EPA600/8-91/049aF
August 1993

Air Quality Criteria for Oxides of Nitrogen

Volume I of III

Environmental Criteria and Assessment Office
Office of Health and Environmental Assessment
Office of Research and Development
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Printed on Recycled Paper

DISCLAIMER

This document has been reviewed in accordance with U S Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use

PREFACE

The U S Environmental Protection Agency (EPA) promulgates the National Ambient Air Quality Standards (NAAQS) on the basis of scientific information contained in criteria documents In 1971, the first air quality criteria document for nitrogen oxides (NO_x) was issued by the National Air Pollution Control Administration, a predecessor of EPA On the basis of scientific information contained in that document, NAAQS were promulgated for nitrogen dioxide (NO_2) at levels of 0 053 ppm (100 $\mu g/m^3$), averaged over 1 year The last full-scale NO_x criteria document revision was completed by EPA in 1982, leading to an Agency decision in 1985 to reaffirm the annual average NO_2 NAAQS of 0 053 ppm The present, revised criteria document, Air Quality Criteria for Oxides of Nitrogen, assesses the current scientific basis for periodic reevaluation of the NO_2 NAAQS in accordance with the provisions identified in Sections 108 and 109 of the Clean Air Act

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

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

Air Quality Criteria for Oxides of Nitrogen

TABLE OF CONTENTS

Volume I — Page

1 EXECUTIVE SUMMARY OF AIR QUALITY CRITERIA FOR OXIDES OF NITROGEN 1-1

2 INTRODUCTION 2-1

3 GENERAL CHEMICAL AND PHYSICAL PROPERTIES OF OXIDES OF NITROGEN AND OXIDES OF NITROGEN-DERIVED POLLUTANTS 3-1

4 AMBIENT AND INDOOR SOURCES AND EMISSIONS OF NITROGEN OXIDES 4-1

5 TRANSPORT AND TRANSFORMATION OF NITROGEN OXIDES 5-1

6 SAMPLING AND ANALYSIS FOR NITROGEN OXIDES AND RELATED SPECIES 6-1

7 AMBIENT AND INDOOR CONCENTRATIONS OF NITROGEN OXIDES . 7-1

8 ASSESSING TOTAL HUMAN EXPOSURE TO NITROGEN DIOXIDE 8-1

Volume II

9 EFFECTS OF NITROGEN OXIDES ON VEGETATION 9-1

10 THE EFFECTS OF NITROGEN OXIDES ON NATURAL ECOSYSTEMS AND THEIR COMPONENTS 10-1

11 EFFECTS OF NITROGEN OXIDES ON VISIBILITY 11-1

12 EFFECTS OF NITROGEN OXIDES ON MATERIALS 12-1

TABLE OF CONTENTS (cont'd)

Volume III Page

13. STUDIES OF THE EFFECTS OF NITROGEN COMPOUNDS ON ANIMALS 13-1

14. EPIDEMIOLOGY STUDIES OF OXIDES OF NITROGEN 14-1

15. CONTROLLED HUMAN EXPOSURE STUDIES OF NITROGEN OXIDES 15-1

16. HEALTH EFFECTS ASSOCIATED WITH EXPOSURE TO NITROGEN DIOXIDE . 16-1

APPENDIX A· GLOSSARY OF TERMS AND SYMBOLS A-1

TABLE OF CONTENTS

	Page
LIST OF TABLES	I-xiv
LIST OF FIGURES	I-xix
AUTHORS	I-xxv
CONTRIBUTORS AND REVIEWERS	I-xxvii
CLEAN AIR SCIENTIFIC ADVISORY COMMITTEE . .	I-xxix
PROJECT TEAM FOR DEVELOPMENT OF AIR QUALITY CRITERIA FOR OXIDES OF NITROGEN	I-xxxi
1 EXECUTIVE SUMMARY OF AIR QUALITY CRITERIA FOR OXIDES OF NITROGEN . .	1-1
1 1 PURPOSE OF THE DOCUMENT	1-1
1 2 INTRODUCTION	1-1
1 3 CHEMICAL AND PHYSICAL PROPERTIES OF NITROGEN OXIDES AND NITROGEN OXIDE-DERIVED POLLUTANTS .	1-1
1 4 EMISSIONS OF NITROGEN OXIDES FROM AMBIENT AND INDOOR SOURCES	1-2
1 5 TRANSPORT AND TRANSFORMATION OF NITROGEN OXIDES . .	1-3
1 6 SAMPLING AND ANALYSIS FOR OXIDES OF NITROGEN AND RELATED SPECIES	1-5
1 7 AMBIENT AND INDOOR CONCENTRATIONS OF OXIDES OF NITROGEN	1-6
1 7 1 Ambient Nitrogen Dioxide Levels	1-6
1 7 2 Indoor Nitrogen Dioxide Levels	1-7
1 8 ASSESSING TOTAL HUMAN EXPOSURE TO NITROGEN DIOXIDE . .	1-8
1 9 EFFECTS OF NITROGEN OXIDES ON VEGETATION	1-9
1 10 EFFECTS OF NITROGEN OXIDES ON ECOSYSTEMS	1-9
1 11 EFFECTS OF NITROGEN OXIDES ON VISIBILITY	1-14
1 12 EFFECTS OF NITROGEN OXIDES ON MATERIALS	1-15
1 13 STUDIES OF THE EFFECTS OF NITROGEN COMPOUNDS ON ANIMALS	1-16
1 14 EPIDEMIOLOGY STUDIES OF NITROGEN DIOXIDE	1-17
1 15 CONTROLLED HUMAN EXPOSURE STUDIES OF OXIDES OF NITROGEN	1-19
1 16 NITROGEN DIOXIDE HEALTH EFFECTS CONCENTRATION-RESPONSE RELATIONSHIPS AND SUBPOPULATIONS POTENTIALLY AT RISK .	1-20
1 16 1 Concentration-Response Relationships	1-20
1 16 2 Subpopulations Potentially at Risk	1-23
2 INTRODUCTION .	2-1
2 1 REGULATORY AND SCIENTIFIC BACKGROUND	2-2

TABLE OF CONTENTS (cont'd)

		Page
2.2	CRITICAL ISSUES . .	2-4
2.3	ORGANIZATION OF THE DOCUMENT	2-5
REFERENCES . . .		2-8
3.	GENERAL CHEMICAL AND PHYSICAL PROPERTIES OF OXIDES OF NITROGEN AND OXIDES OF NITROGEN-DERIVED POLLUTANTS	3-1
3.1	INTRODUCTION AND OVERVIEW	3-1
3.2	NITROGEN OXIDES	3-4
3.2.1	Nitric Oxide . .	3-4
3.2.2	Nitrogen Dioxide .	3-10
3.2.3	Nitrous Oxide	3-10
3.2.4	Nitrogen Trioxide .	3-12
3.2 5	Dinitrogen Trioxide	3-12
3.2.6	Dinitrogen Tetroxide	3-13
3.2.7	Dinitrogen Pentoxide . .	3-13
3.3	NITRATES, NITRITES, AND NITROGEN ACIDS	3-14
3.3.1	Nitric Acid	3-14
3.3.2	Nitrous Acid	3-14
3.3 3	Organic Nitrates	3-15
3.3 4	Aerosol Nitrates	3-16
3.4	AMMONIA .	3-16
3.5	*N*-NITROSO COMPOUNDS	3-17
3.6	SUMMARY .	3-18
3 6 1	Nitrogen Oxides	3-19
3.6 2	Nitrates, Nitrites, and Nitrogen Acids	3-19
3.6.3	*N*-Nitroso Compounds .	3-20
REFERENCES .		3-21
4.	AMBIENT AND INDOOR SOURCES AND EMISSIONS OF NITROGEN OXIDES	4-1
4.1	INTRODUCTION	4-1
4.2	AMBIENT SOURCES OF NITROGEN OXIDES	4-2
4.2.1	Anthropogenic Sources of Nitrogen Oxides	4-3
4.2.1.1	Transportation . .	4-4
4 2.1 2	Stationary Source Fuel Combustion	4-8
4.2 1 3	Industrial Processes .	4-10
4 2 1 4	Solid Waste Disposal .	4-10
4 2 1 5	Miscellaneous Sources .	4-10
4.2 2	Natural Sources of Nitrogen Oxides	4-11
4.2 3	Global Estimates of Nitrogen Oxides Emissions	4-13
4.2 4	Analysis of United States Nitrogen Dioxide Emission Sources, Levels, and Trends . . .	4-14
4 2.5	Comparison of Nitrogen Oxide Emissions Estimates	4-23

TABLE OF CONTENTS (cont'd)

		Page
4 3	INDOOR EMISSION SOURCES OF NITROGEN OXIDES	4-23
4.3.1	Introduction . .	4-23
4 3 2	Formation of Nitrogen Oxides in Combustion in Gas-Fueled Household Appliances	4-24
4 3 3	Gas Stoves Used for Cooking	4-28
4 3 4	Unvented Space Heaters Fueled with Natural Gas and Propane . . .	4-40
4 3 5	Kerosene Heaters .	4-45
4 3 6	Wood Stoves	4-47
4 3 7	Tobacco Products .	4-48
4 3.8	Comparison of Emissions from Sources Influencing Indoor Air Quality	4-49
4 4	SUMMARY OF EMISSIONS OF NITROGEN OXIDES FROM AMBIENT AND INDOOR SOURCES	4-51
REFERENCES	. .	4-53
5	TRANSPORT AND TRANSFORMATION OF NITROGEN OXIDES	5-1
5 1	BACKGROUND	5-1
5 2	THE ROLE OF NITROGEN OXIDES IN OZONE PRODUCTION .	5-3
5 2 1	Urban Plume Chemistry . . .	5-8
5 2 2	Ozone Production in Rural Environments	5-10
5 3	ODD NITROGEN SPECIES .	5-18
5 3 1	Nitric Acid	5-18
5 3 2	Nitrous Acid . . .	5-20
5 3 3	Peroxynitric Acid	5-20
5 3 4	Peroxyacylnitrates	5-21
5 3 5	Nitrate Radical	5-22
5 3 6	Dinitrogen Pentoxide	5-24
5 3 7	Total Reactive Odd Nitrogen Species	5-25
5 3 8	Amines, Nitrosamines, and Nitramines	5-26
5 4	TRANSPORT	5-30
5 4 1	Transport of Reactive Nitrogen Species in Urban Plumes	5-32
5 4 2	Transport and Chemistry in Combustion Plumes	5-34
5 4 3	Regional Transport	5-36
5 5	OXIDES OF NITROGEN AND THE GREENHOUSE EFFECT . .	5-40
5 5 1	Ozone Greenhouse Effects Related to Nitrogen Oxides	5-40
5 5 2	Nitrous Oxide Greenhouse Contributions	5-42
5 6	STRATOSPHERIC OZONE DEPLETION BY OXIDES OF NITROGEN	5-44
5 7	DEPOSITION OF NITROGEN OXIDES	5-48

TABLE OF CONTENTS (cont'd)

			Page
	5.7.1	Dry Deposition of Nitrogen Oxides	5-48
	5 7 2	Methods for Determining Deposition Velocities	5-49
		5 7 2 1 Eddy Correlation .	5-50
		5 7.2.2 Vertical Gradient Methods	5-50
		5.7 2 3 Chamber Methods	5-51
	5 7 3	Deposition of Nitrogen Oxides	5-51
	5.7.4	Nitric Acid Deposition	5-52
	5.7.5	Deposition of Peroxyacetylnitrate	5-52
	5 7.6	Wet Deposition of Nitrogen Oxides	5-52
5.8	SUMMARY AND CONCLUSIONS		5-53
	5 8.1	Ozone Production	5-53
	5 8 2	Production of Odd Nitrogen Species	5-53
	5 8 3	Transport	5-54
		5.8 3 1 General Features	5-54
		5 8.3 2 Transport of Reactive Nitrogen Species in Urban Plumes	5-55
		5 8 3 3 Transport and Chemistry in Combustion Plumes	5-55
		5 8 3 4 Regional Transport	5-55
	5 8 4	Oxides of Nitrogen and the Greenhouse Effect	5-56
		5 8 4 1 Nitrous Oxide Greenhouse Contributions	5-56
		5 8.4 2 Stratospheric Ozone Depletion by Oxides of Nitrogen	5-57
	5.8 5	Deposition of Nitrogen Oxides	5-57
REFERENCES .			5-59
6.	SAMPLING AND ANALYSIS FOR NITROGEN OXIDES AND RELATED SPECIES .		6-1
6.1	INTRODUCTION .		6-1
6 2	NITRIC OXIDE		6-2
	6.2 1	Chemiluminescence	6-2
	6.2 2	Laser-Induced Fluorescence	6-5
	6.2 3	Absorption Spectroscopy	6-6
	6.2.4	Passive Samplers	6-8
	6.2.5	Calibration	6-10
	6.2.6	Intercomparisons	6-10
	6.2.7	Sampling Considerations for Nitric Oxide and Other Nitrogen-Containing Species	6-12
6.3	NITROGEN DIOXIDE		6-12
	6.3.1	Chemiluminescence, Nitric Oxide Plus Ozone	6-13
	6 3.2	Chemiluminescence, Luminol	6-17
	6.3.3	Photofragmentation/Two-Photon Laser-Induced Fluorescence	6-18
	6.3.4	Absorption Spectroscopy	6-19

TABLE OF CONTENTS (cont'd)

			Page
	6 3 5	Wet Chemical Methods	6-21
		6 3 5 1 Griess-Saltzman Method	6-21
		6 3 5 2 Continuous Saltzman Method	6-22
		6 3 5 3 Alkaline Guaiacol Method	6-22
		6 3 5 4 Jacobs-Hochheiser Method	6-23
		6 3 5 5 Sodium Arsenite Method (Manual and Continuous)	6-23
		6 3 5 6 Triethanolamine-Guaiacol-Sulfite Method	6-24
		6 3 5.7 Triethanolamine Method	6-24
	6 3 6	Other Active Methods	6-25
	6 3 7	Passive Samplers	6-27
	6 3 8	Calibration	6-30
	6 3 9	Intercomparisons	6-31
	6 3 10	Designated Methods	6-34
6 4	NITROGEN OXIDES		6-38
6 5	TOTAL REACTIVE ODD NITROGEN OXIDES		6-40
6 6	PEROXYACETYL NITRATE		6-41
	6 6 1	Gas Chromatography-Electron Capture Detection	6-42
	6 6 2	Alkaline Hydrolysis	6-43
	6 6 3	Gas Chromatography—Alternate Detectors	6-43
	6 6 4	Peroxyacetyl Nitrate Stability	6-44
	6 6 5	Calibration	6-45
	6 6 6	Other Organic Nitrates	6-46
6 7	NITRIC ACID		6-47
	6 7 1	Filtration	6-47
	6 7 2	Denuders	6-49
	6 7 3	Chemiluminescence	6-51
	6 7 4	Absorption Spectroscopy	6-52
	6 7 5	Calibration	6-52
	6 7 6	Intercomparisons	6-53
6 8	NITROUS ACID		6-55
	6 8 1	Denuders	6-55
	6.8 2	Chemiluminescence	6-56
	6 8 3	Photofragmentation/Laser-Induced Fluorescence	6-57
	6 8 4	Absorption Spectroscopy	6-57
	6 8 5	Calibration	6-58
	6 8 6	Intercomparisons	6-58
6 9	DINITROGEN PENTOXIDE AND NITRATE RADICALS		6-59
6 10	PARTICULATE NITRATE		6-60
	6 10 1	Filtration	6-60
	6 10 2	Denuders/Filtration	6-64
	6 10 3	Impactors	6-64
	6 10 4	Analysis	6-65
6 11	NITROUS OXIDE		6-69

TABLE OF CONTENTS (cont'd)

		Page
6.12	SUMMARY	6-70
	REFERENCES	6-72
7.	AMBIENT AND INDOOR CONCENTRATIONS OF NITROGEN OXIDES	7-1
7.1	INTRODUCTION	7-1
7.2	AMBIENT AIR CONCENTRATIONS OF NITROGEN OXIDES	7-2
7.2.1	Introduction	7-2
7.2.2	Ambient Air Concentrations of Nitric Acid and Nitrate Aerosol	7-4
7 2.3	Ambient Air Concentrations of Nitric Oxide and Nitrogen Dioxide	7-6
7 2 3 1	Data Availability and Exposure Considerations	7-6
7 2 3 2	Trends in Ambient Nitrogen Dioxide Concentrations	7-8
7 2 3.3	Exposure Patterns Observed for Ambient Nitrogen Dioxide and Nitric Oxide Concentrations—Urban	7-8
7.2 3 4	Exposure Patterns Observed for Ambient Nitrogen Dioxide and Nitric Oxide Concentrations—Rural Forest and Agriculture Areas	7-24
7.3	INDOOR AIR CONCENTRATIONS OF NITROGEN OXIDES	7-32
7.3.1	Background	7-32
7.3.2	Residences Without Indoor Sources	7-38
7.3.3	Residences with Gas Appliances	7-46
7.3 3 1	Average Indoor Concentrations and Estimated Source Contributions	7-47
7 3 3 2	Spatial Distributions	7-59
7 3 3 3	Short-Term Indoor Concentrations	7-60
7.3 4	Unvented Space Heaters	7-65
7 3 4 1	Unvented Kerosene Space Heaters	7-66
7.3 4 2	Unvented Gas Space Heaters	7-71
7.3.5	Other Sources	7-76
7.3.6	Modeling of Indoor Concentrations	7-76
7 3 6 1	Physical/Chemical Models	7-77
7 3 6 2	Statistical/Empirical Models	7-80
7.3.7	Reactive Decay Rate of Nitrogen Dioxide Indoors	7-83
7.4	NITRIC AND NITROUS ACIDS CONCENTRATIONS	7-88
7.5	SUMMARY	7-90
7.5 1	Ambient Nitrogen Dioxide Levels	7-90

TABLE OF CONTENTS (cont'd)

		Page
	7 5.2 Indoor Nitrogen Dioxide Levels	7-91
	REFERENCES	7-95
8	ASSESSING TOTAL HUMAN EXPOSURE TO NITROGEN DIOXIDE	8-1
	8 1 INTRODUCTION	8-1
	8.2 DIRECT METHODS	8-4
	8 2 1 Biomarkers	8-4
	8 2 2 Personal Monitoring	8-5
	8 3 INDIRECT METHODS	8-17
	8 3 1 Personal Exposure Models	8-21
	8 4 SUMMARY	8-24
	REFERENCES	8-26

LIST OF TABLES

Number		Page
1-1	Key Human Health Effects of Exposure to Nitrogen Dioxide—Clinical Studies	1-20
1-2	Key Human Health Effects of Exposure to Nitrogen Dioxide—Epidemiological Studies	1-22
1-3	Key Animal Toxicological Effects of Exposure to Nitrogen Dioxide	1-24
3-1	Theoretical Concentrations of Nitrogen Oxides and Nitrogen Acids That Would Be Present at Equilibrium with Molecular Nitrogen, Molecular Oxygen, and Water in Air at 25 °C, One Atmosphere, 50% Relative Humidity	3-3
3-2	Some Physical and Thermodynamic Properties of the Nitrogen Oxides	3-6
3-3	Theoretical Equilibrium Concentrations of Nitric Oxide and Nitrogen Dioxide in Air (50% Relative Humidity) at Various Temperatures	3-9
3-4	Theoretical Concentrations of Dinitrogen Trioxide and Dinitrogen Tetroxide in Equilibrium with Various Levels of Gaseous Nitric Oxide and Nitrogen Dioxide in Air at 25 °C	3-13
4-1	Major Source Categories .	4-3
4-2	Global Budget of Nitrogen Oxides in the Troposphere	4-13
4-3	Estimates of Nitrogen Oxide Emissions from Anthropogenic and Natural Sources in the United States and Canada	4-14
4-4	Total National Emissions of Nitrogen Oxides, 1940 to 1990	4-15
4-5	Transportation Contribution to United States Nitrogen Oxides Emissions .	4-16
4-6	Breakdown of 1988 Transportation Nitrogen Oxides	4-17
4-7	Emissions of Nitrogen Oxides from Stationary Fuel Combustion Sources, 1970 to 1990 . .	4-18
4-8	Total National Nitrogen Oxide Emissions, 1940 to 2010	4-19

LIST OF TABLES (cont'd)

Number		Page
4-9	Comparison of Anthropogenic and Natural Sources of Nitrogen Oxides Emissions for 1990	4-22
4-10	Comparison of Annual United States Nitrogen Oxide Emissions Estimates from Four Inventories	4-23
4-11	Emission Factors for Nitric Oxide and Nitrogen Dioxide from Burners on Gas Stoves, After Himmel and Dewerth (1974)	4-30
4-12	Emission Factors for Nitric Oxide and Nitrogen Dioxide from Pilot Lights on Gas Stoves, After Himmel and Dewerth (1974)	4-31
4-13	Emission Factors for Nitric Oxide, Nitrogen Dioxide, and Nitrogen Oxides for Top Burners on Gas Stoves Measured with a Sampling Hood and with a Chamber, After Cole et al (1983) and Moschandreas et al (1985)	4-33
4-14	Emission Factors for Nitric Oxide, Nitrogen Dioxide, and Nitrogen Oxides for Ovens, After Cole et al (1983) and Moschandreas et al (1985)	4-34
4-15	Emission Factors for Nitric Oxide and Nitrogen Dioxide from Pilot Lights on Gas Stoves, After Moschandreas et al (1985)	4-35
4-16	Emission Factors for Nitric Oxide and Nitrogen Dioxide from Range-Top Burners of Improved Design, After Cole and Zawacki (1985)	4-36
4-17	Emission Factors for Nitrogen Dioxide from 10 Gas Stoves in Use in Residences, Measured Independently by Research Groups	4-37
4-18	Average Emission Factors for Nitric Oxide, Nitrogen Dioxide, and Nitrogen Oxides from Burners on Gas Stoves Based on Data Reported in the Literature	4-37
4-19	Emission Factors for Nitrogen Oxide and Nitrogen Dioxide for Unvented Space Heaters	4-42
4-20	Emission Factors for Nitrogen Oxide and Nitrogen Dioxide for Convective and Infrared Heaters of Various Designs, Using Natural Gas and Propane . .	4-44

LIST OF TABLES (cont'd)

Number		Page
4-21	Average Emission Factors for Nitric Oxide and Nitrogen Dioxide from Kerosene Heaters, After Leaderer (1982) and Traynor et al (1983b)	4-46
4-22	Average Emission Factors for Nitric Oxide, Nitrogen Dioxide, and Nitrogen Oxides from Various Sources Based on Data Reported in the Literature . .	4-49
5-1	Major Reactions in the Nitrate Radical-Dinitrogen Pentoxide System at Night . .	5-35
5-2	Average Afternoon Background Pollutant Concentrations Measured at Kenosha, Wisconsin	5-38
6-1	Performance Specifications for Nitrogen Dioxide Automated Methods . . .	6-35
6-2	Comparability Test Specifications for Nitrogen Dioxide	6-36
6-3	Reference and Equivalent Methods for Nitrogen Dioxide Designated by the United States Environmental Protection Agency	6-37
6-4	National Precision and Accuracy Probability Limit Values Expressed as Percent for Continuous and Manual Methods for Nitrogen Dioxide .	6-39
7-1	Average Nitrogen Oxides Concentrations Measured at United States Nonurban Monitoring Locations	7-3
7-2	Average Mixing Ratios Measured at Isolated United States Rural Sites and Coastal Inflow Sites . .	7-4
7-3	Average Concentrations of Nitric Acid and Nitrate Ions Measured at Rural Sites	7-5
7-4	Average Concentrations of Nitric Acid and Nitrate Ions Measured at Urban Sites	7-6
7-5	Characterization of Hourly Average Nitrogen Dioxide Concentrations Near Selected Electrical Generating Plants	7-11

LIST OF TABLES (cont'd)

Number		Page
7-6	Maximum Annual Average Nitrogen Dioxide Concentrations Reported in United States Metropolitan Statistical Areas, 1988 to 1990	7-13
7-7	Maximum Hourly Average Nitrogen Dioxide Concentrations Reported in United States Metropolitan Statistical Areas, 1988 to 1990	7-15
7-8	Maximum Hourly Average Nitric Oxide Concentrations Reported in United States Metropolitan Statistical Areas, 1988 to 1990	7-16
7-9	Hourly Incidence of Nitrogen Dioxide Concentrations Greater Than 0 2 ppm for Stations with More Than One Occurrence, 1988	7-20
7-10	Maximum Hourly Average Nitrogen Dioxide Concentrations for Selected United States Rural Forested Sites	7-26
7-11	Characterization of Hourly Average Nitrogen Dioxide Concentrations for Selected United States Forest Sites	7-27
7-12	Maximum Hourly Average Nitrogen Dioxide Concentrations for Selected United States Rural Agricultural Sites	7-28
7-13	Characterization of Hourly Average Nitrogen Dioxide Concentrations for Selected United States Agricultural Sites	7-29
7-14	Maximum Hourly Average Nitric Oxide Concentrations Reported in Rural Areas, 1988 to 1990	7-33
7-15	Average Outdoor Concentrations of Nitrogen Dioxide and Average Indoor/Outdoor Ratios in Homes Without Known Indoor Sources from Field Studies of Private Residences	7-39
7-16	Indoor and Outdoor Concentrations of Nitrogen Dioxide in Homes with Gas Appliances, and the Calculated Average Contribution of Those Appliances to Indoor Residential Nitrogen Dioxide Levels	7-50
7-17	Frequency Distribution for Type of Range from 1985 and 1991 Surveys	7-58
7-18	Average Number of Days of Range Use per Week for Cooking, by Income	7-58

LIST OF TABLES (cont'd)

Number		Page
7-19	Reported Range/Oven Cooking Frequency in 1985 and 1991, by Type of Other Cooking Appliance	7-59
7-20	Summary Statistics for Gas Range Nitrogen Dioxide Maxima Over Several Averaging Times .	7-64
7-21	Two-Week Average Nitrogen Dioxide Levels by Location for Homes in Six Principle Source Categories, New Haven, Connecticut, Area Study, Winter, 1983	7-68
7-22	One-Week Average Nitrogen Dioxide Levels in Homes in North Central Texas by Source Category, with and Without Unvented Gas Space Heater	7-74
7-23	Empirical Statistical Models (Regression) for Residential Nitrogen Dioxide Concentrations Reported from Field Studies of Indoor Levels	7-82
8-1	Electric-Range Home Least Squares Regression Coefficients and T-Statistics .	8-22
8-2	Gas-Range Home Least Squares Regression Coefficients and T-Statistics .	8-23

LIST OF FIGURES

Number		Page
1-1	Nitrogen Cycle	1-10
3-1	Calculated steady states of the free troposphere as a function of nitrogen oxides concentration	3-5
4-1	Production of hydrocarbons, carbon monoxide, and nitrogen oxide as a function of air-fuel ratio	4-5
4-2	National trend in United States nitrogen oxides emissions, 1981 to 1990 .	4-19
4-3	Emission of nitrogen oxides compared with nitrogen oxide standards	4-21
4-4	Laminar blue-flame	4-25
4-5	Emission factors for nitric oxide as a function of gas flow rate	4-39
4-6	Emission factors for nitrogen dioxide as a function of gas flow rate	4-40
5-1	Summary of the gas phase chemistry of nitrogen oxides in the clean troposphere	5-2
5-2	Major chemical reactions affecting oxygen species in the troposphere	5-3
5-3	Major chemical reactions affecting hydrogen species in the troposphere	5-4
5-4	Schematic diagram of the combined reactions of nitrogen, oxygen, and hydrogen	5-5
5-5	Volatile organic compound oxidation in the atmosphere	5-6
5-6	Calculated steady state concentrations in the free troposphere as a function of nitrogen oxides concentration .	5-7
5-7	Summertime (June 1 to August 31) and wintertime (December 1 to February 28) ozone mixing ratio versus nitrogen oxides mixing ratio during the morning and afternoon	5-14
5-8	Summertime ozone mixing ratio versus nitrogen oxides mixing ratio measured during the afternoon hours	5-15

LIST OF FIGURES (cont'd)

Number		Page
5-9	Model calculated daytime change in ozone values (from sunrise to 1630 hours) for summer clear sky conditions is compared to the observed difference between the afternoon (1400 to 1900 hours) and the morning (0700 to 1100 hours) for clear sky conditions	5-16
5-10	Oxygen production per unit nitrogen oxides per day from the NMHC-PO model is plotted as function of nitrogen oxides mixing ratios . .	5-17
5-11	Total reactive odd nitrogen species shortfall	5-26
5-12	Formation and decay of diethylnitrosamine in the dark and in the sunlight from diethylamine and from triethylamine	5-29
5-13	Pollutant levels at the Kenosha, Wisconsin, sampling site before and after passage of the lake-breeze front	5-38
6-1	Absolute error in nitrogen dioxide for 10 seconds in the dark sampling line	6-13
7-1	National trend in the composite annual average nitrogen dioxide concentrations at both National Air Monitoring Station sites and all sites with 95% confidence intervals, 1980 to 1989	7-9
7-2	United States metropolitan area trends in the composite annual average nitrogen dioxide concentration, 1980 to 1989	7-10
7-3	Distribution of peak annual nitrogen dioxide averages in 103 Metropolitan Statistical Areas, 1988 to 1989, as derived by the United States Environmental Protection Agency from Aerometric Information Retrieval System (1991)	7-14
7-4	Monthly 50th, 90th, and 98th percentiles of one-hour nitrogen dioxide concentrations at selected stations, 1986 to 1989, as derived by the United States Environmental Protection Agency from Aerometric Information Retrieval System (1991)	7-18
7-5	Annual average nitrogen dioxide versus second-high one-hour concentration, 1988, 1989, and 1990	7-19

LIST OF FIGURES (cont'd)

Number		Page
7-6	Hourly relative frequency distributions of one-hour nitrogen dioxide values at four selected stations for 1988, with numbers of values greater than 0 2 ppm, as derived by the United States Environmental Protection Agency from Aerometric Information Retrieval System (1991)	7-21
7-7	Percent of one-hour nitrogen dioxide values above 0 03 and 0 05 ppm versus annual averages greater than 0 03 ppm, 1988, as derived by the United States Environmental Protection Agency from Aerometric Information Retrieval System (1991)	7-23
7-8	Relative distributions of one-hour nitrogen dioxide values at selected stations, 1988, as derived by the United States Environmental Protection Agency from Aerometric Information Retrieval System (1991) . . .	7-24
7-9	Seasonal pattern for nitrogen dioxide concentrations at rural and forested Aerometric Information Retrieval System monitoring sites .	7-30
7-10	Diurnal pattern for nitrogen dioxide at rural and forested Aerometric Information Retrieval System monitoring sites	7-31
7-11	Diurnal patterns for nitrogen dioxide monthly average concentrations at selected rural forested Aerometric Information Retrieval System monitoring sites	7-31
7-12	Diurnal patterns for nitrogen dioxide monthly average concentrations at selected rural agricultural Aerometric Information Retrieval System monitoring sites	7-32
7-13	Winter nitrogen dioxide concentrations by site and sampling location .	7-35
7-14	Ratio of average indoor nitrogen dioxide to ambient nitrogen dioxide concentrations by season and location in homes without a nitrogen dioxide source	7-42
7-15	Cumulative frequency distribution of nitrogen dioxide concentrations (one-week sampling period) by location for homes with no known gas appliances for a winter period in Southern California . .	7-43

LIST OF FIGURES (cont'd)

Number		Page
7-16	Cumulative frequency distribution and arithmetic means of nitrogen dioxide concentrations (two-week sampling period) by location for homes with no kerosene heater and no gas range for a winter period in the New Haven, Connecticut, area	7-43
7-17	Cumulative frequency distribution of nitrogen dioxide concentrations (one-week sampling period) by location for homes with no gas appliances for a summer period in Southern California	7-44
7-18	Indoor/outdoor nitrogen dioxide concentration ratios (two-week sampling periods) as a function of time for three homes in the United Kingdom without indoor nitiogen dioxide sources . .	7-45
7-19	Concentrations of nitrogen dioxide from October through March during 1988 and 1989, Albuquerque, New Mexico	7-48
7-20	Indoor versus outdoor nitrogen dioxide in five housing developments in Chattanooga, Tennessee	7-49
7-21	Nitrogen dioxide concentrations across seasons in Albuquerque, New Mexico, bedrooms that do and do not use the gas stove for space heating .	7-56
7-22	Verticle distribution of average nitrogen dioxide concentrations (48-hour sampling periods) measured in nine New York City apartments	7-61
7-23	Mean nitrogen dioxide concentrations (one-week sampling periods) for eight sampling periods by location in the home and type of cooking fuel . .	7-62
7-24	Nitrogen dioxide hourly levels in one home with gas appliances	7-65
7-25	Cumulative frequency distribution and arithmetic means by location, of average nitrogen dioxide levels (two-week sampling periods) during kerosene heater use for residences with one kerosene heater and no gas range, New Haven, Connecticut, area study, winter 1983	7-70
7-26	Cumulative frequency distributions and summary statistics for integrated nitrogen dioxide measurements in two locations (152 study homes)	7-72

LIST OF FIGURES (cont'd)

Number		Page
7-27	Cumulative frequency distributions and summary statistics for indoor nitrogen dioxide concentrations in three groups of monitored homes	7-73
7-28	Nitrogen dioxide box plots for 12 continuously monitored homes . . .	7-75
7-29	Bar graph of nitrogen dioxide removal rate for various materials evaluated in a 1 64-cubic meter test chamber at 50% relative humidity . . .	7-85
7-30	The deposition rates in air changes per hour for nitrogen as a function of percent relative humidity for two surface areas of three materials	7-87
7-31	Concentration distributions for gas-phase species in Boston nitrous acid and nitric acid	7-89
8-1	Average personal nitrogen dioxide exposure for each household compared with outdoor concentrations for summer and winter	8-7
8-2	Average personal nitrogen dioxide exposure for each home compared with average indoor concentrations for summer and winter	8-8
8-3	Comparison of the house average two-week nitrogen dioxide concentrations with the total personal nitrogen dioxide levels measured over the same time period for one adult resident in each house, New Haven, Connecticut, area, winter 1983	8-10
8-4a	Proportion of time spent by women who are full-time homemakers in indoor, outdoor, and in-transit microenvironments	8-20
8-4b	Proportion of time spent by employed persons in indoor, outdoor, and in-transit microenvironments	8-20

AUTHORS

Chapter 1. Executive Summary of Air Quality Criteria for Oxides of Nitrogen

Dr Dennis J Kotchmar
Environmental Criteria and Assessment Office
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Dr Judith A Graham
Environmental Criteria and Assessment Office
U.S Environmental Protection Agency
Research Triangle Park, NC 27711

Mr William G Ewald
Environmental Criteria and Assessment Office
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Dr Lester D. Grant
Environmental Criteria and Assessment Office
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

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

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

Chapter 2 Introduction

Dr Dennis J. Kotchmar
Environmental Criteria and Assessment Office
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Chapter 3: General Chemical and Physical Properties of Oxides of Nitrogen and Oxides of Nitrogen-Derived Pollutants

Dr Robert W. Elias
Environmental Criteria and Assessment Office
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Mr. William G Ewald
Environmental Criteria and Assessment Office
U S. Environmental Protection Agency
Research Triangle Park, NC 27711

AUTHORS (cont'd)

Chapter 4· Ambient and Indoor Sources and Emissions of Nitrogen Oxides

Dr. Charles A. Amann
KAB Engineering
984 Satlerlee Road
Bloomfield Hills, MI 48304-3152

Dr Gregory J McRae
702 Woodland Drive
Ohara Township
Pittsburgh, PA 15238

Dr. Cliff I Davidson
Department of Civil Engineering
Carnegie Mellon University
Pittsburgh, PA 15213

Chapter 5 Transport and Transformation of Nitrogen Oxides

Dr. Halvor Westberg
Laboratory for Atmospheric Research
Washington State University
Pullman, WA 99164-2730

Chapter 6. Sampling and Analysis for Nitrogen Oxides and Related Species

Dr. Joseph E. Sickles II
Atmospheric Research and Exposure Assessment
Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Chapter 7 Ambient and Indoor Concentrations of Nitrogen Oxides

Dr. Robert W Elias
Environmental Criteria and Assessment Office
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dr Allen S LeFohn
A S L Associates
111 Last Chance Gulch
Helena, MT 59601

Dr. Brian Leaderer
Pierce Foundation Laboratory
290 Congress Avenue
New Haven, CT 06519

Mr Tom McMullen
Environmental Criteria and Assessment
Office
U S Environmental Protection Agency
Research Triangle Park, NC 27711

AUTHORS (cont'd)

Chapter 8 Assessing Total Human Exposure to Nitrogen Dioxide

Dr Brian Leaderer
Pierce Foundation Laboratory
290 Congress Avenue
New Haven, CT 06519

CONTRIBUTORS AND REVIEWERS

Dr A Paul Altshuller
Atmospheric Research and Exposure
Assessment Laboratory
U S Environmental Protection Agency
Research Triangle Park, NC 27711

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

Dr Irwin H Billick
Gas Research Institute
8600 West Byrn Mawr Avenue
Chicago, IL 60631

Dr Steven D Colome
Integrated Environmental Services
University Tower, Suite 1090
4199 Campus Drive
Irvine, CA 92715

Dr. Cliff Davidson
Department of Civil Engineering
Carnegie Mellon University
Pittsburgh, PA 15213

Dr. Marcia Dodge
Air and Energy Engineering Research
Laboratory
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Dr Robert Elias
Environmental Criteria and Assessment Office
U S Environmental Protection Agency
Reseach Triangle Park, NC 27711

Dr Don Fox
School of Public Health
ENVR-CB #7400
University of North Carolina
Chapel Hill, NC 27599-7400

Dr Vic Hasselblad
Center for Health Policy Research
Duke University
Durham, NC 27713

Dr Brian Heikes
Graduate School of Oceanography
University of Rhode Island
Narrangansett Bay Campus
Narrangansett, RI 02882-1197

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

Dr Dennis J Kotchmar
Environmental Criteria and Assessment Office
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Mr Douglas Latimer
Latimer & Associates
505 27th Way #301
Boulder, CO 80303

Dr Brian Leaderer
Pierce Foundation Laboratory
Yale University School of Medicine
290 Congress Avenue
New Haven, CT 06519

Mr Frank McElroy
Atmospheric Research and Exposure
Assessment Laboratory
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Dr J David Mobley
Air and Energy Engineering Research
Laboratory
U S Environmental Protection Agency
Research Triangle Park, NC 27711

CONTRIBUTORS AND REVIEWERS (cont'd)

Mr. Warren Porter
U.S. Consumer Products Safety Commission
5401 Westbard Avenue
Room 724
Bethesda, MD 20816

Dr. P. Barry Ryan
Department of Environmental Science and Physiology
Harvard School of Public Health
677 Huntington Avenue
Boston, MA 02115

Dr. Joseph E. Sickles II
Atmospheric Research and Exposure Assessment Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dr. Thomas Stock
University of Texas
School of Public Health
P.O. Box 20186
Houston, TX 77225

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

Mr. John H Wasser
Air and Energy Engineering Research Laboratory
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Dr Hal Westberg
Laboratory for Atmospheric Research
Washington State University
Pullman, WA 99164-2730

Mr James White
Air and Energy Engineering Research Laboratory
U S Environmental Protection Agency
Research Triangle Park, NC 27711

Dr Warren White
6840 Waterman Avenue
St Louis, Missouri 63130

Dr Ron Wyzga
Electric Power Research Institute
3412 Hillview Avenue
P O Box 10412
Palo Alto, CA 94303

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

Oxides of Nitrogen Review

Former Chairman

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

Chairman

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

Members

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

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

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

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

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

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

Consultants

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

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

CLEAN AIR SCIENTIFIC ADVISORY COMMITTEE (cont'd)

Consultants (cont'd)

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

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

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

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

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

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

Dr Warren White
8840 Waterman Avenue
St Louis, MO 63130

Designated Federal Official

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

Staff Secretary

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

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

Scientific Staff

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

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

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

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

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

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

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

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

Technical Support Staff

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

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

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

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

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

Document Production Staff

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

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

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

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

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

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

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

Technical Reference Staff

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

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

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

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

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

1. EXECUTIVE SUMMARY OF AIR QUALITY CRITERIA FOR OXIDES OF NITROGEN

1.1 PURPOSE OF THE DOCUMENT

- The purpose of this document is to present air quality criteria for oxides of nitrogen (NO_x) in accordance with Sections 108 and 109 of the Clean Air Act Section 108 (U S Code, 1991) directs the Administrator of the U S Environmental Protection Agency (EPA) to list pollutants that may reasonably be anticipated to endanger public health and welfare, and to issue air quality criteria for them These air quality criteria are to reflect the latest scientific information useful in indicating the kind and extent of all identifiable effects on public health and welfare that may be expected from the presence of the pollutant in the ambient air

1.2 INTRODUCTION

- The present document, Air Quality Criteria for Oxides of Nitrogen, discusses the latest scientific information useful in deriving criteria to serve as scientific bases for EPA decisions regarding National Ambient Air Quality Standards (NAAQS) for nitrogen dioxide (NO_2) and/or other NO_x compounds The document is comprised of 16 chapters This Executive Summary concisely summarizes key conclusions from the document The following subsections follow the chapter organization

1.3 CHEMICAL AND PHYSICAL PROPERTIES OF NITROGEN OXIDES AND NITROGEN OXIDE-DERIVED POLLUTANTS

- Discussion of the general chemical and physical properties of NO_x and NO_x-derived pollutants is necessary for introduction to the complex chemical and physical interactions that may occur in the atmosphere and other media In this document, NO_x is the sum of NO_2 and nitric oxide (NO), and NO_y refers to the sum of NO_x and other oxidized nitrogen compounds, except nitrous oxide (N_2O) These other compounds include nitric acid (HNO_3), nitrogen trioxide (NO_3), dinitrogen trioxide (N_2O_3), dinitrogen tetroxide (N_2O_4), and dinitrogen pentoxide (N_2O_5) Peroxyacetylnitrate (PAN) is normally included with the NO_y group of compounds

- There are seven oxides of nitrogen that may be present in the ambient air NO, NO_2, N_2O, NO_3, N_2O_3, N_2O_4, and N_2O_5 Of these, NO and NO_2 are generally

present in highest concentrations in the lower troposphere Their interconvertibility in photochemical smog reactions has frequently resulted in their being grouped together under the designation NO_x, although analytic techniques can distinguish clearly between them Of the two, NO_2 has the greater impact on human health

- Nitrous oxide is ubiquitous even in the absence of anthropogenic sources because it is a product of natural biologic processes in soil It is not known, however, to be involved in any photochemical smog reactions Although N_2O is not generally considered to be an air pollutant, it participates in upper atmospheric reactions involving the ozone (O_3) layer

- Although NO_3, N_2O_3, N_2O_4, and N_2O_5 are present in the lower atmosphere only in very low concentrations, even in polluted environments, they play a role in atmospheric chemical reactions leading to the transformation, transport, and ultimate removal of nitrogen compounds from ambient air

- Ammonia (NH_3) is generated, on a global scale, during the decomposition of nitrogenous matter in natural ecosystems, and it may also be produced locally in larger concentrations by human activities such as the maintenance of dense animal populations It is discussed because, through its reaction with HNO_3, resulting in the formation of aerosol nitrate, it plays an important role in determining the atmospheric fate of nitrogen oxides

- Other NO_x-derived compounds that may be found in polluted air include nitrites, nitrates, nitrogen acids, *N*-nitroso compounds, and organic compounds such as the peroxyacyl nitrates ($RC(O)OONO_2$, where R represents any one of a large variety of possible organic groups)

1.4 EMISSIONS OF NITROGEN OXIDES FROM AMBIENT AND INDOOR SOURCES

- Anthropogenic sources of NO_2 emissions include transportation, stationary source fuel combustion, various industrial processes, solid waste disposal, and others, such as forest fires Natural sources of NO_x are lightning, biological and abiological processes in soil, and stratospheric intrusion

- Estimates for 1990 indicate that more than 80% of United States NO_x emissions are emitted by highway vehicles, electric utilities, and industrial boilers Quantitative estimates of the total amount of NO_x emitted to the ambient global atmosphere are available These estimates suggest that 122 to 152 $\times 10^6$ metric tons of NO_x are emitted annually, with about 18 to 19 $\times 10^6$ metric tons emitted in the United States alone

- The important indoor sources of NO_x are gas stoves, unvented space heaters, kerosene heaters, wood stoves, and tobacco products Total emissions and the ratio of NO/NO_2 from gas stoves and space heaters differ according to fuel flow rate and flame adjustment Additional factors, such as the load (e g , cold pot of water), heater type (convective versus radiant), and fuel type (natural gas, propane, or kerosene) may also be important Only limited information is available for wood stoves and tobacco products

1.5 TRANSPORT AND TRANSFORMATION OF NITROGEN OXIDES

- Nitrogen oxides are important chemical species in the planetary boundary layer, as well as in the free troposphere and the stratosphere Nitrogen oxides play important roles in the control of concentrations of radicals in the troposphere, in the production of tropospheric O_3, as an aerosol precursor, and in the production and deposition of acidic species, directly or indirectly

- Combustion processes emit a variety of nitrogen compounds, but chiefly NO, which can be oxidized to NO_2 in ambient air in the presence of O_3 or in a photochemically reactive atmosphere Photolytic decomposition of NO_2 leads to regeneration of NO, producing also an excited oxygen atom that reacts with molecular oxygen to form O_3 Free radicals generated from the oxidative degradation of volatile organic compounds (VOCs) oxidize NO to NO_2 without destroying O_3 Thus, the amount of O_3 formed in ambient air is dependent upon the concentration of NO_x present as well as the concentrations and reactivities of VOC species

- Photochemical processes that include the coupled reactions of NO_x, oxygen species, and free radicals produce not only O_3, but nitrogen-containing products as well These oxidation products include HNO_3, peroxynitric acid, nitrous acid (HONO), $RC(O)O_2NO_2$, N_2O_5, and inorganic and organic nitrates

- Nitric acid is a major sink for active nitrogen and is a contributor to acidic deposition It has been estimated to account for roughly one-third of the total acidity deposited in the eastern United States Potential physical and chemical sinks for HNO_3 include wet and dry deposition, photolysis, reaction with hydroxyl (OH) radicals, and two processes that lead to aerosol production neutralization with gaseous NH_3 and reactions with alkaline soil particles

- Peroxyacyl nitrates are formed from the combination of organic peroxy radicals with NO_2 Peroxyacetylnitrate is the most abundant member of this homologous series of compounds in the lower troposphere It can serve in the troposphere as a temporary reservoir for reactive nitrogen species and can be regionally transported, but it cannot function as a true sink in the lower troposphere because of its thermal instability In the upper troposphere, where temperatures are colder, the lifetime of PAN is longer

- The NO_3 radical is a short-lived radical that is formed in the troposphere primarily by the reaction of NO_2 with O_3 In daylight, NO_3 undergoes rapid photolysis or reaction with NO After sunset, accumulation of NO_3 can occur and is expected to be controlled by the availability of NO_2 and O_3 plus chemical destruction mechanisms involving the formation of N_2O_5 and HNO_3

- Dinitrogen pentoxide, the anhydride of HNO_3, is primarily a nighttime constituent of ambient air because it is formed from the reaction of NO_3 (itself a nighttime species) and NO_2 Dinitrogen pentoxide is thermally unstable, but at the lower temperatures of the upper troposphere, it can serve as a temporary reservoir of NO_3 In the boundary layer, N_2O_5 reacts heterogeneously with water to form HNO_3, which in turn is deposited out

- Amines, nitrosamines, and nitramines are thought to exist in ambient air, but at low concentrations Both nitrosamines and nitramines have short lifetimes in ambient air because they are photolytically decomposed or react with OH radicals and O_3

- The transport and dispersion of the various nitrogenous species are dependent on both meteorological and chemical parameters Advection, diffusion, deposition, and chemical transformations combine to dictate the atmospheric residence times, in turn, atmospheric residence times help determine the geographic extent of transport of a given species Surface emissions are dispersed vertically and horizontally through the atmosphere by tubulent mixing processes that are dependent to a large extent on the vertical temperature structure and wind speed

- As the result of meteorological processes, NO_x emitted in the early morning hours in an urban area will disperse vertically and horizontally (downwind) as the day progresses On sunny summer days, most of the NO_x will have been converted to HNO_3 and PAN by sunset Much of the HNO_3 is removed by deposition as the air mass is transported, but HNO_3 and PAN carried in layers aloft (above the nighttime inversion layer, but below a higher subsidence inversion) can potentially be transported long distances

- Transport of reactive NO_x in regional air masses can occur via several mechanisms (1) mesoscale phenomena, such as mountain-valley wind flow or land-sea breeze circulations (transport for tens to hundreds of kilometers), (2) synoptic weather systems, such as the migratory highs that cross the eastern United States in the summertime (transport for many hundreds of kilometers), and (3) mesoscale phenomena coupled with slow-moving high-pressure systems having weak pressure gradients In the latter interrelated phenomena, mountain-valley or land-water breezes can govern pollutant transport in the immediate vicinity of sources, but the ultimate fate of reactive NO_x species will be distribution into the synoptic system Information remains sparse on NO_x species and their concentrations in synoptic transport systems

- Except for N_2O, the reactive nitrogen species comprising the NO_x and NO_y families in the atmosphere do not absorb infrared radiation and, therefore, do not contribute directly to radiative "greenhouse" forcing They can, however, contribute indirectly to greenhouse processes through the photochemical production of O_3 in the troposphere Nitrous oxide, which is chemically inert in the troposphere, readily absorbs infrared radiation and is among the more significant non-carbon dioxide greenhouse gases Absorption of visible radiation by NO_2 could make this compound a possible source of other climatic influences if atmospheric concentrations become sufficiently higher

- Both wet and dry deposition of NO_x and other nitrogen species occur, but wet deposition is not a significant removal mechanism for NO or NO_2 because both gases are minimally soluble in water Transformation to more highly oxidized forms is necessary for effective wet deposition of NO_x, and the reaction of NO_2 with the OH radical to form HNO_3 appears to be the main source of nitrate ions in precipitation About one-third of the emissions of NO_x in the United States are estimated to be removed by wet deposition

- Dry deposition fluxes for NO_x are highly uncertain, mainly because of analytical problems and the simultaneous occurrence of emission and deposition of NO_x Available data indicate, however, that NO emissions exceed NO deposition and that NO_2 deposition exceeds NO deposition

1.6 SAMPLING AND ANALYSIS FOR OXIDES OF NITROGEN AND RELATED SPECIES

- In 1987, EPA designated a Reference Method and Equivalent Methods for NO_2, which specify a measurement principle and calibration procedures, namely gas-phase chemiluminescence (GP-CLM) with calibration using either gas-phase titration of NO with O_3 or an NO_2 permeation device The Sodium Arsenite Method in both the manual and continuous forms and the Triethanolamine-Guaiacol-Sulfite Method have been designated as Equivalent Methods Subsequently, commercial GP-CLM instruments were designated as Reference Methods The sensitivity of these devices was in the low parts-per-billion range, and, although the GP-CLM instruments were recognized as being susceptible to interferences by other nitroxy species, it was believed that the atmospheric concentrations of these compounds were generally low relative to NO_2

- Information from air quality monitoring networks is now readily available and has shown the GP-CLM instruments to have nominal precision and accuracy of ± 10 to 15% and 20%, respectively, and to have replaced manual methods to a large extent in network applications Although the basic design and performance of the commercial instruments have remained essentially unchanged, researchers have improved GP-CLM measurement technology and have refined other

instrumental methods to permit the determination of NO, NO_2, and NO_y in the low parts-per-trillion range

- A continuous liquid phase CLM device for sensitively detecting NO_2 has been developed and may be suitable to measure NO_2 Passive samplers for NO_2 have been used primarily for workplace and indoor applications, but hold promise for ambient measurements as well Gas chromatography with electron capture detection is useful in the determination of PAN, other organic nitrates, and N_2O

- Laser-induced fluorescence has been introduced to detect NO, NO_2, and HONO with high sensitivity and specificity Tunable-diode laser spectroscopy has been used to detect NO, NO_2, and HNO_3 Long-path spectroscopy has also been used to detect NO, NO_2, HONO, and NO_3 Two-tone frequency modulated spectroscopy holds promise for the sensitive measurement of NO, NO_2, PAN, HNO_3, and N_2O

- Interest in acidification of the environment has resulted in the development of methods for HONO and HNO_3 Integrative methods using denuders have been introduced to permit sensitive determination of these and other species

1.7 AMBIENT AND INDOOR CONCENTRATIONS OF OXIDES OF NITROGEN

1.7.1 Ambient Nitrogen Dioxide Levels

- Nitrogen oxides concentrations in isolated rural sites and coastal inflow areas in the United States generally range from a few tenths to 1 ppb The concentrations in the atmospheric boundary layer and lower free troposphere in remote maritime locations are in the range 0 02 to 0 04 ppb, and concentrations of NO_x in remote tropical forests have been reported to range from 0 02 to 0 08 ppb

- The average concentrations of HNO_3 and nitrate ions (NO_3^-) are generally in the range 0 1 to 20 ppb and 0 1 to 10 ppb, respectively Because there are conflicting reports on the ability of filters to accurately separate HNO_3 from NO_3^- aerosol, it may be more appropriate in some cases to focus on the total NO_3 (HNO_3 + NO_3^-) than on the individual components

