United States
Environmental Protection
Agency

Office of
Research and Development
Washington, DC 20460

EPA/600/8-91/049bA
August 1991
External Review Draft

EPA

Air Quality Criteria for Oxides of Nitrogen

Review Draft

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Volume II of III

NOTICE

This document is a preliminary draft. It has not been formally released by EPA and should not at this stage be construed to represent Agency policy. It is being circulated for comment on its technical accuracy and policy implications.

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Environmental Criteria and Assessment Office
Office of Health and Environmental Assessment
Office of Research and Development
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Research Triangle Park, NC 27711

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Air Quality Criteria for Oxides of Nitrogen

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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) are considered important phytotoxicants. The effects of nitrogen oxides 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 are often expressed as visible foliar injury, premature senescence, increased leaf abscission, and reduced plant growth and yield. These changes at the individual plant level lead to altered reproduction, changes in competitive ability, or reduction of plant vigor. They subsequently are manifested by changes in plant communities and, ultimately, changes in ecosystems. 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.

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. Factors that influence plant response to nitrogen oxides are also included. Since most available data pertained to NO_2, this pollutant receives the most attention. 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 is 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 and other photochemical oxidants. 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 nitrogen oxides 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. Prior to initiation of a study, the desired outcome should be carefully evaluated. Is the goal to develop pollutant exposure-plant response models which 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 which may modify plant response to pollutant exposure under investigation? The answers to these and other questions provide the framework for choosing chamber type, exposure concentration, duration and frequency, plant species and developmental stage, response variables, replication and blocking plans, as well as statistical treatment of the data. This section discusses the various methods used to determine plant response to oxides of nitrogen, including experimental design and data analyses, exposure systems, pollutant climatology and chemistry, and terminology.

9.2.1 Experimental Design and Statistical Analyses

Experimental design refers to the relationship in space and time among replications (or blocks within replications) and treatment factors. 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 (RCBD, RIBD) are most commonly used, frequently blocked over time. Completely randomized designs (CRD, 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 NO_2 are being investigated, the number of treatments increases and study design becomes more complicated. A multi-factor experiment may be conducted as a full (all combinations of factor levels) or partial (some combinations of factor levels) factorial. Treatment factors which 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 which are not so easily contained, such as other pollutant gases, air temperature or radiation levels can be investigated in combination with NO_2 concentration in partial factorial designs, although this approach seems largely confined to O_3/SO_2 mixture studies (Ormrod et al., 1984).

The simpler experimental plans described above (RCBD, CRD) are easily analyzed by traditional 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 NO_2) then an unplanned comparison technique such as multiple range (Duncan new, Sheffe or Student-Newman-Keul) or least significant difference test (Steel and Torrie, 1960). Many of these tests have safeguards which reduce the danger of detecting significant treatment effects when none in fact exist. These tests are not appropriate for qualitative treatments (for example, multiple concentrations of NO_2 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 (independent) or non-orthogonal. This approach is suitable when treatments can be grouped in various ways to generate biologically interesting 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 SO_2 and O_3 on tulip poplar (*Liriodendron tulipifera*) were investigated. The authors developed three orthogonal contrasts, which tested the additivity of O_3 in combination with SO_2 (contrast 1); the effect of $SO_2 + O_3$ on the plants (contrast 2); and compared the effects of O_3 with those of SO_2 (contrast 3):

(1) $[(O_3 - \text{control}) + (SO_2 - \text{control})] = [(O_3 + SO_2) - \text{control}]$

(2) $O_3 + SO_2 = \text{control}$

(3) $O_3 = SO_2$

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 which 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 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 pre-chamber 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 NO_2 from liquid N_2O_4, provided that the container of N_2O_4 is kept at or above 25 °C, which vaporizes N_2O_4 to NO_2. The NO_2 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 NO_2 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):

(i) heating lead nitrate

$$2Pb(NO_3)_2 \leftrightarrow 2PbO + 4NO_2 + O_2$$

(ii) combining nitric acid and copper chips

$$Cu + 4HNO_{3(conc)} \leftrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

(iii) combining nitric acid and sodium nitrate

$$NaNO_2 + 2HNO_{3(dil)} \leftrightarrow NaNO_3 + 2NO_2 + H_2O.$$

Nitrogen dioxide can also be generated by bubbling air through concentrated hot (83 °C) HNO_3 (Oleksyn, 1984):

$$2HNO_3 \leftrightarrow 2NO_2 + H_2O + \frac{1}{2}O_2.$$

The advantage of these methods of NO_2 production is that they cost much less than pressurized cylinders, so are useful to laboratories which are less well equipped. There is a disadvantage in these methods, however, in that the production of NO_2 is highly variable, making good replication of experiments difficult.

Fumigation studies using NO_x usually employ activated charcoal to remove atmospheric SO_2, NO_2, O_3 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. Normally, most if not all NO_2 is 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 $KMnO_4$, is commonly used in this additional filtration. This oxidizes any incoming NO to NO_2 which can then be trapped by activated charcoal.

TABLE 9-1. ADSORPTION CAPACITIES OF ACTIVATED CHARCOAL AT ONE-FIFTH OF THE US OSHA PERMISSIBLE EXPOSURE LIMITS (PEL)* SET FOR PEOPLE

	PEL	Adsorptive Capacity (Weight %)**
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}

*As defined by the 29CER 1910 OSHA Standard dated April 22, 1986.
**Data provided by Westates Carbon Inc., Los Angeles for activated charcoal types G201, G204, G210 and G216 made from coconut-shells.

However, there is an additional complication with O_3 fumigations of plants because inadvertent exposures to NO_x may also occur. Electrical discharge ozonizers are frequently used in O_3 fumigations of plants but some investigators have not heeded warnings given several years ago (Harris et al., 1982) that such ozonizers supplied with ultra-pure air will also form HNO_3 and N_2O_5. For example, an air-fed ozonizer producing 8,650 ppm O_3 also forms 57 ppm HNO_3 and 94 ppm N_2O_5. Production of N_2O_5 can be prevented by the use of pure oxygen instead of air but the formation of HNO_3 is not entirely prevented. An alternative, safer procedure is to use an air-fed ozonizer and bubble the O_3-enriched air through ultra-pure water which 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 N during experimental fumigations with O_3. Some studies of forest decline have lead to reports that increased nitrate leaching can occur when O_3 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 O_3, and hence no deposition of nitrate from the 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 O_3.

9.2.2.2 Chambers

Because NO_2 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 which 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 ab- and adsorption of pollutants on a per unit area of foliage basis, and has been so used in studies of NO_2 phytotoxicity (Elkiey et al., 1982). Other chamber designs have been used for exposing plants to NO_2; these generally differ from CSTR's 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 NO_2: 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 which 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; climatic differences among growing seasons confounding replication over time; and climatic conditions specific to any one year may interact and modify plant

response. While chamberless methods for exposing plants are in use (Zonal Air Pollution System [ZAPS], for example), most data from this exposure system describe plant response to SO_2 (Lee and Lewis, 1977; Muller et al., 1979).

9.2.2.3 Monitoring

The amount of $NO_2/NO_x/NO$ 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 O_3 react in the gaseous phase, NO_2 is produced ($NO + O_3 \rightarrow NO_2 + O_2 + h\nu$). The NO_2 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 NO produced in the reaction. Prior to the reaction with O_3, the NO_2 in the air sample must be converted to NO, which is usually accomplished using a catalyst, such as molybdenum, and heat: $3NO_2 + Mo \rightarrow 3NO + MoO_3$. Since most sources of air to be analyzed contain a mixture of NO and NO_2, the determination of NO_2 concentration is by necessity a two-step process. First the amount of NO in the air is determined by bypassing the $NO \rightarrow NO_2$ converter. Then the air is passed through the converter to determine NO_x, which is the original NO_2 plus the NO which has been converted to NO_2. The difference between these two readings determines NO_2: $NO_2 = NO_x - NO$. 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 N_2 Reference Material. Zero air is defined as air which is free of any contaminants which will cause a detectable response in any mode of the analyzer (NO, NO_2 or NO_x) or react with NO, NO_2 or O_3 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 NO_2 Meter (Mast Co., OH, USA): 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 NO_2 since the chemiluminescent methods are capable of measuring the various oxides of nitrogen, and do so with greater accuracy and sensitivity.

9.2.3 Pollutant Climatology

As NO_2 is a primary, anthropogenic pollutant, its production is not closely linked to meteorological conditions. However, the conversion of NO_2 to NO and the consequent production of O_3 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).

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, 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 O. The oxygen radical (O) is then available to combine with 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 HO_2 to form NO_2 and OH:

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$HO_2 + NO \rightarrow NO_2 + OH.$$

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

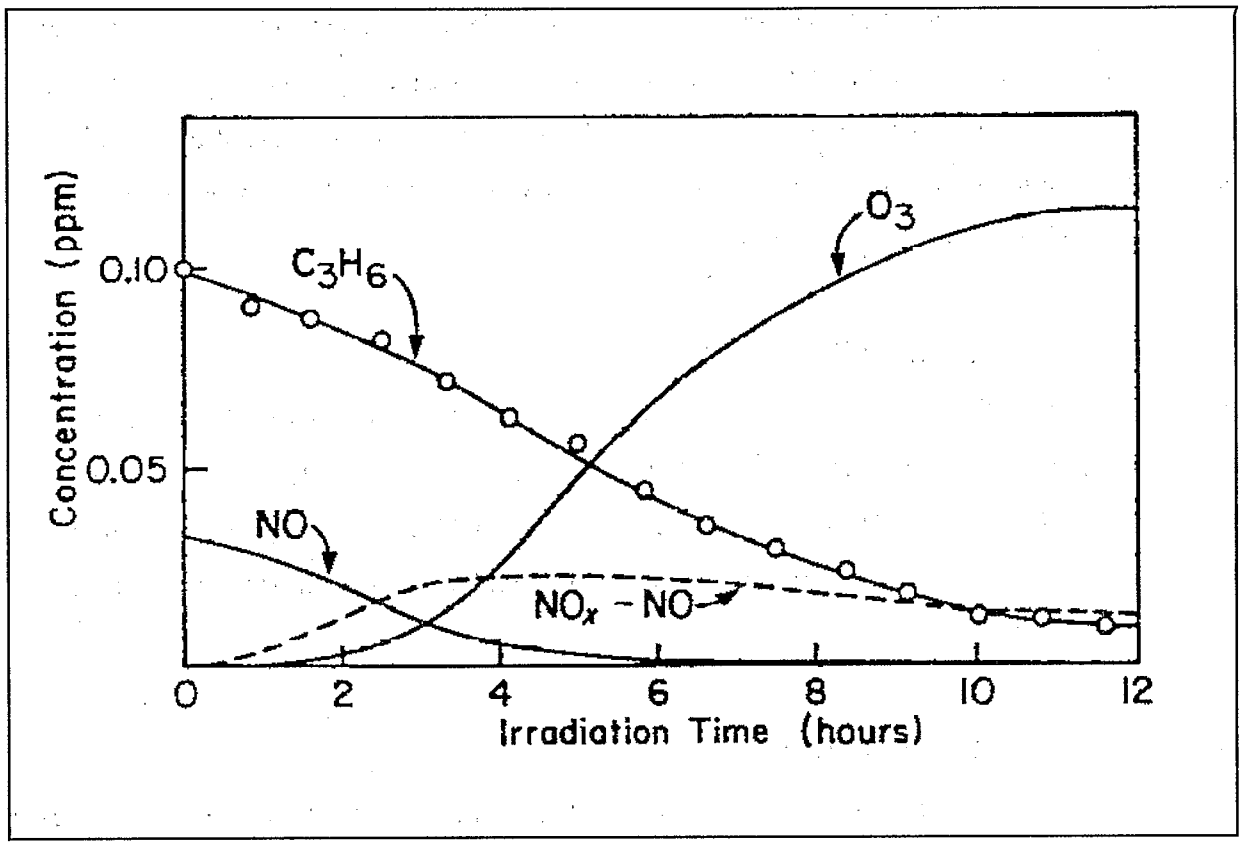

Figure 9-1. Propylene and NO oxidation under artificial illumination. NO is oxidized to NO_2 and other oxides of nitrogen. Ozone concentrations build up after the ratio of NO_2 to NO increases.

Source: Stern (1986).

(Figure 9-3). Once the pollutants have been deposited to vegetation or soil, they become available to the biosphere as toxins.

9.2.5 Terminology

9.2.5.1 Plant Response

Interaction—effect in which plant exposure to a factor modifies plant response to a second factor; these factors may be pollutants, edaphic and atmospheric conditions (such as RH, temperature, soil moisture), or intra-plant (such as age, cultivar). Interaction may be synergistic (plant response to two factors is greater than sum of response to individual

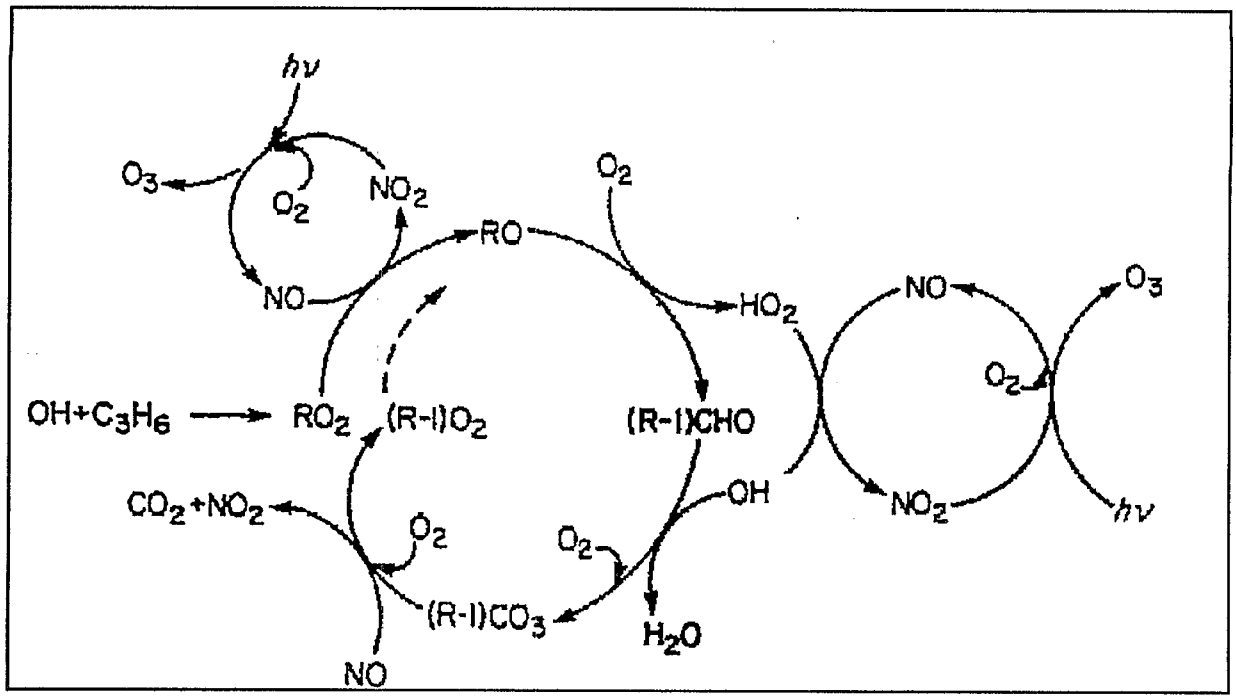

Figure 9-2. The cyclic interaction of free radicals, hydrocarbons, NO, NO_2 and ultraviolet radiation in photochemical smog. In this example hydroxyl radical reacts with propylene at the left side of the diagram forming RO_2. This cycle interacts with NO and molecular O_2. The inorganic NO_x-O_3 cycle is shown on the right side of the diagram with photolysis of NO_2 eventually forming O_3.

Source: Stern (1986).

factors), antagonistic (plant response is less than sum of response to individual factors), or additive (equal to the plant response to individual factors); in addition, the term coalitive is sometimes used to describe plant response to a mixture in the absence of any response to either of the factors alone—in contrast to synergism, where both factors must have an effect on their own.

Damage—plant response to pollutants resulting in loss of intended use or role, for example, agricultural yield, landscaping aesthetics, wildlife habitat.

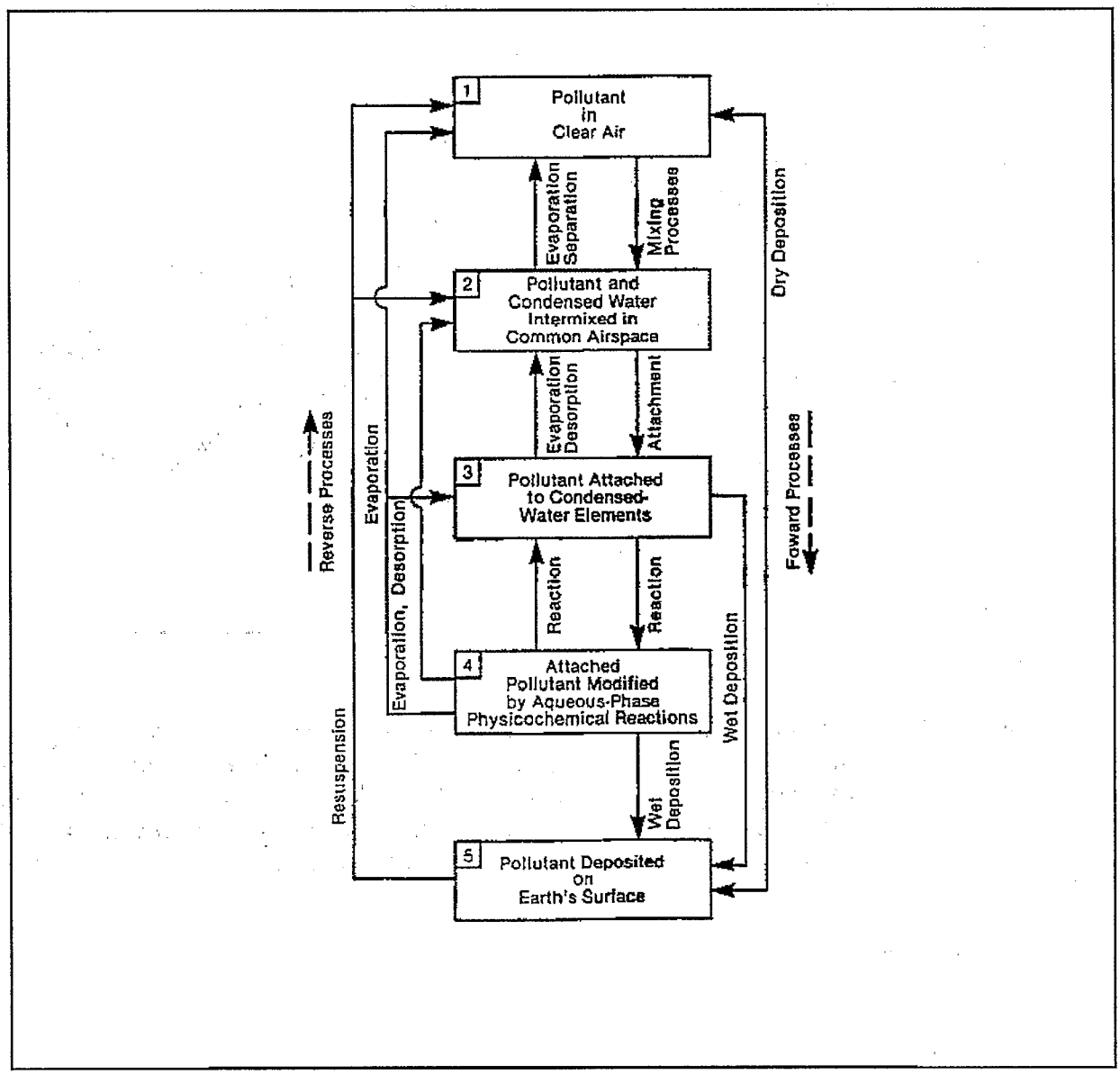

Figure 9-3. Phase interaction diagram for pollutant scavenging processes. Initially, the pollutant may be in the gas phase (Box 1). The presence of water vapor in the atmosphere provides for the intermixing of gaseous pollutants with aqueous droplets in the same space (i.e., in a cloud [Box 2]). The 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 Academy of Sciences (1983), in Stern (1986).

Injury—measurable change in plant structure or function at either the organ, cellular or molecular level, which may or may not lead to damage.

Exposure-response relationships—the generalization of data describing plant response to pollutant exposure by the fitting of a mathematical model, which is generally used for predictive purposes, as it interpolates plant response to pollutant doses for which data have not been gathered.

9.2.5.2 Pollutant Exposure

Concentration—the amount of pollutant in the air expressed either on a v/v (ppm, μL/L) or w/v ($\mu g/m^3$) basis; the v/v basis is usually preferred, as it remains constant over air temperature, whereas $\mu g/m^3$ varies with air temperature.

Duration—the length of time during which the plant is exposed to pollutant treatments; in practical terms is usually measured in h/day for episodic exposures or in days/week or days/growing season for chronic exposure.

Dose—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.

Co-occurrence—pollutant episode during which plants are exposed to two or more gases at the same time.

Sequential—pollutant episode during which two or more gases are presented to the plants one at a time with neither pollutant making more than one appearance.

Complex-sequential—episode during which two or more gases are presented to the plants one at a time, with one or more of the pollutants making more than one appearance.

Chronic exposure—descriptive term for pollutant exposure at a lower concentration for a longer duration; exposures of this type are usually sub-injurious except in very sensitive species or cultivars.

Acute exposure—descriptive term for pollutant exposure at a higher concentration for a shorter duration; exposures of this type usually cause visible injury symptoms in species with a broad range of sensitivities.

Ambient exposure—descriptive term for pollutant exposure which is similar to that which plants would experience when growing in their intended setting; usually implies that pollutant concentration is "dynamic", that is, changes during the exposure period occur in a pattern which simulates the ambient atmosphere.

Episodic exposure—descriptive term for pollutant exposure during which the peak gas concentration approximates the maxima seen in intermittent ambient exposures.

Absorption—removal of gaseous pollutant from the air into the interior of the leaf through the stomates (greatest absorption) or cuticle (least absorption); can be greatly modified by any environmental parameter which influences stomatal opening.

Adsorption—removal of gaseous pollutant from the air by vegetation which is not attributable to stomatal or cuticular absorption; usually involves attachment to and/or modification by such organs as cuticle, trichomes or bark; relatively insensitive to environmental parameters; tends to be related more to species and plant age.

Flux—removal of gaseous pollutant from the air to surfaces (such as vegetation, chambers or buildings); usually described in terms of weight per area per unit time.

Deposition—synonym for flux; deposition may be wet (pollutant dissolved in rain or fog) or dry (in the absence of precipitation).

9.3 MODE OF ACTION

9.3.1 Gas Uptake

9.3.1.1 External NO_x Ratios around Leaves

In order to understand the uptake of oxides of nitrogen (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 (at least every 5 min). 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 which may involve non-aqueous processes prior to entry into cells (see Section 9.4.1.5). 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 N-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 oxide of nitrogen produced is nitrogen monoxide or nitric oxide (NO, Figure 9-4), only a little of which comes from N in the fuel. The majority of the NO is generated from the direct combination of atmospheric O and N within flames (Palmer and Seery, 1973). All ignition reactions involve or produce free radicals (i.e., chemicals which are capable of independent existence which have one or more unpaired electrons in their outer electronic orbitals) such as atomic O and N. NO is also a free radical (.N=O) which, like others, will react so as to lose or gain an electron.

Oxidation of NO by ozone occurs rapidly ($k=1\times10^7\ M^{-1}\ s^{-1}$) even at very low concentrations (Willix, 1976). Altshuller (1956) has calculated that a 50% conversion of NO by 0.1 ppm O_3 would take less than one minute at an NO concentration of 0.1 ppm. 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 which form the pollutant (already described) and those which cause its breakdown. Production of NO and atomic oxygen from NO_2 is the major reverse reaction (Holmes and Daniels, 1934; Ford and Endow, 1957) which is catalyzed by wavelengths of

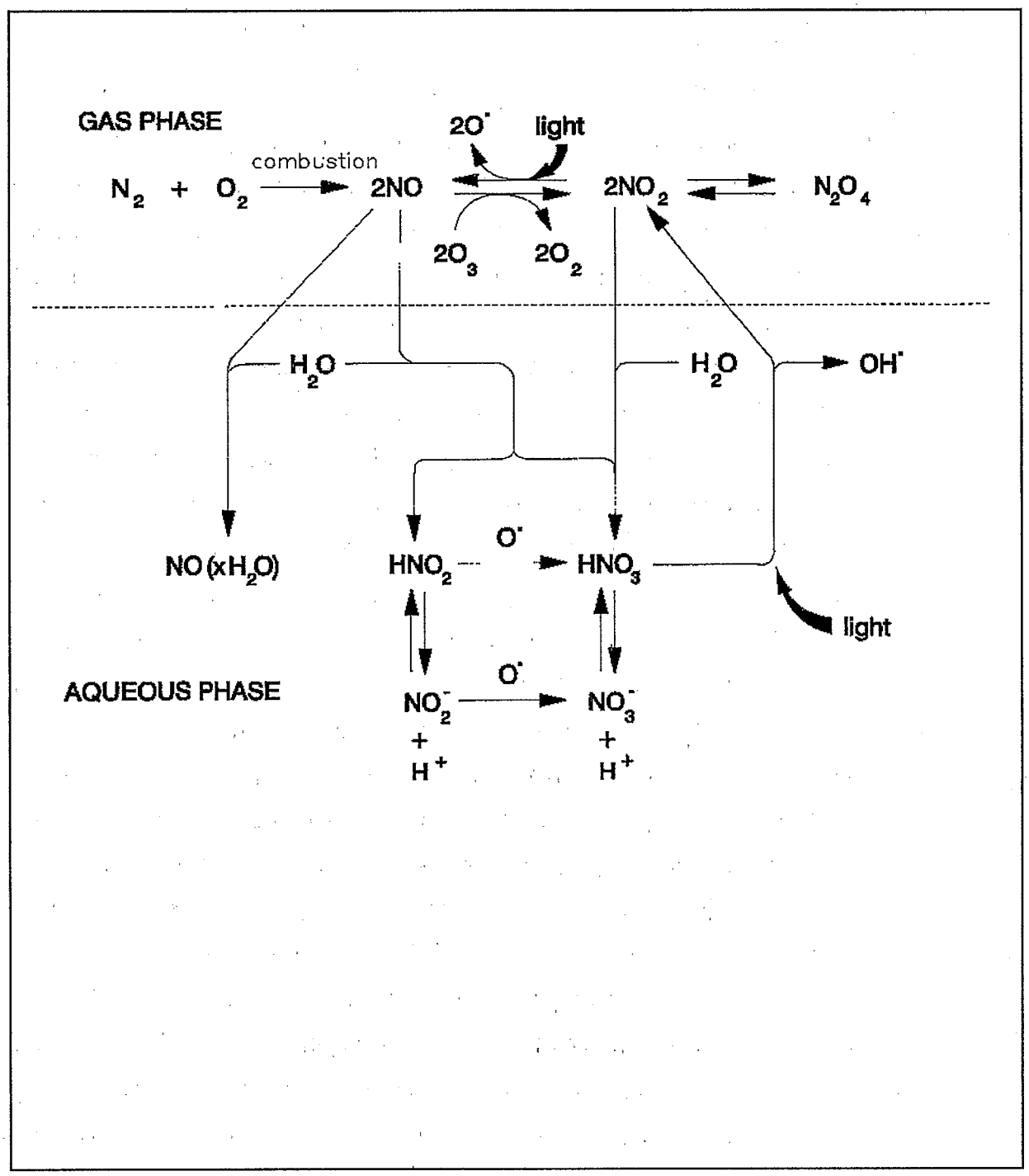

Figure 9-4. Important interconversions of the different forms of NO_x after combustion in the atmosphere and in aqueous solutions in contact with atmospheres containing NO_x.

Source: Rowland et al. (1985).

light less than 440 nm. As a consequence of these forward and back reactions, a wide range of atmospheric NO-to-NO_2 ratios around plants are possible (Fowler and Cape, 1982), depending on levels of light and O_3.

Because the concentration of CO_2 in the atmosphere limits rates of photosynthesis, enrichment of atmospheres with CO_2 (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 CO_2-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 CO_2 to crops. Although the ratio of NO to NO_2 can vary with burner design and method of heating, this ratio is much higher inside (4 parts NO to 1 of NO_2) than outside greenhouses. There are two explanations for this observation even though the glass cut-off effect prevents the light-induced back conversion of NO_2 to NO. First, because the pollutants are monitored close to their source, little time is available for oxidation of NO to NO_2 and, second, the air inside modern greenhouses contains little O_3 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 NO_x

Use of $^{15}NO_2$ 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, Mansfield and Freer-Smith (1981) point out that the molecules must pass through the extracellular water covering the plant cell. Consequently, solubility of a gas in an aqueous medium is an important factor in determining the rate at which it is taken up. Both the gaseous forms of NO and NO_2 are only slightly soluble in pure water but the presence of contaminants such as substituted phenols can alter apparent solubilities (Nash, 1970).

NO_2 differs markedly from NO because it reacts with water and this feature increases significantly the apparent solubility of NO_2 relative to NO. Reaction of NO_2 with water is not just a simple hydration producing nitric acid (HNO_3). 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 which 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 -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 pH 4 can occur.

While the solubility of NO in water has been measured (47.1 ml of gas/L of water at 20 °C and 1 atmosphere), the chemical form of the gas in solution is less certain. 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 is more soluble at lower temperatures than at higher temperatures. Stephen and Stephen (1963) found, for example, 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 produced by NO and NO_2 is markedly different. As already stated, HNO_3 is a strong acid while HNO_2 is regarded as much weaker (pK_a 3.3). Over the probable pH range (5.5-7) of extracellular water (White et al., 1981; Hartung et al., 1988), HNO_3 ionizes fully to form both nitrate ions and protons (see Fig. 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 (N) 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 $^{15}NO_3^-$ produced a similar distribution of ^{15}N (Oghogharie and Pate, 1972) to that found in experiments using $^{15}NO_2$ (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, incorporated into amino acids and subsequently into proteins. Unfortunately, the site of reduction in these studies was not determined. Later experimentation using $^{15}NO_3^-$ in different acid rain treatments (pH 4.0, 3.4, 2.7) of *Phaseolus vulgaris* L. (cv. University of Idaho) showed that the amount of N absorbed by foliage decreased as the rainfall pH was reduced (Evans et al., 1986). Amounts of N accumulated directly from the rain droplets on the leaves into the leaves was found to be only a small percentage of that present in simulated rain and insignificant compared with the amounts of N already present in the leaves. Ammonium and nitrate labeled with ^{15}N have also been used to estimate the amount of foliar uptake of N by red spruce (*Picea rubens* Sarg.) from simulated cloudwater 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 N required for new growth was found to come from ammonium and nitrate in the cloudwater. These conclusions agree with those obtained by Wolfenden and Wellburn (1986) using high performance ion chromatographic (HPIC) analyses of non-aqueously 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 which is relevant to detrimental effects of both wet and dry N deposition on plants. Both cell and tonoplast membranes contain energy(ATP)-dependent H^+-pumps, and the tonoplast pump is strongly inhibited by nitrate (Hager and Bilber, 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 N Uptake Using ^{15}N-labeled Gases

Fumigation experiments using $^{15}NO_2$ have demonstrated that plants take up this gas, that it is converted to nitrite and nitrate, and that only natural modes of N metabolism are involved (Rogers et al., 1979; 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 exposure, glutamine and alanine were strongly labeled while Yoneyama and Sasakawa (1979) and Okano et al. (1984) showed 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., 1979).

In the past, $^{15}N_2$ dilution has been a successful technique to estimate the amount of N fixation by leguminous crops (Fried and Middelboe, 1977) and the same methodology has been adapted to measure the contribution of $^{15}NO_2$ to total N 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 NO_2 (0.5 ppm for 14 d) show absorption rates of 0.57 mg N dm^{-2} d^{-1}—four times those of *Sorghum* (0.16 mg N dm^{-2} d^{-1}). Other species have

intermediate values in the order shown in Table 9-2. They suggested that the total amount of NO_2-derived N 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 C_3 plants) to NO_2 and the relative tolerance of sorghum and maize (both C_4 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 NO_2 uptake and stomatal conductances, a linear relationship (r=0.984) is obtained which does not pass through the origin. From this, Okano et al (1988) concluded that a portion of the NO_2 does not enter the leaf through the stomata.

TABLE 9-2. RATES OF NO_2 ABSORBED AND STOMATAL CONDUCTANCES IN 8 HERBACEOUS SPECIES

Species	Rate (mg N dm^{-2} d^{-1})	Conductance (cm s^{-1})
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 NO_x into Leaves

Both deposition velocities of atmospheric N-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 (Skärby et al., 1981; Johansson, 1987).

NO_x deposited on leaf and stem surfaces either dissociates and is absorbed in the water film covering plant cells or it may react with cuticular wax components in a non-aqueous manner. In excess, NO_2 leads to damaged cuticular surfaces (Fowler et al., 1980). In these circumstances, a small amount of NO_x enters leaves by penetrating the damaged cuticle.

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, Lendzian 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 (two- to six-fold) readily than other air pollutants like SO_2 and 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 N saturation has been achieved does the water permanence increase two- to five-fold, although the barrier towards other gases is unaffected. Uptake of NO_2 and NO into cuticles has also been demonstrated by labeling studies using $^{15}NO_2$ 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 $\mu g\ h^{-1}\ m^{-2}$, a rate of deposition one to two orders of magnitude less than stomatal deposition at similar concentrations of NO_2.

Stomatal behavior, frequency and distribution 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 since a proportion 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 which cause stomatal closure. These include stresses such as low light, humidity or N status (Srivastava et al., 1975a; Law and Mansfield, 1982; Kaji et al., 1980; Yoneyama et al., 1980c). Atmospheric NO_x can also

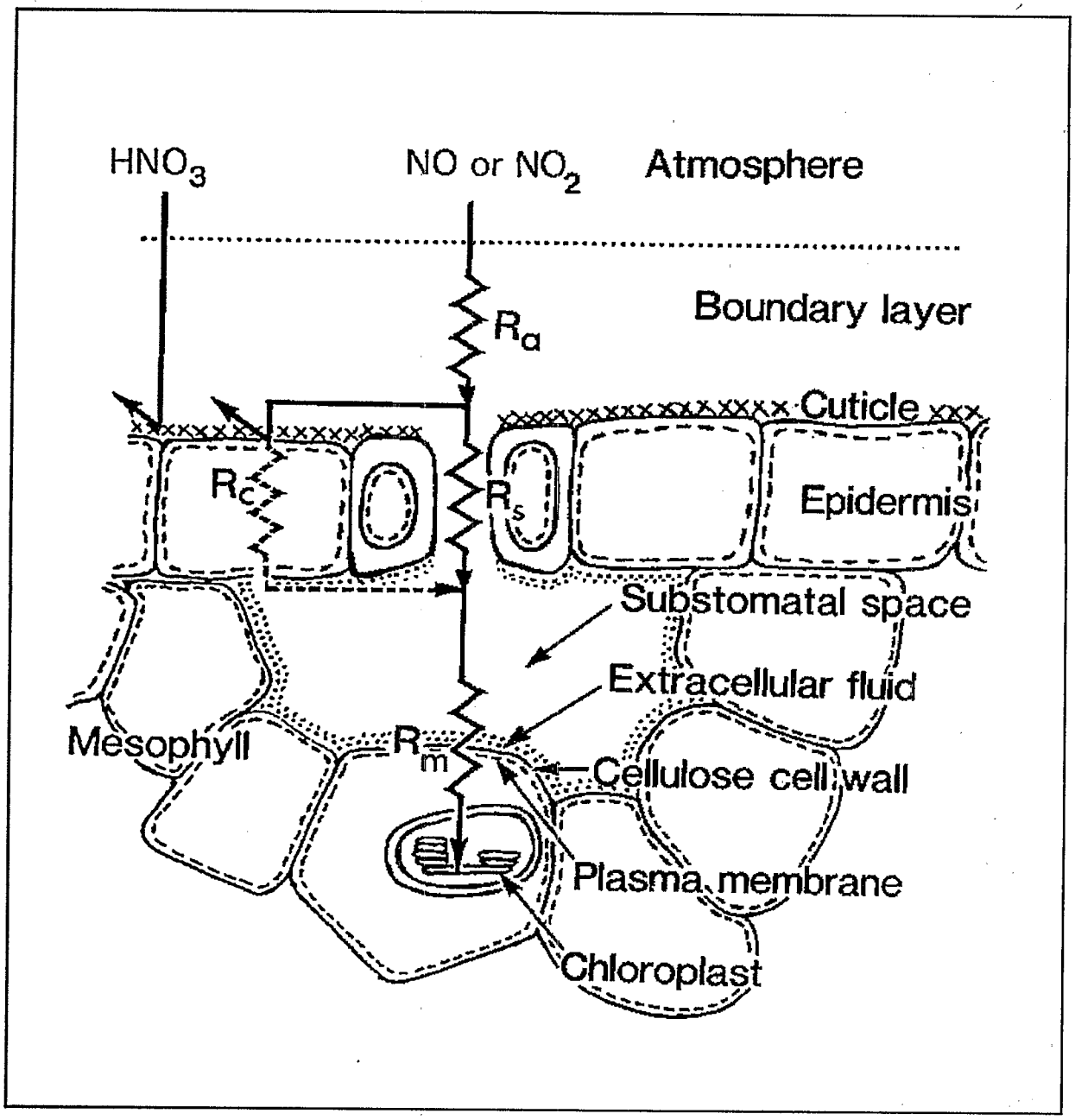

Figure 9-5. Likely access routes for NO_x into a plant leaf. The layer of still air or boundary layer imposes a resistance, R_a, which depend on a number of factors including wind speed. Access is then limited by the degree of stomatal opening, R_s, or to a much lesser extent by penetration through the 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).

cause direct reductions in stomatal conductance (Carlson, 1983) which are then reflected in decreases in transpiration and photosynthesis (see Section 9.4.3.2).

In conclusion, 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 NO_x into Cells

Zeevaart (1976) was the first to suggest that any NO_2 entering a leaf dissolves in the extracellular water of the sub-stomatal 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 50-80% air 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 which 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. Since 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 which 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* 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 9.3.2.1-2).

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 NO_x in Cells

Nitrite is a normal intermediate in the sequential reduction of nitrite to ammonia 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 $^{15}NO_2$ 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., 1984). This process is extremely rapid. For example, radioactive label from atmospheric $^{13}NO_2$ (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.

In general, when bean plants (*Phaseolus vulgaris* L. cv. Kinghorn Wax) are exposed to ambient levels of 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 1-2 h. Similarly, when Yu et al. (1988) fumigated both spinach (*Spinacia oleracea* L. cv. New Asia) and kidney beans (*Phaseolus vulgaris* L. cv. Shin 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 ammonia. 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 four months but could detect no nitrite in the juice from compressed fresh tissues. Likewise, Taylor and Eaton (1966) reported a slight decrease (1.8 meq N g^{-1} fresh wt) in nitrate content from leaves of tomato after 19 days of exposure to NO_2 (0.42-0.54 ppm).

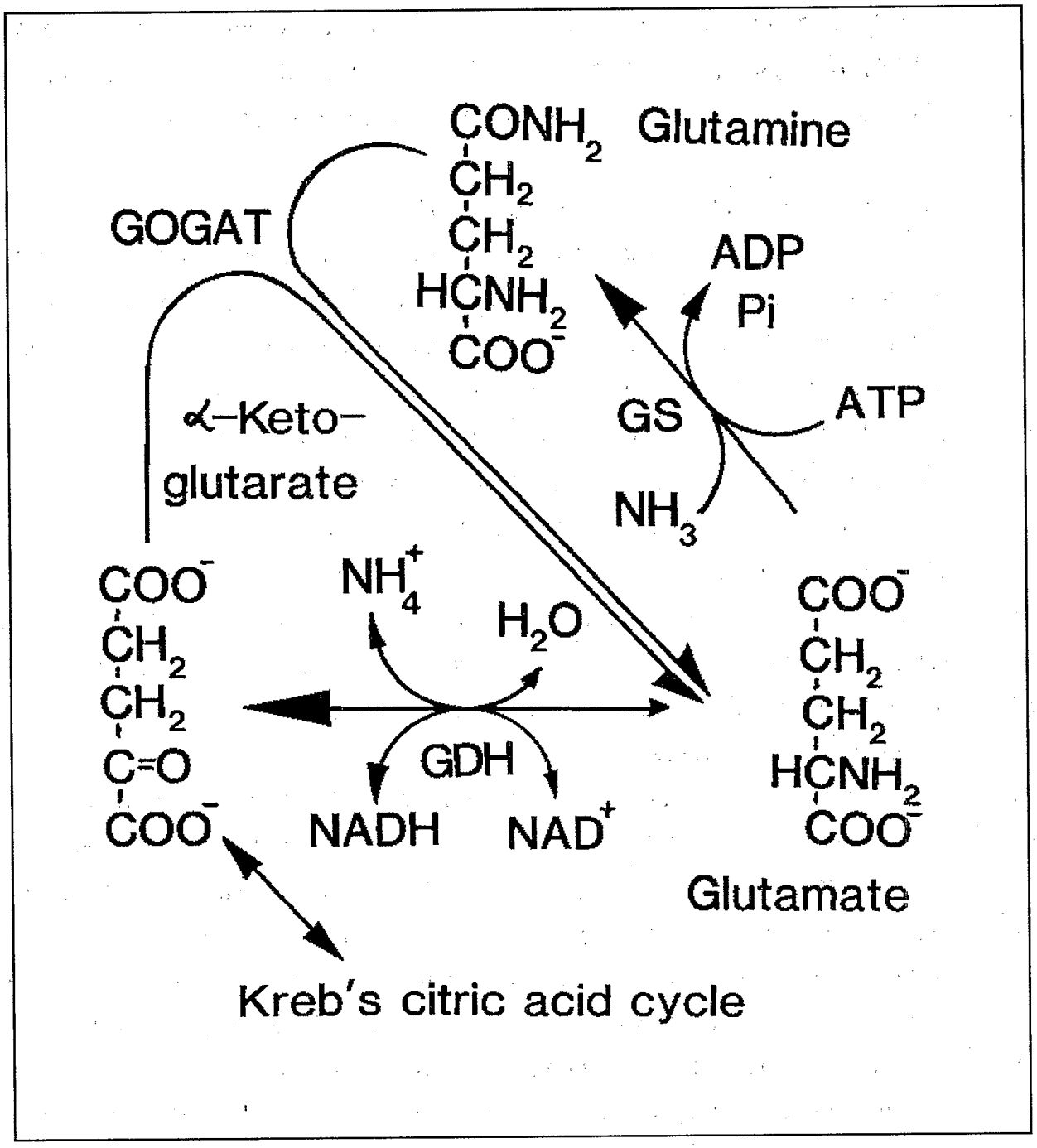

Figure 9-6. Uptake and metabolic pathways involved in the uptake of NO_x into plant leaf tissue from the atmosphere. The enzymes involved include nitrate reductase (NaR), nitrite reductase (NiR), glutamine synthetase (GS), glutamate synthase (GOGAT) and glutamate dehydrogenase (GDH).

Source: Wellburn (1988).

Recent work has shown that changes in levels of total nitrate in response to NO_2 depend upon the amounts of N 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 and Drew, 1988). Hydroponically-grown barley (0.1 mM nitrate) accumulate 85% more nitrate than controls when exposed to 0.3 ppm NO_2 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 (*Phaseolus vulgaris* L. cv. Kinghorn Wax) shoots exposed to 0.5 ppm NO_2 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 N (as opposed to nitrate content) within plant shoots sometimes decline following exposure to NO_x. Elkiey and Ormrod (1981d), for example, found a significant decrease in the total N content of three cultivars of Petunia exposed intermittently to 0.8 ppm NO_2 over four days while similar decreases in shoot total N were found in *Phaseolus vulgaris* L. (cv. Kinghorn Wax) and soybean (*Glycine max* Merr. cv. Williams) with increasing NO_2 concentrations (Srivastava and Ormrod, 1986; Sabaratnam et al., 1988a). The reasons why shoot N levels may decline after exposure to NO_x remain unclear but translocation of additional N from shoots to roots appears to offer a partial explanation. This reallocation of NO_2-derived N 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 $^{14}NO_2$ (0.5 ppm) for 8 days, followed by $^{15}NO_2$ (0.5 ppm) for 3 h and then back to unlabeled NO_2 for one more day (Rowland et al., 1987).

Levels of total N do not always decline. Sinn and Pell (1984) reported that when potato plants were exposed to 0.2 ppm NO_2 for 5 h twice weekly throughout the life cycle of the plant, total N did increase significantly. Similarly, Troiano and Leone (1977) reported that when they exposed tomato plants to 0.025 ppm NO_2 for 80-164 h the N content went in foliage particularly when plants were grown with optimum levels of N in hydroponic culture.

Nitrate and nitrite concentrations in isolated chloroplasts from barley (cv. Patty) exposed to atmospheric NO_2 (0.28 ppm for 1-3 days) have been measured using high

performance ion chromatography (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 and nitrite reductases (see Sections 9.3.2.1, 2). The first enzyme is induced faster than the second so initially more nitrate is converted to nitrite and, when the second catches up, nitrite declines again.

9.3.1.8 Cycling, Partitioning and Elimination of NO_2-derived N

As Section 9.3.1.4 has already mentioned, uptake studies with $^{15}NO_2$ have shown incorporation of label in leaves into glutamine, asparagine, glutamate and alanine. While several groups have also demonstrated transfer of this label into roots, Okano et al. (1984) 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., 1979). 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 $^{15}NO_3^-$, 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 $^{15}NO_3^-$ remaining in the roots was found to be reduced by fumigation with NO_2 especially in those barley seedlings grown at low levels of N 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 seedings well supplied with nitrate, the main effect of atmospheric NO_2 is to increase the amount of reduced N in the roots (Rowland et al., 1987). This was thought to be due to a decrease in the transport of organic N from the roots to the shoots in the xylem stream.

Consequently, the responses of plants to atmospheric NO_2 are very different if the N supply is either limiting or adequate (see also Section 9.3.1.7). If there is sufficient N, there is less redistribution of N and less influence upon roots of N derived from NO_2 taken in by the leaves.

Law and Mansfield (1982) calculated that the input of N 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^{-1} in a growing season of 100 days. Theoretically, such a burner could fulfil virtually all the N requirement of a tomato crop. In practice, greenhouse crops seem to have a limited capacity to utilize N from NO since a supply of NO cannot compensate for the reduction in yield due to a deficiency of soil N (Mansfield and Murray, 1984). This is not true in the case of foliar uptake of NO_2. Faller (1972), for example, fumigated N-deficient sunflowers (*Helianthus annuus*) with NO_2 (0.8-3.1 ppm for 21 days) and found a reduction in the symptoms of N deficiency, 6-28% more growth in the primary leaves but not in the roots, and increases of between 70-116% leaf N and 19-70% root N.

Once pollutant-derived N has been reduced, the form in which it is stored varies (see Section 9.3.1.4). Most, if not all, the common protein amino acids can accumulate ^{15}N derived from $^{15}NO_2$ (Durmishidze and Nutsubidze, 1976; Yoneyama et al. 1980d). However, the extent of ^{15}N accumulation is not only species but also time dependent. As rates of processes involved in uptake and utilization of N vary over 24 h, it is not surprising to find that effects of NO_x also differ over the same period. In spinach and sunflower, exposure to $^{15}NO_2$ 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. Since the plants received NO_2 throughout the whole of this 8 h experiment, this suggests that the controls upon the rates of N metabolism in these plants responded to the pollutant by establishing a new steady-state level and that N 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 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 Sections 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 N-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 ab(*d*)sorbed (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 nitrate reductase (Harper, 1981) activity are both known to be associated with accumulations of nitrite ions and both enzymic (Nelson et al., 1983) or non-enzymic (Klepper, 1979; Nishimura et al., 1986) mechanisms of release have been proposed.

9.3.2 Chemical and Biochemical Responses

9.3.2.1 Nitrate Reductase Activities

Reduction of nitrate and incorporation of reduced N into a wide range of compounds is found in nearly all higher plants (Runge, 1983). Nitrate reductase (NaR or NAD(P)H : nitrate oxidoreductase, EC 1.6.6.2), which catalyses the reduction of nitrate to nitrite (see Figure 9-6), is substrate-induced and hence its levels of activity 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 NO_2 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 NO_2 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 NO_2 (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 CO_2-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 NO_2 for 18 h. In these cultivars, no change in any of the shoot NaR levels occurred with 1.5 ppm NO nor any change 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 NO_2 fumigation (0.5 ppm for 5 days) but only when the supply of N to the roots was low (<1 mM). At similar levels of NO_2 (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 NO_2.

Rates of entry of NO_2 into leaves, however, depend primarily on 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 well as those in the mutants which 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 N 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 N supply to the roots of many non-woody 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 McClean (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 $g^{-1}FW\ h^{-1}$) 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 three-fold 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.

9.3.2.2 Nitrite Reductase

While nitrate reductase (NaR) is located in the cytosol, probably near the cell or plasma membrane, nitrite reductase (NiR ; E.C.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 ammonia 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 30-40 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 N 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. NO produces both nitrite and nitrate ions 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 which preset the level of shoot NiR with respect to nitrate.

During CO_2-enrichment in greenhouses (see Section 9.3.1.1), fumigations with NO of different cultivars of tomato (0.4 ppm for 3 h) or lettuce (cv. Pascal, 0.3 ppm for 8 days) induce 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 NO_2 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 NO_2 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 N is regulated (Wallace and Steer, 1983). Such varietal differences are particularly interesting in view of a growth study conducted by Anderson and Mansfield (1979) which 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 NO_2 or NO (Wellburn et al., 1980).

From fumigation studies of spinach and kidney beans with high levels of NO_2 (3.5-8 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 NO_2 in the light as being mainly due to an accumulation of ammonia rather than of nitrite.

When Yoneyama et al. (1979a) exposed kidney beans (*Phaseolus vulgaris* L. cv. Shin Edogawa), sunflower (*Helianthus annuus* L. cv. Russian Mammoth) and maize (*Zea mays* L. cv. Dento) plants to 4 ppm NO_2 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. While 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 occur, 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.

9.3.2.3 Glutamate Formation and Conversion

In higher plants, ammonia released by NiR is incorporated into glutamate by means of the glutamine synthetase (GS ; E.C.6.3.1.2)/ glutamine oxoglutarate aminotransferase or glutamate synthase (GOGAT ; E.C. 2.6.1.53) cycle (see Figures 9-6 and 9-7) rather than by amination achieved using glutamate dehydrogenase (GDH; E.C. 1.4.1.3; Lea and Miflin, 1974; Miflin 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). That of GDH, by contrast, is confined to mitochondria (Miflin, 1970).

Beans (*Phaseolus vulgaris* L. cv. Kinghorn Wax) exposed to 0.02-0.5 ppm NO_2 for 5 days show increased levels of GOGAT activity (Srivastava and Ormrod, 1984) while levels of related transaminase activities were raised in a sensitive tomato cultivar (Ailsa Craig) when exposed for 14 days to 0.2-0.5 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 0.1-0.5 ppm NO_2 for 6 days although this enzyme is strongly affected by similar SO_2, NH_3, SO_2+ NH_3 and SO_2+ NO_2 fumigations (Wellburn et al., 1976).

It is presumed that GDH operates in a deaminative mode during periods of excess reduced N formation after exposure to atmospheric NO_x while the GS/GOGAT cycle (Figure 9-7) 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 base of expression (e.g., g^{-1} dry weight) which may also change in response to NO_x fumigation. When studying the effects of lower levels of atmospheric NO_2 (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

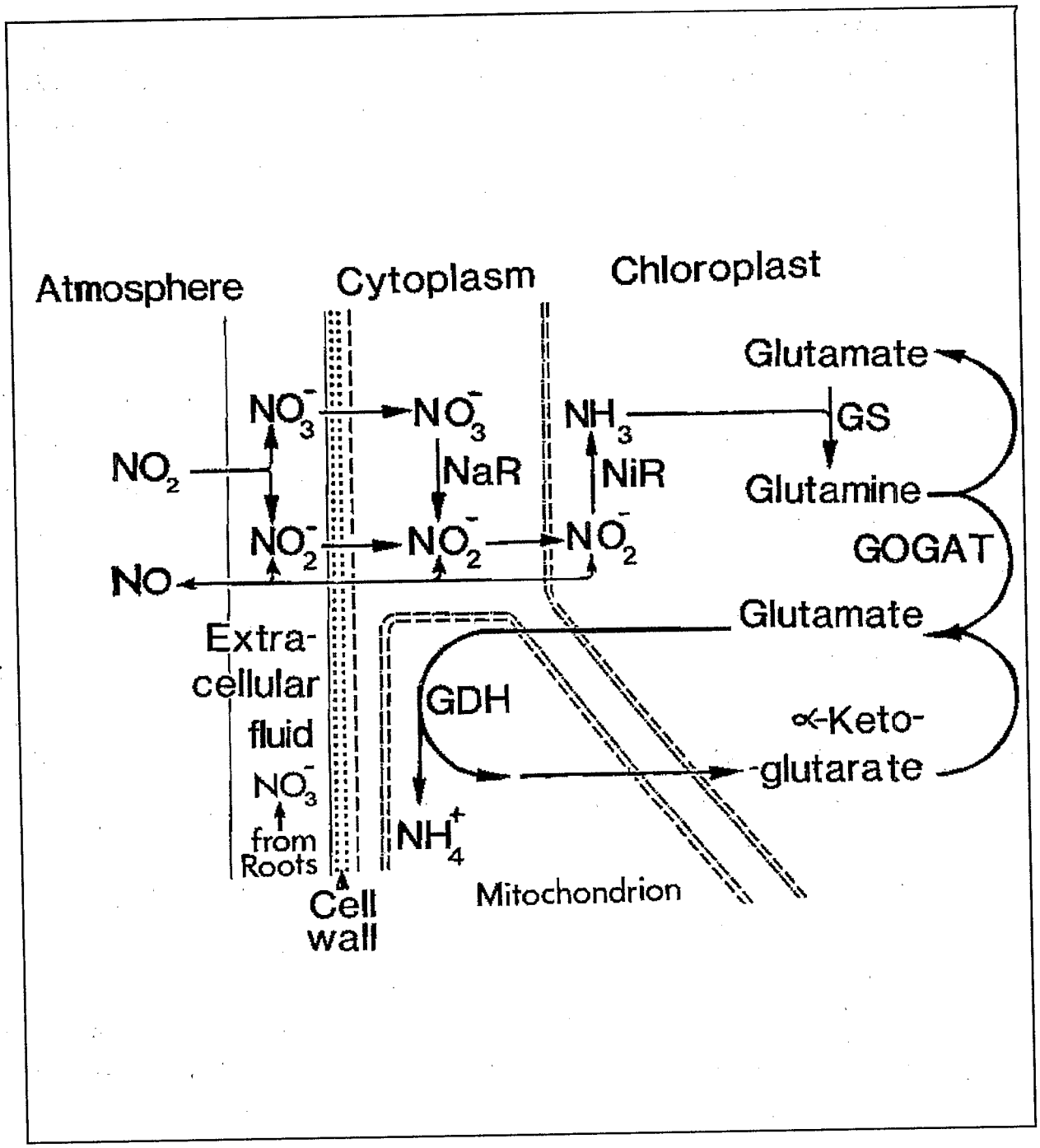

Figure 9-7. The possible interconversions between glutamate, glutamine and α-ketoglutarate which involve the uptake and release of ammonia in plants. The mitochondrial enzyme, glutamate dehydrogenase (GDH) is much more likely to catalyze the deamination of glutamate in the light.

Source: Wellburn (1988).

non-induced conversion of ammonia to glutamate by GS (and 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 (*Spinacia oleracea* L. cv. New Asia) were treated with nitrite (5 mM), either in the light or 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 ammonia fast enough. This then permits uncoupling reactions to take place (see Section 9.3.2.6) which then impairs ATP formation.

9.3.2.4 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 N.

Reports of changes in individual amino acids due to NO_x exposure are contradictory. Takeuchi et al. (1985), for example, report increases of glutamate in squash while 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.

9.3.2.5 Effects of Ammonia

Localized sources of ammonia, 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 H_2S, can add to the effect (Van der Eerden, 1982). Ammonia-affected conifers are usually prone to frost injury (see Section 10.4.2) 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 Brussel 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 ammonia which produce extra ammonium ions inside a plant. Inhibitory effects of ammonium ions acting as uncouplers of phosphorylation in both mitochondria and chloroplasts have long been known. In chloroplasts, this effect of ammonia is highly dependent on both light and pH (Crofts and Walker, 1970). Losada and Arnon (1963) used ammonium levels of 1 mM, equivalent to a dry weight content of 150 $\mu g\ g^{-1}$, to inhibit photophosphorylation. Such levels are frequently found in ammonia-damaged plant tissues. Moreover, tomato plants (cv. Moneymaker) exposed to 2.86 ppm ammonia are only injured in the dark when large amounts of ammonium (200 $\mu g\ g^{-1}$DW) accumulate in plants (Van der Eerden, 1982). In the light, however, this injury does not occur because ammonia is immediately converted to glutamine and asparagine, levels of which rise sharply if temperatures and carbohydrate contents are not limiting. This could explain the extreme sensitivity of conifers to ammonia during the winter.

9.3.3 Physiological Responses

While 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.

9.3.3.1 Dark Respiration

Srivastava et al. (1975a,b) showed that dark respiration in *Phaseolus vulgaris* L. (cv. Pure Gold Wax) was more depressed by high levels of NO_2 (1-7 ppm for 4-8 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 build-up. However, exposure of Scots pine (*Pinus sylvestris* L.) 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 (*Glycine max*. Merr.) but only at the highest levels of NO_2 employed (0.6 ppm for 2-3 h). By contrast, Sabaratnam et al. (1988b) also using soybeans (cv. Williams) found that treatment with 0.2 ppm NO_2 for 7 h day^{-1} 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 NO_2 (7 h day^{-1} for 15 days) enhanced dark respiration during fumigation but this effect disappeared afterwards (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).

9.3.3.2 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 CO_2 using

infrared gas analysis (IRGA) in the light and the dark in order to provide estimates of net photosynthesis. Using IRGA, Hill and Bennett (1970) showed that both NO and NO_2 (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 NO_2 and was reversible. Mixed fumigations with both NO and NO_2 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 due to mixtures of NO_x (0.25-0.4 ppm NO_2 and 0.1-0.15 ppm NO for 1-2 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 NO_2, SO_2, O_3 and HF. However, after 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 NO_2 concentration and length of exposure even though they used high concentrations of NO_2 (1-7 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 NO_2 on peas (*Pisum sativum* L. cv. Feltham First) but at much lower concentrations (0.05-0.25 ppm) for longer (28 days). Subsequently, Capron and Mansfield (1976) exposed tomato (*Lycopersicon esculentum* Mill. cv. Moneymaker) to mixtures of NO and NO_2 (0.10-0.50 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 CO_2 on the third day of exposure but rather less (24% reduction) at 1,000 ppm CO_2. Both these reductions in photosynthesis could not be explained by increases in stomatal resistance.

By contrast, Carlson (1983) fumigated soybeans (*Glycine max* Merr.) with NO_2 (0.2-0.6 ppm for 2-3 h) and was less convinced that NO_2 had a significant effect on net

photosynthesis measured by IRGA although he did find evidence for a reduction in photorespiration with increasing NO_2 concentrations. Likewise, Oleksyn (1984) did not find any effect of NO_2 (0.5-1 ppm) on net photosynthesis during a 2 day exposure of Scots pine (*Pinus sylvestris* L.) seedlings. Saxe (1986a), however, showed that reductions in net photosynthesis in 8 cultivars of 5 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 NO_2. 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 maintains 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 NO_2.

It is now evident that different levels of NO_2 can bring about both increases and decreases of net photosynthesis within the same species. Sabaratnam et al. (1988a) found that low levels of NO_2 (0.2 ppm, 7 h day^{-1} for 5 days) increase net photosynthesis in soybean (*Glycine max* Merr. cv. Williams) at the onset of fumigation and 24 h after fumigation ceases. However, reductions in net photosynthesis are observed at higher levels of NO_2 (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 0.5 ppm NO_2 was insufficient to compensate for the large decrease (51%) of the net assimilation ratio (NAR) which caused a decline in relative growth rate (RGR). These observations are similar to those of Okano et al. (1985b) when they fumigated sunflowers (*Helianthus annuus* L. cv. Russian Mammoth) and maize (*Zea mays* L. cv. Dento) with a range of NO_2 concentrations (up to 1 ppm) for 14 days. At levels of 0.2 ppm, NAR was significantly raised (10%) but, at 0.5 ppm NO_2, was reduced to a similar extent. These changes in NAR could be accounted for by changes in LAR. NAR and RGR also increased when black turtle beans (*Phaseolus vulgaris* L. cv. Domino) were exposed to 0.1 ppm NO_2 (7 h day^{-1}) for 15 days (Sandhu and Gupta, 1989) but the LAR was unaffected.

Assimilation rates of $^{13}CO_2$ determined by ^{13}C-NMR spectroscopy are not in accord with the majority of IRGA studies of the effects of NO_2 on net photosynthesis. This is partly explained by the fact that this technique measures only unidirectional uptake of CO_2 while

IRGA measures bidirectional flow of CO_2. Exposure of kidney beans (*Phaseolus vulgaris* L. cv. Shin Edogawa) to 2 ppm NO_2 for 4 days enhanced $^{13}CO_2$ 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 NO_2 had no effect on $^{13}CO_2$ 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 takes place.

Studies of the effects of NO_2 alone on carbon allocation are rare. Amounts of soluble sugars, especially glucose, in kidney beans (cv. Shin Edogawa) exposed to high levels of NO_2 (2-4 ppm for 7 days) were significantly decreased in the roots by 4 ppm NO_2, 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 NO_2 for this to occur.

Another non-invasive technique which 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), O_3 (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 NO_2 for up to 4 days had virtually no effect on either the pattern of induction or the peak values of emitted fluorescence (Murray, 1984). However, Shimazaki (1988) has been able to demonstrate an effect of NO_2 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 9.3.3.1) lead to the general conclusion that, in many instances, investigators have been dealing with different exposure conditions and with situations where different levels of NO_2 can produce opposing effects. It is now clear that many studies claiming to have fumigated just with NO_2 may have also contained NO but, worse than that, many control treatments which have used activated charcoal to clean the air may have still contained significant levels of NO (see Section 9.3.2). 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 then 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 15-20% 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 NiR activity (see Section 9.3.2.2).

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 affect 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 (RubisCO) are 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 ammonium ions (see Section 9.3.2.5), nitrite has no inhibitory effect on in vitro determinations of the rates of phosphorylation (Asada et al., 1968) which implies that both nitrite and ammonia levels are tightly controlled if the influx of N 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 in 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 O_3 alone and the combined effects of nitrite and sulfite (Robinson and Wellburn, 1983) which could arise from mixed exposures to SO_2 and NO_x. (see Section 9.6.4.4).

This similarity in response between O_3 alone and mixtures of SO_2 and NO_x has been known for some time (Reinert et al., 1975). Furthermore, mixed fumigations of peas (cv. Waverex) with either O_3 alone (0.15 ppm) or with $SO_2 + NO_2 + O_3$ (0.05 ppm each) for 21 days enhance 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 NO_2 (1 ppm, 2 h day^{-1}), significant reductions (17%) in ascorbate levels were detected (Prasad and Rao, 1980).

Wellburn (1985) fumigated barley (cv. Patty) seedlings for 1-3 days with NO_2 (0.28 ppm) and measured the levels of nitrite and nitrate inside the chloroplasts using HPIC. Levels of nitrate actually fell by 45% inside the plastids 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 carried out 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; Foyer, 1986; Heldt et al., 1986). In a wider context, therefore, reduced availability of ATP for synthesis of starch, amino acids and 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 CO_2 (Thomas et al., 1976; Larsson et al., 1985). At levels of 0.5 mM nitrite, CO_2 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 CO_2 and nitrite do not compete for reductant at saturating light intensities. In an attempt to resolve these inconsistencies, Peirson and Elliott (1988) have examined the effect of bicarbonate on the nitrite utilization/concentration interrelationships at the whole plant level. They conclude that, while there are differences between species, fixation of CO_2 and reduction of nitrite only compete at low light levels and high nitrite concentrations. But these are the very conditions that prevail in plants exposed to atmospheric NO_x in northern latitudes. Consequently, this competition for reductant is likely to be a very important component in any physiological explanation of lack of growth caused by NO_x.

9.3.3.3 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 N 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 N balance of plants. More than one possible pathway exists in leaves for the absorption of N from NO_2 (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 ^{15}N-labeled NO_2 have shown uptake by roots after NO_2 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 NO_2 absorbed by the soil is likely to be converted to nitrate and nitrite by soil microorganisms (see Chapter 10.1.3). Yoneyama et al. (1979b) found that although nitrite only accumulates in the upper soil layer, increases in ammonia 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 soil nitrate concentration which had been fumigated with 0.25 ppm NO_2 for 45 days. Some N 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 $^{15}NO_2$ (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 $^{15}NO_2$ 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 N 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 *Phaseolus vulgaris* L. (cv. Kinghorn Wax) seedlings to various levels of NO_2 (0.02 to 0.5 ppm, 6 h day^{-1} for 15 d). They found exposure to atmospheric NO_2 increased the levels of N in the roots but decreased nodule weight and levels of nitrogenase activity. This is what would have been predicted if more

N as a proportion of total N is taken up by the leaves as NO_x since high root N inhibits nodulation.

9.3.4 Tissue and Organ Responses

9.3.4.1 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; Rowland and Gause, 1971; Pryor and Lightsey, 1981). Two types of reactions take place within fatty acids. Attachment of the NO_2 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 NO_2?". Mudd et al. (1984) concluded that the ambient levels of NO_2 are much too low to have such effects.

Ambient levels of O_3, rather than those of NO_2, 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 which favored the idea that attack by O_3 occurs more readily on proteins. Clearly, this whole field should be reexamined and such studies should include mixed effects of NO_2, NO and O_3 upon membranes because a photodynamic equilibrium exists naturally in the atmosphere (Section 9.3.1.1) and some previous O_3 exposures may have inadvertently included various mixtures of NO and NO_2 (Section 9.2.2).

There are strong indications that atmospheric NO_2 inhibits lipid biosynthesis rather than causing damage to existing lipids in membranes. Fumigation of *Pinus banksiana* seedlings with 2 ppm for 2 days inhibited the biosynthesis of phospholipids and galactolipids (Malhotra and Khan, 1984) while 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 the light possibly because adequate amounts of NADPH are not available at night.

9.3.4.2 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 obvious "visible" injury. In the former there is an overall reduction in growth but no obvious signs of visible injury. It is often associated with decreases in transpiration and photosynthesis (see Section 9.3.3.2) but a variety of ultrastructural changes have also been associated with "invisible" air pollution injury (Huttunen and Soikkeli, 1984; Fink, 1988).

Ultrastructural examination of bean leaves exposed to NO_2 has shown changes in the ultrastructure of both mitochondria and chloroplasts due to this pollutant. In an early series of experiments studying the effects of exceptionally large quantities of NO_2 (1% or 1,000 ppt) on *Phaseolus vulgaris*, Dolzmann and Ullrich (1966) observed protrusions from both plastids and mitochondria which appeared to enclose the latter. In later experiments, using lower amounts of NO_2 (0.5-3 ppm for 2-4 h) on broad bean (*Vicia faba* L. cv. Windsor Harlington) leaves, the observed swelling of the plastid thylakoids was interpreted at the time as a response to ionic effects such as a build up of osmotically active compounds which could then have an effect on photosynthesis (Wellburn et al., 1972). During short exposures of 1 h at 0.5 ppm NO_2, this swelling was reduced when the leaves were returned to unpolluted air. What is not certain, as with all studies of this nature, is if such ionic changes actually occur at the time of exposure or during the processing for electron microscopy. Huttunen and Soikkeli (1984) in their review of ultrastructural effects of air pollutants argue for the former and suggest that this type of swelling is a general symptom of acute injury found with many different types of air pollutants because it is also shown by many of their samples and those of others taken from polluted locations outdoors where the pollution climate has not been defined.

In the only other 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, 1982) 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 which accompanies the accumulation of nitrite which accounts for the toxicity (Bingham et al., 1954; Zeevaart, 1976; Lee, 1978). Nitrite ions are reduced inside the chloroplast (Section 9.3.2.2) and therefore all pollutant-derived N 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 9.3.3.2).

Zeevaart (1976) concluded that acidification will only damage plants at high concentrations of NO_2 since nitrite reductase requires six protons from the stroma for every nitrite ion 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 9.6.4.4) which are important, for example, in the regulation of fructose-1,6-*bis*-phosphatase activity (Buchanan et al., 1979).

9.3.5 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 thereafter NO_2 has an inhibitory effect on pigment biosynthesis (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 d^{-1}) 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 d^{-1} for 5 d) had a stimulatory effect on chlorophyll a and total chlorophyll content, while 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 (50-150 ppb each for 7 h) were given along with 50 ppb O_3, ethane as well as ethylene was also evolved but, more significantly, extensive visible injury did occur. Mehlhorn and Wellburn (1987) concluded from these observations that, while 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* from NO_2 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 of some part of the plant, most often in its foliage, that is

*Injury has been defined as "any change in the appearance and/or function of a plant that is detrimental to the plant." American Phytopathological Society. 1974. Glossary of air pollution terms and selected reference list. Phytopathol. News 8: 5-8.

observable by the unaided eye or through a lens of low magnification. Generally, these changes involve the death, discoloration, distortion, or loss of foliar tissue.

Foliar symptoms have a practical significance in three ways. Firstly, they constitute a diminution of the aesthetic or economic value of the plant when this depends upon the appearance of its foliage. Secondly, they offer one diagnostic means for assessing the occurrence of NO_2-induced effects in vicinities of some sources (Taylor and MacLean, 1970; Donagi and Goren, 1979). Thirdly, because symptoms are an easily observed manifestation of a change in the state of the plant, they are a means of determining the nature of the plant's response to NO_2 and the effects of various factors upon it.

9.4.1.1 Characteristics of Foliar Symptoms

There is no single type of symptom that is distinctive for NO_2-induced foliar injury (National Research Council, 1977), and the types induced by NO_2 are similar to those induced by other air pollutants, such as sulfur dioxide (SO_2), hydrogen fluoride (HF), or ozone (O_3) (Matsushima, 1977). The kind of lesion produced and its location on the leaf depend upon concentration of NO_2, 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 different species of plants in the same location. NO_2-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 NO_2 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 NO_2 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 to its upper to lower surface. The resulting necrotic lesions are usually indistinguishable from those produced by SO_2. On most broad-leaved plants, NO_2-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, NO_2-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 leaves. In species with finely dissected compound leaves, such as carrot and parsley, NO_2-induced injury is usually confined to the tips and margins of the leaflets.

Narrow-leaved (monocotyledonous) plants: Acute exposures to NO_2 of narrow-leaved plants most frequently result in a necrosis that is yellow-to-ivory-to-white and 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 NO_2; bleached necrosis begins at the tips and progresses towards the base.

Coniferous plants: Injury to leaves of conifers from acute exposures to NO_2 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 which 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 NO_2-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 four hours or 250 ppm for one hour) (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).

9.4.1.2 Exposure-effect Relationships

Three important characteristics of foliar injury with respect to the structure of 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; (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.

Short-term (Acute) 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 NO_2. Nevertheless, a relationship between the concentration of NO_2 (C_I) required to produce a certain percentage of foliar injury (I) and the duration of exposure was tested in short-term ($\leq$8 hours) exposures with eleven species of plants (Heck and Tingey, 1979) and is given in Equation 1. This represents a development of the O'Gara-Thomas form, which was

[1] $$C_I = a_0 + a_1 I + a_2 T^{-1}$$

derived for the effects of SO_2 (Thomas and Hill, 1935) and is expressed in Equation 2 with the substitution of the terms c_I for $a_0 + a_1$ I and k_I for a_2. The parameter c_I

[2] $$C_I = c_I + k_I T^{-1} \qquad \text{for} \quad C_I \geq c_I$$

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 SO_2-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 3. For the defoliation of citrus by acute exposures to NO_2, it was proposed

[3] $$C_I = c_0 + k_0 T^{-b} \qquad \text{for} \quad C_I \geq c_0 \,;\; 1 \geq b > 0$$

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 hours and concentration of NO_2 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 SO_2 and O_3 (Larsen and Heck, 1976). This is expressed by Equation 4 where: I is the fraction of foliar area injured; C_I is the concentration that

[4] $$C_I = c_m T^{-b} s^z \qquad \text{with} \quad I = \Phi(z)$$

produces this amount of injury with an exposure of duration equal to T (in hours); c_m is the concentration required to produce injury on 50% of the foliar tissue on a plant of median tolerance in a one-hour 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); and, Φ is the integral of the normal distribution function. Although this has not been tested with NO_2, it could be applicable.

These relationships are consistent with what is known about the mechanisms of action of NO_2 (Section 9.3). For example, it can be assumed that the rate of uptake of NO_2 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 3), 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, a NO_2-induced increase in the rate of level of nitrate and nitrite reductase 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 minutes produced about 50% more injury than did three 20-minute exposures separated by intervals of 10 minutes (Matsushima, 1971). Similarly, a series of seven 30-minute exposures declined in effectiveness with an increase in the length of the period between exposures from 10 to 45 minutes (Zahn, 1975).

Based on experimentally derived estimates for the parameters in Equation 1, the concentrations of NO_2 required to produce 5% foliar injury for different durations of exposure are given in Figure 9-8 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 hours to 2 ppm for 8 hours. These concentrations are, respectively, from 120- to 40-fold greater than the NAAQS primary standard of 0.05 ppm, and it has been observed that the ratio of a one-hour maximum concentration to the annual arithmetic mean concentration rarely exceeds the value of 12 (Chapter 8, U.S. Environmental Protection Agency, 1982).

Long-term (Chronic) Exposures

The derivation of an exposure-effect relationship for foliar injury is inherently more problematic for a long-term (chronic) exposure than for an acute 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 exposure, there is the

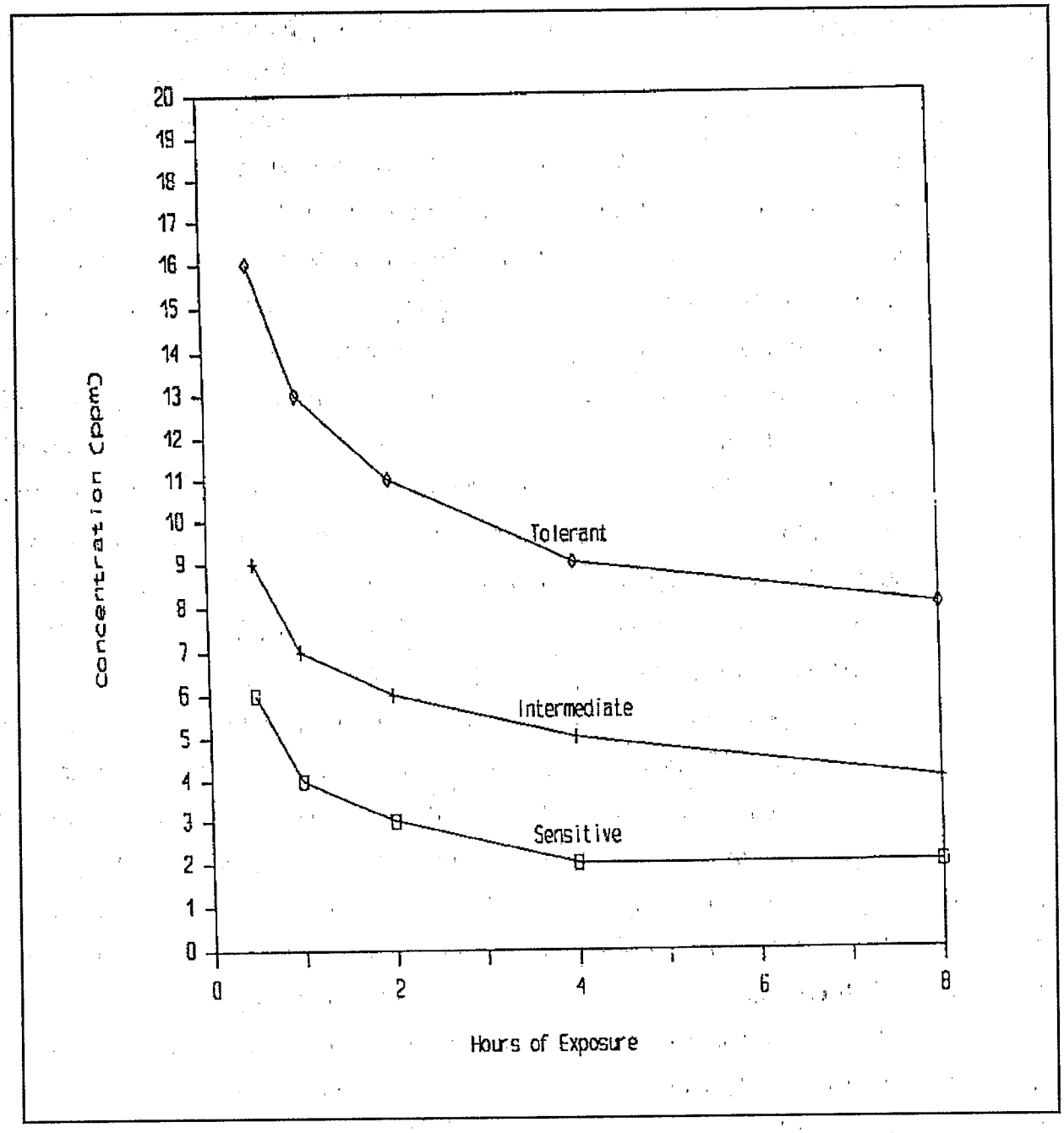

Figure 9-8. Minimum exposures to NO_2 required to produce 5% foliar injury on sensitive, intermediate, and tolerant categories of plants (after Heck and Tingey, 1979).

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 episodes (day/night) 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 9-3.

These results are also summarized in Figure 9-9 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; concentration is expressed as that of NO_x when present and not the arithmetic mean for the entire experimental period. Also present in Figure 9-9 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 (two-fold the annual mean for 10% of the hours); 0.15 ppm for 87 h (three-fold 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 one-hour 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 hours per day for 35 days (total of 140 hours) produced chlorotic lesions on one-third of the clones of eastern white pine (Yang et al., 1982,1983a,b); exposures for 6 hours per day for 28 days (total of 168 hours) 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 continuously for 8 months (Thompson et al., 1970). The mass of leaves dropped tended to increase with the concentration of NO_2 but neither the trend nor the effect of NO_2 at the

TABLE 9-3. COMPILATION OF OCCURRENCE OF FOLIAR SYMPTOMS IN LONG-TERM OR INTERMITTENT EXPOSURES TO NO_x IN EXPERIMENTAL INVESTIGATIONS

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/wk, 56 wk	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 1 of 4 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 1 of 2 cultivars of potato (Petitte and Ormrod, 1988)
0.11	104 h/wk, 8 wk	No injury to orchard grass or Kentucky bluegrass (Ashenden, 1979b)

TABLE 9-3 (cont'd). COMPILATION OF OCCURRENCE OF FOLIAR SYMPTOMS IN LONG-TERM OR INTERMITTENT EXPOSURES TO NO_x IN EXPERIMENTAL INVESTIGATIONS

NO_x ppm	Exposure Duration	Effect (occurrence of foliar lesions)
0.11	104 h/wk, 20 wk	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/wk, 12 wk	No lesions but premature senescence and defoliation in potato (Sinn and Pell, 1984)
0.20	5 h/day, 2 days/wk, 16 wk	No lesions but premature senescence and defoliation in potato (Sinn and Pell, 1984)
0.20	4 h/day, 35 days	Injury to 2 of 3 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 and Totsuka, 1985)
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 wk	No injury to azalea (Sanders and Reinert, 1982a)
0.25	9 h/day, 3 days	No injury to petunia (deCormis 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/wk, 3 wk	No injury to radish (Reinert and Sanders, 1982)

TABLE 9-3 (cont'd). COMPILATION OF OCCURRENCE OF FOLIAR SYMPTOMS IN LONG-TERM OR INTERMITTENT EXPOSURES TO NO_x IN EXPERIMENTAL INVESTIGATIONS

NO_x ppm	Exposure Duration	Effect (occurrence of foliar lesions)
0.30	4 h/day, 35 days	Injury to 2 of 3 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/wk, 3 wk	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/wk, 16 wk	No injury to creosote bush, desert willow, or brittle bush (Thompson et al., 1980)
0.33	5 h/day, 5 days/wk, 32 wk	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 (deCormis and Luttringer, 1977)
[a]0.40	24 h/day, 21 days	No injury to tomato (Wellburn et al., 1976)
[a]0.40	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 (deCormis 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 (deCormis 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 9-3 (cont'd). COMPILATION OF OCCURRENCE OF FOLIAR SYMPTOMS IN LONG-TERM OR INTERMITTENT EXPOSURES TO NO_x IN EXPERIMENTAL INVESTIGATIONS

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 and Totsuka, 1985)
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)
[b]0.7	24 h/day, 21 days	No injury to 4 cultivars of tomato (Mortensen, 1985b)
[b]0.7	24 h/day, 28 days	Injury to 3 of 4 cultivars of tomato (Mortensen, 1985b)
[c]0.85	24 h/day, 18 days	No injury to cucumber (Mortensen, 1985a)
[c]0.85	24 h/day, 22 days	No injury to tomato (Mortensen, 1985a)
[c]0.85	24 h/day, 35 days	No injury to chrysanthemum (Mortensen, 1985a)
[c]0.85	24 h/day, 43 days	No injury to rose or baby's tears (Mortensen, 1985a)
[c]0.85	24 h/day, 55 days	No injury to English ivy (Mortensen, 1985a)
[c]0.85	24 h/day, 77 days	No injury to English ivy or Boston fern (Mortensen, 1985a)
[c]0.85	24 h/day, 104 days	No injury to African violet (Mortensen, 1985a)
[c]0.85	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)
[a]1.0	10 h/day, 139 days	No injury to English or Algerian ivy, rubber tree, benjamin tree, hibiscus, Boston fern; scorching on Dieffenbachia (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	1900 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 9-3 (cont'd). COMPILATION OF OCCURRENCE OF FOLIAR SYMPTOMS IN LONG-TERM OR INTERMITTENT EXPOSURES TO NO_x IN EXPERIMENTAL INVESTIGATIONS

NO_x ppm	Exposure Duration	Effect (occurrence of foliar lesions)
[a]1.0	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., 1986); younger leaves of sunflower were crinkled and darker green (Okano and Totsuka, 1985)
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/wk, 12 wk	No injury to alfilaria (Thompson et al., 1980)
1.0	5 h/day, 5 days/wk, 16 wk	No injury to *Chaenactis carphoclina*, saltbush or burro weed; injury to creosote bush, desert willow, brittle bush (Thompson et al., 1980)
1.0	5 h/day, 5 days/wk, 17 wk	No injury to scorpion weed (Thompson et al., 1980)
1.0	5 h/day, 5 days/wk, 32 wk	No injury to burro weed; injury to brittle bush, creosote bush, desert willow, saltbush (Thompson et al., 1980)
1.2	30 h	
[b]1.5	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)

[a]NO.
[b]20% NO_2 + 80% NO.
[c]0.15 ppm NO_2 + 0.70 ppm NO.
[d]50% NO_2 + 50% NO.
[e]Mean for period.

