen deposition. The organization of this section reflects this complexity. Because an understanding of the ways that nitrogen is cycled through watersheds is critical to our understanding of nitrogen effects, the section begins with a brief description of the nitrogen cycle, and of the transformations of nitrogen that may occur in watersheds. Each of the known possible effects of nitrogen deposition (acidification, eutrophication, and direct toxicity) is discussed separately. Within these discussions, evidence for the importance of nitrogen in causing observed effects is discussed separately from evidence that deposition is the source of the nitrogen observed in affected systems.

10.8.2 The Nitrogen Cycle

Atmospheric nitrogen can enter aquatic systems either as direct deposition to water surfaces, or as nitrogen deposition to the terrestrial portions of a watershed (Figure 10-25, see also Figure 10-1). Nitrogen deposited to the watershed is then routed (e.g., through plant biomass and soil microorganisms) and transformed (e.g., into other inorganic or organic nitrogen species) by watershed processes, and may eventually run off into aquatic systems in forms that are only indirectly related to the original deposition. Much of the challenge of determining when nitrogen deposition is having an effect on aquatic systems depends on our ability to track nitrogen on its path through watersheds. In most cases, this tracking cannot be accomplished outside of a carefully controlled research program, and we are forced to make educated guesses about the likelihood that the nitrogen observed in aquatic systems was originally of atmospheric origin. The strength of these educated guesses will depend, to a large degree, on our ability to identify which nitrogen transformations are occurring and which are not. By eliminating other possible sources or sinks of nitrogen, we are in a stronger position to determine in which cases observed nitrogen effects are caused indirectly by atmospheric deposition. Our understanding of the nitrogen cycle in terrestrial and aquatic ecosystems, therefore, plays a central role in controlling our understanding of deposition effects. The key elements of the nitrogen cycle, particularly those that are thought to be important in determining whether atmospherically derived nitrogen will have an effect on aquatic systems, are discussed briefly in this section (see also Section 10.3).

10.8.2.1 Nitrogen Inputs

Watersheds are generally several orders of magnitude larger than the surface waters that drain them, and so the majority of the atmospheric deposition that may potentially enter aquatic systems falls first on some portion of the watershed. Nitrogen may be deposited to the watershed, or directly to water surfaces, in a variety of forms, including NO_3^- , NH_4^+ , and organic nitrogen in wet and dry deposition. In addition, plants may absorb gaseous nitrogen as NO_x (Rowland et al., 1985) or HNO_3 vapor (Vose et al., 1989), and nitrogen thus absorbed may subsequently enter the watershed nitrogen budget as litter fall, or through the death of plant biomass (Parker, 1983; Olson et al., 1985). These nitrogen constituents

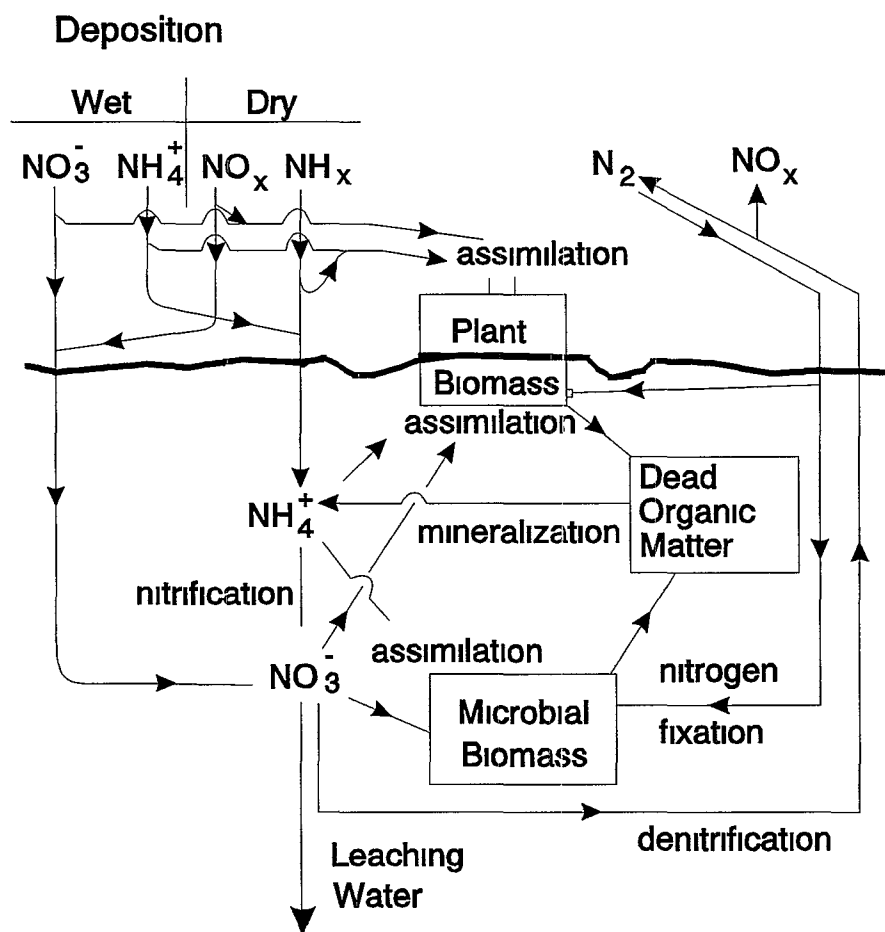


Figure 10-25. A simplified watershed nitrogen cycle. Only the major pathways are shown. The boxes represent major pools of nitrogen in terrestrial ecosystems, and the lines represent the major pathways and processes affecting nitrogen transformations. The wavy line represents the soil surface.

Source Skeffington and Wilson (1988)

are the same as those comprising direct deposition to terrestrial ecosystems recently described by Lindberg et al (1986) (also see Section 10 6)

Concentrations of NO_3^- and NH_4^+ in precipitation vary widely throughout North America, depending largely on the proximity of sampling sites to sources of emissions Galloway et al (1982) report mean concentrations of NO_3^- and NH_4^+ of $2.4 \mu\text{eq/L}$ and $2.8 \mu\text{eq/L}$, respectively, for a site in central Alaska In the Sierra Nevada Mountains of

California, mean concentrations of NO_3^- and NH_4^+ for the period 1985 to 1987 were 5.0 and 5.4 $\mu\text{eq/L}$, respectively (Williams and Melack, 1991a). In a comparison of nitrogen deposition at lake and watershed monitoring sites in the northern United States and southern Canada, Linsey et al. (1987), found NO_3^- concentrations ranging from 15 to 40 $\mu\text{eq/L}$ and NH_4^+ concentrations from 10 to 50 $\mu\text{eq/L}$ in areas considered remote but influenced by prairie dust and long-range acidic deposition, neither ion dominated over the other. In some areas closer to anthropogenic nitrogen sources (e.g., in northeastern United States and southeastern Canada), volume-weighted mean NO_3^- concentrations range from 30 $\mu\text{eq/L}$ (e.g., in the Adirondack and Catskill mountains of New York) to 50 $\mu\text{eq/L}$ (e.g., in the eastern Great Lakes region), whereas mean NH_4^+ concentrations range from 10 to 20 $\mu\text{eq/L}$ in the same areas (Stensland et al., 1986). Ammonium concentrations are highest (ca. 40 $\mu\text{eq/L}$) in the agricultural areas of the midwestern United States.

Deposition of nitrogen will depend on the concentration in precipitation, the volume of water falling as precipitation, and the amount of nitrogen in dry deposition (see Section 10.4 of this report, see also Sisterson et al., 1990). The last of these values (dry deposition) is difficult to measure, and is often estimated as a fraction (e.g., 30 to 40%) of wet deposition (Baker, 1991). Given the range of concentrations mentioned in the previous paragraph, and the volumes of precipitation falling in different regions of North America, estimates of nitrogen deposition rates range from less than 0.2 kg/ha/year in Alaska to 12 kg/ha/year in the northeastern United States (Table 10-19).

Generally NO_3^- dominates over NH_4^+ at sites close to emission sources (Linsey et al., 1987, Altwicker et al., 1986). Dissolved organic nitrogen concentrations are highly variable in precipitation, but often amount to 25 to 50% of inorganic nitrogen deposition values (Linsey et al., 1987, Manny and Owens, 1983, Feller, 1987).

10.8.2.2 Transformations

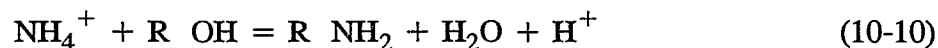
Because the majority of nitrogen deposition falls first on some portion of the watershed, the transformations that nitrogen undergoes within the watershed (e.g., in soils, by microbial action, and in plants) will play a major role in determining what forms and amounts of nitrogen eventually reach surface waters. Much of the following discussion is, therefore, focused on terrestrial processes that alter the forms and rates of nitrogen supply. It is these

processes that, to a large degree, determine whether nitrogen deposition will ever reach lakes, streams, and estuaries, and, therefore, they are very important in controlling the effects of nitrogen deposition. Many of these same processes occur also within surface waters, and a specific discussion of these processes, and their importance, follows the discussion of nitrogen transformations.

Nitrogen Assimilation

Nitrogen assimilation is the uptake and metabolic use of nitrogen by plants (Figure 10-25). Assimilation by both terrestrial and aquatic plants will play a role in determining whether nitrogen deposition affects aquatic systems. Assimilation by the terrestrial ecosystem controls the form of nitrogen eventually released into surface waters, as well as affecting the acid/base status of soil and surface waters. Terrestrial assimilation is a major form of nitrogen removal in watersheds, and may in fact be sufficient to prevent all atmospherically-derived nitrogen from reaching surface waters (Vitousek and Reiners, 1975).

Nitrogen is the most commonly limiting nutrient in forest ecosystems in North America (Cole and Rapp, 1981). Because the primary use of nitrogen in plant biomass is the formation of amino acids, and reduced nitrogen is the most energetically favorable form of nitrogen for incorporation into amino acids, uptake of NH_4^+ is generally favored over uptake of NO_3^- by terrestrial plant species. This demand for NH_4^+ over NO_3^- and the high cation exchange capacity, typical of most temperate forest soils, combine to create the common pattern of low NH_4^+ concentrations in waters draining forested watersheds in the United States. The form of nitrogen used by terrestrial ecosystems strongly affects the acidifying potential of nitrogen deposition (Figure 10-26). Ammonium uptake is an acidifying process (i.e., uptake of NH_4^+ releases one mole of hydrogen per mole of nitrogen assimilated).



The biological uptake of NO_3^- , on the other hand, is an alkalizing process (i.e., uptake of NO_3^- consumes one mole of hydrogen per mole of nitrogen assimilated).

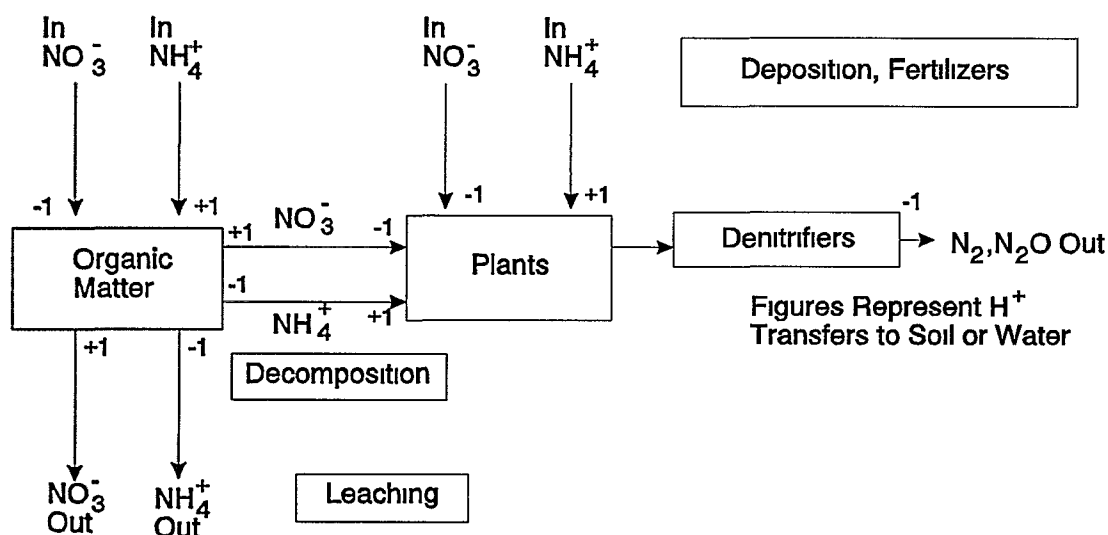
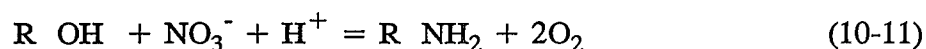


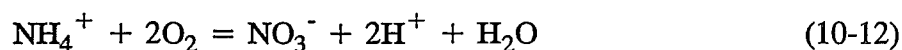
Figure 10-26. The effect of nitrogen transformations on the watershed hydrogen ion budget. One hydrogen ion is transferred to the soil solution or surface water (+1) or from the soil solution or surface water (-1) for every molecule of nitrate or ammonium that crosses a compartment boundary. For example, nitrification follows the pathway for ammonium uptake into organic matter (+1), and is leached out as nitrate (+1), for a total hydrogen ion production of +2 for every molecule of nitrate produced.

Source Skeffington and Wilson (1988)



Nitrification

Nitrification is the oxidation of NH_4^+ to NO_3^- , and is mediated by bacteria and fungi in both the terrestrial and aquatic portions of watersheds. It is an important process in controlling the form of nitrogen released to surface waters by watersheds, as well as in controlling the acid/base status of surface waters (Figure 10-25). Nitrification is a strongly acidifying process, producing two moles of hydrogen for each mole of nitrogen (NH_4^+) nitrified (Figure 10-26):



Because nitrification in forest soils commonly transforms NH_4^+ into NO_3^- , the acidifying potential of deposition (the maximum potential for acidification that is attributable to nitrogen) is often defined as the sum of NH_4^+ and NO_3^- , assuming that all nitrogen will leave the watershed as NO_3^- (e.g., Hauhs et al., 1989)

In most soils, nitrification is limited by the supply of NH_4^+ (Likens et al., 1970, Vitousek et al., 1979), creating a high demand for NH_4^+ on the part of nitrifying soil microbes. This microbial demand for NH_4^+ , coupled with the demand for NH_4^+ on the part of terrestrial plants (discussed above), leads to surface water concentrations of NH_4^+ that are almost always unmeasurable. Nitrification rates may also be limited by inadequate microbial populations, lack of water, allelopathic effects (toxic effects produced by inhibitors manufactured by vegetation), or by low soil pH. Of these other potential limiting factors, soil pH plays an obviously vital role in any discussion of the acidification of surface waters by nitrogen deposition. Nitrification has traditionally been thought of as an acid-sensitive process (Driscoll and Schaefer, 1989, Aber et al., 1989), but high rates of nitrification have been reported from very acid soils (i.e., $\text{pH} < 4.0$) in the northeastern United States (Vitousek et al., 1979, Novick et al., 1984, Rascher et al., 1987) and in Europe (Van Breemen et al., 1982). In the southeastern United States, Montagnini et al. (1989) were unable to find any effect of pH on nitrification, or to stimulate nitrification by buffering acid soils. In a survey of sites across the northeastern United States, McNulty et al. (1990) found no correlation between nitrification rates and soil pH, but found a strong association ($r^2 = 0.77$) with rates of nitrogen deposition. The weight of evidence suggests that nitrification will proceed at low soil pH values as long as the supply of NH_4^+ is sufficient.

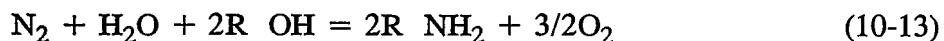
Denitrification

Denitrification is the biological reduction of NO_3^- to produce gaseous forms of reduced nitrogen (N_2 , NO, or N_2O) (Payne, 1981). Denitrification is an anaerobic process (i.e., it proceeds only in environments where oxygen is absent) whose end product is lost to the atmosphere (Figure 10-22). In terrestrial ecosystems, denitrification occurs in anaerobic soils, especially boggy, poorly drained soils, and has traditionally been considered a relatively unimportant process outside of wetlands (Post et al., 1985). It has been suggested, however, that denitrification could be an episodic process, occurring after such events as

spring snow melt and heavy rain storms, when soil oxygen tension is reduced (Melillo et al , 1983). No single equation can describe the denitrification reaction, because several end products are possible. However, denitrification is always an alkalizing process, consuming one mole of hydrogen for every mole of nitrogen denitrified (Figure 10-26). Denitrification can be involved in the production or consumption of N_2O , a product that may have considerable significance as a greenhouse gas (Matson and Vitousek, 1990, Hahn and Crutzen, 1982). In a review of the effects of acidic deposition on denitrification in forest soils, Klemmedtsson and Svensson (1988) conclude that denitrification rates are often limited by the availability of anoxic soil zones, and may, therefore, be relatively insensitive to increases in nitrogen deposition. It has been suggested that the production of N_2O may increase in acidified soils (Knowles, 1982), but few field data are available to test this idea. Rates of N_2O production in soil waters have been shown to increase markedly after forest clear-cutting (Bowden and Bormann, 1986, Melillo et al , 1983), and in areas of both high nitrogen deposition and intensive forest management, N_2O production may be of concern. Nitrous oxide production is strongly influenced by soil temperature, soil NO_3^- concentration, and soil moisture, Davidson and Swank (1990) suggest that one or more of these factors may commonly limit N_2O production in natural systems.

Nitrogen Fixation

Gaseous atmospheric nitrogen (N_2) can be fixed to produce NH_4^+ by a wide range of single-celled organisms, including blue-green algae (cyanobacteria), and various aerobic and anaerobic bacteria. Symbiotic nitrogen-fixing nodules are present on the roots of some early successional forest species (Boring et al , 1988). In headwater streams, nodules on rooting structures of riparian vegetation (e.g., *Alnus* sp.) can also be important nitrogen fixers (Binkley, 1986). Ordinarily, nitrogen fixation has no direct effect on the acid/base status of soil or surface waters.



Nitrogen fixation in excess of biological demand, however, can lead to nitrification or mineralization of organic nitrogen, and, ultimately, lead to acidification of soil or surface waters (Franklin et al , 1968, Van Miegroet and Cole, 1985)

Mineralization

Mineralization is the bacterial decomposition of organic matter, releasing NH_4^+ that can subsequently be nitrified to NO_3^- . Mineralization is an important process in watersheds, as it recycles nitrogen that would otherwise be lost from the system through death of plants, or as leaf litter (Figure 10-22). In a comparative study of mineralization in soils, Nadelhoffer et al (1985) found nitrogen mineralization rates ranging from 50 to 100 kg/ha/year under deciduous tree species, and from 32 to 66 kg/ha/year under coniferous species. These rates should be compared to nitrogen deposition rates of 5 to 12 kg/ha/year for high deposition areas of the Northeast. Nadelhoffer et al (1985) also report estimated rates of nitrogen uptake that were 5 to 20% higher than rates of mineralization, suggesting that mineralization can supply the majority, but not all, of the nitrogen needed for plant growth in these forests.

The effect of mineralization on the acid/base status of draining waters will depend on the form of nitrogen produced. The conversion of organic nitrogen (e.g., from leaf litter) to NH_4^+ consumes 1 mole of hydrogen per mole of nitrogen produced (Figure 10-26), and can be thought of as the reverse of the reaction in Equation 10-10. Organic nitrogen, which is mineralized and subsequently oxidized (nitrified) to NO_3^- (Equation 10-12), produces a net of 1 mole of hydrogen per mole of NO_3^- produced. Because the production of organic nitrogen (i.e., assimilation) can either produce or consume hydrogen (depending on whether NO_3^- or NH_4^+ is assimilated), the net (ecosystem) effect of mineralization depends both on the species entering the watershed and on the species leaving the watershed (Figure 10-26).

In ecosystems where plant growth is limited by the availability of nitrogen, mineralization is also limited by nitrogen, in the sense that additions of nitrogen to the leaf litter will speed decay and increase the rate at which nitrogen is immobilized by decomposers (Melillo et al , 1984, Taylor et al , 1989). Nitrogen limitation of decomposition is in part due to the low nitrogen content typical of litter, resulting from the retranslocation of nitrogen out of leaves during senescence.

10.8.2.3 Nitrogen Saturation

Much of the debate over whether aquatic systems are being affected by nitrogen deposition centers on the concept of nitrogen saturation of forested watersheds. Nitrogen saturation can be defined as a situation where the supply of nitrogenous compounds from the atmosphere exceeds the demand for these compounds on the part of watershed plants and microbes (Aber et al., 1989, Skeffington and Wilson, 1988). Under conditions of nitrogen saturation, forested watersheds that previously retained nearly all of nitrogen inputs, due to a high demand for nitrogen by plants and microbes, begin to have higher loss rates of nitrogen. These losses may be in the form of leaching to surface waters or to the atmosphere through denitrification. These two potential loss pathways have profoundly different impacts on the acid/base status of watersheds and surface waters (see following discussion), and their relative importance in advanced stages of nitrogen saturation will be a decisive characteristic determining the severity of the impact of nitrogen saturation.

Aber et al. (1989) have proposed a hypothetical time course for a watershed response to chronic nitrogen additions (Figure 10-27), describing both the changes in nitrogen cycling that are proposed to occur, as well as the plant responses to changing levels of nitrogen availability. Aber et al. (1989) include in their hypothetical time course a trajectory for the loss of nitrogen to surface water runoff (Figure 10-27), which suggests a simple response (nitrogen leaching) in the later stages of nitrogen saturation. One of the objectives of this document is to establish whether stages equivalent to those shown in Figure 10-27 can be described for surface waters, and to determine whether the response of surface waters to advanced stages of nitrogen saturation is as simple as suggested in Figure 10-27.

Stage 0 of the Aber et al. (1989) conceptual model is the pretreatment condition, where inputs of nitrogen from deposition are at background levels and watershed losses of nitrogen are negligible (Figure 10-27). In Stage 1, increased deposition is occurring, but effects on the terrestrial ecosystem are not evident. For a limiting nutrient such as nitrogen, a fertilization effect might result in increased ecosystem production and tree vigor at Stage 1. Retention of nitrogen is very efficient, and, on an annual basis, little or no nitrogen would be lost to surface waters that drain Stage 1 watersheds. Many forested watersheds in the United States would be considered to exist at this stage.

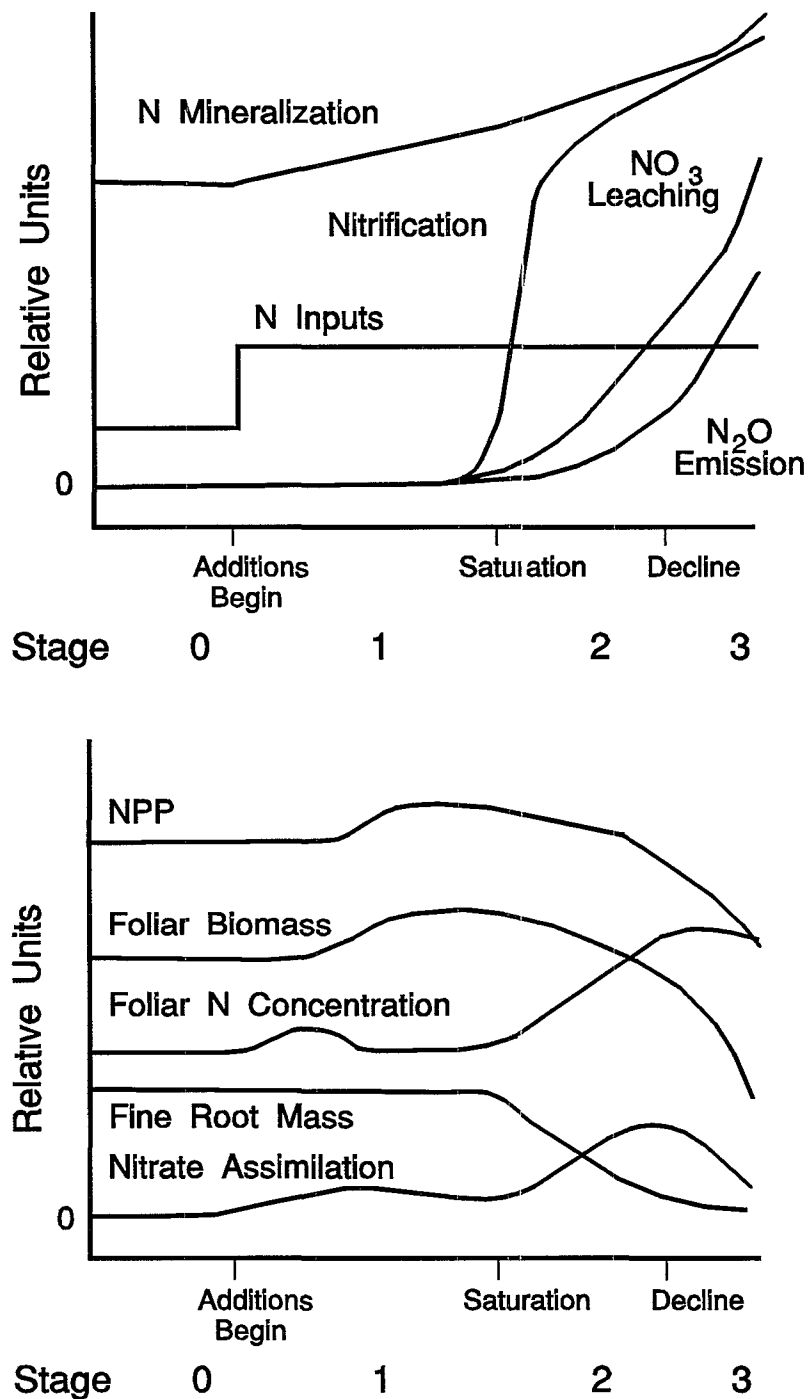


Figure 10-27. Hypothetical time course of forest ecosystem response to chronic nitrogen additions—top: relative changes in rates of nitrogen cycling and nitrogen loss, bottom: relative changes in plant condition (e.g., foliar biomass and nitrogen content, fine root biomass) and function (e.g., net primary productivity and nitrate assimilation) in response to changing levels of nitrogen availability.

In Stage 2 of the Aber et al (1989) hypothetical time course, negative effects occur, but they are subtle, nonvisual, and/or require long time scales to detect. Only in Stage 3 do visible effects on the forests occur, resulting in major environmental impacts. Aber et al (1989) emphasize that different species and environmental conditions could alter the timing of effects illustrated in Figure 10-27.

A number of factors may contribute to a watershed's progression through the stages of nitrogen loss, including elevated nitrogen deposition, stand age, and high soil nitrogen pools. High rates of nitrogen deposition play a clear role, as the ability of forest biomass to accumulate nitrogen must be finite. At very high, long-term rates of nitrogen deposition, the ability of forests and soils to accumulate nitrogen will be exceeded, and the only remaining pathway for loss of nitrogen (other than runoff) is denitrification. As mentioned earlier, high rates of nitrogen deposition may favor increased rates of denitrification, but many watersheds lack the conditions necessary for substantial denitrification (e.g., low oxygen tension, high soil moisture, temperature). Another important factor in nitrogen loss from watersheds is the age of the forest stands. A loss in the ability to retain nitrogen is a natural outcome of forest maturation, as demand for nitrogen on the part of more slowly growing tree species may plateau in later stages of forest development or decline as forests achieve a "shifting-mosaic steady state" (Bormann and Likens, 1979). Uptake rates of nitrogen into vegetation are generally maximal around the time of canopy closure for conifers, and somewhat later (and at higher rates) in deciduous forests due to the annual replacement of canopy foliage in these ecosystems (Turner et al., 1990). Large soil nitrogen pools imply that soil microbial processes that are ordinarily limited by the availability of nitrogen are instead limited by some other factor (e.g., availability of labile organic carbon), and large soil nitrogen pools contribute to the likelihood that watersheds will leach NO_3^- (Johnson, 1992, Joslin et al., 1992). Nitrogen saturation can be seen to occur in a sequence beginning with the fulfillment of vegetation nitrogen demand, followed by the fulfillment of soil microbial nitrogen demand; the existence of large soil nitrogen pools suggests that the second of these requirements may be easily met. The possible importance of all three factors (deposition, stand age, and soil nitrogen) in shifting watersheds from one stage of nitrogen loss to another will be discussed later in the context of surface water evidence of watershed nitrogen saturation.

The loss of nitrogen from watersheds can also be seen to occur in stages, which correspond to the stages of terrestrial nitrogen saturation described by Aber et al (1989). The most obvious characteristics of these stages of nitrogen loss are changes in the seasonal and long-term patterns of surface water NO_3^- concentrations, which reflect the changes in nitrogen cycling that are occurring in the watershed. The nitrogen cycle at Stage 0 is dominated by forest and microbial uptake, and the demand for nitrogen has a strong influence on the seasonal NO_3^- pattern of receiving waters. The "normal" seasonal NO_3^- pattern in a stream draining a watershed at Stage 0 would be one of very low, or immeasurable, concentrations during most of the year, and of measurable concentrations only during snowmelt (in areas where snow packs accumulate over the winter months), or during spring rain storms. The small loss of NO_3^- during the dormant season is a transient phenomenon, and results because snowmelt and spring rains commonly occur in these environments before substantial forest and microbial growth begin in the spring (e.g., winter mineralization of soil organic nitrogen may be an exception to this inactivity [Foster et al, 1989]). As a result, some of the nitrogen stored in soils and/or snowpack may pass through the watershed during extreme hydrologic events and may result in a pulse of elevated NO_3^- concentration. The key surface water characteristics of Stage 0 watersheds are very low NO_3^- concentrations during most of the year, and maximum spring concentrations of NO_3^- that are smaller than concentrations typical of deposition.

At Stage 1, the seasonal pattern typical of Stage 0 watersheds is amplified. It has been suggested that this amplification of the seasonal NO_3^- signal may be the first sign that watersheds are proceeding toward the chronic stages (i.e., Stages 2 and 3 in Figure 10-27) of nitrogen saturation (Driscoll and Schaefer, 1989, Stoddard and Murdoch, 1991), and this suggestion is consistent with the changes in nitrogen cycling that are thought to occur at Stage 1. A conceptual understanding of these changes derives from the most common definition of nutrient limitation. Implicit in the definition of nutrient limitation is the idea that "the current supply rate (of a nutrient) prevents the vegetation from achieving maximum growth rates *attainable within other environmental constraints*" (emphasis added [Binkley et al, 1989]). During the cold season, these environmental constraints can be severe, and maximum attainable growth rates are clearly much lower than in the warm months. Much of this discussion is couched in terms of forest trees, but the same arguments also apply to soil

microbial communities (e.g., decomposers, nitrifiers), which may be as important as vegetation in controlling nitrogen loss from watersheds (Binkley et al., 1989)

Overall limitation of forest growth (in the early stages of nitrogen saturation) is characterized by a seasonal cycle of limitations by physical factors (e.g., cold and diminished light during late fall and winter) and nutrients (primarily nitrogen, during the growing season). The effect of increasing the nitrogen supply (e.g., from deposition) is to postpone the seasonal switch from physical to nutrient limitation during the breaking of dormancy in the spring, and to prolong the seasonal nitrogen saturation that is characteristic of watersheds at this stage. At Stage 1, this switch is enough delayed that substantial NO_3^- may leave the watershed during extreme hydrologic events in the spring. Watershed loss of nitrogen at Stage 1 is still a seasonal phenomenon, and the annual nitrogen cycle is still dominated by uptake, but NO_3^- leaching is less transient than at Stage 0. The key characteristics of Stage 1 watersheds are episodes of surface water NO_3^- that exceed concentrations typical of deposition (e.g., Figure 10-28). Elevated NO_3^- during episodes may result from preferential elution of anions from melting snow (Jeffries, 1990, Johannessen and Henriksen, 1978) or from the contribution of nitrogen mineralization to the soil pool of NO_3^- that may be flushed during high-flow periods (Rascher et al., 1987, Schaefer and Driscoll, in press)

In Stage 2 of watershed nitrogen loss, the seasonal onset of nitrogen limitation is even further delayed, with the effect that biological demand exerts no control over winter and spring nitrogen concentrations, and the period of nitrogen limitation during the growing season is much reduced. The annual nitrogen cycle, which was dominated by uptake at Stages 0 and 1, is instead dominated by nitrogen loss (through leaching and denitrification) at Stage 2, sources of nitrogen (deposition and mineralization) outweigh nitrogen sinks (uptake). The same mechanisms that produce episodes of high NO_3^- during extreme hydrologic events at Stage 1 also operate at Stage 2. But more importantly, NO_3^- leaching can also occur at Stage 2 during periods when the hydrologic cycle is characterized by deeper percolation. If biological demand is sufficiently depressed during the growing season, nitrogen begins to percolate below the rooting zone, and elevated groundwater concentrations of NO_3^- result. Nitrification becomes an important process at Stage 2 (Aber et al., 1989, Figure 10-27), lowered biological demand leads to a buildup of NH_4^+ in soils, and nitrification may be stimulated. This is a pivotal change in the nitrogen cycle because nitrification is such

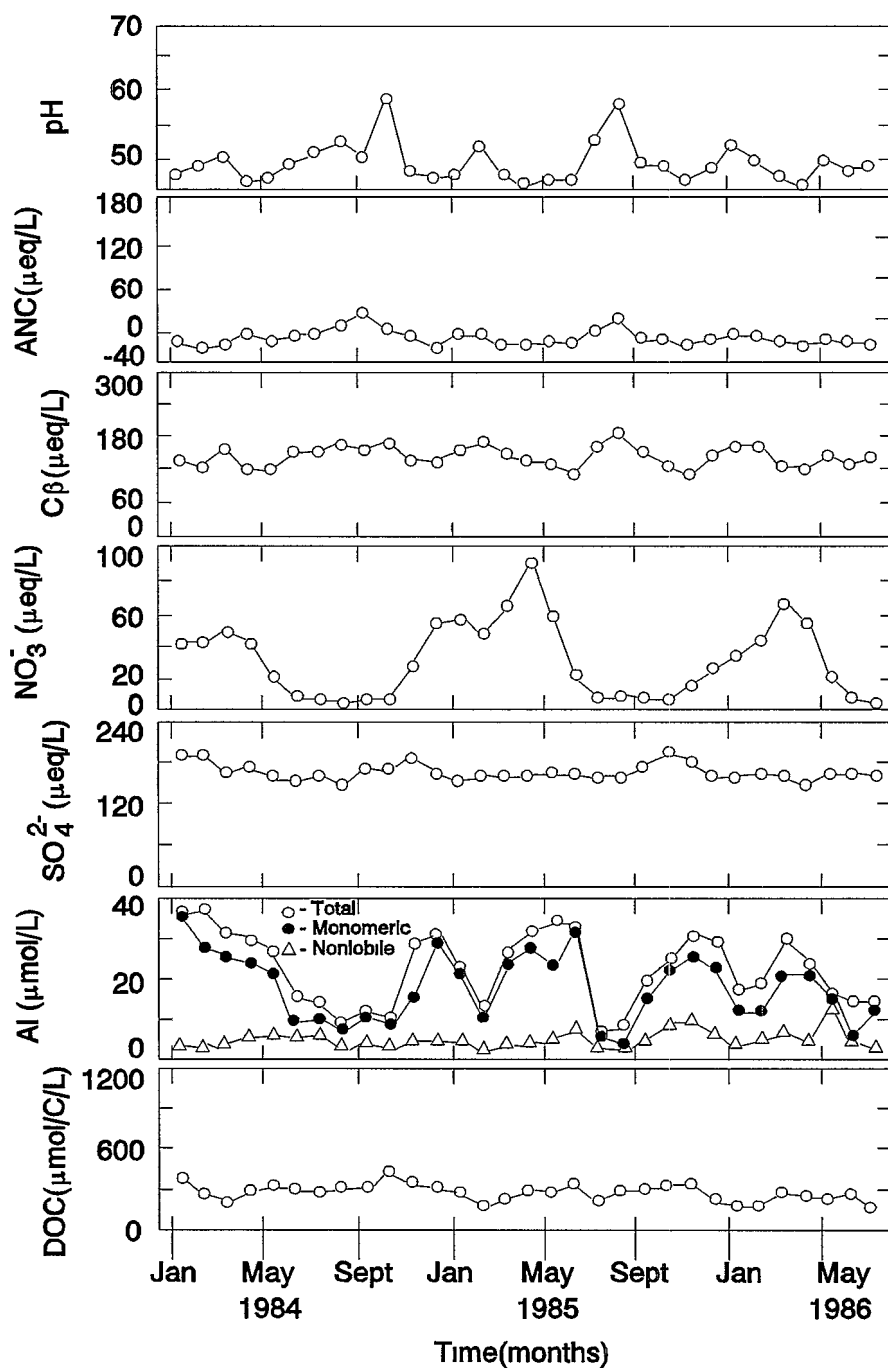


Figure 10-28. Temporal patterns in the chemical characteristics of stream water at Pancake-Hall Creek in the Adirondacks. Sulfate and base cation concentrations are relatively invariant, whereas nitrate concentrations undergo strong seasonality driven by snowmelt. Increases in inorganic monomeric aluminum result when acid neutralizing capacity values fall below zero.

Source Driscoll et al (1989a)

a strongly acidifying process (Figure 10-26). The key characteristics of Stage 2 watersheds are elevated base-flow concentrations of NO_3^- that result from high groundwater concentrations (e.g., Figure 10-29). Episodic NO_3^- concentrations are as high as Stage 1, but the seasonal pattern at Stage 2 is damped by an increase in base-flow concentrations to levels as high as those found in deposition.

In Stage 3, the watershed becomes a net source of nitrogen rather than a sink. Nitrogen retention mechanisms (e.g., uptake by vegetation and microbes) are much reduced, and mineralization of stored nitrogen may add substantially to nitrogen leaving the watershed in runoff or in gaseous forms. As in Stage 2, nitrification rates are substantial. The combined inputs of nitrogen from deposition, mineralization, and nitrification can produce concentrations of NO_3^- in surface waters that exceed inputs from deposition alone. The key characteristics of Stage 3 watersheds are these extremely high NO_3^- concentrations and the lack of any coherent seasonal pattern in NO_3^- concentrations.

Conceptually, the stages of watershed nitrogen loss can be thought of as occurring sequentially, as a single watershed progresses from being strongly nitrogen deficient to strongly nitrogen sufficient. This is consistent with the conceptual model presented by Aber et al. (1989; Figure 10-27), and can be supported by two lines of evidence, presented in the following sections of this paper. The first line of evidence comes from "space for time substitutions" (in the sense of Pickett, 1989), where the occurrence of various stages across a gradient of present-day nitrogen deposition is used as a surrogate for the temporal sequence that a single site might undergo if it were exposed to chronically elevated levels of nitrogen deposition. This technique is commonly applied to current environmental problems where a good historical record is not available (Sullivan, 1991). The second line of evidence comes from long-term temporal trends at single sites, where increases in nitrogen efflux from watersheds (observable as increasing trends in NO_3^- concentration) and changes in the seasonal pattern of NO_3^- concentration can be directly attributed to the combined effects of chronic nitrogen deposition and other factors (e.g., forest maturation). The few cases where individual sites have been observed to progress from Stage 0 to Stage 1 and/or Stage 2 of watershed nitrogen loss are especially useful in establishing that nitrogen saturation occurs as a temporal sequence in areas of high nitrogen deposition. These lines of evidence are discussed in the following sections.

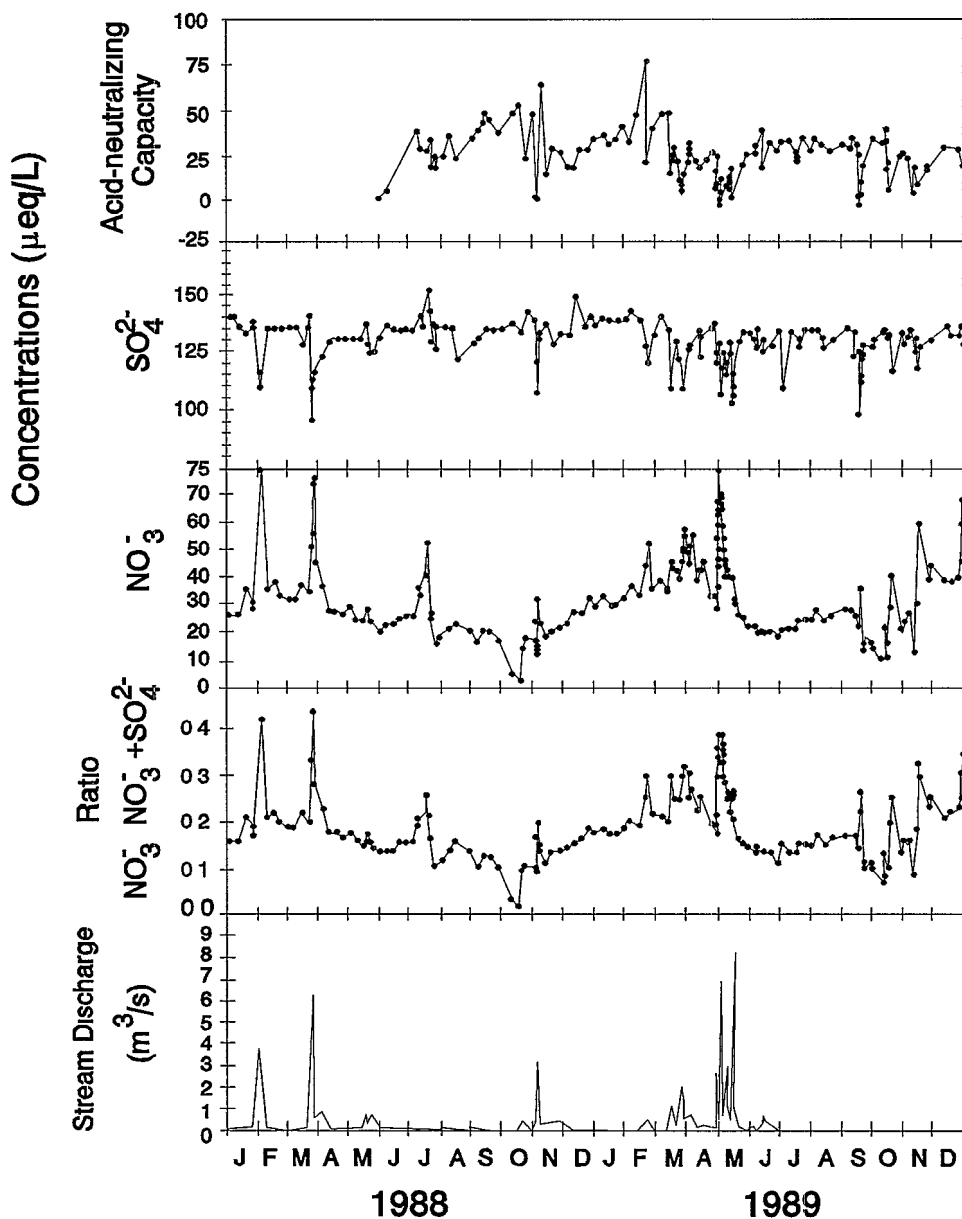


Figure 10-29. Temporal patterns in chemical characteristics of stream water at Biscuit Brook in the Catskill Mountains. All chemical variables undergo strong seasonality, with strong dependence on stream discharge. Values for the ratio of nitrate to nitrate + sulfate approach 0.5 during episodes, and indicate that nitrate is nearly as important an acidifying influence as sulfate during high-flow events.

Source Murdoch and Stoddard (in press a)

10.8.2.4 Processes Within Lakes and Streams

All of the transformations and processes discussed above (primarily in the context of terrestrial ecosystems) also take place in lakes, streams, and estuaries. The emphasis on the transformations that occur in the watershed, before nitrogen reaches surface waters, results from the necessity to establish a linkage between nitrogen deposition and nitrogen effects in aquatic systems, but should not be taken to suggest that nitrogen transformations within aquatic systems are of minor importance in the nitrogen cycle. In a very real sense, nitrogen cycling within the terrestrial ecosystems controls whether nitrogen deposition will reach aquatic systems (and in what concentrations), whereas nitrogen cycling within lakes, streams, and estuaries controls whether the nitrogen will have any measurable effect.

Assimilation by aquatic plants is a key process in the potential eutrophication of surface waters by nitrogen, and may also play a role in their acid/base status. The following discussion of nitrogen assimilation in aquatic systems will deal mainly with the algal and microbial community in phytoplankton (microscopic algal and bacterial species suspended in the water column) and periphyton (algal species growing attached to surfaces). Although macrophytes (macroscopic algal species) are also important in the assimilation of nitrogen, the biomass of phytoplankton and smaller microbes is potentially most reactive to changes in nitrogen supply. Algal uptake is a major component of the eutrophication process, and forms the basis of trophic production in streams and lakes. It can also play a large role in the acid/base status of lakes. Uptake of NO_3^- in lakes is an alkalizing process, consuming 1 mole of hydrogen per mole of nitrogen assimilated (Kelly et al., 1990).

Like terrestrial plants, aquatic plants favor the uptake of NH_4^+ over the uptake of NO_3^- ; NH_4^+ uptake is energetically favorable because NO_3^- must first be reduced before it is physiologically available to algae (Reynolds, 1984). In some circumstances, organic forms of nitrogen are also available for uptake by aquatic plants (reviewed by Healey, 1973). The preferences by algae for the different forms of nitrogen can be related to the history of availability of nitrogen species. In some algal species, the synthesis of the enzyme (nitrate reductase) required to utilize an NO_3^- pool can be induced by high concentrations of NO_3^- in the absence of NH_4^+ (Healey, 1973). The production of nitrate reductase appears to be repressed by the presence of NH_4^+ (Eppley et al., 1979).

The potential uptake rate of inorganic nitrogen is related to ambient inorganic nitrogen concentrations (e.g., Syrett, 1953), that is, cells transferred from nitrogen-deficient media to nitrogen-sufficient media show higher rates of uptake than cells that are grown and remain in nitrogen-sufficient media. McCarthy (1981) summarized several studies that consistently showed that potential (saturated) NH_4^+ uptake rates were greatly enhanced in nitrogen-deficient cells. This relationship is now used along with various other indices as a basis to identify the degree of nitrogen limitation in phytoplankton (Vincent, 1981, Suttle and Harrison, 1988). Under nitrogen-replete conditions, saturated uptake rates are low, but increase with increasing nitrogen deficiency.

A crucial difference between aquatic and terrestrial ecosystems with respect to nitrogen is that nitrogen additions do not commonly stimulate growth in aquatic systems, as seems to be the case in terrestrial systems, and nitrogen limitation may in fact be the exception in aquatic systems rather than the rule. Determining whether nitrogen limitation is a common occurrence in surface waters will play a large role in determining whether nitrogen deposition affects the trophic state of aquatic ecosystems.

The effects of nitrogen supply on uptake and growth rates in phytoplankton and periphyton is the subject of volumes of literature, a summary of which is beyond the scope of this section. However, certain aspects of the limitation of algal growth by the supply of nitrogen and other nutrients will be discussed later as it relates to enrichment effects from nitrogen deposition. For other details on algal nutrition, the reader is referred to reviews by Goldman and Glibert (1982), Button (1985), Kilham and Hecky (1988), and Hecky and Kilham (1988).

Denitrification plays a much larger role in nitrogen dynamics in aquatic ecosystems than it does in terrestrial ones. In streams, rivers, and lakes, bottom sediments are the main sites for denitrification (see Seitzinger, 1988a), although open-water denitrification has also been reported (Keeney et al., 1971). In lake and stream sediments, the main source of NO_3^- , although potentially available from the water column, is NO_3^- produced when organic matter is broken down within the sediments, and the resulting NH_4^+ is subsequently oxidized (Seitzinger, 1988a). Denitrification is an especially important process in large rivers and estuaries, and will play a large role in discussions of nitrogen loading to estuaries and near-coastal systems (see Section 10.8.4.2). In a recent review of denitrification in freshwater

and estuarine systems, Seitzinger (1988a) reported denitrification rates that were 7 to 35 % of nitrogen inputs in large rivers, and 20 to 50 % of inputs in estuaries. Denitrification in aquatic ecosystems is an alkalinizing process, consuming 1 mole of hydrogen for every mole of NO_3^- denitrified.

Estimates of denitrification rates range from 54 to 345 $\mu\text{mol}/\text{m}^2/\text{h}$ in streams with high rates of organic matter deposition, 12 to 56 $\mu\text{mol}/\text{m}^2/\text{h}$ in (nutrient-poor) oligotrophic lakes, 42 to 171 $\mu\text{mol}/\text{m}^2/\text{h}$ in eutrophic lakes, and 77 to 232 $\mu\text{mol}/\text{m}^2/\text{h}$ in estuaries (see Seitzinger, 1988a). These values are in the range where denitrification can deplete NO_3^- pools. Rudd et al. (1990) have reported an increase in the rate of denitrification from less than 0.1 $\mu\text{mol}/\text{m}^2/\text{h}$ to over 20 $\mu\text{mol}/\text{m}^2/\text{h}$ in an oligotrophic lake when nitric acid was added in a whole-lake experimental acidification, suggesting that freshwater denitrification may be limited by NO_3^- availability. Denitrification can account for 76 to 100 % of nitrogen flux at sediment-water interfaces in rivers, lakes, and estuaries (Seitzinger, 1988a). In the Potomac and Delaware rivers, where organic sediment deposition is extreme due to sewage inputs, the loss represents 35 and 20 %, respectively, of external nitrogen inputs. In estuaries, it can represent a 50 % loss. In the deep mud of slow-flowing streams, the process can effectively reduce NO_3^- concentrations in the water column by as much as 200 $\mu\text{eq}/\text{L}$ over a 2 km length of stream (Kaushik et al., 1975, Chatarpaul and Robinson, 1979). This depletion amounts to 75 % of the daily input of NO_3^- during a growing season, and it has been sufficient to consider denitrification as a method for NO_3^- removal in the management of some slow-moving streams having a deep organic substrate (Robinson et al., 1979).

Nitrogen fixation counteracts denitrification losses of nitrogen from surface waters and is fundamental to replenishing fixed forms of nitrogen in all aquatic ecosystems. It is thought to be the main process responsible for maintaining surplus inorganic nitrogen in lakes and streams and is fundamental to the fact that primary production in most lakes and streams is limited by phosphorus (Schindler, 1977). In estuaries, however, there is a higher loss of nitrogen relative to that fixed or imported. The loss may be due to high rates of denitrification (Seitzinger, 1988a), which creates relative nitrogen deficiencies.

Rates of nitrogen fixation are generally related to trophic status in freshwater. Howarth et al. (1988a) show that fixation in low-, medium-, and high-nutrient lakes is generally <0.02, 0.9 to 6.7, and 14.3 to 656.9 $\text{mmol nitrogen}/\text{m}^2/\text{year}$, respectively. Fixation is also

closely correlated with the abundance of blue-green algae (Wetzel, 1983), which suggests that the algae, rather than bacteria, dominate nitrogen fixation in lakes. Although nitrogen fixation does occur in sediments, that source is of minor importance compared to that in the water column. Only in very nutrient-poor lakes, where nitrogen loading from all other sources is small, can nitrogen fixation in sediments gain some significance (e.g., 32% and 6% of total inputs in Lake Tahoe, CA, and Mirror Lake, NH, respectively, Howarth et al., 1988a).

Unlike the nitrogen fixation community in lakes, nitrogen fixers in estuaries are dominated by bacteria, producing rates of 0.1 to 111 mmol nitrogen/m²/year (Howarth et al., 1988a). The highest rates occur in deep organic sediments, but even these are a relatively small percentage of total nitrogen inputs to estuaries (reviewed by Howarth et al., 1988a).

As in terrestrial watersheds, rates of nitrification in lakes and streams are often limited by low concentrations of NH₄⁺. Supply rates of NH₄⁺ from watersheds are often low (except in cases of point-source pollution), and nitrifying organisms have little substrate with which to work. Two exceptions to this generality are cases where NH₄⁺ deposition is extremely high, such as near agricultural areas, and cases where NH₄⁺ is produced within the aquatic system. Experiments on whole lakes and in mesocosms in Canada have confirmed the acidifying potential of ammonium additions from deposition to surface waters (Schindler et al., 1985; Schiff and Anderson, 1987). Ammonium deposition is especially deceptive because in the atmosphere, ammonium can combine as a neutral salt with SO₄²⁻, resulting in precipitation with near-neutral pH values, as seen in the Netherlands (Van Breemen and Van Dijk, 1988). Once deposited, however, the ammonium can be assimilated, leaving an equivalent amount of hydrogen, or it can be nitrified, leaving twice the amount of hydrogen. There is some evidence from Canadian whole-lake experiments that nitrification in lakes is an acid-sensitive process; Rudd et al. (1988) presented data indicating that nitrification was blocked at pH values less than 5.4 in an experimentally acidified lake, leading to a progressive accumulation of NH₄⁺ in the water column.

High NH₄⁺ concentrations may also result in lakes whose deeper waters become anoxic during periods of stratification (usually late winter or late summer). Production of NH₄⁺ (by decomposition) can be substantial under anaerobic conditions, and NH₄⁺ may accumulate in the anoxic water. Nitrification of this NH₄⁺ occurs when lakes mix during spring or fall,

supplying the oxygen necessary for nitrifying organisms to survive (Wetzel, 1983) In estuaries, the processes of nitrification (aerobic) and denitrification (anaerobic) may be closely coupled at the sediment surface, with mineralization in the anaerobic sediments supplying NH_4^+ to nitrifiers at the sediment/water interface (Jenkins and Kemp, 1984) Except in cases where the overlying water becomes anoxic (as may be common in the summer months), the nitrifying organisms supply NO_3^- back to the sediments for subsequent denitrification. In both cases described above (the annual cycle in lakes and the sediment/water interface cycle in estuaries), the main influence of nitrification is to recycle nitrogen within the system and to supply NO_3^- to either denitrifiers or to nitrogen-deficient algae.

In lakes, streams, and estuaries, water is in constant movement, and, to a large extent, the effects of nitrogen cycling on biota are regulated by the local hydrology In lakes, oxidation and reduction reactions are perceived to occur as cycles in the sense that water has a residence time lasting from a few weeks in small ponds to many years in large lakes Nitrogen species are assimilated, they contribute to biological productivity, the organic forms are subsequently mineralized, and the resulting inorganic forms enter various oxidizing and reducing pathways mediated by a microbial community within a single body of water One or more complete cycles can be followed within a single lake before export downstream

In streams, and to some extent in estuaries, nitrogen dynamics are more closely dependent on the physical movements of water As nitrogen compounds are cycled among the biotic and abiotic components of the stream ecosystem, they are subject to downstream transport. Among stream ecologists, this coupling between nutrient cycles and water movement is termed "nutrient spiraling" (e g , Elwood et al , 1980, Newbold et al , 1983) According to this concept, nitrogen cycling occurs in most streams, but little or no recycling occurs in any one place Nitrogen is instead regenerated or transformed at one point in the stream and transported downstream before subsequent reutilization or retransformation (Stream Solute Workshop, 1990) The movement of water can increase nutrient uptake rates and growth rates in freshwater algae (Whitford and Schumacher, 1961, 1964) by continually resupplying nutrients at cell walls This constant replenishment prevents steep concentration gradients from becoming established, as can happen in less active lake water (Gavis, 1976) It also maintains high rates of production and nutrient assimilation Biomass eventually

sloughs from substrata, and drifts as fine particulate organic matter (Meyer and Likens, 1979) for settlement, decomposition, and mineralization downstream. Very high flows associated with intense precipitation events are physically disruptive and can increase the concentration of particulates transported downstream (Bilby and Likens, 1979, Holmes et al, 1980). Efficiencies of nutrient uptake also decrease with increasing flows because of reduced contact time that a given ion has with the reactive substrate (Meyer, 1979).

One important consequence of nutrient spiraling in streams is that any block in the nitrogen cycle upstream can have potential effects on nitrogen conditions downstream. Mulholland et al (1987), for example, have presented experimental evidence that leaf decomposition (mineralization) in streams is inhibited at low pH values. Because mineralization of organic matter is an important process in resupplying nitrogen to organisms downstream, the existence of acidic headwaters could influence biotic conditions in downstream portions of streams where acidification is not important.

10.8.3 The Effects of Nitrogen Deposition on Surface Water Acidification

The acidification processes of lakes and streams are conventionally separated into chronic (long-term) and episodic (event-based) effects. A great deal of emphasis in the past decade has been placed on chronic acidification in general, and on chronic acidification by sulfate in particular (e.g., Galloway et al, 1983, Sullivan et al, 1988, Brakke et al, 1989). This emphasis on SO_4^{2-} has resulted largely because sulfur deposition rates are often higher than those for nitrogen (sulfur deposition rates are approximately twice the rates of nitrogen deposition in the Northeast, Stensland et al, 1986) and because NO_3^- appears to be of negligible importance in surface waters sampled during summer and fall index periods (Linthurst et al, 1986). As mentioned previously, summer and fall are seasons when watershed demand for nitrogen is very high, creating a low probability that nitrogen, in any form, will be leached into soil and surface waters unless the watersheds have achieved nitrogen saturation. Under conditions of low nitrogen deposition (or high nitrogen demand), nitrogen leaking from terrestrial ecosystems, as described earlier, is more likely to be a transient (or seasonal) phenomenon than a chronic one. As a result, the primary impact of nitrogen in surface water acidification will be observed during high-flow seasons, and particularly during snowmelt. It has been estimated that 40 to 640% more streams in the

eastern United States (Florida to the Northern Appalachian Plateau) are acidic during spring episodes than are acidic during spring base flow, whereas the number of acidic Adirondack lakes is estimated to be three times higher during the spring than during the fall (Eshleman, 1988).

Surface waters are conventionally considered acidic if their acid-neutralizing capacity (ANC) is less than zero. The ANC of a lake or stream is a measure of the water's capacity to buffer acidic inputs, and results from the presence of carbonate and/or bicarbonate (or alkalinity), Al, and organic acids in the water (Sullivan et al, 1989). The main purposes of this section are to evaluate the evidence for chronic acidification by nitrogen deposition in North America, and to determine what role nitrogen deposition plays in episodic acidification.

10.8.3.1 Chronic Acidification

In the United States, the most comprehensive assessment of chronic acidification of lakes and streams comes from the National Surface Water Survey (NSWS) conducted as part of the National Acid Precipitation Assessment Program. The NSWS surveyed the acid/base chemistry of both lakes and streams using an "index period" concept. The goal of the index period concept was to identify a single season of the year that exhibited low temporal and spatial variability and that, when sampled, would allow the general condition of surface waters to be assessed (Linthurst et al, 1986). In the case of lakes, the index period selected was autumn overturn (the period when most lakes are mixed uniformly from top to bottom), and in streams, the chosen index period was spring base flow (the period after spring snowmelt and before leaf-out) (Messer et al, 1988). Because of the strong seasonality of the nitrogen cycle in forested watersheds (described earlier), the choice of index period plays a very large role in the assessment of whether nitrogen is an important component of acidification.

The results of the Eastern Lake Survey (Linthurst et al, 1986), based on a probability sampling of lakes during fall overturn, suggest that nitrogen compounds make only a small contribution to chronic acidification in North America. Henriksen (1988) has proposed that the ratio of $\text{NO}_3^- / (\text{NO}_3^- + \text{SO}_4^{2-})$ in surface waters be used as an index of the influence of NO_3^- on chronic acidification status. This index assesses the importance of nitrogen relative to the

importance of SO_4^{2-} , which is usually considered more important in chronic acidification (see above). A value greater than 0.5 indicates that NO_3^- has a greater influence on the chronic acid/base status of surface waters than does SO_4^{2-} . Henriksen (1988) summarized the ratios for acid-sensitive sites worldwide, these results are repeated in Table 10-20. In general, Henriksen's results show that NO_3^- can be almost as important as SO_4^{2-} in some parts of Europe, but that ratios are low in the United States (see also Henriksen and Brakke, 1988).

One problem with Henriksen's approach, however, is that he compares data collected intensively (i.e., through multiple samples per year) with survey data collected during a single index period. The data presented for Adirondack lakes in Table 10-20, for example, were collected monthly over a 2-year period (Driscoll and Newton, 1985), and the apparent difference between the Adirondacks and the rest of central New England (from the regional survey data) could well result from comparing fall values to annual mean values. Annual mean values include high spring NO_3^- concentrations in runoff waters and will, therefore, be higher than concentrations measured only in the autumn. As a result, the ratio values reported in Table 10-20 for the Adirondacks are an indication that NO_3^- may be important in chronic acidification (i.e., NO_3^- makes up about 15% of acid anions), but the low ratios reported for the Eastern Lake Survey are not informative. Unfortunately, no regional lake survey with representative annual, or spring, values exists for the United States, and questions concerning the role of NO_3^- in chronic lake acidification remain unanswered for areas outside of the Adirondacks.