- Analysis of NO_2 data in the Aerometric Information Retrieval System data base for the period 1981 to 1990 indicates a downward trend for the composite United States annual average NO_2 concentration The 1990 composite NO_2 average was 8% less than the 1981 average, and the difference was statistically significant

- The highest hourly and annual ambient NO_2 levels, which are reported from stations in Southern California, can exceed the annual NO_2 NAAQS of 0.053 ppm The seasonal patterns at California stations are usually quite marked

and reach their highest levels during the fall and winter months For most of the other urban sites characterized, the highest monthly average NO_2 concentrations were obtained in the months of November, December, January, or February

- The diurnal patterns of NO_2 for the urban sites showed that, on the average, the highest concentrations occur in the late afternoon and evening hours (1700 to 2200 hours) For those urban areas experiencing hourly NO_2 concentrations >0 2 ppm, the episodic occurrences are experienced usually in the midmorning and afternoon/evening hours

- Based on data collected at rural locations for the period 1979 to 1991, the hourly average NO_2 concentrations for selected U S forest and agricultural sites were <0 10 ppm in most cases As observed for urban locations, a consistent seasonal pattern was distinguishable for both the rural forested and agricultural sites In general, the NO_2 monthly average values were at their highest during the fall and winter months A consistent diurnal pattern was also observed for the rural forested and agricultural sites, late afternoon and evening hours (approximately 1700 to 2200 hours) contained the highest NO_2 concentrations

1.7.2 Indoor Nitrogen Dioxide Levels

- Indoor concentrations of NO_2 are a function of outdoor concentrations, indoor sources (source type, condition of source, source use, etc), infiltration ventilation, air mixing within and between rooms, reactive decay by interior surfaces, and air cleaning or source venting In homes without indoor sources of NO_2, concentrations are lower than outdoor levels due to removal by the building envelope and interior surfaces

- Gas appliances (gas range/oven, water heater, etc) are the major indoor source category for indoor residential NO_2 Nitrogen dioxide levels in homes with gas appliances are higher than those without such appliances and are often higher than levels encountered outdoors Within this catagory, the gas range/oven is a major contributor, especially when used as a supplemental heat source Average indoor concentrations in bedrooms (over a 1- to 2-week measurement period) range from 20 to 120 $\mu g/m^3$ (0 010 to 0 064 ppm) in some homes with gas ranges Homes with gas ranges with pilot lights have higher NO_2 levels than homes that have gas ranges without pilot lights

- Very limited data exist on short-term (3-h or less) average indoor concentrations of NO_2 associated with gas appliance use The limited data suggest that short-term indoor averages of NO_2 are higher than those recorded for outdoors

- Unvented kerosene and gas space heaters are important sources of NO_2 in homes because of both the NO_2 production rate of the heaters and the length of time the heaters are used Field studies indicate that average residential concentrations

(1- or 2-week average levels) exhibit a wide distribution, varying primarily with the amount of heater use and type of heater

- Efforts to model indoor NO_2 levels have employed both (1) physical/chemical and (2) empirical/statistical models These models have been used, with varying success, in explaining measured indoor levels of NO_2 for predicting NO_2 for specific indoor settings, and to estimate indoor concentration distributions Various empirical/statistical models have also been developed from large field-study data bases These employ questionnaire responses and measured physical data (house volume, etc) as key independent variables

- Indoor concentrations of HONO appear to be higher than outdoors, even when indoor NO_2 concentrations do not exceed outdoor levels In homes where unvented combustion sources are used, elevated HONO levels may be associated with direct emissions of HONO from the flame as well as with heterogeneous reactions of the produced NO_2 with water Nitric acid has been measured indoors during a summer period at concentrations lower than ambient

1.8 ASSESSING TOTAL HUMAN EXPOSURE TO NITROGEN DIOXIDE

- Exposure to NO_2 occurs across a number of microenvironments or settings An individual's integrated exposure (E) is the sum of all of the individual NO_2 exposures (E_i) over all time intervals for all microenvironments, weighted by the multiplicative product of the time (f_i) in each microenvironment times the NO_2 concentration (c_i) in the microenvironment The assessment of human exposures to NO_2 can be represented by the following simplified basic model

$$E = \sum_i E_i = \sum_i f_i c_i$$

Accurate assessments of total NO_2 exposure and the environments in which exposures take place are essential to minimize misclassification errors in epidemiologic studies, in defining population exposure distributions in risk assessment, and in developing effective mitigation measures in risk management

- Personal NO_2 exposures can be assessed A limited number of studies have been conducted in which personal exposures to NO_2 were measured using passive monitors These studies generally indicate that outdoor levels of NO_2, although related to and contributing substantially to both personal levels and indoor concentrations, are by themselves poor predictors of personal exposures for most populations Average indoor residential concentrations (e g , whole-house average or bedroom level) tend to be the best predictor of personal exposure, typically explaining 50 to 60% of the variation in personal exposures In selected populations, the indoor residential environment may not be a good

predictor of total exposure because of the higher percentages of time spent in different environments and/or the potential for unusual NO_2 concentrations

1.9 EFFECTS OF NITROGEN OXIDES ON VEGETATION

- Nitrogen oxides emitted into the atmosphere have the potential for influencing plant growth through either the leaves or the roots of plants Of the various nitrogen oxides found in the ambient air, only NO and NO_2 are considered phytotoxic However, the concentrations of gaseous nitrogen oxides in the atmosphere, by themselves or in combination with O_3 or sulfur dioxide, rarely are high enough to influence plant growth

1.10 EFFECTS OF NITROGEN OXIDES ON ECOSYSTEMS

- Nitrogen is an element essential for plant growth Most soils, however, are low in nitrogen, therefore, soil is usually the growth-limiting factor in both agricultural and natural ecosystems Nitrogen governs, to a large extent, the utilization of phosphorus, potassium, and other nutrients Most plants growing in natural ecosystems are adapted to living in soils with low nitrogen levels

- Now, however, because of the nitrogen deposition that has been occurring over many years, forest ecosystems in the temperate regions of the world that at one time were considered to be nitrogen limited are experiencing increased nitrogen deposition The traditionally held view that the growth of forests is nitrogen limited, undoubtedly, has delayed acceptance of the idea that increased nitrogen deposition is a potential source of stress in ecosystems

- Agricultural soils are usually so heavily fertilized that any effects of atmospheric nitrogen deposition cannot be readily observed, therefore, crop (agroecosystem) responses are not considered in the discussion of ecosystem effects because any addition would be considered beneficial

- The mean annual wet nitrate and ammonia deposition in the eastern United States ranges from 2 9 kg/ha at low elevations to 7 to 22 kg/ha at high elevations

- Nitrogen, whether added to the soil from atmospheric deposition, as fertilizer, or formed by nitrification, may (1) be taken up by plants, (2) be taken up by microorganisms, (3) be lost by runoff, or (4) escape as a gas into the atmosphere

- Chronic nitrogen deposition to natural ecosystems in terrestrial habitats alters the following plant and soil processes (1) plant uptake and allocation, (2) litter production and decomposition, (3) immobilization (includes ammonification, the release of ammonium, and nitrification, its conversion to nitrate, during the

decay of litter and soil organic matter), (4) nitrate ion leaching, and (5) trace gas emissions (e.g , nitrous oxides) and can lead to nitrogen saturation (see Figure 1-1)

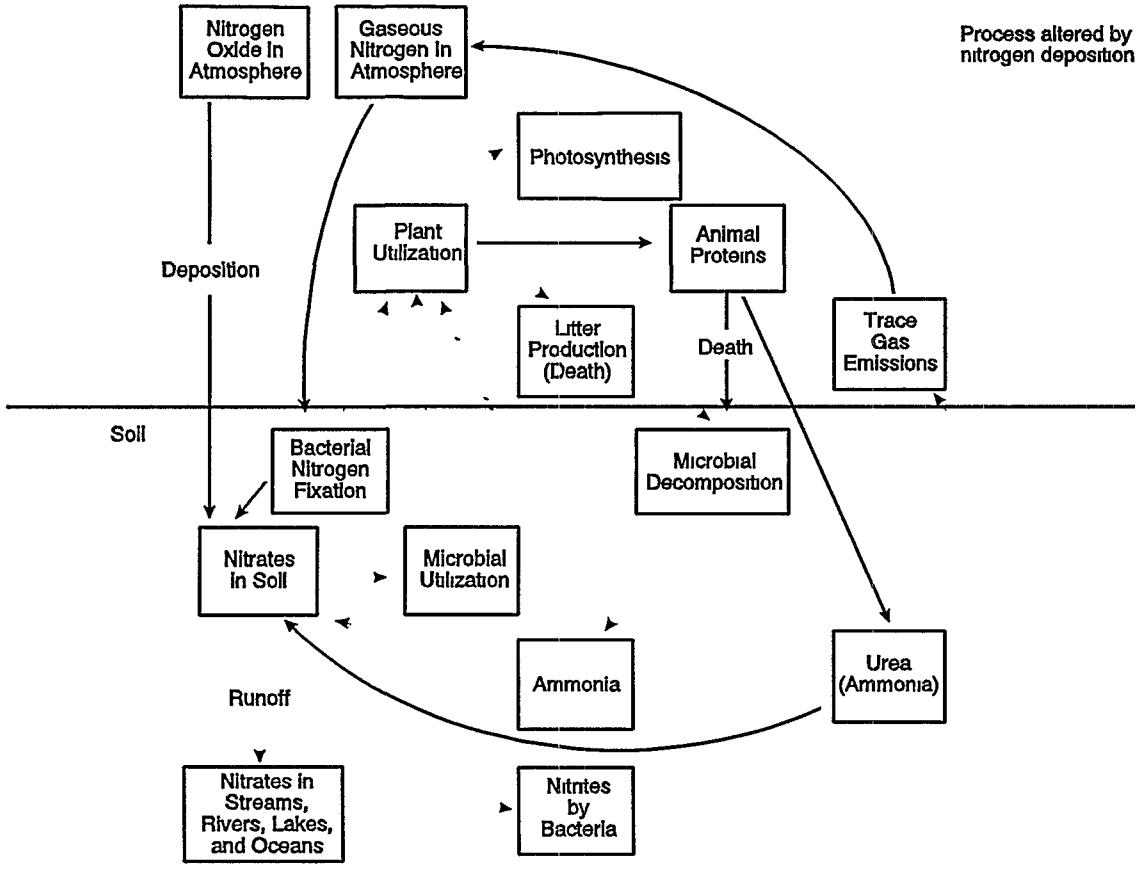


Figure 1-1. Nitrogen cycle (dotted lines indicate processes altered by chronic nitrogen deposition).

- Patterns of nitrogen uptake and carbohydrate allocation directly influence plant growth rates Growth responses are observable over time only if measurements are begun at the time deposition begins The forests in eastern North America today are responding to continuous nitrogen depositions that began no later than the 1930s Therefore, there are probably no pristine forests

  — Nitrogen uptake influences plant photosynthetic capacity and carbohydrate production because approximately 75% of the nitrogen accumulated in a leaf is used during the process of photosynthesis Carbohydrate allocation influences plant growth Plants shift allocation to the shoot or root depending on whether the need is for greater leaf or root growth Excess

soil nitrate shifts carbohydrate allocation to the shoots from the roots and provides nitrogen in a form difficult for plants to metabolize

— The high nitrogen content of leaves associated with increased soil nitrogen is advantageous only if light and water are not limiting because the lack of sunlight limits photosynthetic production of the large amounts of carbohydrates required in the metabolic conversion of nitrates

— Reduced carbohydrate allocation to the roots of plants growing in soil high in nitrogen is associated with increased amino acids in foliage, decreased root biomass, and the loss of the mycorrhizal root fungi necessary for uptake of water and minerals such as nitrogen and phosphorus Foliage of conifers in high nitrogen deposition areas of the United States are low in phosphorus

— The loss of mycorrhizal fungi and nutrient imbalances tend to make conifers more susceptible to drought, other pollutants, and pathogens Drought has been implicated as either triggering or increasing tree decline in forests in both North America and Europe Symptoms of magnesium deficiency and drought have been associated with increased amounts of soil nitrate

- Litter production (leaves, twigs, flowers, fruit, bark fragments, and dead plants) and decomposition of soil organic matter by microorganisms are the most important sources of usable nitrogen in unfertilized ecosystems

  — The nitrogen content of plant tissues influences the size of microbial populations and influences decomposition rates in both terrestrial and aquatic habitats Increased nitrogen in litter increases the amount of nitrogen entering soil and, in turn, alters soil microbial decomposition processes resulting in increased ammonium formation Increases in ammonium levels are expected to result in increased nitrate formation (see Figure 1-1)

  — Increases in the nitrogen content of litter and in litter decomposition rates as well as a change in nitrogen cycling have been observed in the more highly polluted areas of the San Bernardino Mountains of Southern California

- Nitrogen saturation results when continuous additions of nitrogen (nitrogen loading) to the soil exceed the capacity of plants and microorganisms to utilize nitrogen Ecosystems no longer function as a nitrogen sink Saturation implies that some resource other than nitrogen (e g, water and phosphorus for plants, carbon for microorganisms) is limiting biotic function

- Nitrogen saturation in itself need not have a negative impact on ecosystem functioning; brief periods of nitrogen saturation, a result of commercial

fertilization, generally have increased short-term productivity and often produced greater long-term growth

- Nitrate soil levels in excess of plant and microbial demand always result in increased nitrate leaching (i e , runoff [see Figure 1-1])

  — Recent measurements indicating increased nitrogen leaching from certain high-elevation forests in the southern Appalachian Mountains suggest that these forests have reached saturation, cumulative additions have exceeded the capacity of these systems to accumulate nitrogen

  — Nitrate leaching has the potential for mobilizing aluminum and acidifying soils and waters Pulses of nitrate and aluminum (Al^{3+}) have been reported from the Smoky Mountains of North Carolina

  — Nitrate leaching and runoff are probably more important sources of nitrogen in wetlands and aquatic habitats than nitrogen deposition

- Changes in the nitrogen supply can have a considerable impact on the nutrient balance of an ecosystem The nitrogen cycle, the source of all nitrogen required by plants and animals, is mediated in both terrestrial and aquatic habitats almost entirely by microorganisms, making it more sensitive to alterations in available nitrogen

  — Ecosystem response to environmental perturbations is determined by the response of its constituent organisms Response involves alteration of functions (the movement of energy and nutrients) between (1) the individual and its environment, (2) the population and its environment, and (3) the biological community and its environment, the ecosystem (see Figure 1-1)

  — Intense competition among plants for light, water, nutrients, and space, along with the recurrent natural climatic (temperature, wind, rain, and fire) 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

  — Competition for nutrients exists between the various species of plants and between plants and soil microorganisms

  — An increase in the nitrogen supply in both wetlands and soil habitats alters the competitive relationships among plant species Fast growing species that have a high nitrogen requirement are favored

  — In the Netherlands, excess nitrogen deposition has been postulated for (1) the replacement of heathlands by grasses, (2) a shift in composition of the herb layer in forests toward species more commonly found in nitrogen-

rich areas, and (3) the decrease in the past decades of fruiting bodies of mycorrhizal fungi (those growing on tree roots)

- Terrestrial ecosystems suggested as being at risk from deposition of nitrogen-based compounds are (1) heathlands, (2) low meadow vegetation types used for extensive grazing and haymaking, and (3) coniferous forests, especially those at high altitudes

- Ombrotrophic bogs (those dependent on wet and dry atmospheric deposition for their nutrients) are likely to be converted to forested wetlands because the plants normally growing there are unable to compete under increasing nitrogen deposition Increased nitrogen deposition has resulted in bogs in western Europe being converted to grasslands (as indicated above in the Netherlands)

- Wetlands harbor a disproportionate (relative to habitat area) share of the flora that are threatened by extinction Eighteen species of plants, such as the Venus fly trap, formally listed in the Code of Federal Regulation as endangered and an additional 284 species listed as potentially threatened are found principally in wetlands of the conterminous United States Several species on this list are adapted to nitrogen-poor environments and, therefore, are poor competitors in nitrogen-rich habitats

- In the United States, bogs inhabited by sensitive plants (e g , sun dews, pitcher plants, and the endangered Venus fly trap) are found chiefly in the southeast.

- Under anaerobic conditions, such as those found in wetlands, increased denitrification of large nitrate pools could lead to increased release of nitrous oxide to the atmosphere Nitrous oxides have been implicated as being among the gases involved in global warming (see Figure 1-1)

• The effects of nitrogen oxides in aquatic ecosystems fall into three general categories (1) acidification, both chronic and episodic, (2) eutrophication of both fresh water and estuaries, and (3) directly toxic effects

- Episodic acidification is far more common than chronic, and is well documented in streams and lakes in the Adirondack Mountains, for streams in the Catskill Mountains, and in a small proportion of lakes in Vermont and parts of Canada Episodic acidification has been associated with (1) seasonal snow melt and (2) seasonality of snow melt plus increasing nitrate concentrations

- Eutrophication is generally due to the limited availability of phosphorus Toxic effects of nitrogen on biota are associated with the presence of un-ionized ammonia (NH_3) at high pH and not with nitrates

- Concern regarding the possible effects of nitrogen saturation has lead to attempts to develop critical loads A critical load is defined as a quantitative estimate of exposure to one or more pollutants below which significant harmful effects on sensitive elements of the environment do not occur according to present knowledge. The cumulative nitrogen deposition (critical load) required to saturate an ecosystem is a *critical unknown*

1.11 EFFECTS OF NITROGEN OXIDES ON VISIBILITY

- The primary effects of NO_x on visibility are twofold (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

- Nitrogen dioxide and ammonium nitrate, which are the optically active species of NO_x, can contribute significantly to visibility impairment in the form of plumes and hazes

- Nitrogen dioxide causes yellow-brown discoloration, especially in power plant plumes in the western United States

- Nitrogen dioxide and nitrate aerosol are significant contributors to urban haze, especially in urbanized California and other western areas, where their combined share of total light extinction can be 20 to 40% Because of atmospheric conditions in those areas, NO_x are relatively small contributors to light extinction in nonurban areas

- The effects on visibility of NO_2 in plumes can be accurately predicted via models, but the effects of aerosol particles cannot be

- The effects of NO_x emission controls on nitrate aerosol concentrations and resulting visibility effects are nonlinear Also, the large-scale reduction of sulfate, which competes with nitrate for available NH_3, may result in increases in nitrate aerosol concentrations

- 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 aesthetic effects of air pollution-induced changes in atmospheric visibility have been the focus of most economic studies The few studies of effects of visibility changes on commercial operations (such as airports) suggest a very small economic impact from NO_x

- Two studies of visitors to the Grand Canyon National Park show that people would be willing to pay $2 to $3 or $3 to $6 per visitor or per party per day, respectively, to ensure that a thin, dark plume is not visible from a popular observation point A third study indicates a willingness to pay much more than this to preserve and protect for others good atmospheric visibility in the Grand Canyon, but considerable uncertainty exists in the quantitative results of the third study

- The best economic information available for visibility effects associated with NO_x is for changes in visual range in urban areas affected by uniform hazes These values fall between $10 and $100 per year per local household for a 10% change in visual range in major urban areas in California and throughout the eastern United States

- For layered hazes in recreational or residential settings, initial results from one study suggest annual household values of about $30 for a noticeable improvement in visibility conditions in the Denver area, where layered hazes are common

1.12 EFFECTS OF NITROGEN OXIDES ON MATERIALS

- Both NO_x (NO, NO_2) and NO_y (e g , HNO_3) have been shown to cause or accelerate damage to anthropogenic materials exposed to the atmosphere

- Strong evidence exists for the deleterious effects of NO_x on dyes and fabrics The effects observed are mainly fading, discoloration, and loss of strength of textile fibers

- Nitrogen oxides attack metals, but attack by sulfur dioxide (SO_2) is more aggressive because of surface deposition characteristics Damage to metals from NO_x can generally be discounted, except perhaps indoors, where NO_2 may react synergistically with SO_2 or where NO_x deposition on electronic components and magnetic recording equipment may lead to component or system failure

- Although NO_x and NO_y have been reported to play a role in damage to paints and stone, SO_2 and O_3 are thought to be more directly damaging than NO_x and NO_y in typical polluted atmospheres

- Archival and artistic materials, such as paper and artists' paints, have been shown to be susceptible to damage by NO_x, especially NO_2 These are typically materials used indoors

- The highest NO_x levels are found indoors wherever unvented combustion systems are used (e g , gas stoves) Because the widest variety of materials are in indoor use, the principal effects of NO_x on materials may thus occur indoors, but few data are available

- Economic estimates of the monetary value of NO_x damage to anthropogenic materials are few and are inadequate because of the unavailability of reliable damage functions, because they are out of date, or both

1.13 STUDIES OF THE EFFECTS OF NITROGEN COMPOUNDS ON ANIMALS

- Effects of NO_2 observed in laboratory animals (see below) have been confirmed in several animal species, resulting in a conclusion that these effects could occur in humans, if the appropriate exposures were encountered In addition, mathematical dosimetry models suggest that the greatest dose of NO_2 is delivered to the same location in both animal and human lungs (the centriacinar region) Thus, there is general support for a qualitative extrapolation of the data However, the data base is currently inadequate to develop a quantitative animal-to-human extrapolation (i e , the identification of the exposures that would actually evoke similar responses in humans) Exercise increases the total uptake of NO_2 in the respiratory tract of humans and alters the distribution of dose Generally, increased ventilation decreases the percent uptake in the upper respiratory tract and increases the percent uptake in the lower respiratory tract In people who exercise during exposure, this would tend to increase their susceptibility to effects

- Nitrogen dioxide increases susceptibility to both bacterial and viral pulmonary infections in animals This effect is probably due primarily to effects on alveolar macrophages and possibly to changes in the immune system, but other mechanisms cannot be ruled out The lowest observed concentration that increases susceptibility to bacterial lung infections after acute exposure is 2 0 ppm NO_2 (a 3-h exposure study in mice) Acute (17-h) exposures to $\geq$2 3 ppm NO_2 also decrease pulmonary bactericidal activity in mice After long-term exposures (e g , 3 to 6 mo) to 0 5 ppm NO_2, mice have decreased resistance to bacterial lung infections Nitrogen dioxide also increases susceptibility to viral lung infections in mice Subchronic (7-week) exposures to concentrations as low as 0 25 ppm NO_2 can alter the systemic immune system in mice

- When the relationship of NO_2 exposure concentration and duration was studied, concentration had more influence than duration on the health outcome This conclusion is primarily founded on extensive investigations of lung antibacterial defenses of mice, which also indicate that the exposure pattern (e g , baseline level with daily peaks of NO_2 or exposure 24 h/day versus 6 to 7 h/day) has an impact on the study results Another report suggests that lung structural changes are more dependent on exposure concentration than duration

- Nitrogen dioxide exposure causes lung structural alterations in several animal species (e.g., mice, rats, monkeys). Acute exposure effects are of little interest

because of high concentrations required to cause changes Prolonged exposures produce changes in the cells lining the region of the lung where the conducting airways and gas exchange area meet (i e , the centriacinar region) In addition, the tissue in this region (i e , alveolar interstitium) becomes thicker Urban patterns of NO_2 (e g , 0 5-ppm baseline with brief peaks to 1 5 ppm for 6 weeks or exposures to 0 5 ppm NO_2 for 4 to 6 mo) cause these effects in rats

- Several animal studies clearly demonstrate that chronic exposure to NO_2 can cause emphysema of the type seen in human lungs However, to date, only very high, environmentally unrealistic concentrations of NO_2 ($\geq$5 0 ppm) have been reported to cause such effects

- The effects of exposure to mixtures of NO_2 and other pollutants are dependent on the exposure regimen, species, and end point measured Most mixture research involves NO_2 and O_3 and shows that additivity and synergism can occur A similar conclusion can be drawn from the more limited research with NO_2 and sulfuric acid Findings of either additivity or synergism are of concern because of the ubiquitous co-occurring nature of NO_2 and O_3 However, precise extrapolation of these findings to ambient scenarios is confounded because the mixtures used in laboratories (by concentration, concentration ratio, and pattern) do not mimic the ambient air

1.14 EPIDEMIOLOGY STUDIES OF NITROGEN DIOXIDE

- Results from several of a number of indoor air epidemiology studies suggest that increased respiratory symptoms in 5- to 12-year-old children are associated with estimated exposure to NO_2 The associations reported in the majority of the studies did not reach statistical significance at $p \leq 0\ 05$ The consistency of these studies was examined and the evidence synthesized in a combined quantitative analysis (meta-analysis) of the subject studies Subject to assumptions made for the combined analysis, the main conclusion from that analysis was that an increased risk of about 20% for respiratory symptoms and disease corresponded to each increase of 0 015 ppm (28.3 $\mu g/m^3$) in estimated 2-week average NO_2 exposure, where mean weekly concentrations in bedrooms in studies reporting NO_2 levels were predominately between 0 008 and 0 065 ppm NO_2 The measured NO_2 studies gave a higher estimated odds ratio than the surrogate estimates, which is consistent with a measurement error effect The effect of having adjusted for covariates such as socioeconomic status, smoking, and gender was that those studies that adjusted for a particular covariate found larger odds ratios as compared with those that did not

- Several uncertainties need to be considered in interpreting the subject studies and results of the EPA meta-analysis. Measurement error in exposure is potentially one of the most important methodological problems in epidemiological studies of NO_2 Thus, measured NO_2 concentrations are not exposure values per se,

rather, estimating actual exposure requires knowledge of both pollutant levels and related human activity patterns The effects studied may be related to peak exposures, average exposures, or a combination of the two To the extent that health effects depend on peak exposures rather than average exposures, the exposure estimates used in the subject studies and meta-analyses introduce exposure measurement error These studies cannot distinguish between the relative contributions of peak and average exposures and their relationship with the observed health effects Additionally, a by-product of NO_2, HONO, may be a factor in observed health effects However, only very limited health and aerometric data are available that examine such possibilities Also, although the level of similarity and common elements between the health outcome measures in the NO_2 studies provide some confidence in their use in the quantitative analysis, the symptoms and illnesses combined are to some extent different and could indeed reflect different underlying processes Thus, caution is necessary in interpreting the meta-analysis results

- Although there is evidence that suggests that increased estimated NO_2 exposure is associated with increased respiratory symptoms in children aged 5 to 12 years, the exposure estimated may be inadequate to determine a quantitative relationship between estimates of exposure and symptoms The studies with measured NO_2 exposure did so only for periods of 1 to 2 weeks and reported the values as averages. None of the studies attempted to relate the effects seen to the pattern of exposure, such as short-term peaks Furthermore, the extrapolation to possible patterns of ambient exposure is difficult

- In individual indoor studies of infants 2 years of age and younger, no consistent relationship was found between estimates of NO_2 exposure and the prevalence of respiratory symptoms and disease Based on a meta-analyses of these indoor infant studies, subject to the assumptions made for the meta-analysis, the combined odds ratio for the increase in respiratory disease per increase of 0.015 ppm NO_2 was 1 09 with a 95% confidence interval of 0 95 to 1 26, where mean weekly concentrations in bedrooms were predominately between 0 005 and 0.050 ppm NO_2 in studies reporting levels Thus, although the overall combined estimate is positive, it clearly contains the no-effect value of 1 0, (i e , is not statistically significant), and so we cannot conclude that the evidence suggests an effect in infants comparable to that seen in older children

- Other epidemiology studies have attempted to relate some measure of indoor and/or outdoor NO_2 exposure to long-term changes in pulmonary function These changes were marginally significant Most studies did not find any effects, which is consistent with controlled human exposure study data (see Chapter 15) However, there is insufficient epidemiological evidence to make any conclusion about the long- or short-term effects of NO_2 on pulmonary function

1.15 CONTROLLED HUMAN EXPOSURE STUDIES OF OXIDES OF NITROGEN

- Nitrogen dioxide causes decrements in lung function, particularly increased airway resistance in healthy subjects at 2-h concentrations exceeding 2 0 ppm

- Nitrogen dioxide exposure results in increased airway responsiveness in healthy, nonsmoking subjects exposed to concentrations exceeding 1 0 ppm for exposure durations of 1 h or longer

- Nitrogen dioxide exposure at levels above 1 5 ppm may alter numbers and types of inflammatory cells in the distal airways or alveoli, but these responses depend upon exposure concentration, duration, and frequency Nitrogen dioxide may alter function of cells within the lung and production of mediators that may be important in lung host defenses

- Nitrogen dioxide exposure of asthmatics causes, in some subjects, increased airway responsiveness to a variety of provocative mediators, including cholinergic and histaminergic chemicals, SO_2, and cold air However, the presence of these responses appears to be influenced by the exposure protocol, particularly whether or not the exposure includes exercise

- Modest decrements in spirometric measures of lung function (3 to 8%) may occur in some asthmatics and patients with chronic obstructive pulmonary disease (COPD) from brief exposure to concentrations of NO_2 greater than 2 ppm and may also be observed with longer exposures to lower concentrations

- Nitric acid levels in the range of 100 to 200 ppb may cause some pulmonary function responses in adolescent asthmatics, but not in healthy adults Other commonly occurring NO_x species do not appear to cause any pulmonary function responses at concentrations expected in the ambient environment, even at higher levels than in worst-case scenarios However, not all nitrogen oxides acid species have been studied sufficiently

- No association between lung function responses and respiratory symptom responses were observed Furthermore, there is little evidence of a concentration-response relationship for changes in lung function, airway responsiveness, or symptoms at the NO_2 levels that are reviewed here

1.16 NITROGEN DIOXIDE HEALTH EFFECTS: CONCENTRATION-RESPONSE RELATIONSHIPS AND SUBPOPULATIONS POTENTIALLY AT RISK

1.16.1 Concentration-Response Relationships

- Table 1-1 summarizes key health effects observed in controlled human exposure (clinical) studies with NO_2 exposure durations of 0 5 to 3 h The physiological end point that, to date, appears to be the most sensitive indicator of response is a change in airway responsiveness to bronchoconstrictors in asthmatics This increase in airway responsiveness has been observed in some, but not all studies, and only at relatively low NO_2 concentrations within the range 0 2 to 0 3 ppm

TABLE 1-1. KEY HUMAN HEALTH EFFECTS OF EXPOSURE TO NITROGEN DIOXIDE—CLINICAL STUDIES[a]

NO_2 (ppm) (Exposure Duration)	Observed Effects
0 2-0 3 (0 5-2 0 h)	Trend toward increased airway responsiveness to challenges in asthmatics However, no significant effects observed by same or other investigators at NO_2 levels up to 4 ppm Small (4-6%) decreases in FEV_1 or FVC in adult or adolescent asthmatics, in response to NO_2 alone
0 3 (3.75 h)	Small decreases (5-9%) in FVC and FEV_1 in COPD patients with mild exercise No effects seen by other investigators for COPD patients at 0 5-2 0 ppm NO_2
1 5-2 0 (2-3 h)	Increased airway responsiveness to bronchoconstrictors in healthy adults However, effects not detected by other investigators at 2-4 ppm
≥2.00 (1-3 h)	Lung function changes (e g , increased airway resistance) in healthy subjects Effects not found by others at 2-4 ppm

[a]NO_2 = Nitrogen dioxide
FEV_1 = Forced expiratory volume in 1 s
FVC = Forced vital capacity
COPD = Chronic obstructive pulmonary disease

Additionally, small decreases in forced expiratory volume in 1 s (FEV_1) or forced vital capacity (FVC) in adult or adolescent asthmatics have been observed in response to the same levels of NO_2. However, NO_2 concentration-response relationships are not evident for either airway responsiveness or pulmonary function changes A second category of sensitive subjects is patients with COPD. Although small decreases have been observed in FVC and FEV_1 in

COPD patients exposed to 0 3 ppm in one study, no effects were seen in other studies at higher exposure levels At higher exposure levels (more than 1 5 ppm), NO_2 exposure results in increased airway responsiveness and increased airway resistance in healthy adults However, some researchers have not observed any NO_2-induced changes in airway resistance at NO_2 levels between 2 and 4 ppm

- The collective, combined evidence from epidemiology studies examining relationships between estimates of exposure to NO_2 and lower respiratory symptoms and disease in children aged 5 to 12 years (as evaluated by an EPA meta-analysis yielding quantitative estimates of effects) tends to demonstrate that increased risk for respiratory illness among children is associated with exposure to NO_2, as summarized in Table 1-2 In individual indoor studies of infants 2 years of age and younger, no consistent relationship was found between estimates of NO_2 exposure and the prevalence of respiratory symptoms and disease Based on a meta-analyses of these infant studies, the combined odds ratio for the increase in respiratory disease per increase of 0 015 ppm NO_2 was 1 09 with a 95% confidence interval of 0 95 to 1 26 Thus, although the overall combined estimate is positive, it clearly contains the no-effect value of 1 0, (i e , is not statistically significant), and so we cannot conclude that the evidence suggests an effect in infants comparable to that seen in older children (see Table 1-2) Higher levels (>0 3 ppm during a shift at work) in an occupational setting were related to an elevated prevalence of acute respiratory symptoms in adults Also, episodic exposures occurring over a period of 1 h or longer at levels possibly as high as 1 5 ppm or higher have resulted in the occurrence of acute respiratory symptoms Lastly, exceptionally high acute occupational exposures of 25 to 100 ppm NO_2 result in bronchial pneumonia, bronchitis, or bronchiolitis, and very extreme occupational NO_2 exposures (>200 ppm) have been associated with effects that range from hypoxemia and transient obstruction of the airways to death

- Numerous concentration-response studies have been conducted with animals using a wide range of exposure durations and end points, all of which influence the outcome The major classes of effects observed at concentrations less than 1 0 ppm include decrements in host defenses, alterations in lung metabolism (e g , increased lipid peroxidation and antioxidant metabolism), epithelial remodeling of the lower respiratory tract, thickening of the centriacinar interstitium, and a variety of extrapulmonary changes Such findings can be qualitatively extrapolated to humans, but major uncertainties in respiratory tract dosimetry and species sensitivity currently preclude a quantitative extrapolation Substantially higher NO_2 concentrations ($\geq$12 ppm) have caused emphysema as defined by National Institutes of Health criteria

TABLE 1-2. KEY HUMAN HEALTH EFFECTS OF EXPOSURE TO NITROGEN DIOXIDE—EPIDEMIOLOGICAL STUDIES[a]

NO_2 (ppm) (Exposure Duration)	Observed Effects
0 015-ppm increase, where mean weekly concentrations in bedrooms in studies reporting levels were predominately between 0 008 and 0.065 ppm NO_2 (in 1- and 2-week integrated average NO_2 concentration estimating an unspecified long-term average)	A meta-analysis shows an increased risk of lower respiratory symptoms/disease in children 5 to 12 years old associated with exposure estimates of NO_2 levels The 95% confidence interval of the odds ratio was 1 1 to 1 3 (see Chapter 14) Predominant source of exposure contrast is homes with gas stoves vs homes with electric stoves
0.015-ppm increase in annual average of 2-week NO_2 levels, where mean weekly concentrations in bedrooms were predominately between 0 005 and 0 050 ppm NO_2	In individual indoor studies of infants 2 years of age and younger, no consistent relationship was found between estimates of NO_2 exposure and the prevalence of respiratory symptoms and disease Based on a meta-analyses of these infant studies, the combined odds ratio for the increase in respiratory disease per increase of 0 015 ppm NO_2 was 1 09 with a 95% confidence interval of 0 95 to 1 26 Thus, although the overall combined estimate is positive, it clearly contains the no-effect value of 1 0, (i e , is not statistically significant), and so we cannot conclude that the evidence suggests an effect in infants comparable to that seen in older children (see Chapter 14)
>0.3 ppm (average exposure during work shift)	Elevated prevalence of acute respiratory symptoms
Episodic exposure during hockey game to NO_2 levels of 1 5 ppm or higher	Occurrence of acute respiratory symptoms (cough, chest pain, dyspnea)
25 to 100 ppm (episodic occupational exposure)	Bronchial pneumonia, bronchitis, and bronchiolitis induced by exceptionally high NO_2 exposure
>200 ppm (extreme episodic exposures)	Extreme exposure health outcomes range from hypoxemia/transient airway obstruction to death

[a]NO_2 = Nitrogen dioxide

- Results from infectivity studies examining concentration (C) × duration (T, time) of exposure and pattern of exposure indicate that concentration exerted more influence than time of exposure in increasing susceptibility to respiratory bacterial infection in mice Furthermore, the exact pattern of exposure played a major role in experimental outcomes Even so, duration is still important

- For example, as exposures proceed from weeks to months at a given NO_2 concentration, structural changes in the lung become more severe Also, at longer exposure durations, lower NO_2 concentrations cause effects Due to the

large number of animal toxicological studies and the variety of exposure regimes, it is not possible to succinctly display the full range of concentration responses Therefore Table 1-3 lists a few key studies showing the lowest concentrations that caused several types of effects

1.16.2 Subpopulations Potentially at Risk

- Certain groups within the population may be more susceptible to the effects of NO_2 exposure, including persons with preexisting respiratory disease, children, and the elderly The reasons for paying special attention to these groups is that (1) they may be affected by lower levels of NO_2 than other subpopulations or (2) the impact of an effect of given magnitude may be greater Some causes of heightened susceptibility are better understood than others Subpopulations that already have reduced ventilatory reserves (e g , the elderly and persons with asthma, emphysema, and chronic bronchitis) will be more impacted than other groups by decrements in pulmonary function For example, a healthy young person may not even notice a small percentage change in pulmonary function, but a person whose activities are already limited by reduced lung function may not have the reserve to compensate for the same percentage change

- Approximately 10 million persons in the United States have asthma In the general population, asthma prevalence rates increased by 29% from 1980 to 1987 For those under 20 years old, asthma rates increased from approximately 35 to 50 per 1,000 persons, a 45% increase The airways of asthmatics may be hyperresponsive to a variety of inhaled materials, including pollens, cold-dry air, allergens, and air pollutants Asthmatics have the potential to be among the most susceptible members of the population with regard to respiratory responses to NO_2 On the average, asthmatics are much more sensitive to inhaled bronchoconstrictors such as histamine, methacholine, or carbachol The potential addition of an NO_2-induced increase in airway response to the already heightened responsiveness to other substances raises the possibility of exacerbation of this pulmonary disease by NO_2

- Other potentially susceptible groups include patients with COPD, such as emphysema and chronic bronchitis Some of these patients have airway hyperresponsiveness to physical and chemical stimuli A major concern with COPD patients is the absence of an adequate ventilatory reserve, a susceptibility factor described above In addition, the poor distribution of respiratory tract ventilation in COPD may lead to a greater delivery of NO_2 to the segment of the lung that is well ventilated, thus resulting in a greater regional tissue dose Also, NO_2 exposure may alter already impaired defense mechanisms, making this population potentially susceptible to respiratory infection It is estimated that 14 million persons in the United States ($\approx$ 6%) suffer from COPD

TABLE 1-3. KEY ANIMAL TOXICOLOGICAL EFFECTS OF EXPOSURE TO NITROGEN DIOXIDE

Nitrogen Dioxide (ppm) (Exposure Duration)	Species	Observed Effects
0 04 ppm (continuous, 9 mo)	Rat	Increased lipid peroxidation (ethane in exhaled breath)
0.2 ppm (continuous base for 1 year) plus 0 8 ppm (1-h peak, 2×/day, 5 days/week)	Mouse	Increased susceptibility to respiratory infection and decreased vital capacity and respiratory system compliance, compared to control or baseline only
0 25 ppm (7 h/day, 5 days/week, 7 weeks)	Mouse	Systemic effect on cell-mediated immunity
0 3 ppm (2 h/day, 2 days)	Rabbit	Decreased phagocytosis of alveolar macrophages
0.4 ppm (continuous, 4 weeks)	Mouse	Decreased systemic humoral immunity
0 4 ppm (continuous, 9 mo)	Rat	Increased antioxidants and antioxidant metabolism
0.4 ppm (continuous, up to 27 mo)	Rat	Slight increase in thickness of air blood barrier at 18 mo, becoming significant by 27 mo, also alterations in bronchiolar and alveolar epithelium by 27 mo
0 5 ppm (continuous) 3 mo	Mouse	Increased susceptibility to respiratory infection
0.5-28 ppm (6 min to 1 year)	Mouse	Linear increase in susceptibility to respiratory infection with time, increased slope of curve with increased concentration, concentration more important than time
0 5 ppm (continuous base, 6 weeks) plus 1 5 ppm (1-h peak, 2×/day, 5 days/week)	Rat	Alterations in Type 2 cells and increased interstitial matrix of proximal alveolar region, no changes in terminal bronchiolar region of adults

- Based on epidemiology studies, children aged 5 to 12 years constitute a subpopulation potentially susceptible to an increase in respiratory morbidity associated with NO_2 exposure (Chapter 14) In the United States, approximately 18 million children are in the age group 5 to 9 years, whereas around 17 million children are in the age group 10 to 14 years However, the fractions of the numbers of potentially at risk children in various age groups that are actually exposed to NO_2 concentrations/patterns sufficient to induce respiratory morbidity have not been determined

- Another potential susceptible subpopulation group is immunocompromised individuals, who would have an increased susceptibility for infectious pulmonary disease as well as other health effects Such people would hypothetically be more susceptible to agents, such as NO_2, that further compromise host defenses Immunocompromised groups could include those people with abnormalities in polymorphonuclear leukocyte number or function and those with humoral and/or cell-mediated immunity dysfunctions This would include people with reduced

immune function related to kidney transplants, acquired immune deficiency syndrome (AIDS), and chemotherapy Although these immunocompromised groups represent potentially at-risk susceptible populations for NO_2 effects, no human research has examined NO_2 exposure in these groups Thus, there only now exists a hypothesized association with increased susceptibility to NO_2 Although it is clear that NO_2 can affect alveolar macrophages, humoral immunity, and cell-mediated immunity in otherwise normal animals (Chapter 13), the animal-to-human extrapolation cannot yet be made quantitatively Nevertheless, it may be prudent to consider including such reduced immune function groups as susceptible subpopulations at potentially increased risk for NO_2-induced health effects

2. INTRODUCTION

The purpose of this document is to present air quality criteria for oxides of nitrogen (NO_x) in accordance with Sections 108 and 109 of the Clean Air Act (CAA) Section 108 (U S Code, 1991) directs the Administrator of the U S Environmental Protection Agency (EPA) to list pollutants that may reasonably be anticipated to endanger public health and welfare, and to issue air quality criteria for them These air quality criteria are to reflect the latest scientific information useful in indicating the kind and extent of all identifiable effects on public health and welfare that may be expected from the presence of the pollutant in the ambient air

Section 109(a,b) (U S Code, 1991) directs the EPA Administrator to propose and promulgate "primary" and "secondary" National Ambient Air Quality Standards (NAAQS) for pollutants identified under Section 108 Section 109(b)(1) defines a primary standard as a level of air quality, the attainment and maintenance of which in the judgment of the Administrator, based on the criteria and allowing for an adequate margin of safety, is requisite to protect the public health Section 109(d) of the Act (U S Code, 1991) requires periodic review and, if appropriate, revision of existing criteria and standards In addition, Section 109(c) specifically requires the Administrator to promulgate a primary standard for nitrogen dioxide (NO_2) with an averaging time of not more than 3 h, unless no significant evidence is found that such a short-term standard is required to protect health Under Section 109(b) of the CAA, the Administrator must consider available information to set secondary NAAQS that are based on the criteria and are requisite to protect the public welfare from any known or anticipated adverse effects associated with the presence of such pollutants The welfare effects included in the criteria are effects on vegetation, crops, soils, water, animals, manufactured materials, weather, visibility, and climate, as well as damage to and deterioration of property, hazards to transportation, and effects on economic values, personal comfort, and well-being

A variety of NO_x compounds and their transformation products occur naturally in the environment and also result from human activities In addition to NO_2, nitric oxide (NO), nitrous oxide, gaseous nitrous acid, gaseous nitric acid, and both nitrite and nitrate particles

have all been found in the ambient air The formation of nitrosamines in the atmosphere by reaction of NO_x with amines has also been suggested, but not yet convincingly demonstrated Available scientific research on the potential health and welfare effects of NO_x compounds provides the strongest evidence linking specific adverse effects to near-ambient concentrations of NO_2. Therefore, EPA has focused its criteria reviews primarily on health and welfare effects reported to be associated with exposure to NO_2 Nitrogen dioxide is an air pollutant generated mainly by the photochemically initiated oxidation of NO, which is emitted from a variety of mobile and stationary sources At elevated concentrations, NO_2 can adversely affect human health, vegetation, materials, and visibility Nitrogen oxide compounds can also contribute to increased rates of acidic deposition and high ozone concentrations

2.1 REGULATORY AND SCIENTIFIC BACKGROUND

On April 30, 1971, EPA first promulgated the NAAQS for NO_2 under Section 109 of the CAA (Federal Register, 1971) Identical primary and secondary standards for NO_2 were set at 0.053 ppm (100 $\mu g/m^3$), averaged over 1 year The scientific bases for these standards are contained in the original criteria document, Air Quality Criteria for Nitrogen Oxides (U.S. Environmental Protection Agency, 1971) The primary standard set in 1971 was based mainly on community epidemiology studies (Shy et al , 1970a,b, Pearlman et al , 1971) conducted in Chattanooga, TN, which reported respiratory effects in children exposed to low-level NO_2 concentrations over a long-term period

In response to the August 1977 Clean Air Act Amendments, EPA developed the document Health Effects of Short-Term Exposures to Nitrogen Dioxide Air Quality Criteria (U.S. Environmental Protection Agency, 1978b) to serve as the basis for evaluating the need to promulgate a NAAQS for short-term concentrations of NO_2 On December 12, 1978 (Federal Register, 1978), EPA announced that this document on short-term effects of NO_2 would be incorporated into the full revision of the 1971 Air Quality Criteria for Oxides of Nitrogen, which EPA was then in the process of reviewing and updating in accordance with Section 109(d)(1) of the CAA as amended This process resulted in the production of the revised 1982 document, Air Quality Criteria for Oxides of Nitrogen (U S Environmental Protection Agency, 1982a)

In accordance with Sections 108 and 109 of the CAA, in 1985 EPA completed the review of criteria upon which the existing primary and secondary NO_2 NAAQS were based Reevaluation of the Chattanooga studies in view of later information (especially regarding the accuracy of the air quality monitoring method for NO_2 used in the studies) indicated that these studies provide only limited qualitative evidence for an association between health effects and ambient exposures to NO_2 In reviewing the scientific basis for an annual standard, EPA found that evidence showing the most serious health effects associated with chronic NO_2 exposures (e g , emphysematous-like alterations in the lung and increased susceptibility to infection) came from animal studies conducted at concentrations well above those permitted in the ambient air by the current annual standard Major factors impeding use of these studies for standard-setting purposes included limitations of methods for quantitatively extrapolating exposure-response relationships from these animal studies directly to humans However, the seriousness of these effects, coupled with biological similarities between humans and test animals, suggested that there was some risk to human health from long-term exposure to elevated NO_2 levels Other evidence from community epidemiology and gas-stove epidemiology studies provided some qualitative support for concluding that there is a relationship between adverse health effects and repeated, acute exposures to elevated ($\geq$0 2 to 1 0 ppm) NO_2 concentrations or longer term human exposure to near-ambient levels of NO_2 However, concern at that time for limitations associated with these studies (e g , unreliable or insufficient monitoring data and inadequate treatment of potential confounding factors such as humidity and pollutants other than NO_2) then precluded derivation of quantitative exposure-response relationships

Although it is not possible to quantify the margin of safety provided by the existing annual standard, two observations are relevant (1) a 0 053-ppm standard was consistent with the Clean Air Science Advisory Committee's (CASAC's) recommendation (Friedlander, 1982) to set the annual standard at the lower end of the range (0 05 to 0 08 ppm) cited in the Office of Air Quality Planning and Standards (OAQPS) Staff Paper (U S Environmental Protection Agency, 1982b) to ensure an adequate margin of safety against long-term effects and to provide some measure of protection against possible short-term health effects, and (2) a 0 053-ppm standard would keep annual NO_2 concentrations considerably below the long-term exposure levels for which serious chronic effects have been observed in animals

Maintaining the current annual primary standard thus represented, at that time, a prudent public health policy choice aimed at preventing any increased chronic health risk in large, populated U S. urban areas that attain the annual standard On July 19, 1985, EPA announced the final decision to retain the existing annual primary and secondary standards The decision on the need, if any, for a separate short-term standard (less than 3 h) was deferred, pending results from additional research focused on reducing uncertainties associated with evaluating short-term health effects of NO_2

2.2 CRITICAL ISSUES

Based on the available scientific evidence, several critical data bases and associated issues are addressed in this document Some of the key issues addressed are as follows

1. An evaluation of the clinical studies data examining short-term exposure (1 to 3 h) to NO_2 in the range of 0 2 to 0 5 ppm and increased bronchial reactivity in asthmatics is presented

2 The strength and consistency of the epidemiologic data base that relates NO_2 estimates of exposure and an increased rate and/or severity of respiratory symptoms and disease are reviewed Further, a meta-analysis of selected studies is provided that evaluates the combined results of the studies and examines their strength as a whole

3. Controlled human exposure (clinical) and animal toxicological studies that examine the effects of NO_2 on aspects of the respiratory host defense system related to respiratory infection are assessed Also, support from the animal toxicological data for the biologically plausible hypothesis that relates respiratory symptoms and morbidity to NO_2 exposure in epidemiologic studies as being due to respiratory infection is discussed

4. A discussion reviewing the emphysematous potential in humans from exposure to long-term chronic NO_2 exposure is presented

5 Subpopulation groups that may be more susceptible to effects from ambient NO_2 exposure and are potentially at heightened risk are discussed

6. The ecological effects of critical nitrogen loading are also assessed Concentrations of NO and NO_2 in the atmosphere do not often reach phytotoxic levels. Ecosystem exposure to nitrogen compounds, therefore, is mainly through the soil Crops are excluded because they are usually

heavily fertilized Nitrogen in forest soils, however, is usually growth limiting Concern links nitrogen deposition with possible ecological impacts arising from nitrogen saturation Saturation results when continuous additions to soil background nitrogen exceeds the capacity of plants and microorganisms in an ecosystem to utilize and retain nitrogen Increases in soil nitrogen can play a selective role When nitrogen becomes readily available, species or varieties adapted to living in soil with low levels of nitrogen will be replaced by vegetation capable of utilizing the increased supply The concept of critical load, "a quantitative estimate of one or more pollutants below which significant harmful effects on sensitive elements of the environment do not occur according to present knowledge," was developed in Europe This concept, however, has not been widely accepted in the United States because not enough is known concerning the functioning of ecosystems to be able to set critical loads in a completely objective fashion

2.3 ORGANIZATION OF THE DOCUMENT

The present document consists of 16 chapters The Executive Summary for the entire document is contained in Chapter 1, followed by this general introduction in Chapter 2 Chapters 3 through 8 provide background information on physical and chemical properties of NO_2 and related compounds, sources and emissions, atmospheric transport, transformation, and fate of NO_2, methods for the collection and measurement of NO_2, and ambient air concentrations and factors affecting exposure of the general population Chapter 9 evaluates NO_2 effects on crops and natural vegetation, and Chapter 10 discusses effects on terrestrial and aquatic ecosystems Chapter 11 describes effects on visibility, and Chapter 12 describes damage to materials attributable to NO_2 Chapters 13 through 16 evaluate information concerning the health effects of NO_2 More specifically, Chapter 13 discusses respiratory tract deposition of NO_2 and information derived from experimental toxicological studies of animals Chapter 14 discusses epidemiological studies, and Chapter 15 discusses clinical studies Chapter 16 integrates information on critical health issues derived from studies reviewed in the prior three chapters (Chapters 13, 14, and 15)

Neither control techniques nor control strategies for the abatement of NO_x are discussed in this document, although some of the topics included are relevant to abatement strategies Technologies for controlling NO_x emissions and emissions of volatile organic compounds are discussed in documents issued by OAQPS (e g , U S Environmental Protection Agency,

1978b, 1983). Likewise, issues germane to the scientific basis for control strategies, but not pertinent to the development of criteria, are addressed in numerous documents issued by OAQPS.

In addition, certain issues of direct relevance to standard setting are not explicitly addressed in this document, but are instead analyzed in documentation prepared by OAQPS as part of its regulatory analyses Such analyses include (1) discussion of what constitutes an "adverse effect" and delineation of particular adverse effects that the primary and secondary NAAQS are intended to protect against, (2) exposure analyses and assessment of consequent risk, and (3) discussion of factors to be considered in determining an adequate margin of safety. Key points and conclusions from such analyses are summarized in a Staff Paper prepared by OAQPS and reviewed by CASAC. Although scientific data contribute significantly to decisions regarding the above issues, their resolution cannot be achieved solely on the basis of experimentally acquired information Final decisions on items (1) and (3) are made by the Administrator, as mandated by the CAA

A fourth issue directly pertinent to standard setting is identification of populations at risk, which is basically a selection by EPA of the subpopulation(s) to be protected by the promulgation of a given standard This issue is addressed only partially in this document For example, information is presented on factors, such as preexisting disease, that may biologically predispose individuals and subpopulations to adverse effects from exposures to NO_x. The identification of a population at risk, however, requires information above and beyond data on biological predisposition, such as information on levels of exposure, activity patterns, and personal habits Such information is included in the Staff Paper developed by OAQPS.