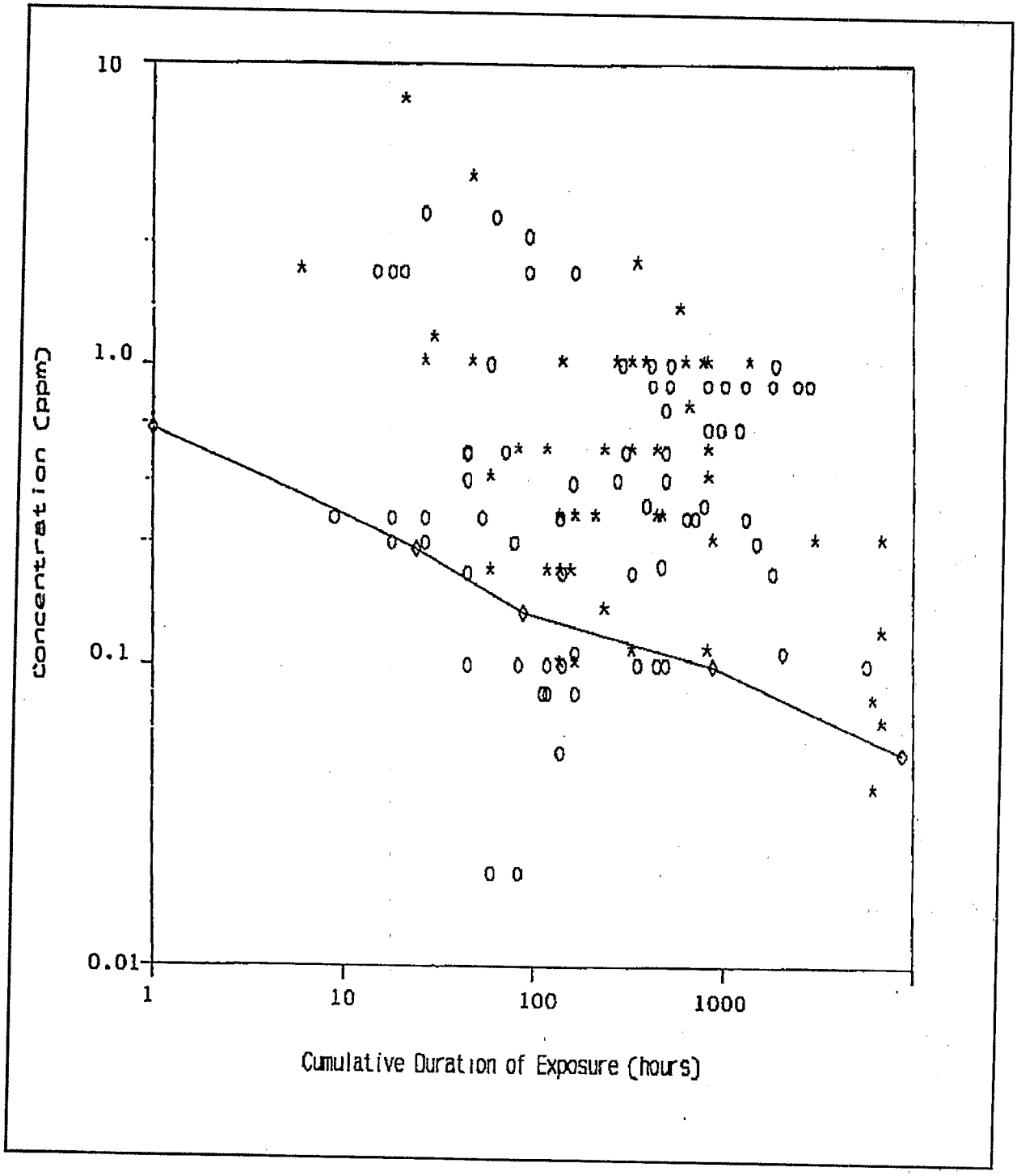

Figure 9-9. Occurrence (*) or absence (o) of foliar injury from NO_x in long-term experimental exposures.

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 NO_2-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 9.B. 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 9-10 with reference to what could be considered an upper boundary of exposures consistent with some characteristics of ambient exposures in the United States.

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 one hour would not be consistent with one-hour maxima observed in ambient monitoring or with the ratios of one-hour 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). Similarly, a mean concentration of greater than 0.2 ppm for a period of 24 hours or more would not be consistent with ambient exposures. Other order statistics

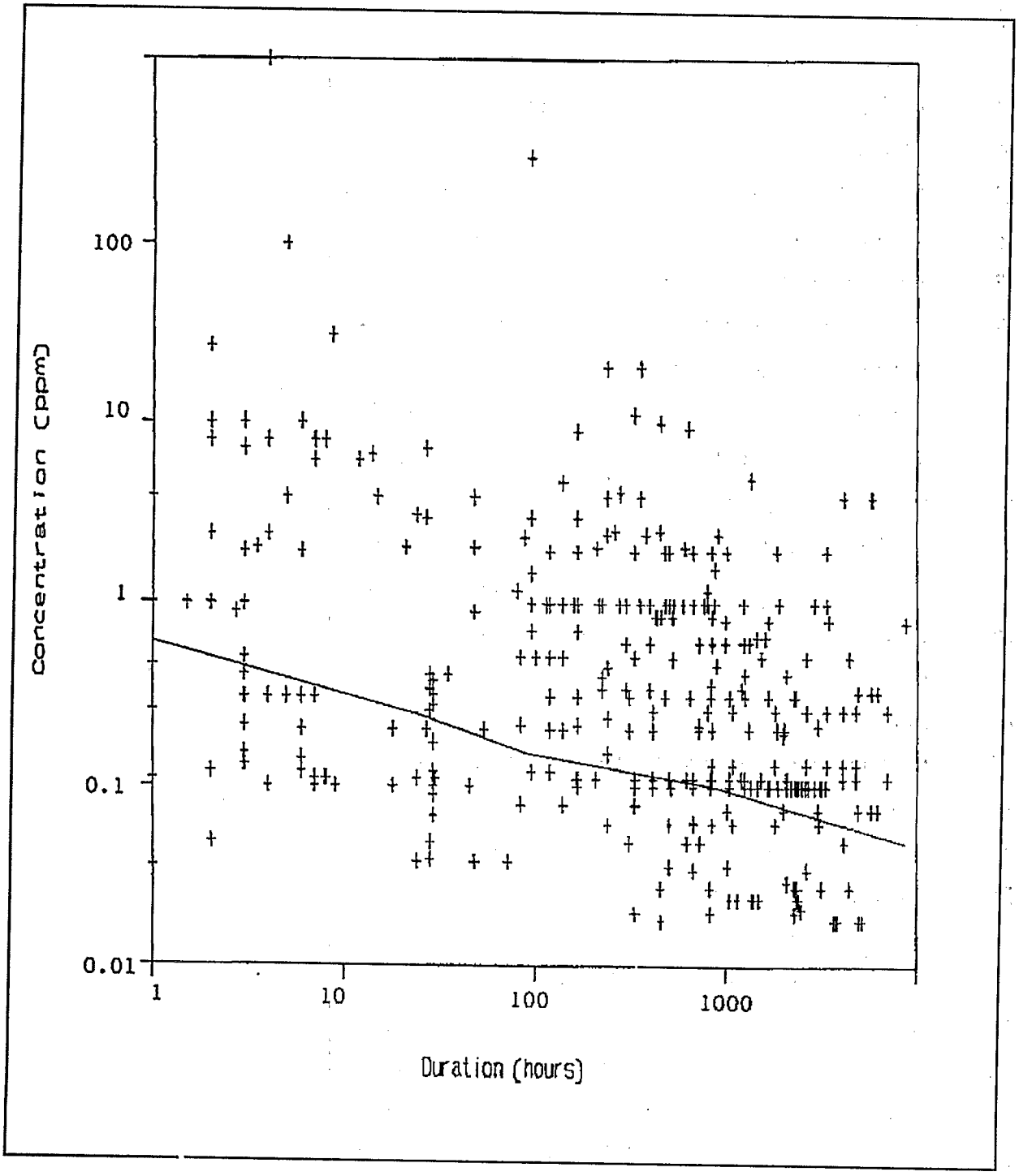

Figure 9-10. Exposures employed in experimental investigations on the effect of NO_x on growth and yield of plants.

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. 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 9-4. 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 9-11) and green bean (Figure 9-12). 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 upon 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 hours per day, 1 day per week, for 3 weeks or (Edelbauer and Maier, 1988) or at 0.1 ppm for 15 days (Elkiey et al., 1988) had no effect on growth; but at 0.12 ppm (2 h/day, 1 day/wk, 3 weeks) it significantly 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).

TABLE 9-4. SOME EFFECTS OF NO_X ON THE GROWTH AND YIELD OF PLANTS WITH RESPECT TO CONCENTRATIONS AND EXPOSURES USED IN EXPERIMENTAL INVESTIGATIONS

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 + NO at 0.012 ppm] (Lane and Bell, 1984).
0.02	5 days	Increase in plant height and decrease in mass and area of leaf depended upon 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 upon 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, 1984).
0.025	7 h/day, 5 days/wk, 3 wk	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 + NO at 0.007 ppm] (Lane and Bell, 1984).
0.03	8 wk	Did not significantly affect mass of plant but advanced bud-break in 6-month-old seedlings of Sitka spruce exposed during dormancy (Freer-Smith and Mansfield, 1987).
0.039	2 h/day, 1 day/wk, 3 wk	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 wk	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/wk, 3 wk	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 wk	No significant effect on mass of roots, stem, or leaves in month-old seedlings of European white birch (Freer-Smith, 1985).

TABLE 9-4 (cont'd). SOME EFFECTS OF NO_X ON THE GROWTH AND YIELD OF PLANTS WITH RESPECT TO CONCENTRATIONS AND EXPOSURES USED IN EXPERIMENTAL INVESTIGATIONS

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 wk	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/wk, 3 wk	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 upon 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., 1982).
0.1	4 h/day, 35 days	Significantly reduced length and mass of needles, depending upon 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 of 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/wk, 8 wk	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 9-4 (cont'd). SOME EFFECTS OF NO_X ON THE GROWTH AND YIELD OF PLANTS WITH RESPECT TO CONCENTRATIONS AND EXPOSURES USED IN EXPERIMENTAL INVESTIGATIONS

NO_x ppm	Exposure Duration	Effect (occurrence of foliar lesions)
0.1	104 h/wk, 21 wk	No effect on mass of Kentucky bluegrass seedlings exposed from emergence (Whitmore and Mansfield, 1983; Whitmore et al., 1982).
0.1	104 h/wk, 22 wk	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/wk, 28 wk	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/wk, 33 wk	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/wk, 60 wk	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 wk	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/wk, 12 wk	No effect on height or mass of plant or on number of inflorescences in *Chaenactis carphoclina* (Thompson et al., 1980).
0.11	5 h/day, 5 days/wk, 17 wk	No significant effect on height or mass of plant or on number of inflorescences in alfilaria, desert marigold, scorpion weed; or, on mass of plant in *Plantago insularis* (Thompson et al., 1980).
0.11	5 h/day, 5 days/wk, 16 wk	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/wk, 32 wk	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 mumber of inflorescences in brittle bush (Thompson et al., 1980).

TABLE 9-4 (cont'd). SOME EFFECTS OF NO_X ON THE GROWTH AND YIELD OF PLANTS WITH RESPECT TO CONCENTRATIONS AND EXPOSURES USED IN EXPERIMENTAL INVESTIGATIONS

NO_x ppm	Exposure Duration	Effect (occurrence of foliar lesions)
0.11	104 h/wk, 4 wk	No effect on mass of green leaves, of dead leaves and stubble, or of roots, leaf area, number of leaves or of tillers in common timothy, Italian ryegrass, (Ashenden and Williams, 1980; Ashenden and Mansfield, 1978) or in orchard grass (Ashenden, 1979b); mass of roots reduced in Kentucky bluegrass (Ashenden, 1979b).
0.11	104 h/wk, 8 wk	No effect on mass of green leaves, of dead leaves and stubble, or of roots, leaf area, number of leaves or 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, of dead leaves and stubble, or of 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 one-year black poplar cuttings (Freer-Smith, 1984; Whitmore et al., 1982).
0.11	104 h/wk, 10 wk	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/wk, 12 wk	Significantly decreased mass of green leaves in orchard grass (Ashenden, 1979), 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 of leaf area and number of leaves in Kentucky ryegrass (Ashenden, 1979).
0.11	104 h/wk, 16 wk	No effect on mass of green leaves, of dead leaves and stubble, or of roots, leaf area, and number of leaves or tillers in orchard grass (Ashenden, 1979) 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, of roots, and of leaf area in Kentucky bluegrass (Ashenden, 1979).
0.11	104 h/wk, 20 wk	No effect on mass of green leaves, of dead leaves and stubble, or of roots, leaf area, 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, 1979) also mass of green leaves, of dead leaves and stubble, and of roots in Kentucky bluegrass (Ashenden, 1979).
0.11	104 h/wk, 22 wk	No effect on growth in mass of stem or roots in one-year black poplar cuttings (Freer-Smith, 1984; Whitmore et al., 1982).
0.12	2 h/day, 1 day/wk, 3 wk	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 9-4 (cont'd). SOME EFFECTS OF NO_X ON THE GROWTH AND YIELD OF PLANTS WITH RESPECT TO CONCENTRATIONS AND EXPOSURES USED IN EXPERIMENTAL INVESTIGATIONS

NO_x ppm	Exposure Duration	Effect (occurrence of foliar lesions)
0.15	10 days	No effect on area of 3rd 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, 1981).
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 wk	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 wk	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/wk, 12-16 wk	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 wk	Significantly decreased masses of stems and leaves and length of shoot in 2 out of 8 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 9-4 (cont'd). SOME EFFECTS OF NO_X ON THE GROWTH AND YIELD OF PLANTS WITH RESPECT TO CONCENTRATIONS AND EXPOSURES USED IN EXPERIMENTAL INVESTIGATIONS

NO_x ppm	Exposure Duration	Effect (occurrence of foliar lesions)
0.3	3 h/day, 3 days in 1 wk	No effect in 30-day-old radish plants (Sanders and Reinert, 1982a).
	6 h/day, 3 days in 1 wk	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 wk	No effect in 30-day-old radish plants (Reinert and Sanders, 1982).
	6 h/day, 9 days in 4 wk	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; but, 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., 1980).
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 upon level of nitrate in 23-day-old green bean seedlings (Srivastava and Ormrod, 1986).

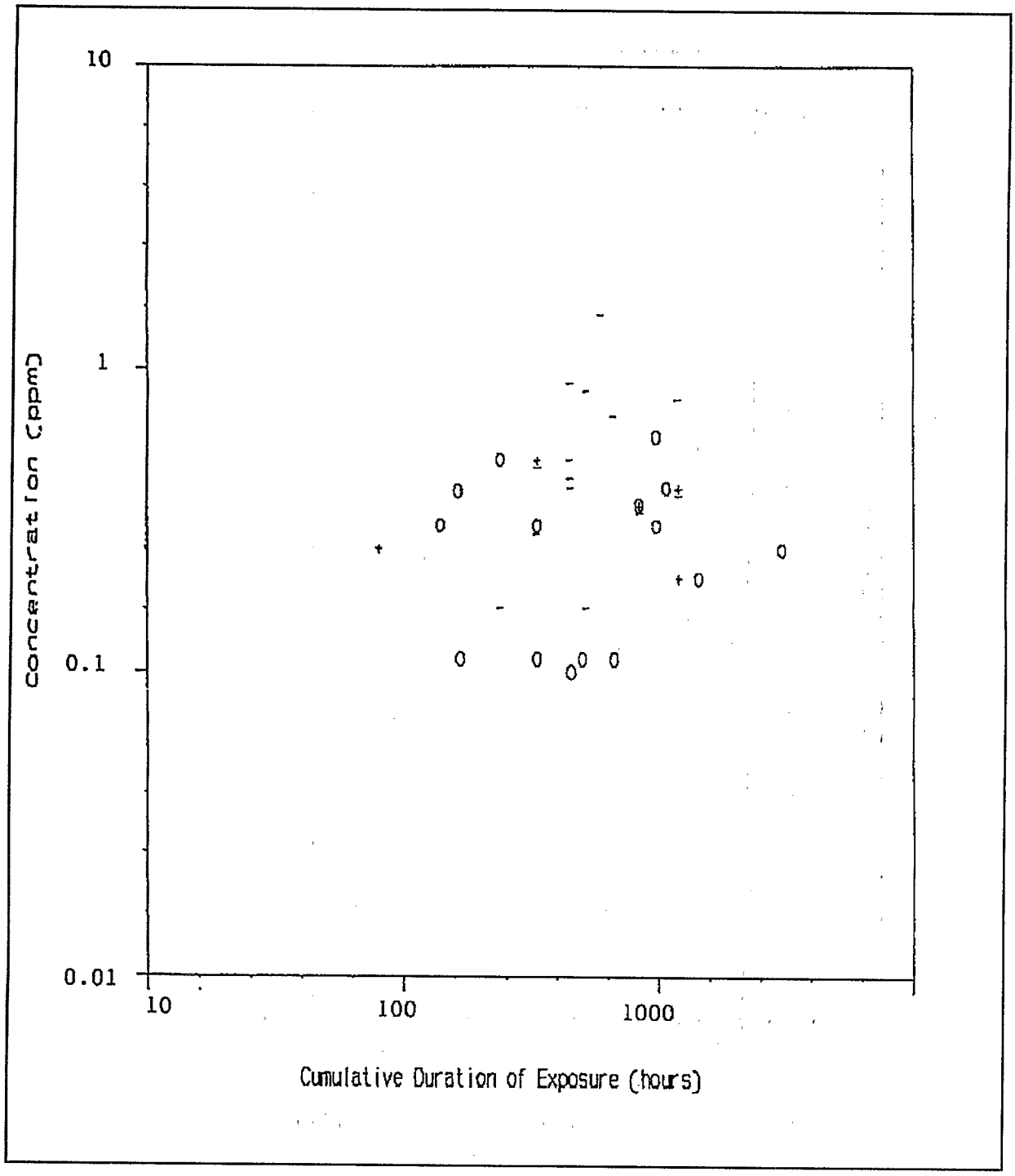

Figure 9-11. Experimental exposures to NO_x resulting in the occurrence of increased (+), decreased (-), or unaffected (o) growth or yield in tomato.

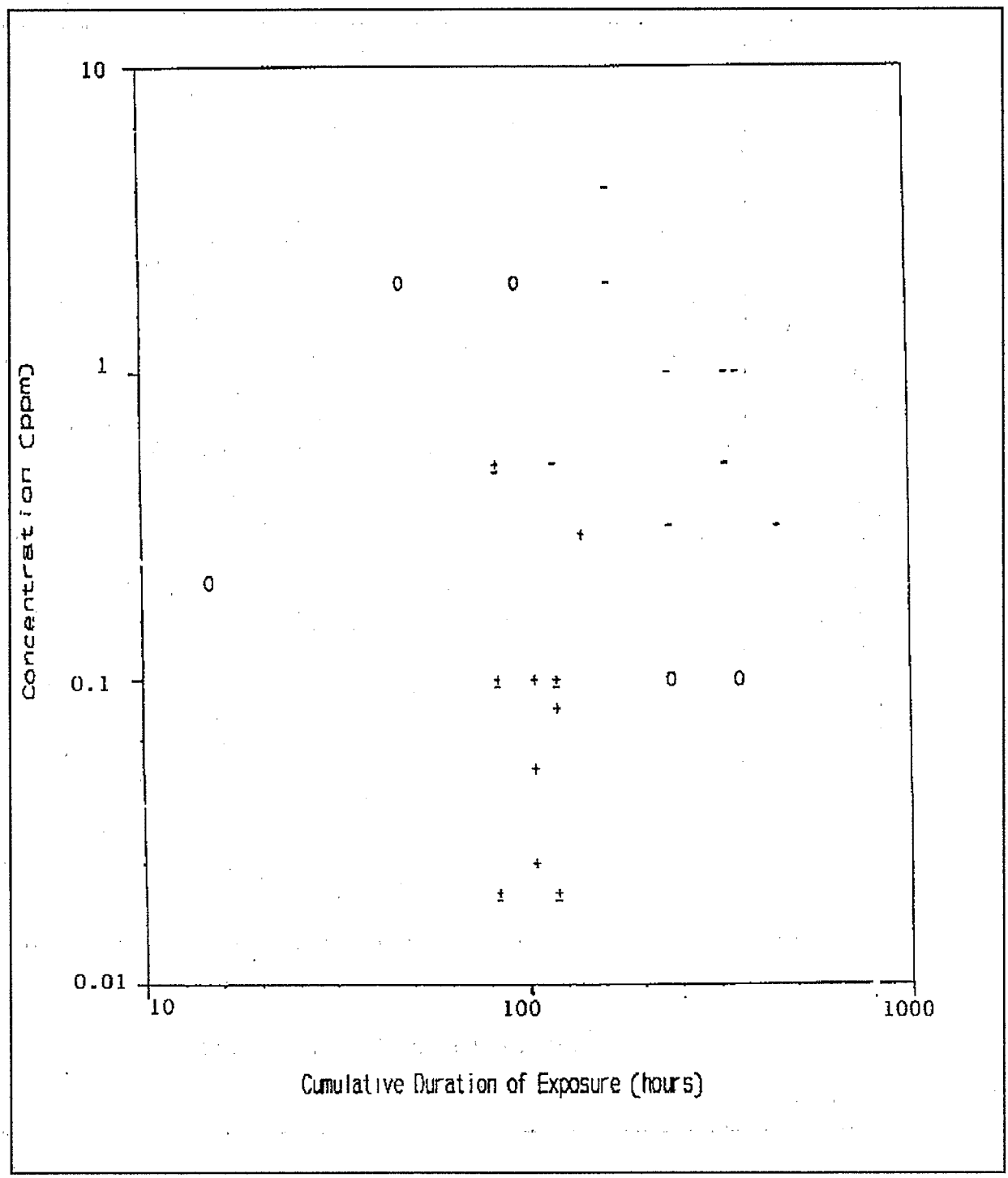

Figure 9-12. Experimental exposures to NO_x resulting in increased (+), decreased (-), or unaffected (o) growth or yield in green bean.

In several species, stimulations of growth occurred at lower concentrations of NO_x than did inhibitions. For example, a one-hour exposure to NO_2 at 0.5 ppm produced a 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 produced a significantly decreased mass of stem in black poplar and a decreased height in Carolina poplar (Eastham and Ormrod, 1986). In radish, exposure to NO_2 at 0.08 ppm, for 3 hours per day for 40 days, produced substantial increases in 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 in 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., 1980), 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 hours per day, 2 days per 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 (for 7, 14, or 15 days) exposures to lower concentrations (0.10 or 0.11 ppm NO_2) had no effect on the growth of younger (20-, 24- or 30-day-old) plants (Petitte and Ormrod, 1984,1988; Elkiey 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 NO_2 ranging from 0.12 to 0.37 ppm for an average of 2.5 hours per event in one year or concentrations from 0.07 to 0.4 ppm for an average of 2.9 hours 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 hours per day, once every 2 days, for 15 events to NO_2 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 at NO_2 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 hours per 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 ppm for 7 hours, when plants were one month 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 NO_2 to charcoal-filtered ambient air. No significant effects of NO_2 with an 8-month 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. Although yield of trees subjected to the lowest concentration of NO_2 was not significantly different from those receiving filtered air, pooled values for the three lower concentrations gave a significant reduction in number of fruit of 51% and mass of fruit of 45% (Thompson et al., 1970).

Five species each of desert annuals and shrubs were subjected to intermittent exposures (5 hours/day for 5 days/week) to NO_2 at 0.11, 0.33, or 1.0 ppm under greenhouse conditions for periods ranging from 9 to 32 weeks (depending upon species). At the lowest

concentration of NO_2, there was no significant effect on height or mass of plant or on number of inflorescences in *Chaenactis carphoclina* after 12 weeks, on mass of plant in *Plantago insularis* 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; (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 hours or less that could produce adverse effects are at concentrations of NO_2 greater than what have been shown to occur in ambient exposures in the United States. In periods of two 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 upon the species of plant, nature of effect, and conditions of exposure.

9.5 FACTORS AFFECTING PLANT RESPONSE TO NO_X

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; (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 9.A). 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 NO_2-induced effects on commercial value (Mortensen, 1985a; Saxe, 1986a; Saxe and Christensen, 1985). The results of several of these studies are summarized in Table 9-5.

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

TABLE 9-5. RELATIVE SENSITIVITIES OF PLANTS TO NITROGEN DIOXIDE[a]

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

TABLE 9-5 (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
Pyracantha	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 plantain	Cheeseweed	Lamb's-quarters
Common mugwort	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

[a]Compiled from Benedict and Breen, 1955; Czech and Northdurft, 1952; Kress and Skelly, 1982; MacLean et al., 1968; Matsushima, 1977; Taylor and MacLean, 1970; Thompson et al., 1980; van Haut and Stratmann, 1967.
[b]Different investigators reported different susceptibilities.

(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 upon the processes (e.g., growth or reproduction) and organ (e.g., leaves, stems, or roots) considered (see Section 9.5.2 and Appendix 9-A). 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.

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 9-6). However, no analyses have been made of the genetic factors that may determine it in crops nor of the statistics that could describe its distribution in natural populations.

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 dose-response relationships. In a concentration-duration factorial design, statistics for the dose-response function for foliar injury yielded about a 48% difference in the threshold dose for one hour between cultivars of oat and about a 40% difference between

TABLE 9-6. INTRASPECIFIC DIFFERENCES IN THE RESPONSES OF PLANTS TO NITROGEN OXIDES

Tomato:

Exposure to NO at 0.4 ppm increased growth in two cultivars ('Sonato' and 'Eurocross BB', and to a greater degree in the former) and decreased growth in two others ('Extase' and 'Adagio', and to a greater degree in the latter) (Anderson & 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 NO_2 at 1.5 ppm on the levels of nitrate or nitrite reductase in leaves and content of nitrate or amines (Murray & Wellburn, 1985).

Eight cultivars were compared in an exposure to NO_x at 0.7 ppm in enriched (1000 ppm) CO_2: 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 NO_2 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 & Pell, 1984).

Four cultivars ('Superior', 'Norchip', 'Kennebec', and 'Russet Burbank') were exposed to NO_2 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 & Ormrod, 1984). When 'Kennebec' and 'Russet Burbank' were exposed to NO_2 at 0.11 ppm as rooted cuttings, fresh mass of roots was decreased in 'Kennebec' (Petitte & Ormrod, 1988). NO_2-induced intumescences of the leaf occurred in 'Kennebec' and 'Russet Burbank' but not in the other two cultivars (Petitte & Ormrod, 1986).

Pepper:

Activity of nitrate reductase in leaves of two cultivars ('Bell Boy' and 'Rumba') was not affected by exposure to NO_2 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 & Wellburn, 1985).

Radish:

Six cultivars were exposed to NO_2 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 NO_2 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 9-6 (cont'd). INTRASPECIFIC DIFFERENCES IN THE RESPONSES OF PLANTS TO NITROGEN OXIDES

Barley:

There was a significant association between increased mass of straw and ambient NO_2 in two cultivars ('Aramir' and 'Claret') but not in two others ('Dram' and 'Golden Promise'); a significant association between increased number of tillers and NO_2 occurred with 'Golden Promise' but not with the other cultivars (Ashmore et al., 1988).

The degree to which exposure to NO_2 at 0.3 ppm altered the level of nitrate reductase varied among mutants deficient in the enzyme; genotype did not affect uptake of NO_2 (Rowland-Bamford et al., 1989).

Oats:

Three cultivars ('Clintland 64', '329-80', and 'Pendek') were classified as susceptible to NO_2-induced foliar injury in a concentration-duration factorial design; based on statistics for the dose-response function, about a 48% difference in threshold dose for one hour was the range (Heck & Tingey, 1979).

Corn:

Both cultivars ('Pioneer 509-W' and 'Golden Cross') were judged tolerant to NO_2-induced foliar injury (Heck & 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 an 40% difference in threshold dose for one hour) (Heck & 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 & Tingey, 1979).

Timothy:

Two cultivars ('Eskimo' and 'S48') differed in growth response to NO_2 at 0.062 ppm when exposed at later stages of development (Whitmore & Mansfield, 1983).

Red fescue:

The growth of two cultivars ('Highlight' and 'Pennlawn') was not affected by NO_2 at 0.15 ppm for 10 days, but foliar injury occurred in 'Pennlawn' (Elkiey & 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 NO_2 (Ashmore et al., 1988).

TABLE 9-6 (cont'd). INTRASPECIFIC DIFFERENCES IN THE RESPONSES OF PLANTS TO NITROGEN OXIDES

Orchard grass:

Two populations (Rainham and 'S26') differed in susceptibility to foliar injury from NO_2 at 4.8 ppm (Taylor & Bell, 1988).

Perennial ryegrass:

Two clones (Rainham and 'S23') differed with respect to growth under exposure to NO_2 at 0.2 ppm and soil-nitrogen (Taylor & Bell, 1988).

Two cultivars ('S23' and 'S24') differed as to the influence of stage of development on the growth reduction produced by NO_2 at 0.062 ppm (Whitmore & Mansfield, 1983).

Effects of NO_2 on levels of nitrite reductase and bioenergetic functions varied among different clones (Wellburn et al., 1981; Wellburn, 1982).

Kentucky bluegrass:

In twelve cultivars, NO_2 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 Skofti') (Elkiey & Ormrod, 1980).

Exposure to NO_2 at 0.15 ppm increased the growth of one cultivar ('Merion') but not in two others ('Cheri' and Touchdown'), that had foliar injury (Elkiey & Ormrod, 1981a).

Exposure to NO_2 at 0.062 ppm decreased growth in one cultivar ('Monopoly') but not in another ('Arima') (Whitmore & Mansfield, 1983).

Among nine cultivars, rates of uptake of NO_2 in light and dark varied over a three- to two-fold range (Elkiey & Ormrod, 1981b).

Petunia:

A comparison of 15 cultivars with respect to foliar injury induced by one-hour exposures to NO_2 at 8, 16, or 32 ppm indicated a range of tolerance (ED_{50}) 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 NO_2 at 0.8 ppm (Elkiey & Ormrod, 1981d). Rate of absorption of NO_2 was less in 'Capri' than in the other two cultivars (Elkiey & Ormrod 1981c).

Japanese morning glory:

Four cultivars ('Heavenly Blue', 'Hamano Yosooi', 'Scarlet O'Hara', and 'Murasaki Jishi') had foliar injury ranging from severe to slight after a one-hour exposure to NO_2 at 0.12 ppm (Matsushima, 1977).

African violet:

With two cultivars ('Lena' and 'Rosa Roccoco') under CO_2 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 9-6 (cont'd). INTRASPECIFIC DIFFERENCES IN THE RESPONSES OF PLANTS TO NITROGEN OXIDES

English ivy:

Two cultivars ('Gloire de Marengo' and 'Harald') were exposed to NO_x at 0.85 ppm under CO_2 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 CO_2 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 NO_2 on photosynthesis, respiration or transpiration (Saxe, 1986a).

Under CO_2 enrichment, NO at 1 ppm affected neither cultivar with respect to mass, height, number of shoots, or production time (Saxe & Christensen, 1984,1985).

Azalea:

Eight cultivars from five hybrid groupings had no foliar injury from NO_2 at 0.25 ppm; however two cultivars (one a Kurume, the other an Indian hybrid) had reduced shoot length (Sanders & Reinert, 1982b).

Orange:

Five varieties of orange showed different sensitivities to defoliation by acute exposures to NO_2 (greater than 25 ppm) (MacLean et al., 1968).

European white birch:

Two clones tended to differ with respect to effects of NO_2 at 0.062 ppm on growth (Wright, 1987).

The relative standard deviation for growth during exposure to a mixture of SO_2 and NO_2, each at 0.05 ppm, was about threefold greater in seedlings than in clonal cuttings (Whitmore & 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 NO_2 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 NO_2 at 0.1 ppm (Kress et al., 1982).

TABLE 9-6 (cont'd). INTRASPECIFIC DIFFERENCES IN THE RESPONSES OF PLANTS TO NITROGEN OXIDES

Eastern white pine:
Eight clones differed with respect to the relationship between concentration of NO_2 (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 NO_2 at 0.1 ppm but no conclusions are possible as to the influence of genetic factors because there was no effect of NO_2 on height or dry masses of top or root of seedlings (Kress & Skelly, 1982).

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 NO_2 among five varieties of orange (MacLean et al., 1968). A comparison of 15 cultivars of petunia at three concentrations of NO_2 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 dose-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 (Elkiey 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 (Petitt 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), but 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., 1982) 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 nitrate or nitrite reductase in leaves and foliar content of nitrate or amines. In addition, the effect of NO_2 on nitrite reductase varied among different clones of perennial ryegrass (Wellburn et al., 1981; Wellburn, 1982), and the effect of NO_2 on nitrate reductase varied among barley mutants deficient in the enzyme (genotype did not affect uptake of NO_2) (Rowland-Bamford et al., 1989).

Cultivar of petunia affected the nitrogen-content of leaves after exposure to NO_2 (Elkiey and Ormrod, 1981d) and the rate of uptake of NO_2 by the leaves (Elkiey and Ormrod 1981c). Among nine cultivars of Kentucky bluegrass, rates of uptake of NO_2 in the dark (adsorption) varied over a two-fold range and rates of uptake in the light above those in the

dark (absorption) varied over a three-fold range (Elkiey and Ormrod, 1981b). The joint-distribution of estimates for rates of absorption and adsorption among these cultivars (Figure 9-13) 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 NO_2 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; for bean, during the transition from vegetative to reproductive growth and during fruit development (van Haut and Stratmann, 1967).

The inhibitory effect of NO_2 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 seven months to NO_2 at 0.062 ppm, Kentucky bluegrass and one cultivar of timothy (but not another) showed a greater reduction of growth by NO_2 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 NO_2 on growth in orchard grass (Whitmore and Mansfield, 1983).

In marigold plants at three ages (seven weeks apart), stage of development did not alter the effect of NO_2 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 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

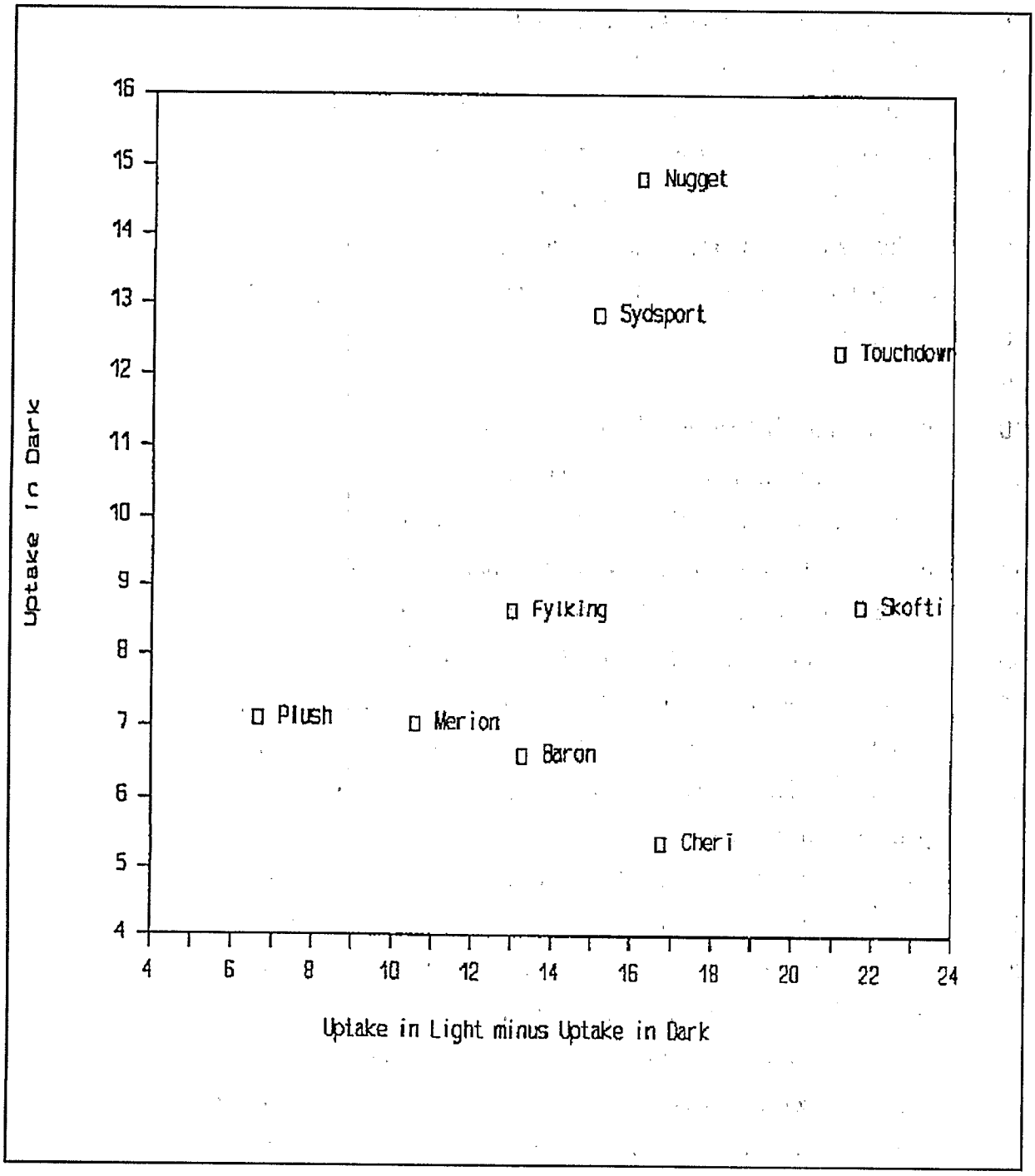

Figure 9-13. Relation between uptake of NO_2 in the dark and in the light for nine cultivars of Kentucky bluegrass; values are $\mu l\ min^{-1}\ dm^{-2}$ leaf area $\times 10^{-2}$ (after Elkiey and Ormrod, 1981).

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; that of larch is the needles of the spur shoots in the first week of emergence; 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; (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; (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, relative humidity (RH), and the gases carbon dioxide (CO_2), ammonia (NH_3), sulfur dioxide (SO_2), ozone (O_3), and hydrogen fluoride (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, and 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 through an extended effect on growth and development indirectly affect the response of plants to NO_x.

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 (ten hours 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 tenfold 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 μmol m^{-2} s^{-1}) 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., 1979).

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 an 11% decrease in rate of transpiration (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 (PFD) and doubled over the range of 0.2 to 420 μE m^{-2} sec^{-1} 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 post-exposure 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 NO_2-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 sensitivite to NO_2-induced foliar injury in the morning than in the afternoon (Zahn, 1975). When subjected to 2-h exposures to NO_2 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 9-14) (van Haut and Stratmann, 1967; van Haut, 1975). There is also some evidence from exposures of bean and sunflower to NO_2 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 nitrite reductase (Yoneyama et al., 1979). 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 CO_2 enrichment (at 1,000 ppm), exposure to 1.5 ppm NO_x (20% NO_2 + 80% NO) for 25 days decreased mass of shoots at all photon flux densities (30, 95, 175, or 250 μmol m^{-2} s^{-1}) but decreased number of leaves and length of stem only at the two lower levels of light intensity (Mortensen, 1986). Daytime exposures to NO_2 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 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

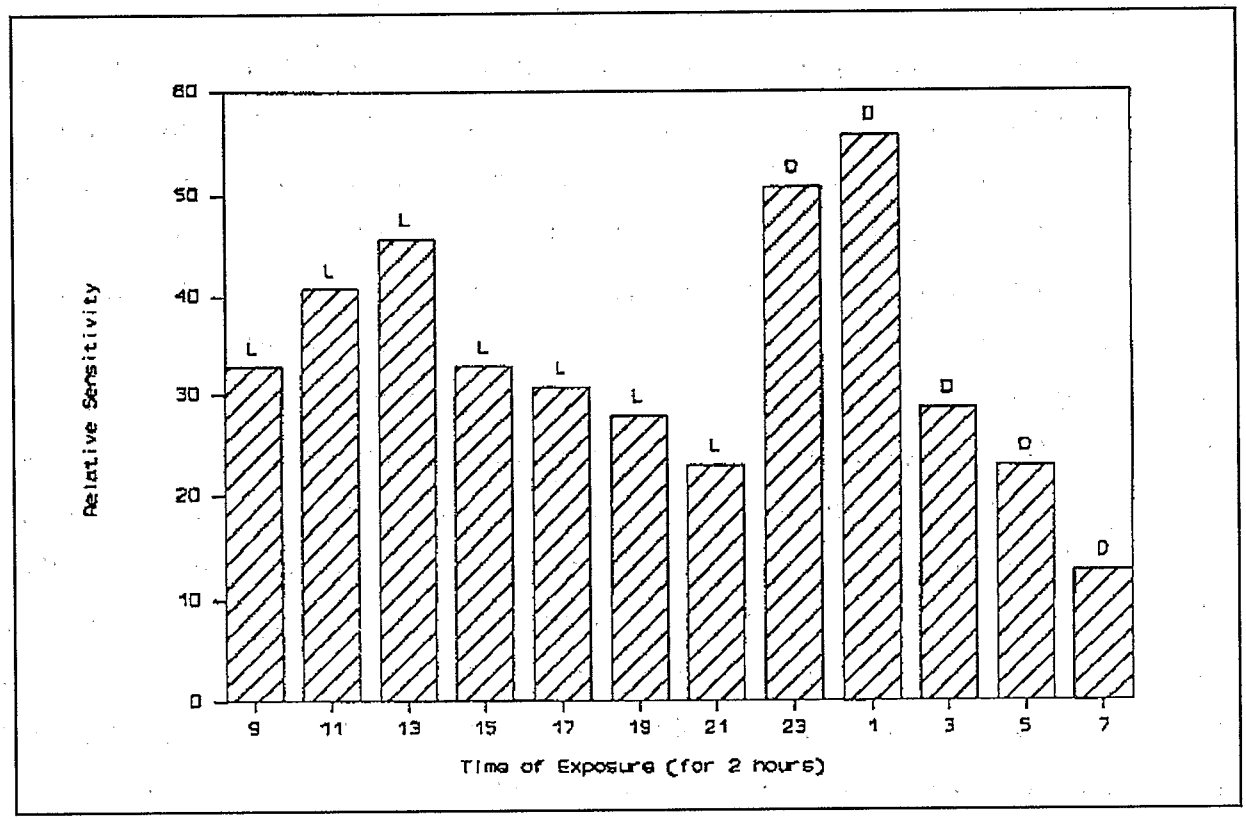

Figure 9-14. Variations in sensitivity of oat seedlings to foliar injury from NO_2 with hour of the day in light (L) and darkness (D) (after van Haut and Stratmann, 1967).

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 photo-environment with a photoperiod of 16 h and photon flux density of 280 μmol m^{-2} s^{-1}; 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 μmol m^{-2} s^{-1}, 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 NO_2 on photosynthetic CO_2 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 NO_2 on dark respiration increased with an increase in temperature (from 39% at 15 °C to 51% at 35 °C). Uptake of NO_2 at 3 ppm by bean leaves increased with increases in temperature over the range of 15 to 35 °C (about a two-fold difference between the lowest and highest temperatures) in the light; however, uptake increased about 75% from 15 to 25 °C but not thereabove in the dark. The inhibition of transpiration in the light by NO_2 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, 1984) or trees (Freer-Smith, 1984) to NO_2. The imposition of low temperatures (less than 0 °C) during a series of exposures to NO_2 could be regarded as a test for changes in cold-tolerance rather than an effect of temperature on the plant's response to NO_2 (Freer-Smith and Mansfield, 1987).

With air temperatures in the range of -6 to 3 °C, there was no measurable uptake of NO or NO_2 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 NO_2-induced foliar injury in Kentucky bluegrass (Elkiey and Ormrod, 1981). Although NO_2 at 0.15 ppm in continuous ten-day exposures had no effect on growth (foliar area) of Kentucky bluegrass when mist was present, NO_2 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, 1981). 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 increased stomatal aperture for 2 to 3 h after each application (Elkiey and Ormrod, 1981). 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 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 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 CO_2 was greater than, equal to, or less than that at normal CO_2 levels depending upon the species of plant (Saxe, 1986a).

Ammonia

Atmospheric NH_3 reduced the severity of foliar symptoms produced by NO_2, but this effect depended upon light intensity and species of plant. In the dark, NH_3 in the range of 2 to 7 ppm reduced foliar injury from a one-hour exposure to NO_2 at 6.4 to 9.0 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 NH_3 was attributed to its neutralization of the nitrous or nitric acids produced in the foliar tissue by NO_2 (Zeevaart, 1976). (cf. 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 NO_2-induced foliar lesions in ten 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 NO_2.

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 (S) 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 S-deficient plants; in another, NO_2 had no effect on plants given complete nutrient but decreased the growth of S-deficient plants (Elkiey and Ormrod, 1981a).

Soil Nitrogen

The availability of inorganic nitrogen (N) 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 upon concentration of NO_x, species of plant, effect measured, degree of N-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 N-deficiency on the sensitivity of the plant to NO_x.

Some data show that NO_x-induced foliar injury *increases* with an increase in N-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., 1979);

(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 post exposure period of 2 days became less severe with increasing levels of nitrate (Srivastava and Ormrod, 1984); (6) foliar injury was more severe in bean grown with deficient nitrogen under acute exposure to 17.2 ppm for 1 hour (Kato et al., 1974).

Other data show that NO_x-induced foliar injury *decreases* with an increase in N-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 (Elkiey 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); (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); (2) injury developed in sunflower supplied with ammonium or nitrite but not in deficient plants or those supplied with nitrate (Yoneyama et al., 1979).

Although NO_x can be a supplemental source of nitrogen for plants in N-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 on growth of NO_x and soil-N on growth have been studied most extensively in the following groups of plants.

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

two other cultivars (Elkiey 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-N and decreased root mass by 29% at low soil-N 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 N-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 N-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-N; produced a slightly greater inhibition of leaves and stem but a 45% reduction in root mass at medium soil-N; and had negligible effects on roots or stem but increased shoot mass by 17% at low soil-N (Matsumaru et al., 1979).

Tomato: Exposures to NO_x at about 2 ppm (in a carbon dioxide enriched atmosphere) had negligible effects (less than 5%) on fruit production (over four months) in plants supplied with 33 or 85 ppm N in soil but reduced production by 13% in plants supplied with 170 ppm N (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^{-1} in solution supplied to the roots (which produced stunted plants), but growth was increased by NO_2 with a five-fold 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 9-15 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; 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 decrease in stem length with no effect on foliar mass with no added nitrate; 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

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 and SO_2. Given the broad variety of pollutant sources in the United States, it is possible that NO_x will co-occur with other compounds, on either a local or 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. To assess the impact of air pollutants on plants in agroecosystems and natural communities, it is necessary to consider the possible impacts from pollutant combinations as well as the effects of individual pollutants.

The publication by Menser and Heggestad (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 ozone or sulfur dioxide 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.

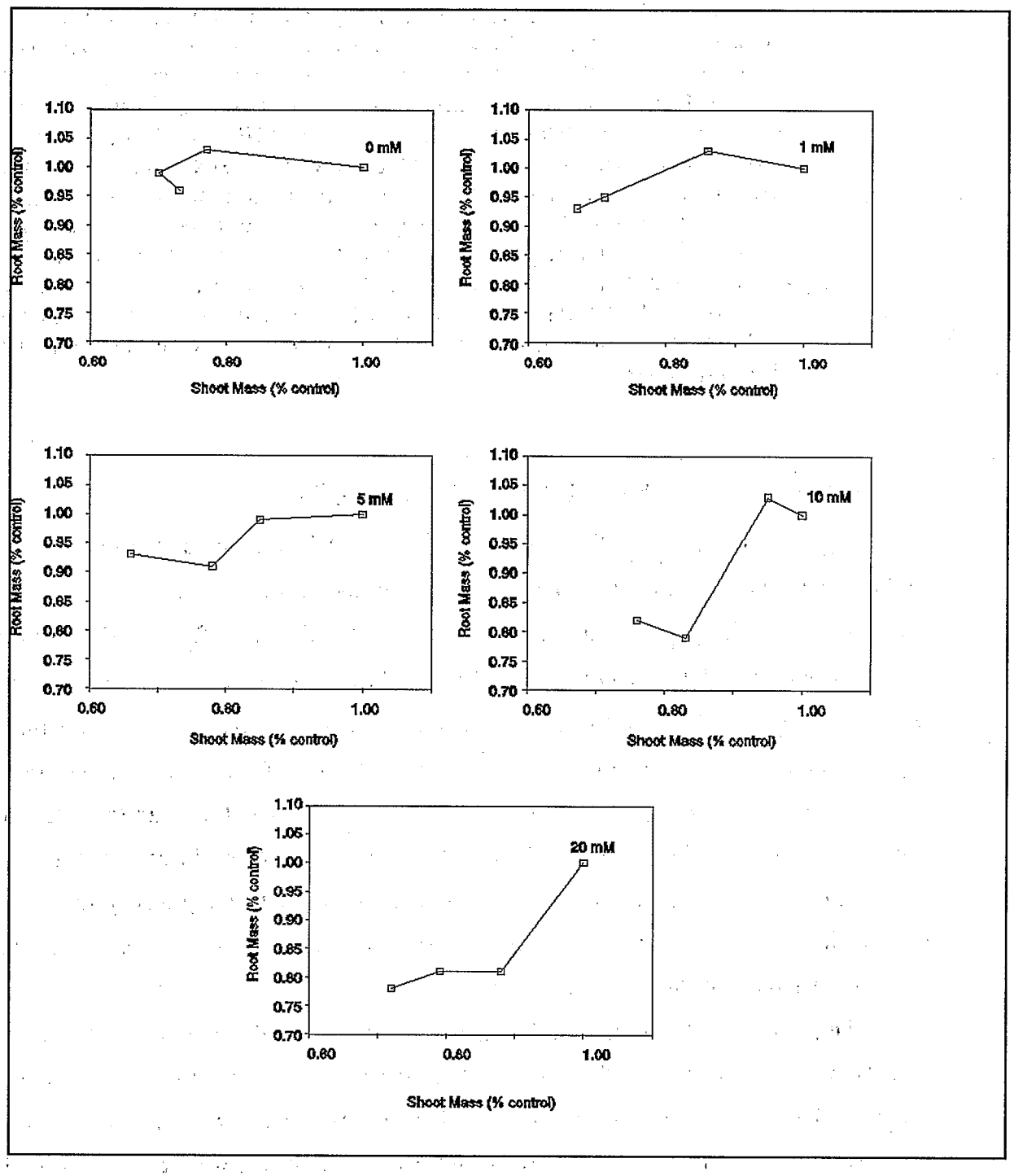

Figure 9-15. Effects of exposure to 0, 0.02, 0.1, or 0.5 ppm NO_2 on the dry weight of roots and shoots of bean seedlings grown in solutions containing 0, 1, 5, 10, or 20 mM nitrate (after Srivastava and Ormrod, 1986).

Plant response to pollutant combinations depends not only on the components of the mixture, but also the concentrations of the individual pollutants, their duration, and temporal succession. Various external and internal growth factors may modify the plant response.

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 determine if the pollutant concentrations and their individual and joint occurrences were reasonable in relation to concentrations and frequency of occurrence monitored in the ambient air. Limited analyses of ambient air monitoring data have studied the frequency of pollutant (NO_2/SO_2 and NO_2/O_3) co-occurrence (Lefohn et al., 1984; Lane and Bell, 1984; Jacobson and McManus, 1985; Lefohn et al., 1987). In general the studies have concluded that (a) the co-occurrence of two-pollutant mixtures lasted only a few hours per episode, (b) the time between episodes is generally large (weeks, sometimes months) and (c) the periods of co-occurrence represent a very small portion of the potential plant growing period.

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 9.6.1, 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 d) singly or in combinations of SO_2 + NO_2 (Wellburn et al., 1981). By contrast, ratios of $NAD(P)H/NAD(P)^+$ and rates of ATP formation were much reduced by SO_2 and SO_2 + 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 *Lolium perenne* L.

(cv. Aberystwyth S23) and mutant material, derived from S23 known to be tolerant of SO_2 (S23 Bell resistant), when fumigated with SO_2 + 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 9.3.2.3). Why low level fumigation with either SO_2 alone or SO_2 + NO_2 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.

Using plastid preparations from fumigated tillers of the SO_2-sensitive grass (*Lolium perenne* L. cv. Aberystwyth S23), the possibility of changes in the levels of NiR activity due to SO_2 , NO_2 or SO_2 + NO_2 have also been investigated (Wellburn et al., 1981). SO_2 has no direct effect upon the levels of NiR activity, even at a relatively high concentration (1 ppm), but NO_2 alone induces a significant increase in NiR after 9 days at 0.25 ppm or after 7 days at 0.5 ppm. This feature has also shown by the SO_2-resistant Helmshore clone after 13 days of fumigation. Most important of all are the combined effects of SO_2 + NO_2 . In such circumstances, the presence of SO_2 completely prevents the rise in NiR activity normally induced by NO_2 alone.

Inhibition of a potential means of detoxification of the products of NO_2 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 NO_2-polluted air (0.068 ppm) were approximately double those in plants growing in clean air. By contrast, the SO_2 + NO_2 treatment failed to increase the levels of NiR normally found in treatments with NO_2 in all grasses. Indeed, with the exception of the S23 Bell SO_2-resistant *Lolium* clone, all levels of NiR activity were significantly depressed below clean-air control levels. The additional presence of SO_2, therefore, prevents the induction of additional NiR activity normally associated with NO_2 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 $O_3 + NO_2$ or $SO_2 + O_3 + NO_2$ 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 NO_2 alone, Klumpp et al. (1989b) showed that nitrate reductase (NaR) activities were enhanced by $O_3 + NO_2$ and $SO_2 + O_3 + NO_2$ treatments in current year needles but reduced in 1-year-old needles. However, responses to the fumigation mixtures were highly dependent upon the availability of Ca and 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-amino-acridine (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 Sections 9.7.1-3). 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 (SO_3^-) which 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 O_3 + NO_2 exposed plants 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 3 soybean varieties (Hark, Beeson and Amsoy) due to SO_2 (2 ppm) + NO_2 (0.5 ppm) were detected in less than 5 h (Amundson and Weinstein, 1981). In this case, NO_2 alone had no effect. Levels of over 1 ppm NO or 2 ppm NO_2 are usually required for this to occur (Darrall, 1989; Saxe and Murali, 1989). Carlson (1983) working in the short term (2-24 h) with soybean (*Glycine max* L.) and up to 0.6 ppm of SO_2, NO_2 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 SO_2 and the SO_2 + NO_2 treatments.

Rates of inhibition of net photosynthesis in sunflowers (*Helianthus annuus* L. cv. Russian Mammoth) induced by NO_2 + O_3 mixtures differ from those of SO_2 + NO_2 or SO_2 + NO_2 + O_3 (Furukawa and Totsuka, 1979). Mixtures of NO_2 (1 ppm) + O_3 (0.2 ppm) decrease rates of net photosynthesis steadily throughout the exposure period (2 h) while mixtures with SO_2 induce an abrupt change to lower steady levels within 30 min. Only in the SO_2 + NO_2 treatment is the extent of the inhibition determined by the levels of NO_2.

Stomatal conductances can also increase at low levels (<0.1 ppm) of SO_2 (Darrall, 1989) and enhance transpiration rates. Levels of either SO_2 or NO_2 (both 0.1 ppm), for example, cause short term increases in transpiration by beans (*Phaseolus vulgaris* L. cv. Canadian Wonder) during the first 3 days of exposure (Ashenden, 1979). By contrast, exposures to SO_2 + NO_2 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 SO_2, NO_2 and SO_2 + NO_2 (0.02-0.06 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 SO_2 + NO_2 as well as by NO_2. Effects of NO_x alone on dark respiration have been discussed elsewhere (Section 9.3.3.1) but various combinations of SO_2 + NO_2 + O_3 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 simulated by various mixtures of NO + NO_2 (2.5-9 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 NO_2 (1-1.15 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 NO_2 alone at concentrations between 0.04 and 0.4 ppm (Darrall, 1989). Nevertheless, adverse interactions between SO_2 and NO_2 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 SO_2, NO_2 or O_3 (0.4 ppm each for 7 days). Darrall (1989) has summarized the details of other mixed fumigations in the literature which 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 (O_3, NO_2 and SO_2), NO_2 is the least likely to cause visible injury because of both its relatively low phytotoxicity and low ambient concentration. In combination with other pollutants, however, NO_2 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 which 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 SO_2.
A survey of six species' sensitivity to SO_2/NO_2 mixtures in 4-h exposures found that neither 2.0 ppm NO_2 nor 0.5 ppm SO_2 alone caused foliar injury (Tingey et al., 1971). However, a

mixture of 0.10 ppm NO_2 and 0.10 ppm SO_2 administered for 4 hours caused foliar injury to pinto bean (*Phaseolus vulgaris*), radish (*Raphanus sativus*), soybean (*Glycine max*), tomato (*Lycopersicon esculentum*), oat (*Avena sativa*) and tobacco (*Nicotiana tabacum*). Exposure to 0.15 ppm NO_2 in combination with 0.1 ppm SO_2 for 4 hours caused greater foliar injury than lower concentrations. Traces of foliar injury were observed at 0.05 ppm NO_2 and 0.05 ppm SO_2; 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 ozone 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 9-7). Fujiwara et al. (1973) found greater-than-additive effects when peas (*Pisum sativum*) 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 9-7).

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 ozone alone (Table 9-7).

Bennett et al. (1975) studied the effects of NO_2 and SO_2 mixtures on radish (*Raphanus sativus*), swiss chard (*Beta vulgaris*), oat (*Avena sativa*) and pea (*Pisum sativum*). Treatments consisted of 1 and 3 hour 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 SO_2 and NO_2. 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 which 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 9-7 do not detail the

TABLE 9-7. VISIBLE INJURY IN CONTROLLED EXPOSURES TO NO_x MIXTURES

Species	Gas Mixture	Exposure	Effect	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 espisode	0/-	Ito et al. (1984)
Carolina poplar	$NO_2 + SO_2$	High espisode	-	Eastham and Ormrod (1986)
		Medium episode	0	
Black poplar		High episode	-	

TABLE 9-7 (cont'd). VISIBLE INJURY IN CONTROLLED EXPOSURES TO NO_x MIXTURES

Species	Gas Mixutre	Exposure	Effect	Reference
Oat	$NO_2 + SO_2$	Medium episode	0	Bennett et al. (1975)
Beet			0	
Radish			-	
Pea			0	
Shore juniper	$NO_2 + SO_2$	Low episode	0	Fravel et al. (1984)
	$NO_2 + SO_2 + O_3$	Medium episode	-	
		Medium episode	-	
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)

+ denotes less effect of mixture than single gases;
0 denotes no different effect of mixture than single gases;
- denotes greater effect of mixture than single gases.

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 9-8). A broad survey of native U.S. species sensitivity to SO_2/NO_2 indicated that the addition of NO_2 to SO_2 (in a 1.0:0.28 proportion) did not cause more injury than did the SO_2 alone (Hill et al., 1974). In addition, the injury from the mixtures resembled that from SO_2 alone—varying with species, it appeared as regions of discolored (tan, grey-brown, yellow-brown, rusty brown) patches of interveinal necrotic tissue.

TABLE 9-8. VISIBLE INJURY IN FIELD CHAMBER AND FIELD EXPOSURES TO NO_x MIXTURES

Species	Gas Mixture	Exposure	Effect	Reference
Desert ecosystems	$NO_2 + SO_2$	High episode	0**	Hill et al. (1971)
Creosote bush	$NO_2 + SO_2$	Medium seasonal	-	Thompson et al. (1980)
Burro weed		High seasonal	-	

\+ denotes less effect of mixture than single gases;
0 denotes no different effect of mixture than single gases;
\- denotes greater effect of mixture than single gases.

The studies described in this section make several points. The first is that NO_2 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 ozone is added. However, the occurrence of injury arises only from mixture concentrations which are much higher than those observed in the ambient environment. The second is that the addition of NO_2 to other gases does not result in unique injury symptoms—the combination usually causes symptoms which resemble those resulting from the other pollutant, or may resemble those from a pollutant not included in the mix. For example, shore juniper injury to NO_2/O_3 resembled O_3 injury and desert native species injury to NO_2/SO_2 resembled SO_2

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 nitrogen dioxide and sulfur dioxide was rare (Jacobson and McManus, 1985). Using minimum concentrations of 0.03 and 0.05 ppm for nitrogen dioxide and sulfur dioxide, 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 nitrogen dioxide and sulfur dioxide is small (Lane and Bell, 1984). The authors characterized 3 months (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 $\geq$0.03 ppm) for at least 1 h anytime during the day (24-h). The pollutant monitoring (based on 110 site years of data for NO_2 and SO_2 and 71 site years for NO_2 and O_3) data were obtained from co-monitoring sites located in both urban and rural areas. The analyses found that the co-occurrences at most rural sites (5 month summer period) were infrequent,

less than 12% of the days. The infrequent co-occurrence is not surprising as most sites experienced only a few h/year when the concentrations of NO_2 or SO_2 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 (nitrogen dioxide and sulfur dioxide) 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 ozone, nitrogen dioxide, and sulfur dioxide that occurred in Holland. Lane and Bell (1984) analyzed 3 months (January through March) of air quality data from central London to design experimental plant exposures which simulated the distributions of sulfur dioxide and nitrogen dioxide. 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 which 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 post-exposure to other gases (Table 9-9). 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

TABLE 9-9. GROWTH/YIELD IN CONTROLLED EXPOSURES TO NO_x MIXTURES

Species	Gas Mixture	Exposure	Effect	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	-	
	$NO_2 + SO_2$	Medium seasonal	0	Reinert and Sanders (1982)
	$NO_2 + O_3$	Medium seasonal	-	
	$NO_2 + SO_2 + O_3$	Medium seasonal	-	
Marigold	$NO_2 + SO_2$	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	Elkiey et al. (1988)
Corn			-	
Kidney bean			0	
Pea			0	
Potato			-	
Tobacco	$NO_2 + SO_2$	Low episode	0/-	Elkiey et al. (1988)
Kidney bean			0/-	
Tomato	$NO_2 + O_3$	Medium episode	0/-	Goodyear and Ormrod (1988)
Kidney bean	$NO_2 + O_3$	High seasonal	-	Ito et al. (1984)
Populus canadensis	$NO_2 + SO_2$	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)
Betula pubescens			-	
European birch	$NO_2 + SO_2$	Low seasonal	0/-	Freer-Smith (1985)

TABLE 9-9 (cont'd). GROWTH/YIELD IN CONTROLLED EXPOSURES TO NO_x MIXTURES

Species	Gas Mixture	Exposure	Effect	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	+	Kress et al. (1982a)
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)

+ denotes less effect of mixture than single gases;
0 denotes no different effect of mixture than single gases;
- denotes greater effect of mixture than single gases.

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 hours, 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 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 14-28), 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 4-6 or 9-11 leaf stage were exposed once for one hour to 0.08 ppm O_3 and 0.21 ppm NO_2. Leaf and stem fresh weights of 4-6 leaf plants were smaller after exposure to the concurrent gases than in control plants. In the second experiment, plants at the 4-6 leaf stage were exposed once to 0.08 ppm O_3 and 0.21 ppm NO_2 either concurrently for one hour or in either sequence, each gas for one hour: 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 which 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. Since this type of exposure is more common in the ambient environment (see introduction), NO_2 mixtures with other ambient pollutants such as SO_2 or O_3 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 NO_2 and SO_2 have been carried out using plants grown under artificial conditions and exposed to concurrent pollutant regimes which are less likely to occur under most ambient situations, but which may occur in the vicinity of a source, such as SO_2/NO_2 near a power plant. These studies may be useful in establishing relative species sensitivities, or identifying modifying factors of plant/pollutant interaction (Table 9-9).

Ten species native to the Mojave/Eastern Mojave-Colorado desert were exposed to high, medium or low concentrations of SO_2 and NO_2 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 NO_2 plus 2.0 ppm SO_2) 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 NO_2 and 0.67 ppm SO_2) and low (0.11 ppm NO_2 and 0.22 ppm SO_2) 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. Since these two species contrast in their growth response to the gas mixture, reduction of flowering in *Ambrosia* may have resulted from generally depressed plant vigour, while flowering in

Encelia may have been directly inhibited by the gas mixture, allowing more photoassimilate to be partitioned to shoot growth—perhaps NO_2 was acting as a fertilizing source of N. 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 SO_2 and NO_2, 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 SO_2 and NO_2. 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 non-stress levels, and relative humidity was high, ensuring that the rate of gas exchange was high. The authors noted that SO_2 did not change plant response to NO_2, so that the mixture posed no greater threat than that from either of the single gases.

The exposure of tomato (*Lycopersicon esculentum*) to continuous SO_2 and NO_2 reduces growth (Marie and Ormrod, 1984). After 14 days in 0.11 ppm SO_2 plus 0.11 ppm NO_2, 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 seven and fourteen 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 SO_2 and NO_2 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 SO_2 and NO_2 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 SO_2 and NO_2 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 concentrations of NO_2 which are non-injurious by themselves, when combined with SO_2.

The exposure of potato (*S. tuberosum*), corn (*Zea mays*), pea (*Pisum sativum*), tobacco (*Nicotiana tabaccum*), and pinto bean (*Phaseolus vulgaris*) to SO_2 (0.15 ppm) and NO_2 (0.10 ppm) continuously for 15 days resulted in little effect on growth (Elkiey 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 one hour per day. Bean leaf area was also reduced by the 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 0.11 ppm NO_2 continuously combined with 0.34 ppm SO_2 for one hour. Kidney bean (*Phaseolus vulgaris* L. 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., 1984). In general, mixture effects were similar to effects of ozone 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 'Modes of Action' 9.6.1.4 for further discussion).

Exposure of *Poa pratensis* 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 which 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 (ppm·days) was related to growth as percent of control; the dose response relationship indicated growth stimulation at low concentrations, followed by growth inhibition which related less to dose as dose increased. Since 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, ppm·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 SO_2/NO_2 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 SO_2/NO_2 mixtures (Ashenden and Mansfield, 1978; Ashenden 1979; Ashenden and Williams, 1980). Although each of the studies is non-replicated, 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 SO_2 and/or NO_2, 5 days per 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 SO_2 was modified by the presence of 0.5 ppm NO_2 (Eastham and Ormrod, 1986). Leaf and stem mass tended to be greater than the control in the presence of NO_2, 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 O_3, NO_2, and SO_2 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 SO_2 and O_3 for radish (*Raphanus sativus*) and marigold (*Tagetes patula*) when 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 SO_2 or O_3 except for a reduction in root and total plant dry weights of marigold exposed to SO_2. A similar study of radish and marigold exposed to 0.3 ppm for 3 or 6 h (respectively), nine times within three weeks indicated that visible injury on radish appeared to be less than additive compared to the single pollutants for NO_2/O_3, and $NO_2/O_3/SO_2$; whereas NO_2/SO_2 appeared to be greater than additive (Reinert and Sanders, 1982). The effect of NO_2/SO_2 and $NO_2/SO_2/O_3$ 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 NO_2 x O_3 interaction only in 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 four 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 and O_3) had no effect in comparison to control, and the plants grew taller than those exposed to SO_2 + NO_2, SO_2 + O_3 or O_3 + SO_2 + NO_2; and 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 SO_2 + O_3 but its addition did decrease growth in response to SO_2 alone. A pair of studies on the effects of $SO_2/NO_2/O_3$ mixtures on a variety of tree species demonstrated that the addition of NO_2 to O_3 + 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 carry out such a large study (Table 9-10). Soybean (*Glycine max* L. cv. Northrup King, 1492) was exposed to NO_2 and SO_2 in the presence of ambient O_3 in a field situation equipped with a Zonal Air Pollutant (delivery) System (ZAPS) (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 SO_2 and 0.06 to 0.40 ppm for NO_2. Nitrogen dioxide exposures had no effect on seed yield in either year, while SO_2 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 SO_2 and NO_2, at concentrations which 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 (13-44%) 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 SO_2 , O_3 and NO_2 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 which included O_3 were more injurious than SO_2 + NO_2 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

TABLE 9-10. GROWTH/YIELD IN FIELD CHAMBER AND FIELD EXPOSURES TO NO_x MIXTURES

Species	Gas Mixture	Exposure	Effect	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	
Baileya pleniradiata	$NO_2 + SO_2$	High seasonal	-	Thompson et al. (1980)
		Medium seasonal	0	
		Low seasonal	0	
Plantago insularis	$NO_2 + SO_2$	High seasonal	0	Thompson et al. (1980)
		Medium seasonal	0	
		Low seasonal	0	
Phacelia crenulata	$NO_2 + SO_2$	High seasonal	-	Thompson et al. (1980)
		Medium seasonal	-	
		Low seasonal	0	
Erodium cicutarum	$NO_2 + SO_2$	High seasonal	-	Thompson et al. (1980)
		Medium seasonal	-	
		Low seasonal	0	
Chaenactis carphoclinia	$NO_2 + SO_2$	High seasonal	-	Thompson et al. (1980)
		Medium seasonal		
		Low seasonal		
White pine	Arsenal emissions	Lifetime	-	Stone and Skelly (1974)
Yellow poplar				
Italian ryegrass	$NO_2 + SO_2$	Low seasonal	-	Ashenden and Williams (1980)
			-	
Orchard grass	$NO_2 + SO_2$	Low seasonal	-	Ashenden and Mansfield (1978)
Italian ryegrass			-	
Timonthy			-	
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)

+ denotes less effect of mixture than single gases;
0 denotes no different effect of mixture than single gases;
- denotes greater effect of mixture than single gases.

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

While 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 which address modification of gas mixture response by external factors have not included single gas treatments, making it difficult to conclude whether the NO_2 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 to 0.04 or 0.05 ppm each of NO_2 and SO_2 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 SO_2 alone (Freer-Smith, 1984). At the lower light intensity, leaf area response to the gas mixture was lower than that observed in the SO_2 treatment.

The response of grass species to SO_2/NO_2 mixtures as modified by light demonstrates that, as in birch, conditions which 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 SO_2 and NO_2 under light and temperature regimes which 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 80-100 ppb SO_2 and NO_2 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

SO_2/NO_2 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 oxides of nitrogen (NO_x) and protection of the plant in part, either by exclusion or detoxification of NO_x.

A model can be constructed that summarizes the material presented. A portion of that model is shown in Figure 9-16. The discussion in this section is organized to follow the movement of gases from the atmosphere into the sites of action within the leaf. Eight major processes will be discussed in sequence, leading from entry into the plant of atmospheric gases 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.

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 through 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

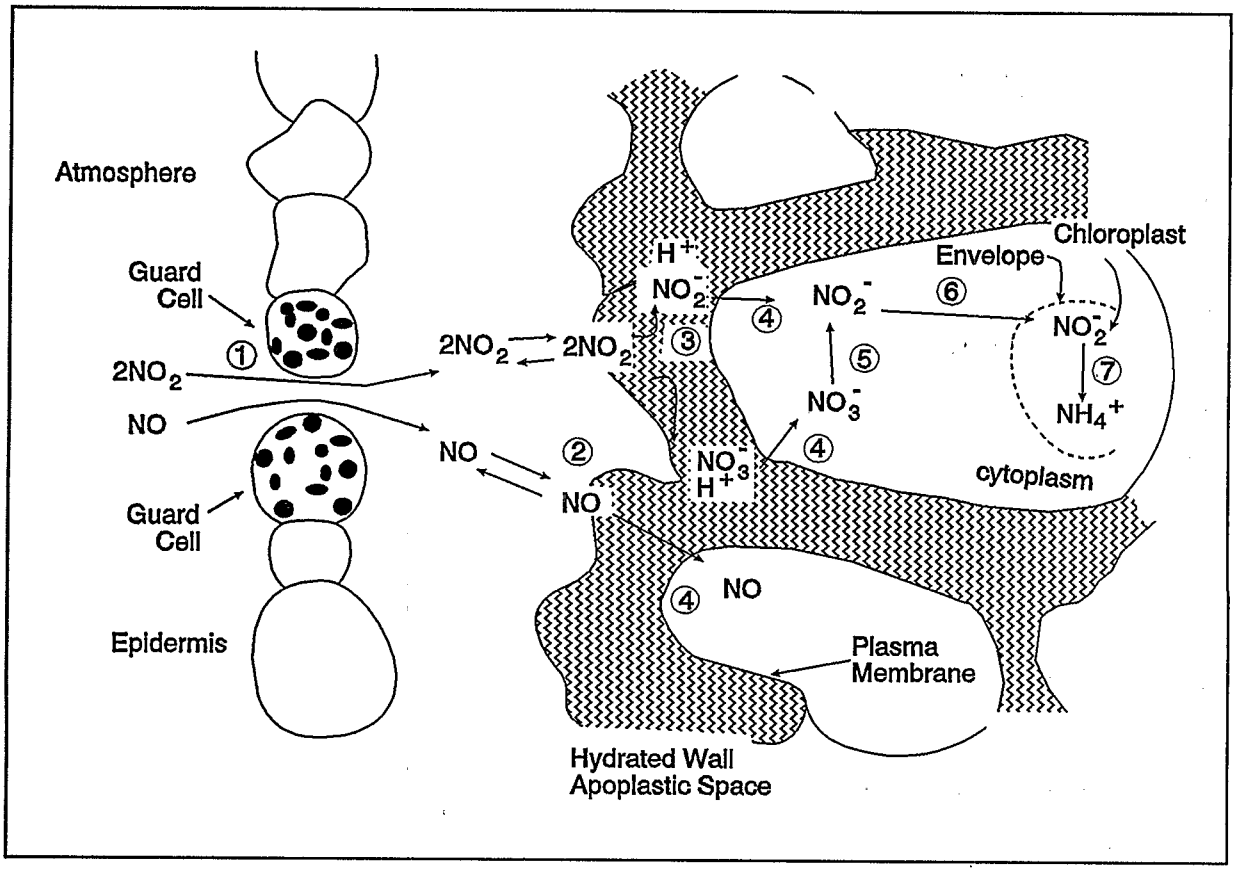

Figure 9-16. A schematic of the movement of gaseous oxides of nitrogen into the mesophyll cells of plant leaves. The diagram has been copied from an electron micrograph and gives approximately the correct relationships. The actual dimensions are very dependent upon the species and growing conditions of the plant. The numbers represent the processes listed in the text.

pathological processes which 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. NO_2 is water soluble and can be incorporated into normal plant nitrogen metabolism, up to a certain concentration. NO is a water insoluble compound and induces free radical reactions. While the exact sequence of reactions is still unknown, it is clear that NO behaves differently than NO_2. The third category contains the remainder of oxides of nitrogen, which are not well defined and whose reactions are poorly understood. For certain gases some processes function similarly, while for others quite differently. Some of these differences will become better defined as the two major components of NO_x (NO and NO_2) are discussed.

Another new finding is that the cell can incorporate NO_2 into normal metabolism, after NO_2 is hydrated to nitric and nitrous acids that exist in ionic form in the aqueous milieu of the cell. Despite the fact that NO_2^- and NO_3^- 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 oxides of nitrogen with different oxidations states (Table 9-11). While 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 NO_2) with their hydrated acidic species ($HONO_2$ 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 N_2O_4, 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

TABLE 9-11. TYPES OF OXIDES OF NITROGEN IN THE GASEOUS PHASE OF AN ATMOSPHERE

Formula	Name	Oxidation State
NO_2	Nitrogen dioxide	(+4)
NO	Nitric oxide	(+2)
$HONO_2$	Nitric acid	(+5)
N_2O_5	Dinitrogen pentoxide	(+5)
HONO	Nitrous acid	(+3)
N_2O_4	Dinitrogen tetroxide	(+4)
$NO_3^{\cdot}$	Nitrate radical	(+5)
N_2O_3	Dinitrogen trioxide	(+3)
NO^+	Nitrosonium ion	(+3)

Species are arranged from the highest to lowest concentrations in general urban atmospheres. Structures and oxidation states are from Pauling (1953).

membrane) and within the cell itself, even if at low levels. The possibility exists for many further reactions of oxides of nitrogen with this compound in the atmosphere and in the cell. Also, compounds such as ozone will give rise to other oxidative compounds, such as O_2^- 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., SO_2 and O_3 with NO_x).

A dynamic equilibrium will be established between O_3, NO_2, and NO in the presence of sunlight (see Chapters 3-5). Further reactions and transformations will occur in the atmosphere that affect NO_x. 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 NO_2 within the cell will be 2.0×10^{-10} M and 1.2×10^{-9} M, respectively*. While these concentrations are small by

*The solubility of NO can be easily measured since it unreactive with water (Schwartz and White, 1981) at 1.93×10^{-3} M/atm. The solubility of the other oxides of nitrogen are more difficult to measure as they react with water. On the basis of equilibrium arguments, Schwarz and White (1981) have given the following solubility coefficients: $NO_2^{\cdot}$, 1.2×10^{-2} M/atm; HNO_3, 2.5×10^5 M/atm; HNO_2, 1×10^5 M/atm.

metabolic standards, they could be quite phytotoxic at a protein level. On the other hand, while 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 nitric acid and nitrous acids which are able to ionize to form nitrate and nitrite. A few of the possible reactions and their kinetic constants are given in Table 9-12 (from Troiano and Leone, 1977; Schwarz and White, 1981; Section 9.3). There are many more possible reactions but their rate constants are unknown, since 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.

9.7.2.1 Foreign Compounds in Plants

Plants can deal with foreign chemicals by several methods (see Levitt, 1980). 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 which 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 since 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. NO_2 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.

TABLE 9-12. POSSIBLE REACTIONS BETWEEN NITROGEN DIOXIDE AND NITRIC OXIDE, AND WATER

Reaction	K_{eq}
1. $2NO_2(g) = 2H^+(a) + NO_2^-(a) + NO_3^-(a)$	2.44×10^2
2. $NO(g) + NO_2(g) = 2H^+(a) + 2NO_2^-(a)$	3.28×10^{-5}
3. $3NO_2(g) = 2H^+(a) + 2NO_3^-(a) + NO(g)$	1.81×10^{-9}

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

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 well as 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, 1981; Ball, 1987), which gives rise to a linear flux law of:

$$j = g\,(C_o - C_i) \qquad (1)$$

where the flux (j) into the internal space of a leaf (in units of mole/m^2sec) is linearly related to the gradient of concentrations from the outside (C_o) inwards (to C_i) (in units of mole/m^3).

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.

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 upon the internal concentration. Furthermore, the internal concentration is critical for reactions which will occur at the cell surfaces, reactions which 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 which enters the leaf are based upon 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. For ozone the internal concentration is very close to zero (Laisk et al., 1989), most probably because ozone is so reactive with cellular chemicals. For CO_2 the internal concentration is clearly not zero; it is slightly less than ambient (10-20% lower) when the stomates limit CO_2 flow and active photosynthesis is occurring (Sharkey et al., 1982).

While the chemical reactivity of NO_2 is not high as O_3, it can react strongly with chemicals contained in certain non-aqueous solvents (Pryor and Lightsey, 1981; Pryor et al., 1982; Giamalva et al., 1987). 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). While 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.

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*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. CO_2, on the other hand, moves to where CO_2 fixation occurs, generally in the mesophyll cells. In addition, Cowan & Farquhar (1977) have redefined the parameters of Equation 1 such that g is measured in mol/m^2-sec and C_o/C_i are measured as partial pressures of the gas. While 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 1 then becomes $j = g\ C_o\ (1-f)$.

Obviously, one method for determining the flux would be to measure directly the accumulation of nitrogen from NO_2. Some measurements have been made, but nitrogen accumulation from the air can not 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 N 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 upon 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 which 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 9-12); and (3) the diffusion to and reaction with their enzymes to convert them into needed biochemicals (nitrate- and nitrite-reductase). The rates for diffusion and conversion are important since 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 occured 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 upon 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 upon 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" at normal temperatures of 0.0585 m/sec. Under these somewhat specialized conditions, the internal concentration of NO_2 ($[NO_2]_i$) can be then calculated when the flux through the stomates is balanced by the accommodation "flux".* For a stomatal conductance of 0.4 cm/sec, 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. (1980), 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 difficulty to be more precise; yet Saxe's data suggest that f was extremely low.