Values of $\text{NO}_3^- / (\text{NO}_3^- + \text{SO}_4^{2-})$ ratios are also available for streams from the National Stream Survey (NSS) (Kaufmann et al., 1988), as well as from other regional stream surveys (e.g., Stoddard and Murdoch, 1991). Median values for each of the regions covered in these surveys are given in Table 10-21. The NSS data have the advantage of having been collected during a spring base-flow index period. This period is been shown to be a good index of mean annual condition for streams (Messer et al., 1988, Kaufmann et al., 1988), but is not an estimate of worst case condition, as concentrations taken during spring snowmelt would be. The Catskill regional data included in Table 10-21 are from a stream survey that included multiple samplings per year (Stoddard and Murdoch, 1991). Several stream regions

**TABLE 10-20. CONCENTRATIONS OF NITRATE, SULFATE, AND RATIOS
OF NITRATE TO THE SUM OF NITRATE AND SULFATE IN RUNOFF WATERS
IN ACIDIFIED AREAS OF THE WORLD^a**

| Location | Year | Concentration ($\mu\text{eq/L}$) | | | Ratio $\text{NO}_3^- / (\text{NO}_3^- + \text{SO}_4^{2-})$ | Sampling Method ^b |
|--------------------------------------|-----------|------------------------------------|-----------------|--------------------|---|---------------------------------|
| | | pH | NO_3^- | SO_4^{2-} | | |
| <u>West Germany</u> | | | | | | |
| Lange Bramke | 1977 | 5.8 | 16 | 233 | 0.06 | Intensive |
| Lange Bramke | 1984 | 6.2 | 49 | 230 | 0.18 | Intensive |
| <u>Bayerischer Wald</u> | | | | | | |
| Rachelsee | 1985 | 4.5 | 77 | 135 | 0.36 | Unknown |
| Gr. Arbersee | 1985 | 4.7 | 98 | 118 | 0.45 | Unknown |
| Kl. Arbersee | 1985 | 4.5 | 93 | 108 | 0.46 | Unknown |
| <u>Poland</u> | | | | | | |
| The Giant Mountains | | | | | | |
| Maly Staw | 1986 | 5.5 | 13 | 92 | 0.12 | Unknown |
| Wielki Staw | 1986 | 4.7 | 40 | 140 | 0.22 | Unknown |
| <u>Czechoslovakia</u> | | | | | | |
| Tatra Mountains | | | | | | |
| av. 53 lakes | 1984 | 6.1 | 37 | 97 | 0.27 | Unknown |
| Jameke | 1980-82 | 4.4 | 2 | 171 | 0.01 | Unknown |
| Popradake | 1980-82 | 6.6 | 40 | 111 | 0.26 | Unknown |
| Vyshe Wahlenbugoro | 1980-82 | 5.6 | 44 | 74 | 0.37 | Unknown |
| Vyshe Furkotake | 1980-82 | 6.3 | 42 | 110 | 0.28 | Unknown |
| <u>Bohemia</u> | | | | | | |
| Carne | 1986 | 4.5 | 93 | 152 | 0.38 | Unknown |
| Certovo | 1986 | 4.2 | 85 | 182 | 0.32 | Unknown |
| Prasilske | 1986 | 4.5 | 40 | 120 | 0.25 | Unknown |
| Plesne | 1986 | 4.7 | 41 | 203 | 0.17 | Unknown |
| Laka (man-made) | 1986 | 5.5 | 45 | 61 | 0.42 | Unknown |
| Zdarske (man-made) | 1986 | 6.5 | 0 | 156 | 0.00 | Unknown |
| Krusne hory Mountains | 1986 | 5.2 | 118 | 1216 | 0.09 | Unknown |
| <u>Sumava Mountains</u> | | | | | | |
| Liz | April '86 | 5.89 | 136 | 390 | 0.26 | Unknown |
| Albrechtec | April '86 | 6.22 | 36 | 358 | 0.09 | Unknown |
| <u>Norway</u> | | | | | | |
| Birkenes | 1973-86 | 4.52 | 9 | 140 | 0.06 | Intensive |
| Storgama | 1973-86 | 4.56 | 12 | 77 | 0.13 | Intensive |
| <u>Sweden</u> | | | | | | |
| Stromyra | 1984-85 | 6.54 | 17 | 180 | 0.09 | Intensive |
| <u>Scotland</u> | | | | | | |
| av. 22 lakes in the Galloway area | 1979 | 4.97 | 21 | 103 | 0.17 | Unknown |

TABLE 10-20 (cont'd). CONCENTRATIONS OF NITRATE, SULFATE, AND RATIOS OF NITRATE TO THE SUM OF NITRATE AND SULFATE IN RUNOFF WATERS IN ACIDIFIED AREAS OF THE WORLD^a

| Location | Year | Concentration ($\mu\text{eq/L}$) | | | Ratio | | Sampling Method ^b |
|--|-------|------------------------------------|------------------------------|-------------------------------|------------------------------|--|------------------------------|
| | | pH | NO ₃ ⁻ | SO ₄ ²⁻ | NO ₃ ⁻ | NO ₃ ⁻ + SO ₄ ²⁻ | |
| <u>United States</u> | | | | | | | |
| <u>Adirondacks</u> | | | | | | | |
| Big Moose Lake | 1980s | 5.1 | 24 | 140 | 0.15 | Monthly | |
| Cascade Lake | | 6.5 | 29 | 139 | 0.17 | Monthly | |
| Darts Lake | | 5.2 | 24 | 139 | 0.15 | Monthly | |
| Merriam Lake | | 6.4 | 26 | 141 | 0.16 | Monthly | |
| Lake Rondaxe | | 5.9 | 23 | 134 | 0.15 | Monthly | |
| Squash Pond | | 4.6 | 24 | 131 | 0.15 | Monthly | |
| Townsend Pond | | 5.2 | 27 | 154 | 0.15 | Monthly | |
| Windfall Pond | | 5.9 | 26 | 141 | 0.16 | Monthly | |
| Bubb Lake | | 6.1 | 16 | 131 | 0.11 | Monthly | |
| Constable Pond | | 5.2 | 17 | 149 | 0.10 | Monthly | |
| Moss Lake | | 6.4 | 26 | 141 | 0.16 | Monthly | |
| Black Pond | | 6.8 | 4 | 130 | 0.03 | Monthly | |
| Clear Pond | | 7.0 | 1 | 139 | 0.00 | Monthly | |
| Heart Lake | | 6.4 | 5 | 106 | 0.05 | Monthly | |
| Otter Lake | | 5.5 | 9 | 138 | 0.06 | Monthly | |
| West Pond | | 5.2 | 10 | 111 | 0.08 | Monthly | |
| Woodruff Pond | | 6.9 | 2 | 147 | 0.01 | Monthly | |
| <u>Eastern Lake Survey^c</u> | | | | | | | |
| Southern Blue Ridge | 1985 | - | 3 | 32 | 0.09 | Fall index | |
| Florida | | - | 1 | 94 | 0.01 | Fall index | |
| Upper Midwest | | - | 0.7 | 57 | 0.01 | Fall index | |
| Upper Great Lakes | | - | 0.6 | 50 | 0.01 | Fall index | |
| Wisconsin | | - | 1.0 | 57 | 0.02 | Fall index | |
| Peninsula, Michigan | | - | 0.6 | 78 | 0.01 | Fall index | |
| Northeastern Minnesota | | - | 0.9 | 62 | 0.01 | Fall index | |
| Maine | | - | 0.2 | 75 | 0.00 | Fall index | |
| Southern New England | | - | 0.8 | 141 | 0.01 | Fall index | |
| Central New England | | - | 0.3 | 101 | 0.00 | Fall index | |
| <u>Canada</u> | | | | | | | |
| <u>Experimental Lakes</u> | | | | | | | |
| Area, Ontario | 1980s | - | 1 | 78 | 0.01 | Intensive | |
| Sudbury, Ontario | 1980s | - | 2 | 252 | 0.01 | Intensive | |
| Kekimikujik, | 1980s | - | 2 | 252 | 0.01 | Intensive | |
| Nova Scotia | | | 3 | 78 | 0.04 | | |

^a NO_3^- = Nitrate ion

SO_4^{2-} = Sulfate ion

^bSampling methods are listed as unknown, monthly, intensive (more frequent than monthly), or based on a single fall index sample

^cMedian value for regional population of lakes

Source: Henriksen (1988)

TABLE 10-21. CONCENTRATIONS OF NITRATE, SULFATE, AND RATIOS OF NITRATE TO THE SUM OF NITRATE AND SULFATE IN STREAMS OF ACID-SENSITIVE REGIONS OF THE UNITED STATES. VALUES ARE MEDIANS FOR REGION (FIRST AND THIRD QUANTILES IN PARENTHESES)^a

| Location | Year | Concentration ($\mu\text{eq/L}$) | | | NO_3^- $\text{NO}_3^- + \text{SO}_4^{2-}$ |
|---|---------|------------------------------------|-----------------|--------------------|--|
| | | pH | NO_3^- | SO_4^{2-} | |
| <u>National Stream Survey^b</u> | | | | | |
| Poconos/Catskills | 1986 | 6.96 | 6 (2-18) | 169 (154-184) | 0.03 (0.01-0.10) |
| Northern Appalachians | | 6.60 | 30 (12-41) | 171 (135-347) | 0.14 (0.02-0.19) |
| Valley and Ridge | | 7.05 | 10 (3-31) | 154 (84-294) | 0.09 (0.01-0.22) |
| Mid-Atlantic Coastal Plain ^c | | 5.98 | - | - | - |
| Southern Blue Ridge | | 6.99 | 8 (2-16) | 17 (10-27) | 0.28 (0.08-0.44) |
| Piedmont | | 6.80 | 2 (0-5) | 48 (19-63) | 0.03 (0-0.20) |
| Southern Appalachians | | 7.33 | 16 (3-32) | 58 (30-104) | 0.32 (0.04-0.40) |
| Ozarks/Ouachitas | | 6.62 | 1 (1-4) | 59 (48-83) | 0.02 (0-0.06) |
| Florida | | 5.48 | 5 (1-10) | 22 (9-30) | 0.19 (0.10-0.25) |
| <u>Catskill Regional Survey^d</u> | | | | | |
| Median value for 51 streams | 1984-86 | 6.60 | 29 (14-47) | 138 (125-151) | 0.17 (0.09-0.26) |

^a NO_3^- = Nitrate ion

SO_4^{2-} = Sulfate ion

^bValues for pH are for entire region (Kaufmann et al., 1988), medians for NO_3^- , SO_4^{2-} , and the $\text{NO}_3^- / (\text{NO}_3^- + \text{SO}_4^{2-})$ ratio exclude sites with potential agricultural or other land-use impacts (Kaufmann et al., 1991)

^cThe influence of agricultural and land use practices could not be ruled out for any of the sites in the Mid-Atlantic Coastal Plain (Kaufmann et al., 1991)

^dFrom Stoddard and Murdoch (1991)

exhibit ratios as high as those reported for the Adirondacks by Henriksen (1988). Several regions in the southeastern United States exhibit high ratios in part because their current SO_4^{2-} concentrations are relatively low. The Southern Blue Ridge, in particular, has the lowest NO_3^- concentrations found in the NSS, and the relatively high $\text{NO}_3^- / (\text{NO}_3^- + \text{SO}_4^{2-})$ ratios in this region could be considered misleading. The stream data do suggest that the Catskills, Northern Appalachians, Valley and Ridge Province, and Southern Appalachians all show some potential for chronic acidification due to NO_3^- . In all of the stream regions in

Table 10-21, as well as the lake regions in Table 10-20, however, chronic acidification is more closely tied to SO_4^{2-} than to NO_3^-

The data presented thus far in this section establish which regions of the country show potential problems with chronic acidification by NO_3^- , but do not indicate whether the source of the NO_3^- is atmospheric deposition. As described earlier, several watershed processes (e.g., mineralization, nitrification, nitrogen fixation) may combine to produce NO_3^- and may be responsible, at least in part, for high NO_3^- concentrations observed in surface waters. On a regional scale, it is not possible to attribute surface water NO_3^- to any single source, but two efforts have been made to relate rates of nitrogen deposition to rates of nitrogen loss from watersheds. Data from the NSS (Kaufmann et al., 1991) suggest a strong correlation between concentrations of stream water nitrogen ($\text{NO}_3^- + \text{NH}_4^+$) at spring base flow and levels of wet nitrogen deposition ($\text{NO}_3^- + \text{NH}_4^+$) in each of the NSS regions (Figure 10-30). The only exception to this relationship is the Pocono/Catskill region, where nitrogen deposition is highest (6 kg/ha/year), but where stream water nitrogen concentrations fall below what is expected, based on results from the other regions. The median stream water NO_3^- value for the Catskills alone (from Stoddard and Murdoch, 1991, Table 10-21) is 29 $\mu\text{eq/L}$, and fits the relationship much more closely, suggesting that watersheds in the southern portion of this region (the Poconos) are retaining nitrogen more strongly than the northern portion. Driscoll et al. (1989a) collected input/output budget data for a large number of watersheds in the United States and Canada, and summarized the relationship between nitrogen export and nitrogen deposition at all of the sites (Figure 10-30). The authors stress that the data illustrated in Figure 10-30 were collected using widely differing methods and over various time scales (from 1 year to several decades). Given the numerous possible sources of NO_3^- and the watershed pathways through which nitrogen may be cycled, the relationships illustrated in Figure 10-30 should not be over-interpreted, nor should they be construed as an illustration of cause and effect. However, the relationships do show that watersheds in many regions of North America are retaining less than 75% of the nitrogen that enters them, and that the amount of nitrogen being leaked from these watersheds is higher in areas where nitrogen deposition is highest. This pattern is consistent with what we would expect if large areas of the eastern United States were experiencing the early stages of nitrogen saturation. Furthermore, both analyses suggest a threshold value of nitrogen

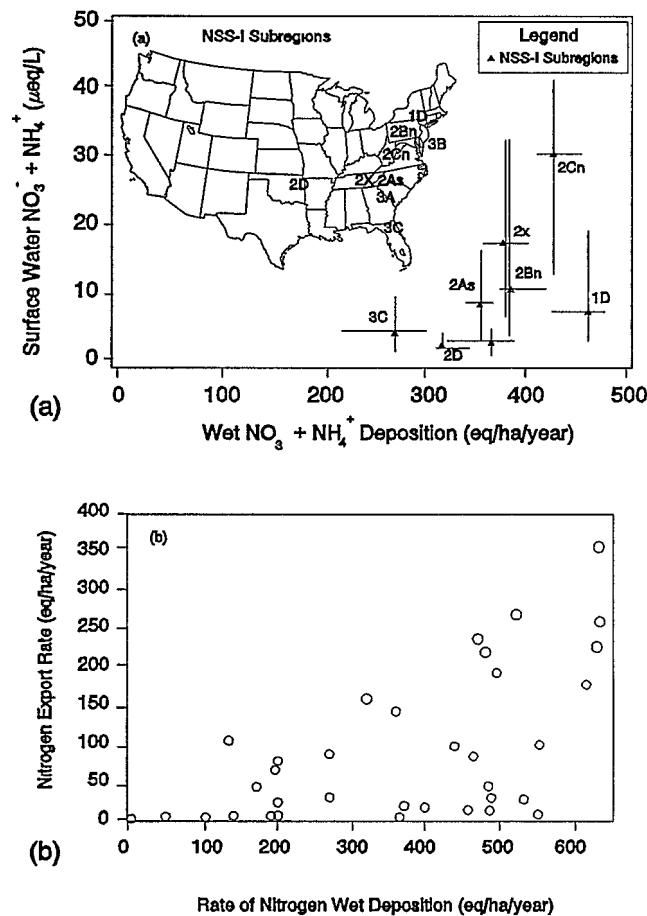


Figure 10-30. Nitrogen deposition and watershed nitrogen loss. (a) Relationship between median wet deposition of nitrogen (nitrate ions plus ammonium ions) and median surface water nitrogen (nitrate ions plus ammonium ions) concentrations for physiographic districts within the National Stream Survey that have minimal agricultural activity. [Subregions are Poconos/Catskills (1D), Southern Blue Ridge Province (2As), Valley and Ridge Province (2Bn), Northern Appalachians (2Cn), Ozarks/Ouachitas (2D), Southern Appalachians (2X), Piedmont (3A), Mid-Atlantic Coastal Plain (3B), and Florida (3C)]. From Kaufmann et al. (1991). (b) Relationship between wet deposition of nitrogen (nitrate ions plus ammonium ions) and rate of nitrogen export for watershed studies throughout North America. Sites with significant internal sources of nitrogen (e.g., from alder trees) have been excluded.

Source Driscoll et al (1989a), additional data from Barker and Witt (1990), Edwards and Helvey (1991), Kelly and Meagher (1986), Katz et al (1985), Buell and Peters (1988), Weller et al (1986), Owens et al (1989), Feller (1987), Stoddard and Murdoch (1991)

deposition (ca 3 kg/ha/year) above which substantial watershed losses of nitrogen might begin to occur

Chronic acidification due to nitrogen deposition is much more common in Europe than in North America (Hauhs et al , 1989) Many sites show chronic increases in nitrogen export from their watersheds (e g , Henriksen and Brakke, 1988, Hauhs, 1989), and at sites with the highest stream water NO_3^- concentrations (i e , Lange Bramke and Dicke Bramke in West Germany), NO_3^- concentrations no longer show the seasonality that is expected from normal watershed processes (Hauhs et al , 1989) Henriksen and Brakke (1988) have reported regional chronic increases in surface water NO_3^- in Scandinavia in the past decade These increases in NO_3^- concentration are associated with increasing concentrations of Al, which is toxic to many fish species (Henriksen et al , 1988, Brown, 1988) There is some evidence that NO_3^- has a greater ability to mobilize toxic Al from soils than does SO_4^{2-} (James and Riha, 1989) Chronic acidification attributable to ammonium deposition has also been demonstrated in the Netherlands (Van Breemen and Van Dijk, 1988, Schuurkes, 1986, 1987) As described earlier, ammonium in deposition can be nitrified to produce both NO_3^- and H^+ , which are subsequently leaked into surface waters Rates of NO_3^- and NH_4^+ deposition are much higher in Europe (in some places deposition is $>2,000$ eq/ha/year, Rosen, 1988) than in the United States (Table 10-19), and it has been suggested that chronic nitrogen acidification is more evident in Europe than in North America because nitrogen saturation (see discussion above) is further progressed in Europe

10.8.3.2 Episodic Acidification

In a recent comprehensive examination, Wigington et al (1990) reported that acidic episodes have now been observed in a wide range of geographic locations in Scandinavia (Norway, Sweden, Finland), Europe (United Kingdom, Scotland, Federal Republic of Germany, Czechoslovakia), and Canada (Ontario, Quebec, Nova Scotia), as well as in the United States They noted that in the United States, episodes have been registered in surface waters in the Northeast, Mid-Atlantic, Mid-Atlantic Coastal Plain, Southeast, Upper Midwest, and West regions In the Mid-Atlantic Coastal Plain and Southeast regions, all of the episodes cataloged to date have been associated with rainfall In contrast, most of the

episodes in the other regions are related to snowmelt, although rain-driven episodes apparently can occur in all regions of the country

The regional importance and severity of episodic acidification have not been quantified, that is, the regional information on chronic acidification that was gained from the NSWS has no parallel in episodic acidification. As a result, all of the information we currently have about the importance of episodes, and the influence of nitrogen deposition on episodes, comes from site-specific studies. It is important to stress that even within a given area, such as the Northeast, major differences can be evident in the occurrence, nature, location (lakes or streams), and timing of episodes at different sites.

Eshleman (1988) has used a simple stream mixing model (Johnson et al., 1969) to predict the number of streams in the NSS that would be acidic during spring episodes, based on their spring base-flow chemistry. In addition, Eshleman used an empirical model relating fall index period lake chemistry to spring episodic chemistry, using data from the U.S. Environmental Protection Agency's (EPA's) Long-Term Monitoring project (Newell et al., 1987), to predict the number of Adirondack lakes that undergo episodic acidification. His results are repeated in Table 10-22. Eshleman's approach has been criticized (see discussion below), largely because it assumes that all lakes, regardless of their baseline ANC, undergo the same relative depression in ANC during episodes (i.e., that the relationship between fall and spring ANC is linear). This assumption ignores any effect of increased NO_3^- during episodes, which may be greater in low ANC lakes (Schaefer et al., 1990, Schaefer and Driscoll, in press). Given this criticism, Eshleman's estimates of the number of episodically acidified systems should probably be considered conservative.

A number of processes contribute to the timing and severity of acidic episodes (Driscoll and Schaefer, 1989). The most important of these processes are

- dilution of base cations (Galloway et al., 1980) by high discharge,
- increases in organic acid concentrations (Sullivan et al., 1986) during periods of high discharge,
- increases in SO_4^{2-} concentrations (Johannessen et al., 1980) during periods of high discharge, and
- increases in NO_3^- concentrations (Galloway et al., 1980, Driscoll and Schafran, 1984, Schofield et al., 1985) during periods of high discharge.

In addition to these factors, which produce the chemical conditions characteristic of episodic events, the likelihood of an *acidic* episode is also influenced by the chemical conditions

TABLE 10-22. ESTIMATES OF THE NUMBER AND PROPORTION OF CHRONICALLY AND EPISODICALLY ACIDIC LAKES AND STREAM REACHES IN THE EASTERN UNITED STATES. CHRONIC CONDITIONS BASED ON RANDOM SAMPLE OF SYSTEMS DURING INDEX CONDITIONS (SPRING BASE FLOW OR FALL OVERTURN). EPISODIC CONDITIONS ESTIMATED FROM TWO-BOX MIXING MODEL (FOR STREAMS), OR EMPIRICAL RELATIONSHIPS BETWEEN FALL INDEX PERIOD AND SPRING SNOWMELT CHEMISTRY (FOR LAKES)

| Subregion | Index Conditions (ANC ^a < 0) | | Episodic Conditions (ANC ^a < 0) | |
|--------------------------------------|---|----------------|--|----------------|
| | Number | Proportion (%) | Number | Proportion (%) |
| <u>Stream Subregions^b</u> | | | | |
| Poconos/Catskills | 209 | 6.4 | 746 | 23.0 |
| Southern Blue Ridge | 0 | 0 | 39 | 2.2 |
| Valley and Ridge | 636 | 4.9 | 1,126 | 8.6 |
| Northern Appalachian Plateau | 499 | 5.8 | 3,224 | 37.2 |
| Ozarks/Ouachitas | 0 | 0 | 75 | 1.8 |
| Southern Appalachians | 121 | 2.5 | 364 | 7.4 |
| Piedmont | 0 | 0 | 0 | 0 |
| Mid-Atlantic Coastal Plain | 1,334 | 11.8 | 3,132 | 27.8 |
| Florida | 678 | 39.2 | 963 | 55.7 |
| <u>Lake Subregions</u> | | | | |
| Adirondacks | 138 | 10.7 | 459 | 35.6 |

^aANC = Acid-neutralizing capacity

^bFor streams, all data are from the upper end of sampled stream reaches (Kaufmann et al , 1988), except for the Southern Blue Ridge, where data from lower ends of stream reaches were used

Source Eshleman (1988)

before the episode begins. Episodes are more likely to be acidic, for example, if the base-flow ANC of the stream or lake is low. In this way, acid anions, especially SO_4^{2-} , can contribute to the severity of an acidic episode, even though they do not increase during the event, by lowering the base-flow ANC of the stream or lake (Stoddard and Murdoch, 1991).

In many cases, all of these processes will contribute to episodes in a single aquatic system. Dilution, for example, probably plays a role in all episodic decreases in ANC and pH in all regions of the United States (Wigington et al , 1990). Dilution results from the increased rate of runoff, and channeling of runoff through shallower soil layers, that occurs

during storms or snowmelt, the shorter contact time produces runoff with a chemical composition closer to that of atmospheric deposition than is typical of base-flow conditions (e.g., Driscoll and Newton, 1985, Peters and Murdoch, 1985, Stoddard, 1987a). Because precipitation is usually more dilute than stream or lake water, storm runoff produces surface waters that are more dilute than during non-runoff periods. In a sense, dilution sets the baseline condition to which the effects of organic acids and atmospherically derived SO_4^{2-} and NO_3^- are added.

Little information exists about the effects of changes in organic acids during episodes. Driscoll et al. (1987a) and Eshleman and Hemond (1985) concluded that organic acids did not contribute to snowmelt episodes in the Adirondacks or in Massachusetts, respectively. At Harp Lake in Canada, organic acidity is believed to remain constant (Servos and Mackie, 1986) or decrease (LaZerte and Dillon, 1984) during snowmelt episodes. Haines (1987) and McAvoy (1989) have documented increases in organic acidity during rain-caused episodes in coastal Maine and in Massachusetts.

Storage of SO_4^{2-} in watersheds, and subsequent release of SO_4^{2-} during episodic events, is well documented in many parts of Europe (Wigington et al., 1990), but has not been commonly found in the United States. Sulfate episodes have been described for the Leading Ridge area of Pennsylvania (Lynch et al., 1986) and at Filsen Creek in Minnesota (Schnoor et al., 1984), but are not widespread. Sulfate does contribute to episodic acidity, however, in the sense that concentrations may remain high during events, and contribute to a lower baseline ANC; the effects of other factors, such as increased NO_3^- , will be in addition to any constant effect of SO_4^{2-} in lowering the baseline ANC (Stoddard and Murdoch, 1991).

The main goal of this section is to determine when increases in NO_3^- concentrations play a significant role in episodic acidification. In the Adirondacks, for example, strong NO_3^- pulses in both lakes (Galloway et al., 1980, Driscoll and Schafran, 1984) and streams (Driscoll et al., 1987b) are apparently the primary factor contributing to depressed ANC and pH during snowmelt. Schaefer et al. (1990) examined the same empirical relationships used for the Adirondack lakes by Eshleman (1988, Table 10-22) and concluded that the magnitude of the episodes experienced by lakes depends strongly on their base cation concentration. They concluded that lakes with high base cation concentrations (and, therefore, high ANC values) undergo episodes that are largely the result of dilution by snowmelt. Low ANC

lakes, on the other hand, undergo episodes that result largely from increases in NO_3^- concentrations. At intermediate ANC levels, lakes are affected by both base cation dilution and NO_3^- increases, and, therefore, these lakes may undergo the greatest increases in acidity during snowmelt episodes (Figure 10-31). The relationship between spring and fall lake chemistry is, therefore, not linear, as assumed by Eshleman (1988), and the number of lakes that become acidic during spring episodes is probably larger than predicted in Table 10-22.

Driscoll et al. (1989a,b) report on a detailed study of nitrogen dynamics in Pancake-Hall Creek in the Adirondack Mountains. This stream is highly acidic, with low and invariant concentrations of base cations, and high and invariant concentrations of SO_4^{2-} (Figure 10-28). Nitrate concentrations were lower than SO_4^{2-} concentrations, and exhibited a distinct seasonal pattern, peak concentrations approached $100 \mu\text{eq/L}$. Short-term changes in NO_3^- were highly correlated, and chemically consistent, with changes in the concentrations of acidic cations (H^+ and Al^{3+}) (Driscoll et al., 1989a). As mentioned earlier, although dilution of base cations and increases in NO_3^- appear to be the primary causes of episodic acidification in Pancake-Hall Creek, these episodes are excursions from an already low baseline ANC, which can be largely attributed to high SO_4^{2-} concentrations.

Stoddard and Murdoch (1991) have concluded that increases in NO_3^- , base cation dilution, and high baseline SO_4^{2-} concentrations all contribute to acidic episodes in Catskill Mountain streams (Figure 10-29). In Biscuit Brook, an intensively-studied stream in the Catskills, concentrations of NO_3^- approach those of SO_4^{2-} during episodes (Murdoch and Stoddard, in press). a) Values for the ratio of $\text{NO}_3^- / (\text{NO}_3^- + \text{SO}_4^{2-})$, as presented in Tables 10-20 and 10-21, illustrate both the general importance of NO_3^- to the acid/base dynamics of this stream, and the increase in importance of NO_3^- during high-flow events (Figure 10-29).

Researchers at the Hubbard Brook Experimental Forest in New Hampshire have been studying the links between atmospheric deposition, watershed processes, and stream water chemistry since 1963 (Likens et al., 1977). In reference Watershed #6, stream water NO_3^- concentrations undergo strong seasonal cycles, with peak concentrations as high as $85 \mu\text{eq/L}$. Both NO_3^- and H^+ concentrations increase during snowmelt at Hubbard Brook, and SO_4^{2-} concentrations decrease slightly (Johnson et al., 1981, Likens, 1985).

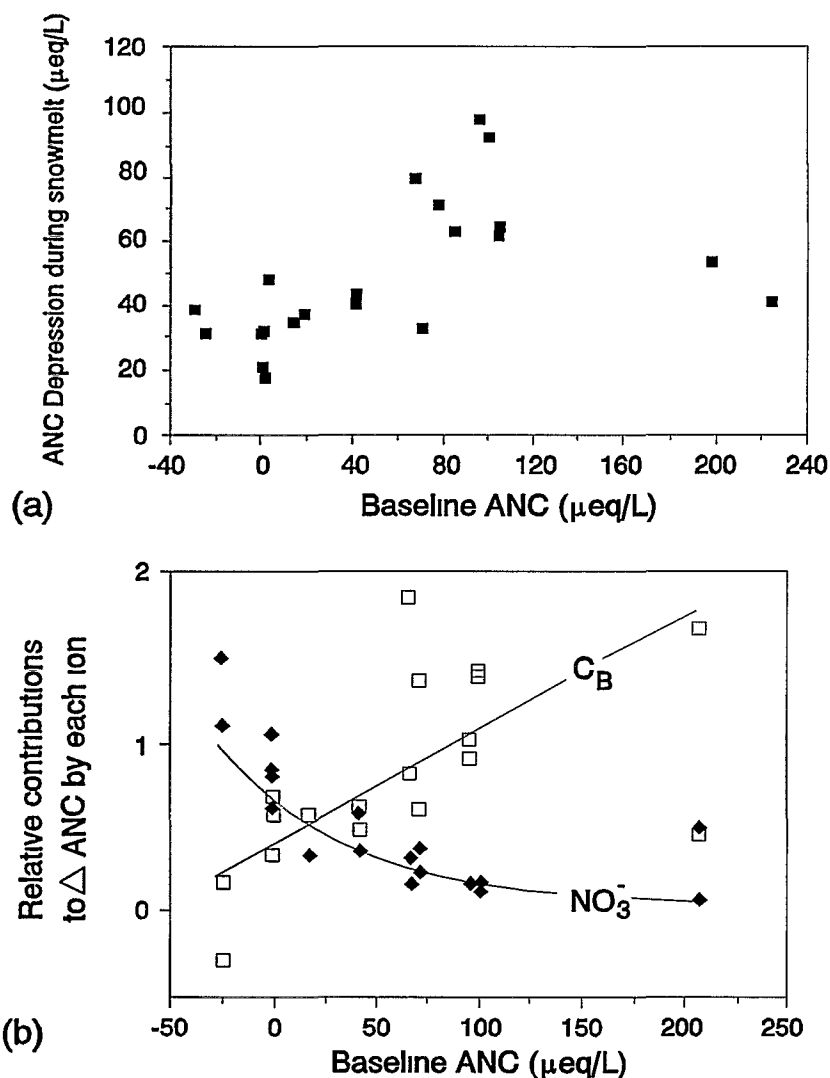


Figure 10-31. Effect of baseline acid-neutralizing capacity and episodic conditions in Adirondack lakes. (a) Relationship between baseline acid-neutralizing capacity and the springtime depression in acid-neutralizing capacity (baseline acid-neutralizing capacity—minimum acid-neutralizing capacity) for 11 lakes sampled in 1986 and 1987. (b) The relative contributions of base cations and nitrate to the springtime acid-neutralizing capacity depressions in Adirondack lakes. Lakes at intermediate acid-neutralizing capacity values undergo the largest springtime depressions in acid-neutralizing capacity. Lakes with lower baseline acid-neutralizing capacity are affected more by nitrate pulses, and lakes with higher baseline acid-neutralizing capacity are affected more by base cation dilution. Solid lines represent best-fit relationships.

Source. Schaefer et al (1990)

The highest recorded NO_3^- concentrations in streams draining undisturbed watersheds in the United States come from the Great Smoky Mountains in Tennessee and North Carolina. Nitrate concentrations in Raven Fork (Jones et al, 1983), Clingman's Creek, and Cosby Creek (Elwood et al, 1991) range from 50 to 100 $\mu\text{eq/L}$, and in all cases are comparable to, or higher than, SO_4^{2-} concentrations. In a survey of stream chemistry at a large number of sites in the Smokies, Silsbee and Larson (1982) reported NO_3^- concentrations ranging from 0.2 to 90 $\mu\text{eq/L}$. NO_3^- concentrations were highest at higher elevations and in areas of old-growth spruce-fir forest that have never been logged. In many cases, NO_3^- concentrations in streams of the Smoky Mountains are higher than nitrogen concentrations in deposition, suggesting both that rates of biological nitrogen uptake are low, and that mineralization rates are high (Joslin et al, 1987). Unfortunately, few data are available to suggest the original source of nitrogen now being mineralized in this region. Unless nitrogen fixation rates have been historically quite high, at least some of the NO_3^- now being leaked from watersheds in the Smokies must have originated as atmospheric deposition. The data of Silsbee and Larson (1982) suggest strongly that forest maturation is linked to the process of NO_3^- leakage from Great Smoky Mountain watersheds, mineralization of soil nitrogen appears to be high only in old-growth forests (Elwood et al, 1991).

In Canada, the influence of NO_3^- on episodic acidification is less universal. Molot et al (1989) and Driscoll et al (1989a) report on numerous episodic events in 15 streams in the Harp, Dickie, and Plastic lake watersheds. Most of these events were driven by base cation dilution, only one event was dominated by increases in NO_3^- concentration. The authors conclude that NO_3^- plays at least a small role in most episodes, and that NO_3^- increases play a greater role in acidic systems than in nonacidic ones.

Small increases in NO_3^- concentrations during hydrologic events have been recorded at sites in a few remaining areas of North America, including northeastern Georgia (Buell and Peters, 1988), where maximum concentrations were approximately 12 $\mu\text{eq/L}$. Several studies have reported the existence of NO_3^- episodes in the western United States, including the North Cascades (Loranger and Brakke, 1988) and the Sierra Nevada (Melack and Stoddard, 1991). In general, the maximum concentrations of NO_3^- observed in the West are less than 15 $\mu\text{eq/L}$, substantially lower than in most of the eastern United States. Lakes in the mountainous West, however, tend to be much more dilute, and, therefore, more sensitive

to acidic deposition than in the East. Thirty-nine percent of lakes in the Sierra Nevada, for example, have ANC values less than 50 $\mu\text{eq/L}$, as do 26% of the lakes in the Oregon Cascades and 17% of the lakes in the North Cascades (Landers et al., 1987). Combined with base cation dilution and small concentrations of SO_4^{2-} , the NO_3^- increases observed during episodes at Emerald Lake, in the Sierra Nevada, have been sufficient to drive the ANC to zero on two occasions in the past 4 years (Williams and Melack, 1991b). Data from the outflow at Emerald Lake in 1986 and 1987 (Figure 10-32) indicate that minimum ANC values are coincident with maximum concentrations of NO_3^- and diluted base cation concentrations. It should be noted, however, that at no time has the pH of Emerald Lake fallen below 5.5, a level commonly considered the threshold for injury to fish populations, and that ANC values of zero can be caused by base cation dilution alone (a natural process). The state of episodic acidification in the Sierra Nevada (and the rest of the West) remains, therefore, uncertain, because few data exist and the data that are available indicate ANC depressions to a value of 0 $\mu\text{eq/L}$, but not below.

Finally, there are some areas of North America where no significant effect of NO_3^- on episodic acidification has been observed. Morgan and Good (1988) report data on 10 streams in the New Jersey Pine Barrens, and found mean annual NO_3^- greater than 1 $\mu\text{eq/L}$ only in disturbed streams (in residential and agricultural watersheds). Swistock et al. (1989) and Sharpe et al. (1984, 1987, 1989) reported data on episodic acidification of several streams in the Laurel Hill area of southwestern Pennsylvania and found that NO_3^- played only a minor role in stream acidification and fish kills. Baird et al. (1987) examined episodic acidification during snowmelt at Cone Pond, NH, and were unable to detect any NO_3^- in inlet water. Cosby et al. (1991) have examined 7 years of data from two streams in Virginia, and found no evidence of NO_3^- episodes; NO_3^- concentrations are always less than 15 $\mu\text{eq/L}$ in these streams. Swank and Waide (1988) reported data from seven undisturbed watersheds at the Coweeta Hydrologic Laboratory in North Carolina, where the volume-weighted mean concentrations of NO_3^- were less than 1.5 $\mu\text{eq/L}$.

Some broad geographic patterns in the frequency of episodes in the United States are now evident. Acidic episodes driven by NO_3^- are apparently common in the Adirondack and Catskill Mountains of New York, especially during snowmelt, and also occur in at least some streams in other portions of the Northeast (e.g., at Hubbard Brook). Nitrate contributes on a

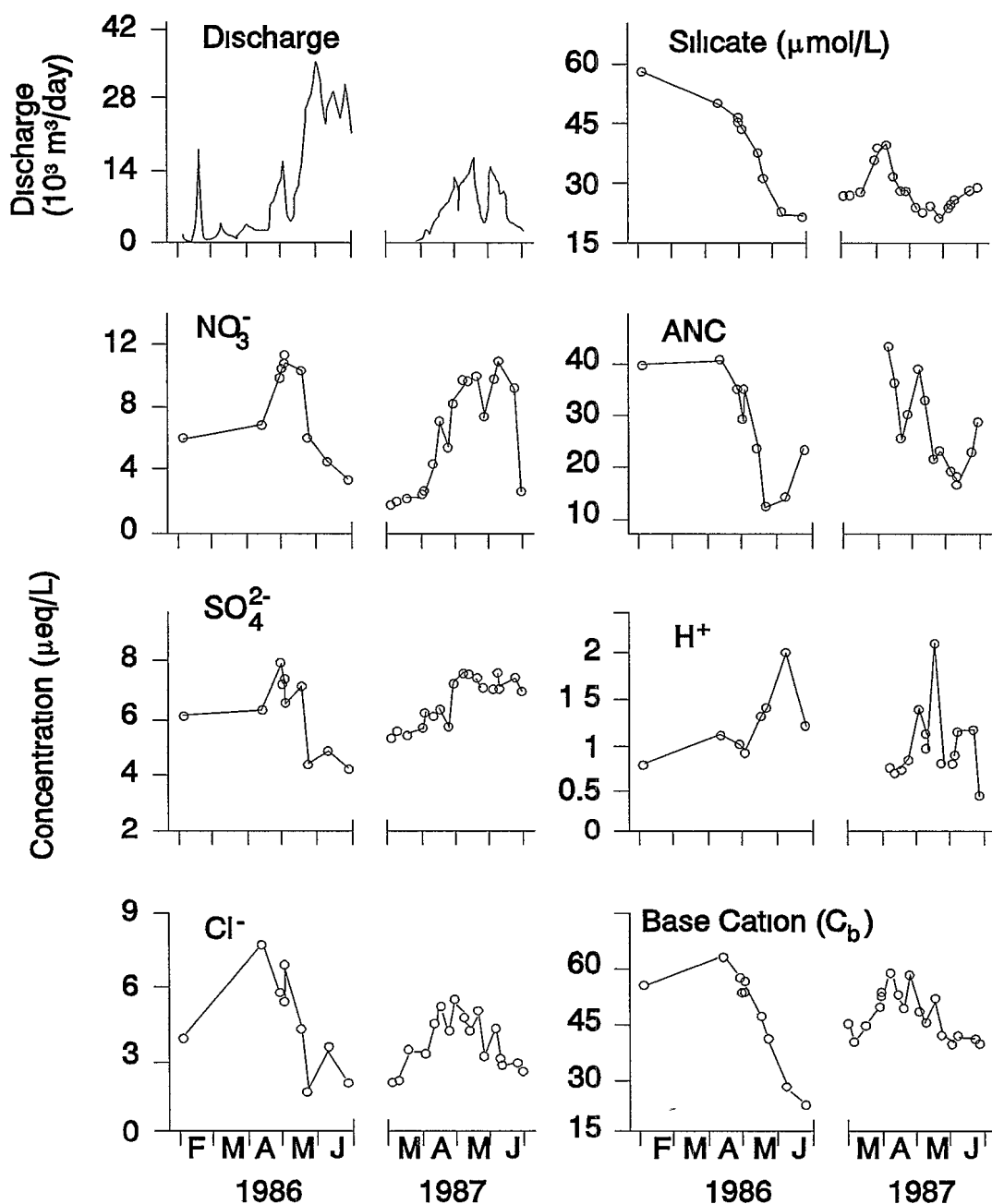


Figure 10-32. Outflow chemistry from two snowmelt seasons (1986 and 1987) at Emerald Lake, a high elevation lake in the Sierra Nevada of California. Nitrate episodes are smaller in magnitude than at sites in the eastern United States, but western lakes may be more susceptible to episodic acidification because of their lower baseline acid-neutralizing capacity than most eastern lakes.

Source Williams and Melack (1991b)

smaller scale to episodes in Ontario, and may play some role in episodic acidification in the western United States. There is little current evidence that NO_3^- episodes are important in the acid-sensitive portions of the southeastern United States outside of the Great Smoky Mountains. We have no information on the importance of NO_3^- in driving episodes in many of the subregions covered by the NSS, including those that exhibited elevated NO_3^- concentrations at spring base flow (e.g., the Valley and Ridge Province and Mid-Atlantic Coastal Plain), because temporally-intensive studies have not been published for these areas.

As was the case with chronic acidification discussed earlier, the mere presence of NO_3^- in acidic episodes should not be construed as proof that nitrogen deposition is having an acidifying effect on surface waters, many other sources of nitrogen exist in watersheds. There is currently little direct evidence linking nitrogen deposition with those acidic episodes that are driven by increases in NO_3^- concentrations, at least partially because the type of data necessary to link deposition to stream water pulses of NO_3^- are extremely difficult to collect. High concentrations of NO_3^- during snowmelt may simply result when NO_3^- stored in the snowpack during the winter months is released while the forest is still dormant. The reduced biological activity typical of the winter months creates less demand for nitrogen, and snowpack NO_3^- may simply run off without entering the nitrogen cycle of the forest or watershed. Several mechanisms, however, will amplify the signal produced by atmospheric deposition of nitrogen to snowpacks. In areas with large snowpacks (e.g., much of the Northeast and all of the mountainous West), ions have been shown to drain from the pack in the early stages of snowmelt, leading to concentrations that are much higher than the average concentration of the snowpack itself (e.g., Jeffries, 1990). This differential elution of acid anions (like NO_3^-) during the initial stages of snowmelt has been shown to be responsible for the elevated NO_3^- concentrations observed in parts of Scandinavia (Johannessen and Henriksen, 1978), Canada (Jeffries, 1990), the Adirondacks (Mollitor and Raynal, 1982), the Midwest (Cadle et al., 1984), and in the Sierra Nevada (Williams and Melack, 1991b). Ammonium deposited to the snowpack as either wet or dry deposition can be subsequently nitrified to NO_3^- in soils, or while still in the snowpack, and can produce NO_3^- concentrations elevated over those calculated from NO_3^- deposition alone (Galloway et al., 1980; Schofield et al., 1985; Cadle et al., 1987; Schaefer and Driscoll, in press). Rates of dry deposition of nitrogen compounds to the snowpack are difficult to measure, but

potentially important, controls on NO_3^- concentrations in snowmelt water (Galloway et al , 1980, Cadle et al , 1987) Jeffries (1990) presents a recent review of snowpack storage and release of pollutants during snowmelt

Some evidence does exist that mechanisms other than atmospheric deposition contribute to NO_3^- episodes, at least on a small scale Rascher et al (1987), for example, have shown that mineralization of organic matter in the soil during the winter months, and subsequent nitrification, contribute substantially to snowmelt NO_3^- concentrations at one site in the Adirondacks Schaefer and Driscoll (in press) have suggested that a similar phenomenon contributes to NO_3^- pulses during snowmelt at 11 Adirondack lakes, and that the contribution from mineralization is greater in low-ANC and acidic lakes Stottlemeyer and Toczydlowski (1990) also report that mineralization contributes to snowmelt NO_3^- at a site on the upper peninsula of Michigan It is not currently known how widespread this phenomenon is Because maximum NO_3^- concentrations are very similar among a large number of streams, Murdoch and Stoddard (in press b) concluded that mineralization probably does not contribute substantially to NO_3^- episodes in the Catskill Mountains due to differences in soil quality, depth, and moisture, mineralization rates are expected to differ among watersheds, and would produce variability in concentrations of NO_3^- among streams There also remains some question of whether NO_3^- produced from mineralization nonetheless results from atmospheric deposition because mineralization recycles nitrogen from leaf litter Mineralization during the winter may simply recycle nitrogen from the leaf fall of the previous autumn, some portion of the nitrogen incorporated into leaves in the summer undoubtedly originates as atmospheric deposition In addition, chronic nitrogen deposition has probably contributed to forest growth in the past (through fertilization), and nitrogen now being mineralized may be the result of such "excess" storage of nitrogen in forest biomass

Earlier in this document (see Section 10 8 2 3) it was suggested that the severity and duration of NO_3^- episodes can be expected to increase as forests become more nitrogen sufficient (see also Driscoll and Schaefer, 1989, Stoddard and Murdoch, 1991) Some of the best information on whether atmospheric deposition is contributing to NO_3^- episodes may, therefore, come from an examination of long-term trends in surface water NO_3^- concentrations

There is some evidence that the occurrence and severity of NO_3^- episodes are increasing. Smith et al (1987a) examined trends in NO_3^- at 383 stream locations in the United States between 1974 and 1981, and reported increases at 167 sites, especially east of the 100th meridian. Many of the increasing trends could be attributed to increased use of fertilizers in agricultural areas, particularly in the Midwest. In addition to agricultural runoff, Smith et al (1987a) identified atmospheric deposition as a major source of NO_3^- in surface waters, particularly in forested basins of the East (e.g., New England and the Mid-Atlantic) and Upper Midwest. Despite widespread use of fertilizers in most of the regions covered by the Smith et al study, they found a high degree of correlation between stream basin yield of NO_3^- and rates of nitrogen deposition.

Historical data are available from 19 large streams in the Catskill Mountains, some of which have been monitored since early in this century (Stoddard and Murdoch, 1991, Stoddard, in review). Trend analyses indicate that NO_3^- concentrations have increased in all of the streams (Table 10-23), with the majority of the increase occurring in the past two decades (1970s and 1980s) (Murdoch and Stoddard, in press b, Stoddard, 1991). These increases are not attributable to other anthropogenic sources of nitrogen, and are similar to trends observed in eight headwaters streams monitored in the 1980s (Murdoch and Stoddard, in press: a, Murdoch and Stoddard, in press b). At four historical Catskill sites where stream discharge data are available, the relationship between NO_3^- concentrations and discharge have changed over the course of the past 4 decades (Figure 10-33). In all cases, the relationships are steeper in the 1980s than in the past, indicating that most of the increase in NO_3^- has occurred at high flows (i.e., episodic NO_3^- concentrations have increased more than base-flow NO_3^- concentrations). The composite average atmospheric NO_2 concentrations have been downward for the past 10 years. Stream concentrations, however, are based on nitrate deposition, not atmospheric concentrations of NO_2 .

Trends in lake water NO_3^- concentrations that are similar to the Catskill stream trends have been reported for Adirondack lakes (Driscoll and Van Dreaseon, in press, Table 10-24). Nine out of 17 Adirondack lakes exhibited significant increases in NO_3^- concentrations, whereas only 1 exhibited a significant decrease (Table 10-24). It is not statistically possible to determine whether episodic NO_3^- concentrations are mostly responsible for the trends in Adirondack lakes because the data record is short (1982 to 1989). Plots of temporal NO_3^-

TABLE 10-23. SLOPES OF NITRATE TRENDS ($\mu\text{eq/L/year}$) IN CATSKILL STREAMS BEFORE 1945, BETWEEN 1945 AND 1970, AND BETWEEN 1970 AND 1990. SLOPES FOR EACH PERIOD ARE CALCULATED FROM BEST-FIT REGRESSION LINES (ANALYSIS OF COVARIANCE ON RANKS, SEE TEXT FOR DETAILS) FITTED TO DATA FROM THE ENTIRE PERIOD OF RECORD. ALL TRENDS ARE SIGNIFICANT AT P LESS THAN 0.05. MEDIAN VALUES AND SAMPLE SIZES FOR EACH PERIOD ARE GIVEN IN PARENTHESES. [-- = Data insufficient for analysis.]

| Site | Change in Nitrate Concentration | | |
|--|---------------------------------|------------------------|------------------------|
| | Before 1945 | 1945-1970 | Between 1970 and 1990 |
| Batavia Kill | +0 24 (11, n = 235) | +0 21 | +0 28 (21, n = 70) |
| Bear Kill above Grand Gorge ^a | -- | -- (27, n = 9) | +0 70 (38, n = 92) |
| Bear Kill above Hardenbergh Falls | +0 34 (18, n = 253) | -- | -- |
| Beaver Kill ^b | +0 05 (4, n = 270) | +0 10 | +1 76 (14, n = 10) |
| Birch Creek above Pine Hill | -- | +0 60 (4, n = 12) | +2 68 (16, n = 75) |
| Birch Creek at Pine Hill | -0 01 (11, n = 287) | +0 68 (6, n = 11) | +0 73 (19, n = 63) |
| Bush Kill | +0 11 (4, n = 235) | +0 00 (7, n = 248) | +2 28 (19, n = 94) |
| Bushnellville Creek ^b | +0 04 (4, n = 267) | +0 25 | +1 57 (17, n = 10) |
| Esopus Creek above Big Indian | +0 08 (4, n = 246) | -- | -- |
| Esopus Creek below Big Indian | -0 16 (7, n = 59) | -0 01 (7, n = 64) | +1 98 (21, n = 93) |
| Esopus Creek at Coldbrook | +0 24 (7, n = 352) | -0 08 (11, n = 784) | +2 00 (19, n = 886) |
| Little Beaver Kill ^b | +0 00 (4, n = 268) | +0 01 | +0 85 (5, n = 10) |
| Manor Kill | -0 12 (11, n = 251) | -0 55 (14, n = 306) | +0 97 (17, n = 96) |
| Neversink River | -- | +0 33 (7, n = 185) | +1 28 (14, n = 104) |
| Rondout Creek | -- | +0 00 (7, n = 12) | +1 79 (8, n = 43) |
| Schoharie Creek at Prattsville | +0 64 (7, n = 238) | -0 13 (14, n = 712) | +1 93 (21, n = 805) |
| Stony Clove Creek ^b | -0 00 (4, n = 272) | +0 08 | +3 77 (24, n = 10) |
| West Kill | +0 19 (7, n = 227) | -- | -- |
| Woodland Creek ^b | +0 02 (4, n = 272) | +0 08 | +3 95 (25, n = 10) |

^aData available for fewer than 2 years in one or more time periods at this site. Trends were not calculated during these time periods at this site, but median values and sample sizes are listed.

^bData for these sites are available only for periods before 1945 and from 1977 to 1979. Trends reported for the periods of missing data are based on regression lines for the entire data set, median values cannot be listed.

Source: Murdoch and Stoddard (in press). ^b

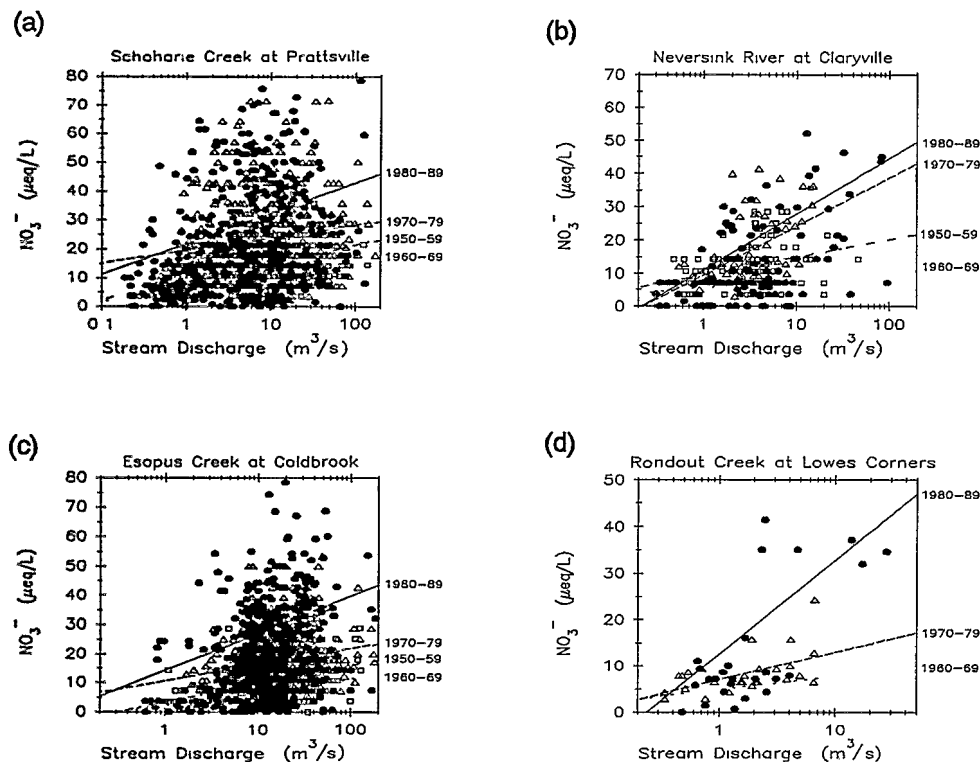


Figure 10-33. Relationship between nitrate concentration and stream discharge for four Catskill streams during four most recent decades. (a) Schoharie Creek at Prattsville, (b) Neversink River at Claryville, (c) Rondout Creek at Lowes Corners, and (d) Esopus Creek at Coldbrook. Regression lines for each decade are from least-squares regression of concentration on the log of stream discharge, and all regressions are significant ($p < 0.05$). All sites indicate that nitrate concentrations at high discharges are higher in the 1970s and 1980s than in previous decades.

Source: Murdoch and Stoddard (in press b)

patterns, however, suggest that base-flow values are relatively unchanged, whereas spring values are increasing (Figure 10-34)

A cautionary note in the interpretation of long-term nitrogen trends is introduced by examination of long-term data from streams at the Hubbard Brook Experimental Forest (HBEF). Data from control Watershed #6 through 1977 suggested a strongly increasing trend in NO_3^- (Schindler, 1987) and have been used to suggest that the HBEF watersheds are

**TABLE 10-24. TRENDS IN NITRATE CONCENTRATIONS FOR ADIRONDACK
LONG-TERM MONITORING LAKES. SLOPES ARE CALCULATED FROM
BEST-FIT REGRESSION LINES (USING ANCOVA ON RANKS)
FITTED TO DATA**

| Lake Name | n ^a | Change in NO ₃ ⁻ (μeq/L/year) ^b | p ^c |
|------------------|----------------|---|----------------|
| Arbutus Lake | 96 | +1 05 | <0 0001 |
| Barnes Lake | 51 | +0 03 | 0 69 |
| Big Moose Lake | 105 | +0 16 | 0 36 |
| Black Lake | 104 | +0 04 | 0 79 |
| Bubb Lake | 88 | -0 11 | 0 53 |
| Cascade Lake | 105 | -0 50 | 0 04 |
| Clear Pond | 104 | +0 51 | <0 0001 |
| Constable Pond | 106 | +1 26 | 0 0003 |
| Dart Lake | 88 | +0 34 | 0 07 |
| Heart Lake | 103 | +0 88 | <0 0001 |
| Lake Rondaxe | 88 | +0 18 | 0 04 |
| Little Echo Pond | 84 | +0 01 | 0 12 |
| Moss Lake | 105 | 0 00 | 0 94 |
| Otter Pond | 93 | +1 50 | <0.0001 |
| Squash Pond | 100 | +1 14 | 0 08 |
| West Pond | 106 | +0 09 | 0 56 |
| Windfall Lake | 88 | 0 14 | 0 82 |

^aNumber of individual observations, the period of record for most sites is from June 1982 to August 1989

^bSlope of analysis of covariance (ANCOVA) model Positive slope indicates an increase in nitrate ions (NO₃⁻), negative number indicates decrease

^cSignificance of regression coefficient for date in ANCOVA model

Source Loftis et al (1989), Driscoll and Van Dreaseon (in press)

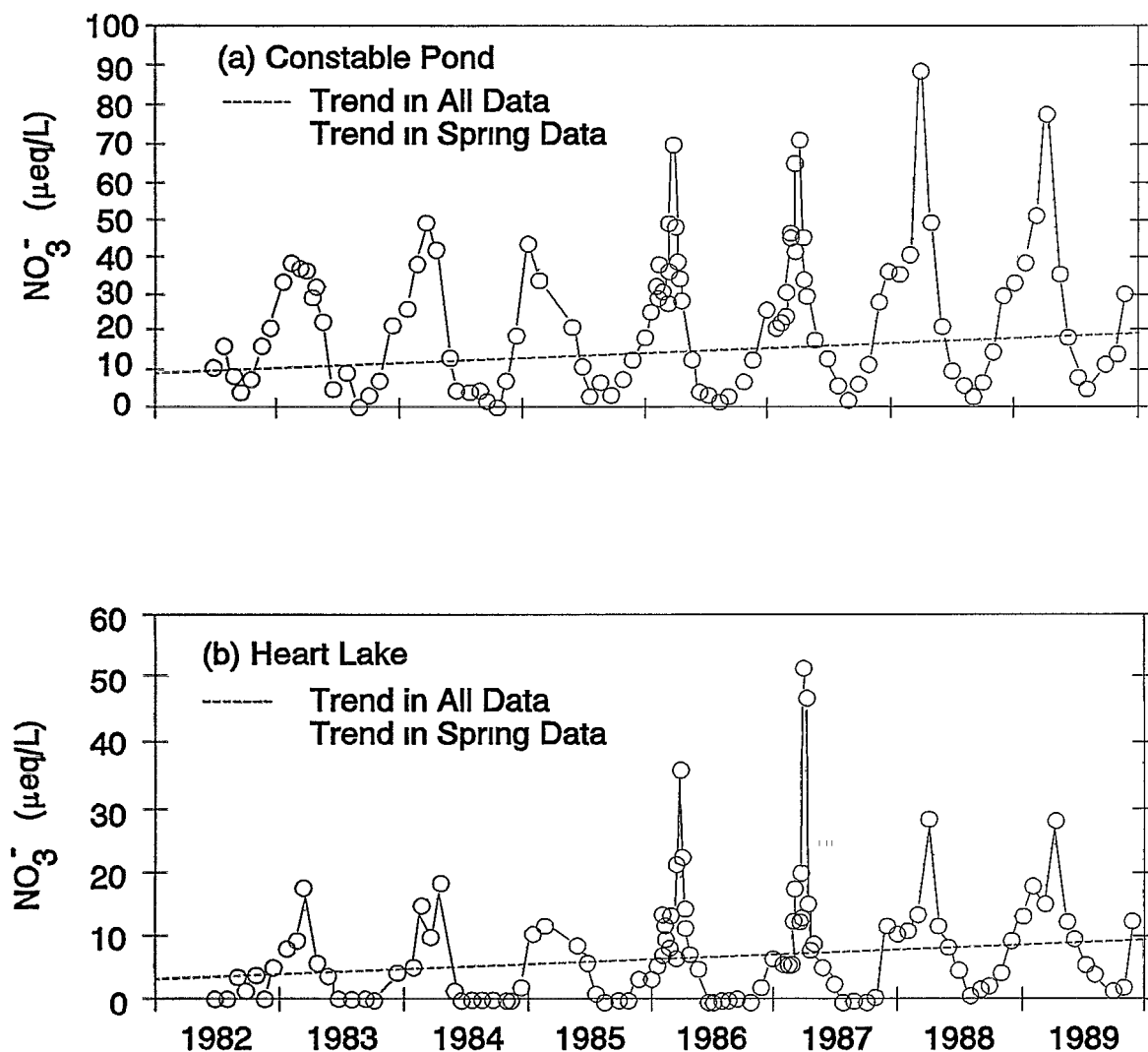


Figure 10-34. Temporal patterns in lake water nitrate concentration for two Adirondack lakes: (a) Constable Pond, and (b) Heart Lake. Both sites exhibit increasing trends in nitrate ion (Table 10-24). The strongly seasonal behavior of nitrate in these lakes suggests that most of the increase has occurred in spring episodic nitrate concentrations.

Source Driscoll and Van Dreason (in press)

undergoing nitrogen saturation (Agren and Bosatta, 1988). Examination of the entire 23-year record (1965 to 1983) from Watershed #6, however, shows no long-term trend (Likens, 1985; Driscoll et al, 1989a) and emphasizes the importance of examining nitrogen processes

in a truly long-term context. Pools of nitrogen associated with soils and forests at HBEF, and elsewhere, are very large (ca 340,000 mol/ha at HBEF, up to 520,000 mol/ha at other sites in the eastern United States, Federer et al , 1989) and long-lived (the turnover rate for nitrogen at HBEF is estimated at 80 years), small changes in the long-term cycling of nitrogen within this system will have profound effects on stream water chemistry (Driscoll et al , 1989a). Although the data reported here for the Catskills can be considered truly long-term (up to 65 years of record), data for the Adirondacks (Driscoll and Van Dreaseon, in press) and other areas of the United States (Smith et al , 1987a) span only 1 to 2 decades, and should be interpreted with caution.

Many of the data discussed above suggest that NO_3^- episodes are more severe now than they were in the past. These surface water nitrogen increases have occurred at a time when nitrogen deposition has been relatively unchanged in the northeastern United States (Husar, 1986, Simpson and Olsen, 1990, Bowersox et al , 1990). If we accept the idea that an increase in the occurrence of NO_3^- episodes is evidence that nitrogen saturation of watersheds is progressing, then current data suggest that current levels of nitrogen deposition (5 to 10 kg/ha/year) are too high for the long-term health of aquatic systems in the Adirondacks, the Catskills, and possibly elsewhere in the Northeast. It is important to note that this supposition is dependent on our acceptance of NO_3^- episodes as evidence of nitrogen saturation. At this point, no measurements of changes in nitrogen cycling have been made to support this.

Similar logic would suggest that levels of nitrogen deposition in the Sierra Nevada (ca 2 kg/ha/year) may be at the upper limit of the levels that would be protective of the long-term health of sensitive, high elevation aquatic systems in the West. The discrepancy between the levels of nitrogen deposition that produce signs of nitrogen saturation in the Northeast and the West is a good illustration of the need to set deposition levels in terms of a "critical load" to specific systems. The deposition levels measured in the eastern and western United States are within the range of nitrogen critical loads (3 to 14 kg/ha/year) suggested by European work in regions of silicate soils of varying sensitivity (Schulze et al , 1989). The Northeast, because of deeper soils and aggrading forests, may be able to absorb higher rates of deposition without serious damage than areas of the mountainous West, where soils are thin and forests are often absent. The abilities of these regions to absorb nitrogen is

a function of the capacities of their watersheds to retain nitrogen. Because these capacities differ from one region to another, the critical loads of nitrogen that will produce signs of degradation also vary from region to region. These differences are at the heart of the critical loads concept of setting deposition limits.

10.8.4 The Effects of Nitrogen Deposition on Eutrophication

The term "eutrophy" generally refers to a state of nutrient enrichment (Wetzel, 1983), but is commonly used to refer to conditions of increased algal biomass and productivity, presence of nuisance algal populations, and a decrease in oxygen availability for heterotrophic organisms. Eutrophication is the process whereby lakes, estuaries, and marine systems progress toward a state of eutrophy. In lakes, eutrophication is often considered to be a natural process, progressing gradually over the long-term evolution of lakes. The process can be significantly accelerated by the additional input of nutrients from anthropogenic sources. The subject of eutrophication has been extensively reviewed by Hutchinson (1973), the National Research Council (1969), and Likens (1972).

Establishing a link between nitrogen deposition and the eutrophication of aquatic systems depends on a determination of two key conditions. The first condition is that the productivity of the system is limited by nitrogen availability. Our current concept of nutrient limitation stems from Liebig's Law of the Minimum (Von Liebig, 1840), which can be paraphrased to suggest that, at any single point in time, ecosystem productivity will be limited by whatever necessary environmental element is in shortest supply. When that necessary environmental element is nitrogen, then the system can be said to be nitrogen limited. The second condition is that nitrogen deposition be a major source of nitrogen to the system. In many cases, the supply of nitrogen from deposition is minor when compared to other anthropogenic sources, such as pollution from either point or nonpoint sources.

10.8.4.1 Freshwater Eutrophication

It is generally accepted that the productivity of fresh waters is limited by the availability of phosphorus, rather than the availability of nitrogen (reviewed by Hecky and Kilham, 1988). Although conditions of nitrogen limitation do occur in freshwater systems (discussed below), they are often either transitory, or the result of high inputs of phosphorus from

anthropogenic sources. At high rates of phosphorus input, phosphorus will cease to be in short supply, and whatever nutrient is then least abundant (often nitrogen) will become limiting. Although additions of nitrogen from deposition will lead to increased productivity in these situations, the primary dysfunction is an excess supply of phosphorus, and these situations will not be discussed further. Often when nitrogen limitation does occur, it is a short-lived phenomenon because nitrogen-deficient conditions favor the growth of blue-green algae (e.g., Smith, 1982), many of which are capable of nitrogen fixation. Because nitrogen-fixing species are not limited by the availability of fixed nitrogen (e.g., NH_4^+ , NO_3^-), they may thrive under conditions where other species are nitrogen limited, and effectively increase rates of nitrogen input to the system by fixation of gaseous nitrogen. High rates of nitrogen fixation may lead to situations where nitrogen can no longer be said to be limiting, and the system often returns to a state of phosphorus limitation. In lakes, nitrogen fixation may be considered a natural mechanism that compensates for deficiencies in nitrogen, and contributes to the long-term evolution and ubiquity of phosphorus limitation (Schindler, 1977).

Nitrogen limitation can occur naturally (i.e., in the absence of anthropogenic phosphorus inputs) in lakes with very low concentrations of both nitrogen and phosphorus, as are common in the western United States and in the Northeast (Suttle and Harrison, 1988). Suttle and Harrison (1988) and Stockner and Shortreed (1988) have suggested that phosphorus concentrations are too low in these systems to allow blue-green algae to thrive because they are poor competitors for phosphorus at very low concentrations (e.g., Schindler et al., 1980, Smith and Kalff, 1982). Thus, diatom communities dominate phytoplankton and periphyton communities in these extremely nutrient-poor (ultraoligotrophic) systems, and rates of nitrogen fixation do not increase because blue-green algae do not become established, regardless of relative nitrogen or phosphorus deficiency. In these systems, the two nutrients are often closely coupled and constant shifts between nitrogen and phosphorus deficiency may occur without obvious changes in community structure. In these situations, additional loading of nitrogen from anthropogenic deposition is likely to have only a small effect on primary productivity because the system quickly becomes phosphorus limited. In a literature survey of 62 separate nutrient limitation studies in lakes, Elser et al. (1990) found that simultaneous additions of nitrogen and phosphorus produced the largest growth response

in 82% of the experiments. These results underline the likelihood that a lake limited by one nutrient may quickly become limited by another if the lake becomes enriched with the original limiting nutrient.

Estimations of nutrient limitation in lake ecosystems follow three major lines of reasoning: (1) evidence from ambient nutrient concentrations and the nutritional needs of algae, (2) evidence from bioassay experiments at various scales, and (3) evidence from nutrient dynamics and input/output studies (Hecky and Kilham, 1988, Howarth, 1988).