The present document includes review and critical evaluation of relevant literature on NO_x through 1993. The material selected for review and comment in the text generally comes from the more recent literature published since 1982, with emphasis on studies conducted at or near NO_x pollutant concentrations found in ambient air Older literature cited in the previous criteria document for NO_x (U S Environmental Protection Agency, 1982a) is generally not discussed. However, as appropriate, some limited discussion is included of older studies judged to be significant because of their potential usefulness in deriving a NAAQS An attempt has been made to discuss key literature in the text and

present it in tables as well Reports of lesser importance for the purposes of this document are typically only summarized in tables

Generally, only published material that has undergone scientific peer review is included In the interest of admitting new and important information, however, some material not yet published in the open literature but meeting other standards of scientific reporting may be included Emphasis has been placed on studies in which NO_2 exposure concentrations were ≤ 5 ppm On this basis, studies in which the lowest concentration employed exceeded this level have been included if they contain unique data, such as documentation of a previously unreported effect or of mechanisms of effects, or if they were multiple-concentration studies designed to provide information on concentration-response relationships In the areas of emphysema, mutagenesis, teratogenesis, and reproductive effects, results of studies conducted at higher levels have been included because of the potential importance of these effects to public health

In reviewing and summarizing the literature, an attempt is made to present alternative points of view where scientific controversy exists As warranted, considerations bearing on the quality of studies are noted

The general policy of EPA is to express concentrations of air pollutants in metric units (e g , in micrograms per cubic meter [$\mu g/m^3$]), as well as in the more widely used units, such as parts per million (ppm) or parts per billion (ppb), which are neither metric nor English units That policy has been followed in those chapters in which most of the data have been obtained from laboratory studies conducted at room temperature (e g , Chapters 13 and 16) Data are presented to a large extent in the units reported by the original researchers Some data, however, are presented both in micrograms per cubic meter and in parts per million to facilitate comparison of data (NO_2 conversions ppm $\times$ 1,882 = $\mu g/m^3$ [e g , 0 053 ppm $\times$ 1,882 = 100 $\mu g/m^3$] and $\mu g/m^3$ $\times$ 0 00053 = ppm [e g , 100 $\mu g/m^3$ $\times$ 0 00053 = 0 053 ppm]) Data reported in parts per million for studies conducted outdoors, such as field and open-top chamber vegetation studies, ambient air monitoring, and research on atmospheric chemistry, have not been converted In these cases, conversion of reported parts per million and parts per billion units is questionable because it assumes standard or uniform temperatures and pressures Deposition studies are reported in micrograms per hectare ($\mu g/ha$)

REFERENCES

Federal Register (1971) National primary and secondary ambient air quality standards F R (April 30) 36 8186-8201

Federal Register. (1978) Air quality criteria document for oxides of nitrogen F R (December 12) 43 58117-58118

Friedlander, S K (1982) CASAC review and closure of the OAQPS staff paper for nitrogen oxides [memorandum to Anne M Gorsuch] July 6

Pearlman, M E ; Finklea, J F , Creason, J P , Shy, C M , Young, M M , Horton, R J M (1971) Nitrogen dioxide and lower respiratory illness Pediatrics 47 391-398

Shy, C M , Creason, J P , Pearlman, M E , McClain, K E , Benson, F B , Young, M M (1970a) The Chattanooga school children study effects of community exposure to nitrogen dioxide 1 Methods, description of pollutant exposure, and results of ventilatory function testing J Air Pollut Control Assoc 20 539-545

Shy, C M , Creason, J P , Pearlman, M E , McClain, K E , Benson, F B , Young, M M (1970b) The Chattanooga school children study effects of community exposure to nitrogen dioxide II Incidence of acute respiratory illness J Air Pollut Control Assoc 20 582-588

U.S. Code. (1991) Clean Air Act, §108, air quality criteria and control techniques, §109, national ambient air quality standards U S C 42 §§7408-7409

U.S. Environmental Protection Agency (1971) Air quality criteria for nitrogen oxides Washington, DC U S Environmental Protection Agency, Air Pollution Control Office, EPA report no AP-84 Available from NTIS, Springfield, VA, PB-197333/BE

U.S Environmental Protection Agency (1978) Health effects of short-term exposures to nitrogen dioxide (air quality criteria) Research Triangle Park, NC Health Effects Research Laboratory, EPA report no EPA-600/8-78-009

U.S Environmental Protection Agency (1982a) Air quality criteria for oxides of nitrogen Research Triangle Park, NC. Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office, EPA report no EPA-600/8-82-026 Available from NTIS, Springfield, VA, PB83-131011

U.S. Environmental Protection Agency (1982b) Review of the national ambient air quality standards for nitrogen oxides· assessment of scientific and technical information, OAQPS staff paper Research Triangle Park, NC. Office of Air Quality Planning and Standards, EPA report no EPA-450/5-82-002 Available from NTIS, Springfield, VA, PB83-132829

3. GENERAL CHEMICAL AND PHYSICAL PROPERTIES OF OXIDES OF NITROGEN AND OXIDES OF NITROGEN-DERIVED POLLUTANTS

3.1 INTRODUCTION AND OVERVIEW

In this chapter, some general chemical and physical properties of oxides of nitrogen (NO_x) and NO_x-derived pollutants are discussed as an introduction to complex chemical and physical interactions that may occur in the atmosphere and other media The information presented mainly summarizes the most salient points drawn from the predecessor NO_x criteria document (U S Environmental Protection Agency, 1982), with appropriate updating on certain important aspects This overview is further augmented throughout the present document as related topics are discussed in depth elsewhere

In this document, NO_x is the sum of nitrogen dioxide (NO_2) and nitric oxide (NO), and NO_y refers to the sum of NO_x and other oxidized nitrogen compounds, except nitrous oxide (N_2O) These include nitric acid (HNO_3), nitrogen trioxide (NO_3), dinitrogen trioxide (N_2O_3), dinitrogen tetroxide (N_2O_4), and dinitrogen pentoxide (N_2O_5) Peroxyacetylnitrate (PAN), although not discussed at great length in this document, is normally included with the NO_y group of compounds

There are seven oxides of nitrogen that may be present in the ambient air NO, NO_2, N_2O, NO_3, N_2O_3, N_2O_4, and N_2O_5 Of these, NO and NO_2 are generally present in highest concentrations in the lower troposphere (Chapter 7) Their interconvertibility in photochemical smog reactions (Chapter 5) has frequently resulted in their being grouped together under the designation NO_x, although analytic techniques can distinguish clearly between them (Chapter 6) Of the two, NO_2 has the greater impact on human health (Chapter 16)

Nitrous oxide is ubiquitous even in the absence of anthropogenic sources because it is a product of natural biologic processes in soil It is not, however, involved in any chemical reactions in the lower atmosphere to any appreciable extent Although N_2O is not generally considered to be an air pollutant, it participates in upper atmospheric reactions involving the stratospheric ozone (O_3) layer, and it is a greenhouse gas (Chapter 5).

Although NO_3, N_2O_3, N_2O_4, and N_2O_5 are present only in very low concentrations, even in polluted environments, they play a role in atmospheric chemical reactions leading to the transformation, transport, and ultimate removal of nitrogen compounds from ambient air

Ammonia (NH_3) is generated, on a global scale, during the decomposition of nitrogenous matter in natural ecosystems, and it may also be produced locally in larger concentrations by human activities such as the maintenance of dense animal populations It is discussed because, through its reaction with HNO_3, resulting in the formation of aerosol nitrate, it plays an important role in determining the atmospheric fate of nitrogen oxides

Other NO_x-derived compounds that may be found in polluted air include nitrites, nitrates, nitrogen acids, *N*-nitroso compounds, and organic compounds such as the peroxyacyl nitrates ($RC(O)OONO_2$, where R represents any one of a large variety of possible organic groups) (Chapter 6)

The peroxyacyl nitrates, of which PAN ($CH_3C(O)OONO_2$) is of most concern in terms of atmospheric concentrations, have been thoroughly reviewed in the recent EPA document *Air Quality Criteria for Ozone and Other Photochemical Oxidants* (U S Environmental Protection Agency, 1986), and are discussed only briefly in this chapter and elsewhere in this document.

The discovery of *N*-nitroso compounds in air, water, and food has led to concern about possible human exposure to this family of compounds, some of which have been shown to be carcinogenic in animals Health concerns also have been expressed about nitrates, which occur as a component of particulate matter in the respirable size range, suspended in ambient air (Chapter 13). Particulate nitrate is produced in atmospheric reactions (Chapter 5) Nitrates may also occur in significant concentrations in drinking water supplies, but this occurrence is not believed to be the result of atmospheric production

Photochemical models predict that up to one-half of the original nitrogen oxides emitted may be converted on a daily basis to nitrates and HNO_3 This atmospheric production of HNO_3 is an important component of acid rain (see Chapter 5)

Table 3-1 summarizes theoretical estimates of the concentrations of the various nitrogen oxides and acids that would be present in an equilibrium state assuming initially only molecules of nitrogen and oxygen at 1 atm pressure, 25 °C, and 50% relative humidity.

TABLE 3-1. THEORETICAL CONCENTRATIONS OF NITROGEN OXIDES AND NITROGEN ACIDS THAT WOULD BE PRESENT AT EQUILIBRIUM WITH MOLECULAR NITROGEN, MOLECULAR OXYGEN, AND WATER IN AIR AT 25 °C, ONE ATMOSPHERE, 50% RELATIVE HUMIDITY

	Concentrations in Hypothetical Atmosphere (ppm)	
Compound	At Equilibrium[a]	In Typical Sunlight-Irradiated, Smoggy Atmosphere[a,b]
Molecular oxygen (O_2)	2.06×10^{5}	2.06×10^{5}
Molecular nitrogen (N_2)	7.69×10^{5}	7.69×10^{5}
Water (H_2O)	1.56×10^{4}	1.56×10^{4}
Nitric oxide (NO)	2.69×10^{-10}	10^{-1}
Nitrogen dioxide (NO_2)	1.91×10^{-4}	10^{-1}
Nitrogen trioxide (NO_3)	3.88×10^{-16}	10^{-8} - 10^{-9}
Dinitrogen trioxide (N_2O_3)	2.96×10^{-20}	10^{-8} - 10^{-9}
Dinitrogen tetroxide (N_2O_4)	2.48×10^{-13}	10^{-7} - 10^{-8}
Dinitrogen pentoxide (N_2O_5)	3.16×10^{-17}	10^{-3} - 10^{-5}
cis-Nitrous acid (HONO)	7.02×10^{-9}	10^{-3}
trans-Nitrous acid (HONO)	1.60×10^{-8}	10^{-3}
Nitric acid ($HONO_2$)	1.33×10^{-3}	10^{-2} - 10^{-3}

[a]Assumes initially only molecules of nitrogen and oxygen at 1 atm pressure, 25 °C, and 50% relative humidity The simulations assume that the sunlight is of fixed intensity, with a solar zenith angle of 40° Photochemical aerosol formation has not been considered here

[b]Theoretical estimates made using computer simulations of the chemical reactions rates in a synthetic smog mixture with hydrocarbons present

Source Demerjian et al (1974)

In polluted, sunlight-irradiated atmospheres concentrations of NO_y species are far above thermodynamic equilibrium concentrations Rather, expected concentrations of pollutants are influenced by emissions and photochemically initiated reactions Table 3-1 lists one set of estimated concentrations of nitrogen oxides and acids expected under more realistic conditions, derived from computer simulations of photochemical smog reactions that might occur in more or less typical urban environments White and Dietz (1984) have postulated that more than one steady state is possible at certain rates of NO_x emissions The calculated steady states of the free troposphere are shown on Figure 3-1 for a range of NO_x concentrations taking into account CH_4 (see White and Dietz, 1984, for all conditions considered). Photolysis rates represent equinoctial diurnal averages at 45° N

3.2 NITROGEN OXIDES

Table 3-2 summarizes some important physical properties of nitrogen oxides under standard temperature and pressure conditions of 25 °C and 1 atm, respectively The remainder of this section describes chemical and physical properties of individual nitrogen oxide species

3.2.1 Nitric Oxide

Nitric oxide is an odorless gas It is also colorless because its absorption bands are all at wavelengths less than 230 nm, well below the visible wavelengths Nitric oxide is only slightly soluble in water (0 006 g/100 g of water at 24 °C and 1 atm pressure) It has an uneven number of valence electrons, but, unlike NO_2, it does not dimerize in the gas phase

Nitric oxide is a principal by-product of combustion processes, arising from the oxidation of molecular nitrogen (N_2) in combustion air and of organically bound nitrogen present in certain fuels such as coal and heavy oil The oxidation of nitrogen in combustion

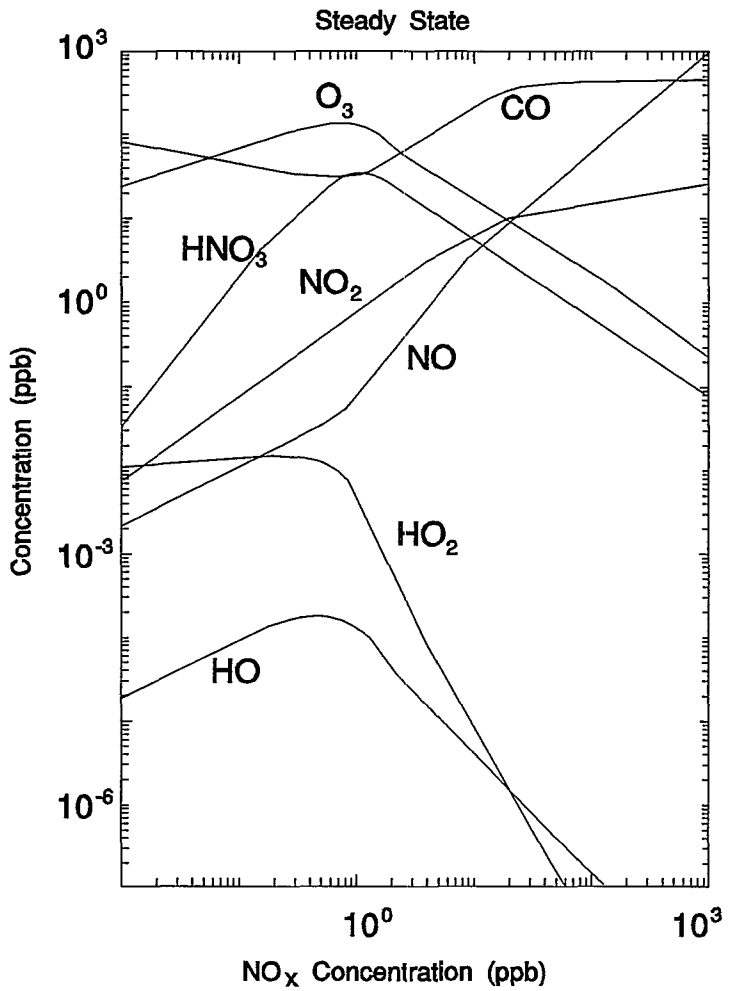


Figure 3-1. Calculated steady states of the free troposphere as a function of NO_x concentration.

Source White and Dietz (1984)

air occurs primarily through a set of reactions known as the extended Zeldovitch mechanism (Zeldovitch, 1946)

$$O_2 + M \rightarrow 2O + M \tag{3-1}$$

$$N_2 + O \rightarrow NO + N \tag{3-2}$$

$$N + O_2 \rightarrow NO + O, \tag{3-3}$$

TABLE 3-2. SOME PHYSICAL AND THERMODYNAMIC PROPERTIES OF THE NITROGEN OXIDES

Oxide	Molecular Weight (g/mol)	Melting Point (°C)[a,b]	Boiling Point (°C)[a,b]	Henry's-law Coefficient at 25 °C (M/atm)[c]	Solubility in 0 °C Water (cm^3 at STP/100 g)[a]	Thermodynamic Functions (Ideal Gas, 1 atm, 25 °C)	
						Enthalpy of Formation (kcal/mol)	Entropy (cal/mol-deg)
Nitric oxide (NO)	30 01	-163 6	-151 8	$1\ 93 \times 10^{-3}$	7 34	21 58	50 347
Nitrogen dioxide (NO_2)	46 01	-11 2	21 2	$1\ 2 \times 10^{-2}$	Reacts with water (H_2O) forming nitric acid ($HONO_2$) and nitrous acid (HONO)	7 91	57 34
Nitrous oxide (N_2O)	44 01	-90 8	-88 5	$2\ 47 \times 10^{-2}$	130 52	19 61	52 55
Dinitrogen trioxide (N_2O_3)	76 01	-102	47 (Decomposes)	$0\ 6 \pm 0\ 2$	Reacts with H_2O, forming HONO	19 80	73 91
Dinitrogen tetroxide (N_2O_4)	92 02	-11 3	21 2	$1\ 4 \pm 0\ 8$	Reacts with H_2O, forming $HONO_2$ and HONO	2 17	72 72
Dinitrogen pentoxide (N_2O_5)	108 01	30	3 24 (Decomposes)		Reacts with H_2O, forming $HONO_2$	2 7	82 8

[a]Matheson Gas Data Book (Matheson Company, 1966)
[b]Handbook of Chemistry and Physics (Weast et al , 1986)
[c]Schwartz and White (1981)

with the additional equation (extended mechanism)

$$N + OH \rightarrow NO + H \tag{3-4}$$

The high activation energy of reaction 3-2 (75 kcal/mol), coupled with its essential function of breaking the strong N_2 triple bond, make this the rate limiting step of the Zeldovitch mechanism Due to the high activation energy, this mechanism for NO production proceeds at a somewhat slower rate than the reactions of fuel constituents and is extremely temperature sensitive (Bowman, 1973) Moreover, the production of atomic oxygen (O) required for the first step is also highly temperature sensitive In the immediate vicinity of a flame, the high temperatures, coupled with the kinetics of the hydrocarbons in the fuel, can drive the O concentration to several times its equilibrium level The local ratio of fuel to air also has a first order effect on the concentration of O (Bowman, 1973)

The reaction kinetics of thermal NO formation is further complicated by the fact that certain hydrocarbon radicals can be effective in splitting the N_2 bond through reactions such as (Fenimore, 1971)

$$CH + N_2 \rightarrow CHN + N \tag{3-5}$$

The rate of oxidation of the fuel (and intermediate hydrocarbon radical fragments) is usually sufficiently rapid that only negligible quantities of the fuel radicals are available to attack the N_2 However, under fuel-rich conditions, this can become the dominant mode of breaking the N_2 bond and, in turn, can be responsible for significant NO formation (Engleman et al , 1976) Such reactions appear to have a relatively low activation energy and can proceed at a rate comparable to oxidation of the fuel Because of the early formation of NO by this mechanism, relative to that formed by the Zeldovitch mechanism, NO thus formed is often referred to as "prompt NO" The importance of this mechanism has not been quantified for practical systems

In fossil fuels such as coal and residual fuel oil, nitrogen compounds are bound within the fuel matrix Typically, Number 6 residual oil contains 0 2 to 0 8% bound nitrogen by weight, and coal typically contains 1 to 2% If this 1% nitrogen were quantitatively

converted to NO_x, it would account for about 2,000 ppm NO_x in the exhaust of a coal-fired unit. In practice, only a portion of these nitrogen compounds is converted to NO_x, with the remainder being converted to N_2 Tests designed to determine the percent of the NO_x emissions due to oxidation of bound nitrogen (Pershing and Wendt, 1976) show that upward of 80% of the NO_x from a coal-fired boiler originates from fuel-bound nitrogen Details of the kinetic mechanisms involved in fuel nitrogen oxidation are uncertain, due in part to the variability of molecular composition among the many types (and sources) of coal and heavy oils and to the complex nature of the heterogeneous processes occurring Experimental evidence does, however, lend some insight into the processes involved A number of fuel-bound nitrogen compounds have been cited (Axworthy and Schuman, 1973, Martin et al , 1971; Turner and Siegmund, 1972), but the degree of conversion to NO_x does not seem to be significantly affected by the compound type Oxides of nitrogen conversions arising from fuel sources seem also to be relatively insensitive to temperature in diffusion flames The most important parameters in determining fuel-bound nitrogen conversion appear to be the local conditions prevailing when the nitrogen is evolved from the fuel Under fuel-rich conditions, this nitrogen tends to form N_2, whereas under fuel-lean conditions, significant amounts of NO_x are formed

Nitric oxide formation kinetics in typical furnaces are not fast enough to reach equilibrium levels in the high temperature flame zone, and the NO destruction mechanisms are far too slow to allow the NO, once formed, to reach equilibrium at typical stack temperatures. This is to say that the NO formation process is kinetically controlled

Nitric oxide and NO_2 produced in relatively large concentrations at high temperatures in combustion processes would revert to lower concentrations characteristic approximately of the equilibrium values shown in Table 3-3 were it not for the fact that combustion equipment rapidly converts a large fraction of the thermal energy available to useful work This results in a rapid cooling of the combustion gases and a "freezing-in" of the produced NO and NO_2 near concentrations characteristic of the high temperature phase of the process

A major implication of the fact that NO_x emissions are defined by the kinetics of the process rather than being an equilibrium phenomenon is that NO_x emissions can be effectively modified by changes in the details of the combustion process For clean fuels such as natural gas or Number 2 distillate oil with no bound nitrogen, the NO formation is

TABLE 3-3. THEORETICAL EQUILIBRIUM CONCENTRATIONS OF NITRIC OXIDE AND NITROGEN DIOXIDE IN AIR (50% RELATIVE HUMIDITY) AT VARIOUS TEMPERATURES

	Concentration ($\mu g/m^3$ [ppm])	
Temperature (K [°C])	Nitric Oxide	Nitrogen Dioxide
298 (24 85)	$3\ 29 \times 10^{-10}$ ($2\ 63 \times 10^{-10}$)	$3\ 53 \times 10^{-4}$ ($1\ 88 \times 10^{-4}$)
500 (226 85)	$8\ 18 \times 10^{-4}$ ($6\ 54 \times 10^{-4}$)	$7\ 26 \times 10^{-2}$ ($3\ 86 \times 10^{-2}$)
1,000 (726 85)	43 (34 4)	3 38 (1 80)
1,500 (1,226 85)	1,620 (1,296)	12 35 (6 57)
2,000 (1,726 85)	9,946 25 (7,957)	23 88 (12 70)

Source National Research Council (1977)

dominated by the Zeldovitch mechanism Thus, combustion modifications that reduce peak flame temperature, limit the gas residence time at peak temperatures, and/or reduce the amount of O available at high temperatures will reduce the NO_x emissions Examples of such modifications include flue gas recirculation, reduced load, reduced combustion air preheat temperature, water injection, and reduced excess air (Bowen and Hall, 1976a,b,c, 1977a,b,c,d,e)

In furnaces fired with coal or heavy oil, the major portion of the NO_x emissions is from fuel-bound nitrogen conversion. Thus, combustion modifications that reduce the availability of oxygen when the nitrogen compounds are evolved will reduce the NO_x produced Examples of such modifications are reduction of the amount of excess air during firing, establishing fuel-rich conditions during the early stages of combustion (staged combustion), or new burner designs that tailor the rate of mixing between the fuel and air streams (Bowen and Hall, 1976a,b,c)

3.2.2 Nitrogen Dioxide

Nitrogen dioxide is a reddish-orange-brown gas with a characteristic pungent odor Although its boiling point is 21 1 °C, the low partial pressure of NO_2 in the atmosphere prevents condensation Nitrogen dioxide is corrosive and highly oxidizing It has an uneven number of valence electrons and forms the dimer N_2O_4 at higher concentrations and lower temperatures, but the dimer is not important at ambient concentrations In the atmosphere, NO can be oxidized to NO_2 by the thermal reaction

$$2NO + O_2 \rightarrow 2NO_2 \tag{3-6}$$

However, this reaction is of minor importance in most ambient situations because other chemical processes are faster Reaction 3-6 is mainly responsible for the NO_2 present in combustion exhaust gases About 5 to 10% by volume of the total emissions of NO_x from combustion sources is in the form of NO_2, although substantial variations from one source to another have been observed Under more dilute ambient conditions, photochemical smog reactions involving hydrocarbons convert NO to NO_2 (Chapter 5)

Nitrogen dioxide's principal involvement in photochemical smog stems from its absorption of sunlight and subsequent decomposition (photolysis) to NO and O Nitrogen dioxide is an efficient absorber of light over a broad range of ultraviolet (UV) and visible wavelengths. Only quanta with wavelengths less than about 430 nm, however, have sufficient energy to cause photolysis It should also be noted that photons having wavelengths less than about 290 nm are largely absorbed in the upper atmosphere The effective range of wavelengths responsible for photolysis of NO_2 at ground level is, therefore, 290 nm to 430 nm Because of its absorption properties, NO_2 produces discoloration and reduces visibility in the polluted lower troposphere

3.2.3 Nitrous Oxide

Nitrous oxide is a colorless gas with a slight odor at high concentrations Nitrous oxide in the atmosphere arises as one product of the reduction of nitrate by a ubiquitous group of bacteria that use nitrate as their terminal electron acceptor in the absence of oxygen

(denitrification) (Brezonik, 1972, Delwiche, 1970, Focht and Verstraete, 1977, Keeney, 1973)

Although N_2O does not participate in the photooxidation reactions that produce undesirable pollutants in the lower troposphere, it is an important atmospheric constituent because it absorbs long-wave length radiation (therefore, serving as a greenhouse gas), and it photolyzes in the stratosphere

Nitrous oxide transported to the stratosphere undergoes photolysis by absorbing UV radiation at wavelengths below 300 nm to produce N_2 and singlet oxygen (Johnston and Selwyn, 1975)

$$N_2O + h\nu \rightarrow N_2 + O('D), \text{ where } h\nu \text{ is a unit of radiant energy} \tag{3-7}$$

The singlet oxygen, formed in reaction 3-7, reacts with more N_2O to produce two sets of products

$$N_2O + O('D) \rightarrow \begin{matrix} N_2 + O_2 \\ \text{and} \\ NO + NO \end{matrix} \tag{3-8}$$

The NO produced enters a catalytic cycle, the net result of which is the regeneration of NO_x and the destruction of O_3

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{3-9}$$

$$O_3 + h\nu \rightarrow O_2 + O \tag{3-10}$$

$$NO_2 + O \rightarrow NO + O_2 \tag{3-11}$$

These reactions are of concern because of the possibility that increased N_2O resulting from denitrification of excess fertilizer may lead to a decrease of stratospheric O_3 (Council for Agricultural Science and Technology, 1976, Crutzen, 1976), with consequent potential for adverse human health effects

3.2.4 Nitrogen Trioxide

Nitrogen trioxide has been identified in laboratory systems containing NO_2/O_3, NO_2/O, and N_2O_5 as an important reactive transient (Johnston, 1966) The reaction of NO_2 and O_3 provides the primary atmospheric source of NO_3

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \tag{3-12}$$

Because it is readily photolyzed by sunlight, NO_3 is only important during the nighttime hours. It reacts rapidly with both inorganic and organic species The reaction with NO_2 produces N_2O_5, which is the anhydride of HNO_3 Nitrogen trioxide is extremely reactive with aldehydes, mercaptans, and olefinic hydrocarbons It may be that the nitrate radical acts as a major sink for these types of organic compounds in the nighttime atmosphere Details of NO_3 radical chemistry are provided in Chapter 5, and a very comprehensive review concerning the NO_3 radical has been published recently (Wayne, 1991)

3.2.5 Dinitrogen Trioxide

In the atmosphere, N_2O_3 (also known as nitrogen sesquioxide) is in equilibrium with NO and NO_2 according to the following equation

$$NO + NO_2 \rightleftarrows N_2O_3 \tag{3-13}$$

The equilibrium concentrations at typical urban levels of NO and NO_2 range from about 10^{-4} $\mu g/m^3$ ($\approx 10^{-7}$ ppm) to 10^{-6} $\mu g/m^3$ ($\approx 10^{-9}$ ppm) (Table 3-4) Dinitrogen trioxide concentrations of this magnitude (i e , $\approx 10^{-8}$ ppm = 10^{-5} ppt) would have little influence on atmospheric chemistry. The rate constants for reaction of N_2O_3 with organics are not large enough to compensate for the low N_2O_3 concentration Dinitrogen trioxide is the anhydride of nitrous acid (HONO) and reacts with liquid water to form the acid

$$N_2O_3 + H_2O \rightarrow 2HONO \tag{3-14}$$

TABLE 3-4. THEORETICAL CONCENTRATIONS OF DINITROGEN TRIOXIDE AND DINITROGEN TETROXIDE IN EQUILIBRIUM WITH VARIOUS LEVELS OF GASEOUS NITRIC OXIDE AND NITROGEN DIOXIDE IN AIR AT 25 °C

	Concentration (ppm)		
Nitric Oxide	Nitrogen Dioxide	Dinitrogen Trioxide	Dinitrogen Tetroxide
0 05	0 05	$1\ 3 \times 10^{-9}$	$1\ 7 \times 10^{-8}$
0 10	0 10	$5\ 2 \times 10^{-9}$	$6\ 8 \times 10^{-8}$
0 50	0 50	$1\ 3 \times 10^{-7}$	$1\ 7 \times 10^{-6}$
1 00	1 00	$5\ 2 \times 10^{-7}$	$6\ 8 \times 10^{-6}$

Source National Research Council (1977)

However, due to the low concentrations of N_2O_3 expected in the atmosphere, this reaction would serve as a minimal source of HONO

3.2.6 Dinitrogen Tetroxide

Dinitrogen tetroxide (also known as nitrogen tetroxide) is the dimer of NO_2 formed by the association of NO_2 molecules It also readily dissociates to establish the equilibrium.

$$2NO_2 \rightleftarrows N_2O_4 \tag{3-15}$$

Table 3-4 presents theoretical predictions of concentrations of N_2O_3 and N_2O_4 in equilibrium with various NO and NO_2 concentrations

3.2.7 Dinitrogen Pentoxide

Dinitrogen pentoxide is a nighttime component of the atmosphere because it is formed in the following reaction between NO_2 and NO_3, the latter of which can exist in appreciable quantities only in the absence of sunlight

$$NO_2 + NO_3 + M \rightleftarrows N_2O_5 \tag{3-16}$$

Nitrogen dioxide, NO_3, and N_2O_5 are in equilibrium, however, the value of the equilibrium constant is somewhat uncertain (Finlayson-Pitts and Pitts, 1986) Even though this uncertainty exists, there should be sufficient quantities of N_2O_5 present to have an impact on nighttime chemistry Dinitrogen pentoxide combines with liquid water to form HNO_3, and in so doing, the equilibrium in reaction 3-16 is shifted to the right, and NO_3 is consumed The overall result of these reactions is the removal of a reactive radical (NO_3) and the formation of an acid (HNO_3) that will be readily removed from the atmosphere by depositional processes

3.3 NITRATES, NITRITES, AND NITROGEN ACIDS

3.3.1 Nitric Acid

Nitric acid in the gaseous state is colorless and photochemically stable in the troposphere. The major pathways for atmospheric formation of HNO_3 involve reaction 3-17 during the daylight period when hydroxyl radicals are present and reaction 3-18 at night The N_2O_5 is formed during the nighttime period as described in Section 3 2 4

$$NO_2 + HO \rightarrow HNO_3 \tag{3-17}$$

$$N_2O_5 + H_2O_{(l)} \rightarrow 2HNO_3 \tag{3-18}$$

Due to its volatility, HNO_3 does not condense into aerosol at concentrations present in the atmosphere. However, HNO_3 can react with NH_3 gas or aerosols containing alkaline crustal material to produce particulate nitrates (Wolff, 1984) Wet and dry deposition of HNO_3 are primary removal mechanisms Neutralization by alkaline gaseous and aerosol materials serves as a sink, as well.

3.3.2 Nitrous Acid

Nitrous acid is an important atmospheric constituent because it photolyzes, yielding a hydroxyl radical Ambient concentrations up to 8 ppb have been recorded in urban atmospheres (Harris et al , 1982) At the present time, the source(s) of HONO is highly

uncertain As indicated in Section 3 2 5, the reaction of NO and NO_2 in the presence of water will produce HONO However, at the concentrations of NO and NO_2 normally found in the atmosphere, this is a negligible source When hydroxyl radicals are present (daytime), HONO can be formed by reaction 3-19 However, because HONO is rapidly destroyed by photolysis, only a very small steady-state concentration of HONO could be produced by this pathway Alternate mechanisms involving heterogeneous reactions have been proposed, but these are difficult to verify. It has been suggested that direct emission of HONO from automobiles may serve as a source (Pitts et al , 1984)

$$NO + OH + M \rightarrow HONO \tag{3-19}$$

3.3.3 Organic Nitrates

Organic nitrates are formed when organic compounds are oxidized in the presence of oxides of nitrogen A large number of alkyl nitrates could be formed by reactions such as 3-20 and 3-21, but few ambient measurements have been reported By far the most studied organic nitrate is PAN, which results from the combination of a peroxyacetyl radical with NO_2 (reaction 3-22)

$$R\text{-}CH_2\text{-}O + NO_2 \rightarrow RCH_2\text{-}ONO_2 \tag{3-20}$$

$$RCH_2O\text{-}O + NO \rightarrow RCH_2ONO_2 \tag{3-21}$$

$$CH_3C(O)OO + NO_2 \rightarrow CH_3C(O)OONO_2 \tag{3-22}$$

Peroxyacetyl nitrate was first identified as a component of Los Angeles smog Since that time, it has been shown to be ubiquitous in the atmosphere Peroxyacetyl nitrate is thermally labile, with a lifetime of only minutes at temperatures above 25 °C However, at the lower temperatures aloft in the troposphere, PAN has a sufficiently long lifetime to act as a storage reservoir for NO_2 Peroxyacetyl nitrate slowly decomposes through reactions with the hydroxyl radical and sunlight (see Chapter 5)

3.3.4 Aerosol Nitrates

Particulate ammonium nitrate is produced when NH_3 reacts with HNO_3 The reaction is reversible under atmospheric conditions, with a temperature- and relative-humidity-dependent equilibrium constant Stelson and Seinfeld (1982) have calculated the equilibrium concentrations of gaseous NH_3 and HNO_3 and the resulting solid or aqueous ammonium nitrate using fundamental thermodynamic principles The system is very complex and must also include sulfate, because NH_3 will preferentially react with sulfuric acid to give ammonium bisulfate and ammonium sulfate A summary of the physics and chemistry of the NH_3-sulfuric acid-HNO_3 system has been provided by Seinfeld (1986)

3.4 AMMONIA

Ammonia is a colorless gas with a pungent odor It is extremely soluble in water, forming the ammonium and hydroxy (OH^-) ions Ammonia is the only gaseous basic compound present in appreciable concentrations in the atmosphere It reacts rapidly with sulfuric acid to form ammonium bisulfate and sulfate aerosols Ammonia is removed from the atmosphere by wet and dry deposition It will react slowly with hydroxyl radical As shown in reaction 3-23, this produces amide (NH_2) radicals, which can be oxidized to NO_x products or serve as a sink for NO and NO_2 via reactions of the types shown in reactions 3-24 and 3-25 The atmospheric fate of the NH_2 radical is not well understood at present.

$$NH_3 + OH \rightarrow NH_2 + H_2O \tag{3-23}$$

$$NH_2 + NO \rightarrow N_2 + H_2O \tag{3-24}$$

$$NH_2 + NO_2 \rightarrow N_2O + H_2O \tag{3-25}$$

3.5 *N*-NITROSO COMPOUNDS

Organic nitroso compounds contain a nitroso group (-N = O) attached to a nitrogen or carbon atom According to Magee (1971), *N*-nitroso compounds generally can be divided into two groups—one group includes the dialkyl, alkylaryl, and diaryl nitrosamines, and the other includes the alkyl and aryl nitrosamides

The principal chemical reaction involved in the formation of *N*-nitrosamines is that of the secondary amines with HONO Nitrosation is effected by agents having the structure ONX, where X = *O*-alkoxyl, nitrite ion (NO_2^-), nitrate ion, halogen, tetrafluoroborate, hydrogen sulfate, or OH^- The equilibrium reaction of nitrosonium ion (ON^+), HONO, and NO_2^-,

$$ON^+ + OH^- \rightleftarrows HNO_2 \rightleftarrows H^+ + NO_2^-, \qquad (3\text{-}26)$$

is shifted to the right at pH > 7 The simplest form of nitrosation of amines involves electrophilic attack by the ON^+ and subsequent deprotonation

Mirvish (1970) studied the kinetics of dimethylnitrosamine nitrosation and pointed out that the chief nitrosating agent at pH 1 is N_2O_3, the anhydride of HONO, which forms reversibly from two HONO molecules The formation of nitrosamines is dependent on the pK of the amine

Nitroso compounds are characteristically photosensitive and the nitroso group is split by UV radiation Gaseous nitrosamines may be denitrosated by visible light Absorption spectra of several nitrosamines are given in the literature (Rao and Bhaskar, 1969), the characteristic spectra show a low intensity absorption maximum around 360 nm and an intense band around 235 nm Nitrosamines show three relatively intense bands in the infrared region of 7 1 to 7 4 μm, 7.6 to 8 6 μm, and 9 15 to 9 55 μm Nuclear magnetic resonance, infrared, UV, and mass spectrometry spectra have been reviewed by Magee et al (1976)

Atmospheric reactions involving nitrosamines are discussed in Chapter 5

3.6 SUMMARY

There are seven nitrogen oxides that may be present in the ambient air NO, NO_2, N_2O, NO_3, N_2O_3, N_2O_4, and N_2O_5 Of these, NO and NO_2 are generally present in highest concentrations in polluted atmospheres Their interconvertibility in photochemical smog reactions has frequently resulted in their being grouped together under the designation NO_x, although analytic techniques can distinguish clearly between them Of the two, NO_2 is the more toxic and irritating compound

Nitrous oxide is ubiquitous even in the absence of anthropogenic sources because it is a product of natural biologic processes in soil Nitrous oxide is inert in the lower troposphere, so it is not a participant in photochemical smog reactions Although N_2O is not generally considered to be an air pollutant, it is a greenhouse gas and a reactant in upper atmospheric reactions involving the stratospheric O_3 layer

Nitrogen trioxide, N_2O_3, N_2O_4, N_2O_5, and HNO_3 all play a role in atmospheric chemical reactions leading to the transformation, transport, and ultimate removal of nitrogen compounds from ambient air

Ammonia is emitted during the decomposition of nitrogenous matter in natural ecosystems, but it may also be produced locally by human activities such as the maintenance of dense animal populations It reacts with HNO_3 in the troposphere to produce ammonium nitrate aerosol Deposition of this aerosol then serves as a sink for the oxides of nitrogen

Compounds derived from NO_x, including nitrites, nitrates, nitrogen acids, *N*-nitroso compounds, and organic compounds such as the peroxyacyl nitrates ($RC(O)OONO_2$, where R represents any one of a large variety of possible organic groups), may also be found in polluted air.

The peroxyacyl nitrates, of which PAN ($CH_3C(O)OONO_2$) is of most concern in terms of atmospheric concentrations, have been thoroughly reviewed in the recent EPA document *Air Quality Criteria for Ozone and Other Photochemical Oxidants* (U S Environmental Protection Agency, 1986)

The discovery of *N*-nitroso compounds (some of which have been shown to be carcinogenic in animals) in air, water, and food has led to concern about possible human exposure to this family of compounds Health concerns also have been expressed about HNO_3 vapor and particulate nitrates, occurring as a component of particulate matter in the

respirable size range, suspended in ambient air These nitrates are produced in atmospheric reactions Nitrates may also occur in significant concentrations in public and private drinking water, but this occurrence is not believed to be the result of atmospheric production

Photochemical models predict that up to one-half of the original nitrogen oxides emitted may be converted on a daily basis to nitrates and HNO_3 This atmospheric production of HNO_3 is an important component of acidic rain and is a major contributor to the dry deposition flux of acid gases to the earth's surface

3.6.1 Nitrogen Oxides

Nitric oxide is an odorless and colorless gas It is a major by-product of the combustion process, arising both from the oxidation of N_2 in the combustion air and of nitrogen compounds bound in the fuel molecule The amount of NO formed from the oxidation of N_2 is dependent upon such parameters as peak flame temperature, quantity of combustion air, and gas residence time in the combustion chamber The amount of NO arising from oxidation of fuel-bound nitrogen does not seem to depend significantly on either the type of nitrogen compound involved or the flame temperature, but instead depends on the specific air-to-fuel ratio at various stages in combustion and the nitrogen content of the fuel

Nitrogen dioxide is produced in minor quantities in the combustion process (5 to 10% of the total oxides of nitrogen) In terms of significant atmospheric loading in populated areas, NO_2 arises mainly from the photochemically initiated conversion of NO to NO_2 by a variety of chemical processes in the atmosphere Nitrogen dioxide is corrosive and highly oxidizing Its reddish-orange-brown color arises from its preferential absorption of blue light Because of its strong absorption in this range (and also in the UV spectrum), NO_2 can cause visibility reduction and affect the spectral distribution of solar radiation in the polluted, lower atmosphere

3.6.2 Nitrates, Nitrites, and Nitrogen Acids

Other compounds derived from NO_x by means of atmospheric chemical processes include nitrites, nitrates, nitrogen acids, organic compounds, such as the peroxyacyl nitrates, and, possibly, the *N*-nitroso compounds

Nitric acid, a strong acid and powerful oxidizing agent, is colorless and photochemically stable in the gaseous state Its high volatility prevents condensation into droplets in the atmosphere It can, however, react with NH_3 and alkaline aerosol materials to form aerosol nitrates.

3.6.3 *N*-Nitroso Compounds

The *N*-nitroso family comprises a wide variety of compounds, all containing a nitroso group (-N = O) attached to a nitrogen or carbon atom Their formation in the atmosphere has been postulated to proceed through chemical reaction of amines with NO_x and NO_x-derivatives in gas phase reactions and/or through atmospheric reactions involving aerosols. Nitroso compounds are characteristically photosensitive and the nitroso group is split by the UV radiation in sunlight Gaseous nitrosamines may also be denitrosated by visible light.

REFERENCES

Axworthy, A E , Schuman, M (1973) Investigation of the mechanism and chemistry of fuel nitrogen conversion to nitrogen oxides in combustion In Proceedings, coal combustion seminar, June, Research Triangle Park, NC Research Triangle Park, NC U S Environmental Protection Agency, Office of Research and Development, pp 9-41, EPA report no EPA-650/2-73-021 Available from NTIS, Springfield, VA, PB-224210

Bowen, J S , Hall, R E , eds (1976a) Proceedings of the stationary source combustion symposium Volume I Fundamental research, September 1975, Atlanta, GA Washington, DC U S Environmental Protection Agency, Office of Research and Development, EPA report no EPA-600/2-76-152a Available from NTIS, Springfield, VA, PB-256320

Bowen, J S , Hall, R E , eds (1976b) Proceedings of the stationary source combustion symposium Volume II Fuels and process research and development, September 1975, Atlanta, GA Washington, DC U S Environmental Protection Agency, Office of Research and Development, EPA report no EPA-600/2-76-152b Available from NTIS, Springfield, VA, PB-256321

Bowen, J S , Hall, R E , eds (1976c) Proceedings of the stationary source combustion symposium Volume III Field testing and surveys, September 1975, Atlanta, GA Washington, DC U S Environmental Protection Agency, Office of Research and Development, EPA report no EPA-600/2-76-152c Available from NTIS, Springfield, VA, PB-257146

Bowen, J S , Hall, R E , eds (1977a) Proceedings of the second stationary source combustion symposium Volume I Small industrial, commercial, and residential systems, August-September, New Orleans, LA Research Triangle Park, NC U S Environmental Protection Agency, Office of Research and Development, EPA report no EPA-600/7-77-073a Available from NTIS, Springfield, VA, PB-270923.

Bowen, J S , Hall, R E , eds (1977b) Proceedings of the second stationary source combustion symposium Volume II Utility and large industrial boilers, August-September, New Orleans, LA Research Triangle Park, NC U S Environmental Protection Agency, Office of Research and Development, EPA report no EPA-600/7-77-073b Available from NTIS, Springfield, VA, PB-271756/9

Bowen, J S , Hall, R E , eds (1977c) Proceedings of the second stationary source combustion symposium Volume III Stationary engine, industrial process combustion systems, and advanced processes, August-September, New Orleans, LA Research Triangle Park, NC U S Environmental Protection Agency, Office of Research and Development, EPA report no EPA-600/7-77-073c Available from NTIS, Springfield, VA, PB-271757/7

Bowen, J S , Hall, R E , eds (1977d) Proceedings of the second stationary source combustion symposium Volume IV Fundamental combustion research, August-September, New Orleans, LA Research Triangle Park, NC U S Environmental Protection Agency, Office of Research and Development, EPA report no EPA-600/7-77-073d Available from NTIS, Springfield, VA, PB-274029

Bowen, J S , Hall, R E , eds (1977e) Proceedings of the second stationary source combustion symposium Volume V Addendum, August-September, New Orleans, LA Research Triangle Park, NC U S Environmental Protection Agency, Office of Research and Development, EPA report no EPA-600/7-77-073e Available from NTIS, Springfield, VA, PB-274897

Bowman, C T (1973) Kinetics of nitric oxide formation in combustion processes In Fourteenth symposium (international) on combustion, August 1972, University Park, PA Pittsburgh, PA The Combustion Institute, pp 729-738

Brezonik, P L (1972) Nitrogen sources and transformations in natural waters In Allen, H E , Kramer, J R , eds Nutrients in natural waters New York, NY John Wiley & Sons, Inc , pp 1-50

Council for Agricultural Science and Technology (1976) Effect of increased nitrogen fixation on stratospheric ozone Ames, IA Iowa State University, Department of Agronomy, report no 53, January 19

Crutzen, P. J (1976) Upper limits on atmospheric ozone reductions following increased application of fixed nitrogen to the soil Geophys Res Lett 3 169-172

Delwiche, C C (1970) The nitrogen cycle Sci Am 223 137-147

Demerjian, K L , Kerr, J A , Calvert, J G (1974) The mechanism of photochemical smog formation In· Pitts, J N , Jr , Metcalf, R L , Lloyd, A C , eds Advances in environmental science and technology, v 4. New York, NY John Wiley & Sons, pp 1-262

Engleman, V S , Siminski, V J , Bartok, W (1976) Mechanism and kinetics of the formation of NO_x and other combustion pollutants Phase II Modified combustion Research Triangle Park, NC U S Environmental Protection Agency, Industrial Environmental Research Laboratory, EPA report no EPA-600/7-76-009b Available from NTIS, Springfield, VA, PB-258875

Fenimore, C P. (1971) Formation of nitric oxide in premixed hydrocarbon flames In Thirteenth symposium (international) on combustion, August 1970, Salt Lake City, UT Pittsburgh, PA The Combustion Institute; pp 373-380

Finlayson-Pitts, B J , Pitts, J N , Jr (1986) Atmospheric chemistry fundamentals and experimental techniques New York, NY John Wiley & Sons, pp 961-1007

Focht, D. D , Verstraete, W (1977) Biochemical ecology of nitrification and denitrification Adv Microb Ecol 1 135-214

Harris, G W , Carter, W P L , Winer, A M , Pitts, J N , Jr , Platt, U , Perner, D (1982) Observations of nitrous acid in the Los Angeles atmosphere and implications for predictions of ozone-precursor relationships Environ Sci Technol 16 414-419

Johnston, H S (1966) Experimental chemical kinetics In Gas phase reaction rate theory New York, NY The Ronald Press Company, pp 14-34

Johnston, H S , Selwyn, G S (1975) New cross sections for the absorption of near ultraviolet radiation by nitrous oxide (N_2O) Geophys Res Lett 2 549-551

Keeney, D R (1973) The nitrogen cycle in sediment-water systems J Environ Qual 2 15-29

Magee, P. N (1971) Toxicity of nitrosamines their possible human health hazards Food Cosmet Toxicol 9 207-218

Magee, P. N., Montesano, R , Preussmann, R (1976) N-nitroso compounds and related carcinogens In Searle, C. E , ed Chemical carcinogens Washington, DC American Chemical Society, pp 491-625 (ACS monograph 173)

Martin, G B , Pershing, D W , Berkau, E E (1971) Effects of fuel additives on air pollutant emissions from distillate-oil-fired furnaces Research Triangle Park, NC U S Environmental Protection Agency, Office of Air Programs, report no AP-87 Available from NTIS, Springfield, VA, PB-213630

Matheson Company, Inc (1966) Matheson gas data book 4th ed East Rutherford, NJ The Matheson Company, Inc

McConnell, J C (1973) Atmospheric ammonia J Geophys Res 78 7812-7821

Mirvish, S S (1970) Kinetics of dimethylamine nitrosation in relation to nitrosamine carcinogenesis J Natl Cancer Inst 44 633-639

National Research Council (1977) Nitrogen oxides Washington, DC National Academy of Sciences

Pershing, D W , Wendt, J O L (1976) Pulverized coal combustion the influence of flame temperature and coal composition on thermal and fuel NO_x In Sixteenth symposium (international) on combustion, August, Cambridge, MA Pittsburgh, PA The Combustion Institute, pp 389-399

Pitts, J N , Jr , Biermann, H W , Winer, A M , Tuazon, E C (1984) Spectroscopic identification and measurement of gaseous nitrous acid in dilute auto exhaust Atmos Environ 18 847-854

Rao, C N R , Bhaskar, K R (1969) Spectroscopy of the nitroso group In Feuer, H , ed The chemistry of the nitro and nitroso groups part 1 New York, NY Interscience Publishers, pp 137-163

Schwartz, S E , White, W, H (1981) Solubility equilibria of the nitrogen oxides and oxyacids in dilute aqueous solution Adv Environ Sci Eng 4 1-45

Seinfeld, J H (1986) Atmospheric chemistry and physics of air pollution New York, NY John Wiley & Sons

Stelson, A W , Seinfeld, J H (1982) Thermodynamic prediction of the water activity, NH_4NO_3 dissociation constant, density and refractive index for the NH_4NO_3-$(NH_4)_2SO_4$-H_2O system at 25°C Atmos Environ 16 2507-2514

Turner, D W , Siegmund, C W (1972) Staged combustion and flue gas recycle potential for minimizing NO_x from fuel oil combustion Presented at The American Flame Research Committee Flame Days, September, Chicago, IL

U S Environmental Protection Agency (1982) Air quality criteria for oxides of nitrogen Research Triangle Park, NC Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office, EPA report no EPA-600/8-82-026 Available from NTIS, Springfield, VA, PB83-131011

U S Environmental Protection Agency (1986) Air quality criteria for ozone and other photochemical oxidants Research Triangle Park, NC Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office, EPA report nos EPA-600/8-84-020aF-eF 5v Available from NTIS, Springfield, VA, PB87-142949

Wayne, R P , Barnes, I , Biggs, P , Burrows, J P , Canosa-Mas, C E , Hjorth, J , Le Bras, G , Moortgat, G K , Perner, D , Poulet, G , Restelli, G , Sidebottom, H (1991) The nitrate radical physics, chemistry, and the atmosphere Atmos Environ Part A 25 1-203

Weast, R C , Astle, M J , Beyer, W H , eds (1986) CRC handbook of chemistry and physics a ready-reference book of chemical and physical data 67th ed Boca Raton, FL CRC Press, Inc , pp B-111 - B-112

Wolff, G T (1984) On the nature of nitrate in coarse continental aerosols Atmos Environ 18 977-981

White, W. H , Dietz, D. (1984) Does the photochemistry of the troposphere admit more than one steady state? Nature (London) 309 242-244

Zeldovich, J. (1946) The oxidation of nitrogen in combustion and explosions Acta Physicochim URSS 21: 577-628

4. AMBIENT AND INDOOR SOURCES AND EMISSIONS OF NITROGEN OXIDES

4.1 INTRODUCTION

Sources of emissions of nitrogen oxides (NO_x) in the ambient environment and indoors play a major role in the determination of nitrogen dioxide (NO_2) levels that are observed in the ambient air and indoors Nitrogen dioxide levels are discussed in Chapter 7 Ambient emission sources include both anthropogenic and natural categories Anthropogenic sources primarily consist of emissions from various transportation vehicles, fuel combustion from stationary sources, industrial processes, solid waste disposal and other sources such as forest fires Natural sources of NO_2 emissions include lightning, stratospheric injection and release from soils and the oceans Indoor sources include gas stoves used for cooking, unvented space heaters fueled with natural gas and propane, kerosene heaters, wood stoves and tobacco products Knowledge of emission sources and patterns for NO_x is important for air quality planning

The present chapter, in Section 4 2, first discusses ambient sources of NO_x and breaks these down into anthropogenic and natural categories (Sections 4 2 1 and 4 2 2, respectively) Next, a brief discussion of global estimates of NO_x emissions is presented in Section 4 2 3 Then an analysis of U S NO_x emission sources, levels, and trends is discussed in Section 4 2 4, followed by Section 4 2 5, a comparison of NO_x emission estimates The chapter then describes indoor NO_x emission sources in Section 4 3, including discussion of the formation of NO_x in combustion in gas-fueled household appliances (Section 4 3 2) Then, specific indoor sources are discussed in the following sections (1) gas stoves used for cooking (Section 4 3 3), (2) unvented space heaters fueled with natural gas and propane (Section 4 3 4), (3) kerosene heaters (Section 4 3 5), (4) wood stoves (Section 4 3 6), and (5) tobacco products (Section 4 3 7) Next, a comparison of emissions from these indoor sources and their influence on indoor air quality is discussed in Section 4 3 8 Finally, the chapter is summarized in Section 4 4

4.2 AMBIENT SOURCES OF NITROGEN OXIDES

Ambient sources of NO_x can be classified into anthropogenic and natural categories Most of the anthropogenic data for Section 4 2 1 was derived from the National Air Pollutant Emissions Estimate 1940 to 1990 (U S Environmental Protection Agency, 1991a), and a majority of the material for the natural source category for Section 4 2 2 was adopted from the National Acid Precipitation Assessment Program Technology Report on Emissions Involved in Acidic Deposition Processes (Placet et al , 1991)

Ideally, national emission estimates should result when the emissions of each individual source in the country are added together However, this "bottom-up" approach is not feasible for a national estimate, and, therefore, emission estimates presented here are based on the "top-down" calculation approach When using the "top-down" estimating procedure, emissions are determined through the application of the formula

$$\text{Emissions} = \text{Activity Level} \times \text{Emission Factor} \times (1 - \text{Removal Efficiency})$$

The activity levels (e g., kilograms of coal consumed) are activities that are associated with pollutant releases The emission factors (e g , grams of NO_x emission per kilogram of coal consumed) are estimated values that relate the quantity of a pollutant to some measure of activity. The removal efficiency represents the fraction of emissions removed through the application of control devices.