Rowland-Bamford and Drew (1988) also attempted to determined the internal level of NO_2. Their experiments on Barley at low light levels (20-25% of the level of full sunlight) indicated that the level of internal NO_2 was, at best, only about 5-10% that of the external level (at 0.3 ppm). That level was lowest in the morning and rose significantly in the

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*This balance occurs when the accommodation coefficient (R_a) times the internal concentration ($[NO_2]_i$) times the average speed of the molecules (which depends upon the gas temperature) equal the real gas conductance (g) times the difference between the external and internal gas concentration. If the internal concentration is defined as $f \times [NO_2]$ where $[NO_2]$ is the external concentration, then $f = g/(R_a+g)$.

afternoon. Interestingly, at the lowest light intensity, the net flux rate (per unit of light) was quite low, while at higher light levels, the flux rate became nearly a thousand-fold 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 nitrite reductase 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 N-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. While some authors believe that NO can be converted into soluble compounds, chemical investigations (Wellburn, 1990; Equation 2 of Table 9-12) suggest that NO is relatively insoluble and, by itself, non-reactive 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). Since unbounded free radicals are relatively rare in biological systems, the path of diffusion will be long and the rate of reaction slow. Therefore, the internal concentration of NO should be similar to the external concentration, and the stomates will exert only a small effect upon 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 9-12). At concentrations of 0.1 ppm, the amount of NO_2^- which can be formed from both NO and NO_2 would be $2.3 \times 10^{-8}/[H^+]$ M, where the $[H^+]$ is the local concentration. If the combined reaction between NO and NO_2 occurred within the acidic cell wall ($[H^+]$ = ca. 3×10^{-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., 1990). 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 x $[NO_2]_o$, 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:

$$[NO_2^-][NO_3^-] = 2.44 \times 10^2 [NO_2]^2 f^2 / [H^+]^2 \quad (2)$$

For $[NO_2] = 0.1$ ppm, this becomes:

$$[NO_2^-][NO_3^-] = 2.44 \times 10^{-4} f^2 \quad (2)$$

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 uM, respectively. Thus, $[NO_2^-][NO_3^-] = 10^{-4} \times 5 \times 10^{-3} = 5 \times 10^{-7}$ M^2. Thus either f = 2-3% 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 Compounds

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 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 too far from its normally balanced state, such that the plant could not restore 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 NOx compounds and (2) what is meant by the "normal" state and how far can plants deviate from that state without permanent damage 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 ammonia (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 ammonia can be used by the plant. NO_x which falls upon the soil has the potential of being easily converted by microbial or chemical action and so can be readily adsorbed by the roots. Ground deposited NO_x can enter the metabolic pathway readily through the soil/root interface, although deposition can overload the soil/plant systems (see chapter 10). Gaseous NO_x which enters through the leaf can likewise be converted through enzyme systems which can handle the derived compounds.

The chemical species which will be dealt with are nitrous acid, ammonium ion, and nitric acid. The first two are a weak acid and weak base, respectively (see Equations 3 and 4 below), and, therefore, their actual chemical forms are dependent upon 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, nitric acid is such a strong acid that it exists predominantly as a nitrate ion under all biological conditions.

$$HNO_2 == H^+ + NO_2^- \quad (pK = 3.3) \tag{3}$$

$$NH_4^+ == H^+ + NH_3 \quad (pK = 9.2) \tag{4}$$

$$HNO_3 == H^+ + NO_3^- \quad (pK = -1.3) \tag{5}$$

While plants can use both ammonium and nitrate, nitrate seems to be safer even in high concentrations for the plant and, thus, is classed as a "relatively innocuous" compound (Miflin, 1980). Nitrite seems to be a compound whose concentration is highly regulated and is maintained at low levels within the plant. Ammonium seems likewise to be highly regulated and its concentration is also kept at low levels. The biological protocol to prevent high ammonia levels is to convert, as rapidly as possible, ammonium to amino groups.

Nitrate is converted first to nitrite via the enzyme, nitrate reductase, with the resulting nitrite being converted to ammonia by another enzyme, nitrite reductase. The full conversion of nitrate into ammonia requires 8 electrons or the equivalent of 4 molecules of NAD(P)H per molecule of NO_3^-. Since each NAD(P)H has a free energy content of about 28 kcal/mole, one mole of $NO_3^- \rightarrow NH_4^+$ requires about 115 kcal/mole 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 gain. 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, ammonia 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 μmole N/g FW h^{-1}* and then move into the shoots at a rate of

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*g FW is grams of fresh weight of plant material.

1.25 μmole N/g FW h^{-1}. The NH_4^+ pools were 3.85 and 0.45 μmole/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 μmole/g FW with an external NH_4^+ level of 88 mM (Mayer et al., 1990). Rates of nitrate reductase have been measured to be 4-6 and 2-3 μmole/g FW h^{-1} for barley and corn roots, respectively (Siddiqui et al., 1990). Wellburn (1984) measured nitrate- and nitrite-reductase activities in tomato (resistant to NO_2 exposures) as 3.6 to 5.4 μmole/g FW h^{-1}, respectively. Woodin et al. (1985) measured nitrate reductase as 0.4 μmole/g FW h^{-1}, yet upon NO_3^- fertilization that value rose five-fold in less than a day to 2 μmole/g FW h^{-1}. Thus, it seems that the rate of nitrogen reduction can range from 0.4 to 5 μmole/g FW h^{-1}, depending upon 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 N (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 since much more nitrogen is added by the grower as fertilizer. In natural regions, for example, 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 9-17), 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 active transport and so its rate can be saturated (see Glass et al., 1990; Siddiqi et al., 1990). Although space does not permit a complete discussion, detailed reports are given in Durzan and Steward (1983); Hayes (1986); and Goh and Hayes (1986). Many of the past experiments performed on the competition of soil nitrogen and NO_x-derived nitrogen do not fully appreciate these facts. The soil level is often much too high and the added NO_x causes

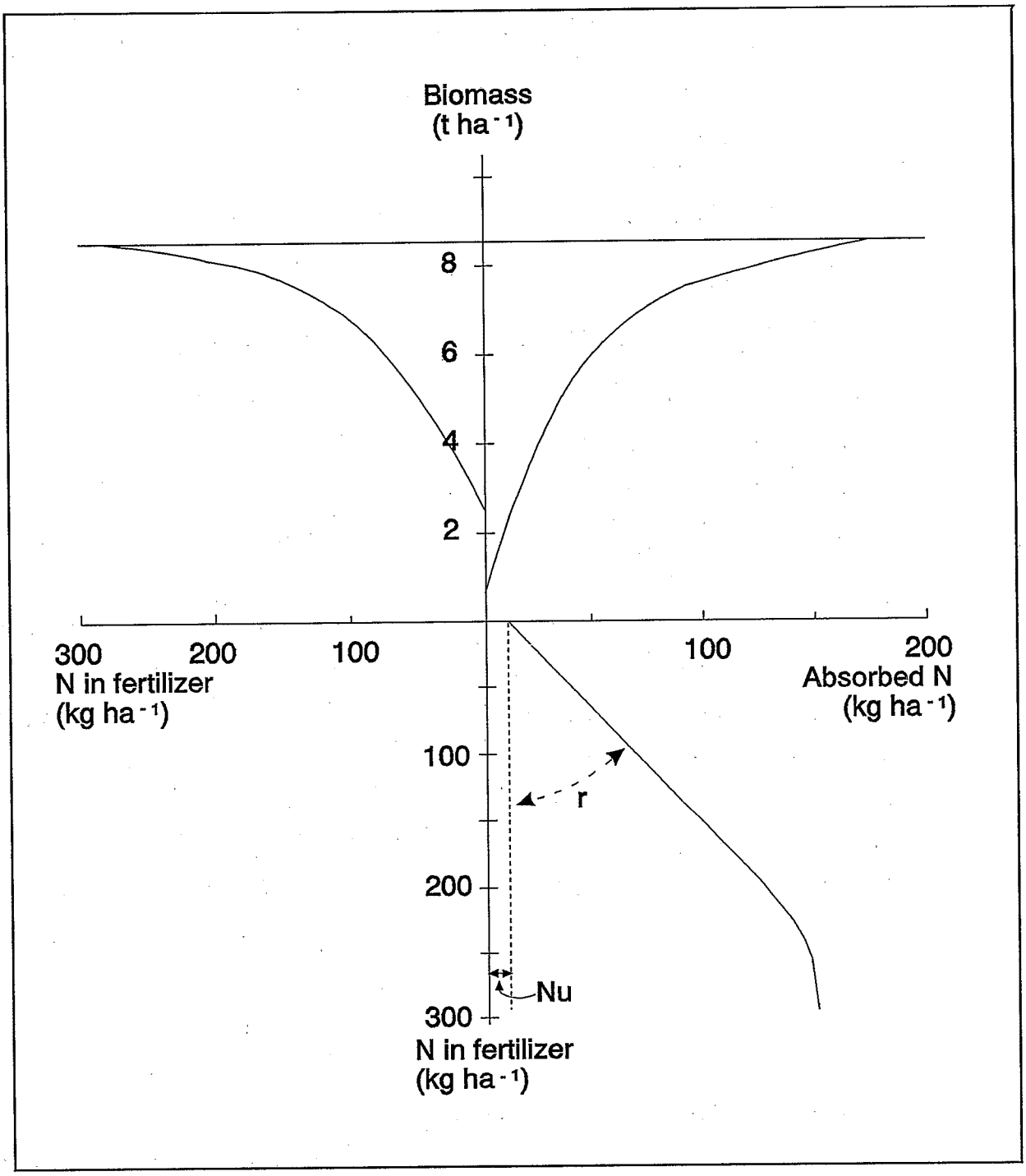

Figure 9-17. The relationship between applied nitrogen, soil nitrogen, and biomass production for a C_4 grass. (Taken from Penning de Vries, 1982). Nu is the nitrogen absorbed from the unfertilized soil and r is the recovery fraction of the fertilizer nitrogen.

only small changes in growth or total nitrogen. For example, few changes are obtained in bean growth experiments with soil nitrate levels of 10-20 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 9-18). 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 ammonia (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 a weak acid $[HNO_3]$, 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 since it is uncharged and can diffuse rapidly through the membrane. Thus, equilibrium means:

$$[H^+]_1 [NO_2^-]_1 = [H^+]_2 [NO_2^-]_2 \qquad (6)$$

For the weak base $[NH_3]$, the equilibrium condition of $K_b = [H^+] [NH_3] / [NH_4^+]$ likewise holds on both sides of the membrane. Here the concentration of NH_3 is the same on both sides, since it is uncharged and can diffuse rapidly (Crofts, 1967). The equilibrium condition then gives rise to:

$$[NH_4^+]_1 [NH_4^+]_2 = [H^+]_1 [H^+]_2 \qquad (7)$$

side 1		side 2
$NH_4^+ = H^+ + NH_3$	===	$NH_3 + H^+ = NH_4^+$
$NO_2^- + H^+ = HNO_2$	===	$HNO_2 = H^+ + NO_2^-$

Figure 9-18. 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 (See Walker and Crofts, 1970). In other words, the diffusion of uncharged species is fast enough to maintain a chemical potential equilibrium.

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 (HNO_2 + 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 total 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. Since the K_a for ammonia 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 value 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 ammonia 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 pH

The above arguments are critical for understanding how nitrogen species can move through biological organisms. Ammonium can accumulate in spaces of low pH, while nitrite can accumulate in spaces of high pH (compared with neighboring spaces). This is not true for strong acids such as nitric acid, which in biological organisms is completely dissociated to nitrate. 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 upon 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 μm thickness, this would be 2.5×10^{-9} equ/cm^2 wall. Moorvan et al. (1979) measured only about 7.5×10^{10} 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 uncontrolled by the cell (Taiz, 1984; Lutten et al., 1990) Once these acids are inside the cell, their metabolism and conversion to ammonium ion 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 N. He argues that uptake of phosphate and sulfur with conversion of ammonium into amino acids interact to keep this number small. This is not true for ammonia 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 N accumulated from NO_2 in sunflower is roughly 7.2×10^{-10} mol N/g FW sec^{-1}. Using Raven's number from above, there is about 2.4×10^{-7} 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, 1970]). 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 N 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 since 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 stomate and, therefore, the stomatal aperture 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 nitrate reductase. 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 9-13. NADH from respiration (and glycolysis) drives the reduction of nitrate to nitrite within the cytoplasm. 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 since the internal pH of the chloroplast stroma is higher than that of the cytoplasm (at about 8 to 8.5 when the leaf is illuminated, see arguments above). Normally, nitrite is reduced by a 6-electron process via photosynthesis. Although the evidence is somewhat contradictory (see Robinson, 1988, and 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 9-13. In darkness nitrite can not 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 ammonia are also toxic. Ammonia acts as an uncoupler of photophosphorylation. Thus, a critical limit in concentration must exist for both molecules for normal cells. While Table 9-13 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 upon the use of ammonia 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 ammonia (200 ppm) nor a decline in photosynthesis and growth; metabolites derived from nitrate seem to be well regulated under most circumstances.

If nitrate is added to the ammonia fertilizer (at 10% of ammonium), the level of ammonia within the plant remains low (200-600 ppm); again nitrate metabolites aid in the regulation of ammonia levels (Goyal et al., 1982). Under these conditions, the internal concentration of nitrate remains low—at about 500 ppm—for ammonia 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, while 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).

TABLE 9-13. 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 NO_3^- inward [Siddiqui et al., 1990].)

V_{max}: 0.3 - 3 μmol/g FW h^{-1}
K_m: 60-100 μM

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

$$NO_3^- + NAD(P)H = NO_2 + H_20 + NAD(P)$$

V_{max}: 3 - 5 μmol/g FW h^{-1}

	K_m,μM
NO_3^-	4,500
NADPH	15
NADH	9

C. Nitrite Reductase. (Enzyme associated with ferredoxin within the photosynthetic electron transport chain [Losada and Paneque, 1977; Wellburn, 1990].)

$$NO_2^- + (Fd)red = NH_4^+ (Fd)oxid$$

V_{max}: 3 - 5 μmol/g FW h^{-1}

	K_m,μM
Ferredoxin (Fd)	10
NO_2^-	100

D. Glutamine Synthetase. (Enzyme within plant tissue [Durzan and Steward, 1983].)

$$Glutamate + NH_3 + ATP = Glutamine + ADP + Pi$$

V_{max}: 5.4 - 9.9 μmol/g FW h^{-1}

	K_m,μM
Glutamate	3,000-12,000
NH_3	10-20
ATP	100-1,000

TABLE 9-13 (Cont'd). ENZYME PARAMETERS FOR CRITICAL ENZYMATIC STEPS IN PLANT USE OF NITROGEN COMPOUNDS

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

Glutamine = Oxoglutaric Acid + NAD(P)H = 2 Glutamate = $NAD(P)^+$

V_{max}: 1.8 - 3.6 μmol/g FW h^{-1}

	K_m,μM
Glutamine	300-1,500
Oxoglutarate	40-600
NAD(P)H	7-30

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

Oxaloacetate + Glutamate = Oxoglutarate = Asparate

K_m (acids) = 1 -40 mM

G. Asparagine Synthetase.

Asparate + Glutamine/NH_3 + ATP = Asparagine + Glutamate + ATP + P-P/H_2O

	K_m,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 - 100 μmole/g FW h^{-1}

9.7.4.6 Amine Metabolism

The metabolic pathway of nitrogen in the chloroplast is summarized in Figure 9-19. 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).

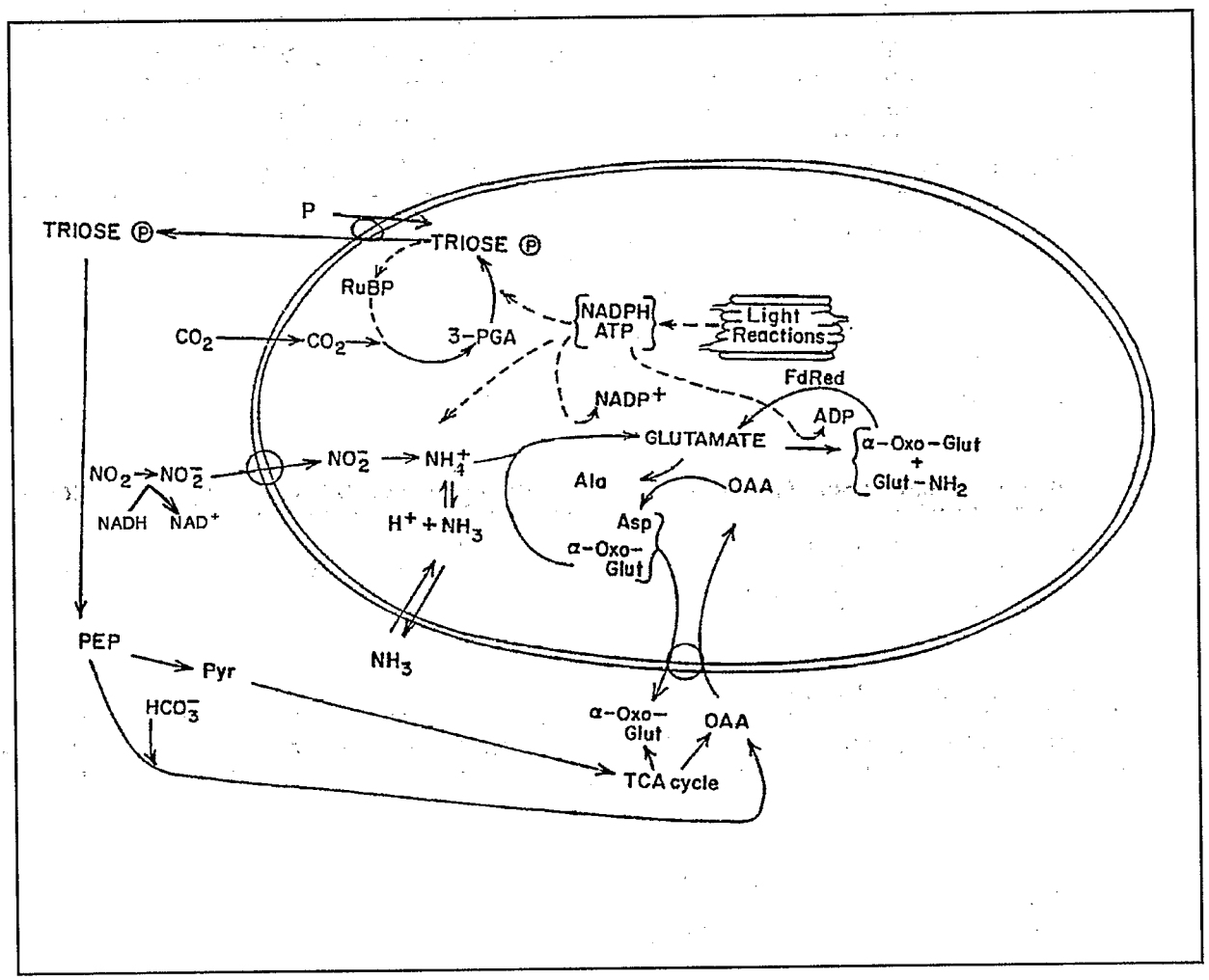

Figure 9-19. A generalized pathway of amino acid biosynthesis involving the chloroplast within the leaf. Abbreviations are: RuBP, ribulose 1,5-bisphosphate; PGA, 3-phosphoglyceric acid; Fd, ferredoxin; a-oxo-glut, a-oxo-glutarate; glut-NH_2, glutamine; Ala, alanine; asp, aspartic acid; OAA, oxalacetic acid; PEP, phosphopyruvic acid; Pyr, pyruvic acid; triose-P, triose phosphate (either dihydroxyacetone phosphate or glyceraldehyde 3-phosphate).

The photosynthetic process generates ammonia which 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 ammonia low and is carried out by the glutamate cycle coupling the equations shown under D and E in Table 9-13:

$$NH_4^+ + \text{glutamate} + \text{oxoglutarate} + ATP + NADPH = 2\ \text{glutamate} + ADP + Pi + NADP^+ \quad (14)$$

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 to 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 9-13) 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.

9.8 REGULATORY MAINTENANCE OF REDUCED NITROGEN COMPOUNDS (DETOXIFICATION)

As summarized above, NO_x exposure can overload the nitrogen metabolism pathways, as seen in Figure 9-16 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

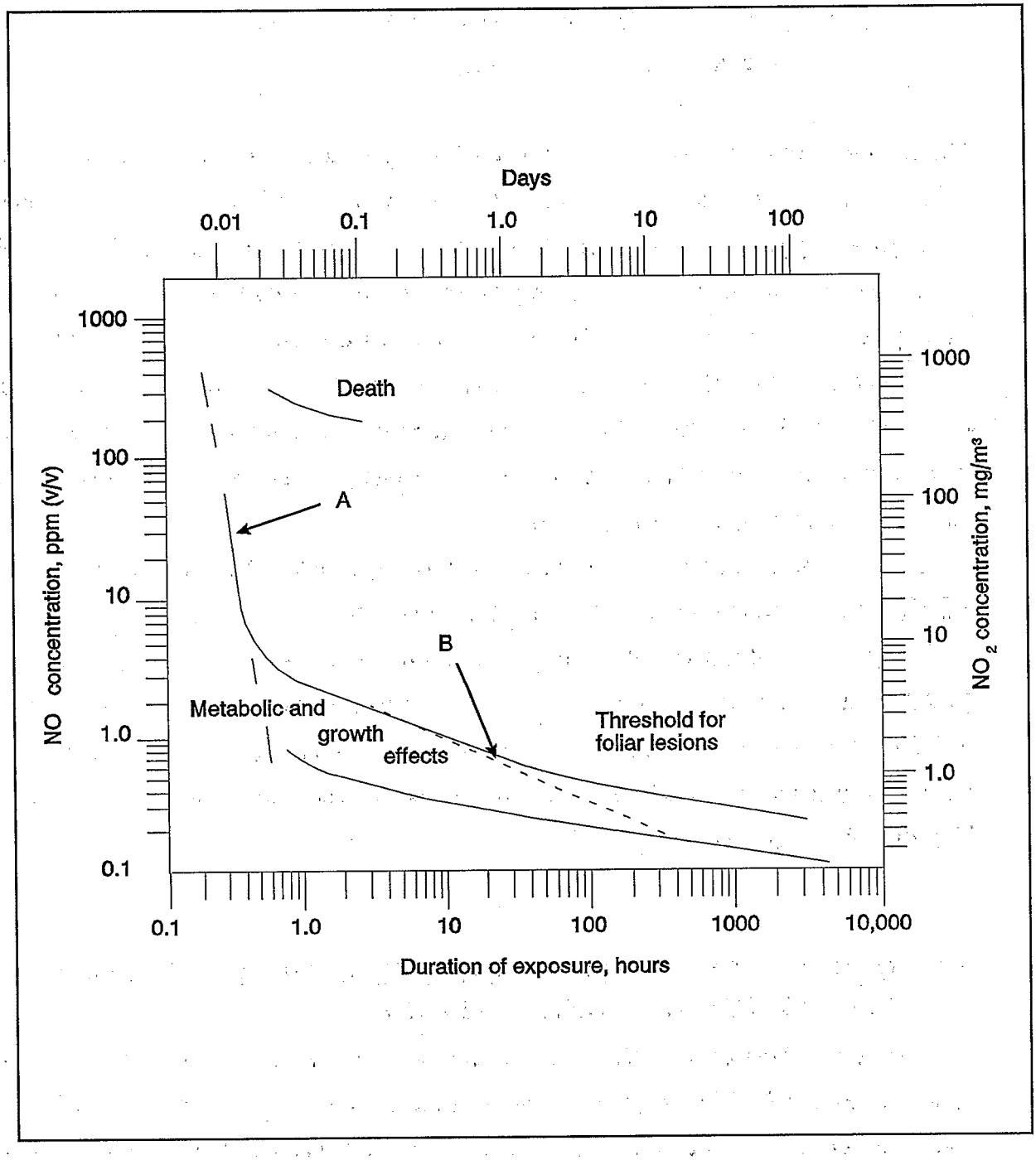

Figure 9-20. The relationship between the onset of either foliar lesions or metabolic and growth effects and the effective dose of NO_2. The curves contain data points of plant exposures above which effects were observed. The curve was taken from the 1982 criteria document (U.S. Environmental Protection Agency, 1982) and Figure 9-8, presented earlier.

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, 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 non-linearly dependent upon 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. Explanation for these curved boundaries is unknown. Understanding of the metabolic events surrounding NO_x conversion into metabolically active amines may help in discovering that explanation.

9.8.1 NO_x Incorporation with Non-toxic 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-N 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 be broken into two sections easily in which the relation between duration and concentration is nearly linear. Only the curve which marks the beginning of threshold foliar injury will be examined. The first section (Section A) extends from about 0.13 to 0.78 hours (8 to 47 minutes) 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:

$$C^n \times T = D_o \tag{15}$$

where C is the external concentration in ppm, T is the time in hours, and D_o and n are constants. This formula is fitted to the curves and the following values for each section for the constants are found to be:

Section	Time region	n(power)	D_o
A	15 - 50 min	0.30	1.6
B	3 h - 14 days	2.90	55.4

Section A represents very high levels of NO_2, which occur infrequently in nature. While 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 which enters the plant could be determined with proper measurements.

For the longer time periods at concentrations presently occurring 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 well match the reactions which are observed; the internal levels may be very low and stomatal aperture would influence reactions greatly. The ability of the plant to utilize the nitrite and ammonia 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 which 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 ammonia pool. If the flow of nitrogen into that pool exceeds the flow out, many metabolites, including ammonia, 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 2-3% 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.

9.9 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 which 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 ammonia.

9.9.1 Concept of Exposure Index

Data presented previously (in Figure 9-20) clearly showed that the concept of dose (concentration x exposure time) is not valid, as the effects of NO_2 are decidedly nonlinear. Most of the exposure data presented in Table 9-3 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 9-3. 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 able to exclude NO_x. Those plants which increase in mass are often those which 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 Ca^{+2} and K^+ imbalances (Goh and Hayes, 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 9-3 (Section 9.4.2) into a gross quantitative measure of (a) no effect, (b) decrease, or (c) 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/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 which 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 (concentration) versus log (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

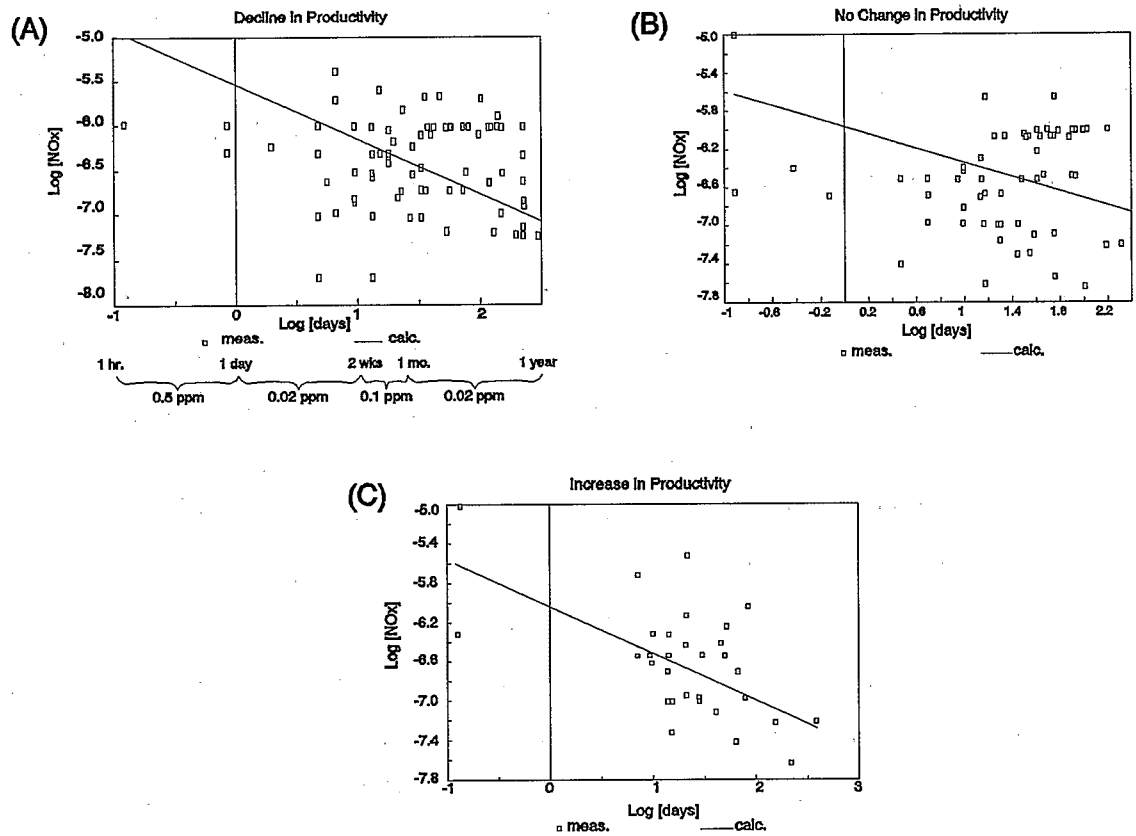

Figure 9-21. Diagram of studies of NO_x on plant productivity. This figure is similar to Figure 9-20; however, separate experiments are shown by individual symbols as a function of log (concentration of NO_2) and log(duration of exposure). The data are from Table 9-3. All the data in each sub-figure 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, top) Decline in productivity (exponent=2.7±0.2; r^2=0.200; n=87); (B, middle) No observed effect upon productivity (exponent=1.7±0.2; r^2=0.200; n=87); (C, bottom) 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.

dependence of dose (time × 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 upon 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 of a day to 2 weeks can cause an increase while for longer exposures (greater than one month), increases can be induced by as low as 0.024 ppm.

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

(1) While there are no absolute limits, for the most part a lower concentration will cause some shift in productivity (higher or lower) with longer times of exposure.

(2) The concept of a strict dose (concentration x 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 15).

(3) Under varied circumstances within the range of NO_2 exposure given in Figure 9-21, a given species will be either affected or not affected by NO_2. 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 upon productivity. The data are less clear for very long exposures; it may be that very low concentrations over a year's exposure may be enough to cause ecological problems. The lack of data make any conclusion premature.

9.9.2 Inhibited Processes

As previously stated, excess nitrate causes little injury to the plant; however, excess nitrite and ammonia 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'Neil et al., 1983, K_i = 10 mM), while ammonia 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 as well as normal carbon fixation is severely limited, thus inhibiting photosynthesis. Under high light or saturating CO_2, nitrite can intercept electrons and so inhibit NADPH used for CO_2 fixation. Under most conditions some believe that nitrogen reduction does not directly compete for reducing equivalences and so would not slow CO_2 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 ammonia 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 ammonia and NO_x exposure has not been established by research.

NO_2 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 which are largely unknown at the present time are expected to play a major role. Most of the chemical studies which indicate that NO_2 can react with double bonds of fatty acids are done in organic or non-polar solutions. The majority of these highly reactive compounds behave differently in polar solvents.

NO is even a 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 which indicate that it reacts rapidly with free radicals have been carried out in non-polar solvents and are, therefore, suspect. To be sure, there are many biochemical reactions which 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 since 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 15-30%). Since 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 SO_2 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., 1985). 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 (Malhatra 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 which 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 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 ammonia 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 since they cannot be exported. With a decline in available export carbohydrates, growth, 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).

9.9.3 Pollutants in Combination

The data collected for pollutants in combination do not give a coherent picture. Under most cases, 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 which 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 upon the nature of the pollutant and its interaction with the normal physiology. For example, ozone 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 will link directly to the formation of those compounds from nitrogen. One expects interactions but how they will develop is difficult to predict presently, since the interrelationships are many and currently difficult to model.

In any event, studies of co-occurrence of NO_2/SO_2 and NO_2/O_3 (Lefohn et al., 1984; Lane and Bell, 1984; Jacobson and McManus, 1985; Lefohn et al., 1987) concluded that (a) the co-occurrence of two-pollutant mixtures lasted only a few hours per episode, (b) the time between episodes is generally large (weeks, sometimes months), and (c) 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:	
Vegetable Crops:	
Onion	*Allium cepa* L.
Leek	*Allium ampeloprasum* L.
Tampala	*Amaranthus tricolor* L.
Celeriac	*Apium graveolens* L. var *rapaceum* (Mill.) Gaud.-Beaupr.
Beet	*Beta vulgaris* L.
Swiss chard	*Beta vulgaris* L.
Kale	*Brassica oleraceae* L. var *acephala* DC
Broccoli	*Brassica oleraceae* L. var *botrytis* L.
Cabbage	*Brassica oleraceae* L. var *capitata*
Kohlrabi	*Brassica oleraceae* L. var *gongylodes*
Turnip	*Brassica rapa* L.
Green pepper	*Capsicum annuum* L. var *annuum*
Chick pea	*Cicer arietinum* L.
Endive	*Cichorium endivia* L.
Taro	*Colocasia esculenta* (L.) Schott var *antiquorum* (Schott) F.J.Hubb and Rehd.
Cucumber	*Cucumis sativus* L.
Squash	*Cucurbita maxima* Duch.
Carrot	*Daucus carota* L. var *sativus* Hoffm.
Strawberry	*Fragaria chiloensis* (L.) Duchesne.
Woodland strawberry	*Fragaria vesca* L.
Sweet potato	*Ipomea batatas* (L.) Lam.
Garden lettuce	*Lactuca sativa* L.
Tomato	*Lycopersicon lycopersicum* (L.) Karst. ex Farw.
Currant tomato	*Lycopersicon pimpinellifolium* (Jusl.) Mill.
Parsnip	*Pastinaca sativa* L.
Parsley	*Petroselinum crispum* (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	*Phaseolus vulgaris* L.
Garden pea	*Pisum sativum* L.
Radish	*Raphanus sativus* L.
Rhubarb	*Rheum rhabarbarum* L.
Black salsify	*Scorzonera hispanica* L.
Eggplant	*Solanum melongena* L.
Potato	*Solanum tuberosum* L.
Spinach	*Spinacia oleracea* L.
Broad bean	*Vicia faba* L.
Watermelon	*Citrullus lanatus* (Thunb.) Matsum. and Nakai
Field crops:	
Oats	*Avena sativa* L.
Sugar beet	*Beta vulgaris* L.
Rape	*Brassica napus* L.
Buckwheat	*Fagopyrum esculentum* Moench.
Soybean	*Glycine max* (L.) Merrill
Upland cotton	*Gossypium hirsutum* L.
Common sunflower	*Helianthus annuus* L.
Barley	*Hordeum vulgare* L.
Tobacco	*Nicotiana tabacum* L.
Paddy rice	*Oryza sativa* L.
Castor bean	*Ricinus communis* L.
Common rye	*Secale cereale* L.
Sesame	*Sesamum indicum* L.
Sorghum	*Sorghum bicolor* (L.) Moench
Common wheat	*Triticum aestivum* L.
Durum wheat	*Triticum turgidum* L.
Maize	*Zea mays* L.
Forage, Pasture, Turf:	
Bentgrass	*Agrostis capillaris* L.
Redtop	*Agrostis gigantea* Roth.

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

Common Name[a]	Scientific Name
Creeping bentgrass	*Agrostis stolonifera* L. var *palustris* (Huds.) Farw.
Colonial bentgrass	*Agrostis tenuis* Sibth.
Smooth brome	*Bromus inermis* Leyss.
Orchard grass	*Dactylis glomerata* L.
Red fescue	*Festuca rubra* L.
Italian ryegrass	*Lolium multiflorum* Lam.
Perennial ryegrass	*Lolium perenne* L.
Alfalfa	*Medicago sativa* L.
Mat-grass	*Nardus stricta* L.
Common timothy	*Phleum pratense* L.
Annual bluegrass	*Poa annua* L.
Kentucky bluegrass	*Poa pratensis* L.
Red clover	*Trifolium pratense* L.
Crimson clover	*Trifolium incarnatum* L.
Spring vetch	*Vicia sativa* L.
Hedge vetch	*Vicia sepium*
Floricultural:	
Flossflower	*Ageratum houstonianum* Mill.
Common snapdragon	*Antirrhinum majus* L.
Sprenger asparagus	*Asparagus densiflorus* (Knuth) Jessop Cv. *Sprengeri*
Begonia	*Begonia* sp.
Hollyhock begonia	*Begonia gracilis* HBK
Begonia	*Begonia multiflora* Benth.
King begonia	*Begonia rex* Putz.
China aster	*Callistephus chinensis* (L.) Nees
Oxeye daisy	*Chrysanthemum leucanthemum* L.
Florist's chrysanthemum	*Chrysanthemum Xmorifolium* Ramat.
Painted leaf	*Coleus shirensis* Gürke
Lily-of-the-valley	*Convalaria majalis* L.
Dahlia	*Dahlia pinnata* 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	*Dieffenbachia maculata* (Lodd.) G.Don
Golden pothos	*Epipremnum aureum* (Linden and André) Bunt.
Spring heather	*Erica carnea* L.
Summer hyacinth	*Galtonia candicans* (Bak.) Decne.
Garden gladiolus	*Gladiolus Xhortulanus* L.H.Bailey
Plantain lily	*Hosta* sp.
Patience plant	*Impatiens wallerana* Hook. f.
Japanese morning-glory	*Ipomoea nil* (L.) Roth.
Palm-Beach-bells	*Kalanchoe blossfeldiana* Poelln.
Sweet pea	*Lathyrus odoratus* L.
Daffodil	*Narcissus pseudonarcissus* L.
Boston fern	*Nephrolepis exaltata* (L.) Schott
Garden geranium	*Pelargonium Xhortorum* L.H.Bailey
Geranium	*Pelargonium zonale* (L.) L'Her. ex Ait.
Common garden petunia	*Petunia Xhybrida* Hort. Vilm.-Andr.
Fairy primrose	*Primula malacoides* Franch.
German primrose	*Primula obconica* Hance
Common African violet	*Saintpaulia ionantha* H.Wendl.
Common salvia	*Salvia officinalis* L.
Baby's-tears	*Soleirolia soleirolii* (Req.) Dandy
French marigold	*Tagetes patula* L.
Tulip	*Tulipa gesnerana* L.
Periwinkle	*Vinca* sp.
Common periwinkle	*Vinca minor* L.
Common zinnia	*Zinnia elegans* Jacq.
Weeds and Native:	
Bear's garlic	*Allium ursinum* L.
Redroot	*Amaranthus retroflexus* L.
Adam-and-Eve	*Arum maculatum* L.
Common mugwort	*Artemesia vulgaris* 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	*Baileya pleniradiata* Harv. and Gray
Beggar-tick	*Bidens frondosa* L.
White mustard	*Brassica hirta* Moench
Crunch-weed	*Brassica kaber* (DC) L.C.Wheeler var *pinnatifida* (Stokes) L.C.Wheeler *Chaenactis carphoclinia* Gray
Lamb's-quarters	*Chenopodium album* L.
Goosefoot	*Chenopodium murale* L.
Canada thistle	*Cirsium arvense* (L.) Scop.
Jimsonweed	*Datura stramonium* L.
Crabgrass	*Digitaria* sp.
Horseweed	*Erigeron canadensis* L.
Alfilaria	*Erodium cicutarium* (L.) L'Her.
Japanese clover	*Lespedeza striata* (Thunb. ex J.Murr.) Hook. and Arn.
Lupine	*Lupinus angustifolius* L.
Mallow	*Malva parviflora* L.
Wood melic	*Melica uniflora* Retz.
Mint	*Mentha piperita* L.
Millet grass	*Milium effusum* L.
Sensitive plant	*Mimosa pudica* L.
? Tobacco	Nicotiana glutinosa
Wild tobacco	*Nicotiana rustica* L.
European wood sorrel	*Oxalis acetosella* L.
Scorpion weed	*Phacelia crenulata* Torr. ex S.Wats. *Plantago insularis* Eastw.
Common plantain	*Plantago major* L.
Dock	*Rumex ambiguous*
Broad-leaved dock	*Rumex obtusifolius* L.
Bladder campion	*Silene vulgaris* (Moench) Garcke
Common chickweed	*Stellaria media* (L.) Cyrillo
Common dandelion	*Taraxicum officinale* 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	*Viola reichenbachiana* Jord. ex Boreau
Devil's tongue	
Trees and Shrubs:	
Fruits:	
	Citrus aurantium L. *Citrus natsudaidai*
Grapefruit	*Citrus Xparadisi* Macfady
Sweet orange	*Citrus sinensis* (L.) Osbeck *Citrus unshu*
Japanese persimmon	*Diospyros kaki* L.f.
Common apple	*Malus pumila* Mill.
Peach	*Prunus persica* (L.) Batsch.
Wild pear	*Pyrus communis* L.
Currant	*Ribes* sp.
Grape (American hybrids)	*Vitis vinifera*
Fox grape	*Vitis labrusca* L.
Ornamentals:	
Japanese aucuba	*Aucuba japonica* Thunb.
Bougainvillea	*Bougainvillea spectabilis* Willd.
Boxwood	*Buxus microphylla* Siebold and Zucc.
Common camellia	*Camellia japonica* L.
Karanda	*Carissa carandas* L.
Croton	*Codiaeum variegatum* (L.) Blume
Algerian ivy	*Hedera canariensis* Willd.
English ivy	*Hedera helix* L.
Benjamin tree	*Ficus benjamina* L.
Rubber plant	*Ficus elastica* Roxb. ex Hornem.
Hybrid fuchsia	*Fuchsia Xhybrida* Hort. ex Vilm.
Common gardenia	*Gardenia jasminoides* Ellis
Chinese hibiscus	*Hibiscus rosa-sinensis* L.
Hortensia	*Hydrangea macrophylla* (Thunb.)Ser. subsp. *macrophylla*

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	*Ixora coccinea* L.
Glossy privet	*Ligustrum lucidum* Ait.
Paperbark tree	*Melaleuca quinquenervia* (Cav.) S.T.Blake
Common oleander	*Nerium oleander* L.
Fragrant olive	*Osmanthus fragrans* (Thunb.) Lour.
Japanese pittosporum	*Pittosporum tobira* (Thunb.) Ait.
Firethorn	*Pyracantha coccinea* M.J.Roem.
Azalea	*Rhododendron canescens*
Catawba rhododendron	*Rhododendron catawbiense* Michx.
Cultivated rose	*Rosa* sp.
Natural:	
Hedge maple	*Acer campestre* L.
Box elder	*Acer negundo* L.
Japanese maple	*Acer palmatum* Thunb.
Norway maple	*Acer platanoides* L.
Red maple	*Acer rubrum* L.
Black alder	*Alnus glutinosa* (L.) Gaertn.
White alder	*Alnus incana* (L.) Moench
Burro weed	*Ambrosia dumosa* (Gray) Payne
Four-wing saltbush	*Atriplex canescens* (Pursh.) Mutt
European white birch	*Betula pendula* Roth.
Downy birch	*Betula pubescens* J.F.Ehrh.
European hornbeam	*Carpinus betulus* L.
Hornbeam (?)	*Carpinus caucasica* Gros.
Australian pine	*Casuarina cunninghamiana* Miq.
Desert willow	*Chilopsis linearis* Cav.
Camphor tree	*Cinnamomum camphora* (L.) J.Presl. *Corylus betulus*
Russian olive	*Elaeagnus angustifolia* L.
Brittle bush	*Encelia farinosa* 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	*Eucalyptus camadulensis* Dehnh.
Spindle tree	*Euonymus japonica* Thunb.
European beech	*Fagus silvatica* L.
White ash	*Fraxinus americana* L.
European ash	*Fraxinus excelsior* L.
Green ash	*Fraxinus pennsylvanica* Marsh.
Maidenhair tree	*Gingko biloba* L.
Honeylocust	*Gleditsia triacanthos* L.
English walnut	*Juglans regia* L.
Creosote bush	*Larrea divaricata* Cav.
Sweetgum	*Liquidambar styraciflua* L.
Yellow poplar	*Liriodendron tulipifera* L.
Toringo crab apple	*Malus Sieboldii* (Regel) Rehd.
American sycamore	*Platanus occidentalis* L.
Carolina poplar	*Populus canadensis* Moench
Black poplar	*Populus nigra* L.
Hybrid poplar	*Populus nigra* x *P. maximowiczii*
Hybrid poplar	*Populus maximowiczii* x *P. planteirensis*
Sargent cherry	*Prunus sargentii* Rehd.
Japanese pear	*Pyrus pyrifolia* (Burm.f.) Nakai
White oak	*Quercus alba* L.
Oak	*Quercus iberica* Stev.
Oak	*Quercus imeretina* Stev.
Shira oak	*Quercus myrsinaefolia* Blume
English oak	*Quercus robur* L.
Pin oak	*Quercus palustris* Muenchh.
Willow oak	*Quercus phellos* L.
Black locust	*Robinia pseudoacacia* L.
European elderberry	*Sambucus nigra* L.
White beam	*Sorbus aria* (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	*Syringa vulgaris* L.
Small-leaved European linden	*Tilia cordata* Mill.
Large-leaved lime	*Tilia platyphyllos* Scop.
American elm	*Ulmus americana* L.
Scotch elm	*Ulmus glabra* Huds.
Sweet viburnum	*Viburnum odoratissima* Ker-Gawl. var. *awabuki* (C.Koch) Zab.
Summer grape	*Vitis aestivalis* Michx.
Japanese zelkova	*Zelkova serrata* (Thunb.) Mak.
Conifers:	
Silver fir	*Abies alba* Mill.
White fir	*Abies concolor* (Gord.) Lindl. ex Hildebr.
Nikko fir	*Abies homolepis* Siebold and Zucc.
Caucasian fir	*Abies nordmanniana* (Steven) Spach
Deodar cedar	*Cedrus deodara* (D.Don) G.Don
Port-Orford-cedar	*Chamaecyparis lawsoniana* (A.Murr.) Parl.
Hinoki cypress	*Chamaecyparis obtusa* (Siebold and Zucc.) Endl.
Japanese cedar	*Cedrus deodara* (Roxb.) Loud.
Shore juniper	*Juniperus conferta* Parl.
European larch	*Larix decidua* Mill.
Japanese larch	*Larix kaempferi* (Lamb.) Carrière
Norway spruce	*Picea abies* (L.) Karst.
White spruce	*Picea glauca* (Moench) Voss
Blue spruce	*Picea pungens* Engelm.
Red spruce	*Picea rubens* Sarg.
Sitka spruce	*Picea sitchensis* (Bong.) Carr.
Japanese red pine	*Pinus densiflora* Sieb. and Zucc.
Shortleaf pine	*Pinus echinata* Mill.
Pine	*Pinus elodarica* Medw.
Mountain pine	*Pinus mugo* Turra
Austrian pine	*Pinus nigra* 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	*Pinus pinaster* Ait.
Pitch pine	*Pinus rigida* Mill.
Eastern white pine	*Pinus strobus* L.
Scots pine	*Pinus sylvestris* L.
Loblolly pine	*Pinus taeda* L.
Japanese black pine	*Pinus thunbergiana* Franco
Virginia pine	*Pinus virginiana* Mill.
Douglas-fir	*Pseudotsuga menziesii* (Mirb.) Franco
English yew	*Taxus baccata* L.
Lichens:	*Anaptychia neoleucomelanena* *Lecanora chrysoleuca* *Parmelia praesignis* *Usnea cavernosa*

[a] Common 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 NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop				
NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
Vegetable crops:				
Swiss chard (*Beta vulgaris* L.)				
0.3	10 h/da, 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 (*Chicorium endivia* L.)				
1.0	620 hours over 1 month	Yield (-37), owing to reduced growth of foliage.[l] (Zahn, 1975)	GH/FE	G-S
Garden lettuce (*Lactuca sativa* L.)				
0.5[h]	16 days	Mass of plant (-11*); 30 days old; CO_2 at 1,200 ppm. (Caporn, 1989)	GH	ChLum
0.85[c]	33 days	Mass of plant (0); seedlings; CO_2 at 1000 ppm. (Mortensen, 1985a)	CE	?
0.9[b]	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[b]	16 days 22 days	Mass of plant (-18*); 30 days old; CO_2 at 1,200 ppm. (Caporn, 1989) Mass of plant (-32*); 36 days old; CO_2 at 1,200 ppm. (Caporn, 1989)	GH	ChLum
Green pepper (*Capsicum annuum* L. var *annuum*)			GH	ChLum
2.0[g]	over 110 days	Mass of plant (-20), yield of fruit (-17), delayed fruiting (10 days); CO_2 at 2,000 ppm.[l] (Law and Mansfield, 1982)	GH	?
Tomato (*Lycopersicon lycopersicum* [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

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop				
NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
0.11	1 weeks	Leaf area (-2), mass of leaves (+4), of stem (-1), of roots (+5); 4-week-old plants. (Marie and Ormrod, 1984)	CE	B942
	2 weeks	Leaf area (-9), mass of leaves (-2), of stem (-3), of roots (+7); 5-week-old plants. (Marie and Ormrod, 1984)	CE	B942
	3 weeks	Leaf area (-16), mass of leaves (+11), of stem (+19), of roots (+11); 6-week-old plants. (Marie and Ormrod, 1984)	CE	B942
	4 weeks	Leaf area (-9), mass of leaves (+6), of stem (+10), of roots (+9); 7-week-old plants. (Marie and Ormrod, 1984)		
0.16	10 days	Mass of 5th leaf (-33*); exposures started when 3rd or 4th true leaf appeared. (Taylor and Eaton, 1966)	CE	B942
	22 days	Mass (-20**) and area (-19**) of 5th leaf; exposures started when 3rd or 4th true leaf appeared. (Taylor and Eaton, 1966)	CE	Saltzman
0.2	60 days	Leaf area (-31).[1] (Natori and Totsuka, 1980)		
0.2[a]	50 days	Mass of plant (+96*, +2, or -7), leaf area (+120*, +4, or -5); 0, 1x, or 2x additions of fertilizer to soil; plants 9 to 10 weeks old. (Anderson and Mansfield, 1979)	CE	Saltzman
0.21	1 hour	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 GH	ChLum ChLum
0.25	80 hours	Mass of leaves (-6 or +17**), mass of stem (0 or +26); N-nutrient level at 28 or 140 mg/liter; 5-week-old plants. (Troiano and Leone, 1977)	CSTR/GH	B952
	125 hours	Number of fruit (-11), mass per fruit (-13), mass of plant (-41); increased senescence and abscission of foliage.[1] (Spierings, 1971)	CE/GH	MastTM
0.28	14 days	Fresh mass (-18*) or dry mass (-6) of 5th leaf; exposures started when 3rd or 4th true leaf appeared. (Taylor and Eaton, 1966)	GH,CE	Saltzman

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop				
NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
0.3	10 h/da, 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 ppmN-nutrient; 5-week-old plants.[1] (Matsumaru et al., 1979)	CE/GH	ChLum
	41 days	No effect on growth.[1] (Ishikawa, 1976)	CE/GH GH,CE	ChLum Saltzman
0.35[a]	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 hours	Mass of leaves (-8 or +14), mass of stem (0 or +16); N-nutrient level at 28 or 140 mg/liter; 5-week-old plants. (Troiano and Leone, 1977)	CE/GH	MastTM
0.4[a]	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).[1] (Spierings, 1971)	GG,CE	Saltzman
[a]	50 days	Mass of plant (+38*, -24*, or -44*), leaf area (+21*, -28*, or -44*); 0, 1x, or 2x 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 5th leaf; exposures started when 3rd or 4th true leaf appeared. (Taylor and Eaton, 1966)	CE	Saltzman
0.5	10 days	Length of shoot (+11), mass of leaves (-22).[1] (Spierings, 1971)	GH,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[b]	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

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop				
NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
0.6	41 days	No effect on growth.[1] (Ishikawa, 1976)		
0.7[b]	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 CE	Saltzman ChLum
0.8[a]	50 days	Mass of plant (-6, -17*, or -31*), leaf area (-11, -7, or -31*); 0, 1x, or 2x additions of fertilizer to soil; plants 9 to 10 weeks old. (Anderson and Mansfield, 1979)	GH	ChLum
0.85[c]	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[f]	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[b]	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
Eggplant (*Solanum melongena* 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.[1] (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.[1] (Ishikawa, 1976).		

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
Greenbean (*Phaseolus vulgaris* L.)				
0.02	5 days 6 h/da, 14 days	Plant height (+23*, +16*, +6*, +4, +8*), mass of leaf (+7, 0, -8*, -12*, -5*), area of leaf (+3, 0, 0, -9, -9*); unifoliolate leaf; depended upon level of nitrate (0, 1, 5, 10, 20 mM); 12-day-old seedlings. (Srivastava and Ormrod, 1984)	CE	ChLum
		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 upon level of nitrate (0, 1, 5, 10, 20 mM); 23-day-old seedlings. (Srivastava and Ormrod, 1986)	CE	ChLum
0.025	7 h/da, 5 da/wk, 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/da, 5 da/wk, 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/da, 40 days	Mass of plant (+25*), mass of roots (+1); 40-day-old plants. (Runeckles and Palmer, 1987)	GH	Mast
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*); unifoliolate leaf; depended upon 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) and mass of leaves (+9), of stems (+6), of roots (0), or of flowers (-4).[1] (Totsuka et al., 1978)	CE	ChLum
	15 days	Growth in leaf area (-6) and mass of leaves (-4), of stem (-1), of roots (+14), or of flowers and fruit (-13).[1] (Totsuka et al., 1978).	CE	ChLum
	15 days	Mass of plant (-3 to +11); (depended on experiment) exposed at 4- to 6-leaf stage. (Elkiey et al., 1988)	CE	B952
	7 h/da, 5 da/wk, 3 weeks	Mass of shoot (+98*), mass of roots (+178*), of number of pods (+86*), number of seeds (+29*), mass of seeds (+46*); 57-day-old plants. (Sandhu and Gupta, 1989)	GH	CSI
	6 h/da, 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 upon level of nitrate (0, 1, 5, 10, 20 mM); 23-day-old seedlings. (Srivastava and Ormrod, 1986)	CE	ChLum

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
0.21	1 h/da, 15 days	Mass of plant (-3); exposed at 4- to 6-leaf stage. (Elkiey et al., 1988)		
0.3	10 h/da, 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
0.5	6 h/da, 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 upon level of nitrate (0, 1, 5, 10, 20 mM); 23-day-old seedlings. (Srivastava and Ormrod, 1986)	CE CE	Saltzman ChLum
	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*); unifoliolate leaf; depended upon 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) and mass of leaves (-11), of stem (-23), of roots (-36), or of flowers (-39).[1] (Totsuka et al., 1978)	CE	ChLum
	14 days	Growth depression.[1] (cited in Taylor et al., 1975)		
	15 days	Growth in leaf area (-25) and mass of leaves (+5), of stem (-13), of roots (-53), or of flowers and fruit (-82).[1] (Totsuka et al., 1978)	CE	ChLum
	639 hours over 2 months	Yield (-27) with number of fruit (-19) and mass per fruit (-10).[1] (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

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop	NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
Garden pea (*Pisum sativum* L.)					
	0.039	2 h/da, 1 da/wk, 3 weeks	Mass of plant (-5), leaf area (±10); (added to continuous exposure of 0.0094 ppm); 5-week-old plants. (Edelbauer and Maier, 1988)	CE	ChLum
	0.1	15 days	Mass of plant (-3); exposed at 4- to 6-leaf stage. (Elkiey et al., 1988)	GH CE	ChLum B952
	0.12	2 h/da, 1 da/wk, 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 Maier, 1988)	GH	ChLum
Cucumber (*Cucumis sativus* L.)					
	0.2	67 days	Leaf area (+17).[1] (Natori and Totsuka, 1980)	CE	ChLum
	0.3	10 h/da, 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
	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[c]	18 days	Mass of plant (-9); seedlings; CO_2 at 1,000 ppm. (Mortensen, 1985a)	CE	ChLum
Woodland strawberry (*Fragaria vesca* L.)					
	1.0	213 hours over 7 weeks	No significant effect on yield.[1] (Zahn, 1975)	CE	?
Carrot (*Daucus carota* L. var *sativus* Hoffm.)					
	2.1	357 hours over 50 days	Yield of roots (-30).[1] (Zahn, 1975).	GH/FE	G-S

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
Radish (*Raphanus sativus* L.)				
0.08	3 h/da, 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 hours	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/da, 3 da/wk, 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/da, 3 da/wk, 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 hours	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 hours over 38 days	Mass of root (-13) and mass of plant (-27).[1] (Zahn, 1975)		
Field crops:			CSTR/GH	ChLum
Oats (*Avena sativa* L.)			CSTR/GH	ChLum
30	1 hour	No effect on growth; 3-month-old plants.[1] (Czech and Nothdurft, 1952)	CE	ChLum
Barley (*Hordeum vulgare* 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 NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
Species or Crop				
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 hours	Length of leaf (+27).[1] (Zahn, 1975)		
100	1 hour	Adverse effect on grain development.[1] (Czech and Nothdurft, 1952)	CE	ChLum
Paddy rice (*Oryza sativa* L.)				
0.3	51 days	Number of ears (+18), mass of grain (+1), mass of straw (0).[1] (Fujiwara, 1973; Ishikawa, 1976)	CE	ChLum
0.6	51 days	Number of ears (+29), mass of grain (+36), mass of straw (+5).[1] (Fujiwara, 1973).		
Common rye (*Secale cereale* L.)				
100	1 hour	Adverse effect on grain development.[1] (Czech and Nothdurft, 1952)	GH/FE FE,GH	G-S ?
Sorghum (*Sorghum bicolor* [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 (*Triticum aestivum* L.)				
0.08	3 h/da, 38 days	Mass of plant (+6), mass of roots (-18); 38-day-old plants. (Runeckles and Palmer, 1987)	GH	Mast
1.0	334 hours in 40 days	No significant effect on yield, mass per grain (+10), stalk growth (-12).[1] (Zahn, 1975)	GH/FE	G-S

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
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 hours	Length of leaf (+27).[1] (Zahn, 1975)		
100	1 hour	Adverse effect on grain development.[1] (Czech and Nothdurft, 1952)	CE	ChLum
Paddy rice (*Oryza sativa* L.)				
0.3	51 days	Number of ears (+18), mass of grain (+1), mass of straw (0).[1] (Fujiwara, 1973a; Ishikawa, 1976)	CE	ChLum
0.6	51 days	Number of ears (+29), mass of grain (+36), mass of straw (+5).[1] (Fujiwara, 1973a; Ishikawa, 1976).		
Common rye (*Secale cereale* L.)				
100	1 hour	Adverse effect on grain development.[1] (Czech and Nothdurft, 1952)	GH/FE FE,GH	G-S ?
Sorghum (*Sorghum bicolor* [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 (*Triticum aestivum* L.)				
0.08	3 h/da, 38 days	Mass of plant (+6), mass of roots (-18); 38-day-old plants. (Runeckles and Palmer, 1987)	GH	Mast
1.0	334 hours in 40 days	No significant effect on yield, mass per grain (+10), stalk growth (-12).[1] (Zahn, 1975)	GH/FE	G-S

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop				
NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
30	1 hour	No effect on yield.[1] (Czech and Nothdurft, 1952)	FE,GH	?
100	1 hour	Decreased filling of head.[1] (Czech and Nothdurff, 1952).	FE,GH	?
300	1 hour	Decreased mass of grains.[1] (Czech and Nothdurff, 1952).	FE,GH	?
Maize (*Zea mays* L.)				
0.1	15 days	Increased mass of plant (+13) and leaf area; 15-day-old seedlings.[1] (Elkiey 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/da, 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 N-nutrient; 4-week-old plants.[1] (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/da, 4-5 da/wk, 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/da, 4-5 da/wk, 4 week(?)	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

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
Buckwheat (*Fagopyrum esculentum* Moench.)				
0.3	30 days	Height (-3), number of leaves (+22), leaf mass (-33), stem mass (-43).[1] (Fujiwara, 1973; Ishikawa, 1976)	CE	ChLum
0.6	30 days	Height (-11), number of leaves (+23), leaf mass (-33), stem mass (-36).[1] (Fujiwara, 1973; Ishikawa, 1976)		
Soybean (*Glycine max* [L.] Merrill)				
0.1	7 h/da, 5 days	Relative growth rate of plant (+4); 5-week-old plants. (Sabaratnam and Gupta, 1988)	GH,CE	Saltzman
	3 h/da, once/2 da, 4 weeks	Mass of leaves (+5), of stem (0), of roots (+6), or of nodules (-1), and number of nodules (-4*); 7-week-old plants. (Klarer et al., 1984)	GH,CE	Saltzman
0.2	7 h/da, 5 days	Relative growth rate of plant (+3); 5-week-old plants. (Sabaratnam and Gupta, 1988)	CE CSTR	CSI ChLum
	3 h/da, once/2 da, 4 weeks	Mass of leaves (+9), of stem (+5), of roots (+2), or of nodules (+2), and number of nodules (-15*); 7-week-old plants. (Klarer et al., 1984)		
0.3	7 h/da, 5 days	Relative growth rate of plant (+1); 5-week-old plants. (Sabaratnam and Gupta, 1988)		
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/da, 5 days	Relative growth rate of plant (-47*); 5-week-old plants. (Sabaratnam and Gupta, 1988)	CE	CSI
	7 hours	Number of pods (-32*), number of seeds (-13*), mass of seeds (-34*); exposed when 1 month old, harvested 80 days later. (Gupta and Sabaratnam, 1988)	ZAPS	ChLum

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop	NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
	1.0	7 hours	Number of pods (-64*), number of seeds (-46*), mass of seeds (-58*); exposed when 1 month old, harvested 80 days later. (Gupta and Sabaratnam, 1988).	ZAPS CE CE CE	ChLum CSI CSI CSI
Common sunflower (*Helianthus annus* L.)					
	0.1	10 days	Growth in leaf area (-11) and mass of leaves (-3), of stem (-16), or of roots (-26).[1] (Totsuka et al., 1978)	CE	ChLum
		15 days	Growth in leaf area (+26) and mass of leaves (+27), of stem (+9), of roots (+37), or of flowers (-24).[1] (Totsuka et al., 1978)	CE	ChLum
	0.2	14 days	Leaf area (-4*), mass of leaves (+2), mass of stem (+8), mass of roots (+16); 28-day-old plants. (Okano et al., 1985a)	CE	ChLum
		38 days	Leaf area (+11).[1] (Natori and Totsuka, 1980)		
	0.3	7 days	Leaf area (+13, +6, or +10), mass of leaves (+23**, +6, or +14), mass of stem (+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 CE	ChLum ChLum
		10 h/da, 14 days	Leaf area (+3 or +31**), mass of leaf (-1 or +11*), mass of stem (-10 or +19*), mass of roots (-3 or +4); daytime or nightime exposure; 4-week-old plants. (Yoneyama et al., 1980c)	CE/GH	ChLum
		14 days	Mass of leaves (+17, -14, or -11), mass of stem (-5, -22, or -14), mass of roots (-7, -45, or -11); plants grown at 26, 105, or 260 ppmN-nutrient; 4-week-old plants.[1] (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 stem (-22**), mass of roots (-11); 28-day-old plants. (Okano et al., 1985a)		
	0.78	8 h/da, 21 days	Height (+6), mass of plant (+8); N-deficient plants.[1] (Faller, 1972)	CE	ChLum

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop				
NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
1.0	10 days	Growth in leaf area (-30) and mass of leaves (+1), of stem (-32), or of roots (-44).[1] (Totsuka et al., 1978)		
	15 days	Growth in leaf area (+6) and mass of leaves (+16), of stem (-26), of roots (-23), or of flowers (-74).[1] (Totsuka et al., 1978).	CE	ChLum
	14 days	Leaf area (-12**), mass of leaves (+2), mass of stem (-34**), mass of roots (-37**); 28-day-old plants. (Okano et al., 1985a)	GH CE	? ChLum
2.0	7 days	Leaf area (+35**, -6, -18**), mass of leaves (+42**, +17**, or -4), mass of stem (-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/da, 21 days	Height (+16), mass of plant (+10); N-deficient plants.[1] (Faller, 1972)	CE	ChLum
Sugar beet (*Beta vulgaris* L.)				
10	1 hour	No effect.[1] (Czech and Nothdurft, 1952)	CE	ChLum
30	1 hour	No effect.[1] (Czech and Nothdurff, 1952).		
100	1 hour	Decreased growth.[1] (Czech and Nothdurff, 1952)..		
Potato (*Solanum tuberosum* L.)			GH	?
0.1	15 days	Mass of plant (+13); 30-day-old plants. (Elkiey et al., 1988)		
0.11	7 days	Leaf area (-17 to +2), mass of leaves (-16 to +16), mass of stem (-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 stem (-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	?

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop	NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
	0.11	14 days	Leaf area (-15 to -7), mass of leaves (-9 to -3), mass of stem (-21 to +10); (depending on cultivar) in 20-day-old plants from sprouts. (Petitte and Ormrod, 1984)	CE CE	B952 B952
			Leaf area (-7), mass of leaves (-3), mass of stem (+1), mass of roots (+4); in 24-day-old plants from rooted cuttings. (Petitte and Ormrod, 1988)	CE CE	B952 B952
	0.2	5 h/da, 2 da/wk, 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 hour	No effect.[1] (Czech and Nothdurft, 1952)	FE,GH	?
	30	1 hour	No effect.[1] (Czech and Nothdurff, 1952)	FE,GH	?
	300	1 hour	Inhibited tuber formation.[1] (Czech and Nothdurff, 1952)	FE,GH	?
Tobacco (*Nicotiana tabacum* L.)					
	0.10	15 days	Mass of plant (-2 to +4), leaf area increased; (depended on experiment); exposed at 4- to 6-leaf stage.[1] (Elkiey et al., 1988)	CE	B952
	0.21	1 h/da, 15 days	Mass of plant (-2); exposed at 4- to 6-leaf stage. (Elkiey 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
Grasses:					
Redtop (*Agrostis gigantea* Roth.)					
	0.15	10 days	Area of 3rd youngest leaf (-12); 48 days old at start. (Elkiey and Ormrod, 1980)	CE	B942
Creeping bentgrass (*Agrostis stolonifera* L.)					
	0.15	10 days	Area of 3rd youngest leaf (-8); 48 days old at start. (Elkiey and Ormrod, 1980)	CE	B942
Colonial bentgrass (*Agrostis tennuis* Sibth.)					
	0.15	10 days	Area of 3rd youngest leaf (-13); 48 days old at start. (Elkiey and Ormrod, 1980)	CE	B942

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop				
NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
Orchard grass (*Dactylis glomerata* L.)				
0.024[j]	to 153 days	Percent dead leaf mass (-10) or mass of shoots (+4); plants 183 days old. (Lane and Bell, 1984)		
0.1	104 h/wk, 7 months	Mass of shoot (-5 or -14); exposed from emergence or 6 weeks later. (Whitmore and Mansfield, 1983)	FE	B952
0.11	104 h/wk, 4 weeks	Mass of green leaves (-25), of dead leaves and stubble (-29), or of roots (-13), leaf area (-24), number of leaves (-18), or of tillers (-9); seedlings 6 weeks old at start. (Ashenden, 1979a)	GH	?
	8 weeks	Mass of green leaves (-31**), of dead leaves and stubble (-20), or of roots (-20), leaf area (-24*), number of leaves (-7), or of tillers (-5); seedlings 6 weeks old at start. (Ashenden, 1979a)	GH	ChLum
	12 weeks	Mass of green leaves (-30*), of dead leaves and stubble (-24), or of roots (-12), leaf area (-25), number of leaves (-20), or of tillers (-17); seedlings 6 weeks old at start. (Ashenden, 1979a)	GH	ChLum
	16 weeks	Mass of green leaves (-3), of dead leaves and stubble (-19), or of roots (-18), leaf area (+6), number of leaves (-5), or of tillers (-5); seedlings 6 weeks old at start. (Ashenden, 1979a)	GH	ChLum
	20 weeks	Mass of green leaves (-7), of dead leaves and stubble (-46**), or of roots (-11), leaf area (-21), number of leaves (-33), or of tillers (-1); seedlings 6 weeks old at start. (Ashenden, 1979a)	GH	ChLum
Red fescue (*Festuca rubra* L.)				
0.15	10 days	Area of 3rd youngest leaf (-1 to +4); two cultivars; 48 days old at start. (Elkiey and Ormrod, 1980)	GH	ChLum
Italian ryegrass (*Lolium multiflorum* Lam.)				
0.11	104 h/wk, 4 weeks	Mass of green leaves (-3), of dead leaves and stubble (-6), or of roots (-14), leaf area (-14), number of leaves (-11), or of tillers (-21); seedlings 5 weeks old at start. (Ashenden and Williams, 1980; Ashenden and Mansfield, 1978)	CE	B942

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop				
NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
	8 weeks	Mass of green leaves (-13), of dead leaves and stubble (0), or of roots (+5), leaf area (-12), number of leaves (+4), or of tillers (+6); seedlings 5 weeks old at start. (Ashenden and Mansfield, 1978)	GH	ChLum
	12 weeks	Mass of green leaves (-14), of dead leaves and stubble (-23*), or of roots (-47**), leaf area (-27), number of leaves (+24), or of tillers (+10); seedlings 5 weeks old at start. (Ashenden and Mansfield, 1978)	GH	ChLum
	16 weeks	Mass of green leaves (-13), of dead leaves and stubble (-13), or of roots (-17), leaf area (-9), number of leaves (+20), or of tillers (-3); seedlings 5 weeks old at start. (Ashenden and Mansfield, 1978)	GH	ChLum
	20 weeks	Mass of green leaves (-10), of dead leaves and stubble (-5), or of roots (+35), leaf area (+1), number of leaves (-18), or of tillers (-17); seedlings 5 weeks old at start. (Ashenden and Mansfield, 1978)	GH	ChLum
Perennial ryegrass (*Lolium perenne* L.)				
0.018[d]	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, 1984)	FE	TM
0.028[e]	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, 1984)	FE	TM
0.024[j]	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, 1984)	FE	B952
0.1	104 h/wk, 7 months	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 3rd 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 N-level in soil; two populations. (Taylor and Bell, 1988)		
Common timothy (*Phleum pratense* L.)				
0.018[d]	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, 1984)	FE	TM

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
Species or Crop				
0.028[e]	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, 1984)	FE	TM
0.024[j]	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, 1984)	FE	B952
0.1	104 h/wk, 7 months	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/wk, 4 week	Mass of green leaves (-25), of dead leaves and stubble (-19), or of roots (-25), leaf area (-26), number of leaves (-8), or 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), of dead leaves and stubble (+15), or of roots (+12), leaf area (+13), number of leaves (+5), or of tillers (+2); seedlings 5 weeks old at start. (Ashenden and Mansfield, 1978)	GH	ChLum
	12 weeks	Mass of green leaves (-25), of dead leaves and stubble (-29), or of roots (-30*), leaf area (-20), number of leaves (-19), or of tillers (-17); seedlings 5 weeks old at start. (Ashenden and Mansfield, 1978)	GH	ChLum
	16 weeks	Mass of green leaves (-12), of dead leaves and stubble (-2), or of roots (-25*), leaf area (-16), number of leaves (+12), or of tillers (+11); seedlings 5 weeks old at start. (Ashenden and Mansfield, 1978)	GH	ChLum
	20 weeks	Mass of green leaves (+14), of dead leaves and stubble (-12), or of roots (+1), leaf area (+30), number of leaves (+10), or of tillers (-6); seedlings 5 weeks old at start. (Ashenden and Mansfield, 1978)	GH	ChLum
Kentucky bluegrass (*Poa pratensis* L.)				
0.1	104h/wk, 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 months	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	?

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop				
NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
0.11	104 h/wk, 4 weeks	Mass of green leaves (-18), of dead leaves and stubble (-7), or of roots (-33**), leaf area (-10), number of leaves (-24), or of tillers (0); seedlings 6 weeks old at start. (Ashenden, 1979a)	GH	ChLum
	8 weeks	Mass of green leaves (-30**), of dead leaves and stubble (-27*), or of roots (-23*), leaf area (-29*), number of leaves (-23*), or of tillers (-13); seedlings 6 weeks old at start. (Ashenden, 1979a)	GH	ChLum
	12 weeks	Mass of green leaves (-33**), of dead leaves and stubble (-20*), or of roots (-37**), leaf area (-34**), number of leaves (-36**), or of tillers (-15); seedlings 6 weeks old at start. (Ashenden, 1979a)	GH	ChLum
	16 weeks	Mass of green leaves (-34**), of dead leaves and stubble (-25*), or of roots (-42**), leaf area (-29**), number of leaves (-14), or of tillers (-19); seedlings 6 weeks old at start. (Ashenden, 1979a)	GH	ChLum
	20 weeks	Mass of green leaves (-29**), of dead leaves and stubble (-27*), or of roots (-47**), leaf area (-17), number of leaves (-12), or of tillers (-9); seedlings 6 weeks old at start. (Ashenden, 1979a)	GH	ChLum
0.15	10 days	Area of 3rd youngest leaf (-20 to +8); significant (-18*) in 1 out of 12 cultivars; 48 days old at start. (Elkiey and Ormrod, 1980)		
	10 days	Fresh mass of leaves (-17 to +16), leaf area (-10* to +22*); depended upon cultivar and environmental conditions; 45-day-old seedlings. (Elkiey and Ormrod, 1981a)	GH	ChLum
Fruits:				
Navel orange (*Citrus sinensis* [L.] Osbeck)				
1X ambient[i] for 8 months		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
2X ambient[i] for 8 months		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

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
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 (*Malus pumila* Mill.)				
0.1	104 h/wk, 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 (*Ribes* sp.)				
1.0	213 hours over 8 weeks	Yield (-12).[l] (Zahn, 1975)		
Floricultural crops:			FE	?
Florist's chrysanthemum (*Chrysanthemum Xmorifolium* Ramat.)				
0.85[c]	35 days	Mass of plant (-7 or +1); young plants of two cultivars; CO_2 at 1000 ppm. (Mortensen, 1985a)	FE	?

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
Dumb cane (Dieffenbachia maculata [Lodd.] G.Don.)				
1.0[a]	139 days	Mass of plant (-27*), height (+8*), number of lateral shoots (-23*); CO_2 at 1000 ppm. (Saxe and Christensen, 1984,1985)	GH/FE CE GH	G-S ? Chlum
Benjamin tree (*Ficus benjamina* L.)				
1.0[a]	147 days	Mass of plant (-25*), height (-7); CO_2 at 1000 ppm. (Saxe and Christensen, 1984,1985)	GH	ChLum
Rubber plant (*Ficus elastica* Roxb. ex Hornem.)				
1.0[a]	128 to 136 days	Mass of plant (-28*), height of plant (-21*), total leaf area (-18); CO_2 at 1000 ppm. (Saxe and Christensen, 1984,1985)	GH	ChLum
Algerian ivy (*Hedera canariensis* Willd.)				
1.0[a]	101 days	Mass of plant (-1), length of shoots (0); CO_2 at 1000 ppm. (Saxe and Christenden, 1984, 1985)		
English ivy (*Hedera helix* L.)				
0.85[c]	55 or 77 days	Mass of plants (-10 or 0); young plants of two cultivars; CO_2 at 1000 ppm. (Mortensen, 1985a)	GH	ChLum
1.0[a]	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 (*Hibiscus rosa-sinensis* L.)				
1.0[a]	112 or 133 days	Mass of plant (±1), height of plant (+1), number of shoots (0); CO_2 at 1,000 ppm. (Saxe and Christenden, 1984, 1985)	GH	ChLum
Palm-Beach-bells (*Kalanchoe blossfeldiana* Poelln.)				
0.85[c]	54 days	Mass of plant (+8); young plants; CO_2 at 1,000 ppm. (Mortensen, 1985a)	GH	ChLum
Boston fern (*Nephrolepis exaltata* [L]. Schott)				
0.85[c]	76 days	Mass of plant (-7); young plants; CO_2 at 1,000 ppm. (Mortensen, 1985a)	CE	?

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
Species or Crop				
1.0[a]	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 (*Rhododendron canescens*)				
0.25	3 h/da, 6 days over 4 weeks	Mass of stems (-10*), mass of leaves (-7*), shoot length (-18*) in 2 out of 8 cultivars; 1-year-old plants. (Sanders and Reinert, 1982a)	GH	ChLum
Cultivated rose (*Rosa* sp.)				
0.85[c]	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 hours over 8 weeks	No effect.[1] (Zahn, 1975)		
African violet (*Saintpaulia ionantha* H. Wendl.)				
0.85[c]	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 (*Soleirolia soleirolii* [Req.] Dandy)				
0.85[c]	43 days	Mass of plant (+2); young plants; CO_2 at 1,000 ppm. (Mortensen, 1985a)	GH/FE	G-S
French marigold (*Tagetes patula* L.)				
0.3	6 h/da, 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/da, 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:			CSTR/GH	ChLum
Desert marigold (*Baileyia pleniradiata* Harv. and Gray)				
0.11	5 h/da, 5 da/wk, 17 weeks	Height (-4), mass of plant (+6), number of inflorescences (+10). (Thompson et al., 1980)	CSTR/GH	ChLum
0.33	5 h/da, 5 da/wk, 17 weeks	Height (+6), mass of plant (+30), number of inflorescences (+61*). (Thompson et al., 1980)		

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop	NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
	1.0	5 h/da, 5 da/wk, 17 weeks	Height (0), mass of plant (+26), number of inflorescences (+65*). (Thompson et al., 1980)		
(*Chaenactis carphoclina* Gray)					
	0.11	5 h/da, 5 da/wk, 12 weeks	Height (-23), mass of plant (+56), number of inflorescences (+40).[1] (Thompson et al., 1980)	GH	ChLum
	0.33	5 h/da, 5 da/wk, 12 weeks	Height (-2), mass of plant (+49), number of inflorescences (-6).[1] (Thompson et al., 1980)	GH	ChLum
	1.0	5 h/da, 5 da/wk, 12 weeks	Height (-3), mass of plant (+26), number of inflorescences (+35).[1] (Thompson et al., 1980)	GH	ChLum
Alfilaria (*Erodium cicutarium* [L.] L'Her.)					
	0.11	5 h/da, 5 da/wk, 16 weeks	Height (-9), mass of plant (-5), number of inflorescences (-16). (Thompson et al., 1980)	GH	ChLum
	0.33	5 h/da, 5 da/wk, 16 weeks	Height (+28*), mass of plant (+24), number of inflorescences (-2). (Thompson et al., 1980)	GH	ChLum
	1.0	5 h/da, 5 da/wk, 16 weeks	Height (+8), mass of plant (0), number of inflorescences (-17). (Thompson et al., 1980)	GH	ChLum
Mint (*Mentha piperita* L.)					
	0.08	3 h/da, 56 days	Mass of plant (+4), mass of roots (-6); rooted cuttings. (Runeckles and Palmer, 1987)	GH	Mast
Scorpion weed (*Phacelia crenulata* Torr. ex S.Wats.)					
	0.11	5 h/da, 5 da/wk, 17 weeks	Height (+9), mass of plant (-10), number of inflorescences (-5). (Thompson et al., 1980)	GH	ChLum
	0.33	5 h/da, 5 da/wk, 17 weeks	Height (+3), mass of plant (+2), number of inflorescences (+2). (Thompson et al., 1980)	GH	ChLum

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop	NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
	1.0	5 h/da, 5 da/wk, 17 weeks	Height (+20), mass of plant (+12), number of inflorescences (+4). (Thompson et al., 1980)	GH	ChLum
(*Plantago insularis* Eastw.)					
	0.11	5 h/da, 5 da/wk, 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/da, 5 da/wk, 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/da, 5 da/wk, 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:					
White alder (*Alnus incana* [L.] Moench)					
	0.1	104 h/wk, 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	?
Burro weed (*Ambrosia dumosa* [Gray] Payne)					
	0.11	5 h/da, 5 da/wk, 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

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop	NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
	0.33	5 h/da, 5 da/wk 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/da, 5 da/wk 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
Four-wing saltbush (*Atriplex canescens* [Pursh.] Mutt)					
	0.11	5 h/da, 5 da/wk 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/da, 5 da/wk 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/da, 5 da/wk 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 (*Betula pendula* 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); month-old seedlings. (Freer-Smith, 1985)	CE	?