Much of the acceptance of the idea that freshwater lakes are primarily phosphorus limited stems from the close correlations between phosphorus concentrations and lake productivity or algal biomass (usually measured as chlorophyll concentration) that have been observed in a large number of lake studies (e.g., Dillon and Rigler, 1974, Schindler, 1977, 1978, reviewed by Reynolds, 1984, Peters, 1986). More recently, researchers have begun to question the ubiquity of the phosphorus-chlorophyll relationship, and to identify some of the factors that lead to the large variability observed in this relationship in nature (e.g., Smith and Shapiro, 1981, Smith, 1982, Pace, 1984, Hoyer and Jones, 1983, Prairie et al., 1989). Notably, researchers have found that the relationship is not linear, as previously supposed, but sigmoidal (McCauley et al., 1989), and that the slope of the relationship is significantly affected by nitrogen concentrations, particularly at high concentrations of phosphorus ($> 10 \mu\text{eq/L}$) that are likely to be caused by anthropogenic inputs. McCauley et al. (1989) found that nitrogen had little effect on the phosphorus-chlorophyll relationship at low concentrations of phosphorus. This effect is expected in nutrient-poor lakes, where the primary effect of nitrogen additions would be to push lakes into a phosphorus-deficient condition.

Arguments based on ambient nutrient concentrations stem from the early work of Redfield (1934), who examined the concentrations of nutrients within the cells of nutrient-sufficient algae from marine systems worldwide, and found surprisingly consistent results for the ratio of carbon to nitrogen to phosphorus concentrations (106:16:1), deviations from these ratios are taken to be evidence that one nutrient or another is limiting to algal growth (e.g., nitrogen: phosphorus [N:P] ratio values below 16:1 suggest nitrogen limitation, values above 16:1 suggest phosphorus limitation). Because the relative supply rates of phosphorus and nitrogen will determine whether one or the other nutrient is in short supply, it has been

suggested that the ratio of the two nutrients (i.e., total nitrogen to total phosphorus) can be used as an index of nutrient limitation (Chiaudani and Vighi, 1974, Rhee, 1978, Schindler, 1976, 1977, 1978). Various researchers have extended interpretation of the Redfield ratio to include ambient nutrient concentrations in water (Redfield's original work was with intracellular concentrations), and applied the nutrient ratio criteria to waters supplying lakes to determine the likely limiting conditions that these waters will produce (e.g., Schindler, 1977, Smith and Shapiro, 1981, Prairie et al., 1989). This method has the potential to illustrate regional patterns and has gained some support from the results of bioassay experiments (see below). This idea has been refined recently to exclude from the ratio those forms of nitrogen and phosphorus that are not biologically available (e.g., especially organic forms of nitrogen), with the result that good predictions of nutrient limitation can now be made from ratios of total dissolved inorganic nitrogen (DIN) to total phosphorus (TP) (Morris and Lewis, 1988).

Morris and Lewis (1988) conducted nutrient addition bioassays on natural assemblages of phytoplankton from many lakes, and compared their results to DIN:TP values measured in the lakes at the same time as the experiments were conducted. They found that lakes with DIN:TP values less than 9 (using molar concentrations) could be limited by either nitrogen or phosphorus (often additions of both nutrients were required to stimulate growth), whereas lakes with DIN:TP values less than 2 were always limited by nitrogen. The discrepancy between the 16:1 Redfield ratio and the 2:1 ratio suggested by Morris and Lewis (1988) may result from measuring ambient, rather than cellular, nutrient concentrations and from the variety of critical nitrogen:phosphorus (N:P) ratios exhibited by different species in nature (Suttle and Harrison, 1988).

If a critical DIN:TP value less than 2 is applied to lakes from the Eastern Lake Survey (Linthurst et al., 1986) and Western Lake Survey (Landers et al., 1987), it is possible to estimate the number of nitrogen-limited lakes in some regions of the United States (Table 10-25). Lakes with total phosphorus concentrations greater than $2.0 \mu\text{eq/L}$ have been excluded from this analysis because many of them may have experienced anthropogenic inputs of phosphorus (Vollenweider, 1968, Wetzel, 1983). This test is, therefore, a conservative one for nitrogen limitation, both because the DIN:TP value chosen (< 2) is a conservative measure of nitrogen limitation (Morris and Lewis, 1988) and because some

TABLE 10-25. ESTIMATED NUMBER AND PROPORTION OF NITROGEN-LIMITED LAKES IN SUBREGIONS OF THE UNITED STATES SAMPLED BY THE NATIONAL SURFACE WATER SURVEY. ESTIMATES ARE BASED ON MOLAR RATIOS OF TOTAL INORGANIC NITROGEN CONCENTRATIONS (NITRATE + AMMONIUM) TO TOTAL PHOSPHORUS CONCENTRATIONS

| Subregion | Number of Lakes in Subregion | Estimated Number of Nitrogen- Limited Lakes | Proportion of Population Nitrogen-Limited (%) |
|--|------------------------------------|---|---|
| <u>Eastern Lake Survey^a</u> | | | |
| Adirondacks (1A) | 1,684 | 16 4 | 1 0 |
| Poconos/Catskills (1B) | 1,986 | 228 5 | 11 5 |
| Central New England (1C) | 2,003 | 54 9 | 2 7 |
| Southern New England (1D) | 2,667 | 144.7 | 5 4 |
| Northern New England (1E) | 2,388 | 91 3 | 3 8 |
| Northeastern Minnesota (2A) | 2,132 | 316 2 | 14 8 |
| Upper Peninsula, Michigan (2B) | 1,698 | 305 8 | 18 0 |
| Northcentral Wisconsin (2C) | 1,707 | 248 2 | 14 5 |
| Upper Great Lakes Area (2D) | 6,147 | 1345 4 | 21 9 |
| Southern Blue Ridge (3A) | 538 | 11 5 | 2 1 |
| Florida (3B) | 8,053 | 2 5 | 0 0 |
| <u>Western Lake Survey^b</u> | | | |
| California (4A) | 2,806 | 535 8 | 19 1 |
| Pacific Northwest (4B) | 2,200 | 609 1 | 27 7 |
| Northern Rockies (4C) | 3,335 | 739 9 | 22 2 |
| Central Rockies (4D) | 2,970 | 788 7 | 26 6 |
| Southern Rockies (4E) | 2,195 | 455 2 | 20 7 |

^aData from Kanciruk et al. (1986), excluding lakes with total phosphorus > 2 $\mu\text{mol/L}$

^bData from Eilers et al. (1987), excluding lakes with total phosphorus > 2 $\mu\text{mol/L}$

lakes with naturally high concentrations of phosphorus may be excluded, these lakes are more likely to be nitrogen-limited than lakes with low phosphorus concentrations. The proportions of lakes that can be considered nitrogen-limited vary widely from region to region, with the greatest number being found, as expected, in the West. The highest

proportion was found in the Pacific Northwest (27.7% of lakes exhibited low DIN:TP ratios), but all subregions of the West contained substantial numbers of nitrogen-limited lakes. The smallest proportions were found in the Southeast (2.5% of the lakes in the entire region exhibited low DIN:TP ratios) and the Northeast (5%). One surprise in this analysis is the number of lakes in the Upper Midwest that appear to be nitrogen-limited, taken as a whole, this region had 19% of its lakes with DIN:TP ratios less than 1.

A more direct indication of nutrient limitation than is available from nutrient ratios can be gained from bioassay experiments, where a small volume of natural lake water is enclosed and various known concentrations of potentially limiting nutrients are added (e.g., Melack et al., 1982, Setaro and Melack, 1984, Stoddard, 1987b). A growth response (usually measured as an increase in biomass) in treatments containing an added nutrient constitutes evidence of limitation by that nutrient. The results of such experiments are available for only a few selected nutrient-poor lakes, however, and indicate a variety of responses including strong phosphorus limitation (Melack et al., 1987), limitation by phosphorus and Fe (Stoddard, 1987b), simultaneous nitrogen and phosphorus limitation (i.e., the two nutrients are so closely balanced that addition of one alone simply leads to limitation by the other, Gerhart and Likens, 1975, Suttle and Harrison, 1988, Dodds and Prisco, 1990), and limitation primarily by nitrogen (Morris and Lewis, 1988, Goldman, 1988). No clear pattern of nitrogen or phosphorus limitation develops from an examination of these few studies.

The potential for nitrogen deposition to contribute to the eutrophication of freshwater lakes is probably quite limited. Eutrophication by nitrogen inputs will only be a concern in lakes that are chronically nitrogen limited. This condition occurs in some lakes that receive substantial inputs of anthropogenic phosphorus, and in many lakes where both phosphorus and nitrogen are found in low concentrations (e.g., Table 10-25). In the former case, the primary dysfunction of the lakes is an excess supply of phosphorus, and controlling nitrogen deposition would be an ineffective method of water quality improvement. In the latter case, the potential for eutrophication by nitrogen addition (e.g., from deposition) is limited by low phosphorus concentrations, additions of nitrogen to these systems would soon lead to nitrogen-sufficient, and phosphorus-deficient, conditions. Increases in nitrogen deposition to some of the regions in Table 10-24 would probably lead to measurable increases in algal

biomass in those lakes with low DIN TP ratios and substantial total phosphorus concentrations, but the number of lakes that meet these criteria is likely to be quite small

10.8.4.2 Estuaries and Coastal Waters

Estuarine and coastal water ecosystems exist at the transition between freshwater systems and the open ocean. These transition zones share some characteristics with both freshwater and marine systems, but they also have some unique properties that lead to different responses to NO_x deposition and a correspondingly different set of concerns. They are at the end of a long series of nitrogen transport and transformation processes involving interactions with vegetation, soils, groundwater, small streams, lakes, and rivers. At each step in this series, the processes vary temporally and spatially and may be subject to a variety of human influences. This transition zone integrates complex and fluctuating processes that are distributed over what are sometimes very large watersheds.

The transition zones between fresh- and saltwater systems are subject to natural processes that are not observed elsewhere in aquatic systems, such as tidal flows and salinity changes. They are also subject to substantial human influence. Estuaries provided natural ports and are among the most productive ecosystems on the planet (Begon et al., 1986). Thus, they became an obvious location for cities, with accompanying demands for wastewater disposal. The history of human use of estuaries and lands around estuaries make it more difficult to isolate the effects of a particular anthropogenic contaminant on ecosystem characteristics. The conservative approach used above to assess the impact of nitrogen deposition on freshwater eutrophication (excluding all systems with anthropogenic impacts other than atmospheric deposition) is not possible for estuaries and coastal waters, all estuarine systems, and most coastal waters, have been subjected to human impacts, often for several centuries.

Estuaries are bodies of water, more or less isolated from the rest of the ocean, where fresh water and salt water mix. This generally produces a salinity gradient, and often leads to stratification of water, with the heavier salt water below a layer of fresh water. Estuaries are also subject to tidal effects and may be strongly influenced by river flows. In combination, these forces tend to produce quite complex water circulation patterns with significant biological consequences. For example, water currents within Chesapeake Bay

concentrate and circulate the dinoflagellate *Gyrodinium uncatenum*, which is responsible for red tides in that estuary (Tyler et al , 1982) Circulation patterns within estuaries may also influence patterns of habitat use by fish (e g , Pietrafesa et al , 1986)

Boynton et al (1982) described a classification of estuaries into four categories that were designed to reflect the primary factors influencing algal production and the variability that exists among estuaries

- *Fjords* have deep basin waters and shallow underwater sills connecting them with the sea, providing slow exchange with adjacent sea waters,
- *Lagoons* are shallow, well-mixed, slowly flushed, and only slightly influenced by riverine inputs,
- *Embayments* are deeper than lagoons, often stratified, only slightly influenced by freshwater inputs, and have good exchange with the ocean, and
- *River-Dominated Estuaries* are a more diverse group of systems, all of which exhibit seasonally depressed salinities due to riverine inputs and variable degrees of stratification

The physical and chemical structure of estuaries will strongly shape the movement and transformation of nitrogen compounds Aston (1980) has provided a list of features of estuaries that have a controlling influence on the geochemistry of contaminants and nutrients

- (1) The tidal mixing of fresh and sea waters on a semidiurnal or diurnal time scale, with corresponding changes in the volume of water in an estuary, produces temporal changes in the contributions of nutrients and dissolved gases from marine and freshwater sources For example, estuaries are generally enriched in nutrients relative to ocean waters due to the local influences of land drainage and often pollution
- (2) The circulation, and especially the stratification, of some estuaries can create vertical and horizontal variations of the concentrations of nutrients and dissolved gases within an estuary
- (3) Estuarine topography may give rise to particularly restricted circulations (e g , in fjords, where the mixing of external sea water with the estuarine waters is greatly reduced), and the restricted mixing leads to unusual chemical environments (e g , oxygen-deficient waters)
- (4) The circulation patterns in coastal waters and estuaries lead to the deposition of various types of sedimentary material The deposition and resuspension of sediments may

influence the budgets of dissolved constituents, including nutrients and gases, in estuarine waters

- (5) Chemical reactions occurring during the mixing of river water with sea water may lead to the removal or addition of the dissolved nutrients. Also, the changes in temperature and salinity during estuarine mixing influence the solubility of dissolved gases, and thus influence their removal or addition in an estuary
- (6) Biological production and metabolism have significant influences on the occurrence and distribution of nutrients and some gases (e.g., CO₂ and oxygen) in estuarine waters. The biological communities in estuaries tend to be species-poor because few species are able to tolerate the extremes in environment to which they are exposed. What species do thrive, however, are often productive

In fact, estuaries may be extremely productive. Fisheries yields in estuaries are higher per unit area than in lakes (Nixon, 1988). This appears not to be related to primary production, but rather to the efficiency of utilization of the primary production. The input of nutrients from outside the ecosystem may be a major determinant of overall fisheries production levels (Day et al., 1982). The economic importance of estuaries may be simply indicated by McHugh's (1976) estimate that in 1970, 69% (by weight) of fish landings in the United States were estuary dependent.

Estuaries and coastal waters receive substantial amounts of weathered material (and anthropogenic inputs) from terrestrial ecosystems and from exchange with sea water. As a result, they tend to be very well buffered, acidification is not a concern in any of these areas. The same load of weathered material and anthropogenic inputs that makes estuaries and coastal areas insensitive to acidification, however, makes them very prone to the effects of eutrophication. Eutrophication of these areas has some very specific and damaging consequences, especially the creation of anoxic bottom waters, blooms of nuisance algae, and replacement of economically important species by less-desirable ones (e.g., Mearns et al., 1982; Jaworski, 1981). Eutrophication, for example, has been suggested as the causal factor in the disappearance of the striped bass (*Morone saxatilis*) fishery in Chesapeake Bay (Price et al., 1985), the increasing spatial extent of anoxic bottom waters during the summer season is the proposed mechanism (e.g., Officer et al., 1984). Anoxia is also thought to have had disastrous effects on surf clams (*Spisula solidissima*) in the New York Bight (Swanson and Parker, 1988) and the blue crab (*Callinectes sapidus*) habitat in Chesapeake Bay (Officer et al., 1984). In 1971, blooms of the red tide dinoflagellate *Ptychodiscus brevis* in the Gulf

of Mexico were responsible for the deaths of approximately 100 tons of fish daily, the high nutrient concentrations typical of eutrophic conditions have been linked to many blooms of nuisance algae (Paerl, 1988)

Establishing a link between nitrogen deposition and the eutrophication of estuaries and coastal waters depends on a determination (as it does in fresh water—see above) of two key conditions. The first condition is that the productivity of these systems is limited by nitrogen availability. The second condition is that nitrogen deposition be a major source of nitrogen to the system. In many cases, the supply of nitrogen from deposition is minor when compared to other anthropogenic sources, such as pollution from either point or nonpoint sources.

Few topics in aquatic biology have received as much attention in the past decade as the debate over whether estuarine and coastal ecosystems are limited by nitrogen, phosphorus, or some other factor (reviewed by Hecky and Kilham, 1988). In a seminal paper published in 1971, Ryther and Dunstan (1971) used evidence of ambient nutrient concentrations and the results of bioassay experiments to conclude that nitrogen limited the productivity of waters along the south shore of Long Island and in the New York Bight. They noted that, during blooms of algae in these areas, inorganic nitrogen concentrations often decreased to levels below detection, whereas inorganic concentrations of phosphorus remained high. From this evidence, they deduced that phosphorus could not be a limiting factor, but that nitrogen could be. They conducted bioassay experiments, suspending in small bottles single-species cultures of either *Nannochloris atomus* or *Skellatonema costatum*, the two algal species that were dominant in the blooms in each location, in filtered sea water with additions of either ammonium or phosphorus. Ryther and Dunstan (1971) found that both species increased dramatically in ammonium-enriched bottles, but that phosphorus-enriched bottles were no different than controls, and that this response was consistent at a large number of sites throughout the south shore of Long Island and in the New York Bight. They concluded that "nitrogen is the critical limiting factor to algal growth and eutrophication in coastal marine waters" (Ryther and Dustan, 1971).

Since the publication of this influential paper, many researchers have accepted the notion that coastal waters and estuaries are limited primarily by nitrogen (e.g., Boynton et al., 1982, Nixon and Pilson, 1983), to the point where nitrogen limitation in marine

waters, and phosphorus limitation in fresh waters, has become near dogma (Hecky and Kilham, 1988). More recently, some oceanographers have begun to question the ubiquity of nitrogen-limitation in estuarine and coastal marine waters (e.g., Smith, 1984, Howarth, 1988), and it seems clear that evidence for nutrient limitation in these systems must be analyzed on a case-by-case basis. Experiments to confirm widespread nitrogen limitation in estuaries have not been conducted, and nitrogen limitation cannot be assumed to be the rule (Hecky and Kilham, 1988).

Estimations of nutrient limitation in estuaries and coastal marine ecosystems follow the same three major lines of reasoning as arguments about freshwater nutrient limitation (see Section 10.8.4.1). (1) evidence from ambient nutrient concentrations and the nutritional needs of algae, (2) evidence from bioassay experiments at various scales, and (3) evidence from nutrient dynamics and input/output studies (Hecky and Kilham, 1988, Howarth, 1988).

As explained earlier, arguments based on ambient nutrient concentrations stem from the early work of Redfield (1934), who examined the concentrations of nutrients within the cells of nutrient-sufficient algae from marine systems worldwide, and found surprisingly consistent results for the ratio of carbon to nitrogen to phosphorus concentrations (106:16:1, using molar concentrations), deviations from these ratios are taken to be evidence that one nutrient or another is limiting to algal growth (e.g., molar N:P ratio values below 16:1 suggest nitrogen limitation, values above 16:1 suggest phosphorus limitation). Various researchers have extended interpretation of the Redfield ratio to include ambient nutrient concentrations in water (Redfield's original work was with intracellular concentrations), and applied the nutrient ratio criteria to waters supplying estuaries and coastal systems to determine the likely limiting conditions that these waters will produce (e.g., Ryther and Dunstan, 1971, Jaworski, 1981). The biotic response (i.e., biostimulation) is not measured using this approach, but is instead inferred from geochemical principles, in this sense, the nutrient-ratio approach measures potential nutrient limitation rather than actual limitation. Boynton et al. (1982) summarized nutrient ratio information for a number of estuarine systems, these results are repeated in Table 10-26. At the time of maximum primary productivity, a majority of the estuaries they surveyed (22 out of 27) had N:P ratios well below the Redfield ratio and may have been nitrogen limited.

**TABLE 10-26. MOLAR RATIOS OF DISSOLVED INORGANIC NITROGEN
TO DISSOLVED INORGANIC PHOSPHORUS IN A VARIETY OF
ESTUARIES^a**

| Estuary | DIN DIP Ratio at Time of Maximum Productivity | Annual Range in DIN DIP Ratio |
|-----------------------------------|---|----------------------------------|
| Pamlico River, NC | 0.2 | 0-3 |
| Roskeeda Bay, Ireland | 0.3 | 0-1 |
| Narragansett Bay, RI | 0.5 | 0.5-14 |
| Bedford Basin, Nova Scotia | 0.8 | 0.5-8 |
| Beaufort Sound, NC | 1.0 | 0.5-16 |
| Chincoteague Bay, MD | 1.2 | 1-10 |
| Western Wadden Sea, Netherlands | 1.3 | 1.3-120 |
| Eastern Wadden Sea, Netherlands | 1.5 | 1.5-56 |
| Peconic Bay, NY | 1.5 | 1-4 |
| Mid-Patuxent River, MD | 1.8 | 1.8-53 |
| Southeastern Kaneohe Bay, HI | 2.0 | Not reported |
| St. Margarets Bay, Nova Scotia | 0.2 | 1-7 |
| Central Kaneohe Bay, HI | 2.8 | Not reported |
| Long Island Sound, NY | 3.9 | 1-6 |
| Lower San Francisco Bay, CA | 6.0 | 4.5-8.5 |
| Upper San Francisco Bay, CA | 6.0 | 0.5-16 |
| Barataria Bay, LA | 6.2 | 6-16 |
| Victoria Harbor, British Columbia | 6.2 | 6-15 |
| Mid-Chesapeake Bay, MD | 7.6 | 7-225 |
| Duwamish River, WA | 8.5 | 8-16 |
| Upper Patuxent River, MD | 9.2 | 9-61 |
| Baltic Sea | 15 | Not reported |
| Redfield Ratio N:P = 16:1 | | |
| Loch Etive, Scotland | 18 | 12-125 |
| Hudson River, NY | 20 | 16-30 |
| Vostock Bay, U.S.S.R. | 20 | 5-22 |
| Apalachicola Bay, FL | 20 | 5-22 |
| High Venice Lagoon, Italy | 48 | 48-190 |

^aDIN = Dissolved inorganic nitrogen, DIP = Dissolved inorganic phosphorus

^bN:P = Nitrogen phosphorus

Source: Boynton et al. (1982)

The data in Table 10-26, as well as from many other studies, suggest that N:P ratios vary widely within a single system from season to season. D'Elia et al. (1986), for example, report ratios for the Patuxent River estuary that vary from over 20:1 during the winter to less than 1:1 during the summer. This variability suggests that estuarine algae may be limited by different nutrients at different seasons.

The ambient nutrient ratio approach has been criticized widely because it ignores several factors known to be important to algal growth. The use of only inorganic nutrient species in the ratios, for example, has been criticized because many algal species are known to utilize organic forms, especially of phosphorus (Howarth, 1988), the nutrient ratios listed for freshwater systems (see freshwater eutrophication section, above) were based on concentrations of total inorganic nitrogen and total phosphorus because these are thought to be better estimators of the nutrient species actually available to algae (Morris and Lewis, 1988). Algal growth may also be more dependent on the supply rates of nutrients than on their ambient concentrations (Goldman and Glibert, 1982; Healey, 1973), many species of algae may, therefore, not be limited by nutrients whose ambient concentrations are so low as to be undetectable. Broecker and Peng (1982) have echoed the earlier conclusions of Redfield himself (1958) in pointing out that biologically mediated nitrogen fixation, and loss rates of nitrogen from the surface waters of marine ecosystems, interact with terrestrial nutrient inputs and tend to push the N:P ratio in the particulate (i.e., living) fraction of water toward a "geochemically balanced" ratio (i.e., the Redfield ratio of 16:1 [see Section 10.8.4.1]). Thus ratios within the biologically active portion of the ecosystem (particularly the algae) may approach 16:1 despite much lower ratios in the abiotic portion of the ecosystem. Taken as a whole, the evidence for nitrogen limitation from ambient nutrient concentrations in estuaries and coastal waters must be considered equivocal.

A second, and more direct, line of evidence for nutrient limitation in estuaries and coastal waters comes from bioassay experiments. These experiments have been conducted in both freshwater and marine systems at a number of scales from small single-species cultures (Level I experiments), to small enclosures of natural algal assemblages (Level II), to intermediate-sized enclosures (mesocosms) of natural assemblages (Level III), to whole-system (so far largely limited to whole lakes) treatments (Level IV, levels as defined by Hecky and Kilham, 1988). These experiments, therefore, progress along a gradient of

"naturalness" from studies substantially different from the real world (Level I) to those that simulate natural conditions very closely (Levels III and IV). Interpretation of the results of these experiments, therefore, follows the same gradient, with more confidence being placed in the results of studies at the upper (i.e., more natural) end of the gradient (Hecky and Kilham, 1988, Howarth, 1988). The results of Level I experiments on single-species cultures of algae, like the original experiments of Ryther and Dunstan (1971), are especially difficult to interpret because threshold N:P ratios for individual species are known to vary substantially. Suttle and Harrison (1988) report limitation at ratios from 7:1 to 45:1 for single species. At all scales, the experimental procedure used for experimental nutrient additions is fairly similar, with various nutrients being added either alone or in combination, and the growth in treated enclosures being compared to growth in control enclosures.

Level I and Level II experiments have been conducted in a wide variety of estuaries and coastal waters (e.g., Thomas, 1970, Ryther and Dunstan, 1971, Vince and Valiela, 1973, Smayda, 1974, Goldman, 1976, Graneli, 1978) and often suggest nitrogen limitation. Two studies have suggested seasonal changes from nitrogen limitation to phosphorus limitation (D'Elia et al., 1986, McComb et al., 1981), in both cases, nitrogen-deficient conditions were found during the peak of annual productivity in the summer. The results of experiments at Levels I and II suggest that nitrogen limitation is at least a common, if not ubiquitous, phenomenon in coastal and estuarine waters. This interpretation has been challenged by Smith (1984) and Hecky and Kilham (1988) because the experiments were conducted at such an unrealistic spatial scale. In particular, Level I and II experiments measured only the short-term response of algae present at the time the experiments were run, they did not allow natural mechanisms such as species replacement and nitrogen fixation to take place.

Only a few examples of Level III bioassays exist for estuarine and coastal ecosystems. The best known of these have been conducted at the Marine Ecosystem Research Laboratory (MERL) at the University of Rhode Island. The MERL tanks are large (13-m^3), relatively deep (5-m) cylinders, with natural sediments and filtered seawater inputs. They are designed to mimic the environment of Narragansett Bay, including the mixing, flushing, temperature, and light regimes (Nixon et al., 1984). In the original experiments conducted in the MERL tanks, nutrients were added with ratios that matched those of sewage entering Narragansett Bay, but at concentrations that ranged from 1 to 32 times those in the bay itself, the

experiments were run for 28 mo. Algal abundance, primarily diatoms, increased with the level of nutrient enrichment, but not on a 1:1 basis. Productivity increased only by a factor of 3.5 in the 32-time treatment, suggesting that something other than nutrients was limiting for at least a portion of the experiment (Oviatt et al., 1986). Oviatt et al. (1989) have suggested that, in treatments with high levels of nutrient enrichment, grazing by zooplankton controlled algal abundances to low levels, and that the upper limit to productivity was set by self-shading in the algal community. Further experiments conducted with varying nutrient ratios suggested that diatoms in the low-nutrient (one-time) treatments were limited by silica, and not by either nitrogen or phosphorus (Doering et al., 1989). Sewage inputs to many estuaries, including Narragansett Bay, are deficient in silica (Officer and Ryther, 1980), and silica concentrations often fall to very low levels during winter diatom blooms in this area (Pratt, 1965). Taken as a whole, the results of the MERL experiments suggest a complex picture for Narragansett Bay, where no nutrient is strongly limiting to algal biomass through much of the year, and where algal abundances during winter blooms are controlled ultimately by the concentrations of silica.

In another Level III bioassay experiment, D'Elia et al. (1986) simulated the environment of the Patuxent River estuary, a tributary to Chesapeake Bay, in 0.5-m³ enclosures. Their results had a strong seasonal component. Supplements of nitrogen, either as NO₃⁻ or as NH₄⁺, stimulated growth during the low-flow, late-summer season. This corresponds to the time period when N:P ratios in the estuary are low (1:1 or lower). Phosphorus additions stimulated growth during the late-winter, high-flow season, when N:P ratios typically exceed 20:1. Peaks in algal abundance occurred in the summer, when anoxic conditions in bottom waters in Chesapeake Bay are common, and when algae appear to be nitrogen-deficient.

Thus far, only one Level IV experiment has been conducted in estuarine waters, and only preliminary results are available. Sewage treatments supplying nutrients to the Himmerfjard basin, a brackish fjord in the Stockholm archipelago on the eastern coast of Sweden, have been deliberately altered to produce varying levels of phosphorus and nitrogen loads since 1983 (Graneli et al., 1990). Between 1983 and 1985, phosphorus removal at the plant was deliberately reduced to produce a 10-fold increase in orthophosphate, and additional sewage inputs were routed into the basin to increase total nitrogen inputs by 30 to

40% At the same time as nutrient manipulations were being carried out, measurements were made of nitrogen cycling in the basin, and algal bioassays were conducted to determine nutrient limitation Preliminary results suggest that nitrogen is limiting at low nutrient concentrations (i.e., typical of near-coastal regions unaffected by anthropogenic inputs), and that limiting nutrients in areas affected by anthropogenic inputs are determined by the supply ratios of nitrogen and phosphorus (Graneli et al., 1990) Because small changes in the supply of either phosphorus or nitrogen in the Himmerfjärd basin have caused changes in the identity of the limiting nutrient (i.e., increases in phosphorus quickly lead to nitrogen limitation, and vice versa), the authors suggest that management of both nitrogen and phosphorus is necessary to reduce eutrophication in the basin

The remaining line of evidence used to infer nutrient limitation in estuarine and coastal marine ecosystems comes from studies of nutrient dynamics, and especially of input/output budgets In many ways, the results of these studies help to integrate the sometimes contradictory results gleaned from studies of nutrient ratios and bioassay experiments at different levels of complexity Smith (1984) summarized the studies conducted on four subtropical bays and concluded that phosphorus is more likely to be limiting in these systems than nitrogen, and that physical factors are often more important than either nutrient Smith noted that in the systems that had high throughputs of water (i.e., embayments according to the Boynton et al. [1982] criteria, see earlier description), incoming ratios of nutrients were matched very closely by the ratios in the outgoing water This suggests that algal growth is having little effect on nutrient levels, and that nutrients do not limit productivity In systems that flush more slowly (i.e., lagoons or fjords in the Boynton et al. [1982] classification), any deficiencies in nitrogen in the incoming water can be made up by nitrogen fixation on the ocean bottom, and phosphorus is, therefore, more likely to be limiting

The question of why nitrogen deficiencies in marine systems are not simply made up by nitrogen fixation, as suggested by Smith (1984), is central to the issue of whether estuaries and coastal waters are primarily limited by nitrogen or not In lakes (see the description in Section 10.8.4.1), conditions of nitrogen deficiency often produce blooms of planktonic blue-green algae, which fix atmospheric nitrogen and act to return the algal community to a condition of nitrogen sufficiency (Schindler, 1977, Flett et al., 1980) Only when N:P ratios are extremely low and blue-green algae are unable to fix enough nitrogen to bring the ratio

up to the Redfield proportions do lakes remain nitrogen limited (Howarth et al , 1988a)

Why, then, doesn't the same phenomenon (nitrogen fixation by blue-green algae) occur in nitrogen-deficient marine systems? A major difference in the biogeochemistry of lakes and estuaries is that nitrogen fixation by free-living algae (phytoplankton) rarely occurs in estuaries, even when the N:P ratios of incoming water suggest severe nitrogen limitation

Howarth et al (1988b), for example, surveyed a large number of estuaries along the Atlantic coast of the United States and found no instances in which nitrogen-fixing blue-green algae made up more than 1% of the algal biomass

A number of explanations for this lack of nitrogen fixation in estuaries have been proposed, including shorter water residence times (faster flushing rates) than lakes, greater turbulence than in lakes, and lower concentrations of micronutrients (especially Fe and molybdenum) needed for the biochemical pathways in nitrogen fixation (Howarth, 1988, Howarth et al , 1988b)

Of these, only the last argument really holds true in a comparison of lakes and estuaries

Howarth and Cole (1985) and Cole et al. (1986) have determined that the high concentrations of sulfate in marine systems interfere with the assimilation of molybdenum by marine algae, and propose that low rates of molybdenum availability are, in turn, limiting to rates of nitrogen fixation in many systems

Molybdenum limitation, however, has not been experimentally demonstrated in many marine environments

In fact, many nutrient addition bioassays conducted in benthic environments have shown that the availability of organic matter and of oxygen-depleted microenvironments tightly control marine microbial nitrogen fixation potentials (Paerl et al , 1987, Paerl and Prufert, 1987).

Because the enzymes needed for nitrogen fixation are readily inactivated by oxygen, rates of fixation may be limited by energy availability (i.e., the supply of carbon reductant) and ambient oxygenation

By and large, nitrogen-deficient marine waters are depleted in readily oxidizable organic matter and are well oxygenated

When high rates of nitrogen fixation do occur in marine systems, they are usually associated with bottom-dwelling (benthic) algae (Howarth, 1988), these habitats are relatively enriched with organic matter and support localized oxygen-depleted microenvironments (Paerl et al , 1987)

Iron is also required for nitrogen fixation, and may limit rates of nitrogen fixation in some freshwater lakes (Wurtsbaugh and Horne, 1983), concentrations of Fe in seawater are often much lower than in fresh water, and although little direct evidence of limitation of nitrogen fixation by low Fe concentrations exists, it is certainly a likely condition (Howarth et al ,

1988b) It is difficult at this point in the debate over marine nitrogen fixation to state anything definitively beyond the fact that nitrogen fixation is not common in marine waters (Carpenter and Capone, 1983, Howarth et al , 1988a) One possible conclusion from the debate among researchers in this field (e g , Howarth et al , 1988b, Paerl et al , 1987) is that planktonic nitrogen fixers may be limited by micronutrient availability, whereas benthic nitrogen fixers are limited by availability of organic carbon and high ambient oxygen levels, but both factors, as well as others, probably operate in both environments Light, for example, appears to play a role in clear, tropical lagoons (Potts and Whitton, 1977, Wiebe et al , 1975) because benthic nitrogen-fixing algae in these environments require light for photosynthesis The presence of benthic nitrogen fixation in Smith's (1984) subtropical lagoons may help explain the apparent contradiction between his predictions of phosphorus limitation and experimental results suggesting nitrogen limitation in slowly flushed systems

Nixon and Pilson (1983) have summarized the results of numerous input/output studies in estuaries and coastal waters and related the inputs of various nutrients to algal biomass Their results for nitrogen are repeated in Figure 10-35 and are supported by a similar analysis conducted by Boynton et al (1982) for algal productivity The relationship between nitrogen inputs and mean algal biomass in marine systems is certainly much weaker than the relationship between phosphorus and biomass in lakes (e g , Schindler, 1978), but is nonetheless suggestive of a general pattern of nitrogen limitation in these systems (Figure 10-35) Seasonal effects on nutrient ratios, grazing by zooplankton, and physical factors such as light, circulation patterns, and turbidity all lend uncertainty to the relationship Perhaps the most important aspect of the relationship is the apparent strong dependence of annual maximum chlorophyll concentrations (Figure 10-35b) on nitrogen inputs ($r^2 = 0.57$, $p < 0.0001$) Many of the most severe impacts of eutrophication are experienced during summer algal blooms, these seem to be more strongly dependent on nitrogen than biomass in other seasons (e g , D'Elia et al , 1986).

In summary, there does seem to be confirmatory evidence of nitrogen limitation in many estuarine and coastal marine ecosystems This conclusion is a general rule, rather than an absolute one, and other limiting factors certainly occur in some locations, and during some seasons In general, ratios of nitrogen to phosphorus in inputs to estuaries and coastal waters are much lower than in lakes (Hecky and Kilham, 1988, Howarth, 1988), and this

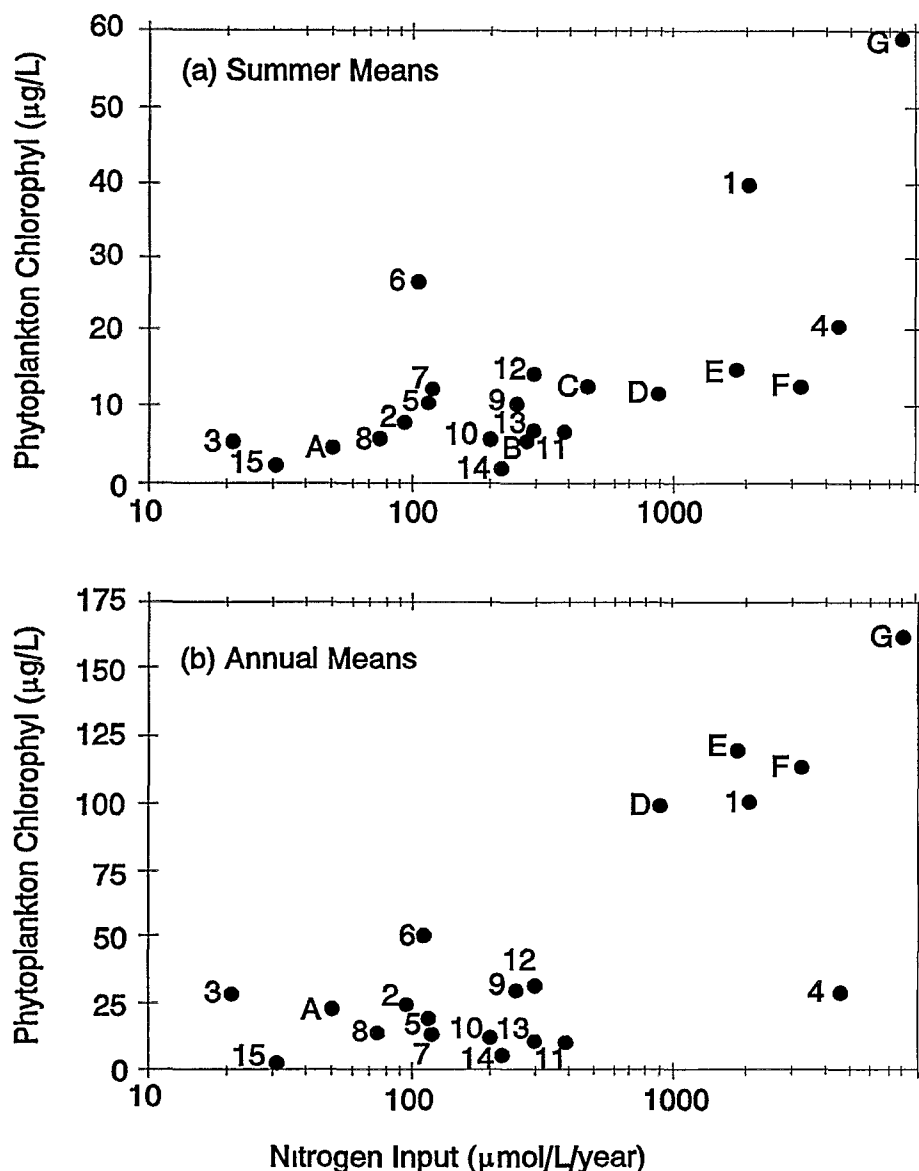


Figure 10-35. Concentrations of (a) mean algal chlorophyll and (b) annual maximum chlorophyll, in the midregion of various estuaries (1 to 15) and in the Marine Ecosystem Research Laboratory experimental ecosystems (A to G) as a function of the input of dissolved inorganic nitrogen. 1 - Providence River estuary, RI; 2 - Narragansett Bay, RI; 3 - Long Island Sound; 4 - Lower New York Bay; 5 - Delaware Bay; 6 - Patuxent River estuary, MD; 7 - Potomac River estuary, MD; 8 - Chesapeake Bay; 9 - Pamlico River estuary, NC; 10 - Apalachicola Bay, FL; 11 - Mobile Bay, AL; 12 - Barataria Bay, LA; 13 - North San Francisco Bay, CA; 15 - Kaneohe Bay, HI. Note change in scale on vertical axis.

Source Nixon and Pilson (1983)

probably contributes strongly to the apparent difference between lakes and marine systems in their nutrient limitation. These low ratios, however, result largely from sewage inputs (Ryther and Dunstan, 1971, Jaworski, 1981, Howarth, 1988), and whether atmospheric deposition of nitrogen contributes to eutrophication in these systems will depend strongly on the relative inputs of nitrogen from these two sources. As stated in the introduction to this section, any question of negative impacts on estuaries and coastal waters from nitrogen deposition depends both on a determination of nitrogen limitation and on a determination that atmospheric deposition is a major contributor of nitrogen to these ecosystems.

Anthropogenic sources of nitrogen to estuaries and coastal waters include point sources (such as sewage plant outfalls), fertilizer and animal wastes in runoff, and atmospheric deposition (predominantly due to NO_x from combustion and ammonium from agricultural activity). Atmospheric deposition may be supplied directly to the surfaces of estuaries or coastal waters or may be supplied indirectly to the watershed and subsequently transported to the coast by river flow. As discussed earlier, nitrogen can be deposited in a variety of forms, two of the contentious issues in determining the impact of NO_x on estuarine ecosystems are estimating the total deposition and the uncertainty in the relative proportion contributed by the different forms, especially between dry and wet deposition (e.g., Fisher et al., 1988a).

Runoff inputs to estuaries may be the most variable of the nitrogen inputs. They vary with watershed area, precipitation rates, land-use patterns (especially the use of fertilizer), and rates of atmospheric deposition. Spring runoff represents a major input of nutrients to estuarine and coastal systems. Runoff inputs vary seasonally (e.g., Jaworski, 1981) and from year to year (e.g., Boynton et al., 1982; Jaworski, 1981). Nitrate inputs to estuaries increase markedly during flooding conditions (Biggs and Cronin, 1981), and are at least partially responsible for the finding that nitrogen is less likely to be limiting in the winter and spring than in the summer (above).

Point sources of nutrients may be particularly important near urbanized areas. Sewage inputs contribute more than half of the inorganic nitrogen content to a number of major estuaries in the United States: Long Island Sound (67%), New York Bay (82%), Raritan Bay (86%), San Francisco Bay (73%), and Delaware Bay (50%) (Nixon and Pilson, 1983).

Natural and anthropogenic sources of nitrogen to coastal waters may result in the same form of nitrogen (e.g., NO_3^-) being transported by the same route (e.g., river input). Their effects will, therefore, be indistinguishable, and it becomes impossible to assign "responsibility" for a problem to a particular source. This has obvious consequences for policy decisions because, for example, there are many possible regulatory actions that could all result in the reduction of nitrate input to a particular estuary. It may be more cost effective, for example, to increase the efficiency of nitrogen removal in sewage treatment than to reduce NO_x emissions, even if NO_3^- inputs from atmospheric deposition are increasing.

The first published attempt to determine the relative importances of nitrogen from deposition, and nitrogen from runoff, was that of Correll and Ford (1982) for the Rhode River estuary, a tributary to the Chesapeake Bay. Correll and Ford assumed in their analysis that all atmospheric nitrogen deposited on the watershed was retained, and that the only atmospheric inputs of nitrogen to the estuary were those that fell directly on the water surface. This estimate should, therefore, be considered a lower limit to the importance of atmospheric deposition because some terrestrial watersheds do show retention capacities lower than 100% (see discussion of nitrogen saturation, above). Correll and Ford (1982) conclude that, on an annual basis, atmospheric and watershed sources of nitrogen to the Rhode River are approximately equal. During the summer and fall, a period when the Chesapeake Bay undergoes substantial anoxia, precipitation inputs of nitrogen may slightly exceed those from watershed runoff. It is important to note that the watershed of the Rhode River estuary is small relative to the estuary itself (the watershed is less than six times the size of the estuary). These results should be extrapolated with caution to situations where watershed sizes may be orders of magnitude larger than those of the waters that drain them. The entire Chesapeake Bay, for example, is approximately one-fifteenth the size of its watershed, and the relative importance of nitrogen falling directly on the water surface would, therefore, be smaller relative to terrestrial inputs.

Paerl (1985) has determined that NO_3^- -enriched rain falling on the waters of Bogue Sound (an embayment), the Continental Slope, and the Gulf Stream (all off the east coast of North Carolina) increased algal biomass as much as fourfold, and that rain falling directly on the ocean surface accounted for as much as 10 to 20% of the volume of water supplied to

these near-coastal areas. More recent work (Paerl et al., 1990) indicates that rainfall additions as low as 0.5% by volume stimulated algal primary production and biomass in these nitrogen-limited waters. Paerl (1985) and Paerl et al. (1990) did not estimate the proportion of the total nitrogen inputs to these areas that entered as precipitation, but they do suggest that algal blooms initiated by direct inputs of nitrogen from large rain storms could be sustained by NO_3^- -enriched runoff from nearby land masses. Terrestrial inputs of nitrogen (from runoff) usually lag rainfall by 4 to 5 days in this region. These studies appear to be unique in showing a direct link between nitrogen deposition and algal productivity, but do not provide enough information to estimate the overall importance of deposition to the maintenance of high algal biomass in these waters.

10.8.4.3 Evidence for Nitrogen Deposition Effects in Estuarine Systems—Case Studies

Complete nitrogen budgets, as well as information on nutrient limitation and seasonal nutrient dynamics, have been compiled for two large estuaries, the Baltic Sea and Chesapeake Bay, and for the Mediterranean Sea. In the case of the Mediterranean, Loye-Pilot et al. (1990) suggest that 50% of the nitrogen load originates as deposition falling directly on the water surface. In the case of the Baltic and Chesapeake, deposition of atmospheric nitrogen has been suggested as a major contributor to the eutrophication of the estuaries (see below). Data for other coastal and estuarine systems are less complete, but similarities between these two systems and other estuarine systems suggest that their results may be more widely applicable. The discussion in this document is limited to these two "case studies," with some speculation about how other estuaries may be related.

The Baltic Sea

The Baltic Sea is perhaps the best-documented available case study of the effects of nitrogen additions in causing estuarine eutrophication. Like many other coastal waters, the Baltic Sea has experienced a rapidly increasing anthropogenic nutrient load; it has been estimated that the supply of nitrogen has increased by a factor of 4, and phosphorus has increased by a factor of 8, since the beginning of the century (Larsson et al., 1985). The first observable changes attributable to eutrophication of the Baltic were declines in the concentration of dissolved oxygen in the 1960s (Rosenberg et al., 1990). Decreased

dissolved oxygen concentrations result when decomposition in deeper waters is enhanced by the increased supply of sedimenting algal cells from the surface water layers to the sediments. In the case of the Baltic, the spring algal blooms that now result from nutrient enrichment consist of large, rapidly sedimenting algal cells, which supply large amounts of organic matter to the sediments for decomposition (Enoksson et al , 1990) Since the 1960s, researchers in the Baltic have documented increases in algal productivity, increased incidence of nuisance algal blooms, and periodic failures and unpredictability in fish and Norway Lobster catches (Fleischer and Stibe, 1989, Rosenberg et al , 1990)

It has now been shown by a number of methods that algal productivity in nearly all areas of the Baltic Sea is limited by nitrogen Nitrogen-to-phosphorus ratios range from 6:1 to 60:1 (Rosenberg et al , 1990), but the higher ratios are only found in the remote, and relatively unimpacted, area of the Bothnian Bay (between Sweden and Finland) Productivity in the spring (the season of highest algal biomass) is fueled by nutrients supplied from deeper waters during spring overturn (Graneli et al , 1990), deep waters are low in nitrogen and high in phosphorus, resulting in N:P ratios near 5 (Rosenberg et al , 1990), suggesting potential nitrogen limitation when deep waters are mixed with surface waters Low N:P ratios in deep water result from denitrification in the deep sediments (Shaffer and Ronner, 1984). Primary productivity measurements in the Kattegat (the portion of the Baltic between Denmark and Sweden) correlate closely with uptake of NO_3^- , but not of phosphate ions (Rydberg et al , 1990) Level II and III nutrient enrichment experiments conducted in near-shore areas of the Baltic, as well as in the Kattegat, indicate nitrogen limitation at most seasons of the year (Graneli et al , 1990) Growth stimulation of algae has also been produced by addition of rain water to experimental enclosures, in amounts as small as 10% of the total volume (Graneli et al , 1990), rain water in the Baltic is enriched in nitrogen, but is phosphorus-poor In portions of the Baltic where freshwater inputs keep the salinity low, blooms of the nitrogen-fixing blue-green alga *Aphanizomenon flos-aquae* are common (Graneli et al , 1990), blue-green algal blooms are common features of nitrogen-limited freshwater lakes (see Section 10.6.4.1), but are usually absent from marine waters

Nitrogen budget estimates indicate that the Baltic Sea as a whole receives 1×10^9 kg/year of nitrogen, of which 3.9×10^8 kg/year (37%) comes directly from atmospheric deposition (Rosenberg et al , 1990) Fleischer and Stibe (1989) report that the

nitrogen flux from agricultural watersheds feeding the Baltic have been decreasing since about 1980, but that the nitrogen contribution from forested watersheds is increasing, they cite both increases in nitrogen deposition and the spread of modern forestry practices as causes for the increase. It should be noted, however, that the Baltic also experiences a substantial phosphorus load from agricultural and urban lands, and that phosphorus inputs may help to maintain nitrogen-limited conditions (Graneli et al., 1990). If the Baltic had received consistent nitrogen additions (e.g., from the atmosphere or from agricultural runoff) in the absence of phosphorus additions, it might well have evolved into a phosphorus-limited system some time ago.

The physical structure of the Baltic Sea, with a shallow sill limiting exchange of water with the North Sea (see the definition of a fjord, above) contributes to the eutrophication of the basin by trapping nutrients in the basin once they reach the deeper waters. Because the larger algal cells that result from nutrient enrichment in the basin provide more nutrients to the deep water through sedimentation, and because only shallow waters have the ability to exchange with the North Sea, it is estimated that less than 10% of nutrients added to the Baltic are exported over the sill to the North Sea (Wulff et al., 1990). Throughout much of the year, especially during the dry months, productivity in the Baltic is maintained by nutrients recycled within the water column (Enoksson et al., 1990). The trapping of nutrients within the basin and recycling of nutrients from deeper waters by circulation patterns suggest that eutrophication of the Baltic is a self-accelerating process (Enoksson et al., 1990), with a long time lag between reductions of inputs and improvements in water quality.

Chesapeake Bay

The most complete attempts to estimate the relative importance of atmospheric deposition to the overall nitrogen budget of an estuary or coastal ecosystem in the United States were completed for Chesapeake Bay by the Environmental Defense Fund (EDF) (Fisher et al., 1988a, Fisher and Oppenheimer, 1991) and by Versar, Inc. (Tyler, 1988) in 1988. Neither of these reports has been published in a peer-reviewed arena, but the issue of atmospheric contributions to the eutrophication of the Chesapeake has been widely discussed.

(and criticized), particularly after the publication of the EDF report, and bears close examination for these reasons

Both reports conclude that atmospheric deposition makes a substantial contribution (25 to 40% of total inputs) to the nitrogen budget of Chesapeake Bay. In both cases, nitrogen budgets for the bay were constructed via a number of steps, each of which involved simplifying assumptions that bear further examination. Both reports calculate inputs from atmospheric deposition to the bay itself (Step #1), atmospheric deposition to the watershed (#2), fertilizer application in the watershed (#3), generation of animal wastes in the watershed (#4), inputs from urban land use (#5), and point source inputs (#6). Once the total inputs to the watershed and bay were estimated, both reports calculated the proportion of the inputs that were retained by the watershed (Step #7) and the proportion that were retained within the rivers and tributaries feeding the bay (#8).

The two reports had different goals, which make their results difficult to compare. The EDF report (Fisher et al., 1988a, Fisher and Oppenheimer, 1991) estimated the proportions of both NO_3^- and NH_4^+ deposition to the total nitrogen budget of the Chesapeake (including all forms of nitrogen, and both base flow and storm flows). The Versar report (Tyler, 1988), on the other hand, estimated only contributions of NO_3^- , because NH_4^+ does not result from the burning of fossil fuels, and excluded base-flow contributions. In addition, the Versar report used a range of values both for the watershed contributions made by each nitrogen source (deposition, fertilizers, etc.) and for the fraction of the inputs retained by the watershed (transfer coefficients). This results in a wide range of budget values for each of the sources, and for the relative importance of NO_3^- deposition to the budget, which complicates any comparison of the results of the two studies. Nonetheless, the two reports used similar methods in developing their budgets, and a combined discussion of the uncertainties involved in each of the steps listed above is warranted.

The results for the two budgets are presented in Table 10-27. Since the publication of these budgets, additional information on such issues as dry deposition and retention of nitrogen by forested watersheds has become available. This new information has been compiled to produce a third "refined" budget, which is also presented in Table 10-27. The assumptions that were used to construct the refined budget are outlined in each of the discussions of individual budgeting steps below.

TABLE 10-27. THREE NITROGEN BUDGETS FOR CHESAPEAKE BAY

| Source of Nitrogen | EDF Budget (kg × 10 ⁸ /year) | | Versar Budget (kg × 10 ⁸ /year) | | Refined Budget (kg × 10 ⁸ /year) | |
|--|--|------------------|---|--------|--|------------------|
| Direct Deposition | | | | | | |
| Nitrate Ions | 0 8 | | 0 7 | | 0 6 | |
| Ammonium Ions | 0 4 | | - ^a | | 0 3 | |
| Nitrogen Load to Bay (from direct deposition) ^b | 1 3 | | 0 7 | | 0 8 | |
| Forests | | | | | | |
| Nitrate Ion Deposition | 9 0 | | 8 4 | | 6 4 | |
| Ammonium Ion Deposition | 4 9 | 80% | - ^a | 95% | 3 5 | 84 6% |
| Watershed Retention | 0 8 | 50% | 0 2 | 50% | 0 7 | 35% |
| In-Stream Retention | 1 4 | | 0 2 | | 1 0 | |
| Atmospheric Nitrate Ion Load to Bay (from forests) | | | | | | |
| Nitrogen Load to Bay (from forests) ^b | | | | | | |
| Pasture Land | | | | | | |
| Nitrate Ion Deposition | 2 4 | | 1 7 | | 1 3 | |
| Ammonium Ion Deposition | 1 3 | 95% ^c | - ^a | 94-99% | 0 7 | 95% ^d |
| Animal Wastes | 14 5 | 50% ^c | 11 8 | 50% | 19 5 | 35% |
| Watershed Retention | 0 7 | | 0 01-0 06 | | 0 13 | |
| In-Stream Retention | 1 5 | | 0 07-0 4 | | 0 8 | |
| Atmospheric Nitrate Ion Load to Bay (from pastures) | | | | | | |
| Nitrogen Load to Bay (from pastures) ^b | | | | | | |
| Cropland | | | | | | |
| Nitrate Ion Deposition | 2 5 | | 2 8 | | 2 1 | |
| Ammonium Ion Deposition | 1 4 | 70% | - ^a | 76-99% | 1 1 | 95% |
| Fertilizers | 15 8 | | 4 1-27 0 | 50% | 15 8 | 35% |
| Watershed Retention | 0 8 | | 0 01-0 3 | | 0 07 | |
| In-Stream Retention | 5 9 | | 0 06-3 6 | | 0 6 | |
| Atmospheric Nitrate Ion Load to Bay (from cropland) | | | | | | |
| Nitrogen Load to Bay (from cropland) ^b | | | | | | |
| Residential/Urban | | | | | | |
| Nitrate Ion Deposition | 0 4 | | 0 7 | | 0 6 | |
| Ammonium Ion Deposition | 0 3 | 35% | - ^a | 62-96% | 0 3 | 50% |
| Watershed Retention | 0 3 | 0% | 0 01-0 14 | 20% | 0 1 | 35% |
| In-Stream Retention | 0 4 | | 0 01-0 14 | | 0 3 | |
| Atmospheric Nitrate Ion Load to Bay (from urban areas) | | | | | | |
| Nitrogen Load to Bay (from urban areas) ^b | | | | | | |
| Point Sources | 3 4 | | 2 0-3 2 | | 3 4 | |
| NITRATE ION LOAD TO BAY (FROM DEPOSITION) | 3 5 | | 0 94-1 48 | | 1 53 | |
| TOTAL NITROGEN LOAD TO BAY^b | 13 94 | | 3 03-8 26 | | 6 82 | |
| Percent of Nitrogen from Nitrate Ion Deposition | 25% | | 18-31% ^e | | 22 5% | |

^aThe Versar Budget (Tyler, 1988) does not calculate loads of ammonium ions (NH₄⁺)

^bFor the Environmental Defense Fund (EDF) Budget (Fisher et al , 1988a, Fisher and Oppenheimer, 1991) and refined budget, total nitrogen load to the bay includes both nitrate ion (NO₃⁻) and NH₄⁺. The Versar Budget (Tyler, 1988) includes only NO₃⁻

^cWatershed and in-stream retention values for pastureland in the EDF Budget apply only to animal wastes. For atmospheric deposition, the cropland retention value (70%) was used

^d95% retention was used for animal wastes, 85% retention was used for deposition (see text)

^eThe range of contributions of NO₃⁻ deposition to the total budget were calculated by comparing maximum-to-maximum estimates and minimum-to-minimum estimates. These combinations are more likely to occur during extreme (e.g., very wet or very dry) years

The major uncertainty involved in calculating direct inputs to the Chesapeake from atmospheric deposition (Step #1, above) is estimation of the contribution of dry deposition (see also Section 10.2). Both reports use actual deposition monitoring data (i.e., from NADP/National Trends Network) to estimate the nitrogen load from wet deposition and then assume that the rate of dry deposition of nitrogen in the watershed is equal to the rate of wet deposition. As discussed earlier (see Section 10.8.2 on nitrogen inputs), the measurement of dry deposition is a much vexed issue, and most researchers make educated guesses of rates of dry deposition by assuming that they are some fraction of wet deposition rates. The assumption that dry deposition is equal to wet deposition is probably reasonable for areas directly adjacent to emissions sources (Summers et al., 1986), but the ratio of dry deposition to the sum of wet and dry deposition may fall as low as 0.2 in locations remote from sources. For example, Barrie and Sirois (1986) estimated that dry deposition contributed 21 to 30% of total NO_3^- deposition in eastern Canada. Baker (1991) concludes that dry deposition of NO_3^- is approximately 40% of wet deposition, whereas dry deposition of NH_4^+ is approximately 34% of wet deposition (resulting in ratios of dry deposition to wet plus dry deposition of 0.29 and 0.25, respectively) for areas remote from emissions. In the most complete analysis of dry and wet deposition of NO_3^- to date, Sisterson et al. (1990) reported ratios of dry deposition to wet plus dry deposition of 0.35 for two locations inside or near the borders of the Chesapeake Bay watershed (State College, PA, and West Point, NY). Based on the results of these studies, it seems that the assumption made in the two Chesapeake Bay nitrogen budgets (i.e., that dry deposition is equal to wet deposition) probably overestimates the importance of dry deposition. The 0.35 ratio is used in constructing the refined budget in Table 10-27.

The two reports (Fisher et al., 1988a, Fisher and Oppenheimer, 1991, Tyler, 1988) also present different values for the direct contribution of wet deposition to the bay because they use different methods to estimate the spatial pattern of deposition in the bay and its watershed. The EDF report uses wet deposition values from the nearest NADP collector, and the Versar report extrapolates deposition values from isopleth maps of NO_3^- deposition. In addition, the Versar report includes direct atmospheric inputs to the tributaries of the bay, as well as to the bay itself (Table 10-27). Aside from problems with estimating dry deposition, it seems likely that the approach used in the Versar report for estimating

deposition is more precise than that used in the EDF report. The Versar values for wet deposition were, therefore, used in the refined budget, after adjusting them to reflect a 35% contribution from dry deposition. Ammonium deposition was calculated for the refined budget by applying the ratio of NH_4^+ to NO_3^- deposition reported in the EDF report to the estimated NO_3^- deposition values from the Versar report (i.e., these values assume that the spatial pattern in NH_4^+ deposition is the same as the spatial pattern for NO_3^- deposition).

The uncertainties involved in estimating nitrogen deposition to the Chesapeake Bay watershed (Step #2) are similar to those for estimating direct deposition. It seems likely that, by assuming dry deposition is equal to wet deposition, both reports overestimate the dryfall contribution to deposition. Differences between the estimates of wet deposition presented in the two reports result from the same methodological differences used in estimating direct inputs (i.e., use of the nearest NADP collector versus extrapolated values from isopleth maps) and from slight differences in the estimates of the coverage of each land-use type. The Versar method produces slightly lower estimates of atmospheric nitrogen inputs to the basin (Table 10-27) and, as in the case with estimates of direct deposition to the bay, the Versar method probably produces better estimates of basin-wide deposition loads than the EDF approach. The refined budget uses the Versar values for wet NO_3^- deposition (adjusted to reflect a 0.35 ratio for dry deposition, as above) and estimates of NH_4^+ deposition based on the Versar spatial deposition pattern and the EDF estimate of NH_4^+ deposition, as above.

The EDF report (Fisher et al., 1988a, Fisher and Oppenheimer, 1991) uses county agricultural reports and U.S. Census Bureau data to calculate the application rates of fertilizers to the counties (and portions thereof) in the Chesapeake Bay watershed (Step #3, above). The Versar report (Tyler, 1988) calculates the total fertilizer load (from NO_3^-) to the watershed by applying a correction factor to the level of fertilizer application recommended by the U.S. Department of Agriculture; the correction factor was based on local officials' best guesses of actual fertilizer application rates (e.g., 30 to 60% of the recommended rates). Because it deals only with NO_3^- loading, the Versar approach also necessitates making an assumption about the proportion of nitrogen fertilizers that are applied as NO_3^- , as opposed to NH_4^+ or urea; the report assumes that 60% of the nitrogen added is in the form of NO_3^- , but presents no data to support this assumption. Because it is more direct in nature, the EDF approach to estimating fertilizer inputs seems to be more defensible.

than the Versar approach, and the EDF estimate is, therefore, used in the refined budget. The EDF estimate of 15.8×10^6 kg/year is near the bottom range of fertilizer loads estimated by the Versar report (Table 10-27).

The EDF (Fisher et al., 1988a, Fisher and Oppenheimer, 1991) and Versar (Tyler, 1988) reports use the same estimate (from the EDF report) for the contribution by animal wastes (Step #4, above) to the nitrogen budget. The EDF report used county agricultural statistics to calculate the total number of farm animals of different types in the Chesapeake Bay watershed. These population numbers were then multiplied by published estimates of the amount of nitrogenous wastes excreted by each type of animal annually, to produce an estimate of 19.5×10^6 kg/year. As in the estimates of fertilizer NO_3^- inputs, the Versar report assumed that 60% of animal nitrogenous wastes were in the form of NO_3^- , this estimate seems especially difficult to justify when it is used both for animal wastes and for fertilizers, as there is no reason to expect both nitrogen sources to have the same composition. The EDF estimate of 19.5×10^6 kg/year is used for the refined budget.

In both reports, atmospheric deposition is considered to be the only source of nitrogen to urban areas (Step #5, above). As pointed out in the Versar report (Tyler, 1988), this is likely to be an underestimate because it ignores fertilizer applications to lawns and gardens. Because fertilizers applications are seasonal, and the area of urban land in the basin is small (about 3% of the total), this underestimate is considered unimportant. As mentioned earlier, the EDF (Fisher et al., 1988a, Fisher and Oppenheimer, 1991) and Versar reports use slightly different methods to calculate wet deposition. The primary difference between the two estimates of nitrogen loading to urban areas (Table 10-27), however, is in their estimate of the proportion of the basin in residential and urban land use (5×10^5 ha in the EDF report versus 8×10^5 ha in the Versar report). In neither case does the nitrogen contribution from urban lands (<2% of the total loading to the watershed) play a significant role in the budgets. The Versar estimate of deposition to urban areas is used in the refined budget, with the same adjustments applied as for the deposition to the watershed and directly to the bay (above).

Both reports used the same EPA estimates of point source inputs to the Chesapeake Bay watershed (Step #6, above), the lower value presented in the Versar report (Tyler, 1988) is the estimated proportion of point source inputs that are in the form of NO_3^- , again assuming

that NO_3^- is 60% of the total inorganic nitrogen. The upper limit to the range of point source inputs presented by the Versar report is a more recent (1988) estimate from the Chesapeake Bay Program. There seems to be little reason not to use the original EDF value (Fisher et al., 1988a, Fisher and Oppenheimer, 1991) of 32.9×10^6 kg/year (Table 10-27), and this value is used in the refined budget.