The methods used for preparing the data presented in this section are as similar as possible to those used for the Aerometric Information Retrieval System (AIRS) data preparation (U S. Environmental Protection Agency, 1991b) The source files include the results of investigations of millions of sources of air pollution Sources are categorized into two main classifications· (1) "point" sources (e g , petroleum refineries and utility boilers) are facilities, plants, or activities for which individual records are maintained in the source file; and (2) "area" sources (e.g , motor vehicles) are those activities for which aggregated source and emission information are maintained for entire source categories

National activity data for individual source categories are obtained from many different publications. Emission factors, however, are generally obtained from the U S Environmental Protection Agency's (EPA's) *Compilation of Air Pollutant Emission Factors*,

AP-42 (U S Environmental Protection Agency, 1985), and from the EPA's mobile source emission factor model (U S Environmental Protection Agency, 1989)

4.2.1 Anthropogenic Sources of Nitrogen Oxides

Table 4-1 provides the major source categories and subcategories of anthropogenic NO_x emissions The following sections briefly describe the methodology for estimating the annual emissions by major source categories

TABLE 4-1. MAJOR SOURCE CATEGORIES[a]

Category	Subcategory
Anthropogenic Sources	
Transportation	Highway Vehicles (Gasoline- and Diesel-Powered) Aircraft Railroads Vessels Off-Highway Vehicles and Machinery
Stationary Source Fuel Combustion	Electric Utilities Industrial Boilers Commercial and Institutional Boilers and Furnaces Residential Furnaces and Space Heaters
Industrial Processes	Chemical Manufacturing Petroleum Refining Primary and Secondary Metals Iron and Steel Mills Mineral Products Food Production and Agriculture Industrial Organic Solvent Use Petroleum Production and Marketing
Solid Waste Disposal	Incineration Open Burning
Miscellaneous	Forest Fires[b] Other Burning (Agricultural Burning, Coal Refuse Burning, and Structure Fires) Miscellaneous Organic Solvent Evaporation

[a]U S Environmental Protection Agency (1991a)
[b]For the purpose of this report, forest fires are considered anthropogenic sources, although some fires may be caused by nature

4.2.1.1 Transportation

This category includes gasoline- and diesel-powered motor vehicles, aircraft, railroads, vessels, and off-highway vehicles

The dominant gasoline-fueled powerplant is a homogeneous-charge spark-ignition engine. "Homogeneous charge" implies that an effort is made to provide a uniformly mixed charge of fuel and air in the cylinder prior to combustion This necessitates introduction of the fuel into the air upstream of the engine cylinder

In contrast, the diesel is a stratified-charge compression-ignition engine The fuel is injected into the cylinder beginning near the end of the compression stroke This produces a nonuniform mixture that ranges from 100% fuel at the exit from the injector nozzle to 0% fuel in other regions of the cylinder

Both of these engines require a higher average cylinder-gas temperature during the expansion stroke than during the compression stroke in order to produce useful output work, and the combustion process provides that difference At the high temperatures reached during combustion, a small fraction of the cylinder air forms NO If chemical equilibrium existed at all times in the cylinder, that NO would disappear as the cylinder gas cooled during expansion. The nitrogen atoms in the NO would revert to molecular nitrogen and the oxygen atoms would either revert to molecular oxygen or appear in water or an oxide of carbon. The engine cycle is completed so quickly, however, that chemical equilibrium cannot be established and some of the NO is discharged with the exhaust gas

Ultimately, the NO exhausted from the tailpipe oxidizes over time to NO_2 In fact, a small amount of the NO formed during combustion may already experience that oxidation before exiting the tailpipe. Because emission standards are expressed on a mass basis, all oxides of nitrogen exhausted from the tailpipe are assigned the molecular weight of NO_2 and are referred to as NO_x.

Federal regulation of NO_x from U S automobiles and light trucks began in 1973 and regulation of NO_x from heavy-duty trucks began in 1984 Regulation of unburned hydrocarbons (HCs) and carbon monoxide (CO) emitted from these vehicles began even earlier. The fuel economy of automobiles and light trucks (i e , light-duty vehicles [LDVs]) is also subject to federal standards

Because of the significance of all these regulations to engine and vehicle design, it is helpful to understand their interactions Emission trends for NO_x, HCs, and CO, all expressed in terms of mass per unit of engine output energy, are illustrated in Figure 4-1 for a homogeneous-charge engine with ignition timing set for best fuel economy Thermal efficiency, which is proportional to fuel economy, is also shown

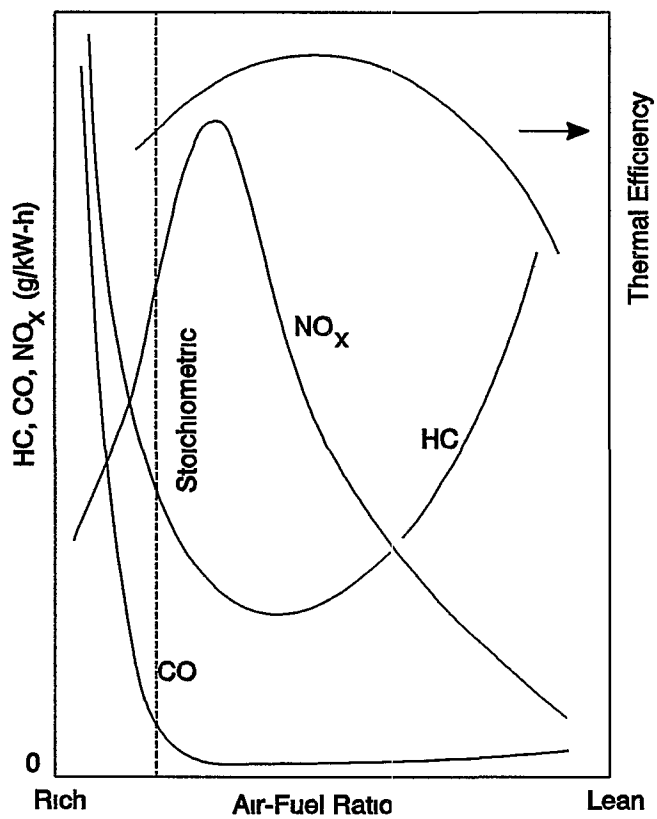


Figure 4-1. Production of hydrocarbons, carbon monoxide, and nitrogen oxide as a function of air-fuel ratio.

Source Heywood (1988)

Nitrogen oxide production is seen in Figure 4-1 to peak just to the lean side of the chemically correct, or stoichiometric, air-fuel ratio It is evident that NO_x can be kept low by running with a rich mixture, but the associated effects on HCs, CO, and fuel economy are evident Similarly, operating with a very lean mixture lowers NO_x

To meet current emissions standards, gasoline-fueled LDVs employ a catalyst-based exhaust aftertreatment system that, when the mixture is tightly controlled about the stoichiometric ratio, is able to effect substantial reductions in all three regulated emissions Unfortunately, the catalysts used are ineffective in reducing engine-out NO_x in lean mixtures To date, efforts to develop a lean-mixture NO_x catalyst system with both high efficiency and good durability have been unsuccessful Therefore, the only viable aftertreatment strategy today necessitates using oxidizing (for HCs and CO) and reducing (for NO_x) catalysts and, for most engine operating conditions, a stoichiometric mixture The catalysts used are now typically packaged together to make what is known as a three-way catalytic converter

Two other techniques have been used to decrease NO_x emissions, but they are adjuncts to, rather than replacements for, the three-way catalyst One is to delay the timing of combustion in the cycle by retarding the spark This lowers peak cylinder-gas temperature, hence NO production, but is undesirable for its adverse effect on fuel economy The second is to use exhaust-gas recirculation (EGR) back into the engine intake With a stoichiometric air-fuel ratio, EGR serves as a diluent to decrease combustion temperature With a fast-burn combustion-chamber design, a little EGR can actually improve the fuel economy of a stoichiometric engine somewhat, but excessive EGR deteriorates drivability

Because of its charge stratification, the diesel engine is able to operate at much leaner overall air-fuel ratios than the homogeneous-charge engine In fact, at a given operating speed, diesel load is controlled by varying the overall air-fuel ratio rather than by manipulating an intake throttle as on the homogeneous-charge engine However, the low NO_x production that might be expected from Figure 4-1 with such a lean mixture does not occur. As injected fuel vaporizes and diffuses into the surrounding cylinder air, from the spectrum of local air-fuel ratios established in the diesel, conditions for autoignition and combustion are most favorable around the stoichiometric ratio Thus, much of the fuel burns locally in a mixture-ratio range near that for peak NO_x production in Figure 4-1, irrespective of the lean cylinder-average mixture

As is true of the homogeneous-charge engine, NO_x from the diesel can be decreased by delaying the timing of combustion through retardation of injection timing, but with an adverse effect on fuel economy Exhaust-gas recirculation is also effective in lowering NO_x at partial engine loads, but normally that increases particulate matter (PM)

Heavy-duty diesels typically consume most of their fuel at high loads, where the cylinder-average air-fuel ratio is usually already set at the rich end of the acceptable range for diesel combustion (although still leaner than stoichiometric), as limited by the time available for proper mixing of fuel and air Under these conditions, additional combustion diluent in the form of EGR is unwelcome, so EGR is generally not a useful NO_x-reduction option in heavy-duty applications

The federal government is examining introduction of alternative fuels in metropolitan areas with the poorest air quality Included on the list of options are methanol, natural gas, reformulated gasoline, ethanol, liquefied petroleum gas (LPG), and hydrogen A discussion of alternative fuels, however, is outside the scope of this document

Highway Vehicles

Emissions from gasoline- and diesel-powered motor vehicles are based on vehicle miles traveled and emission factors Eight vehicle categories are considered gasoline-powered automobiles, diesel-powered automobiles, light-duty gasoline trucks (<6,000 lb), light-duty gasoline trucks (6,000 to 8,500 lb), light-duty diesel trucks, heavy-duty gasoline trucks and buses, heavy-duty diesel trucks and buses, and motorcycles Emission factors were obtained from the MOBILE4 model (U S Environmental Protection Agency, 1989) This model was designed to be used as a tool for estimating exhaust and running loss emissions from highway vehicles in nonattainment areas and in urban air sheds The revised model, MOBILE5a, updated and corrected May 20, 1993 (Federal Register, 1993), estimates higher NO_2 emissions

Aircraft

Emissions from aircraft are based on the number of take-offs and landings reported by the Federal Aviation Administration (U S Department of Transportation, Annual a) and on AP-42 emission factors for various types of aircraft

Railroads

Emissions for railroads are based on diesel and residual fuel oil consumption by railroads as reported by the Energy Information Administration (U S Department of Energy, Monthly). Average emission factors were used as applicable for each fuel type

Vessels

The consumption of diesel fuel, residual oil, and coal by vessels operating inside the United States boundaries was obtained from the U S Department of Energy (Monthly, Annual· a, Annual. b) Gasoline consumption is based on national boat and motor registrations, together with usage factors (gallons per motor per year) (U S Department of Energy, Monthly) and marine gasoline sales, as reported by the U S Department of Transportation (Annual b) The estimates of fuel consumption are multiplied by AP-42 emission factors In the case of coal-fired vessels, an average emission factor for coal combustion in boilers was used

Off-Highway Vehicles

This source category includes farm tractors, other farm machinery, construction equipment, industrial machinery, small general utility engines, such as lawn mowers and snowmobiles; and motorcycles Fuel use is estimated for each subcategory from equipment population data and an annual fuel-use factor (Hare and Springer, 1973a,b,c), together with fuel deliveries of diesel fuel reported by the U S Department of Energy (Monthly) and gasoline sales reported by the U S Department of Transportation (Annual b) for off-highway use

4.2.1.2 Stationary Source Fuel Combustion

This category includes electric utilities (including boilers) combined cycle combustion turbines, combustion (gas) turbines, cogeneration units, and internal combustion (diesel), industrial boilers, commercial and institutional boilers and furnaces, and residential furnaces and space heaters. However, because the emission factors for stationary sources depend on the fuel used by each source, this section is divided into the following sections coal, fuel

oil, natural gas, wood, and other fuels The NO_x emissions summary, presented in Section 4 2 3, is presented both by fuel type and by stationary source

Coal

The consumption of bituminous coal, lignite, and anthracite coal by various end users is reported by the U S Department of Energy (Annual b, Annual c) Most coal is consumed by electric utilities The reported fuel consumption by source category was multiplied by an average emission factor for NO_x For coal, fuel nitrogen is generally the principal source of NO_x emissions (Bartok and Sarofim, 1991)

Fuel Oil

Residual oil, distillate oil, and kerosene are burned by electric utilities, industrial boilers, commercial and institutional boilers, furnaces, and residential heaters
The consumption of each fuel type by end users is reported by the U S Department of Energy (Monthly) Average emission factors are calculated and applied to the consumption data As with coal, fuel nitrogen is generally the principal source of NO_x emissions (Bartok and Sarofim, 1991)

Natural Gas

Natural gas consumption is also reported by the U S Department of Energy for various end-user groups (U S Department of Energy, Annual d) The AP-42 emission factors were used to calculate the emissions The "thermal mechanism" is generally the principal source of NO_x emissions for natural gas (Bartok and Sarofim, 1991)

Wood and Other Fuels

Consumption of wood has been estimated by the U S Department of Energy (1982, 1984) for wood stoves and residential fireplaces Consumption of bagasse is based on data reported in AIRS (U S Environmental Protection Agency, 1991b) Sales of liquified petroleum gas are reported by the U S. Department of Energy (Annual a) Coke and coke-oven gas consumption values are obtained from Gschwandtner et al (1990) These consumption values were multiplied by appropriate emission factors obtained either from

AIRS (U.S. Environmental Protection Agency, 1991b) or AP-42 (U S Environmental Protection Agency, 1985) As with natural gas, the "thermal mechanism" is generally the principle source of NO_x emissions (Bartok and Sarofim, 1991)

4.2.1.3 Industrial Processes

Production data for industries that produce the majority of emissions were obtained from available publications Generally, the Minerals Yearbook (U S Department of the Interior, Annual) and the Current Industrial Reports (U S Department of Commerce, Annual: a), published by the Bureau of Census, provided most of the necessary data Average emission factors were applied to the various production data Average nationwide control efficiency values for various processes were obtained either from published reports (Shannon et al., 1971, Vandegrift et al , 1971a,b), the 1985 National Acid Precipitation Assessment Program (NAPAP) emission inventory (Saeger et al , 1989), or AIRS (U S Environmental Protection Agency, 1991b)

Petroleum product storage and petroleum marketing operations (including gasoline, crude oil, and distillate fuel oil storage and transfer, gasoline bulk terrains and bulk plants, and retail gasoline service stations) are included as industrial processes Also included are industrial surface coating and degreasing operations, graphic arts (printing and publishing), and dry cleaners

4.2.1.4 Solid Waste Disposal

The emissions from this category are based on an assumed solid waste generation rate of 5.5 lb/capita/day This value was originally based on a study of solid waste collection and disposal practices (U S Department of Health, Education, and Welfare, 1968) This value is adjusted each year based on information contained in AIRS (U S Environmental Protection Agency, 1991b) Average emission factors are applied to the estimated quantities of solid waste disposal.

4.2.1.5 Miscellaneous Sources

This major source category includes forest fires, agricultural burning, coal refuse burning and structure fires

Forest Fires

The U S Forest Service of the Department of Agriculture and the U S Department of the Interior publish information on the number of forest fires, their location, and the acreage burned each year The amount of forest biomass burned and controlled burning of forest areas each year are estimated per acre by Yamate (1974) Average emission factors were applied to the estimated quantities of materials burned

Agricultural Burning

A study was conducted by the EPA to obtain local agricultural and air pollution control agency estimates of the number of acres and quantity of material burned per acre in agricultural burning operations (Yamate, 1974) These data have been updated and used to estimate emissions based on average emission factors

Coal Refuse Burning

Estimates of the number of burning coal-refuse piles existing in the United States are reported by the Bureau of Mines (McNay, 1971) This publication presents a detailed discussion of the nature, origin, and extent of this source of pollution Rough estimates of the quantity of emissions were made using this information by applying average emission factors for coal combustion It should be noted that the number of coal-refuse piles had become negligible by 1975

Structure Fires

The U S Department of Commerce (Annual b) publishes information on the number and type of structures damaged by fires each year Emissions are estimated by applying average emission factors for wood combustion to these statistics

4.2.2 Natural Sources of Nitrogen Oxides

Nitrogen oxides can be naturally produced by lightning, biological and abiological processes in soil, stratospheric intrusion, and chemical or photochemical processes in the oceans There are four source categories for natural NO_x emissions lightning, soils, stratospheric injection, and oceans

Lightning

The release of energy generated by lightning produces the extremely high temperatures required to convert atmospheric nitrogen and oxygen to NO Quantitative estimates of NO_x production have been derived from different methods One method (Borucki and Chameides, 1984) uses three general factors (1) the frequency of lightning flashes, (2) energy dissipated per flash, and (3) the NO_x production per unit of energy dissipated Another method (Albritton et al , 1984) used nitrate deposition data from remote oceanic and polar sites where NO_x from intracloud lightning is expected to be the dominant precursoi Estimates of lightning-based NO_x emissions for North America (Placet et al , 1991) range from 1 2 to 1.7 Tg/year of NO_2

Soils

At this time, the biological or abiological pathway to NO_x production of the soils is still being debated (Placet et al , 1991) In spite of the uncertainties, four local variables emerge as possible factors that influence NO_x emissions soil temperature, soil moisture content, soil vegetation cover, and soil nutrients (Placet et al , 1991) The NAPAP has estimated national emissions of NO_x from soils to be 1 2 Tg/year

Stratospheric Injection

Nitrous oxide (N_2O) is released into the troposphere from various sources on the Earth's surface However, because there are no significant loss processes for N_2O in the troposphere, this N_2O is transported to the stratosphere, where it is photodissociated or oxidized. A portion of the NO produced by these processes in the stratosphere subsides into the troposphere. Because it has been extensively modeled, the magnitude of the NO_x emissions from this source is probably more well known than from any other natural source (Placet et al , 1991) Crutzen and Schmailz (1983) estimated global NO_x emissions from stratospheric injection to be 0 5 Tg/year For the United States, stratospheric injection is probably the source of less than 0 1 Tg/year of NO_x (Placet et al , 1991)

Oceans

Production of NO from the ocean is attributed to the photolysis of nitrite dissolved in seawater (Zafiriou and McFarland, 1981) On a global basis, oceans are a small natural source of NO_x Given the lifetime of NO_x in the atmosphere—a few days or less (Liu et al , 1987)—the transport of NO_x into the United States is negligible (Placet et al , 1991), with the possible exception of some local scale transport of NO_x that may be measurable

4.2.3 Global Estimates of Nitrogen Oxides Emissions

Global sources for NO_x appear to be on the order of 150 Tg of NO_x per year (see Table 4-2) (Logan, 1983) Similar estimates for global sources of NO_x are given in Bauer (1982) and Stedman and Shetter (1983)

TABLE 4-2. GLOBAL BUDGET OF NITROGEN OXIDES IN THE TROPOSPHERE[a]

	Nitrogen Oxides (Tg/year)[b]	
Source	Ehhalt and Drummond	Logan
Production		
Fossil-Fuel Combustion	42 (26-58)	63 (44-88)
Biomass Burning	36 (18-52)	36 (13-76)
Release from Soils	17 (3-30)	25 (13-50)
Lightning Discharges	15 7 (6-25)	25 (6-63)
Ammonia Oxidation	10 (4-15)	(0-31)
Ocean Surface (biologic)	--	3
High-Flying Aircraft	1 (0 6-1 2)	--
Stratosphere	2 (0 9-2 8)	1 5
Total Production	122 (60-186)	152 (79-310)

[a]Derived from estimates according to Ehhalt and Drummond (1982) and Logan (1983)
[b]Mean (low range—high range)

Note Values may not sum due to independent rounding

As with the emission estimates for the United States, emissions from anthropogenic sources (fossil fuel combustion and biomass fires associated with agriculture) appear to exceed the emissions from natural sources (lightning and soils) For the global estimate, the ratio of emissions from anthropogenic sources to the emissions from natural sources is on the

order of 2. For the emission estimates for the United States (see Table 4-3) this ratio is approximately 9.

TABLE 4-3. ESTIMATES OF NITROGEN OXIDE EMISSIONS FROM ANTHROPOGENIC AND NATURAL SOURCES IN THE UNITED STATES AND CANADA (MILLIONS OF METRIC TONS/YEAR OF NITROGEN DIOXIDE EQUIVALENT EMISSIONS)

Emission Source	Emissions		Percent of Total [b]
	Best Estimate	Range[a]	
Anthropogenic sources[c]			
Highway vehicles	8 1	6 2 - 10 5	32
Power plants	6 0	5 0 -7 2	23
Industrial combustion	4 1	3 4 - 4 9	16
Other	4 3	3 4 - 5 4	17
Total anthropogenic[d]	22 6	18 0 - 28 0	88
Natural sources[e]			
Lightning	1	0 3 - 2	4
Soil	2	0 3 - 5	8
Stratospheric injection	<0 1	NA[f]	≈0
Total natural[d]	3	0 6 - 7	12
Total[d]	26	19 - 35	100

[a]Based on uncertainties in Table 4-5 for anthropogenic source categories
[b]Percentages are based on "best estimate" values
[c]Includes Canada and the United States Values for the United States are the "best estimate" for 1985 shown in Table 4-5
[d]Values may not sum to totals due to independent rounding
[e]Values are for North America from Table 4-6
[f]NA = Not available

Source. U S Environmental Protection Agency (1991a)

4.2.4 Analysis of United States Nitrogen Dioxide Emission Sources, Levels, and Trends

Table 4-4 presents the total emissions of NO_x in the United States from 1940 to 1990 Preliminary estimates for 1990 indicate that over 80% of the national NO_x emissions are emitted by highway vehicles, electric utilities, and industrial boilers Nitrogen oxides emissions for stationary fuel sources have grown steadily from 1940 through 1990 Between

TABLE 4-4. TOTAL NATIONAL EMISSIONS OF NITROGEN OXIDES, 1940 TO 1990 (teragrams/year)[a]

Source Category	1940	1950	1960	1970	1980	1990
Transportation						
Highway Vehicles	1 4	2 2	3 8	6 3	7 9	5 6
Aircraft	0 0	0 0	0 0	0 1	0 1	0 1
Railroads	0 6	0 9	0 7	0 6	0 8	0 5
Vessels	0 1	0 1	0 1	0.1	0 2	0 2
Other Off-Highway Vehicles	0 2	0 4	0 5	0 8	1 0	1 1
Transportation Total	2 3	3 6	5 1	8 0	9 8	7 5
Stationary Source Fuel Combustion						
Electric Utilities	0 6	1 2	2 3	4 4	6 4	7 3
Industrial	2 3	2 9	3 7	3 9	3 1	3 3
Commercial-Institutional	0 2	0 3	0 3	0 9	0 3	0 2
Residential	0 3	0 3	0 4	0 4	0 4	0 4
Fuel Combustion Total	3 4	4 7	6 7	9 1	10 1	11 2
Industrial Processes						
Petroleum Refining	0 1	0 1	0 2	0 2	0 2	0 2
Chemicals	0 0	0 0	0 1	0 2	0 2	0 1
Iron and Steel Mills	0 0	0 1	0 1	0 1	0 1	0 0
Pulp Mills	0 0	0 0	0 0	0 0	0 0	0 0
Mineral Products	0 1	0 1	0 1	0 2	0 2	0 2
Industrial Processes Total	0 2	0 3	0 5	0 7	0 7	0 6
Solid Waste Disposal						
Incineration	0 0	0 1	0 1	0 1	0 0	0 0
Open Burning	0.1	0 1	0 2	0 3	0 1	0 1
Solid Waste Total	0 1	0 2	0 3	0 4	0 1	0 1
Miscellaneous						
Forest Fires	0 7	0 4	0 2	0 2	0 2	0 2
Other Burning	0 2	0 2	0 2	0 1	0 0	0 0
Miscellaneous Total	0 9	0 6	0 4	0 3	0 2	0 3
Total of All Sources	6 9	9 4	13 0	18 5	20 9	19 6

[a]U S Environmental Protection Agency (1991a)

the years 1940 and 1980, NO_x emissions from transportation sources nearly quintupled, but decreased by 30% from 1980 to 1990

In the recent past, the U S transportation system has been responsible for 40 to 50% of the annual national NO_x emissions, as indicated in Table 4-5 (U S Environmental Protection Agency, 1991a) From 1982 through 1989, that percentage contribution has been decreasing at an average rate of 2 5%/year

TABLE 4-5. TRANSPORTATION CONTRIBUTION TO U.S. NITROGEN OXIDES EMISSIONS

Year	Millions of Metric Tons	Percent of U S Total
1978	9 8	46 4
1979	10 1	46 8
1980	9 8	46 9
1981	10 0	47 8
1982	9 4	47 0
1983	8 9	46 1
1984	8 8	44 4
1985	8 9	44 7
1986	8 3	43 5
1987	8 1	41 8
1988	8 1	40 5
1989	7 9	39 7

Source U S Environmental Protection Agency (1991a)

In 1988, the highway sector produced 76% of the NO_x from the transportation system, as shown in Table 4-6 (U S Environmental Protection Agency, 1990) This amounted to 31% of the national NO_x emissions for that year Among the contributors to the balance from the transportation system were air, marine, and rail vehicles As seen from Table 4-6, in 1988, 62% of the NO_x from highway vehicles came from gasoline engines and 38% came from diesel engines

Table 4-7 shows the emissions of NO_x from stationary fuel combustion sources categorized by fuel type For the 1990 data, the combustion of coal accounted for 63% of the NO_x emissions from stationary sources The majority of the emissions came from coal

TABLE 4-6. BREAKDOWN OF 1988 TRANSPORTATION NITROGEN OXIDES

Type[a]	Millions of Metric Tons	Percent of Highway Total
Gasoline LDV	3 55	57 8
Gasoline HDV	0 25	4 1
Motorcycle	0 01	0 2
Diesel LDV	0 03	0 5
Diesel HDV	2 30	37 5
Nonhighway	1 95	----
Total	8 09	

[a]LDV = Light-duty vehicle
HDV = Heavy-duty vehicle

Source U S Environmental Protection Agency (1990)

combustion in electric utilities Coal combustion accounted for 88% of the NO_x emissions for electric utilities, while accounting for 61% of the fossil-fuel electric utility-generating capacity (U S Department of Energy, 1991) Natural gas accounts for 29% of the NO_x emissions from stationary sources In the industrial boiler category, natural gas accounts for nearly 72% of the NO_x emissions Nitrogen oxides related to the combustion of coal increased 82% from 1970 to 1990 During the same time, NO_x from fuel oil and natural gas decreased 45 and 20%, respectively

Table 4-8 presents U S NO_x emissions from 1940 to 1990 and current estimates of future NO_x emissions from highway vehicles, industrial sources, electric utilities, and all other sources These emission trends are shown in Figure 4-2 The projections account for the expected net effect of all provisions of the Clean Air Act (CAA) as amended in 1990 These include the NO_x emission limits prescribed for utility boilers under the acid rain provisions, the Tier I automobile tailpipe standards, and application of technology-based requirements to nonutility boilers (generally greater than 100 tons/year) in ozone (O_3) nonattainment areas and the Northeast Ozone Transport Region The estimates do not fully incorporate New Source Review requirements, such as offsets and lowest achievable emission rates in nonattainment areas, nor do they incorporate additional controls required based on attainment demonstration modeling They also do not attempt to estimate the extent

TABLE 4-7. EMISSIONS OF NITROGEN OXIDES FROM STATIONARY FUEL COMBUSTION SOURCES, 1970 TO 1990 (teragrams/year)[a]

Source	1970	1980	1990
Coal			
Electric Utilities	3 17	5 15	6 42
Industrial	0 70	0 40	0 67
Commercial-Institutional	0 02	0 02	0 03
Residential	0 02	<0 01	<0 01
Coal Total	3 91	5 57	7 12
Fuel Oil			
Electric Utilities	0 39	0 44	0 27
Industrial	0 3	0 22	0 10
Commercial-Institutional	0 19	0 14	0 08
Residential	0 11	0 08	0 09
Fuel Oil Total	0 99	0 85	0 54
Natural Gas			
Electric Utilities	0 88	0 78	0 59
Industrial	2 77	2 24	2 37
Commercial-Institutional	0 11	0 12	0 12
Residential	0 22	0 22	0 20
Natural Gas Total	3 98	3 36	3 28
Wood			
Industrial	0 09	0 12	0 15
Residential	0 04	0 08	0 07
Wood Total	0 13	0 20	0 22
Other Fuels			
Industrial	0 05	0 07	0 03
Residential	0 06	0 03	0 03
Other Fuels Total	0 11	0 10	0 06
Fuel Combustion Total	9 12	10 08	11 22

Note Values may not sum due to independent rounding

[a]U S. Environmental Protection Agency (1991a)

TABLE 4-8. TOTAL NATIONAL NITROGEN OXIDE EMISSIONS, 1940 TO 2010 (teragrams/year)[a]

Source	1940	1950	1960	1970	1980	1990	2000	2010
Highway Vehicles	1 4	2 2	3 8	6 3	7 9	5 6	3 0	2 9
Electric Utilities	0 6	1 2	2 3	4 4	6 4	7 3	6 1	7 4
Industrial Sources[b]	2 5	3 2	4 2	4 6	3 8	3 9	3 5	4 1
Other	2 4	2 8	2 7	3 2	2 8	2 8	3 0	3.2
Total	6 9	9 4	13 0	18 5	20 9	19 6	15 6	17 6

[a]U S Environmental Protection Agency (1991a)
[b]Includes industrial fuel combustion and processes

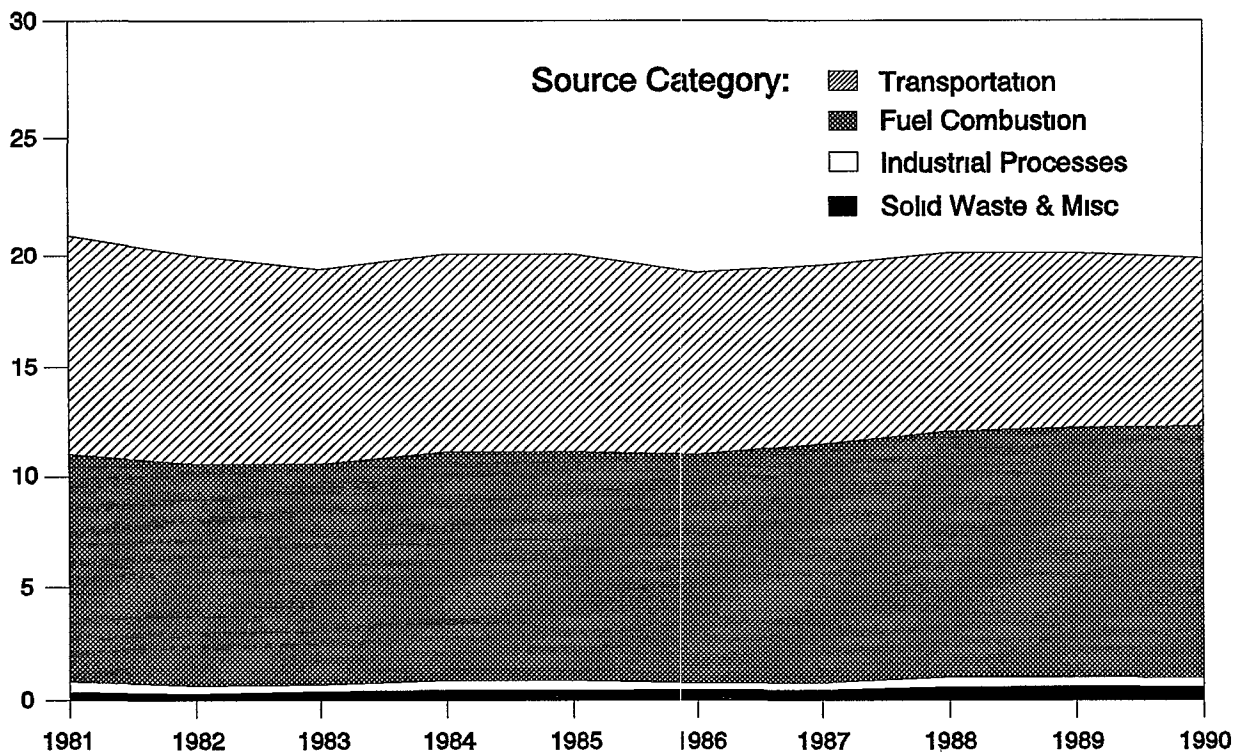


Figure 4-2. National trend in U.S. nitrogen oxides emissions, 1981 to 1990 (10^6 metric tons per year).

to which any areas might be exempted from NO_x stationary source controls under CAA Section 182(f).

Projections of NO_x emissions from highway vehicles are based on projected vehicle miles traveled and MOBILE4 1 emission factors These emission factors reflect current emission control standards and Tier I motor vehicle emission standards of the CAA (Tier II standards are not reflected because these are discretionary) As a result of these standards, NO_x emissions from highway vehicles are expected to decrease by almost 50% from 1990 to 2000.

Federal Tier I standards for 1994 and California's series of low-emission vehicle (LEV) standards call for further reductions in NO_x, regardless of the fuel used Specifically, these standards are 0.4 g/mi NO_x for Tier I and California's transitional low-emission vehicle, and 0.2/mi for the LEV and ultra-low-emission vehicle

An indication of the effectiveness of NO_x regulation on the NO_x per highway vehicle is provided in Figure 4-3. Nitrogen oxide standards for both LDVs and diesel HDVs are traced by the stairsteps The estimate plotted for the average highway vehicle was made in the following way. Available NO_x data from the entire transportation sector were multiplied by 0 778, the average ratio of highway-vehicle energy consumption to total transportation energy consumption over the 12-year period illustrated (U S Environmental Protection Agency, 1991a). This product was then used to calculate the ratio to the total annual miles traveled by all highway vehicles The resulting estimate, which involves an assumption that NO_x mass produced is proportional to energy consumption for cars, diesel trucks, locomotives, jet liners, and pipelines alike is obviously not quantitatively correct, but the trend is believed to be valid This estimated average is seen to track the trends in NO_x emission standards remarkably well

Future reductions in NO_x standards, therefore, suggest a likely continued downtrend in NO_x grams per mile for highway vehicles The total NO_x contributed will depend, of course, on the product of grams per mile of NO_x per vehicle and the total annual miles driven. Table 4-5 suggests that since 1979, the decrease in NO_x per vehicle-mile has more than compensated for any increase in total miles driven

Additional measures being scheduled to decrease the average grams NO_x per mile from passenger cars are (1) advanced on-board diagnostics systems to signal the driver of engine

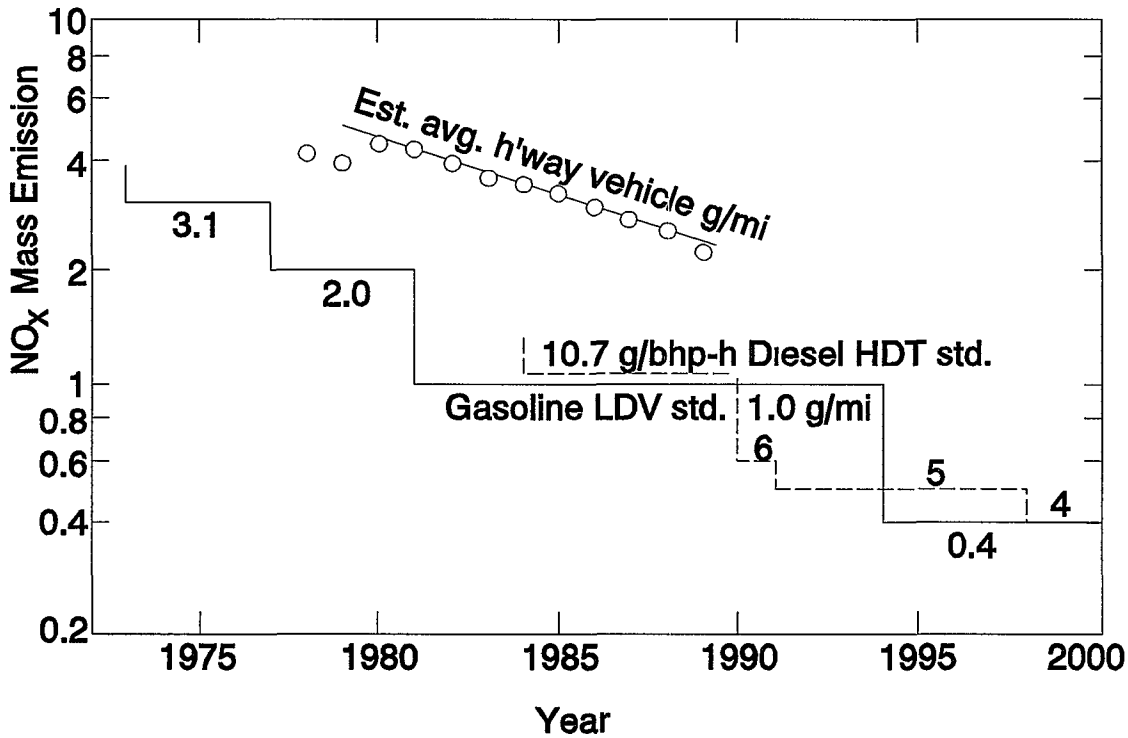


Figure 4-3. Emission of nitrogen oxides compared with nitrogen oxide standards.

Source· U S. Environmental Protection Agency (1990)

and emissions-control system malfunctions, and (2) expanded and improved inspection and maintenance procedures These steps will augment the impact of emissions standards Most cars on the road today have control systems required to meet emission standards at 50,000 mi As of 1990, approximately 60% of these cars had been driven more than 50,000 mi, and about a quarter of registered cars were built before the NO_x reducing catalyst and electronic control had seen widespread application (U.S Environmental Protection Agency, 1991a)

By 2000, all electric utility units with capacities greater than 25 MW are expected to meet new emission limits imposed by the CAA Also, new or modified electric power units will be subject to revised performance standards As a result, NO_x emissions from electric utilities are expected to decrease by 16% in the next 10 years The analysis for utilities was performed under the assumption that low-NO_x combustion technology would be employed to

meet the NO_x provisions of Title IV The 6 1 Tg estimate for electric utilities in 2000 is approximately 1.8 Tg (2 million short tons) less than what would have been emitted by utilities without controls implemented as a result of the CAA Amendments of 1990

Estimates of future NO_x emissions from industrial sources are based on state-level growth factors and the expected application of reasonable available control technology where required. As a result, a 10% reduction is expected in NO_x emissions from industrial sources from 1990 to 2000 This reduction may be more than offset by increases in emissions between 2000 and 2010 The future trend of stationary source NO_x emissions is presently uncertain because it is not known whether O_3 nonattainment areas will be exempt from the proposed New Source Review policy that requires lowest achievable emission reductions and offsets for new major sources

Table 4-9 presents the estimated emissions of NO_x from anthropogenic and natural sources for 1990 As shown, anthropogenic sources account for nearly 90% of the NO_x emissions

TABLE 4-9. COMPARISON OF ANTHROPOGENIC AND NATURAL SOURCES OF NITROGEN OXIDES EMISSIONS FOR 1990[a]

Sources	Emissions (Tg)	Percent of Total
Anthropogenic		
Transportation	7 5	34
Stationary	11 2	51
Industrial Processes	0 6	3
Solid Waste	0 1	<1
Misc.	0 3	<1
	19 7	89
Natural		
Lightning	1 2	5
Soils	1 2	5
Stratosphere	<0 1	<1
Oceans	<0 1	<1
	2 4	11
Total	22 1	100

[a]U.S Environmental Protection Agency (1991a), and Placet et al (1991)

4.2.5 Comparison of Nitrogen Oxide Emissions Estimates

Table 4-10 compares several sources of NO_x emission estimates These include the NO_x emission estimates of the 1985 NAPAP Emissions Inventory (Version 2) (Saeger et al , 1989), the EPA long-term trends estimates (U S Environmental Protection Agency, 1990), NAPAP month and state current emission trends (MSCET) estimates (Kohout et al , 1990), and the 1982 Electric Power Research Institute (EPRI) Inventory (Heisler et al , 1988) For 1985 data, total emissions from the NAPAP, EPA, and MSCET inventories differ by less than 9% The EPRI inventory estimate of 20 7 Tg is higher than the 1982 EPA and MSCET estimates, which are 19 6 and 18 8 Tg, respectively

TABLE 4-10. COMPARISON OF ANNUAL U.S. NITROGEN OXIDE EMISSIONS ESTIMATES FROM FOUR INVENTORIES[a]

	Emissions (Tg/year)			
Source Category	NAPAP Inventory[b]	EPA Trends[c]	MSCET[d]	EPRI[e]
Electric Utilities	6 0	6 8	6 2	7 2
Nonutility Combustion	3 5	3 4	3 6	4 4
Transportation	8 0	8 9	7 6	7 9
Other Sources	1 0	0 7	0 8	1 2
Total	18 6	19 8	18 2	20 7

[a]Note Values may not sum to totals due to independent rounding
NAPAP = National Acid Precipitation Assessment Program
EPA = U S Environmental Protection Agency
MSCET = Month and state current emission trends
EPRI = Electric Power Research Institute
[b]Saeger et al (1989)
[c]U S Environmental Protection Agency (1990)
[d]Kohout et al (1990)
[e]Heisler et al (1988)

4.3 INDOOR EMISSION SOURCES OF NITROGEN OXIDES

4.3.1 Introduction

This section summarizes emissions of NO_x from combustion sources commonly found in the indoor residential environment that affect indoor air quality There are several reasons for considering these emissions First, such information is needed to understand the

fundamental physical and chemical processes influencing emissions This understanding can be used to help develop strategies for reducing emissions Second, examining emissions from several types of sources and source categories can help identify the relative importance of each source in affecting indoor air quality This information can guide decisions by house occupants on combustion appliance purchases and methods of using such appliances Finally, studying emissions from indoor sources can provide source strength input data needed for indoor air quality modeling Predicting indoor airborne concentrations is important for estimating the total exposure of individuals to NO_x

This section begins with a brief discussion of the physics and chemistry of nitrogen oxides formation in flames Several major source categories are then considered These include gas stoves used for cooking, unvented gas space heaters, unvented kerosene heaters, wood stoves primarily used for heating, and tobacco products For each category, several studies will be discussed, including the measurement methods used and the resulting data Following these presentations, the emissions of NO_x for all categories will be compared

Note that several types of vented appliances commonly found indoors usually emit NO_x to the outdoors. Examples include furnaces, water heaters, and clothes dryers using gas, as well as stoves and furnaces using wood, coal, and other fuels Under some circumstances, these sources may contribute to elevated NO_x levels indoors, for example, Hollowell et al (1977) reported high NO and NO_2 concentrations in a house where a vented forced-air gas-fired heating system was used Elevated concentrations may also be a problem with malfunctioning vented appliances Other data (e g , Fortmann et al , 1984), however, suggested that fugitive emissions of NO_x from vented appliances are small Because the importance of unvented appliances to indoor NO_x levels is well-documented, this chapter focuses on emissions from such appliances

4.3.2 Formation of Nitrogen Oxides in Combustion in Gas-Fueled Household Appliances

Many household appliances incorporate laminar flames in which the input fuel is premixed with a known amount of air before being subjected to combustion As an example, Figure 4-4 shows a diagram of a single-port flame fueled with natural gas, taken from a review by the Institute of Gas Technology (Zawacki et al , 1986) The figure is somewhat

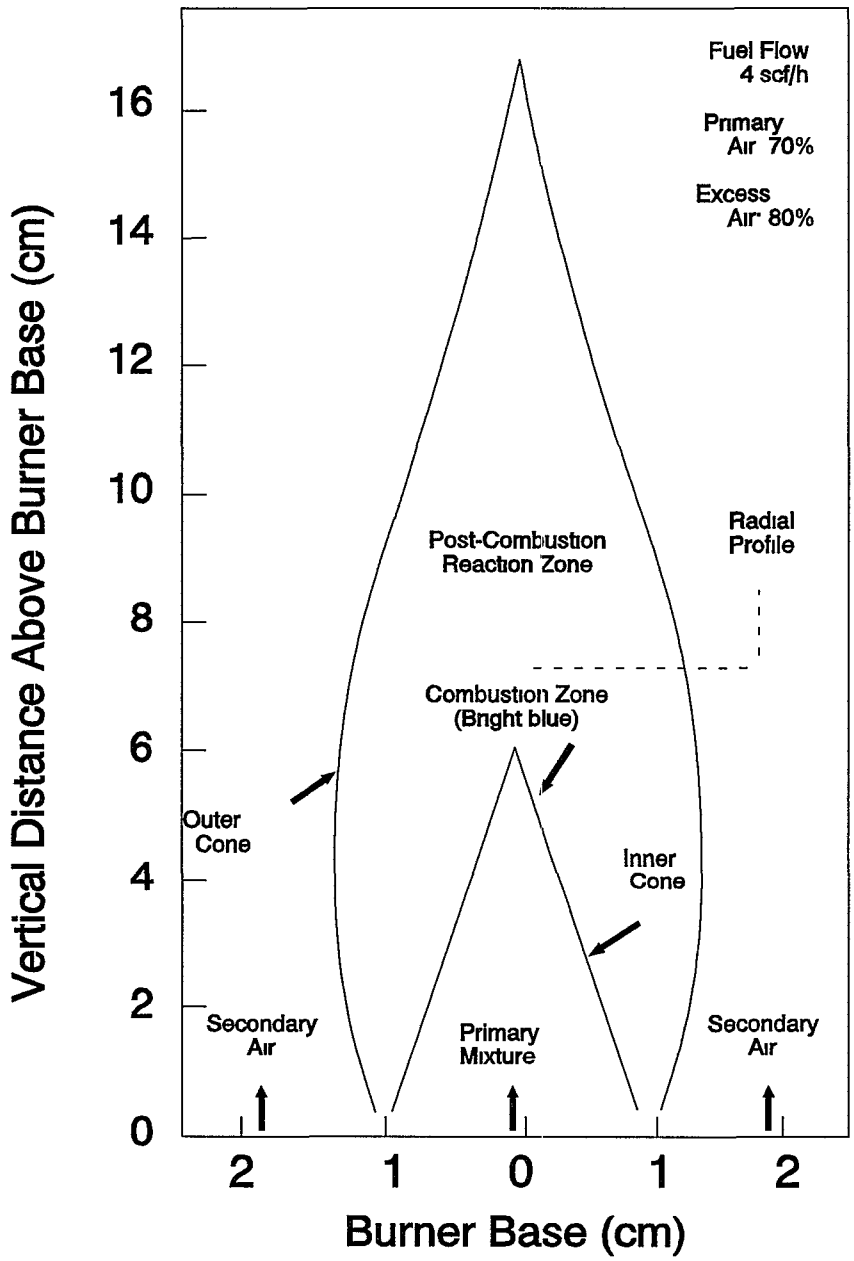


Figure 4-4. Laminar blue-flame. Reproduced from Zawacki et al. (1986). Permission to be obtained.

simplified in that most appliances include burners with several flame ports, the combustion product distributions are affected by interference from adjacent flames Nevertheless, the single flame model has been used successfully to approximate the behavior of more complex systems.

The primary mixture consists of gas and 40 to 70% of the air required for complete combustion. Excess air needed for complete combustion is provided through an annular region surrounding the central port The combustion takes place in a thin layer surrounding the inner cone, termed the combustion zone A number of intermediate products are formed in this zone, including molecular hydrogen, CO, and radical species such as hydroxyl, atomic oxygen, and atomic nitrogen Significant amounts of the major products, carbon dioxide (CO_2) and water, are also formed here

As the combustion products flow outward, other reactions occur in a luminous secondary reaction zone, termed the postcombustion reaction zone The maximum temperatures in the flame occur at the boundary of the outer cone defined by these reactions Beyond this boundary, the combustion products mix with secondary air, resulting in a rapid temperature decrease

Many investigators have considered NO and NO_2 production in this type of combustion process, as reviewed by Zawacki et al (1986) The NO concentration peaks at the outer cone boundary, where production is assisted by high temperatures The low molecular oxygen content there prevents production of NO_2 The latter species is produced at a slightly greater radial distance from the flame center, where oxygen provided by secondary air reacts with the high NO concentration Overall, the production of NO is highest in regions of maximum temperature Thus, NO production may be particularly high at "hot spots" in the flame (Hayhurst and Vince, 1980)

It is of interest to consider the chemical reactions involved in the formation of NO and NO_2 in this system At high temperatures (>1,600 K), NO is produced primarily by the reactions first proposed by Zeldovich (1946)

$$O + N_2 \rightarrow NO + N$$
$$N + O_2 \rightarrow NO + O$$

Coutant et al (1982) observed that NO also appears to form around the base of the flame where the temperatures are too low for the Zeldovich mechanism to occur (about 1,350 K) They hypothesize reactions of the form

$$CN, NH + O_2 \rightarrow NO + \text{products},$$

which may be important at high as well as low temperatures in the flame These authors use the work of Fenimore (1971) to further hypothesize a number of specific reactions to produce CN and NH

$$CH_4 + O \rightarrow CH_3 + OH$$
$$CH_3 + OH \rightarrow CH_2 + H_2O$$
$$CH_3 + N_2 \rightarrow HCN + NH_2$$
$$CH_2 + N_2 \rightarrow HCN + NH$$

After NO is produced from the reaction of CN and NH with O_2 as shown above, oxidation to NO_2 occurs via the reaction.

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

With sufficient oxygen present, the HO_2 would come from the reaction of oxygen with methane

$$CH_4 + O_2 \rightarrow HO_2 + CH_3,$$

or from reactions with formaldehyde or CHO as proposed by Peeters and Mahnen (1973)

$$CH_2O, CHO + O_2 \rightarrow HO_2 + CHO, CO$$

Knowledge of these reactions has been used to design burners that may have smaller NO_x emissions For example, reducing the flame temperature decreases the production of

NO, use of infrared tiles to lower the temperature has been shown to be an effective strategy in decreasing NO emissions (Zawacki et al , 1986) The emissions of CO, however, tend to increase under these conditions because of reduced oxidation of CO to CO_2 Fuel type may affect temperature and hence NO_x emissions propane combustion is much hotter than that of natural gas, resulting in greater NO emissions Other factors such as the level of primary aeration, use of recirculation of combustion products, and control of air currents near the burner have been shown to affect NO_x emissions, the reader is referred to Zawacki et al (1986) for more detail

It is important to note that our understanding of NO_x emissions even from simple combustion systems is far from complete Reuther et al (1988) summarize data from 12 investigations of premixed stoichiometric air/methane combustion, and conclude that wide variations in reported emissions are probably due to differences in measurement protocol Reuther et al recommend that standardized measurement techniques be established for further investigation of NO_x emissions

Besides studies of simple well-controlled combustion, a number of investigators have measured NO_x emissions from common household appliances in the laboratory and in the field. Data resulting from these measurements are briefly reviewed below.