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
0.1	104 h/wk, 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/wk, 10 months	Mass of shoot (-11), mass of roots (-23). (Wright, 1987)	FE	?
	13 months	Height (0), stem diameter (+5), mass of shoot (+16), mass of roots (+14); different clone from above. (Wright, 1987)	FE	?
Downy birch (*Betula pubescens* J.F.Ehrh.)				
0.1	104 h/wk, 22 week	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/wk, 2 months	Height (-22). (Wright, 1987)	GH	?
	13 months	Height (-3), stem diameter (0), mass of shoot (+5), mass of roots (0). (Wright, 1987)	GH	?
Desert willow (*Chilopsis linearis* Cav.)				
0.11	5 h/da, 5 da/wk, 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/da, 5 da/wk, 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/da, 5 da/wk, 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 (*Cinnamomum camphora* 4[L.] J.Presi.)				
0.3	30 days	Mass of plant (+10), leaf area (+2); 1- to 2-year-old plants. (Okano et al., 1989)	CE	ChLum

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop					
NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]		Facility[m]	Monitor[n]
Brittle bush (*Encelia farinosa* Gray ex Torr.)					
0.11	5 h/da, 5 da/wk, 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
0.33	5 h/da, 5 da/wk, 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/da, 5 da/wk, 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 (*Euonymus japonica* 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 (*Fraxinus americana* L.)					
0.1	6 h/da, 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 (*Fraxinus pennsylvanica* Marsh.)					
0.1	6 h/da, 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 (*Larrea divaricata* Cav.)					
0.11	5 h/da, 5 da/wk, 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

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
0.33	5 h/da, 5 da/wk, 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/da, 5 da/wk, 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 (*Liquidambar styraciflua* L.)				
0.1	6 h/da, 28 days	Height (-32), shoot mass (-25), root mass (-27*); 6- to 8-week-old seedlings. (Kress and Skelly, 1982)	CSTR/GH	ChLum
Common oleander (*Nerium oleander* L.)				
0.3	30 days	Mass of plant (+17*), leaf area (+3); 1- to 2-year-old plants. (Okano et al., 1989)		
American sycamore (*Platanus occidentalis* L.)				
0.1	6 h/da, 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., 1982)	CE	ChLum
Carolina poplar (*Populus canadensis* Moench)				
0.5	1 hour	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 hour	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 (*Populus maximowiczii* x *Populus* 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

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
Black poplar (*Populus nigra* L.)				
0.1	104 h/wk, 22 weeks	Stem height (+3), leaf area (+15), mass of shoot (+18); second-year cuttings. (Freer-Smith, 1984; Whitmore and Freer-Smith, 1982)	FE	?
	60 weeks	Stem height (0), mass of shoot (-13); second-year cuttings. (Whitmore and Freer-Smith, 1982)	FE	?
0.11	104 h/wk, 8 weeks	Growth in mass of leaves (-22), of stem (-14), of roots (-16); number of leaves (-43**), area per leaf (+45*); one-year cuttings. (Freer-Smith, 1984; Whitmore et al., 1982)	FE	?
	10 weeks	Mass of leaves (-27), of stem (-20), of roots (-21); during winter. (Whitmore and Freer-Smith, 1982)	FE	?
	22 weeks	Growth in mass of stem (-25), of roots (-38); one-year cuttings. (*idem*)	FE	?
0.5	1 hour	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
1.0	1 hour	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 (*Quercus mysinaefolia* 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 (*Quercus phellos* L.)				
0.1	6 h/da, 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 (*Tilia cordata* Mill.)				
0.1	104 h/wk, 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 bivurnum (*Biburnum odoratissima* Ker-Gawl. var *awabuki*)				
0.3	30 days	Mass of plant (+20), leaf area (-5); 1- to 2-year-old plants. (Okano et al., 1989)		

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop				
NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
Japanese zelkova (Zelkova serrata [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 (*Larix decidua* L.)				
1.0	537 hours over 2 months	No effect.[1] (Zahn, 1975)	GH/FE	G-S
Norway spruce (*Picea abies* [L.] Karst.)				
1.3	1900 hours over 5 months	Linear growth of current year (-7), linear growth of following year (-17).[1] (Zahn, 1975)	GH/FE	G-S
Sitka spruce (*Picea sitchensis* [Bong.] Carr.)				
0.03	8 weeks	Mass of plant (-5 to +18); advanced bud-break (*); 6-month-old seedlings exposed during dormancy; harvested 6 weeks after exposure. (Freer-Smith and Mansfield, 1987)	CE	?
Pitch pine (*Pinus rigida* Mill.)				
0.1	6 h/da, 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 (*Pinus strobus* L.)				
0.05	4 h/da, 35 days	Length of needles (<-10); 2-year-old ramets. (Yang et al., 1982,1983b)	CSTR/GH	ChLum
0.1	4 h/da, 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/da, 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

APPENDIX 9B (cont'd). TABULATION OF EFFECTS OF NO_x ON GROWTH, REPRODUCTION, AND YIELD OF PLANTS IN EXPERIMENTAL INVESTIGATIONS

Species or Crop	NO_x ppm	Exposure Duration	Effect (% deviation from treatment without NO_x)[k]	Facility[m]	Monitor[n]
Loblolly pine (*Pinus taeda* L.)					
	0.1	6 h/da, 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 (*Pinus virginiana* Mill.)					
	0.1	6 h/da, 28 days	Height (-13), mass of shoot (-1), mass of roots (-7); 6- to 8-week-old seedlings. (*idem*)		

[a] NO
[b] 20% NO_2 and 80% NO
[c] NO_2 at 0.15 + NO at 0.7 ppm
[d] NO_2 at 0.006 + NO at 0.012 ppm
[e] NO_2 at 0.021 + NO at 0.007 ppm
[f] NO_2 at 0.5 + NO at 0.4 ppm
[g] NO (with NO_2 at 0.05 ppm)
[h] NO (with NO_2 at 0.15 ppm)
[i] Range of 0 to 0.2 ppm
[j] Control was NO_2 at 0.009 ppm, background SO_2 at 0.003 ppm.
[k] Statistical significance of the effect, as provided in the source, is indicated by * for $0.01 < \alpha \leq 0.05$ and by ** for $\alpha \leq 0.01$.
[l] Statistical information not provided.
[m] Experimental facilities are denoted by: ZAPS, zonal air pollution system in open field; FE, field exposure chamber; GH, greenhouse; CSTR/GH, continuous-flow stirred-tank reactor in a green house; CE, controlled environment chamber.
[n] Monitoring methods for NO_x are denoted by: ChLum, for gas-phase chemiluminescent devices; Saltzman, for impingement in Saltzman reagent; TM for triethanolamine method; GS for Griess-Saltzman method; LGS for Lyshkow-modified Griess-Saltzman method; B852, B942 or B952 for Beckman 852, 942A or 952A monitors; CSI for Columbia Scientific, model 1600 Monitor.

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, NO_2). This chapter explains the known effects of nitrogen compounds (e.g., nitrogen oxides, nitrate, nitric acid) 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.

Since the mid-1980s the view has emerged that the atmospheric deposition of inorganic nitrogen has impacted aquatic and terrestrial ecosystems. It is known that in many areas of the United States the atmospheric input of nitrogen compounds is significant (U.S. Environmental Protection Agency, 1982), however, the impacts are generally unknown or considered benign. Although, the evidence linking nitrogen deposition with ecological impacts is tenuous there has been a growing concern (Skeffington and Wilson, 1988). This concern has been magnified because (1) the atmospheric concentrations of nitrogen compounds have increased in North America and most European countries, and (2) ecosystems formerly limited by nitrogen have become nitrogen saturated via atmospheric deposition. These concerns have led to attempts 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).

This chapter is organized into six main sections that are presented in the following sequence: (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 on wetlands and bogs of nitrogen loading; and (6) discussion of the effects on aquatic ecosystems of nitrogen loading.

10.1.2 Ecosystems

Ecosystems are composed of populations of "self-supporting" and "self maintaining" living plants, animals and microorganisms interacting among themselves and with the non-living 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), 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, esthetic 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 its 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).

10.1.2.1 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 determines 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 plant species that have a capacity to tolerate the competitional stresses (Kozlowlski, 1980). Pollutant stresses are superimposed upon the naturally occurring competitional 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.

10.1.2.2 Ecosystem Functions

Ecosystem function refers to the suite of processes and interactions among its components and their environment that involve movement of nutrients and energy through a community as organic matter. The more nutrients 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 (CO_2) 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). Its 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).

10.1.2.3 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 upon their genetic constitution (genotype), 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 non-living environment. Air pollutants, for example, that limit carbon fixation will shift allocation to new leaves, while 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, 1988).

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 determine accurately 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 possible changes in the nitrogen cycle that may result.

10.1.3 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 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 ecosystems may be upsetting the relationships that exist among the various components and thus changing 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, a pollutant that can be converted chemically or biologically into ammonia, nitrate, or nitrite can be used by plants. Nitrogen oxides which 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 which enters through the leaves can also be converted for plant use since most leaves have enzyme systems which 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, fresh water and oceanic habitats; only the microorganisms which 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); (2) sedimentation of particulate forms of inorganic nitrogen; and (3) sorption (e.g., of ammonium ions 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,

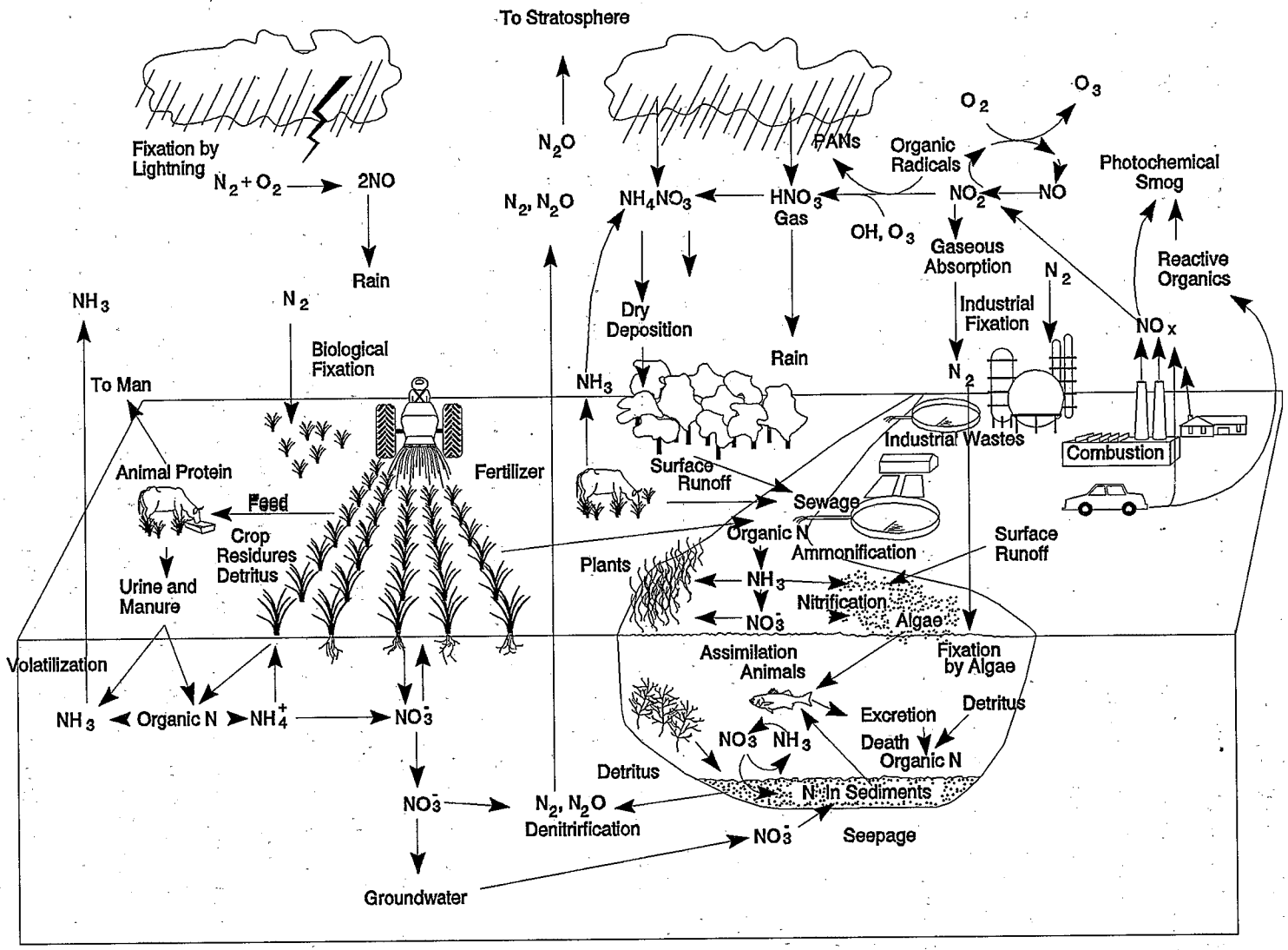


Figure 10-1. Schematic representation of the nitrogen cycle, emphasizing human activities that affect fluxes of nitrogen.

Source: National Research Council (1978).

(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 ammonia 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 can utilize nitrogen in the form of ammonium or nitrate with equal efficiency and either form can be converted by plants 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 ammonia. 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 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 nitrogen oxide emissions from 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. Crops can utilize only a proportion of the nitrogen fertilizers (containing nitrates, ammonium salts, anhydrous or liquid ammonia, or urea) added to the agricultural soils; leaching and runoff results (Sprent, 1987). Also, ammonia 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).

10.1.3.1 Biological Nitrogen Fixation

Nitrogen fixation, the conversion of molecular nitrogen gas (N_2) to ammonium (NH_4^+), is accomplished by a limited number of free-living and symbiotic (living in the roots of leguminous plants) bacteria. The ammonia (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.

10.1.3.2 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 while 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).

10.1.3.3 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 are converted into ammonium. The ammonium may be (1) assimilated by terrestrial or aquatic plants and microorganism, (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 ammonia (NH_3) may escape into the atmosphere during the process. Its volatilization is a purely physical process whereby ammonia, in equilibrium with ammonium (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).

10.1.3.4 Nitrification

Nitrification is the two-step process during which microorganisms first convert ammonium (NH_4^+) to nitrite (NO_2^-) and then to nitrate (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 reduced 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 nitrous oxide 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 the ground water, or
- escape as gas to the atmosphere (Buckman and Brady, 1969).

10.1.3.5 Denitrification

Denitrification is an anaerobic bacterial process during which nitrates are converted into atmospheric nitrogen gas. Nitrates (NO_3^-), are converted into nitrites (NO_2^-), then gaseous nitrous oxide (N_2O) and finally into nitrogen gas (N_2), which escapes into the atmosphere. Under acidic conditions in the soil, nitrites rarely accumulate but are spontaneously decomposed into nitric oxide (NO). Under alkaline conditions, they are biologically converted into nitrous oxide and molecular nitrogen (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. The photochemical decomposition of nitrous oxides is the main stratospheric source of nitrogen oxides (Delwiche, 1977). Nitrous oxide has been implicated in global warming (Bolle et al., 1986).

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 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.

10.2 DRY DEPOSITION RATES OF REACTIVE "N" 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, biogeochemical cycling, and may help explain how pollutants affect plants (Baldocchi et al., 1987, 1988; Hosker and Lindberg, 1982; Taylor et al., 1988).

Dry deposition characteristics of nitrogen dioxide (NO_2), nitric oxide (NO), nitric acid vapor (HNO_3), ammonia (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 N deposited on landscape surfaces, and by dissolving in aerosols NH_3 may enhance HNO_3 removal in wet precipitation (Erisman et al., 1988). Therefore, ammonia deposition data is included here. Deposition data is unavailable for other potentially important reactive forms of N: nitrous acid (HNO_2), dinitrogen pentoxide (N_2O_5), and the gaseous nitrate radical (NO_3). Pernitrate 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 (N_2O), the most abundant nitrogen oxide, 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 nitrogen oxides 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 nitrogen oxides are usually below or at the detection limits of available monitoring equipment (concentrations range from <0.003 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 nitrogen oxide concentrations are around 0.07 ppm with values ranging from <0.005 to 0.4 ppm.

A number of recent studies in remote areas have shown that air concentrations of NO, NO_2, and HNO_3 are commonly less than 0.005 ppm with HNO_3 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, NO_2 and HNO_3 concentrations have been measured in the 0.010-0.030 ppm and 0.001-0.003 ppm ranges, respectively (Bytnerowicz

et al., 1987; 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 N 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. World Health Organization (1987) also provides an extended discussion of deposition of N forms important to the establishment of air quality guidelines.

10.2.1 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 Diederen, 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. Although not yet applied to pollutant gas deposition, Matson and Harriss (1988) have suggested the use of aircraft-based measurements to study gas exchange over wide landscape areas.

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 N 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 Diederen, 1985) are two examples of the problems often encountered. Many N 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 discussion of the benefits and/or pitfalls of the canopy measurement techniques.

Comparisons between throughfall or precipitation nitrate and ammonium ion concentrations have also been used to calculate particulate N deposition to forest canopies (Gravenhorst et al., 1983; Lovett and Lindberg, 1984). However, the reactivity of trace N 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^- vs. 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 ^{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).

10.2.2 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:

$$F_c = V_d * (C_z - C_o) \quad (1)$$

where F_c is flux to the canopy in nmol m^{-2} s^{-1}, C_z is the concentration at the height of the measurement (nmol m^{-3}), C_o is the concentration at receptor sites in the canopy (nmol m^{-3}), and V_d is the overall deposition velocity in units of m s-1. The V_d is the reciprocal of the total canopy resistance to flux. An analogous equation can be derived for leaf-level, chamber measurements:

$$F_1 = K_1 * (C_a - C_i) \quad (2)$$

where F_1 is flux to leaves, C_a is the concentration of pollutant in the air around the leaf, C_i is the concentration of pollutant in or on the leaf (often equal to 0), and K_1 is the conductance of the leaf to pollutant gas transfer.

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:

$$V_d = K_1 * LAI \quad (3)$$

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.

10.2.3 Processes Governing Deposition of Gases and Particles

Dry deposition of gases and particles to foliar and non-foliar surfaces refers to the transfer of N 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 10.2.4 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.

TABLE 10-1. FACTORS INFLUENCING DRY DEPOSITION OF REACTIVE NITROGEN COMPOUNDS (Modified after Sehmel, 1980)

	Chemical Properties of Depositing Material		Receptor
Micrometeorological Variables	Particles	Gases	Surface Variables
Aerodynamic resistance: -mass transfer -heat -momentum -1/deposition velocity	Particle size: -diameter -density -agglomeration	Partial Pressure -solubility -concentration Chemical activity/ reactions	Abiotic features Accommodation: -dew -exudates -wax -pubescence
Diffusion effect of: -canopy structure -extent of fetch	Diffusion: -Brownian -eddy -eddy Impaction	Diffusion: -molecular	Reactive sites: -area -prior loading -adsorption -absorption
Friction velocity Surface roughness length Zero plane displacement Wind velocity Turbulence	Gravitational settling Electrostatic effects		
Temperature			Biotic features Stomatal -conductance -diurnal pattern
Relative humidity			Plant metabolic rate -assimilation -cell pH
Precipitation Solar radiation			

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 μm exhibit a variable deposition velocity (V_d) between 5 and 110 mm s^{-1} dependent on frictional velocities, while a minimum particle deposition velocity has been shown for particles in the size range 0.1-1 μm (Figure 10-2).

(2) Deposition velocity of particles (V^d) is approximately a linear function of friction velocity.

(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).

Theoretically based models for predicting particle deposition velocities have recently been published by Bache (1979a, 1979b), 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 vs. 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 vs. 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).

10.2.4 Deposition of "N" Forms 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

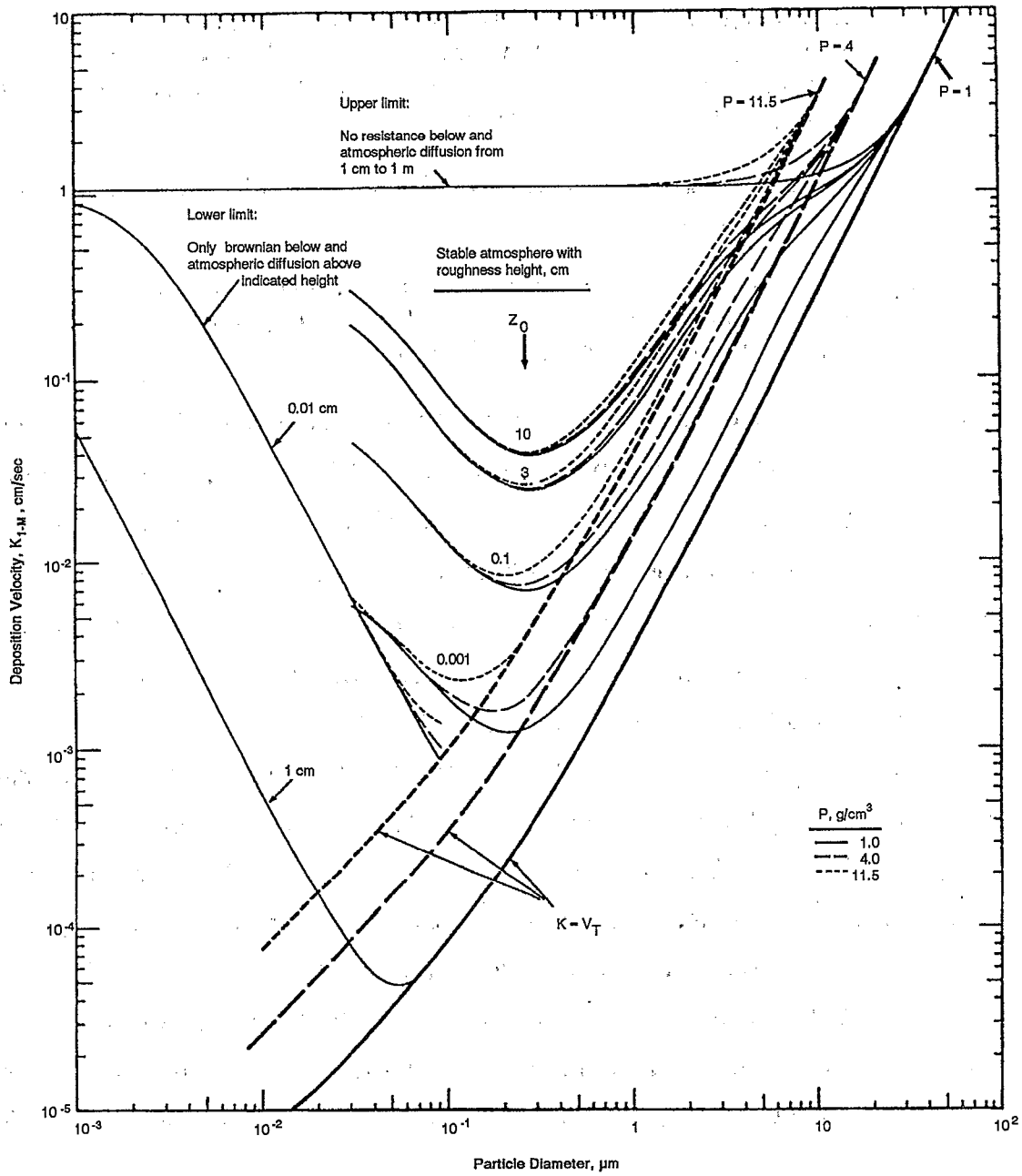


Figure 10-2. Predicted deposition velocities (V_d) at 1 meter for a friction velocity of 30 cm s^{-1} and particle densities of 1,4, and 11.5 g cm^{-3} (Sehmel, 1980).

TABLE 10-2. CONDUCTANCE (K_1) OF NO_2 TO LEAF SURFACES

Species	Concentration ppmv ($\mu g/m^{-3}$)[a]	$[K_1]^{bc}$ mm s^{-1}	Method	Reference
Austrian pine (*Pinus nigra*)	0.400	0.3[d]	Chamber	Elkiey et al. (1982)
Barley (*Hordeum vulgare*)	0.3	0.5	Chamber	Rowland-Bamford and Drew (1988)
	0.3	0.5	^{15}N	Rowland-Bamford and Drew (1988)
Bean (*Phaseolus vulgaris*)	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	0.8	Chamber	Srivastava et al. (1975)
	3	0.85	Chamber	Srivastava et al. (1975)
	7	0.63	Chamber	Srivastava et al. (1975)
Chinese hibiscus (*Hibiscus rosa-sinensis*)	1.0	0.69	Chamber	Saxe (1986)
	1.0	0.79	Chamber	Saxe (1986)
	4.0	0.54	Chamber	Saxe (1986)
	4.0	0.65	Chamber	Saxe (1986)
Cucumber (*Cucumis sativus*)	0.500	1.1	^{15}N	Okano et al. (1988)
Diffenbachia maculata	1.0	0.49	Chamber	Saxe (1986)
	4.0	0.31	Chamber	Saxe (1986)
Douglas fir (*Pseudotsuga mensiesii*) [Mirb.] Franco	0.400	0.2[d]	Chamber	Elkiey et al. (1982)
English ivy (*Hedera helix*)	1.0	0.56	Chamber	Saxe (1986)
	4.0	0.29	Chamber	Saxe (1986)
European White Birch (*Betula pendula*)	<0.06	3.2	NA[e]	Freer-Smith (1983)
	0.400	0.2	Chamber	Elkiey et al. (1982)
Ficus benjamina	0.400	0.1	Chamber	Elkiey et al. (1982)
	1.0	0.47	Chamber	Saxe (1986)
	4.0	0.19	Chamber	Saxe (1986)
Hedera canariensis	1.0	0.62	Chamber	Saxe (1986)
	4.0	0.35	Chamber	Saxe (1986)
Honey locust (*Gleditsia triancanthos*)	0.400	0.2	Chamber	Elkiey et al. (1982)
Indian rubber (*Ficus elastica*)	1.0	0.86	Chamber	Saxe (1986)
	4.0	0.69	Chamber	Saxe (1986)
Loblolly pine (*Pinus taeda*)	0.020	0.6	Chamber	Hanson et al. (1989)

TABLE 10-2 (cont'd). CONDUCTANCE (K_1) OF NO_2 TO LEAF SURFACES

Species	Concentration ppmv ($\mu g/m^{-3}$)[a]	$[K_1]^{bc}$ mm s^{-1}	Method	Reference
Lombardy poplar (*Populus nigra*)	<0.06	2.9	NA	Freer-Smith (1983)
Maize (*Zea mays*)	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 (*Sorbus aria*)	0.400	0.2	Chamber	Elkiey et al. (1982)
Nephrolepsis exaltala	1.0	0.48	Chamber	Saxe (1986)
	4.0	0.22	Chamber	Saxe (1986)
Norway spruce (*Picea abies*)	0.400	0.2[d]	Chamber	Elkiey et al. (1982)
Petunia (*Petunia hybrida*)	0.400	0.6	Chamber	Elkiey and Ormrod (1981)
Prunus sargentii	0.400	0.1	Chamber	Elkiey et al. (1982)
Radish (*Raphanus sativus*)	0.500	1.9	^{15}N	Okano et al. (1988)
Red maple (*Acer rubrum*)	0.020	1.8	Chamber	Hanson et al. (1989)
Red spruce (*Picea rubens*)	0.020	0.4	Chamber	Hanson et al. (1989)
Spruce (*Picea sp.*) dormant	0.006-0.03	<<0.3	Chamber	Granat and Johansson (1983)
Scots pine (*Pinus sylvestris*)				
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 (K_1) OF NO_2 TO LEAF SURFACES

Species	Concentration ppmv ($\mu g/m^{-3}$)[a]	$[K_1]$[bc] mm s^{-1}	Method	Reference
Sunflower (*Helianthus annus*)	0.2	1.1	^{15}N	Okano et al. (1986)
	0.3	3.0	^{15}N	Okano and Totsuka (1986)
	0.5	2.3	^{15}N	Okano et al. (1986)
	0.5	2.2	^{15}N	Okano et al. (1986)
	1.0	2.1	^{15}N	Okano et al. (1986)
	2.0	3.4	^{15}N	Okano and Totsuka (1986)
Sweet pepper (*Capsicum annum*)	1.5	0.02-1.6	Chamber	Rowland et al. (1985)
	NA	1.3	NA	Law and Mansfield (1982)
Sycamore maple (*A. platanoides*)	0.400	0.1	Chamber	Elkiey et al. (1982)
Sycamore (*Platanus occidentalis*)	0.020	4.1	Chamber	Hanson et al. (1989)
Sorghum (*Sorghum vulgare*)	0.500	0.6	^{15}N	Okano et al. (1988)
Tobacco (*Nicotiana tabacum*)	0.500	1.3	^{15}N	Okano et al. (1988)
Tomato (*Lycopersicon esculentum*)	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 (*Fraxinus americana*)	0.020	0.7	Chamber	Hanson et al. (1989)
White oak (*Quercus alba*)	0.020	1.3	Chamber	Hanson et al. (1989)
White fir (*Abies concolor*)	0.400	0.3[d]	Chamber	Elkiey et al. (1982)
White pine (*Pinus strobus*)	0.020	0.4	Chamber	Hanson et al. (1989)
Yellow-Poplar (*Liriodendron tulipifera*)	0.020	1.5	Chamber	Hanson et al. (1989)

[a]For NO_2 at 25 °C [1 $\mu g/m^{-3}$ = 0.000531 ppmv].
[b]Data are presented as a range or the mean of reported values.
[c]Data for broadleaved plants and conifers are presented on a one-sided and total leaf area basis, respectively.
[d]Based on a one-sided leaf area.
[e]NA = not available.
[f]Negative values represent evolution of NO_2 from leaves.

leaf-level or canopy-level measurements. If a cited paper lumped data for NO and NO_2 together as NO_x, that data is presented in Table 10-2 along with the information on NO_2, but it is indicated as being for NO_x. If the original authors did not calculate K_1 or V_d,

TABLE 10-3. DEPOSITION VELOCITY (V_d) OF NO_2 TO PLANT CANOPY SURFACES

Species	Concentration ppmv ($\mu g/m^{-3}$)[a]	$[V_d]^{bc}$ mm s^{-1}	Method	Reference
Alfalfa (*Medicago sativa*)				
	0.05	19	Chamber	Hill (1971)
	0.1	20	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)	0.017 (32.4)	1.0-3.0	Flux grad.	Delany and Davies (1983)
pasture (NO_x)	NA[d]	-26-15	Flux grad.	Duyzer et al. (1983)
Oats (*Avena sativa*)				
	0.08	12.5	Chamber	Hill (1971)
day	0.08	12.5	Chamber	Tingey (1968)
night	0.08	4.2	Chamber	Tingey (1968)
Soybean (*Glycine max [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 (*Picea* sp.) (NO_x)				
	0.018	28	Gradient	Enders and Teichmann (1986)
	0.029	20	Gradient	Enders and Teichmann (1986)

[a]For NO_2 at 25 °C [1 $\mu g/m^{-3}$ = 0.000531 ppmv].
[b]Data are presented as a range or the mean of reported values.
[c]Data are based on ground area under the canopy.
[d]NA = not available.

concentration and flux data from the original papers were used in Equations 1 or 2 to generate the values reported in the following tables.

10.2.4.1 Nitrogen Dioxide

Direct measurements of NO_2 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 (Elkiey et al., 1982; Grennfelt et al., 1983; Rogers et al., 1979) and fewer still for woody plants using near-ambient concentrations of NO_2 (Hanson et al., 1989; Johansson, 1987; Skärby

TABLE 10-4. CONDUCTANCE (K_1) OF NO TO LEAF SURFACES

Species	Concentration ppmv ($\mu g/m^{-3}$)[a]	$[K_1]^{bc}$ mm s^{-1}	Method	Reference
Chinese hibiscus (Hibiscus rosa-sinensis)	4.0	0.22	Chamber	Saxe (1986)
Diffenbachia maculata	4.0	0.34	Chamber	Saxe (1986)
English ivy (*Hedera helix*)	4.0	0.10	Chamber	Saxe (1986)
Ficus benjamina	4.0	0.10	Chamber	Saxe (1986)
Hedera canariensis	4.0	0.13	Chamber	Saxe (1986)
Indian rubber (*Ficus elastica*)	4.0	0.34	Chamber	Saxe (1986)
Nephrolepsis exaltala	4.0	0.22	Chamber	Saxe (1986)
Pine/spruce dormant	0.0005-0.002	<<0.3	Chamber	Granat and Johansson (1983)
Scots pine (*Pinus sylvestris*)				
dormant (field)	variable	<<0.1	Chamber	Johansson (1987)
dormant (lab)	0.122 (150)	0.04	Chamber	Skarby et al. (1981)
	0.244 (300)	0.04	Chamber	Skarby et al. (1981)
	0.407 (500)	0.05	Chamber	Skarby et al. (1981)

[a]For NO at 25 °C 1 $\mu g/m^{-3}$ = 0.000814 ppmv.
[b]Data are presented as a mean or range of reported values.
[c]Data for broadleaved plants and conifers are presented on a one-sided and total leaf area basis, respectively.

TABLE 10-5. DEPOSITION VELOCITY (V_d) OF NO TO PLANT CANOPY SURFACES

Species	Concentration ppmv ($\mu g/m^{-3}$)[a]	$[V_d]^{bc}$ mm s^{-1}	Method	Reference
Alfalfa	0.100	1.7	Chamber	Bennett and Hill (1973)
(*Medicago sativa*)	0.050	1.0	Chamber	Hill (1971)

[a]For NO at 25 °C 1 $\mu g/m^{-3}$ = 0.000814 ppmv.
[b]Data are the mean or a range of reported values.
[c]Data are based on ground area under the canopy.

TABLE 10-6. CONDUCTANCE (K_1) OF HNO_3 TO LEAF SURFACES

Species	Concentration ppmv ($\mu g/m^{-3}$)[a]	$[K_1]^{bc}$ mm s^{-1}	Method	Reference
American elm (*Ulmus americana*)	1.2 - 0.012	12	Chamber	Dasch (1989)
Austrian pine (*Pinus nigra*)	0.012-1.2	2.0	Chamber	Dasch (1989)
Pin oak (*Quercus palustris*)	0.012-1.2	4.4	Chamber	Dasch (1989)
Red maple (*Acer rubrum*)	0.02-0.03	3.3[c]	Chamber	Hanson et al. (1991)
Red spruce (*Picea rubens*)	0.058-0.067	2.6	Chamber	Hanson et al. (1991)
Sycamore (*Platanus occidentalis*)	0.02-0.07	1.1	Chamber	Hanson et al. (1991)
White oak (*Quercus alba*)	0.04-0.07	2.2	Chamber	Hanson et al. (1991)
White pine (*Pinus strobus*)	37-500 (95-1,288)	0.4-0.8	Chamber	Marshall and Cadle (1989)

[a]For HNO_3 at 25 °C 1 $\mu g/m^{-3}$ = 0.000388 ppmv.
[b]Data for broadleaved plants and conifers are presented on a one-sided and total leaf area basis, respectively.
[c]The data from Hanson et al. (1991) represent cuticular deposition only.

et al., 1981). Tables 10-2 and 10-3 provide a comprehensive listing, by plant species, of current data on the deposition of NO_2 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 to 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 NO_2 concentrations (Sinn et al., 1984; Srivastava et al., 1975; Skärby et al., 1981). At low concentrations of NO_2 (0.0013 ppmv [2.4 $\mu g\ m^{-3}$]), Johansson (1987) observed no deposition in Scots pine. Johansson suggested that his data indicated a "compensation point" at which rates of NO_2 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 NO_2 deposition at concentrations common across many non-urban areas of the United States (i.e., areas of NO_2 concentration <0.005 ppmv). However, more recent observations have shown that sunflower (*Helianthus annuus*) does not exhibit an NO_2 compensation point (Föerstel et al., 1989). Additional discussion of the deposition of NO_2 into leaves can be found in Section 9.4.1.

TABLE 10-7. DEPOSITION VELOCITY (V_d) OF HNO_3 TO CANOPY SURFACES

Species	Concentration ppmv ($\mu g/m^{-3}$)[a]	$[K_1]^{bc}$ mm s^{-1}	Method	Reference
Barley (*Hordeum*)	NA	77	Flux grad.	Harrison et al. (1989)
Beets (*Beta*)	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^{-1}	NA	14	NA	Fowler et al. (1989)
wind = 4 m s^{-1}	NA	50	NA	Fowler et al. (1989)
Forest	0.001-0.002	22-50	Flux grad.	Meyers et al. (1989)
	NA	20-50	Model	Hicks et al. (1985)
	NA	20-60	Model	Hicks and Meyers (1988)
wind = 1 m s^{-1}	NA	40	NA	Fowler et al. (1989)
wind = 4 m s^{-1}	NA	100	NA	Fowler et al. (1989)
Grass (pasture)	<0.001 (2)	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	3-18	Flux grad.	van Aalst & Diederen
	NA	7-37	Flux grad.	(1985)
wind = 1 m s^{-1}	NA	5	NA	Harrison et al. (1989)
wind = 4 m s^{-1}	NA	23	NA	Fowler et al. (1989)
				Fowler et al. (1989)
Pine (*Pinus*)	0.001	20-70	Leaf Wash	Dasch (1987)
Potato (*Solanum*)	NA	4	Flux grad.	Harrison et al. (1989)
Spruce (*Picea*)	NA	60-120	Model	Hicks et al. (1985)
Wheat (*Triticum*)	NA	50-260	Flux grad.	Dollard et al. (1987)

[a]For HNO_3 at 25 °C 1 $\mu g/m^{-3}$ = 0.000388 ppmv.
[b]Data are means or a range of the reported values.
[c]Data are based on ground area under the canopy.
[d]NA = not available.

Numerous studies have confirmed the control of stomatal aperture on NO_2 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 NO_2 deposition.

Until recently it was assumed that cuticular deposition of NO_2 was negligible. Recent studies by Lendzian and Kerstiens (1988) and Kisser-Priesack et al. (1987) clearly

TABLE 10-8. CONDUCTANCE (K_1) OF NH_3 TO LEAF SURFACES

Species	Concentration ppmv ($\mu g/m^{-3}$)[a]	$[K_1]^{bc}$ mm s^{-1}	Method	Reference
Bean (*Phaseolus vulgaris*)				
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 (*Gossypium hirsutum*)	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 (*Calluna/Molina*)	NAd	4	Estimated	Duyzer et al. (1987)
Italian rygrass (*Lolium multiflorum*)	22.6 (16)	3	Chamber	Lockyer and Whitehead (1986)
	735 (520)	28	Chamber	Lockyer and Whitehead (1986)
Maize (*Zea mays*)	0.034 (24)	6.5	Chamber	Hutchinson et al. (1972)
	0.320	4	Chamber	Rogers and Aneja (1980)
Oats (*Avena*)	0.200	13	Chamber	Rogers and Aneja (1980)
Orchard grass	0.283	10	Chamber	Rogers and Aneja (1980)
Populus euramericana	0.072	0.5-5	Chamber	van Hove et al. (1989)
	0.143	0.5-9	Chamber	van Hove et al. (1989)
Soybean (*Glycine max*)	0.037 (26)	4	Chamber	Hutchinson et al. (1972)
	0.170	11	Chamber	Rogers and Aneja (1980)
Sunflower (*Helianthus annuus*)	0.045 (31)	4	Chamber	Hutchinson et al. (1972)
Tomato (*Lycopersicon esculentum*)	0.148	10	Chamber	Rogers and Aneja (1980)
Tobacco (*Nicotiana tabacum*)	0.173	6	Chamber	Rogers and Aneja (1980)
Wheat (*Triticum*)	0.277	15	Chamber	Rogers and Aneja (1980)

[a]For NH3 at 25 °C 1 $\mu g/m^{-3}$ = 0.00143 ppmv.
[b]Data are the mean or a range of reported values.
[c]K_1 is based on a one-sided leaf area.
[d]NA = not available.

TABLE 10-9. DEPOSITION VELOCITY (V_d) OF NH3 TO PLANT CANOPY SURFACES

(Data showing net efflux of ammonia from fertilized crop landscapes are not included in this table.)

Species	Concentration ppmv ($\mu g/m^{-3}$)[a]	$[V_d]^{bc}$ mm s^{-1}	Method	Reference
Bean (*Phaseolus vulgaris*)	0.100	4	Chamber	Aneja et al. (1986)
Fescue (*Festuca arundinacea*)	0.603	12	Chamber	Aneja et al. (1986)
Heather/purple moor grass (*Calluna/Molina*)	NA[d]	19	Flux grad.	Duyzer et al. (1987)
Maize (*Zea mays*)	0.250	3	Chamber	Aneja et al. (1986)
Oats (*Avena sativa*)	0.200	10	Chamber	Aneja et al. (1986)
Orchard grass (*Dactylis glomerata*)	0.576	10	Chamber	Aneja et al. (1986)
Pine (*Pinus* sp.)	NA	18-26	Flux grad.	Duyzer et al. (1987)
Soybean (*Glycine max* [L.] Merr.)	0.075	6	Chamber	Aneja et al. (1986)

[a]For NH_3 at 25 °C 1 $\mu g/m^{-3}$ = 0.00143 ppmv.
[b]Data are means or a range of reported values.
[c]Data are based on ground area under the canopy.
[d]NA = not available.

demonstrate cuticular deposition rates (see the discussion in Section 9.4.1). However, cuticular deposition rates are 1 to 2 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 N deposition to landscapes are attempted.

Whole-canopy measurements of NO_2 deposition conducted in laboratory or field situations (Table 10-3) yield daytime overall deposition velocities (V_d) between 1 and 28 mm s^{-1}. Duyzer et al. (1983) and van Aalst and Diederen (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 10.2.4.3) 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 0_3 can also lead to errors in whole-canopy

TABLE 10-10. MEASURED DEPOSITION VELOCITIES OF NITRATE (NO_3^-) AND AMMONIUM (NH_4^+)

Species	Deposition Velocity NO_3^-	Deposition Velocity NH_4^+	Method	Reference
American elm (*Ulmus americana*)	11	NA	Leaf wash	Dasch (1987)
Austrian pine (Pinus nigra)	5-13	0.1-0.6	Leaf wash	Dasch (1987)
Beech (Fagus silvatica)	13	10	Throughfall	Höefken and Gravenhorst (1982)
	7-17	6-13	Throughfall	Gravenhorst et al. (1983)
winter	6-16	2-8	Throughfall	Gravenhorst et al. (1983)
Ceanothus crassifolius	4.1[a]	4.4	Leaf wash	Bytnerowicz et al. (1987)
Chestnut oak (*Quercus prinus*)				
	5.5	NA	Throughfall	Lovett and Lindberg (1984)
dormant	7.1	NA	Throughfall	Lovett and Lindberg (1984)
Heather/moor grass (*Calluna/Molina*)	NA[b]	1.8	Flux grad.	Duyzer et al. (1987)
Laurel (*Kalmia latifolia*)	NA	0.3-1.4	Leaf wash	Tjepkema et al. (1981)
Norway spruce (*Picea abies*)				
	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 (*Quercus palustris*)	7-11	NA	Leaf wash	Dasch (1987)
Privet				
(*Ligustrum japonicum*)	2.2-5.4	NA	Leaf wash	John et al. (1985)
(*Ligustrum ovalifolium*)	1-2.1	NA	Leaf wash	John et al. (1985)
Soybean (*Glycine max*)	2.4	NA	Leaf wash	Dolske (1988)
White pine (*Pinus strobus*)	NA	0.3-1.4	Leaf wash	Tjepkema et al. (1981)

[a]Particle NO_3^- deposition data typically includes some NO_3^- from HNO_3 vapor.
[b]NA = not available.

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 nitrogen oxides. Their data showed that deposition of NO_x predominated in the morning hours while 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 ozone, 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 micormeteorologically 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 type of plant species. A simple average of the species specific data in Table 10-2 for *non-dormant* 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_1) for broadleaf tree and crop plants was approximately 1.3 mm s^{-1}, and for conifers and house plants between 0.5 and 1.0 mm s^{-1}. Hanson et al. (1989) documented a similar pattern. Elkiey et al. (1982) reported data on the foliar sorption of NO_2 to ten ornamental woody plants using an NO_2 concentration of 400 nl l^{-1}. 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 which 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.

10.2.4.2 Nitric Oxide

A comparison of tree and crop data between Tables 10-2 and 10-4, or Tables 10-3 and 10-5 shows that the K_i 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 than for 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 (Skärby 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 nitrogen oxides 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.

10.2.4.3 Nitric Acid Vapor

The dry deposition characteristics of HNO_3 vapor suggest substantially higher deposition for HNO_3 than for other nitrogen oxides. Micrometeorological measurement of the overall deposition velocity of HNO_3 to pasture grass (see papers by various authors in Table 10-7), showed an average V_d for HNO_3 of 29 mm s^{-1}. Other studies on crop canopies showed V_d values for HNO_3 over a range from 4-260 mm s^{-1}. Using throughfall nitrate and ambient HNO_3 concentrations, Dasch (1987) calculated the V_d for an Austrian pine (*Pinus nigra*)

stand to be 67 mm s^{-1} at the stand perimeter and 17 mm s^{-1} at interior stand locations. Dollard et al. (1987) reported V_d values as high as 260 mm s^{-1} 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 HCl 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^{-1} depending on wind speeds (Table 10-7). Forest landscapes also showed a range of V_d from 40 to 100 mm s^{-1} 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^{-1} for the low elevation broadleaf forests, and a V_d between 60-120 mm s^{-1} 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^{-1} for slow and fast wind speeds, respectively. Fowler (1984) calculated that the atmospheric resistance to deposition of pollutants would increase from 2 to 4 fold depending on the nature of the landscape vegetation with a change in windspeed from 1 to 4 m s^{-1}. 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^{-1} to be an appropriate mean V_d with a range between 20 and 60 mm s^{-1}.

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 10-6) and found a mean K_1 for two hardwoods to be 8.2 mm s^{-1} and a K_1 for *Pinus nigra* to be 2 mm s^{-1}. 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^{-1}. Hanson et al. (1991) measured HNO_3 conductances to foliage of four tree species under low humidity conditions and found a K_1 ranging from 1 to 3.3 mm s^{-1}. Because low humidity caused stomatal closure, their measurements did not include deposition to leaf internal spaces. Vose and Swank (1990) used a ^{15}N labeling technique to assess HNO_3 deposition to white pine foliage and found rates of

"non-extractable" HNO_3 absorption between 5 and 53 nmol g^{-1} s^{-1}. These data were not included in Table 10-6 because the surface adsorbed HNO_3 was removed in a water rinse prior to assaying nonextractable ^{15}N-labeled HNO_3. Taylor et al. (1988) compared foliar deposition characteristics of HNO_3 vapor to that of other pollutant gases and suggested that 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 SO_2. Vose and Swank (1990) conducted a study of HNO_3 deposition to foliar surfaces using ^{15}N labeled HNO_3 has confirmed the cuticular pathway for HNO_3 deposition.

10.2.4.4 Ammonia

Ammonia deposition data is 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^{-1} and a V_d for canopies of 7.4 mm s^{-1}. 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 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 micrometerological 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) has reported V_d for ammonia to heather-purple moor grass (*Calluna, Molinia* sp.) canopies to be 19 mm s^{-1}, and V_d to Corsican pine (*Pinus nigra var. maritime*) canopies ranged between 18 and 26 mm s^{-1}. 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^{-1} 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 μmol g fresh weight^{-1} h^{-1} at 30 and 300 ppmv, respectively, was measured in sunflower leaves using high concentrations of ^{15}N labeled NH_3 (Berger et al., 1986). ^{15}N labeled NH_3 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^{-1} (Cowling 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 μg 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 40-70 μg m^{-3}.

Denmead et al. (1976) found that ungrazed pasture was capable of absorbing most NH_3 released from the ground while grazed pasture lost NH_3 to the atmosphere. Their observations, while 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.

10.2.4.5 Particles (Nitrate and Ammonium)

Direct measurements of aerosol-associated N 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 (Bytnerowicsz et al., 1987; Dasch, 1987; Lindberg and Lovett, 1985; van Aalst and Diederen, 1985). The average V_d for nitrate and ammonium (Table 10-10) was greater if determined from throughfall measurements (12 and 10 mm s^{-1}) than if determined from individual leaf washing experiments (6 and 2 mm s^{-1}). 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 10.2). Lindberg and Lovett (1985) estimated dry deposition of nitrate to deciduous forest leaves to be 5.7 $\mu g\ m^{-2}\ h^{-1}$, 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) the contribution of HNO_3 dry deposition to NO_3^- on the foliage surface could not be separated 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 with a mean of 2.4 mm s^{-1}. 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^{-1}, Table 10-10) was determined using flux gradient analysis of NH_4^+ particles trapped in filtered air leaving denuder tubes.

10.2.5 Deposition of "N" Forms to Non-Foliar 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 NO_2 deposition of NO_2 to normal or wetted bark of three broadleaf and one conifer tree species was similar among species

SURFACES TO REACTIVE NITROGEN GASES

Species	Concentration ppmv ($\mu g/m^{-3}$)	$[K_1]^{ab}$ mm s^{-1}	Method	Reference
Nitrogen dioxide				
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	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	3.0	NA	van Aalst (1982)
Snow	0.006-0.03	$<<0.3$	Chamber	Granat and Johansson (1983)
Nitric Oxide				
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	<0.01	NA	van Aalst (1982)
Snow	0.0005-0.002	$<<0.3$	Chamber	Granat and Johansson (1983)
Nitric Acid Vapor				
Bark	0.06-0.07	7.4	Chamber	Hanson et al. (1991)
Snow				
-18 °C	0.014 (36)[a]	<0.2	Chamber	Johansson and Granat (1986)
-8	0.014 (36)	0.4	Chamber	Johansson and Granat (1986)
-5	0.014 (36)	0.4	Chamber	Johansson and Granat (1986)
-4	0.014 (36)	1.2	Chamber	Johansson and Granat (1986)
-3	0.014 (36)	1.0	Chamber	Johansson and Granat (1986)
-2	0.014 (36)	5.7	Chamber	Johansson and Granat (1986)

[a]Data are presented as a range or the mean of reported values.
[b]Data are based on total area for bark and litter, and ground area for snow, forest floor, and soil.

(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^{-1} and were within a factor of 2 of K_1 values for plant leaf surfaces. HNO_3 conductance to bark was nearly an order of magnitude greater than for NO_2 (Hanson et al., 1991; 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 (Table 10-11; Judeikis and Wren, 1978). 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 Γ-irradiation and concluded that microorganisms were responsible, not so much for absorption of NO_2, but its conversion into nitrate. Mortland (1965) and Sundaresan et al. (1967) documented mechanisms for NO deposition by soil based 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).

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 (Table 10-11; Granat and Johansson, 1983; Johansson and Granat, 1986). 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 2-5 mm s^{-1} by aerodynamic resistances.

10.3 EFFECTS ON VEGETATION AND SOILS

10.3.1 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 be 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 an ecosystem'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 (N) is unique among nutrients in that its retention and loss is regulated almost exclusively by biological processes. Whereas other major nutrients (P, S, K, Ca, Mg, 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. Since NO_3^- is poorly adsorbed to oils (in contrast to SO_4^{2-} and ortho-phosphate; Hingston et al., 1967), nitrification in excess of plant and microbial demand for N 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 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^--N being 10 mg N/L).

Soils are by far the largest N pool in forest ecosystems, usually exceeding 85% of total ecosystem capital (Cole and Rapp, 1981). Yet most soil N is inert and unavailable for either uptake or leaching, with only a rather loosely-defined "mineralizeable" pool being

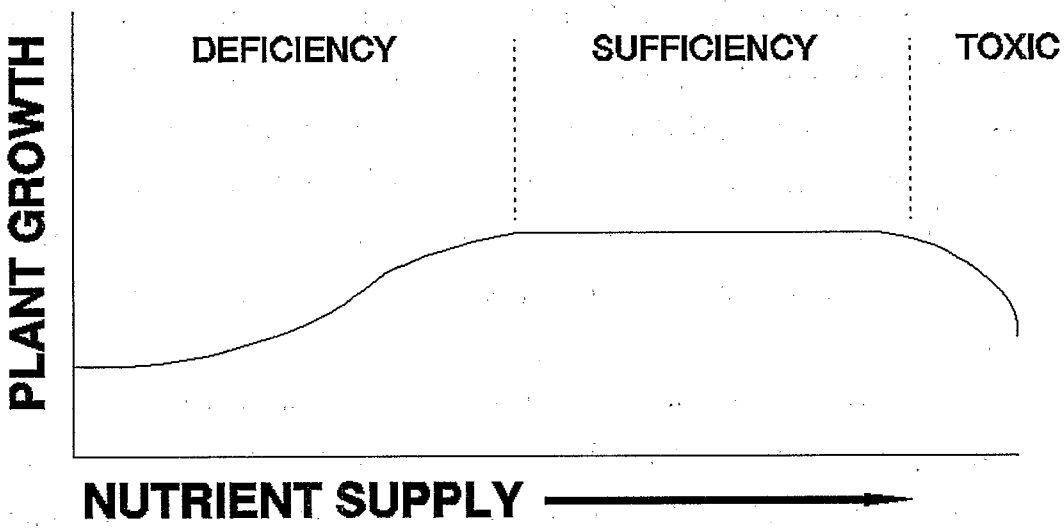


Figure 10-3. Schematic representation of the response of natural ecosystems to nutrient inputs.

biologically active (Aber et al., 1989). This "mineralizeable pool", the size of which is typically defined either by in situ incubation of soils or litter, is that portion of soil N that heterotrophs (decomposers), autrotrophs (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 N-rich red alder (*Alnus rubra*) forests in Washington (apparently a result of cessation of N-fixation; Biggar and Cole, 1983; Van Miegroet et al., 1989) does not support earlier predictions that nitrate leaching following disturbance is usually greatest in sites with inherently better N 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., in press) 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 will focus upon forest ecosystems, because of their sensitivity to both the positive and negative effects of N deposition discussed above. Arid and semi-arid 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 N deposition on arid and semi-arid 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 N (100-300 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.

10.3.2 Pollutant N Inputs and Nitrogen Cycling in Natural Ecosystems: A Brief Review

An evaluation of the effects of pollutant N deposition on terrestrial vegetation and soils must begin with considerations of how these pollutant inputs affect terrestrial N cycles. The general subject of terrestrial N cycling was reviewed in section 10.1.3; only a few of the more germane details are repeated here. Not all potential effects of pollutant N inputs can be described from the perspective of a generic N cycle, however: there are secondary effects such as effects of excessive vegetation uptake upon susceptibility to attack by pests and pathogens and to climatic damage, for example, that cannot be described from the N cycle alone.

Nitrogen, unlike Ca, K, Mg, P, or S, seldom forms large soil inorganic pools which 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., 1985). Since NO_3^- is poorly adsorbed to soils, nitrification in excess of plant and microbial demand for N 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 N; (2) dry deposition of these forms plus nitric acid 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 N 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 nitrifiying bacteria compete for it (Figure 10-4, top). This competition for N among heterotrophs, plants, and nitrifiying bacteria plays a major role in determining the degree to which a vegetation growth increase will occur and the degree to which incoming N is retained within the ecosystem. It has been assumed that nitrifiers are poor competitors for N compared to heterotrophs and plants (Vitousek et al., 1982; Riha et al., 1986; see also review by Davidson et al., 1991). This assumption has recently been challenged by Davidson et al. (1991). Using ^{15}N techniques, these authors found significant nitrification and microbial NO_3^- uptake (12 to 46% of N 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 NO_3^- and that nitrifiers were quite able competitors for N. They also point out that NO_3^- 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.

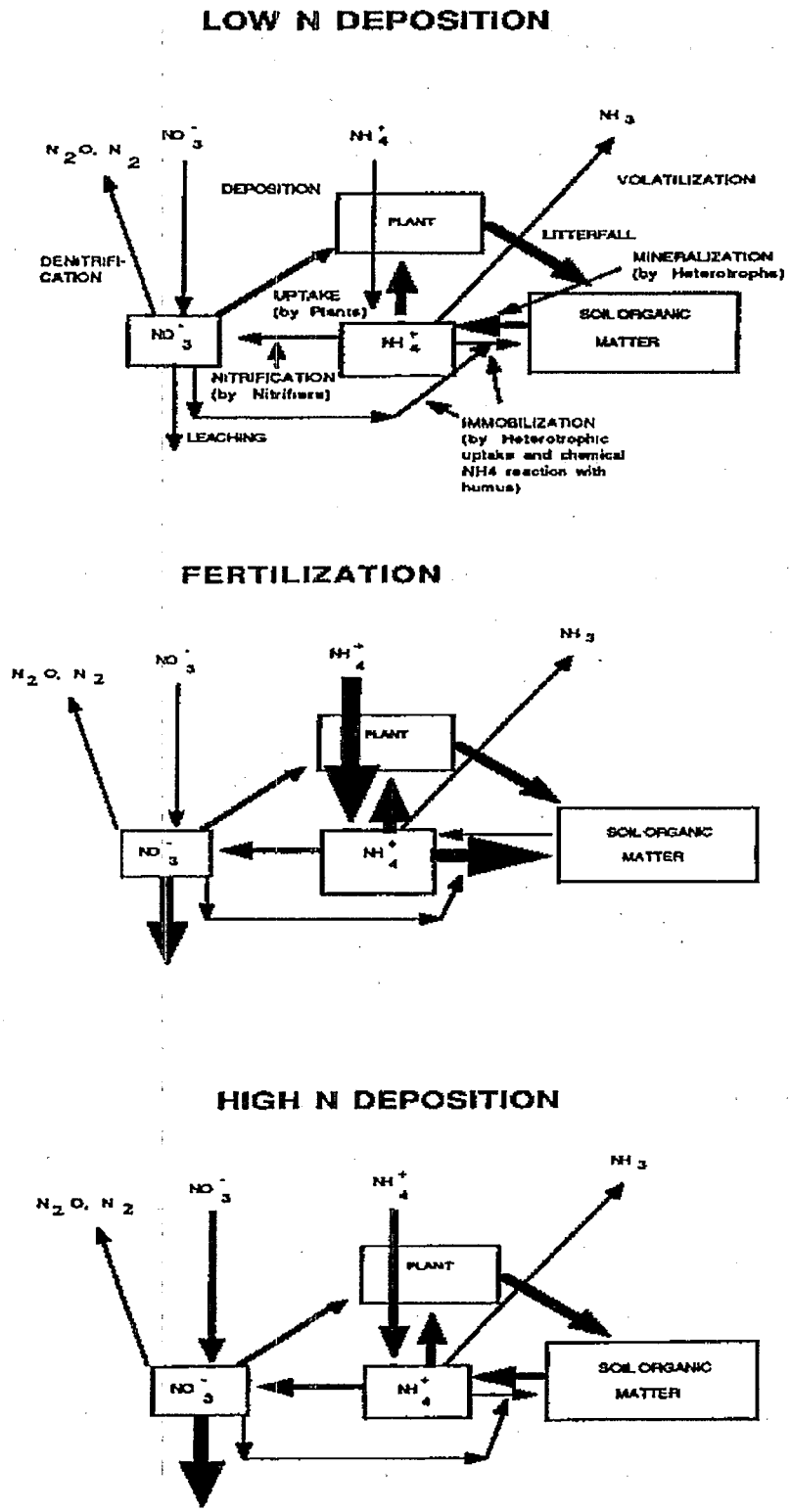


Figure 10-4. Schematic representation of the fate of incoming N in N-poor (top), fertilized (center), and high-N input systems.

Heterotroph demand for N (both NH_4^+ and NO_3^-) depends upon the supply of labile organic C substrates (as well as temperature and moisture conditions). Thus, adding labile organic C 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 C 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 N deficiency in Douglas fir (*Pseudotsuga menziesii*) trees, presumably by stimulating heterotrophic competition for N. 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 N 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 increased in the supply of N". There are clearly problems with this definition in that ecosystems that are low in N but limited by another nutrient (such as P) may not experience an increase in primary production in response to N input *unless* P is added first (e.g., Pritchett and Comerford, 1982). Other definitions for nitrogen saturation reviewed by Skeffington and Wilson (1988) include: "when external N input and N mineralization from the soil exceed the capacity of the ecosystem organisms to absorb more N", 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" (p. 379). 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 N-deficient ones, have some small pool of ammonium and nitrate within the soil and litter components. Using the definition of Aber et al. (1989) 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 (P)-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 N and release virtually no nitrate. Furthermore, as noted above, P-deficient ecosystems will frequently accumulate substantially more N once P limitations are satisfied.

While 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 N accumulation cannot occur, even though other nutrient limitations are satisfied. This definition will be used in the following discussion.

It is important to note is that additional N inputs to an N-saturated ecosystem will cause equivalent leaching losses of NO_3^- regardless of the chemical form of the N entering the system (NH_4^+, NO_3^-, or organic) to the extent that (1) N 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 N on ecosystem acidification and nitrate leaching, an omission which substantially underestimates the acidification potential of atmospheric N 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 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 alleopathic 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 which (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 N-rich forest ecosystems in Wisconsin of 0.2 to 2.1 kg ha^{-1} yr^{-1}, values that are worthy of including in N 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 N loss mechanism. Curiously, however, Westerman and Tucker (1978) and Klubek et al. (1978) found that denitrification rather than NH_3 volatilization is the major N 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 N inputs to desert ecosystems in the southwestern U.S. have been lost to the atmosphere since the last glaciation. They stop short of giving values for NO_x and N_2 (denitrification) vs. NH_3 (volatilization) losses, but point out that the importance of learning more about the nature of gaseous N losses from these systems, especially in the case of N_2O given its importance to the ozone layer and as a greenhouse gas.

Vegetation demand for N depends upon 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 N input, however. Several studies have shown that demonstrated net N 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 N 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 N export from ecosystems such as fire and harvesting will naturally push ecosystems toward a state of greater N demand or even N deficiency. Frequent fire is normally thought of as an especially effective way of maintaining low ecosystem N status. However, studies on the effects of fire upon soil N have produced conflicting results. Some authors have reported total N contents that were not significantly changed within 1-2 years of burning whereas others have reported significant losses. Jurgensen et al. (1981) found that broadcast burning caused a minor net loss of N (approximately 100 kg/ha) from a clearcut site in Montana, and concluded that plant re-establishment benefitted from the increased N availability following this prescribed burn. Wells (1971) noted that while the periodic prescribed burns has 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 N (550-990 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 N status has a great deal to do with fire intensity.

10.3.3 Fate of Nitrogen in Forest Ecosystems: Contrasts Between Fertilizer and Pollutants

The prospects for forests becoming "nitrogen saturated" from atmospheric N 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 N saturation typically consider vegetation uptake and increment as the primary factors controlling forest ecosystem N retention, and attribute little potential for soil N accumulation, despite the fact that soils comprise the largest ecosystem N 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 N (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 N via fertilization vs. slow, steady inputs via atmospheric deposition.

Fertilization studies differ from pollutant N deposition in two important respects. Pollutant N 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 N deposition enters the ecosystem as a slow, steady input in rather low concentrations, whereas the fertilizer is typically applied in 1-5 large doses. Nitrate applications or urea applications to N-rich sites can result in substantial nitrate leaching losses of fertilizer N (e.g., Overrein, 1969; Matzner et al., 1983; Tschaplinski et al., in press). However, most studies show minimal loss of fertilizer N via leaching following single, large applications of ammonium or urea to N-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 vs. slow, steady applications of N, 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 N deposition.

10.3.3.1 Case Studies of Forest Fertilization at Differing Intervals

Ingestad (1980) has demonstrated in greenhouse experiments that optimum nitrogen uptake and growth by plants can be achieved by adjusting N inputs to the rate of plant growth. In these experiments the rate of N supply (i.e., flux density, or N input per unit area per unit time) was proven to be the critical variable, not necessarily the concentration of N in the uptake solution. Field experiments comparing standard fertilization with simultaneous irrigation and fertilization (IF) have also demonstrated the superior growth response and fertilizer N recovery by adjusting the flux density of N input (through the IF treatments) as compared to adding either one or a few large doses of N as in conventional fertilization (Aronsson and Elowson, 1980; Ingestad, 1980; Landsberg, 1986).

These authors (Aronsson and Elowson, 1980; Ingestad 1980; Landsberg, 1986) do not report the effects of slow, steady inputs of N 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-N applications of 100 kg/ha/yr for 3 years in quarterly (25 kg N/ha/3 mo) and annual (100 kg N/ha, in March) to young loblolly pine (*Pinus taeda*) and yellow-poplar (*Liriodendron tulipifera*) 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 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 benefitted nitrifiers more than trees.

In a later study, in a more N-rich site nearby, exactly the opposite results were obtained in a study comparing a single urea-N applications of 50, 150, and 450 kg N/ha with multiple (three times at 37.5 kg N/ha) applications to a young sycamore (*Platanus occidentalis*) plantation (Tschaplinski et al., in press). 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

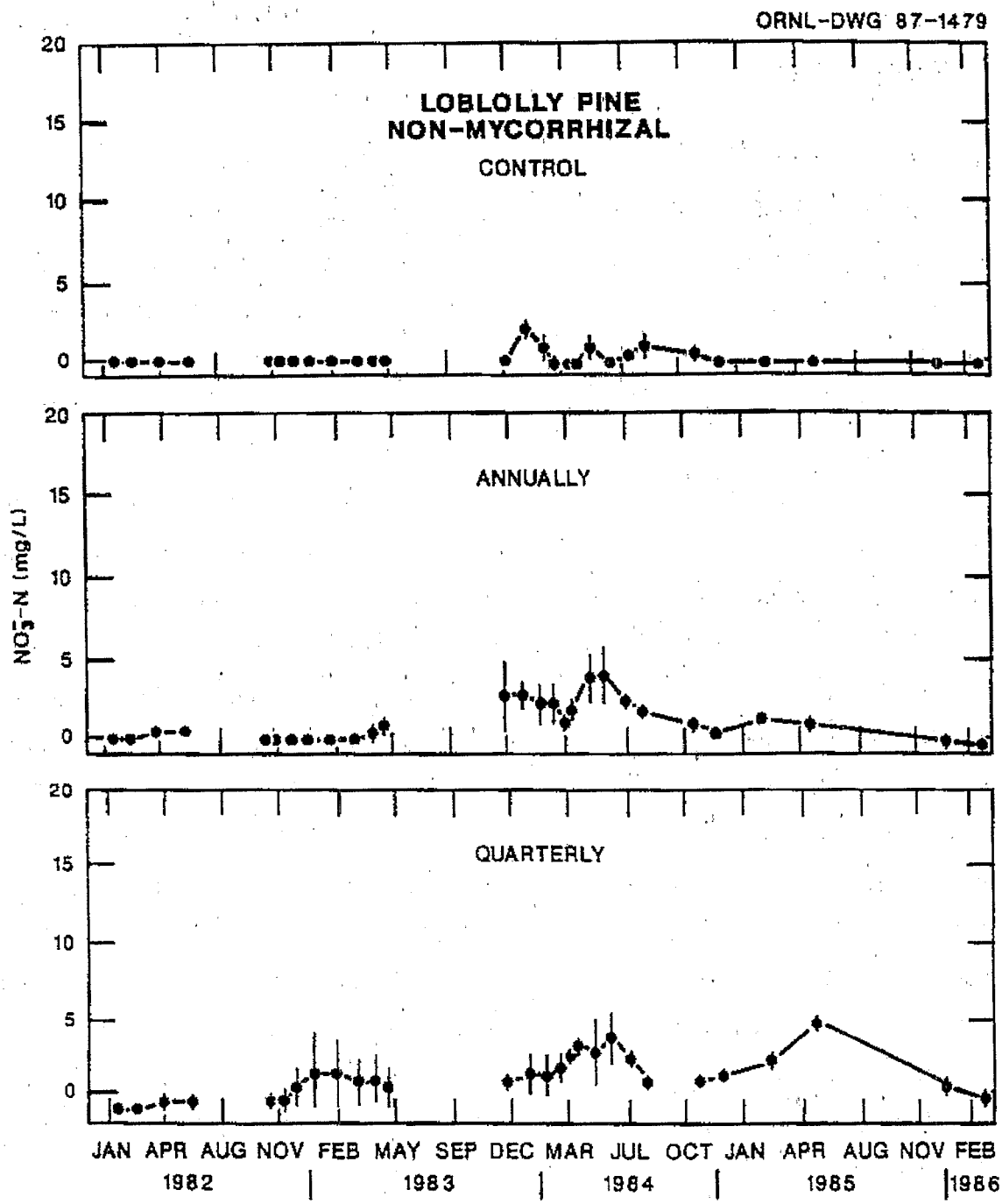
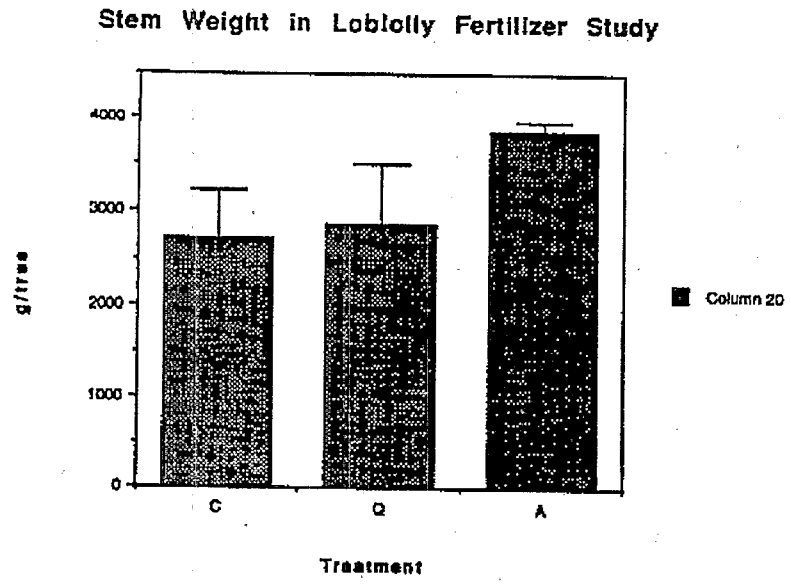


Figure 10-5. Soil solution nitrate concentrations in untreated control (top), annually fertilized (100 kg urea-N ha^{-1} yr^{-1}, center) and quarterly-fertilized (25 kg urea-N ha^{-1} 3 mo^{-1}, bottom) loblolly pine plots. (After Johnson and Todd, 1988.)



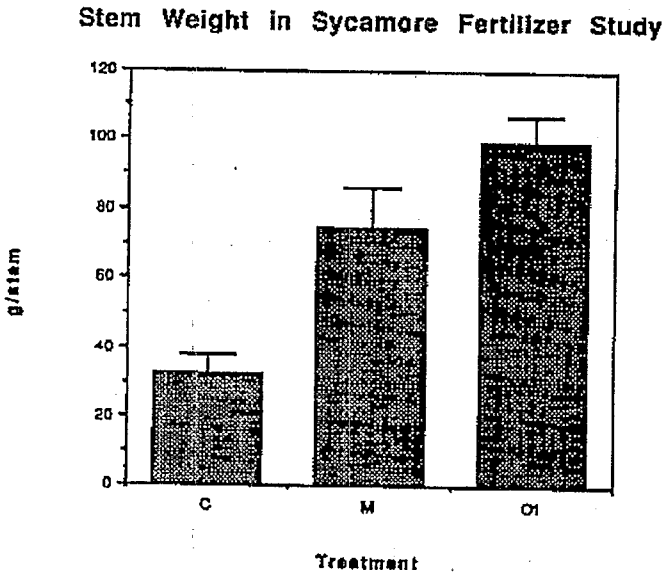


Figure 10-6. Top: Growth of loblolly pine in untreated (C), annual (A) (100 kg urea-N ha^{-1} yr^{-1}, center) and quarterly (Q) (25 kg urea-N ha^{-1} 3 mo^{-1}, center) applications of urea-N. (After Johnson and Todd, 1988.) Bottom: Growth of American sycamore in untreated (C), multiple (37.5 kg urea-N ha^{-1}, 3 times) and single (450 kg N ha^{-1}) applications of urea-N. (After Tschaplinski et al., in press.)

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 N-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 25-30 days in the N-poor site and 0-4 days in the N-rich site (Johnson and Todd, 1988; Tschaplinski et al., in press). According to Sabey et al. (1959) delay period for the onset nitrate production is closely related to the initial population of nitrifying bacteria. These results imply that slow, steady inputs of N characteristic of pollutant inputs may cause more rapid N-saturation in low-N ecosystems than conventional, single-shot fertilization would, but the opposite would be true in high-N 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 N in excess of plant demand regardless of timing and without delays caused by heterotrophic uptake.

10.3.3.2 Fate of N from Pulse Fertilization vs. Atmospheric Deposition

Forest fertilization has proven quite successful in producing growth increases in N-deficient forests, even though trees typically recover only 5-50% of fertilizer N in aboveground biomass (the very high tree recovery found by Bockheim et al., 1986, being exceptional; Table 10-12). Increased N in the soil is not mirrored directly by more N uptake except at low levels (see Chapter 9). Fertilizer N 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 N retention: (1) N uptake by soil heterotrophic organisms, and (2) non-biological, chemical reactions between ammonia and soil organic matter (Foster et al., 1985a). The overall result is that the retention of N on an ecosystem level is usually quite high (averaging 60% of applied N; Table 10-12). Furthermore, fertilizer recovery in trees,

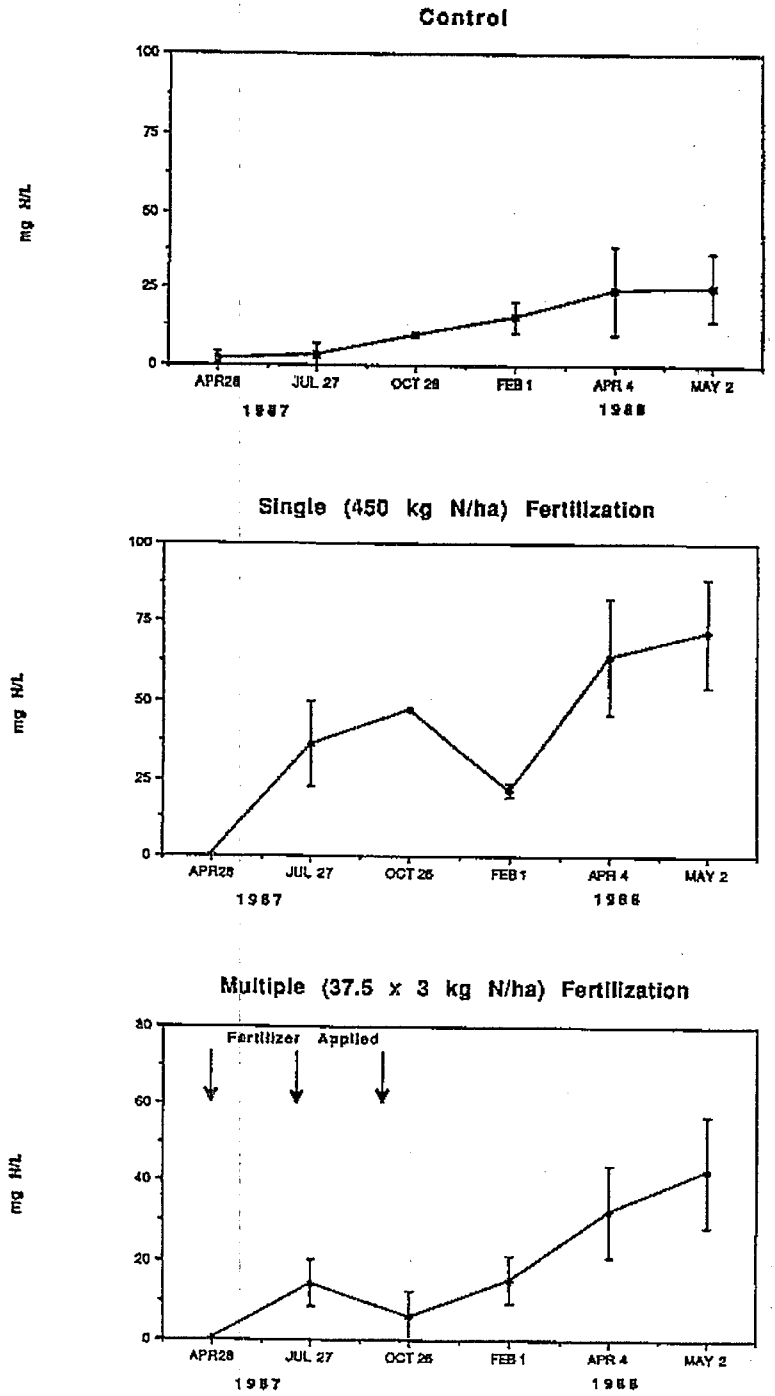


Figure 10-7. Soil solution nitrate concentrations in untreated (top), single (450 kg N ha^{-1}, center), and multiple (37.5 kg urea-N ha^{-1}, 3 times, bottom) applications of urea-N. (After Tschaplinski et al., in press.)

TABLE 10-12. NITROGEN FERTILIZER RECOVERY BY VEGETATION AND SOILS IN VARIOUS STUDIES

Location	Species and Age Type and Amount* (kg/ha)	Fertilizer Recovery (kg/ha and percent)	Vegetation Recovery (kg/ha and percent)	Soil	Reference
Florida	*Pinus eliottii*, 11	AS,56	6 (11%)	17 (30%)	Mead and Pritchett (1975)
Florida	*Pinus eliottii*, 11	AS,224	24 (11%)	40 (18%)	Mead and Pritchett (1975)
Mississippi	*Pinus taeda*, 5	AN,112	16 (14%)	-	Baker et al. (1974)
Mississippi	*Pinus taeda*, 6	AN,224	31 (28%)	-	Baker et al. (1974)
Mississippi	*Pinus taeda*, 5	AN,224	31 (14%)	-	Baker et al. (1974)
Mississippi	*Pinus taeda*, 6	AN,224	146 (65%)	-	Baker et al. (1974)
New Zealand	*Pinus radiata*, 14	NS,960	120 (13%)	488 (51%)	Baker et al. (1986)
New Zealand	*Pinus radiata*, 13	U,224	80 (40%)	120 (60%)	Worsnop and Will (1980)
Ontario	*Pinus banksiana*, 45	U,300	76 (25%)	79 (26%)	Morrison and Foster (1977)
Scotland	*Pinus nigra*, 36	AS,252	136 (54%)	176 (67%)	Miller et al. (1976)
Scotland	*Pinus nigra*, 36	AS,504	228 (45%)	78 (15%)	Miller et al. (1976)
Scotland	*Pinus nigra*, 36	AS,1008	366 (36%)	303 (30%)	Miller et al. (1976)
Scotland	*Pinus nigra*, 36	AS,1512	495 (32%)	229 (15%)	Miller et al. (1976)
Sweden	*Pinus sylvestris*, 130	AN,224	19 (19%)	46 (46%)	Melin et al. (1983)
Sweden	*Pinus sylvestris*, 120	U,150	12 (8%)	74 (49%)	Nommik and Moller (1981)
Sweden	*Pinus sylvestris*, 120	U,300	21 (7%)	87 (29%)	Nommik and Moller (1981)
Sweden	*Pinus sylvestris*, 120	U,600	36 (6%)	102 (17%)	Nommik and Moller (1981)
Sweden	*Pinus sylvestris*, 120	AN,150	29 (19%)	32 (21%)	Nommik and Moller (1981)
Sweden	*Pinus sylvestris*, 120	AN,300	60 (20%)	48 (16%)	Nommik and Moller (1981)
Sweden	*Pinus sylvestris*, 120	AN,600	90 (12%)	72 (12%)	Nommik and Moller (1981)
Tennessee	*Pinus taeda*, 4	U,300	25 (8%)	-	Johnson and Todd (1988)
Western Washington	*Pseudotsuga menziesii*, 52	NS,224	94 (42%)	124 (55%)	Heilman and Gessel (1963)
Western Washington	*Pseudotsuga menziesii*, 38	NS,224	204 (50%)	206 (51%)	Heilman and Gessel (1963)
Western Washington	*Pseudotsuga menziesii*, 30	NS,400	72 (13%)	284 (51%)	Heilman and Gessel (1963)
Western Washington	*Pseudotsuga menziesii*, 32	NS,560	75 (13%)	687 (123%)	Heilman and Gessel (1963)
Western Washington	*Pseudotsuga menziesii*, 38	NS,560	149 (20%)	337 (46%)	Heilman and Gessel (1963)
Wisconsin	*Pinus resinosa*, 37	AN,100	125 (125%)	-	Bockheim et al. (1986)

*U=Urea, AS=Ammonium Sulfate, AN=Ammonium Nitrate, NS=Not Specified.

soil, and the total ecosystem increase with the rate of fertilization and show no sign of levelling off even at rates of fertilizer N input of up to 1,500 kg/ha (Figures 10-8 to 10-10).

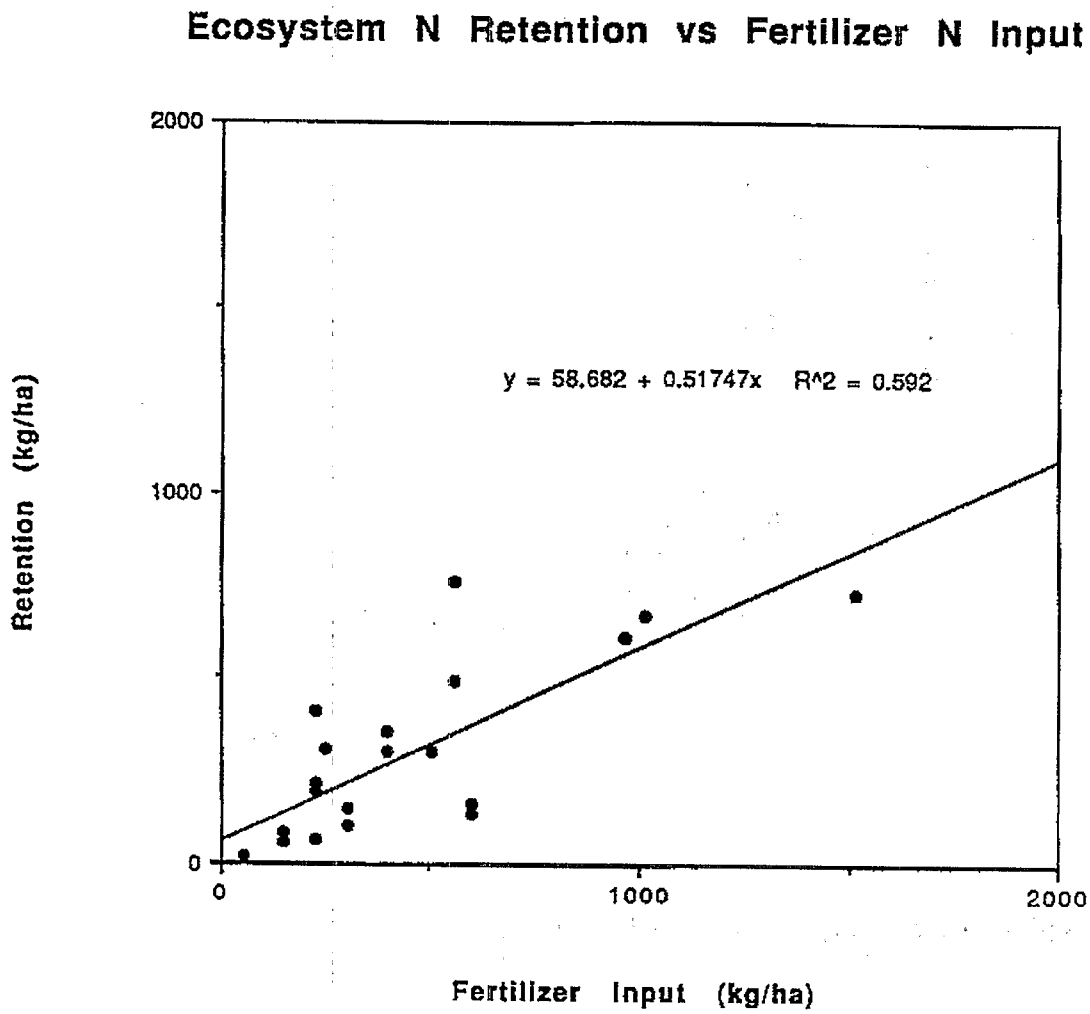


Figure 10-8. Ecosystem recovery of fertilizer N as a function of fertilizer N input.