Perhaps the greatest source of uncertainty in both nitrogen budgets is created when the proportions of nitrogen inputs that are retained within the watershed are estimated (Step #7, above). Both reports use a variety of methods to calculate separate transfer coefficients for each land use type, and in some cases, for different sources of nitrogen within a single land-use type. In particular, the Versar report (Tyler, 1988) compares calculated loads (as described in the preceding paragraphs) to calculated runoff from each land-use type (from Smullen et al., 1982) and estimates a range of transfer coefficients from these calculated values. Because the error inherent in the calculated values is amplified when they are compared, this method seems especially problematic. Often, the calculated transfer coefficients differ greatly from coefficients measured for single basins within the Chesapeake Bay watershed. The transfer coefficients for each land-use type are discussed in detail below. It should be emphasized that all of the nitrogen budgets discussed below deal only with inorganic forms of nitrogen (i.e., NO_3^- and NH_4^+). Outputs of organic nitrogen from watershed can be substantial (e.g., Correll and Ford, 1982), and organic forms can result from atmospheric deposition sources when watershed processes route nitrogen through the biotic portion of the ecosystem. Given this possible source of error, the nitrogen retention values presented below should probably be considered maximum estimates.

Estimating watershed retention of nitrogen in forested watersheds is difficult, primarily because so few data are available, and the applicability of single watershed values to wide areas of the Chesapeake Bay watershed is untested. The Versar (Tyler, 1988) report compares calculated deposition loads (Table 10-27) to estimates of runoff from forests (from Smullen et al., 1982) to yield a transfer coefficient of 4.8%. As discussed above, this estimate must be considered very uncertain, because of the combined errors introduced by comparing two calculated values. The EDF report (Fisher et al., 1988a, Fisher and Oppenheimer, 1991) found literature values that ranged from 50% (in the Mid-Appalachians) to 97% (in the Coastal Plain), and used 80% as a "reasonable mid-range estimate." Given

the range of possible retention values, it seems unlikely that any single number would be a reasonable estimate for the entire Chesapeake Bay watershed. Some additional nitrogen retention values are given in Table 10-28, based on published nitrogen budgets for watersheds in or near the Chesapeake Bay basin. These are arranged according to physiographic regions, in order to illustrate the spatial variability in watershed nitrogen retention. Of the values in Table 10-28, only those of Kaufmann et al. (1991) are applicable to broad spatial areas, because they are based on a probability sampling of streams in each region. These values assume that NO_3^- concentrations at spring base flow are representative of annual mean concentrations (Kaufmann et al., 1988, Messer et al., 1988). If the retention coefficients for each physiographic region are weighted by the proportion of the Chesapeake Bay watershed in each physiographic region (from Smullen et al., 1982), an area-weighted retention coefficient of 84.6% results, this figure was used for the refined budget (Table 10-27). The 84.6% figure agrees remarkably well with the data presented in Figure 10-28b (Driscoll et al., 1989a), which suggest an interpolated coefficient of 84.7% at the levels of deposition calculated for the Chesapeake Bay watershed (8.9 kg/ha total deposition, or 5.8 kg/ha of wet deposition).

Nitrogen retention by pasturelands is generally thought to be very high. Both the EDF (Fisher et al., 1988a; Fisher and Oppenheimer, 1991) and the Versar (Tyler, 1988) reports estimate retention coefficients in the 94 to 99% range. As with forest nitrogen retention, the EDF estimate is based on published values from watershed studies, whereas the Versar estimate is based on comparisons of calculated loads and calculated runoff. The EDF estimate (95%) is based primarily on a study by Kuenzler and Craig (1986, as reported in Fisher et al., 1988a, Fisher and Oppenheimer, 1991) on pastureland in the Chowan River, NC, watershed. Similar results (94.4% retention) have been reported for unfertilized pasture lands in Ohio by Owens et al. (1989), where NO_3^- losses were lower from pastureland than from nearby undisturbed forests (86% retention). Nitrogen retention coefficients reported here were recalculated to include dry deposition (at 35% of total deposition), as was the case for forest nitrogen budgets reported above. The EDF report applies the 95% retention rate only to animal wastes, and uses a 70% retention coefficient for atmospheric deposition. Because they are primarily in the form of particulate organic matter, it seems reasonable to assume that animal wastes will be more strongly retained than deposition. The refined

**TABLE 10-28. RETENTION OF NITROGEN IN WATERSHEDS IN OR
NEAR THE CHESAPEAKE BAY BASIN, FROM PUBLISHED REPORTS.
ALL NITROGEN LOADS HAVE BEEN REESTIMATED BASED ON MEASURED
WET DEPOSITION, AND A 35% CONTRIBUTION TO TOTAL DEPOSITION
FROM DRY DEPOSITION**

| Physiographic Region | Nitrogen Load (10 ⁶ eq/year) ^a | Nitrate Ion Export (10 ⁶ eq/year) | Percent Retention | Source |
|---|---|--|----------------------|--------------------------------|
| Poconos/Catskills ^b | - | - | 88 3 | Kaufmann et al (1991) |
| Biscuit Brook, NY | 878 | 214 | 75 7 | Stoddard and Murdoch (1991) |
| Northern Appalachians ^b | - | - | 72 7 | Kaufmann et al (1991) |
| Southwestern Pennsylvania | 1,192 | 264 | 78 0 | Barker and Witt (1990) |
| Southwestern Pennsylvania ^b | - | - | 94 5 | Sharpe et al (1984) |
| Fernow, WV | 1,506 | 607 | 59 5 | Helvey and Kunkle (1986) |
| Eastern Tennessee | 707 | 36 | 94 6 | Kelly (1988) |
| Valley and Ridge ^b | - | - | 78 5 | Kaufmann et al (1991) |
| Catoctin Mountains, MD | 593 | 250 | 57 5 | Katz et al (1985) |
| Shenandoah National Park, VA | 557 | 3 | 99 5 | Shaffer and Galloway (1983) |
| Mid-Atlantic Coastal Plain ^b | - | - | 90 9 | Kaufmann et al (1991) |
| Chesapeake Bay, MD | 1,000 | 10 | 99 0 | Weller et al (1986) |
| Piedmont ^b | - | - | 90 2 | Kaufmann et al (1991) |
| Northern Georgia | 486 | 11 | 97 7 | Buell and Peters (1988) |
| Southern Blue Ridge ^b | - | - | 88 3 | Kaufmann et al (1991) |

^aNitrogen loads are calculated from published wet deposition estimates, extrapolated to total deposition according to a 0.35 dry wet plus dry ratio (see text)

^bRetention estimates are calculated by comparing mean concentrations of precipitation to mean concentrations in stream water. Estimates from Kaufmann et al (1991) are from the National Stream Survey (Kaufmann et al, 1988) and are for the population of streams within each physiographic province

budget, therefore, applies the 95 % retention figure for animal wastes, and an 85 % retention coefficient (as for forests, above) for nitrogen from deposition (Table 10-27)

The ability of croplands to retain nitrogen is generally high because most of the nitrogen applied to crops as fertilizer is removed as biomass during harvest (Lowrance et al , 1985; Groffman et al , 1986) Both the EDF (Fisher et al , 1988a, Fisher and Oppenheimer, 1991) and the Versar (Tyler, 1988) budgets compare estimates of fertilizer and deposition loads to estimates of runoff from croplands to calculate nitrogen transfer coefficients Use of loads estimates from a number of sources creates a range of retention coefficients from 70 % (Fisher et al , 1988a; Fisher and Oppenheimer, 1991) to 99 % (Tyler, 1988) Published values from studies of cropland watersheds are all toward the higher end of this range Peterjohn and Correll (1984) measured a retention coefficient of 93.2 % for a fertilized corn field in Maryland. Groffman et al (1986) reported 100 % retention of fertilizer nitrogen in a sorghum field in the Georgia piedmont, lower retention coefficients (76.1 %) were measured during the winter, but the planting of crimson clover (a nitrogen-fixing legume) as a winter cover crop complicates the interpretation of these figures Lowrance et al (1985) reported nitrogen budgets for four cropland watersheds with a variety of crops in the Georgia Coastal Plain, with retention coefficients ranging from 97.8 to 100 % Nitrogen retention coefficients reported here were recalculated to include dry deposition (at 35 % of total deposition), as was the case for forest and pastureland nitrogen budgets reported above A retention coefficient of 95 %, as used for the refined budget (Table 10-27) is near the middle of the range of published values Fertilizer inputs are generally in the same inorganic forms as atmospheric deposition, and there seems no reason to apply different retention values to fertilizer and deposition sources of nitrogen

Published reports of nitrogen retention in urban lands are apparently unavailable The EDF report (Fisher et al , 1988a, Fisher and Oppenheimer, 1991) simply chose a retention coefficient midway between their cropland value (70 %) and complete runoff from impervious surfaces (100 %). The Versar report (Tyler, 1988) calculates transfer coefficients from estimated loads (from deposition) and estimated runoff, and gives a range of 62 to 96 % (Table 10-27) There is little justification for choosing any particular value The 50 % value used for the refined budget (Table 10-27) is chosen only to provide a "ball-park" value,

slightly higher or lower values, when applied to the relatively small atmospheric loads falling on urban areas, will not substantially change the conclusions presented here

The final assumption that affects the nitrogen budgets concerns the proportion of watershed runoff that is lost during transport through rivers to the bay (Step 8, above) Denitrification in slow-moving lotic waters can significantly reduce the load of nitrogen delivered to estuarine waters (see Section 10.8.2.4) In the absence of any measured loss rates, both the EDF (Fisher et al., 1988a, Fisher and Oppenheimer, 1991) and the Versar (Tyler, 1988) reports adopt the 50% loss value suggested by the Chesapeake Bay Program (Smullen et al., 1982) More recently, denitrification values have been published for two rivers, the Potomac, which supplies water directly to Chesapeake Bay, and the Delaware, which is adjacent to the Chesapeake Bay watershed (summarized in Seitzinger, 1988a) Seitzinger and Garber (1987) estimated that 35% of the dissolved inorganic nitrogen ($\text{NO}_3^- + \text{NH}_4^+$) load to the Potomac River was lost through denitrification Seitzinger (1988b) measured denitrification rates at six locations in the tidal portion of the Delaware River and estimated that 20% of the dissolved inorganic nitrogen load was lost through denitrification Both of these studies were conducted in the relatively flat, slow-moving and tidal portions of rivers, where denitrification rates are likely to be maximal, due to the existence of anoxic sediments Data from smaller streams suggest that lower rates of nitrogen retention (10 to 15%) are more likely to occur in headwater streams (Triska et al., 1990, Duff and Triska, 1990) In light of these lower measured rates of nitrogen loss, the 50% figure used in the EDF and Versar budgets seems insupportable for riverine losses, loss rates as high as 50% have been measured only in estuarine waters (e.g., Narragansett Bay, Seitzinger et al., 1984, the Baltic Sea, Larsson et al., 1985) The refined budget uses a figure of 35%, reflecting the only known value for a river feeding the Chesapeake itself (Seitzinger and Garber, 1987), and may still overestimate in-stream retention in small streams

When the three budgets are compared, they suggest a wide range in estimated contributions from individual sources of nitrogen (e.g., estimates of cropland inputs vary from 0.03×10^6 kg/year for the "best case" Versar budget to 59.8×10^6 kg/year for the EDF budget), but a surprisingly consistent percentage contribution from atmospheric NO_3^- deposition (18 to 31%) to the total budget (Table 10-27) All three budgets suggest that a large amount of nitrogen enters the bay from deposition, the 15.9×10^6 kg/year estimate

from the refined budget corresponds to a nitrogen load of 44 metric tons per day entering Chesapeake Bay from deposition directly to the bay and the watershed. The caveat presented earlier concerning organic forms of nitrogen should probably be repeated here, the estimates of atmospheric NO_3^- contributions to the bay ignore all but the inorganic nitrogen fractions. Organic nitrogen can be a substantial contributor to the nitrogen in runoff, and could potentially have a large atmospheric deposition component. Many of the estimates that went into these budgets are relatively certain. For example, we have good data on wet deposition, and can extrapolate to total deposition with reasonable certainty given recent estimates of dry deposition within the watershed (e.g., Sisterson et al., 1990). The biggest uncertainty in estimating atmospheric NO_3^- loading to the bay results from the figure for retention of nitrogen by forested watersheds. This influence results from the fact that most of the watershed (ca. 80%) is forested, small changes in the retention coefficients can have a large effect on the estimated load to the bay from these watersheds. The retention coefficient calculated for the refined budget (84.6%) is our current best estimate, based on regional estimates of retention within each of the physiographic regions in the Chesapeake Bay basin, however, it still contains considerable uncertainty. The retention coefficients listed in Table 10-28 suggest that retention can vary from less than 60% to more than 99% in individual watersheds. Many more values from individual watersheds are needed before we can be certain how representative the values for each physiographic region are.

Taken as a whole, the budgets suggest that deposition is approximately equal in importance to point-source supplies of nitrogen, and is possibly more important than agricultural sources of nitrogen (Table 10-27). The fact that three different approaches (i.e., the three budgets in Table 10-27) yield similar results lends weight to the suggestion that atmospheric nitrogen contributes substantially to the eutrophication of the Chesapeake Bay. The detrimental effects of eutrophication have been discussed earlier (see Section 10.8.4.1). These results are surprising, given the emphasis usually placed on reducing point-source inputs to the bay in order to improve water quality (e.g., Chinchilli, 1989, Caton, 1989). Based on the results of nutrient limitation work discussed earlier, it seems clear that the control of nitrogen inputs is important to the control of eutrophication in the Chesapeake Bay. The results of the budget exercises discussed here suggest that any

program for nitrogen control should include the control of nitrogen deposition, as well as point and nonpoint sources

Some corroboration of the budgets presented here is provided by recent attempts at calculating nitrogen mass balances for the Upper Potomac River Basin (Groffman and Jaworski, 1991, Jaworski and Linker, 1991) These studies apply both the EDF budget technique and an "input-output analysis matrix" to calculate nitrogen loads and nitrogen exports attributable to various sources within the Upper Potomac watershed (approximately 18% of the entire Chesapeake Bay watershed) The latter technique combines model estimates of edge-of-field exports of nitrogen for different land-use types with a watershed mass balance, where measurements or estimates of loads (e g , point sources, fertilization, etc) are balanced against measured or estimated outputs (e g , crop harvest, river export) and the difference is attributed either to storage of nitrogen within the watershed or to denitrification and volatilization (gaseous losses) When applied to the Upper Potomac River Basin, the EDF technique estimates that 10.6×10^6 kg/year of nitrogen that leaves the watershed originated as atmospheric deposition (45 % of the total export) The second technique estimates that 8.2×10^6 kg/year of the nitrogen leaving the watershed originated as deposition (or 25 % of the total export) The major difference between the two estimates is in the total export values (23.8×10^6 kg/year and 32.1×10^6 kg/year, respectively) The value for the input-output analysis matrix is likely to be the best estimate for the Upper Potomac because it is based on actual mass balance estimates of river export The same discrepancy would apparently not exist if the input-output analysis matrix technique were applied to the entire Chesapeake watershed, as the estimates of load to the bay from the EDF technique match current best estimates of actual loads very closely (140×10^6 kg/year for the EDF method, 130×10^6 kg/year for best current estimates, Fisher and Oppenheimer, 1991) Given the similarities in the two estimates of Upper Potomac River export attributable to atmospheric deposition, and the unlikelihood that estimates for total river export for the entire Chesapeake would differ as much as the estimates for the Potomac do, the Upper Potomac River basin study lends substantial credence to the EDF technique The improvements made to the EDF method in this document and presented in the "refined budget" (Table 10-28) seem, therefore, to represent the best available information on atmospheric nitrogen loading to the Chesapeake Bay

Finally, atmospheric NO_3^- inputs to the Chesapeake Bay should be put into the context of seasonal nitrogen limitation of algal productivity in the bay. As was discussed earlier, the bay may undergo seasonal shifts in nutrient limitation, from phosphorus limitation in late winter and early spring to nitrogen limitation during summer and fall (e.g., D'Elia et al., 1982, D'Elia et al., 1986). If atmospheric NO_3^- is to have a significant effect on algal biomass, it would need to be present during the late summer, low-flow, high-biomass period. However, much of the NO_3^- load occurs during the spring, when river flows and NO_3^- leakage from watersheds are high (e.g., Lowrance and Leonard, 1988). In the case of the Baltic Sea, discussed earlier, nutrients were largely trapped within the estuary by sedimentation processes and minimal water exchange with the North Sea. Does the Chesapeake Bay act in a similar manner to trap nutrients, providing a mechanism for springtime loads of NO_3^- to influence summertime productivity? Unfortunately, few measurements of the nutrient retention capacities of the Chesapeake Bay are available, but some estimates have been made. Smullen et al. (1982) estimated, based on some measurements of current and nutrient concentrations at the mouth of the bay and a simple box model, that virtually all of the nitrogen entering the bay was retained. Nixon (1987) and Nixon et al. (1986) question this conclusion, and point out that such high nutrient retention rates should result in very high nutrient concentrations in the sediments, which have not been found. Based on estimates of sediment nutrient concentrations, Nixon et al. (1986) calculated that only approximately 5% of nitrogen entering the bay is retained. The argument of Nixon et al. (1986), however, seems to ignore the potential effect of denitrification in maintaining low sediment nitrogen concentrations, despite high rates of retention by the bay. Fisher et al. (1988b) use longitudinal profiles of nutrient concentrations throughout the bay to estimate that 33 to 71% of nitrogen entering the bay is retained. These lower estimates of nitrogen retention suggest that nitrogen entering the Bay during spring runoff does have the potential to affect productivity in the Bay during the critical summer months. They also suggest, however, that the Chesapeake Bay could return to background nitrogen concentrations within several flushing times of the bay, or within several years (Fisher et al., 1988b), if nutrient control strategies were put in place.

It is impossible to determine at this point whether the Chesapeake Bay example is an unusual one in terms of the relative importance of atmospheric nitrogen inputs. Jaworski

(1981) gives crude nitrogen budgets for four estuaries and embayments in the United States, his results suggest that the Chesapeake Bay receives an unusually large proportion of nitrogen (68%) from land runoff (which includes agricultural and deposition sources) Jaworski's (1981) budgets indicate that wastewater discharges are more important in the Hudson River (New York) and San Joaquin River (California) estuaries (63 and 47% of inputs, respectively, but these estimates do not include deposition), and the Potomac River estuary has equal inputs from wastewater and land runoff Of Jaworski's four systems, the Chesapeake Bay is the least influenced by point-source pollution, but it also receives larger inputs from point sources than many estuaries in the United States (e g , the Apalachicola Bay, Nixon and Pilson, 1983) If one views all estuarine and coastal waters as lying along a gradient from high to low influence by point-source pollution, then the relative importance of deposition to the nitrogen budget will change as one moves along the gradient. The general applicability of the nitrogen budget results from the Chesapeake Bay will depend on where the bay falls along this gradient

10.8.5 Direct Toxicity Due to Nitrogen Deposition

In addition to the effects of acidification and eutrophication, nitrogen deposition could potentially contribute to directly toxic effects in surface waters Toxic effects on freshwater biota result from un-ionized NH_3 that occurs in equilibrium with ionized NH_4^+ and hydroxide (OH^-) High NH_3 concentrations are associated with lesions in gill tissue, reduced growth rates of trout fry, reduced fecundity (number of eggs), increased egg mortality, and increased susceptibility of fish to other diseases, as well as a variety of pathological effects in invertebrates and aquatic plants (reviewed in U S Environmental Protection Agency, 1985) Most analytical methods for ammonium actually measure the sum of NH_3 and NH_4^+ , which is commonly referred to as NH_4^+ ; for clarity, the sum of ammonium and NH_3 will be referred to here as total ammonia (T- NH_3) No single toxic concentration for T- NH_3 can be established because the relative contribution of NH_3 to T- NH_3 , and the toxicity of NH_3 , vary with the pH and temperature (Emerson et al , 1975) and the ionic strength (Messer et al , 1984) of the water The proportion of NH_3 increases at higher temperatures and increasing pH Because of the variability in NH_3 toxicity, new criteria have recently been developed that calculate the toxicity as a function of pH, temperature, and ionic strength (U S

Environmental Protection Agency, 1985) The new regulations require the calculation of a "final chronic value" (FCV) and "final acute value" (FAV), 4-day average concentrations of NH_3 cannot exceed the FCV more often on average than once every 3 years, nor can 1-h average concentrations exceed one-half of the FAV more often on average than once every 3 years.

Critical concentrations of NH_3 that cause the various effects are wide ranging and are related to site specific temperature and pH values For example, the concentration values at which 50% of the test organisms die within 48 h (48-h LC_{50}) for *Daphnia magna*, a common invertebrate found in lake zooplankton, range from 38 to 350 $\mu\text{mol/L}$ T- NH_3 over a temperature range from 19.6 to 25 °C and pH range of 7.4 to 8.6 (U S Environmental Protection Agency, 1985) However, results of toxicity tests on stream insects showed that 96-h LC_{50} values ranged from 128 to 421 $\mu\text{mol/L}$ T- NH_3 at relatively constant chemical conditions. The 96-h LC_{50} values for rainbow trout ranged from 11.4 to 78.5 $\mu\text{mol/L}$ T- NH_3 Fingerlings tend to be less sensitive than older life stages, and lower oxygen concentrations increased sensitivity to NH_3 Variation in temperature, pH, acclimation time, and CO_2 concentrations also appeared to explain some variation in responses Effler et al (1990) calculated FCV and FAV values for Onondaga Lake, an urban lake in Syracuse, NY, that is heavily polluted with municipal sewage For both salmonid and nonsalmonid fishes, the FCV values varied (with time of year) from 1.4 to 2.9 $\mu\text{mol/L}$ One-half FAV values for nonsalmonids varied from 3.6 to 28.6 $\mu\text{mol/L}$ (acute toxicity information for salmonids is not given). At typical pH (pH = 8) and temperature (temperature = 20 °C) values for Onondaga Lake, the minimum FCV value of 1.4 $\mu\text{mol/L}$ corresponds to a T- NH_3 concentration of 36 $\mu\text{mol/L}$, this concentration is always exceeded in the lake (Effler et al , 1990)

Onondaga Lake is unusual in being very productive, and so tends to be warmer and have a higher pH than many lakes At lower pH values (pH = 7) and lower temperatures (15 °C), the percentage of T- NH_3 that is free NH_3 drops dramatically (Emerson et al , 1975), so that the FCV values reported for Onondaga Lake would not be exceeded until a T- NH_3 concentration of 785 $\mu\text{mol/L}$ was reached Currently no areas of North America are known to experience rates of NH_4^+ deposition that are sufficient to produce such high concentrations in surface waters Given current maximal concentrations of NH_4^+ in deposition (40 $\mu\text{mol/L}$; Stensland et al , 1986) and reasonable maximum rates of dry

deposition and evapotranspiration (dry deposition equal to 100% of wet deposition and evapotranspiration equal to 50% of deposition), maximum NH_4^+ concentrations in surface waters will be less than 160 $\mu\text{mol/L}$. If all nitrogen in deposition ($\text{NO}_3^- + \text{NH}_4^+$) were ammonified, maximum potential NH_4^+ concentrations attributable to deposition would be approximately 280 $\mu\text{mol/L}$, and would be unlikely to be toxic except in unusual circumstances. Because NH_4^+ is rapidly oxidized to NO_3^- in watershed soils and under well-oxygenated conditions in lakes and streams, the likelihood of reaching toxic concentrations are extremely limited. Toxic levels would be more likely in systems that have oxygen deficits, high organic matter loading (which would increase oxygen demand and contribute ammonium through mineralization processes), and direct inputs of NH_3 (i.e., near feedlot operations). In such cases, it would probably be more effective to remove the local causes of oxygen depletion and organic matter loading, than to reduce atmospheric inputs of nitrogen. It appears from the information above that the potential for directly toxic effects attributable to nitrogen deposition in the United States is very limited.

10.9 DISCUSSION AND SUMMARY

10.9.1 Introduction

Since the mid-1980s, the view has emerged that the deposition of atmospheric inorganic nitrogen has impacted aquatic and terrestrial ecosystems (Aber et al., 1989; Ellenberg, 1987; Van Breeman and Van Dijk, 1988). It is known that in many areas of the United States, the atmospheric input of nitrogen compounds has been significant (U.S. Environmental Protection Agency, 1982, Sections 10.4 and 10.7.2), however, the impacts have generally been unknown or considered benign. Although, the evidence linking nitrogen deposition with ecological impacts has been tenuous, there has been a growing concern (Skeffington and Wilson, 1988). This concern has been magnified because continuous deposition of atmospheric concentrations of nitrogen compounds (particularly HNO_3 and NO_3^-) in North America and most European countries has resulted in ecosystems once limited by nitrogen receiving nitrogen in excess of plant and microbial demand. These concerns have led to the efforts in Europe to develop "critical loads" of nitrogen for various ecosystems. A critical load is defined as "a quantitative estimate of an exposure to one or more pollutants below

which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge" (Nilsson and Grennfelt, 1988) The concept of critical load has not received wide acceptance in North America Current information indicates that "nitrogen-saturated" forests are relatively rare and limited in extent, especially managed forests In addition, because of the great variation in both natural forest nitrogen uptakes and management intensity, it is not reasonable to assign one critical load to all forest ecosystems

10.9.2 Ecosystems

Ecosystems are composed of populations of "self-supporting" and "self-maintaining" living plants, animals, and microorganisms interacting among themselves and with the nonliving chemical and physical environment within which they exist (Odum, 1989, Billings, 1978; Smith, 1980) Ecosystems usually have definable limits and may be large or small (e g., fallen logs, forests, grasslands, cultivated or uncultivated fields, ponds, lakes, rivers, estuaries, oceans, the earth) (Odum, 1971, Smith, 1980, Barbour et al , 1980) The environmental conditions of a particular area or region determine the boundaries of the ecosystem as well as the organisms that can live there (Smith, 1980) Together, the environment, the organisms, and the physiological processes resulting from their interactions form the life-support systems that are essential to the existence of any species on earth, including man (Odum, 1989)

Human welfare is dependent on ecological systems and processes Natural ecosystems are traditionally spoken of in terms of their structure and functions Ecosystem structure includes the species (richness and abundance) and their mass and arrangement in an ecosystem. This is an ecosystem's standing stock—nature's free "goods" (Westman, 1977) Society reaps two kinds of benefits from the structural aspects of an ecosystem (1) products with market value such as fish, minerals, forest and pharmaceutical products, and genetic resources of valuable species (e g , plants for crops, timber, and animals for domestication) and (2) the use and appreciation of ecosystems for recreation, aesthetic enjoyment, and study (Westman, 1977).

Structure within ecosystems involves several levels of organization The most visible are (1) the individual and its environment, (2) the population and its environment, and (3) the

biological community and its environment, the ecosystem (Billings, 1978) Ecosystems function as energy and nutrient transfer systems Through the process of photosynthesis, vegetation accumulates, uses, and stores carbon compounds (energy) to maintain physiological processes and to build plant structure Carbohydrates and other compounds accumulated and stored by plants are the basic source of food (energy and nutrients) for the majority of animals and microorganisms Energy moves unidirectionally and ultimately dissipates into the environment Nutrients are recycled into the system Because the various ecosystem components are chemically interrelated, stresses placed on individual components, such as those caused by nitrogen deposition and loading, can produce perturbations that are not readily reversed and will significantly alter the ecosystem (Guderian and Kueppers, 1980)

10.9.3 The Nitrogen Cycle

Nitrogen, one of the main constituents of the protein molecules essential to all life, is recycled within ecosystems (see Section 10.1) Most organisms cannot use the molecular nitrogen found in the earth's atmosphere It must be transformed by terrestrial and aquatic microorganisms into a form other organisms can use The transformations of nitrogen as it moves through the ecosystem is referred to as the nitrogen cycle Mature natural ecosystems are essentially self-sufficient and independent of external additions Modern technology, by either adding nitrogen or removing nitrogen from ecosystems, can upset the relationships that exist among the various components, and thus change their structure and functioning

10.9.4 Nitrogen Deposition

The removal (dry deposition) of reactive nitrogen gases from the atmosphere occurs along several pathways leading to foliage, bark, or soil, with pathways to foliage being predominant during the growing season The prevalence of any particular type of deposition is a function of (1) the physicochemical properties of nitrogen compounds, (2) their ambient concentration, and (3) the presence of suitable receptor sites in the landscape (e.g., leaves with open stomata) Average canopy-level measurements (Table 10-29) exhibit the following pattern or tendency towards dry deposition $\text{HNO}_3 > \text{NH}_3 = \text{NO}_2 > \text{NO}$ Although the leaf-level data for crops are incomplete (NO and HNO_3 data are not available), the leaf

**TABLE 10-29. MEAN DEPOSITION CHARACTERISTICS OF REACTIVE
NITROGEN GASES AT THE LEAF OR CANOPY SCALE OF
RESOLUTION FOR CROP OR TREE SPECIES**

| Compound | Leaf-Level Measures | Canopy-Level Measures |
|---------------------------------|---------------------------|---------------------------|
| | K_1 (mm/s) ^a | V_d (mm/s) ^a |
| Summary for Crop Species | | |
| Nitric Oxide | ND ^b | 1 3 |
| Nitrogen Dioxide | 1 2 | 7 7 |
| Nitric Acid | ND ^b | 19 8 |
| Ammonia | 4 5 | 6 6 |
| Summary for Tree Species | | |
| Nitric Oxide | <0 3 | ND ^b |
| Nitrogen Dioxide | 1 1 | 24 |
| Nitric Acid | 2 1 | 41 |
| Ammonia | 1 8 | 22 |

^aMeans are the average for *all* species studied. However, measurements on dormant plant materials, foliage with low stomatal conductance, and data recorded in the dark were excluded. The values listed as K_1 (leaf conductance) and V_d (deposition velocity) for particles represent the leaf-wash and throughfall measurement techniques, respectively.

^bND = No data were available.

conductance (K_1) data for trees shows a similar pattern. These patterns are consistent with the observations of Bennett and Hill (1973), and can be partially explained by gas solubility characteristics (Taylor et al., 1988). Particle deposition data averaged across species and experimental techniques shows approximately three times greater nitrate aerosol deposition (7.8 mm/s) than for ammonium (2 mm/s). However, the high average V_d for NO_3^- is probably excessively high due to the unavoidable inclusion of nitrate from HNO_3 in measurements of nitrate deposition.

With the possible exception of HNO_3 vapor, deposition characteristics of reactive nitrogen compounds are highly variable and dramatically influenced by environmental conditions that affect stomatal conductance. The tight relationship between stomatal

conductance and the deposition of NO and NO₂ implies that gaseous deposition of reactive NO_x is greatly reduced in the dark, when stomata close (Hanson et al , 1989, Saxe, 1986, Hutchinson et al , 1972) Deposition of gaseous nitrogen forms is usually proportional to ambient concentrations, but "compensation concentrations" at which no uptake occurs (i e , <0.003 to 0.005 ppmv) have been reported for NO₂ and NH₃ Data for NO, NO₂, and HNO₃ (Grennfelt et al , 1983, Johansson, 1987, Marshall and Cadle, 1989, Skarby et al , 1981), from the vegetation dormant period, show a reduced potential for deposition Conversely, particulate nitrate and ammonium deposition do not appear to be affected by the season of the year (Gravenhorst et al , 1983, Lovett and Lindberg, 1984)

The preceding information on gases and particles indicates that methods for measuring gas or particulate deposition may produce dramatically different results Leaf-level measures of deposition (K_1) for NO, NO₂, and HNO₃ were 4 to 10 times lower than estimates obtained using micrometeorological canopy-level measurements (V_d) This discrepancy can largely be explained once canopy area instead of ground area is factored into the canopy-based measurements

The canopy-level V_d measurement has been criticized because it attempts to pool environmental, physiological, and morphological characteristics into a single descriptive measurement (i e , it attempts to do too much, Taylor et al , 1988) The result of this oversimplification is that V_d for even a single trace gas varies substantially in space and time However, average K_1 and V_d values for NH₃ on crop species were comparable, perhaps because crop canopies are more uniform and closer to the ground Particle deposition is governed by a different set of principles (see Section 10.2.3) and the same relationships between leaf and canopy level measurements may not be applicable

Daytime rates of NO_x or NH₃ deposition can also be approximated from ambient concentrations of the gases (U S Environmental Protection Agency, 1982, Hicks et al , 1985) and deposition constants such as those presented in Table 10-29 Hanson et al (1989) used such information with conservative estimates of concentration to approximate total nitrogen deposition from NO₂ to various forest stands They predicted NO₂-nitrogen inputs between 0.04 and 1.9 kg nitrogen/ha/year for natural forests and inputs up to 12 kg nitrogen/ha/year for forests in urban environments For a forested watershed, Grennfelt and Hultberg (1986) calculated the annual deposition of NO₂ plus HNO₃ to be in the range from

3.6 to 5.1 kg nitrogen/ha/year Hill (1971) estimated the removal of NO_2 from the atmosphere in Southern California to be approximately 109 kg nitrogen/ha/year

Preliminary particle deposition measurements and calculated dry deposition estimates of reactive nitrogen gases indicate significant nitrogen inputs to terrestrial systems Barrie and Sirois (1986) estimated that dry deposition contributed 21 to 30% of total NO_3^- deposition in eastern Canada Lovett and Lindberg (1986) concluded that dry deposition of nitrate is the largest form of inorganic nitrogen deposited to oak-hickory forests in eastern Tennessee Annual estimates of NH_3 deposition have been reported (Cowling and Lockyer, 1981, Sinclair and Van Houtte, 1982), but numerous reports of NH_3 evolution from foliage under conditions of high soil nitrogen confound simple estimates of annual NH_3 -nitrogen deposition Lovett (1992) summarized research data for a number of forested sites in North America and Norway and concluded that dry deposition of nitrogen typically occurs at annual rates approximately equal to nitrogen deposited in precipitation

Because gaseous deposition is difficult to measure accurately or continuously at the landscape level of resolution, estimates of dry nitrogen deposition must rely on models Rigorous models of pollutant deposition have been developed (Hicks et al , 1985, Baldocchi, 1988; Baldocchi et al , 1987) and will be needed in the future for accurate determination of reactive nitrogen gas and particle deposition to forest stands and ecosystems Although progress has been made in understanding and modeling the processes that control the dry deposition of nitrogen containing compounds, additional research will be required to minimize errors in predictions of total dry nitrogen deposition to specific regions and under a range of environmental conditions

Increased efforts have been made to establish both wet and dry deposition rates of nitrogen to various types of ecosystems These current deposition data are important because they provide a basis for evaluating potential effects against "suggested critical levels" Although the concept of critical nitrogen loading has not been widely adopted in North America, for reasons discussed in Sections 10.5.8, 10.5.9, and 10.6.3.1, a comparison of total nitrogen deposition data for North America with proposed critical loads for Europe provide a comparison of the status of terrestrial systems with respect to changes that might be expected from elevated levels of nitrogen deposition Figure 10-19 summarizes wet deposition data for nitrate and ammonium in the United States Because the data are for wet

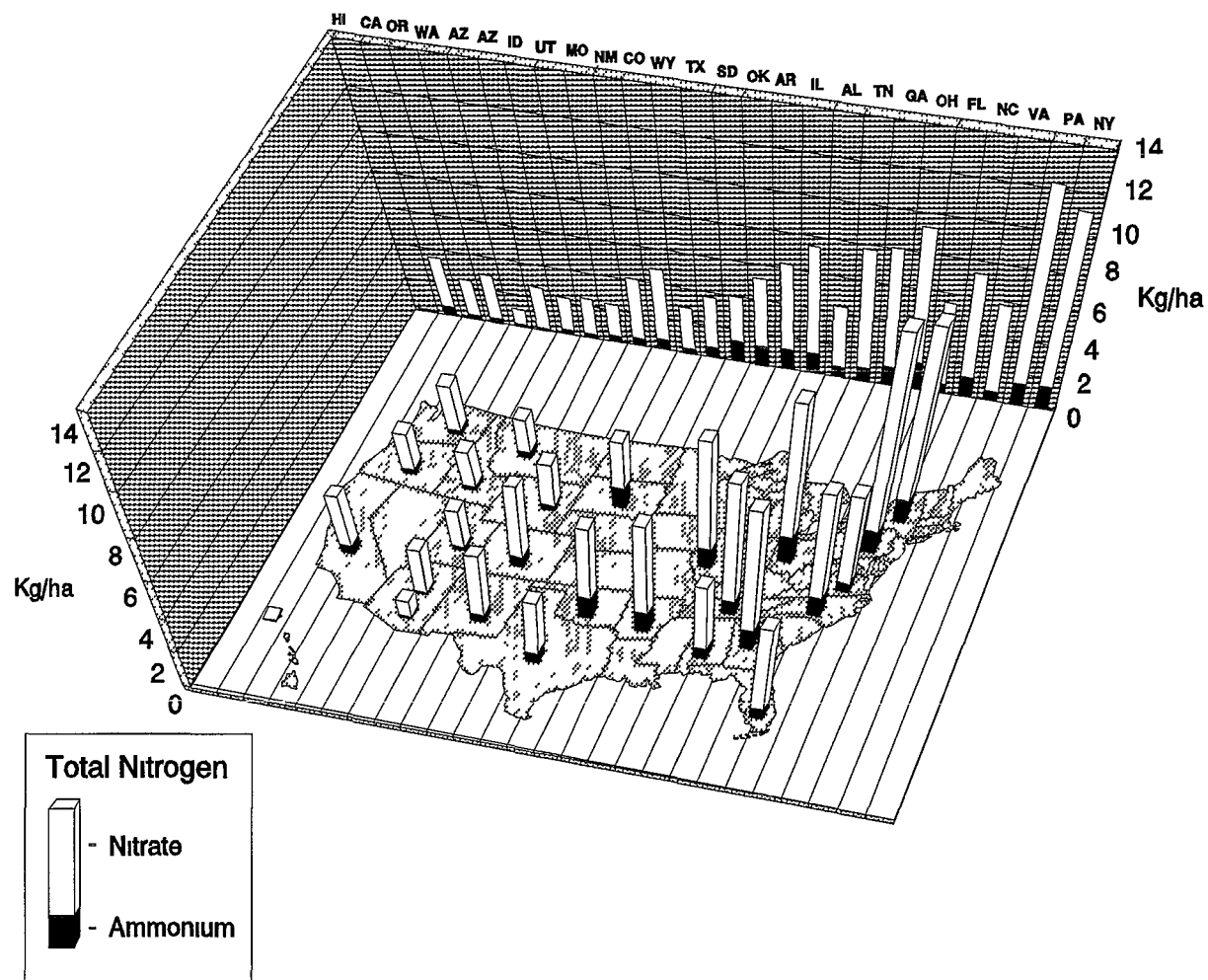


Figure 10-19. Mean annual wet nitrate and ammonium deposition to various states located throughout the United States.

Source Data from the National Atmospheric Deposition Program (1988) are for a single year, and data summarized by Bohm (1991) are for the period 1985 through 1988

deposited forms of nitrogen, they represent an underestimate of the total nitrogen deposition to the ecosystems. Table 10-14 summarizes information regarding the total (wet and dry) deposition of nitrogen to a variety of ecosystems/forest types or regional areas in North America and Europe.

10.9.5 Effects of Deposited Nitrogen on Soils

The effects of nitrogen deposition on biological systems must be viewed from the perspective of the amount of nitrogen in the system, the biological demand for nitrogen, and the amount of deposition. If nitrogen is deposited on a nitrogen-deficient ecosystem, a growth increase will likely occur. If nitrogen is deposited on an ecosystem with adequate supplies of nitrogen, nitrate leaching will eventually occur. Nitrate leaching is usually deemed undesirable in that it can contaminate groundwater and lead to soil acidification.

This analysis focuses on forest ecosystems, but considers arid ecosystems as well. Agricultural lands are excluded from this discussion because crops are routinely fertilized with amounts of nitrogen (100 to 300 kg/ha) that far exceed pollutant inputs even in the most heavily polluted areas. Pollutant nitrogen inputs to grasslands and arid soils can be expected to produce increased growth in some instances, despite water limitations (e.g., Fisher et al., 1988c). However, these systems are obviously not subject to the soil acidification and groundwater NO_3^- pollution problems that might occur in more humid areas. Excess nitrogen deposited on these ecosystems leaves via either denitrification or NH_4^+ volatilization (see review by Woodmansee, 1978).

The biological competition for atmospherically deposited nitrogen among heterotrophs (decomposing microorganisms), plants, and nitrifying bacteria, combined with the chemical reactions between NH_4^+ and humus in the soil, determine the degree to which vegetation growth increase will occur and the degree to which incoming nitrogen is retained within the ecosystem. Until recently, nitrifying bacteria were thought to be poor competitors for nitrogen, with heterotrophs being the most effective competitors and plants being intermediate. Recent studies of soil nitrogen dynamics using ^{15}N (Davidson et al., 1990) and thorough analyses of forest nitrogen budgets suggest that these assumptions and perhaps our conceptual model of soil nitrogen cycling need modification. Specifically, nitrification may be proceeding at a significant level without the appearance of NO_3^- in soils or soil solution if

**TABLE 10-14. MEASUREMENTS OF VARIOUS FORMS OF
ANNUAL NITROGEN DEPOSITION TO NORTH AMERICAN AND
EUROPEAN ECOSYSTEMS**

| Site Location/ Vegetation | Forms of Nitrogen Deposition (kg/ha) ^a | | | | Total ^b | Reference |
|-------------------------------|---|------|-----------|-------|--------------------|------------------------------|
| | Wet | | Dry | | | |
| | Cloud | Rain | Particles | Gases | | |
| <u>United States</u> | | | | | | |
| California, Chaparral | -- | 8 2 | -- | -- | 23 ^c | Riggan et al (1985) |
| California, Sierra Nevada | -- | -- | -- | -- | (2) | Williams and Melack (1991a) |
| Georgia, Loblolly pine | -- | 3 7 | 1 0 | 4 2 | 9 | Lovett (1992) |
| North Carolina, Loblolly pine | -- | 8 7 | 2 2 | 4 1 | 15 | Lovett (1992) |
| North Carolina, Hardwoods | -- | 4 8 | 0 5 | -- | 5 3 | Swank and Waide (1988) |
| North Carolina, White pine | -- | 3 7 | 0 9 | 2 7 | 7 | Lovett (1992) |
| North Carolina, Red spruce | 8 7 | 6 2 | 3 6 | 8 6 | 27 | Lovett (1992) |
| New Hampshire, Deciduous | -- | 7 0 | -- | -- | (7) | Likens et al (1970) |
| New Hampshire, Deciduous | -- | 9 3 | -- | -- | (9) | Likens (1985) |
| New York, Red spruce | 7 3 | 6 1 | 0 2 | 2 3 | 16 | Lovett (1992) |
| New York, Mixed deciduous | -- | 4 8 | 0 8 | 2 5 | 8 | Lovett (1992) |
| Tennessee, Mixed deciduous | -- | 2 9 | 4 1 | 6 1 | 13 | Kelly and Meagher (1986) |
| Tennessee, Oak forest #1 | -- | 3 2 | 4 4 | 4 0 | 12 | Kelly and Meagher (1986) |
| Tennessee, Oak forest #2 | -- | 2 9 | 4 4 | 4 0 | 11 | Kelly and Meagher (1986) |
| Tennessee, Oak forest #1 | -- | 6 9 | 1 3 | -- | 8 | Kelly (1988) |
| Tennessee, Oak forest #2 | -- | 6 0 | 1 2 | -- | 7 | Kelly (1988) |
| Tennessee, Oak forest | -- | 4 5 | 1 8 | 3 8 | 10 | Lindberg et al (1986) |
| Tennessee, Loblolly pine | -- | 4 3 | 0 6 | 1 4 | 9 | Lovett (1992) |
| Washington, Douglas fir | -- | 2 9 | 1 3 | 0 6 | 5 | Lovett (1992) |
| Washington, Douglas fir | -- | 1 0 | -- | -- | (1) | Henderson and Harris (1975) |
| <u>U S Regions</u> | | | | | | |
| Adirondacks | -- | 6 3 | 4 7 | -- | 11 | Driscoll et al (1989a) |
| Midwest | -- | 4 2 | 2 9 | -- | 7 1 | Driscoll et al (1989a) |
| Northeast | -- | 21 7 | -- | -- | 22 | Munger and Eisenreich (1983) |
| Northwest | -- | 16 6 | -- | -- | 17 | Munger and Eisenreich (1983) |
| Southeast | -- | 20 6 | -- | -- | 21 | Munger and Eisenreich (1983) |
| Southeast Appalachians | -- | 4 2 | 3 1 | -- | 7 3 | Driscoll et al (1989a) |

**TABLE 10-14 (cont'd). MEASUREMENTS OF VARIOUS FORMS OF
ANNUAL NITROGEN DEPOSITION TO NORTH AMERICAN AND
EUROPEAN ECOSYSTEMS**

| Site Location/ Vegetation | Forms of Nitrogen Deposition (kg/ha) ^a | | | | Total ^b | Reference |
|------------------------------------|---|------|-------------------|-------|--------------------|---------------------------------|
| | Wet | | Dry | | | |
| | Cloud | Rain | Particles | Gases | | |
| <u>Canada</u> | | | | | | |
| Alberta (southern) | -- | 7 3 | 12 2 | -- | 19 5 | Peake and Davidson (1990) |
| British Columbia | -- | 5 5 | -- | -- | (5) | Feller (1987) |
| Ontario | -- | 3 7 | -- | -- | (4) | Linsey et al (1987) |
| Ontario (southern) | -- | 2 3 | 1 4 | -- | 3 7 | Ro et al (1988) |
| <u>Federal Republic of Germany</u> | | | | | | |
| Spruce (Southeast slope) | -- | 16 5 | -- | -- | 16 5 | Hantschel et al (1990) |
| Spruce (Southwest slope) | -- | 24 3 | -- | -- | 24 3 | Hantschel et al (1990) |
| <u>Netherlands</u> | | | | | | |
| Oak-birch | -- | -- | -- | -- | 24-56 ^c | Van Breemen and Van Dijk (1988) |
| Deciduous/spruce | -- | -- | -- | -- | 21-42 ^c | Van Breemen and Van Dijk (1988) |
| Scots pine | -- | -- | -- | -- | 17-64 ^c | Van Breemen and Van Dijk (1988) |
| Douglas fir | -- | -- | -- | -- | 17-64 ^c | Van Breemen and Van Dijk (1988) |
| Douglas fir | -- | 19 3 | 95 7 ^d | -- | 115 | Draaijers et al (1989) |
| <u>Norway</u> | | | | | | |
| Spruce | -- | 10 3 | 0 7 | 0 2 | 11 2 | Lovett (1992) |
| | -- | -- | -- | -- | 3-19 ^c | Royal Society (1983) |
| <u>United Kingdom</u> | | | | | | |
| Spruce forest | 1 9 | 8 0 | -- | 13 5 | 23 4 | Fowler et al (1989a) |
| Cotton grass moor | 0 4 | 8 0 | -- | 4 0 | 12 4 | Fowler et al (1989a) |

^a-- Symbolizes data not available or, in the case of cloud deposition, not present

^bMeasurements of total deposition data that do not include both a wet and dry estimate probably underestimate total nitrogen deposition and are enclosed in parentheses

^cTotal nitrogen deposition was based on bulk deposition and throughfall measurements and does include components of wet and dry deposition

^dIncludes deposition from gaseous forms

NO_3^- is rapidly taken up by heterotrophs. It is also clear that trees can be very effective competitors for atmospherically deposited nitrogen in nitrogen-deficient ecosystems. Finally, the role of chemical reactions between NH_4^+ and humus need to be investigated, such reactions have been shown to be very important in fertilization studies, and they may also play a major role in unfertilized ecosystems. If this is the case, the fundamental assumption that nitrogen retention is controlled primarily by biological processes may be erroneous.

Nitrification and NO_3^- leaching become significant only after heterotroph and plant demand for nitrogen are substantially satisfied, a condition that has been referred to as "nitrogen-saturated". Nitrogen-saturated forest ecosystems are very rare in the United States, but do occur in some slow-growing, high-nitrogen input areas (e.g., high-elevation southern Appalachians). Additions of nitrogen in any biologically available form (NH_4^+ , NO_3^- , or organic) to a nitrogen-saturated system will cause equivalent leaching of NO_3^- , except in those very rare systems where nitrification is inhibited by factors other than competition from heterotrophs and plants. Considering the effects of NO_3^- only will result in a substantial underestimation of the acidification potential of atmospheric deposition in nitrogen-saturated ecosystems.

Vegetation demand for nitrogen depends on a number of growth-influencing factors including temperature, moisture, availability of other nutrients, and stand age. Uptake rates decline as forests mature, especially after the cessation of the buildup of nutrient-rich foliar biomass following crown closure. Thus, nitrogen-saturation tends to be more common in older forests than in younger forests because nitrogen demand is less. Processes that cause net nitrogen export from ecosystems, such as fire and harvesting, will naturally push ecosystems toward a state of lower nitrogen-saturation or even nitrogen deficiency. Intense fires cause a large loss of ecosystem nitrogen capital, but frequent, low-intensity fires may have little effect.

A review of the literature on forest fertilization and nitrogen-cycling studies under various levels of pollutant nitrogen input reveals some interesting contrasts that pertain to the relative roles of heterotrophs, plants, and nitrifiers discussed above. Forest fertilization has proven quite successful in producing growth increases in nitrogen-deficient forests, even though trees typically recover only 5 to 50% of fertilizer nitrogen (Table 10-12). On an ecosystem level, however, retention of nitrogen is usually quite high (often 70 to 90% of

TABLE 10-12. NITROGEN FERTILIZER RECOVERY BY VEGETATION AND SOILS IN VARIOUS STUDIES

| Location | Species and Age (years) | Fertilizer Type and Amount (kg/ha) ^a | Vegetation Recovery (kg/ha and percent) | Soil Recovery (kg/ha and percent) | Reference |
|-------------|-------------------------------|--|--|--|----------------------------|
| Florida | <i>Pinus eliottii</i> , 11 | AS,56 | 6 (11%) | 17 (30%) | Mead and Pritchett (1975) |
| Florida | <i>Pinus eliottii</i> , 11 | AS,224 | 24 (11%) | 40 (18%) | Mead and Pritchett (1975) |
| Mississippi | <i>Pinus taeda</i> , 5 | AN,112 | 16 (14%) | - | Baker et al (1974) |
| Mississippi | <i>Pinus taeda</i> , 6 | AN,224 | 31 (28%) | - | Baker et al (1974) |
| Mississippi | <i>Pinus taeda</i> , 5 | AN,224 | 31 (14%) | - | Baker et al (1974) |
| Mississippi | <i>Pinus taeda</i> , 6 | AN,224 | 146 (65%) | - | Baker et al (1974) |
| New Zealand | <i>Pinus radiata</i> , 14 | NS,960 | 120 (13%) | 488 (51%) | Baker et al (1986) |
| New Zealand | <i>Pinus radiata</i> , 13 | U,224 | 80 (40%) | 120 (60%) | Worsnop and Will (1980) |
| Ontario | <i>Pinus banksiana</i> , 45 | U,300 | 76 (25%) | 79 (26%) | Morrison and Foster (1977) |
| Scotland | <i>Pinus nigra</i> , 36 | AS,252 | 136 (54%) | 176 (67%) | Miller et al (1976) |
| Scotland | <i>Pinus nigra</i> , 36 | AS,504 | 228 (45%) | 78 (15%) | Miller et al (1976) |
| Scotland | <i>Pinus nigra</i> , 36 | AS,1008 | 366 (36%) | 303 (30%) | Miller et al (1976) |
| Scotland | <i>Pinus nigra</i> , 36 | AS,1512 | 495 (32%) | 229 (15%) | Miller et al (1976) |
| Sweden | <i>Pinus sylvestris</i> , 130 | AN,224 | 19 (19%) | 46 (46%) | Melin et al (1983) |
| Sweden | <i>Pinus sylvestris</i> , 120 | U,150 | 12 (8%) | 74 (49%) | Nommik and Moller (1981) |
| Sweden | <i>Pinus sylvestris</i> , 120 | U,300 | 21 (7%) | 87 (29%) | Nommik and Moller (1981) |
| Sweden | <i>Pinus sylvestris</i> , 120 | U,600 | 36 (6%) | 102 (17%) | Nommik and Moller (1981) |

TABLE 10-12 (cont'd). NITROGEN FERTILIZER RECOVERY BY VEGETATION AND SOILS IN VARIOUS STUDIES

| Location | Species and Age (years) | Fertilizer Type and Amount (kg/ha) ^a | Vegetation Recovery (kg/ha and percent) | Soil Recovery (kg/ha and percent) | Reference |
|--------------------|----------------------------------|--|--|--|---------------------------|
| Sweden | <i>Pinus sylvestris</i> , 120 | AN,150 | 29 (19%) | 32 (21%) | Nommik and Moller (1981) |
| Sweden | <i>Pinus sylvestris</i> , 120 | AN,300 | 60 (20%) | 48 (16%) | Nommik and Moller (1981) |
| Sweden | <i>Pinus sylvestris</i> , 120 | AN,600 | 90 (12%) | 72 (12%) | Nommik and Moller (1981) |
| Tennessee | <i>Pinus taeda</i> , 4 | U,300 | 25 (8%) | - | Johnson and Todd (1988) |
| Western Washington | <i>Pseudotsuga menziesu</i> , 52 | NS,224 | 94 (42%) | 124 (55%) | Heilman and Gessel (1963) |
| Western Washington | <i>Pseudotsuga menziesu</i> , 38 | NS,224 | 204 (50%) | 206 (51%) | Heilman and Gessel (1963) |
| Western Washington | <i>Pseudotsuga menziesu</i> , 30 | NS,400 | 72 (13%) | 284 (51%) | Heilman and Gessel (1963) |
| Western Washington | <i>Pseudotsuga menziesu</i> , 32 | NS,560 | 75 (13%) | 687 (123%) | Heilman and Gessel (1963) |
| Western Washington | <i>Pseudotsuga menziesu</i> , 38 | NS,560 | 149 (20%) | 337 (46%) | Heilman and Gessel (1963) |
| Wisconsin | <i>Pinus resinosa</i> , 37 | AN,100 | 125 (125%) | - | Bockheim et al (1986) |

^aAS = Ammonium sulfate, AN = Ammonium nitrate, NS = Not specified, U = Urea

Source Johnson (1992)

applied nitrogen, Table 10-12), primarily due to fertilizer nitrogen retention in the litter and soil, including nonbiological reactions between NH_4^+ and humus. Fertilization studies differ from pollutant nitrogen deposition in several important respects: (1) pollutant nitrogen deposition enters the ecosystem at the canopy level, whereas fertilizer is typically (but not always) applied to the soil, (2) fertilization leads to high concentrations of NH_4^+ and, in the case of urea, high pH, both of which are conducive to nonbiological reactions between soil humus and NH_4^+ , and (3) pollutant nitrogen deposition enters the ecosystem as a slow, steady input in rather low concentrations, whereas the fertilizer is typically applied in one to five large doses. Both plants and nitrifying bacteria are favored by slow, steady inputs of nitrogen, possibly giving them a competitive advantage over heterotrophs for pollutant nitrogen inputs. A review of the literature on nitrogen cycling in unfertilized forests, with differing levels of pollutant nitrogen input supports this hypothesis. Ecosystem-level recovery of atmospherically deposited nitrogen (typically less than 50% and often 0%, Table 10-13 and Figure 10-8) is lower than of fertilizer nitrogen (typically 70 to 90% of applied nitrogen, Table 10-12 and Figure 10-11). It also appears that vegetation retention of incoming nitrogen in unfertilized forests is somewhat higher than in fertilized forests, whereas soil (heterotroph) retention of atmospherically deposited nitrogen is much lower. In forests with very low atmospheric nitrogen inputs, it appears as if the soil is being "mined" for the nitrogen necessary to supply vegetation, an indication that plants are actually out-competing heterotrophs for nitrogen. In forests with high atmospheric nitrogen inputs, heterotrophic nitrogen uptake appears to be minimal, perhaps because of limitations by organic substrates or other nutrients.

Because nitrification results in the creation of HNO_3 within the soil, there are concerns that elevated nitrogen inputs to nitrogen-saturated systems will result in soil acidification and Al mobilization. There are very few proven, documented cases in which excessive atmospheric nitrogen deposition has caused soil acidification (e.g., in forests in the Netherlands subject to very high nitrogen deposition levels, 40 to 80 kg/ha/year), but there is no doubt that the potential exists for many mature forests with low uptake rates, given high enough inputs for a sufficiently long time. The amount of nitrogen deposition required will vary with the ecosystem. The greatest uncertainty in assessing and projecting rates of soil

**TABLE 10-13. NITROGEN INPUTS, OUTPUTS, AND VEGETATION INCREMENTS
IN VARIOUS FOREST ECOSYSTEMS**

| Location | Species | Input (kg/ha/year) | Leaching (kg/ha/year) | Net Retention (kg/ha/year) ^a | Vegetation Increment (kg/ha/year) | Calc Soil Retention (kg/ha/year) ^b | Reference |
|----------------|--|-----------------------|--------------------------|---|---|---|---|
| New Hampshire | Northern hardwood | 6 5 | 4 0 | 2 5 (38%) | 9 0 (138%) | -6 5 (-100%) | Bormann et al (1977) |
| Washington | <i>Pseudotsuga menziesii</i> | 1 7 | 0 6 | 1 1 (65%) | 10 0 (588%) | -8 9 (-523%) | Cole and Rapp (1981) |
| Germany | <i>Fagus sylvatica</i> | 21 8 | 4 4 | 17 4 (80%) | 4 1 (19%) | 13 3 (61%) | Cole and Rapp (1981) |
| Germany | <i>Picea abies</i> | 21 8 | 14 9 | 6 9 (32%) | 2 2 (56%) | 4 7 (22%) | Cole and Rapp (1981) |
| U S S R | <i>Picea abies</i> | 1 1 | 0 9 | 0 2 (18%) | 9 0 (818%) | -8 8 (-800%) | Cole and Rapp (1981) |
| Tennessee | <i>Liriodendron tulipifera</i> | 7 7 | 3 5 | 4 2 (55%) | 7 1 (93%) | -2 9 (-60%) | Cole and Rapp (1981) |
| Washington | <i>Abies amabilis</i> | 1 3 | 2 7 | -1 4 (-108%) | | | Turner and Singer (1976) |
| Wisconsin | Aspen-mixed hardwood | 5 6 | 0 05 | 5 5 (99%) | 26 0 (464%) | -20 5 (-364%) | Pastor and Bockheim (1984) |
| Oregon | <i>Pseudotsuga menziesii</i> | 2 0 | 1 5 | 0 5 (25%) | -2 8 (-140%) | 2 3 (115%) | Sollins et al (1980) |
| Washington | <i>Alnus rubra</i> | 70 0 ^c | 71 0 | - | 7 1 | | Van Miegroet and Cole (1984) |
| Holland | <i>Quercus robur</i> , <i>Betula pendula</i> | 54 5 | 78 5 | -24 0 (44%) | 6 0 (11%) | -30 0 (-55%) | Van Breemen et al (1987) |
| Holland | <i>Quercus robur</i> | 56 2 | 28 1 | 28 2 (50%) | 24 0 (43%) | 4 2 (7%) | Van Breemen et al (1987) |
| Holland | <i>Quercus robur</i> | 44 6 | 22 5 | 22 1 (50%) | 17 0 (38%) | 5 1 (11%) | Van Breemen et al (1987) |
| Holland | Mixed deciduous | 62 8 | 87 6 | 24 8 (39%) | | | Van Breemen et al (1987) |
| Tennessee | Mixed deciduous | 13 0 | 3 1 | 9 9 (76%) | 13 5 (104%) | -3 6 (-2 7%) | Henderson and Harris (1975) |
| Ontario | <i>Acer saccharum</i> | 7 8 | 18 2 | -10 4 (-133%) | | | Foster and Nicholson (1988) |
| North Carolina | Mixed deciduous | 7 0 | 0 3 | 6 7 (96%) | 7 1 (101%) | -0 4 (5%) | Swank in Johnson and Lindberg (1992) ^d |
| Washington | <i>Abies amabilis</i> | 2 5 | 1 3 | 1 2 (48%) | 3 6 (144%) | -2 4 (-96%) | Cole and Van Miegroet in Johnson and Lindberg (1992) ^d |
| North Carolina | <i>Picea rubens</i> | 5 9 | 21 6 | -15 7 (-266%) | 0 5 (8%) | -16 2 (-275%) | Johnson et al (1991) |
| North Carolina | <i>Picea rubens</i> | 26 0 ^a | 20 5 | 5 5 (21%) | 1 8 (7%) | 3 7 (14%) | Johnson et al (1991) |
| North Carolina | <i>Pinus strobus</i> | 7 1 ^a | 0 3 | 6 8 (96%) | 6 6 (93%) | -0 2 (-3%) | Swank in Johnson and Lindberg (1992) ^d |

**TABLE 10-13 (con't). NITROGEN INPUTS, OUTPUTS, AND VEGETATION INCREMENTS
IN VARIOUS FOREST ECOSYSTEMS**

| Location | Species | Input (kg/ha/year) | Leaching (kg/ha/year) | Net Retention (kg/ha/year) ^a | Vegetation Increment (kg/ha/year) | Calc Soil Retention (kg/ha/year) ^b | Reference |
|----------------|-----------------------------|-----------------------|--------------------------|---|---|---|---|
| Maine | <i>Picea rubens</i> | 7 6 | 0 3 | 7.3 (96%) | - | - | Fernandez in Johnson and Lindberg (1992) ^d |
| Tennessee | <i>Pinus taeda</i> | 9 7 ^a | 0 6 | 9 1 (94%) | 6 6 (18%) | 2 5 (25%) | Johnson and Lindberg in Johnson and Lindberg (1992) ^d |
| Georgia | <i>Pinus taeda</i> | 9 0 ^a | 0 2 | 8 8 (98%) | - | - | Ragsdale in Johnson and Lindberg (1992) ^d |
| Ontario | Northern hardwood | 7 5 | 23 0 | -15 5 (-207%) | 1 3 (17%) | -16 8 (-224%) | Foster in Johnson and Lindberg (1992) ^d |
| New York | Spruce-fir | 16 0 ^a | 2 8 | 13 2 (83%) | 10 8 (180%) | 2 4 (15%) | Friedland in Johnson and Lindberg (1992) ^d |
| Florida | <i>Pinus elioti</i> | 6 0 ^a | 0 2 | 5 8 (97%) | 1 8 (30%) | 4 0 (67%) | Gholz in Johnson and Lindberg (1992) ^d |
| North Carolina | <i>Pinus taeda</i> | 14 0 ^a | 2 4 | 11 6 (83%) | 70 1 (500%) | -58 5 (418%) | Binkley and Knoerr in Johnson and Lindberg (1992) ^d |
| Norway | <i>Picea abies</i> | 10 8 ^a | 0 6 | 10 2 (96%) | 9 7 (91%) | 0 5 (5%) | Stuanes in Johnson and Lindberg (1992) ^d |
| Washington | <i>Pseudotsuga menziesu</i> | 4 8 | 0 4 | 4 4 (2%) | 5 4 (113%) | -1 0 (13%) | Cole and Van Miegroet in Johnson and Lindberg (1992) ^d |
| New York | Northern hardwood | 9 5 ^a | 1 5 | 8 0 (84%) | 1 1 (12%) | 6 9 (73%) | Mitchell and Sheppard in Johnson and Lindberg (1992) ^d |

^aInput — Leaching

^bInput — Leaching — Vegetation Increment

^cEstimated input by fixation

^dRefers to principal investigators for the specific data set summarized in Johnson and Lindberg (1992)

Source Johnson (1992)

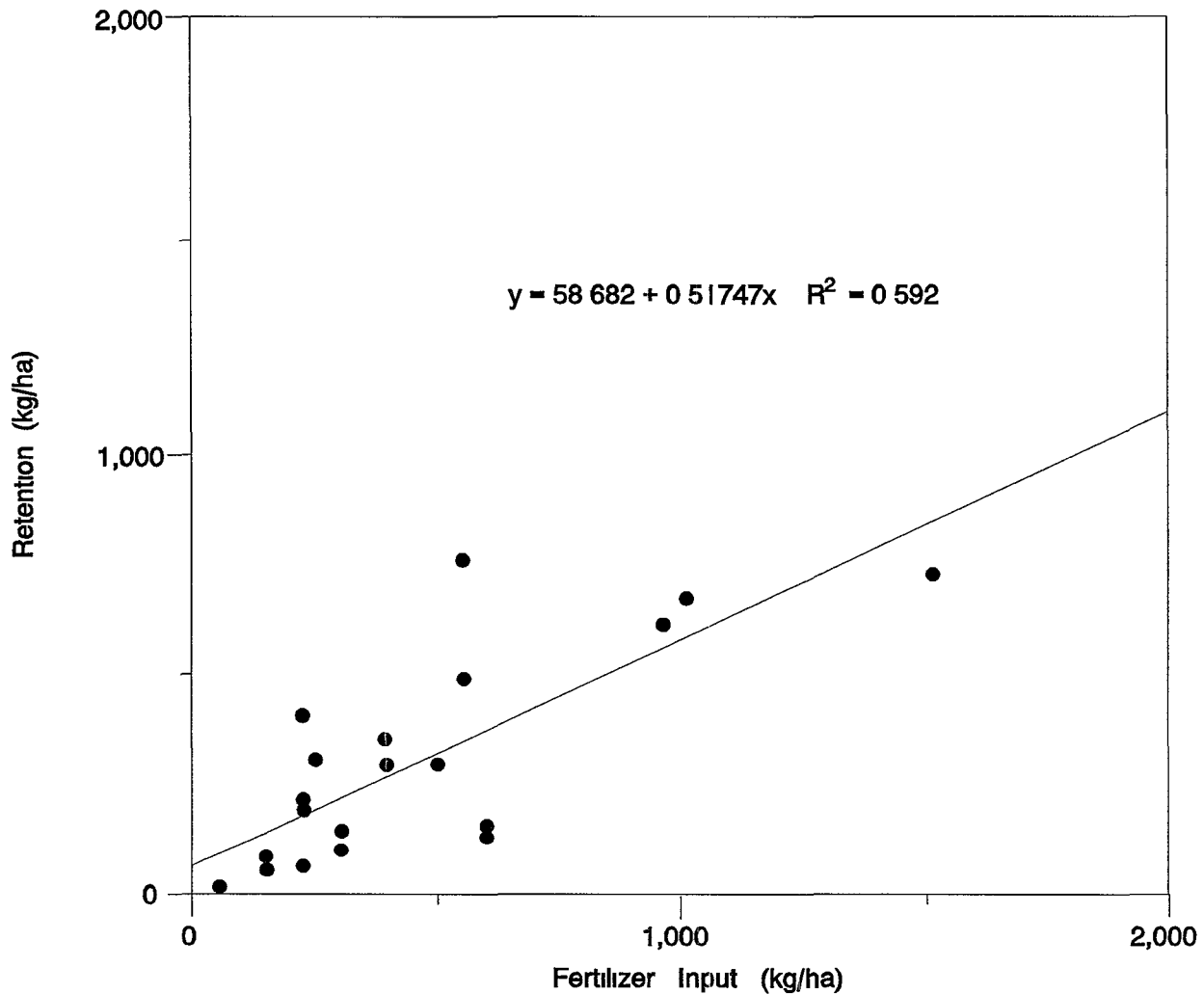


Figure 10-8. Ecosystem recovery of fertilizer nitrogen as a function of fertilizer nitrogen input.