4.3.3 Gas Stoves Used for Cooking

Several research programs have investigated NO_x emissions from stoves fueled with natural gas and propane Most of these studies have included a number of other pollutants as well, such as CO, aldehydes, and unburned HCs This summary only addresses the NO_x emission data. Furthermore, only studies using fuels of composition commonly found in the United States are included For additional information on emissions from other types of gas, the reader is referred to Yamanaka et al (1979) and Caceres et al (1983)

One of the earliest studies of gas stove emissions was conducted by Himmel and DeWerth (1974) at the American Gas Association Laboratories A total of 18 commercially available residential stoves were examined The authors estimated that the population of stoves tested was representative of at least 90% of the total population of gas stoves in use within the United States at that time

The emissions were sampled using a 28-cm diameter, 25-cm high quartz hood The combustion exhaust gases were drawn through the top of the hood, passed through a cold trap to reduce moisture content, and directed into pollutant analyzers These investigators used the standard American National Standard Institute (ANSI) pot filled with water as a load The ANSI pot is chrome-plated brass, having dimensions 19 cm in diameter by 15 cm in height The quartz hood was positioned over the burner and pot such that the CO_2 concentration in the emissions was approximately 2% This value was selected to provide a reasonably concentrated sample that did not have an excessive correction factor when calculating the air-free pollutant concentration

$$\text{Air-Free Pollutant Concentration} = \frac{\text{Ultimate } CO_2}{\text{Sample } CO_2} \times \text{Sample Pollutant Concentration}, \quad (4\text{-}1)$$

where the air-free and sample pollutant concentrations are given on a dry-weight basis Ultimate CO_2 refers to the concentration expected based on stoichiometric considerations The combustion process was allowed to reach steady-state before recording data

This procedure was applied to each of four top burners on 16 stoves, and to three top burners on each of 2 additional stoves Oven and broiler burners were also sampled, as were the pilot lights for all types of burners Tests were conducted using well-adjusted blue flames, and also poorly adjusted yellow flames In limited additional testing, emissions from the burners were sampled with water-filled cooking pots made of different materials quartz, pyrex, aluminum, copper, steel, iron, and Pyroceram

An overall summary of the data for burner operation is presented in Table 4-11 The top burners were operated at maximum heat input rate, which was close to the rated 158 kJ/min (9,000 BTU/h) for some of the stoves and 211 kJ/min (12,000 BTU/h) for others The oven and broiler burners were operated at heat input rates ranging from 193 kJ/min (11,000 BTU/h) to 422 kJ/min (24,000 BTU/h) The data show that emissions of NO are generally in the range of 16 to 24 μg/kJ (0 037 to 0 056 lb/10^6 BTU), whereas emissions of NO_2 are in the range of 5 to 14 μg/kJ (0 012 to 0 033 lb/10^6 BTU) Exceptions include an infrared burner with a very low NO emission factor and a pyrolytic self-cleaning oven with a relatively high NO emission factor Table 4-11 also shows emission factors as a function of heat input rate for a top burner on one of the stoves

TABLE 4-11. EMISSION FACTORS FOR NITRIC OXIDE AND NITROGEN DIOXIDE FROM BURNERS ON GAS STOVES, AFTER HIMMEL AND DEWERTH (1974)

	Number of Burners	Flame Type	Emission Factor for Nitric Oxide (μg/kJ)	Emission Factor for Nitrogen Dioxide (μg/kJ)
Top Burners	70	Blue	20 4 ± 4 4	8 4 ± 2 22
Top Burners	70	Yellow	16 0 ± 5 0	13 5 ± 5 4
Ovens and Broilers	27	Blue	22 2 ± 5 5	5 5 ± 1 91
Ovens and Broilers	27	Yellow	16 6 ± 7 8	11 5 ± 8 1
Top Burners with Thermostat	6	Blue	20 7 ± 3 0	10 5 ± 3 2
Top Burners, 142 kJ/min	35	Blue	20 5 ± 4 0	7 5 ± 1 30
Top Burners, 190 kJ/min	35	Blue	20 6 ± 4 4	8 6 ± 2 35
Infrared Burners	2	Blue	3 5	5 2
Ovens and Broilers with Catalytic Clean	8	Blue	24 0 ± 7 1	5 1 ± 2 74
Ovens and Broilers with Catalytic Clean	8	Yellow	18 5 ± 10 8	7 44 ± 2 48
Pyrolytic Self Clean Oven	1	750 °F[a]	38 1	14 4
Top Burner of One Stove, 150 kJ/min	1	Yellow	22 5	10 2
Top Burner of One Stove, 79 kJ/min	1	Yellow	9 42	14 0
Top Burner of One Stove, 39 kJ/min	1	Yellow	1 45	15 3

[a]Temperature setting as given in the original reference

As the heat input rate increases, the data show that the emission factor for NO increases, but the emission factor for NO_2 decreases

Emission factors for pilot lights associated with the top burners and with the ovens and broilers are shown in Table 4-12 Three types of top burner pilot lights and two types of oven and broiler pilot lights were tested The data show that emission factors for NO and NO_2 average roughly 12 9 and 7 3 μg/kJ (0 030 and 0 016 lb/10^6 BTU), respectively, for

TABLE 4-12. EMISSION FACTORS FOR NITRIC OXIDE AND NITROGEN DIOXIDE FROM PILOT LIGHTS ON GAS STOVES, AFTER HIMMEL AND DEWERTH (1974)

	Pilot Type[a]	Emission Factor for Nitric Oxide (μg/kJ)	Emission Factor for Nitrogen Dioxide (μg/kJ)
Top Burners	I	13.7	7 83
Top Burners	II	13 2	6 83
Top Burners	III	11 9	7 35
Ovens/Broilers	I	0 265	14 4
Ovens/Broilers	II	1 01	10 7

[a]Types of pilot lights on top burners

I A free standing single flame that is surrounded by a flashtube assembly

II Same as above with a shield or baffle around the flame The baffle typically comes up to about one-half of the flame height, protects the flame from drafts and tends to channel the combustion air supply Combustion air supply openings may be in the baffle, or inside or outside the baffle on the range top

III Same as II with the addition of a shield above the flame This shield can be a flat baffle or an arch-type baffle The baffle appears to be for the purpose of keeping the range top cool Type III seems to be the most popular of the three pilot types

Types of pilot lights on ovens and broilers

I A constant input pilot which typically is a horizontally oriented flame positioned directly below a flame sensing element

II Similar to I, but operated in two fuel input modes (1) a standby pilot mode and (2) ignition mode, where a secondary fuel supply ignites the burner The standby pilot mode is not directed onto a flame sensing element, whereas the ignition flame is Generally this type of pilot is primary aerated

the top burner pilots For the oven and broiler pilots, the NO emission factor is very small, the original data show high variability, with individual measurements ranging from near zero to 2 2 μg/kJ (0 005 lb/10^6 BTU) The NO_2 emission factor is not as variable

Himmel and DeWerth (1974) also conducted statistical tests with the emission factor data to determine the influence of various parameters on the total NO_x emissions. Results showed that the heat input rate and the number of burners in operation each had a significant effect on emissions at the 99% confidence level Cooking utensil material had a significant effect at the 95%, but not at the 99%, level The supporting grate material, grate height,

and whether or not the oven was in operation had no significant effect on the top burner NO_x emissions There was no significant difference in NO_2 emitted from stove to stove, although differences in total NO_x were observed The front burners had 13% higher emission factors for NO_2 than the rear, attributed to differences in entertainment of secondary air to feed the flame. The authors also discussed experimental burners that may be effective in reducing NO_x emissions from top burners They concluded that controlling the ingress of secondary air to the flame could reduce NO_x emissions by about 50% Reducing flame temperature with a screen or other heat absorber in the flame could reduce NO_x emissions by as much as 68%, whereas operating a burner at 100% plus primary aeration could reduce NO_x emissions by as much as 66%.

Cole et al. (1983) and Moschandreas et al (1985) conducted a variety of emissions tests with top burners, ovens, broilers, and pilot lights The tests for the top burners were conducted using two methods The first method was similar to that of Himmel and DeWerth (1974) involving a quartz hood placed directly over the burner The second method involved placing a stove in a 33-m^3 (1,150-ft^3) all-aluminum chamber with controlled air exchange (1 to 5 air changes per hour) and temperature characteristics, emissions were determined by measuring the ambient concentrations in the chamber and using a one-compartment mass balance model to calculate the source strength, as in the experiments of Cote et al (1974)

Four top burners on each of three ranges were tested using the quartz hood Both lean gas with a heating content of 36,600 kJ/m^3 (983 BTU/ft^3) and rich gas with a heating content of 38,100 kJ/m^3 (1,022 BTU/ft^3) were used Some of the tests were conducted with a properly adjusted blue flame, and others used a poorly adjusted yellow flame The tests were conducted at maximum heat inputs, which were in the range of 140 to 175 kJ/min (8,000 to 10,000 BTU/h).

The results of these tests are shown in Table 4-13 The data show average values for both lean and rich gas Note that both the NO and the NO_2 emission factors agree well with those of the Himmel and Dewerth study obtained using similar sampling procedures All of these values refer to steady-state conditions A limited amount of data were also reported showing variations in emission factor with time before reaching steady-state, results showed that emissions of NO increase during the approach to steady-state, whereas NO_2 emissions decrease until a steady condition is achieved

TABLE 4-13. EMISSION FACTORS FOR NITRIC OXIDE, NITROGEN DIOXIDE, AND NITROGEN OXIDES FOR TOP BURNERS ON GAS STOVES MEASURED WITH A SAMPLING HOOD AND WITH A CHAMBER, AFTER COLE ET AL. (1983) AND MOSCHANDREAS ET AL. (1985)[a]

	Flame Type	Emission Factor for Nitric Oxide (μg/kJ)	Emission Factor for Nitrogen Dioxide (μg/kJ)	Emission Factor for Nitrogen Oxides (μg/kJ)
Sampling Hood	Blue	18 ± 1 1	9 9 ± 1 1	36 ± 2 0
Sampling Hood	Yellow	16 ± 0 7	14 ± 1 1	39 ± 1 0
Chamber, Mass Balance	Blue	16 ± 1 1	10 ± 2 0	35 ± 2 6
Chamber, Mass Balance	Yellow	11 ± 1 8	16 ± 3 5	33 ± 3 0
Top Burner of One Stove, 145 kJ/min	Blue	15 ± 0 4	7 3 ± 0 4	29 ± 0 9
Top Burner of One Stove, 121 kJ/min	Blue	13 ± 0 4	8 6 ± 0 4	29 ± 0 4
Top Burner of One Stove, 24 kJ/min	Blue	20 ± 0 9	8 6 ± 0 4	23 ± 1 3
Top Burner of One Stove, 13 kJ/min	Blue	0 86 ± 0.4	14 ± 2 6	16 ± 2 6

[a]The first four rows refer to tests conducted at maximum heat input rate, values of average and standard deviation in these tests are computed based on three values, each representing the average of 9 to 24 measurements on a single stove Values given for the chamber mass balance tests are for sampling 12 to 29 min after turning on the stove

The chamber tests involved operating one burner on each of the same three stoves, using blue and yellow flames Results are also shown in Table 4-13 The data from these tests agree reasonably well with the results of direct sampling using the quartz hood, suggesting the viability of either method

Moschandreas et al (1985) also examined the influence of heat input rate on emissions Measurements were made with one stove operated in the chamber at four heat input rates The results, shown in Table 4-13, are in qualitative agreement with Himmel and Dewerth increasing the heat input rate increases NO, but decreases NO_2 emission factors Additional

tests conducted by Moschandreas et al (1985) showed that NO and NO_2 emissions decreased with increasing relative humidity in their chamber

As with the burner emissions, NO and NO_2 emissions from ovens were measured using two different techniques The first method involved use of a sampling probe positioned at the oven flue outlet on the back of the range The second method involved placing the stove in the chamber, as before Average heat input rates ranged from 90 to 340 kJ/min (5,100 to 19,500 BTU/h). Table 4-14 shows the results of the oven emissions tests using the first method. The original data show that results for the second method of testing agree well with those in Table 4-14 and therefore are not shown

TABLE 4-14. EMISSION FACTORS FOR NITRIC OXIDE, NITROGEN DIOXIDE, AND NITROGEN OXIDES FOR OVENS, AFTER COLE ET AL. (1983) AND MOSCHANDREAS ET AL. (1985)[a]

	Type of Gas	Emission Factor for Nitric Oxide (μg/kJ)	Emission Factor for Nitrogen Dioxide (μg/kJ)	Emission Factor for Nitrogen Oxides (μg/kJ)
Range 1, Bake	Rich	14 ± 3 2	11 ± 1 5	41 ± 5 4
Range 1, Broil	Lean	29 ± 0 3	7 1 ± 0 8	53 ± 0 9
Range 2, Broil	Lean	22 ± 0 1	9 7 ± 0 3	44 ± 0 3
Range 2, Broil	Rich	22 ± 0 3	9 9 ± 0 1	41 ± 0 5
Range 3, Bake	Lean	14 ± 0 1	13 ± 0 7	35 ± 1 5
Range 3, Broil	Lean	23 ± 0 3	12 ± 0 1	47 ± 0 5
Range 3, Broil	Rich	23 ± 0 2	11 ± 0 4	46 ± 0 6
Range 3, Self-clean	Rich	27 ± 1 0	12 ± 0 2	54 ± 1 8

[a]Bake test. Thermostat at 500 °F, burner cycles normally
Broil test· Thermostat at broil, burner on continuously
Self-clean test Thermostat at clean, programmed burner sequential operation

Finally, Moschandreas et al (1985) determined emissions from three pilot lights in one of the ranges using the chamber method Results are shown in Table 4-15 The two top pilots had a combined heat input rate of 4 4 kJ/min (250 BTU/h), compared with the single bottom pilot heat input rate of 15 kJ/min (850 BTU/h) Despite the lower heat input rate of the top pilots, both NO and NO_2 emissions were substantially greater from the top pilots Overall, the emissions in Table 4-15 are similar to those of the pilot lights tested by Himmel and DeWerth (1974).

TABLE 4-15. EMISSION FACTORS FOR NITRIC OXIDE AND NITROGEN DIOXIDE FROM PILOT LIGHTS ON GAS STOVES, AFTER MOSCHANDREAS ET AL. (1985)

	Air Exchange Rate[a]	Emission Factor for Nitric Oxide (μg/kJ)	Emission Factor for Nitrogen Dioxide (μg/kJ)
All three pilots	1 0	7 3 ± 0 9	8 6 ± 1 3
All three pilots	2 5	7 3 ± 1 3	9 0 ± 0 9
All three pilots	5 0	9 0 ± 2 6	12 ± 1 7
Two top pilots	1 0	17 ± 1 7	11 ± 3 0
Bottom pilot	1 0	3 9 ± 1 3	8 2 ± 1 3

[a]Air exchange rates refer to chamber operating conditions

Tests conducted by Fortmann et al (1984) involved two top burners on each of two stoves, operated with a blue flame at maximum heat input rate A sheet metal sampling hood covering all four burners was used, following the procedures of Yamanaka et al (1979) A water-filled stainless steel pot (22-cm diameter by 17-cm high) was used as a load. These tests gave average steady-state emission factors of 17 μg/kJ (0 040 lb/10^6 BTU) for NO and 12 μg/kJ (0 028 lb/10^6 BTU) for NO_2 Later tests by the same research group involved one of these stoves sampled with a Teflon-coated hood (Borrazzo et al , 1987) Experiments were performed during initial start-up and at steady-state Results for steady-state operation showed average emission factors of 17 μg/kJ (0 039 lb/10^6 BTU) for NO and 12 μg/kJ 0 028 lb/10^6 BTU) for NO_2 For initial start-up, emissions of NO increased and those of NO_2 decreased until steady-state was achieved, in qualitative agreement with the data of Cole et al (1983) Both Fortmann et al (1984) and Borrazzo et al (1987) also sampled at several heat input rates Results showed that although there is considerable variability, NO emissions generally increase and NO_2 emissions decrease with increasing heat input rate Cole and Zawacki (1985) prepared a literature survey of emissions from gas-fired appliances, including gas stoves Within the summary, they report emissions of NO_x from two Gas Research Institute studies of advanced design burners The American Gas Association design involves stainless steel inserts applied to conventional burners The Shukla and Hurley (1983) design incorporates a new infrared jet burner Preliminary results are presented in Table 4-16 Reductions are seen in the improved burners

TABLE 4-16. EMISSION FACTORS FOR NITRIC OXIDE AND NITROGEN DIOXIDE FROM RANGE-TOP BURNERS OF IMPROVED DESIGN, AFTER COLE AND ZAWACKI (1985)

	Heat Input Rate (kJ/min)	Emission Factor for Nitric Oxide (μg/mkJ)	Emission Factor for Nitrogen Dioxide (μg/mkJ)
American Gas Association Standard Burner	158	20 2	14 6
American Gas Association 2-Ring Insert	158	9 04	12 5
American Gas Association 3-Ring Insert	158	8 61	10 8
Shukla and Hurley Infrared	118	2 6	1 3
Shukla and Hurley Infrared	72 1	2 2	1 3
Shukla and Hurley Infrared	45 7	1.7	0 86

Measurements of emissions from ten gas stoves currently in use in residences were obtained by Tikalsky et al (1987) The emissions were measured using the hood method of Himmel and DeWerth (1974) Data from each stove were obtained independently by two research groups in order to obtain comparative data The results are shown in Table 4-17

Overall, the emission factors are similar to those reported in the literature from other studies. Although the overall mean values reported by the two groups are in agreement, results of the individual tests for each burner showed significant differences between the two groups. The original data also showed greater variability in the results of these field tests compared with results of laboratory tests reported in the literature The emissions did not appear to vary with gas flow rate for the conditions of this study.

Summary of Emissions from Gas Stoves

Table 4-18 lists average emission factors for range-top burners and for oven and broiler burners operated at maximum heat input rate Data are shown for both well-adjusted blue flames and for poorly adjusted yellow flames Each of the averages is based on the total number of stoves tested for that category using data from the above studies For top burners with blue flames, a total of 27 values are represented, for yellow flames, there are a total of

TABLE 4-17. EMISSION FACTORS FOR NITROGEN DIOXIDE FROM 10 GAS STOVES IN USE IN RESIDENCES, MEASURED INDEPENDENTLY BY RESEARCH GROUPS (TIKALSKY ET AL., 1987)
(Values shown are arithmetic averages and standard deviations.)

	Gas Flow Rate	Emission Factors Measured by Group 1 (μg/kJ)	Emission Factors Measured by Group 2 (μg/kJ)
Right Front Burner	High	15 ± 3	14 ± 6
Right Front Burner	Medium	15 ± 5	15 ± 8
Right Front Burner	Low	14 ± 3	26 ± 35[a]
Left Rear Burner	High	16 ± 3	15 ± 6
Left Rear Burner	Medium	16 ± 3	15 ± 6
Left Rear Burner	Low	18 ± 4	17 ± 6
Oven, Bake		13 ± 9	12 ± 6
Oven, Broil		19 ± 14	16 ± 7

[a]Average influenced significantly by one extreme value

TABLE 4-18. AVERAGE EMISSION FACTORS FOR NITRIC OXIDE, NITROGEN DIOXIDE, AND NITROGEN OXIDES FROM BURNERS ON GAS STOVES BASED ON DATA REPORTED IN THE LITERATURE

	Flame Type	Factor for Nitric Oxide (μg/kJ)	Factor for Nitrogen Dioxide (μg/kJ)	Factor for Nitrogen Oxides (μg/kJ)
Top Burners	Blue	20 0 ± 4 5	10 2 ± 3 1	41 0 ± 8 2
Top Burners	Yellow	16 9 ± 4 5	15 0 ± 4 8	42 0 ± 9 1
Ovens and Broilers	Blue	21 9 ± 6 3	7 23 ± 3 01	40 9 ± 8 6
Ovens and Broilers	Yellow	19 8 ± 9 6	11 4 ± 5 7	39 0 ± 10 8

23 values (24 for NO_x) Averages for the oven and broiler burners represent 20 blue-flame and 16 yellow-flame values Where data are reported for both oven and broiler burners for a single stove, the values have been averaged to produce one emission factor for the oven and broiler category for that stove Values are generally very similar for emissions from these

two types of burners on the same stove Overall, the results show that well-adjusted blue flames emit more NO but less NO_2 than poorly adjusted yellow flames Emission factors from range-top burners are comparable to those from oven and broiler burners Note that the emission factors from Tikalsky et al (1987) have not been included in these averages because flame type (blue or yellow) was not specified

A recent literature survey, which includes most of the studies cited in this section, has examined data from range-top burners for the purpose of identifying factors that significantly influence emissions of NO, NO_2, and total NO_x (Davidson et al , 1987) The data were used with several statistical tests First, analysis of variance was used to investigate the importance of three binary factors in explaining the observed variations in emissions The factors considered were (1) type of combustion (poorly adjusted or well adjusted), (2) burner position (front or rear), and (3) method of sampling (direct with a hood or indirect with a chamber). The results showed that roughly one-third of the variance in the base 10 logarithm of the emission factor (log EF) for NO_2 can be explained by noting whether the combustion is poorly adjusted or well adjusted For NO and total NO_x, the fraction of total variance in log EF explained by this factor depends on the subset of the data chosen Values of the fraction range from 0 088 to 0 56, depending on whether the subset of data involved front or rear burners, and whether the measurements were conducted with a hood or in a chamber. Burner position and method of sampling were both relatively unimportant in explaining the observed variance for NO, NO_2, or NO_x

The emission factor data were then used to estimate coefficients in various multivariate regression models. The first regression model incorporated several factors type of combustion, burner position, method of sampling, the three two-way interactions among these factors, and (M-1) binary factors corresponding to the M stoves for which data were available Subsequent multivariate regression models were constructed by sequentially eliminating a factor or factors from the previous model Results of these tests showed that stove differences were significant at the 95% level in explaining the variance in NO_2 and NO_x emission factor Type of combustion was significant for NO and NO_2 Burner position had a smaller but still statistically significant effect in explaining variance in NO_2 emissions Similarly, the method of sampling had a small but statistically significant effect for NO_x emissions.

The influence of gas flow rate (heat input rate) on emission factors was investigated separately Statistical tests were not run for this factor due to lack of data and due to the presence of detailed data for only one study Results of plotting all of the data for NO and NO_2 are shown in Figures 4-5 and 4-6, respectively. The graphs illustrate wide variations in emission factors, apparently due to varying stove characteristics, testing conditions, and other nonuniformities among the data sets However, there are general trends toward increasing emissions for NO and decreasing emissions for NO_2 as flow rate increases Note that the detailed data of Borrazzo et al (1987) in these figures suggest that the emission/gas flow rate relationships are complex, despite the general trends

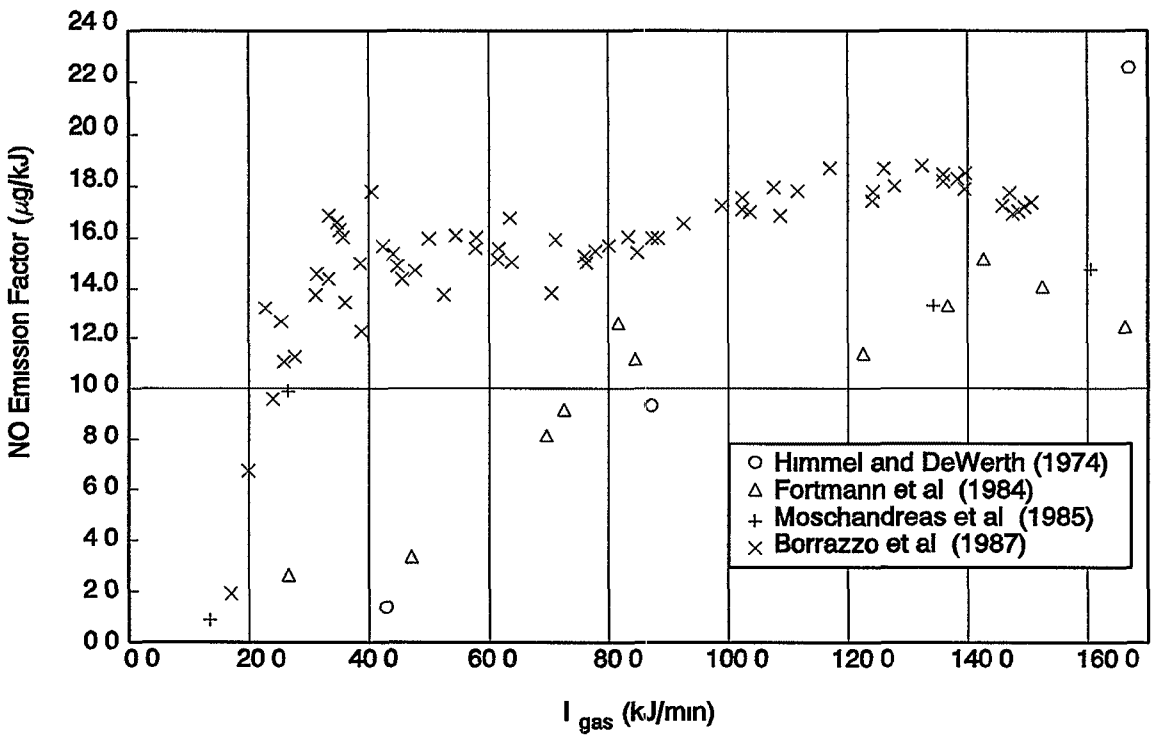


Figure 4-5. Emission factors for nitric oxide as a function of gas flow rate.

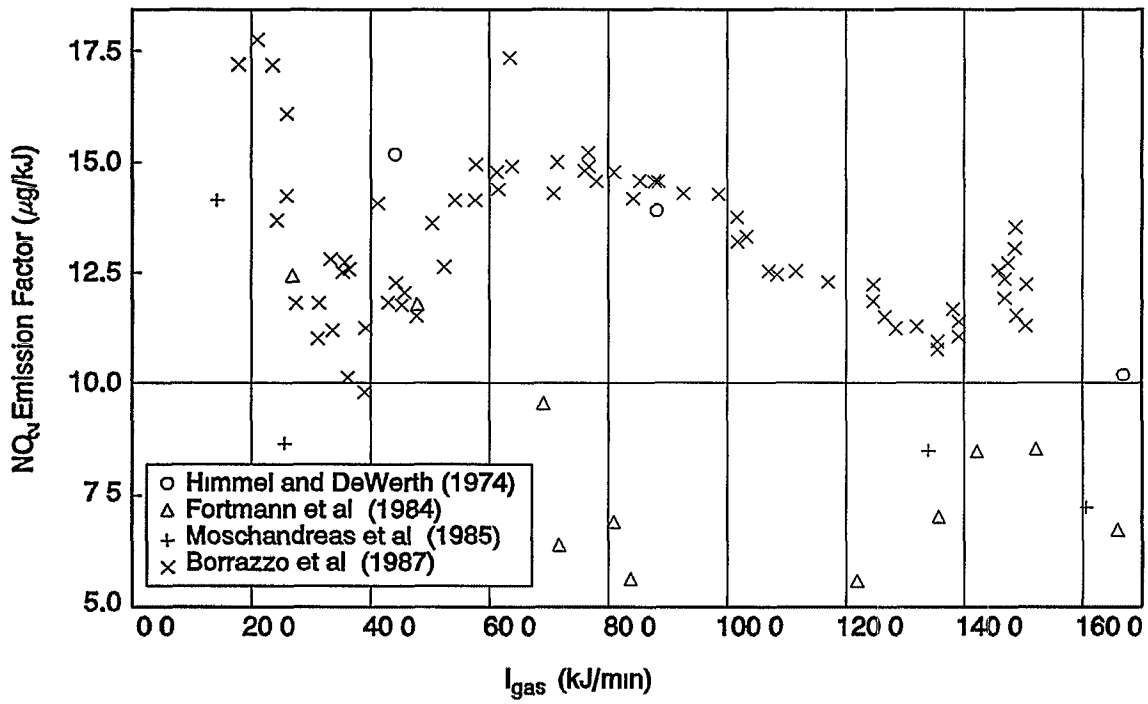


Figure 4-6. Emission factors for nitrogen dioxide as a function of gas flow rate.

4.3.4 Unvented Space Heaters Fueled with Natural Gas and Propane

A number of studies have considered emissions of NO_x from unvented space heaters As with the stove emissions studies, several different types of heaters and a variety of measurement techniques were used This section summarizes these studies Much of the information has been taken from the literature review of Cole and Zawacki (1985) It is important to note that the emission factors for heaters must be interpreted differently from those for stoves, due to differences in use profiles

Thrasher and DeWerth (1979) studied emissions from five heaters by measuring NO and NO_2 concentrations in the flue products during well-adjusted blue-flame operation All of the heaters had cast iron Bunsen burners with drilled ports Three of the heaters had suspended radiant tiles above the flame, whereas two did not The heat input rates varied from 86.1 to 661 kJ/min (4,900 to 37,600 BTU/h) Results of these tests are given in

Table 4-19 The data show that the emission factors are not monotonically related to heat input rate, the influence of the radiant tiles is unclear based on these tests These investigators also examined emissions during poorly adjusted yellow-flame operation No definite conclusions could be reached when results of these tests were compared with blue-flame emissions

Traynor et al (1983a) examined eight heaters using a 27-m^3 (953-ft^3) environmental chamber operated at 0 5 air changes per hour Emissions were computed based on airborne concentrations in the chamber using the mass balance method Heaters with cast iron Bunsen burners of both drilled- and slotted-port designs were used Heat input rates varied from 188 to 830 kJ/min Emission factors for NO, NO_2, and NO_x are shown in Table 4-19

In addition to these chamber tests, Traynor et al (1983a) operated four of the heaters in an experimental research house with a volume of 240 m^3 The tests in the house showed greater total NO_x emissions than were measured in the chamber with the same heaters However, the ratios of NO_2 emissions to NO_x emissions measured in the house with each heater were much smaller than the corresponding ratios measured in the chamber These differences were attributed to the much longer time periods of heater operation in the house as compared with the chamber tests

Previous work by Traynor et al (1984a) involved heaters without oxygen depletion sensors (ODSs) which were all fueled by natural gas This subsequent set of tests involved ODS-equipped heaters that were fueled by both natural gas and propane Infrared as well as convective heaters were used The measurements were conducted in the same manner as employed previously All tests were run under well-tuned conditions at full heat input Results are shown in Table 4-19 Nitrogen dioxide emissions from the infrared heaters average about one-third of those from convective heaters, whereas NO_x emissions from the infrared heaters are an order of magnitude smaller Nitric oxide emissions from the infrared heaters are very small, below the limits of the measurement methods in some cases No significant differences are observed between propane and natural gas heaters

In other tests, Traynor et al (1984a) considered emissions during short-term use before the heaters were able to warm up completely Compared with the longer-term emissions in Table 4-19, the tests showed slightly lower NO_2 and NO_x emissions for the infrared heaters

TABLE 4-19. EMISSION FACTORS FOR NITROGEN OXIDE (μg/kJ) AND NITROGEN DIOXIDE (μg/kJ) FOR UNVENTED SPACE HEATERS

Study	Distinguishing Features	Heat Input Rate (kJ/min)	Emission Factor for Nitrogen Oxide (μg/kJ)	Emission Factor for Nitrogen Dioxide (μg/kJ)	Emission Factor for Nitrogen Oxides (μg/kJ)
Thrasher and DeWerth (1979)[a]	With radiant tiles	661	47	5 2	77
	No radiant tiles	86 1	35	7 3	60
	No radiant tiles	176	24	2 2	39
	With radiant tiles	311	27	6 0	47
	With radiant tiles	156	34	6 0	56
Traynor et al (1983a)[b]	Drilled port	188	9 5	20	34
	Drilled port	656	22	12	43
	Drilled port	830	16	20	47
	Slotted port	424	16	11	36
	Slotted port	592	19	9 5	39
Traynor et al (1984a)[c]	Infrared, P	245	0 1	5 9	5 9
	Infrared, N	263	0 1	5 2	5 2
	Infrared, N	317	0 1	6 2	6 2
	Convective, P, drilled port	335	28 7	12 4	56 5
	Convective, N, ribbon port	486	17 8	12 9	40 1
	Convective, P, slotted port	626	28 2	10	53 2
Billick et al (1984), Moschandreas et al (1985), and Zawacki et al (1984)[d]	Bunsen, no radiant tiles	186	18	9 9	35
	Bunsen, no radiant tiles	186	15	15	37
	Bunsen, with radiant tiles	255	22	9 0	42
	Catalytic, no radiant tiles	207	0 09	0 1	0 3
	Catalytic, no radiant tiles	207	0	1 3	1 3
	Radiant (ceramic), no radiant tiles	260	0 39	3 8	4 3
	Radiant (ceramic), no radiant tiles	260	0	4 7	4 7

[a]For convective heaters with drilled ports using natural gas
[b]For convective heaters with radiant tiles using natural gas
[c]For convective heaters with radiant tiles and for infrared heaters fueled with natural gas (N) and propane (P)
[d]For heaters with bunsen, catalytic, and ceramic tile burners using natural gas

Similarly, the short-term emissions of NO_x for the convective heaters were slightly lower than the longer term emissions

Billick et al (1984), Moschandreas et al (1985), and Zawacki et al (1984) examined four heaters of different burner designs Two of the heaters had ribbon-port Bunsen burners, one had a catalytic burner, and one had a ceramic-tile burner The Bunsen burners were used in the well-adjusted blue-flame mode The units were operated at their respective maximum heat input rates, which varied from 186 to 260 kJ/min (10,600 to 14,800 BTU/h) The tests involved direct measurements of the exhaust gases for all heaters, three of the heaters were also tested in a 33-m^3 (1,150-ft^3) chamber using the mass balance method The results, shown in Table 4-19, indicate that the NO_2 emission factors measured in the chamber are much greater than those determined using the direct testing for each of the three heaters The opposite is true for the NO emission factor

These researchers also investigated ways of reducing emissions by using various inserts in the flame of one of the Bunsen burner heaters They found that ceramic rod inserts used to reduce the temperature of the flame reduced NO emissions by 44%, although NO_2 emissions were unchanged and CO emissions increased

In more recent work, Zawacki et al (1986) considered natural gas and propane heaters These included three convective and four infrared heaters fueled with natural gas, two propane convective heaters, and one propane infrared heater Tests were conducted using three measurement methods a probe, a sampling hood, and a chamber Some of the heaters were the same ones used previously by Traynor et al (1984a)

Results are shown in Table 4-20 Statistical analyses were performed on these data by the investigators, the differences were generally insignificant between emissions determined with the probe and with the hood for NO, NO_2, and NO_x However, NO emissions obtained with the chamber method were smaller than those obtained with the other two methods This was attributed to the vitiated atmosphere maintained within the chamber at the low air exchange rates used Overall, the results were in general agreement with the data of Traynor et al (1984a)

TABLE 4-20. EMISSION FACTORS FOR NITROGEN OXIDE AND NITROGEN DIOXIDE (μg/kJ) FOR CONVECTIVE AND INFRARED HEATERS OF VARIOUS DESIGNS, USING NATURAL GAS AND PROPANE (ZAWACKI ET AL., 1986)

Distinguishing Features[a]	Test Method	Rated Input Rate (kJ/min)	Emission Factor for Nitrogen Oxide (μg/kJ)	Emission Factor for Nitrogen Dioxide (μg/kJ)	Emission Factor for Nitrogen Oxides (as Nitrogen Dioxide) (μg/kJ)
CBR, no RT, N	Probe	176	17 7	9 8	35 3
	Hood		16	10 9	35 4
	Chamber		9 7	8 4	23 3
CBR, with RT, N	Probe	264	21 7	8 4	41 9
	Hood		20 7	9 1	40 8
	Chamber		11	10 4	27 2
Infrared, N	Probe	264	0 6	1 8	2 7
	Hood		0 005	2 8	2 8
	Chamber		0 005	3 5	3 5
Infrared, N	Probe	304	1 7	2 6	5 1
	Hood		0 5	4 1	4 8
	Chamber		0 3	5 3	5 7
Convective, slotted port, with RT, P	Probe	703	39 8	7 6	68 6
	Hood		39 3	7 6	67 9
	Chamber		28 3	8	51 2
Convective, drilled port, with RT, P	Probe	352	44 4	8 4	76 4
	Hood		43 9	8 1	75 4
	Chamber		31 8	10 5	59 3
CBR, with RT, N	Probe	527	13	23 3	43 3
	Hood		14 5	20	43 1
	Chamber		5 3	19	27 1
Infrared P	Probe	316	0 9	1 6	3
	Hood		0 5	3	3 9
	Chamber		0 4	3 3	4

[a]CBR = Convective ribbon burners
RT = Radiant tiles
N = Natural gas
P = Propane.

Summary of Emissions from Unvented Gas Space Heaters

This section has summarized the findings of five separate investigations, with the data given in Tables 4-19 and 4-20 The tables show that, on the average, convective space heaters have emissions of NO roughly three times the emissions of NO_2 The influence of radiant tiles on emissions is not clear Heaters with catalytic burners, radiant ceramic-tile

burners, and improved-design steel burners (radiant and Bunsen) have much smaller NO and NO_2 emissions than heaters with conventional cast-iron Bunsen burners

These data also indicate that measurement of emissions with a probe, sampling hood, or chamber can all yield equivalent results under certain conditions Zawacki et al (1986) suggest the use of a sampling hood as the preferred method, because of its versatility and ease in use

4.3.5 Kerosene Heaters

In this section, the results of three studies reporting NO_x emissions for portable kerosene heaters are examined Yamanaka et al (1979) examined emissions from six radiant and five convective kerosene heaters Emissions were sampled using a hood positioned over the heater Results were presented only for total NO_x (as NO_2) The emission factors for the radiant heaters averaged 13 $\pm$ 1 8 μg/kJ, whereas the emission factors for the convective heaters averaged 70 $\pm$ 6 8 μg/kJ Overall heat input rates for the 11 heaters were in the range 110 to 200 kJ/min

Leaderer (1982) measured emissions of NO, NO_2, and other pollutants from one radiant and one convective kerosene heater The heaters were rated at 169 kJ/min (9,600 BTU/h) and 153 kJ/min (8,700 BTU/h), respectively Measurements were performed in a 34-m^3 (1,200-ft^3) chamber operated at 100 air changes per hour Emission factors were determined by mass balance The data were obtained at three different heat input rates for each heater, there were three sets of runs for each heat input rate

Results are shown in Table 4-21 Emission factors for NO from the radiant heater are very small, whereas those from the convective heater are more than an order of magnitude greater For NO_2, the emission factors are also greater from the convective heater than from the radiant heater, but only by factors of 1 5 to 3

Traynor et al (1983b) tested two radiant and two convective kerosene heaters Emission factors were determined by the mass balance method, using airborne concentrations measured in a 27-m^3 chamber operated at 0 4 air changes per hour Two types of tests were conducted In the first type, the heater was fired in the chamber and allowed to run for 1 h In the second type, the heater was fired outside the chamber and allowed to warm up for 10 min The heater was then brought into the chamber for a 1-h run

TABLE 4-21. AVERAGE EMISSION FACTORS FOR NITRIC OXIDE AND NITROGEN DIOXIDE FROM KEROSENE HEATERS, AFTER LEADERER (1982) AND TRAYNOR ET AL. (1983b)

	Type of Heater	Heat Input Rate (kJ/min)	Emission Factor for Nitric Oxide (μg/kJ)	Emission Factor for Nitrogen Dioxide (μg/kJ)	Emission Factor for Nitrogen Oxides (μg/kJ)
Leaderer	Radiant, new	144	0 45 ± 0 05	4 4 ± 0 2	5 1 ± 0 2
Leaderer	Radiant, new	113	0 08 ± 0 05	5 0 ± 0 2	5 1 ± 0 2
Leaderer	Radiant, new	84 4	0	5 9 ± 0 3	5 9 ± 0 3
Leaderer	Convective, new	158	17 ± 0 3	7 0 ± 0 4	33 ± 0 6
Leaderer	Convective, new	97 9	12 ± 0 6	15 ± 0 3	33 ± 1 0
Leaderer	Convective, new	37 3	11 ± 0 9	17 ± 1 0	34 ± 1 7
Traynor et al	Radiant, new	137	1 3 ± 0 7	4 6 ± 0 8	6 6 ± 1 3
Traynor et al.	Radiant, 1 year old	111	2 1	5 1	8 3
Traynor et al	Convective, new	131	25 ± 0 7	13 ± 0 8	51 ± 1 3
Traynor et al	Convective, 5 years old	94 8	11 ± 0 1	32 ± 2 8	49 ± 2 8

Results are shown in Table 4-21 The data are the averages of both types of tests for the two convective heaters and for the new radiant heater. The 1-year-old radiant heater was studied using only the second type of test The original data show little difference in emission factor between the two types of tests Overall, the results are similar to those of Leaderer (1982), showing smaller emission factors for radiant as compared with convective heaters.

The data reported by Traynor et al (1983b) in Table 4-21 refer to operation at the maximum wick length In additional tests, these investigators reduced the length of the wick to half of the full setting of the wick control knob (radiant heater) or until the flame was half the length as it was previously (convective heater) Results showed slightly smaller NO emissions for both heater types, for NO_2, the emissions were comparable to those of the full wick for the radiant heater, but about double those of the full wick for the convective heater

Apte and Traynor (1986) reviewed data obtained by a Lawrence Berkeley Laboratory group on emissions from two-stage kerosene heaters The two-stage burners resemble those of radiant kerosene heaters, except that there is a second chamber above the radiant element where additional combustion air is introduced In this region, the flame temperature is allowed to rise and the combustion process is more complete Emissions of NO from the two-stage heater are slightly greater than those from radiant heaters due to the higher flame temperature, although emissions of NO_2 as well as of CO and unburned HCs are lower The data presented in this section show that emission factors of NO and NO_2 for radiant kerosene heaters are generally much smaller than those for convective kerosene heaters Emissions of NO from two-stage heaters are only slightly greater than those from radiant heaters, whereas emissions of NO_2 are the lowest of the three heater types Most of the NO_x emissions from radiant heaters are in the form of NO_2, for convective heaters that are two-stage heaters, the emissions of NO and NO_2 are of comparable magnitude There are insufficient data to evaluate changes in emissions as kerosene heaters age

4.3.6 Wood Stoves

The use of wood stoves for residential space heating has become increasingly popular in recent years Because of this, a number of studies have examined pollutant emissions from wood stoves Some of these studies have measured emission factors based on concentrations in the flue gases, such information would be useful for assessing the contribution of wood stove emissions to ambient air quality Very little information is available, however, on fugitive emissions from wood stoves into the indoor living space

In a detailed literature survey, Smith (1987) reports that emissions of pollutants from wood stoves are highly variable, depending on the type of wood used, stove design, the way the stove is used, and other factors He reports emission factors for NO_x and other pollutants for wood stoves used in developing countries Many of these stoves are unvented, resulting in excessive indoor concentrations as the combustion products are exhausted into the room This information is not applicable to the United States, where virtually all wood stoves are vented to the outdoors

Traynor et al (1984b) have studied wood stoves used in a house (three airtight and one nonairtight) For each experiment, airborne concentrations of several pollutants were

measured inside and outside the house during operation of one of the stoves The results showed that all indoor and outdoor concentrations of NO and NO_2 were below 0 02 ppm Indoor airborne concentrations of some of the other pollutants were high during use of the nonairtight stove, however The airtight stoves had little influence on indoor concentrations of any pollutants In another study, Traynor et al (1982) found elevated airborne concentrations of NO and NO_2 in three occupied houses during operation of wood stoves and a wood furnace The concentrations were highly variable, however, and the authors caution that additional tests would be needed to determine the influence of wood stoves on indoor concentrations of NO_x and other pollutants

Because of the paucity of data, it is difficult to reach quantitative conclusions regarding the importance of wood stoves However, the limited information available suggests that wood stoves are not a major contributor to NO_x exposures indoors This is consistent with the small NO emission rates expected from the low temperature combustion processes characteristic of wood stoves

4.3.7 Tobacco Products

A number of studies have compared concentrations of NO_x and other pollutants in houses with smokers and houses without smokers In general, these studies have shown that concentrations are greater in the homes of smokers There are few data available, however, on NO_x emission factors of tobacco products

A few studies have reported emissions of NO_x from cigarettes while sampling both sidestream and mainstream smoke together Woods (1983) report 0 079 mg/cigarette for NO_2, and the University of Kentucky (undated) reports 1 56 mg/cigarette for NO_x (as NO) Moschandreas et al. (1985) lists emissions of 2 78 mg/cigarette for NO and 0.73 mg/cigarette for NO_2 The National Research Council (1986) reports total NO_x emissions of 100 to 600 μg/cigarette for mainstream smoke, with values 4 to 10 times greater for sidestream smoke According to this reference, virtually all of the emitted NO_x is in the form of NO, once emitted, the NO is gradually oxidized to NO_2 Thus, environments containing cigarette smoke may have higher concentrations of both NO and NO_2 than environments without such smoke

4.3.8 Comparison of Emissions from Sources Influencing Indoor Air Quality

This section has considered emissions of NO_x from gas stoves, heaters using natural gas or propane, kerosene heaters, wood stoves, and tobacco products A significant number of appliances in the first three categories have been tested, emission factors in these categories have been averaged and are shown in Table 4-22 Note that all data for a single appliance have been averaged before being used as an input to compute the grand averages shown in the table This procedure has been followed even when a single appliance has been tested by more than one group (e g , Tables 4-19 and 4-21) Some of the reported data are given as values below a specified limit of detection, these values have been taken as zero in this analysis Only data for the hood measurement technique have been used in Table 4-22 For kerosene heaters, the NO_x values include the data of Yamanaka et al (1979), whereas the NO and NO_2 values include only the data of Leaderer (1982) and Traynor et al (1983b)

TABLE 4-22. AVERAGE EMISSION FACTORS FOR NITRIC OXIDE, NITROGEN DIOXIDE, AND NITROGEN OXIDES FROM VARIOUS SOURCES BASED ON DATA REPORTED IN THE LITERATURE

	Number of Appliances	Emission Factor for Nitric Oxide (μg/kJ)	Emission Factor for Nitrogen Dioxide (μg/kJ)	Emission Factor for Nitrogen Oxides (μg/kJ)
Range-Top Burners	27	20 0 ± 4 5	10 2 ± 3 1	41 0 ± 8 2
Ovens and Broilers	20	21 9 ± 6 3	7 23 ± 3 01	40 9 ± 8 6
Unvented Gas Heaters (Cast-Iron Bunsen Burners)	15	22 9 ± 9 6	10 8 ± 5 3	45 4 ± 11 4
Kerosene Heaters (Convective)	5	15 2 ± 6 02	16 8 ± 9 3	55 1 ± 17 7[a]
Kerosene Heaters (Radiant)	5	0 79 ± 0 90	5 00 ± 0 58	9 69 ± 3 68[b]

[a]Total number of convective kerosene heaters tested for NO_x = 10
[b]Total number of radiant kerosene heaters tested for NO_x = 11

These data show that emissions of NO_x are about 65 to 75% NO and 25 to 35% NO_2 for range-top burners, for ovens and broilers fueled with natural gas, and for convective heaters fueled with natural gas and propane In contrast, convective kerosene heaters have emissions of NO and NO_2 that are roughly comparable Radiant heaters using natural gas,

propane, or kerosene all have emissions of NO that are negligible compared with those of NO_2.

For gas stoves, emission factors of NO and NO_2 from range-top burners operating at maximum heat input rate are comparable to those from the oven and broiler burners Well-adjusted blue flames emit slightly more NO and slightly less NO_2 than poorly adjusted yellow flames. The emission factor of NO increases as the heat input rate increases on top burners, and the emission factor of NO_2 decreases as the heat input rate increases When first starting a range-top burner with a cold load (e g , a water-filled pot), the emission factor of NO is initially small, but steadily increases as the load warms up The emission factor of NO_2, on the other hand, is initially high, but steadily decreases Pilot lights associated with range-top burners have emission factors comparable to or slightly smaller than emission factors for the burners Pilot lights associated with oven and broiler burners have NO emission factors much smaller than those of the burners themselves, although NO_2 emission factors are comparable

Emission factors for NO and NO_2 from convective natural gas and propane heaters with Bunsen burners are similar to emission factors from natural gas stoves Emission factors of NO from convective kerosene heaters are slightly smaller than those from gas stoves and convective gas heaters, whereas emission factors of NO_2 are slightly greater Emission factors of NO from radiant heaters using natural gas, propane, or kerosene are very small, whereas those for NO_2 are about one-third of the respective convective heater emissions There appears to be little difference in emission factor from a warmed kerosene heater compared with emissions from a cold start The length of the wick can affect emissions a smaller wick yields smaller NO emissions, but possibly greater NO_2 emissions Two-stage kerosene heaters have smaller emissions of NO_2 than do either convective or radiant kerosene heaters

Emissions of NO_x to the indoor environment from wood stoves are not expected to be significant given the low combustion temperatures involved No data are available to allow quantification of such emissions, however

Only limited data are available on NO_x emissions from tobacco Nearly all of the emitted NO_x from cigarettes is in the form of NO, although oxidation to NO_2 occurs over

time periods of several minutes following emission Sidestream smoke from a cigarette contains up to an order of magnitude more NO than mainstream smoke

The emission factors given in Table 4-22 can be used with indoor air quality models to predict indoor airborne concentrations of NO_x, provided input data for other parameters included in the model are available Examples of such parameters include air exchange characteristics of the house, outdoor airborne concentrations of NO_x, and appliance usage patterns The last parameter is especially important very little information is available on the frequency of use of stoves and other combustion sources Information on the way occupants influence air exchange, such as by opening windows and doors, is also very limited For many situations, our ability to predict indoor airborne concentrations is limited by our lack of understanding of occupant behavior, rather than by lack of data on emission factors

4.4 SUMMARY OF EMISSIONS OF NITROGEN OXIDES FROM AMBIENT AND INDOOR SOURCES

Anthropogenic sources of NO_2 emissions include transportation, stationary source fuel combustion, various industrial processes, solid waste disposal, and others, such as forest fires Natural sources of NO_x are lightning, biological and abiological processes in soil, and stratospheric intrusion Estimates for 1990 indicate that over 80% of the United States NO_x emissions are emitted by highway vehicles, electric utilities, and industrial boilers

Quantitative estimates of the total amount of NO_x emitted to the ambient global atmosphere are available These estimates suggest that 122 to 152 $\times 10^6$ metric tons of NO_x are emitted annually, with about 18 to 19 $\times 10^6$ metric tons emitted in the United States alone

The important indoor sources of NO_x are gas stoves, unvented space heaters, kerosene heaters, wood stoves, tobacco products, and infiltration of ambient air containing NO_x Total emissions and the ratio of NO/NO_2 from gas stoves and space heaters differ according to fuel flow rate and flame adjustment Additional factors, such as the load (e g , cold pot of water), heater type (convective versus radiant), and fuel type (natural gas, propane, or

kerosene) may also be important Only limited information is available for wood stoves and tobacco products.