Table 10-13 gives a summary of N budgets from the nutrient cycling literature and from the recently completed Integrated Forest Study (IFS; Johnson and Lindberg, in press). In this summary, atmospheric inputs are compared with outputs via soil solution or streamwater (primarily as NO_3^-) and vegetation increment, or the N necessary to build perennial tissues in

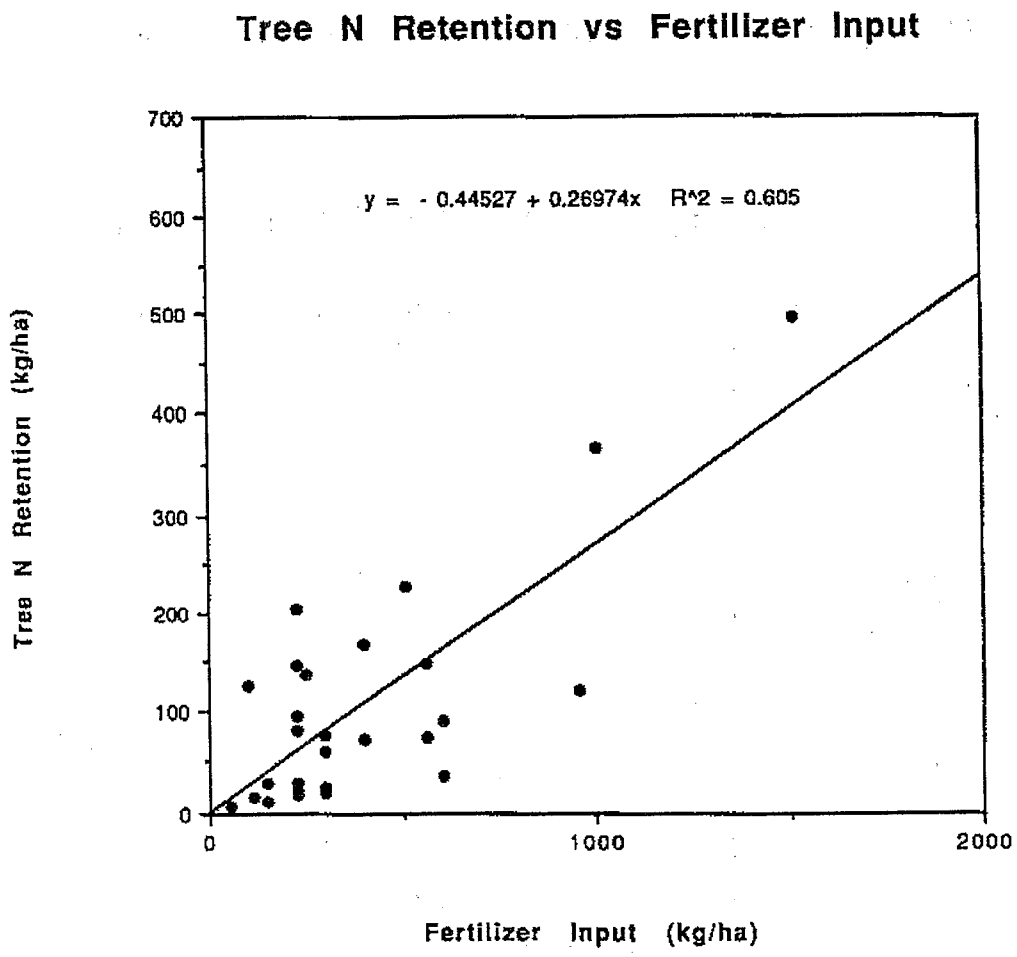


Figure 10-9. Tree recovery of fertilizer N as a function of fertilizer N input.

biomass (bole, branches). It should be noted that the studies prior to IFS measured N deposition principally by bulk precipitation, which substantially underestimates N 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 N deposition values reported there are often much greater than those that would have been reported using bulk collectors. For that reason, the IFS data is shown separately from previous data in Figures 10-11 to 10-13. It should also be noted that vegetation N uptake values in each of these systems are much

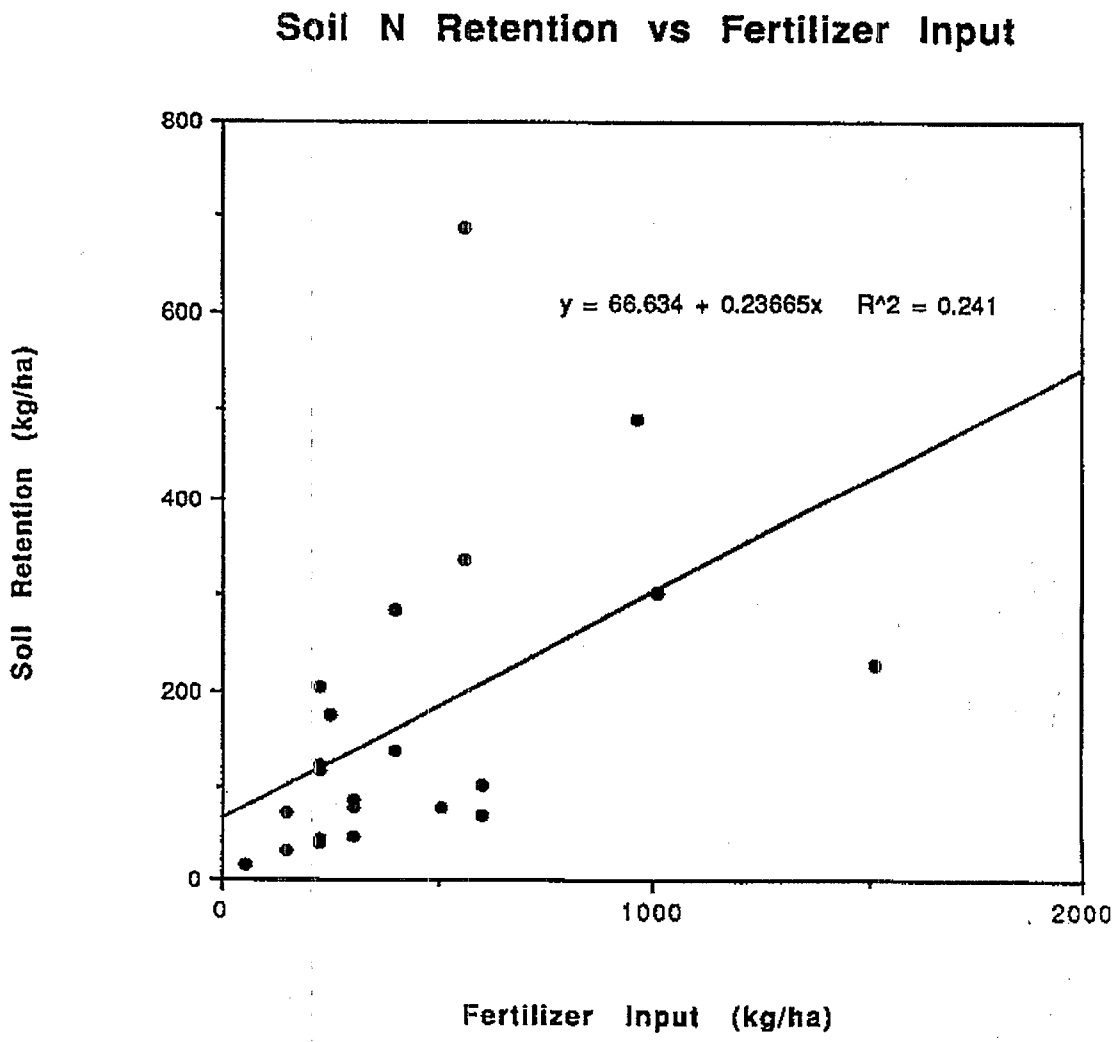


Figure 10-10. Soil recovery of fertilizer N as a function of fertilizer N input.

higher than vegetation increment, since uptake includes N taken up and returned annually via litterfall and foliar leaching. Vegetation increment was chosen for this analysis because it represents the net N demand of growing vegetation which must be satisfied from sources external to the N cycle (atmospheric deposition or soil "mining").

The data in Table 10-13 and Figures 10-11 to 10-13 reveal some interesting contrasts between ecosystem retention of fertilizer vs atmospherically-deposited N. First, total ecosystem retention of atmospherically-deposited N ranges from over 99% to -266%, with no

TABLE 10-13. NITROGEN INPUTS, OUTPUTS, AND VEGETATION INCREMENTS IN VARIOUS FOREST ECOSYSTEMS

Location	Species	Input	Leaching	Input-Output	Vegetation Increment	Reference
		----------kg/ha/yr----------				Cole and Rapp (1981)
USSR	*Picea abies*	1.1	0.9	+0.1	9.0	Turner and Singer (1976)
Washington	*Abies amabilis*	1.3	2.7	-1.4	-	
Washington	*Pseudotsuga menziesii*	1.7	0.6	+1.1	10.0	Cole and Rapp (1981)
Oregon	*Pseudotsuga menziesii*	2.0	1.5	+0.5	-2.8	Sollins et al. (1980)
Wisconsin	Aspen-Mixed Hardwood	5.6	0.05	+5.1	26.0	Pastor and Bockheim (1984)
New Hampshire	Northern hardwood	6.5	4.0	+2.5	9.0	Bormann et al. (1977)
Tennessee	*Liriodendron tulipifera*	7.7	3.5	+4.2	7.1	Cole and Rapp (1981)
Ontario	*Acer saccharum*	7.8	18.2	-10.4	-	Foster and Nicolson (1988)
Tennessee	Mixed deciduous	13.0	3.1	+9.9	13.5	Henderson and Harris (1975)
Germany	*Fagus sylvatica*	21.8	4.4	+17.4	4.1	Cole and Rapp (1981)
Germany	*Picea abies*	21.8	14.9	+6.9	12.2	Cole and Rapp (1981)
Holland	*Quercus robur*	44.6	22.5	+22.1	17.0	van Breemen et al. (1987)
Holland	*Quercus robur, Betula pendula*	54.5	78.5	-24.0	6.0	van Breemen et al. (1987)
Holland	*Quercus robur*	56.2	28.1	+28.1	24.0	van Breemen et al. (1987)
Holland	Mixed deciduous	62.8	87.6	-24.8	-	van Breemen et al. (1987)
Washington	*Alnus rubra*[*]	70.0	71.0	-1.0	7.1	Van Miegroet and Cole (1984)

[*]N-fixing species.

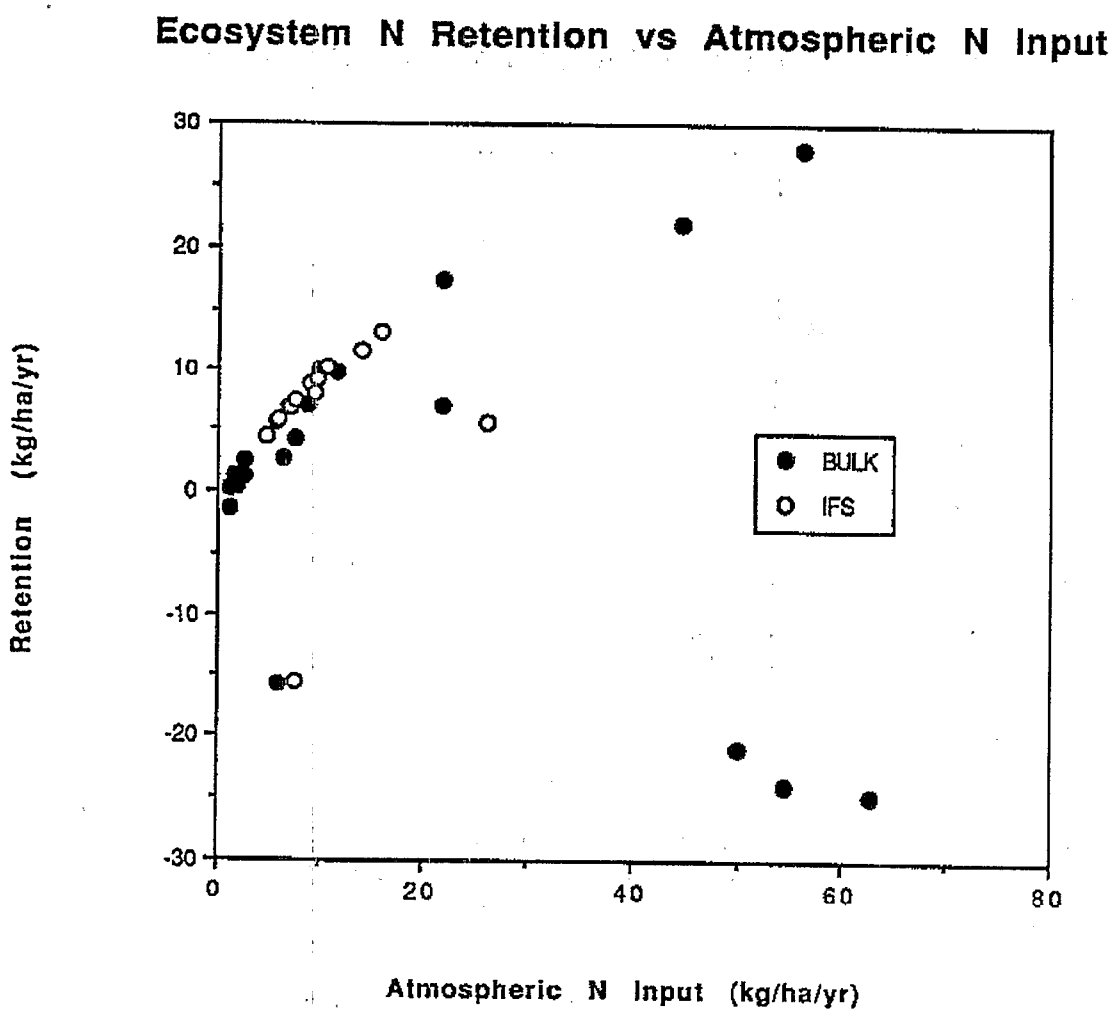


Figure 10-11. Ecosystem N retention as a function of atmospheric N input.

apparent relationship to atmospheric input (Figure 10-10). Secondly, vegetation N increment accounts for nearly all ecosystem N retention in most (19 of 24) cases, and calculated soil N retention is low and frequently negative (14 of 23 cases) (Table 10-13; Figures 10-12 and 10-13). There is no relationship between atmospheric N deposition and either tree increment or calculated soil retention (Figures 10-12 and 10-13).

The pattern of calculated soil N vs deposition in Figure 10-13 suggests that heterotrophs are very poor competitors for N, even at very low N input levels. Indeed, it appears as if the

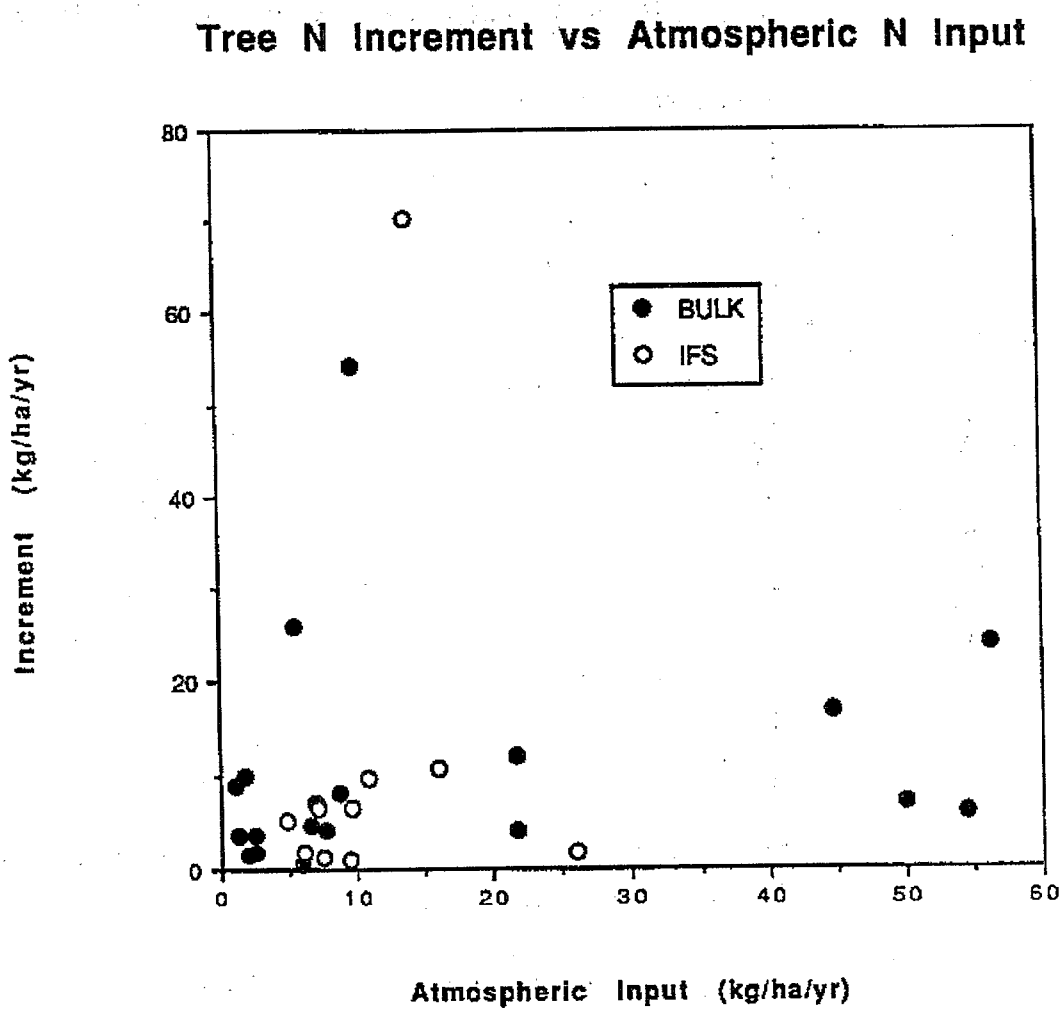


Figure 10-12. Tree N increment as a function of atmospheric N input.

soil is being "mined" for the N necessary to supply vegetation increment systems with very low atmospheric N inputs. This is readily apparent when N output is plotted as a function of input minus vegetation increment (Figure 10-14). Input minus increment can be thought of as N 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 N to supply tree needs or that there is an unmeasured N input contributing to tree N needs. In either case the data suggest that, contrary to views expressed in the literature (see review above), trees are, in the end, more effective competitors for N than soil heterotrophs. Similarly, the nearly 1:1

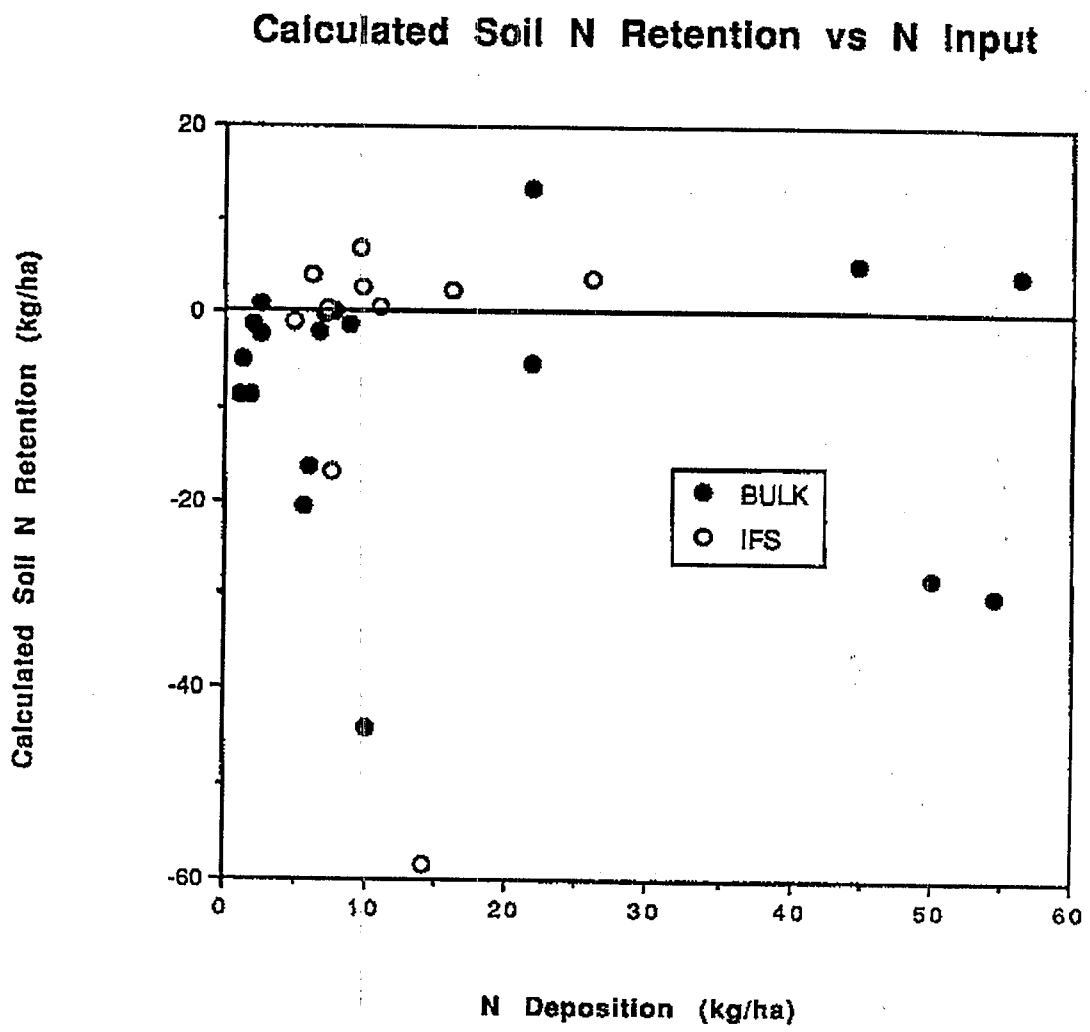


Figure 10-13. Calculated soil N retention (Input-increment-leaching) as a function of atmospheric N input.

relationship between N output and input-increment after the latter exceeds 0 ($r^2 = 0.84$) indicates that N 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 N retention and loss patterns between fertilizer and nutrient cycling/air pollution studies. Firstly, heterotrophic demand for N in fertilized sites is likely to be greater than in sites

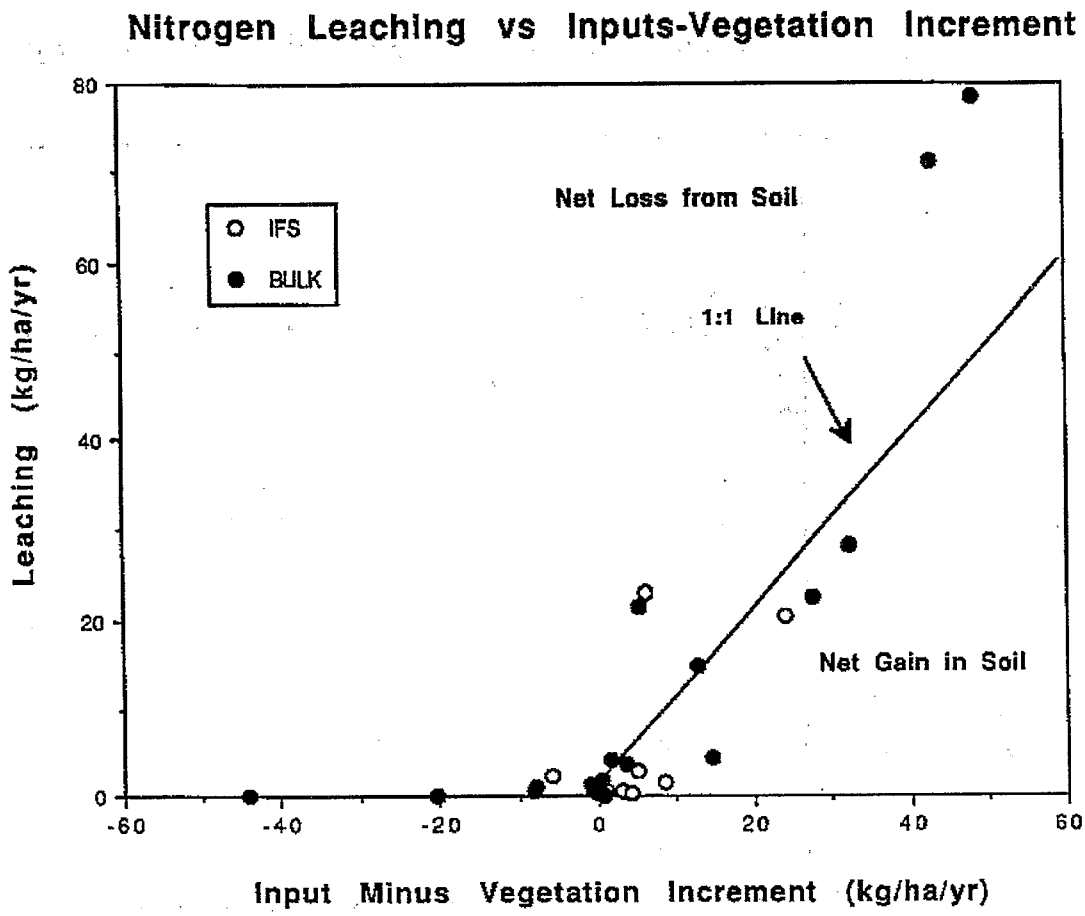


Figure 10-14. N leaching as a function of atmospheric N input minus tree N increment. Points above the 1:1 line imply net soil loss, and points below the line imply net soil retention.

subjected to chronically elevated atmospheric N inputs. Fertilizer N is typically applied to N-deficient ecosystems where N demand by soil heterotrophs is likely to be high, whereas heterotrophic demand for N may have been substantially satisfied in sites with chronically high atmospheric N inputs. Heterotrophic activity in fertilized sites is also likely to be stimulated by mobilization of soil organic C which typically occurs after fertilization (especially with urea; Ogner, 1972; Foster et al., 1985a). Secondly, as noted above, the slow, steady inputs of N via air pollution, like slow, steady inputs of fertilizer N probably

favor nitrification. Thirdly, non-biological retention of N is likely to be greater with fertilization than atmospheric deposition. Ammonium (NH_4^+) and ammonia (NH_3) fixation in 2:1 clays is likely to be substantially increased 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, non-labile 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 N inputs.

10.3.4 Effects of Pollutant N Inputs on Soils

10.3.4.1 Soil Biota

The most obvious and immediate effects of pollutant N inputs on soils are those on the microbial community. An increased activity of heterotrophs and nitrifiers associated with increased decomposition and nitrification rates would seem a likely result of increased N inputs. Studies of microbial responses to N fertilization have produced mixed results, however. Kelly and Henderson (1978) found increased bacterial activity but reduced invertebrate populations one year after fairly high levels of urea fertilization (550 and 1,100 kg N/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 ammonium nitrate and potassium chloride caused a reduction in soil microbial activity (as measured by carbon dioxide evolution) for at least three 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 N typical of fertilization studies as opposed to the slow, steady inputs of N at lower concentration typical of pollutant inputs. Aside from the limited information on effects on nitrifiers, virtually nothing is known as to as to the effects of slow, steady inputs of N on soil microbial communities.

10.3.4.2 Soil Chemistry

The foremost concern about long-term, capacity-controlled effects of excessive N 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 N 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 cations are adsorbed, are occupied with base cations (Ca^{2+}, Mg^{2+}, and K^+) as opposed to Al^{3+} and 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.

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 upon 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 10-20% 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.

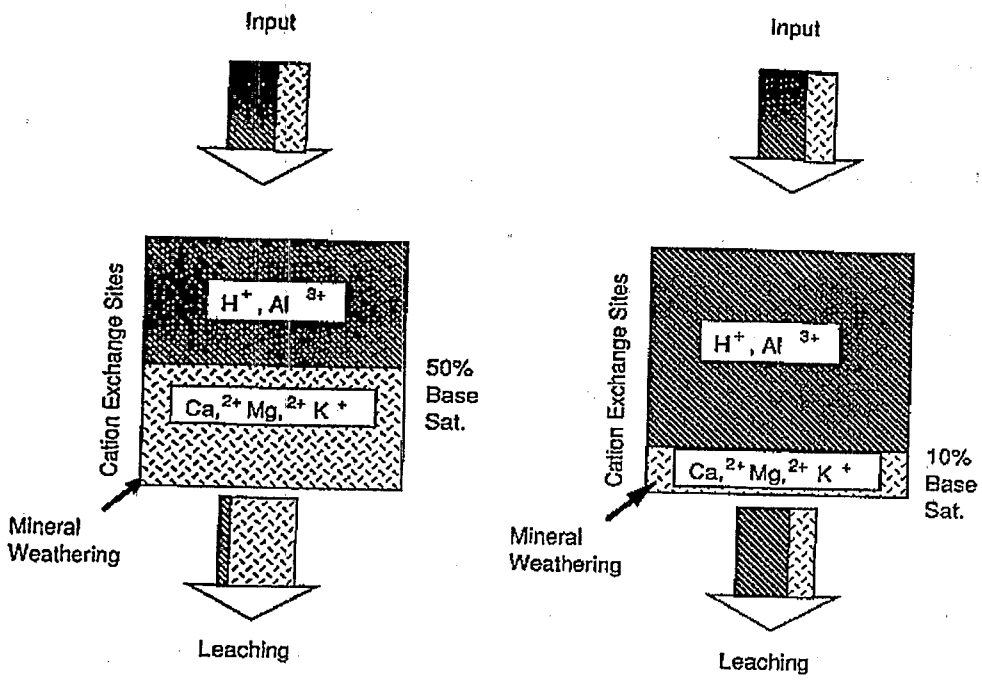


Figure 10-15. Schematic diagram of cation exchange for base cations, Al^{3+} and H^+ in circumneutral (50% base saturation, left) and acid (10% base saturation, right) soils.

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. We noted such a situation with respect to Ca^{2+} in an oak-hickory forest on Walker Branch watershed, Tennessee (Johnson et al., 1985). 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 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 Fe and 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

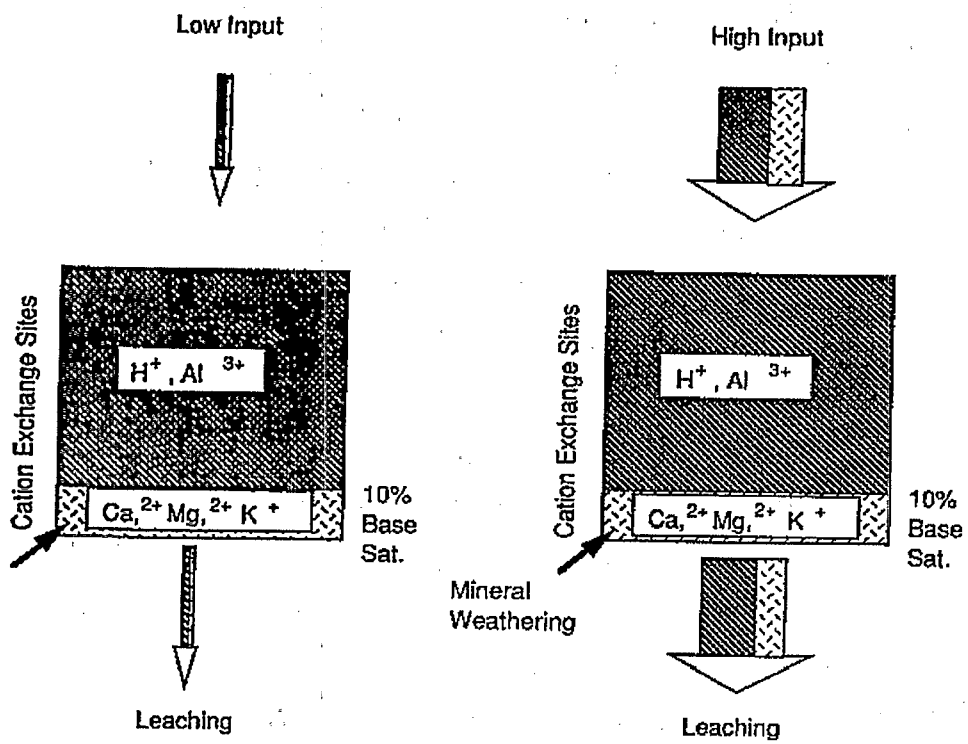


Figure 10-16. Schematic diagram of cation exchange for base cations, Al^{3+} and H^{+} in acid soils with low (right) and high (left) atmospheric deposition rates.

soil. The former method gives a better estimate of current 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, while 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 (e.g., 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 (e.g., 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 N 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 very few proven, documented cases in which excessive atmospheric N deposition has caused soil acidification, but there is no doubt that the potential exists, given high enough inputs for a sufficiently long time. Van Breemen et al. (1982, 1987) report high acidification pressure on forests of The Netherlands subject to very high inputs of N from nearby agricultural activities (often considerably in excess of 50 kg $N \cdot ha^{-1} \cdot yr^{-1}$; van Breemen et al., 1982, 1987; Nilsson and Grennfelt, 1988). The hydrogen ion 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 N deficiency may outweigh the detriments of soil acidification. For instance, Van Miegroet and Cole (1984) found that excessive N_2 fixation by red alder (*Alnus rubra*) caused large increases in NO_3^- leaching and a significant amount of soil acidification relative to adjacent Douglas-fir (*Psuedotusga menziesii*) stands, yet Douglas-fir growth is invariably superior on sites formerly occupied by red alder due to the differences in N status (Tarrant and Miller, 1963; Binkley, 1983; Van Miegroet et al., 1991).

10.3.5 Effects on Natural Waters

A major recent concern over the effects of soil acidification due to atmospheric deposition of both N 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 N 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: $Al^{3+} > Ca^{2+}, Mg^{2+} > K^+, Na^+, H^+$. 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 streamwaters 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 U.S. (Galloway et al., 1980; Driscoll et al., 1989). In less acid systems, NO_3^- pulses may be associated with base cations rather than Al^{3+}, and H^+: Foster et al. (1989) note pulses of NO_3^- and base cations in soil solutions and streams at the Turkey Lakes site in Ontario. Driscoll et al. (1989) reviewed the North

American data relevant to the role of nitrogen in the acidification of surface waters and explored relationships between atmospheric N deposition, soil C/N ratio and streamwater 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 streamwater nitrate concentrations.

10.3.6 Effects of Pollutant N Deposition upon Vegetation Nutrient Status

Because N is the most commonly limiting nutrient for growth in forest ecosystems in North America (Cole and Rapp, 1981), deposition of N in any biologically available form to most forest ecosystems is likely to produce increased vegetation growth to some extent. The degree of response will depend upon the amount of N deposited, the N demand for vegetation, and the competition from soil heterotrophic organisms for this N, as described above. In addition to changes in growth, increased N deposition can cause significant changes in tree physiological function, susceptibility to insect and disease attack, and even plant community structure. In this section, we will briefly review plant physiological responses related to increased N nutrition (see Section 11.4 for more in depth coverage), and give a more in-depth review of soil-mediated effects of N deposition on vegetation and an update on plant community/successional changes that seem to be occurring in high-deposition areas of Europe.

10.3.6.1 Physiological Effects of Excess N Inputs

Nitrogen addition can have several impacts upon 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*) to SO_2 injury (Cotrufo and Berry, 1970). Nitrogen fertilization usually depressed 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 N inputs might be expected.

Several hypotheses posed to explain current forest declines in eastern North America invoke the effects of excess N deposition upon 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 N 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 N 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 an 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 red spruce response to nitrogen lend no support to the various hypotheses for N-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 upon laboratory studies with detached shoots. DeHayes et al. (1989) found that treatment of red spruce seedlings with ammonium nitrate *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 U.S., perhaps with some additional exacerbation due to the direct effects of acid mist on foliage (Lucier et al., 1990). There is some evidence to suggest that indirect effects of nitrogen saturation, namely nitrate and aluminum leaching, may be contributing factors to red spruce decline in the southern Appalachians, and this literature is reviewed below.

10.3.6.2 Soil-Mediated Effects on Vegetation

N inputs in excess of tree and heterotrophic N 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 N status will greatly outweigh the detrimental effects of decreased availability of other nutrients. For instance, the benefits of N fixation during a red alder (*Alnus rubra*) stage to subsequent Douglas-fir (*Pseudotsuga menziesii*) forests in the Pacific Northwest are well-documented despite the fact that excessive N fixation during the red alder stage causes considerable P immobilization and soil acidification (Van Miegroet and Cole, 1984). In other cases,

effects of excessive N deposition may be clearly deleterious to plant nutrition. Boxmann et al. (1988) report that excessive NH_4^+ deposition to soils in which nitrification is inhibited causes serious nutritional imbalances and even toxic effects to some forests in The Netherlands. According to Boxmann et al. physiological mechanisms for these effects might include inhibition of photosynthetic phosphorylation, starch synthesis, protein synthesis (causing a buildup of amino acids), chlorophyll synthesis, and saturation of membrane lipids with NH_4^+, reducing their ion selectivity and making them more permeable. Increased membrane permeability may allow potentially toxic ions to be taken up (e.g., Al^{3+}) and allow nutrient ions to be released (e.g., Ca^{2+}). Deleterious effects of excess N deposition can occur via soil interactions as described above, or via aboveground processes. 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 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., Rehfuess, 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. (in press) 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 N, (up to 10,000 kg N/ha) and atmospheric N deposition was also quite high (26 kg N ha^{-1} yr^{-1}), both of which contribute to the high rates of NO_3^- leaching at these sites. The peak *total* Al concentrations (70 μM/L) associated with these NO_3^- pulses were below the threshold for *monomeric* Al where visible injury to red spruce seedlings occurs in laboratory studies (200 μM/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 80-90% of total Al in these soil solutions was in monomeric form, and inhibition of Ca

and Mg uptake at monomeric Al levels of well below 200 μM/L has been noted (Thornton et al., 1987). In this vein, 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 an hypothesis for the decline of red spruce in which Al inhibits Ca uptake, Ca deficiency reduces cambial growth (since 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, A.H. Johnson (1983) finds no support for the Al hypothesis in the seriously declining forests of Camel's Hump, Vermont. He found that while the degree of decline increases with elevation, both Al concentration and Al:Ca ratios in fine roots decrease with elevation while the degree of dieback and decline increases 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) conclude 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 damage 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.

10.3.6.3 Ecosystem-Level Responses to N Deposition

Growth responses to increased N 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 N deposition may not be deemed desirable in wilderness areas. Different genera and species respond differentially to increased N availability; for instance, deciduous species (aniosperms) generally have a greater demand for N 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 N additions to abandoned old fields in Minnesota. Thus, there is a real possibility for changes in ecosystem composition with increased N loading. Changes from heathland to grassland in Holland have been attributed to high rates of N deposition (Roelofs et al., 1987). Ellenberg (1987) points to further species changes in Central European ecosystems as a likely consequence of elevated N. 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 N via host-pathogen interactions. Increased N 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 P and N to sites deficient in these elements increased the incidence of fusiform rust in slash pine. On the other hand, increased N 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 N inputs produces changes in stand structure which produce 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*) to grasses in The Netherlands, note that N fertilization leads to increased growth of grasses only when *Calluna* stands are opened up by beetle attacks. By increasing the N concentration of heather foliage, high N input stimulates larval growth and increases body weight of beetles.

The effects of increased N inputs on host-pathogen interactions remain largely speculative; insufficient research on this subject has been done to make many 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 N deposition, both positive and negative, on host-pathogen interactions.

10.3.7 Critical Loads for Atmospheric N Deposition

Recently, there have been efforts to set critical loads for N deposition for natural ecosystems (Nilsson and Grennfelt, 1988; Fox et al., 1989; Schulze et al., 1989). 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" (p. 17, Nilsson and Grennfelt, 1988; p. 451, Schulze et al., 1989). The critical loads for N 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:

$$\text{BC leaching} \leq \text{BC weathering} + \text{BC deposition} - \text{BC growth} \qquad (1)$$

where BC=base cations. Equation (1) is perhaps best understood by rearranging:

$$\text{BC leaching} + \text{BC growth} \leq \text{BC weathering} + \text{BC deposition} \qquad (2)$$

Equation (2) 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:

$$\text{Nitrate leaching} + \text{Sulfate leaching} \leq \text{BC leaching} \qquad (3)$$

The authors state that equation (3) 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" (<) as well as the "equal to" (=) sign in Equation (3) 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 aluminum and hydrogen ions are present to significant extent in soil solutions.

Combining (1) and (3), the authors obtain:

$$\text{Acceptable Nitrate Leaching} \leq \text{BC weathering} + \text{BC deposition} - \text{BC growth} - \text{Sulfate leaching} \quad (4)$$

In obtaining Equation (4), the authors assumed (without stating so) that only the "equal to" (=) and not the "less than" sign in Equation (3) applied; in short, they assumed that all base cation leaching was due to nitrate + sulfate leaching, and that no H^+ and Al^{3+} leaching occurred.

To estimate nitrate leaching, the authors use the nitrogen balance equation:

$$\text{N input} \leq \text{N growth} + \text{N immobilization} - \text{N mineralization} + \text{N denitrification} - \text{N fixation} + \text{N leaching} \quad (5)$$

Again, this equation is best understood by rearranging:

$$\text{N leaching} \geq (\text{N input} + \text{N fixation} + \text{N mineralization}) - (\text{N growth} + \text{N immobilization} + \text{N denitrification}) \quad (6)$$

Equation (6) can be thought of as a mass balance equation for the soil inorganic N 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 input), fixation (N fixation), and release from soil organic matter during decomposition (N mineralization). The non-leaching outputs include plant uptake (N growth), heterotrophic uptake (N immobilization), and denitrification (N denitrification). The remainder must be leaching (N leaching). It is assumed in their analysis that N denitrification and N fixation are negligible in forest ecosystems and that N immobilization − N mineralization, which is the

net annual N accumulation in the soil, equals only 1-3 kg N· $ha^{-1} \cdot yr^{-1}$. The latter numbers are based upon an estimate of the net N accumulation in soils of Sweden since the last glaciation (obtained by dividing nominal soil N content values by the number of years since glaciation). Soil N accumulation rates can be much higher: Jenkinson (1970) documents net annual soil N accumulations of over 50 kg · $ha^{-1} \cdot yr^{-1}$ 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 N accumulation was greater than thought possible from atmospheric deposition alone and may have been in part due to the action of free-living N-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 N accumulations of only 23 kg · $ha^{-1} \cdot yr^{-1}$ 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 3-5 kg N · $ha^{-1} \cdot yr^{-1}$ for raised bogs to a high of 5-20 kg N · $ha^{-1} \cdot yr^{-1}$ for deciduous forests. A critical concentration for nitrate in groundwater (10 mg N/L) is then calculated based upon an assumption of precipitation surplus (precipitation minus evapotranspiration) of 100 to 400 mm yr^{-1}, giving values of 10 to 40 kg N · $ha^{-1} \cdot yr^{-1}$.

In contrast to the rather quantitative approach taken at the Skokloster Workshop, a far more subjective approach is taken in determining critical N loads for wilderness areas in the U.S. Forest Service-sponsored workshop held at Cary Arboretum, Millbrook, New York 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 N cycling in wilderness areas is quite scarce at best, and in many areas completely lacking" (p. 12). Despite the lack of N cycling data, the authors provide guesses at "green" and "red" line values for specific wilderness areas ranging from 3-10 kg N kg · $ha^{-1} \cdot yr^{-1}$ for "green" values and 10-15 kg · $ha^{-1} \cdot yr^{-1}$ for "red" values. These values quantitatively similar to

those obtained in the Skokloster workshop, and actually show very little spread between "green" and "red" lines.

10.3.8 An Evaluation of Critical Loads Calculations for N 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 1-3 kg N · ha^{-1} · yr^{-1} 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 10.3.3. Having stated that, however, it should also be noted that both heterotroph and ecosystem-level recovery of atmospherically-deposited N seems to be lower than that of fertilizer N, as also noted also in Section 10.3.3. The authors of the critical load document (Nilsson and Grennfelt, 1988) recognize that N 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 50-100 years). Nonetheless, even "temporary" retention of atmospherically-deposited N could be significant: if N-deficient systems can retain as much as 600 kg N · ha^{-1} in the soil by heterotrophs (see Table 10-13), an atmospheric N input of 25 kg · ha^{-1} · yr^{-1} could be retained for 24 years. Recall that Jenkinson (1970) found an average annual N accumulation of about 25 kg · ha^{-1} · yr^{-1} in soils at the Rothamsted Experiment Station in England over an 80-year period (1888-1962). This accumulation, which was calculated by differences in measured soil N content over time, is of special interest in that it actually *exceeded* estimated atmospheric N deposition over that period. It seems clear that estimates of atmospheric N inputs to these sites are low, due either to underestimates of dry deposition or N-fixation

A critical unknown in soil heterotrophic N 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 N from the irrigation and fertilizer experiments noted above (Aronsson and Elowson, 1980; Ingestad, 1980; Landsberg, 1986) can increase substantially with increasing N deposition rate, bringing into question calculations of N sequestering by trees from areas that are not N-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, BC weathering. While 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 amounts of minerals and cation nutrients left in soils 8,000-12,000 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 which formed the basis of the Skokloster document is based upon preventing soil acidification. Implicit in this goal is the assumption that soils reach and remain in some kind of steady-state, non-acid 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 N 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 judgements inevitably come into play in setting critical loads for pollutant deposition of nutrients, especially in the case of N.

The "green" and "red" lines for N 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 argument. Given the fact that wilderness areas, especially those in the western U.S., 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 N deposition rates in some parts of the western U.S., (1-2 kg $\cdot$ ha^{-1} $\cdot$ yr^{-1}; Table 10-13), it seems likely that increases of up to 10 kg $\cdot$ ha^{-1} $\cdot$ yr^{-1} will result in some increases in plant growth, plant health, and, quite possibly, changes in species composition. The judgement 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 N demand is satisfied in these slow-growing ecosystems), but remain open to serious question over the long term.

10.3.9 Conclusions

There is little doubt that N deposition has a pronounced effect on many, if not most terrestrial ecosystems. Because most forest ecosystems in North America are N deficient, one of the most noticeable initial changes in response to increased N deposition is likely to be a growth increase. Whether this 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, value judgements by society.

All current information indicates that such "N-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 upon the degree to which forests become N saturated. The critical load values given in the Skolster document (Nilsson and Grennfelt, 1988) are unlikely to produce N-saturation in highly-productive, intensively-managed forests of the timberbelts in the southeastern and northwestern U.S. that are frequently harvested and/or subjected to control burning. Indeed, there is considerable concern that intensive management practices in these forests are causing N depletion (Boyle and Ek, 1972).

Given the great variation in both natural forest N 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 N ha^{-1} yr^{-1}, whereas a value as low as 10 kg N ha^{-1} yr^{-1} may be produce undesired growth increases in very slow-growing virgin forests in wilderness areas. Given some knowledge about forest uptake rates and current N status, critical loads might be calculated on a site-by-site basis, but regional values will invariably prove invalid for many (if not most) forests within the region to which they are applied.

10.4 TERRESTRIAL ECOSYSTEM EFFECTS—VEGETATION

Subsequent to the dry or wet deposition of N forms from the atmosphere (Section 10.2) nitrogen containing compounds can impact the terrestrial ecosystem through direct effects on plant metabolic processes, or indirectly by modifying the nitrogen cycle and associated soil chemical properties. However, interpretation of the effects of N deposition at the level of the ecosystem becomes difficult because of the complex interactions which exist between biological, physicochemical, and climatic factors (U.S. Environmental Protection Agency, 1982).

10.4.1 Direct Effects

Direct effects of reactive nitrogen compounds on terrestrial ecosystems are defined as those effects that impact individual plants by disturbing "normal" physiological processes. Because information on the direct effects of NO and NO_2 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 nitric acid vapor on vegetation and essentially no information on its effects on ecosystems. Norby et al. (1989) reported that nitric acid 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 nitric acid 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 ammonia, a reduced nitrogen gas, have been summarized by Van Der Eerden (1982), however, ammonia 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 ammonia 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 ammonia fumigation and concluded that the following concentrations produced no adverse effects:

0.107 ppmv (75 $\mu g\ m^{-3}$), yearly average
0.858 ppmv (600 $\mu g\ m^{-3}$), daily average
14.3 ppmv (10,000 $\mu g\ m^{-3}$) 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 mg m^{-3} (37 ppmv), three 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 ammonia producing the leaf effects (37 ppmv) exceeds normal ambient levels for the U.S., but it is representative of reported high concentration episodes in Europe (Gmur et al., 1983). Cowling and Lockyer (1981) reported beneficial effects of ammonia 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 $\mu g\ m^{-3}$ NH_3 on *Populus euramericana* L. over a 6 to 8-week period and found increases in photosynthesis at 100 $\mu g\ m^{-3}$, but no changes in stomatal characteristics up to that level of NH_3.

10.4.2 Indirect Effects

Indirect effects of dry nitrogen deposition to terrestrial ecosystems result from the addition of nitrogen to ecosystems at a rate above that experienced during normal successional processes leading to ecosystem eutrophication. Positive 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 10.3 and 10.5). However, if atmospheric additions of nitrogen exceed the "buffering" capacity of an ecosystem, alterations in soil chemistry are expected to take place (see Section 10.3). Inputs of nitrogen to natural systems are hypothesized to alleviate deficiencies and allow increased growth of some plants, but in doing so may also impact interplant competitive relationships which would result in altered species composition and diversity in sensitive ecosystems (U.S. Environmental Protection Agency, 1982; Ellenberg, 1987). Schulze (1989) has also proposed that excessive additions of nitrogen lead to nutrient deficiencies of other elements (Ca, Mg). Aber et al. (1989) outlined a hypothetical progression of the effects of excessive nitrogen additions for northern forest ecosystems, and concluded that these systems have a limited capacity to accumulate nitrogen.

In addition to the potential for increasing plant productivity through fertilization, the deposition of nitrogen from the atmosphere to ecosystems has been hypothesized to disrupt normal nutrient cycles and physiological processes, resulting in increased susceptibility of forests to other environmental stresses (Lindberg et al., 1987; Nihlgård, 1985; McLaughlin, 1985; Schulze, 1989). Physiological imbalances resulting from excessive nitrogen additions are also hypothesized to disrupt the winter hardening process (Nihlgård, 1985; Friedland et al., 1984; Waring, 1987), produce nutrient imbalances (Nihlgård, 1985; Waring, 1987; Schulze, 1989), and altered carbon allocation patterns within plants (Nihlgård, 1985; McLaughlin, 1985). 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 (Grennfelt and Hultberg, 1986; Nihlgård, 1985). 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 might 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. For example, Roelofs et al. (1987) proposed that ammonia/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+}

(2) nitrogen enrichment leading to "abnormal" plant growth rates and altered competitive relationships.

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 which showed no additional winter injury of high elevation conifer forests when fertilized with 40 kg total nitrogen ha^{-1} yr^{-1}. 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^{-1} yr^{-1}. At the very high rates of application of 480 kg N ha^{-1} yr^{-1} 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 negative effects, but some indication of increased growth since 1960 that could be the result of atmospheric N deposition was indicated for Norway spruce. Miller and Miller (1988) concluded that fertilizer trials are not be appropriate for extrapolation as indicators of forest response to N 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.

De Temmerman et al. (1988) provided data showing increased fungal outbreaks and frost damage on several pines species exposed to very high ammonia deposition rates (>350 kg ha^{-1} yr^{-1}). 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 10.2), has also been suggested to favor outbreaks of insect pests (Waring and Pitman, 1985; White, 1984). Schulze (1989) presents a clear progression of evidence which indicates that canopy uptake of nitrogen together with root uptake has caused a nitrogen imbalance in Norway spruce leading to forest 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). The authors established that the changing nature of unmanaged heathlands in the Netherlands, where *Calluna vulagris* 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 vulagris* and *Molinia caerulea* 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 dominate 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 N ha^{-1} yr^{-1}. Liljelund and Torstensson (1988) have shown clear signs of vegetation changes in response to nitrogen deposition rates of 20 kg ha^{-1} yr^{-1}. 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. 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.

10.4.3 N Saturation, Critical Loads, and Current Deposition

Ecosystem nitrogen saturation and the definition of the critical levels of total N 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 N saturated ecosystems (1) no response to additional N (2) growth reductions

in response to added N or (3) added N leads to increased losses of nitrate in streamwater, and concluded that the third was most reasonable (see also Section 10.3). Brown et al. (1988) reported that a recent workshop concluded that N saturation could be best defined as occurring when N outputs from ecosystems exceeded inputs. This conclusion was based on a model of plant/soil N saturation put forth by Ågren 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 N saturation leads to the possibility of defining a critical N load (deposition rate) at which no change or deleterious impacts will occur to an ecosystem (Nilsson, 1986). 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).

10.4.3.1 Critical N Loads That Have Been Proposed

Skeffington and Wilson (1988) summarized and discussed the following possible criteria as potentially useful for defining appropriate critical N loads on ecosystems:

- Prevent nitrate levels in drinking or surface waters from rising above standard levels
- Ensure proton production less than weathering rate
- Maintenance of a fixed ammonia-base cation balance
- Maintenance N inputs below N outputs (the N saturation approach)
- 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 sulfur for Dutch forest ecosystems based on the following: N 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 N and S deposition in the Netherlands exceed acceptable levels.

Schulze et al. (1989) have also proposed critical loads for N 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 10.3.6). 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 3-14 kg N ha^{-1} yr^{-1} for silicate soils or 3 to 48 kg

N ha^{-1} yr^{-1} for calcareous based soils. Other critical loads have been proposed at rates of nitrogen deposition ranging from as little as 1 to levels near 100 Kg N ha^{-1} yr^{-1} depending on the impacts considered acceptable and the criteria used to define the critical load.

Critical loads less than 30 kg ha^{-1} yr^{-1} have been proposed based on criteria to minimize species changes (van Breeman and van Dijk, 1988; Liljelund and Torstensson, 1988). Using the criteria that ecosystem nitrogen inputs should not exceed outputs, critical loads have been proposed as low as 1-5 kg N ha^{-1} yr^{-1} for poorly productive sites with low productivity or in the range from 5-30 kg N ha^{-1} yr^{-1} 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 N load Skeffington and Wilson (1988) concluded that "we do not understand ecosystems well enough to set a critical load for N 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).

These oligotrophic ecosystems are considered at risk from atmospheric nitrogen inputs 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 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 N deposition (World Health Organization, 1987).

10.4.3.2 Current Rates of Total N Deposition

Application of the concept of critical N loading has not yet been widely adopted in North America (based on amount of published data), but a comparison of total N 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, 10-15, and 10-16 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 the four categories depending on its origin: cloudwater, precipitation, dry particles, and gaseous forms. Table 10-15 summarizes wet deposited nitrate and ammonium deposition data for various states that were part of the National Acid Deposition Program. Table 10-16 specifically addresses the issue of relationships between ecosystems nitrogen inputs and outputs. Data in these tables indicates that total deposition of nitrogen in North America is typically less than rates found for many areas in Europe. North American sites would appear to have total N deposition rates less than 25 kg N ha^{-1} yr^{-1}. 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 northeastern United Sates and southern Canada (Olsen, 1989). Peak values were 5 and 25 kg ha^{-1} yr^{-1} for ammonium and nitrate, respectively. Similar wet deposition data for 1987 showed peak deposition rates of 3.5 and 16 kg ha^{-1} yr^{-1} 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^{-1} yr^{-1}) occurred between lakes Michigan and Ontario. They also found the temporal pattern of nitrate deposition was quite even

TABLE 10-14. MEASUREMENTS OF VARIOUS FORMS OF ANNUAL N DEPOSITION TO NORTH AMERICAN AND EUROPEAN ECOSYSTEMS

Site Location/ Vegetation	Forms of N deposition (Kg ha^{-1}) Wet: Cloud	Wet: Rain	Dry: Particles	Dry: Gases	Total	Reference
United States						
CA, Chaparral	--[a]	8.2	--	--	23[b]	Riggan et al. (1985)
CA, Sierra Nevada	--	--	--	--	(2)[c]	Williams and Melack (in press)
GA, Loblolly pine	--	3.7	1.0	4.2	9	Lovett (1991)
NC, Loblolly pine	--	8.7	2.2	4.1	15	Lovett (1991)
NC, Hardwoods	--	4.8	0.5	--	5.3	Swank and Waide (1988)
NC, White pine	--	3.7	0.9	2.7	7	Lovett (1991)
NC, Red spruce	8.7	6.2	3.6	8.6	27	Lovett (1991)
NH, Deciduous	--	7	--	--	(7)	Likens et al. (1970)
NH, Deciduous	--	9.3	--	--	(9)	Likens (1985)
NY, Red spruce	7.3	6.1	0.2	2.3	16	Lovett (1991)
NY, Mixed deciduous	--	4.8	0.8	2.5	8	Lovett (1991)
TN, Mixed deciduous	--	2.9	4.1	6.1	13	Kelly and Meagher (1986)
TN, Oak forest #1	--	3.2	4.4	4.0	12	Kelly and Meagher (1986)
TN, Oak forest #2	--	2.9	4.4	4.0	11	Kelly and Meagher (1986)
TN, Oak forest #1	--	6.9	1.3	--	8	Kelly (1988)
TN, Oak forest #2	--	6.0	1.2	--	7	Kelly (1988)
TN, Oak forest	--	4.5	1.8	3.8	10	Lindberg et al. (1986)
TN, Loblolly pine	--	4.3	0.6	1.4	9	Lovett (1991)
WA, Douglas fir	--	2.9	1.3	0.6	5	Lovett (1991)
WA, Douglas fir	--	1	--	--	(1)	Henderson and Harris (1975)
U.S. Regions						
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)
S.E. Appalachians	--	4.2	3.1	--	7.3	Driscoll et al. (1989a)
Canada						
Alberta (southern)	--	7.3	12.2[c]	--	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)

TABLE 10-14 (cont'd). MEASUREMENTS OF VARIOUS FORMS OF ANNUAL N DEPOSITION TO NORTH AMERICAN AND EUROPEAN ECOSYSTEMS

Site Location/ Vegetation	Forms of N deposition (Kg ha^{-1}) Wet: Cloud	Wet: Rain	Dry: Particles	Dry: Gases	Total	Reference
Fed. Rep. Germany						
Spruce (SE slope)	--	16.5	--	--	16.5	Hantschel et al. (1990)
Spruce (SW slope)	--	24.3	--	--	24.3	Hantschel et al. (1990)
Netherlands						
Oak-birch	--	--	--	--	24-56[b]	van Breemen and van Dijk (1988)
Deciduous/spruce	--	--	--	--	21-42[b]	van Breemen and van Dijk (1988)
Scots pine	--	--	--	--	17-64[b]	van Breemen and van Dijk (1988)
Douglas fir	--	--	--	--	17-64[b]	van Breemen and van Dijk (1988)
Douglas fir	--	19.3	95.7[c]	--	115	Draaijers et al. (1989)
Norway						
Spruce	--	10.3	0.7	0.2	11.2	Lovett (1991)
	--	--	--	--	3-19[b]	Royal Society (1983)
United Kingdom						
Spruce Forest	1.9	8.0	na	13.5	23.4	Fowler et al. (1989)
Cotton grass moor	0.4	8.0	na	4.0	12.4	Fowler et al. (1989)

[a]-- Symbolizes data not available or in the case of cloud deposition not present.
[b]Total nitrogen deposition was based on bulk deposition and throughfall measurements and does include components of wet and dry deposition.
[c]Measurements of total deposition data that do not include both a wet and dry estimate probably underestimate total nitrogen deposition and are enclosed in parentheses.
[d]Includes deposition from gaseous forms.

throughout the year (Schwartz, 1989). Wet deposition of ammonium (NH_4^+) in Europe ranges between 3.5 and 17.3 kg NH_4^+ ha^{-1} yr^{-1} (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

TABLE 10-15. MEAN ANNUAL WET NITRATE AND AMMONIUM DEPOSITION TO VARIOUS STATES LOCATED THROUGHOUT THE UNITED STATES*

		Forms of N deposition (Kg ha^{-1})			
Location	No. of Sites	Nitrate	Ammonium	Total[a]	Reference[b]
Pennsylvania	3	10.9	1.3	12.2	National Atmospheric Deposition Program (1988)
New York	5	9.7	1.4	11.1	National Atmospheric Deposition Program (1988)
Ohio	2	7.6	1.7	9.3	National Atmospheric Deposition Program (1988)
Georgia	1	6.9	1.1	8.0	National Atmospheric Deposition Program (1988)
Tennessee	1	6.9	0.8	7.7	National Atmospheric Deposition Program (1988)
Illinois	4	6.2	1.3	7.5	National Atmospheric Deposition Program (1988)
N. Carolina	4	6.2	1.1	7.3	National Atmospheric Deposition Program (1988)
Arkansas	1	5.0	1.3	6.3	National Atmospheric Deposition Program (1988)
Virginia	1	5.3	0.5	5.8	National Atmospheric Deposition Program (1988)
Florida	2	4.9	0.6	5.5	National Atmospheric Deposition Program (1988)
Oklahoma	3	4.1	1.3	5.4	National Atmospheric Deposition Program (1988)
Colorado	4	4.3	0.6	4.9	Böhm (1991)
Alabama	1	3.7	0.6	4.3	National Atmospheric Deposition Program (1988)
New Mexico	4	3.6	0.5	4.1	Böhm (1991)
S. Dakota	1	2.7	1.3	4.0	National Atmospheric Deposition Program (1988)
Texas	3	3.1	0.6	3.7	National Atmospheric Deposition Program (1988)

TABLE 10-15 (cont'd). MEAN ANNUAL WET NITRATE AND AMMONIUM DEPOSITION TO VARIOUS STATES LOCATED THROUGHOUT THE UNITED STATES*

		Forms of N deposition (Kg ha^{-1})			
Location	No. of Sites	Nitrate	Ammonium	Total[a]	Reference[b]
California	5	2.9	0.6	3.5	Böhm (1991)
Washington	3	2.7	0.3	3.0	Böhm (1991)
Wyoming	3	2.5	0.4	2.9	Böhm (1991)
Arizona	1	2.6	0.2	2.8	Böhm (1991)
Utah	1	2.5	0.3	2.8	Böhm (1991)
Idaho	1	2.3	0.3	2.6	Böhm (1991)
Oregon	4	2.1	0.3	2.4	Böhm (1991)
Montana	4	1.9	0.4	2.3	Böhm (1991)
Arizona	1	1.0	0.2	1.2	National Atmospheric Deposition Program (1988)
Hawaii	1	0.08	0.01	0.1	National Atmospheric Deposition Program (1988)

*The states are presented in order of the greatest annual N deposition.
[a]Total deposition data is for wet deposited forms only and as such represents an underestimate of the total nitrogen loading received by these geographic areas.
[b]Data from National Atmospheric Deposition Program (1988) are for a single year, and data summarized by Böhm (1991) are for the period from 1985 through 1988.

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 nitrogen dioxide have been predicted (Hanson et al., 1989; Hill, 1971; Kelly and Meagher, 1986). Duyzer et al. (1987) has also predicted that dry deposition of ammonia can reach levels as high as 54 kg ha^{-1} yr^{-1} in areas of high ambient concentration (0.017 ppmv). Typical values of ammonia deposition in

TABLE 10-16. NITROGEN INPUT/OUTPUT RELATIONSHIPS FOR SEVERAL ECOSYSTEMS

Site/Vegetation	Inputs	Efflux[a]	Reference
United States			
FL, slash pine	5.9[b]	0	Van Miegroet et al. (1991)
GA, Loblolly pine	9[b]	0	Van Miegroet et al. (1991)
ME, spruce	7.5[b]	0	Van Miegroet et al. (1991)
NC, Loblolly pine	15[b]	0	Van Miegroet et al. (1991)
NC, Oak-Hickory	8.2[c]	3.2	Cole and Rapp (1981)
NC, Red spruce	27.1[b]	11-20	Van Miegroet et al. (1991)
NC, White pine	8.8[c]	0.2	Cole and Rapp (1981)
NC, White pine	7.4[b]	0	Van Miegroet et al. (1991)
NH, N. Hardwood	6.5	4.0	Bormann et al. (1977)
NH, N. Hardwood	23.6	17.4	Likens et al. (1977)
NY, Deciduous	8[b]	1	Van Miegroet et al. (1991)
NY, Red spruce	15.9[b]	3	Van Miegroet et al. (1991)
OR, Douglas fir	2.0	1.5	Sollins et al. (1980)
TN, Loblolly pine	8.7[b]	0-2	Van Miegroet et al. (1991)
TN, Hardwood	13.2[b]	4.4	Kelly and Meagher (1986)
TN, Hardwood	13.0	3.1	Henderson and Harris (1975)
TN, Hardwood	8.7	1.8	Cole and Rapp (1981)
TN, Oak forest	7-8[d]	1.25	Kelly (1988)
TN, Oak forest	11.5[b]	3.2	Kelly and Meagher (1986)
TN, Shortleaf/pine	8.7	1.8	Cole and Rapp (1981)
TN, Yellow/poplar	7.7	3.5	Cole and Rapp (1981)
WA, Douglas fir	1.7	0.6	Cole and Rapp (1981)
WA, Douglas fir	4.7[b]	0	Van Miegroet et al. (1991)
WA, Red alder	70[b]	71	Van Miegroet and Cole (1984)
WA, Silver fir	1.3	2.7	Turner and Singer (1976)
WI, N.hardwoods	5.6	0.05	Pastor and Bockheim (1984)
Canada			
Ontario (maple)	7.8	18.2	Foster and Nicolson (1988)
Fed. Rep. Germany			
Norway spruce	21.8	14.9	Cole and Rapp (1981)
Beech	21.8	4.4	Cole and Rapp (1981)
Netherlands			
Oak	45	22	van Breemen et al. (1987)
Oak-Birch	54	78	van Breemen et al. (1987)
Oak	56	28	van Breemen et al. (1987)
Mixed deciduous	63	68	van Breemen et al. (1987)

TABLE 10-16 (cont'd). NITROGEN INPUT/OUTPUT RELATIONSHIPS FOR SEVERAL ECOSYSTEMS

Site/Vegetation	Inputs	Efflux[a]	Reference
Norway			
Spruce	11.2[b]	0	Van Miegroet et al. (1991)
Sweden			
Coniferous	2.1	0.6-1	Rosen (1982)
United Kingdom			
Mixed hardwood	5.8	12.6	Cole and Rapp (1981)
U.S.S.R.			
Norway spruce	1.1	0.9	Cole and Rapp (1981)

[a]An estimate based on nitrogen losses from the soil profile or from streamflow out of a watershed.
[b]Includes precipitation, cloud (where appropriate), particulate and gaseous forms of nitrogen deposition.
[c]Includes nitrogen inputs from precipitation and particulate forms of deposition.
[d]Mean of two oak forests in east Tennessee.

central Europe and Scandinavia range between 20 and 40 kg ha^{-1} yr^{-1} (Grennfelt and Hultberg, 1986).

Based on the current rates of N deposition (loading) occuring in North America (Tables 10-14 through 10-16) and the proposed critical N outlined in previous sections (Sections 10.3.6 and 10.4.3.1) one might conclude that current rates of N deposition in North America are sufficient to induce minor changes in some ecosystems (i.e., rates of deposition in N. America exceed some of the proposed critical load levels). 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 currently resulting from N 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 total 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 be in the range of 2-4 kg N ha^{-1} yr^{-1}. Higher levels of atmospheric nitrogen deposition are also expected to lead to increased rates of N_2O emissions.

10.5 ECOSYSTEM EFFECTS—WETLANDS AND BOGS

10.5.1 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^- (nitrate) or NH_4^+ (ammonium), 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.

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 CH_4 (methane) (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 N_2O (nitrous oxide). 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 $\times$ 10^6 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 (5-6 $\times$ 10^9 metric tons/y, Rotty, 1983) or the net uptake of CO_2-C by the ocean (1.6 $\times$ 10^9 metric tons/y, 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 ozone 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 nitrogen oxides 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), 1776 species are listed for the conterminous United States (Federal Register, 1985), and 302 of these (17%) occur principally in wetland habitats. The national list of plant species that occur in wetlands includes 6,728 entries (Reed, 1988), and since 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 10-17) 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., 1983). The net loss of wetland habitats during these two decades is equivalent to an annual rate of loss of 1,852 km^2/yr (= 715 sq. miles per 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.

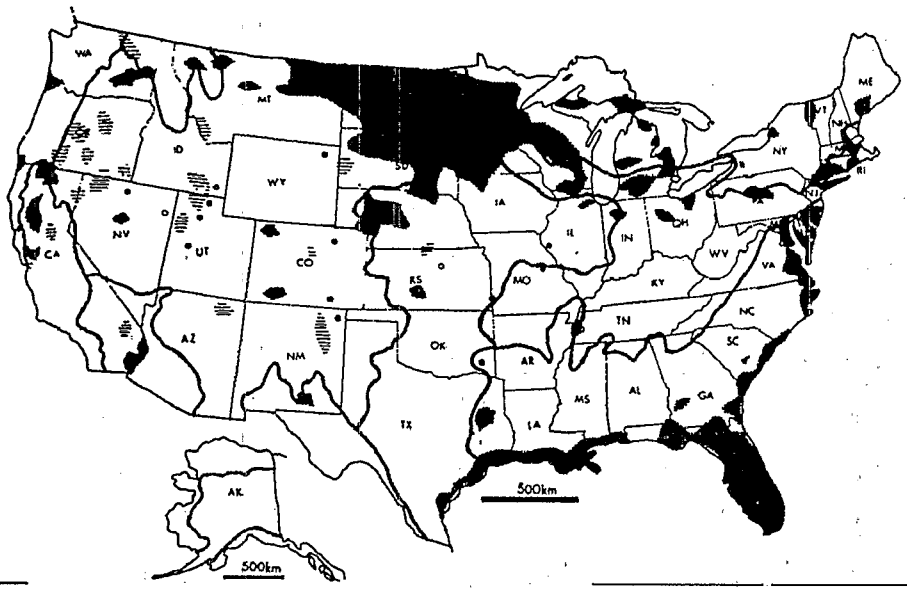


Figure 10-17. Map of the United States showing location of the major groups of inland freshwater marshes (from Hofstetter, 1983, p. 213). Contours delineate physiographic regions.

10.5.2 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) modelled the fate of nitrogen oxide emissions to the atmosphere and concluded that dry deposition accounts for greater than one-half of the total nitrogen oxide deposition in North America.

The rate of bulk NO_3^- deposition has been shown to be positively correlated with the concentration of nitrogen dioxide (NO_2) in 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 months. NO_2 concentrations (2 week averages) ranged from near zero to 25 $\mu g/m^3$ 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 N/litre.

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 N ha^{-1} yr^{-1} compared to a bulk deposition rate of 23.4 kg N ha^{-1} yr^{-1}. The same phenomenon was observed by Woodin and Lee (1987) who collected 1.45x 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 suggests that the deposition of solutes by this mechanism is important, and that bulk precipitation samplers underestimate total deposition.

Table 10-17 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 N ha^{-1} yr^{-1}. Other studies, however, indicate that wet NO_3^- deposition alone exceeds 15 kg N ha^{-1} yr^{-1} over most of the midwest, and 20 kg N ha^{-1} yr^{-1} in portions of the northeast United States (Zemba et al., 1988).

TABLE 10-17. BULK DEPOSITION OF NITROGEN IN NORTH AMERICAN WETLANDS (kg N ha^{-1} yr^{-1})

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)

NR = not reported.

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^{-1} yr^{-1} have been reported (Press and Lee, 1982; Ferguson et al., 1984). The combination of NO_3^- and NH_4^+ deposition down-wind of Manchester and Liverpool is reported to be 32 kg N ha^{-1} yr^{-1} (Lee et al., 1986). Nitrogen deposition in fens near Utrecht was 21 kg N ha^{-1} yr^{-1} of inorganic nitrogen and 3 to 5 kg N ha^{-1} yr^{-1} of organic nitrogen in bulk precipitation and 18 kg N ha^{-1} yr^{-1} of inorganic nitrogen in dry deposition (Koerselman et al., 1990). Roelofs (1983) reported that wet deposition alone of nitrogen in The Netherlands averages 15 kg N ha^{-1} yr^{-1} and is as great as 20-60 kg N ha^{-1} yr^{-1} in areas of intensive stockbreeding, 75-90% 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 (Buijsman, 1987). Annual NH_3 emissions from animal excreta in The Netherlands are reported to be 230 kt yr^{-1} (Van der Molen et al., 1989) or about 60 kg ha^{-1} yr^{-1} 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 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 N (8.4 kg/ha) in 13 months compared to total nitrogen in runoff from 2,050 ha of watershed of 10,000 kg N. 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 kg/ha × 2,050 ha = 17,220 kg) exceeded total runoff from the watershed to the wetland (10,000 kg), deposition could have contributed indirectly through runoff the majority of nitrogen entering the wetland. But the contributions of other nitrogen sources to runoff, such as fixation, fertilizer, and animal waste, were not given.

10.5.3 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 (nitrous oxide) or N_2 (nitrogen gas). 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 10.1.3.

Table 10-18 the nitrogen budgets are presented of wetlands that exhibit a wide range of nitrogen inputs. The two bog sites (Table 10-18) are representative of wetlands that contain 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, creating a surface that contains no mineral sediment. The peat in ombrotrophic bogs is raised above the elevation of the surrounding land so that they receive neither runoff from uplands nor inputs from ground water. 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 10-18. The bog ecosystems represented in Table 10-18 are located in Minnesota (Urban and Eisenreich, 1988) and Massachusetts (Hemond, 1983).

In bog ecosystems, the most important nitrogen inputs are from wet and dry deposition (see the line labelled precipitation in Table 10-18). The total input of nitrogen in these examples is about 10 kg N ha^{-1} yr^{-1}, 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 N ha^{-1} yr^{-1}. The outputs are accounted for by denitrification (1 to 1.8 kg N ha^{-1} yr^{-1}) 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

TABLE 10-18 NITROGEN BUDGETS OF SELECTED WETLANDS
(kg N ha^{-1} yr^{-1})

Location and Wetland Type:	UK Salt Marsh[1]	MA Salt Marsh[2]	Dutch Rech. Fen[3]	Dutch Disc. Fen[3]	French Heath[4]	MA Bog[5]	MN Bog[6]
INPUTS:							
Precipitation	NR	7.9	43.7[¶]	42.0[¶]	8.1	7.5	8.6
Fixation	3.36	68.0	2.1	12.7	1.3	3.36	0.5
Surf., ground or tidal water	43.4[#]	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[$]	274.0[†]	90.0[†]	82.0	38.0	66.0
Mineralization	194.9	193.0[$]	244.0[‡]	79.0[‡]	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
Surf. or subsurface DIN export	2.4[@]	102.0	2.1	6.7	3.0	2.0	0
Surf. or subsurface ON export	43.0[@]	552.0	45.8[§]	80.4[§]	3.0	1.0	2.0
Total		797.4	49.3	88.2		4.0	3.8

DIN = Dissolved inorganic nitrogen.
ON = Dissolved and particulate organic nitrogen.
NR = Not Reported.
[1]Abd. Aziz and Nedwell (1986a,b): salt marsh dominated by *Puccinellia maritima* (a grass).
[2]Valiela and Teal (1979): salt marsh dominated by *Spartina alterniflora*.
[3]Koerselman et al. (1990): Dutch eutrophic recharge and mesotrophic discharge fens, respectively.
[4]Rozé (1988): mesophilous heathland (shrub bog) dominated by *Erica ciliaris* (heath) and *Ulex minor*.
[5]Urban and Eisenreich (1988): ombrotrophic *Sphagnum* bog forested with black spruce (*Picea mariana*) and with an understory of shrubs and sedges.
[6]Hemond (1983): ombrotrophic bog dominated by *Sphagnum*.
[$]Calculated from Morris et al. (1984) and Valiela et al. (1984).
[#]Represents the net exchange of NO_3- (the major component) and small particulate organic nitrogen rather than an absolute rate.
[@]Represents the net exchange of DON (the major component), NH_4+, and large particulate organic nitrogen rather than an absolute rate.
[¶]Includes bulk plus dry deposition of inorganic and organic nitrogen.
[†]From Verhoeven et al. (1988), assuming a root:shoot quotient of 1.0.
[‡]From Verhoeven et al. (1988).
[§]Includes primarily hay harvested by mowing.

input of inorganic nitrogen. For example, wetfall contributed more than 95% of the NH_4^+ and NO_3^- entering the 1,000 km^2 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

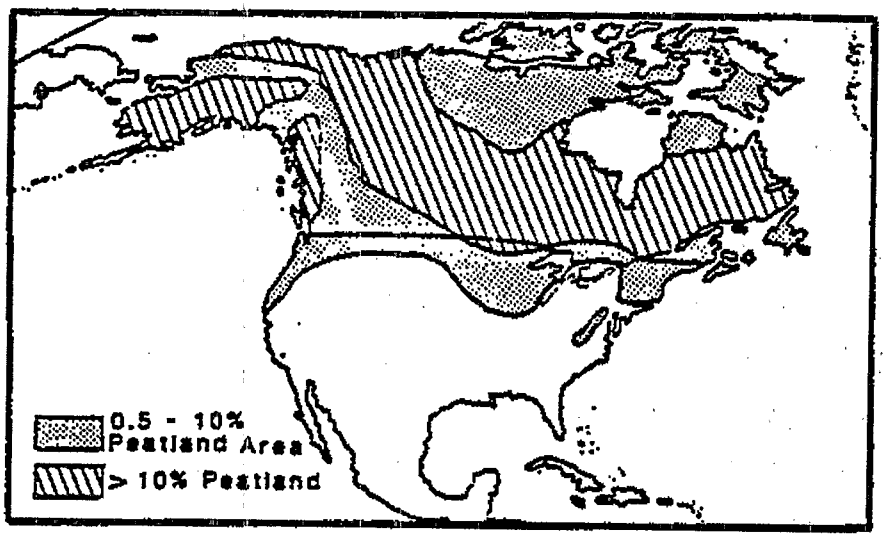


Figure 10-18. Distribution of North American peatlands (from Mitsch and Gosselink, 1986, p. 288).

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 10-18) 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 (Rozé, 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 10-18), 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 ground water

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 ground water (Verhoeven et al., 1988). However, atmospheric nitrogen deposition in these fens supplies more nitrogen than all other inputs combined (Table 10-18).

The coastal salt marsh ecosystems in Table 10-18 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, ground water. 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, since the diffusion gradients for NH_4^+ and DON normally favor diffusion out of the sediment. These surface and ground water sources of nitrogen are one to two orders of magnitude greater than inputs from precipitation (Table 10-18). In the Massachusetts salt marsh, ground water inputs of NO_3^- and DON are important and account for 60 and 56 kg N ha^{-1} yr^{-1}, respectively, of the total inputs (Valiela and Teal, 1979). In contrast, the Essex (UK) marsh is not influenced by ground water (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 N ha^{-1} yr^{-1}), DON (337 kg N ha^{-1} yr^{-1}), and particulate organic nitrogen (139 kg N ha^{-1} yr^{-1}) (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 10-18), 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 N ha^{-1} yr^{-1}), NO_3^- (25 kg N ha^{-1} yr^{-1}), DON (380 kg N ha^{-1} yr^{-1}), and particulate organic nitrogen (17 kg N ha^{-1} yr^{-1}) (Valiela and Teal, 1979).

Nitrogen inputs and outputs in tidal water were given as net exchanges of different nitrogen components in the Essex (UK) study (Abd. Aziz and Nedwell, 1986b) rather than 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 10-18). However, valid comparisons can be made of the net exchanges. There is a large net export of DON (43 kg N ha^{-1} yr^{-1}) from the Essex marsh (Abd. Aziz and Nedwell, 1986b), and this is consistent with the net DON loss in tidal water of 45 kg N ha^{-1} yr^{-1} 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 10-18. Nitrogen assimilation by the plant communities varies from 38 to 66 kg N ha^{-1} yr^{-1} in the bog ecosystems compared to 225 to 274 kg N ha^{-1} yr^{-1} in the salt marsh and fen ecosystems, respectively. The nitrogen cycle in the bog and heathland ecosystems is largely closed (Figure 10-19). In contrast, the nitrogen cycle in salt marshes and fens is open, and there is a great exchange of nitrogen with adjacent systems (Figure 10-19). In all these ecosystems, the rate of nitrogen mineralization almost balances plant assimilation in the manner of a closed cycle (Table 10-18). 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 10-18).