Source Johnson (1992)

acidification is the estimation of weathering rates (i.e., the release of base cations from primary minerals)

Soil acidification is usually thought of as an undesirable effect, but in some cases, the benefits of alleviating nitrogen deficiency clearly outweigh the detriments of soil acidification (e.g., the benefits of nitrogen fixation by red alder always outweigh the detriments of soil acidification to succeeding Douglas fir stands in the Pacific Northwest)

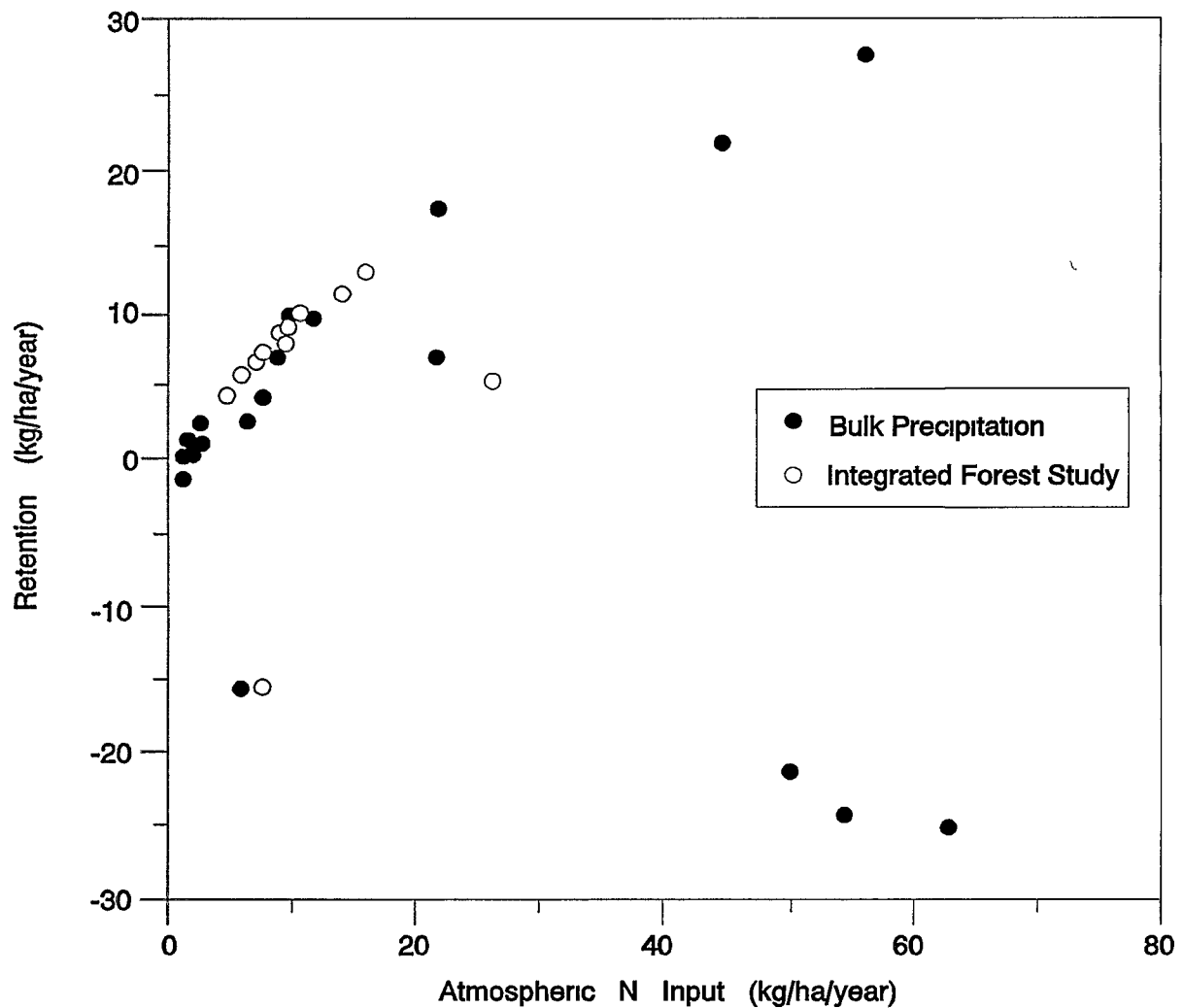


Figure 10-11. Ecosystem nitrogen retention as a function of atmospheric nitrogen input.

Source Johnson (1992)

Increased concentrations of NO_3^- or any other mineral acid anion (e.g., SO_4^{2-} or Cl^-) in soil solution lead to increases in the concentrations of all cations in order to maintain charge balance in solution. Equations describing cation exchange in soils dictate that as the total anion (and cation) concentrations increase, individual cation concentrations increase as follows: $\text{Al}^{3+} > \text{Ca}^{2+}$ and $\text{Mg}^{2+} > \text{K}^+, \text{Na}^+, \text{and } \text{H}^+$. Thus, soil-solution Al^{3+} concentrations increase not only as the soil acidifies (i.e., as the proportion of Al^{3+} on the

exchange complex increases) but also as the total ionic concentration of soil solution increases

There are several cases in which Al^{3+} concentrations in natural waters have been shown to be positively correlated with NO_3^- concentrations Ulrich (1983) noted NO_3^- - Al^{3+} pulses in soil solutions from the Solling site in Germany during warm, dry years He hypothesized that these nitrate-induced Al^{3+} pulses caused root injury and were a major contributor to what he termed "forest decline" observed in Germany during the mid-1980s This hypothesis is disputed by other German forest scientists who point out that forest decline occurred on base-rich as well as base-poor soils (the base-rich soils not being subject to Al^{3+} pulses) (e g , Rehfuss, 1987), Van Breemen et al (1982, 1987) and Johnson et al (1991) noted NO_3^- - Al^{3+} pulses in soil solutions from forest sites in the Netherlands and in the Smoky Mountains of North Carolina Aluminum toxicity is one of several nitrogen-related hypotheses posed to explain what has been termed forest decline in both countries Other hypotheses include weather extremes and climate change, Mg and K deficiencies that occur in sites naturally low in these nutrients, and foliar damage due to acid mist Researchers on aquatic effects of acid deposition have long noted springtime pulses of NO_3^- , Al^{3+} , and H^+ in acid-affected surface waters of the northeastern United States (Galloway et al., 1980, Driscoll et al , 1989b)

10.9.6 Effects of Nitrogen on Ecosystems

Ecosystems respond to environmental stresses through their constituent organisms (see Section 10.1) Plant populations, when exposed to any environmental stress, can exhibit four different reactions (1) no response—the individuals are resistant to the stress, (2) the most severe response—mortality of all individuals and local extinction of the extremely sensitive populations, (3) physiological accommodation—growth and reproductive success of individuals are unaffected because the stress is physiologically accommodated, and (4) differential response—members of the population respond differentially, with some individuals exhibiting better growth and reproductive success due to genetically determined traits (Taylor and Pitelka, 1992, Garner, 1992) The primary effect of air pollution on the more susceptible members of the plant community is that they can no longer compete effectively for essential nutrients, water, light, and space, and are eliminated The extent of

change that may occur in a community depends on the condition and type of community, as well as the pollutant exposure (Garner, 1992)

Plant responses are foliar or soil mediated. Subsequent to the dry and wet deposition of nitrogen forms from the atmosphere (Section 10.4), nitrogen-containing compounds can impact the terrestrial ecosystems when they enter plant leaves and alter metabolic processes (Chapter 9) or by modifying the nitrogen cycle and associated soil chemical properties (Section 10.5). Changes in biochemistry that result in reduced vigor and growth and decrease the plant's ability to compete for light, water, space, and nutrients can be manifested as changes in plant populations, communities, and, ultimately, ecosystems (Chapter 9, Section 10.2). Interpretation of the effects of wet- and dry-deposited nitrogen compounds at the ecosystem level is difficult because of the interconversion of nitrogen compounds and the complex interactions that exist between biological, physicochemical, and climatic factors (Section 10.2, U.S. Environmental Protection Agency, 1982). Nevertheless, reactive nitrogen compounds have been hypothesized to impact ecosystems through modifications of individual plant physiological processes upon entering plants through the foliage, or through alterations in the nitrogen status of the ecosystem.

Very little information is available on the direct effects of HNO_3 vapor on vegetation, and essentially no information is available on its effects on ecosystems. Norby et al. (1989) reported that HNO_3 vapor (0.075 ppmv) induced NRA in red spruce foliage. The effects of NH_3 , a reduced nitrogen gas, have been summarized by Van der Eerden (1982); however, NH_3 concentrations seldom reach phytotoxic levels in the United States (U.S. Environmental Protection Agency, 1982). In contrast, high NH_3 concentrations have been observed in Europe (Van Dijk and Roelofs, 1988). Van der Eerden (1982) summarized available information on the direct response of crop and tree species to NH_3 fumigation and concluded that the following concentrations produced no adverse effects: 0.107 ppmv ($75 \mu\text{g}/\text{m}^3$) yearly average, 0.858 ppmv ($600 \mu\text{g}/\text{m}^3$) daily average, and 14.3 ppmv ($10,000 \mu\text{g}/\text{m}^3$) hourly average. Submicron ammonium sulfate aerosols have been shown to affect foliage of *Phaseolus vulgaris* L. (Gmur et al., 1983). Three-week exposure to a concentration of $26 \text{ mg}/\text{m}^3$ (37 ppmv) produced leaf chlorosis, necrosis, and loss of turgor.

Because current ambient concentrations of NO , NO_2 , and NH_3 are low across much of the United States, except in certain highly populated urban areas, significant direct effects of

these nitrogen compounds on ecosystems seems unlikely at the current time. Concentration and effects data are unavailable for making similar conclusions regarding other reactive nitrogen compounds like HNO_3 vapor or the gaseous nitrate radical.

Serious consideration is currently being given to hypotheses that excess total nitrogen deposition may impact plant productivity directly or through changes in soil chemical properties. Furthermore it has been proposed that excess nitrogen deposition to ecosystems can modify interplant competitive balances, leading to changes in species composition and/or diversity. The uptake of nitrogen and its allocation is of overriding importance in plant metabolism and governs, to a large extent, the utilization of phosphorus, potassium, and other nutrients, and plant growth. Nitrogen is the mineral nutrient that most frequently limits growth in both agricultural and natural systems (Chapin et al., 1987). Normally, the acquisition of nitrogen is a major carbon expense for plants. Plants expend a predominant fraction of the total energy available to them in the form of carbohydrates in the acquisition of nitrogen. Absorption of nitrogen from the soil requires constant and extensive root growth to meet the needs of a rapidly growing plant because soil pools of nitrogen, ammonium, or nitrate in the immediate vicinity of the roots are usually so small that they are quickly depleted (Section 10.3).

Increased nitrogen deposition has been associated with changes in the following plant and soil processes involved in nutrient cycling: (1) plant uptake and allocation, (2) litter production, (3) immobilization (includes the processes of ammonification [the release of ammonium] and nitrification [the conversion of ammonium to nitrate during the decay of litter and soil organic matter]), (4) NO_3^- leaching, and (5) trace gas emission (Aber et al., 1989, Figure 10-17). Changes in tree physiology include altered nutrient uptake and carbohydrate allocation, which directly alters the rate of photosynthesis and influences growth rate and mycorrhizae formation, and increased leaf nitrogen (Chapin et al., 1987, Waring, 1985). Susceptibility to insect and disease attack have also been attributed to alteration in tree physiology (Chapin et al., 1987, Waring, 1987, Shigo, 1973, Hollis et al., 1975, Weetman and Hill, 1973).

Increased nitrogen inputs can affect tree resistance to insects and disease either positively or negatively. Alleviating nitrogen deficiency may increase plant resistance to pathogen attack, but it may also reduce the production of phenols in plant tissues, thereby

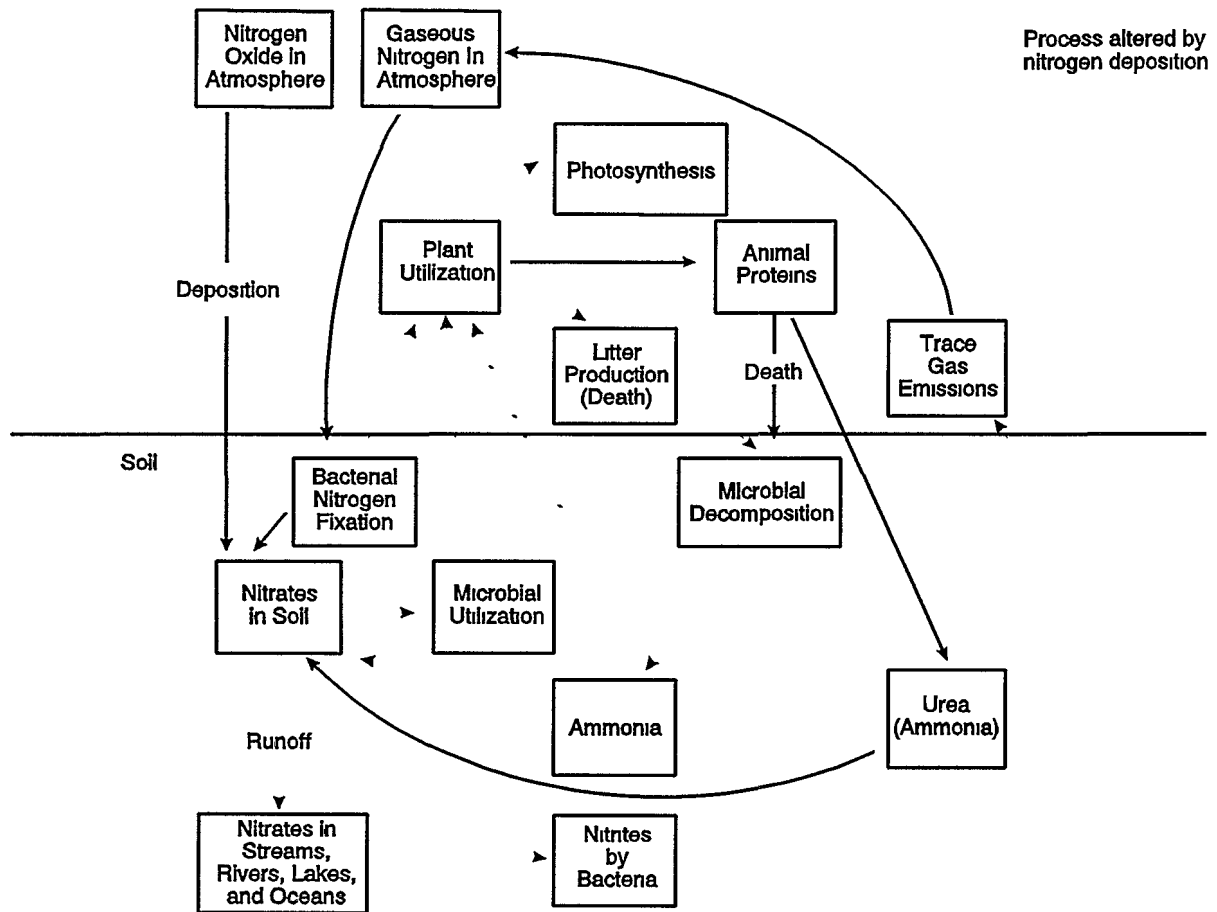


Figure 10-17. Nitrogen cycle (dotted lines indicate processes altered by chronic nitrogen deposition).

Source Garner (1992)

reducing resistance to pathogen attack To date, there is little research to show how increased nitrogen inputs affect susceptibility to pathogen attack, but the potential for either increased susceptibility or protection is significant

The nitrogen-photosynthesis relationship is critical to the growth of trees because in the leaves of plants with C_3 photosynthesis (the pathway used by most of the world's plants), approximately 75% of the total nitrogen is contained in the chloroplasts and is used during photosynthesis (Chapin et al , 1987) As a rule, plants allocate resources most efficiently when growth is equally limited by all resources When a specific resource such as nitrogen limits growth, plants adjust by allocating carbohydrates to the organs that acquire the most

strongly limiting resources, however, when nitrogen is abundant, allocation is to the formation of new leaves

Plants do not necessarily benefit from added nitrogen. More nitrogen in the soil is not mirrored by increased uptake except at low levels (Section 10.3). Among boreal and subalpine conifers and other vegetation adapted to resource-poor environments, nitrogen added to the soil may not increase growth. The nitrate reductase enzyme activity in roots and shoots determines the pattern of nitrate assimilation. The photosynthetic capacity of conifer foliage is low and not greatly enhanced by increasing the nitrogen content (Waring and Schlesinger, 1985). High leaf nitrogen content is not always an advantage when other resources, among which are light and water, are limited. When photosynthesis is measured at light saturation, leaf nitrogen is closely correlated with photosynthetic capacity. But when light is low, photosynthesis increases very little, if at all, with increasing leaf nitrogen (Chapin et al., 1987). In dense conifer forests, lack of sunlight makes the metabolic conversions of nitrate inefficient because production of large amounts of carbohydrates and other light-driven reactions become limiting (Zeevaart, 1976). When nitrogen is no longer limiting, deficiencies of other nutrients may occur (Aber et al., 1989; Kenk and Fischer, 1988). Competition, under the above circumstances, favors deciduous tree species, plants characteristic of resource-rich environments, rather than conifers (Waring, 1987).

Excessive NH_4^+ deposition (40 to 80 kg/ha/year) to soils in which nitrification is inhibited causes serious nutritional imbalances and even toxic effects to some forests in the Netherlands (Boxman et al., 1988). Deleterious effects of excess nitrogen deposition (40 to 80 kg/ha/year) can occur via aboveground processes as well. K and Mg deficiencies in declining Dutch forests are thought to be caused by excessive foliar leaching due to high inputs of NH_4^+ (Roelofs et al., 1985).

Growth responses to increased nitrogen inputs resulted in changes in species composition in ecosystems in the Netherlands (Van Breeman and Van Dijk, 1988). Species respond differentially to increased nitrogen availability, creating the potential for changes in ecosystem composition with increased nitrogen loading. Changes from heathland to grassland in Holland have been attributed to current rates of nitrogen deposition (Roelofs et al., 1987). Ellenberg (1987) points to further species changes in Central European ecosystems as a likely consequence of elevated nitrogen. He states that "More than 50% of

the plant species in Central Europe can only compete on stands that are deficient in nitrogen supply."

De Temmerman et al (1988) found increased fungal outbreaks and frost damage on several pine species exposed to very high NH_3 deposition rates ($> 350 \text{ kg/ha/year}$) Numbers of species and fruiting bodies of fungi have also decreased concomitantly with nitrogen deposition in Dutch forests (Van Breemen and Van Dijk, 1988) Schulze (1989) presents a clear progression of evidence that indicates that canopy uptake of nitrogen together with root uptake has caused a nitrogen imbalance in Norway spruce, leading to its decline

Excessive nitrogen inputs to terrestrial ecosystems can cause differential competitive advantage among plants within a heathland (Heil and Bruggink, 1987, Heil et al , 1988) In unmanaged heathlands in the Netherlands, *Calluna vulgaris* is being replaced by grass species as a consequence of the eutrophic effect of acidic rainfall and large nitrogen inputs arising from intensive farming practices in the region *Calluna* is an evergreen with a long growing season, which normally permits it to compensate for its slow growth rate so that it competes successfully with the faster growing *Molinia* (grass) under normal nutrient-limiting conditions However, a large increase in the nitrogen supply improves the competitive advantage of *Molinia*, increasing its growth rate so that it becomes the dominant species in the heathland. Roelofs et al (1987) observed that nitrophilous grasses (*Molinia* and *Deschampsia*) are displacing slower growing plants (*Erica* and *Calluna*) on heathlands in the Netherlands, and suggested that a correlation existed between this change and nitrogen loading. Van Breemen and Van Dijk (1988) found a substantial displacement of heathland plants by grasses from 1980 to 1986 and also observed increases in nitrophilous plants in forest herb layers Ellenberg (1988) suggested that ionic inputs (NO_3^- and NH_4^+) influence competition between organisms long before toxic effects appear on individual plants These changes in the Netherlands have occurred under nitrogen loadings of between 20 and 60 kg nitrogen/ha/year Liljelund and Torstensson (1988) have shown clear signs of vegetation changes in response to nitrogen deposition rates of 20 kg/ha/year

Evidence is accumulating that the assumed O_3 -specific effects of forests within the Los Angeles basin are not strictly the result of O_3 exposures but, in part, due to the co-deposition of oxides of nitrogen, specifically HNO_3 The environment is seldom optimal in either natural or agricultural communities It is not unusual, therefore, for plants growing

in natural habitats to encounter multiple stresses. Plant responses to multiple stresses depend on resource (carbon and nitrogen) interactions at levels ranging from the cell to the ecosystem (Chapin et al., 1987). At the present time, data dealing with the response of trees or other vegetation to the combined stresses of O_3 exposure above ground and nitrate deposition through the soil are sparse, however, when the responses of plants exposed to O_3 alone and to nitrate deposition alone are considered, it is possible to conceptualize how exposure to the two in combination could affect vegetation. Both O_3 exposure and nitrate uptake can affect the processes of photosynthesis, carbohydrate allocation, and nutrient uptake. The impact of a reduced carbon supply to the shoot or to the roots and the effect on subsequent allocation of nitrogen, as well as other nutrients, can be deduced from

Figure 10-17

The importance of the nitrogen-photosynthesis relationship and the allocation of nitrogen and carbon on plant growth has been discussed in the previous section. Patterns of carbon allocation directly influence the growth rate (McLaughlin et al., 1982, U.S. Environmental Protection Agency, 1986, Garner et al., 1989). The ready availability of nitrogen in the soil and its uptake influence the process of photosynthesis by increasing carbohydrate demand and shifting allocation (Figure 10-17) from the roots, to the shoots. To increase carbohydrate production in order to utilize increased leaf nitrogen, plants compensate by producing more leaves.

Exposure to O_3 inhibits photosynthesis and increases carbohydrate demand in plants that already have a high carbohydrate demand. Ozone is the most phytotoxic of the ambient air pollutants. Many controlled studies using both herbaceous and woody vegetation have demonstrated inhibition of photosynthesis and premature senescence of leaves by O_3 exposure (Garner et al., 1989, U.S. Environmental Protection Agency, 1986). Exposure of sensitive trees to O_3 decreases growth and vigor by inhibiting photosynthesis, decreasing carbohydrate production and allocation to the roots, and interfering with mycorrhizae formation (McLaughlin et al., 1982, Tingey and Taylor, 1982, U.S. Environmental Protection Agency, 1986, Garner et al., 1989).

Both increased soil nitrogen and O_3 exposure can affect nutrient uptake. When nitrogen is readily available, other nutrients (e.g., phosphorus and calcium) can become limiting. Decreased carbohydrate allocation to roots, a result of O_3 exposure, interferes with

mycorrhizae formation and, subsequently, nutrient uptake. Limiting carbohydrate production and nutrient availability suppresses growth (McLaughlin et al., 1982, Mooney and Winner, 1988; U.S. Environmental Protection Agency, 1986). The combined stresses resulting from increased soil nitrogen and ambient O₃ exposure, therefore, have the capability of severely impacting plant growth.

10.9.7 Nitrogen Saturation, Critical Loads, and Current Deposition

Ecosystem nitrogen saturation and the definition of the level of total nitrogen deposition at which critical changes begin to appear in sensitive ecosystems have been the subject of recent conferences in Europe (Nilsson and Grennfelt, 1988, Brown et al., 1988, Skeffington and Wilson, 1988). The Workshop held at Skokloster, Sweden, in March 1988 (Nilsson and Grennfelt, 1988) adopted the following definition for a critical load: "A quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge." In the Skokloster Report (Nilsson and Grennfelt, 1988) and subsequent publications synthesizing much of the information, nitrogen critical loads were aimed "to protect soils from long-term chemical changes with respect to base saturation" (Nilsson and Grennfelt, 1988, Schulze et al., 1989). The critical loads were estimated using two equations. Based on the equations and estimates of the various parameters within them, the authors calculated critical loads for various forest ecosystems. Their values ranged from a low of 3 to 5 kg nitrogen/ha/year for raised bogs to a high of 5 to 20 kg nitrogen/ha/year. It is important to recognize that the magnitude of such a critical load will be site and species specific because it is highly dependent on initial soil chemistries and biological growth potentials (i.e., nitrogen demands).

The aim of the nitrogen saturation concept is to make it possible to define a critical load for nitrogen (deposition rate) at which no change or deleterious impacts will occur to an ecosystem (Nilsson, 1986). Problems exist, however, with implementing the concept. Establishing a critical load depends on the criteria used (e.g., one critical load would be required to prevent species change and another would be required to prevent community change) (Liljelund and Torstensson, 1988).

Skeffington and Wilson (1988) point out that intrinsic in all definitions of a critical load is the notion that there is a load at which no long-term effects occur. The complexity of the nitrogen cycle and ecosystem diversity make defining a critical load for nitrogen very difficult. The following possible criteria may be useful for defining appropriate critical nitrogen loads on ecosystems

- prevent nitrate levels in drinking or surface waters from rising above standard levels,
- ensure proton production less than weathering rate,
- maintain a fixed NH_3 -base cation balance,
- maintain nitrogen inputs below nitrogen outputs (the nitrogen-saturation approach), and
- minimize accelerations in the rates of ecological succession (vegetation changes due to altered interspecific competition)

In summarizing the results of a recent conference on critical nitrogen loading, after discussing various options for setting a critical nitrogen load, Skeffington and Wilson (1988) concluded that "we do not understand ecosystems well enough to set a critical load for nitrogen deposition in a completely objective fashion." Brown et al. (1988) further concluded that there was probably no universal critical load definition that could be applied to all ecosystems, and a combination of scientific, political, and economic considerations would be required for the application of the critical load concept.

The following terrestrial ecosystems have been suggested as being at risk from the deposition of nitrogen-based compounds

- heathlands with a high proportion of lichen cover,
- low meadow vegetation types used for extensive grazing and haymaking, and
- coniferous forests, especially those at high altitudes (World Health Organization, 1987)

The above oligotrophic ecosystems are considered at risk from atmospheric nitrogen deposition because plant species normally restricted by low nutrient concentrations could gain a competitive advantage, and their growth at the expense of existing species would change the "normal" species composition and displace some species entirely (Ellenberg, 1987, Waring, 1987). Sensitive natural ecosystems, unlike highly manipulated agricultural systems, may be prone to change from exposure to dry deposited nitrogen compounds because processes of natural selection whereby tolerant individuals survive may not be keeping pace.

with the current levels of atmospheric nitrogen deposition (World Health Organization, 1987)

There is little doubt that nitrogen deposition has had an effect on many ecosystems in Europe. Kauppi et al (1992) report that biomass of European forest increased during the 1971 to 1990 period. This is in stark contrast to earlier claims of forest decline. The authors attribute this growth increase to increases in nitrogen deposition and base their conclusions on a comparison of the magnitude of increases in nitrogen deposition and responses shown by European forests to nitrogen fertilizer. It is logical to assume that the same growth increase would occur in many forests in North America (especially western North America) with increased deposition, given known nitrogen deficiencies and responses to nitrogen fertilization (Aber et al, 1989, Gessel et al, 1973)

However, because ecosystems have a variable capacity to buffer changes caused by elevated inputs of nitrogen, it is difficult to make general conclusions about the type and extent of change (if any) currently resulting from nitrogen deposition in North America. More research needs to be conducted in this area to determine if the hypothesized effects of excess nitrogen deposition are taking place and to determine the sensitivity of a wide range of natural ecosystems to nitrogen loading.

10.9.8 Effects of Nitrogen on Wetlands and Bogs

The anaerobic (oxygen-free) nature of their waterlogged soils is the feature that sets wetlands apart. Anaerobic wetland soils favor the accumulation of organic matter and losses of mineral nitrogen to the atmosphere through denitrification reactions (the conversion of nitrate to gaseous nitrogen by microbes). Nitrogen deposition can impact plant and microbial processes either directly or indirectly by acidifying the environment. An increase in nitrogen supply through atmospheric deposition or other means alters the competitive relationships among plant species such that fast-growing nitrophilous species (species that have a high nitrogen requirement) are favored. Microbial rates of decomposition, nitrogen fixation (the conversion of gaseous nitrogen to ammonium), nitrification (the conversion of ammonium to nitrate), and dissimilatory nitrate reduction (conversion to gaseous nitrogen or ammonium) are all affected. Acidification below pH 4 to 5.7 blocks the nitrogen cycle by inhibiting nitrification, and the accumulation of NH_4^+ in the environment represses nitrogen fixation.

(Roelofs, 1986, Schuurkes et al , 1986, 1987, Rudd et al , 1988) The proportion of N_2O produced by denitrification reactions increases with decreasing pH below 7, and the absolute rate of production of N_2O increases with increasing eutrophication (nutrient enrichment of the environment) (Focht, 1974) This is potentially important on a global scale because of chemical reactions with N_2O in the atmosphere that result in a loss of O_3

The importance of atmospheric nitrogen deposition to the community structure (species composition and interrelationships) of wetlands increases as rainfall increases as a fraction of the total water budget Primary production (plant growth) in wetlands is commonly limited by nitrogen availability Primary production is proportional to the rate of internal nitrogen cycling, which is influenced by the quantity of mineralizable soil nitrogen as well as the supply of nitrogen to the ecosystem from the atmosphere or surface flow Total nitrogen inputs range from about 10 kg nitrogen/ha/year in ombrotrophic bogs (rain-fed bogs), which receive water only through precipitation, to 750 kg nitrogen/ha/year or more in intertidal wetlands with large ground and surface hydrologic inputs

From studies of nine North American wetlands, bulk nitrogen deposition ranges from 5.5 to 12 kg nitrogen/ha/year and occurs in the form of NO_3^- , NH_4^+ , and dissolved organic nitrogen in roughly equal proportions More recent studies, however, suggest that these rates are too low and that the wet deposition of NO_3^- alone is greater than 15 kg nitrogen/ha/year over much of eastern North America (Zemba et al , 1988) Dry deposition, which probably accounts for greater than 50% of total deposition, adds to the total Leaf capture of nitrogen in fog droplets is a third form of deposition that is locally important Applications of nitrogen fertilizer in the field, ranging from 7 to 3,120 kg nitrogen/ha/year, have increased standing biomass by 6 to 413% Other nutrients, like phosphorus, become secondarily limiting to primary production after nitrogen inputs reach a threshold Fertilization and increased atmospheric deposition have increased the dominance of grass species over other plant species in bogs, and extreme eutrophication is associated with a decrease in plant species diversity

Single additions to vegetated wetland soils of ^{15}N -labeled mineral nitrogen at rates of about 100 kg nitrogen/ha/year indicate that up to 93% of applied NH_4^+ is rapidly assimilated into organic matter within a single growing season The majority of the labeled nitrogen is lost from the system after 3 years by the combined processes of advective transport in water

(carried in moving water) of particulate organic matter, advective and diffusive transport of dissolved nitrogen, and denitrification. In the absence of plants, the major fate of inorganic nitrogen applied to wetland soils is loss to the atmosphere by denitrification.

Peat-forming *Sphagnum* spp. are largely absent from bogs in western Europe where bulk deposition rates are about 20 to 40 kg nitrogen/ha/year, and soft-water communities once dominated by isoetids in the Netherlands have been converted to later successional stages dominated by *Juncus* spp. (rush) and *Sphagnum* spp. or to grasslands. Heathlands dominated by shrubs have also converted to grasslands. Experimental studies indicate that ombrotrophic bogs can be maintained if nitrogen inputs are less than 20 kg nitrogen/ha/year. Increased productivity associated with eutrophication is accompanied by increased rates of transpiration (evaporation of water from leaf surfaces), which can alter wetland hydrology and influence the direction of wetland succession. By this mechanism, one modeling study suggests that a succession (change) from open ombrotrophic bog to forested wetland occurs when a threshold of 7 kg nitrogen/ha/year is exceeded. These estimates are consistent with conclusions from studies of species distributions that place the limit for many species from 10 to 20 kg nitrogen/ha/year (Liljelund and Torstensson, 1988).

Fourteen percent (18 species) of the plant species from the conterminous United States that are formally listed as endangered, and an additional 284 species listed as potentially threatened (Code of Federal Regulations, 1987), are found principally in wetland habitats. Some of the endangered plants, like the green pitcher plant, are known to be adapted to infertile habitats and are threatened by current levels of nitrogen deposition in parts of North America. Plant species that are threatened by high nitrogen deposition are not confined to wetland habitats, however, but are common across many ecosystem types (Ellenberg, 1988).

10.9.9 Effects of Nitrogen on Aquatic Systems

Nitrogen deposition has not historically been considered a serious threat to the integrity of aquatic ecosystems.

Assessment of the aquatic effects of NO_x depends on a close examination of the processes by which nitrogen may enter streams, lakes and estuaries. Sources of nitrogen may include (1) atmospheric deposition directly to the water surface, (2) deposition to the watershed that is subsequently routed to the drainage waters, (3) gaseous uptake by plants

that is subsequently routed, by way of litter fall and decomposition, to drainage waters, and (4) nitrogen fixation, either in the water itself, or in watershed soils. In addition, numerous processes act to transform nitrogen species into forms that are only indirectly related to the original deposition or fixation. These transformations include (1) nitrogen assimilation (the biological uptake of inorganic nitrogen species), (2) nitrification (the oxidation of ammonium to nitrate), (3) denitrification (the biological reduction of nitrate to form gaseous forms of nitrogen, N_2 , NO, or N_2O), and (4) mineralization (the decomposition of organic forms of nitrogen to form ammonium). The multiple sources of nitrogen to aquatic systems, and the complexities of nitrogen transformations in water and watersheds, have the effect of decoupling nitrogen deposition from nitrogen effects, and reduce our ability to attribute known aquatic effects to known rates of nitrogen deposition. Although it is not currently possible to trace the pathway of nitrogen from deposition through any given watershed and into drainage waters, we can, in areas of the United States where nonatmospheric sources of nitrogen are small, begin to infer cases where nitrogen deposition is having an impact on aquatic ecosystems.

Any discussion of the aquatic effects of NO_x must focus on the concept of nitrogen saturation. Nitrogen saturation can be defined as a situation where the supply of nitrogenous compounds from the atmosphere exceeds the demand for these compounds on the part of watershed plants and microbes (Skeffington and Wilson, 1988, Aber et al., 1989). Under conditions of nitrogen saturation, forested watersheds that previously retained nearly all of nitrogen inputs, due to a high demand for nitrogen by plants and microbes, begin to supply more nitrogen to the surface waters that drain them. Our conceptual understanding of nitrogen saturation suggests that, in aquatic systems, the earliest stages of nitrogen saturation will be observable as increases in the severity and duration of springtime pulses of nitrate.

The aquatic effects of NO_x can be divided into three general categories:

(1) acidification, both chronic and episodic, (2) eutrophication of both fresh waters and estuaries, and (3) directly toxic effects.

10.9.9.1 Acidification

Acidification effects are traditionally divided into chronic (long-term) and episodic (short-term effects usually observable only during seasons of high runoff) effects. Nitrate,

the dominant form of inorganic nitrogen in almost all aquatic systems, is commonly present in measurable concentrations only during winter and early spring, when terrestrial demand for nitrogen is low because plants in the watershed are dormant. Nitrogen will, therefore, only be a problem in chronic acidification in rare cases where the process of nitrogen saturation is very much progressed. Chronic acidification by nitrogen can be conclusively demonstrated only in parts of Europe (e.g., Hauhs, 1989, Hauhs et al., 1989, Van Breemen and Van Dijk, 1988).

Episodic acidification by nitrate is far more common than chronic acidification, and is well documented for streams (Driscoll et al., 1987b) and lakes (Galloway et al., 1980, Driscoll et al., 1991, Schaefer et al., 1990) in the Adirondack Mountains, for streams in the Catskill Mountains (Stoddard and Murdoch, 1991, Murdoch and Stoddard, in press b), and in a small proportion of lakes in Vermont (Stoddard and Kellogg, in press), as well as in many parts of Canada (Jeffries, 1990) and Europe (e.g., Hauhs et al., 1989).

Based on intensive monitoring data, it is possible to divide lakes and streams into three groups, based on their seasonal NO_3^- behavior. In many parts of the country, nitrogen demand on the part of the terrestrial ecosystem is sufficiently high that no leakage of NO_3^- from watersheds occurs, even when nitrogen deposition rates are relatively high, and cold temperatures should limit the biological demand for nitrogen. Lakes and streams in these areas show no evidence that nitrogen deposition is producing adverse aquatic effects.

In a second group of lakes and streams, NO_3^- concentrations show strong seasonality, with peak concentrations during snowmelt or following large rain events. In many cases, these episodic increases in NO_3^- , along with already low baseline ANC are sufficient to cause short-term acidification and potential adverse biological effects. It is important to note that seasonal increases in NO_3^- concentrations can be produced by normal watershed processes; lowered terrestrial demand for nitrogen during the dormant season, for example, creates a strong likelihood that springtime drainage waters will show NO_3^- concentrations that are elevated over summer and fall concentrations. Mineralization of organic matter during the cold months of winter, coupled with low biological demand for nitrogen, can produce high winter concentrations of NO_3^- in soil water that is subsequently flushed into drainage waters during spring snowmelt or during large rain storms. Although the seasonal pattern of elevated NO_3^- concentrations in this group of lakes and streams can be considered

normal, the severity of the NO_3^- episodes that these systems experience can be strongly influenced by the amount of nitrogen stored in the snowpack over the course of the winter. If biological demand for nitrogen is still low at the onset of snowmelt, the entire store of snowpack NO_3^- can be flushed into drainage waters in the very early stages of snowmelt (e.g., Johannessen and Henriksen, 1978, Jeffries, 1990).

The third group of lakes and streams exhibits both the strong seasonality in NO_3^- concentration described in the previous paragraph, and increasing trends in NO_3^- concentrations. Because the early stages of nitrogen saturation are expected to produce increases in NO_3^- concentrations, especially during episodes, long-term increases in NO_3^- may represent the strongest evidence that nitrogen deposition is responsible for aquatic effects. In all cases where increasing trends in NO_3^- have been documented in the United States (Smith et al., 1987b, Stoddard and Murdoch, 1991, Murdoch and Stoddard, in press b, Driscoll and Van Dreaseon, in press), they have occurred at a time when nitrogen deposition is relatively constant (e.g., Simpson and Olsen, 1990). Increased leakage of NO_3^- from watersheds in these areas, therefore, represents a long-term decrease in the ability of watersheds to retain nitrogen. A likely cause of such long-term changes is a lowering in the demand for nitrogen as a nutrient on the part of the terrestrial ecosystem, which may result from long-term high rates of nitrogen deposition to affected watersheds (e.g., Aber et al., 1989), forest maturation (Elwood et al., 1991), or, more likely, a combination of both factors.

The locations of lake and stream sites in each of the three NO_3^- groups are shown on maps of the Northeast (Figure 10-36), the Southeast (Figure 10-37), and the West (Figure 10-38). In order to assess which lake and stream sites fall into each group, it was necessary to have data collected over several years (at least 3 years) and on a relatively intensive sampling schedule (at least four times per year, to illustrate seasonal patterns). These criteria exclude many sources of data, most notable are those from the NSWS (Linthurst et al., 1986, Landers et al., 1987, Kaufmann et al., 1988), and limit the conclusions that can be drawn concerning the spatial extent of aquatic effects attributable to nitrogen deposition. Nonetheless, the maps illustrate the existence of severe problems in the Northeast (especially the Adirondack and Catskill Mountains) and the Southeast (in the

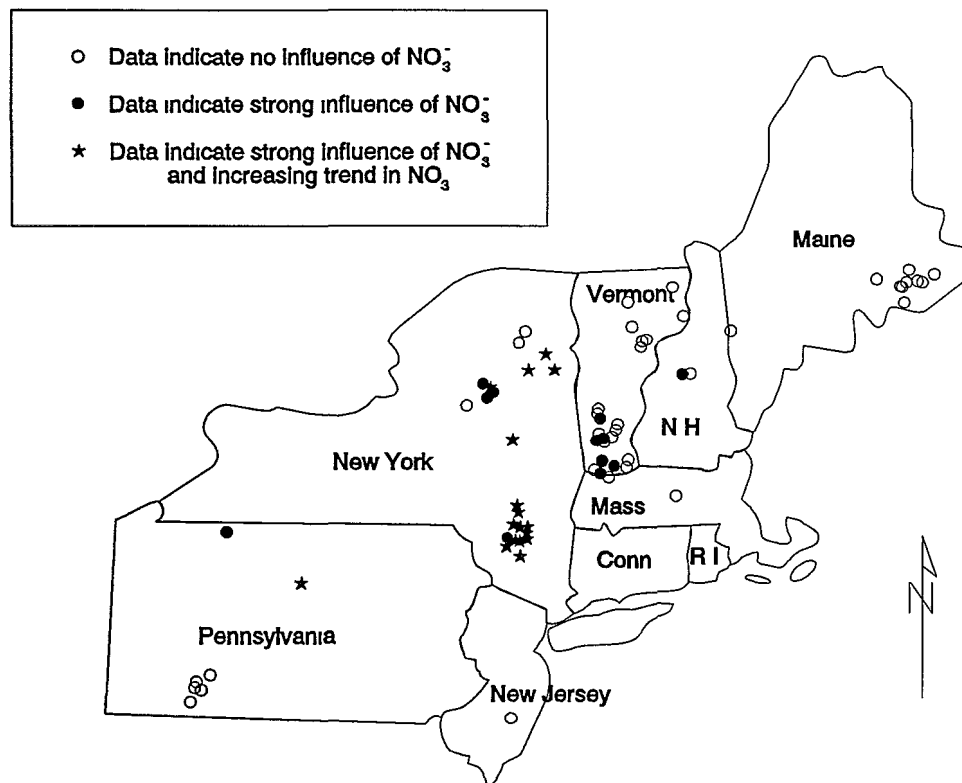


Figure 10-36. Location of acid-sensitive lakes and streams in the northeastern United States where the importance of nitrate to seasonal water chemistry can be determined.

Source: Kahl et al (1991), Wigington et al (1990), Driscoll et al (1987a), Driscoll and Van Dreason (in press), Kramer et al (1986), Murdoch and Stoddard (in press a), Eshleman and Hemond (1985), Morgan and Good (1988), Baird et al (1987), Likens (1985), Sharpe et al (1984), Stoddard and Kellogg (in press), DeWalle et al (1988), Barker and Witt (1990), Schofield et al (1985), Phillips and Stewart (1990)

Mid-Appalachians and Great Smoky Mountains), and the potential for future problems in the West.

It is also possible to draw correlations between rates of nitrogen deposition and rates of nitrogen loss from watersheds, although these analyses cannot indicate causal relationships, they can suggest patterns that merit further attention. Two independent attempts have been made to relate deposition and watershed nitrogen export in the United States, and both suggest similar conclusions. Kaufmann et al (1991) used data from the NSS (Kaufmann

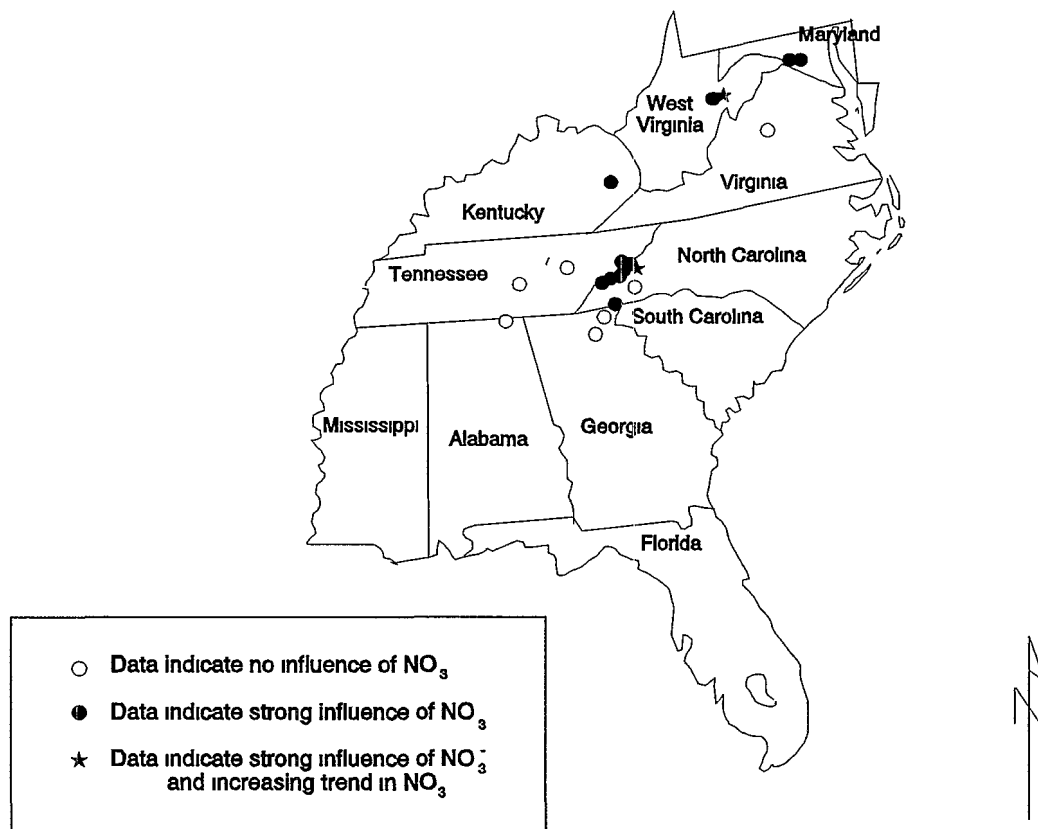


Figure 10-37. Location of acid-sensitive lakes and streams in the southeastern United States where the importance of nitrate ions to seasonal water chemistry can be determined.

Source Elwood et al (1991), Cosby et al (1991), Elwood and Turner (1989), Buell and Peters (1988), Swank and Waide (1988), Jones et al (1983), Silsbee and Larson (1982), Katz et al (1985), Weller et al (1986), Wigington et al (1990), Kramer et al (1986), Edwards and Helvey (1991)

et al , 1988) and interpolated wet deposition values (of $\text{NO}_3^- + \text{NH}_4^+$) to correlate deposition and surface water dissolved inorganic nitrogen concentrations ($\text{NO}_3^- + \text{NH}_4^+$) in large physiographic regions of the eastern United States (Figure 10-39) The NSS was a probability-based sample of streams, sampled at spring base flow in 1987, because it is probability-based, the results from the relatively small number of streams sampled in the NSS can be extrapolated to the population of streams within each of the nine regions sampled The results of the correlation suggest a strong correspondence between median wet deposition of nitrogen in a region and the median spring base-flow concentration of nitrogen

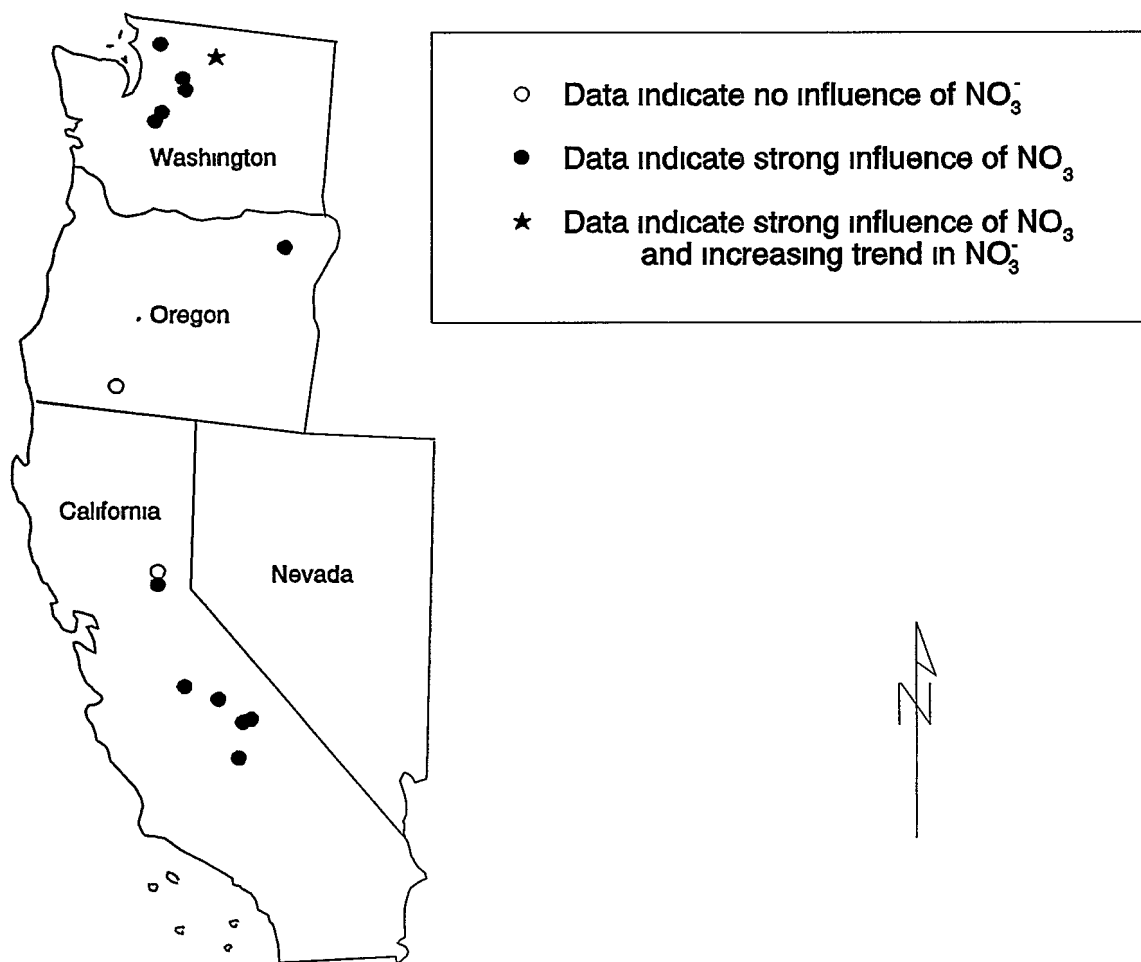


Figure 10-38. Location of acid-sensitive lakes and streams in the western United States where the importance of nitrate ions to seasonal water chemistry can be determined.

Source Melack and Stoddard (1991), Stoddard (1987a), Loranger et al (1986), Wightington et al (1990), Kramer et al (1986), Welch et al (1986), Eilers et al (1990), Gilbert et al (1989)

in a region In addition, the results suggest a threshold rate of wet nitrogen deposition of approximately 3 kg nitrogen/ha/year, above which significant losses of nitrogen from watersheds can begin to occur

Driscoll et al. (1989a) collected input/output budget data for a large number of undisturbed forested watersheds in the United States and Canada, and summarized the

relationship between nitrogen export (of NO_3^-) and wet nitrogen deposition (of $\text{NO}_3^- + \text{NH}_4^+$). These data are supplemented in Figure 10-39 with some published input/output data that were not included in the original figure. Driscoll et al. (1989a) stress that the data were collected using widely differing methods and over various time scales (from 1 year to several decades). Like the data of Kaufmann et al. (1991, Figure 10-39), these budget data suggest a threshold rate of wet nitrogen deposition of approximately 3 kg nitrogen/ha/year, above which significant export of NO_3^- from watersheds may occur.

10.9.9.2 Eutrophication

Assigning responsibility for the eutrophication of lakes and estuaries to NO_x requires a determination of two key conditions. The first is that the productivity of the aquatic system be limited by the availability of nitrogen, rather than by some other nutrient or physical factor. The second is that nitrogen deposition be a significant source of nitrogen to the system. In many cases of eutrophication, the supply of nitrogen from deposition is minor when compared to other anthropogenic sources, such as pollution from either point or nonpoint sources.

It is generally accepted that the productivity of fresh waters is limited by the availability of phosphorus, rather than the availability of nitrogen (reviewed by Hecky and Kilham, 1988). Conditions of nitrogen limitation do occur in lakes, but are often either transitory, or the result of high inputs of phosphorus from anthropogenic sources. Often when nitrogen limitation does occur, it is a short-term phenomenon because nitrogen-deficient conditions favor the growth of nitrogen-fixing blue-green algae (e.g., Smith, 1982). Because nitrogen-fixing species are not limited by the availability of fixed nitrogen (e.g., NH_4^+ or NO_3^-), they may thrive under conditions where other species are nitrogen limited, and may effectively increase rates of nitrogen input to the system (by fixation of gaseous nitrogen) beyond the levels where system productivity can be said to be nitrogen limited. It appears that nitrogen limitation may occur naturally (i.e., in the absence of anthropogenic phosphorus inputs) in lakes with very low concentrations of both nitrogen and phosphorus, as are common in the western United States and in the Northeast. Suttle and Harrison (1988) and Stockner and Shortreed (1988) suggest that phosphorus concentrations are too low in these systems to allow blue-green algae to thrive, because they are poor competitors for phosphorus at very

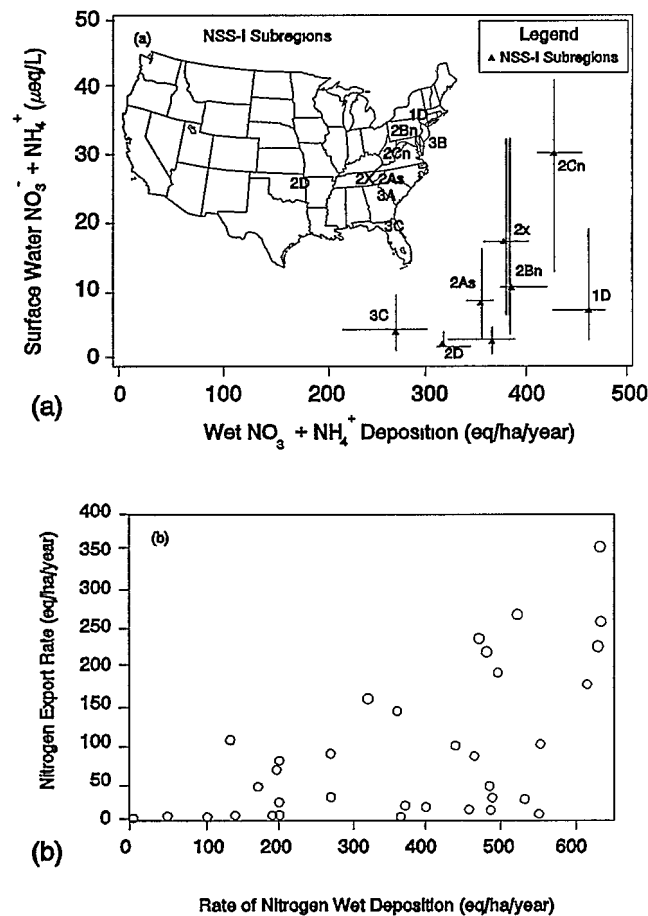


Figure 10-39. (a) Relationship between median wet deposition of nitrogen (nitrate ions plus ammonium ions) and median surface water nitrogen (nitrate ions plus ammonium ions) concentrations for physiographic districts within the National Stream Survey that have minimal agricultural activity. [Subregions are Poconos/Catskills (1D), Southern Blue Ridge Province (2As), Valley and Ridge Province (2Bn), Northern Appalachians (2Cn), Ozarks/Ouachitas (2D), Southern Appalachians (2X), Piedmont (3A), Mid-Atlantic Coastal Plain (3B), and Florida (3C)]. From Kaufmann et al. (1991). (b) Relationship between wet deposition of nitrogen (nitrate ions plus ammonium ions) and rate of nitrogen export for watershed studies throughout North America. Sites with significant internal sources of nitrogen (e.g., from alder trees) have been excluded.

Source Driscoll et al (1989a), additional data from Barker and Witt (1990), Edwards and Helvey (1991), Kelly and Meagher (1986), Katz et al (1985), Buell and Peters (1988), Weller et al (1986), Owens et al (1989), Feller (1987), Stoddard and Murdoch (1991)

low concentrations Results of the NSWS (Kanciruk et al , 1986, Eilers et al , 1987) suggest that the largest number of potentially nitrogen-limited lakes in the United States occur in the West (20 to 30% of the population of lakes sampled by NSWS), and particularly in the Pacific Northwest, although significant numbers may also occur in the Upper Midwest (15 to 25% of population) In all cases, because the concentrations of both nitrogen and phosphorus are low, additional inputs of nitrogen may have a limited potential to cause eutrophication because their input will quickly lead to a switch in the limiting nutrient, additions of nitrogen to these systems would soon lead to nitrogen-sufficient and phosphorus-deficient conditions Increases in nitrogen deposition to some regions would probably lead to measurable increases in algal biomass in lakes with both low concentrations of dissolved nitrogen and substantial concentrations of phosphorus, but the number of lakes that meet these criteria naturally (i.e., that do not have large anthropogenic inputs of phosphorus) is likely to be quite small

Few topics in aquatic biology have received as much attention in the past decade as the debate over whether estuarine and coastal ecosystems are limited by nitrogen, phosphorus, or some other factor (reviewed by Hecky and Kilham, 1988) Numerous geochemical and experimental studies have suggested that nitrogen limitation is much more common in estuarine and coastal waters than in freshwater systems Experiments to confirm widespread nitrogen limitation in estuaries have not been conducted, however, and nitrogen limitation cannot be assumed to be the rule Taken as a whole, the productivity of estuarine waters of the United States correlates more closely with supply rates of nitrogen than of other nutrients (Nixon and Pilson, 1983) Specific instances of phosphorus limitation (Smith, 1984) and of seasonal switching between nitrogen and phosphorus limitation (D'Elia et al , 1986, McComb et al , 1981) have been observed and stand as exceptions to the general rule of nitrogen limitation in marine ecosystems Nitrogen-fixing blue-green algae are rarely abundant in estuarine waters (Howarth et al , 1988a), and so nitrogen-deficient conditions may continue indefinitely in these systems, unless nitrogen supply exceeds the biological demand for nitrogen

Estimation of the contribution of nitrogen deposition to the eutrophication of estuarine and coastal waters is made difficult by the multiple direct anthropogenic sources (e.g., from agriculture and sewage) of nitrogen against which the importance of atmospheric sources

must be weighed. Estuaries and coastal areas are natural locations for cities and ports, and most of the watersheds of major estuaries in the United States have been substantially developed. The crux of any assessment of the importance of nitrogen deposition to estuarine eutrophication is establishing the relative importance of direct anthropogenic effects (e.g., sewage and agricultural runoff) and indirect effects (e.g., atmospheric deposition). In the United States, a large effort has been made to establish the relative importance of sources of nitrogen to the Chesapeake Bay (e.g., D'Elia et al., 1982, Smullen et al., 1982, Fisher et al., 1988b, Tyler, 1988). Estimates of the contribution of nitrogen to the Chesapeake Bay from each individual source are very uncertain, estimating the proportion of nitrogen deposition exported from forested watersheds is especially problematic, but critical to the analysis because about 80% of the Chesapeake Bay basin is forested. Nonetheless, three attempts at determining the proportion of the total NO_3^- load to the bay attributable to nitrogen deposition all produced estimates in the range of 18 to 31% (Table 10-27). Supplies of nitrogen from deposition exceed supplies from all other nonpoint sources to the bay (e.g., agricultural runoff, pastureland runoff, urban runoff), and only point-source inputs represent a greater input than deposition.

10.9.9.3 Direct Toxicity

Toxic effects of nitrogen on aquatic biota result from un-ionized NH_3 , which occurs in equilibrium with ionized NH_4^+ and OH^- . Ammonia concentrations approach toxic concentrations most commonly at high pH and temperature values, which are most typical of heavily polluted lakes and streams (e.g., Effler et al., 1990). In the well-oxygenated conditions typical of unpolluted lakes and streams (as well as in most watersheds), NH_4^+ is rapidly oxidized to NO_3^- , which does not have toxic effects on aquatic organisms. Within the typical range of pH and temperature that unpolluted lakes and streams experience, toxic concentrations of NH_3 resulting from nitrogen deposition would be extremely unusual. At a pH of 7 and a temperature of 15 °C, for example, concentrations of total NH_4^+ would have to reach over 750 $\mu\text{mol/L}$ before chronically toxic concentrations of free NH_3 would develop. Currently, no areas of North America are known to experience rates of nitrogen deposition that are sufficient to produce such high concentrations of total NH_4^+ in surface waters.