Two factors, ambient and indoor NO_x emissions, form the primary bases that determine air concentrations and exposure in the human environment

REFERENCES

Albritton, D L , Liu, S C , Kley, D (1984) Global nitrate deposition from lightning In Aneja, V P , ed Environmental impact of natural emissions proceedings of an Air Pollution Control Association specialty conference, March, Research Triangle Park, NC Pittsburgh, PA Air Pollution Control Association

Apte, M G , Traynor, G W (1986) Comparison of pollutant emission rates from unvented kerosene and gas space heaters In Proceedings of the ASHRAE conference IAQ '86 managing indoor air for health and energy conservation, April, Atlanta, GA Atlanta, GA American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc , pp 405-416

Bartok, W , Sarofim, A F (1991) Fossil fuel combustion a source book New York, NY John Wiley & Sons, Inc

Bauer, E (1982) Natural and anthropogenic sources of oxides of nitrogen (NO_x) for the troposphere Washington, DC U S Department of Transportation, Federal Aviation Administration, report no FAA-EE-82-7 Available from NTIS, Springfield, VA, AD-A134516

Billick, I , Johnson, D , Moschandreas, D , Relwani, S (1984) An investigation of operational factors that influence emission rates from gas appliances In Berglund, B , Lindvall, T , Sundell, J , eds Indoor air proceedings of the 3rd international conference on indoor air quality and climate, v 4, chemical characterization and personal exposure, August, Stockholm, Sweden Stockholm, Sweden Swedish Council for Building Research, pp 181-187 Available from NTIS, Springfield, VA, PB85-104214

Borrazzo, J E , Osborn, J F , Fortmann, R C , Keefer, R L , Davidson, C I (1987) Modeling and monitoring of CO, NO and NO_2 in a modern townhouse Atmos Environ 21 299-311

Borucki, W J , Chameides, W L (1984) Lightning estimates of the rates of energy dissipation and nitrogen fixation Rev Geophys Space Phys 22 363-372

Caceres, T , Soto, H , Lissi, E , Cisternas, R (1983) Indoor house pollution appliance emissions and indoor ambient concentrations Atmos Environ 17 1009-1013

Cole, J T , Zawacki, T S (1985) Emissions from residential gas-fired appliances Chicago, IL Institute of Gas Technology, report no GRI-84/0164 Available from NTIS, Springfield, VA, PB85-174928

Cole, J T , Zawacki, T S , Macriss, R A , Moschandreas, D J (1983) Constituent source emission rate characterization of three- gas fired domestic ranges Presented at 76th annual meeting of the Air Pollution Control Association, June, Atlanta, GA Pittsburgh, PA Air Pollution Control Association, paper no 83-64 3

Cote, W A , Wade, W A , III, Yocom, J E (1974) A study of indoor air quality Washington, DC U S Environmental Protection Agency, Office of Research and Development, EPA report no EPA-650/4-74-042 Available from NTIS, Springfield, VA, PB-238556

Coutant, R W , Merryman, E L , Levy, A (1982) Formation of NO_2 in range-top burners Environ Int 8 185-192

Crutzen, P J , Schmailz, U (1983) Chemical budgets of the stratosphere Plant Space Sci 31 1009-1032

Davidson, C I , Borrazzo, J E , Hendrickson, C T (1987) Pollutant emission factors for gas stoves a literature survey Research Triangle Park, NC U S Environmental Protection Agency, Air and Energy Engineering Research Laboratory, EPA report no EPA-600/9-87-005 Available from NTIS, Springfield, VA, PB87-171328

Ehhalt, D H , Drummond, J W (1982) The tropospheric cycle of NO_x In Georgii, H W , Jaeschke, W , eds Chemistry of the unpolluted and polluted troposphere proceedings of the NATO Advanced Study Institute, September-October 1981, Corfu, Greece Boston, MA D Reidel Publishing Company, pp 219-251 (NATO Advanced Study Institutes series C—mathematical and physical sciences v 96)

Federal Register (1993) Air pollution control, motor vehicle emission factors—notice of model availability F R (May 20) 58 29409-29410

Fenimore, C. P (1971) Formation of nitric oxide in premixed hydrocarbon flames In Thirteenth symposium (international) on combustion, August 1970, Salt Lake City, UT Pittsburgh, PA The Combustion Institute, pp 373-380

Fortmann, R C , Borrazzo, J E , Davidson, C I (1984) Characterization of parameters influencing indoor pollutant concentrations In Berglund, B , Lindvall, T , Sundell, J , eds Indoor air proceedings of the 3rd international conference on indoor air quality and climate, v 4, chemical characterization and personal exposure, August, Stockholm, Sweden Stockholm, Sweden Swedish Council for Building Research, pp. 259-264 Available from NTIS, Springfield, VA, PB85-104214

Gschwandtner, G , Barnard, W , Carlson, P (1990) Feasibility of including regional and temporal VOC emissions estimates in the EPA emissions trends report Research Triangle Park, NC U S Environmental Protection Agency, Office of Air Quality Planning and Standards, EPA report no EPA/450/4-91/005A Available from NTIS, Springfield, VA, PB92-216910/XAB

Hare, C. T., Springer, K J (1973a) Exhaust emissions from uncontrolled vehicles and related equipment using internal combustion engines part 3—motorcycles Ann Arbor, MI U S Environmental Protection Agency, Office of Mobile Source Air Pollution Control, EPA report no APTD-1492 Available from NTIS, Springfield, VA, PB-224884/7

Hare, C T , Springer, K J (1973b) Exhaust emissions from uncontrolled vehicles and related equipment using internal combustion engines Final report Part 5 heavy-duty farm, construction, and industrial engines Washington, DC U S Environmental Protection Agency, Office of Air Quality Planning and Standards, report no APTD-1494 Available from NTIS, Springfield, VA, PB-232507

Hare, C T , Springer, K J (1973c) Exhaust emissions from uncontrolled vehicles and related equipment using internal combustion engines part 4—small air-cooled spark ignition utility engines Ann Arbor, MI U S Environmental Protection Agency, Office of Air and Water Programs, publication no APTD-1493 Available from. NTIS, Springfield, VA, PB-224885

Hayhurst, A N , Vince, I M (1980) Nitric oxide formation from nitrogen flames The importance of "prompt" nitric oxide Prog Energy Combust Sci 6 35-51

Heywood, J B (1988) Internal combustion engine fundamentals New York, NY McGraw-Hill Book Co , Inc ; p. 571

Heisler, S. L , Collins, H , Collins, J , Hayden, P , Lurmann, F , Yeransian, T , Young, J (1988) Interim emissions inventory for regional air quality studies Palo Alto, CA Electric Power Research Institute, report no EPRI EA-6070

Himmel, R L , DeWerth, D W (1974) Evaluation of the pollutant emissions from gas-fired ranges Cleveland, OH American Gas Association Laboratories, report no 1392

Hollowell, C D , Budnitz, R J , Traynor, G W (1977) Combustion-generated indoor air pollution In Kasuga, S , Suzuki, N , Yamada, T , Kimura, G , Inagaki, K , Onoe, K , eds Proceedings of the fourth international clean air congress, May, Tokyo, Japan Tokyo, Japan Japanese Union of Air Pollution Prevention Associations, pp 684-687

Kohout, E J , Miller, D J , Nieves, L A , Rothman, D S , Sancks, C L , Stodolsky, F , Hanson, D A , (1990) Current emission trends for nitrogen oxides, sulfur dioxide, and volatile organic compounds by month and state methodology and results Argonne, IL Argonne National Laboratory, Environmental Assessment and Information Sciences Division, report no ANL/EAIS/TM-25 Available from NTIS, Springfield, VA, DE92008666

Leaderer, B P (1982) Air pollutant emissions from kerosene space heaters Science (Washington, DC) 218 1113-1115

Liu, S C , Trainer, M , Fehsenfeld, F C , Parrish, D D , Williams, E J , Fahey, D W , Huebler, G , Murphy, P C (1987) Ozone production in the rural troposphere and the implications for regional and global ozone distributions J Geophys Res [Atmos] 92 4191-4207

Logan, J A (1983) Nitrogen oxides in the troposphere global and regional budgets J Geophys Res C Oceans Atmos 88 10785-10807

McNay, L M (1971) Coal refuse fires, an environmental hazard Washington, DC U S Department of the Interior, Bureau of Mines, information circular 8515

Moschandreas, D J , Relwani, S M , O'Neill, H J , Cole, J T , Elkins, R H , Macriss, R A (1985) Characterization of emission rates from indoor combustion sources Chicago, IL Gas Research Institute, report no GRI 85/0075 Available from NTIS, Springfield, VA, PB86-103900

National Research Council (1986) Environmental tobacco smoke measuring exposures and assessing health effects Washington, DC National Academy Press

Peeters, J , Mahnen, G (1973) Structure of ethylene-oxygen flames Reaction mechanism and rate constants of elementary reactions In Weinberg, F J , ed Combustion Institute European Symposium 1973 papers for presentation at the symposium, September, University of Sheffield, United Kingdom New York, NY Academic Press, pp 53-58

Placet, M , Battye, R E , Fehsenfeld, F C , Bassett, G W (1991) Emissions involved in acidic deposition processes In Irving, P M , ed Acidic depostion state of science and technology, volume I, emissions, atmospheric processes, and deposition Washington, DC The U S National Acid Precipitation Assessment Program (State of science and technology report no 1)

Reuther, J J , Billick, I H , Gaynor, A J (1988) The measurement of NO_2 from gas flames Combust Flame 71 331-335

Saeger, M , Langstaff, J , Walters, R , Modica, L , Zimmerman, D , Fratt, D , Dulleba, D , Ryan, R , Demmy, J , Tax, W , Sprague, D , Mudgett, D , Werner, A S (1989) The 1985 NAPAP emissions inventory (version 2) development annual data and modelers' tapes Research Triangle Park, NC U S Environmental Protection Agency, Air and Energy Engineering Research Laboratory, EPA report no EPA/600/7-89/012A Available from NTIS, Springfield, VA, PB91-119669/XAB

Shannon, L J , Gorman, P G , Reichel, M (1971) Particulate pollutant system study, volume II—fine particle emissions Durham, NC U S Environmental Protection Agency, Air Pollution Control Office, EPA report no APTD-0744 Available from NTIS, Springfield, VA, PB-203531

Shukla, K C ; Hurley, J R (1983) Development of an efficient, low NO_x domestic range cooktop Thermo Electron Corporation research report, GRI contract no 5081-241-0544

Smith, K R (1987) Biofuels, air pollution, and health a global review New York, NY Plenum Press (Lester, R K , Andelin, J , eds Modern perspectives in energy)

Statutes-at-Large (1988) Alternative motor fuels act of 1988, PL 100-494, October 14, 1988 Stat 102 2441-2453

Stedman, D H , Shetter, R E (1983) The global budget of atmospheric nitrogen species In Schwartz, S E , ed Trace atmospheric constituents properties, transformations, and fates New York, NY John Wiley & Sons, pp 411-454 (Nriagu, J O , ed Advances in environmental science and technology v 12)

Thrasher, W. H , DeWerth, D W (1979) Evaluation of the pollutant emissions from gas-fired room heaters Cleveland, OH American Gas Association Laboratories, research report no 1515

Tikalsky, S , Reisdorf, K , Flickinger, J , Totzke, D , Haywood, J , Annen, L , Kanarek, M , Kaarakka, P , Prins, E (1987) Gas range/oven emissions impact analysis [final report (July 1985-December 1987)] Chicago, IL Gas Research Institute, report no GRI-87/0119 Available from NTIS, Springfield, VA, PB88-232756

Traynor, G W , Allen, J R , Apte, M G , Dillworth, J F , Girman, J R , Hollowell, C D , Koonce, J F , Jr (1982) Indoor air pollution from portable kerosene-fired space heaters, wood-burning stoves, and wood-burning furnaces In Proceedings of the Air Pollution Control Association specialty conference on residential wood and coal combustion, March, Louisville, KY Pittsburgh, PA Air Pollution Control Association, pp 253-263

Traynor, G. W , Girman, J R , Allen, J R , Apte, M G , Carruthers, A R , Dillworth, J F , Martin, V M (1983a) Indoor air pollution due to emissions from unvented gas-fired space heaters Presented at 76th annual meeting of the Air Pollution Control Association, June, Atlanta, GA Pittsburgh, PA Air Pollution Control Association, paper no 83-9 6

Traynor, G W , Allen, J R , Apte, M G , Girman, J R , Hollowell, C D (1983b) Pollutant emissions from portable kerosene-fired space heaters Environ Sci Technol 17 369-371

Traynor, G W , Apte, M G , Carruthers, A R , Dillworth, J F , Grimsrud, D T (1984a) Pollutant emission rates from unvented infrared and convective gas-fired space heaters Berkeley, CA U S Department of Energy, Lawrence Berkeley Laboratory, report no LBL-18258 Available from NTIS, Springfield, VA, DE85 010647/XAB

Traynor, G W , Apte, M G , Carruthers, A R , Dillworth, J F , Grimsrud, D T , Gundel, L A (1984b) Indoor air pollution to emissions from wood burning stoves Presented at 77th annual meeting of the Air Pollution Control Association, June, San Francisco, CA Pittsburgh, PA Air Pollution Control Association, paper no 84-33 4

U.S. Department of Commerce (Annual a) Current industrial reports Washington, DC Bureau of the Census

U S Department of Commerce (Annual b) Statistical abstract of the United States Washington, DC Bureau of the Census

U S. Department of Energy (1982) Estimates of U S wood energy consumption from 1949 to 1981 Washington, DC Energy Information Administration, Office of Coal, Nuclear, Electricity, and Alternate Fuels; publication no DOE/EIA-0341 Available from NTIS, Springfield, VA, DE82020578

U S Department of Energy (1984) Estimates of U S wood energy consumption 1980-1983 Washington, DC Energy Information Administration, Office of Coal, Nuclear, Electric and Alternate Fuels, publication no DOE/EIA-0341(83) Available from NTIS, Springfield, VA, DE85003669/XAB

U S Department of Energy (1991) Inventory of power plants in the United States 1990 Washington, DC Energy Information Administration, report no DOE/EIA-0095(90) Available from NTIS, Springfield, VA, DE92-002711

U S Department of Energy (Annual a) Petroleum supply annual Washington, DC Energy Information Administration

U S Department of Energy (Annual b) Coal distribution January-December Washington, DC Energy Information Administration

U S Department of Energy (Annual c) Electric power annual Washington, DC Energy Information Administration

U S Department of Energy (Annual d) Natural gas annual Washington, DC Energy Information Administration

U S Department of Energy (Monthly) Petroleum marketing monthly Washington, DC Energy Information Administration

U S Department of Health, Education, and Welfare (1968) National survey of community solid waste practices Cincinnati, OH Public Health Service, PHS publication no 1867

U S Department of the Interior (Annual) Minerals yearbook Washington, DC Bureau of Mines

U S Department of Transportation (Annual a) FAA air traffic activity Washington, DC Federal Aviation Administration

U S Department of Transportation (Annual b) Highway statistics Washington, DC Federal Highway Administration

U S Environmental Protection Agency (1985) Compilation of air pollutant emission factors, volume I stationary point and area sources, volume II mobile sources 4th ed Research Triangle Park, NC Office of Air Quality Planning and Standards, EPA report no AP-42-ED-4-VOL-1 and AP-42-ED-4-VOL-2 Available from NTIS, Springfield, VA, PB86-124906 and PB87-205266

U S Environmental Protection Agency (1989) User's guide to MOBILE4 (Mobile Source Emission Factor Model) Ann Arbor, MI Office of Mobile Sources, EPA report no EPA-AA-TEB-89-01 Available from NTIS, Springfield, VA, PB89-164271

U S Environmental Protection Agency (1990) National air pollutant emission estimates, 1940-1988 Research Triangle Park, NC Office of Air Quality Planning and Standards, EPA report no EPA/450/4-90/001 Available from NTIS, Springfield, VA, PB90-199266/HSU

U S Environmental Protection Agency (1991a) National air pollutant emission estimates 1940-1990 Research Triangle Park, NC U S Environmental Protection Agency, Office of Air Quality Planning and Standards, EPA report no EPA/450/4-91/026 Available from NTIS, Springfield, VA, PB92-152859

U S Environmental Protection Agency (1991b) AIRS facility subsystem Research Triangle Park, NC Office of Air Quality and Standards, National Air Data Branch

U.S. Environmental Protection Agency (1992) National air pollutant emission estimates, 1900-1991 Research Triangle Park, NC Office of Air Quality Planning and Standards, EPA report no EPA/454/R-92/013 Available from NTIS, Springfield, VA, PB93-157808/XAB

University of Kentucky (n d) Physical and analytical data on IR4F reference cigarettes from Tobacco and Health Research Institute Lexington, KY [as cited in Moschandreas et al (1985)]

Vandegrift, A E , Shannon, L J , Gorman, P G , Lawless, E W , Sallee, E E , Reichel, M (1971a) Particulate pollutant system study, volume I—mass emissions Durham, NC U S Environmental Protection Agency, Air Pollution Control Office, EPA report no APTD-0743 Available from NTIS, Springfield, VA, PB-203128

Vandegrift, A E , Shannon, L J , Lawless, E W , Gorman, P G , Sallee, E E , Reichel, M (1971b) Particulate pollutant system study, volume III—handbook of emission properties Durham, NC U S Environmental Protection Agency, Air Pollution Control Office, EPA report no APTD-0745 Available from NTIS, Springfield, VA, PB-203522

Woods, J E (1983) Sources of indoor air contaminants ASHRAE Trans 89 462-497

Yamanaka, S., Hirose, H , Takada, S (1979) Nitrogen oxides emissions from domestic kerosene-fired and gas-fired appliances Atmos Environ 13 407-412

Yamate, G. (1974) Emissions inventory from forest wildfires, forest managed burns, and agricultural burns Research Triangle Park, NC U S Environmental Protection Agency, Office of Air Quality Planning and Standards, EPA report no EPA-450/3-74-062 Available from NTIS, Springfield, VA, PB-238766

Zafiriou, O. C ; McFarland, M (1981) Nitric oxide from nitrite photolysis in the central equatorial Pacific J Geophys Res. C· Oceans Atmos 86 3173-3182

Zawacki, T. S ; Cole, J T , Huang, V M S , Banasiuk, H , Macriss, R A (1984) Efficiency and emissions improvement of gas-fired space heaters Task 2 Unvented space heater emission reduction [final report] Chicago, IL· Gas Research Institute, report no GRI-84/0021 Available from NTIS, Springfield, VA, PB84-237734.

Zawacki, T. S ; Cole, J T , Jasionowski, W J , Macriss, R A (1986) Measurement of emission rates from gas-fired space heaters Chicago, IL Gas Research Institute, report no GRI-86/0245

Zeldovich, J. (1946) The oxidation of nitrogen in combustion and explosions Acta Physicochim URSS 21 577-628

5. TRANSPORT AND TRANSFORMATION OF NITROGEN OXIDES

5.1 BACKGROUND

Even in the clean, unpolluted troposphere, nitrogen oxides (NO_x) play an important role in natural atmospheric processes They regulate the oxidizing power of the free troposphere by controlling the buildup and fate of free radical species Consequently, the concentration of NO_x is a critical factor in determining ozone (O_3) production and volatile organic compound (VOC) chemistry under natural circumstances, and even more so under circumstances of added anthropogenic emissions

Much of the tropospheric chemistry discussed in this chapter is based on the cyclic reactions of nitrogen (Figure 5-1), oxygen (Figure 5-2), and hydrogen (Figure 5-3) These are schematically combined in Figure 5-4 to show the complexity of interactions among these three groups of gaseous compounds Collectively, these four diagrams, along with Figure 5-5, provide a visual reference for the series of individual reactions discussed throughout the chapter White and Deitz (1984) demonstrated the complexity of these interactions and the calculated steady state concentrations of other species of gaseous compounds in the troposphere as a function of NO_x concentration (Figure 5-6)

In urban environments, the oxides of nitrogen react with VOCs in the presence of sunlight to produce oxidants such as O_3 and peroxyacetylnitrate (PAN) There are many urban areas in the United States that are not in compliance with the National Ambient Air Quality Standards for O_3 Therefore, the involvement of NO_x in this photochemical process must be critically examined when considering O_3 control strategies On a global basis, increasing O_3 levels in the troposphere are of concern because of the ability of O_3 to absorb outgoing radiation and, thus, contribute to the greenhouse warming of the earth's atmosphere In recent years, acidic deposition has created a great deal of concern in the eastern United States The oxides of nitrogen contribute to atmospheric acidity through their conversion to nitric acid (HNO_3)

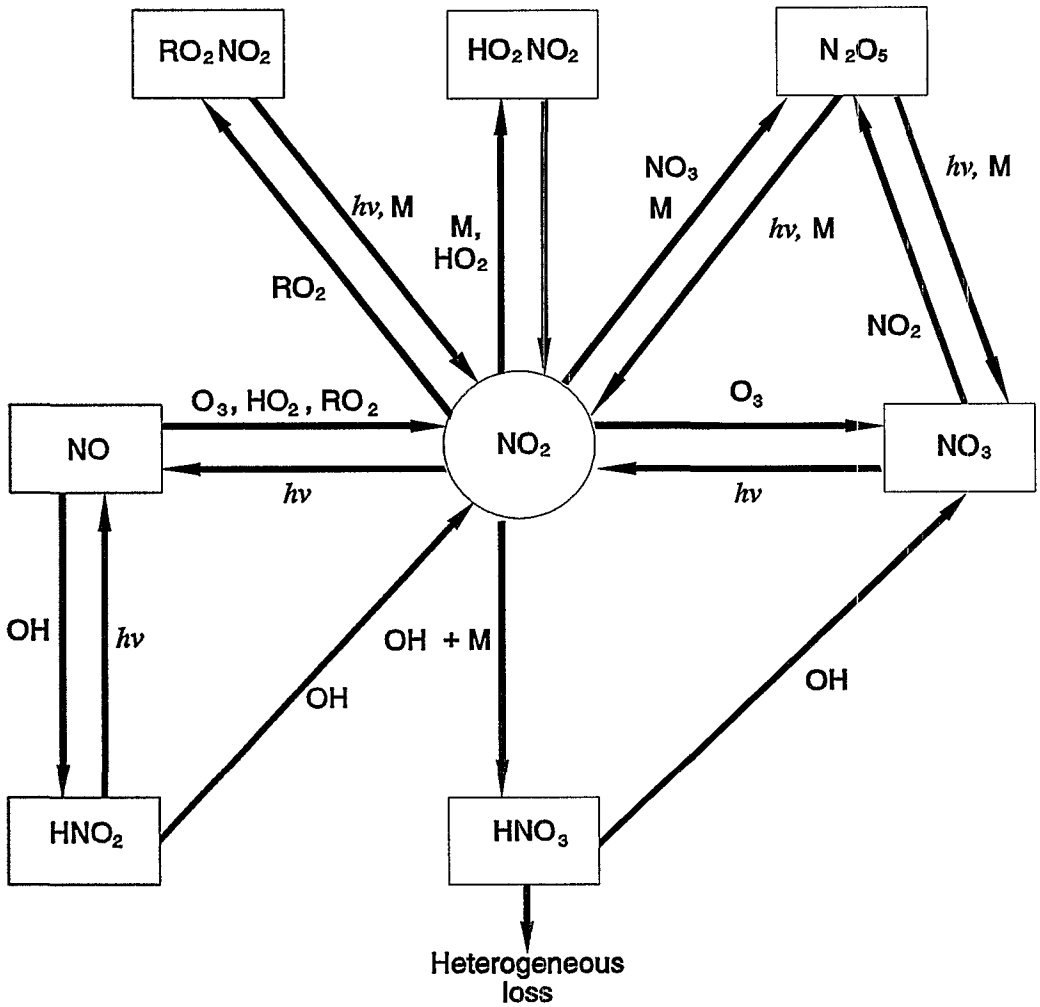


Figure 5-1. Summary of the gas phase chemistry of NO_x in the clean troposphere.

Source Finalyson-Pitts and Pitts (1986)

On a global scale, the chemistry of NO_x compounds is important because it plays a major role in controlling free radical concentrations The buildup and fate of species such as $HO_2^{\cdot}$, $^{\cdot}OH$, and RO_2 (where R is an organic moiety) is very dependent on the concentration of nitric oxide (NO) that is present As will be discussed later in this chapter, the levels of NO_x present can regulate the oxidizing power of the free troposphere

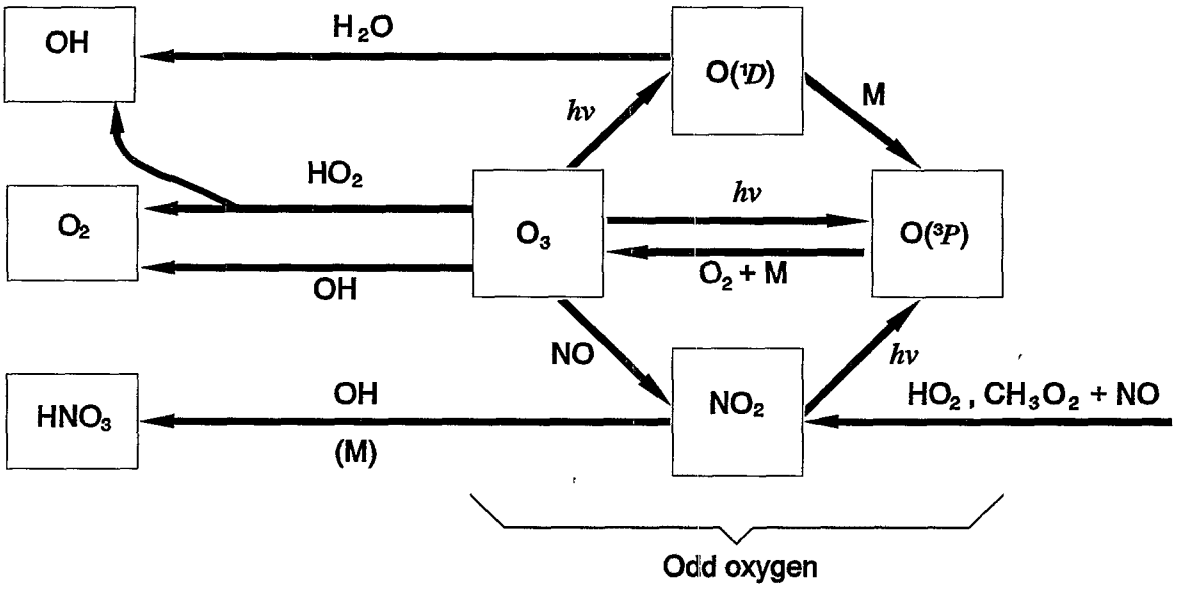


Figure 5-2. Major chemical reactions affecting oxygen species in the troposphere. Molecules acting as third bodies are denoted as 'M' (e.g., N_2, O_2, Ar, H_2O).

Source Finalyson-Pitts and Pitts (1986)

In summary, the atmospheric chemistry of the oxides of nitrogen has an important impact on (1) the production of O_3, (2) acidification in the atmosphere, and (3) control of radical concentrations in the clean troposphere

In the ensuing portions of this chapter, the chemical mechanisms that relate to each of these impacts will be described An important complement to the chemistry is the dispersion and geographical movement of the oxides of nitrogen and their oxidation products This chapter will address the factors that control the transport of these species within the atmosphere

5.2 THE ROLE OF NITROGEN OXIDES IN OZONE PRODUCTION

Solar radiation triggers a series of reactions in the atmosphere between gaseous organic molecules and NO_x This chemistry involves a variety of unstable excited molecules and

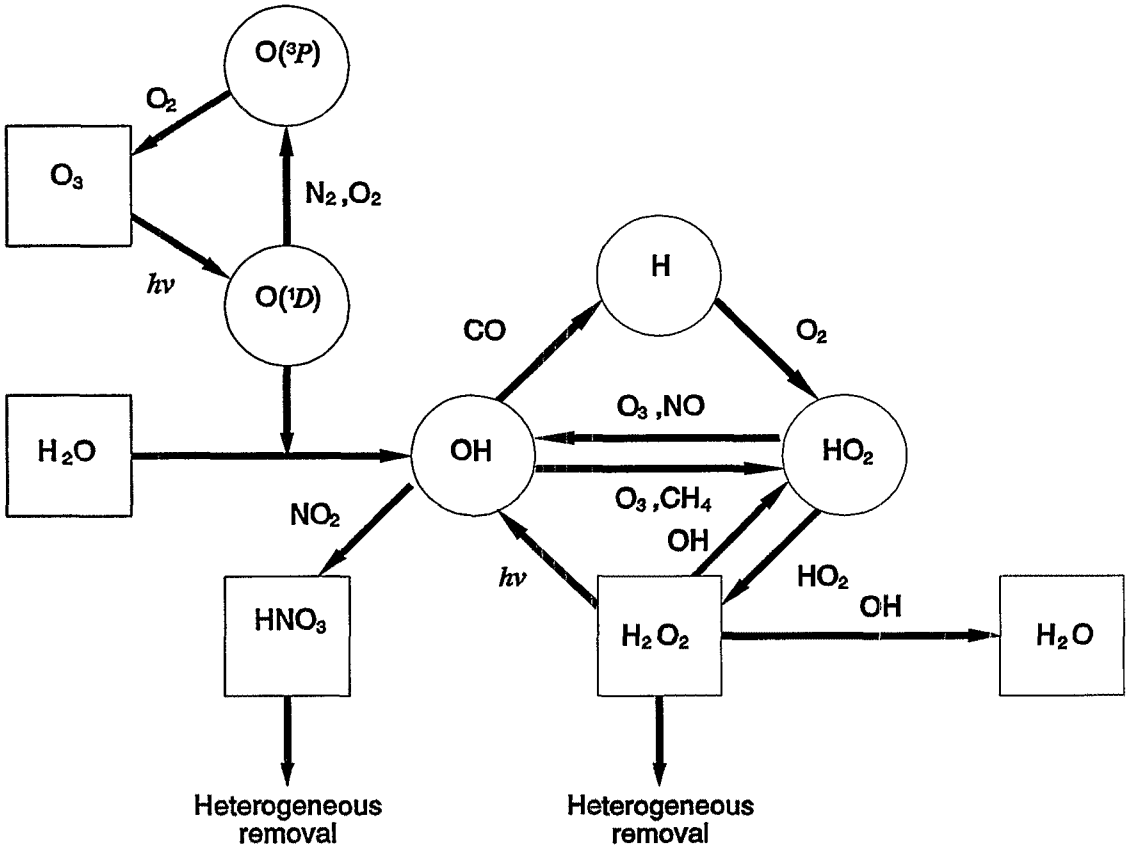


Figure 5-3. Major chemical reactions affecting hydrogen species (OH, H, H_2O, H_2O_2) in the troposphere.

Source· Finalyson-Pitts and Pitts (1986)

molecular fragments that lead to the production of secondary pollutants In urban plumes, O_3 is the predominant product of these reactions The amount of NO_x present can determine whether the photochemical reactions lead to the production or consumption of O_3

Nitrogen oxides are emitted in most combustion processes, with NO being the major constituent. Upon entering the ambient atmosphere, the NO can be oxidized quite rapidly in the presence of O_3 or in a photochemically reactive atmosphere to nitrogen dioxide (NO_2) The conversion of NO to NO_2 can occur via reactions shown in Equations 5-1 and 5-2, as follows:

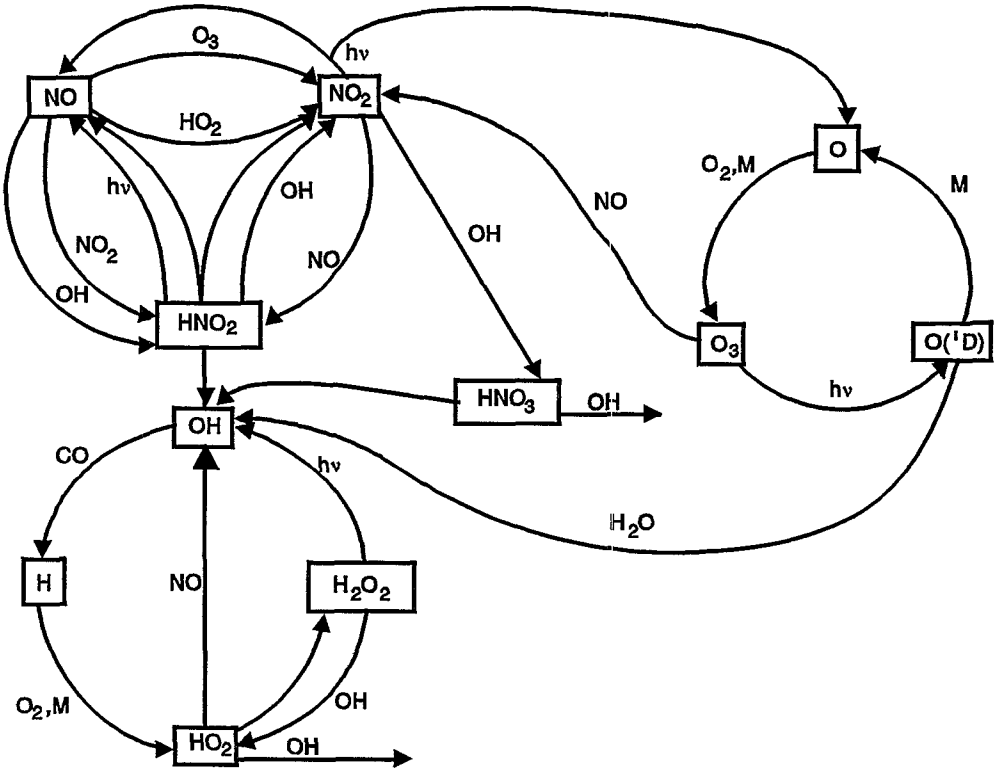


Figure 5-4. Schematic diagram of the combined reactions of nitrogen, oxygen, and hydrogen.

Source Carmichael and Peters (1984)

$$2NO + O_2 \rightarrow 2NO_2 \quad (5\text{-}1)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (5\text{-}2)$$

Reaction with molecular oxygen as the oxidizing agent is relatively slow, however, and is only important in the immediate vicinity of a source where NO concentrations are elevated Thus, in ambient air, Equation 5-1 is negligible At typical ambient levels of NO, Equation 5-2, which destroys a molecule of O_3, represents a more important mechanism by which NO is converted to NO_2 During the daytime, NO_2 absorbs sunlight at wavelengths less than 430 nm and decomposes to NO and a triplet-P oxygen atom as represented by Equation 5-3 The highly reactive oxygen atom forms O_3 through collisions with oxygen molecules In Equation 5-4, the M represents a third molecule (such as molecular nitrogen,

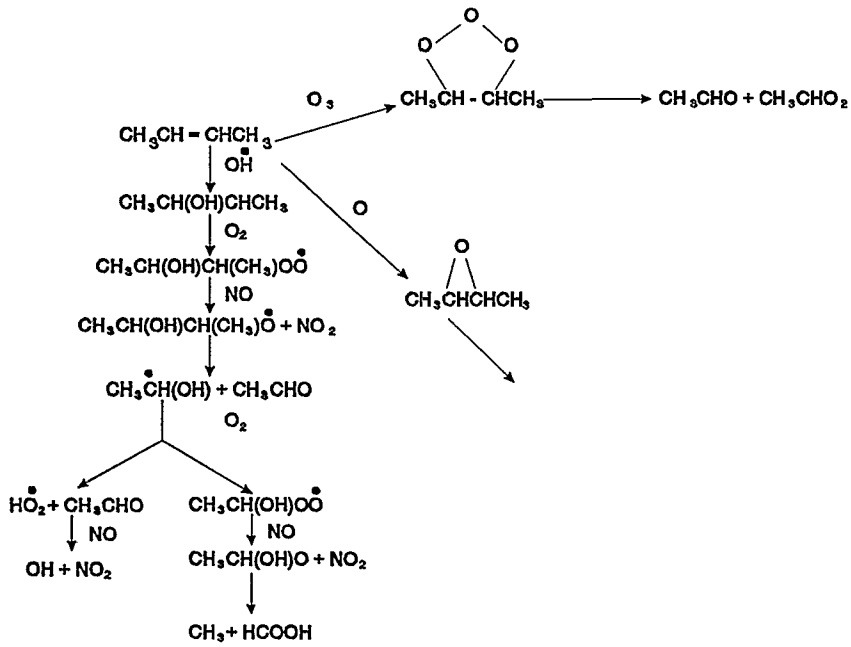


Figure 5-5. Volatile organic compound oxidation in the atmosphere.

Source. Atkinson and Carter (1984)

molecular oxygen, etc) that absorbs excess vibrational energy from the newly formed O_3 molecules.

$$NO_2 + h\nu \rightarrow NO + O(^3P) \tag{5-3}$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \tag{5-4}$$

The net effect of Equations 5-2 through 5-4 is an equilibrium in which NO, NO_2, and O_3 concentrations are interdependent

$$NO_2 + O_2 + h\nu \leftrightharpoons NO + O_3$$

In the absence of competing reactions, the NO, NO_2, and O_3 are expected to reach a steady-state condition, with their concentrations defined by the following relationship

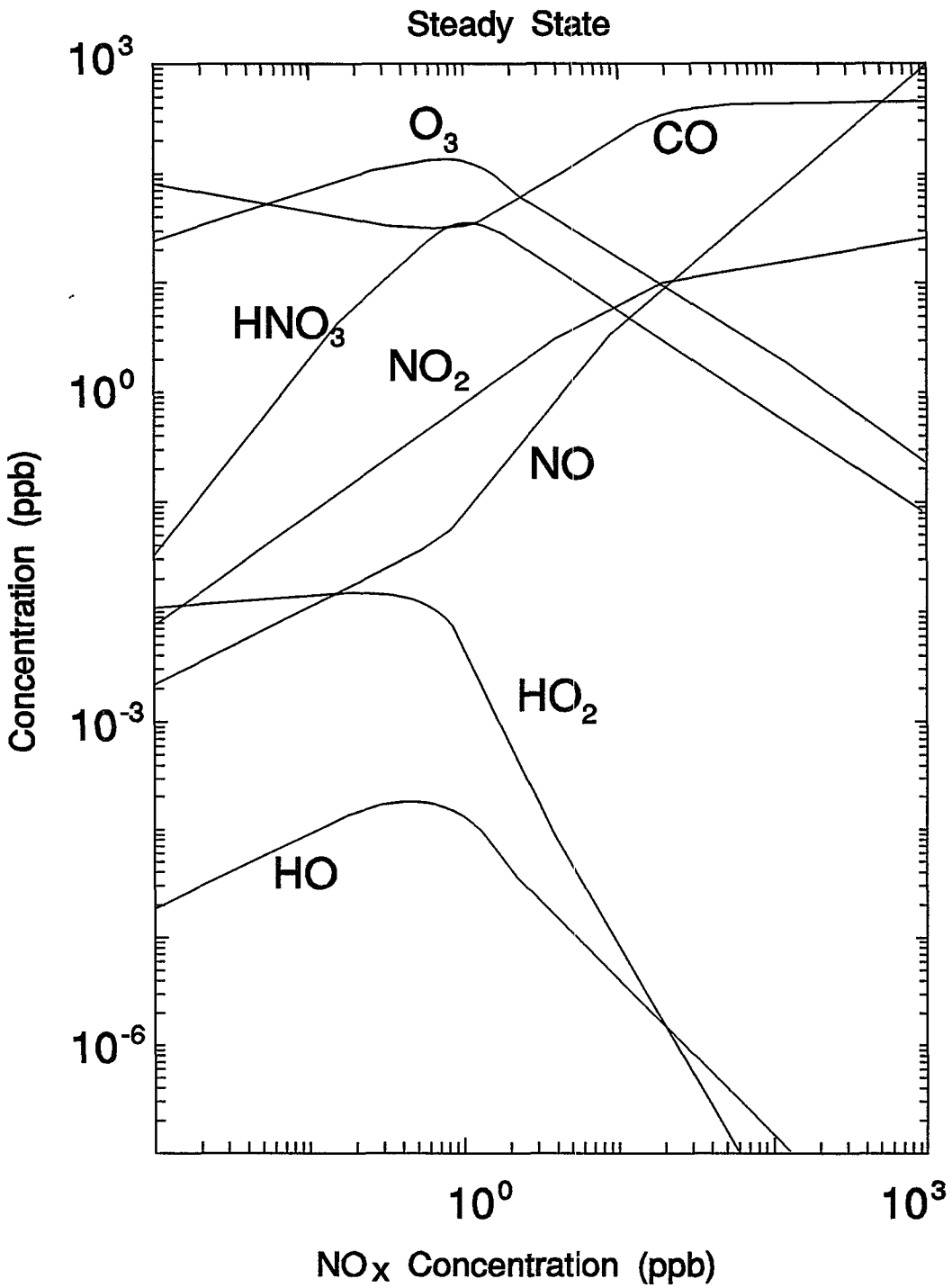


Figure 5-6. Calculated steady state concentrations in the free troposphere as a function of nitrogen oxides concentration. Conditions described by White and Dietz (1984).

Source White and Dietz (1984)

$$[O_3]_{ss} = \frac{JNO_2\ [NO_2]}{k_2\ \ [NO]},$$

where JNO_2 is the photolysis rate for Equation 5-3 and k_2 is the rate constant for Equation 5-2.

Even in the cleanest daytime atmospheres, however, sufficient quantities of HO_2 and various organic $RO_2^{\cdot}$ (where R is an organic moiety) radicals will be present that can compete with O_3 for converting NO to NO_2 Thus, Equations 5-5 and 5-6 increase the $[NO_2]/[NO]$ ratio, which leads to an increase in O_3 levels

$$NO + HO_2 \rightarrow NO_2 + OH \qquad (5\text{-}5)$$

$$NO + RO_2 \rightarrow NO_2 + RO \qquad (5\text{-}6)$$

In these reactions, NO is converted to NO_2 without destroying an O_3 molecule, as occurs in Equation 5-2; and consequently, O_3 levels will build up in the atmosphere The peroxy radicals in Equations 5-5 and 5-6 can be initially formed by photolysis of aldehydes and, subsequently, from other reactions associated with the photoxidation of VOCs

These peroxy radical reactions oxidize NO to NO_2 without destroying O_3 In effect, NO and NO_2 are cycled catalytically, with the original NO_x concentration remaining essentially unchanged; but the O_3 concentration builds up The amount of O_3 formed is dependent on the concentration of NO_x present as well as the amounts and reactivity of VOCs available. In urban plumes, O_3 concentrations in excess of 200 ppb are not uncommon in many areas of the United States However, in NO_x-rich plumes, such as those emanating from fossil-fuel burning power plants, O_3 buildup is not observed until the NO_x is diluted with ambient air.

5.2.1 Urban Plume Chemistry

During the early morning hours, urban plumes typically contain a multitude of VOCs and oxides of nitrogen (primarily NO) In the larger cities, during 0600 to 0900 hours, nonmethane VOC (NMHC) levels generally average between 250 and 1,000 ppbC at the

surface During the same period, NO_x concentrations fall in the range 20 to 150 ppb, which leads to typical VOC to NO_x ratios of 7 to 15 Ozone levels in the early morning urban air mass are near zero due to scavenging by NO (Equation 5-2) Because the reaction in Equation 5-2 is very rapid, O_3 concentrations cannot increase until most of the NO has been converted to NO_2 As indicated earlier, this will occur as sunlight energy becomes sufficient to generate HO_2 and RO_2 Reactions such as Equations 5-3 and 5-4 then increase the NO_2 to NO ratio

It is inappropriate in this document to discuss in detail the VOC chemistry involved in oxidant formation Volatile organic compound reactions have been reviewed by many authors (Atkinson, 1990, Atkinson and Carter, 1984) The VOCs serve as a source of free radicals that propogate the series of chemical reactions leading to oxidant production The process is initiated by the reaction of a VOC with an oxidizing species present in the atmosphere An example of this process is depicted in Figure 5-5

Of the three oxidizing species shown in Figure 5-5, the OH, radical is considered to be by far the most important Several different production mechanisms for the OH radical have been recognized Nitrous acid, which accumulates in urban areas during the nighttime hours (Harris et al , 1982), will photolyze at sunrise, yielding OH radicals as illustrated in Equation 5-7

$$HONO + h\nu \rightarrow OH + NO \qquad (5\text{-}7)$$

The photolysis of aldehydes will also lead to OH production Formaldehyde has been shown to be present in significant quantities during the morning hours Photolysis of formaldehyde generates OH radicals through the sequence shown below (Finlayson-Pitts and Pitts, 1986)

$$CH_2O + h\nu \rightarrow H + HCO \qquad (5\text{-}8)$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad (5\text{-}9)$$

$$HCO + O_2 \rightarrow HO_2 + CO \qquad (5\text{-}10)$$

$$HO_2 + NO \rightarrow NO_2 + OH \qquad (5\text{-}11)$$

The third source of OH radicals is via photolysis of O_3 and subsequent reaction of the excuted atomic oxygen atoms ($O[^1D]$) that are produced with atmospheric water vapor

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \quad (5\text{-}12)$$

$$O(^1D) + H_2O \rightarrow 2\ OH \quad (5\text{-}13)$$

This source is probably not very important during the early hours of urban plume chemistry because O_3 levels are typically very low However, as the day progresses and O_3 levels build up, it certainly becomes more important especially in the free troposphere and in pristine areas.

The amount of O_3 produced in an urban plume is dependent on the absolute amounts of VOCs, oxides of nitrogen, and sunlight In a particular urban area where the VOC to NO_x ratio remains relatively constant under conditions of high solar intensity, the greater the concentrations of VOCs and NO_x, the greater will be the production of O_3 However, care must be exercised when comparing oxidant production in different urban areas Simulations of the atmospheric chemistry of O_3 formation have shown that the VOC to NO_x ratio can be quite important in O_3 formation At very low ratios where NO is present in relatively high concentrations, O_3 cannot build up because of scavenging by the NO (Equation 5-2) At the high VOC to NO_x ratios, there is insufficient NO_x to propogate the radical reactions that lead to O_3 production. Urban VOC to NO_x ratios are generally in the range of 5 to 15 In urban areas with higher VOC to NO_x ratios, NO_x control will aid in reducing O_3 production The opposite is true when urban VOC to NO_x ratios are low In this latter case, reducing NO_x emissions will likely result in increased O_3 production

5.2.2 Ozone Production in Rural Environments

Ozone producing reactions identical to those described in urban plumes will occur in rural environments, provided there are sufficient quantities of VOCs and oxides of nitrogen present. Because the magnitude of natural VOC emissions is considerably larger than natural NO_x emissions, there are generally sufficient quantities of VOCs present with the result being that the production of O_3 is limited by the oxides of nitrogen Rural environments can be characterized as follows, according to their NO_x concentrations.

(1) regions in which NO_x levels average less than 50 ppt—this condition is generally limited to clean maritime areas, most of the free troposphere, and possibly some remote continental locations in the southern hemisphere,

(2) areas with NO_x concentrations ranging from about 50 to 200 ppt—clean continental regions in the northern hemisphere comprise this category;

(3) semipolluted environments with average NO_x concentrations ranging between 1 and 10 ppb—this condition is typical of much of the eastern United States and probably rural areas in the industrialized countries of Europe and Asia

In the cleanest atmospheres, methane and carbon monoxide (CO) are the species present in highest concentrations Consequently, they, along with the oxides of nitrogen, are important participants in the photochemical reactions that control trace gas concentrations Crutzen (1988) and Penkett (1991) have pointed out that O_3 can be produced and destroyed by the methane and CO oxidation cycles, depending on the concentrations of NO present For example, the carbon monoxide oxidation cycles can proceed by either of the reaction sequences shown below

$$CO + OH \rightarrow CO_2 + H \quad (5\text{-}14a)$$

$$H + O_2 + M \rightarrow HO_2 + M \quad (5\text{-}14b)$$

$$HO_2 + NO \rightarrow HO + NO_2 \quad (5\text{-}14c)$$

$$NO_2 + h\nu \rightarrow NO + O \quad (5\text{-}14d)$$

$$\underline{O + O_2 + M \rightarrow O_3 + M} \quad (5\text{-}14e)$$

$$\text{*Net} \quad CO + 2O_2 \rightarrow CO_2 + O_3 \quad (5\text{-}14f)$$

$$CO + OH \rightarrow CO_2 + H \quad (5\text{-}15a)$$

$$H + O_2 + M \rightarrow HO_2 + M \quad (5\text{-}15b)$$

$$\underline{HO_2 + O_3 \rightarrow OH + 2O_2} \quad (5\text{-}15c)$$

$$\text{*Net} \quad CO + O_3 \rightarrow CO_2 + O_2 \quad (5\text{-}15d)$$

Whether reaction series 5-14 or 5-15 predominates is dependent on the NO concentration the rate constant for Equation 5-14c is about 5,000 times larger than that for Equation 5-15c Thus, at $[O_3]/[NO]$ ratios less than 5,000, the O_3 production sequence (5-14) is more

important, whereas the O_3 destruction sequence (5-15) predominates when NO levels are extremely low At background O_3 levels of 20 to 40 ppb, the 5,000 ratio corresponds to NO levels of 10 ppt or less Similarly, for the oxidation of methane, the following net reactions can be derived depending on the NO levels (Crutzen, 1988)

$$CH_4 + 4O_2 \rightarrow CH_2O + H_2O + 2O_3 \quad (5\text{-}16)$$

$$CH_2O + 4O_2 \rightarrow CO + 2\,OH + 2O_3 \quad (5\text{-}17)$$

$$CH_2O + 2O_2 \rightarrow CO + H_2O + O_3 \quad (5\text{-}18)$$

Equation 5-17 results from a series of reactions that are initiated by photodissociation of the formaldehyde and subsequent oxidation of NO to NO_2 via HO_2 radicals Equation 5-18 involves nearly the same sequences of steps, but is initiated by reaction of the formaldehyde with OH radicals. It is apparent from net Equations 5-16, 5-17, 5-18, and 5-14f that oxidation of methane to CO and then to carbon dioxide (CO_2) will yield a gain in O_3 molecules in environments with sufficient NO present

In NO-depleted environments, a loss of O_3 is expected to occur due to a series of reactions represented by the net Equations 5-19 to 5-21 and 5-15d

$$CH_4 + OH + OH_2 \rightarrow CH_2O + 2H_2O \quad (5\text{-}19)$$

$$CH_2O + 2O_3 \rightarrow CO + 2O_2 + 2\,OH \quad (5\text{-}20)$$

$$CH_2O + O_3 \rightarrow CO + H_2O + O_2 \quad (5\text{-}21)$$

Thus, it is expected that in all but NO-deficient environments (NO $<$ 10 ppt), O_3 production will occur during the daytime hours when conditions are conducive for photochemical processes. In the context of this document, it is of greatest interest to study the environments with adequate NO in order to see if there is a quantitative relationship between NO_x levels and the amount of O_3 that is photochemically produced

Research studies at a mountain site in Colorado (Niwot Ridge) have provided the best understanding of NO_x-O_3 relationships in rural areas (Parrish et al , 1986) When winds are from the west, the Niwot site is fumigated by clean air that is devoid of recent anthropogenic emissions. Nitrogen dioxide levels in these westerly air masses are typical of those

associated with clean continental environments (Category 2)—namely between 10 and 200 ppt However, the Niwot site is less than 100 km from the Denver-Boulder metropolitan areas Occasionally, upslope winds advect polluted air that originates in this urban region to the mountain site Under upslope flow conditions, NO_x levels generally exceed 800 ppt and range up to a few parts per billion Figures 5-7a and 5-7b show the relationship between low NO_x levels and O_3 at Niwot Ridge The two lines in each figure represent morning and afternoon relationships The best fit lines during the morning hours include data collected during the 0700 to 1100 hours time periods, when the nocturnal inversion has burned off but photochemical O_3 production has not fully developed It is evident that there is little dependence of O_3 on NO_x during the winter and only a slight dependence during the morning hours in the summer The slope of summer-morning best fit line is 1 9 $\pm$ 2 8 In contrast to the morning behavior, a large dependence of O_3 on NO_x is seen in the afternoon summertime data The slope of the least-squares fit is 16 8 $\pm$ 2 6. Thus, the daily photochemical production of O_3 amounts to about 17 ppbv O_3/day/ppbv NO_x

Kelly et al (1984) made similar measurements at sites in South Dakota, Virginia and Louisana Their data provided a value of 6 ppbv O_3/ppbv NO_x for the daily photochemical production of O_3 This is considerably less than the value of 17 found at Niwot Ridge and could be due to the fact that the Kelly et al data covered the time period between 1000 and 1400 hours, when the daily solar flux was not at its maximum Also, the average NO_x levels were higher (2 to 9 ppbv) at the three sites monitored by Kelly et al (1989). Based on Niwot Ridge data, O_3 production per unit NO_x becomes smaller at NO_x concentrations above 1 ppb Figure 5-8 shows the summertime O_3 mixing ratio measured during the afternoon hours (1500 to 2000 hours) versus the concurrently measured NO_x mixing ratio Starting at about 0 5 ppb NO_x, O_3 values exhibit a general increase up to approximately 3 ppb Above and below this range of NO_x levels, there is no apparent dependence of O_3 on NO_x levels in the ambient data from Niwot Ridge Recent photochemical modeling results of Liu et al (1987) agree fairly well with the O_3-NO_x relationships derived from ambient data at Niwot Ridge

Figure 5-9 compares calculated change in O_3 values (Q) with ambient measurement data (open circles with error bars) at the Colorado site The model included nonmethane VOC chemistry, surface deposition of trace gases, and the dilution effect of trace gases due

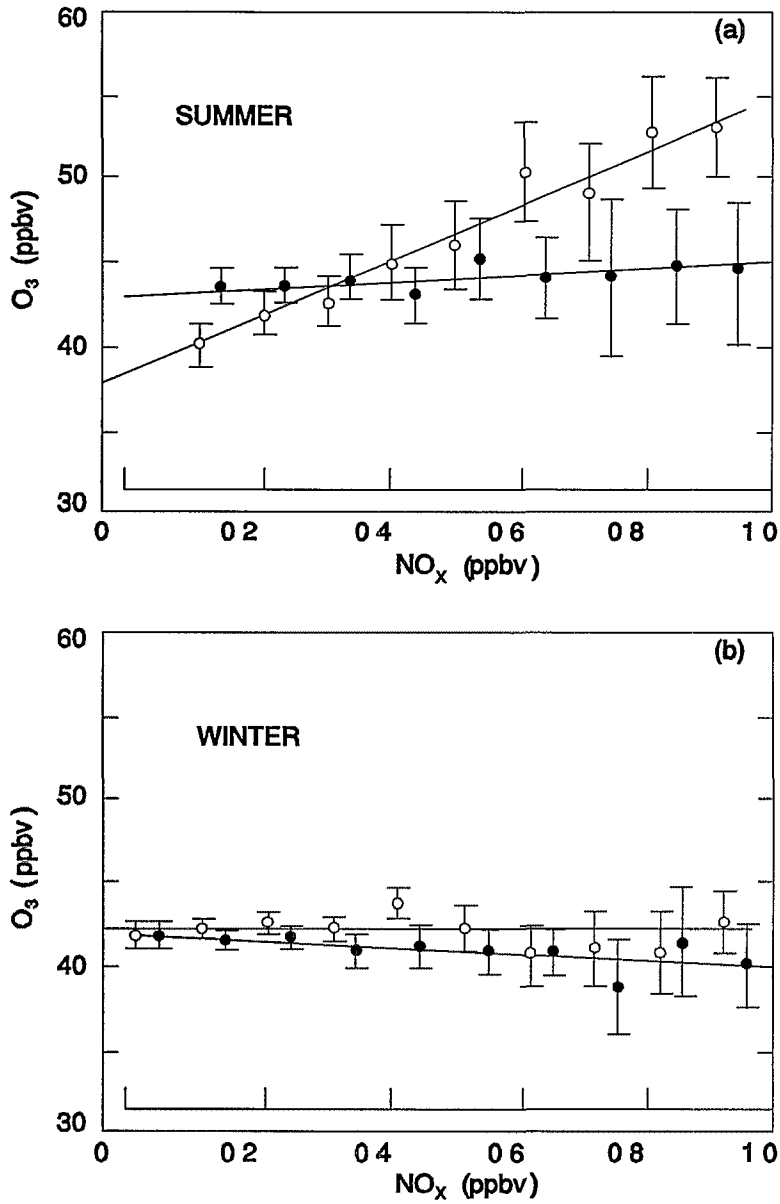


Figure 5-7. (a) Summertime (June 1 to August 31) and (b) wintertime (December 1 to February 28) ozone mixing ratio versus nitrogen oxides mixing ratio during the morning and afternoon. Filled circles are used for the morning values; open circles are used for the afternoon values. Each point is an average concentration of ozone for all nitrogen oxides concentration values in a parts-per-billion-volume interval. The vertical error bars give the 95% confidence limits for the average deduced from the standard deviation of the measurements and the number of measurements in each nitrogen oxides interval. The lines give the linear, least squares fit to the data averages. For clarity, the morning points and the linear fits have been offset horizontally as indicated by the second abscissas.