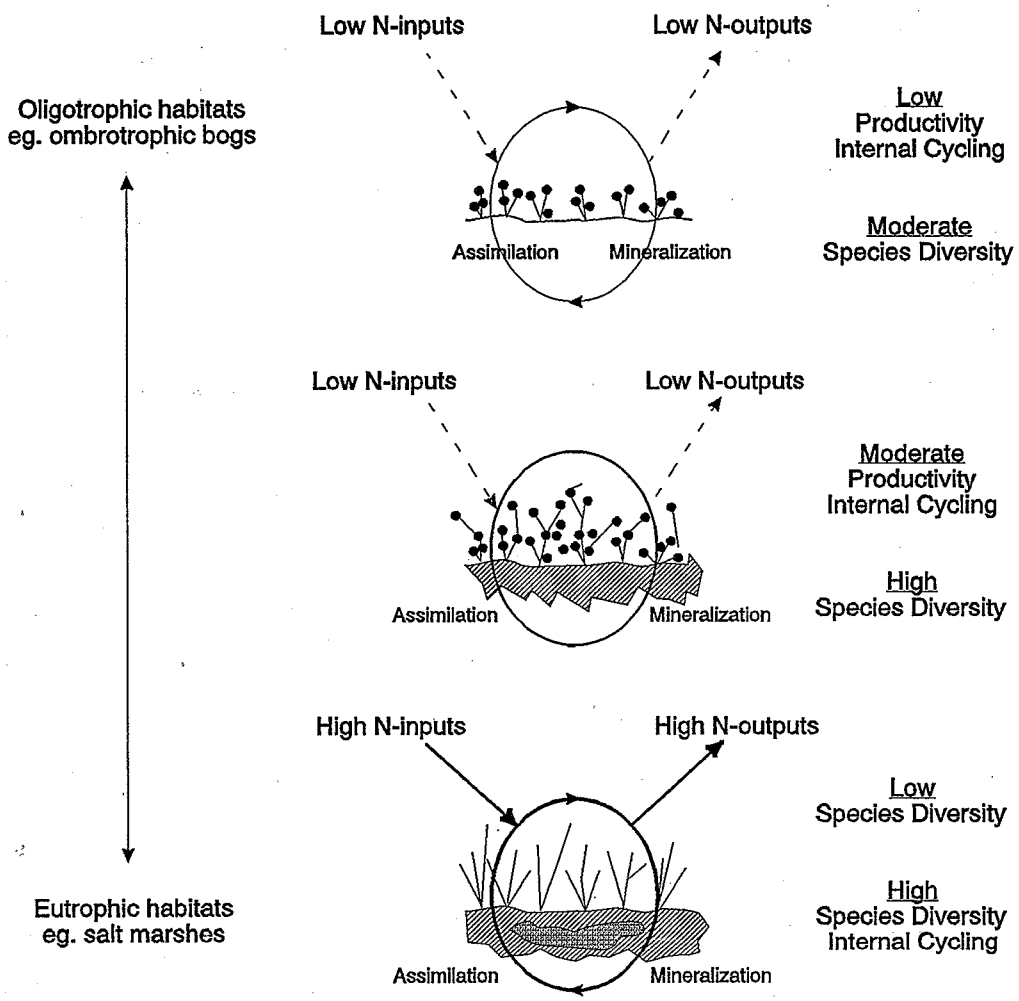


Figure 10-19. Conceptual relationships among trends in nitrogen cycling, productivity, and species diversity along a gradient from oligotrophic (nutrient-poor) to eutrophic (nutrient-rich) habitats.

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 10-19).

10.5.4 Effects of Nitrogen Loading on Wetland Plant Communities

10.5.4.1 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 10-19. 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 N ha^{-1} yr^{-1} (Table 10-19), and in most studies these have been 1 to 2 orders of magnitude greater than rates of atmospheric deposition (Table 10-17). These applications stimulated increases in standing biomass by 6 to 413% (Table 10-19).

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 sub-arctic salt marsh by 175%, while 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 P_i (inorganic phosphate) 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 yr at a rate of 200 kg N ha^{-1} yr^{-1}, but sites fertilized with 40 kg P ha^{-1} yr^{-1} did show a significant increase in biomass (Aerts and

TABLE 10-19. RESULTS OF NITROGEN FERTILIZATION EXPERIMENTS IN WETLAND ECOSYSTEMS

Salt Marsh Ecosystems	Rate of N Application (kg ha^{-1} yr^{-1})	Length of Study (yr)	Control[1] Biomass (g/m^2)	Percent[2] Increase	N-form Applied	Reference
Spartina	200	1	1,660	16	NH_4^+	Patrick and Delaune (1976)
Spartina	200	1	816	25	NH_4NO_3	Gallagher (1975)
Spartina	220	3	320	131	Sludge	Valiela et al. (1975)
Spartina	650	3	320	269	Urea	Valiela et al. (1975)
Spartina	670	2	250	120	Sludge	Valiela and Teal (1974)
Spartina	1,040	1	450	100	NH_4^+	Haines (1979)
Spartina	3,120	2	235	413	NH_4^+	Morris (1988)
Puccinellia	320	2	64	175	NH_4^+	Cargill and Jefferies (1984)
Puccinellia	320	2	64	73	NO_3^-	Cargill and Jefferies (1984)
Carex	320	2	65	146	NH_4^+	Cargill and Jefferies (1984)
Panicum hemitomon	30	1	1,320	6	NH_4^+	DeLaune et al. (1986)
Panicum hemitomon	100	1	1,320	42	NH_4^+	DeLaune et al. (1986)
Typha glauca	1,350	2	1,726	36	NH_4NO_3	Neely and Davis (1985a)
Sparganium eurycarpum	1,350	2	637	86	NH_4NO_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)

[1]Control biomass is the maximum, nonfertilized aboveground standing crop
[2]Percent increase indicates the response of control biomass during the year of fertilization at the indicated rate of application, computed as 100x(Experimental-Control)/Control

Berendse, 1988). Thus, wetlands are not universally limited by nitrogen. However, as discussed above (Atmospheric Nitrogen Inputs - 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. (horesetail) had a smaller biomass contribution upon

fertilization. This tendency toward a change in species composition or dominance has been observed in other fertilization experiments also. Jefferies and Perkins (1977) found species-specific changes in stem density at a Norfolk, England salt marsh after fertilizing monthly with 610 kg NO_3^--N ha^{-1} yr^{-1} or 680 kg NH_4^+-N ha^{-1} yr^{-1} over a period of 3-4 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 10-19). 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 10-19 pertain to growth of aboveground biomass only. In several of these studies, measurements of belowground biomass were also made (Valiela and Teal, 1974; Haines, 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) is clear 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 10-19 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 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 N ha^{-1} yr^{-1} 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.

10.5.4.2 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. ^{15}N is a stable isotope comprising 0.37% of naturally occurring nitrogen. It can be quantified together with the more common isotope of nitrogen, ^{14}N, 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 N ha^{-1} in one application as $^{15}NH_4^+$ 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 $^{15}NH_4^+$ 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 $^{15}NH_4^+$ from the sediment.

Lindau et al. (1988) made single additions of either $^{15}NO_3^-$ or $^{15}NH_4^+$, equivalent to 100 kg N ha^{-1}, 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 $^{15}NH_4^+$ 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 since 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 $^{15}NH_4^+$ 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 N ha^{-2}. After 21 days, 0.5 to 2.3% of the added nitrogen was recovered in the flood water, largely as NO_3^-, and 13.6 to 17.8% 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 slurrys of marl and peat sediments from the Florida Everglades (Gordon et al., 1986) demonstrated that 10-34% of NO_3^- added at levels of 10 and 100 μM (1 μM = 14 μg N/litre) 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 slurrys 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 $^{15}NH_4^+$ placed below the soil surface in a Louisiana salt marsh dominated by *Spartina alterniflora*. The

singular application of $^{15}NH_4^+$ was equivalent to 72 kg N ha^{-1}. 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 1.2% 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^{-1} of $^{15}NH_4^+$-N 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 $^{15}NH_4^+$ to the flood water 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 N ha^{-1} $season^{-1}$. 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, while 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.

10.5.4.3 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, 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 N-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 a nutrient 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 non-diazotrophs 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. Decomposition rate is decreased by acidification (Leuven and Wolfs, 1988; Hendrickson, 1985), but the degree of inhibition is dependent upon the buffering capacity of

the litter (Gallagher et al., 1987). Nitrification is also affected by acidification. Nitrification was inhibited at pH 4-5 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% 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 ozone.

Finally, NO_3^- and NH_4^+ have been shown to influence the relative and absolute production of endproducts 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 slurrys incubated anaerobically with 250 μM NO_3^-. As the nitrate concentration was increased, up to 2 mM (1 mM = 14 mg N/litre), the proportion of the nitrate which 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 Sakdinan, 1978; Blackmer and Bremner, 1978). Seitzinger et al. (1983 and 1984) observed higher ratios of N_2O: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-N m^{-2} day^{-1}, respectively, to 1.5 and 2.9 mg N_2O-N m^{-2} day^{-1} after amending the sediments with 1.2-1.5 g NH_4^+-N 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-N as N_2O from submerged soils amended with 34 g NO_3^--N m^{-2} and 12 g NH_4^+-N 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).

10.5.4.4 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. While 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, *Sarracenis 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. 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 of poor nitrogen supply. 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 (Figure 10-20, 10-21).

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 and Lee, 1980; 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 yr, with the virtual elimination of the dominant 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,

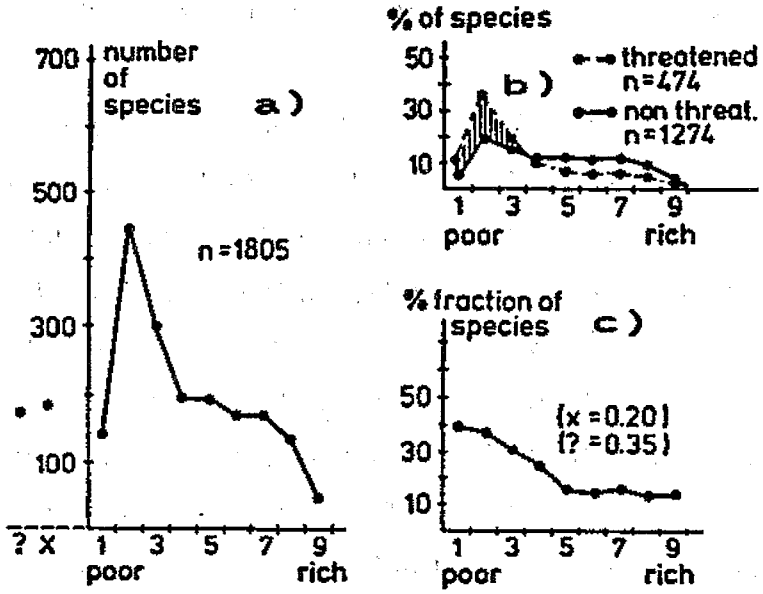


Figure 10-20. Distribution of 2,164 Central European plant species in the gradient of nitrogen indicator values (from Ellenberg, 1988, p. 379).

(a) "?" not known; "x" indifferent
"1" most pronounced nitrogen deficiency
"3" poor in nitrogen
"5" just sufficient in nitrogen
"7" more often found at places rich in N
"8" nitrogen indicator
"9" surplus nitrogen to polluted with N
"2", "4", "6" intermediate

(b) most of the threatened species can only compete on nitrogen-deficient stands (57 "potentially threatened" species not regarded).

(c) the fraction of threatened species within the total of species in a given class of nitrogen indicator value is deminishing with better nitrogen supply. It remains constant from value "5" upwards (see above).

although studies of this particular area should be interpreted cautiously because of its long history of exposure to multiple pollutants. The combination of NO_3^- and NH_4^+ deposition, about 32 kg N ha^{-1} yr^{-1}, is more than double the deposition rates in the Berwyn Mountains in North Wales, which still support healthy *Sphagnum* communities, and contributes significantly to a supraoptimal nitrogen supply (Lee et al., 1986). In The Netherlands there has been a great decline during the past 3 decades in communities dominated by iosetids in soft water areas and their conversion to later successional stages dominated by grasslands or

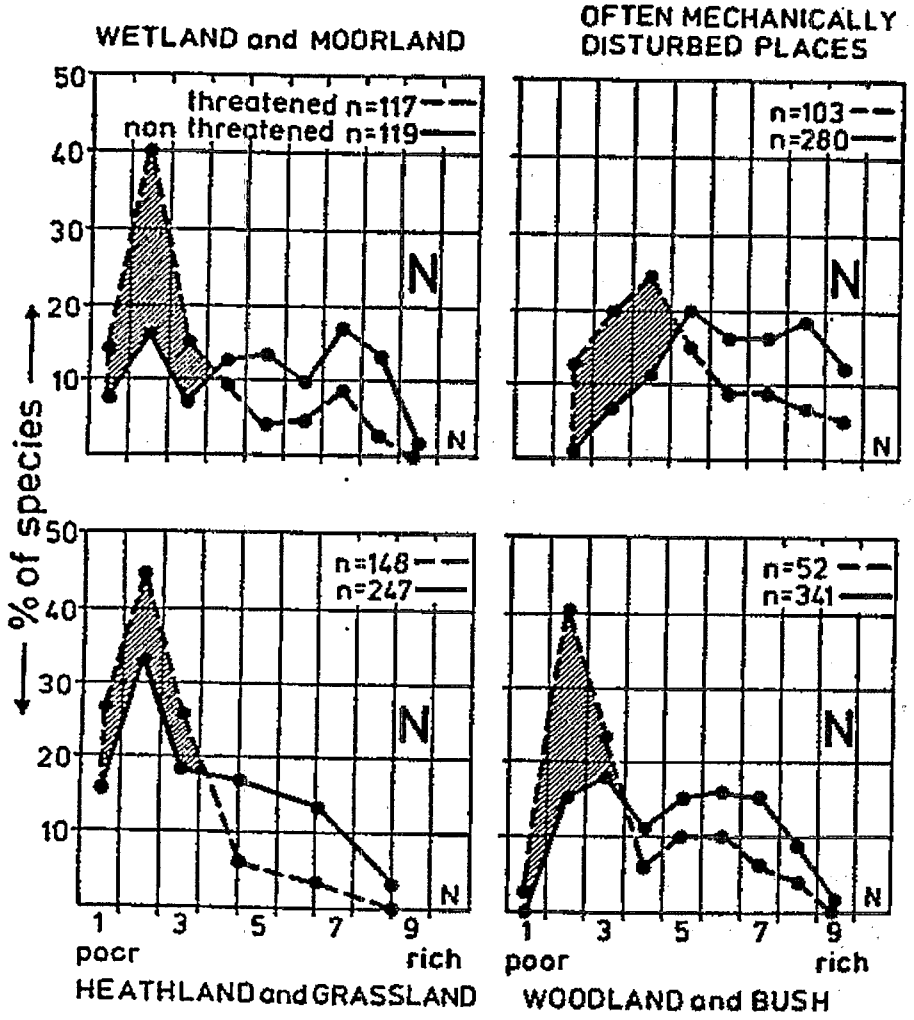


Figure 10-21. Distribution of Central European plant species along a gradient of nitrogen indicator values (see Figure 10-20) across ecosystem types (from Ellenberg, 1988, p. 380).

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 400-500 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 (3-24 per 0.25 m^2) occurs at intermediate standing crops (60-500 g/m^{-2}) and the lowest density of species (2-5 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).

10.5.4.5 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 N, S, Pb, Fe, and P increased significantly, but the concentration of K did not. The greatest change observed was for nitrogen which increased by absolute amounts that varied from 17.7 mg per gram 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). Since 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 N deposition is 43 kg N ha^{-1} yr^{-1}, is supra-optimal 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 N ha^{-1} yr^{-1} 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 N 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* and/or *Deschampsia flexuosa* (grasses) expand at the expense of *Erica tetralix* or *Calluna vulgaris* (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, while 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 carried out to identify the mechanisms of nitrogen control over species composition. This is a non-trivial task since 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 either 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 (63-73%) in plants that are characteristic of soft waters (low Ca^{2+} and Mg^{2+}), while NH_4^+ strongly dominated the nutrition (85-90%) 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^--N ha^{-1} yr^{-1} plus 19 kg NH_4^+-N ha^{-1} yr^{-1} in simulated rain; when given 0.25X that amount of NO_3^- and 1.5X (and 4X) 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 a NO_3^- input of 4.71 kg N ha^{-1} yr^{-1}, including 1.6 kg N ha^{-1} yr^{-1} 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 less at 1,000 or 100 μM NH_4^+, while Press et al. (1986) observed that the best growth of this same species occurred in N-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 two-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, while 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 H_2SO_4 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^{-1} yr^{-1}, and that the annual nitrogen deposition should not be greater than 1,380 mol ha^{-1} yr^{-1} or 19.4 kg N ha^{-1} yr^{-1} (NO_3^- + 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 N ha^{-1} yr^{-1} and for oligotrophic (nutrient-poor) bogs is probably about 10 kg N ha^{-1} yr^{-1}. These limits are exceeded currently in the United States where wet nitrate deposition alone exceeds 15 kg N ha^{-1} yr^{-1} over most of the midwest, New York, and New England (Zemba et al., 1988).

10.6 AQUATIC EFFECTS OF NITROGEN OXIDES

10.6.1 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 nitrogen oxides. 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 non-atmospheric 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 nitrogen oxide 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 de-coupling 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.

10.6.2 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 10-22). 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

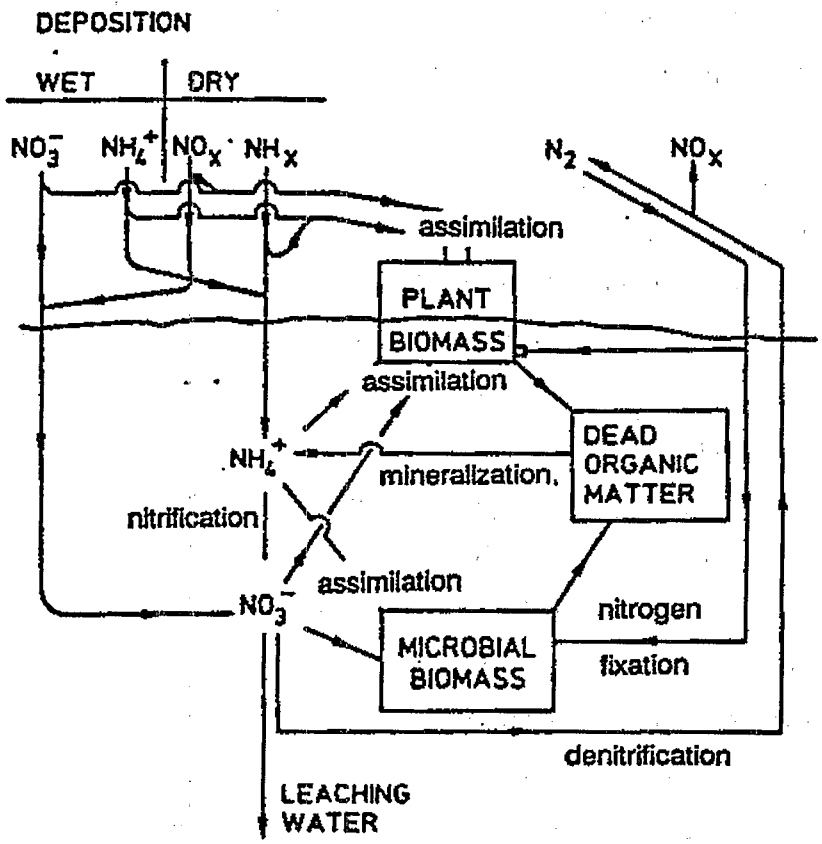


Figure 10-22. A simplified watershed nitrogen cycle. Only the major pathways are shown. The boxes represent major pools of nitrogen in terrestrial ecosystems, and the lines represent the major pathways and processes affecting nitrogen transformations. The wavy line represents the soil surface. Modified from Skeffington and Wilson (1988).

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.

10.6.2.1 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 nitrate (NO_3^-), ammonium (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 nitric acid 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 are the same as those comprising direct deposition to terrestrial ecosystems recently described by Lindberg et al. (1986) also Section 10.4.

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 $\mu eq \cdot L^{-1}$ and 2.8 $\mu eq \cdot L^{-1}$, 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 1985-1987 were 5.0 and 5.4 $\mu eq \cdot L^{-1}$, respectively (Williams and Melack, in press a). 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 $\mu eq \cdot L^{-1}$ and NH_4^+ concentrations from 10 to 50 $\mu eq \cdot L^{-1}$ 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 $\mu eq \cdot L^{-1}$ (e.g., in the Adirondack and Catskill mountains of New York) to 50 $\mu eq \cdot L^{-1}$ (e.g., in the eastern Great Lakes region), while mean NH_4^+ concentrations range from 10 to 20 $\mu eq \cdot L^{-1}$ in the same areas (Stensland et al., 1986). Ammonium concentrations are highest (ca. 40 $\mu eq \cdot L^{-1}$) in the agricultural areas of the mid-western 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., in press). The last of these values (dry deposition) is difficult to measure, and is often estimated as a fraction (e.g., 30-40%) 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 12 eq · ha^{-1} · yr^{-1} in Alaska to near 800 eq · ha^{-1} · yr^{-1} in the northeastern United States (Table 10-20).

TABLE 10-20. RATES OF NITROGEN DEPOSITION IN SEVERAL AREAS OF NORTH AMERICA

	eq · ha^{-1} · yr^{-1}			
Area	NO_3^-	NH_4^+	Total	Source
Alaska[a] (Poker Flat)	6.9	4.8	11.7	Galloway et al. (1982)
Sierra Nevada, CA[b] (Emerald Lake)	79	85	164	Williams and Melack (in press, a)
Ontario, Canada[c] (Experimental Lakes Area)	125	140	265	Linsey et al. (1987)
British Columbia, Canada[c]	260	130	390	Feller (1987)
Upper Midwest[d]	300	210	510	Driscoll et al. (1989a)
Southeastern U.S.[e] (Walker Branch, TN)	540	180	720	Lindberg et al. (1986)
New Hampshire[c]	464	200	664	Likens (1985)
Catskills[a]	580	292	874	Stoddard and Murdoch (1991)
Adirondacks[d]	590	190	780	Driscoll et al. (1989a)

[a]Dry deposition estimated as 35% of total deposition.
[b]Dry deposition sampled as part of snowpack; no correction for dry deposition made.
[c]Bulk precipitation measurements; no correction for dry deposition made.
[d]Values corrected for dry deposition based on ratios in Hicks (1989).
[e]Includes estimates for dry deposition and gaseous uptake of nitrogen areas, DON can occur in greater concentrations than the inorganic species (Moore and Nuckols, 1984).

Generally NO_3^- dominates over NH_4^+ at sites close to emission sources (Linsey et al., 1987; Altwicker et al., 1986). Dissolved organic nitrogen (DON) 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).

10.6.2.2 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 10-22). 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^- contributes to 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 effects strongly the acidifying potential of nitrogen deposition (Figure 10-23). Ammonium uptake is an

acidifying process (i.e., uptake of NH_4^+ releases one mole of hydrogen per mole of nitrogen assimilated):

$$NH_4^+ + R \cdot OH = R \cdot NH_2 + H_2O + H^+ \qquad \text{(Eq. 10.6-1)}$$

The biological uptake of NO_3^-, on the other hand, is an alkalinizing process (i.e., uptake of NO_3^- consumes one mole of hydrogen per mole of nitrogen assimilated):

$$R \cdot OH + NO_3^- + H^+ = R \cdot NH_2 + 2O_2 \qquad \text{(Eq. 10.6-2)}$$

Nitrification

Nitrification is the oxidation of ammonium (NH_4^+) to nitrate (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 10-22). Nitrification is a strongly acidifying process, producing two moles of hydrogen for each mole of nitrogen (NH_4^+) nitrified (Figure 10-23):

$$NH_4^+ + 2O_2 = NO_3^- + 2H^+ + H_2O \qquad \text{(Eq. 10.6-3).}$$

Because nitrification in forest soils commonly transforms NH_4^+ into NO_3^-, the acidifying potential of deposition (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^+ which 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

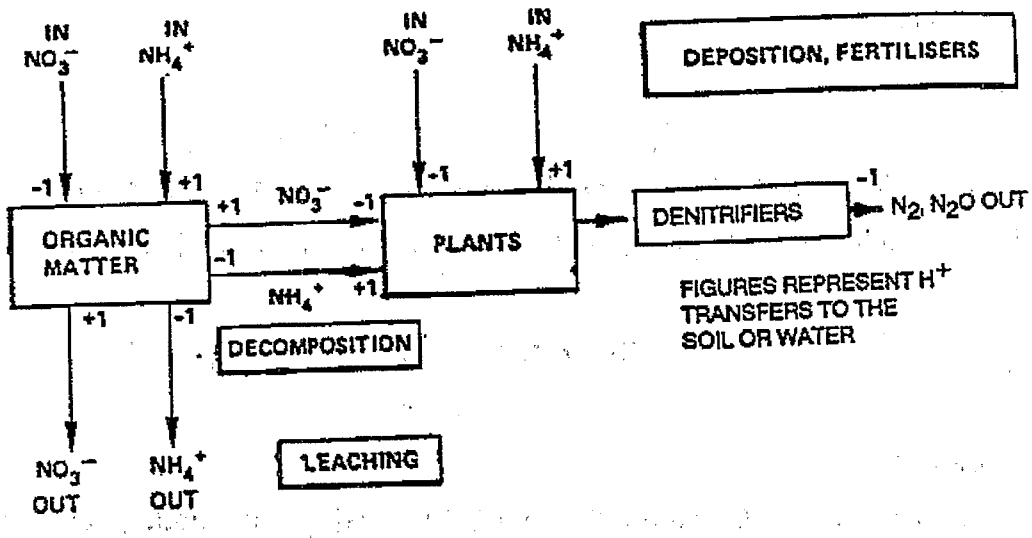


Figure 10-23. The effect of nitrogen transformations on the watershed hydrogen ion budget. One hydrogen ion is transferred to the soil solution or surface water (+1) or from the soil solution or surface water (-1) for every molecule of NO_3^- or NH_4^+ which crosses a compartment boundary. For example, nitrification follows the pathway for NH_4^+ uptake into organic matter (+1), and is leached out as NO_3^- (+1), for a total hydrogen ion production of +2 for every molecule of NO_3^- produced. Modified from Skeffington and Wilson (1988).

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., 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 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 alkalinizing process, consuming one mole of hydrogen for every mole of nitrogen denitrified (Figure 10-23). Denitrification can be involved in the production or consumption of N_2O, a product which 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, Klemedtsson and Svensson (1988) conclude that denitrification rates are often limited by the availability of oxygen, 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:

$$N_2 + H_2O + 2R \cdot OH = 2R \cdot NH_2 + {}^{3}/_{2}O_2 \qquad \text{(Eq. 10.6-4)}$$

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 3,600 to 7,600 eq $\cdot$ $ha^{-1} \cdot yr^{-1}$ under deciduous tree species, and from 2,300 to 4,700 eq $\cdot$ $ha^{-1} \cdot yr^{-1}$ under coniferous species. These rates should be compared to nitrogen deposition rates of 400-800 eq $\cdot$ $ha^{-1} \cdot yr^{-1}$ for high deposition areas of the Northeast. Nadelhoffer et al. (1985) also report estimated rates of nitrogen uptake that were 20 to 80% 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 one mole of hydrogen per mole of nitrogen produced (Figure 10-23), and can be thought of as the reverse of the reaction in Equation 10.6-1. Organic nitrogen which is mineralized and subsequently oxidized (nitrified) to NO_3^- (Equation 10.6-3) produces a net of one 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 10-23).

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.

10.6.2.3 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 (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.

The major aspects of the nitrogen saturation concept can be described by a simple analogy. In this analogy, forested watersheds are likened to a dry sponge. When a sponge is dry, it has a high capacity to absorb water deposited on its surface, just as a nitrogen-deficient forest has a high capacity to accumulate nitrogen from deposition. The capacities of both the forest and the sponge are related to the rate of supply of nitrogen or water, respectively, at least in the early stages of nitrogen or water addition. That is, if we pour water slowly onto the sponge it will retain nearly all of it, but if the water is poured quickly the sponge will retain most of the water, while some leaks out. This same characteristic in forests results in the common seasonal pattern for streams that drain forested watersheds. During seasons of low nitrogen deposition (e.g., during dry seasons) nearly all of the deposited nitrogen is retained in soils and forest biomass, and stream water concentrations of nitrogen are low or undetectable. When nitrogen deposition is at a high rate, however, it may exceed (temporarily) the capacity of the system to absorb nitrogen, and some will leak into the streams that drain the watersheds. This simplified pattern of low

nitrogen concentrations in streams during dry seasons, and high concentrations during wet seasons, is a very common one.

Returning to the sponge analogy, we know that if we add water to the sponge at a constant rate over some period of time, eventually the sponge will become saturated; its capacity to absorb water will be very low, and the rate of water leakage from the sponge will depend on the rate of water addition. In a similar manner, the capacity of forested ecosystems to retain nitrogen may be exceeded by long-term high rates of nitrogen deposition. At some critical point in this process, forested watersheds will begin chronically "leaking" nitrogen to the streams that drain them. This is the phenomenon commonly thought of as nitrogen saturation. The major difference between this simple sponge analogy and the cycling of nitrogen in nitrogen-deficient forests is that the forests have nitrogen-retaining capacities (i.e., biological demands for nitrogen) which vary with season, depending on whether forest growth is occurring or not (i.e., nitrogen retention is higher during the growing season). One major effect of this complexity is to amplify the seasonal differences in nitrogen leakage. This amplification results when the growing season coincides, as it does in most forested areas, with a period of lower deposition (late spring and summer); many forests are dormant during the seasons of highest atmospheric deposition (winter and early spring) and so both supply and demand favor the leakage of some nitrogen from the system.

Aber et al. (1989) have proposed a hypothetical time course for a watershed response to chronic nitrogen additions (Figure 10-24), describing both the changes in nitrogen cycling that are proposed to occur, as well as the plant responses to changing levels of nitrogen availability. The four stages (Figure 10-24), correspond to those described by Smith (1974) and Bormann (1982) for ecosystem response to pollution loading. Stage 0 is the pre-treatment condition. In Stage 1, increased deposition is occurring, but effects on the ecosystem are not evident. Many forested watersheds in the United States would be considered to exist at this stage. 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 little or no nitrogen would be lost to surface waters that drain Stage 1 watersheds.

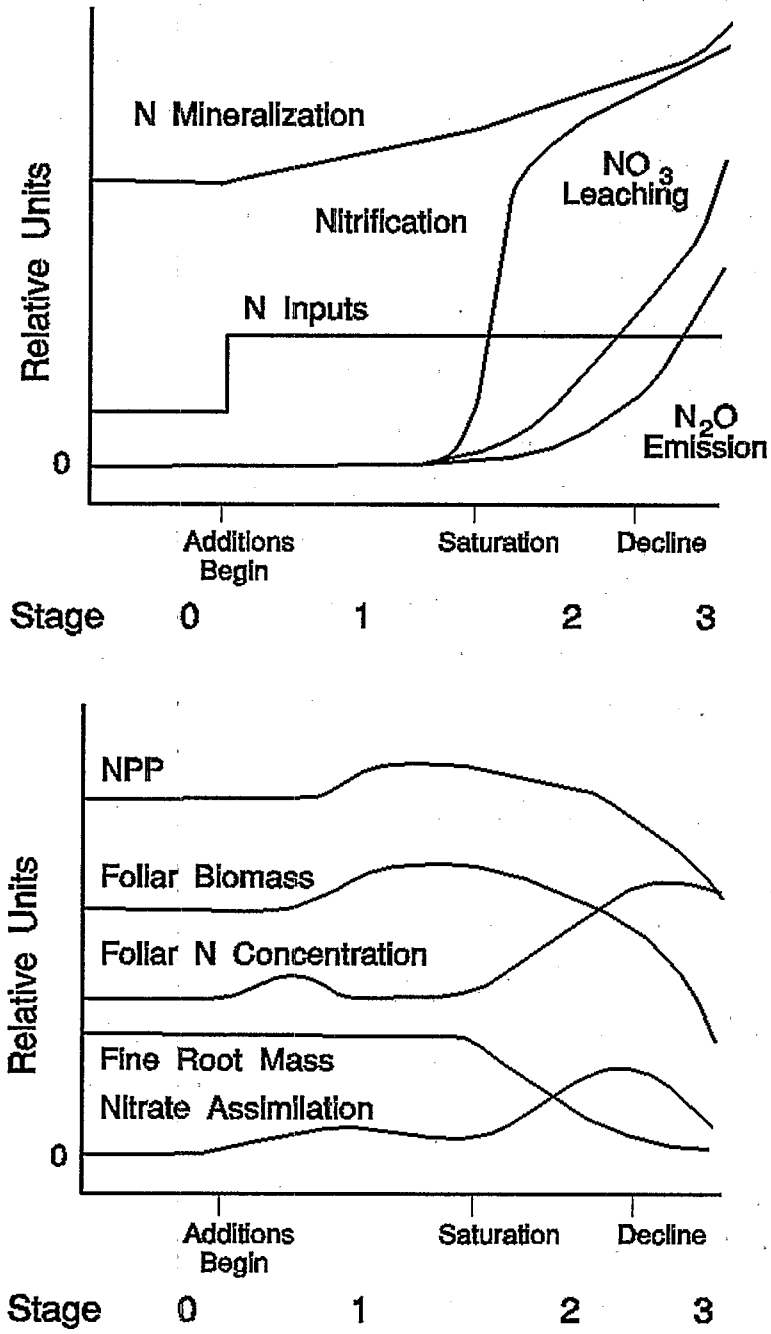


Figure 10-24. Hypothetical time course of forest ecosystem response to chronic nitrogen additions. Top: relative changes in rates of nitrogen cycling and nitrogen loss. Bottom: relative changes in plant condition (e.g., foliar biomass and nitrogen content, fine root biomass) and function (e.g, net primary productivity (NPP) and nitrate assimilation) in response to changing levels of nitrogen availability. From Aber et al. (1989).

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. Stage 2 could be considered to correspond to the "damp" stage of the sponge analogy, where rapid rates of water addition will cause leakage; if nitrogen is added over short time scales (e.g., in storms) to Stage 2 watersheds, leakage of NO_3^- would result. 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 10-24).

The high capacity of forested watersheds to retain nitrogen is responsible for the concept that nitrogen deposition does not affect aquatic ecosystems. However, as nitrogen saturation proceeds, the ability of watersheds to retain nitrogen decreases, and the potential for nitrogen effects in aquatic systems grow. One of the major tasks in assessing nitrogen effects on surface waters is the recognition of the early stages of nitrogen saturation. It has been suggested (Grennfelt and Hultberg, 1986; Driscoll and Schaefer, 1989; Stoddard and Murdoch, 1991) that chronic nitrogen leakage from forested watersheds (Stage 3 in Figure 10-24) will be preceded by an amplification of the seasonal pattern in surface water nitrogen. The rationale behind this suggestion stems from the idea that biological activity is probably not limited be a single nutrient or physical factor year-round. Forest growth, for example, is probably limited by temperature during the winter months (Likens et al., 1977; Vitousek, 1977), and passes through a phase in the spring when growth is limited either by temperature or by nitrogen, depending on whether nitrogen deficiency or cold is more severe at any given point in time. As forests become more nitrogen sufficient (i.e., as nitrogen saturation proceeds), the period of temperature limitation is likely to be extended further and further into the spring season, or to be replaced by a period of limitation by some other nutrient or physical factor. This longer period of low nitrogen demand (on the part of forests) is likely to produce larger or longer periods of elevated nitrogen concentrations in lakes and streams during spring snow melt. This extended period of low demand for nitrogen need not extend very far into the spring snowmelt season in order to cause nitrogen episodes, as soil water charged with nitrogen may be quickly transported to soils zones below the rooting zone (i.e., below the soil level where biological uptake can affect the nitrogen concentration) by the movement of water during snow melt (Murdoch and Stoddard, in

review). A number of other mechanisms can produce similar results, but there are few data to support their existence. These mechanisms include:

- An increase in the length or severity of the winter. By delaying the onset of snow melt, longer winters would allow a larger accumulation of nitrogen in the snow pack, and could prolong the period of temperature limitation in forests, lowering the demand for nitrogen as the dormant period is ending. Limited available evidence, however, suggests that winters have become shorter rather than longer, and that snow melt is occurring earlier in the year now than it did 20 years ago (Schindler et al., 1990).

- Prolonged defoliation of forest trees (e.g., by insect outbreaks) could lower the forest demand for nitrogen and potentially increase NO_3^- concentrations in runoff water during the growing season. Defoliation should have little effect on snowmelt NO_3^- concentrations, however, because these episodes occur largely in deciduous forest that are devoid of leaves during the dormant (winter) season.

- Increases in nitrogen deposition. These could result in more severe NO_3^- episodes, independent of any change in nitrogen saturation, by producing a larger accumulation of nitrogen in winter snow packs. Because most snow melts while the forest is still largely dormant, an increase in nitrogen storage in the snowpack could lead to an increase in the severity of snowmelt NO_3^- episodes, without any long-term change in nitrogen retention occurring. There is no evidence, however, that nitrogen deposition is increasing anywhere in North America (Simpson and Olsen, 1990; Bowersox et al., 1990). Estimates of nitrogen deposition calculated from NO_x emissions in the Northeast suggest that nitrogen deposition increased more-or-less linearly from the turn of the century until 1970, but has remained relatively constant in the past 20 years (Husar, 1986). The longest available records of nitrogen deposition for a site in the Northeast (Hubbard Brook Experimental Forest) suggest that rates of nitrogen deposition peaked in the early 1970s and have either decreased (NH_4^+) or remained constant (NO_3^-) since then (Likens et al., 1984; Hedin et al., 1987).

A change in the ability of forests to retain nitrogen remains, therefore, the most likely mechanism producing increases in snowmelt NO_3^- episodes. According to this scenario, the earliest symptoms of nitrogen saturation of soils may be most visible as increases in the severity of nitrogen episodes in the surface waters.

10.6.2.4 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), while 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 alkalinizing process, consuming one 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 a 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 which 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 10.6.4.2). 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 one mole of hydrogen for every mole of NO_3^- denitrified.

Estimates of denitrification rates range from 54 to 345 $\mu mol \cdot m^{-2} h^{-1}$ in streams with high rates of organic matter deposition, 12 to 56 $\mu mol \cdot m^{-2} h^{-1}$ in (nutrient-poor) oligotrophic lakes, 42 to 171 μmol $\mu mol \cdot m^{-2} h^{-1}$ in eutrophic lakes and 77 to 232 $\mu mol \cdot m^{-2} h^{-1}$ 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 $\mu mol \cdot m^{-2} h^{-1}$ to over 20 $\mu mol \cdot m^{-2} h^{-1}$ in an oligotrophic lake when nitric acid was added in a whole-lake experimental acidification, suggesting that freshwater denitrification may 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 deep mud of slow flowing streams, the process can effectively reduce NO_3^- concentrations in the water column by as much as 200 $\mu eq \cdot L^{-1}$ 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 mmol · N · m^{-2} · yr^{-1} 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, California, and Mirror Lake, New Hampshire, 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 · N · m^{-2} · yr^{-1} (Howarth et al., 1988a). 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 NH_4^+. Supply rates of NH_4^+ 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 NH_4^+ deposition is extremely high, such as near agricultural areas, and cases where NH_4^+ 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 it can combine as a neutral salt with SO_4^{2-}, 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 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 NH_4^+ in the water column.

High NH_4^+ concentrations may also result in lakes whose deeper waters become anoxic during periods of stratification (usually late winter or late summer). Production of NH_4^+ (by decomposition) can be substantial under anaerobic conditions, and NH_4^+ may accumulate in

the anoxic water. Nitrification of this NH_4^+ 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, 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 spiralling" (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 spiralling 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.

10.6.3 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 sulfate (SO_4^{2-}) has resulted largely because sulfur deposition rates are often higher than those for nitrogen (S deposition rates are approximately twice the rates of N 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, while supply rates (from deposition) are low, 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 snow melt. It has been estimated that 40% to 640% more streams in the eastern U.S. are acidic during spring episodes than are acidic during spring base flow, while 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), aluminum 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.

10.6.3.1 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 (NAPAP). 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), while in streams the chosen index period was spring base flow (the period after spring snow melt 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 NO_3^-:NO_3^-+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 10-21. In general, Henriksen's results show that NO_3^- can be as important as SO_4^{2-} in some parts of Europe, but that ratios are low in the United States, except for selected Adirondack systems (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 10-21, for example, were collected monthly over a two 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 and will be therefore be higher than concentrations measured only in the autumn. As a result, the high ratio values reported in Table 10-21 for the Adirondacks are a good 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 NO_3^-:NO_3^-+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 10-22. The NSS data have the advantage of having been collected during a spring baseflow 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 snow melt would be. The Catskill regional data included in Table 10-22 are from a stream survey which included multiple samplings per year (Stoddard and Murdoch, 1991). Several stream regions exhibit ratios as high as those reported for the Adirondacks by Henriksen (1988). Several

TABLE 10-21. CONCENTRATIONS OF NITRATE, SULFATE, AND RATIOS OF NITRATE TO THE SUM OF NITRATE AND SULFATE IN RUNOFF WATERS IN ACIDIFIED AREAS OF THE WORLD (FROM HENRIKSEN, 1988)

Location	Year	pH	$\mu eq \cdot L^{-1}$ NO_3^-	$\mu eq \cdot L^{-1}$ SO_4^{2-}	$NO_3^-:NO_3^- + SO_4^{2-}$	Sampling Method[a]
West Germany						
Lange Bramke	1977	5.8	16	233	0.06	Intensive
Lange Bramke	1984	6.2	49	230	0.18	Intensive
Bayerischer Wald						
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
Poland						
The Giant Mts.						
Maly Staw	1986	5.5	13	92	0.12	Unknown
Wielki Staw	1986	4.7	40	140	0.22	Unknown
Czechoslovakia						
Tatra Mts.						
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
Bohemia						
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 Mts.	1986	5.2	118	1216	0.09	Unknown
Sumava Mts.						
Liz	Apr 86	5.89	136	390	0.26	Unknown
Albrechtec	Apr 86	6.22	36	358	0.09	Unknown
Norway						
Birkenes	1973-86	4.52	9	140	0.06	Intensive
Storgama	1973-86	4.56	12	77	0.13	Intensive
Sweden						
Stromyra	1984-85	6.54	17	180	0.09	Intensive
Scotland						
Av 22 lakes in the Galloway area	1979	4.97	21	103	0.17	Unknown

TABLE 10-21 (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 (FROM HENRIKSEN, 1988)

Location	Year	pH	$\mu eq \cdot L^{-1}$ NO_3^-	$\mu eq \cdot L^{-1}$ SO_4^{2-}	$NO_3^-:NO_3^- + SO_4^{2-}$	Sampling Method[a]
United States						
Adirondacks						
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
Eastern Lake Survey[b]						
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
NE Minnesota		-	0.9	62	0.01	Fall index
Maine		-	0.2	75	0.00	Fall index
S New England		-	0.8	141	0.01	Fall index
C New England		-	0.3	101	0.00	Fall index
Canada						
Experimental Lakes Area, Ontario	1980s	-	1	78	0.01	Intensive
Sudbury, Ontario	1980s	-	2	252	0.01	Intensive
Kekimkujik, Nova Scotia	1980s	-	2	252	0.01	Intensive
			3	78	0.04	

[a]Sampling methods are listed as either monthly, intensive (more frequent than monthly) or based on a single fall index sample.
[b]Median value for regional population of lakes.

TABLE 10-22. 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 QUARTILES IN PARENTHESES)

Location	Year	pH	$\mu eg \cdot L^{-1}$ NO_3^-	SO_4^{2-}	$NO_3^-:NO_3^- + SO_4^{2-}$
	National Stream Survey[a]				
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[b]		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)
Catskill Regional Survey[c]					
Median value for 51 streams	1984-86	6.60	29 (14-47)	138 (125-151)	0.17 (0.09-0.26)

[a]Values for pH are for entire region (Kaufmann et al., 1988); medians for NO_3^-, SO_4^{2-} and the $NO_3^-:NO_3^- + SO_4^{2-}$ ratio exclude sites with potential agricultural or other land use impacts (Baker et al., in press).
[b]The influence of agricultural and land use practices could not be ruled out for any of the sites in the Mid-Atlantic Coastal Plain (Baker et al., in press).
[c]From Stoddard and Murdoch (1991).

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 $NO_3^-:NO_3^-+SO_4^{2-}$

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 10-22, as well as the lake regions in Table 10-21, 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, and 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 streamwater nitrogen ($NO_3^- + NH_4^+$) at spring base flow and levels of wet nitrogen deposition ($NO_3^- + NH_4^+$) in each of the NSS regions (Figure 10-25a). The only exception to this relationship is the Pocono/Catskill region, where nitrogen deposition is highest (450 eq $\cdot$ $ha^{-1} \cdot yr^{-1}$), but where stream water nitrogen concentrations fall below what is expected, based on results from the other regions. The median streamwater NO_3^- value for the Catskills alone (from Stoddard and Murdoch, 1991; Table 10-22) is 29 $\mu eq \cdot L^{-1}$, 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. (1989) 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 10-25b). The authors stress that the data illustrated in Figure 10-25b were collected using widely differing methods and over various time scales (from one 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 10-25 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

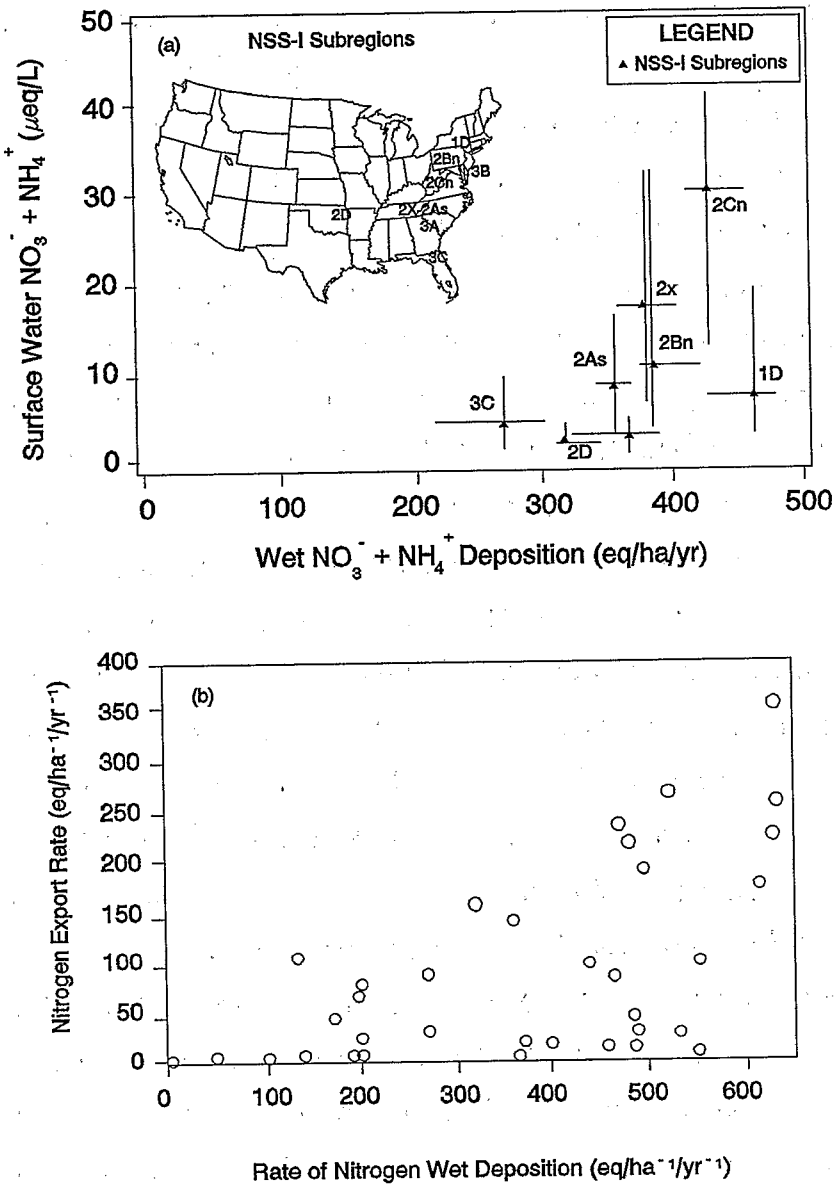


Figure 10-25. (a) Relationship between median wet deposition of nitrogen (NO_3^- + NH_4^+) and median surface water nitrogen (NO_3^- + NH_4^+) concentrations, for physiographic districts within the National Stream Survey that have minimal agricultural activity. [Subregions are: Poconos/Catskills (1D), 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 Baker et al. (in press). (b) Relationship between wet deposition of nitrogen (NO_3^- + NH_4^+) 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. Data from Driscoll and Schaefer (1989).

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 deposition (between 200 and 300 eq $\cdot$ $ha^{-1} \cdot yr^{-1}$) 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 which 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 aluminum, 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 aluminum 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 hydrogen ions, 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 $\cdot$ $ha^{-1} \cdot yr^{-1}$; Rosen, 1988) than in the United States (Table 10-20), 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.

10.6.3.2 Episodic Acidification

In a recent comprehensive examination, Wigington et al. (1989) 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 the United States. In the United States, they noted that 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 snow melt, 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 baseflow chemistry. In addition, Eshleman used an empirical model relating fall index period lake chemistry to spring episodic chemistry, using data from EPA's Long-Term Monitoring (LTM) project (Newell et al., 1987), to predict the number of Adirondack lakes that undergo episodic acidification. His results are repeated in Table 10-23. 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

TABLE 10-23. 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 BASEFLOW OR FALL OVERTURN). EPISODIC CONDITIONS ESTIMATED FROM TWO-BOX MIXING MODEL (FOR STREAMS), OR EMPIRICAL RELATIONSHIPS BETWEEN FALL INDEX PERIOD AND SPRING SNOW MELT CHEMISTRY (FOR LAKES) (FROM ESHLEMAN, 1988)

	Index Conditions (ANC <0)		Episodic Conditions (ANC <0)	
Subregion[a]	Number	Proportion (%)	Number	Proportion (%)
Stream subregions				
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
Lake subregions				
Adirondacks	138	10.7	459	35.6

[a]For 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.

- 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 before the episode begins. Episodes are more likely to be acidic, for example, if the baseflow 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 baseflow 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., 1989). Dilution results from the increased rate of runoff, and channeling of runoff through shallower soil layers, that occurs during storms or snow melt; the shorter contact time produces runoff with a chemical composition closer to that of atmospheric deposition than is typical of baseflow 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 is added the effects of organic acids and atmospherically derived SO_4^{2-} and NO_3^-.

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., 1989), 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 snow melt. Schaefer et al. (1990) examined the same empirical relationships used

for the Adirondack lakes by Eshleman (1988; Table 10-23), and conclude that the magnitude of the episodes experienced by lakes depends strongly on their base cation concentration. They conclude that lakes with high base cation concentrations (and therefore high ANC values) undergo episodes that are largely the result of dilution by snow melt. 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 10-26). 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 10-23.

Driscoll et al. (1989a, 1989b) 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 10-27). Nitrate concentrations were lower than SO_4^{2-}, and exhibited a distinct seasonal pattern; peak concentrations approached 100 $\mu eq \cdot L^{-1}$. Short-term changes in NO_3^- were highly correlated, and chemically consistent, with changes in the concentrations of acidic cations (hydrogen and aluminum) (Driscoll et al., 1989a). As mentioned earlier, while 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 10-28). 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 review). Values for the ratio of NO_3^- to $NO_3^- + SO_4^{2-}$, as presented in Tables 10-21 and 10-22, 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 10-28).

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^-

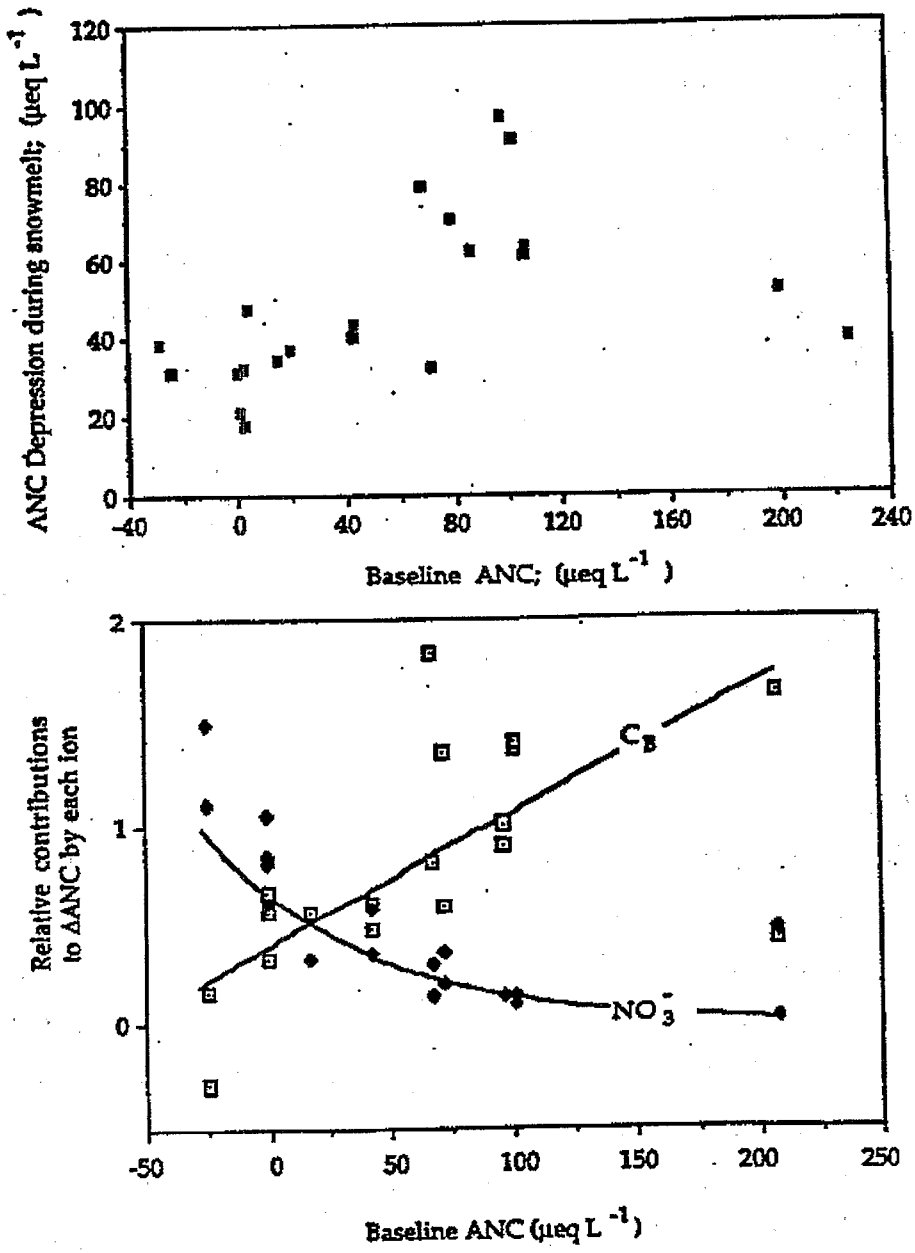


Figure 10-26. Effect of baseline acid neutralizing capacity (ANC) and episodic conditions in Adirondack lakes. (a) Relationship between baseline ANC and the springtime depression in ANC (baseline ANC - minimum ANC) for 11 lakes sampled in 1986 and 1987. (b) The relative contributions of base cations (C_B) and nitrate (NO_3^-) to the springtime ANC depressions in Adirondack lakes. Lakes at intermediate ANC values undergo the largest springtime depressions in ANC. Lakes with lower baseline ANC are affected more by NO_3^- pulses, and lakes with higher baseline ANC are affected more by base cation dilution. Solid lines represent best-fit relationships. Both figures are from Schaefer et al. (1990).

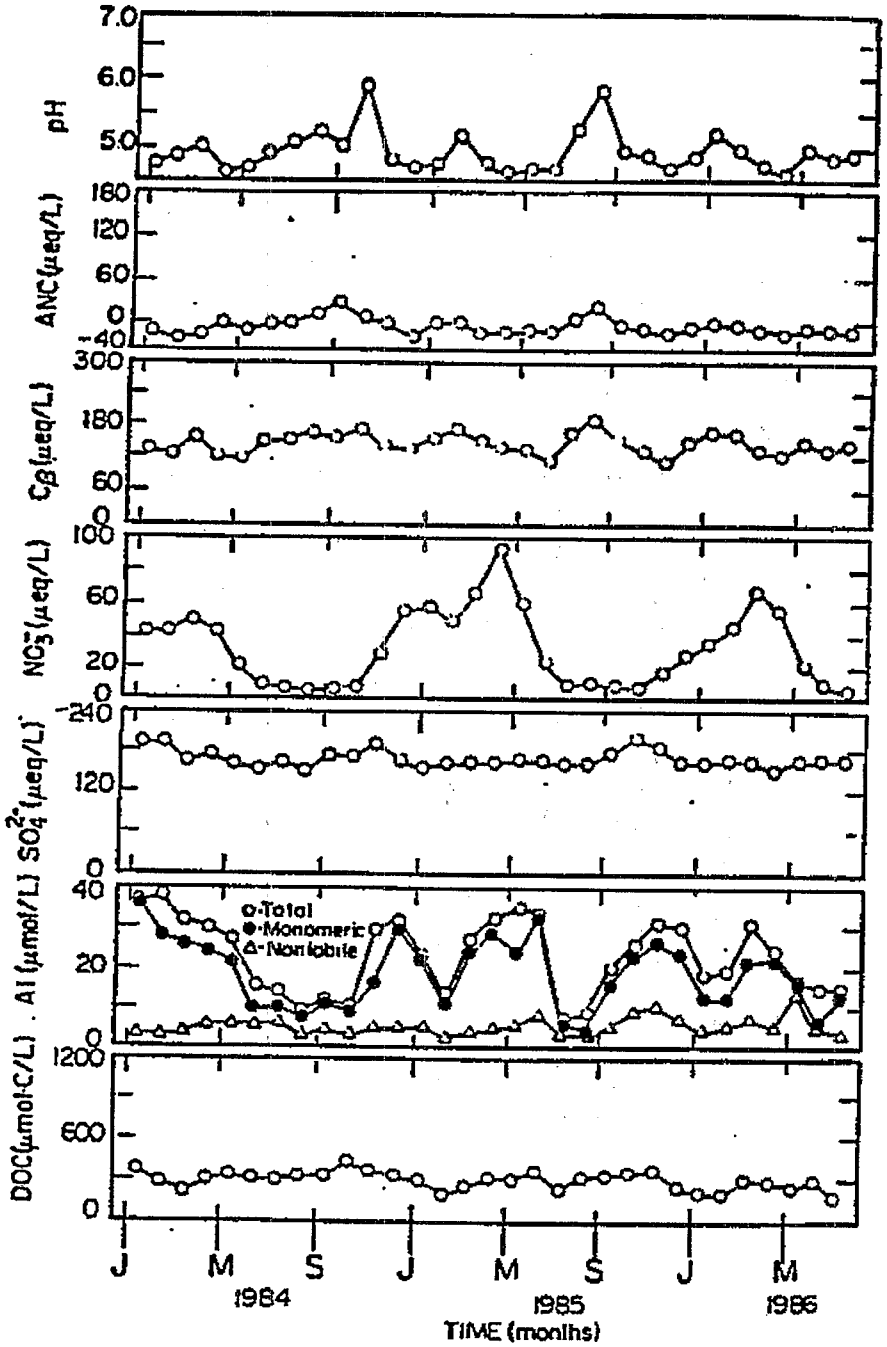


Figure 10-27. Temporal patterns in the chemical characteristics of stream water at Pancake-Hall Creek in the Adirondacks. Sulfate and base cation concentrations are relatively invariant, while NO_3^- concentrations undergo strong seasonality driven by snow melt. Increases in inorganic monomeric aluminum result when ANC values fall below zero. From Driscoll et al. (1989a).

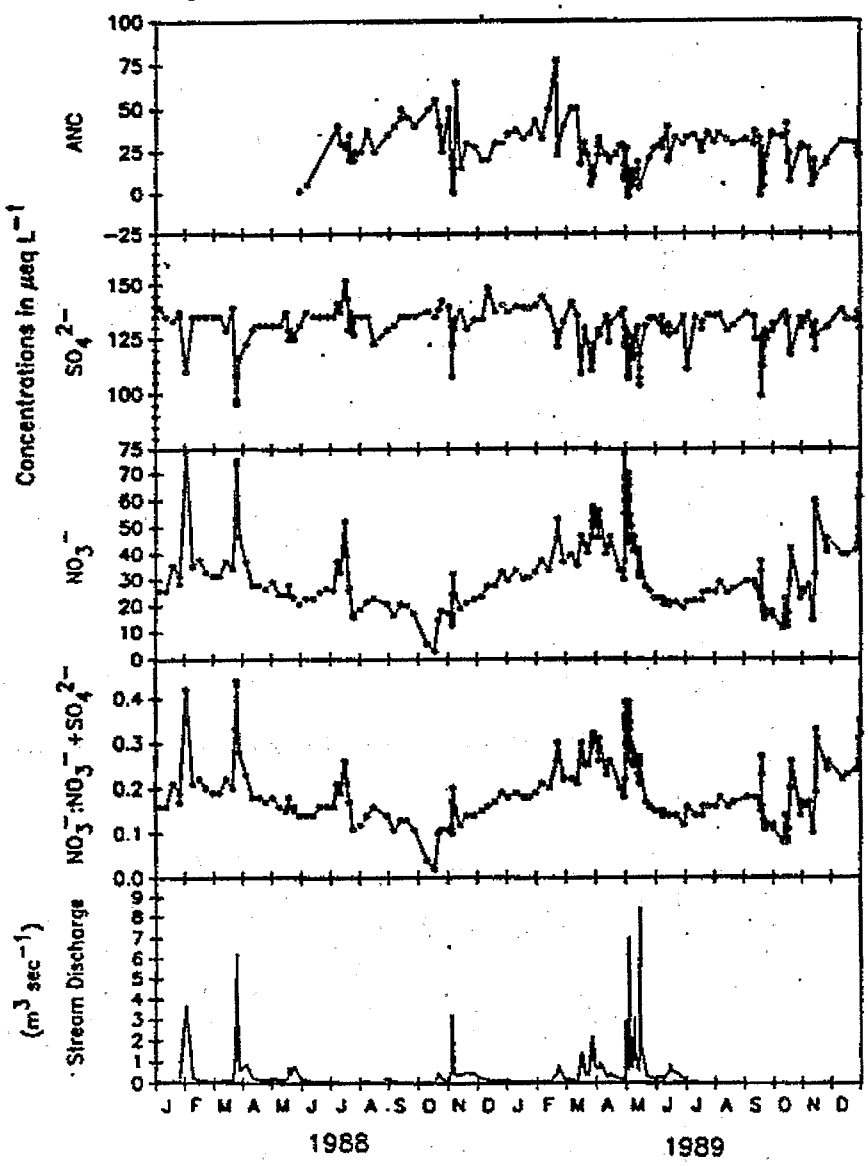


Figure 10-28. Temporal patterns in chemical characteristics of stream water at Biscuit Brook in the Catskill Mountains. All chemical variables undergo strong seasonality, with strong dependence on stream discharge. Values for the ratio of NO_3^- to $NO_3^- + SO_4^{2-}$ approach 0.5 during episodes, and indicate that NO_3^- is nearly as important an acidifying influence as SO_4^{2-} during high flow events. Data from Murdoch and Stoddard (in review).

concentrations undergo strong seasonal cycles, with peak concentrations as high as 85 $\mu eq \cdot L^{-1}$. Both NO_3^- and hydrogen ion concentrations increase during snow melt at Hubbard Brook, while SO_4^{2-} concentrations decrease slightly (Johnson et al., 1981; Likens, 1985).

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 $\mu eq \cdot L^{-1}$, 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 $\mu eq \cdot L^{-1}$; 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 non-acidic 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 ca. 12 $\mu eq \cdot L^{-1}$. Several studies have reported the existence of NO_3^- episodes in the western United States, including the North

Cascades (Loranger and Brakke, 1988), and Sierra Nevada Mountains (Melack and Stoddard, 1991). In general, the maximum concentrations of NO_3^- observed in the West are less than 15 $\mu eq \cdot L^{-1}$, 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 $\mu eq \cdot L^{-1}$, 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 ANC to zero on two occasions in the past 4 years (Williams and Melack, in press b). Data from the outflow at Emerald Lake in 1986 and 1987 (Figure 10-29) 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 (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 $\mu eq \cdot L^{-1}$, but not below.

Finally, there are some areas of North America where no significant affect 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 $\mu eq \cdot L^{-1}$ 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 snow melt at Cone Pond, New Hampshire, 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 $\mu eq \cdot L^{-1}$ in these streams. Swank and Waide (1988) reported data from 7 undisturbed watersheds at the Coweeta Hydrologic Laboratory in North Carolina, where the volume-weighted mean concentrations of NO_3^- were less than 1.5 $\mu eq \cdot L^{-1}$.

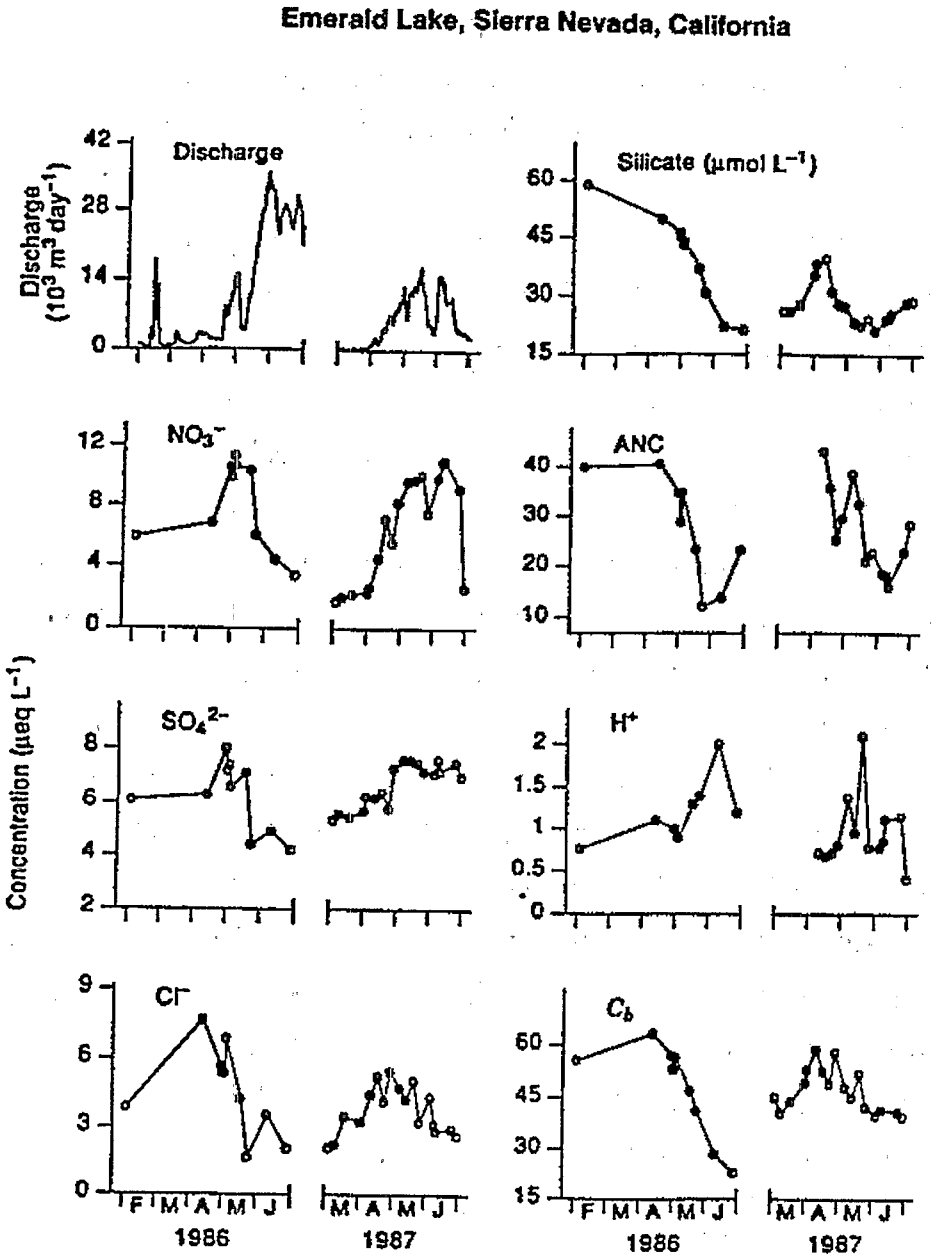


Figure 10-29. **Outflow chemistry from two snowmelt seasons (1986 and 1987) at Emerald Lake, a high elevation lake in the Sierra Nevada mountains of California. Nitrate episodes are smaller in magnitude than at sites in the eastern United States, but western lakes may be more susceptible to episodic acidification because of their lower baseline acid neutralizing capacity than most eastern lakes.**

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 snow melt, and also occur in at least some streams in other portions of the Northeast (e.g., at Hubbard Brook). Nitrate contributes on a 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 baseflow (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 snow melt may simply result when NO_3^- stored in the snow pack 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 runoff without entering the nitrogen cycle of the forest or watershed. Several mechanisms, however, will amplify the signal produced by atmospheric deposition of nitrogen to snow packs. In areas with large snow packs (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 snow melt, 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 snow melt 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, in press b). 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 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 snow melt.

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 snow melt at 11 Adirondack lakes, and that the contribution from mineralization is greater in low ANC and acidic lakes. Stottlemyer 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. Murdoch and Stoddard (in review) conclude that mineralization probably does not contribute substantially to NO_3^- episodes in the Catskill Mountains, because maximum NO_3^- concentrations are very similar among a large number of streams; 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 none-the-less 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 10.6.2.3) 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) identify 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 10-24), with the majority of the increase occurring in the past two decades (Murdoch and Stoddard, in review; Stoddard, in review). These increases are not attributable to other anthropogenic sources of nitrogen, and are similar to trends observed in 8 headwaters streams monitored in the 1980s (Murdoch and Stoddard, in press; Murdoch and Stoddard, in review). At four historical Catskill sites where stream discharge data are available, the relationships between NO_3^- concentration and discharge have changed over the course of the past 4 decades (Figure 10-30). 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 baseflow NO_3^- concentrations).

Trends in lake water NO_3^- concentrations that are similar to the Catskill stream trends have been reported for Adirondack lakes (Table 10-25; Driscoll et al., in review). Nine out of seventeen Adirondack lakes exhibited significant increases in NO_3^- concentrations, while only one exhibited a significant decrease (Table 10-25). It is not statistically possible to determine whether episodic NO_3^- concentrations are mostly responsible for the trends in

TABLE 10-24. SLOPES OF NITRATE TRENDS ($\mu eq \cdot L^{-1} \cdot yr^{-1}$) IN CATSKILL STREAMS BEFORE 1945, BETWEEN 1945 AND 1970, AND AFTER 1970. 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 <0.05. MEDIAN VALUES AND SAMPLE SIZES FOR EACH PERIOD ARE GIVEN IN PARENTHESES. [-- = DATA INSUFFICIENT FOR ANALYSIS.] FROM MURDOCH AND STODDARD (IN REVIEW)

Site	Change in Nitrate Concentration		
	Before 1945	1945-1970	After 1970
Batavia Kill	+0.24 (11, n=235)	+0.21	+0.28 (21, n=70)
Bear Kill above Grand Gorge[b]	--	-- (27, n=9)	+0.70 (38,n=92)
Bear Kill above Hardenbergh Falls	+0.34 (18, n=253)	--	--
Beaver Kill[a]	+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[a]	+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[a]	+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[a]	-0.00 (4, n=272)	+0.08	+3.77 (24, n=10)
West Kill	+0.19 (7, n=227)	--	--
Woodland Creek[a]	+0.02 (4, n=272)	+0.08	+3.95 (25, n=10)

[a]Data for these sites are available only for periods before 1945 and from 1977-79. Trends reported for the periods of missing data are based on regression lines for the entire data set; median values cannot be listed.
[b]Data 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.

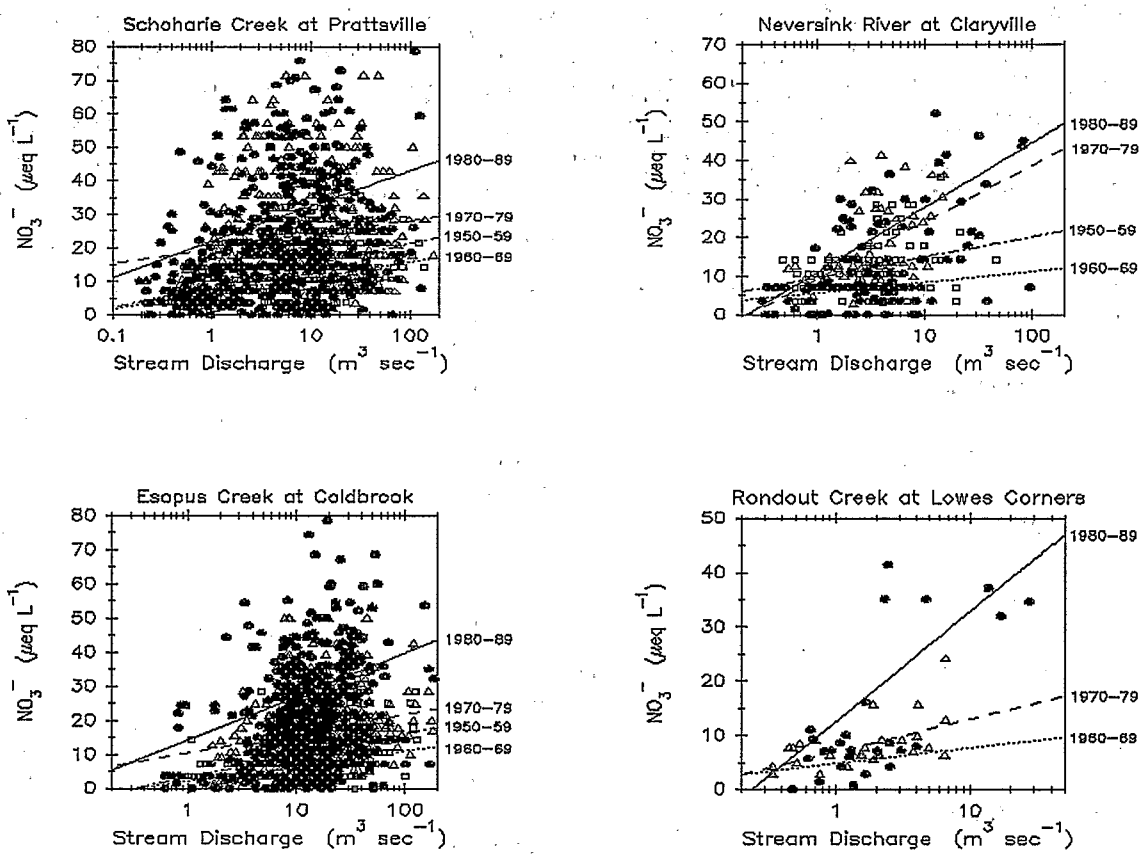


Figure 10-30. Relationship between nitrate concentration and stream discharge for four Catskill streams during four most recent decades: (a) Schoharie Creek at Prattsville, (b) Neversink River at Prattsville, (c) Rondout Creek at Lowes Corners, and (d) Esopus Creek at Coldbrook. Regression lines for 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 NO_3^- concentrations at high discharges are higher in the 1970s and 1980s than in previous decades. From Murdoch and Stoddard (in review).

Adirondack lakes, because the data record is short (1982-89). Plots of temporal NO_3^- patterns, however, suggest that baseflow values are relatively unchanged, while spring values are increasing (Figure 10-31).

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

TABLE 10-25. TRENDS IN NITRATE CONCENTRATIONS FOR ADIRONDACK LONG-TERM MONITORING LAKES. SLOPES ARE CALCULATED FROM BEST-FIT REGRESSION LINES (USING ANCOVA ON RANKS; LOFTIS et al., 1989) FITTED TO DATA. DATA ARE FROM DRISCOLL et al. (IN REVIEW)

Lake Name	n[a]	Change in NO_3^-[b] ($\mu eq \cdot L^{-1} \cdot yr^{-1}$)	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

[a]Number of individual observations; the period of record for most sites is from June, 1982, to August, 1989.
[b]Slope of ANCOVA model. Positive slope indicates an increase in NO_3^-, negative number indicates decrease.
[c]Significance of regression coefficient for date in ANCOVA model.

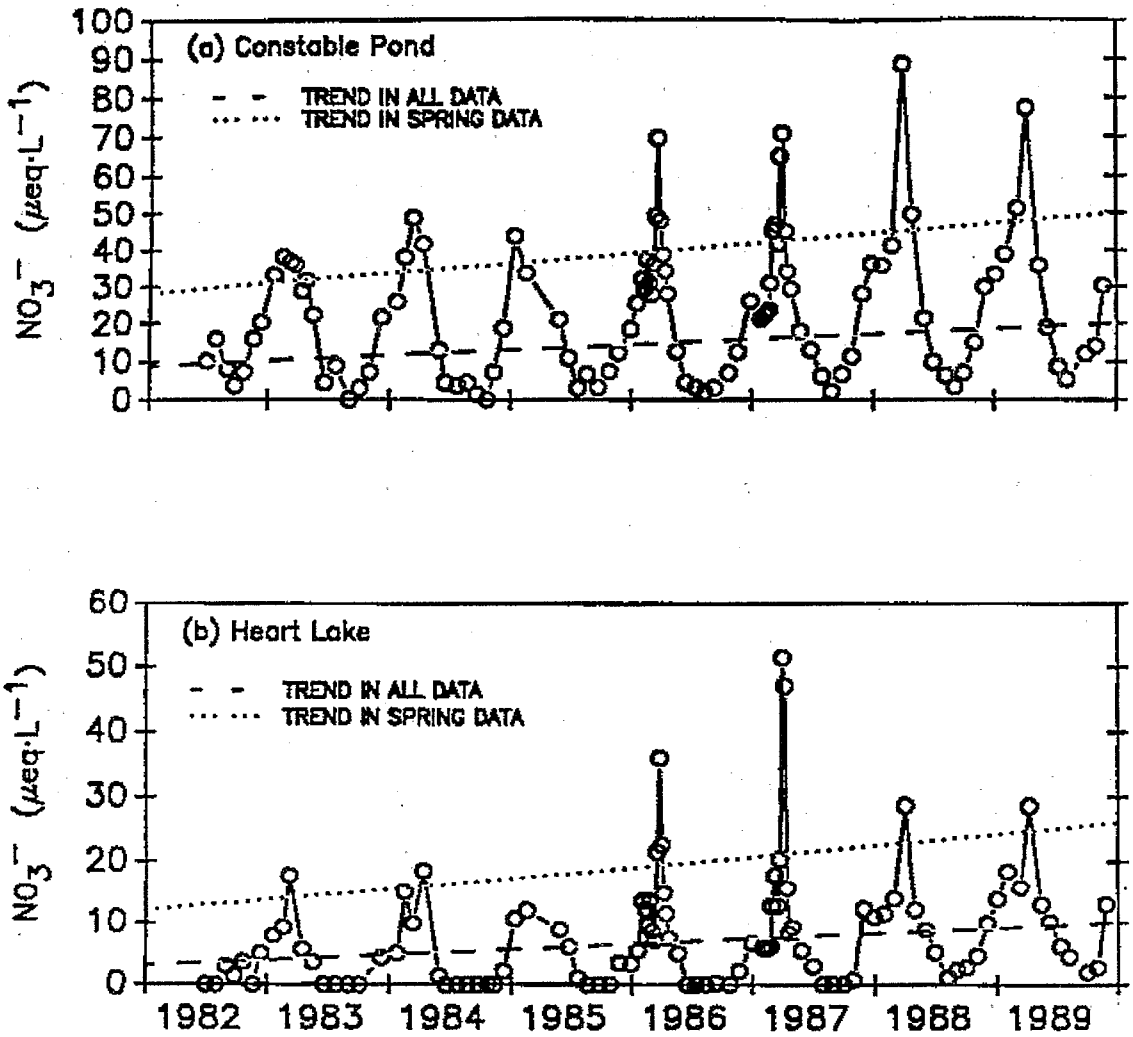


Figure 10-31. Temporal patterns in lake water NO_3^- concentration for two Adirondack lakes, (a) Constable Pond, and (b) Heart Lake. Both sites exhibit increasing trends in NO_3^- (Table 10-25). The strongly seasonal behavior of NO_3^- in these lakes suggests that most of the increase has occurred in spring episodic NO_3^- concentrations.

in NO_3^- (Schindler, 1987), and have been used to suggest that the HBEF watersheds are undergoing nitrogen saturation (Agren and Bosatta, 1988). Examination of the entire 23-year record (1965-1983) 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 moles/ha at HBEF, up to 520,000 moles/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). While the data reported here for the Catskills can be considered truly long-term (up to 65 years of record), data for the Adirondacks (Driscoll et al., in review) and other areas of the United States (Smith et al., 1987a) span only one to two 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 (350-700 eq $\cdot$ ha^{-1} $\cdot$ yr^{-1}) are too high the 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. 150 eq $\cdot$ ha^{-1} $\cdot$ yr^{-1}) may be at the upper limit of the levels that would be protective of the long-term health of sensitive 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 (210 to 1,000 eq $\cdot$ ha^{-1} $\cdot$ yr^{-1}) 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.

10.6.3.3 Biological Effects

In addition to affecting acid/base chemistry, there is considerable evidence that episodic events affect biological systems. J. Baker et al. (1989) have reviewed the scientific evidence of biological effects attributable to surface water acidification, and have documented evidence of: (1) fish kills during spring episodes in Norwegian rivers; (2) loss of stocked trout from re-acidifying Adirondack lakes after liming; (3) decreased density of acid-sensitive benthic invertebrates in whole stream experiments simulating episodic acidification; and (4) loss of acid-sensitive mayfly and stonefly species from two Ontario stream sites experiencing acidic episodes.

Although biological responses to acidification are complex, research over the past decade has provided us with a strong understanding of the relationship between changes in surface water chemistry associated with acidification and responses in biological communities. In short, shifts in water chemistry during acidification can affect biological communities and processes both directly (e.g., physiological stress, toxicity) and indirectly (e.g., changes in food availability, predation). From a biological perspective, changes in several ions (e.g., hydrogen, aluminum, and calcium), not just pH, are important. The scientific literature contains a number of comprehensive reviews of acidification effects on aquatic biota (cf., National Research Council Canada, 1981; Altshuller and Linthurst, 1984; Baker and Christensen, 1991; J. Baker et al., 1989); interested readers are referred to these documents for detailed description of the state-of-science.

10.6.4 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 non-point sources.