TABLE 10-27. THREE NITROGEN BUDGETS FOR THE CHESAPEAKE BAY

| Source of Nitrogen | EDF Budget (10 ⁸ kg/year) | | Versar Budget (10 ⁸ kg/year) | | Refined Budget (10 ⁸ kg/year) | |
|--|---|------------------|--|--------|---|------------------|
| Direct Deposition | | | | | | |
| Nitrate Ions | 0 8 | | 0 7 | | 0 6 | |
| Ammonium Ions | 0 4 | | - ^a | | 0 3 | |
| Nitrogen Load to Bay (from direct deposition) ^b | 1 3 | | 0 7 | | 0 8 | |
| Forests | | | | | | |
| Nitrate Ion Deposition | 9 0 | | 8 4 | | 6 4 | |
| Ammonium Ion Deposition | 4 9 | 80% | - ^a | 95% | 3 5 | 84 6% |
| Watershed Retention | 0 8 | 50% | 0 2 | 50% | 0 7 | 35% |
| In-Stream Retention | 1 4 | | 0 2 | | 1 0 | |
| Atmospheric Nitrate Ion Load to Bay (from forests) | | | | | | |
| Nitrogen Load to Bay (from forests) ^b | | | | | | |
| Pasture Land | | | | | | |
| Nitrate Ion Deposition | 2 4 | | 1 7 | | 1 3 | |
| Ammonium Ion Deposition | 1 3 | 95% ^c | - ^a | 94-99% | 0 7 | 95% ^d |
| Animal Wastes | 14 5 | 50% ^c | 11 8 | 50% | 19 5 | 35% |
| Watershed Retention | 0 7 | | 0 01- | | 0 13 | |
| In-Stream Retention | 1 5 | | 0 06 | | 0 8 | |
| Atmospheric Nitrate Ion Load to Bay (from pastures) | | | 0 07- | | | |
| Nitrogen Load to Bay (from pastures) ^b | | | 0 4 | | | |
| Cropland | | | | | | |
| Nitrate Ion Deposition | 2 5 | | 2 8 | | 2 1 | |
| Ammonium Ion Deposition | 1 4 | 70% | - ^a | 76-99% | 1 1 | 95% |
| Fertilizers | 15 8 | | 4 1- | 50% | 15 8 | 35% |
| Watershed Retention | 0 8 | | 27 0 | | 0 07 | |
| In-Stream Retention | 5 9 | | 0 01- | | 0 6 | |
| Atmospheric Nitrate Ion Load to Bay (from cropland) | | | 0 3 | | | |
| Nitrogen Load to Bay (from cropland) ^b | | | 0 06- | | | |
| | | | 3 6 | | | |
| Residential/Urban | | | | | | |
| Nitrate Ion Deposition | 0 4 | | 0 7 | | 0 6 | |
| Ammonium Ion Deposition | 0 3 | 35% | - ^a | 62-96% | 0 3 | 50% |
| Watershed Retention | 0 3 | 0% | 0 01- | 20% | 0 1 | 35% |
| In-Stream Retention | 0 4 | | 0 14 | | 0 3 | |
| Atmospheric Nitrate Ion Load to Bay (from urban areas) | | | 0 01- | | | |
| Nitrogen Load to Bay (from urban areas) ^b | | | 0 14 | | | |
| Point Sources | 3 4 | | 2 0-3 2 | | 3 4 | |
| NITRATE ION LOAD TO BAY (FROM DEPOSITION) | 3 5 | | 0 94- | | 1 53 | |
| | | | 1 48 | | | |
| TOTAL NITROGEN LOAD TO BAY ^b | 13 94 | | 3 03- | | 6 82 | |
| | | | 8 26 | | | |
| % of Nitrogen from NO ₃ ⁻ deposition | 25% | | 18- | | 22 5% | |
| | | | 31% ^e | | | |

^aThe Versar Budget (Tyler, 1988) does not calculate loads of ammonium ions (NH₄⁺)

^bFor the Environmental Defense Fund (EDF) Budget (Fisher et al , 1988a, Fisher and Oppenheimer, 1991) and refined budget, total nitrogen load to the bay includes both nitrate ions (NO₃⁻) and NH₄⁺. The Versar Budget (Tyler, 1988) includes only NO₃⁻

^cWatershed and in-stream retention values for pastureland in the EDF Budget apply only to animal wastes. For atmospheric deposition, the cropland retention value (70%) was used.

^d95% retention was used for animal wastes, 85% retention was used for deposition (see text in Section 10 8 4 3)

^eThe range of contributions of NO₃⁻ deposition to the total budget were calculated by comparing maximum-to-maximum estimates and minimum-to-minimum estimates. These combinations are more likely to occur during extreme (e.g., very wet or very dry) years.

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11. EFFECTS OF NITROGEN OXIDES ON VISIBILITY

Clear days are an important aesthetic resource for us all. They also carry commercial value for tourism and real estate. Thus, the appearance of layers of smoggy haze over cities and across rural vistas is one of the most widely noticed effects of air pollution (Sloane and White, 1986).

Emissions of nitrogen oxides (NO_x) can contribute significantly to visibility impairment, or the "layers of smoggy haze" noted by Sloane and White. They can have aesthetic impact because they can cause a yellow-brown discoloration of the atmosphere when present in plumes or in urban, regional, and layered haze. They can also reduce visual range, thereby diminishing the contrast of distant objects viewed through an atmosphere containing NO_x .

Only some of the species in the NO_x family, however, are optically active and thus able to affect atmospheric visibility. Figure 11-1 illustrates the major categories (including atmospheric oxidation products) of NO_x species and the two species that have an effect on visibility: nitrogen dioxide (NO_2), a gas that absorbs light, chiefly at the blue end of the visible spectrum, and nitrate aerosols, particles that scatter light. The other forms of NO_x that occur in ambient air, nitric oxide (NO), nitrous acid (HONO), and nitric acid (HNO_3), are optically inactive gases and therefore do not contribute to visibility impairment. (Peroxyacetyl nitrate [PAN], HONO , and HNO_3 , however, interfere with chemiluminescence NO_2 measurements and therefore would indirectly affect the estimation of the effects of NO_2 on visibility.) Thus, depending on the form in which NO_x exists in the atmosphere, NO_x may or may not play a significant role overall in visibility. For example, nitrate aerosol may never form from HNO_3 in certain warm climates, in areas with low ambient atmospheric concentrations of ammonia (NH_3), or in areas with high ambient concentrations of acid sulfate, since acid sulfate reacts with ammonium nitrate (NH_4NO_3), thereby releasing nitric acid.

Nitrogen oxides have been found to play a significant role in the aesthetic impact caused by combustion emission sources such as power plants. This impact is dominated by the yellow-brown coloration caused by NO_2 relatively near the source (within 100 km). Nitrate aerosols have been found to play a significant role in the haze observed in urban

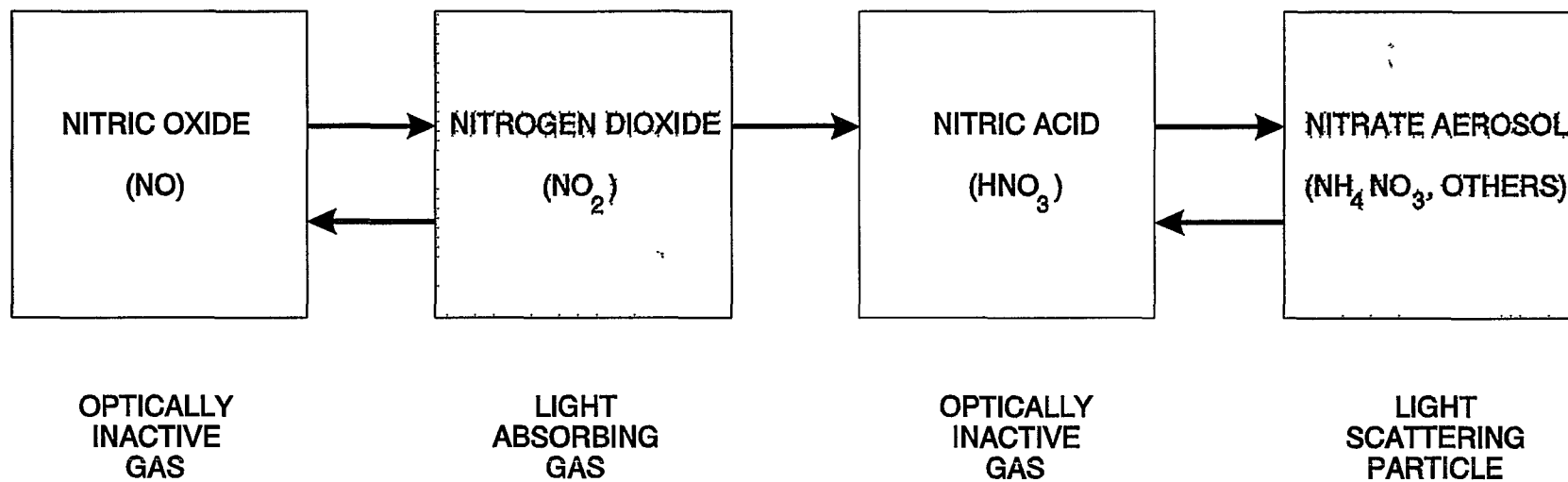


Figure 11-1. The family of nitrogen oxides and those that impair visibility.

areas in the western United States, particularly during winter and near significant ammonia sources (such as cattle feedlots) Nitrate aerosols, along with sulfate, may also play a significant role in the formation of wintertime layered haze that has been observed in the vicinity of large, isolated power plants

Although NO_x has a clearly defined effect on visibility (aesthetic impacts and visual range reduction), in most areas of the country visibility impairment is usually dominated by other species, such as sulfate and elemental and organic carbon particles Also, it should be noted that brownish atmospheric discoloration may be caused by particles such as sulfate and not solely by NO_2 and nitrate

11.1 OVERVIEW OF LIGHT SCATTERING AND ABSORPTION

The visibility effects of the optically active forms of NO_x , NO_2 and nitrate aerosols, can best be illustrated by reviewing some of the fundamentals of atmospheric optics The deterioration of visibility is the result of the absorption and scattering of light by gaseous molecules and suspended solid or liquid particles (Middleton, 1952) Absorbed light is transformed into other forms of energy, such as heat, whereas scattered light is reradiated in all directions

The effect of the intervening atmosphere on the visibility and coloration of a viewed object, such as the horizon sky, a distant mountain, or a cloud, can be calculated by solving the radiative transfer equation along the line of sight (see schematic in Figure 11-2) This equation can be solved if the light extinction properties of the intervening atmosphere are known

The change in the light intensity of a specific wavelength, or spectral radiance $I(\lambda)$, as a function of distance along the line of sight can be calculated as follows (Chandrasekhar, 1960, Latimer and Samuelson, 1975, 1978, Latimer et al , 1978, White et al , 1986)

$$\frac{dI(\lambda)}{dr} = -b_{\text{ext}}(\lambda)I(\lambda) + J(\lambda, \theta) b_{\text{scat}}(\lambda), \quad (11-1)$$

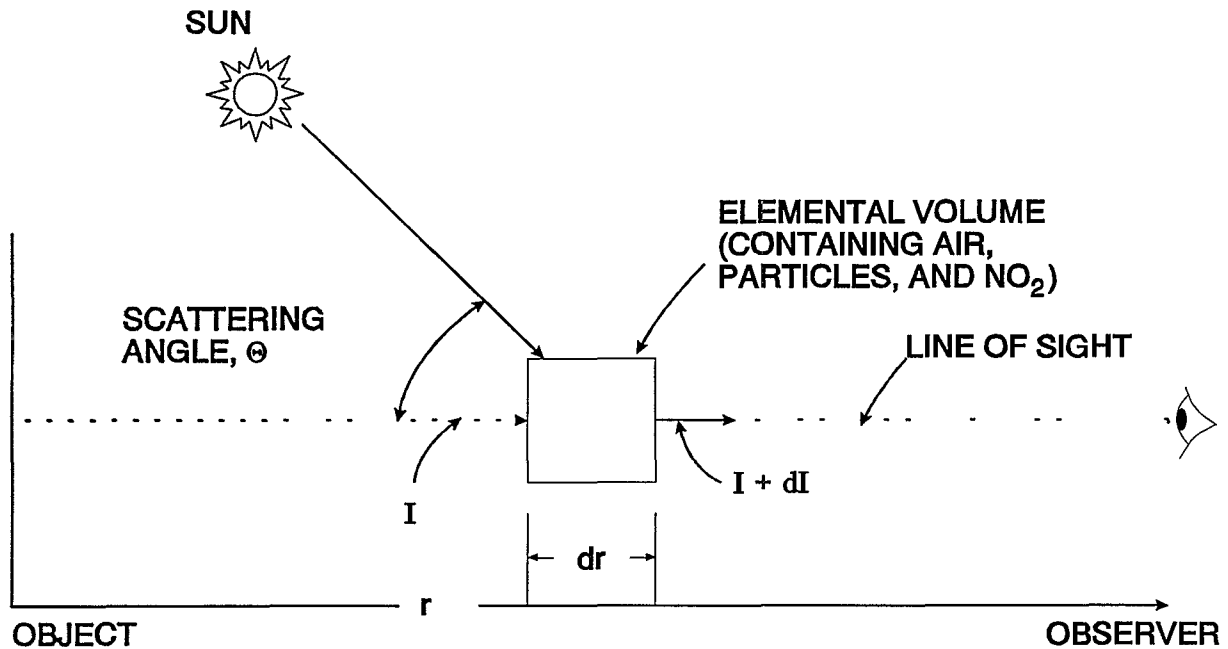


Figure 11-2. Schematic of an elemental volume of haze along a line of sight.

Source Latimer and Ireson (1980)

where

$I(\lambda)$ = the spectral light intensity of wavelength λ ,

r = the distance along the line of sight from the object to the observer (see Figure 11-2 for definitions),

$J(\lambda, \Theta)$ = source function,

$b_{\text{scat}}(\lambda)$ = the light scattering coefficient, and

$b_{\text{ext}}(\lambda)$ = the light extinction coefficient, the sum of scattering and absorption

An examination of Equation 11-1 indicates that light can be both removed and added to the line of sight. The first term on the right side of this equation represents the rate at which light is removed from the line of sight and the second term is the rate at which it is added. If the first term is larger than the second, the net effect is a decrease in light intensity.

(darkening) of an observed object as one moves along the line of sight (see upper curve in Figure 11-3). If the second term is larger than the first, the net effect is an increase in light intensity (brightening) of an observed object. The darkening effect, the first term, is dependent on total light extinction (b_{ext}), which is the sum of light scattering and absorption. The brightening effect, the second term, is dependent only on light scattering (b_{scat}). Thus, light absorption can only darken objects viewed through the atmosphere, whereas light scattering can either brighten or darken viewed objects. Since NO_2 is a gas that preferentially absorbs blue light, it always tends to darken and discolor the sky and objects viewed through the atmosphere. Because nitrate aerosol scatters light, it can either brighten or darken the sky and objects.

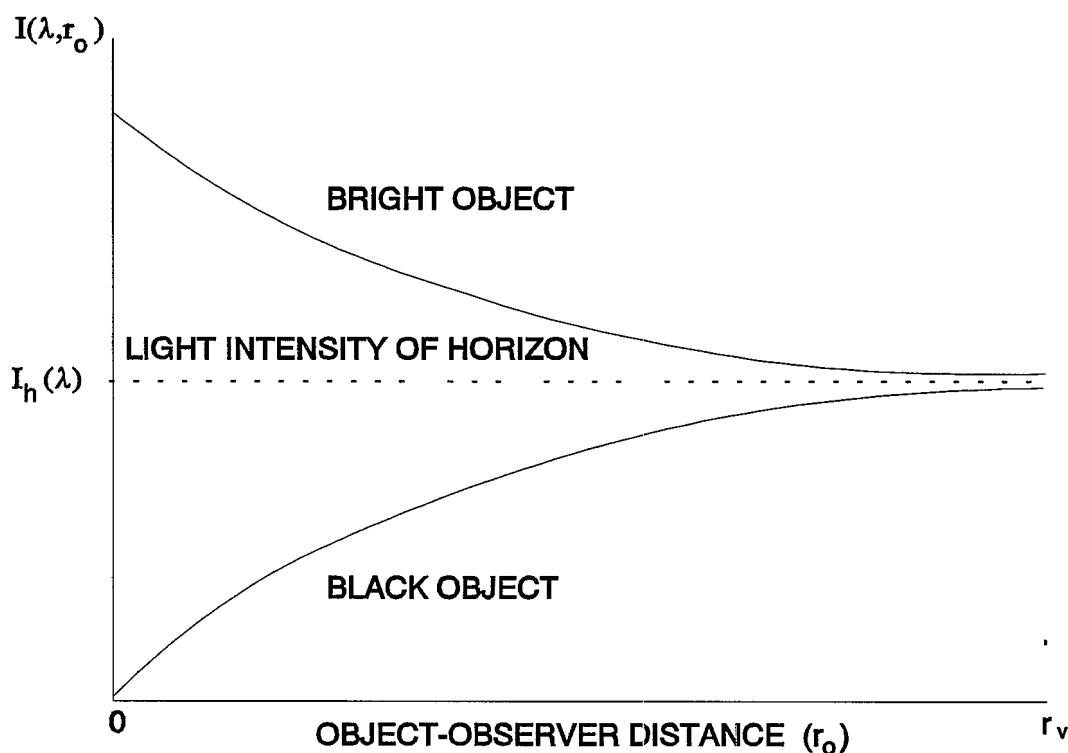


Figure 11-3. Effect of a homogeneous atmosphere on light intensity of bright and dark objects as a function of distance along a line of sight.

Source: Latimer and Ireson (1980), adapted from Middleton (1952)

The light extinction (b_{ext}) coefficient is the optical equivalent of ambient pollutant concentration. This parameter (as well as its scattering and absorption components) has units of inverse distance (e.g., m^{-1} , km^{-1} , Mm^{-1}). These coefficients can be considered to be the equivalent light extinction, scattering, or absorption cross-sectional area (m^2) per unit volume of ambient air (m^3). In Equation 11-1, the light extinction coefficient is the sum of its light scattering and light absorption components

$$b_{\text{ext}}(\lambda) = b_{\text{scat}}(\lambda) + b_{\text{abs}}(\lambda) = (b_{\text{sg}} + b_{\text{sp}}) + (b_{\text{ag}} + b_{\text{ap}}) \quad (11-2)$$

The first term, b_{sg} , is the scattering coefficient attributable to gases and is the result primarily of Rayleigh scattering caused by gases in the atmosphere (chiefly nitrogen and oxygen). The second term, b_{sp} , is the scattering coefficient from particles suspended in the atmosphere (aerosols). Nitrate aerosol contributes to this term, along with other aerosols, including sulfates, organic and elemental carbon, and other particulate matter, both fine ($<2.5 \mu\text{m}$ in diameter) and coarse ($>2.5 \mu\text{m}$ in diameter). The third term, b_{ag} , is the absorption coefficient resulting from gases. Nitrogen dioxide is the only significant contributor to this term in the visible spectrum. The fourth and last term, b_{ap} , is the absorption coefficient resulting from particles. This term is dominated by the effect of elemental carbon (soot), a combustion product found, for example, in diesel engine exhaust.

Except in very clean areas of the western United States, natural b_{sg} is a small fraction of b_{ext} , b_{sp} usually dominates b_{ext} , and fine-particle b_{sp} usually dominates total b_{sp} (White, 1990).

All of these components of total light extinction, as well as total extinction itself, are functions of the wavelength of light. As discussed in more detail later, the atmospheric discoloration caused by NO_x (both NO_2 and nitrate aerosol) can be explained by the wavelength-dependent nature of NO_2 light absorption and nitrate light scattering effects. Both scattering and absorption from these NO_x species are stronger at the blue end of the visible spectrum (wavelength $\lambda = 0.4 \mu\text{m}$) than at the red end ($\lambda = 0.7 \mu\text{m}$).

The scattering or absorption coefficient can be determined from the product of the concentration of an optically active species and its light scattering or specific absorption efficiency (β). This efficiency is commonly stated in units of m^2/g . When the ambient

concentration ($\mu\text{g}/\text{m}^3$) of a given species is multiplied by its extinction efficiency (m^2/g), the extinction coefficient of that species, in units of inverse megameters (Mm^{-1}), is obtained

The light extinction efficiency for particles is a strong function of particle size (see Figure 11-4) Fine particles, those with diameters $< 2.5 \mu\text{m}$, are much more effective per unit mass in scattering light than are coarse particles, those with diameters $> 2.5 \mu\text{m}$ Particle scattering efficiency is a maximum for particles having a diameter of approximately $0.5 \mu\text{m}$ Coarse particles have scattering efficiencies that are approximately an order of magnitude smaller (see Figure 11-4)

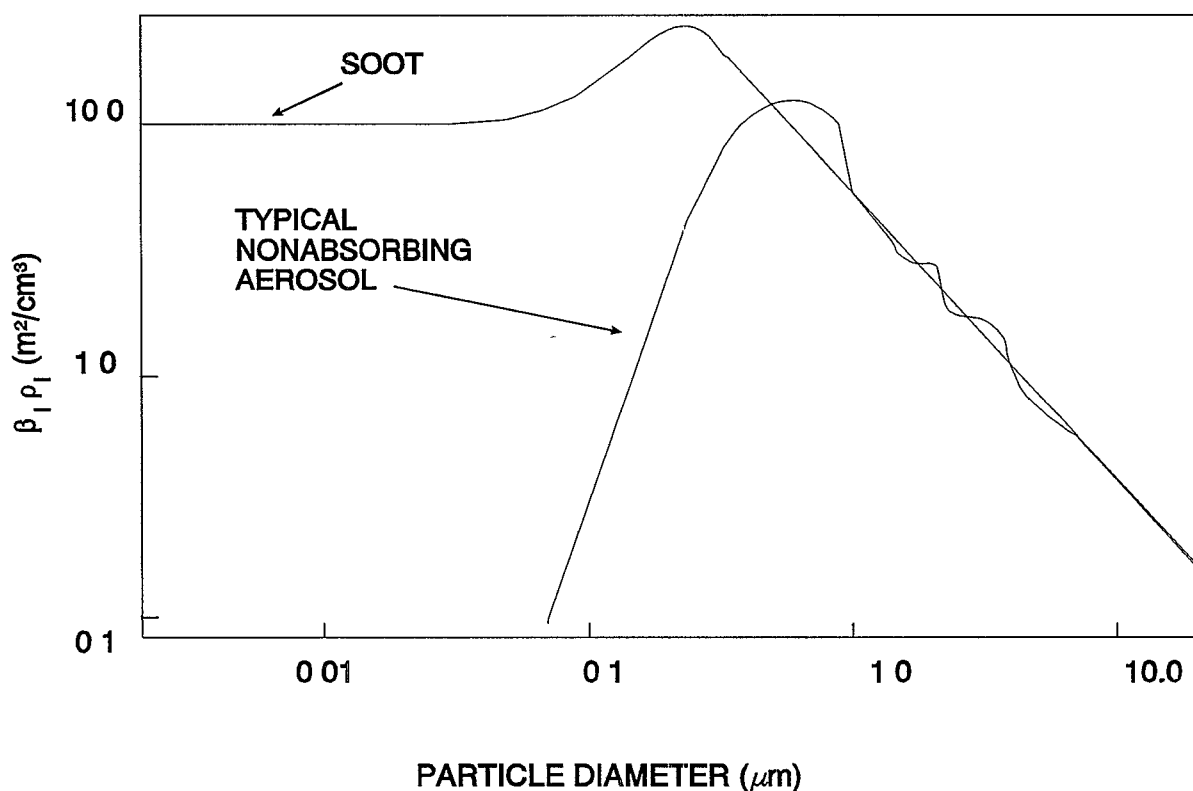


Figure 11-4. Light extinction efficiency at $\lambda = 0.55 \mu\text{m}$ as a function of particle size for soot and for typical, nonabsorbing atmospheric aerosol.

Source Latimer (1988a) after Bergstrom (1973)

Nitrate particles can be either coarse or fine. Milford and Davidson (1987) reviewed the sizes of particulate sulfate and nitrate in the atmosphere, nitrate mass median diameters ranged from 0.23 to 4.2 μm in 16 different measurement sets. Wolff (1984) noted that in continental environments nitrate can exist as either coarse or fine particles, however, in a number of summertime studies in the eastern United States, nitrate concentrations were quite low and nitrate occurred primarily in the coarse mode (Wolff, 1984; Mamane and Dzubay, 1986). Wolff explained this qualitatively by the reaction of alkaline soil dust with HNO_3 , nitrate aerosol is not formed in the submicron mode if temperatures are high or if NH_3 is not available or is tied up with sulfate. It should be noted, however, that the data of Wolff (1984) were collected using methods later found to have significant artifact problems. In coastal environments, nitrate may also be primarily in the coarse mode because of reaction with sea salt (Yoshizumi, 1986; Wall et al., 1988; Orel and Seinfeld, 1977; Mamane and Mehler, 1987). Richards (1983) suggested that coarse-particle nitrate may form from nighttime oxidation involving nitrogen pentoxide-water reactions on the surfaces of particles. Nitrate is in the submicron fine mode when it reacts directly with NH_3 to form NH_4NO_3 (Orel and Seinfeld, 1977; Wolff, 1984). The submicron nitrate forms when conditions are favorable (abundant ambient NH_3 and moderate temperatures).

Nitrate aerosol in the size range of 0.1 to 2.5 μm is most effective per unit mass in scattering light. For particles having a typical density (ρ) of 2 g/cm^3 and a diameter of 0.5 μm , Figure 11-4 shows that the scattering efficiency at the middle of the visible spectrum ($\lambda = 0.55 \mu\text{m}$) is approximately 5 m^2/g . By contrast, the average NO_2 absorption efficiency over the wavelengths 0.45 to 0.65 μm , centered on 0.55 μm , is 0.144 m^2/g (Latimer and Ireson, 1988, based on Dixon, 1940). Thus, the extinction efficiency of nitrate aerosol can be more than an order of magnitude greater than that for NO_2 . As discussed in the next section, the extinction efficiencies of both nitrate aerosol and NO_2 gas are strong functions of the wavelength, being larger at the blue end ($\lambda = 0.4 \mu\text{m}$) of the visible spectrum.

11.2 ATMOSPHERIC DISCOLORATION CAUSED BY NITROGEN OXIDES

As Finlan (1981) so aptly stated "Many of the most beautiful sights in nature are caused by wavelength-dependent light scattering. It can be truly exhilarating to see the beauty of the blue sky or to witness a rainbow, a sunset, or a sunrise. Unfortunately, the physical processes responsible for these beautiful sights also cause much of the color that we often see in smogs and hazes over cities."

The undesirable yellow or whisky-brown color of hazes has been an ongoing topic of discussion in the literature for more than 20 years. Hodkinson (1966) described the effects that NO_2 could produce on the color of the atmosphere. Charlson and Ahlquist (1969), however, argued that wavelength-dependent scattering was the primary cause of atmospheric discoloration in most situations. Horvath (1971) countered with the argument that any color caused by wavelength-dependent light scattering that removed light from the line of sight would be offset by the additional light scattered into the line of sight by the same wavelength-dependent scattering. Thus, he thought that any color would be the result of the absorption of blue light by NO_2 . He did conclude, however, that if extremely bright objects were viewed through an aerosol, a discoloration could result. Charlson et al. (1972) measured NO_2 concentrations and the wavelength dependence of the light-scattering coefficient in Pasadena, CA, during August and September 1970 and concluded that NO_2 had a significant effect on atmospheric color 20% of the time. Sloane (1987) applied Mie theory to calculate the effects of urban haze mixtures of NO_2 and elemental carbon (soot). She found that soot can offset the coloration caused by NO_2 , even though both species absorb preferentially at the blue end of the spectrum. Husar and White (1976) performed careful atmospheric optics calculations using Mie scattering theory (Kerker, 1969) to assess the relative roles of wavelength-dependent light scattering by particles and wavelength-dependent light absorption caused by NO_2 . They found that particles typical of Los Angeles haze could cause yellow-brown discoloration when the sun was behind the observer (scattering angle $\Theta > 90^\circ$), and typical NO_2 concentrations could perceptibly add to this color. More detailed analysis by Finlan (1981) confirmed the importance of scattering angle and the size distribution and refractive index of the aerosol in determining atmospheric color.

Atmospheric color can be studied theoretically by solving Equation 11-1 for the spectral radiance or light intensity of an object observed at distance r as follows (Middleton, 1952, Latimer and Samuelsen, 1975, 1978, Latimer et al , 1978, Husar and White, 1976, White et al., 1986).

$$I_r = I_0 \exp(-\tau) + J [1 - \exp(-\tau)], \quad (11-3)$$

where

I_r, I_0 = spectral light intensities at distance r from an object and at the object itself,

τ = optical depth between the object and the observer ($= \int b_{\text{ext}} dr$),

J = the source function (the second term in Equation 11-1, divided by b_{ext})

Equation 11-3 can be used to evaluate the effect of a uniform concentration of NO_2 on atmospheric coloration. The ratio of the intensity of the horizon sky (h) with and without a given concentration of NO_2 can be calculated from Equation 11-3 as follows (Hodkinson, 1966, Robinson, 1968; White, 1982)

$$I_{h\text{NO}_2}/I_{h0} = (1 + b_{\text{ag}}/b_{\text{scat}})^{-1} \quad (11-4)$$

The light absorption coefficient for NO_2 , b_{ag} , is a strong function of wavelength. Figure 11-5 shows the wavelength dependence of the NO_2 light absorption efficiency over the ultraviolet and visible spectrum (Davidson et al , 1988). The light efficiency, σ , is the ratio of the light absorption coefficient to the NO_2 concentration. The value at the blue end of the visible spectrum, $\lambda = 0.4 \mu\text{m}$, is $5.9 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ or $1.45 \text{ km}^{-1} \text{ ppm}^{-1}$, is nearly six times larger than the value at the center of the visible spectrum at a green wavelength $\lambda = 0.55 \mu\text{m}$, which is $1.0 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ (or $0.24 \text{ km}^{-1} \text{ ppm}^{-1}$). This value at $\lambda = 0.55 \mu\text{m}$ of $0.24 \text{ km}^{-1} \text{ ppm}^{-1}$ is considerably less than the value of $0.33 \text{ km}^{-1} \text{ ppm}^{-1}$ derived from earlier measurements (Dixon, 1940). When Equation 11-4 is evaluated as a function of wavelength (λ), and the λ -dependence of b_{scat} is neglected, the curves shown

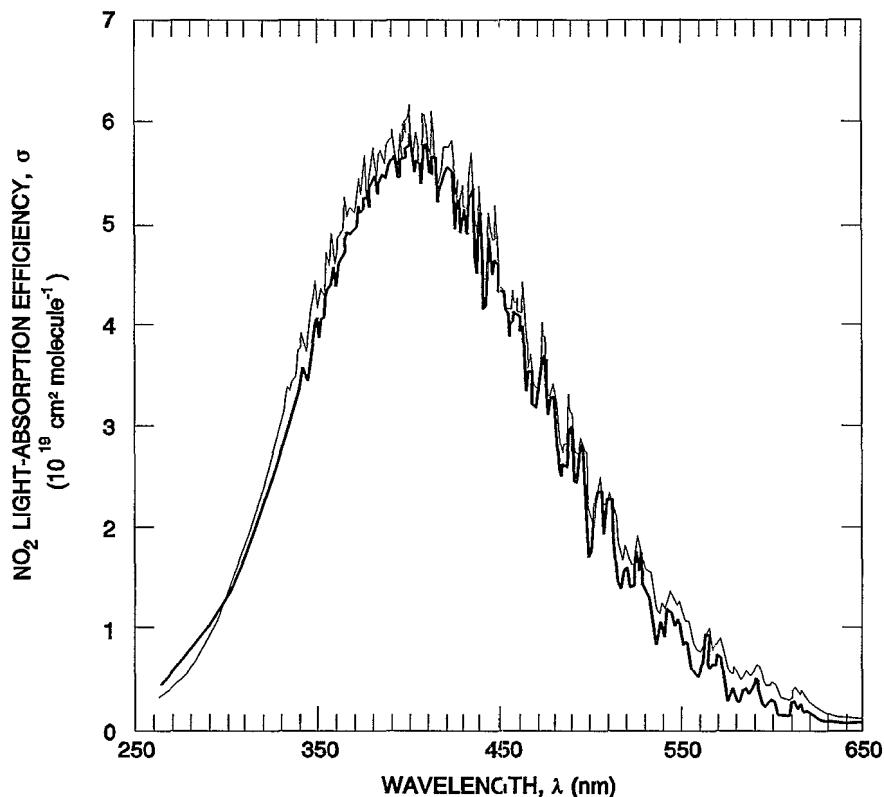


Figure 11-5. Light absorption efficiency of nitrogen dioxide estimated for $-30.2\text{ }^{\circ}\text{C}$ (thin line) and $124\text{ }^{\circ}\text{C}$ (dark line). (To obtain units of $\text{ppm}^{-1}\text{ km}^{-1}$, multiply $\text{cm}^2\text{ molecule}^{-1}$ by 2.46×10^{18} .)

Source Davidson et al (1988)

in Figure 11-6 are obtained for the horizon-sky light-intensity ratio (Hodkinson, 1966, White, 1982) Nitrogen dioxide causes a darkening effect, especially at the blue end of the visible spectrum For example, with an NO_2 -visual range product of 0.3 ppm-km , the horizon sky light intensity at $\lambda = 0.4\text{ }\mu\text{m}$ is about 14% less than it would be without NO_2 and would thus be quite noticeably discolored (yellow or brown) This concentration-visual range product could be caused by 0.03 ppm ($60\text{ }\mu\text{g/m}^3$) NO_2 associated with a visual range of 10 km, which is typical of urban haze (Note $0.03\text{ ppm} \times 10\text{ km} = 0.3\text{ ppm-km}$)

Atmospheric aerosols, including particulate nitrates, can also cause atmospheric discoloration (Ahlquist and Charlson, 1969, Husar and White, 1976) The scattering coefficient of particles smaller than $1.5\text{ }\mu\text{m}$ in diameter can be strongly dependent on the

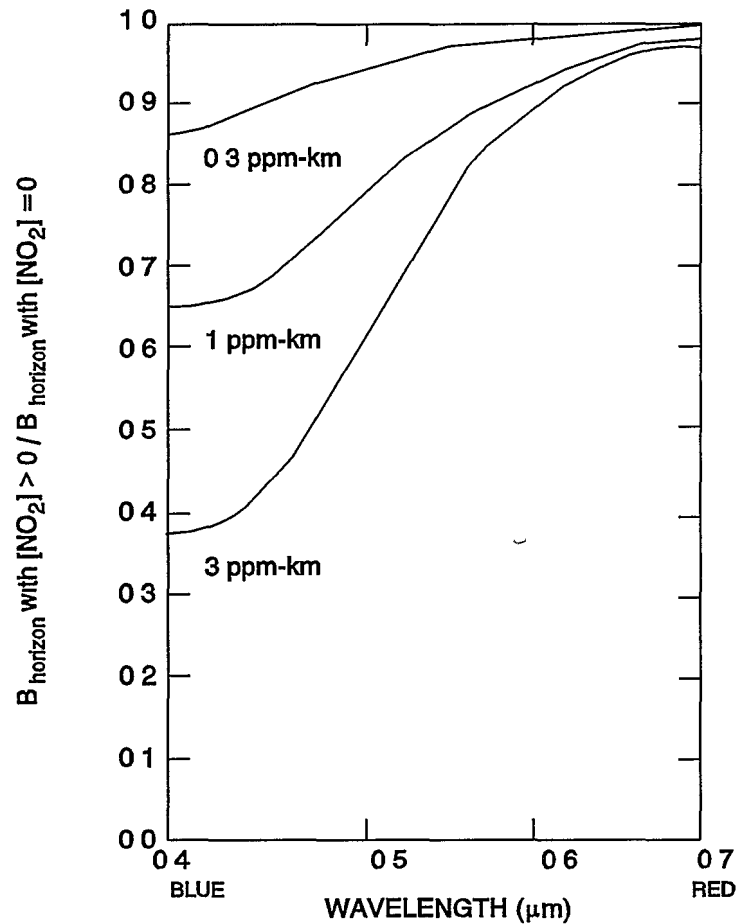


Figure 11-6. Effect of nitrogen dioxide on horizon sky brightness as a function of the wavelength of light; relative horizon brightness, $b_{\text{scat}}/(b_{\text{scat}} + b_{\text{ag}})$ for selected values of the product of nitrogen dioxide concentration and visual range assuming that $b_{\text{scat}} = 3/(\text{visual range})$.

Source White (1982) adapted from Hodkinson (1966)

wavelength of light, as shown in Table 11-1 (Latimer and Ireson, 1980) For example, an aerosol with a mass median diameter of $0.5 \mu\text{m}$ has a light scattering coefficient b_{scat} that is inversely proportional to wavelength λ . Thus, light scattering at the blue end ($\lambda = 0.4 \mu\text{m}$) of the visible spectrum would be 75% greater ($7/4 = 1.75$) than at the red end ($\lambda = 0.7 \mu\text{m}$). Because the light-scattering coefficient caused by aerosols and the light-absorption coefficient caused by NO_2 are both wavelength-dependent, both can cause atmospheric discoloration.

**TABLE 11-1. WAVELENGTH DEPENDENCE OF LIGHT SCATTERING
COEFFICIENT AS A FUNCTION OF PARTICLE
LOGNORMAL SIZE DISTRIBUTION**

| Mass Median Diameter (DG) ^a (μm) | α ^b |
|---|----------------|
| 0.1 | 2.8 |
| 0.2 | 2.1 |
| 0.3 | 1.6 |
| 0.4 | 1.2 |
| 0.5 | 1.0 |
| 0.6 | 0.7 |
| 0.8 | 0.5 |
| 1.0 | 0.2 |
| >5 | 0 |

^aGeometric standard deviation $\sigma_g = 2$

^bα is defined as follows

$$b_{\text{scat}}(\lambda_1) = b_{\text{scat}}(\lambda_2) \left[\frac{\lambda_1}{\lambda_2} \right]^{-\alpha}$$

(appropriate for $0.4 < \lambda < 0.7 \mu\text{m}$)

Source Latimer and Ireson (1980)

Husar and White (1976) formulated the problem of atmospheric coloration rigorously in terms of radiative transfer theory. A solution was derived from theory and from aerosol size distributions measured in Los Angeles. They found that aerosol (without NO₂) could cause yellow-brown discoloration, and that this discoloration would increase as NO₂ concentrations increase and as the scattering angle, Θ, increases. Noticeable discoloration from NO₂ was found to occur at concentrations as low as 0.05 ppm. The discoloration effect caused by particles, unlike that caused by NO₂, is dependent on the scattering angle, Θ, with most intense effects occurring in situations in which the sun is behind the observer (Θ > 90°). In addition, when the viewed object has a light intensity greater than the horizon-sky light intensity (the I_h asymptote in Figure 11-3), light scattered by fine particles would cause a darkening and discoloring effect because of the wavelength-dependent light scattering.

Waggoner et al. (1983) used teleradiometer measurements to determine the color of the winter haze in Denver that is commonly known as the "brown cloud." Although this haze

appeared to be brown in contrast to the blue sky above, they found that its spectral light-intensity distribution was gray and was caused primarily by aerosol rather than NO_2 . These findings were consistent with the conclusions of Horvath (1971) and of Husar and White (1976) that yellow haze could appear brown if it were darker than the viewing background. The chromatic adaptation of the human eye-brain system (Cornsweet, 1970) also explains why a gray haze may appear yellow or brown. An observer that has adapted to the color of the blue sky will visually perceive a gray haze as the complementary color to that adaptation (i.e., yellow or brown).

11.3 VISUAL RANGE REDUCTION CAUSED BY NITROGEN OXIDES

At some distance from a black object, an observer can no longer distinguish between the intensity of it and the sky. This limit of perceptibility is defined by a threshold (liminal) contrast that is just noticeable to a human observer. The distance at which the contrast of a black object against the horizon sky equals this threshold is called the visual range or, commonly, visibility. Although a range of values for the threshold contrast from about 1 to 20% is supported by the literature (Middleton, 1952, U.S. Environmental Protection Agency, 1979, Latimer, 1988b, Griffing, 1980, Dzubay et al., 1982), the threshold human visual perception threshold is commonly assumed to be a contrast of 2%.

Koschmieder (1924) developed a formula for visual range, which is based on the assumptions that the threshold contrast is 2%, that the atmosphere is uniform and cloud-free, and that the curvature of the Earth can be ignored when evaluating horizon light intensity. The Koschmieder equation is simply

$$r_v = -\ln(C_{\min})/b_{\text{ext}}, \quad (11-5)$$

where

- r_v = the visual range,
- C_{\min} = the contrast perceptibility threshold, and
- b_{ext} = the light extinction coefficient, as defined previously

If the commonly accepted threshold of 2% is used above, the Koschmieder equation becomes

$$r_v = 3.9/b_{\text{ext}}, \quad (11-6)$$

the most common form of the equation. If the perceptibility threshold is assumed to be 5%, which appears to correlate best with common airport visibility measurements (Samuels, 1973, Johnson, 1981, Latimer, 1988b), the equation becomes

$$r_v = 3/b_{\text{ext}} \quad (11-7)$$

Note that as the light extinction coefficient increases, visual range decreases. This inverse relationship suggests that increases in atmospheric concentrations of light scattering and absorbing species will cause a decrease in visibility. Figure 11-7 illustrates this relationship for fine particles assumed to have a scattering efficiency of $4 \text{ m}^2/\text{g}$ (U.S. Environmental Protection Agency, 1979). Because both of the optically active NO_x species, NO_2 and nitrate aerosol, contribute to the absorption and scattering components of light extinction (b_{ext}), they both tend to reduce visual range.

If it is not uniformly distributed in the atmosphere, NO_2 may not contribute to a reduction in the contrast of a distant object and hence to visual-range reduction. This can happen when NO_2 is located relatively close to the observer (e.g., in a plume or haze layer). In such a situation, the light absorbed by NO_2 reduces the light intensity of both the sky and the dark object equally, so that the sky and object are darkened but their contrast remains unaffected. Latimer and Samuelsen (1975, 1978) developed a formula to account for this effect for atmospheres containing NO_2 plumes.

11.4 NITRATE PHASE CHANGES AND HYGROSCOPICITY

Assessment of the role played by nitrate particles in urban, regional, and layered haze and in plumes is more difficult than for sulfates since certain of the nitrate aerosols (e.g., NH_4NO_3) can volatilize during sample collection because of their volatile nature. Unlike sulfate, which is always in the particulate phase, nitrate often remains in the gas

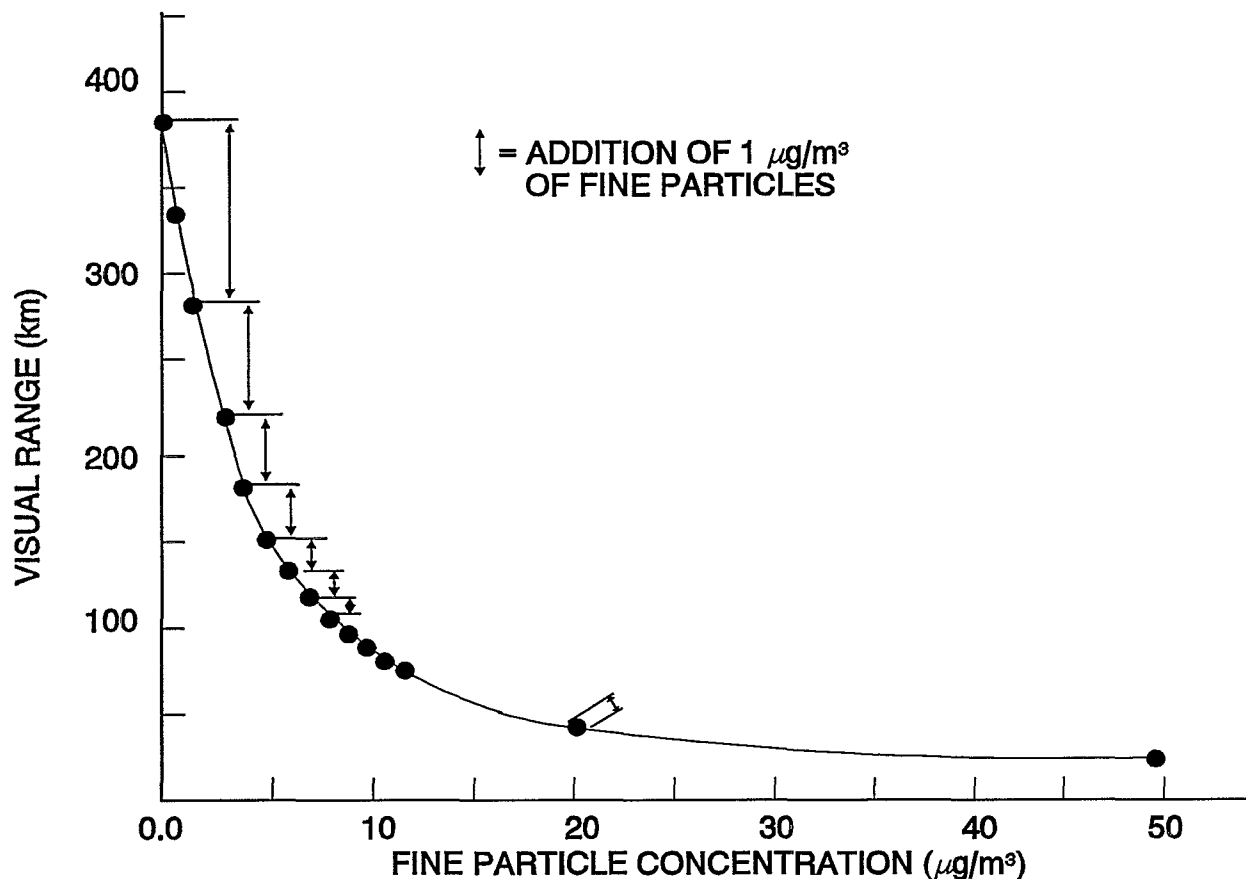


Figure 11-7. Effect on visual range of incrementally adding $1 \mu\text{g}/\text{m}^3$ of fine particles having a light extinction efficiency of $4 \text{ m}^2/\text{g}$. (Greater light extinction efficiencies and visibility reduction than shown here would occur with sulfate and nitrate aerosols at high relative humidities. See text.)

Source U S Environmental Protection Agency (1979)

phase as HNO_3 . In order for condensation of particulate nitrate (NH_4NO_3) to occur, there must be sufficient atmospheric NH_3 to react with HNO_3 . Furthermore, the vapor pressure of NH_4NO_3 is strongly temperature-dependent, so that even if NH_3 is present in the atmosphere nitrate particles may not condense because of moderate or high temperatures. The volatility of particulate NH_4NO_3 contributes to the difficulty and uncertainties in most measurement programs carried out to date. These difficulties regarding phase changes are complicated even more by the fact that NH_4NO_3 is deliquescent, it absorbs water from the atmosphere at

moderate to high relative humidities. Thus, like sulfate, the scattering efficiency of NH_4NO_3 is enhanced by associated liquid water in the particle droplet.

The issue of changes in phase between gas and aerosol is a key uncertainty in understanding, measuring, and mathematically modeling the impacts of nitrate aerosol (Sloane and White, 1986).

Just as a cloud produces a dramatic visual effect when only a small fraction of the water vapor changes phase, a substantial haze results if only a fraction of the gaseous pollutant mass enters a condensed phase. In this regard, visibility is unique among air pollution effects; it depends not only on the amount of air pollution but in addition on its phase. This peculiarity greatly complicates the prediction of visibility impairment and aerosol measurement procedures because the equilibrium between the condensed and gaseous phases can be fragile.

Ammonium nitrate particles will form only if (1) sufficient ambient NH_3 is present to neutralize any acidic sulfates and gas-phase HNO_3 and (2) temperatures and relative humidities are such that the thermodynamic equilibrium favors the formation of nitrate aerosol (Stelson et al., 1979; Stelson and Seinfeld, 1982; Saxena et al., 1986; Sloane and White, 1986). Until acidic sulfate compounds are fully neutralized as ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), they react with NH_4NO_3 , releasing HNO_3 vapor (Saxena et al., 1986). If sufficient gas-phase NH_3 is left after sulfate neutralization and temperatures are low enough, NH_4NO_3 aerosol will condense. At relative humidities above 62%, the deliquescent point for NH_4NO_3 , water vapor is taken up in the nitrate particle (droplet), forming a water solution (Saxena et al., 1986). At these higher relative humidities, a new equilibrium is established favoring more nitrate in the particulate phase (Sloane and White, 1986).

The net result of all of the nitrate phase interactions is that particulate NH_4NO_3 "can build up only in locations where sufficient ammonia is present to neutralize the sulfuric acid. This occurs, for example, in Los Angeles and Denver, where sulfate concentrations are relatively low compared to concentrations of ammonia" (Milford and Davidson, 1987). White and Macias (1987) attribute the extremely low nitrate aerosol concentrations observed in the intermountain West to very low ambient HNO_3 and NH_3 concentrations and to the warm temperatures during the nonwinter months. Thus, the conditions can be summarized under which fine nitrate particles are most likely to form: high ambient concentrations of NH_3 and HNO_3 (e.g., Los Angeles, Denver), low ambient concentrations of sulfate (e.g., most of the western United States), low temperatures (e.g., winter), and high humidities.

(e.g., winter, coastal sites) Conversely, fine nitrate particles are least likely to form under the following conditions low ambient concentrations of NH_3 and HNO_3 (e.g., intermountain West), high ambient concentrations of sulfate (e.g., the eastern United States), high temperatures (e.g., summer), and low relative humidities (e.g., the Southwest) Furthermore, if sufficient coarse particles exist that can react with HNO_3 (e.g., sea salt, alkaline soil dust), coarse nitrate particle formation is favored As subsequent discussion bears out, these generalizations based on thermodynamic equilibrium explain much of observed nitrate aerosol behavior

The volatility of particulate nitrate makes its measurement difficult and uncertain (Sloane and White, 1986) Significant positive and negative artifacts can occur with different measurement techniques using different filter media (see Section 6.1) Thus, in evaluating empirical studies of the importance of nitrate to total light extinction, it is important to consider the complications caused by uncertainty in nitrate particle measurements

Further complicating the definition of the role of nitrate is the fact that nitrate particles will absorb water vapor, becoming water solutions, at high humidities (above 62%) The water associated with the nitrate results in scattering efficiencies per unit mass of nitrate that are much larger than dry particle efficiencies The effect on light-scattering efficiencies of liquid water associated with aerosols has been known for a long time, but the specific effect of associated water is difficult to quantify Empirical studies have used a nonlinear relative humidity term to attempt to account for this effect

Tang and coworkers (Tang et al., 1981, Tang, 1982) developed a computer model for calculating the optical properties of nitrate particles, both alone and in combination with sulfate, as a function of particle size and relative humidity This model was based on multicomponent aerosol thermodynamic theory as a function of particle chemical composition and relative humidity Light-scattering efficiencies were calculated from resulting particle sizes using Mie scattering theory Figures 11-8 through 11-12 summarize the light-extinction coefficients for $1 \mu\text{g}/\text{m}^3$ of sulfate or nitrate aerosol, or both, as a function of humidity Figure 11-8 shows that pure $(\text{NH}_4)_2\text{SO}_4$ exhibits a deliquescent point at 80% relative humidity. At humidities above 80%, water vapor condenses, thereby increasing the aerosol particle size, volume, and light scattering At humidities below 80%, the extinction efficiencies range from 1 to $4 \text{ m}^2/\text{g}$ of sulfate, whereas above 80% humidity, extinction

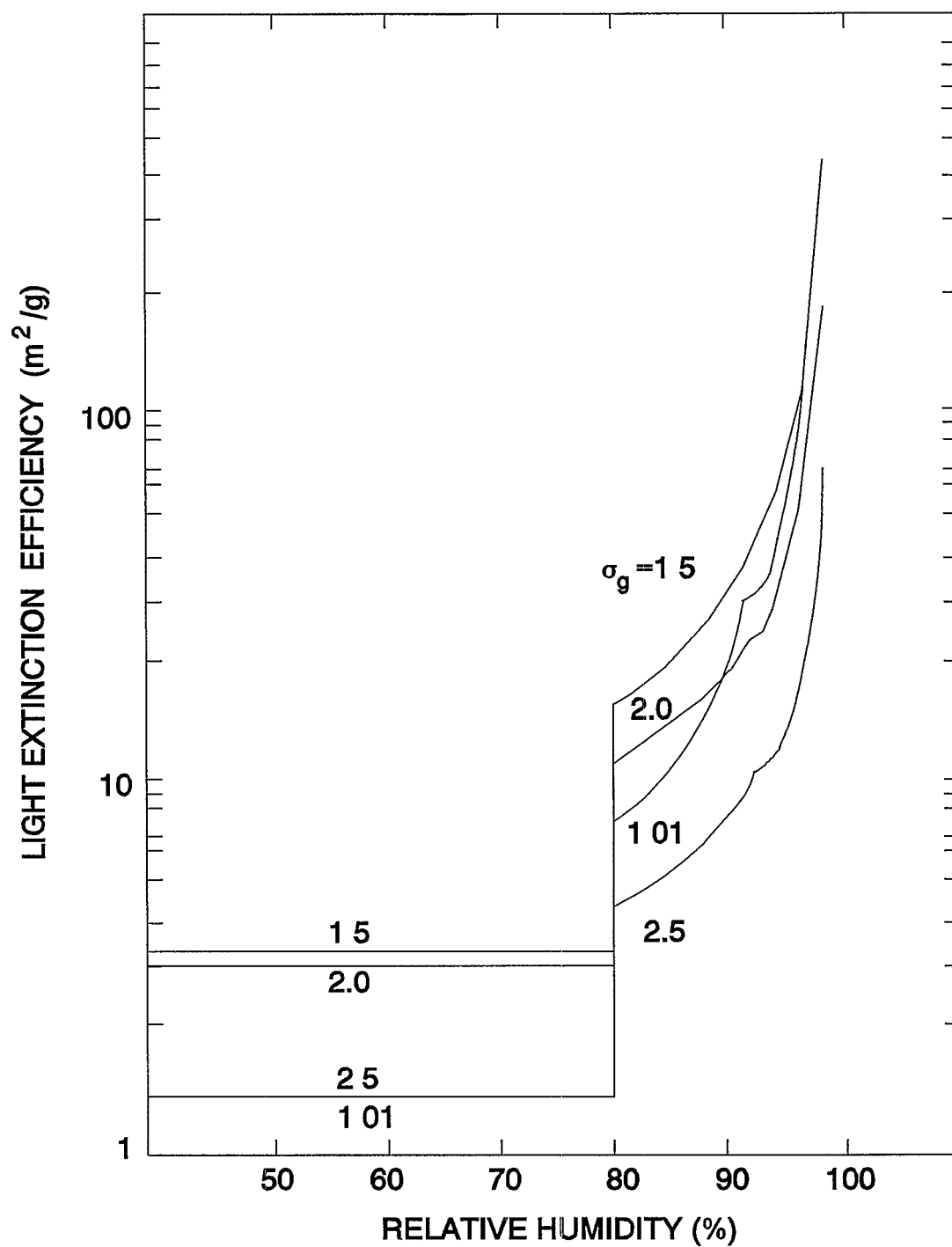


Figure 11-8. Light extinction efficiency for ammonium sulfate aerosol as a function of relative humidity; with ammonium sulfate having lognormal particle size distributions characterized by $D_g = 0.2 \mu\text{m}$ and $\sigma_g = 1.01, 1.5, 2.0,$ and 2.5 . (Multiply values by 1.375 to obtain efficiencies per unit mass of sulfate anion.)

Source Modified after Tang et al (1981)

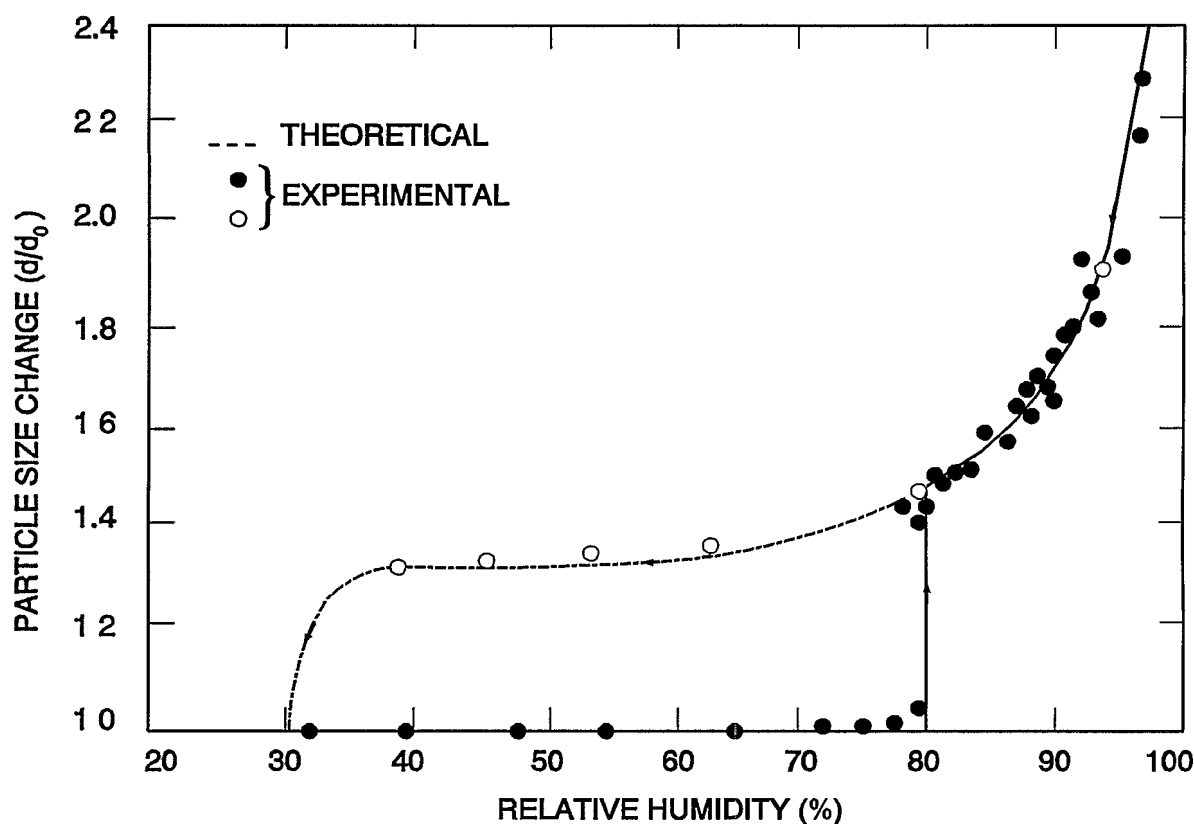


Figure 11-9. Particle size change for ammonium sulfate aerosols in a moist atmosphere at 25° C.

Source Tang et al (1981)

efficiencies can increase considerably above $10 \text{ m}^2/\text{g}$. Figure 11-9 illustrates the hysteresis effect, that is, the ability of the particle to hold on to liquid water, that can result when relative humidity is slowly decreased. Figure 11-10 shows the increase in light extinction of pure NH_4NO_3 aerosol as a function of relative humidity. At and above the deliquescent point at 62% humidity, the scattering efficiency increases by a factor of two or more because of the condensed water vapor associated with the nitrate particle. Figures 11-11 and 11-12 show the effects of humidity on the light extinction efficiencies of different mixtures of sulfate and nitrate aerosols. Externally mixed aerosols, those in which the sulfate and nitrate exist on different particles, exhibit the separate deliquescent points for $(\text{NH}_4)_2\text{SO}_4$ (80% RH) and NH_4NO_3 (62% RH). Internally mixed aerosols, in which the sulfate and nitrate occur

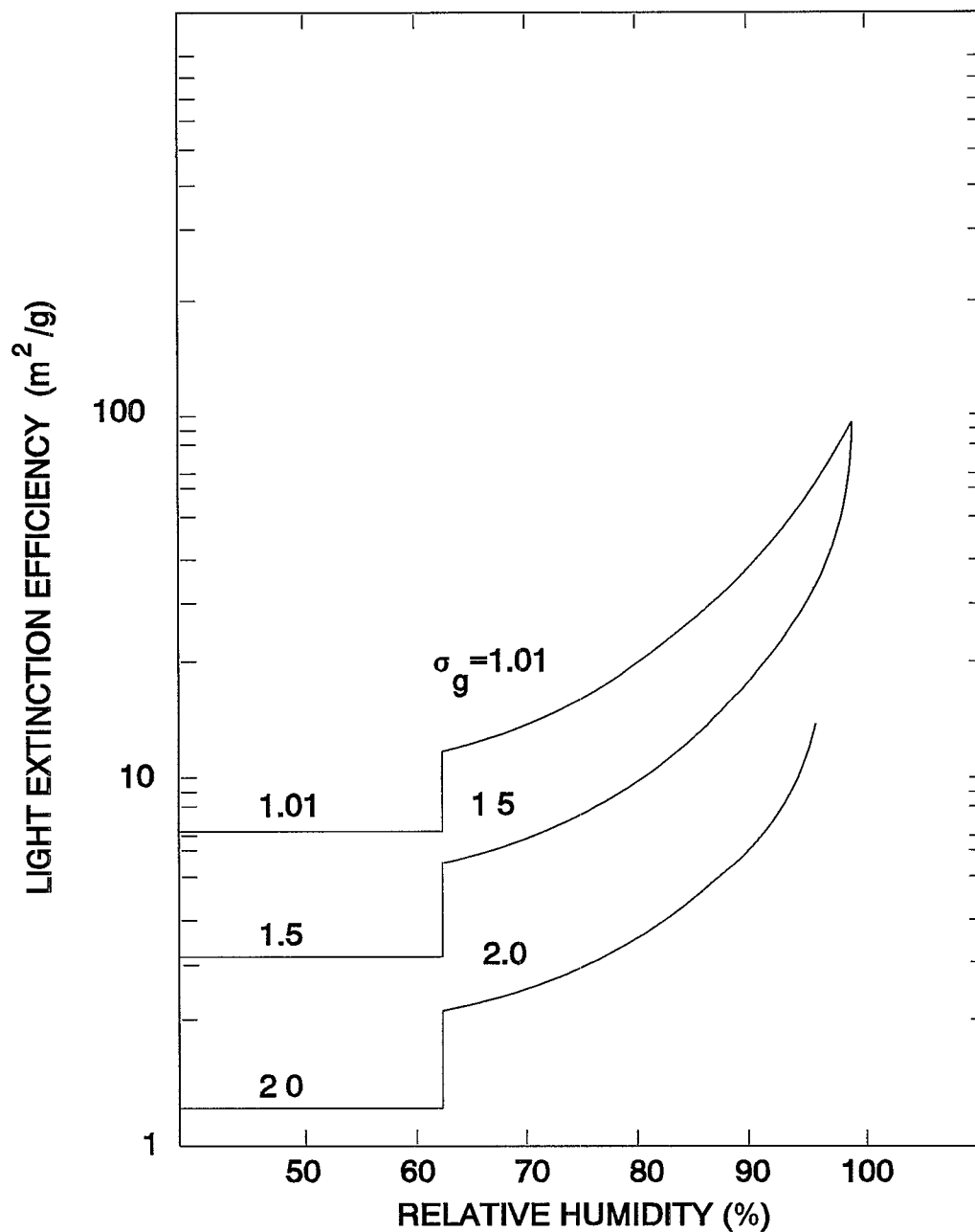


Figure 11-10. Light extinction efficiency for ammonium nitrate aerosol as a function of relative humidity; with ammonium nitrate aerosol having lognormal particle size distribution characterized by $D_g = 0.6 \mu\text{m}$ and $\sigma_g = 1.01$, 1.5, and 2.0. (Multiply by 1.29 to obtain efficiencies per unit mass of nitrate anion.)