Source. Parrish et al. (1986)

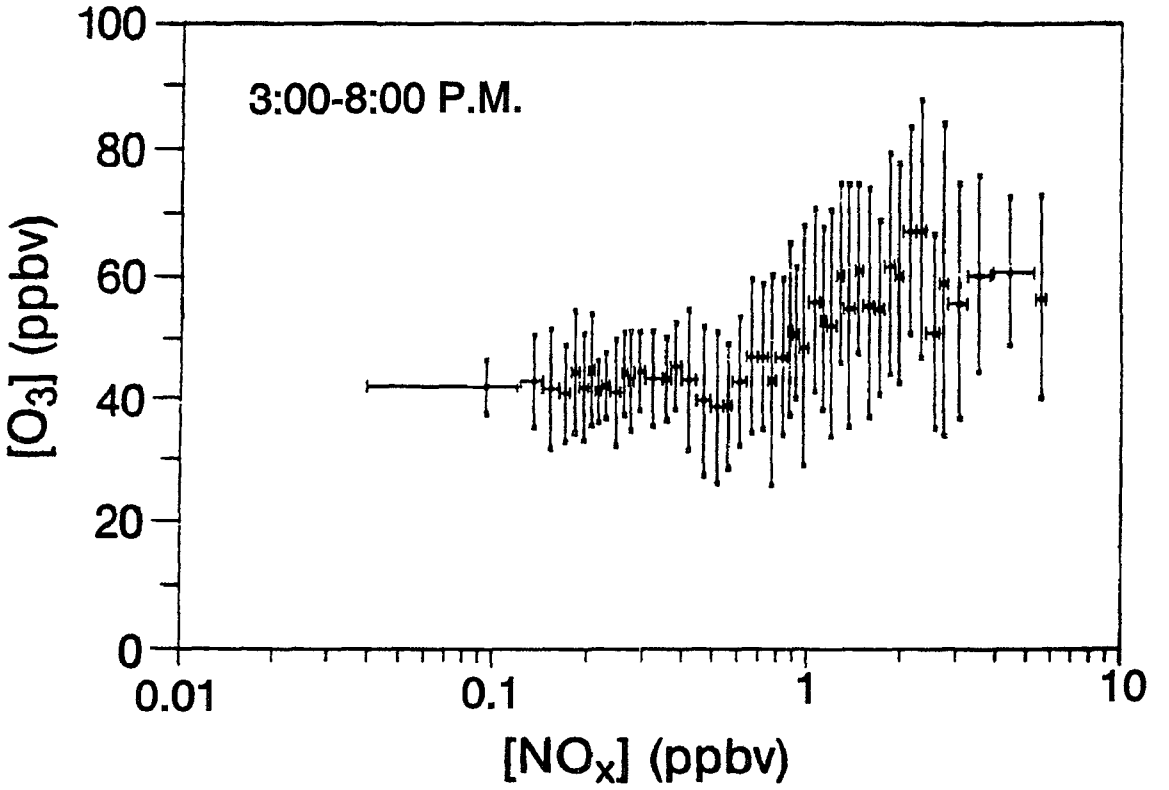


Figure 5-8. Summertime ozone mixing ratio versus nitrogen oxides mixing ratio measured during the afternoon hours.

Source Parrish et al (1986)

to changes in the daily inversion height The solid lines in Figure 5-9 represents the model calculated dependence of O_3 on NO_x Several scenarios were examined in the model, with that represented by the NMHC-PO line being deemed the most appropriate for the Niwot site Below 1 ppb NO_x, the model overestimates the O_3 buildup by a factor of 2 This is suspected to result from an overestimation of odd hydrogen radical concentrations Although the modeled results always exceed the measured values, the agreement becomes better at higher NO_x concentrations and the general shape of the calculated and measured curves are very comparable An important feature of the net daily O_3 change shown in Figure 5-9 is the nonlinear relationship with NO_x Both calculations and measurements indicate that

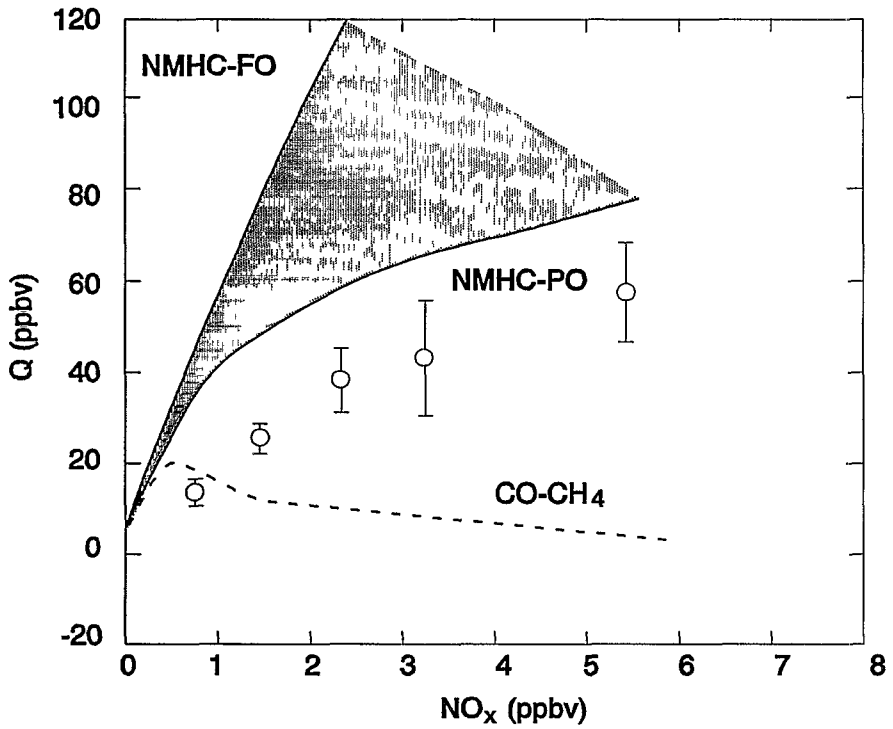


Figure 5-9. Model calculated daytime change (Q) in ozone values (from sunrise to 1630 hours) for summer clear sky conditions is compared to the observed difference between the afternoon (1400 to 1900 hours) and the morning (0700 to 1100 hours) for clear sky conditions. Open circles with error bars are ambient measurement data at the Colorado site. The dashed line is calculated from a model without nonmethane VOCs. The shaded area represents calculated values from a model with anthropogenic nonmethane VOCs. The lower envelope of the shaded area is calculated by assuming no overnight retention of secondary VOCs (NMHC-PO), whereas the upper envelope assumes buildup of secondary VOCs to their steady state values (NMHC-FO).

Source Liu et al (1987)

O_3 production increases more rapidly at low concentrations of NO_x This is demonstrated in more detail in Figure 5-10 The two curves in Figure 5-10 show the calculated average daily O_3 production per unit concentration of NO_x (ΔP) versus the NO_x concentration for summer and winter conditions The shape of the two curves is similar for the two seasons, however, the summertime daily O_3 production values are approximately a factor of 10 larger This is ue to the higher photochemical activity in the summer The decline in daily O_3 production

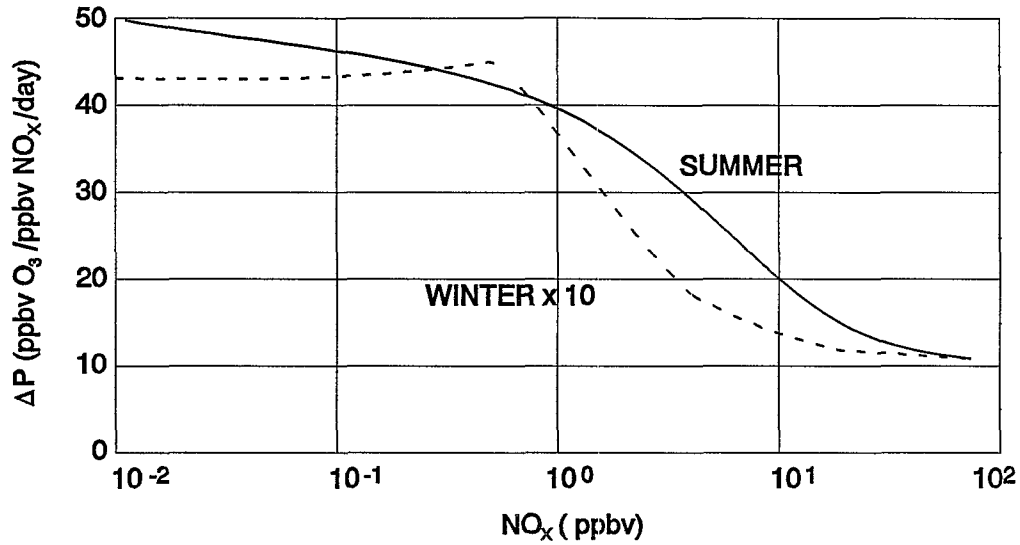


Figure 5-10. Oxygen production per unit nitrogen oxides per day (ΔP) from the NMHC-PO model is plotted as function of nitrogen oxides mixing ratios. A constant nonmethane volatile organic compound to nitrogen oxides ratio is assumed; see text for details. The solid line gives summer values. The dashed line gives the winter values multiplied by 10.

Source Liu et al (1987)

rate at NO_x concentrations larger than 1 ppb reported by Liu et al (i e , Figure 5-9) is consistant with other modeling results Photochemical smog models suggest that the degree of nonlinearity is a function of the ratio of NMHC to NO_x and the relative abundance of various VOCs

As pointed out by Liu et al (1987), the nonlinearity of the O_3 production-NO_x dependence may have important implications for regional and global O_3 budgets Clearly, as atmospheric turbulence and advection dilute NO_x emissions, the efficiency of O_3 production will be enhanced For the United States, Liu and co workers have estimated an average summer column O_3 production rate due to the reactions involving anthropogenic NO_x and NMHCs that is 20 times larger than the downward flux from the stratosphere If the O_3 production from natural NO_x emissions is also considered, the proportion of O_3 production in the eastern and central regions of the United States that is associated with human activities amounts up to 50 to 80% These findings are supported in a recent report by Trainer et al (1987) that compared model predicted O_3 buildup with observed values at a

rural site in central Pennsylvania These authors concluded that photochemistry of NO_x, which is mainly of athropogenic origin, and isoprene from biogenic sources can lead to elevated O_3 levels

5.3 ODD NITROGEN SPECIES

Up to this point, there has been little discussion of the nitrogen containing products that are produced from NO_x in tropospheric photochemical reactions These oxidation products, which are commonly referred to as odd nitrogen species, include HNO_3, peroxynitric acid (HO_2NO_2), nitrous acid (HONO), peroxyacylnitrates ($RC(O)O_2NO_2$), dinitrogen pentoxide (N_2O_5), nitrate radical (NO_3), and organic nitrates

5.3.1 Nitric Acid

Nitric acid is a strong mineral acid that contributes to acidic deposition problems in the United States According to recent estimates, HNO_3 accounts for roughly one-third of the total acidity deposited in the eastern United States (Calvert and Stockwell, 1983) In terms of atmospheric photochemistry, HNO_3 is a major sink for active nitrogen. During the daytime hours, HNO_3 is formed by the reaction of NO_2 with the OH radical

$$NO_2 + OH + M \rightarrow HNO_3 + M \tag{5-22}$$

Equation 5-22 serves as a chain terminating step in the photochemistry that produces urban smog This is a relatively fast reaction that can produce significant amounts of HNO_3 over a period of a few hours During nighttime, the heterogenous reaction between gaseous N_2O_5 and liquid water is thought to be a source of HNO_3 The sequence of reactions that produce N_2O_5 and, subsequently, HNO_3 are as follows

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{5-23}$$

$$NO_3 + NO_2 \rightarrow N_2O_5 \tag{5-24}$$

$$N_2O_5 + H_2O \rightarrow HNO_3 \tag{5-25}$$

This pathway to HNO_3 is not viable in the daytime because the NO_3 photolyzes rapidly and, therefore, is not present in sufficient quantities to react with NO_2 The NO_3 will abstract a hydrogen atom from VOCs, aldehydes, and mercaptans, which in theory provides another nighttime source of HNO_3

$$\begin{matrix} \text{R-H} \\ \text{RC(O) -H} \\ \text{RS-H} \end{matrix} + NO_3 \rightarrow HNO_3 + \text{other products} \qquad (5\text{-}26)$$

The importance of this reaction pathway to HNO_3 is not well understood at the present time (see NO_3 discussion)

Logan (1983) has estimated a lifetime of 1 to 10 days for HNO_3 in the lower troposphere This variability results from the fact that the primary removal mechanism is deposition Kelly (1987) indicates that HNO_3 disappears faster than explained by dry deposition, and suggests that HNO_3 reactions with coarse soil particles and subsequent dry deposition may be important The loss of HNO_3 by rainout is subject to precipitation frequency, whereas the dry depositional loss varies with the surface cover and dispersion characteristics within the boundary layer Chemical destruction mechanisms for HNO_3 do exist, however, their importance is not well understood or is suspected to be minor in the lower troposphere For example, HNO_3 can be destroyed through photolysis or reaction with OH

$$HNO_3 + OH \rightarrow NO_3 + H_2O \qquad (5\text{-}27)$$

$$HNO_3 + h\nu \rightarrow NO_2 + OH \qquad (5\text{-}28)$$

Equations 5-27 and 5-28 are slow and, therefore, probably can't compete with the depositional losses of HNO_3 in the boundary layer Neutralization of HNO_3 through reaction with gaseous ammonia (NH_3) is another potential sink for HNO_3

$$HNO_3 + NH_3 \leftrightharpoons NH_4\,NO_3 \qquad (5\text{-}29)$$

The importance of Equation 5-29 as a removal mechanism for HNO_3 is not well understood The interaction with NH_3 has been reported to influence surface fluxes of HNO_3 (Huebert et al., 1988) Furthermore, it has proven difficult to separate the deposition of aerosol nitrate and ammonium ion from deposition due to HNO_3, NO_2, and NH_3 (Hanson and Lindberg, 1991)

5.3.2 Nitrous Acid

Little is known about the distribution and concentration of HONO in various ambient atmospheres. There have been a few measurements in urban environments (Harris et al , 1982). During the daytime, HONO levels are expected to be low because it photolyzes rapidly.

$$HONO + h\nu \rightarrow HO + NO \tag{5-30}$$

This reaction likely serves as a source of OH radicals during the morning in urban regions where HONO may accumulate during the nighttime hours The most likely production mechanisms for HONO include

$$HO + NO + M \rightarrow HONO + M \tag{5-31}$$

$$NO + NO_2 + H_2O \rightarrow 2HONO \tag{5-32}$$

Equation 5-31 will only lead to a buildup of HONO during the late afternoon and evening hours, when sunlight intensities are low but some OH radicals are still present Equation 5-32 can produce HONO throughout the nighttime hours The reaction probably involves a multistep sequence analogous to Equations 5-23 and 5-24 that produce HNO_3 Dinitrogen trioxide is the anhydride of HONO and reacts with liquid water to form the acid

5.3.3 Peroxynitric Acid

Although this oxidized form of HNO_3 has never been measured, it is expected to be present in the upper troposphere Models suggest concentrations in the 10 to 100 ppt range at altitudes above 6 km (Singh, 1987, Logan, 1983) Peroxynitric acid is thermally unstable,

consequently, boundary-layer concentrations are expected to be extremely low (<1 ppt) Peroxynitric acid is formed through the combination of a HO_2 radical with NO_2

$$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M \tag{5-33}$$

In the upper troposphere, HO_2NO_2 is destroyed by photolysis or by reaction with OH

$$HO_2NO_2 + h\nu \rightarrow HO_2 + NO_2 \tag{5-34}$$

$$HO_2NO_2 + OH \rightarrow \text{products} \tag{5-35}$$

5.3.4 Peroxyacylnitrates

Peroxyacetylnitrate is the most abundant of this family of nitrates The next higher homolog, peroxypropionyl nitrate (PPN), is generally less than 10% of the PAN concentration, with higher molecular weight species such as peroxybenzoyl nitrate expected to be present at even lower levels Peroxyacetylnitrate is the only member of this family of compounds that has been extensively studied It is a strong oxidant and, therefore, can have adverse effects on human health and can cause plant damage if ambient concentrations become high enough Of greatest interest to this chapter is the role PAN plays in atmospheric chemistry Based on its primary means of formation,

$$CH_3C(O)OO + NO_2 \rightarrow CH_3C(O)O_2NO_2, \tag{5-36}$$

it might be expected that PAN would serve as a sink for oxides of nitrogen This is not true, however, because PAN is thermally unstable and is much more likely to produce NO_2 through the reverse of Equation 5-36 than to be removed by depositional process If the lifetime of PAN was determined by its thermal decomposition, the lifetime would be approximately 1 h at 25 °C, 2 days at 0 °C, 5 mo at −23 °C, and 42 years at −43 °C Based on these estimated lifetimes, it was suggested that PAN could be the principal form of reactive nitrogen in the upper troposphere (Singh and Hanst, 1981) In reality, because PAN reacts with OH radical and photolyzes, its mean lifetime cannot exceed 3 mo

$$CH_3C(O)O_2NO_2 + h\nu \rightarrow \text{products} \quad (5\text{-}37)$$

$$CH_3C(O)O_2NO_2 + OH \rightarrow \text{products} \quad (5\text{-}38)$$

Equations 5-37 and 5-38 are slow compared to the thermal degradation of PAN at temperatures above 0 °C and, therefore, are unimportant in determining the summertime boundary-layer fate of this reactive nitrogen compound

There is no question that PAN can serve as a storage reservoir for NO_2 In the summertime boundary layer, PAN concentrations will be decreased somewhat by dry depositional losses over land (deposition velocity of approximately 0 25 cm/s), but it is very likely that a significant fraction of the PAN produced in urban plumes can be transported into the regional environment For example, PAN lifetimes of about 5 and 20 h have been calculated at 20 and 10 °C, respectively In transport layers above a nighttime surface inversion, PAN could be transported several hundred kilometers Even during transport conditions where mixing occurs down to the surface, PAN is expected to persist because it is continually being produced

5.3.5 Nitrate Radical

The NO_3 radical is a short-lived oxide of nitrogen that is formed by the reaction of NO_2 with O_3

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (5\text{-}39)$$

Other sources of NO_3 exist (Wayne et al , 1991), however, Equations 5-3 to 5-39 serve as the primary tropospheric production mechanism for NO_3 Photolysis of NO_3 is rapid, resulting in a lifetime of about 5 s at midday Furthermore, NO_3 reacts rapidly with NO, which limits its lifetime both during the daylight and nighttime hours At NO concentrations of 320 pptv, the lifetime of NO_3 due to reaction with NO is similar to that for photolysis ($\approx$5 s) Thus, in urban regions where NO concentrations normally exceed 300 pptv, the reaction with NO will control the NO_3 lifetime

At night, NO_3 concentrations on the order of 0 3 ppt have been measured in clean tropospheric air, with recorded levels ranging up to 430 ppt in urban areas (Wayne et al ,

1991) After sunset, the buildup of NO_3 is expected to be controlled by the availability of NO_2 and O_3 plus the main chemical destruction mechanisms

$$NO_3 + NO_2 \rightarrow NO + NO_2 + O_2 \quad (5\text{-}40)$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \quad (5\text{-}24)$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \quad (5\text{-}25)$$

In clean background environments, it has been reported that measured NO_3 levels are significantly less than predicted from a consideration of Equations 5-39, 5-40, 5-24, and 5-25 alone This implies that some additional loss mechanism must be occurring Speculation has centered around four different loss processes (Platt et al , 1981, Noxon et al , 1980)

(1) heteorogenous losses of NO_3 and/or N_2O_5 on particle surfaces,
(2) reactions with water vapor,
(3) reaction of NO_3 with NO, and
(4) NO_3 reaction with organic compounds

Based on modeling results, Heikes and Thompson (1983) suggest that the low NO_3 concentrations could result from the reaction of NO_3 with NO, provided sufficient quantities of NO are present at night In the absence of NO, heterogenous loss of NO_3 and N_2O_5 could account for lower than expected NO_3 levels, provided that their sticking coefficients are greater than 10^{-3}

Wayne et al (1991) have studied the nighttime chemistry of NO_3 and conclude that simple analyses are useful, but generally insufficient for interpreting NO_3 behavior They suggest that a numerical simulation is required in order to accurately assess NO_3 observations in individual data sets Perner et al (1991) have conducted such a modeling exercise, and their results suggest that nighttime concentrations of NO_3 can be reduced by the presence of naturally emitted monoterpene Thus, in regions when reactive organic compounds are present in nighttime air masses, lower than anticipated NO_3 concentrations may be due to scavenging by organic species

Reactions of NO_3 with organic species have garnered considerable interest in recent years. Kinetic studies have shown NO_3 to be very reactive toward a variety of organic compounds. For example, at NO_3 levels of approximately 100 ppt, the lifetime of monoterpene VOCs due to NO_3 oxidation will be less than 10 min This, then, might be an important nighttime sink for both biogenic VOCs and the NO_3 radical (Winer et al , 1984) At this time, little is known about the mechanisms or products that result from the reaction of organics with NO_3. It is expected that hydrogen abstraction reactions will yield HNO_3 and organic radicals.

$$\text{R-H} + NO_3 \rightarrow HNO_3 + RO_2 \qquad (5\text{-}26)$$

$$\text{RCHO} + NO_3 \rightarrow HNO_3 + \text{RCO} \qquad (5\text{-}26)$$

With olefinic or aromatic VOCs, organic nitrates are expected to predominate

$$\text{R-CH} = CH_2 + NO_3 \rightarrow \text{RCH-}CH_2ONO_2 \rightarrow \text{products} \qquad (5\text{-}41)$$

$$\text{Ar-OH} + NO_3 \rightarrow \text{ArO} + HNO_3 \rightarrow \text{Ar(OH)}NO_2 \qquad (5\text{-}42)$$

5.3.6 Dinitrogen Pentoxide

Dinitrogen pentoxide is the anhydride of HNO_3 As indicated in the previous section, it is formed from NO_3 and NO_2 Because NO_3 is present only at night, N_2O_5 is primarily a nighttime species as well and is thermally unstable, decomposing to NO_3 and NO_2 At high altitudes in the troposphere, where temperatures are low, N_2O_5 can act as a temporary reservoir for NO_3 Dinitrogen pentoxide photolyzes at wavelengths less than 330 mm to give, once again, NO_3 and NO_2 This provides the major source of NO_3 production in the stratosphere

Dinitrogen pentoxide reacts heterogeneously with water on the surface of hydrometers to form HNO_3. This serves as the main nighttime production mechanism for HNO_3, and because HNO_3 is readily deposited by dry and wet deposition, it provides an important mechanism for removal of NO_x from the atmosphere The importance of the gas-phase reaction between N_2O_5 and water vapor is not well understood (Logan, 1983)

$$N_2O_5 + H_2O(g) \rightarrow 2HNO_3 \quad (5\text{-}43)$$

An upper limit of 13 to 21 cm^3/molecule/s has been reported for the rate coefficient (Tuazon et al , 1983) Wayne et al (1991) has pointed out that even with this low rate coefficient, the gas-phase reaction of N_2O_5 and water vapor could contribute significantly to the atmospheric formation of HNO_3 However, until the rate constant is established with greater certainty, the prominence of this reaction as a source of HNO_3 will remain obscure There are a few reports of N_2O_5 reacting with aromatic VOCs such as naphthalene and pyrene (Pitts et al , 1985, Atkinson et al , 1986), and nitroarenes appear to be the product of the reaction

5.3.7 Total Reactive Odd Nitrogen Species

The total reactive odd nitrogen species are referred to as NO_y It is expected that NO, NO_2, PAN, and HNO_3 comprise the bulk of the NO_y present in the ambient atmosphere This has been tested by measuring these individual compounds at the same time as a total NO_y measurement is performed (Fahey et al , 1986) The sum of the individual species should equal the NO_y concentration if NO, NO_2, HNO_3, and PAN are the only nitrogen compounds present Figure 5-11 shows a plot of the $(NO_y)_i/NO_y$ ratio versus NO_y, $(NO_y)_i$ is the sum of measured odd nitrogen compounds A ratio of 1 0 implies that the sum of the individual species is equal to the total NO_y These all were summertime measurements at Point Arena on the California coast, Niwot Ridge in Colorado, and Scotia Range in central Pennsylvania Both at the Point Arena and Niwot sites, there is a significant odd nitrogen shortfall Approximately 45% of the odd nitrogen species are unaccounted for at the Niwot site During the winter months, the $(NO_y)_i$ shortfall is not nearly as large ($\approx$5%), which implies that the unknown component is most likely photochemically produced Organic nitrates, in particular methyl nitrate and higher homologs of PAN, have been suggested as the missing component Calvert and Madronich (1987) have recently reported that organic nitrates should be important products of photochemistry Although the importance of the organic nitrates is recognized, evidence for their existence in the atmosphere is sparse and often only circumstantial Therefore, it is unknown whether or not they constitute the missing NO_y fraction at Niwot Ridge and elsewhere

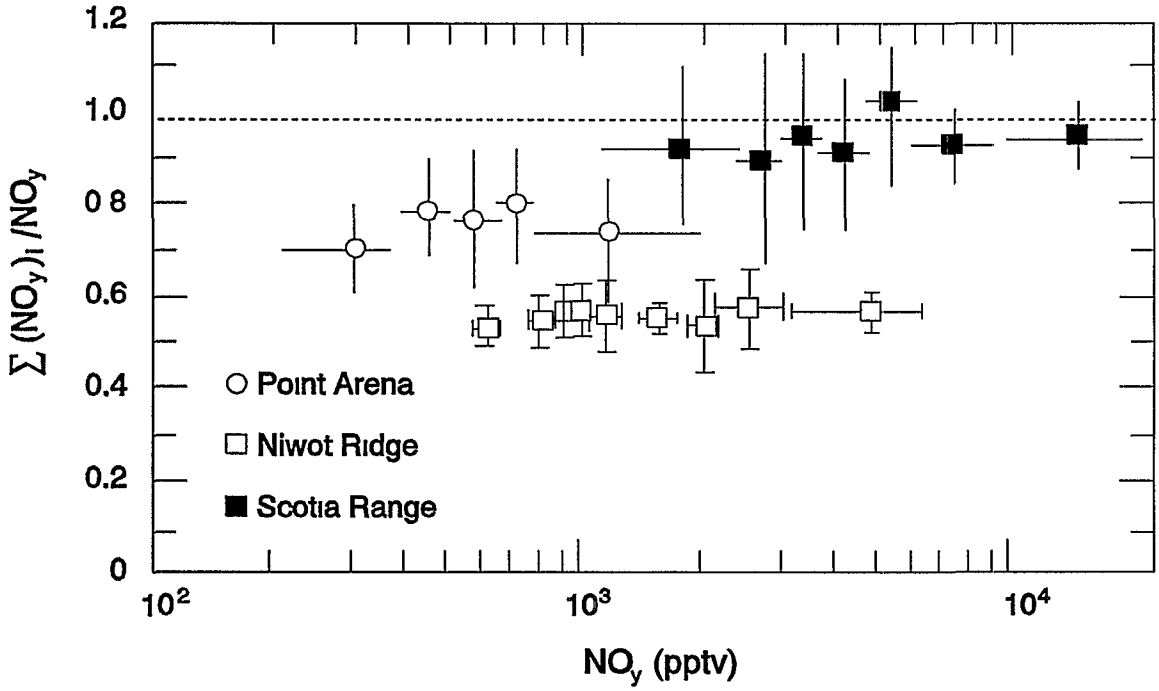


Figure 5-11. Total reactive odd nitrogen species shortfall.

Source Fahey et al (1986)

5.3.8 Amines, Nitrosamines, and Nitramines

The concentration of amines in the atmosphere is thought to be low, although there are few data available to confirm this hypothesis The highest concentrations would be expected in the vicinity of various sources (e g , cattle feed lots, sewage treatment facilities, waste incinerators, industrial plants) that utilize or produce amines

Nitrosamines and nitramines are produced in the troposphere through photochemical reactions involving alkyl amines and the oxides of nitrogen (NO and NO_2) Because both nitrosamines and nitramines have proven to be carcinogenic in animals, considerable interest has centered around the tropospheric sources and distribution of these organonitrogen compounds. In the preceeding NO_x Criteria Document (U S Environmental Protection Agency, 1982), three chemical mechanisms were described for the formation of nitrosamines in the atmosphere

(1) reaction of gaseous amines with NO_x and HONO (nonphotochemical),

(2) photochemical reactions of amines with NO_x in the gas phase, and

(3) heterogenous formation processes involving atmospheric aerosols

All three of these pathways involve reactions of amines with the oxides of nitrogen and/or HNO_3 The dark reaction (nonphotochemical) and heterogenous mechanism are poorly understood In the former case, there are conflicting reports concerning reaction rates and yields of nitrosamine products formed It is quite likely that at least part of the dark Equations 5-32 and 5-44 that are believed to convert amines to nitrosamines occur on the walls of chambers used to study these processes (Finlayson-Pitts and Pitts, 1986)

$$NO + NO_2 + H_2O \rightarrow 2HONO \qquad (5\text{-}32)$$

$$R_2NH + HONO \rightarrow R_2NNO + H_2O \qquad (5\text{-}44)$$

Therefore, caution must be exercised when extrapolating laboratory smog chamber studies to the real atmosphere Laboratory studies conducted in the late 1970s (Hanst et al , 1977, Grosjean et al., 1978, Pitts et al , 1978) indicated low yields (3%) of nitrosamine production in the dark If this is true, boundary layer concentrations of nitrosamines should be low during the nighttime hours

Because there do not appear to be any recent studies that clarify the nonphotochemical conversion of amines to nitrosamines, the reader is referred to the 1982 NO_x Criteria Document for a more thorough discussion of this subject

As is the case with most heterogenous chemical transformations in the atmosphere, nitrosation in aerosols is highly speculative The absorption of basic amines by acidic aerosol droplets followed by reaction with nitrite, HONO, or other species could, theoretically, lead to the formation of nitrosamines (U S Environmental Protection Agency, 1976) Whether or not the nitrosamines so produced could withstand photodecomposition and/or further oxidation is unknown

There is good evidence that photolysis of gaseous amines in the presence of NO_x will produce nitrosamines and nitramines Figure 5-12 shows the concentration time profiles for diethylnitrosamine in photooxidation experiments involving diethyl- and triethylamine in the presence of NO and NO_2 Diethylnitrosamine appears shortly after the reactants are mixed in a darkened chamber This is presumably due to the dark Equations 5-32 and 5-44 discussed previously The diethylnitrosamine that formed in the dark rapidly decayed, although there was clearly additional generation of this compound from triethylamine followed by its decomposition after continued photolysis Pitts et al (1978) derived the following sequence of reactions to explain the photochemical transformations

$$(C_2H_5)_3N + OH \rightarrow (C_2H_5)_2NCHCH_3 + H_2O$$

$$\downarrow O_2$$

$$\downarrow (NO \rightarrow NO_2)$$

$$HO_2 + (C_2H_5)_2NC(O)\text{-}CH_3 \xleftarrow{O_2} (C_2H_5)_2NC(O)HCH_3 \rightarrow (C_2H_5)_2NCHO + CH_3\cdot$$

$$\downarrow$$

$$CH_3CHO + (C_2H_5)_2N \xrightarrow{NO_2} (C_2H_5)_2NNO_2$$

$$\downarrow NO$$

$$(C_2H_5)_2NNO$$

In the case of diethylamine, hydrogen abstraction can occur from the nitrogen as well This probably accounts for the significantly higher yield of nitramines observed from secondary amines compared to tertiary amines

$$R_2NH + OH \rightarrow R_2N + H_2O \qquad (5\text{-}45)$$

$$R_2N + NO_2 \rightarrow R_2NNO_2 \qquad (5\text{-}46)$$

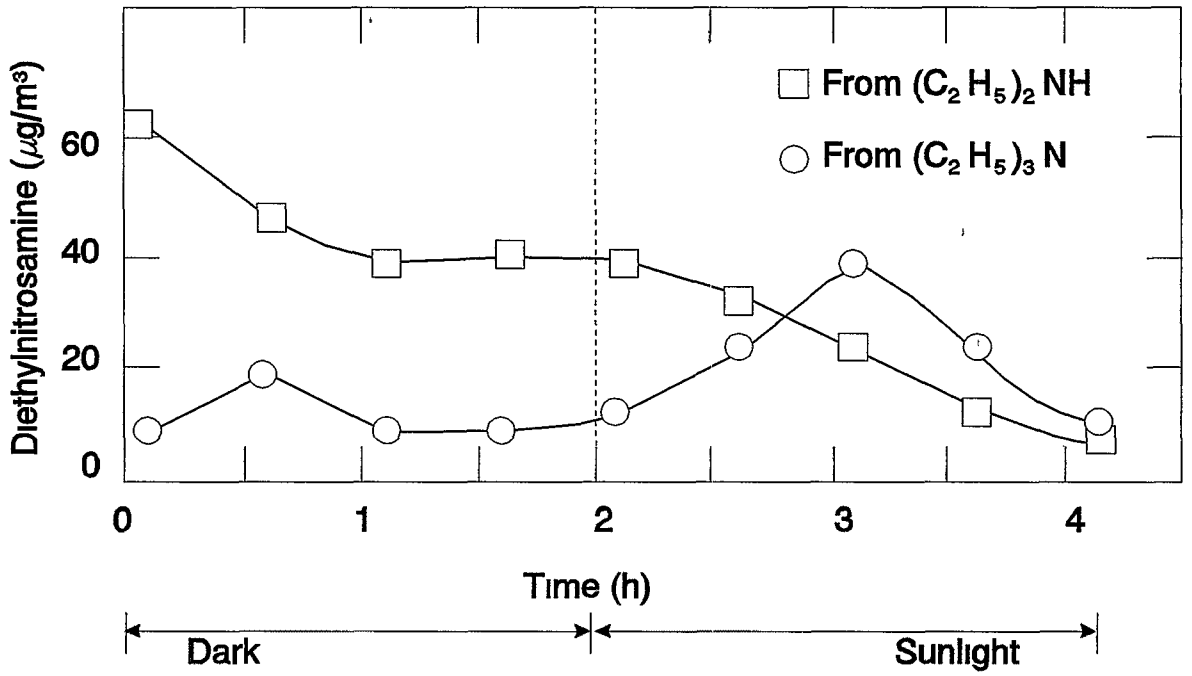


Figure 5-12. Formation and decay of diethylnitrosamine in the dark and in the sunlight from diethylamine (open squares) and from triethylamine (open circles).

Source U S Environmental Protection Agency (1982)

In the case of diethylamine, hydrogen abstraction can occur from the nitrogen as well This probably accounts for the significantly higher yield of nitramines observed from secondary amines compared to tertiary amines.

The nitrosamines and nitramines have limited lifetimes in the atmosphere due to photolytic decomposition and/or reactions with OH radical and O_3 Nitrosamines absorb light in the ultraviolet region (325 to 375 mm) efficiently and are rapidly photolyzed Tuazon et al (1984) estimated that dimethylnitrosamine has a half-life of about 5 min at Los Angeles latitudes during the midsummer daytime Photolysis will control the fate of nitrosamines in the troposphere because the reactions with OH and O_3 are relatively slow (Tuazon et al , 1984) The lifetime of dimethylnitrosamine due to reaction with OH ([OH] = 1×10^6 cm^{-3}) has been estimated to be 4 days If the reaction with O_3 was the lifetime determining process at 100 ppb O_3, the lifetime of dimethylnitrosamine would exceed 1 year

The situation is somewhat different with nitramines They have low light absorption cross sections and do not photolyze readily Nitramines react very slowly with O_3 (lifetime of dimethylnitramine $\approx$4 years) but will be removed from the atmosphere through reaction with OH radical For example, the estimated lifetime for dimethylnitramine is about 3 days at an OH concentration of 1×10^6 cm^{-3} (Tuazon et al , 1984) Little is known about the mechanism or products formed in the reaction of nitramines with OH

5.4 TRANSPORT

The transport and dispersion of the various odd nitrogen species are dependent on both meteorological and chemical parameters Advection, diffusion, deposition, and chemical transformations combine to dictate the atmospheric residence time of a particular trace gas Nitrogenous species that undergo slow chemical changes in the troposphere, and are not readily removed by depositional processes, can have atmospheric lifetimes of several months Gases with lifetimes on the order of months can be dispersed over continental scales and possibly even over an entire hemisphere At the other extreme are gases that undergo rapid chemical transformation and/or depositional losses that limit their atmospheric residence times to a few hours or less Dispersion of these short-lived species may be limited to only a few kilometers from their point of emission

Surface emissions are dispersed vertically and horizontally through the atmosphere by turbulent mixing processes that are dependent to a large extent on the vertical temperature structure and wind speed On the vertical scale, transport can occur in three separate layers

(1) The daytime and/or nighttime mixed layer—this layer can extend from the surface up to a few hundred meters at night or several thousand meters during the daytime

(2) A layer that exists during the nighttime above a low level surface inversion and below the daytime mixing height—this layer will generally fall in the 200 to 2,000 m altitude (above ground level) band

(3) The free troposphere—this transport zone is above the boundary layer mixing region

During the warm, summertime period when the impact of reactive nitrogen species is the greatest, vertical mixing follows a fairly predictable diurnal cycle A surface inversion normally develops during the evening hours and persists throughout the nighttime and morning period, until broken by surface heating While the inversion is in place, surface NO_x emissions can lead to relatively high, local concentrations because of the restricted vertical dispersion Following the breakup of a nighttime surface inversion, vertical mixing will increase and surface-based emissions will disperse to higher altitudes The extent of vertical mixing during the daytime is often controlled by synoptic weather features. Elevated temperature inversions associated with high pressure systems are common in many parts of the United States An elevated inversion in the Los Angeles Basin traps pollutants in the lower 600 m of the atmosphere In the midwestern and northeastern regions of the United States, summertime afternoon mixing levels normally range between 1,600 and 1,800 m (Holzworth, 1967) Horizontal dispersion of trace gases in the mixing layer is caused by horizontal turbulence and vertical wind shear For mesoscale and synoptic scale transport, mean wind shear is the dominant cause for dispersion

The dispersion processes described above coupled with chemical transformations of a particular reactive nitrogen compound dictate transport distances in the troposphere A reasonable understanding exists concerning the short-term (daylight hours) fate of NO_x emitted in urban areas during the morning hours As described in detail in Section 5 2 1, NO_x emitted in the early morning hours in an urban area will disperse vertically and move downwind as the day progresses On sunny summer days, most of the NO_x will have been converted to HNO_3 and PAN by sunset Much of the HNO_3 will be removed by depositional processes as the air mass moves along After dusk, an upper portion of the daytime mixed layer will be decoupled from the surface due to formation of a low-level radiation inversion Transport will continue in this upper level during the nighttime hours and although photochemical processes will cease, other dark phase chemical reactions can proceed There are no reports of plume measurement studies that have tracked plumes for more than one daylight period Thus, nothing is known concerning the fate of the remaining nitrogenous species that become entrapped in the layer above the nighttime surface inversion and below a higher subsidence inversion Peroxyacetylnitrate and HNO_3, if carried along in this layer, could be transported long distances

5.4.1 Transport of Reactive Nitrogen Species in Urban Plumes

The most extensive studies of the fate of nitrogen species in urban plumes have been reported by Spicer and co-workers They have examined the behavior of reactive nitrogen compounds in plumes emanating from Los Angeles, CA (Spicer et al , 1979), Phoenix, AZ (Spicer et al , 1978); Boston, MA (Spicer, 1982a), and Philadelphia, PA (Spicer and Sverdrup, 1981). The nitrogen budget derived from Boston plume measurements provides a good example of the fate of reactive nitrogen compounds in urban plumes Nitrogen oxides concentrations at short distances from Boston varied from about 30 to 130 ppb After travel times of 4 to 7 h, NO_x concentrations in the plume were in the 5- to 10-ppb range Removal rates of NO_x were calculated from measured NO_x, PAN, and HNO_3 concentrations Dilution effects were accounted for by using tracers of opportunity such as CO, acetylene, and trichloroflurometh ane The plume was monitored by aircraft to distances as far as 150 km east of Boston This corresponded to reaction times of as much as 7 5 h The NO_x removal rate ranged from 0 14 to 0 24 h^{-1} for four different days This corresponds to NO_x lifetimes (1/removal rate) of 4 2 to 7 1 h (Altshuller, 1986) These lifetimes apply to sunny, summertime, moderately polluted plume conditions with transport mainly over water Nitrogen oxides depositional losses during over-water transport should be very small In the Boston plume, the chemical loss of NO_x is equal to the appearance of nitrate products (HNO_3, PAN, and NO_3) On an August 18, 1978, flight, an overall NO_x loss rate of 0.24 h^{-1} was obtained During the same measurement period, a value of 0 23 h^{-1} was calculated for the conversion rate of NO_x to nitrate products

Somewhat lower NO_x loss rates have been reported from data collected in Los Angeles (Chang et al , 1979). Chang and coworkers derived a value of 0 04 h^{-1} as a lower limit for the yearly average daytime NO_x removal rate Calvert (1976) estimated the NO_x removal rate to be approximately 0 09 h^{-1} during the midmorning to early afternoon hours It has been suggested that the values derived from Los Angeles data probably represent only a portion of the true NO_x loss rate because of NO_x measurement interferences by HNO_3 and PAN. However, the 0 09 h^{-1} value derived by Calvert agrees well with recent estimates in the Detroit metropolitan area (Kelly, 1987) Using a combination of captive outdoor irradiation experiments, photochemical modeling, and ambient measurements, Kelly obtained an NO_x removal rate of approximately 0 1 h^{-1} It was determined that HNO_3 accounted for

67 to 84% of the nitrogen-containing products This led to the conclusion that HNO_3 formation will control the chemical lifetime of NO_x on photochemically active days

Based on a calculated formation rate of HNO_3, Kelly was able to estimate the expected ambient HNO_3 concentrations in the Detroit plume The predicted concentrations always exceeded the measured ambient HNO_3 concentrations by a significant amount (3 to 4 times) In order to reconcile this difference, Kelly hypothesized that once formed, HNO_3 was rapidly removed from the urban plume Several removal mechanisms were considered, with incorporation into coarse atmospheric aerosol deemed to be most likely Based on Kelly's analysis, approximately 70% of the gaseous NO_x in Detroit's morning atmosphere is photochemically converted to products by sundown In the absence of sinks, the product distribution would be $\approx$75% HNO_3, $\approx$20% PAN, and the remaining 5% as other organic nitrates However, removal of HNO_3 as coarse nitrate leads to a maximum HNO_3 concentration that is only 20 to 30% of that expected in the absence of the aerosol sink Because the coarse nitrate aerosol is quickly removed by sedimentation, the majority of the nitrogen-containing species emitted and produced in the Detroit urban area are not transported long distances downwind

It should be kept in mind that the studies just described in Boston, Los Angeles, and Detroit addressed only the daytime fate of reactive nitrogen species The nighttime chemistry of odd nitrogen compounds in urban environs is poorly understood Nighttime emissions of NO will react with O_3 to produce NO_2 as long as there is sufficient O_3 present Often the O_3 reservior that exists aloft over urban areas is decoupled from the surface layer at night by a low-level radiation inversion Under these conditions, the O_3 supply is not replenished, and once it has been used up, NO will no longer be oxidized to NO_2 via reaction with O_3 As described earlier, during nighttime periods when O_3 is present, it can react with NO_2 to form NO_3 The NO_3 radical is very reactive, consequently, its concentration remains low ($\approx$1 to 500 ppt) It reacts rapidly with NO so as the night progresses and NO levels increase, NO_3 concentrations will fall

$$NO_3 + NO \rightarrow 2NO_2 \qquad (5\text{-}47)$$

Other sinks for NO_3 include the reactions with organic species (Equations 5-26, 5-41, and 5-42) and NO_2, which produces N_2O_5 (Equation 5-24) The N_2O_5 will react with water to form HNO_3 (Equation 5-25). It can also react with VOCs, which may produce significant quantities of nitro-substituted polycyclic aromatics (Pitts, 1987)

Chemical models have been employed to try to sort out the nighttime NO_x chemistry (Stockwell and Calvert, 1983, Jones and Seinfeld, 1983, Russell et al , 1985) Russell et al (1985) were able to get reasonable agreement between predicted and measured time profiles of NO_3, NO_2, and O_3 during nighttime hours in the Los Angeles Basin The reactions of importance to nighttime chemistry and the rate constants as employed in the Russell et al model are listed in Table 5-1 In order to accurately model this nighttime NO_x chemistry, atmospheric concentrations of NO, NO_2, NO_3, O_3, water vapor, and organic species must be known. In addition, meteorological factors (such as mixing conditions, temperature, etc) are important An entire data set such as this is not currently available for modeling purposes Consequently, concentrations must be estimated for unmeasured species From the rate constants shown in Table 5-1, it is obvious that NO can play a very critical role in nighttime chemistry. Nitric oxide very rapidly scavenges NO_3 For example, Russell et al calculated an NO_3 concentration of 12 ppt in the Los Angeles surface layer when 1 ppb NO is present and over 200 ppt NO_3 when NO is negligible Dinitrogen pentoxide is another species that can significantly influence nighttime chemistry The magnitudes of the various N_2O_5 loss processes (see Table 5-1) are not well understood Due to the transient character of N_2O_5, it has been difficult to determine the homogenous gas-phase reaction rate constant with water vapor, the deposition velocity, and heterogenous interactions with ambient particulate matter

5.4.2 Transport and Chemistry in Combustion Plumes

Interest in the NO_x chemistry of power plant plumes increased significantly following the 1974 report by Davis et al that O_3 could be generated through a series of reactions involving sulfur and nitrogen constituents within this type of plume In subsequent studies, it was pointed out that the well-known photochemical reactions involving oxides of nitrogen and VOCs are the more likely mechanisms of O_3 buildup in power-plant plumes (Miller et al., 1978). Because the VOC to NO_x ratio in these plumes is very low, the VOCs must

TABLE 5-1. MAJOR REACTIONS IN THE NITRATE RADICAL-DINITROGEN PENTOXIDE SYSTEM AT NIGHT

Reaction	Rate Constant 298 K (ppm min units)	Reference and Comments[a]
$NO_2 + O_3 \xrightarrow{7} NO_3 + O_2$	$k_7 = 0\ 05$	1
$NO + NO_3 \xrightarrow{8} 2NO_2$	$k_8 = 29560$	1
$NO_2 + NO_3 \xrightarrow{44} N_2O_5$	$k_{44} = 2510$	2
$N_2O_5 \xrightarrow{45} NO_2 + NO_3$	$k_{45} = 2\ 9$	1, 3
$N_2O_5 + H_2O \xrightarrow{46} 2HNO_3$	$k_{46} = 1\ 9 \times 10^{-6}$	4
$NO_3 + HCHO \xrightarrow{53} HNO_3 + HO_2 + CO$	$k_{53} = 0\ 86$	5
$NO_3 + RCHO \xrightarrow{54} RCO_3 + HNO_3$	$k_{54} = 3\ 6$	5, 6
$NO_3 + OLE \xrightarrow{56} RPN$	$k_{56} = 12\ 4$	5, 7, 8, 9
$NO_2 + NO_3 \xrightarrow{57} NO + NO_2 + O_2$	$k_{57} = 0\ 59$	10
N_2O_5 + aerosol $\rightarrow 2HNO_3$	$k^*_{N_2O_5}$	11
NO_3 + aerosol $\rightarrow$ aerosol	$k^*_{NO_3}$	11

[a](1) Baulch et al (1982), (2) Tuazon et al (1984), (3) Malko and Troe (1982), (4) Tuazon et al (1983), (5) Atkinson and Lloyd (1984), (6) the rate constant used for the NO_3 reaction with high aldehydes is that measured for acetaldehyde, (7) the value used for the rate constant of the NO_3 reaction with olefins is that measured for the nitrate radical reaction with propene, (8) the ultimate products of reaction (56) are reported to be nitroxyperoxyalkyl nitrates and dinitrates (Bandow et al , 1980), (9) Bandow et al (1980), (10) Atkinson and Lloyd (1984), (11) Russell et al (1985)

Source Russell et al (1985)

be mixed into the power-plant plume as it moves downwind Excess O_3 concentrations of 20 to 50 ppb above ambient have been reported in plumes after several hours of downwind transport However, an O_3 buildup is not found in all power-plant plumes (Hegg et al , 1977, Ogren et al , 1977, White, 1977) The single most important ingredient appears to be the availability of reactive VOCs in the dilution air Aircraft measurements have shown little enhancement of inorganic and particulate nitrate concentrations in power-plant plumes (Hegg and Hobbs, 1979)

Due to the difficulties associated with tracking and making accurate measurements in a narrow power-plant plume, little information is available concerning the fate of reactive nitrogen species in these plumes Hegg et al (1977) have reported measurements in four different NO_x-rich power-plant plumes Out to distances of 90 km and travel times up to 4 h, no O_3 enhancements were observed in any of these plumes Measured NO_2/NO ratios in these plumes were generally in the 1 to 2 range This is considerably below the value of 10, which has been shown in laboratory experiments to be the minimum ratio at which appreciable O_3 generation can occur As a consequence, smog chamber and modeling studies have been employed to study NO_x transformation rates Smog chamber experiments under a variety of conditions expected in real atmospheres yield NO_x lifetimes varying from about 1 to 7 h (Spicer et al , 1981) The fastest conversion times were observed when VOC to NO_x ratios were high (≈ 15) and the VOC mix included those species typically found in urban atmospheres Nitric acid and PAN were the major nitrogen-containing products observed in the chamber reactions Generally, they accounted for between 70 and 90% of the nitrogenous species present at the end of the final irradiation period The PAN/HNO_3 ratio varied depending on the initial VOC to NO_x ratio Less PAN was produced in cases where organic levels were initially low

The smog chamber studies imply that the NO_x lifetime in a power-plant plume can vary from a few hours to more than a day, depending on environmental conditions Under conditions of low VOC levels (e g , rural areas or aloft above a surface inversion), the NO_x lifetime will be sufficiently long to allow NO_x input to regional air masses

5.4.3 Regional Transport

Transport of reactive nitrogen species in regional air masses can involve several mechanisms Mesoscale phenomena such as land-sea breeze circulations or mountain-valley wind flows will transport pollutants over distances of tens to hundreds of kilometers On a larger scale, synoptic weather systems such as the migratory highs that cross the eastern United States in the summertime influence air quality over many hundreds of kilometers The accumulation and fate of nitrogen compounds will differ somewhat between the mesoscale and synoptic systems Mountain-valley and land-water transport mechanisms have dual temporal scales due to their dependence on solar heating However, in the larger scale

synoptic systems, reactive nitrogen species can build up over multiday periods The residence time of air parcels within a slow moving high-pressure system can be as long as 6 days (Vukovich et al , 1977)

In many cases, the transport mechanisms mentioned above are interrelated For example, slow-moving high-pressure systems that migrate across the eastern United States are characterized by weak pressure gradients Thus, mountain-valley or land-water breezes can dictate pollutant transport in the immediate vicinity of sources, but the eventual fate of reactive nitrogen species will be distribution into the synoptic system

Combined studies of air quality and meteorology along the western shore of Lake Michigan have clearly documented this relationship (Lyons and Cole, 1976, Westberg et al , 1981) Data shown in Table 5-2 and Figure 5-13 were collected near Kenosha, WI, during the period August 14 to 22, 1976 During this time, a strong, slow-moving high-pressure system traveled across the Great Lakes Region Degradation of air quality in southeastern Wisconsin was clearly associated with both synoptic transport and mesoscale (lake breeze) advection during this 9-day period August 14 was the first day during which the effects of the advancing high-pressure system were observed in southeastern Wisconsin Northerly flow associated with the leading edge of the anticyclone persisted through August 16 As can be seen in Table 5-2, pollutant levels were low during that period with northerly winds. From August 18 to 22, however, meteorology along the western shore of Lake Michigan was controlled by synoptic features characteristic of the trailing edge of an anticyclone and the local lake-breeze phenomenon Thus, gradient winds were from the southwest, but during the afternoon hours, a shift to southeasterly flow occurred as the lake-breeze front moved inland Figure 5-13 shows pollutant profiles recorded about 5 mi inland on the afternoons of August 18 and 19 Pollutant levels increased dramatically following passage of the lake-breeze front on both of these days These high pollutant levels were most likely the result of emissions from the Chicago-Hammond-Gary urban complex During the night and early morning hours, the plume from this industrial region drifts in a northerly direction over the lake Morning sunlight serves to initiate photochemical processes in the contaminated air mass over Lake Michigan High levels of secondary pollutants such as O_3 and NO_2 developed by early afternoon, when the air mass is transported onshore by the lake-breeze

TABLE 5-2. AVERAGE AFTERNOON BACKGROUND POLLUTANT CONCENTRATIONS MEASURED AT KENOSHA, WISCONSIN

	O_3 (ppb)	NO (ppb)	NO_2 (ppb)	NMTHC (ppbC)	CO (ppm)	$CFCl_3$ (ppt)
North wind	37	2	3	123	0 4	163
South wind	94	3	7	213	0 6	229

Source Westberg et al (1981)

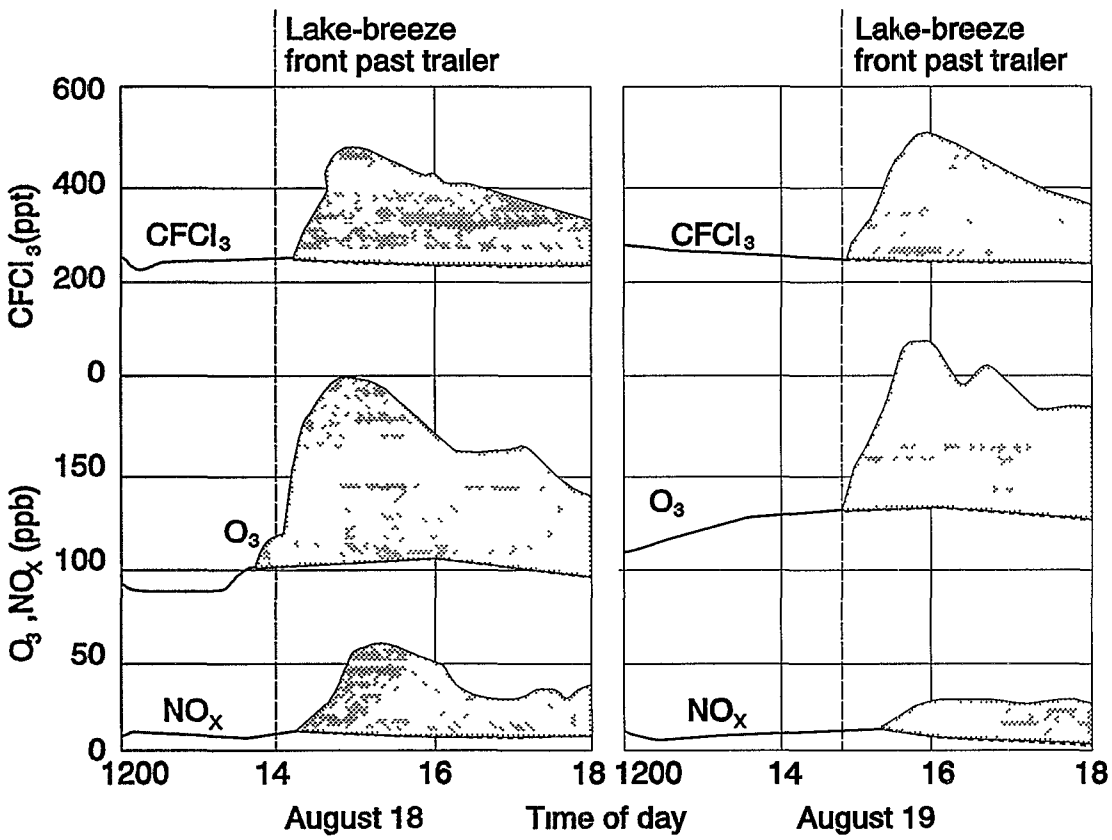


Figure 5-13. Pollutant levels at the Kenosha, WI, sampling site before and after passage of the lake-breeze front.