10.6.4.1 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). While 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. While 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 which 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 ($>10\ \mu eq \cdot L^{-1}$) 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., 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:total phosphorus) can be used as an index of nutrient limitation (Chiandani 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 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), while 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 and cellular, nutrient concentrations, and from the variety of critical 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 10-26). Lakes with total phosphorus concentrations greater than 2.0 $\mu eq \cdot L^{-1}$ 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 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 sub-regions 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 one.

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

TABLE 10-26. 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

Sub-Region	Number of Lakes in Sub-Region	Estimated Number of Nitrogen Limited Lakes	Proportion of Population N-Limited (%)
Eastern Lake Survey[a]			
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
Western Lake Survey[b]			
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

[a]Data from Kanciruk et al. (1986); excluding lakes with total phosphorus > 2 $\mu mol \cdot L^{-1}$.
[b]Data from Eilers et al. (1987); excluding lakes with total phosphorus > 2 $\mu mol \cdot L^{-1}$.

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 iron (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 Priscu, 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 10-26). 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 10-25 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.

10.6.4.2 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 freshwater and marine systems, but they also have some unique properties that lead to different responses to nitrogen oxide 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 which are distributed over what are sometimes very large watersheds.

The transition zones between fresh and salt water systems are subject to natural processes which 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 waste water 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*, 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 which 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 which have a controlling influence on the geochemistry of contaminants and nutrients:

(a) The tidal mixing of fresh and sea waters on a semi-diurnal 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 fresh water sources. For example, estuaries are generally enriched in nutrients relative to ocean waters due to the local influences of land drainage and often pollution.

(b) 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.

(c) 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, for example oxygen-deficient waters.

(d) 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.

(e) 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.

(f) Biological production and metabolism have significant influences on the occurrence and distribution of nutrients and some gases (e.g., carbon dioxide 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 freshwater—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 non-point 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, while 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 *Skelatonema 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, p. 1008).

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 freshwaters, 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 can not 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 10.6.4.1): (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 10-27. 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.

The data in Table 10-27, 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 freshwaters systems (see freshwater eutrophication section, above) were based on concentrations of total inorganic nitrogen and total phosphorus because these are thought to

TABLE 10-27. MOLAR RATIOS OF DISSOLVED INORGANIC NITROGEN (DIN) TO DISSOLVED INORGANIC PHOSPHORUS (DIP) IN A VARIETY OF ESTUARIES. FROM BOYNTON et al. (1982)

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
S.E. 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, B.C.	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, USSR	20	5-22
Apalachicola Bay, FL	20	5-22
High Venice Lagoon, Italy	48	48-190

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). 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 measure only the short-term response of algae present at the time the experiments are run; they do 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 the 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 1X to 32X 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 32X 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 (1X) 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 m^3 enclosures. Their results had a strong seasonal component. Supplements of nitrogen, either as NO_3^- or as NH_4^+, 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 Himmerfjärd 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 (Granéli 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 30-40%. 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 (Granéli 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 sub-tropical 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 through-puts of water (i.e., "embayments" according to Boynton et al.'s [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 Boynton et al.'s [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 description in freshwater eutrophication section), 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-greens) 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 iron and molybdenum) needed for the biochemically 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 iron in seawater are often much lower than in freshwater, and while little direct evidence of limitation of nitrogen fixation by low iron 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, while 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) sub-tropical

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 10-32, 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 none-the-less suggestive of a general pattern of nitrogen-limitation in these systems (Figure 10-32a). 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 10-32b) 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 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

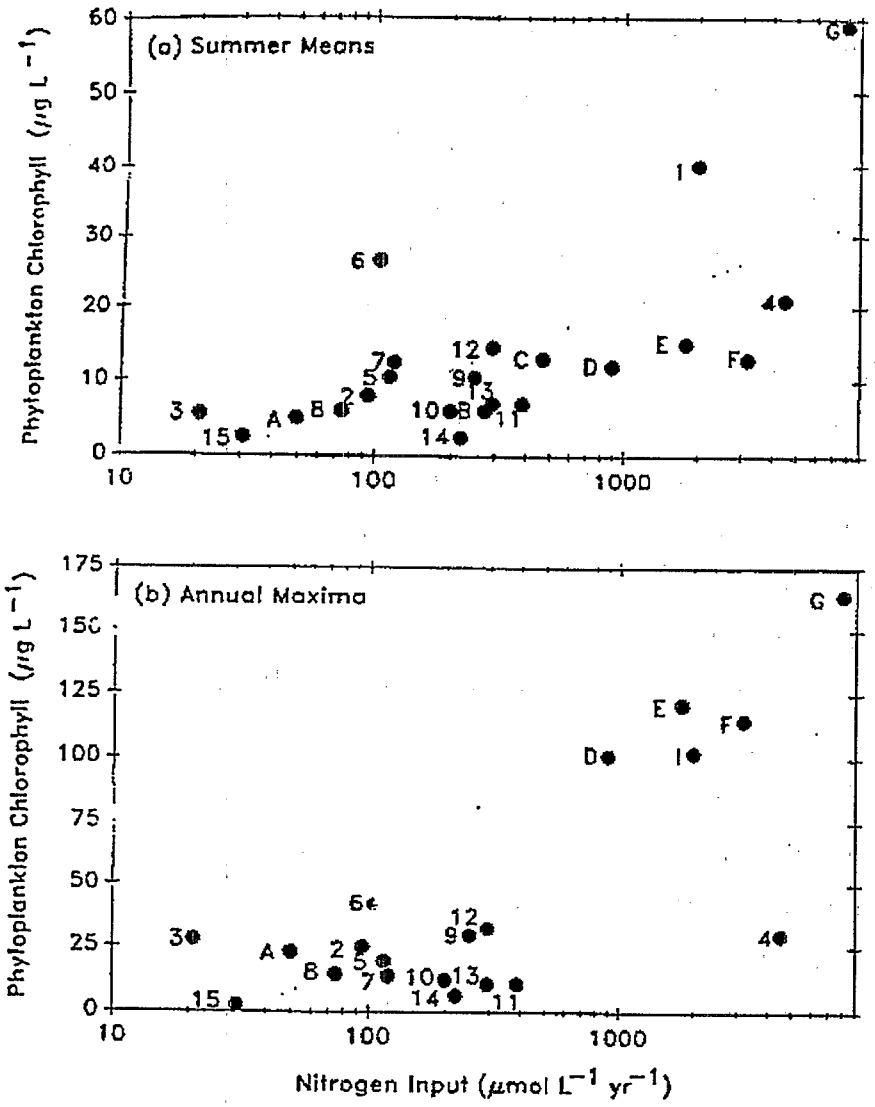


Figure 10-32. Concentrations of (a) mean algal chlorophyll, and (b) annual maximum chlorophyll, in the mid region of various estuaries (1-15) and in the MERL experimental ecosystems (A-G) as a function of the input of dissolved inorganic nitrogen. 1 - Providence River estuary, Rhode Island; 2 - Narragansett Bay, Rhode Island; 3 - Long Island Sound; 4 - lower New York Bay; 5 - Delaware Bay; 6 - Patuxent River estuary, Maryland; 7 - Potomac River estuary, Maryland; 8 - Chesapeake Bay; 9 Pamlico River estuary, North Carolina; 10 - Apalachicola Bay, Florida; 11 - Mobile Bay, Alabama; 12 - Barataria Bay, Louisiana; 13 - N. San Francisco Bay, California; 15 - Kaneohe Bay, Hawaii. Doted lines are from least squares regression, and are included to show strength of relationships; they do not imply causation. Note change in scale on vertical axis. Figure redrawn from Nixon and Pilson (1983).

deposition (predominantly due to nitrogen oxides from combustion and ammonium from agricultural activity). Atmospheric deposition may be supplied directly to the surfaces of estuaries or coastal waters, or 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 nitrogen oxides 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, since, for example, there are many possible regulatory actions which 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, since 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 four-fold, and that rain falling directly on the ocean surface accounted for as much as 10-20% 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 4-5 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.

10.6.4.3 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 the 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 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 values 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 (Granéli 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 nitrogen to phosphorus ratios in deep water result from denitrification in the deep sediments (Shaffer and Rönner, 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 PO_4^{3-} (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 (Granéli 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 (Granéli et al., 1990); rain water in the Baltic is enriched in nitrogen, but 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 (Granéli 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 7.6×10^{10} eq · yr^{-1} of nitrogen, of which 2.8×10^{10} eq · yr^{-1} (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 ca. 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 (Granéli 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 (i.e., 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.

The 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 the Chesapeake Bay by the Environmental Defense Fund (EDF; Fisher et al., 1988a), 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 (25-40% of total inputs) to the nitrogen budget of the Chesapeake Bay. In both cases, nitrogen budgets for the Bay were constructed via a number of steps, each of which involved simplifying assumptions which 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) 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 baseflow 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 baseflow 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. None-the-less, 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 10-28. 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 10-28. The assumptions that were used to construct the refined budget are outlined in each of the discussions of individual budgeting steps below.

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/NTN) 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 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^-

TABLE 10-28. THREE NITROGEN BUDGETS FOR THE CHESAPEAKE BAY

Source of Nitrogen	EDF Budget ($eq \times 10^9 \cdot yr^{-1}$)		Versar Budget ($eq \times 10^9 \cdot yr^{-1}$)		Refined Budget ($eq \times 10^9 \cdot yr^{-1}$)	
Direct Deposition						
NO_3^-	0.6		0.5		0.4	
NH_4^+	0.3		-[a]		0.2	
N Load to Bay (from direct deposition)[b]	0.9		0.5		0.6	
Forests						
NO_3^- Deposition	6.4		6.0		4.6	
NH_4^+ Deposition	3.5	80%	-[a]	95%	2.5	84.6%
Watershed Retention	0.6	50%	0.15	50%	0.5	35%
In-stream Retention	1.0		0.15		0.7	
Atmospheric NO_3^- Load to Bay (from forests)						
N Load to Bay (from forests)[b]						
Pasture Land						
NO_3^- Deposition	1.7		1.2		0.9	
NH_4^+ Deposition	0.9	95%[c]	-[a]	94-99%	0.5	95%[d]
Animal Wastes	13.9	50%[c]	8.4	50%	13.9	35%
Watershed Retention	0.5		0.01-0.04		0.09	
In-stream Retention	1.1		0.05-0.3		0.6	
Atmospheric NO_3^- Load to Bay (from pastures)						
N Load to Bay (from pastures)[b]						
Cropland						
NO_3^- Deposition	1.8	}70%	2.0		1.5	
NH_4^+ Deposition	1.0		-[a]	76-99%	0.8	95%
Fertilizers	11.3		5.9-19.3	50%	11.3	35%
Watershed Retention	0.6		0.010.2		0.05	
In-stream Retention	4.2		0.04-2.6		0.4	
Atmospheric NO_3^- Load to Bay (from cropland)						
N Load to Bay (from cropland)[b]						
Residential/Urban						
NO_3^- Deposition	0.3		0.5		0.4	
NH_4^+ Deposition	0.2	35%	-[a]	62-96%	0.2	50%
Watershed Retention	0.2	0%	0.01-0.1	20%	0.1	35%
In-stream Retention	0.3		0.01-0.1		0.2	
Atmospheric NO_3^- Load to Bay (from urban areas)						
N Load to Bay (from urban areas)[b]						
Point Sources	2.4		1.4-2.3		2.4	
NO_3^- LOAD TO BAY (FROM DEPOSITION)	2.50		0.67-1.06		1.09	
TOTAL NITROGEN LOAD TO BAY[b]	9.95		2.16-5.90		4.87	
% of N from NO_3^- deposition	25%		18-31%[e]		22.5%	

[a]The Versar Budget (Tyler, 1988) does not calculate loads of NH_4^+.
[b]For the EDF Budget (Fisher et al., 1988a) and refined budget total nitrogen load to the Bay includes both NO_3^- and NH_4^+. The Versar Budget (Tyler, 1988) includes only NO_3^-.
[c]Watershed 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.
[d]95% retention was used for animal wastes; 85% retention was used for deposition (see text).
[e]The range of contributions of NO_3^- 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.

deposition in eastern Canada. Baker (1991) concludes that dry deposition of NO_3^- is ca. 40% of wet, while dry deposition of NH_4^+ is approximately 34% of wet (resulting in ratios of dry 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. (in press) report ratios of dry to wet plus dry deposition of 0.35 for two locations inside or near the borders of the Chesapeake Bay watershed (State College, Pennsylvania, and West Point, New York). 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) probably overestimates the importance of dry deposition. The 0.35 ratio is used in constructing the refined budget in Table 10-28.

The two reports (Fisher et al., 1988a; 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; 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 10-28). 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, 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, vs. extrapolated values from isopleth maps), and 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 10-28) 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) 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 11.3×10^9 eq $\cdot$ yr^{-1} is near the bottom range of fertilizer loads estimated by the Versar report (Table 10-28).

The EDF (Fisher et al., 1988a) 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 13.9×10^9 eq $\cdot$ yr^{-1}. 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 seem 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 13.9×10^9 eq $\cdot$ yr^{-1} 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) 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 10-28), 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 vs. 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 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) of 2.35×10^9 eq $\cdot$ yr^{-1} (Table 10-28), 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 10-28) 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) 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 10-29, 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 10-29, 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 baseflow 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 10-28). The 84.6% figure agrees remarkably well with the data presented in Figure 10-16b (Driscoll et al., 1989a), which suggest an interpolated coefficient of 84.7% at the levels of deposition calculated for the

TABLE 10-29. WATERSHED RETENTION OF NITROGEN IN WATERSHEDS IN OR NEAR THE CHESAPEAKE BAY BASIN, FROM PUBLISHED REPORTS. ALL NITROGEN LOADS HAVE BEEN RE-ESTIMATED BASED ON MEASURED WET DEPOSITION, AND A 35% CONTRIBUTION TO TOTAL DEPOSITION FROM DRY DEPOSITION

Physiographic Region	eq × $10^6 \cdot yr^{-1}$ N Load[a]	eq × $10^6 \cdot yr^{-1}$ NO_3^- Export	% 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 (1982)
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)

[a]Nitrogen loads are calculated from published wet deposition estimates, extrapolated to total deposition according to a 0.35 dry:wet plus dry ratio (see text)
[b]Retention 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.

Chesapeake Bay watershed (636 eq · ha^{-1} total deposition, or 413 eq · ha^{-1} of wet deposition).

Nitrogen retention by pasturelands is generally thought to be very high. Both the EDF (Fisher et al., 1988a) and Versar (Tyler, 1988) reports estimate retention coefficients in the 94-99% range. As with forest nitrogen retention, the EDF estimate is based on published values from watershed studies, while 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) on pastureland in the Chowan River 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 budget therefore applies the 95% retention figure for animal wastes, and an 85% retention coefficient (as for forests, above) for nitrogen from deposition (Table 10-28).

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) and 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) 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) report 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) report 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 10-28) 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) 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 10-28). There is little justification for choosing any particular value. The 50% value used for the refined budget (Table 10-28) 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 10.6.2.4). In the absence of any measured loss rates, both the EDF (Fisher et al., 1988a) and 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 the Chesapeake Bay, and the Delaware, which is adjacent to the Chesapeake Bay watershed (summarized in Seitzinger, 1988a). Seitzinger (1987) estimated that 35% of the dissolved inorganic nitrogen ($NO_3^- + NH_4^+$) 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 (10-15%) 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; 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, 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 0.04×10^9 eq $\cdot$ yr^{-1} for the "best case" Versar budget, to 4.2×10^9 eq $\cdot$ yr^{-1} for the EDF budget), but a surprisingly consistent percentage contribution from atmospheric NO_3^- deposition (18 - 31%) to the total budget (Table 10-28). All three budgets suggest that a large amount of nitrogen enters the Bay from deposition; the 1.1×10^9 eq $\cdot$ yr^{-1} estimate from the refined budget corresponds to a nitrogen load of 19 tons per day entering the 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., in press). The biggest uncertainty in estimating atmospheric NO_3^- loading to the Bay comes 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 10-29 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 10-28). The fact that three different approaches (i.e., the three budgets in Table 10-28) yield similar results lends weight to the suggestion that atmospheric nitrogen contributes substantially to the eutrophication of the Chesapeake Bay. 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 non-point sources.

Finally, atmospheric NO_3^- inputs to the Chesapeake 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 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 the 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) calculate that only ca. 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 through 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 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), while 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.

10.6.5 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 ammonia (NH_3) that occurs in equilibrium with ionized ammonium (NH_4^+) and 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 ammonia (NH_3) and ammonium (NH_4^+), which is commonly referred to as NH_4^+; for

clarity, the sum of ammonium and ammonia will be referred to here as total ammonia ($T\text{-}NH_3$). No single toxic concentration for $T\text{-}NH_3$ can be established, because the relative contribution of NH_3 to $T\text{-}NH_3$, 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 which 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 three years, nor can 1-h average concentrations exceed one-half of the FAV more often on average than once every three 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, 48-h LC_{50} values (the concentration at which 50% of the test organisms die within 48 h) for *Daphnia magna*, a common invertebrate found in lake zooplankton, range from 38 to 350 $\mu mol \cdot L^{-1}$ $T\text{-}NH_3$ over a temperature range from 19.6 °C 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 $\mu mol \cdot L^{-1}$ $T\text{-}NH_3$ at relatively constant chemical conditions. The 96-h LC_{50} values for rainbow trout range from 11.4 to 78.5 $\mu mol \cdot L^{-1}$ $T\text{-}NH_3$. 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) calculate FCV and FAV values for Onondaga Lake, an urban lake in Syracuse, New York, that is heavily polluted with municipal sewage. For both salmonid and non-salmonid fishes, the FCV values varied (with time of year) from 1.4 to 2.9 $\mu mol \cdot L^{-1}$. One-half FAV values for non-salmonids varied from 3.6 to 28.6 $\mu mol \cdot L^{-1}$ (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 $\mu mol \cdot L^{-1}$ corresponds to a $T\text{-}NH_3$ concentration of 36 $\mu mol \cdot L^{-1}$; 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 μmol · L^{-1} 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 μmol L^{-1}, Stensland et al., 1986) and reasonable maximum rates of dry deposition and evapotranspiration (dry 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 μmol · L^{-1}. If all nitrogen in deposition (NO_3^- + NH_4^+) were ammonified, maximum potential NH_4^+ concentrations attributable to deposition would be approximately 280 μmol · L^{-1}, and unlikely to be toxic except in unusual circumstances. Since 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 ammonia (i.e., near feed lot 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.

10.7 DISCUSSION AND SUMMARY

10.7.1 Introduction

Since the mid-1980s the view has emerged that the atmospheric deposition of inorganic nitrogen has impacted aquatic and terrestrial ecosystems. In many areas of the United States it is known that the atmospheric input of nitrogen compounds has been significant (U.S. Environmental Protection Agency, 1982, Section 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 (1) the atmospheric concentrations of nitrogen compounds have increased in North America and most European countries and (2) ecosystems formerly limited by nitrogen have become nitrogen saturated via atmospheric deposition. These concerns have led to the efforts 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).

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), 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).

Ecosystems have both structure and function. The most visible levels of organization are: (1) the individual and its environment; (2) the population and its environment; and (3) the biological communty and its environment, the ecosystem (Billings, 1978). Ecosystems function as energy and nutrient transfer systems. Vegetation through the process of photosynthesis accumulates, uses, and stores carbon compounds (energy), to maintain their physiological processes amd to build plant structure. Carbohydrates and other compounds accumluated 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.

10.7.2 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 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 may be upsetting the relationships that exist among the various components and thus changing its structure and functioning.

10.7.3 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 10-30) exhibit the following pattern or tendency towards dry deposition $HNO_3 > NH_3 = NO_2 > NO$. Although the leaf-level data for crops is incomplete (NO and HNO_3 data are not available), the leaf conductance (K_1) data for trees shows a similar pattern. These patterns are consistent with 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^{-1}) than for ammonium (2 mm s^{-1}). However, the high average depositon velocity (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 nitric acid vapor, deposition characteristics of reactive nitrogen compounds are highly variable and dramatically influenced by environmental conditions that effect stomatal conductance. The tight relationship between stomatal conductance and the deposition of NO and NO_2 implies that gaseous deposition of reactive nitrogen oxides is greatly reduced in the dark when stomata close (Hanson et al., 1989; Saxe,

TABLE 10-30. MEAN DEPOSITION CHARACTERISTICS OF REACTIVE NITROGEN GASES AT THE LEAF OR CANOPY SCALE OF RESOLUTION FOR CROP OR TREE SPECIES

Compound	Leaf Level Measures K_1 (mm s^{-1})[a]	Canopy Level Measures Vd (mm s^{-1})[a]
Summary for Crop Species		
NO	ND[b]	1.3
NO_2	1.2	7.7
HNO_3	ND	19.8
NH_3	4.5	6.6
Summary for Tree Species		
NO	<0.3	ND
NO_2	1.1	24
HNO_3	2.1	41
NH_3	1.8	22

[a]Means 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 and V_d for particles represent the leaf wash and throughfall measurement techniques, respectively.
[b]ND; No data for crop plants were available.

1986; Hutchinson et al., 1972). Deposition of gaseous N forms is usually proportional to ambient concentrations, but "compensation concentrations" at which no uptake occurs (i.e., <0.003-0.005 ppmv) have been reported for NO_2 and NH_3. Data for NO, NO_2, and HNO_3 (Grennfelt et al., 1983; Johansson, 1987; Marshall and Cadle 1989; Skärby 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, NO_2, and HNO_3 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 deposition velocity measurement (V_d) 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 over simplification 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 NH_3 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 nitrogen oxide or ammonia 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 10-30. Hanson et al. (1989) used such information with conservative estimates of concentration to approximate total N deposition from nitrogen dioxide to various forest stands. They predicted NO_2-N inputs between 0.04 and 1.9 kg N ha^{-1} yr^{-1} for natural forests and inputs up to 12 kg N ha^{-1} yr^{-1} for forests in urban environments. For a forested watershed, Grennfelt and Hultberg (1986) calculated the annual deposition of NO_2 plus HNO_3 to be in the range from 3.6 to 5.1 kg N ha^{-1} yr^{-1}. Hill (1971) estimated the removal of NO_2 from the atmosphere in Southern California to be approximately 109 kg N ha^{-1} yr^{-1}.

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 N confound simple estimates of annual NH_3-N deposition. Lovett (1991) 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 the modeling process 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 as they provide a basis to evaluate potential effects against "suggested critical levels". Although the concept of critical nitrogen loading has not yet been widely adopted in North America (based on amount of published data), a comparison of total nitrogen deposition data for North America and proposed critical loads provide a reasonable comparison of the status of terrestrial systems with respect to changes expected from elevated levels of nitrogen deposition. Table 10-31 summarizes wet deposition data for nitrate and ammonium in the United States. Since the data are for wet deposited forms of nitrogen, they represent an underestimate of the total nitrogen deposition to the ecoystems. Table 10-32 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.

10.7.4 Effect of Deposited Nitrogen on Forest Vegetation and Soils

The effects of N deposition upon biological systems must be viewed from the perspective of the amount of N in the system, the biological demand for N, and the amount of deposition. If N is deposited on an N-deficient ecosystem, a growth increase will likely occur. If N is deposited on an ecosystem with adequate supplies of N, nitrate leaching will eventually occur. Nitrate leaching is usually deemed undesireable in that it can contaminate groundwater and lead to soil acidification.

TABLE 10-31. MEAN ANNUAL WET NITRATE AND AMMONIUM DEPOSITION TO VARIOUS STATES LOCATED THROUGHOUT THE UNITED STATES. THE STATES ARE PRESENTED IN ORDER OF THE GREATEST ANNUAL N DEPOSITION

		Forms of N Deposition (Kg ha^{-1} yr^{-1})		
Location	No. of Sites	Nitrate	Ammonium	Total[a]
Pennsylvania	3	10.9	1.3	12.2
New York	5	9.7	1.4	11.1
Ohio	2	7.6	1.7	9.3
Georgia	1	6.9	1.1	8.0
Tennessee	1	6.9	0.8	7.7
Illinois	4	6.2	1.3	7.5
N. Carolina	4	6.2	1.1	7.3
Arkansas	1	5.0	1.3	6.3
Virginia	1	5.3	0.5	5.8
Florida	2	4.9	0.6	5.5
Oklahoma	3	4.1	1.3	5.4
Colorado	4	4.3	0.6	4.9
Alabama	1	3.7	0.6	4.3
New Mexico	4	3.6	0.5	4.1
S. Dakota	1	2.7	1.3	4.0
Texas	3	3.1	0.6	3.7
California	5	2.9	0.6	3.5
Washington	3	2.7	0.3	3.0
Wyoming	3	2.5	0.4	2.9
Arizona	1	2.6	0.2	2.8
Utah	1	2.5	0.3	2.8
Idaho	1	2.3	0.3	2.6
Oregon	4	2.1	0.3	2.4
Montana	4	1.9	0.4	2.3
Arizona	1	1.0	0.2	1.2
Hawaii	1	0.08	0.01	0.1

[a]Total deposition data is for wet deposited forms only and as such represents an underestimate of the total nitrogen loading received by these geographic areas.

TABLE 10-32. MEASUREMENTS OF VARIOUS FORMS OF ANNUAL NITROGEN DEPOSITION TO NORTH AMERICAN AND EUROPEAN ECOSYSTEMS. MEASUREMENTS OF TOTAL DEPOSITION DATA THAT DO NOT INCLUDE BOTH A WET AND DRY ESTIMATE PROBABLY UNDERESTIMATE TOTAL NITROGEN DEPOSITION AND ARE ENCLOSED IN PARENTHESES

Site	Forms of N Deposition (Kg ha^{-1} yr^{-1})				
	Wet		Dry		
Location/Vegetation	Cloud	Rain	Particles	Gases	Total
United States					
CA, Chaparral	--[a]	8.2	--	--	23[b]
CA, Sierra Nevada	--	--	--	--	(2)
GA, Loblolly pine	--	3.7	1.0	4.2	9
NC, Hardwoods	--	4.8	0.5	--	5.3
NC, White pine	--	3.7	0.9	2.7	7
NY, Red spruce	7.3	6.1	0.2	2.3	16
TN, Oak forest #2	--	6.0	1.2	--	7
WA, Douglas fir	--	1	--	--	(1)
U.S. Regions					
Adirondacks	--	6.3	4.7	--	11
Canada					
Alberta (southern)	--	7.3	12.2[c]	--	19.5
British Columbia	--	5.5	--	--	(5)
Ontario	--	3.7	--	--	(4)
Ontario (southern)	--	2.3	1.4	--	3.7
Fed. Rep. Germany					
Spruce (SE slope)	--	16.5	--	--	16.5
Netherlands					
Oak-birch	--	--	--	--	24-56[b]
Douglas fir	--	--	--	--	17-64[b]
Douglas fir	--	19.3	95.7[c]	--	115
Norway					
Spruce	--	10.3	0.7	0.2	11.2

[a]--Symbolizes data not available or in the case of cloud deposition not present.
[b]Total nitrogen deposition was based on bulk deposition and throughfall measurements and does include components of wet and dry deposition.
[c]Includes deposition from gaseous forms.

This analysis focuses upon forest ecosystems, because they are sensitive to both the positive and negative effects of N deposition. Agricultural lands are excluded from this discussion because crops are routinely fertilized with amounts of N (100-300 kg/ha) that far exceed pollutant inputs even in the most heavily polluted areas. Pollutant N inputs to grasslands and arid soils can be expected to produce increased growth in some instances, despite water limitations (e.g., Fisher et al., 1988). 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 N deposited on these ecosystems leaves via either denitrification or NH_4^+ volatilization (see review by Woodmansee, 1978).

The biological competition for atmospherically-deposited N 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 N is retained within the ecosystem. Until recently, nitrifying bacteria were thought to be poor competitors for N, with heterotrophs the most effective competitors and plants intermediate. Recent studies of soil N dynamics using ^{15}N (Davidson et al., 1990) and a through analyses of forest N budgets suggest that these assumptions and perhaps our conceptual model of soil N cycling need modification. Specifically, nitrification may be proceeding at a significant level without the appearance of NO_3^- in soils or soil solution if NO_3^- is rapidly taken up by heterotrophs. It is also clear that trees can be very effective competitors for atmospherically-deposited N in N-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 N retention is controlled primarily by biological processes may be erroneous.

Nitrification and NO_3^- leaching become significant only after heterotroph and plant demand for N are substantially satisfied, a condition that has been referred to as "nitrogen-saturated" or "N-saturated". Additions of N in any biologically-available form (NH_4^+, NO_3^-, or organic) to an N-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 N-saturated ecosystems.

Vegetation demand for N depends upon a number of growth-influencing factors including temperature, moisture, availibility 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, N-saturation tends to be more common in older forests than in younger forests. Processes that cause net N export from ecosystems such as fire and harvesting will naturally push ecosystems toward a state of lower N-saturation or even N deficiency. Intense fire causes a large loss of ecosystem N capital, but frequent, low intensity fires may have little effect.

A review of the literature on forest fertilization and N cycling studies under various levels of pollutant N input reveals some interesting contrasts that pertain to the the relative roles of heterotrophs, plants, and nitrifiers discussed above. Forest fertilization has proven quite successful in producing growth increases in N-deficient forests, even though trees typically recover only 5-50% of fertilizer N (Table 10-33). On an ecosystem level, however, retention of N is usually quite high (often 70-90% of applied N; Table 10-33), primarily due to fertilizer N retention in the litter and soil, including non-biological reactions between NH_4^+ and humus. Fertilization studies differ from pollutant N deposition in several important respects: (1) pollutant N 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 non-biological reactions between soil humus and NH_4^+, and (3) pollutant N deposition enters the ecosystem as a slow, steady input in rather low concentrations, whereas the fertilizer is typically applied in 1-5 large doses. Both plants and nitrifying bacteria are favored by slow, steady inputs of N, possibly giving them a competative advantage over heterotrophs for pollutant N inputs. A review of the literature on N cycling in unfertilized forests with differing levels of pollutant N input supports this hypothesis. Ecosystem-level recovery of atmospherically-deposited N (typically less than 50% and often 0%; Table 10-34 and Figure 10-33) is lower than of fertilizer N (typically 70-90% of applied N; Table 10-33 and Figure 10-34). It also appears as if vegetation retention of incoming N in unfertilized forests is somewhat higher than in fertilized forests whereas soil (heterotroph) retention of

TABLE 10-33. NITROGEN FERTILIZER RECOVERY BY VEGETATION AND SOILS IN VARIOUS STUDIES

Location	Species and Age Type and Amount (kg/ha)	Fertilizer Recovery* (kg/ha and percent)	Vegetation Recovery (kg/ha and percent)	Soil	Reference
Florida	*Pinus eliottii*, 11	AS,56	6 (11%)	17 (30%)	Mead and Pritchett (1975)
Florida	*Pinus eliottii*, 11	AS,224	24 (11%)	40 (18%)	Mead and Pritchett (1975)
Mississippi	*Pinus taeda*, 5	AN,112	16 (14%)	-	Baker et al. (1974)
Mississippi	*Pinus taeda*, 6	AN,224	31 (28%)	-	Baker et al. (1974)
Mississippi	*Pinus taeda*, 5	AN,224	31 (14%)	-	Baker et al. (1974)
Mississippi	*Pinus taeda*, 6	AN,224	146 (65%)	-	Baker et al. (1974)
New Zealand	*Pinus radiata*, 14	NS,960	120 (13%)	488 (51%)	Baker et al. (1986)
New Zealand	*Pinus radiata*, 13	U,224	80 (40%)	120 (60%)	Worsnop and Will (1980)
Ontario	*Pinus banksiana*, 45	U,300	76 (25%)	79 (26%)	Morrison and Foster (1977)
Scotland	*Pinus nigra*, 36	AS,252	136 (54%)	176 (67%)	Miller et al. (1976)
Scotland	*Pinus nigra*, 36	AS,504	228 (45%)	78 (15%)	Miller et al. (1976)
Scotland	*Pinus nigra*, 36	AS,1008	366 (36%)	303 (30%)	Miller et al. (1976)
Scotland	*Pinus nigra*, 36	AS,1512	495 (32%)	229 (15%)	Miller et al. (1976)
Sweden	*Pinus sylvestris*, 130	AN,224	19 (19%)	46 (46%)	Melin et al. (1983)
Sweden	*Pinus sylvestris*, 120	U,150	12 (8%)	74 (49%)	Nommik and Moller (1981)
Sweden	*Pinus sylvestris*, 120	U,300	21 (7%)	87 (29%)	Nommik and Moller (1981)
Sweden	*Pinus sylvestris*, 120	U,600	36 (6%)	102 (17%)	Nommik and Moller (1981)
Sweden	*Pinus sylvestris*, 120	AN,150	29 (19%)	32 (21%)	Nommik and Moller (1981)
Sweden	*Pinus sylvestris*, 120	AN,300	60 (20%)	48 (16%)	Nommik and Moller (1981)
Sweden	*Pinus sylvestris*, 120	AN,600	90 (12%)	72 (12%)	Nommik and Moller (1981)
Tennessee	*Pinus taeda*, 4	U,300	25 (8%)	-	Johnson and Todd (1988)
Western Washington	*Pseudotsuga menziesii*, 52	NS,224	94 (42%)	124 (55%)	Heilman and Gessel (1963)
Western Washington	*Pseudotsuga menziesii*, 38	NS,224	204 (50%)	206 (51%)	Heilman and Gessel (1963)
Western Washington	*Pseudotsuga menziesii*, 30	NS,400	72 (13%)	284 (51%)	Heilman and Gessel (1963)
Western Washington	*Pseudotsuga menziesii*, 32	NS,560	75 (13%)	687 (123%)	Heilman and Gessel (1963)
Western Washington	*Pseudotsuga menziesii*, 38	NS,560	149 (20%)	337 (46%)	Heilman and Gessel (1963)
Wisconsin	*Pinus resinosa*, 37	AN,100	125 (125%)	-	Bockheim et al. (1986)

*U=Urea, AS=Ammonium Sulfate, AN=Ammonium Nitrate, NS=Not Specified.

TABLE 10-34. NITROGEN INPUTS, OUTPUTS, AND VEGETATION INCREMENTS IN VARIOUS FOREST ECOSYSTEMS

Location	Species	Input	Leaching	Input-Output	Vegetation Increment	Reference
		----------kg/ha/yr----------				
USSR	*Picea abies*	1.1	0.9	+0.1	9.0	Cole and Rapp (1981)
Washington	*Abies amabilis*	1.3	2.7	-1.4	-	Turner and Singer (1976)
Washington	*Pseudotsuga menziesii*	1.7	0.6	+1.1	10.0	Cole and Rapp (1981)
Oregon	*Pseudotsuga menziesii*	2.0	1.5	+0.5	-2.8	Sollins et al. (1980)
Wisconsin	Aspen-Mixed Hardwood	5.6	0.05	+5.1	26.0	Pastor and Bockheim (1984)
New Hampshire	Northern hardwood	6.5	4.0	+2.5	9.0	Bormann et al. (1977)
Tennessee	*Liriodendron tulipifera*	7.7	3.5	+4.2	7.1	Cole and Rapp (1981)
Ontario	*Acer saccharum*	7.8	18.2	-10.4	-	Foster and Nicolson (1988)
Tennessee	Mixed deciduous	13.0	3.1	+9.9	13.5	Henderson and Harris (1975)
Germany	*Fagus sylvatica*	21.8	4.4	+17.4	4.1	Cole and Rapp (1981)
Germany	*Picea abies*	21.8	14.9	+6.9	12.2	Cole and Rapp (1981)
Holland	*Quercus robur*	44.6	22.5	+22.1	17.0	van Breemen et al. (1987)
Holland	*Quercus robur, Betula pendula*	54.5	78.5	-24.0	6.0	van Breemen et al. (1987)
Holland	*Quercus robur*	56.2	28.1	+28.1	24.0	van Breemen et al. (1987)
Holland	Mixed deciduous	62.8	87.6	-24.8	-	van Breemen et al. (1987)
Washington	*Alnus rubra**	70.0	71.0	-1.0	7.1	Van Miegroet and Cole (1984)

*N-fixing species.

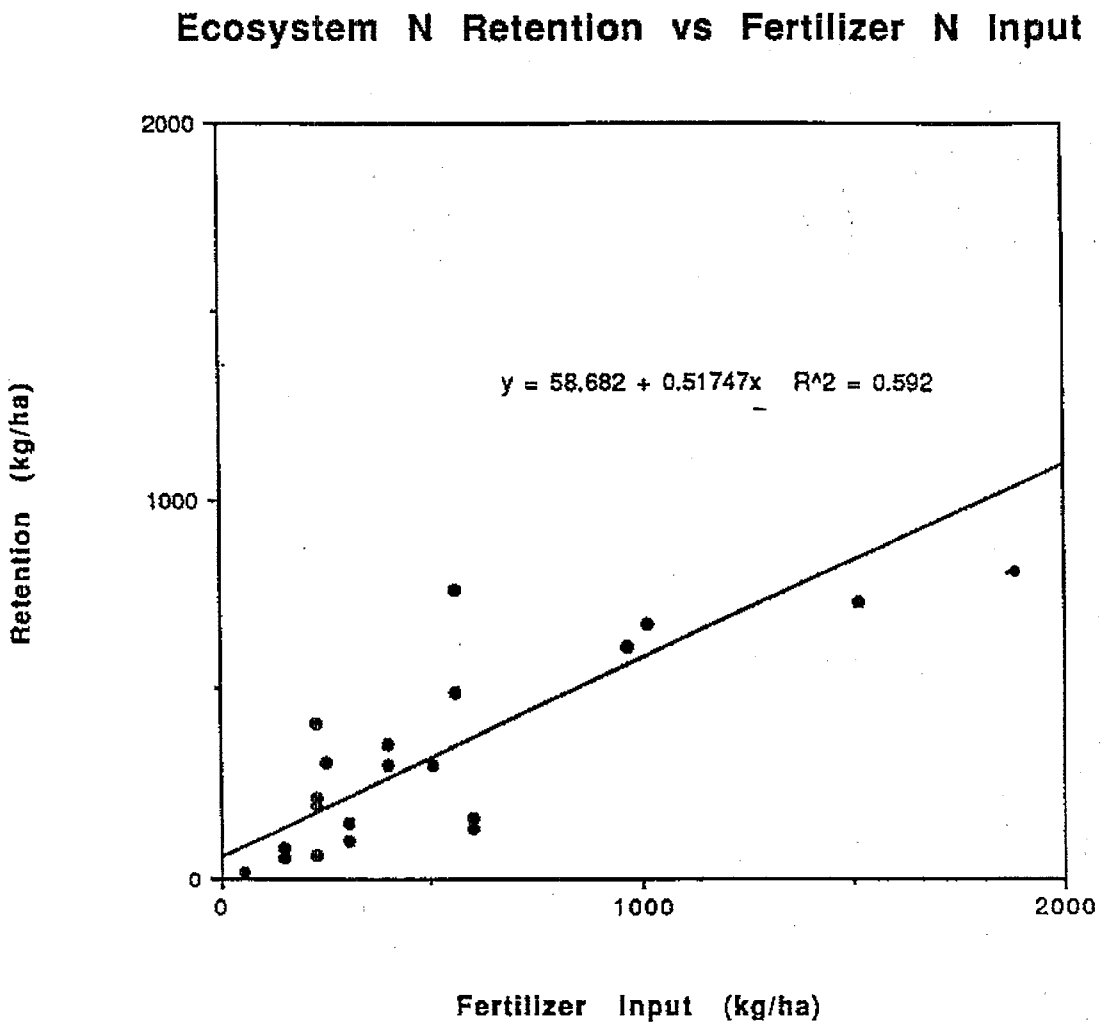


Figure 10-33. Ecosystem recovery of fertilizer N as a function of fertilizer N input.

atmospherically-deposited N is much lower. In forests with very low atmospheric N inputs, it appears as if the soil is being "mined" for the N necessary to supply vegetation, an indication that plants are actually out-competing heterotrophs for N. In forests with high atmospheric N inputs, heterotrophic N uptake appears to be minimal, perhaps because of limitations by organic substrates or other nutrients.

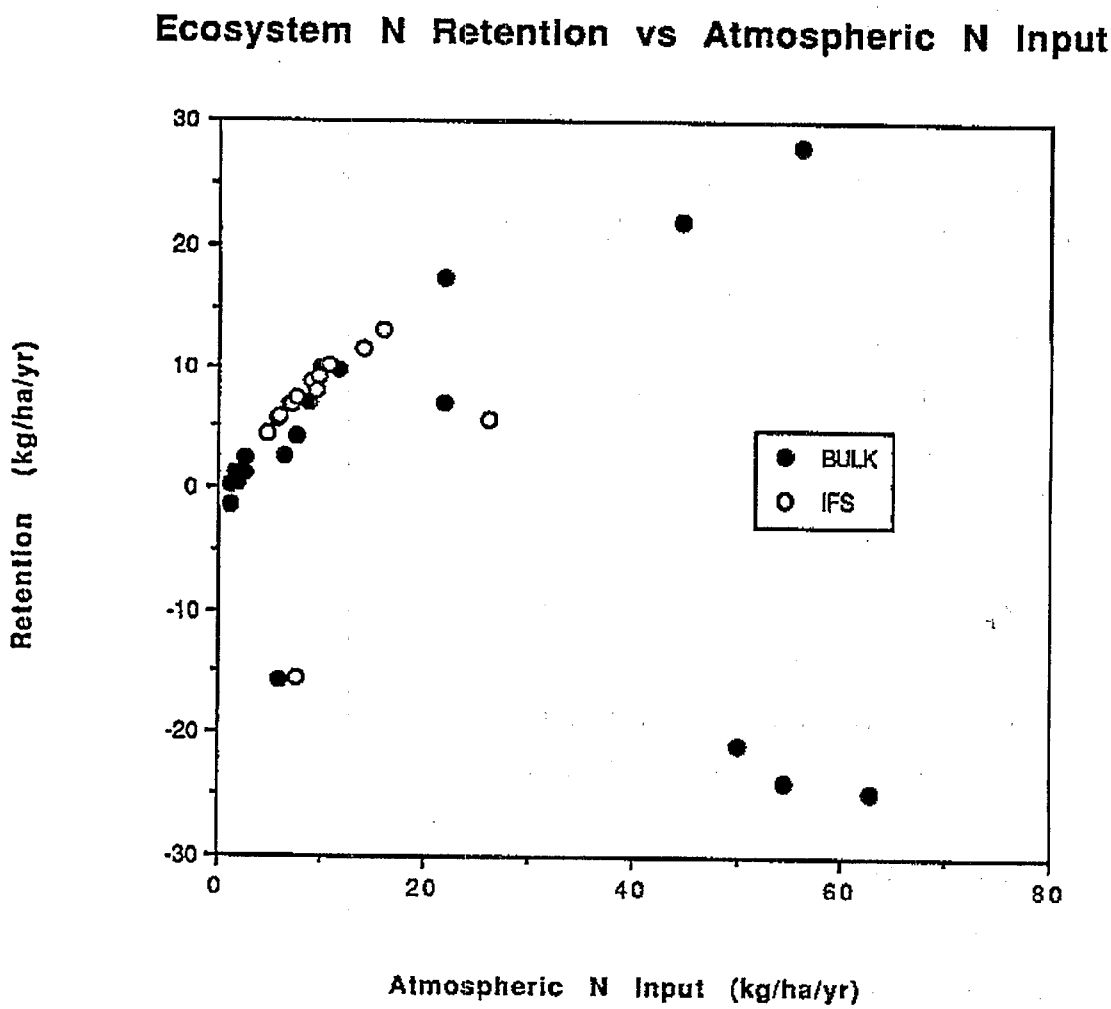


Figure 10-34. Ecosystem N retention as a function of atmospheric N input.

Since nitrification results in the creation of nitric acid within the soil, there are concerns that elevated N inputs to N-saturated systems will result in soil acidification and aluminum mobilization. There are very few proven, documented cases in which excessive atmospheric N deposition has caused soil acidification (e.g., in forests in The Netherlands subject to very high N deposition levels), 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

greatest uncertainty in assessing and projecting rates of soil 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 undesireable effect, but in some cases, the benefits of alleviating N deficiency clearly outweigh the detriments of soil acidification (e.g., the benefits of N-fixation by red alder always outweigh the detriments of soil acidification to succeeding Douglas fir stands in the Pacific Northwest).

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: $Al^{3+} > Ca^{2+}, Mg^{2+} > K^+, Na^+, H^+$. 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 damage and and were a major contributor to forest decline observed in Germany during the mid 1980's. 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., Rehfuess, 1987). Van Breemen et al. (1982, 1987) and Johnson et al. (in press) note 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 forest decline in both countries. Other hypotheses include weather extremes and climate change, Mg and K deficiencies which 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 U.S. (Galloway et al., 1980; Driscoll et al., 1989).

Increased N deposition can cause significant changes in tree physiological function, susceptibility to insect and disease attack, and even plant community structure. Several hypotheses posed to explain current forest declines in eastern North America invoke the

effects of excess N deposition upon physiological processes. These physiological responses generally invoke altered carbohydrate allocation causing increased sensitivity to drought, frost, or insect attack. To date, however, experimental evidence has not supported these hypotheses.

Excessive NH_4^+ deposition to soils in which nitrification is inhibited causes serious nutrional imbalances and even toxic effects to some forests in The Netherlands (Boxman et al., 1988). Deleterious effects of excess N deposition 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 N inputs may result in changes in species composition. Species respond differentially to increased N availability, creating the potential for changes in ecosystem composition with increased N loading. Changes from heathland to grassland in Holland have been attributed to current rates of N deposition (Roelofs et al., 1987). Ellenberg (1987) points to further species changes in Central European ecosystems as a likely consequence of elevated N. He states that "More than 50% of the plant species in Central Europe can only compete on stands that are deficient in nitrogen supply".

Increased N inputs can affect tree resistance to insect and desease either positively or negatively. Alleviating N deficiency may increase plant resistance to pathogen attack, but it may also reduce the production of phenols in plant tissues, thereby reducing resistance to pathogen attack. To date, there is little research to show how increased N inputs affect susceptibility to pathogen attack, but the potential for either positive or negative effects is significant.

10.7.5 Effects of Nitrogen on Terrestrial Vegetation

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 which exist between biological, physicochemical, and climatic factors. Nevertheless, reactive nitrogen compounds have been hypothesized to impact ecosystems directly through modifications of individual plant physiological processes, or indirectly through alterations in the nitrogen status of the ecosystem.

Very little information is available on the direct effects of nitric acid vapor on vegetation and essentially no information on its effects on ecosystems. Norby et al. (1989) reported that nitric acid vapor (0.075 ppmv) induced nitrate reductase activity (NRA) in red spruce foliage. The effects of ammonia, a reduced nitrogen gas, have been summarized by Van der Eerden (1982), however, ammonia concentrations seldom reach phytotoxic levels in the United States (U.S. Environmental Protection Agency 1982). In contrast, high ammonia concentrations in Europe have been observed (van Dijk and Roelofs, 1988). Van der Eerden (1982) summarized available information on the direct response of crop and tree species to ammonia fumigation and concluded that the following concentrations produced no adverse effects:

0.107 ppmv (75 μg m^{-3}), yearly average
0.858 ppmv (600 μg m^{-3}), daily average
14.3 ppmv (10,000 μg 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 mg 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 nitric acid 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 may be modifying interplant competitive balances leading to changes in species composition and/or diversity.

De Temmerman et al. (1988) found increased fungal outbreaks and frost damage on several pines species exposed to very high ammonia deposition rates (>350 kg ha^{-1} yr^{-1}). Numbers of species and fruiting bodies of fungi have also increased concomitantly with nitrogen deposition in Dutch forests (van Breemen and van Dijk, 1988). Schulze (1989) presents a clear progression of evidence which indicates that canopy uptake of nitrogen

together with root uptake has caused a nitrogen imbalance in Norway spruce leading to forest 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 vulagris* is being replaced by grass species, as a consequnce 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 N ha^{-1} yr^{-1}. Liljelund and Torstensson (1988) have shown clear signs of vegetation changes in response to nitrogen deposition rates of 20 kg ha^{-1} yr^{-1}.

10.7.6 N Saturation, Critical Loads, and Current Deposition

Ecosystem nitrogen saturation and the definition of the critical N deposition levels have been the subject of recent conferences (Nilsson and Grennfelt, 1988; Brown et al., 1988; Skeffington and Wilson, 1988). Miller and Miller (1988) proposed three definitions for N saturated ecosystems:

1. No response to additional N,
2. Growth reductions in response to added N or,
3. Added N leads to increased losses of nitrate in streamwater.

They concluded that third was most reasonable. Brown et al. (1988), however, reported that a recent workshop, based on a model of plant/soil N saturation put forth by Agren and Bosatta (1988), concluded that N saturation could best be defined as occurring when N losses from ecosystems exceeded inputs. 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 makes it possible to define a critical N load (deposition rate) at which no change or deleterious impacts will occur to an ecosystem (Nilsson, 1986). 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). 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 N cycle and ecosystem diversity make defining a critical load for N very difficult. The following possible criteria may be useful for defining appropriate critical N loads on ecosystems:

1. Prevent nitrate levels in drinking or surface waters from rising above standard levels
2. Ensure proton production less than weathering rate
3. Maintenance of a fixed ammonia-base cation balance
4. Maintenance N inputs below N outputs (the N saturation approach)
5. Minimize accelerations in the rates of ecological succession (vegetation changes due to altered interspecific competition).

De Vries (1988) defined criteria for a combined critical load for nitrogen and sulfur for Dutch forest ecosystems using the following: N 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 N and S deposition in The Netherlands exceed acceptable levels.

Schulze et al. (1989) proposed critical loads for N 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 Section 10.3.6). 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 3-14 Kg N ha^{-1} yr^{-1} for silicate soils or 3 to 48 kg N ha^{-1} yr^{-1} for calcareous based soils. Other critical loads have been proposed at rates

of nitrogen deposition ranging from as little as 1 to levels near 100 Kg N ha^{-1} yr^{-1} depending on the impacts considered acceptable and the criteria used to define the critical load.

Using criteria to minimize species change, critical loads less than 30 kg ha^{-1} yr^{-1} have been proposed (van Breeman and van Dijk, 1988; Liljelund and Torstensson, 1988). When using the criteria that ecosystem nitrogen inputs should not exceed outputs, critical loads have been proposed as low as 1-5 kg N ha^{-1} yr^{-1} for poor productive sites with low productivity or in the range from 5-30 kg N ha^{-1} yr^{-1} 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 summarizing the results of a recent conference on critical nitrogen loading, after discussing various options for setting a critical N load, Skeffington and Wilson (1988) concluded that "we do not understand ecosystems well enough to set a critical load for N 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 N deposition (World Health Organization, 1987).

There is little doubt that N deposition has a prounced effect on many if not most terrestrial ecosystems. Since most forest ecosystems in North America are N deficient, one of the most noticeable initial changes in response to increased N deposition is likely to be a growth increase. Whether this growth increase is deemed desireable or undesireable in a particular ecosystem is entirely a matter of management objectives (timber production or wilderness preservation), and, ultimately, value judgements by society. For instance, improved growth and vitality due to increased N deposition may not be deemed desireable in wilderness areas. A blanket statement as to the benefit or damage due to N deposition cannot be made, but it is logical to assume that increased N deposition would be considered beneficial, on balance, to most North American forests. Exceptions to this will certainly occur, and have already been noted in specific situations such as high-elevation forests with low vegetation demand and high atmospheric N input.

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.

10.7.7 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^+ (ammonium) in the environment represses nitrogen fixation (Roelofs, 1986; Schuurkes et al., 1986, 1987; Rudd et al., 1988). The proportion of N_2O (nitrous oxide) 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 ozone.

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 N ha^{-1} yr^{-1} in ombrotrophic bogs (rain-fed bogs), which receive water only through precipitation, to 750 kg N ha^{-1} yr^{-1} 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 N ha^{-1} yr^{-1} and occurs in the form of NO_3^- (nitrate), NH_4^+ (ammonium), 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 N ha^{-1} yr^{-1} 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 N ha^{-1} yr^{-1}, 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-labelled mineral nitrogen at rates of about 100 kg N ha^{-1} yr^{-1} indicate that up to 93% of applied NH_4^+ is rapidly assimilated into

organic matter within a single growing season. The majority of the labelled 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 20-40 kg N ha^{-1} yr^{-1}, 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 N ha^{-1} yr^{-1}. 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 modelling study suggests that a succession (change) from open ombrotrophic bog to forested wetland occurs when a threshold of 7 kg N ha^{-1} yr^{-1} 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 N ha^{-1} yr^{-1} (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).

10.7.8 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 nitrogen oxides 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 de-coupling nitrogen deposition from nitrogen effects, and reduce our ability to attribute known aquatic effects to known rates of nitrogen deposition. While 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 non-atmospheric 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 nitrogen oxides 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 nitrogen oxides can be divided into three general categories: (1) acidification, both chronic and episodic; (2) eutrophication of both freshwaters and estuaries; and (3) directly toxic effects.

10.7.8.1 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 review), 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 snow melt, or following large rain events. In many cases, these episodic increases in NO_3^-, along with already low baseline acid neutralizing capacity (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 snow melt or during large rain storms. While 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 snow pack over the course of the winter. If biological demand for nitrogen is still low at the onset of snow melt, the entire store of snowpack NO_3^- can be flushed into drainage waters in the very early stages of snow melt (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., 1987; Stoddard and Murdoch, 1991; Murdoch and Stoddard, in review; Driscoll et al., in review) 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 streams sites in each of the three NO_3^- groups are shown on maps of the Northeast (Figure 10-35) the Southeast (Figure 10-36) and the West (Figure 10-37). 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 4 times per year, to illustrate seasonal patterns). These criteria exclude many sources of data, most notable those from the National Surface Water Survey (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

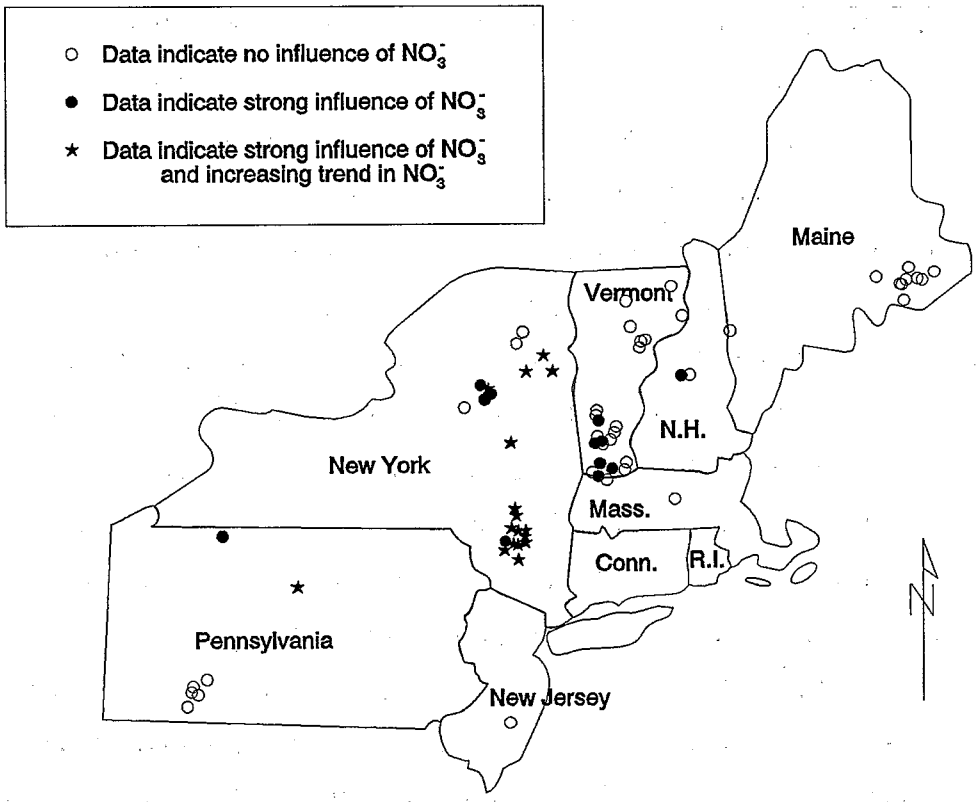


Figure 10-35. Location of acid-sensitive lakes and streams in the northeastern United States where the importance of NO_3^- to seasonal water chemistry can be determined. Data from: Kahl et al. (1991); Wigington et al. (1989); Driscoll et al. (1987a); Driscoll et al. (in review); Kramer et al. (1986); Murdoch and Stoddard (in review); 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).

nitrogen deposition. None-the-less, the maps illustrate the existence of severe problems in the Northeast (especially the Adirondack and Catskill Mountains), and the Southeast (in the Mid-Appalachians and Great Smoky Mountains), and the potential for future problems in the West.

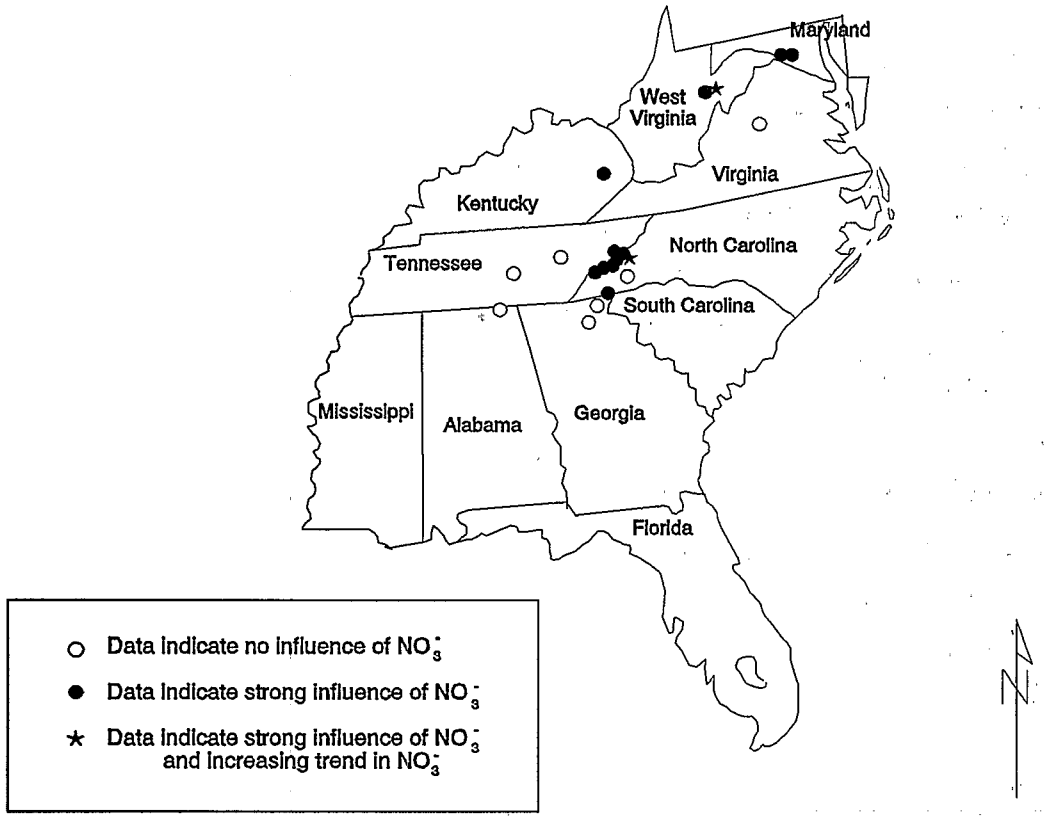


Figure 10-36. Location of acid-sensitive lakes and streams in the southeastern United States where the importance of NO_3^- to seasonal water chemistry can be determined. Data from: Elwood et al. (1991); Cosby et al. (1991); Elwood and Turner (1989); Buell and Peters (1988); Swank and Waide (1988); Jones et al. (1983); Silsbee and Larson (1982); Katz et al. (1985); Weller et al. (1986); Wigington et al. (1989); Kramer et al. (1986); Edwards and Helvey (1991).

It is also possible to draw correlations between rates of nitrogen deposition, and rates of nitrogen loss from watersheds; while 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 National Stream Survey (NSS; Kaufmann et al., 1988) and interpolated wet deposition values (of $NO_3^- + NH_4^+$) to correlate deposition and surface water dissolved inorganic nitrogen concentrations

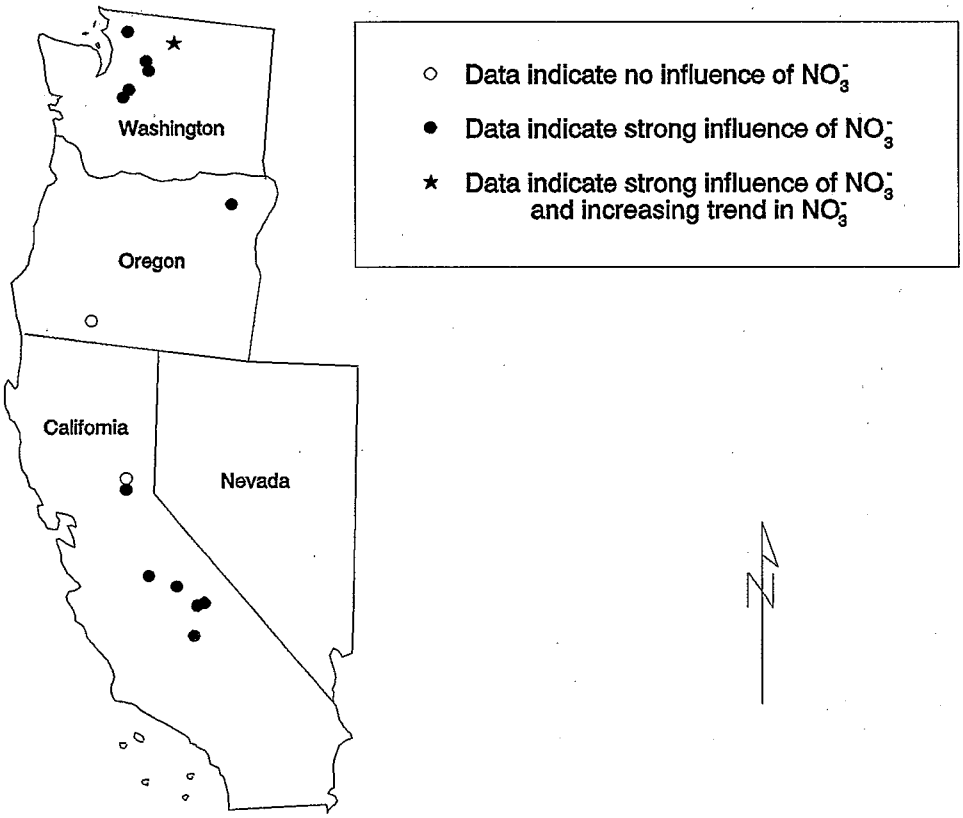


Figure 10-37. Location of acid-sensitive lakes and streams in the western United States where the importance of NO_3^- to seasonal water chemistry can be determined. Data from: Melack and Stoddard (1991); Stoddard (1987a); Loranger et al. (1986); Wigington et al. (1989); Kramer et al. (1986); Welch et al. (1986); Eilers et al. (1990); Gilbert et al. (1989).

($NO_3^- + NH_4^+$) in large physiographic regions of the eastern United States (Figure 10-38a). 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 9 regions sampled. The results of the correlation suggest a strong correspondence between

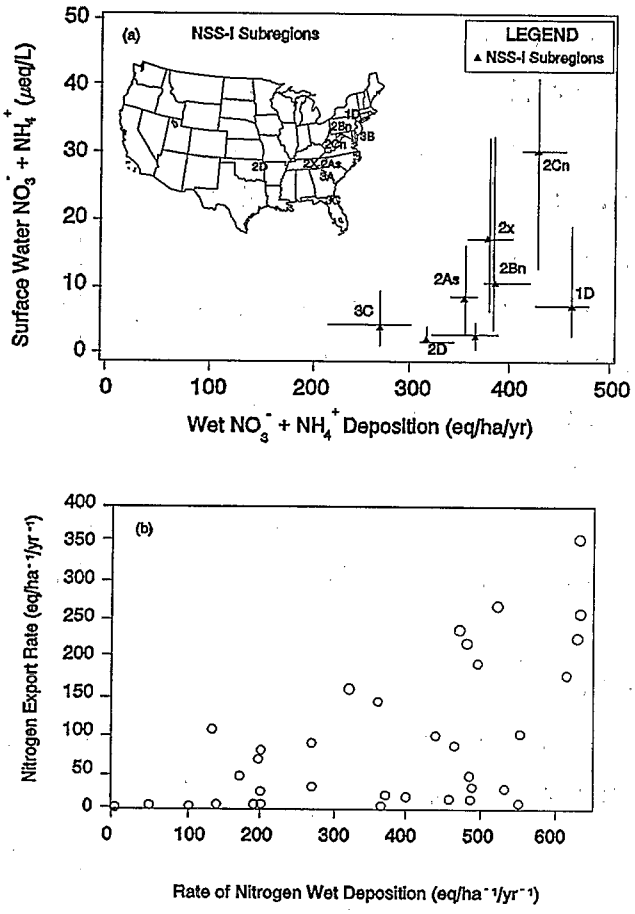


Figure 10-38. (a) Relationship between median wet deposition of nitrogen (NO_3^- + NH_4^+) and median surface water nitrogen (NO_3^- + NH_4^+) concentrations, for physiographic districts within the National Stream Survey that have minimal agricultural activity. [Subregions are: Poconos/Catskills (1D), 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 (NO_3^- + NH_4^+) 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. Original figure from Driscoll et al. (1989a); additional data from Barker and Witt (1990), Edwards and Helvey (1991), Kelly (1986), Katz et al. (1985), Buell and Peters (1988), Weller et al. (1986), Owens et al. (1989), Feller (1987), Stoddard and Murdoch (1991).

median wet deposition of nitrogen in a region, and the median spring base-flow concentration of nitrogen in a region. In addition, the results suggest a threshold rate of wet nitrogen deposition of approximately 2.8 kg N ha^{-1} yr^{-1} 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 $NO_3^- + NH_4^+$). These data are supplemented in Figure 10-38b 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 one year to several decades). Like the data of Kaufmann et al. (1991, Figure 10-38a), these budget data suggest a threshold rate of wet nitrogen deposition of ca. 2.8 kg N ha^{-1} yr^{-1} above which significant export of NO_3^- from watersheds may occur.

10.7.8.2 Eutrophication

Assigning responsibility for the eutrophication of lakes and estuaries to nitrogen oxides 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 non-point 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 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 low concentrations. Results of the National Surface Water Survey (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 (20-30% of the population of lakes sampled by NSWS), and particularly in the Pacific Northwest, although significant numbers may also occur in the Upper Midwest (15-25% 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., 1988; 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 ca. 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 produce estimates in the range of 18 to 31% (Table 10-35). Supplies of nitrogen from deposition exceed supplies from all other non-point sources to the Bay (e.g., agricultural runoff, pastureland runoff, urban runoff), and only point source inputs represent a greater input than deposition.

10.7.8.3 Direct Toxicity

Toxic effects of nitrogen on aquatic biota result from un-ionized ammonia (NH_3), which occurs in equilibrium with ionized ammonium (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,

TABLE 10-35. THREE NITROGEN BUDGETS FOR THE CHESAPEAKE BAY

Source of Nitrogen	EDF Budget (eq × $10^9 \cdot yr^{-1}$		Versar Budget (eq × $10^9 \cdot yr^{-1}$		Refined Budget (eq × $10^9 \cdot yr^{-1}$	
Direct Deposition						
NO_3^-	0.6		0.5		0.4	
NH_4	0.3		-[a]		0.2	
N Load to Bay (from direct deposition)[b]	0.9		0.5		0.6	
Forests						
NO_3^- Deposition	6.4		6.0		4.6	
NH_4^+ Deposition	3.5		-[a]		2.5	
Watershed Rentention		80%		95%		84.6%
In-stream Retention		50%		50%	0.5	35%
Atmospheric NO_3^- Load to	0.6		0.15		0.7	
Bay (from forests)	1.0		0.15			
N Load to Bay (from forests)[b]						
Pastureland						
NO_3^- Deposition	1.7		1.2		0.9	
NH_4^+ Deposition	0.9		-[a]		0.5	
Animal Wastes	13.9		8.4		13.9	
Watershed Retention		95%[c]		94-99%		95%[d]
In-stream Retention		50%[c]		50%		35%
Atmospheric NO_3^- Load to Bay (from pastures)	0.5		0.01-0.04		0.09	
N Load to Bay (from pastures)[b]	1.1		0.05-0.3		0.6	
Cropland						
NO_3^- Deposition	1.8		2.0		1.5	
NH_4^+ Deposition	1.0		-[a]		0.8	
Fertilizers	11.3		5.9-19.3		11.3	
Watershed Retention		70%		76-99%		95%
In-stream Retention		70%		50%		35%
Atmospheric NO_3^- Load to Bay (from cropland)	0.6		0.0-0.2		0.05	
N Load to Bay (from cropland)[b]	4.2		0.04-2.6		0.4	
Residential/Urban						
NO_3^- Deposition	0.3		0.5		0.4	
NH_4^+ Deposition	0.2		-[a]		0.2	
Watershed Retention		35%		62-96%		50%
In-stream Retention		0%		20%		35%
Atmospheric NO_3^- Load to Bay (from urban areas)	0.2		0.01-0.1		0.1	
					0.2	
N Load to Bay (from urban areas)[b]	0.3		0.01-0.1			

TABLE 10-35 (cont'd). THREE NITROGEN BUDGETS FOR THE CHESAPEAKE BAY

Source of Nitrogen	EDF Budget (eq × $10^9 \cdot yr^{-1}$	Versar Budget (eq × $10^9 \cdot yr^{-1}$	Refined Budget (eq × $10^9 \cdot yr^{-1}$
Point Sources	2.4	1.4-2.3	2.4
NO_3^- LOAD TO BAY (FROM DEPOSITION	2.50	0.67-1.06	1.09
TOTAL NITROGEN LOAD TO BAY[b]	9.95	2.16-5.90	4.87
% of N from NO_3^- depostion	25%	18-31%	22.5%

[a]The Versar Budget (Tyler, 1988) does not calculate loads of NH_4^+.
[b]For the EDF Budget (Fisher et al., 1988a) and refined budget total nitrogen load to the Bay includes both NO_3^- and NH_4^+. The Versar Budget (Tyler, 1988) includes only NO_3^-.
[c]Watershed 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.
[d]95% retention was used for animal wastes; 85% retention was used for deposition (see text).
[e]The range of contributions of NO_3^- 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.

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 $\mu mol \cdot L^{-1}$ 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.

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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 nitrogen oxides.

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 (NO_3^-), particles that scatter light. The other forms of NO_x that occur in ambient air, nitric oxide (NO), nitrous acid (HNO_2), and nitric acid (HNO_3), are optically inactive gases and therefore do not contribute to visibility impairment. (Nitrous acid, however, interferes 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 nitric acid in warm climates; in areas with low ambient atmospheric concentrations of ammonia (NH_3); or in areas with high ambient concentrations of sulfate ($SO_4^=$), since sulfate preferentially reacts with available atmospheric ammonia.

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 areas;

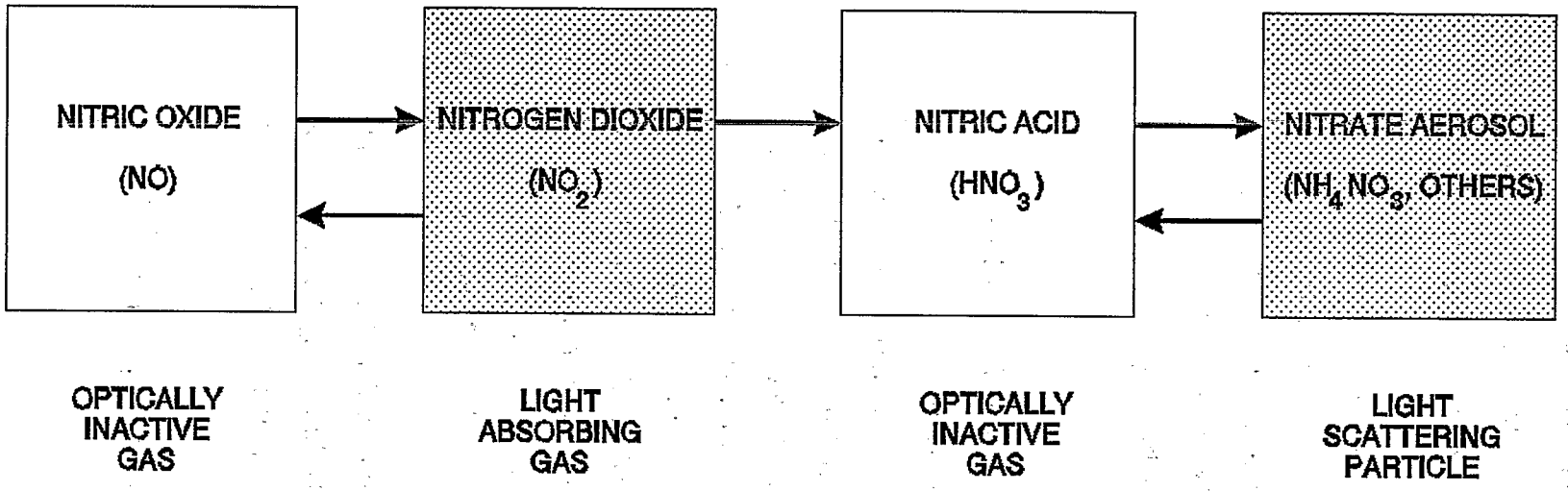

Figure 11-1. The family of nitrogen oxides and those that impair visibility.

particularly during winter and near significant ammonia sources (such as cattle grazing fields and 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 non-nitrogenous 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, nitrogen dioxide (NO_2) and nitrate aerosols (NO_3^-), 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, while scattered light is re-radiated 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 radiation 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 Samuelsen, 1975, 1978; Latimer et al., 1978; White et al., 1986):

$$\frac{dI(\lambda)}{dr} = -b_{ext}(\lambda)I(\lambda) + \left[\frac{p(\lambda,\theta)}{4\pi}F_s(\lambda) + D\right]b_{scat}(\lambda) \qquad (11\text{-}1)$$

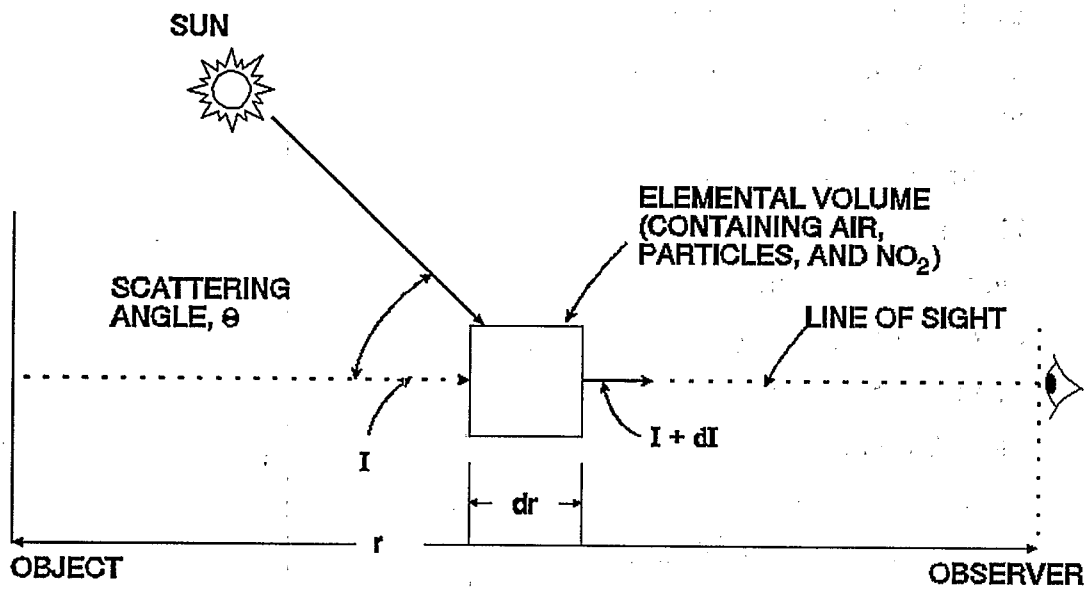

Figure 11-2. Schematic of an elemental volume of haze along a line of sight.

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),

$p(\lambda,\theta)$ = the scattering distribution or phase function for the scattering angle θ,

$F_s(\lambda)$ = the solar flux (watt/m^2/μm) incident on the line of sight,

D = the diffuse light source term. (Diffuse light emanates from directions other than that of the sun. This light results from light scattered from other portions of the atmosphere and light reflected from the surface of the Earth and from clouds.)

$b_{scat}(\lambda)$ = the light scattering coefficient, and

$b_{ext}(\lambda)$ = 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, while 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, while 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. Since nitrate aerosol scatters light, it can either brighten or darken the sky and objects. In Equation 11-1, the light extinction coefficient is the sum of its light scattering and light extinction components:

$$b_{ext}(\lambda) = b_{scat}(\lambda) + b_{abs}(\lambda) = (b_{sg} + b_{sp}) + (b_{ag} + b_{ap}). \qquad (11\text{-}2)$$

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 N_2 and O_2). 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 ($< 2.5\ \mu m$ in diameter) and coarse ($> 2.5\ \mu m$ 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.

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

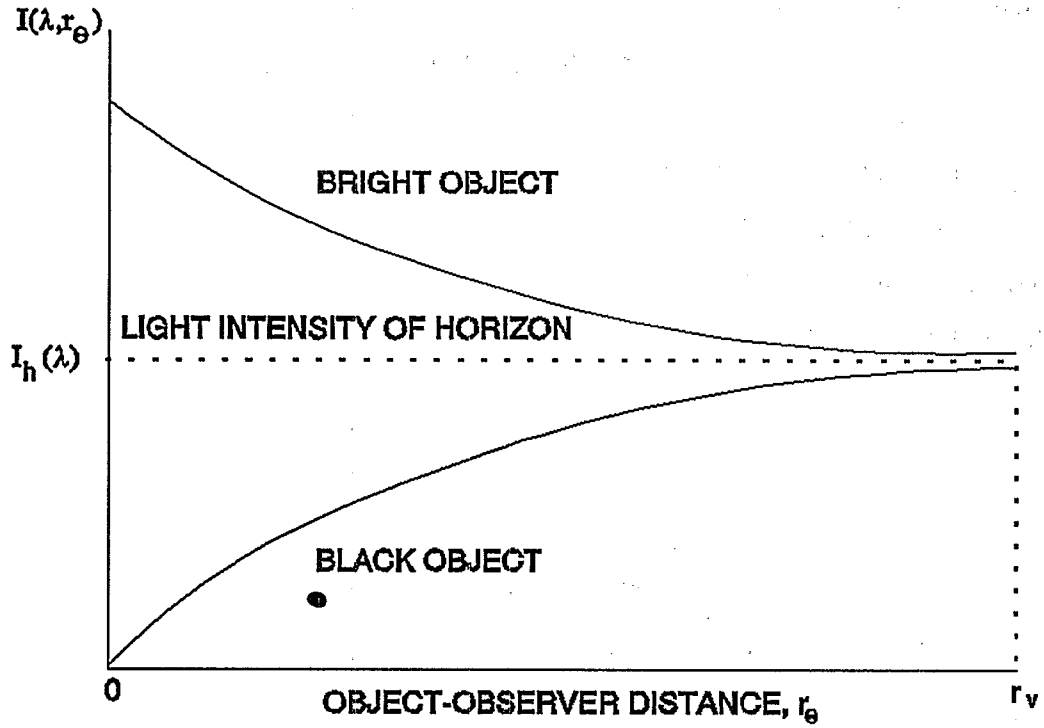

Figure 11-3. Effect of a homogeneous atmosphere on light intensity of bright and dark objects as a function of distance along a line of sight.

Source: Latimer and Ireson (1980).

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 $\lambda = 0.4\ \mu m$) than at the red end ($\lambda = 0.7\ \mu m$).

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). 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 ($\mu g/m^3$) 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 (absorption, b_{ap}, and especially scattering, b_{sp}) is a strong function of particle size (see Figure 11-4). Fine particles, those with diameters less than 2.5 μm, are much more effective per unit mass in scattering light than are coarse particles, those with diameters > 2.5 μm. Particle scattering efficiency is a maximum

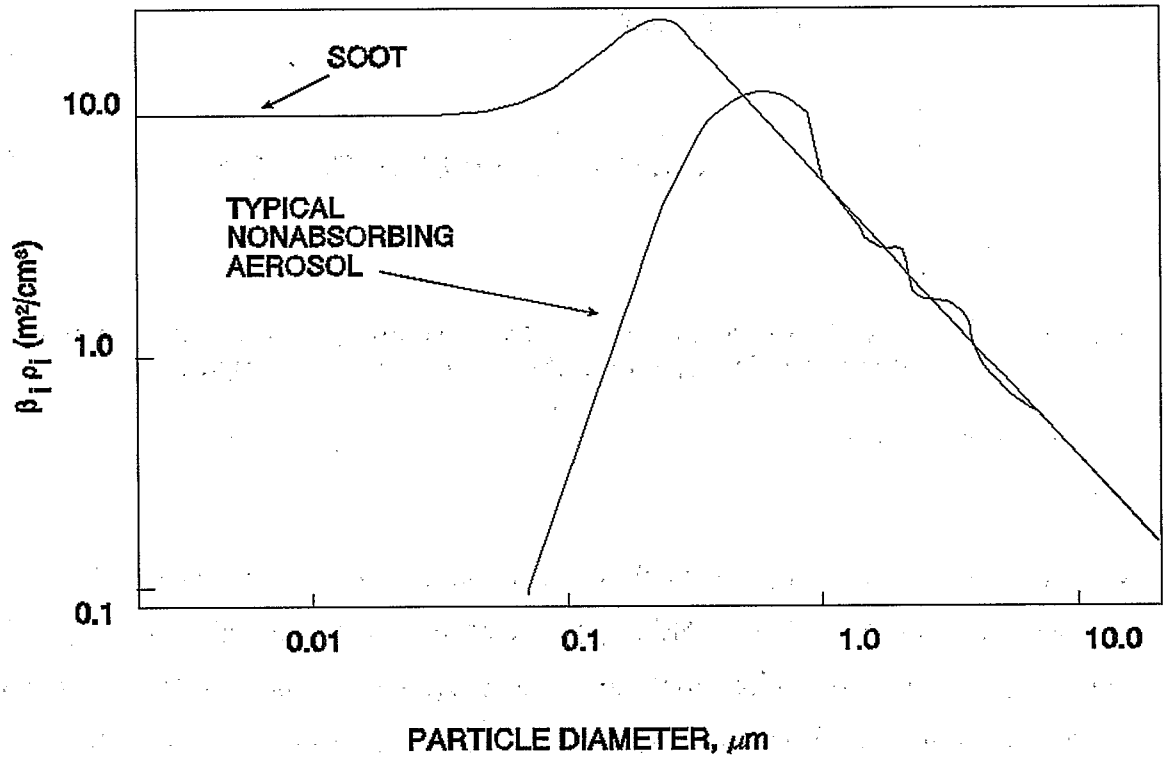

Figure 11-4. Light extinction efficiency at λ = 0.55 μm as a function of particle size for soot and for typical, nonabsorbing atmospheric aerosol.