Source Modified after Tang et al (1981)

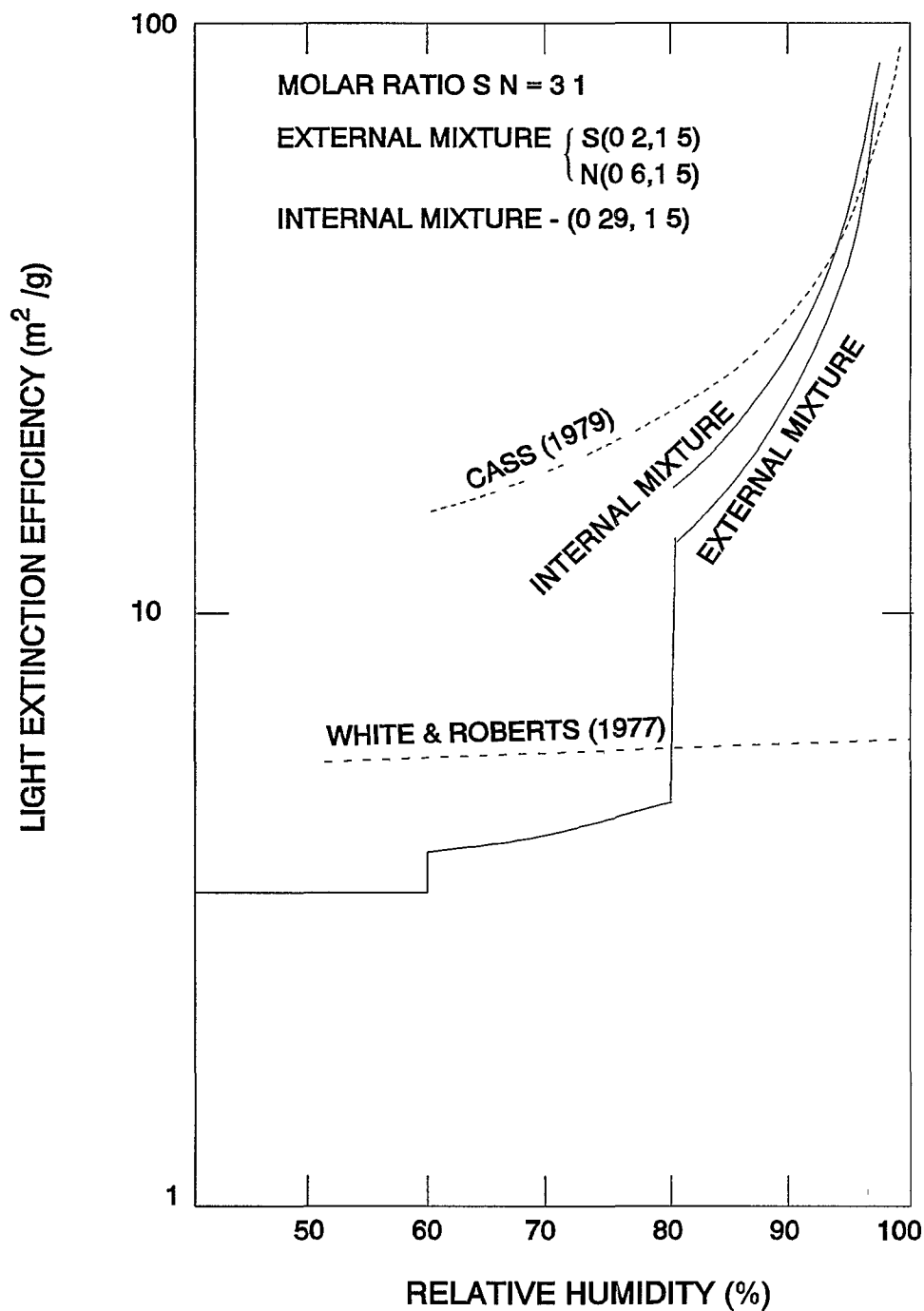


Figure 11-11. Light scattering coefficient for $1 \mu\text{g}/\text{m}^3$ of a dry sulfate/nitrate aerosol mixture as a function of relative humidity; b_{scat} versus relative humidity for externally and internally mixed sulfate and nitrate aerosols (S:N = 3:1) for indicated size distributions (D_g , α_g).

Source. Modified after Tang et al (1981), corrected by Tang (1982)

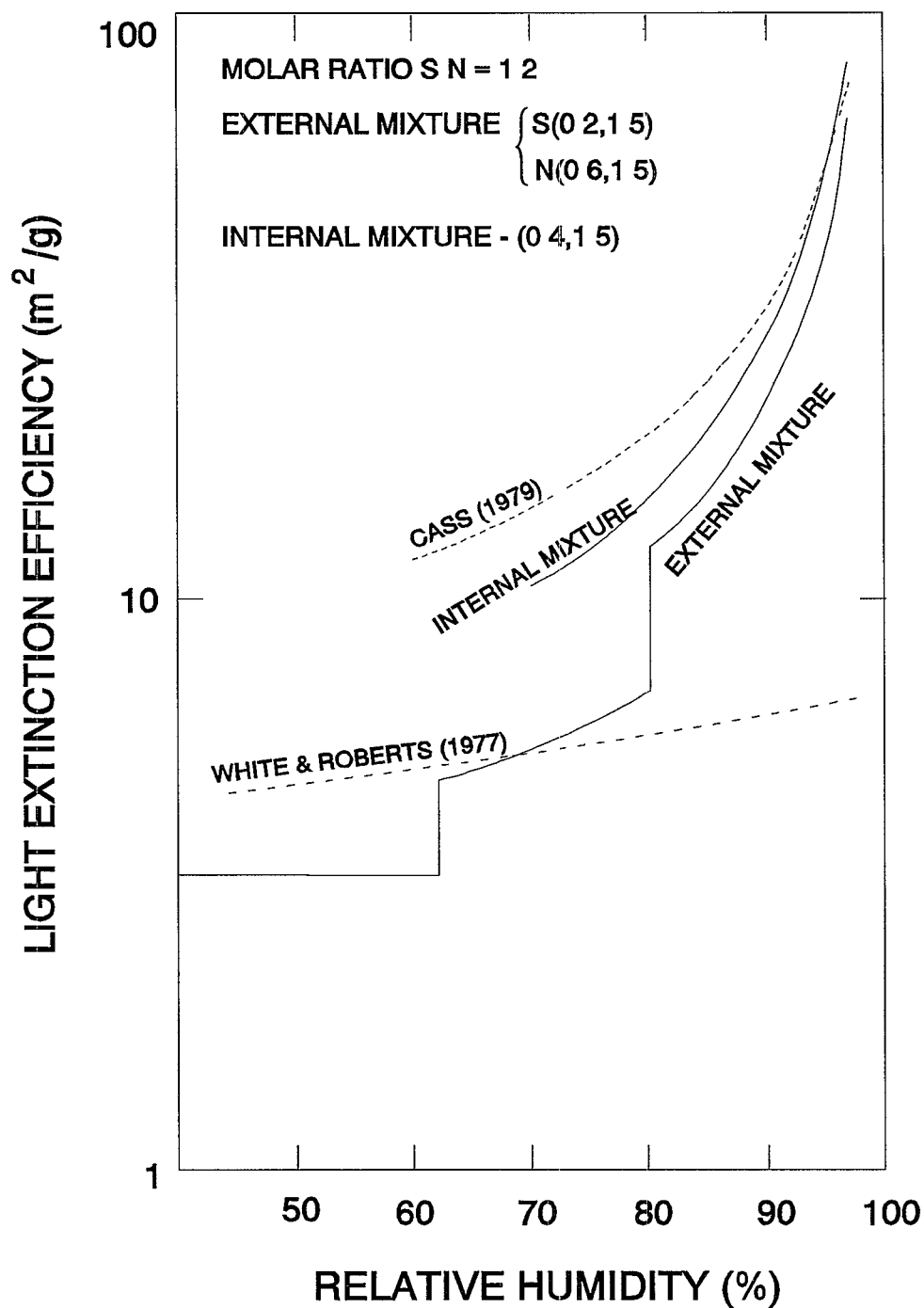


Figure 11-12. Light extinction efficiency for $1 \mu\text{g}/\text{m}^3$ of a dry sulfate/nitrate aerosol mixture as a function of relative humidity; b_{scat} versus relative humidity for externally and internally mixed sulfate and nitrate aerosols (S:N = 1:2) for indicated size distributions (D_g, σ_g).

Source Modified after Tang et al (1981), corrected by Tang (1982)

mixed within the same particle, do not exhibit distinct deliquescent points and have more water associated with them at a given humidity, and hence have larger light-extinction efficiencies. The sulfate and nitrate aerosol mixtures may also exhibit hysteresis effects in situations where humidity is reduced, thereby causing a haze to linger.

11.5 MEASUREMENTS OF THE CONTRIBUTION OF NITROGEN OXIDES TO URBAN AND REGIONAL HAZE

This section presents the various estimates of the contribution of NO_2 and NH_4NO_3 aerosols to light extinction. The discussion is broken into two sections: (1) recent state-of-the-art measurements, and (2) earlier measurements having significant positive or negative biases. As mentioned earlier in this chapter and also in Section 6.10 of this document, earlier measurements of nitrate aerosol were plagued by significant positive and negative artifacts. Glass filters had positive artifacts (i.e., overestimated nitrate concentrations), whereas Teflon® filters had negative artifacts (i.e., underestimated nitrate concentrations). The best measurements of nitrate are made with a denuder and nylon filter combination. There are relatively few studies with the state-of-the-art measurement technology; these studies are discussed first. For historical completeness, additional studies with significant nitrate measurement artifacts are summarized next.

11.5.1 Recent State-of-the-Art Measurements

Appel et al. (1983, 1985) studied the chemical composition of aerosol in July and August 1982 using state-of-the-art denuder difference measurements in three California cities: San Jose, Riverside, and Los Angeles. Mean nitrate anion concentrations were $4.4 \mu\text{g}/\text{m}^3$ (17% of the total fine particle mass of $22.3 \mu\text{g}/\text{m}^3$) in San Jose, $17.4 \mu\text{g}/\text{m}^3$ (37% of the total fine particle mass of $47.5 \mu\text{g}/\text{m}^3$) in Riverside, and $10.2 \mu\text{g}/\text{m}^3$ (17% of the total fine particle mass of $61.5 \mu\text{g}/\text{m}^3$) in Los Angeles.

Solomon et al. (1992) have reported the results of a 1-year measurement program conducted throughout the South Coast Air Basin in the greater Los Angeles area during 1986, based on state-of-the-art denuder/nylon-filter measurements. Most of the HNO_3 in the area was found in the aerosol phase, and a substantial fraction (about 42%) of the nitrate was

coarse Fine-particle NH_4NO_3 concentrations ranged from 6.2 to 18.2 $\mu\text{g}/\text{m}^3$ and averaged 10.4 $\mu\text{g}/\text{m}^3$ for seven metropolitan area sites. The background site had a fine-particle nitrate concentration of 1.1 $\mu\text{g}/\text{m}^3$. This is a substantial fraction of total fine-particulate mass in the Los Angeles area (23.1 to 42.1 $\mu\text{g}/\text{m}^3$) measured in 1982, reported by Gray et al. (1986).

Lewis et al. (1986) measured the chemical composition of fine and coarse fractions of the aerosol for 20 days in January 1982. With their denuder/nylon-filter combination, they measured a daytime fine-particle NH_4NO_3 mass of 3.4 $\mu\text{g}/\text{m}^3$, 18% of the daytime fine-particle total mass of 19.0 $\mu\text{g}/\text{m}^3$.

Watson et al. (1988) and Sloane et al. (1991) measured the chemical composition of the fine-particle mass, making 7-h daytime measurements ($n = 24$) during the winter of 1987-1988. The Micro-Orifice Uniform Deposit Impactor (MOUDI) was used to measure fine-particle mass in several size ranges. Nitrate measurements were considered accurate based on a prior comparison of impactor and denuder/nylon-filter measurements. Ammonium nitrate averaged 3.4 $\mu\text{g}/\text{m}^3$, 21% of the total fine-particle mass of 16.4 $\mu\text{g}/\text{m}^3$. Particle size distributions were measured for two distinctly different days during this measurement period: a high-relative-humidity day with prolonged northeasterly flow and a relatively low-humidity, stagnant day. During the high-humidity day, the light-extinction efficiency for nitrate anion was 7.2 m^2/g (6.6 m^2/g for light scattering and 0.6 m^2/g for light absorption). During the stagnant, lower-humidity day, the light-extinction efficiency for nitrate anion was 3.6 m^2/g (3.0 m^2/g of scattering and 0.6 m^2/g for absorption).

Watson et al. (1991) studied the chemical composition of the haze in Phoenix from September 25, 1989, through January 22, 1990. The mean NH_4NO_3 and total fine-particle mass concentrations over the entire time period and the four measurement sites were 4.4 and 22.3 $\mu\text{g}/\text{m}^3$, respectively, for morning measurements and 4.8 and 15.5 $\mu\text{g}/\text{m}^3$, respectively, for afternoon measurements. Thus, nitrate contributed 19% of the fine-particle mass in the morning and 31% of the fine-particle mass in the afternoon. The light-scattering efficiency of nitrate anion was fit with the following equation: $2.3 + [1.7/(1 - \mu)] \text{ m}^2/\text{g}$, where μ is relative humidity defined as percentage divided by 100. Thus, for 50% RH, the nitrate anion scattering efficiency is 5.7 m^2/g .

Stevens et al. (1988) reported measurements made during the winter of 1986-1987 in Boise, ID. Nitrate aerosol was a significant component of total light extinction, contributing

13% of the fine-particle mass. Less than 10% of the total nitrate was left in the vapor phase as HNO_3 . Measurements in this study were made using an annular denuder followed by Teflon[®] and nylon filters.

Malm et al (1989) evaluated the contribution of nitrate aerosol, along with larger contributions from sulfate and carbonaceous aerosols, to wintertime visibility impairment in the scenic Southwest near Grand Canyon and Canyonlands national parks. Nitrate concentrations during January and February 1987 at Grand Canyon averaged 0.1 to $0.3 \mu\text{g}/\text{m}^3$. Multiple linear-regression analysis suggested that nitrate particles had an average scattering efficiency of $4.7 \text{ m}^2/\text{g}$ and contributed 6 to 14% of the fine-particle light extinction during the wintertime study. Nitrate was generally a much smaller contributor, however, to light extinction than sulfates, which contributed 62 to 72% of fine-particle extinction, and organics, which contributed 15 to 16%.

Richards et al (1991) measured aerosol composition in and near the Grand Canyon during January through March 1990. Ammonium nitrate was 6.4 to 10.4% of the fine-particle mass at three locations in the Grand Canyon.

11.5.2 Earlier Measurements

Because these earlier measurements have significant positive and negative nitrate artifacts, they are less accurate than the previous studies. Such biases should be kept in mind.

White and Roberts (1977) studied the statistical relationships between light-scattering coefficient and the aerosol constituents of Los Angeles area smog measured during the summer and early fall of 1973 as part of ACHEX (Aerosol Characterization Experiment). Using linear-regression techniques, they estimated that nitrate aerosols contributed, on average, about 27% of the total light-scattering coefficient. Nitrates were found to have a light-scattering efficiency, having units of m^2/g of nitrate anion, of $2.9 + 6.5 \mu^2$, where μ is the relative humidity as previously defined. Thus, at a humidity of 50%, the light scattering coefficient of nitrates was estimated to be $4.5 \text{ m}^2/\text{g}$. Appel et al (1985) have commented that White and Roberts (1977) may have seriously underestimated nitrate scattering efficiencies because the glass-fiber filters used to collect aerosol samples had a strong

positive artifact (i.e., gaseous HNO_3 was deposited on the filter, thereby inflating the nitrate aerosol measurement)

Cass (1979) used linear and nonlinear regression to study the relationships between sulfate and nitrate concentrations and visibility in Los Angeles from 1965 through 1974. Sulfates and nitrates were found to be significant contributors to total light extinction. The best fits to measured visibility were obtained with regression coefficients of the form, $\beta/(1 - \mu)$, where μ is the relative humidity as defined previously. This is indicative of hygroscopic or deliquescent properties of sulfate and nitrate. The values for β for sulfate and nitrate anion were 5.3 and 3.3 m^2/g , respectively. At 50% RH, this would yield overall respective light-extinction efficiencies for sulfate and nitrate anions and associated water of 10.7 and 6.6 m^2/g . The nitrate measurements used by Cass were subject to positive artifacts. The nitrate data were 24-h averages, whereas the extinction data were daytime averages. Light extinction was derived from visual-range observations rather than nephelometer or transmissometer measurements. A Koschmieder constant of 3.9 rather than 3.0 as recommended in Equation 11-7 was used, thereby biasing extinction values high. It is not clear whether the two positive biases would cancel each other out.

Trijonis et al. (1982) investigated the visibility-aerosol relationship in California using data from 34 locations. They found that NO_2 contributed a rather uniform 7 to 11% of total light extinction (b_{ext}) throughout California. Although they were not of adequate quality to make definitive statements, the data suggest that nitrates are more important contributors to b_{ext} in northern California, where they may contribute 10 to 40% of b_{ext} .

Outside of California, the most significant urban hazes that have been shown to be associated with NO_x occurred in the winter in Denver and Phoenix. Nitrogen oxides, both NO_2 and nitrate aerosol, were found to be significant contributors to the winter haze in Denver (Groblicki et al., 1981), even with the significant negative artifacts of the measurement techniques used. Multivariate statistical analysis (regression) was used to analyze the relationships between light scattering and absorption and concentrations of particles and gases measured on 41 consecutive days in November and December 1978. Most of the light extinction was found to be caused by particles $< 2.5 \mu\text{m}$ in diameter. Elemental carbon (soot) was found to be the most significant contributor, accounting for 37% of light extinction above natural Rayleigh background. Sulfate (and associated water) was

found to contribute 20%, nitrate (and associated water), 17%, and organic carbon, 13%, the remaining fine-particle matter contributed 7%, and NO₂ contributed 6%. All measurements were based on a wavelength of light of 0.475 μm (Hasan and Dzubay, 1983). If the contribution of nitrate and NO₂ are combined, the total NO_x contribution to Denver winter haze is 23%, second only to the contribution of elemental carbon, however, this is probably an underestimate of the NO_x contribution because of the negative nitrate artifact.

Still, data from the Groblicki et al. (1981) study may be better than some of the other data for Denver because of the cold temperatures and high NH₃ concentrations found in Denver during the study.

Wolff et al. (1981) determined the emission source contributions to the Denver winter haze. Of the total NO_x contribution to the winter haze of 23% (also an underestimate because of the negative nitrate artifact), combustion of natural gas, oil, and coal (in power plants and boilers) accounted for more than half (14%), and automotive contributions were the largest part of the remainder (9%). Hasan and Dzubay (1983) developed estimates of light extinction efficiency of various aerosol components of the 1978 Denver winter haze using both regression analysis and Mie scattering theory based on measured particle size distributions. For nitrate anion, regression gave a scattering efficiency of 3.1 to 3.2 m²/g, whereas theoretical calculations yielded a scattering efficiency of 4.8 to 4.9 m²/g.

Solomon and Moyers (1984) studied the contributors to light extinction in Phoenix during January 1983, when winter hazes were observed. Elemental carbon was estimated to be the largest contributor to light extinction, at 41% of b_{ext}, on average. Approximately equal contributions resulted from nitrate (15%), organic carbon (15%), and sulfate (13%). However, these estimates are biased because they used the Groblicki et al. (1981) regression equations. The contribution from NO₂ averaged 3.2%. Solomon and Moyers (1986) reported that the fine nitrate aerosol measured in Phoenix in January 1983 was 13.4% of the total fine-particle mass, comparable to the 12.2% contribution of nitrate found in Denver during November and December 1978 and much higher than the contribution reported in other major metropolitan and rural areas. However, they concluded that their nitrate measurements were significantly positively biased. They concluded that motor vehicle emissions accounted for most of the nitrate and other fine-particle mass that caused the observed haze.

Few studies of the role of nitrate aerosol in visibility impairment have been conducted outside of the western United States. Nitrate aerosol contributions appear to be lower in the eastern United States than in California and other western U.S. areas, perhaps because of higher sulfate concentrations competing for the available atmospheric NH_3 .

Using multiple linear-regression techniques, Trijonis and Yuan (1978a) found that nitrate did not account for any of the observed light extinction in most of the cities in the northeastern and north central United States. Nitrates accounted for 8% of total light extinction in Columbus, OH. There the light extinction efficiency of nitrate was estimated from regression analysis to be in the range of 6 to 9 m^2/g .

Wolff et al. (1982) found that nitrate contributed minimally to light extinction in Detroit during July 1981. Fine-particle nitrate averaged $0.2 \mu\text{g}/\text{m}^3$, coarse-particle nitrate was higher, at $1 \mu\text{g}/\text{m}^3$. This was consistent with other measurements made in the eastern United States (Ferman et al., 1981), where little nitrate was found in the fine fraction. Nitrogen dioxide contributed 4% of b_{ext} in the Wolff et al. study (1982).

Dzubay et al. (1982) studied the relationships between visibility and aerosol composition during summer in Houston, TX. Nitrate was found mainly on coarse particles and was determined to be an insignificant (0.5%) contributor to the total light extinction. It was conjectured that fine nitrate aerosol did not condense because the sulfate was not fully neutralized (i.e., there was insufficient NH_3 to react with HNO_3), and that HNO_3 condensed on the alkaline coarse particles, which were a significant sink for nitrate. Nitrate particle measurement artifacts may also have been a major factor in this study. Nitrogen dioxide contributed 4.7% of b_{ext} .

Colbeck and Harrison (1984) found significant quantities of nitrate aerosol in northwest England. Visibility there was strongly correlated with both nitrate and sulfate concentrations. Diederer et al. (1985) investigated the nature of the haze in western Netherlands during the period 1979 to 1981. Ammonium nitrate aerosol was found to contribute 35% of total b_{ext} , and NO_2 to contribute 2%.

Bravo et al. (1988) found high concentrations of nitrate aerosol and NO_2 in Mexico City ($6.4 \mu\text{g}/\text{m}^3$ and 0.07 ppm, respectively), however, the relative contributions of these species to the total light extinction budget were small (5 and 2.5%, respectively) because of

the much higher concentrations of other aerosol species. Total light extinction was dominated by soot (31%), sulfate (30%), organics (15%), and other species (16%).

The effects of NO_2 and nitrate on regional haze outside of urban areas appear to be less significant than their effects on urban hazes. Nitrogen oxides may not be significant in these nonurban regional hazes because of low concentrations of HNO_3 and NH_3 , high ambient temperatures, and low humidities in the West, and because of high sulfate concentrations in the East that compete for available NH_3 .

Macias et al (1981) found that nitrate made small or negligible contributions to regional haze at one site in Arizona on several monitoring days in the summer and winter of 1979, although on one day NH_4NO_3 was about 8% of the fine-particle mass. However, these measurements were negatively biased.

White and Macias (1987) found very low concentrations of nitrate aerosol in the nonurban, intermountain West. Measurements of nitrate aerosol concentrations averaged $0.09 \mu\text{g}/\text{m}^3$. Nitrate was very episodic, however, with major contributions to this average arising from a small number of episodes. Higher concentrations were observed in the North and at all sites during the winter. White and Macias (1987) commented that during the winter the measurements may have underestimated nitrate aerosol concentrations by as much as a factor of three because of nitrate volatilization from the filters.

Trijonis et al (1988) analyzed data collected in the Mohave Desert of California over a 2-year period, 1983 to 1985, to determine the species contributing to light extinction. They found that for both average and worst-case conditions the sum of particulate nitrate and NO_2 contributed $13 \pm 5\%$ of non-Rayleigh b_{ext} , however, nitrate measurements were subject to artifacts.

Mathai and Tombach (1987), in their review of visibility and aerosol measurements in the eastern United States, concluded that fine nitrate concentrations averaged $1 \mu\text{g}/\text{m}^3$. In the studies they summarized, fine-particle nitrate had been measured for very short (week and month) periods and concentrations had ranged from 0.2 to 0.9 $\mu\text{g}/\text{m}^3$.

Wolff and Korsog (1989) found that NO_2 (averaging 4 ppb) accounted for less than 1% of total light extinction in the Berkshire Mountains of Massachusetts in the summer of 1984. Sulfate and associated water caused most (77%) of the light extinction. Nitrate aerosol was not found. The measurements of Vossler et al (1989) at Deep Creek Lake in

Maryland and of Pierson et al (1987) in the Allegheny Mountains were consistent with the Berkshire Mountains study, NO_2 averaged 4 ppb, and nitrate aerosol concentrations were very small relative to sulfate. The latter two studies, unlike the Berkshire study, used the more accurate denuder-nylon filter samples.

Dzubay and Clubb (1981) found that for summer conditions in Research Triangle Park, NC (nonurban but near urban areas), the sum of the scattering and absorption coefficients by species accounted for about 90% of the measured b_{ext} . Particle scattering caused most of the light extinction (75%), followed by Rayleigh scattering from air (7%) and particle light absorption (7%), NO_2 light absorption accounted for only 2% of total light extinction.

11.6 MODELING REGIONAL AND URBAN HAZE EFFECTS

Latimer et al (1985a) used a Lagrangian regional visibility model and emission inventories for the southwestern United States to estimate the effects of manmade emission sources on regional visibility in 1980 and 1995. In this assessment, nitrate aerosol was found to be a potentially significant contributor to the manmade portion of nonurban regional haze. While manmade sulfate sources were found to be the largest contributors to haze, contributing over half (50 to 60%) of the manmade fraction, nitrate was estimated to be the next largest contributor (10 to 20%). Although manmade organic and elemental carbon contributions to regional haze were found to be small (less than 10% of the manmade fraction), biogenic organic aerosol was estimated to be a large contributor to total light extinction (the sum of natural and manmade fractions).

In this modeling study, it was cautioned that the estimates of the contribution of nitrate to the manmade total were uncertain because of uncertainties in the relative distribution of the nitrate anion (NO_3^-) between optically inactive HNO_3 and light-scattering NH_4NO_3 aerosol. This uncertainty resulted largely from the uncertainty regarding background concentrations of NH_3 , which is essential to the formation of NH_4NO_3 aerosol. On the basis of thermodynamic equilibrium considerations, the study showed that nitrate aerosol would be most likely to condense in winter and least likely in summer. Nitrate aerosol was found to be a significant portion of increases in regional haze projected for the period 1980 to 1995. Latimer et al (1985b, 1986) evaluated the performance of this regional visibility model by

comparing model calculations with particulate, visibility, and wet deposition measurements performed by the U S Environmental Protection Agency (EPA), the National Park Service, and the Electric Power Research Institute. This comparison showed that model predictions of sulfate and nitrate concentrations and light extinction were only slightly biased and were highly correlated with actual measurements. The average nitrate aerosol concentration predicted by the model was $0.22 \mu\text{g}/\text{m}^3$, approximately 2.4 times the average measured during the Western Regional Air Quality Study in 1981 of $<0.1 \mu\text{g}/\text{m}^3$ that was reported in Tombach et al (1987) and the value of $0.09 \mu\text{g}/\text{m}^3$ reported by White and Macias (1987), however, these latter studies had negative artifacts.

Latimer et al (1986) and Latimer (1988c) applied this regional visibility model to the case of winter layered haze observed near the national parks in Utah and Arizona. An average nitrate aerosol concentration of $0.35 \mu\text{g}/\text{m}^3$ was predicted. This value compares reasonably well with the average of $0.16 \mu\text{g}/\text{m}^3$ measured during a special study in 1986 (Latimer, 1988c) and the average of $0.38 \mu\text{g}/\text{m}^3$ measured during the WHITEX experiment in 1987 (Malm and Iyer, 1988). However, the model underpredicted the observed sulfate concentrations by a factor of two to four. Although considerable uncertainty exists over the accuracy of nitrate measurements (Malm and Gebhard, 1988), nitrate may be a significant contributor to winter layered haze (approximately 15 to 25% of extinction from manmade sources, according to Malm et al, 1989), even though sulfate appears to be the dominant contributor.

Latimer (1988a) developed a spreadsheet template for calculating the effect of changes in aerosol species concentration on total light extinction and visibility. As part of that effort, available measurements of chemical composition and concentration of particles and of visibility or light extinction were compiled. Using an assumed nitrate light-scattering efficiency of $8 \text{ m}^2/\text{g}$, Latimer (1988a) estimated the relative contribution of nitrate to total light extinction in numerous locations where both aerosol and visibility data were available. Nitrate generally contributed less than 10% to total extinction, except in Portland, OR, where it was 11 to 14%, Denver, CO, 16%, Los Angeles, CA, 20%, and Riverside, CA, 40%. Latimer (1988a) found that measured visual ranges agreed well with visual ranges derived from the measured aerosol constituents and their respective light-extinction efficiencies.

Russell and Cass (1986) developed a Lagrangian trajectory model that incorporates gaseous and aerosol chemistry and aerosol equilibrium. This model was applied to a smog episode in Southern California. Predictions from the model compared well with measurements of O_3 , NO_2 , HNO_3 , NH_3 , PAN, and particulate nitrate. When the model was used to investigate alternative control techniques for nitrate aerosol, NO_x emission control was found to produce a nearly proportional (linear) reduction in total nitrate (HNO_3 vapor plus particulate nitrate) and slightly greater than proportional reductions in particulate nitrate. Particulate nitrate concentrations were found to be effectively reduced by reducing NH_3 emissions, especially from farm-related activities.

Russell et al (1988a,b) developed and applied a grid-based Eulerian airshed model that incorporates a chemical reaction mechanism for gaseous and aerosol species. The model was compared with measurements and the model calculations of aerosol nitrate concentrations were found to be in good agreement with measurements.

Pilinis and Seinfeld (1987) developed the SEQUILIB model, which consists of thermodynamic equilibrium relationships that describe the behavior of the HNO_3 , NH_4NO_3 , NH_3 , NH_4^+ , $SO_4^{=}$, Cl^- , and H_2O chemical system (Stelson and Seinfeld, 1982a,b,c, Bassett and Seinfeld, 1983, 1984, Saxena et al, 1986, Pilinis et al, 1987). This model calculates the equilibrium concentrations of these species in the gas and aerosol phases. A model of this type is essential for calculating the amount of aerosol nitrate formed and the water content of hygroscopic aerosols. This model was applied in the Phoenix winter haze study (Watson et al, 1991) to assess the degree of nitrate and NH_3 control required to reduce NH_4NO_3 aerosol concentrations.

Reactive plume models have been developed (Joos et al, 1987, Hudischewskyj and Seigneur, 1989) that incorporate such equilibrium models and aerosol coagulation models to calculate aerosol size distributions of nitrate and other aerosols. Zhang (1991) has developed mathematical models to calculate light-extinction efficiency from aerosol composition.

11.7 ROLE OF NITROGEN OXIDES IN PLUME VISUAL IMPACT

Much of the regulatory attention that has been given to visibility during the past decade has focused on the issue of the visibility impacts of plumes from individual emission sources.

This plume visual impact is commonly called "plume blight" (U S Environmental Protection Agency, 1979) Particularly in areas of pristine background visibility, such as the intermountain West, the visual impact of plumes such as those from power plants can be quite significant as far as 100 km from sources (U S Environmental Protection Agency, 1979; Latimer, 1979, 1980) Considerable work has been carried out during the past decade to develop and evaluate computer models of plume visual impact and to develop technical guidance for plume visual impact evaluation as part of the implementation of EPA's visibility regulations under the visibility protection provisions of the Clean Air Act Nitrogen dioxide has been found to be a significant contributor to plume visual impact from modern, well-controlled power plants

The contrast of a plume against an optically thick horizon-sky background can be calculated by solving Equation 11-1 (Latimer et al , 1978, White et al , 1986)

$$C_{\text{plume}} = [J_{\text{plume}}/J_{\text{back}} - 1] [1 - \exp(-\tau_{\text{plume}})] [\exp(-b_{\text{ext}} r_p)], \quad (11-8)$$

where

C_{plume} = contrast of the plume against the horizon sky $([I_{\text{plume}} - I_{\text{sky}}]/I_{\text{sky}})$,

J = source function defined previously,

τ_{plume} = optical thickness of the plume $(\int b_{\text{ext}} dr)$,

b_{ext} = extinction coefficient of the intervening background atmosphere between the plume and the observer, and

r_p = distance between the plume and the observer

For a pure NO_2 plume, the first term (in the first pair of square brackets) equals -1, and therefore C_{plume} is always negative, signifying a dark plume If one also assumes either that the plume is very close to the observer ($r_p \approx 0$) or that the intervening atmosphere is optically thin ($b_{\text{ext}} \approx 0$), then the last term in this equation equals 1, and the following equation for an NO_2 plume is obtained

$$C_{\text{plume}} = -[1 - \exp(-\tau_{\text{plume}})] = -[1 - \exp(\int_{\text{plume}} b_{\text{ag}} dr)] \quad (11-9)$$

If one assumes that C_{plume} must equal at least 0.02 for a plume to be visible, then the plume optical thickness (τ_{plume}) must be at least 0.02. For a plume that is 1 km wide, this optical depth can be caused by 0.065 ppm ($122 \mu\text{g}/\text{m}^3$) of NO_2 at $\lambda = 0.55 \mu\text{m}$ or by 0.012 ppm ($22 \mu\text{g}/\text{m}^3$) at $\lambda = 0.4 \mu\text{m}$. For a plume 10 km wide, the same effect could be caused by NO_2 concentrations one-tenth as large. Melo and Stevens (1981) found that under typical conditions a plume NO_2 optical thickness corresponding to 90 ppm-m (or 0.090 ppm in a 1 km wide plume) was required to make a plume just visible against a blue horizon-sky background. Using a predecessor of the PLUVUE models (Johnson et al., 1980, Seigneur et al., 1984), Latimer (1980) investigated the relationship between NO_x emission rates from power plants and plume contrast and other optical parameters. He found that the yellow-brown coloration of the power plant plume was dominated by NO_2 for the modeled cases. Melo and Stevens (1981) confirmed the dominant importance of NO_2 to coloration in an actual power plant plume. Latimer (1979, 1980) modeled the visual impacts of power plants of various sizes and NO_x emission rates and concluded that yellow-brown plumes could be observed as far as 100 to 150 km away from a power plant, but only on a few days per year.

White and Patterson (1981) developed nomographs that allow one to determine the optical properties and relative importance of emitted particles and NO_2 as a function of the scattering angle and the particle size distribution. Vanderpol and Humbert (1981) identified NO_2 as the primary plume colorant when particle size was greater than $0.5 \mu\text{m}$. Haas and Fabrick (1981) performed a sensitivity analysis to investigate the effects of NO_2 and particles in plumes on various indicators of color and contrast.

In studies of the Navajo Generating Station plume in the southwestern United States as part of the VISTTA project, Richards et al. (1981) never found particulate nitrate, even though HNO_3 vapor was formed at rates 3 to 10 times the rate at which sulfate aerosol was formed. They concluded that nitrate aerosol did not condense because of inadequate background concentrations of NH_3 . Hegg and Hobbs (1983) measured the constituents of another power-plant plume in the Southwest and found rapid formation of both HNO_3 and nitrate aerosol. Nitrate aerosol constituted 15 to 75% of the nitrate in the plume. Measured plume aerosol size was primarily in the $0.25\text{-}\mu\text{m}$ range. Approximately equal contributions to plume light extinction were made by particles and NO_2 . The reason the Hegg and Hobbs (1983) findings were quite different from those of Richards et al. (1981) is not clear, but the

findings may have differed because background NH_3 concentrations differed at the respective sites

Also as part of the VISTTA study, Blumenthal et al (1981) measured the dispersion, chemistry, and optical properties of the Navajo Generating Station. On the basis of this measurement program, they concluded that NO_2 was the primary plume colorant, that secondary aerosol formation could be neglected within 100 km of the source, and that the PLUVUE model adequately characterized observed effects. Bergstrom et al (1981) evaluated the PLUVUE model using VISTTA data and found that the model performed reasonably well, but that it slightly overpredicted observed plume visual impacts. Sensitivity analyses performed indicated that NO_2 was the principal plume colorant.

The most detailed evaluation of plume visibility models was carried out as part of the VISTTA study (White et al , 1985, 1986). Four plume visibility models, including the two versions of PLUVUE (Latimer and Samuelsen, 1975, 1978, Latimer et al , 1978, Johnson et al., 1980, Seigneur et al , 1984), the ERT visibility model (Drivas et al , 1980), PHOENIX (Eltgroth, 1982), and the Los Alamos visibility model (Williams et al 1980, 1981), were evaluated by comparison with field measurements of plume concentrations, optical parameters, and observed plume color and contrast made at the Navajo Generating Station, well-controlled for particulate, at less well-controlled power plants in the Midwest, and at an uncontrolled smelter in the Southwest. Of the four, the first two, the PLUVUE and ERT models, were found to be most accurate in predicting the plume visual impacts observed in the field measurement programs. The plume contrast for the power plant with modern particulate controls could be adequately explained accounting just for the plume NO_2 concentrations; particulates did not play a significant role. In the study of strong particulate emission sources (White et al , 1986), the performance of PLUVUE II and the ERT models was less satisfactory than for the NO_2 -dominated plumes. However, the relatively poor performance of these two models may have resulted in large part from the imprecise specification of model inputs (particle size and background sky radiance). Model performance was found to depend strongly on model input specification.

11.8 SUMMARY OF EFFECTS ON VISIBILITY

Emissions of NO_x can contribute significantly to visibility impairment in the form of plumes and hazes. Nitrogen dioxide and NH_4NO_3 are the optically active species of NO_x . Other species, including NO and HNO_3 , are gases with insignificant optical effects. Nitrogen dioxide is a gas that preferentially absorbs blue light, thus tending to cause yellow-brown atmospheric discoloration. There is agreement among many studies that NO_2 is a strong and consistent colorant. Aerosols, however, including nitrate, can cause atmospheric discoloration, particularly when bright objects are observed or the sun is behind the observer.

Nitrogen dioxide has been shown to be the most significant plume colorant for the yellow-brown power plant plumes that have been observed, primarily in the western United States, and that are of current regulatory concern to EPA and the States.

Nitrogen dioxide and nitrate aerosol are significant contributors to urban haze, especially in California and the western United States. Their combined share of total extinction can be 20 to 40% of total light extinction in such urban areas. In nonurban areas, NO_x appears to be a relatively small contributor to light extinction because NO_2 , nitrate aerosol, and NH_3 concentrations tend to be lower or because moderate or high temperatures tend to prevent nitrate aerosol from condensing. Nitrate aerosol does not appear in high concentration in areas of high concentrations of acid sulfate, such as the eastern United States, mainly because acidic sulfate compounds consume the available atmospheric NH_3 that is needed to condense nitrate aerosol from HNO_3 vapor.

Theoretical models have been developed for describing the chemical reactions that result in the formation of optically active NO_x species, aerosol dynamics of nitrate aerosol, chemical equilibrium of nitrate-water aerosols, the light scattering and absorption properties as a function of the wavelength of light, and effects on visual range, haze contrasts, and atmospheric color. The available comparison of plume visibility models suggests that the effects of plume NO_2 can be accurately predicted but that model predictions of the effects of aerosol particles are less adequate. Limited work has been done to develop and test models for urban, layered, and regional haze, but much more work is clearly needed.

Measurement of nitrate aerosol is complicated by its volatility. However, newer measurement techniques based on the use of denuders have provided reliable measurements.

Because older techniques (such as Teflon[®] filters) can seriously underestimate nitrate aerosol concentrations, care must be taken when interpreting data obtained by those techniques

Work is needed to understand the apparently nonlinear effects of NO_x emission controls on nitrate aerosol concentrations and resulting visibility effects. Also, work is needed to understand the effects of sulfur dioxide emission controls on nitrate aerosol production, because the large-scale reduction of sulfate, which competes with nitrate for available NH₃, may result in increases in nitrate aerosol

11.9 ECONOMIC VALUATION OF EFFECTS ON VISIBILITY FROM NITROGEN OXIDES

The primary effects of NO_x on visibility were described in previous sections of this chapter and are believed to be (1) discoloration, producing a brownish color seen in plumes, layered hazes, and uniform hazes, and (2) reductions in visual range (increases in light extinction), especially in urban areas in the western United States. This section discusses the available economic evidence concerning the value of preventing or reducing these types of effects on visibility. Economic studies have not focused specifically on NO_x-associated changes in visibility for the most part, but some studies have considered the types of visibility effects that are associated with NO_x. The following summary of economic estimation methods and available results is brief. For more detail see Chestnut and Rowe (1990a), Mitchell and Carson (1989), Fischhoff and Furby (1988), Cummings et al (1986), and Rowe and Chestnut (1982)

11.9.1 Basic Concepts of Economic Valuation

Visibility has value to individual economic agents primarily through its impact upon activities of consumers and producers. Studies of the economic impact of visibility degradation by air pollution have focused on consumer activities. Most economic studies of the effects of air pollution on visibility have focused specifically on the aesthetic effects to the individual. Some commercial activities, such as airport operations, may be affected by visibility degradation by air pollution, but available evidence suggests that the economic magnitude of NO_x effects on commercial operations probably is very small. In a 1985

report, EPA concluded that some percentage of the visibility impairment incidents sufficient to affect air traffic activity might be attributable, at least in part, to manmade air pollutants (possibly 2% to 12% in summer in the eastern United States), but according to the information presented previously in this chapter, NO_x would not be expected to be a significant contributor to these incidents

It is well established that people notice those changes in visibility conditions that are significant enough to be perceptible to the human observer, and that visibility conditions affect the well-being of individuals. This has been verified in scenic and visual air quality rating studies (Middleton et al , 1983, Latimer et al , 1981, Daniel and Hill, 1987), through the observation that individuals spend less time at scenic vistas on days with lower visibility (MacFarland et al , 1983), and through use of attitudinal surveys (Ross et al , 1987). The intent of visibility-related economic studies has been to put a dollar value on changes in well-being associated with visibility degradation.

Welfare economics defines a dollar measure of the change in individual well-being (referred to as utility) that results from a change in the quality of any public good, such as visibility, as the change in income that would cause the same change in well-being as that caused by the change in the quality of the public good. One way of defining this measure of value is to determine the maximum amount the individual would be willing to pay to obtain improvements or prevent degradation in the public good (see Freeman [1979] for more detail). For most goods and services traded in markets, this measure can be derived from analysis of market transactions. For non-market goods, such as visibility, this economic measure of value must be derived some other way.

For purposes of this discussion, consumer values for changes in visibility can be divided into use and non-use values (there are slight variations in the way these are defined by different economists). Use values are related to the direct influence of visibility on the current and expected future activities of an individual at a site. Non-use values are the values an individual places on protecting visibility for use by others (bequest value) and on knowing that it is being protected regardless of current or future use (existence value). Total value, combining use and non-use, is sometimes called preservation value.

11.9.2 Economic Valuation Methods for Visibility

Two main economic valuation methods have been used to estimate dollar values for changes in visibility conditions in various settings (1) the contingent valuation method (CVM), and (2) the hedonic property value method. Both methods have important limitations, and uncertainties surround the accuracy of available results for visibility. Ongoing research continues to address important methodological issues, but at this time some fundamental questions remain unresolved (Chestnut and Rowe, 1990a, Mitchell and Carson, 1989, Fischhoff and Furby, 1988, Cummings et al, 1986). Recognizing these uncertainties is important, but the body of evidence as a whole suggests that economic values for changes in visibility conditions are probably substantial in many cases and that a sense of the likely magnitude of these values can be derived in some instances from the available results (Chestnut and Rowe, 1990a).

11.9.2.1 Contingent Valuation Method

The CVM involves the use of surveys to elicit values that respondents place on changes in visibility conditions (see Rowe and Chestnut [1982], Mitchell and Carson [1989], and Cummings et al [1986] for more details on this method). The most common variation of the CVM relies on questions that directly ask respondents to estimate their maximum willingness to pay (WTP) to obtain or prevent various changes in visibility conditions. The potential changes in visibility conditions are usually presented to the respondents by means of photographs and verbal descriptions, and some hypothetical payment mechanism, such as a general price increase or a utility bill increase, is posed.

The CVM offers economists the greatest flexibility and potential for estimating use and non-use values for visibility. There are many types of changes in visibility for which total values cannot be derived from market data. As a result, most recent visibility value applications use the CVM. This approach continues to be controversial, however, and there are those who question whether the results are useful for policy analysis (Fischhoff and Furby, 1988, Kahneman and Knetsch, 1992). Smith (1992) has responded to some of the questions raised about the CVM, but a consensus on its usefulness and reliability has not been reached in the economics community. Cummings et al (1986) and Mitchell and Carson (1989) have conducted the most comprehensive reviews of the CVM approach to date and

have concluded that there is sufficient evidence to support the careful use of results from well-designed CVM studies in certain applications

Among the fundamental issues concerning the application of CVM for estimating visibility values are (1) the ability of researchers to present visibility conditions in a manner relevant to respondents and to design instruments that can elicit unbiased values, and (2) the ability of respondents to formulate and report values with acceptable accuracy. As with any survey instrument, it is important that the presentation be credible, realistic, and as simple as possible. The optimal level of detail and the most critical pieces of information necessary in the presentation to respondents to obtain useful CVM responses continue to be topics of research and discussion. Another important issue in CVM visibility research concerns the ability of respondents to isolate values related to visibility aesthetics from other potential benefits of air pollution control such as protection of human health. Preliminary results (Irwin et al, 1990, Carson et al, 1990) suggest that simply telling respondents before asking the WTP questions to include only visibility is not adequate and may cause some upward bias in the responses.

11.9.2.2 Hedonic Property Value Method

The hedonic property value method uses relationships between property values and air quality conditions to infer values for differences in air quality (see Rowe and Chestnut [1982] and Trijonis et al [1984] for more detail on this method). The approach is used to determine the implicit, or "hedonic," price for air quality in a residential housing market, based on the theoretical expectation that differences in property values that are associated with differences in air quality will reveal how much households are willing to pay for different levels of air quality in the areas where they live. The major strength of this approach is that it uses real market data that reflect what people actually pay to obtain improvements in air quality in association with the purchase of their homes. The method can provide estimates of use value, but non-use values cannot be estimated with this method.

There are many theoretical and empirical difficulties in applying the hedonic property value method for estimating values for changes in visibility, but the most important limitation is the difficulty in isolating values for visibility from other effects of air pollution at the residence. Hedonic property value studies to date provide estimates of total value for all

perceived impacts resulting from air pollution at the residence, including health, visibility, soiling, and damage to materials and vegetation. The potential for estimating separate values for visibility with this method is limited for two reasons. First, the actual effects of air pollution often are highly correlated, making it difficult to separate them statistically using objective measures. Second, individuals are likely to perceive a correlation between these effects and to act accordingly in their housing decisions, even if the effects are actually separable using objective measures.

11.9.3 Studies of Economic Valuation of Visibility

Economic studies have estimated values for two types of visibility effects potentially related to NO_x : (1) use and non-use values for preventing the types of plumes caused by power plant emissions, visible from recreation areas in the southwestern United States, and (2) use values of local residents for reducing or preventing increases in urban hazes in several different locations.

11.9.3.1 Economic Valuation Studies for Air Pollution Plumes

Three CVM studies have estimated on-site use values for preventing an air pollution plume visible from recreation areas in the southwestern United States (Table 11-2). One of these studies (Schulze et al., 1983) also estimated total preservation (use and non-use) values held by visitors and non-visitors for preventing a plume at the Grand Canyon. A fourth study concerning a plume at Mesa Verde National Park (Rae, 1983) was not included because of methodological problems with the contingent ranking approach used (Ruud, 1987). The plumes in all three studies were illustrated with actual or simulated photographs showing a dark, thin plume across the sky above scenic landscape features, but specific measures such as contrast and thickness of the plume were not reported. Respondents were told that the source of the plume was a power plant or an unspecified air pollution source. In one study (Brookshire et al., 1976), a power plant was visible in the photographs.

The estimated on-site use values for the prevention or elimination of the plume ranged from about \$3 to \$6 (1989 dollars) per day per visitor-party at the park. These value estimates are comparable to values obtained in these and other studies for preventing fairly significant reductions in visual range caused by haze at parks and recreation areas in the

TABLE 11-2. ECONOMIC VALUATION STUDIES FOR AIR POLLUTION PLUMES

| Study | Location of Plume | Study Subjects | Year of Interviews | Type of Value | Valuation Method | Payment Vehicle | Mean Results (\$ 1989) |
|-------------------------|--|---|--------------------|--|--|-------------------------------|---|
| Schulze et al (1983) | Grand Canyon National Park | Urban residents who have visited or plan to visit Grand Canyon | 1980 | Daily use value at park per household | Contingent valuation, direct WTP ^a question | Daily park entrance fee | \$6 17 per day at park per household |
| | | Urban residents in Denver, Los Angeles, Chicago, Albuquerque, visitors and non-visitors | 1980 | Monthly preservation value per household | Contingent valuation, direct WTP ^a question | Monthly utility bill increase | \$5 31 per month per household |
| MacFarland et al (1983) | Grand Canyon National Park | Park visitors | 1980 | Daily use value at park per visitor-party (household) | Contingent valuation, direct WTP ^a question | Daily park entrance fee | \$2 84 per day at park per visitor-party (household) |
| Brookshire et al (1976) | Glen Canyon National Recreation Area (Lake Powell) | Nearby residents and lake visitors | 1974 | Daily use value at recreation area per visitor-party (household) | Contingent valuation, direct WTP ^a question | Daily entrance fee | Visitors \$3 32 per day additional to prevent visible plume Residents \$2 21 per day additional to prevent visible plume |

^aWTP = Willingness to pay

Southwest A potential problem common to all of these studies is the use of daily entrance fees as a payment vehicle Respondents may have anchored on the then-typical \$2 per day fee and stated an acceptable proportional increase in entrance fees rather than reporting a maximum willingness to pay This may have caused some downward bias in the responses, but empirical exploration of this question is needed An alternative payment vehicle to consider might be total expenditures for the trip to the park

The results of the Schulze et al (1983) study suggest that on-site use values may be easily dwarfed by total preservation values held by the entire population For example, with average annual visitation at the Grand Canyon of about 1.3 million visitor-parties (about three people per party), annual on-site use values for preventing a visible plume every day would be about \$8 million based on the Schulze et al results, whereas the implied preservation value for preventing a visible plume most days (the exact frequency was not specified) at the Grand Canyon would be about \$5.7 billion each year when applied to the total United States population There is, however, considerable uncertainty in the preservation value estimates from this study Chestnut and Rowe (1990b) found that the Schulze et al. (1983) preservation value estimates for haze at national parks in the Southwest are probably overstated by a factor of two or three and the same probably applies to the preservation value estimates for plumes

11.9.3.2 Economic Valuation Studies for Urban Haze

Six economic studies concerning urban haze caused by air pollution are summarized in Table 11-3 Five of these are CVM studies and one is a hedonic property value study Although many other hedonic property value studies concerning air quality have been conducted (see Trijonis et al [1984] and Rowe and Chestnut [1982] for reviews), the study by Trijonis et al (1984) is the only one that has used visibility as the measure of air quality

The magnitudes of the changes in visual range considered in each study vary, making direct comparisons of the results difficult In Table 11-3 implicit values obtained for a 10% change in visual range are reported to allow a comparison of results across the studies Values for a 10% change are shown to illustrate the range of results across the different studies These estimates are based on a model developed for comparison purposes that

TABLE 11-3. ECONOMIC VALUATION STUDIES ON URBAN HAZE

| Study | Location | Year | Valuation Method ^a | Payment Vehicle | Presentation/Definition of Change in Visibility | Implied Mean Annual WTP ^a for a 10% Change in Visual Range (\$ 1989) |
|----------------------------------|---|---------|---|--|--|---|
| PART I UNIFORM URBAN HAZE | | | | | | |
| <u>Western Cities</u> | | | | | | |
| Loehman et al (1981) | San Francisco | 1980 | Contingent valuation, direct WTP question | Monthly utility bill increases | Change in frequency distribution illustrated with local photos for 3 levels of air quality | \$106 per household |
| Brookshire et al (1982) | Los Angeles | 1978 | Contingent valuation, direct WTP question | Monthly utility bill increases | Change in average visibility illustrated with local photos for 3 levels of air quality | \$10 per household |
| Trijonis et al (1984) | San Francisco | 1978-79 | Hedonic property value | | Light extinction based on airport visibility data | \$208-231 per household |
| | Los Angeles | 1978-79 | Hedonic property value | | Light extinction based on airport visibility data | \$112-226 per household |
| <u>Eastern Cities</u> | | | | | | |
| Tolley et al (1986) | Chicago, Atlanta, Boston, Mobile, Washington, D C , Miami, Cincinnati | 1982 | Contingent valuation, direct WTP question | Monthly payment for visibility improvement program | Change in average visibility illustrated with Chicago photos for levels of air quality | \$8-51 per household |

TABLE 11-3 (cont'd). ECONOMIC VALUATION STUDIES ON URBAN HAZE

| Study | Location | Year | Valuation Method ^a | Payment Vehicle | Presentation/Definition of Change in Visibility | Implied Mean Annual WTP ^a for a 10% Change in Visual Range (\$ 1989) |
|--|------------|------|---|--|--|---|
| PART I (cont'd). UNIFORM URBAN HAZE | | | | | | |
| Rae (1984) | Cincinnati | 1982 | Contingent valuation, direct WTP question | Monthly payment for visibility improvement program | Change in average visibility illustrated with Chicago photos for 3 levels of air quality | \$48 per household |
| PART II. URBAN HAZE WITH BORDER | | | | | | |
| Irwin et al (1990) | Denver | 1989 | Contingent valuation, direct WTP question | General higher prices each year | 1-step change in 7-point air quality scale, illustrated with photos | <u>Preliminary</u> results indicate mean annual WTP of about \$100 per household for a 1-step change in the 7-point scale, with about one-third of the value attributed to visibility alone |

^aWTP = Willingness to pay

assumes economic values are proportional to the percentage change in visual range. Values for a 20% change, for example, would be about twice as large as those shown for a 10% change, given the underlying comparison model. Each of these studies relied on a reasonably representative sample of residents in the study area, such that a range of socioeconomic characteristics and of neighborhood pollution levels was included in each sample.

The first five studies in Table 11-3 all focused on changes in urban hazes with fairly uniform features that can be described as changes in visual range. The sixth study (Irwin et al., 1990) focused on visual air quality in Denver, where a distinct edge to the haze is often noticeable, making visual range a less useful descriptive measure because it would vary depending on the viewpoint of the individual and whether the target was in or above the haze layer. The studies conducted in Denver and in the California cities are the most relevant because hazes in these cities are likely to have a higher NO_x component than in the eastern cities, but none of these studies focused specifically on NO_x .

Both of the CVM studies in California asked respondents to consider health and visual effects but used different techniques to have respondents partition the total values. They found that, on average, respondents attributed about one-third to one-half of their total values to aesthetic visual effects. In spite of many similarities in the approaches used, the CVM results for San Francisco are notably higher than for Los Angeles when adjusted to a comparable percentage change in visual range. One potentially important difference in the presentations was that Loehman et al. (1981) defined the change in visibility as a change in a frequency distribution rather than simply a change in average conditions. This type of presentation is more realistic but more complex, and it is unclear how it may affect responses relative to presentation of a change in the average. It is possible that the distribution presentation might elicit higher WTP responses because it may focus respondents' attention on the reduction in the number of relatively bad days (and on the increase in the number of relatively good days), whereas the associated change in the average may not appear as significant. The implied change in average conditions in the Loehman et al. (1981) San Francisco study was considerably smaller than that presented in the Brookshire et al. (1982) Los Angeles study, which may have also resulted in a higher value when adjusted to a

comparable size change in average visual range because of diminishing marginal utility (i.e., the first incremental improvement is expected to be worth more than the second)

The California studies in Los Angeles and San Francisco provide some interesting comparisons because two different estimation techniques were applied for the same locations. Property value results for changes in air quality for both cities were found to be higher than comparable values (for changes in total air quality) obtained in the CVM studies. This is as expected given the theoretical underpinnings of each estimation method, although Graves et al. (1988) have reported that subsequent analysis of the property value data revealed that the estimates are more variable than the original results suggest. These property value results are not reported here because they are for changes in air pollution indices that are not tied to visual air quality.

The property value study results reported in Table 11-3 from Trijonis et al. (1984) were estimated using light extinction as the measure of air quality. However, as discussed in the previous section on the hedonic property value method, these estimates are still likely to include perceived benefits to human health for reductions in air pollution as well as values for visual aesthetics. Consistent with this expectation, the results for a 10% change in light extinction are higher than the CVM results for visual range changes for the same cities. Respondents in several CVM studies have reported that, on average, they would attribute to visibility aesthetics about one-fourth to one-half of their total WTP for improvements in air quality. This would imply that the Trijonis et al. results may reflect \$25 to \$100 for a change in visibility alone.

The results for the uniform urban haze studies in cities in the eastern United States fall between the respective CVM results for the California cities. The changes in visual range presented in these studies were similar to those presented in the Los Angeles study. In all of the eastern studies respondents were simply asked to consider only the visual effects when answering the WTP questions. This approach is now considered to be inadequate (Irwin et al., 1990; Carson et al., 1990).

A recent study that has not as yet completed the peer-review process has applied the approach recommended in recent methodological explorations to estimate values for changes in visibility. McClelland et al. (1991) conducted a mail survey in 1990 in Chicago and Atlanta. Residents were asked what they would be willing to pay to have an improvement in

air quality, which amounted to about a 14% improvement in annual average visual range. Respondents were then asked to say what percentage of their response was attributable to concern about health effects, soiling, visibility, or other air quality impact. Respondents, on average, attributed about 20% of their total WTP to visibility. The authors conducted two analyses and adjustments on the responses. One was to estimate and eliminate the potential selection bias resulting from non-response to the WTP questions (including what has been called protest responses). The other was to account for the potential skewed distribution of errors caused by the skewed distribution of responses (the long tail at the high end). Both of these adjustments caused the mean value to decrease. The annual average household WTP for the designated visibility improvement was \$39 before the adjustments and \$18 after the adjustments. This adjusted mean value implies about \$13 per household for a 10% improvement in visual range. This is at the low end of the range of estimates shown in Table 11-3. If peer-review of this research effort confirms the appropriateness of the study design and analysis, the results suggest that greater confidence should be placed in the lower end of the range of results shown in Table 11-3 because this study represents an improvement in approach over the other eastern-cities studies.

Irwin et al (1990) have reported preliminary results for the Denver study (Part II, Table 11-3). Comparison of these preliminary results with results from other studies is difficult because the photographs used to illustrate different levels of air quality were not tied to visual range levels. Instead, they were rated on a seven-point air quality scale by the respondents, who were then asked their maximum WTP for a one-step improvement in the scale. This study reports some important methodological findings. One of these is confirmation that simply asking respondents to think only about visibility results in higher WTP responses for visibility changes than when respondents are asked to give WTP for the change in air quality and then to say what portion of that total they would attribute to visibility only. The latter approach produced a mean WTP estimate for a one-step change in visibility that was about one-half the size of the mean WTP estimate given when respondents were simply asked to think only about visibility. This may result from the effect of budget constraints on marginal values (the respondent has less to spend on visibility when he also is buying health), however, the authors express the concern that some, but not all, of the value for health may be included in the response when respondents are told to think only about

visibility. They recommend that respondents be asked to give total values for changes in urban air quality and then be asked to say what portion is for visibility

11.9.4 Summary of Economic Valuation

Visibility has value to individual economic agents primarily through its impact upon activities of consumers and producers. Most economic studies of the effects of air pollution on visibility have focused on the aesthetic effects to the individual, which are, at this time, believed to be the most significant economic impacts of visibility degradation caused by air pollution in the United States. It is well established that people notice those changes in visibility conditions that are significant enough to be perceptible to the human observer, and that visibility conditions affect the well-being of individuals.

Welfare economics defines a dollar measure of the change in individual well-being (referred to as utility) that results from the change in the quality of any public good, such as visibility, as the change in income that would cause the same change in well-being as that caused by the change in the quality of the public good. One way of defining this measure of value is to determine the maximum amount the individual would be willing to pay to obtain improvements or prevent degradation in the public good. Two economic valuation techniques have been used to estimate willingness to pay for changes in visibility: (1) the contingent valuation method, and (2) the hedonic property value method. Both methods have important limitations, and uncertainties exist in the available results. Recognizing these uncertainties is important, but the body of evidence as a whole suggests that economic values for changes in visibility conditions are probably substantial in some cases, and that a sense of the likely magnitude of these values can be derived from available results in some instances. Economic studies have estimated values for two types of visibility effects potentially related to NO_x : (1) use and non-use values for preventing the types of plumes caused by power plant emissions, visible from recreation areas in the southwestern United States, and (2) use values of local residents for reducing or preventing increases in urban hazes in several different locations.

Available evidence suggests that visitors to major recreation areas in the southwestern United States value the prevention of manmade plumes visible from the recreation area. The results of two studies suggest values per visitor-party per day in the range of \$3 to \$6 (1989

dollars) in additional park entrance fees to ensure that a thin, dark plume is not visible from a popular observation point at Grand Canyon National Park. A similar study at Lake Powell found somewhat smaller values, in the range of \$2 to \$3 per day. Schulze et al. (1983) found that total preservation values held by visitors and non-visitors for preventing a plume visible from the Grand Canyon may substantially overwhelm on-site use values based on a few dollars per day at the site, however, considerable uncertainty exists in the quantitative results of this study, given the pioneering nature of the effort.

The best economic information available for visibility effects associated with NO_x is for on-site use values related to changes in visual range in urban areas caused by uniform haze. These values fall roughly between \$10 and \$100 per year per local household for a 10% change in visual range in major urban areas in California and throughout the eastern United States. Reasonable extrapolations of on-site use values (with an order-of-magnitude range of uncertainty) could be made from these studies for estimates of changes in visual range that are attributable to changes in NO_x levels in these and other major urban areas, where NO_x contributes to uniform haze that can be characterized by changes in visual range. Available results with regard to visual range in urban areas appear to be sufficient to determine the importance of visibility values (on-site use) related to NO_x -caused uniform haze in urban areas relative to other potential benefits of NO_x controls, and to provide order-of-magnitude estimates of such visibility values. To do so, however, would require estimates of the changes in visual range that might be expected as a result of NO_x controls.

Extrapolations to less urbanized areas or to other visibility changes, or both, would require additional assumptions and might introduce additional uncertainty. Because each of the studies completed to date has some important weaknesses and limitations, it would be desirable to continue to enhance the geographic extent and the technical breadth of issues addressed in these studies to arrive at a broader and more defensible set of estimates.

Very little work has been done regarding layered hazes in recreation or residential settings. Preliminary results from Irwin et al. (1990) suggest annual residential household values of about \$30 for a noticeable improvement in visibility conditions in the Denver area, where layered hazes are common. More information is needed about the specific visual characteristics of such hazes that are most important to viewers, as well as about the value people may place on reducing or preventing them.

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12. EFFECTS OF NITROGEN OXIDES ON MATERIALS

12.1 INTRODUCTION

Materials exposed to the atmosphere in both indoor and outdoor environments may suffer undesirable physical and chemical changes. Although many of these changes occur whether or not pollutants are present, the rate at which these changes occur can be influenced by pollutant concentrations. Nitrogen oxides (NO_x), including nitric oxide (NO), nitrogen dioxide (NO_2), and nitric acid (HNO_3), are known to affect the fading of dyes, the strength of fabrics, plastics, and rubber products, the corrosion of metals, and the use-life of electronic components, paints, and masonry. Although the materials damage potential of sulfur oxides (SO_x) has been extensively studied, much less research has been reported for NO_x . Graedel and McGill (1986) have pointed out, however, that sulfur dioxide (SO_2) concentrations are generally decreasing across the country. Levels of NO_x increased through 1985 but declined from 1985 through 1991 (U.S. Environmental Protection Agency, 1992). The amount of materials damage attributable to NO_x can therefore be expected not to increase. This chapter discusses the impact of NO_x on a number of categories of materials. Emphasis is placed on those experiments and materials in which degradation was observed.

To understand the results of materials exposure to NO_x , it is important to appreciate the influence of several factors on the materials damage process:

- 1 The environment in which materials are exposed,
- 2 The mechanisms that cause damage in different exposures,
- 3 The wet and dry deposition processes that influence damage rates, and
- 4 The chemical interactions of NO_x species with materials and with other components of the environment, for example, other airborne pollutants and moisture

It is also necessary to understand the experimental techniques used to study damage processes and the limitations of these study techniques, as well as the results of the studies. Finally, if

estimates of the costs of materials damage are desired, an understanding of the economic estimation procedures is needed. A useful survey of the topic of air pollution damage to materials is contained in Jorg et al (1985)

12.1.1 Environmental Exposures of Materials

The materials affected by NO_x occur in both indoor and outdoor environments. Outdoor materials will be exposed to NO_x concentrations such as those discussed in Chapter 7 plus stresses caused by a wide range of temperatures and humidities, sunlight, and precipitation. Identical materials exposed in nearby locations may be damaged at very different rates depending on their microenvironments (e.g., building stone sheltered by an overhang will be damaged at a different rate than stone openly exposed on the face of the same structure). Most materials exposed for extended periods to the outdoor environment are selected or designed to withstand these exposures and, therefore, they degrade at a slow rate. Materials that may be subject to NO_x damage and that are widely used outdoors include paints, cement and concrete, stone, architectural and statuary metals, plastics, and elastomers.

Indoor concentrations of NO_x are discussed in Chapter 7. Although indoor environments are free of many of the extreme environmental stresses present outdoors, NO_x concentrations may be significantly higher in some indoor environments (e.g., where unvented gas appliances are in use) and the materials exposed indoors may be more sensitive. Virtually all the materials found outside are also found indoors to some extent, however, additional materials such as paper, fine textiles, and electronic components are more common in indoor than outdoor environments. In addition, paint formulations intended for indoor applications are different from those formulations intended for outdoor use.

12.1.2 Mechanisms of Materials Damage

Damage to exposed materials results from attack through both physical and chemical processes, and damage is induced both by pollution and by other agents. Physical processes include erosion by windborne particles, differential heating, and frost attack. Chemical processes include corrosion, biological attack (e.g., mildew), direct attack by acid mists, and gaseous and particle deposition and subsequent reactions (Tombach, 1982, Yocom and Baer,

1983) It is difficult to distinguish a single causative agent for observed damage to exposed materials because many agents, together with a number of environmental stresses, act on a surface throughout its life. Even some extensively studied systems (such as the effect of SO₂ pollution on metals) are not thoroughly understood, and there is work still needed to understand the interaction of NO_x with the variety of materials in use today.

12.1.3 Deposition Processes

For them to cause damage to a material, atmospheric pollutants such as NO_x must come in contact with the material. Oxides of nitrogen are deposited on material surfaces through both wet and dry deposition processes (Tombach, 1982). Dry deposition processes for gaseous NO_x include Brownian or molecular diffusion to the surface, Stefan flow toward surfaces where moisture is condensing, thermophoresis toward cold surfaces, and diffusiphoresis toward evaporating surfaces. In addition, particles containing NO_x can be transported to a material surface through gravitational settling or inertial impaction of the particles on the surface. Wet deposition (e.g., acid rain) processes include the scavenging of gaseous NO_x or particles containing absorbed NO_x into precipitation or fog droplets that impact the surface. The rate at which deposition processes transport NO_x to the surface is dependent on the NO_x concentrations in the environment, the chemistry and geometry of the surface, the concentrations of other atmospheric constituents, and the turbulent transfer properties of the air (Lipfert, 1989).

The transfer of pollutants from the atmosphere to a surface is often visualized in terms of the "multiple resistance analogy" (Sherwood et al., 1990). In this analogy, the rate of mass transfer of pollutants is modeled as a series of resistances to the mass transfer

$$R_T = R_a + R_b + R_c \quad (12-1)$$

The total resistance, R_T , is made up of the sum of "free air" turbulent transfer resistance, R_a , the near-surface, quasi-laminar boundary layer resistance, R_b , and the surface uptake resistance, R_c . The aerodynamic resistance, R_a , is dominated by atmospheric turbulence. The boundary layer resistance, R_b , depends on the aerodynamics of flow immediately adjacent to the surface and the molecular diffusivity of the pollutant. The

surface resistance, R_c , depends on the physical and chemical interactions of the surface and the pollutant. Depending on the aerodynamic conditions, and the physical and chemical state of the surface, any of these terms can be the rate-limiting step for the transfer.

The inverse of the total resistance is the deposition velocity, V_d (in units of cm/s). The deposition velocity is the ratio of flux of mass to the surface ($\text{g}/\text{cm}^2 \text{ s}$) to the free air concentration of the pollutant (g/cm^3).

In a laboratory study, Edney et al. (1986) measured the deposition of NO_2 and various other compounds to both wet and dry galvanized steel. A large "smog chamber" (an environmental chamber designed to simulate photochemical processes) was used for the study; NO_2 , propylene (C_3H_6), and SO_2 were introduced in various combinations to study deposition processes. Galvanized steel was exposed both dry and wet with artificial dew cycles caused by cooling the samples. An experiment with a dry surface and NO_2 alone yielded a deposition velocity for NO_2 -to-galvanized steel of 0.05 cm/s . A similar test with SO_2 yielded an SO_2 -to-galvanized steel deposition velocity of 0.8 cm/s , or deposition about 16 times greater for SO_2 than for NO_2 . Dry deposition of NO_2 on galvanized steel is thus significantly slower than the dry deposition of SO_2 . These researchers suggest that, for the purposes of developing a damage function representative of typical polluted atmospheres, NO_2 dry deposition on galvanized steel can be ignored.

In a test with an NO_2 and C_3H_6 mixture, Edney et al. (1986) simulated smog conditions that might be similar to Southern California conditions (i.e., smog with very low SO_2 concentrations). This experiment was allowed to proceed in the smog chamber for 336 h (2 weeks) with a total time of induced dew of 196 h in 7-h periods. At the end of the experiment, concentrations in the gas phase and in dew on the surface of the galvanized steel were measured. Results are shown in Table 12-1. Fairly small amounts of nitrite ions (NO_2^-) and nitrate ions (NO_3^-) were found on the surface and relatively little zinc was freed (corroded). Clearly, however, the NO_2 and other reactants had reacted to form a number of species.

A test with NO_2 , C_3H_6 , and SO_2 was also run for comparison. After 25 h, with a total time of wetness of 14 h for the galvanized steel, the gas and surface-dew concentrations shown in Table 12-2 were measured. The gaseous species concentrations were similar to those found in the previous test, except for SO_2 . Again, little nitrate or nitrite was found in

**TABLE 12-1. SMOG CHAMBER REACTIONS OF NITROGEN DIOXIDE
AND PROPYLENE AND DEPOSITION OF REACTION PRODUCTS
ON GALVANIZED STEEL**

| Chemical Species | Gas-Phase Concentration (ppb) | Surface-Dew Concentration (nmol/cm ²) |
|------------------------------|-------------------------------------|---|
| O ₃ | 134 | --- |
| CH ₃ CHO | 254 | --- |
| HCHO | 621 | 133 |
| PAN | 57 | --- |
| NO _x -PAN | 359 | --- |
| HNO ₃ | 7 | --- |
| NO ₂ ⁻ | --- | 11 |
| NO ₃ ⁻ | --- | 77 |
| SO ₄ ⁼ | --- | 1 |
| Zn | --- | 77 |

Source Edney et al (1986)

**TABLE 12-2. SMOG CHAMBER REACTIONS OF NITROGEN DIOXIDE,
PROPYLENE, AND SULFUR DIOXIDE AND DEPOSITION OF
REACTION PRODUCTS ON GALVANIZED STEEL**

| Chemical Species | Gas-Phase Concentration (ppb) | Surface-Dew Concentration (nmol/cm ²) |
|------------------------------|-------------------------------------|---|
| O ₃ | 240 | --- |
| HCHO | 1,150 | 560 |
| PAN | 114 | --- |
| NO _x -PAN | 159 | --- |
| HNO ₃ | 9 | --- |
| SO ₂ | 1,190 | --- |
| NO ₂ ⁻ | --- | 4 |
| SO ₃ ⁼ | --- | 595 |
| NO ₃ ⁻ | --- | 19 |
| SO ₄ ⁼ | --- | 91 |
| Zn | --- | 441 |

Source Edney et al (1986)

the dew on the surface of the galvanized steel, especially when compared to the SO_x deposition. Furthermore, far more zinc was found in solution (i.e., corroded) when SO_2 was added to the NO_2 - C_3H_6 mixture

The above laboratory studies illustrate both the complex nature of the NO_x chemistry and the relatively low deposition rate of NO_x on galvanized steel. In a subsequent field experiment, Edney et al. (1987) measured the ion concentrations for dry deposition and in rainwater runoff from galvanized steel samples exposed outdoors in Research Triangle Park, NC. The dry deposition ratio of sulfate ions ($\text{SO}_4^{=}$) to NO_3^- was 3.4, again illustrating the relatively low deposition velocity of NO_x compared to SO_x for galvanized steel, this time under outdoor exposure conditions. This ratio might change as ambient concentrations of SO_x and NO_x change. These researchers speculated that the NO_3^- resulted from dry deposition of HNO_3 and particulate nitrate. The ratio of dry to total nitrate deposition was 0.46, suggesting that wet and dry deposition appeared to play about equal roles in nitrate deposition. Regression analysis of the ion concentration showed that the NO_3^- did not significantly relate to the zinc in solution concentrations, however, $\text{SO}_4^{=}$ concentrations were in a one-to-one relationship with dissolved zinc. Edney et al. (1987) concluded that NO_x is not effectively deposited on galvanized steel surfaces and that sulfates dominate galvanized steel corrosion.

Although NO_x deposition to galvanized steel may be insignificant, Spicer et al. (1987) found that there is a significant range of removal rates of NO_2 by common indoor materials. Samples of 35 materials (surface area 3.3 m^2) were exposed in chambers to $282 \mu\text{g}/\text{m}^3$ (0.15 ppm) NO_2 (initial condition) at 50% relative humidity (RH) for 12 h and the rate of NO_2 removal was measured. The results of these experiments are shown in Figure 12-1. Galvanized metal ducts were near the low end of removal rates measured in the Spicer et al. (1987) experiments. Many common indoor materials (wallboard, wool carpet) were found to have very high removal rates. Nitric oxide gaseous concentrations were also monitored during these experiments and were often found to increase as NO_2 levels decreased. The author suggested that judicious selection of indoor materials might be considered as a means of indoor NO_2 control. However, it was not possible from these experiments to determine the amount of NO_x accumulating on the surfaces of these materials, nor could conclusions be drawn on any damage to indoor materials that might result from exposure to NO_2 .

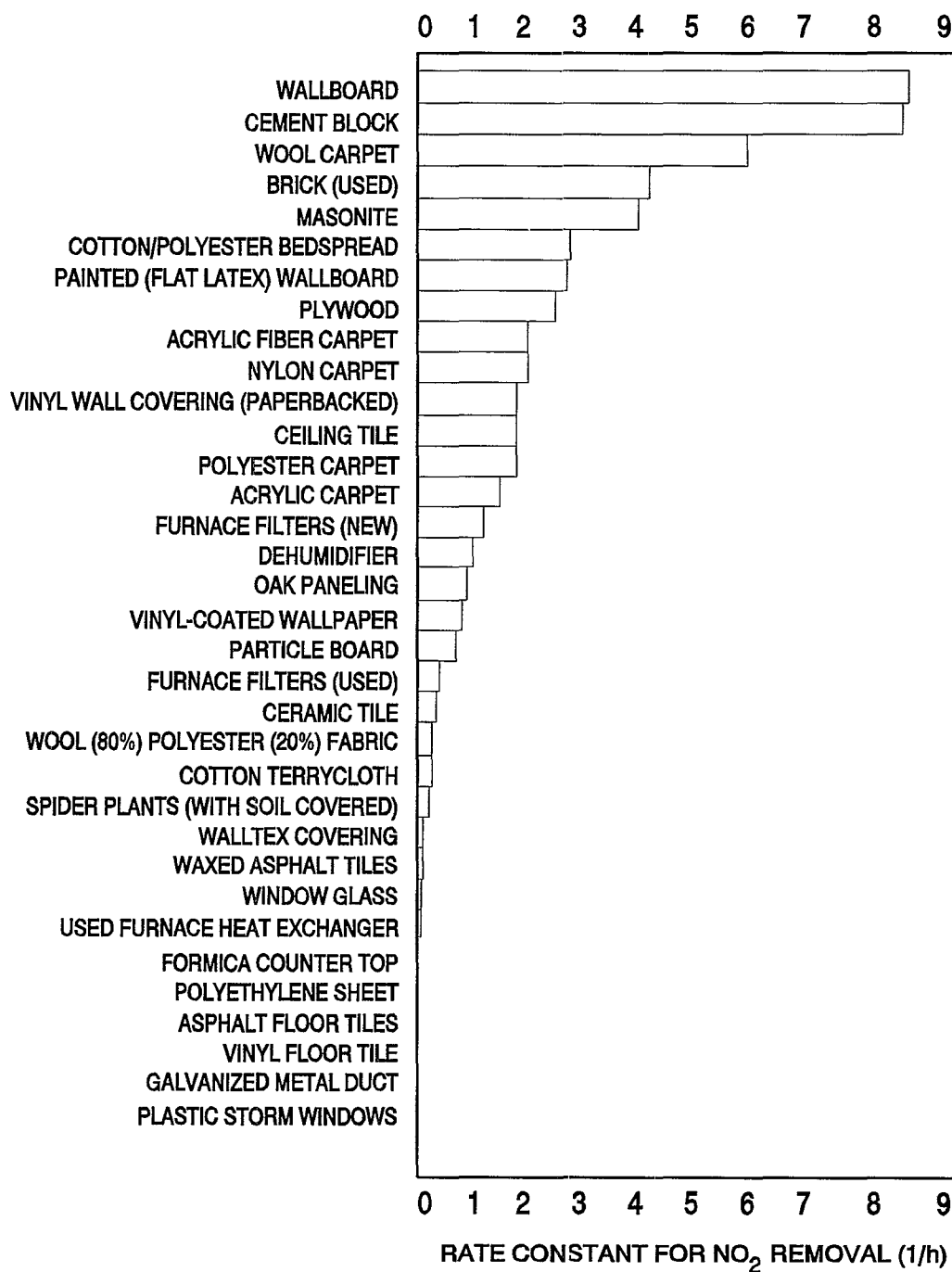


Figure 12-1. Bar graph of nitrogen dioxide removal rate for various materials evaluated in a 1.64-m³ test chamber at 50% relative humidity.

Source Spicer et al (1987)

Miyazaki (1984) conducted a similar experiment, exposing common interior materials in a chamber to initial concentrations of $1,645 \text{ mg/m}^3$ (875 ppm) NO_2 and $1,124 \text{ mg/m}^3$ (914 ppm) NO . A summary of these results is shown in Table 12-3. The trend in these data is similar to that reported by Spicer et al (1987), with wool carpeting and cement showing relatively high deposition velocities for NO_2 . Vinyl floor tile, glass, and metals showed relatively low deposition velocities for NO_2 . Insulation board and an ester/acrylic carpet, materials not tested by Spicer et al (1987), had the highest deposition velocities. Miyazaki (1984) also found that NO_2 deposition rates increased if turbulence, humidity, and temperature were each increased in the chamber. Increased turbulence escalates the rate of delivery of NO_2 to the surface. Increased humidity probably results in dissolution of NO_2 . Increased temperature causes faster reaction rates.

The deposition rates reported by Miyazaki appear to be low compared to the rates reported by Edney et al (1986). The reason for the discrepancy is not apparent, however, the differences may have been caused by different levels of turbulence in the two experimental chambers. Caution should be used in applying data from Miyazaki (1984) for more than comparative purposes.

12.1.4 Chemical Interactions of Nitrogen Oxides Species

Not only is there wide variation in the deposition of NO_x to different surfaces but NO_x species themselves are reactive and their interactions with other atmospheric constituents are complex. Bassett and Seinfeld (1983) proposed a chemical equilibrium model for the behavior of NO_x , SO_x , ammonia (NH_3), and water in the atmosphere that is instructive for understanding the role of NO_x in materials damage. Nitrogen species (NO , NO_2 , HNO_3 , etc.) are present as gases and in particulates (liquid and solid) and are deposited on material surfaces. Nitric acid is potentially the NO_x species most directly damaging to materials and is formed by photochemically initiated reactions involving NO_x in the atmosphere. Under dry conditions, HNO_3 can deposit on a surface and can cause direct damage. If liquid water is present, HNO_3 exists in equilibrium between the liquid phase in water solution and the gaseous phase in the atmosphere. However, Bassett and Seinfeld (1983) showed that in the presence of atmospheric NH_3 and sulfuric acid (H_2SO_4), the HNO_3 gas-phase versus liquid-phase equilibrium is shifted toward the gas phase. Thus, as nitrates accumulate on the

**TABLE 12-3. DEPOSITION VELOCITIES OF NITROGEN DIOXIDE AND
NITRIC OXIDE FOR INTERIOR MATERIALS**

| Interior Material | Deposition Velocity (cm/s) ^a | |
|---|--|--------|
| | NO ₂ | NO |
| Flooring materials | | |
| Carpet 1 (Acrylic fiber) | 0 03 | 0 0003 |
| Carpet 2 (Acrylic fiber) | 0 02 | --- |
| Carpet 3 (Acrylic fiber) | 0 02 | --- |
| Carpet 4 (Wool) | 0 06 | --- |
| Carpet 5 (30% Ester, 70% Acrylic fiber) | 0 10 | --- |
| Tatami facing | 0 01 | 0 003 |
| Needle punch | 0 01 | 0 0008 |
| Bath mat (100% Cotton) | 0 05 | --- |
| Floor sheet 1 (Vinyl chloride) | 0 001 | 0 00 |
| Floor sheet 2 (Vinyl chloride) | 0 003 | --- |
| Floor sheet 3 (Vinyl chloride) | 0 003 | --- |
| Plastic tile | 0 003 | --- |
| Ceramic tile | 0 004 | --- |
| Wall materials | | |
| Wallpaper 1 | 0 002 | 0 00 |
| Wallpaper 2 | 0 002 | --- |
| Printed plywood | 0 001 | --- |
| Ceiling materials | | |
| Insulation board | 0 11 | 0 00 |
| Painted insulation board | 0 06 | 0 001 |
| Plaster board | 0 02 | 0 003 |
| Wooden cement board | 0 03 | 0 003 |
| Asbestos cement board | 0 04 | --- |
| Fittings | | |
| Glass | 0 00 | 0 0008 |
| Painted stainless steel | 0 0008 | 0 001 |
| Painted wood | 0 003 | 0 0003 |
| Curtain | 0 0008 | 0 0003 |
| Fusuma paper | 0 003 | 0 002 |
| Shoji paper | 0 0003 | 0 0003 |

^aThese values were averaged from the results of the experiments at 20 to 26 °C, 40 to 60% relative humidity

Source Modified from Miyazaki (1984)

surface of a material, much of the accumulated nitrate mass may be evaporated into the atmosphere as HNO_3 . Baedecker et al (1990) believe that this mechanism explains why most *post facto* microanalytical investigations of damaged surfaces reveal very small amounts of nitrogen species, whereas sulfates are frequently present. It is also possible that, because of their soluble nature, nitrate compounds have been washed off the damaged surfaces prior to analysis. Wolff et al (1990) reported the results of a field study during which pollutant fluxes were analyzed. They found that $\text{SO}_4^{=}$ accounted for 79%, on average, of the total acidity of the wet deposition, whereas NO_3^- was responsible for 21% of the acidity. The findings of Wolff et al (1990) indicate that, in polluted atmospheres containing SO_2 and condensing moisture, it is possible that NO_x currently plays a relatively small role compared to SO_2 in causing the observed damage to most materials.

12.1.5 Materials Damage Experimental Techniques

Because of the number of possible damaging agents and the complexity of synergistic interactions, deposition processes, and exposure scenarios, researchers have typically relied on controlled environmental chambers to quantify the damage rates attributable to specific agents such as NO_x . Often materials exposure chamber studies are conducted at high concentrations or at elevated temperatures and humidities in order to see damage within a reasonable exposure period. In addition, some chamber studies are conducted at low flow rates that poorly simulate mass transfer properties in the natural environment and lead, therefore, to underestimation of real-world deposition rates. Also, the sequence in which materials are exposed to different pollutants can affect the formation of protective corrosion films, and this process is sometimes poorly simulated in chambers. Although such studies are useful, care should be exercised in the extrapolation of data and conclusions based on chamber studies to effects expected from ambient exposures.

The alternative to chamber studies has been ambient exposure studies. In these exposure studies, the materials of interest are usually exposed to ambient conditions at several locations representing a spectrum of environmental variables (e.g., temperature, sunshine, humidity, pollutant concentrations). Statistical and chemical analyses are then used to assess the contribution of the measured environmental variables to the materials damage. Again, the number of possible agents and the complexity of synergistic interactions makes it

difficult to apportion observed damage among all the possible causes. Franey and Graedel (1985) reviewed the pollutant species that induce damage under actual ambient exposure conditions, and have suggested that for any chamber study to be realistic, moisture, radiation, carbon dioxide, reduced sulfur, a chlorine-containing gas, and a nitrogen-containing gas must be included. Because of the difficulties involved in apportioning the causes of materials damage, reliable appraisals of the damage induced by NO_x exposure alone are not yet available.

Both chamber studies and ambient exposure studies have come to rely on sophisticated surface chemistry analytical techniques, as well as traditional bulk chemistry analyses and measurements of physical properties. Additionally, moisture collected from the samples (runoff) has been analyzed for its chemical constituents. The objective of these efforts is to understand the chemical reactions occurring on the sample surfaces.

Generally, little evidence of NO_x species has been found in these analyses. As noted in the previous section, much of the NO_x will be converted into HNO_3 and subsequently will be evaporated back into the atmosphere. Thus, if HNO_3 is leading to damage, it may not be adequately accounted for in either surface chemical or runoff chemical analyses, and its role in the damage process could be underestimated. Better experimental techniques are needed, both for investigating materials damage on the whole and for determining the role played by NO_x .

12.2 EFFECTS OF NITROGEN OXIDES ON DYES AND TEXTILES

12.2.1 Fading of Dyes by Nitrogen Oxides

Textile and dye manufacturers have recognized the problem of dye fading induced by NO_x for some time. Rowe and Chamberlain (1937) reported that dyes fade because of the presence of NO_x in combustion effluents. Carpets, upholstery, and drapes that have been subjected to elevated NO_x levels in buildings using unvented gas heat have been observed to fade within a year when dyes not resistant to NO_x fading have been used. Fading is exacerbated when susceptible fabrics are dried in gas-fired clothes dryers, in which the concentrations of NO_2 can reach $3,760 \mu\text{g}/\text{m}^3$ (2.0 ppm) (McLendon and Richardson, 1965). Moreover, dryer exhaust is sometimes vented to the indoor environment to conserve heat and

humidity, thus increasing indoor concentrations of NO_x . Textile and dye manufacturers have responded to NO_x -induced deterioration by seeking out and using NO_x -resistant dyes or inhibitors that forestall fading. Fading from NO_x has been observed on acetate, cotton, nylon, rayon, silk, wool, and polyester.

Nitrogen oxide-induced ("gas-fume") fading received serious attention when blue disperse dyes were found to deteriorate significantly on cellulose acetate. Salvin and coworkers (1952) pointed out that NO_2 is soluble in cellulose acetate, and that during laboratory tests significant fading of dyes on the material can be observed within an hour. Hemphill et al. (1976) tested a spectrum of dyes on various fabrics and found that NO_2 caused significant fading on the cellulose acetate samples. Salvin and Walker (1959) and Salvin (1964) showed that alternative dyeing processes are available to minimize the impact of NO_x -induced fading on cellulose acetate, but that in many cases these substitute processes and dyes are more expensive to use than the processes and dyes they replaced.

Belom (1973) exposed a variety of fabrics and dyes to $120 \mu\text{g}/\text{m}^3$ (0.1 ppm) and $1,230 \mu\text{g}/\text{m}^3$ (1 ppm) of NO , and $90 \mu\text{g}/\text{m}^3$ (0.05 ppm) and $940 \mu\text{g}/\text{m}^3$ (0.5 ppm) of NO_2 for 12 weeks in an environmental exposure chamber. He found that "appreciable" to "very much" (the most severe category) fading occurred at both concentrations of NO for cottons with direct, reactive, and vat blue dyes, cellulose acetate with disperse blue dyes, and nylon with a blue dye. The cellulose acetate samples exposed to NO_2 had generally greater amounts of color change than the samples exposed to NO . In addition, NO_2 affected cotton with direct and reactive red dyes, cotton with reactive blue dye, and rayon with direct red dye. Belom (1972) conducted tests on 67 dye-fabric combinations at 11 urban and rural sites nationwide for 3-month exposures. The tests were conducted outdoors using chambers designed to let the ambient air circulate around the samples but to exclude sunlight. Using multiple regression analysis, he sought to determine which pollutants played a significant role in the observed change of colors on the fabrics. He found that SO_2 concentrations were significant for 23 fabrics, ozone (O_3) was significant for 8 fabrics, and NO_2 was significant for 7 fabrics. Fabric-dye combinations affected by NO_2 included cellulose acetate with red and blue disperse dyes, cotton muslin with reactive red and blue dyes, wool flannel with acid blue dye, and the NO_x gas-fading control ribbon recommended by the American Association of Textile Chemists and Colorists (AATCC) for testing NO_x fading.

Cotton is the most widely used natural textile fiber and, again, significant gas-fume fading has been noted. Haynie et al (1976) exposed plum-colored cotton drapery fabric to NO_2 in a chamber for 1,000 h and found that serious fading occurred. Based on extrapolation, they predicted that the use-life of draperies exposed to $100 \mu\text{g}/\text{m}^3$ (0.053 ppm) NO_2 would decrease 19%. In Beloin's chamber study described above, dyes on cotton were found to experience "noticeable" to "much" fading when exposed to NO and "noticeable" to "very much" fading when exposed to NO_2 . McLendon and Richardson (1965) found that blue-dyed cotton fabric became green after repeated NO_x exposures in gas-fired dryers and that the NO_x exposure caused white fabric to "yellow". Salvin (1969) reported the results of sheltered, outdoor exposures of dyed cottons for 90 days in Los Angeles. Thirty-one colors of direct, vat, reactive, and sulfur dyes were tested and fifteen faded substantially. The author concluded that NO_x and O_3 were primarily responsible. Hemphill et al (1976) also demonstrated NO_x -induced fading of vat, direct, and reactive dyes on cotton at concentrations of $940 \mu\text{g}/\text{m}^3$ (0.5 ppm) in a chamber for a 5-h exposure.

Imperial Chemical Industries Limited (1973), a supplier of dyes for synthetics, issued a technical bulletin on the gas-fume fastness of dyes used for nylon (polyamide). Nylons have high resistance to wear and thus are often used as carpeting. In this application, nylons are exposed to indoor atmospheres for long periods. Imperial Chemical Industry's bulletin showed that several of the commercially available dyes faded noticeably on nylon when exposed to NO_x fumes and advised that these dyes not be used. The susceptible dyes fade, become duller in appearance, or acquire a redder or yellower cast. Hemphill et al (1976) demonstrated that certain blue and red dyes on nylon fade substantially when exposed to $940 \mu\text{g}/\text{m}^3$ (0.5 ppm) NO_2 . Beloin's (1973) chamber study found that "appreciable" to "very much" fading occurred on nylon fabrics exposed to NO or NO_2 . In outdoor exposures in Los Angeles, Salvin (1964) found that nylon faded only slightly to very slightly.

Other fabrics have been tested for dye gas-fading resistance as well. Hemphill et al (1976) investigated dye fading of rayon. They found that two of the dyes tested, Direct Blue 86 and Direct Red 79, showed "noticeable" to "significant" fading. Beloin (1973) found that rayon withstood NO exposure with only a trace of fading, but exhibited "very much" fading when exposed to NO_2 . In checking orlon, Hemphill et al (1976) found minimal dye fading. Salvin (1964) found that wool did not fade significantly in Los Angeles ambient exposures,

but Hemphill et al (1976) showed moderate fading of red dye on wool in chamber exposures Polyester exhibited very good dye-fading resistance in Salvin's Los Angeles study (1964).

Whitmore and Cass (1989) report the results of a chamber study in which various art materials were evaluated for color change due to NO₂ exposure in the absence of light The air in the exposure chamber was stirred and maintained at 24 °C and 50% RH for the 12-week exposure periods The NO₂ concentration was 940 µg/m³ (0.5 ppm) and the NO concentration was 48 µg/m³ (0.04 ppm) They tested 23 different natural dyes traditionally used in Japan on silk and found that, in most cases, the changes were small The largest color change occurred for enju (a dye made from the Japanese pagoda tree) Whitmore and Cass rated the change as noticeable

The AATCC encourages textile manufacturers and suppliers to test dye and fabric combinations for NO_x fading These tests are routinely performed and NO_x-susceptible dye and fabric combinations rarely are produced in large quantities for the open market (Tew, 1990).

12.2.2 Degradation of Textile Fibers by Nitrogen Oxides

Nitrogen oxides not only affect fabric color, but can also alter the physical characteristics of the fibers themselves, especially synthetic fibers Jellinek (1970) and Jellinek et al. (1969) reported significant chain-scissioning of nylon after NO₂ exposure Chain-scissioning is the breaking of the molecular structure that makes up a polymer and it results in a loss of strength Vijayakumar et al (1989) found statistically significant amounts of damage to nylon textiles exposed for 28 days to 0.1 ppm and 0.5 ppm concentrations of HNO₃ Zeronian et al (1971) investigated the impact of NO₂ on acrylic, modacrylic, nylon, and polyester yarn The yarns were continuously exposed in chambers for 1 week to simulated sunlight and 3,760 µg/m³ (2.0 ppm) NO₂ The yarn strength and rupture energies were reduced for all materials The most seriously affected was nylon yarn, which lost approximately 30% of its strength and 33% of its rupture energy as compared to control samples exposed without NO₂ The least affected was polyester, with about a 13% decrease in strength The loss of strength of the acrylics was intermediate between the other two yarns.

12.3 EFFECTS OF NITROGEN OXIDES ON PLASTICS AND ELASTOMERS

Plastics are highly polymerized materials, mostly synthetics, combined with other constituents such as hardeners, fillers, and reinforcing agents (Hawley, 1981). Plastics include fluorocarbon resins, phenolics, polyimides, polyethylene, acrylic polymers, polystyrene, polyurethane, and numerous other synthetic compounds. Major uses of plastics include automobile bodies and components, boat hulls, building and construction materials (pipe, siding, flooring), packaging (bottles, vapor barriers, drum linings), textiles (carpets, cordage, hosiery), organic coatings such as paint and varnish vehicles, adhesives, electrical components, and numerous other applications. Use of plastics in the United States in 1980 was estimated at approximately 60 billion pounds per year, or double the 1970 consumption. Further development of and greater reliance on plastics are expected to increase the demand for them in the future.

Elastomers are synthetic polymers with the ability to stretch to at least twice their normal length and retract rapidly to near their normal length when released. Examples of elastomers include butyl, nitrile, and polysulfide rubber, and neoprene. Elastomers are used for vibration dampers, wire coatings, fabrics, automobile tires, bumpers, and windshield wipers, and other applications.

Plastics and elastomers are subject to deterioration on exposure to ultraviolet (UV) radiation, O_3 , SO_2 , and NO_x . Jellinek et al (1969) and Jellinek (1970) reported a series of experiments in which a variety of polymers and elastomers were exposed to UV radiation and pollutants in chamber experiments. Jellinek et al (1969) reported the following results for high concentration (nearly pure) NO_2 exposures:

- 1 Polyethylene minimal effect except for an increase in viscosity
- 2 Polypropylene some cross-linking (forming of additional chemical bonds) of the polymer, although not as much as when exposed to SO_2
- 3 Polystyrene some chain-scissioning (breaking of chemical bonds)
- 4 Polymethyl methacrylate some chain-scissioning (breaking of chemical bonds)
- 5 Polyvinyl chloride loss of chlorine due to reaction with NO_2

6. Polyacrylonitrile no significant change
7. Nylon chain-scissioning occurs
8. Butyl rubber chain-scissioning
9. Polyisoprene appreciable chain-scissioning
10. Polybutadiene. cross-linking occurs

They concluded that damage to elastomers was generally greater than damage to plastics, but that O_3 -induced damage was probably more important than NO_2 -induced degradation

Jellinek (1970) reported findings for the same series of plastics and elastomers at NO_2 concentrations of $1,880 \mu g/m^3$ and $9,400 \mu g/m^3$ (1 and 5 ppm) for 1 h exposures. At these levels polymethyl methacrylate, nylon, and butyl rubber were found to suffer chain-scissioning. Polyethylene, polypropylene, polyisoprene, and polybutadiene exhibited cross-linking.

Krause et al. (1989) exposed polyvinyl chloride, polyurethane, glass-fiber-reinforced polyester, and alkyd resin for 5 years in glass chambers to either $5,000 \mu g/m^3$ NO_2 , $5,000 \mu g/m^3$ SO_2 , $2,500 \mu g/m^3$ O_3 , or a mixture of the pollutants. The exposure cells were kept at a humidity of 50 to 60%. Half of each chamber was exposed to sunlight through UV-transmitting glass. The other half was kept dark. The investigators found that most of the degradation was caused by sunlight, with significantly less degradation occurring from dark exposures to pollutants.

Haynie et al. (1976) exposed tire rubber and vinyl house siding to NO_2 , SO_2 , O_3 , radiation, and humidity in a chamber. Two NO_2 concentrations, 94 and $940 \mu g/m^3$ (0.05 and 0.5 ppm), were used with exposure times of 250, 500, and 1,000 h. Various combinations of other pollutants, radiation, and humidity were used in the exposures. The primary cause of damage to rubber was O_3 exposure, and NO_2 actually seemed to inhibit the rate of O_3 -induced damage. No appreciable damage to vinyl siding was observed. The National Research Council (1977) notes that discoloration and deterioration of strength of foam rubber occurs from NO_2 exposure.

12.4 EFFECTS OF NITROGEN OXIDES ON METALS

12.4.1 Role of Nitrogen Oxides in the Corrosion Process

Atmospheric corrosion of metals is a serious problem and air pollution is known to accelerate corrosion processes. Sulfur oxides and chlorides are the atmospheric contaminants most frequently implicated in the corrosion of metals. Nitrogen oxides are also involved but have received less attention. Moisture enables these contaminants to form aggressive acids that attack the metal surface and promote electrochemical reactions. For this reason, both pollutant concentrations and the "time of wetness" (i.e., how long liquid water is present on the surface of the material) for exposed surfaces are important in determining the amount of damage that will occur.

For most metals, NO_x alone as an attacking agent is much less aggressive than sulfur or chlorine compounds. Svedung et al. (1983), Kucera (1986), and Johansson (1986), however, have pointed out the synergistic impact of NO_x on atmospheric corrosion mechanisms. Using an exposure chamber, Kucera (1986) showed that carbon steel corrodes rapidly when exposed to $3,421 \mu\text{g}/\text{m}^3$ SO_2 and 90% RH, but very slowly when exposed to SO_2 at the same concentration and 50% RH. At 50% RH, steel corrodes about three times more quickly when exposed to NO_2 ($5,640 \mu\text{g}/\text{m}^3$). However, when both NO_2 and SO_2 at the same concentrations are present at 50% RH, the corrosion rate is approximately 30 times the rate seen with SO_2 alone. Kucera noted that the presence of NO_2 increases the rate of deposition of SO_2 on the metal surface. Johansson (1986), also using an exposure chamber, showed that NO_2 deposition leads to the formation of hygroscopic nitrate-containing corrosion products on the surface of the metal. These corrosion products, in turn, absorb moisture onto the surface, making the moisture available to mobilize other ions (such as sulfates and chlorides) and thus leading to active corrosion at much lower relative humidities than if NO_2 were not present. Effectively, NO_2 acts to increase the time of wetness for the surfaces. Svedung et al. (1983) showed similar results for gold-coated brass (a common electrical contact), with NO_2 -containing atmospheres accelerating degradation at all humidity levels between 40 and 80%.

In the outdoor environment, the deposition of NO_2 is limited, for most materials, by the surface uptake resistance, and NO_2 is more slowly adsorbed than SO_2 . In the experiments conducted by Svedung et al. (1983), Kucera (1986), and Johansson (1986), low flow rates

were used in the exposure chambers. During low-flow conditions, the deposition rate becomes limited by the surface boundary layer resistance and the effective deposition rates of NO_2 and SO_2 will become more nearly equal. Thus, the conclusion from chamber studies that NO_x is synergistic with SO_2 may not be applicable in outdoor environments. In indoor exposures of materials, however, the conclusions of Svedung et al., Kucera, and Johansson are applicable.

12.4.2 Effects of Nitrogen Oxides on Economically Important Metals

Steel

Steel is the most widely used structural metal and is available in a wide variety of types with varying percentages of alloying elements. Basically, steel consists of iron containing 0.02 to 1.5% carbon. The corrosion behavior of common construction steels (carbon steels, containing about 0.2% carbon) is similar, and rusting of exposed surfaces proceeds rapidly. Low-alloy steels, containing chromium, nickel, copper, molybdenum, phosphorus, and vanadium in the range of a few percent or less for the total inclusion, are substantially stronger and offer improved resistance to atmospheric corrosion. Specialty steels, such as stainless steels containing over 10% chromium, are designed to be highly corrosion-resistant, but are also much more costly. Bare steel is not usually exposed to the environment, but rather is painted to prevent rust and premature failure. Nevertheless, except where specifically noted, the following discussion concerns common construction steel that is boldly exposed with no coatings.

Samples of enameled steel were exposed at 57 of the National Air Surveillance Network locations (Haynie and Upham, 1974), for 1- and 2-year exposure cycles. Sulfur dioxide and particulate matter concentrations, relative humidity, and particulate chemistry were monitored at the sites. Corrosion rates for the steel samples, determined from weight loss measurements, were correlated against the pollution measurements. Haynie and Upham (1974) concluded that either SO_2 or particulate sulfate, or both, were significant in causing steel corrosion. Particulate nitrate (PN) was not statistically significantly related to the observed corrosion, however, their measurement techniques for PN were unreliable. Measurements of gaseous NO_x species were not made.

Johansson (1986) showed in a low-flow chamber study that gaseous NO_2 adsorbs on steel surfaces and reacts with water to form HNO_3 and HONO . Construction steel was exposed continuously for 6 weeks to $376 \mu\text{g}/\text{m}^3$ or $5,640 \mu\text{g}/\text{m}^3$ (0.2 or 3.0 ppm) NO_2 and different levels of moisture and SO_2 . He determined that the deposition rate of NO_2 was much lower than the deposition rate for SO_2 and that steel exposed to NO_2 alone, in the absence of other pollutants, will slowly acquire a thin oxide layer (rust) that protects the underlying steel from further damage. Unfortunately, the nitrates formed during the corrosion process are hygroscopic and act to adsorb further moisture from the atmosphere at around 50% RH and above. If it is also present, SO_2 , which does not form hygroscopic corrosion products but does have a higher deposition rate than NO_2 (Johansson, 1986), reacts with this moisture to form strong acids that corrode the surface very rapidly. In addition to its hygroscopic effect, Johansson suggested that NO_2 might increase the oxidation rate of SO_2 to $\text{SO}_4^{=}$, and thus enhance corrosion. At relative humidities in excess of 90%, the synergistic effect of NO_2 is lost because at these high humidity levels moisture forms on the surface whether or not NO_2 is present. In fact, Henriksen and Rode (1986) have suggested that NO_2 may actually inhibit SO_2 -induced steel corrosion at 95% RH.

Haynie (1986) analyzed data from 30-mo exposures of weathering steels at nine sites around St. Louis, MO, as part of the U.S. Environmental Protection Agency's Regional Air Pollution Study. Weathering steels are architectural steels specifically formulated to rapidly develop a surface corrosion layer that protects the underlying substrate steel. The exposure samples were co-located with air quality monitoring stations. Haynie (1986) statistically analyzed the observed corrosion in relation to meteorological and air quality variables. He found that the sample weight change was positively correlated with the SO_2 levels, but negatively correlated with NO_2 . He concluded that NO_2 decreases the solubility of the corrosion layer.

Haynie et al. (1976) studied weathering steel in an exposure chamber. Although they concluded that NO_2 did not have as significant an impact as SO_2 on the indicated corrosion, a review of the data showed that at low relative humidities the samples showed somewhat more damage at high NO_2 concentrations ($940 \mu\text{g}/\text{m}^3$ [0.5 ppm]) than at low concentrations ($94 \mu\text{g}/\text{m}^3$ [0.05 ppm]).

Galvanized Steel and Zinc

Because most carbon steels rust readily when exposed to moist air, a layer of zinc is frequently coated or galvanized onto the surface. The zinc acts to protect the substrate steel electrochemically by preferentially corroding away, leaving the steel rust-free. Zinc galvanized steel is used for many outdoor purposes, including chain-link fences, highway guard rails and sign posts, roofing, and automobile body panels.

Whitbeck and Jones (1987) studied the accumulation of nitrates on galvanized steel in an exposure chamber. They exposed the galvanized steel to $18,800 \mu\text{g}/\text{m}^3$ (10 ppm) of NO_2 (much higher than ambient air levels) and measured the nitrate formation as a function of time on the sample surface. They found that the formation of nitrates was linear with time. Haynie et al. (1976) included galvanized steel in their chamber study discussed above and concluded that the effects of SO_2 are much more significant than those of NO_2 .

These results are further supported by the field investigations reported by Cramer et al. (1988). They found that SO_2 is more readily absorbed on galvanized surfaces than NO and NO_2 and that SO_2 -induced corrosion probably dominates corrosion by NO_x in most environments. In relatively dry environments, Cramer et al. (citing Johansson, 1986) pointed out that NO_2 can participate in a reaction to oxidize SO_2 and form H_2SO_4 , which is very aggressive to galvanized surfaces. Edney et al. (1987) statistically analyzed the results of exposures of galvanized steel and chemical analyses of the runoff rainwater from the samples. They found that the amount of deposited $\text{SO}_4^{=}$ dominated the amount of deposited NO_3^- , and that $\text{SO}_4^{=}$ and NO_3^- deposition rates were strongly correlated at the field exposure site. From the regression analysis, therefore, $\text{SO}_4^{=}$ was found to dominate the corrosion of galvanized steel and NO_3^- was found not to be a significant contributor to corrosion at this location. Subsequent analysis of data from the same site by Spence et al. (1988), using a more complete regression model, found no statistically significant effects of pollution on either galvanized steel or weathering steel exposed for 3 years. The site used for this experiment, Research Triangle Park, NC, is relatively rural and SO_2 and NO_2 concentrations are fairly low. The analysis of Spence et al. suggests that natural weathering processes dominate over corrosion at this site.

Although rarely used alone as a construction material, zinc is used for galvanizing and as an alloying metal and its corrosion behavior has been investigated. Johansson (1986)

exposed zinc to NO_2 and SO_2 in a low-flow exposure chamber. He showed that NO_2 alone had little impact, but that small amounts, $376 \mu\text{g}/\text{m}^3$ (0.2 ppm), were strongly synergistic when combined with SO_2 . As the NO_2 concentration in the mixture was increased from $376 \mu\text{g}/\text{m}^3$ to $5,640 \mu\text{g}/\text{m}^3$ (0.2 ppm to 3.0 ppm) and the SO_2 concentrations were held constant, there was little change in the rate of corrosion.

Kucera (1986) has noted that, in the open air, zinc tends to form a layer of sulfates and carbonates on the surface that acts to passivate the metal. This layer is basic, and if rain with a pH value of 4 or less washes the surface, the layer is removed, exposing the substrate metal. In this way zinc is sensitive to acid deposition, so that any pollutant, including NO_x , that adds to the acidity of the environment is damaging to zinc.

Hermance (1966) and Hermance et al. (1971) reported the impact of nitrates on zinc-containing nickel-brass wire springs used in telephone relays. They pointed out that hygroscopic nitrate salts collected on the springs and moisture formed on the surface at any relative humidity exceeding 50%. The nitrate deposition resulted in attack on the zinc in the springs and premature failure of the relays. In addition, Graedel and McGill (1986) have pointed out that NO_2 is known to be moderately aggressive towards nickel. Ultimately, the telephone companies were forced to replace zinc-containing nickel-brass springs in areas with high NO_x levels, such as Los Angeles. Henrikson and Rode (1986) showed that at 95% RH the synergistic effects of NO_2 and SO_2 were not detectable for zinc corrosion. At high humidities, SO_2 appears to dominate zinc corrosion.

Aluminum

Aluminum is widely used because of its corrosion resistance and is second only to steel in the amount of metal in use. Aluminum is often exposed without coatings, such as paint, and is used for architectural trim, aircraft, small buildings, cooking utensils, etc. Kucera (1986) noted that the time of wetness of aluminum surfaces correlates with NO_x concentrations, but could not conclude that NO_x was of any practical importance in the aluminum corrosion process. Johansson (1986) demonstrated in a chamber study that NO_2 did not significantly adsorb on aluminum but that at 90% RH NO_2 was synergistic with SO_2 and caused nearly three times the corrosion caused by either pollutant alone. Henriksen and Rode (1986) showed that NO_2 inhibits SO_2 -induced aluminum corrosion at 95% RH. In a

chamber study, Loskutov et al (1982) demonstrated that the interaction of NO₂ and water on an aluminum surface was a complex process. They concluded that adsorbed water acted to displace NO₂ on the surface, and that metal corrosion occurred simultaneously with the adsorption/displacement process but slowed substantially as water displaced NO_x.

Vijayakumar et al (1989) exposed aluminum to 940 and 1,880 µg/m³ (0.5 and 1 ppm) NO₂ in a chamber for 28 days. They found no statistically significant impact of NO₂ on aluminum. They also exposed aluminum to 252 and 1,260 µg/m³ (0.1 and 0.5 ppm) HNO₃ and determined that there was statistically significant damage and that the rate of the damaging reaction was relatively rapid.

Copper

Copper is used for architectural trim, electrical components, and heat transfer coils in air conditioners. Chamber studies (Schubert, 1978, Rice et al, 1981) have shown that NO₂ has little impact on copper at concentrations up to 2,444 µg/m³ (1.3 ppm). Rice et al (1980a) concluded from a multiple-city exposure study that hydrogen sulfide (H₂S), SO₂, and O₃ all had more impact than NO_x on copper. Kucera (1986), Johansson (1986), and Henriksen and Rode (1986), using chamber studies, found that NO₂ and SO₂ in combination was synergistic and increased the observed corrosion rate of copper by 10 to 20 times the rate observed with single-gas exposures under low-flow-rate conditions.

Nickel

Nickel is used as a coating material to protect other metals from corrosion and is particularly resistant to environments that aggressively attack steels, aluminums, and a variety of other metals (e.g., marine environments). Rice et al (1980a) investigated the indoor corrosion of nickel in several urban areas and found that SO₂, NO₂, and chlorides played a significant role in accelerating nickel corrosion. In a chamber study, Rice et al (1980b) found that NO₂ attacked nickel but that SO₂ and chlorine (Cl₂) were more aggressive than NO₂. Graedel and McGill (1986) have listed NO₂ as being moderately aggressive toward nickel.

12.4.3 Effects of Nitrogen Oxides on Electronics

Although the impact of air pollution on architectural and structural metals in the outdoor environment has been recognized for some time, the attack of NO_x on electronic components, generally used in indoor environments, is a more recently recognized problem. Telephone companies first reported the problem, noting failures of wire-spring relays in telephone switching offices located in regions with high NO_x levels (Hermance, 1966, McKinney and Hermance, 1967, Hermance et al, 1971). Nitrogen oxides were depositing on the springs and eventually leading to stress corrosion failures. Here, the cost of the failed part, the spring, was a minor consideration compared to the loss of service. Eventually, technology made the wire-spring relays obsolete, but, meanwhile, inconveniences and costs were incurred as the result of these failures.

Most of the gold used for industrial purposes is used to inhibit corrosion in electrical contacts. Svedung et al (1983) tested the corrosion resistance of gold-plated brass, one of the most common contact materials, in an atmosphere containing $940 \mu\text{g}/\text{m}^3$ (0.5 ppm) NO_2 . They found that NO_2 -containing environments were more aggressive than SO_2 environments at all relative humidities from 40 to 80%. As found with common metals, an environment containing a mixture of NO_2 and SO_2 was even more damaging. Samples of gold contacts exposed to mixed-gas atmospheres became partly covered by visible corrosion after 2 to 3 h. Kucera (1986) reported similar findings for electrolytic copper contacts. Buildup of corrosion layers on electrical contacts causes loss of conductivity and possible failure of the contact.

Voytko and Gulinger (1988) exposed gold, nickel, and palladium samples electroplated on copper substrates to an atmosphere containing 100 ppb NO_2 , 100 ppb H_2S , and 10 ppb Cl_2 at 60% RH for 332 h. These samples were designed to simulate typical electrical contact materials. They found that all coatings developed "pores" that allowed the substrate copper to corrode and that the "solderability" of the specimens generally decreased after exposure. Graedel and McGill (1986) reviewed the impact of pollutants on a variety of materials, and listed NO_2 as being moderately aggressive to solder.

Abbott (1987) exposed electrical contacts made of cobalt-hardened gold over sulfamate-nickel to different pollutant mixtures in a laboratory test environment. He found that H_2S and SO_2 , both singly and in combination, were fairly benign to the contact surfaces,

producing only mild pore corrosion even as concentrations approached 1 ppm. The reaction became more severe when NO_2 was added to the mixture. A mixture of 0.1 ppm each of H_2S , SO_2 , and NO_2 was more aggressive than 0.5 ppm H_2S plus 1.0 ppm SO_2 . Abbott also estimated that approximately 30% of indoor electrical and electronic equipment environments are corrosive enough to result in pore corrosion and film creep that could lead to component failure.

Freitag et al. (1980) investigated the corrosion of magnetic recording heads of the types used in computers. They found that exposure to 0.3 ppm each of NO_2 and SO_2 led to the formation of corrosion products on the heads. This corrosion would lead to a degradation of the magnetic properties of the recording head.

12.5 EFFECTS OF NITROGEN OXIDES ON PAINTS

Paints are by far the dominant class of manmade materials exposed to the atmosphere in both indoor and outdoor environments. Paint systems are used to protect substrate materials such as wood, steel, and stucco from damaging environmental agents, including moisture, sunlight, and pollutants. Paints are also applied for aesthetic reasons. Paints are broadly classified as architectural coatings (e.g., house paints, stains, varnishes), product coatings (e.g., furniture finishes, automotive paints, appliance coatings), and special-purpose coatings (e.g., bridge paints, swimming pool coatings, highway marking paint).

Although paints are designed to erode uniformly and repainting is expected, any damaging process that exposes the substrate material or discolors the finish more rapidly than natural weathering results in premature failure of the paint system and leads to the need for more frequent maintenance and thus to increased costs. Major paint manufacturers routinely conduct proprietary tests of their coatings, and some information is available in the open literature about the effects of NO_x on selected paint systems. Because paint formulations vary widely, however, results obtained for one paint may not be directly applicable to other paints.

Spence et al. (1975) investigated the effects of various pollutants on oil-based house paint, vinyl coil coating, and acrylic coil coating. A chamber study approach was used with 1,000 h of exposure to 94 and 940 $\mu\text{g}/\text{m}^3$ (0.05 and 0.5 ppm) NO_2 in combination with

various levels of SO_2 , O_3 , and humidity. The coil coatings were very resistant to all pollutants and showed little change over the course of the experiment. The oil-based house paint was found to be most sensitive to SO_2 and humidity, but increased concentrations of NO_2 led to increased sample weights. This implies that the NO_2 was reacting with the paint in some way, although whether this reaction was significant was not discussed.

Haynie and Spence (1984) reported results of exposures of latex and oil exterior house paints for 30 mo at nine sites around St. Louis, MO. They reported that NO_x became incorporated into the latex paint film and suggested that it reacted with the polymers that make up the paint. Similar results were reported for oil-based paint and brown staining.

Vijayakumar et al. (1989) exposed samples of high- and low-carbonate paints to NO_2 and HNO_3 for 28 days in an exposure chamber. They found statistically significant damage to low-carbonate paints at $940 \mu\text{g}/\text{m}^3$ (0.5 ppm) NO_2 , but not at $1,880 \mu\text{g}/\text{m}^3$ (1 ppm) NO_2 . The amount of damage was slight. At $1,260 \mu\text{g}/\text{m}^3$ (0.5 ppm) HNO_3 , however, both carbonate and noncarbonate paints were damaged.

12.6 EFFECTS OF NITROGEN OXIDES ON STONE AND CONCRETE

Air pollution has been known to damage both building and statuary stone. Many famous edifices, such as the Parthenon in Athens, have been the subject of studies of air pollution-induced damage to building stone. Calcareous stone, such as limestone, marble, and carbonate cemented sandstone, is subject to air pollution attack. Silicate stone, such as granite, slate, and noncarbonate sandstone, is much less susceptible. The effects of SO_2 deposition on calcareous stone are well documented because calcium sulfate (gypsum) has limited solubility and remains on protected stone surfaces as a gypsum coating. Calcium nitrate resulting from direct NO_x attack is both very soluble and hygroscopic and thus washes off the stone surface almost as soon as it is exposed to rain. Livingston and Baer (1983) suggest that the solubility of calcium nitrate has caused many researchers to overlook NO_x deposition to stone. Thus, although few data are available, NO_x may have a significant effect on certain types of stone.

The interaction of NO_x with building stone is complex. Not only will nitrogen compounds interact directly with the stone, but various endolithic bacteria present in the stone result in biochemical interactions (Baumgaertner et al., 1990). *Nitrosomonas* species oxidize ammonium to HONO and *Nitrobacter* species oxidize HONO to HNO_3 . Production of these acids results in direct chemical attack to calcareous stone and concrete. Baumgaertner et al. (1990) have also reported that the surface of construction stone is a significant source of NO, apparently biologically produced. On the other hand, NO_2 and NH_3 are absorbed by the stone.

Baedecker et al. (1990) summarized the work of several researchers for the National Acid Precipitation Assessment Program (NAPAP). They noted that by far the greatest chemical erosion of calcareous stone results from the natural constituents of clean rain. Carbon dioxide dissolved in rain forms carbonic acid that reacts with the calcium of the stone. Baedecker et al. (1990) estimated that wet-deposited hydrogen ions from all acid species account for about 20% of the chemical weathering of the NAPAP limestone and marble samples. Dry deposition of SO_2 was responsible for approximately 6 to 10% of the chemical weathering and dry deposition of HNO_3 (believed to be the major form of NO_y attack) accounted for 2 to 6% of chemical erosion. They noted that an adequate model for predicting dry deposition of HNO_3 to stone is not available, and suggested that this topic needs further research.

Mansfeld (1980) performed a statistical analysis of damage incurred on marble samples exposed for 30 mo at nine air quality monitoring sites around St. Louis, MO. He concluded that NO_3^- and total suspended particulate levels best correlated with observed stone degradation, however, the analytical techniques used may be questionable and could have resulted in inappropriate conclusions. Livingston (1985) reviewed current studies regarding the impact of NO_x on calcareous stone. He concluded that sulfates dominate the damage to stone, but that NO_x can play a role. Livingston also showed that the reaction of stone with SO_2 is thermodynamically favored over the reaction with NO_2 , and that if both pollutants are present more calcium sulfate than calcium nitrate will be formed. Amoroso and Fassina (1983) have suggested that the primary impact of NO_x on stone may be its role in oxidizing SO_2 to form sulfate and eventually H_2SO_4 . Although this is not a direct NO_x attack, it does lead to the degradation of stone.

Johansson et al (1988) exposed limestone, marble, and travertine to SO_2 and NO_x for 6 weeks at various concentration combinations in the parts-per-million and sub-parts-per-million range. The exposure chamber flow rates were low, with a net "wind speed" over the samples of only 0.004 m/s. The investigators found that significantly more gypsum formation occurred with the combinations of pollutants than with either pollutant alone. The low flow rates in the chamber, however, make these data questionable for direct application to outdoor exposures.

Concrete is a widely used construction material and dominates infrastructure construction (bridges, highways, water and sewer systems). Webster and Kukacka (1985) surveyed the construction industry and the technical literature for information regarding the impact of pollutants on concrete and cement. They speculate that HONO and HNO_3 are more damaging than H_2SO_4 to concrete on brief exposures because they convert calcium hydroxide to very soluble calcium nitrate. They also believe that even highly diluted HNO_3 solutions can bring about extensive destruction to concrete.

12.7 EFFECTS OF NITROGEN OXIDES ON PAPER AND ARCHIVAL MATERIALS

Paper is the primary storage medium for permanent records ranging from personal photographs to the Constitution of the United States. The National Research Council (1986) noted that NO_2 and other "acid gases" are expected to promote the failure of the cellulose fibers that make up paper. They recommended that the storage condition standards suggested by the National Institute of Standards and Technology be followed and that NO_x levels in archives, libraries, and museums not exceed $5 \mu\text{g}/\text{m}^3$.

Baer and Banks (1985) have pointed out a particular problem with NO_x pollution that libraries, museums, and archives face. In the nineteenth century, cellulose nitrate was produced in large quantities as the first plastic and was used in a wide variety of products. The common uses included photographic film, "acetate" recording disks, pre-vinyl imitation leather, adhesives, and finishes. As cellulose nitrate ages, it continuously emits NO_x . If large quantities of books with artificial leather bindings (or replacement bindings using pyroxylin-impregnated cloth) or of early photographic film are stored, NO_x indoor emissions,

which can be significant, may cause elevated concentrations unless the storage area is adequately vented. In extreme cases of nitrate film storage in sealed vaults with no ventilation, the resulting gas pressure "may be enough to force out masonry walls." If cellulose nitrate film is stored in sealed containers, NO_x concentrations can build up to the point of causing an autocatalytic reaction that can end in spontaneous combustion. Several collections of historic motion picture films have been destroyed in fires resulting from this process.

Salmon et al. (1990) measured nitrogen species deposition during two seasons in five museums in Los Angeles and measured outdoor concentrations of NO_x species, as well. They noted that previous studies that attributed the damage to NO_2 may have actually been seeing damage induced by "co-pollutant" species, such as HNO_3 . Concentrations of HNO_3 within the museums were in the range of 1 to 40% of the outdoor concentrations. They measured apparent HNO_3 deposition velocities to vertical surfaces inside the museums, and found values of approximately 0.18 to 2.37 cm/s. They suggested that the deposition of total inorganic nitrate (gas-phase plus aerosol-phase) onto vertical surfaces is dominated by gas-phase species (probably HNO_3 vapor). A further study of HNO_3 removal by air-handling systems was conducted at one museum, and Salmon et al. (1990) found that approximately 40% of the HNO_3 was removed by deposition within the ventilation system. It was suggested that very low measured values of HNO_3 within galleries may be misleading. Deposition of HNO_3 on surfaces within the museums, probably including the collection, was rapid and potentially induced damage.

Whitmore and Cass (1989), in the chamber study described in Section 12.2.1, tested a selection of natural and synthetic artists' colorants applied to paper. Nitric acid was carefully removed from the chamber environment for these studies, and the NO_2 concentration was $940 \mu\text{g}/\text{m}^3$ (0.5 ppm). Seventeen natural organic colorants, 18 synthetic organic colorants, and 7 inorganic colorants were tested in the absence of light for 12 weeks of exposure. Changes in color were measured with a spectrophotometer. The paper itself exhibited slight yellowing as the result of exposure, and several of the natural colorants showed noticeable color changes. For many of these samples, there was yellowing as measured by decreased reflectance of blue light. Four of the synthetic organic colorants and two of the inorganic colorants showed measurable changes. The authors noted that the cumulative NO_2 dose to

which the samples were exposed was roughly equivalent to 2 years of exposure in an unprotected museum in downtown Los Angeles. They concluded that the damage to a few of the samples should be regarded as unacceptable.

12.8 COSTS OF MATERIALS DAMAGE FROM NITROGEN OXIDES

Cost estimates for materials damage have been based on two distinct approaches. The first technique, the "top-down approach", involves determining the dollar value of a material produced each year and then estimating the percentage of that value that is lost each year from pollutant-induced damage. The advantage of this approach is its ease of application. However, it is not rigorous and is likely to contain significant errors. For example, using the top-down approach, it is not possible to determine the pollutant exposure levels of the materials because there is no way to determine the locations in which the materials are deployed. All that can be done is to use gross averages for exposures with this technique.

The second technique is the "bottom-up approach", in which as much detail as possible is gathered regarding the geographic distribution of materials, the spatially resolved pollutant concentrations and other variables, and the costs of repairs and replacement. The bottom-up approach is more rigorous and demanding in terms of data requirements, and may yield a closer estimate of actual costs than the top-down, production approach. The accuracy of either approach is unknown. The methodology of cost estimation for materials damage needs further research and development.

The costs of some types of NO_x -induced damage to textiles were estimated by the National Research Council (1977). The following estimates, in 1977 dollars and based on 1977 production rates and pollutant concentrations, were made:

1. \$53 million incurred from dye fading on acetate fibers. This includes costs for more expensive, fade-resistant dyes, inhibitors, research, quality control, fade losses at the manufacturing and retail level, and reduced product life at the consumer level as the result of fading.

- 2 \$22 million incurred from dye fading on cotton fibers. This includes estimates of cotton fabrics exposed in polluted areas, percentages of dyes known to be susceptible to NO_x fading, and yearly loss in use-life
3. \$22 million incurred from dye fading on viscose rayon and rayon blends with nylon, polyester, or acetate. This includes reduced wear-life for sensitive dye shades

Estimates of the costs of other types of losses caused by adverse NO_x impacts on textiles and fibers are not available. Loss of strength and shortened use-life may be a significant cost for fibers used for industrial purposes. According to the National Research Council (1977), 18 to 20% of all fibers produced are used by industry for items such as tarpaulins, cords, and rope. Loss of strength for fibers used for these purposes shortens use-life and may present a safety hazard.

Estimates of the costs of NO_x-induced damage to plastics and elastomers are not reported in the literature. The damages suffered through cross-linking and chain-scissioning are loss of strength, increased cracking, and discoloration. As the use of these compounds for construction and automotive applications increases, the amount of exposure to NO_x will increase and the disbenefit costs of this exposure are expected to increase.

No overall estimates of the costs of NO_x-induced damage to metals and electronics are available. For metallic corrosion in general, the costs are large. The paint and coatings industry, for example, produces a spectrum of products designed to prevent rust on steel and these coatings would not be needed if corrosion were not a problem.

Damage to paints, concrete, and stone produces potentially one of the largest economic disbenefits of NO_x-induced materials damage because the use of these materials is widespread. In 1987, sales by the paints and coatings industry alone approached \$10 billion. The costs of infrastructure replacement because of concrete degradation can be seen as part of the annual highway budgets. Damage to historic stone structures and statues is mostly a cultural cost and is not readily calculated.

All of the foregoing cost estimates are either based upon old information (e.g., the National Research Council data were compiled in 1977) or are not specific for NO_x-induced damage. Also, the materials reported are only a subset of all materials exposed to NO_x.

Recent and specific NO_x -induced materials damage cost estimates are not available in the literature. This is an area of research that requires attention and updating.

12.9 SUMMARY OF THE EFFECTS OF NITROGEN OXIDES ON MATERIALS

Nitrogen oxides have been shown to cause or accelerate damage to manmade materials exposed to the atmosphere. Nitrogen oxides atmospheric and surface chemistry is complex and there are many compounds, including NO , NO_2 , and HNO_3 , that can contribute to this damage.

Strong evidence exists for the negative impact of NO_x on dyes and fabrics. Many varieties of dyes are known to fade, become duller, or acquire a different cast, and white fabrics may "yellow" from exposure to NO_x . Nitric oxide and NO_2 were found to be significant causes of color change for various fabric and dye combinations exposed in ambient air. Fade-resistant dyes and inhibitors have been developed, but are generally more costly to employ. Nitrogen oxides also attack textile fibers, resulting in a loss of strength. Nylon, in particular, appears to be susceptible to NO_2 damage. Plastics and elastomers are subject to NO_2 reactions that cause discoloration and changes in physical properties, including loss of strength.

Although NO_x attacks metals, attack by SO_2 is more aggressive, partly because in outdoor environments the uptake of NO_2 is limited by surface resistance and SO_2 deposits more rapidly. There is evidence that HNO_3 attacks aluminum, but that NO_2 is not directly damaging to aluminum. Damage to metals from NO_x can generally be discounted, except perhaps in indoor exposures, where NO_2 may react synergistically with SO_2 . Also largely indoors, NO_x is deposited on electronic components and magnetic recording equipment and may lead to failures in these systems. Nitrogen dioxide leads to pore corrosion on the gold-plated surfaces of electrical contacts, leading to component failure.

The influence of NO_x on paints and stone has not been clearly demonstrated. Many researchers have reported that NO_x and NO_y (e.g., HNO_3) play a role in damaging these materials, but most concede that SO_2 and O_3 are more directly damaging than NO_x and NO_y in typical polluted atmospheres. Nitrogen oxides, along with other "acid pollutants", attack

the cellulose fibers in paper, leading to discoloration and weakened structure. Nitrogen dioxide has been shown to affect art supply colorants adversely and thus can damage works of fine art.

The highest NO_x levels are to be found indoors where unvented combustion systems (e.g., gas stoves) are used and the widest variety of materials are routinely exposed. Therefore, the principal effects of NO_x -induced damage to materials are probably seen in the indoor environment. Few data are available regarding materials deterioration indoors.

The presence of NO_x will shorten the use-life of susceptible materials, and generally the rate of damage is proportional to the pollutant concentration. Adequate NO_x damage functions for a wide variety of materials are not available. Consequently, practical cost/benefit analyses of permissible NO_x levels vis-a-vis shortened use-life estimates may be impossible. Cost estimates for NO_x -specific damage at existing concentrations are available only for dye fading (\$97 million annually in 1977 dollars), and these estimates are very out of date.

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