Source: Latimer (1988a) after Bergstrom (1973).

for particles having a diameter of approximately 0.5 μm. Coarse particles have scattering efficiencies that are approximately an order of magnitude smaller (see Figure 11-4).

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; however, in a number of summertime studies in the eastern U.S., 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 ammonia 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 N_2O_5-H_2O reactions on the surfaces of particles. Nitrate is in the submicron fine mode when it reacts directly with ammonia to form ammonium nitrate (Orel and Seinfeld, 1977; Wolff, 1984). The submicron nitrate forms when conditions are favorable (abundant ambient ammonia 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 (λ = 0.55 μm) 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 (λ = 0.4 μm) 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, California, during August and September 1970 and concluded that NO_2 had a significant effect on atmospheric color 20 percent 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 $\theta > 90°$), 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):

$$I_r(\lambda) = I_0(\lambda) \exp(-\tau) + J\,[1 - \exp(-\tau)], \qquad (11\text{-}3)$$

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 ($= \int b_{ext}\, dr$),

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):

$$I_{hNO_2}/I_{h0} = (1 + b_{ag}/b_{ext})^{-1} \qquad (11\text{-}4)$$

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 coefficient over the visible spectrum (Dixon, 1940; Latimer and Ireson, 1980). The value at the blue end of the visible spectrum, $\lambda = 0.4\ \mu m$, is 1.71 $km^{-1}\ ppm^{-1}$, more than five times larger than the value at the center of the visible spectrum at a green wavelength $\lambda = 0.55\ \mu m$ (0.33 km^{-1} ppm^{-1}), and approximately 100 times larger than at the red end of the spectrum at a wavelength of 0.7 μm (0.017 km^{-1} ppm^{-1}). When Equation 11-4 is evaluated as a function of wavelength (λ), the curves shown 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

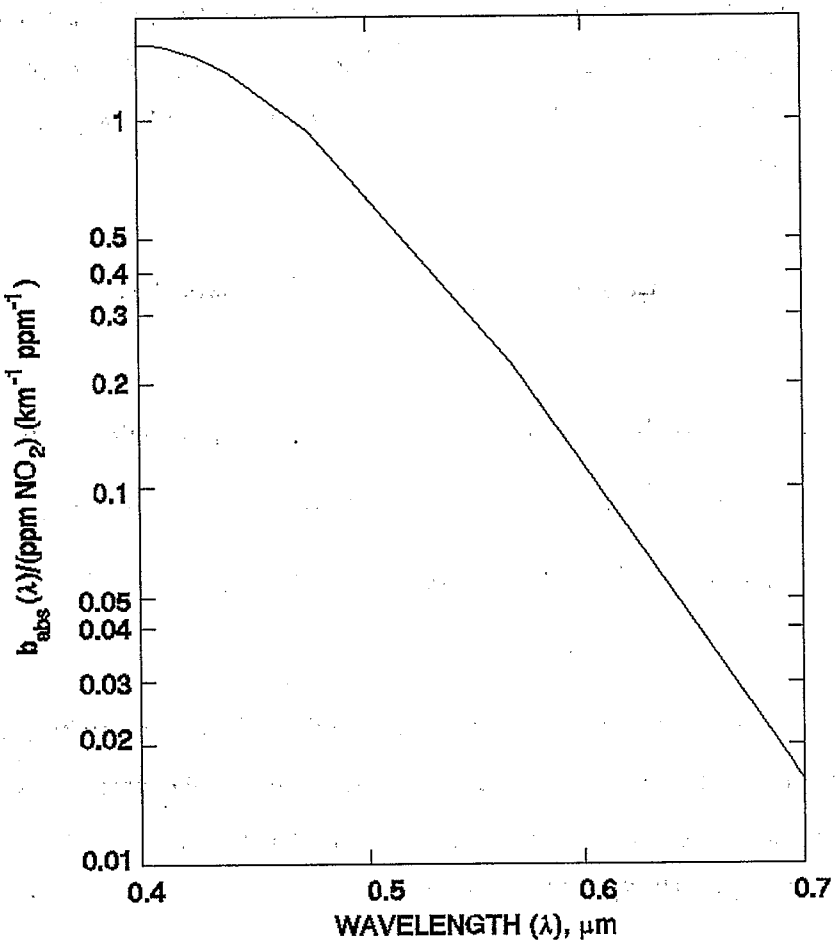

Figure 11-5. Light absorption efficiency of nitrogen dioxide as a function of the wavelength of light in the visible spectrum, 0.4 μm < λ < 0.7 μm.

Source: Latimer and Ireson (1980) after Dixon (1940).

product of 0.3 ppm-km, the horizon sky light intensity at $\lambda = 0.4$ μm is about 14 percent 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 $\mu g/m^3$) NO_2 associated with a visual range of 10 km (typical of urban haze) and by 0.0015 ppm (3 $\mu g/m^3$) NO_2 associated with a visual range of 200 km (typical of much of the nonurban western U.S.).

Atmospheric aerosols, including particulate nitrates, can also cause atmospheric discoloration (Ahlquist and Charlson, 1969; Husar and White, 1976). The scattering

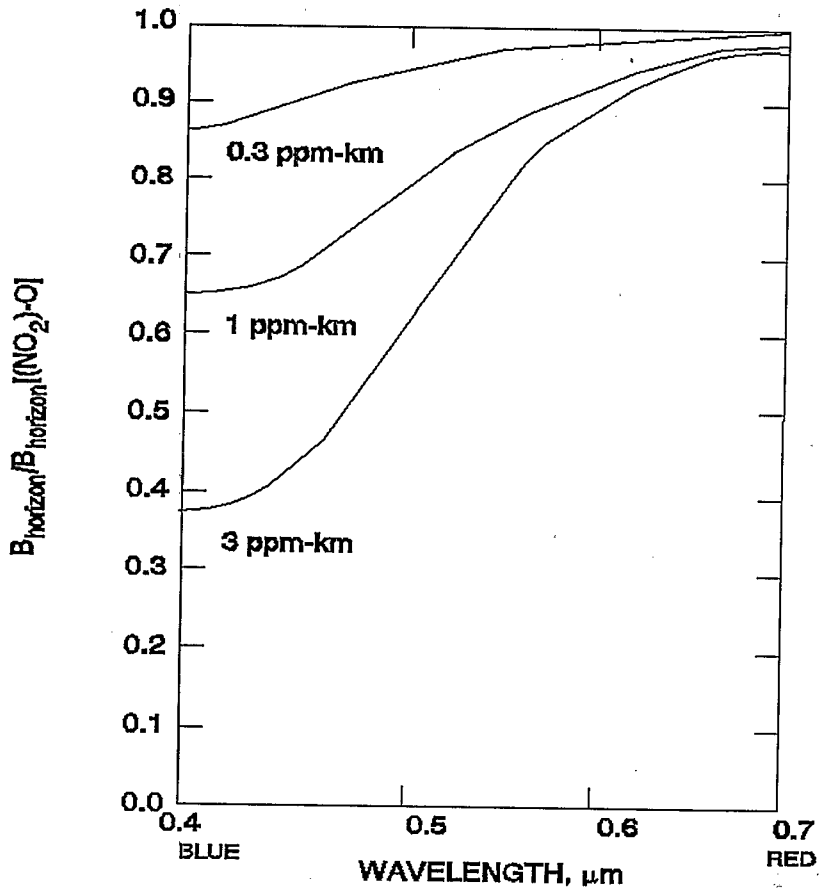

Figure 11-6. Effect of nitrogen dioxide on horizon sky brightness as a function of the wavelength of light; relative horizon brightness, $b_{ext}/(b_{ext} + b_{ag})$ for selected values of the product of NO_2 concentration and visual range assuming that b_{ext} = 3/(visual range).

Source: White (1982) adapted from Hodkinson (1966).

coefficient of particles smaller than 1.5 μm in diameter can be strongly dependent on the 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 μm has a light scattering coefficient b_{scat} which is inversely proportional to wavelength λ. Thus, light scattering at the blue end (λ = 0.4 μm) of the visible spectrum would be 75 percent greater (7/4 = 1.75) than at the red end (λ = 0.7 μm). Since 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 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

[a]Geometric standard deviation $\sigma_g = 2$.
[b]α is defined as follows:

$$b_{scat}(\lambda_1) = b_{scat}(\lambda_2) \left[\frac{\lambda_1}{\lambda_2}\right]^{-\alpha}$$

(appropriate for $0.4 < \lambda < 0.7$ μm).

Source: Latimer and Ireson (1980).

Husar and White (1976) formulated the problem of atmospheric coloration rigorously in terms of radiation transfer theory. A solution was derived from theory and from aerosol size distributions measured in Los Angeles. They found that aerosol (without NO_2) could cause yellow-brown discoloration, and that this discoloration would increase as NO_2 concentrations increase and as the scattering angle θ increases. Noticeable discoloration from NO_2 was found to occur at concentrations as low as 0.05 ppm. The discoloration effect caused by particles, unlike that caused by NO_2, is dependent on the scattering angle, θ, with most intense effects occurring in situations in which the sun is behind the observer ($\theta > 90°$). 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 scatter.

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 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 which 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 5 percent is supported by the literature (Middleton, 1952; U. S. Environmental Protection Agency, 1979; Latimer, 1988b), the threshold human visual perception threshold is commonly assumed to be a contrast of 2 percent.

Koschmieder (1924) developed a formula for visual range, which is based on the assumptions that the threshold contrast is 2 percent, 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:

$$r_v = -\ln(C_{min})/b_{ext}, \qquad (11\text{-}5)$$

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 percent is used above, the Koschmieder equation becomes

$$r_v = 3.9/b_{ext}, \qquad (11\text{-}6)$$

the most common form of the equation. If the perceptibility threshold is assumed to be 5 percent, which appears to correlate best with common airport visibility measurements (Johnson, 1981; Latimer, 1988b), the equation becomes:

$$r_v = 3/b_{ext}. \qquad (11\text{-}7)$$

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 m^2/g (U.S. Environmental Protection Agency, 1979). Since 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

The role played by nitrate particles in urban, regional, and layered haze and in plumes is currently uncertain because of the volatile nature of this species. Unlike sulfate, which is always in the particulate phase, nitrate often remains in the gas phase as nitric acid. In order for condensation of particulate nitrate (ammonium nitrate, NH_4NO_3) to occur, there must be sufficient atmospheric ammonia to react with nitric acid. Furthermore, the vapor pressure of ammonium nitrate is strongly temperature-dependent, so that even if ammonia is present in the atmosphere nitrate particles may not condense because of moderate or high temperatures.

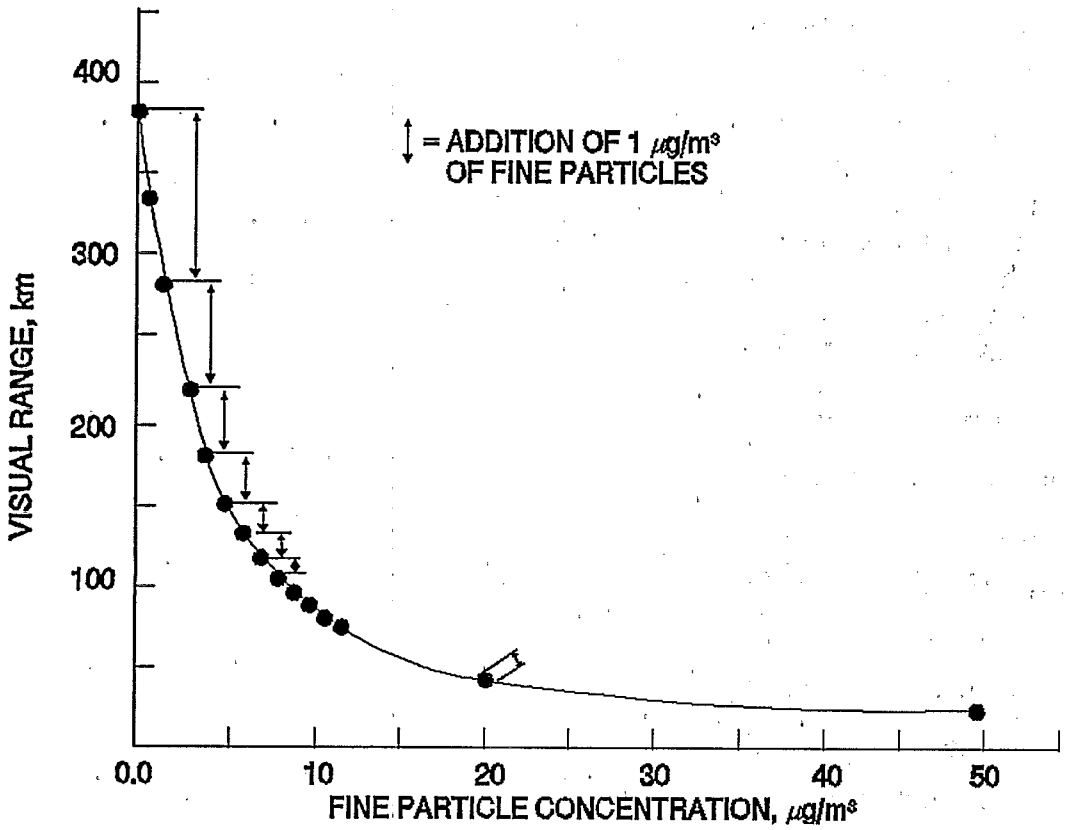

Figure 11-7. Effect on visual range of incrementally adding 1 $\mu g/m^3$ of fine particles having a light extinction efficiency of 4 m^2/g. (Greater light extinction efficiencies and visibility reduction than shown here would occur with sulfate and nitrate aerosols at high relative humidities. See text.)

Source: U.S. Environmental Protection Agency (1979).

The volatility of particulate ammonium nitrate 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 ammonium nitrate is deliquescent; it absorbs water from the atmosphere at moderate to high relative humidities. Thus, like sulfate, the scattering efficiency of ammonium nitrate 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 ammonia is present to neutralize gas phase nitric acid (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). Ammonia reacts preferentially with acidic sulfate compounds until it is fully neutralized as ammonium sulfate (Saxena et al., 1986). If sufficient gas phase ammonia is left after sulfate neutralization and temperatures are low enough, ammonium nitrate aerosol will condense. At relative humidities above 62 percent, the deliquescent point for ammonium nitrate, 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 ammonium nitrate "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 nitric acid and ammonia concentrations and to the warm temperatures during the non-winter months. Thus, the conditions can be summarized under which fine nitrate particles are most likely to form: high ambient concentrations of ammonia and nitric acid (e.g., Los Angeles, Denver), low ambient concentrations of sulfate (e.g., most of the western U.S.), 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 ammonia and

nitric acid (e.g., intermountain West), high ambient concentrations of sulfate (e.g., the eastern U.S.), high temperatures (e.g., summer), and low relative humidities (e.g., the Southwest). Furthermore, if sufficient coarse particles exist that can react with nitric acid (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 extreme volatility of particulate nitrate makes its measurement extremely difficult and uncertain (Sloane and White, 1986). Significant positive and negative artifacts can occur with different measurement techniques using different filter media. Glass fiber filters have a significant positive nitrate particle artifact because they tend to sorb nitric acid vapor (Appel et al., 1985). Significant particle nitrate loss from quartz filters in storage was noted by Dunwoody (1986). Teflon filters may have a significant negative artifact because nitrate is volatilized during or after the sampling, resulting in a potential underestimation of nitrate particle mass. Volatilization losses of fine particle nitrate are likely to be even greater for a Teflon filter loaded with acid sulfate than from a clean filter. As reported by a number of researchers, actual particle nitrate concentrations tend to be about 20 to 50 percent higher than Teflon-based measurements, on an annual average basis (Appel et al., 1981; Stevens, 1987; John, 1986; Cadle, 1985). However, others (White and Macias, 1987; Malm and Gebhard, 1988) suggest that at least during winter conditions nitrate particle measurements might be low by factors of three to five. The denuder/nylon-filter method may be the most accurate measurement technique (Malm et al., 1989; Allegrini and De Santis, 1989; Stevens et al., 1988; Mulawa and Cadle, 1985); however, only limited data are available that were obtained with this technique. 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 percent). 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 et al. (1981) 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. Figure 11-8 through 11-12 summarize the light extinction coefficients for 1 $\mu g/m^3$ of sulfate or nitrate aerosol, or both, as a function of humidity. Figure 11-8 shows that pure ammonium sulfate exhibits a deliquescent point at 80 percent relative humidity. At humidities above 80 percent, water vapor condenses, thereby increasing the aerosol particle size, volume, and light scattering. At humidities below 80 percent, the extinction efficiencies range from 1 to 4 m^2/g of sulfate; while above 80 percent humidity, extinction efficiencies can increase considerably above 10 m^2/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 ammonium nitrate aerosol as a function of relative humidity. At and above the deliquescent point at 62 percent 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 ammonium sulfate (80 percent RH) and ammonium nitrate (62 percent RH). Internally mixed aerosols, in which the sulfate and nitrate occur mixed within the same particle, do not exhibit distinct deliquescent points and have less water associated with them at a given humidity; and hence have lower 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.

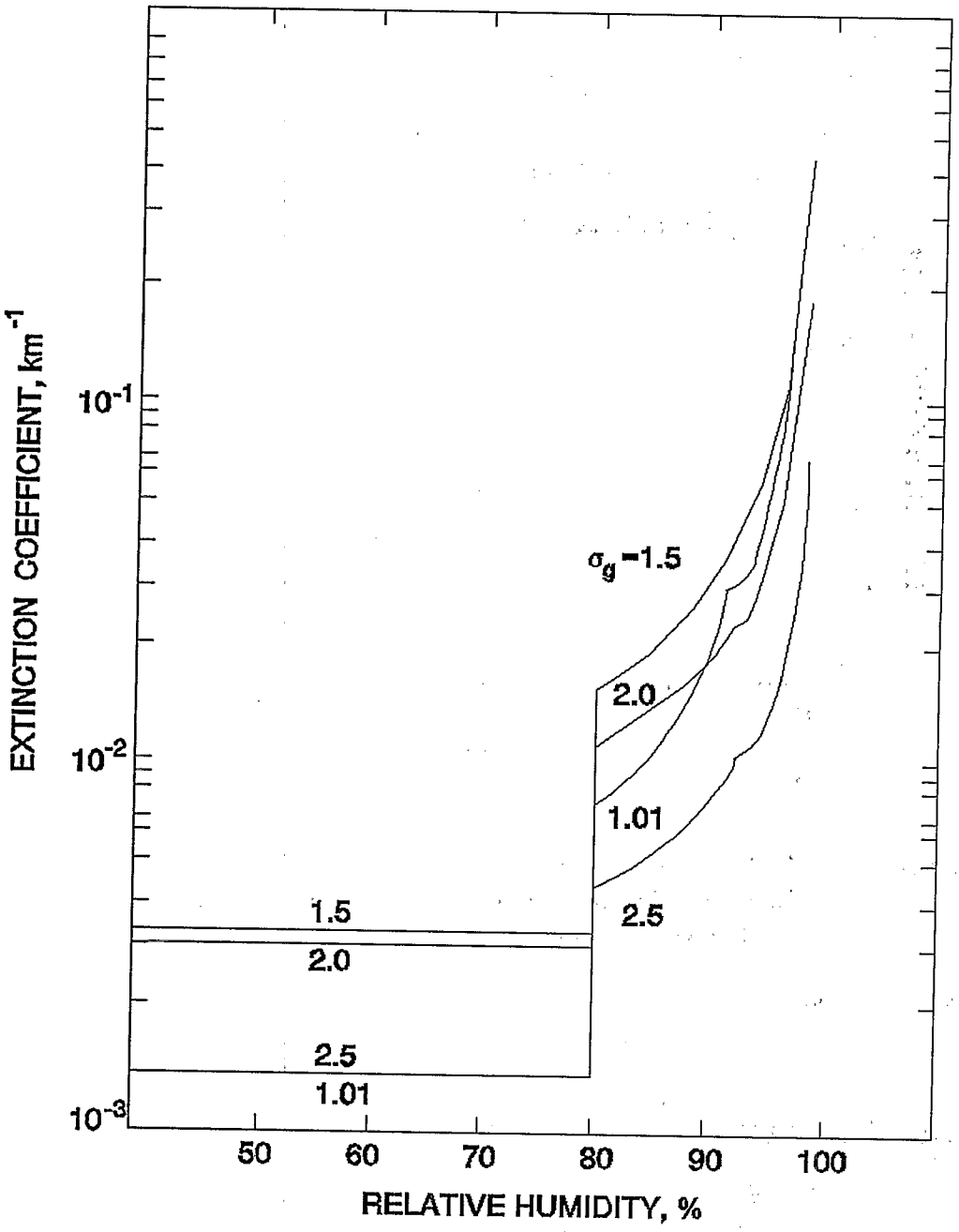

Figure 11-8. Light scattering coefficient for 1 $\mu g/m^3$ of sulfate or nitrate aerosol as a function of relative humidity; b_{scat} versus relative humidity for ammonium sulfate aerosol (having particle size distributions characterized by D_g = 0.2 μm and α_g = 1.01, 1.5, 2.0, and 2.5).

Source: Tang et al. (1981).

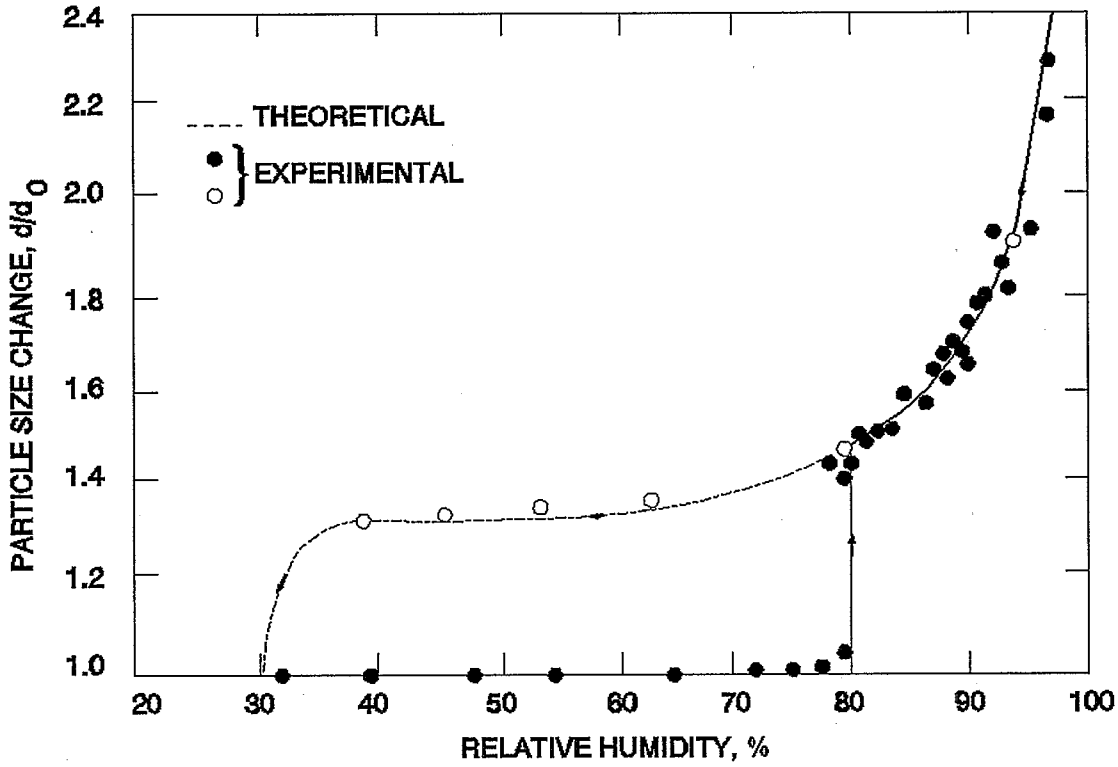

Figure 11-9. Light scattering coefficient for 1 $\mu g/m^3$ of sulfate or nitrate aerosol as a function of relative humidity; b_{scat} versus relative humidity for ammonium sulfate aerosol showing the effect of hysteresis.

Source: Tang et al. (1981).

11.5 ROLE OF NITROGEN OXIDES IN URBAN HAZE

The most significant effects of nitrogen dioxide and especially nitrate aerosols have been observed in urban hazes, especially in western urban areas such as those in California; and in wintertime urban hazes, such as those in Phoenix and Denver. The importance of nitrate has been studied empirically by many researchers, but the caveats noted above regarding measurement uncertainties should be kept in mind when interpreting these studies. In addition, research has been carried out in recent years on theoretical approaches for analyzing urban haze chemical reactions and aerosol coagulation.

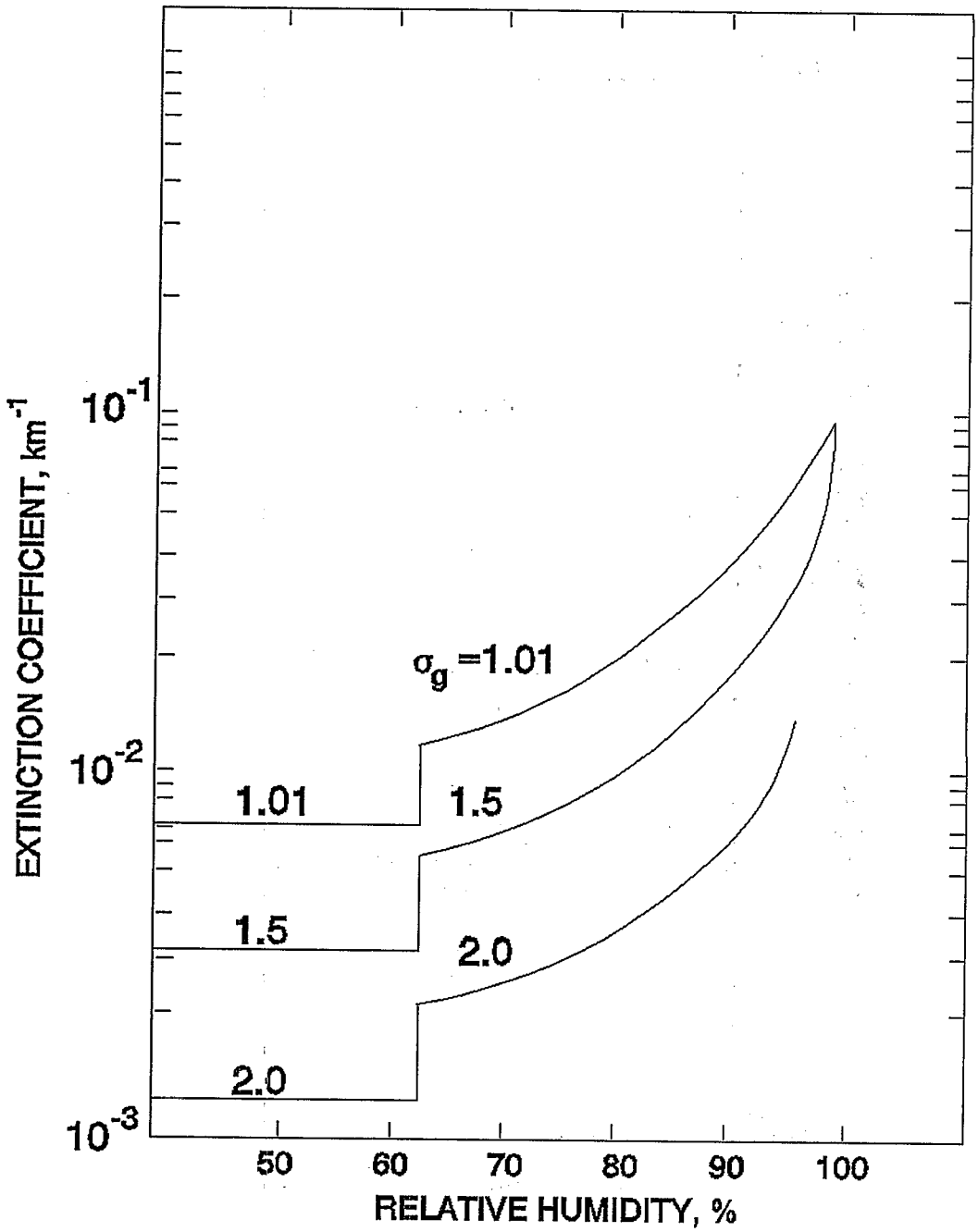

Figure 11-10. Light scattering coefficient for 1 $\mu g/m^3$ of sulfate or nitrate aerosol as a function of relative humidity; b_{scat} versus relative humidity for ammonium nitrate aerosol (having particle size distributions characterized by D_g = 0.6 μm and α_g = 1.01, 1.5, and 2.0).

Source: Tang et al. (1981).

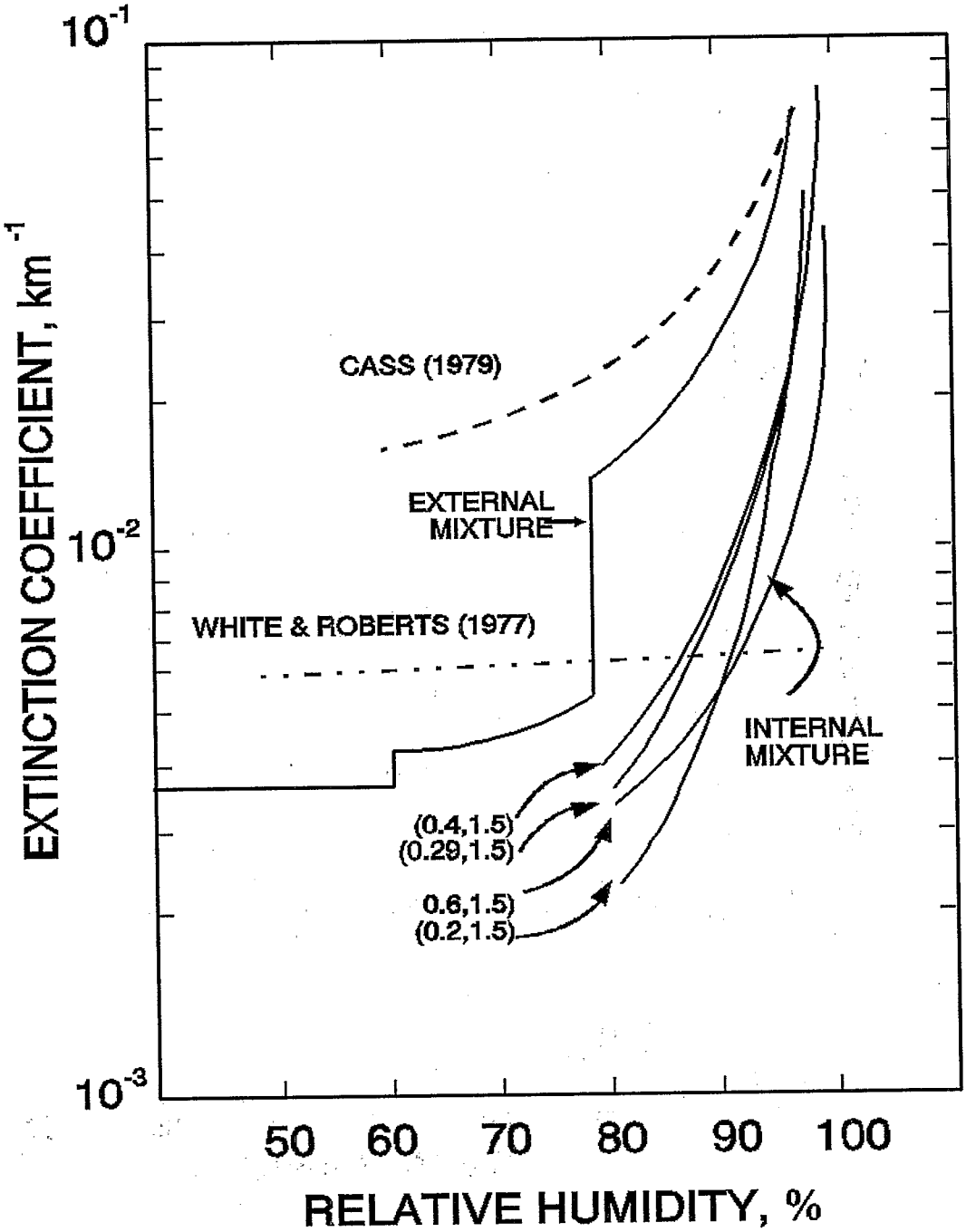

Figure 11-11. Light scattering coefficient for 1 $\mu g/m^3$ of sulfate or nitrate aerosol as a function of relative humidity; b_{scat} versus relative humidity for externally and internally mixed sulfate and nitrate aerosols (S:N = 3:1) for indicated size distributions (D_g, α_g).

Source: Tang et al. (1981).

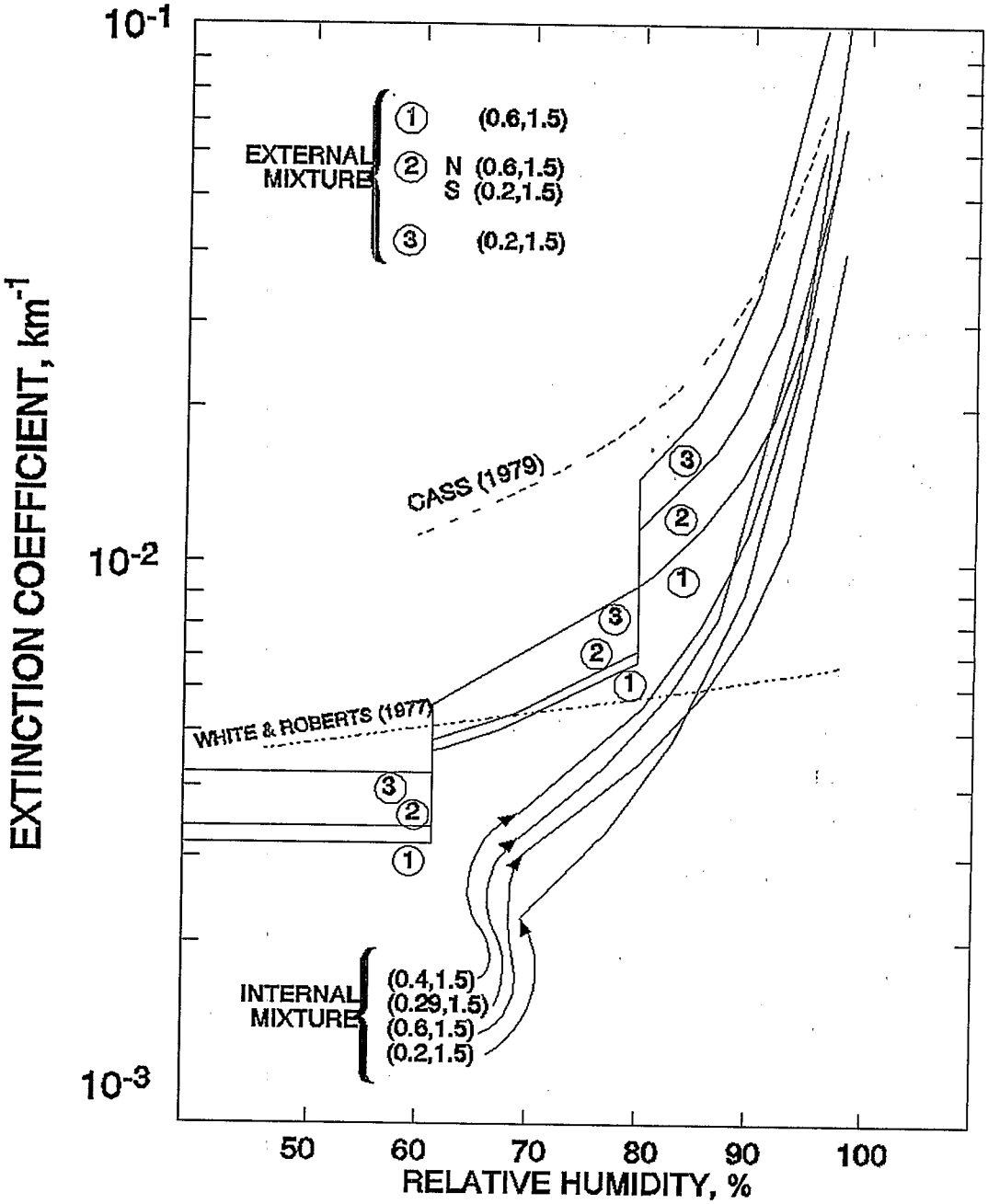

Figure 11-12. Light scattering coefficient for 1 $\mu g/m^3$ of sulfate or nitrate aerosol as a function of relative humidity; b_{scat} versus relative humidity for externally and internally mixed sulfate and nitrate aerosols (S:N = 1:2) for indicated size distributions (D_g, α_g).

Source: Tang et al. (1981).

11.5.1 California Urban Areas

The most work has been done and the most significant effects of NO_x have been observed in California, especially in the Los Angeles area. 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 the Aerosol Characterization Experiment (ACHEX). Using linear regression techniques, they estimated that nitrate aerosols contributed, on average, about 27 percent of the total light scattering coefficient. Nitrates were found to have a light scattering efficiency, having units of m^2/g of nitrate anion (multiply anion mass by 1.3 to obtain total ammonium nitrate mass), of $1.7 \pm 3.9\ \mu^2$, where μ is the relative humidity (in percent divided by 100). Thus, at a humidity of 50 percent, the light scattering coefficient of nitrates was estimated to be $2.7\ m^2/g$. 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 regression to study the relationships between sulfate and nitrate concentrations and visibility in Los Angeles over the decade, 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 were 4.1 and $2.5\ m^2/g$, respectively. For a relative humidity of 50 percent, this would yield overall respective light extinction efficiencies for sulfate and nitrate and associated water of 8.2 and $5\ m^2/g$.

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 percent 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 percent of b_{ext}.

In probably the most accurate assessment of the role of nitrate, Appel et al. (1985) studied the relationship between light extinction and aerosol composition using empirical data

from three California cities: San Jose, Riverside, and Los Angeles. Multiple linear regression was used to relate aerosol concentrations to measured light extinction. Emphasis was placed in the study on minimizing the sampling artifacts that may have caused substantial errors in previous studies. A linear regression equation that related concentrations of aerosol species and NO_2 to measured b_{ext} provided a very good fit ($r = 0.96$), with average agreement within 6 percent. The regression coefficient for fine particle nitrate was found to be higher than in other studies. The coefficient, interpreted as the light extinction efficiency of nitrate and associated water, was $6.3(1 + \mu)$ m^2/g, where μ is the relative humidity as defined previously. Using the average humidity of 46 percent measured during the sampling yields a nitrate light extinction efficiency of 9.4 m^2/g. The average sulfate extinction efficiency was comparable: 8.6 m^2/g for the average humidity of the sampling period. Nitrate aerosol, on average, contributed 36 percent of total light extinction in these three cities; NO_2 contributed 8 percent.

The contributions of various aerosol constituents to total light extinction at two locations in the Los Angeles area in 1980 were estimated by Pratsinis et al. (1984). Particulate nitrate aerosol contributed 4 and 1 percent and NO_2 contributed 7 and 6 percent of the light extinction in Lennox and Duarte, respectively. The contributions of the NO_x species were considerably less than those from sulfate (31 to 53 percent), organics (13 to 23 percent), and elemental carbon (14 to 21 percent). Gray et al. (1984) determined that nitrate aerosol contributed 13 percent of the light extinction in downtown Los Angeles in 1982.

11.5.2 Urban Areas in the Western United States

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; Lewis et al., 1986). 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 μm in diameter. Elemental carbon (soot) was found to be the most significant contributor, accounting for 37 percent of light extinction above natural Rayleigh background. Sulfate

(and associated water) was found to contribute 20 percent, nitrate (and associated water) 17 percent, and organic carbon 13 percent; the remaining fine particle matter contributed 7 percent, and NO_2 contributed 6 percent. All measurements were based on a wavelength of light of 0.475 μm (Hasan and Dzubay, 1983). The contribution of NO_2 would have been larger at the blue end of the visible spectrum. If the contribution of nitrate and NO_2 are combined, the total NO_x contribution to Denver winter haze is 23 percent, second only to the contribution of elemental carbon. 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 percent, combustion of natural gas, oil, and coal (in power plants and boilers) accounted for more than half (14 percent), while automotive contributions were the largest part of the remainder (9 percent). 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 ammonium nitrate aerosol, regression gave a scattering efficiency of 2.4 to 2.5 m^2/g, while theoretical calculations yielded a scattering efficiency of 3.7 to 3.8 m^2/g.

Solomon and Moyers (1984) studied the contributors to light extinction in Phoenix, Arizona, during January 1983, when winter hazes were observed. Elemental carbon was by far the largest contributor to light extinction, at 41 percent of b_{ext}, on the average. Approximately equal contributions resulted from nitrate (15 percent), organic carbon (15 percent), and sulfate (13 percent). The contribution from NO_2 averaged 3.2 percent. Solomon and Moyers (1986) reported that the fine nitrate aerosol measured in Phoenix in January 1983 was 13.4 percent of the total fine particle mass, comparable to the 12.2 percent 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. They concluded that motor vehicle emissions accounted for most of the nitrate and other fine particle mass that caused the observed haze.

Dzubay et al. (1982) studied the relationships between visibility and aerosol composition during summer in Houston, Texas. Nitrate was found mainly on coarse particles and was determined to be an insignificant (0.5 percent) 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 ammonia 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 percent of b_{ext}.

Stevens et al. (1988) reported measurements made during the winter of 1986-1987 in Boise, Idaho. There nitrate aerosol was a significant component of total light extinction, contributing 13 percent of the fine particle mass. Less than 10 percent of the total nitrate was left in the vapor phase as nitric acid. This study represents one of the few good sources of fine particle nitrate data; measurements in this study were made using an annular denuder followed by Teflon® and nylon filters.

11.5.3 Urban Areas in the Eastern United States, Europe, and Mexico

Few studies of the role of nitrate aerosol in visibility impairment have been conducted outside of the western United States. Furthermore, because of the significant problems inherent in measuring particulate nitrate (discussed in preceding sections), the studies described here may not have accurately measured particulate nitrate concentrations. This problem should be kept in mind. Nitrate aerosol contributions appear to be lower in the eastern United States than in California and other western U.S. cities, perhaps because of higher sulfate concentrations competing for the available atmospheric ammonia. 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 percent of total light extinction in Columbus, Ohio. 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 $\mu g/m^3$; coarse particle nitrate was higher, at 1 $\mu g/m^3$. 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 percent of b_{ext} in the Wolff et al. study (1982).

Colbeck and Harrison (1984) found significant quantities of nitrate aerosol in northwest England. Visibility there was strongly correlated with both nitrate and sulfate concentrations. Diederen 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 percent of total b_{ext}, and NO_2 to contribute 2 percent.

Bravo et al. (1988) found high concentrations of nitrate aerosol and NO_2 in Mexico City (6.4 $\mu g/m^3$ and 0.07 ppm); however, the contributions of these species to the total light extinction budget were relatively small (5 and 2.5 percent) because of the much higher concentrations of other aerosol species. Total light extinction was dominated by soot (31 percent), sulfate (30 percent), organics (15 percent), and other species (16 percent).

11.5.4 Modeling Urban Haze Effects

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 most effectively reduced by reducing ammonia (NH_3) emissions, especially from farm-related activities.

Russell et al. (1988) developed 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.

11.6 ROLE OF NITROGEN OXIDES IN NONURBAN REGIONAL HAZE

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 nitric acid (HNO_3) and ammonia (NH_3), high ambient temperatures, and low humidities in the West; and because of high sulfate concentrations in the East that compete for available ammonia.

11.6.1 Nonurban Areas of the Western United States

As noted previously (Section 11.5.3), few studies of the role of nitrate aerosol in visibility impairment have been conducted outside of the western United States. Furthermore, because of the significant problems inherent in measuring particulate nitrate (discussed in preceding sections), the studies described below may not have accurately measured particulate nitrate.

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 ammonium nitrate was about 8 percent of the fine particle mass.

White and Macias (1987) found very low concentrations of nitrate aerosol in the nonurban, intermountain West. Measurements of nitrate aerosol concentrations averaged 0.09 $\mu g/m^3$. 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 percent of b_{ext}.

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 $\mu g/m^3$. Multiple linear regression analysis suggested that nitrate particles had an average scattering efficiency of 4.7 m^2/g and contributed 6 to 14 percent 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 percent of fine particle extinction, and organics, which contributed 15 to 16 percent.

11.6.2 Nonurban Areas of the Eastern United States

Mathai and Tombach (1987), in their review of visibility and aerosol measurements in the eastern United States, concluded that fine nitrate concentrations averaged 1 $\mu g/m^3$. 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 $\mu g/m^3$.

Wolff and Korsog (1989) found that NO_2 (averaging 4 ppb) accounted for less than 1 percent of total light extinction in the Berkshire Mountains of Massachusetts in the summer of 1984. Sulfate and associated water caused most (77 percent) 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, North Carolina (nonurban but near urban areas), NO_2 light absorption accounted for only 2 percent of total light extinction. Particle scattering caused most of the light extinction (75 percent), followed by Rayleigh scattering from air (7 percent) and particle light absorption (7 percent).

11.6.3 Modeling Regional 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 percent) of the manmade fraction, nitrate was estimated to be the next largest contributor (10 to 20 percent). Although manmade organic and elemental carbon contributions to regional haze were found to be small (less than 10 percent 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 the optically inactive nitric acid (HNO_3) and the light-scattering ammonium nitrate aerosol (NH_4NO_3). This uncertainty resulted largely from the uncertainty regarding background concentrations of ammonia (NH_3), which is essential to the formation of ammonium nitrate 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, 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 relatively unbiased and were highly correlated with actual measurements. The average nitrate aerosol concentration predicted by the model was 0.22 $\mu g/m^3$, approximately 2.4 times the average measured during the Western Regional Air Quality Study in 1981 of < 0.1 $\mu g/m^3$ that was reported in Tombach et al. (1987) and the value of 0.09 $\mu g/m^3$ reported by White and Macias (1987).

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 $\mu g/m^3$ was predicted. This value compares reasonably well with the average of 0.16 $\mu g/m^3$ measured during a special study in 1986 (Latimer, 1988c) and the average of 0.38 $\mu g/m^3$ 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 percent of extinction from manmade sources (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 particle chemical composition and concentration and visibility or light extinction were compiled. Using an assumed nitrate light-scattering efficiency of 8 m^2/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 percent to total extinction, except in Portland, Oregon, where it was 11 to 14 percent; Denver, Colorado, 16 percent; Los Angeles, California, 20 percent; and Riverside, California, 40 percent. Latimer (1988a) found that measured visual ranges agreed well with visual ranges derived from the measured aerosol constituents and their respective light extinction efficiencies.

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 plume visual impact computer models and to develop technical guidance for plume visual impact evaluation as part of the implementation of U.S. 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):

$$C_{plume} = [J_{plume}/J_{back} - 1]\,[1 - \exp(-\tau_{plume})]\,[\exp(-b_{ext}\, r_p)], \qquad (11\text{-}8)$$

where

C_{plume} = contrast of the plume against the horizon sky $([I_{plume} - I_{sky})/I_{sky}]$;

J = source function defined previouly;

τ_{plume} = optical thickness of the plume ($\int b_{ext}\, dr$);

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 ($b_{ext} \approx 0$), then the last term in this equation equals 1, and the following equation for an NO_2 plume is obtained:

$$C_{plume} = -[1 - \exp(-\tau_{plume})] = -[1 - \exp(\int_{plume} b_{ag}\, dr)]. \qquad (11\text{-}9)$$

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 $\mu g/m^3$) of NO_2 at $\lambda = 0.55\ \mu m$ or by 0.012 ppm (22 $\mu g/m^3$) at $\lambda = 0.4\ \mu m$. 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-km (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 μm. 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 a power plant plume in the southwestern United States as part of the VISTTA project, Richards et al. (1981) never found particulate nitrate even though nitric acid 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 ammonium ion. Hegg and Hobbs (1983) measured the constituents of another power-plant plume in the Southwest and found rapid formation of both nitric acid and nitrate aerosol. Nitrate aerosol constituted 15 to 75 percent of the nitrate in the plume. Measured plume aerosol size was primarily in the 0.25 μm 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 ammonia 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 a coal-fired power plant plume in the Southwest. 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 a large power plant in the

Southwest, well-controlled for particulate, and at less well-controlled power plants in the Midwest and 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 CONTRIBUTIONS OF NITROGEN OXIDES TO THE LIGHT EXTINCTION BUDGET

Trijonis (1987) evaluated the relative contributions of NO_2 and nitrate aerosol to visibility by comparing the light extinction caused by these NO_x species to total light extinction for field studies in which the total light extinction and the chemical composition of the haze were measured simultaneously. Tables 11-2 and 11-3 summarize the results for NO_2 and nitrate aerosol, respectively. The contribution of NO_2 to light absorption was obtained by multiplying the NO_2 concentration by its light absorption efficiency at 0.55 μm (0.33 Mm^{-1} ppb^{-1}). The relative contribution of NO_2 ranged from $<$ 1 percent of total light extinction in the rural East to as high as 9 percent in urban areas. Nitrate aerosols generally contributed less than 10 percent, except in California urban areas and in Denver during the winter, where the fraction of total light extinction attributable to nitrate was as high as 34 percent. It should be noted, however, that these estimates may be lower bounds because of nitrate measurement problems resulting from the volatility of sampled nitrates.

Trijonis (1987) summarized his assessment of the contribution of the two NO_x species as shown in Table 11-4.

These estimates may be somewhat high for the rural situations if nitrate aerosol concentrations are limited because of low nitric acid and ammonia concentrations,

TABLE 11-2. NITROGEN DIOXIDE CONTRIBUTIONS TO TOTAL LIGHT EXTINCTION

Regions and Data Sets	Average NO_2 Concentration, ppb		Average Total Extinction, Mm^{-1}		Total Extinction From NO_2, %	
METROPOLITAN - WEST						
A. SPECIAL FIELD PROGRAMS						
1. Appel et al. (1983): One month at Los Angeles and Riverside in the summer of 1982. See footnote a.	S[b]	49	S	290	S	6
2. Appel et al. (1983): One month at San Jose in the summer of 1982. See footnote a.	S	19	S	95	S	7
3. Lewis et al. (1986): Three weeks at Denver in the winter of 1982. See footnote a.	W	29	W	120	W	8
4. Groblicki et al. (1981): Four weeks at Denver in the winter of 1978. See footnote a.	W	45	W	190	W	8
5. Zak et al. (1984): Two months at Albuquerque in the winter (Jan-Feb) of 1983.	W	29	W	220	W	4
B. ROUTINE MONITORING DATA						
1. Trijonis et al. (1982): One to sixteen years of data at 26 California metropolitan sites, mostly in the mid-1970's. See footnote c.		41		150		9
2. SAROAD Data: Three or more years of data at 62 metropolitan sites in the 1980's. See footnote c.		29		110		9
RURAL - WEST						
A. SPECIAL FIELD PROGRAMS		3		50		2
1. RESOLVE Special Study (Trijonis et al. [1987]): Thirteen weeks of sampling at Edwards and China Lake, CA.						
B. ROUTINE MONITORING DATA						
1. SAROAD Data: Three or more years of data at 15 rural sites in the 1980's. See footnote c.		11		70		5

TABLE 11-2 (cont'd). NITROGEN DIOXIDE CONTRIBUTIONS TO TOTAL LIGHT EXTINCTION

Regions and Data Sets	Average NO_2 Concentration, ppb		Average Total Extinction, Mm^{-1}		Total Extinction From NO_2, %	
METROPOLITAN - EAST						
A. SPECIAL FIELD PROGRAMS						
1. Dzubay et al. (1982): One week at Houston in September 1980. See footnote a.	S	24	S	232	S	4
2. Wolff et al. (1982): One week at Detroit in July 1981.	S	33	S	230	S	5
B. ROUTINE MONITORING DATA						
1. SAROAD Data: Three or more years of data at 85 metropolitan sites in the 1980's. See footnote c.		22		150		5
A. SPECIAL FIELD PROGRAMS						
1. Cadle et al. (1985): Eighteen weeks in northern Michigan in winter 1983-1984. See footnote c.	W[b]	2	W	100	W	0.7
2. Ferman et al. (1981): One month at Shenandoah Valley, VA, in the summer of 1981. See footnote c.	S	2	S	280	S	0.2
B. ROUTINE MONITORING PROGRAMS						
1. SAROAD Data: Three or more years of data at 25 rural sites in the 1980's. See footnote c.		13		150		3

[a]Reported extinction values are corrected for nephelometer wavelength, nephelometer calibration, missing coarse particle scattering, and/or Rayleigh scatter.
[b]bS,W=Data are restricted to a single season, summer (S) or winter (W). Results are seasonally biased and also may be nonrepresentative because of small sample size.
[c]Total extinction estimated from airport visibility data (Trijonis et al., 1987; Trijonis, 1982a,b; Trijonis and Yuan, 1978a,b). Average total extinction is estimated as 0.7 x (3.9/AMVR), where AMVR is airport median visual range (Trijonis et al., 1987).

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TABLE 11-3. NITRATE CONTRIBUTIONS TO TOTAL LIGHT EXTINCTION

Regions and Data Sets	Average Fine NO_3^- Concentration, $\mu g/m^3$		Average Total Extinction, Mm^{-1}		Total Extinction From Nitrate Aerosols %	
A. LOS ANGELES METROPOLITAN AREA	S[c]	10.7	S	290	S	34
1. Appel et al. (1983): One month at Lost Angeles and Riverside in summer of 1982. See footnotes a, b.	S	5.8	S	180	S	25
2. John et al. (1985): Four days of sampling at West Los Angeles in the summer of 1983. See footnotes d, e.		>3.1		210		>12
3. SAROAD Data: Two to five years of IP Network data at Azusa, Los Angeles, and Riverside from 1979-1983. See footnotes e,f.						
B. SAN FRANCISCO METROPOLITAN AREA						
1. Appel et al. (1983): One month at San Jose in the summer of 1982. See footnotes a, b.	S	3.4	S	95	S	33
2. John et al. (1985): Four days of sampling at San Jose in the summer of 1982. See footnotes a, b.	S	1.4	S	100	S	11
3. SAROAD Data: Two to four years of IP Network data at Livermore, Richmond, San Francisco, and San Jose from 1979-1983. See footnotes e, f.		>1.5		110		>11
C. DENVER METROPOLITAN AREA						
1. Lewis et al. (1986): Three weeks at Denver in the winter of 1982. See footnotes b, e.	W	2.2	W	150	W	11
2. Groblicki et al. (1981): Four weeks at Denver in the winter of 1978. See footnotes a, b.	W	6.1	W	190	W	14
D. PORTLAND METROPOLITAN AREA						
1. Shah et al. (1984): Approximately 30 days per site at four Portland area locations from summer 1977 to spring 1978. See footnotes a, b.		>1.8 g		110		7
E. ROUTINE NITRATE DATA AT 32 METROPOLITAN LOCATIONS						
1. SAROAD Data: One to five years of IP Network data at 32 metropolitan locations from 1979-1983. See footnotes e, f.		>1 .17 g		100		>9

TABLE 11-3 (cont'd). NITRATE CONTRIBUTIONS TO TOTAL LIGHT EXTINCTION

Regions and Data Sets	Average NO_2 Concentration, ppb		Average Total Extinction, Mm^{-1}		Total Extinction From NO_2, %	
RURAL - WEST						
A. SPECIAL FIELD PROGRAMS						
1. RESOLVE Special Study (Trijonis et al. [1988]): Thirteen weeks of sampling at Edwards and China Lake, CA. See footnote a.		0.9		50		9
2. John et al. (1985): Four days of sampling in mountains northeast of Los Angeles in summer 1983. See footnote d, e.	S	2.5	S	140	S	9
3. John et al. (1985): Four days of sampling in remote Kern County in summer 1982. See footnotes d, e.	S	0.9	S	95	S	5
B. ROUTINE NITRATE DATA FROM TEFLON FILTERS						
1. SAROAD Data: One to four years of IP Network data at 9 rural locations from 1979-1983. See footnotes e, f.		>0.3		40		>4
2. WRAQS Network (White and Macias [1987]): One year at 11 sites in the mountain/desert West in 1981-1982. See footnotes e, f.		>0.1		25		>2
METROPOLITAN - EAST						
A. SPECIAL FIELD PROGRAMS						
1. Cadle (1985): One year at Warren, MI, in 1981-1982. See footnotes e, f, h.		1.2		190		7
2. Dzubay et al. (1982): One week at Houston, TX, in September 1980. See footnotes b,e.	S[d]	>0.4		190	S	>2
3. Wolff et al. (1982): One week at Detroit in July 1981. See footnotes e, h.	S	>0.2	S	230	S	>1
B. ROUTINE NITRATE DATA FROM TEFLON FILTERS						
1. SAROAD Data: One to five years of IP Network data at 59 metropolitan locations from 1979-1983. See footnotes e, f.		>0.4		150		>3

TABLE 11-3 (cont'd). NITRATE CONTRIBUTIONS TO TOTAL LIGHT EXTINCTION

Regions and Data Sets	Average NO_2 Concentration, ppb		Average Total Extinction, Mm^{-1}		Total Extinction From NO_2, %	
RURAL - EAST						
A. SPECIAL FIELD PROGRAMS						
1. Stevens (1987): Several months of sampling at Research Triangle Park, NC, in the 1980s. See footnotes e, f.		0.7		170		4
2. Pierson et al. (1987); Mathai and Tombach (1987): One month of sampling at two rural sites in Pennsylvania in summer 1983. See footnotes b, e.	S	0.5	S	280	S	2
3. Stevens et al. (1980): One week at Smoky Mountains in September 1980. See footnotes e, f, i.	S	0.3	S	200	S	2
4. Cadle et al. (1985): Eighteen weeks in northern Michigan in winter 1983-1984. See footnotes e, f, h.	W	0.8	2	100	W	8
B. ROUTINE NITRATE DATA FROM TEFLON FILTERS						
1. SAROAD Data: One to four years of IP Network data at nine rural sites from 1979-1983. See footnotes e, f.		>0.6[g]		120		>5

[a]Extinction efficiency for nitrates specific to this data set is derived in cited reference.

[b]Reported extinction values (and any propagated effects on NO_3 scattering efficiencies) are corrected for nephelometer wavelength, nephelometer calibration, missing coarse particle scattering, and/or Rayleigh scatter.

[c]S,W=Data are restricted to a single season, summer (S) or winter (W). Results are seasonally biased and also may be nonrepresentative because of small sample size.

[d]Non-Rayleigh part of extinction for these California sites is estimated as five times measured fine particle mass as suggested by data from Trijonis et al. (1987), Appel et al. (1983), and Trijonis and Davis (1981).

[e]Nitrate aerosol is taken as 1.29 $[NO_3^-]$ to account for mass of ammonium cation. Scattering efficiency for nitrate aerosol is then taken as 4 m^2/g in rural West, 6 m^2/g in urban West, and 8 m^2/g in rural and urban East (Trijonis et al., 1987; Shah et al., 1984; Appel et al., 1983; White, 1981).

[f]Total extinction is estimated from airport visibility data (Trijonis et al., 1987; Trijonis, 1982a,b; Trijonis and Yuan, 1978a,b). Average total extinction is estimated as 0.7 x (3.9/AMVR), where AMVR is airport median visual range (Trijonis et al., 1987).

[g]Nitrate concentrations represent lower bound because samples were collected on Teflon filters. Note that lower bound on nitrate concentrations does not necessarily translate into a lower bound for nitrate contributions to extinction (third column) because of compensating effects in estimating nitrate scattering efficiency for some of the studies.

[h]Fine aerosol nitrate is computed from total aerosol nitrate using simultaneously collected size distribution data for nitrates.

[i]Total extinction is also estimated at this site as nine times average fine particle mass based on data in Trijonis (1982a).

TABLE 11-4. PERCENTAGE CONTRIBUTION OF NITROGEN OXIDES TO TOTAL LIGHT EXTINCTION

Location	Contribution to Extinction, %		
	NO_2	Nitrate	Total NO_x
Metropolitan West	8 ± 1.5	15 ± 4	23 ± 4.5
Rural West	4 ± 2	6 ± 2	10 ± 3
Metropolitan East	5 ± 1.5	5 ± 2	10 ± 2.5
Rural East	2 ± 1.5	5 ± 2	7 ± 2.5

competition from sulfate for ammonia, and temperatures and humidities that favor the retention of nitrate in the gas phase.

11.9 SUMMARY OF EFFECTS ON VISIBILITY

Emissions of NO_x can contribute significantly to visibility impairment in the form of plumes and hazes. Nitrogen dioxide (NO_2) and ammonium nitrate aerosol (NH_4NO_3) are the optically active species of NO_x. Other species, including nitric oxide (NO) and nitric acid (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 percent 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 ammonia concentrations tend to be lower or because moderate or high temperatures tend to prevent nitrate aerosol from condensing. Nitrate aerosol does not appear

in areas of high concentrations of sulfate, such as the eastern United States, mainly because acidic sulfate compounds consume the available atmospheric ammonia that is needed to condense nitrate aerosol from nitric acid 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 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.

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 SO_2 emission controls on nitrate aerosol production, because the large-scale reduction of sulfate, which competes with nitrate for available ammonia, may result in increases in nitrate aerosol.

11.10 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 (1989), Mitchell and Carson (1989), Fischhoff and Furby (1988), Cummings et al. (1986), and Rowe and Chestnut (1982).

11.10.1 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. 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, the U.S. Environmental Protection Agency concluded that only a small percentage of the visibility impairment incidents sufficient to affect air traffic activity can be attributed primarily to manmade air pollutants (2% to 12% in summer in the eastern United States); and according to the information presented previously in this chapter, NO_x would not be expected to be a significant contributor to these incidents. Most economic studies of the effects of air pollution on visibility have, therefore, focused on the aesthetic effects to the individual.

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.

11.10.2 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, 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, 1989; 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, 1989).

11.10.2.1 Contingent Valuation Method

The contingent valuation method (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; 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). 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 the ability of researchers to present visibility conditions in a manner relevant to respondents and to design instruments that can elicit unbiased values; and 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 continues to be a topic 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.

11.10.2.2 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 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.

11.10.3 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.

11.10.3.1 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 11-5). 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

TABLE 11-5. 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 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 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 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 question	Daily entrance fee	Visitors: $3.32 per day additional to prevent visible plume Residents: $2.21 per day additional to prevent visible plume

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 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 WTP. 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 3 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, while 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 (1990) found that the Schulze et al. (1983) 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 plume estimates.

11.10.3.2 Economic Valuation Studies for Urban Haze

Six economic studies concerning urban haze caused by air pollution are summarized in Table 11-6. 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), this California study (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 11-6 implicit values obtained for a 10 percent change in visual range are reported to allow a comparison of results across the studies. These estimates are based on an assumption that economic values are proportional to the percentage change in visual range. All of these studies relied on not exactly random, but more or less representative samples of residents in each of the selected urban areas. A range of socioeconomic characteristics and of neighborhood pollution levels was included in each sample.

The first five studies in Table 11-6 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.

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 both cities were found to be higher than comparable values obtained in the CVM studies, although Graves et al. (1988) have reported that subsequent analysis of the property value data revealed that the WTP estimates are more variable than the original results suggest. The higher property value results are expected because those results are likely to reflect concern about health as well as aesthetic effects of air pollution.

TABLE 11-6. ECONOMIC VALUATION STUDIES ON URBAN HAZE
PART I. UNIFORM URBAN HAZE

Study	Location	Year	Valuation Method	Payment Vehicle	Presentation/Definition of Change in Visibility	Implied Mean Annual WTP for a 10% Change in Visual Range, $ 1989
Western Cities						
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 increase	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
Eastern Cities						
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 to $51 per household
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

TABLE 11-6. ECONOMIC VALUATION STUDIES ON URBAN HAZE
PART II. URBAN HAZE WITH BORDER

Study	Location	Year	Valuation Method	Payment Vehicle	Presentation/Definition of Change in Visibility	Results, $ 1989
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	Preliminary results indicate mean annual between $100 and $200 per household for a 1-step change in the 7-point scale, with about one-third of the value attributed to visibility alone

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) while 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 turned out to be 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 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).

Irwin et at. (1990) have reported preliminary results for the Denver study (Part II, Table 11-6). The data obtained in this study are being analyzed further and a final report on the project is expected to be available in 1991. Comparison of the results of this study with those 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 than when respondents are asked to give WTP for the change in air quality and then say what portion of that total is attributable to visibility only. Values for health and visibility combined exceeded those for visibility alone (when respondents were simply told to think only about visibility). This may result simply 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 for 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.

11.10.4 Conclusions

The current reliance on and continuing methodological uncertainties in the contingent valuation method for obtaining economic estimates related to changes in visibility means future methodological research related to CVM may provide important information relevant to interpreting previous and designing new visibility value studies using CVM. Some evidence is beginning to emerge as to those factors in CVM applications that appear to have the most effect on visibility value estimates and that, therefore, need to receive more attention. Among these factors are:

1. The treatment of related air pollution effects such as health;
2. The geographic location of the impact;
3. Whether values are obtained in a single or multiple good context, and are appropriately adjusted for non-visibility components;
4. Whether a frequency distribution presentation of visibility is used;
5. Various features of the hypothetical context of the WTP questions; and
6. Survey implementation and data handling procedures.

Available estimates of economic values for plumes are directly applicable for only a thin, dark plume present on most days in the sky at Grand Canyon National Park, and possibly at a few other national parks in the Southwest. There is little empirical evidence (from economics studies to date) about how the values would vary with the frequency, location, or visual characteristics of a plume. Available results do suggest the potential

importance of considering total preservation values, rather than only on-site use values, in any assessment of the economic impact of NO_x plumes visible from major recreation areas.

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 percent 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. Extrapolations to less urbanized areas and/or to other visibility changes 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. Available results with regard to visual range in urban areas, however, 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 would require estimates of the changes in visual range that might be expected as a result of NO_x controls.

Very little work has been done regarding layered hazes in recreation or residential settings. The work conducted in Denver (Irwin et al., 1990) is the only study in this category. More information is needed about what visual characteristics of such hazes are most important to viewers, as well as on the value people may place on reducing or preventing them. A related question that is relevant for NO_x, but that has not been addressed in economic studies to date, is the effect of variations in air pollution color (in plumes or hazes) on visibility values. In order to apply available economic values for changes in layered hazes to changes in NO_x levels, a link would need to be made between NO_x levels (and changes that might result from control efforts) and visual characteristics of layered hazes that can be tied to the economic values.

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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. While 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 and NO_x levels are increasing. The relative proportion of materials damage attributable to NO_x can therefore be expected to increase. This section 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, a qualitative understanding of the

economic estimation procedures is needed. A useful survey of the topic of air pollution damage to materials is contained in Joerg et al. (1987).

12.1.1 Environmental Exposures to 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 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 extensively studied systems (such as the effect of SO_2 pollution on metals) are not thoroughly understood, and there is extensive 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 NO_x must come in contact with the material. They 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 diffusiophoresis 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 being determined by a series of resistances to the mass transfer. 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. Thus,

$$R_T = R_a + R_b + R_c. \qquad (12\text{-}1)$$

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, which has units of cm/s. The deposition velocity is the ratio of flux of mass to the surface (g/cm^2 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 and NO_2, propylene (C_3H_3), 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 velocity for the deposition of 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 sixteen times greater for SO_2 than for NO_2. Clearly, dry deposition of NO_2 on galvanized steel is significantly slower than the dry deposition of SO_2. These researchers suggest that, for the purposes of developing a damage function, NO_2 dry deposition on galvanized steel can be ignored.

In a test with an NO_2 and propylene 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 hours (2 weeks) with a total time of induced dew of 196 hours 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_3, 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 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_3 mixture.

TABLE 12-1. SMOG CHAMBER REACTIONS OF NO_2 AND C_3H_3 AND DEPOSITION OF REACTION PRODUCTS ON GALVANIZED STEEL

Chemical Species	Gas-Phase Concentration, ppb	Surface-dew Concentration, nmol/cm^2
O_3	134	---
CH_3CHO	254	---
HCHO	621	133
PAN	57	---
NO_x-PAN	359	---
HNO_3	7	---
NO_2^-	---	11
NO_3^-	---	77
$SO_4^=$	---	133
Zn	---	77

Source: Edney et al. (1986).

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 $SO_4^=$ 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. 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, $SO_4^=$ concentrations were in a one-to-one relationship with dissolved zinc. Edney et al. (1987) concluded that NO_x is

TABLE 12-2. SMOG CHAMBER REACTIONS OF NO_2, C_3H_3, AND SO_2 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).

not effectively deposited on galvanized steel surfaces and that sulfates dominate galvanized steel corrosion.

While 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 μg/m^3 (0.15 parts per million [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, probably of material similar to the metal used by Edney et al. (1987), 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

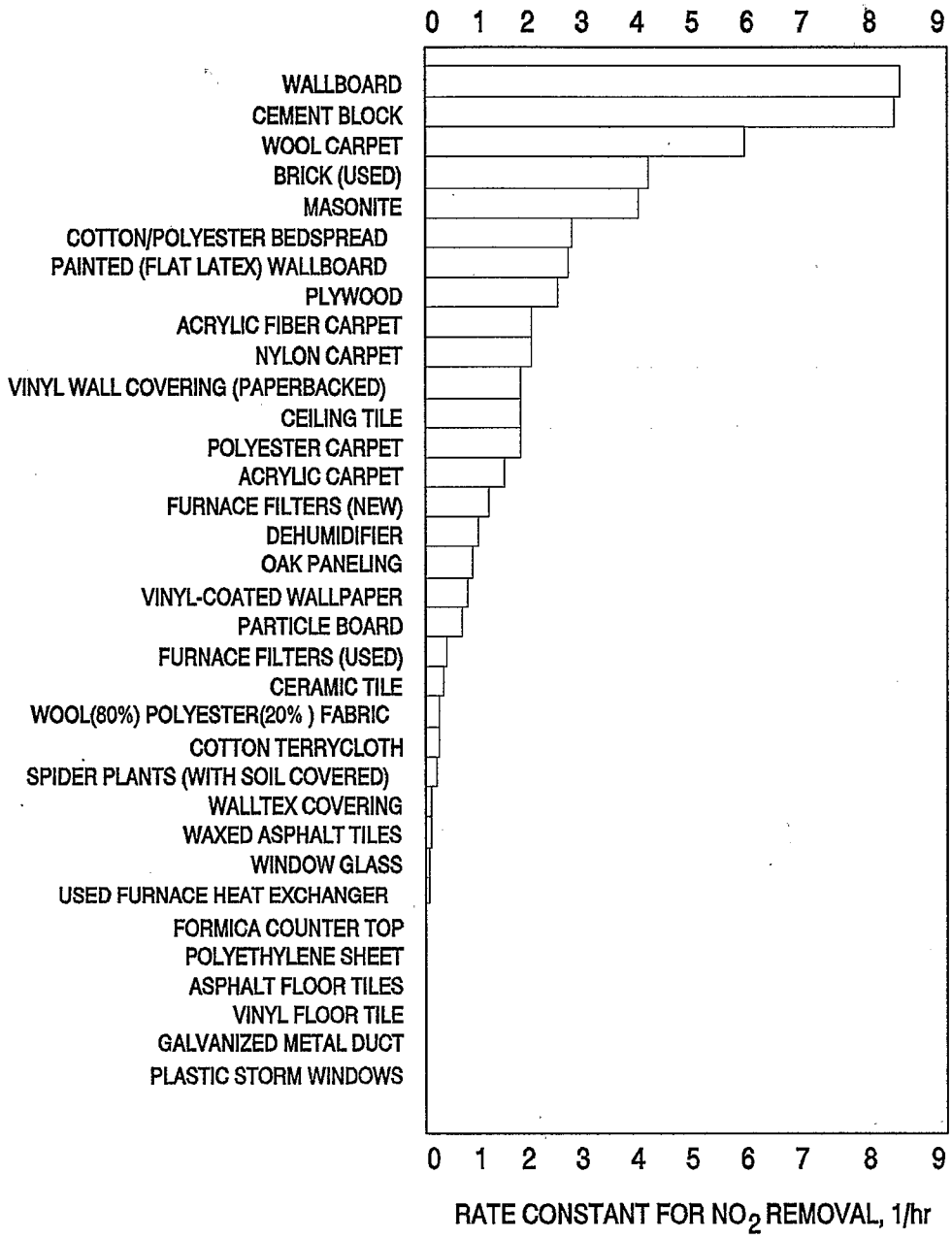

Figure 12-1. Bar graph of NO_2 removal rate for various materials evaluated in a 1.64 m^3 test chamber at 50% RH.

Source: Spicer et al. (1987).

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.

Miyazaki (1984) conducted a similar experiment exposing common interior materials in a chamber to initial concentrations of 1,645 mg/m^3 (875 ppm) NO_2 and 1,124 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 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 Oxide 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, ammonium (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 photochemical 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

TABLE 12-3. DEPOSITION VELOCITIES OF NO_2 AND NO FOR INTERIOR MATERIALS

Interior Material	Deposition Velocity, cm/s	
	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

These values were averaged from the results of the experiments at 20-26 °C, 40-60% RH.

Source: Modified from Miyazaki (1984).

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 NH_3 and sulfuric acid (H_2SO_4), constituents found in the atmosphere, the HNO_3 gas-phase versus liquid-phase equilibrium is shifted toward the gas phase. Thus, as nitrates accumulate on the surface of a material much of the accumulated nitrate mass can 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 $SO_4^=$ are frequently present. Thus, 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 to underestimation of real-world deposition rates. Also, the sequence with which materials are exposed to different pollutants can affect the formation of protective corrosion films, and this process is sometimes poorly simulated in chambers. While such studies are useful, care should be exercised in the extrapolation of data and conclusions based on chamber studies to 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 (CO_2), reduced sulfur, a chlorine-containing gas, and a nitrogen-containing gas must be included. Because of the difficulties involved in apportioning the causes of damages, 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 (run-off) has been analyzed for its chemical constituents. The objectives of these efforts are 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, 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 $\mu g/m^3$ (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, 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.

Beloin (1973) exposed a variety of fabrics and dyes to 120 $\mu g/m^3$ (0.1 ppm) and 1,230 $\mu g/m^3$ (1 ppm) of NO, and 90 $\mu g/m^3$ (0.05 ppm) and 940 $\mu g/m^3$ (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. Beloin (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 for testing NO_x fading.

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).

The American Association of Textile Chemists and Colorist 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.

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 fiber themselves. Jellinek (1970) and Jellinek et al. (1969) reported significant chain scissioning of nylon after NO_2 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 HNO_3. Zeronian et al. (1971) investigated the impact of NO_2 on acrylic, modacrylic, nylon, and polyester yarn. The yarns were continuously exposed in chambers for 1 week to simulated sunlight and 3,760 $\mu g/m^3$ (0.2 ppm) NO_2. 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 NO_2. 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

12.3.1 Chemical Changes Induced by Nitrogen Oxides

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 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 radiation (UV), 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 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_x, 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 exposures with the other pollutants, radiation, and humidity conditions were used. 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., the duration for which the material surface has liquid water present) 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 $\mu g/m^3$ SO_2 and 90% RH, but very slowly when exposed to SO_2 at the same concentration and 50% RH. At 50% RH humidity, steel corrodes about three times more quickly when exposed to NO_2 (5,640 $\mu g/m^3$). 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 may become nearly equal. Thus, the conclusion 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 may be applicable.

12.4.2 Effect 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 enameling steel were exposed at 57 of the National Air Site 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 were determined from weight loss measurements, and these data 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, 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 nitrous acid (HNO_2). Construction steel was exposed continuously for 6 weeks to 376 $\mu g/m^3$ or 5,640 $\mu g/m^3$ (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, if no other pollutants were available, steel exposed to NO_2 alone 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 relative humidities around 50% 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 $SO_4^=$, 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 relative humidities of 95%.

Haynie (1986) analyzed data from 30 months of exposures of weathering steels at nine sites around St. Louis, MO, as part of the U.S. Environmental Protection Agency's (EPA's) Regional Air Pollution Study (RAPS). Weathering steels are architectural steels specifically formulated to rapidly develop a surface corrosion layer that protects the underlying substrate steel. The exposure samples were collated with air quality monitoring stations. Haynie (1986) statistically analyzed the observed corrosion versus 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. While 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 $\mu g/m^3$, 0.5 ppm) than at low concentrations (94 $\mu g/m^3$, 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 $\mu g/m^3$ (10 ppm) of NO_2 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 sulfuric acid (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 $SO_4^=$ dominated the amount of deposited NO_3^-, and that $SO_4^=$ and NO_3^- deposition rates were strongly correlated at the field exposure site. The regression analysis, therefore, found that $SO_4^=$ dominated the corrosion of galvanized steel and that NO_3^- was not 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 was strongly synergistic when combined with SO_2. As the NO_2 concentration in the mixture was increased from 376 $\mu g/m^3$ to 5,640 $\mu g/m^3$ (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-aluminum corrosion at 95% RH. In a chamber study, Loskutov et al. (1982) demonstrated that the interaction of NO_2 and water on an aluminum surface was a complex process. They concluded that adsorbed water acted to displace NO_x 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 $\mu g/m^3$ (0.5 and 1 ppm) NO_2 in a chamber for 28 days. They found no statistically significant impact of NO_2 on aluminum. They also exposed aluminum to 252 and 1,260 $\mu g/m^3$ (0.1 and 0.5 ppm) HNO_3 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 NO_2 has little impact on copper at concentrations up to 2,444 $\mu g/m^3$ (1.3 ppm). Rice et al. (1980a) concluded from a multiple-city exposure study that hydrogen sulfide (H_2S), SO_2, and O_3 all had more impact than NO_x on copper. Kucera (1986), Johansson (1986), and Henriksen and Rode (1986), using chamber studies, found that the NO_2 and SO_2 combined was synergistic and increased the observed corrosion rate of copper by ten to twenty 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 SO_2, NO_2, and chlorides played a significant role in accelerating nickel corrosion. In a chamber study, Rice et al. (1980b) found that NO_2 attacked nickel but that SO_2 and chlorine (Cl_2) were more aggressive than NO_2. Graedel and McGill (1986) have listed NO_2 as being moderately aggressive toward nickel.

12.4.3 Effects of Nitrogen Oxides on Electronics

While 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 with 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 $\mu g/m^3$ (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 Guilinger (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" which 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, even as concentrations approached 1 ppm, producing only mild pore corrosion. The reaction became more severe when NO_2 was added to the mixture. A mixture of 0.1 ppm H_2S plus 0.1 ppm SO_2 plus 0.1 ppm 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 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).

While 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 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 $\mu g/m^3$ (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 months 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 $\mu g/m^3$ (0.5 ppm) NO_2, but not at 1,880 $\mu g/m^3$ (1 ppm) NO_2. The amount of damage was slight. At 1,260 $\mu g/m^3$ (0.5 ppm) HNO_3, however, both carbonate and non-carbonate 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 Taj Mahal and 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 non-carbonate 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 dark 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, while 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 spp.* oxidize ammonium to nitrous acid and *Nitrobacter spp.* oxidize HNO_2 to HNO_3. Production of these acids results in direct chemical attack to calcareous stone and concrete. Baumgartner et al. 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. 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_x 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 months at nine air quality monitoring sites around St. Louis, MO. He concluded that NO_3 and total suspended particulate (TSP) 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 ppm and sub-ppm 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 HNO_2 and HNO_3 are more damaging than H_2SO_4 to concrete on brief exposures because they convert the $Ca(OH)_2$ 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 $\mu g/m^3$.

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 rebinding 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 buildup 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.

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 since 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 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, 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. Jirillo et al. (1987), however, have reported the costs of preservation of Italian artistic properties as 69,697 thousand million lira, with a sizable fraction of the damage attributed by the authors to acid deposition.

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. 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. Fade-resistant dyes and inhibitors have been developed, but are generally more costly to employ. Nitrogen oxides also attack textile fibers and result in a loss of strength. Plastics and elastomers are subject to NO_x reactions that cause discoloration and changes in physical properties, including loss of strength. The rate of NO_x-induced deterioration to plastics and elastomers is generally overshadowed, however, by O_3-induced damage. Although NO_x attacks metals, attack by SO_2 is more aggressive. Damage to metals from NO_x can generally be discounted, except perhaps in indoor exposures, where NO_x 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. The influence of NO_x on paints and stone has not been clearly demonstrated. Many authors indicate that NO_x plays a role in damaging these materials, but most concede that SO_2 and O_3 are more directly damaging. Nitrogen oxides, along with other "acid pollutants," attack the cellulose fibers in paper, leading to discoloration and weakened structure.

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, cost/benefit analyses of permissible NO_x levels vis-a-vis shortened use-life estimates could be misleading. 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.

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, but few data are available regarding materials deterioration indoors. This is an area of needed research.

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