Source· Westberg et al (1981)

The pollutants associated with the local, mesoscale lake-breeze system certainly get incorporated into the larger scale synoptic circulation and contribute to the increased levels associated with southwesterly flow (see Table 5-2) The distribution of odd nitrogen species within these anticyclones will depend on rates of chemical conversion and deposition

The studies just described provide little detailed information about oxides of nitrogen behavior under various regional transport scenarios At the time those studies were conducted, sophisticated NO_x and NO_y monitoring instrumentation was not generally available Consequently, we only know that NO_x levels were near the detection limit of the instrumentation ($\approx$1 to 2 ppb) in synoptic air masses advected into the United States from Canada and that NO_x concentrations increased significantly after a period of residence over industrialized regions of the United States The composition of odd nitrogen species in the aged air mass is not well known However, more recent studies may be able to provide better insight into oxides of nitrogen chemistry in regional air masses (Fahey et al , 1986; Luke and Dickerson, 1987) For example, Luke and Dickerson (1987) have reported NO_x and NO_y measurements off the east coast of the United States They subdivided the atmosphere along their flight tracks into two-dimensional boxes and calculated the flux of nitrogen species through each box A calculated gross nitrogen flux of 0 5 Tg/year was derived using this methodology Luke and Dickerson emphasize that the 0 5 Tg/year flux should be viewed with caution because it results from the combination of an annually averaged wind field and an NO_y data base of limited time resolution Sampling flights were conducted during the period January 3 to 11, 1986

Even though the Luke and Dickerson flux number is subject to considerable uncertainty, it is interesting to compare it to earlier flux estimates that were derived by less direct methods Logan (1983) calculated a nitrogen flux of 1 7 Tg/year by balancing the regional nitrogen budget of eastern North America Galloway et al (1984) estimated that 1 1 to 3 2 Tg/year are transported eastward off the Atlantic coast More recently, Galloway and Whelpdale (1987) have reduced their flux estimate downward to 0 8 to 1 2 Tg/year This flux corresponds to approximately 25% of the NO_x emitted to the atmosphere of eastern North America based on Logan's (1983) NO_x emission estimate of 4 5 Tg nitrogen/year

5.5 OXIDES OF NITROGEN AND THE GREENHOUSE EFFECT

The oxygenated nitrogen species typically assumed to comprise the NO_x and NO_y families, as discussed in previous sections of this chapter, do not absorb infrared radiation, and, therefore, do not contribute to direct radiative "greenhouse" forcing Nitrogen dioxide is an efficient absorber of visible radiation, and it has been proposed as a possible source of additional climatic influences, assuming atmospheric concentrations were to become sufficiently large (Wuebbles, 1989) The previously described NO_x species can, however, contribute indirectly to the greenhouse process through the photochemical production of O_3, a known greenhouse gas Additionally, nitrous oxide (N_2O), which is chemically inert in the troposphere, readily absorbs longwave radiation and is among the more significant non-CO_2 greenhouse gases.

5.5.1 Ozone Greenhouse Effects Related to Nitrogen Oxides

On a per mole basis, Rodhe (1990) estimated tropospheric O_3 to be more effective at absorbing infrared radiation than CO_2 Measured background tropospheric O_3 concentrations, particularly in the northern hemisphere, have shown an apparent increase over the past few decades, although the uncertainties are generally large (Logan, 1985; Oltmans and Kohmyr, 1986, Angell, 1988) Rodhe estimates the current annual rate of increase in global tropospheric O_3 as 0 5% Using a one-dimensional model, Lacis et al (1990) showed the direction of the O_3-induced radiative forcing to be sensitive to the vertical O_3 distribution. Tropospheric O_3 increases, as well as stratospheric decreases, could both lead to surface warming Ozone concentration changes in the upper troposphere and lower stratosphere, where temperatures are at a minimum compared to surface temperatures, are the most effective in producing surface layer temperature changes (Wuebbles, 1989) It should be noted, however, that Lacis et al (1990) calculated a net O_3-induced 0 05 °C (±0.05 °C) surface cooling for mid-latitude regions during the 1970s Based on limited observational O_3 column data, the modeled surface cooling caused by decreases in stratospheric O_3 outweighed warming effects brought on by tropospheric O_3 increases

The photochemical relationship of NO_x to the formation of tropospheric O_3 has been previously described in Section 5 2 It is generally regarded that due to the relatively short atmospheric lifetime of O_3, local (urban) sources of O_3 do not contribute significantly to the

upper tropospheric global O_3 levels (Machta, 1983) Sources of greenhouse-important tropospheric O_3 are presumably an equal combination of downward injection of stratospheric O_3 and O_3 precursors (NO_x) during intrusion episodes and upper tropospheric photochemical production (Liu et al , 1980, Fishman, 1985, Wuebbles et al , 1989) Of particular interest then, is the mechanisms by which NO_x species can be transported and dispersed sufficiently throughout the mid to upper troposphere to result in the formation of upper-level O_3 The processes of mesoscale and synoptic transport (see Section 5 4 3) in combination with transformation of NO_x to reservoir species, such as peroxy- and organic nitrates, could serve to relay the O_3 precursor species to the remote troposphere Singh et al (1985) submitted that PAN, in particular, would be an effective long-range transport mechanism for boundary layer NO_x, thereby influencing background levels of O_3, as well as other important oxidation compounds (i e , OH radicals)

Another proposed anthropogenic source of mid and upper tropospheric, as well as stratospheric, O_3 precursors (NO_x and VOCs) is via the exhaust of high-flying jet aircraft (Liu et al , 1980, Kinnison et al , 1988) Liu et al estimated a potential 7 to 15% increase in upper tropospheric O_3 over the northern hemisphere due to high-flying subsonic aircraft for the decade of the 1970s They compared this to an average observed 8% increase over the same hemisphere from 1966 to 1977 Nitrogen oxides are also known to be produced in conjunction with lightning discharges (Logan, 1983) While investigating lightning, followed by upward transport, as a potential source for stratospheric NO_y, Ko et al (1986) showed that significant levels, above background, of tropospheric NO_y can be produced, especially in the tropical latitudes

In a recent World Meteorological Organization Assessment Document (World Meteorological Organization, 1991) dealing with the status of atmospheric O_3, an international group of scientists provided the following conclusions concerning tropospheric O_3-NO_x relationships

(1) Increases in NO_x and other O_3 precursor species can lead to increases in tropospheric O_3

(2) The increase in these precursors could be the reason for the approximately 10% per decade increase in O_3 measured at northern mid-latitudes over the past two decades

(3) Estimates of O_3 production from NO_x emissions vary depending on the model employed; thus, the usefulness of such calculations is limited

(4) Given the key role NO_x plays in tropospheric O_3 chemistry, high priority should be given to observations of NO_x compounds

As briefly mentioned earlier, O_3 perturbations within the stratosphere, particularly the lower regions, can produce surface temperature changes of equal or greater magnitude than O_3 changes within the troposphere (Lacis et al , 1990) In the lower to mid-stratosphere, at middle latitudes, the destruction of stratospheric O_3 proceeds via a series of complex, catalyzed reactions involving the HO_x and ClX families of free radicals These reactions, as summarized by Johnston (1982), are as follows

$$NO + O_3 \rightarrow NO_2 + O_2 \quad \left[\begin{array}{l}\text{direct}\\ \text{catalyzed by } HO_x\\ \text{catalyzed by ClX}\end{array}\right. \tag{5-48}$$

$$O_3 + h\nu \rightarrow O + O_2 \tag{5-49}$$

$$NO_2 + O \rightarrow NO + O_2, \tag{5-50}$$

where, because Equation 5-50 is the rate determining step, the gross rate of stratospheric O_3 depletion through reactions of NO_x can be approximated by

$$-d[O_3]/dt = 2\, k_{5\text{-}41}\, [O]\, [NO_2] \tag{5-51}$$

In polar (high-latitude) regions, especially in the Antarctic where favorable conditions often exist, additional NO_y/ClX heterogenous reactions on the particulate surfaces of polar stratospheric clouds can further enhance stratospheric O_3 depletion (see Section 5 6), thereby increasing the likelihood of greenhouse forcing

5.5.2 Nitrous Oxide Greenhouse Contributions

Chemically unreactive in the troposphere, N_2O readily absorbs infrared radiation and is estimated to be responsible for approximately 4 to 5% of the theorized greenhouse effect

(Hansen et al , 1989, Rodhe, 1990) At present atmospheric mixing ratios (307 to 310 ppbv), N_2O, on a per mole basis, is given to be 200 times more effective than CO_2 as an absorber of heat radiation (Wuebbles, 1989, Rodhe, 1990) Nitrous oxide in the troposphere is thought to originate predominately through soil denitrification (McElroy, 1980, Machta, 1983) Additionally, anthropogenic sources, especially high-temperature combustion, may also release significant amounts of N_2O Wuebbles (1989) estimated that as much as 40% of atmospheric N_2O to be a product of anthropogenic processes (fossil fuel combustion, 21%, biomass burning, 5%, fertilized soils, 5%, cultivated natural soils, 10%) Other researchers (Hao et al , 1987, Muzio and Kramlich, 1988) have proposed that the contribution of fossil fuel combustion may by significantly less Thiemens and Trogler (1991) calculated that the commercial manufacture of nylon releases, on a global basis, approximately 6 6 $\times 10^8$ kg of N_2O annually This would account for about 0 03% of the current tropospheric levels, or about 10% of the observed annual increase

Although there are as yet some questions in the partitioning of N_2O sources, the atmospheric levels of N_2O have been observed to be increasing at an annual rate of 0 2 to 0 3% (Machta, 1983, Wuebbles et al , 1989, Rodhe, 1990) With an atmospheric lifetime of 150 years (Rodhe, 1990, Levander, 1990), it can be seen that given an increase in atmospheric loading, N_2O will become an increasingly more important greenhouse gas Levander (1990) using a 0 2% rate of increase in N_2O emissions, predicted that after 50 years, the resulting buildup in N_2O would be 350 times more effective at absorbing infrared radiation than an equivalent amount of CO_2 emissions The Levander estimate is somewhat larger than that listed for N_2O in the Scientific Assessment of Ozone Depletion 1991 (World Meteorological Organization, 1991) document A global warming potential of 270 was calculated for 50 years in the future An N_2O lifetime of 132 years was employed in the World Meterological Organization calculation

Nitrous oxide does not decompose until it is transported to the stratosphere The main sink for stratospheric N_2O is the reaction with $O(^1D)$ (Johnston, 1982, Logan, 1983, Wuebbles, 1989) The products of such reactions are the primary sources for stratospheric NO_x, which, as previously mentioned, catalytically react to deplete stratospheric O_3 and partially supply NO_x species to the upper troposphere during intrusion episodes

5.6 STRATOSPHERIC OZONE DEPLETION BY OXIDES OF NITROGEN

Oxides of nitrogen, from anticipated high-altitude supersonic aircraft exhaust, were first proposed as a destruction mechanism for stratospheric O_3 in the early 1970s (Crutzen, 1970, Johnston, 1971). Since then, the relationship between stratospheric odd nitrogen species, NO_y ($NO + NO_2 + NO_3 + HNO_3$ + chlorine nitrate [$ClNO_3$] + $N_2O_5 + HO_2NO_2$), has received considerable attention

The primary source of stratospheric NO_y is thought to be via the reaction of $O(^1D)$ and N_2O (Johnston, 1982, Logan, 1983, Wuebbles, 1989),

$$O(^1D) + N_2O \rightarrow 2\ NO \tag{5-52}$$

Significant sources of N_2O were discussed in Section 5 5 2 Jackman et al (1980) list other possible, less significant, sources of stratospheric odd nitrogen as NO_y production by lightning in the troposphere followed by upward transport, nuclear bomb blasts, thermospheric NO_y production with downward transport, and NO_y produced during ionizing events (i.e , solar proton episodes) Additionally, recent renewed interest in stratospheric, intercontinental passenger jet aircraft has likewise restimulated research into the sensitivity of stratospheric O_3 to potential aircraft exhaust (Kinnison et al , 1988, Kinnison and Wuebbles, 1989).

In the mid-latitude and lower- to mid-stratospheric regions, as mentioned in Section 5.5.1 (Equations 5-48 to 5-51), NO cycles through NO_2 for a net destruction of two molecules of O_3

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{5-48}$$

$$O_3 + h\nu \rightarrow O + O_2 \tag{5-49}$$

$$NO_2 + O \rightarrow NO + O_2 \tag{5-50}$$

$$\text{Net}\ \ 2O_3 \rightarrow 3O_2$$

It is known, however, that catalytic reactions involving chlorinated compounds within the stratosphere can be even more effective as an O_3 depletion mechanism These reactions, although not specifically involving NO_x in the O_3 destruction reaction, are an important

component of the overall reaction system The homogeneous ClO dimer reaction sequences, which are most important, as proposed by Molina and Molina (1987), are as follows

$$2\ ClO + M \rightarrow Cl_2O_2 + M \quad (5\text{-}53)$$
$$Cl_2O_2 + h\nu \rightarrow Cl + ClOO \quad (5\text{-}54)$$
$$ClOO + M \rightarrow Cl + O_2 + M \quad (5\text{-}55)$$
$$2Cl + 2O_3 \rightarrow 2ClO + 2O_2 \quad (5\text{-}56)$$
$$\text{Net } 2O_3 \rightarrow 3O_2$$

Fahey et al (1989) showed a similar ClO dimer reaction sequence, differing only by the self-decomposition of dichlorine dioxide and the photolysis of diatomic chloride The actual O_3 depletion mechanism (Equation 5-56) is the same in both reaction schemes.

$$2ClO + M \rightarrow Cl_2O_2 + M \quad (5\text{-}53)$$
$$Cl_2O_2 + M \rightarrow Cl_2 + O_2 + M \quad (5\text{-}57)$$
$$Cl_2 + h\nu \rightarrow 2Cl \quad (5\text{-}58)$$
$$2Cl + 2O_3 \rightarrow 2ClO + 2O_2 \quad (5\text{-}56)$$
$$\text{Net. } 2O_3 \rightarrow 3O_2$$

McElroy et al (1986a) also proposed the following chlorine/bromine oxidation cycle as an important stratospheric O_3 depletion mechanisms

$$Br + O_3 \rightarrow BrO + O_2 \quad (5\text{-}59)$$
$$Cl + O_3 \rightarrow ClO + O_2 \quad (5\text{-}60)$$
$$ClO + BrO \rightarrow Cl + Br + O_2 \quad (5\text{-}61)$$
$$\text{Net } 2O_3 \rightarrow 3O_2$$

The roles of Equations 5-53 to 5-61 in the stratospheric O_3 depletion are generally limited in the mid-latitude regions by the reaction of ClO and BrO with NO_2, which forms the unreactive $ClNO_3$ and bromine nitrate ($BrNO_3$) (McElroy et al , 1986a)

$$ClO + NO_2 + M \rightarrow ClNO_3 + M \quad (5\text{-}62)$$

$$BrO + NO_2 + M \rightarrow BrNO_3 + M \quad (5\text{-}63)$$

In the atmospheric regions mentioned above, where oxygenated nitrogen compounds are generally much more prevalent than chlorine compounds, Equations 5-62 and 5-63 act as important sinks for ClO and BrO, but as an insignificant sink for NO_2 (McElroy and Salawitch, 1989) Therefore, in order for Equations 5-53 to 5-61 to become significant, NO_2 must be removed from the reaction sequences or transformed into a less reactive species

Of more importance is that after the reaction sequences occur, the initial scavengers, NO or ClO, are reformed so the sequence can continue unabated until something removes them from the sequence and terminates the reactions One ClO molecule can destroy 100,000 O_3 molecules under normal conditions

Several heterogeneous reactions, believed to occur on the ice surfaces of polar stratospheric clouds (PSCs), have been proposed that act to sequester or remove (by deposition) reactive odd nitrogen This, then, initiates the more effective O_3 depletion chlorine and chlorine/bromine cycles The proposed heterogeneous reactions involve the reactions of $ClNO_3$ and N_2O_5 with hydrogen chloride (HCl) and water, presumably in the solid phase, on PSCs particulate surfaces (Molina et al , 1987; Tolbert et al , 1987, Tolbert et al., 1988a).

$$ClNO_3 + HCl \rightarrow Cl_2 + HNO_3 \quad (5\text{-}64)$$

$$ClNO_3 + H_2O \rightarrow HOCl\ HNO_3 \quad (5\text{-}65)$$

$$N_2O_5 + HCl \rightarrow ClNO_2 + HNO_3 \quad (5\text{-}66)$$

$$N_2O_5 + H_2O \rightarrow 2\ HNO_3 \quad (5\text{-}25)$$

Leu (1988) also suggested recombination of ClO on the surface of PSCs,

$$ClO + ClO \rightarrow Cl_2 + O_2 \quad (5\text{-}67)$$

However, much uncertainty still remains regarding the mechanism and the importance of Equation 5-67 to the heterogeneous reactions associated with stratospheric O_3 depletion

Polar stratospheric clouds are commonly formed at altitudes in the 10- to 20-km range over the Antarctic, and, to a lesser extent, over the Arctic, during the respective winter months (McCormick et al , 1982) Model calculations that have included both heterogeneous (Equations 5-64 to 5-66) and homogeneous mechanisms have simulated the observed Antarctic O_3 depletion patterns reasonably well (McElroy et al , 1986b, Solomon et al , 1986, Wofsy et al , 1988, Fahey et al , 1989) Additionally, the model calculations of Douglass and Stolarski (1989) have demonstrated that such heterogeneous reactions may have a noticeable impact on the $O_3/NO_y/ClX$ chemistry of the Arctic stratosphere, even though arctic PSCs are less common and less persistent

McElroy et al (1986a) and others have suggested that the HNO_3 formed in the above heterogeneous reactions could condense, along with water, resulting in the formation of PSCs at temperatures warmer than the ice point of water The embellished formation of PSCs would, in turn, enhance the efficiency of the heterogeneous reactions of the polar stratospheric O_3 depletion mechanisms Laboratory experiments by Hanson and Mauersberger (1988) showed the HNO_3 trihydrate formed at stratospheric conditions condensed approximately 7 K above the ice point

Recent investigations have suggested there is still considerable uncertainty in the precise mechanisms of the theorized polar stratospheric heterogeneous chemistry Wolff et al (1989) presented data that contradicted the findings of earlier investigators (Molina et al , 1987, Wofsy et al , 1988) pertaining to the incorporation and movement of HCl within ice crystals Wolff et al (1989) found HCl is not readily incorporated into ice crystals, but rather strongly partitioned along grain boundaries They proposed that the HCl may be present in some form other than solid (i e , liquid surface film, grain boundary liquid, chemisorbed to the ice surface, reactant on super-cooled droplet), thereby supplying the HCl as required by current theories

Other mechanisms for the release of active chlorine from the reservoir species ($ClNO_3$ and N_2O_5), which would initiate the homogeneous O_3 depletion cycle, have been presented by Tolbert et al (1988b) and Finlayson-Pitts et al (1989) Laboratory studies by Tolbert et al (1988b) suggested that the heterogeneous reactions suspected to occur on PSCs may also occur on atmospheric sulfuric acid aerosols This would have the effect of extending the latitude and lowering the altitude at which the proposed heterogeneous reactions could occur

Finlayson-Pitts et al (1989) found that $ClNO_3$ and N_2O_5 react with sodium chloride particles at 298 K similarly to the previously discussed polar stratospheric reactions

$$ClNO_3 + NaCl(s) \rightarrow Cl_2 + NaNO_3(s) \quad (5\text{-}68)$$

$$N_2O_5 + NaCl(s) \rightarrow ClNO_2 + NaNO_3(s) \quad (5\text{-}69)$$

These additional mechanisms, which result in photochemically active chlorine (O_3-depleting) species, indicate that reactions similar to the stratospheric heterogeneous reactions may also impact tropospheric chemistry. Additional research may also result in the inclusion of these mechanisms in polar, and possibly global, stratospheric chemistry

5.7 DEPOSITION OF NITROGEN OXIDES

Oxides of nitrogen and related nitrogen-containing species can be removed from the atmosphere by dry and/or wet deposition Dry deposition consists of transfer of a gaseous species from the atmosphere to an underlying surface, where the gas is chemically or biologically assimilated Wet deposition requires incorporation of NO_x into cloud and/or precipitation particles, followed by delivery to the earth's surface Wet deposition rates are highly variable because they depend on atmospheric advection and mixing processes, storm dynamics, atmospheric chemical transformations, and physiochemical processes in the cloud environment

5.7.1 Dry Deposition of Nitrogen Oxides

The general procedure for calculating dry deposition fluxes (F) is to multiply deposition velocity (V_d) for a particular trace gas by its air concentration (C) at some reference height above the surface.

$$F = V_d C$$

The deposition velocity is an experimentally determined parameter, which depends on meteorological conditions, surface, and trace gas characteristics In order to apply deposition

velocity to a diversity of conditions, V_d can be broken down into the reciprocal sum of three individual resistances

$$V_d = 1/(Ra + Rb + Rc)$$

Ra is an aerodynamic resistance related to the atmospheric turbulence above the surface, *Rb* accounts for resistance associated with the thin boundary layer that exists very close to the surface, and *Rc* defines the sink capacity of the surface itself

The aerodynamic resistance (*Ra*) is a function of a number of physical and meteorological parameters, including friction velocity, height above the surface, surface roughness, length, and turbulence class In most cases, *Ra* cannot be calculated directly, and approximations must be invoked Various formulations have been described by Hicks et al (1987)

Molecular diffusion becomes the primary transport pathway in the thin layers close to the depositional surface Therefore, *Rb* is a function of the molecular diffusivity of the depositing gas As with *Ra*, normally it is difficult to evaluate *Rb* precisely because surface roughness is highly variable and, consequently, difficult to parameterize in deposition models

For many gases, the surface uptake resistance (*Rc*) is the most difficult to evaluate and is dependant on the sink capacity of the depositional surface, which is a function of numerous physical, chemical, and biological processes Transport through stomatal openings on leaf surfaces, for example, is a function of solar radiation, leaf temperature, leaf water potential, etc

5.7.2 Methods for Determining Deposition Velocities

Deposition velocities (V_d) are defined as the ratio of surface fluxes to air concentrations at some height above the surface (e g , 2 m) In order to determine V_d, the vertical flux (rate of transport per unit area) and fluctuations of a trace gas must be measured The most common methods employed include eddy correlation, vertical gradients, and enclosure-based systems

5.7.2.1 Eddy Correlation

This is the most direct method for measuring vertical fluxes It requires fast response and sensitive detection of trace gases, along with the simultaneous measurement of vertical velocity Vertical velocity is generally determined with a sonic anemometer The limiting feature associated with the eddy correlation technique is availability of fast-response chemical sensors. Of the nitrogen-containing trace gases, only NO and NO_2 have detection systems of sufficient speed to utilize the eddy correlation method

The fast response limitation is eliminated in a variation of eddy correlation known as eddy accumulation Vertical air movement is still monitored with a sonic anemometer, but instead of having a colocated fast response chemical sensor, a pump is used to fill two air sampling devices Air is pumped into one of the containers when movement is upward (as sensed by the sonic anemometer) and into the second container when air is subsiding The mass of the trace gas of interest in each container is then determined using conventional analytical techniques As long as sample integrity is maintained in the collection device, eddy accumulation could be used to measure the flux of such nitrogenous gases as PAN and PPN; organic nitrates, and, possibly, HNO_3

5.7.2.2 Vertical Gradient Methods

These methods involve the measurement of trace gas concentrations at several levels above the surface The vertical concentration profile is proportional to the flux of the trace gas of interest

$$F = Kz(dc/dz)$$

The proportionality constant (Kz) is normally estimated from concurrently measured meteorological parameters or by assuming that it is the same for another quantity as for the trace gas of interest For example, sensible heat flux can be measured by eddy correlation This allows calculation of the transfer (diffusion) coefficient (Kz), which can then be combined with concurrent vertical profile measurements of a trace gas to determine its flux The main limitation of this latter procedure is the requirement that sources and sinks of the trace gas and heat flux are similarly distributed

5.7.2.3 Chamber Methods

A volume of air is enclosed above a depositional surface (soil, water, etc) by one of two types of chambers In closed circulation chambers, trace gas fluxes are determined by periodically collecting samples from the chamber and calculating the change in concentration with time In the closed or static mode, the chamber remains over the surface of interest only long enough to make the measurement By contrast, dynamic or open chambers generally are kept in place for several hours or even days In this latter case, a continuous flow of air passes through the enclosure When chamber methods are utilized for determining NO_x depositional fluxes, special care must be exercised to eliminate the following problems (Mosier, 1989)

(1) Uptake or production of NO and NO_2 by chamber wall material—corrections must be made when fluxes of NO and NO_2 are very small

(2) Changes in aerodynamic mixing close to the surface—airflows through the chamber should mimic the natural environment as closely as possible

(3) If reaction times for species of interest are similar to the enclosure residence time, corrections must be made This is generally true for open chambers where NO, NO_2, and O_3 are present

(4) For NO, the net exchange above the surface has been shown to be dependent on the concentration Thus, a "compensation point" exists above which there will be uptake of NO and below which NO emission will occur Therefore, in order to get representative information, NO concentrations in chamber air must be as close as possible to those in ambient air

5.7.3 Deposition of Nitrogen Oxides

Nitrogen oxides dry deposition fluxes are still very uncertain Results from many micrometeorological studies exhibit large scatter in NO_x fluxes This is due both to analytical problems (i e , interference from other nitrogen-containing species) and to the fact that NO_x exchange includes simultaneous emission and deposition It is generally believed that NO emission exceeds NO deposition, and that NO_2 deposition is greater than NO deposition (Johansson, 1989) Deposition velocities (V_d) for NO have been reported to range from less than 0 1 to approximately 0 2 cm/s For NO_2, reported V_d values generally fall in the range 0 3 to 0 8 cm/s (Hanson and Lindberg, 1991) Because NO normally constitutes a

small fraction ($\approx 10\%$) of the atmospheric NO_x concentration, the dry deposition of NO to terrestrial surfaces can be neglected as a sink for removal of atmospheric NO_x

5.7.4 Nitric Acid Deposition

The surface uptake resistance for HNO_3 deposition to terrestrial surfaces has been shown to be very small (Huebert and Robert, 1985) Therefore, when aerodynamic and diffusional processes bring gaseous HNO_3 in contact with a surface, the HNO_3 molecules will deposit at nearly 100% efficiency Consequently, deposition velocities are larger than those for NO and NO_2 Terrestrial values for V_d reportedly range between 0 5 and 3.0 cm/s. Nitric acid deposition velocities over water surfaces are somewhat lower, falling in the 0.3 to 0 7 cm/s range

5.7.5 Deposition of Peroxyacetylnitrate

Very little information exists concerning PAN deposition rates A V_d of 0 25 cm/s has been reported over a grass and soil surface (Garland and Penkett, 1976) In their study of the photochemistry of biogenic emissions in the Amazon Basin, Jacob and Wofsy (1988) assumed for PAN a V_d value of 2 cm/s A high value was selected because of the large surface area associated with the tropical vegetation canopy It is expected that the deposition velocity over water surfaces would constitute the other extreme, with values as low as 0.01 cm/s having been proposed (Andreae et al , 1988) Deposition velocities for PAN will probably remain uncertain due to the difficulties associated with making accurate PAN measurements

5.7.6 Wet Deposition of Nitrogen Oxides

Wet deposition is not a significant atmospheric removal mechanism for NO and NO_2 These two gases are minimally soluble in water and, therefore, must be transformed to more highly oxidized forms for wet removal to become effective The reaction of NO_2 with OH radical to produce HNO_3 appears to be the main source of the nitrate ion measured in precipitation It is estimated that about one-third of United States NO_x emissions are removed by wet deposition processes (Hicks et al , 1991)

5.8 SUMMARY AND CONCLUSIONS

Nitrogen oxides are important chemical species in the planetary boundary layer, as well as in the free troposphere and the stratosphere Nitrogen oxides play important roles (1) in the control of concentrations of radicals in the clean troposphere, (2) in the production of tropospheric O_3, (3) as an aerosol precursor, and (4) in the production and deposition of acidic species, directly or indirectly

5.8.1 Ozone Production

Combustion processes emit a variety of nitrogen compounds, but chiefly NO, which is rapidly oxidized to NO_2 in ambient air, primarily by O_3 Photolytic decomposition of NO_2 then leads to regeneration of NO, producing also an excited oxygen atom that reacts with molecular oxygen to form O_3 In the absence of competing reactions, NO, NO_2, and O_3 reach an equilibrium described by the steady-state equation

Competing reactions exist, however, so that free radicals (HO_2 , RO_2) generated from the oxidative degradation of volatile organic compounds (VOCs) oxidize NO to NO_2 without destroying O_3 Thus, the amount of O_3 formed in ambient air is dependent upon the concentration of NO_x present as well as the concentrations and reactivities of VOC species

5.8.2 Production of Odd Nitrogen Species

Photochemical processes that include the coupled reactions of NO_x, oxygen species, and free radicals produce not only O_3, but nitrogen-containing products as well These oxidation products include HNO_3, HO_2NO_2, HONO, $RC(O)O_2NO_2$, N_2O_5, and inorganic and organic nitrates

Nitric acid is a major sink for active nitrogen and is a contributor to acidic deposition It has been estimated to account for roughly one-third of the total acidity deposited in the eastern United States (Calvert and Stockwell, 1983) Potential physical and chemical sinks for HNO_3 include wet and dry deposition, photolysis, reaction with OH radicals, and neutralization by gaseous NH_3, which leads to aerosol production

Peroxyacyl nitrates are formed from the combination of RO_2 radicals with NO_2 Peroxyacetylnitrate is the most abundant member in the lower troposphere of this homologous series of compounds It can serve in the troposphere as a temporary reservoir

for reactive nitrogen species and can be regionally transported, but it cannot function as a true sink in the lower troposphere because of its thermal instability In the upper troposphere, where temperatures are colder, the lifetime of PAN is longer, but is only about 3 mo because PAN is photolyzed and also reacts with OH radicals

The NO_3 radical is a short-lived radical that is formed in the troposphere primarily by the reaction of NO_2 with O_3 In daylight, NO_3 undergoes rapid photolysis or reaction with NO. After sunset, accumulation of NO_3 can occur and is expected to be controlled by the availability of NO_2 and O_3 plus chemical destruction mechanisms involving the formation of N_2O_5 and HNO_3.

Dinitrogen pentoxide, the anhydride of HNO_3, is primarily a nighttime constituent of ambient air because it is formed from the reaction of NO_3 (itself a nighttime species) and NO_2. Dinitrogen pentoxide is thermally unstable, but at the lower temperatures of the upper troposphere, it can serve as a temporary reservoir of NO_3 In the boundary layer, N_2O_5 reacts heterogeneously with water to form HNO_3, which in turn is deposited out

Amines, nitrosamines, and nitramines are thought to exist in ambient air, but at low concentrations. Both nitrosamines and nitramines have short lifetimes in ambient air because they are photolytically decomposed (nitrosamines) and/or react with OH radicals and O_3 (nitramines and nitrosamines)

5.8.3 Transport

5.8.3.1 General Features

The transport and dispersion of the various nitrogenous species are dependent on both meteorological and chemical parameters Advection, diffusion, deposition, and chemical transformations combine to dictate the atmospheric residence time of a particular trace gas In turn, atmospheric residence times help determine the geographic extent of transport of a given species Surface emissions are dispersed vertically and horizontally through the atmosphere by tubulent mixing processes that are dependent to a large extent on the vertical temperature structure and wind speed

As the result of meteorological processes, NO_x emitted in the early morning hours in an urban area will disperse vertically and horizontally (downwind) as the day progresses On sunny summer days, most of the NO_x will have been converted to HNO_3 and PAN by

sunset Much of the HNO_3 is removed by deposition as the air mass is transported, but HNO_3 and PAN carried in layers aloft (above the nighttime inversion layer, but below a higher subsidence inversion) can potentially be transported long distances

5.8.3.2 Transport of Reactive Nitrogen Species in Urban Plumes

Studies of the fate of reactive nitrogen species in daytime urban plumes indicate removal rates ranging from 0 04 h^{-1} in Los Angeles (Chang et al , 1979), to 0 1 h^{-1} in Detroit (Kelly, 1987), to 0 14 to 0 24 h^{-1} (for four different, nonconsecutive days) in Boston (Spicer, 1982a) In the Detroit study, HNO_3 accounted for 67 to 84% of the nitrogenous transformation products, but still fell short of predicted HNO_3 levels Removal by incorporation into coarse atmospheric aerosol was postulated as a major sink for HNO_3 and as the cause of the discrepancy between measured and predicted levels (Kelly, 1987)

The nighttime chemistry of NO_y is poorly understood Nighttime concentrations of NO_3 show a typical pattern of increase until O_3 is no longer available, followed by a decrease as NO emissions cannot be oxidized by O_3 to NO_2, but react instead with the NO_3

5.8.3.3 Transport and Chemistry in Combustion Plumes

Ozone buildup in power-plant plumes appears to be the result of mixing of VOCs into the plume as it moves downwind because the VOC/NO_x ratio in these plumes is quite low An O_3 buildup is not found in all power-plant plumes, however (e g , Hegg et al , 1977, Ogren et al , 1977, White, 1977), and the most important factor in the in-plume formation of O_3 appears to be the availability of reactive VOCs in the dilution air

Little information is available on the fate of reactive nitrogen species in NO_x-rich plumes Aircraft measurements have shown little increase in inorganic and particulate nitrate concentrations in power-plant plumes (Hegg and Hobbs, 1979) Chamber and modeling studies indicate that in NO_x-rich but VOC-poor plumes, the NO_x lifetime will be long enough to allow NO_x to be incorporated into regional air masses (Spicer et al , 1981)

5.8.3.4 Regional Transport

Transport of reactive NO_x in regional air masses can occur via several mechanisms (1) mesoscale phenomena, such as mountain-valley wind flow or land-sea breeze circulations

(transport for tens to hundreds of kilometers), (2) synoptic weather systems, such as the migratory highs that cross the eastern United States in the summertime (transport for many hundreds of kilometers), and (3) mesoscale phenomena coupled with slow-moving high-pressure systems having weak pressure gradients In the latter interrelated phenomena, mountain-valley or land-water breezes can govern pollutant transport in the immediate vicinity of sources, but the ultimate fate of reactive NO_x species will be distribution into the synoptic system

Information remains sparse on NO_x species and their concentrations in synoptic transport systems Calculated fluxes for the northeastern, Atlantic coast area (Luke and Dickerson, 1987; Galloway et al , 1984, Galloway and Whelpdale, 1987) correspond to about 25% of the NO_x emitted to the atmosphere of eastern North America, using Logan's (1983) emission estimate of $4\ 5 \times 10^{12}$ g nitrogen/year

5.8.4 Oxides of Nitrogen and the Greenhouse Effect

Except for N_2O, the reactive nitrogen species comprising the NO_x and NO_y families in the atmosphere do not absorb infrared radiation and, therefore, do not contribute directly to radiative "greenhouse" forcing They can, however, contribute indirectly to greenhouse processes through the photochemical production of O_3 in the troposphere Ozone absorbs infrared radiation more effectively per mole than CO_2 (Rodhe, 1990)

Nitrous oxide, which is chemically inert in the troposphere, readily absorbs infrared radiation and is among the more significant non-CO_2 greenhouse gases Absorption of visible radiation by NO_2 could make this compound a possible source of other climatic influences if atmospheric concentrations become sufficiently higher (Wuebbles, 1989)

5.8.4.1 Nitrous Oxide Greenhouse Contributions

Nitrous oxide is thought, on a per mole basis, to be 200 times more effective than CO_2 as an absorber of heat radiation (Wuebbles, 1989, Rodhe, 1990) It is estimated at present levels to be responsible for about 4 to 5% of the theorized greenhouse effect (Hansen et al , 1989; Rodhe, 1990) Assuming a 0 2% per year increase, Levander (1990) predicted that the increased atmospheric mixing ratio of N_2O after 50 years would result in an even greater efficiency (350 times) in infrared radiation absorption compared to expected CO_2 levels

5.8.4.2 Stratospheric Ozone Depletion by Oxides of Nitrogen

In mid-latitudes and lower to mid-stratospheric regions, cyclic reactions initiated by the oxidation of NO by O_3 lead to the net destruction of two molecules of O_3 per cycle Among the stratospheric O_3-depletion mechanisms that have been proposed, however, are much more important reactions involving the dimerization of ClO in the presence of a third body, M, and subsequent sequences in which the monomer is regenerated and two O_3 molecules are destroyed (Fahey et al , 1989, Molina and Molina, 1987) McElroy et al (1986a) also proposed chlorine (Cl) and bromine (Br) oxidation cycles as an important stratospheric O_3-depletion mechanism In this mechanism, the dimerization and regeneration of ClO, coupled with the oxidation of Br and Cl by O_3, are limited by the reaction of ClO and BrO with NO_2 to form the unreactive $ClNO_3$ or $BrNO_3$ (McElroy et al , 1986a) Reactions of ClO and BrO with NO_2 are important sinks for the halogen oxides, but are insignificant sinks for NO_2 (McElroy and Salawitch, 1989)

Sequestering of reactive NO_y by heterogeneous reactions on the ice surfaces of polar PSCs has been proposed as a means of removing NO_2 Its removal allows other O_3-depleting cycles to proceed (Molina et al , 1987, Tolbert et al , 1987, Tolbert et al , 1988a) Dinitrogen pentoxide has been implicated in these heterogeneous reactions

5.8.5 Deposition of Nitrogen Oxides

Both wet and dry deposition of NO_x and other nitrogen species occur, but wet deposition is not a significant removal mechanism foi NO or NO_2 because both gases are minimally soluble in water Transformation to more highly oxidized forms is necessary for effective wet deposition of NO_x, and the reaction of NO_2 with the OH radical to form HNO_3 appears to be the main source of nitrate ion in precipitation About one-third of the emissions of NO_x in the United States is estimated to be removed by wet deposition (Hicks et al , 1991)

Dry deposition fluxes for NO_x are highly uncertain, mainly because of analytical problems and the simultaneous occurrence of emission and deposition of NO_x Available data indicate, however, that NO emissions exceed NO deposition and that NO_2 deposition exceeds NO deposition Reported V_d values for respective nitrogen species are $<0\ 1$ to $\approx 0\ 2$ cm/s for NO, 0 3 to 0 8 cm/s for NO_2, and 0 5 to 3 0 cm/s for HNO_3 over land and

0.3 to 0 7 cm/s for HNO_3 over water (Huebert and Robert, 1985) The few data that exist show deposition rates for PAN of 0 01 cm/s over water (Andreae et al , 1988) and 0 25 cm/s (Garland and Penkett, 1976) to 2 0 cm/s (Jacob and Wofsy, 1988) over land

REFERENCES

Altshuller, A P (1986) The role of nitrogen oxides in nonurban ozone formation in the planetary boundary layer over N America, W Europe and adjacent areas of ocean Atmos Environ 20 245-268

Andreae, M O , Browell, E V , Garstang, M , Gregory, G L , Harriss, R C , Hill, G F , Jacob, D J , Pereira, M C , Sachse, G W , Setzer, A W , Silva Dias, P L , Talbot, R W , Torres, A L , Wofsy, S C (1988) Biomass-burning emissions and associated haze layers over Amazonia J Geophys Res [Atmos] 93 1509-1527

Angell, J K (1988) An update through 1985 of the variations in global total ozone and north temperate layer-mean ozone J Appl Meteorol 27 91-97

Atkinson, R (1990) Gas-phase tropospheric chemistry of organic compounds a review Atmos Environ Part A 24 1-41

Atkinson, R , Carter, W P L (1984) Kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmospheric conditions Chem Rev 84 437-470

Atkinson, R , Lloyd, A C (1984) Evaluation of kinetic and mechanistic data for modeling of photochemical smog J Phys Chem Ref Data 13 315-344

Atkinson, R , Winer, A M , Pitts, J N , Jr (1986) Estimation of night-time N_2O_5 concentrations from ambient NO_2 and NO_3 radical concentrations and the role of N_2O_5 in night-time chemistry Atmos Environ 20 331-339

Bandow, H , Okuda, M , Akimoto, H (1980) Mechanism of the gas-phase reactions of C_3H_6 and NO_3 radicals J Phys Chem 84 3604-3608

Baulch, D L , Cox, R A , Crutzen, P J , Hampson, R F , Kerr, J A , Troe, J , Watson, R T (1982) Evaluated kinetic and photochemical data for atmospheric chemistry supplement 1 J Phys Chem Ref Data 11 327-496

Calvert, J G (1976) Hydrocarbon involvement in photochemical smog formation in Los Angeles atmosphere Environ Sci Technol 10 256-262

Calvert, J G , Madronich, S (1987) Theoretical study of the initial products of the atmospheric oxidation of hydrocarbons J Geophys Res [Atmos] 92 2211-2220

Calvert, J G , Stockwell, W R (1983) Acid generation in the troposphere by gas-phase chemistry Environ Sci Technol 17 428A-443A

Carmichael, G R , Peters, L K (1984) An Eulerian transport/transformation/removal model for SO_2 and sulfate—I Model development Atmos Environ 18 937-951

Chang, T Y , Norbeck, J M , Weinstock, B (1979) An estimate of the NO_x removal rate in an urban atmosphere Environ Sci Technol 13 1534-1537

Crutzen, P J (1970) The influence of nitrogen oxides on the atmospheric ozone content Q J R Meteorol Soc 96 320-325

Crutzen, P J (1988) Tropospheric ozone an overview In Isaksen, I S A , ed Tropospheric ozone—regional and global scale interactions proceedings of the NATO advanced workshop on regional and global ozone interaction and its environmental consequences, June 1987, Lillehammer, Norway Dordrecht, The Netherlands D Reidel Publishing Company, pp 3-32 (NATO advanced science institutes studies series C, mathematical and physical sciences v 227)

Davis, D D., Smith, G , Klauber, G (1974) Trace gas analysis of power plant plumes via aircraft measurement O_3, NO_x, and SO_2 chemistry Science (Washington, DC) 186 733-736

Douglass, A R , Stolarski, R S (1989) Impact of heterogeneous reactions on stratospheric chemistry of the Arctic Geophy. Res Lett 16 131-134

Fahey, D. W ; Hubler, G , Parrish, D D , Williams, E J , Norton, R B , Ridley, B A , Singh, H B , Liu, S C , Fehsenfeld, F C (1986) Reactive nitrogen species in the troposphere measurements of NO, NO_2, HNO_3, particulate nitrate, peroxyacetyl nitrate (PAN), O_3, and total reactive odd nitrogen (NO_y) at Niwot Ridge, Colorado J Geophys Res [Atmos] 91 9781-9793

Fahey, D. W ; Murphy, D M , Kelly, K K , Ko, M K W , Proffitt, M H , Eubank, C S , Ferry, G V , Loewenstein, M , Chan, K R (1989) Measurements of nitric oxide and total reactive nitrogen in the Antarctic stratosphere observations and chemical implications J Geophys Res [Atmos] 94 16665-16681

Finlayson-Pitts, B J , Ezell, M J , Pitts, J N , Jr (1989) Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N_2O_5 and $ClONO_2$ Nature (London) 337 241-244

Finlayson-Pitts, B J ; Pitts, J N , Jr (1986) Atmospheric chemistry fundamentals and experimental techniques New York, NY John Wiley & Sons, pp 961-1007

Fishman, J. (1985) Ozone in the troposphere In Whitten, R C , Prasad, S , eds Ozone in the free atmosphere New York, NY Van Nostrand Reinhold, pp 161-194

Galloway, J N., Whelpdale, D M , Wolff, G T (1984) The flux of S and N eastward from North America Atmos Environ 18 2595-2607

Galloway, J N , Whelpdale, D M (1987) WATOX-86 overview and western North Atlantic Ocean S and N atmospheric budgets Global Biogeochem Cycles 1 261-281

Garland, J A , Penkett, S A (1976) Absorption of peroxy acetyl nitrate and ozone by natural surfaces Atmos Environ 10 1127-1131

Grosjean, D ; Van Cauwenberghe, K , Schmid, J , Pitts, J N , Jr (1978) Formation of nitrosamines and nitramines by photooxidation of amines under simulated atmospheric conditions In Proceedings of the fourth joint conference on sensing of environmental pollutants, November 1977, New Orleans, LA Washington, DC: American Chemical Society, pp 196-199

Hansen, J., Lacis, A , Prather, M (1989) Greenhouse effect of chlorofluorocarbons and other trace gases J Geophys Res [Atmos] 94 16417-16421

Hanson, D , Mauersberger, K (1988) Solubility and equilibrium vapor pressures of hydrogen chloride dissolved in polar stratospheric cloud materials ice and the trihydrate of nitric acid Geophys Res Lett 15 1507-1510

Hanson, P J , Lindberg, S E (1991) Dry deposition of reactive nitrogen compounds a review of leaf, canopy and non-foliar measurements Atmos Environ Part A 25 1615-1634

Hanst, P L , Spence, J W , Miller, M (1977) Atmospheric chemistry of *N*-nitroso dimethylamine Environ Sci Technol 11 403-405

Hao, W M , Wofsy, S C , McElroy, M B , Beer, J M , Toqan, M A (1987) Sources of atmospheric nitrous oxide from combustion J Geophys Res [Atmos] 92 3098-3104

Harris, G W , Carter, W P L , Winer, A M , Pitts, J N , Jr , Platt, U , Perner, D (1982) Observations of nitrous acid in the Los Angeles atmosphere and implications for predictions of ozone-precursor relationships Environ Sci Technol 16 414-419

Hegg, D A , Hobbs, P V (1979) Some observations of particulate nitrate concentrations in coal-fired power plant plumes Atmos Environ 13 1715-1716

Hegg, D , Hobbs, P V , Radke, L F , Harrison, H (1977) Ozone and nitrogen oxides in power plant plumes In Dimitriades, B , ed International conference on photochemical oxidant pollution and its control proceedings, v I, September 1976, Raleigh, NC Research Triangle Park, NC U S Environmental Protection Agency, Environmental Sciences Research Laboratory, pp 173-183, EPA report no EPA-600/3-77-001a Available from NTIS, Springfield, VA, PB-264232

Heikes, B G , Thompson, A M (1983) Effects of heterogeneous processes on NO_3, HONO, and HNO_3 chemistry in the troposphere J Geophys Res C Oceans Atmos 88 10883-10895

Hicks, B B , Baldocchi, D D , Meyers, T P , Hosker, R P , Jr , Matt, D R (1987) A preliminary multiple resistance routine for deriving dry deposition velocities from measured quantities Water Air Soil Pollut 36 311-330

Hicks, B B , Draxler, R R , Albritton, D L , Fehsenfeld, F C , Dodge, M , Schwartz S E , Tanner, R L., Hales, J M , Meyers, T P , Vong, R J (1991) Atmospheric processes research and process model development In Irving, P M , ed Acidic deposition state of science and technology, volume I, emissions, atmospheric processes and deposition Washington, DC The U S National Acid Precipitation Assessment Program (State of science and technology report no 2)

Holzworth, G C (1967) Mixing depths, wind speeds and air pollution potential for selected locations in the United States J Appl Meteorol 6 1039-1044

Huebert, B J , Luke, W T , Delany, A C , Brost, R A (1988) Measurements of concentrations and dry surface fluxes of atmospheric nitrates in the presence of ammonia J Geophys Res [Atmos] 93 7127-7136

Huebert, B J , Robert, C H (1985) The dry deposition of nitric acid to grass J Geophys Res [Atmos] 90 2085-2090

Jackman, C H , Frederick, J E , Stolarski, R S (1980) Production of odd nitrogen in the stratosphere and mesosphere an intercomparison of source strengths J Geophys Res C Oceans Atmos 85 7495-7505

Jacob, D J , Wofsy, S C (1988) Photochemistry of biogenic emissions over the Amazon forest J Geophys Res [Atmos] 93 1477-1486

Johansson, C (1989) Fluxes of NO_x above soil and vegetation In Andreae, M O , Schimel, D S , eds Exchange of trace gases between terrestrial ecosystems and the atmosphere report of the Dahlem workshop, February, Berlin, Federal Republic of Germany New York, NY John Wiley & Sons, pp 229-246

Johnston, H. (1971) Reduction of stratospheric ozone by nitrogen oxide catalysts from supersonic transport exhaust Science (Washington, DC) 173 517-522

Johnston, H S (1982) Odd nitrogen processes In Bower, F A , Ward, R B , eds Stratospheric ozone and man volume I Boca Raton, FL CRC Press, Inc , pp 87-140

Jones, C. L , Seinfeld, J H (1983) The oxidation of NO_2 to nitrate—day and night Atmos Environ 17 2370-2373

Kelly, N A (1987) The photochemical formation and fate of nitric acid in the metropolitan Detroit area ambient, captive-air irradiation and modeling results Atmos Environ 21 2163-2177

Kelly, N A , Wolff, G T , Ferman, M A (1984) Sources and sinks of ozone in rural areas Atmos Environ 18 1251-1266

Kelly, T J., McLaren, S E , Kadlecek, J A (1989) Seasonal variations in atmospheric SO_x and NO_y species in the Adirondacks Atmos Environ 23 1315-1332

Kinnison, D. E., Wuebbles, D J , Johnston, H S (1988) A study of the sensitivity of stratospheric ozone to hypersonic aircraft emissions Presented at First international conference on hypersonics flight in the 21st century, September, Grand Forks, ND Livermore, CA U S Department of Energy, Lawrence Livermore National Laboratory, Atmospheric and Geophysical Sciences Division, report no UCRL-98314 Available from NTIS, Springfield, VA, DE89-001240

Kinnison, D E , Wuebbles, D J (1989) Preventing depletion of stratospheric ozone—implications on future aircraft emissions Livermore, CA Lawrence Livermore National Laborabory, report no UCRL-99926-Rev 1 Available from NTIS, Springfield, VA, DE89-013779

Ko, M. K. W , McElroy, M B , Weisenstein, D K , Sze, N D (1986) Lightning a possible source of stratospheric odd nitrogen J Geophys Res [Atmos] 91 5395-5404

Lacis, A A , Wuebbles, D J , Logan, J A (1990) Radiative forcing of climate by changes in the vertical distribution of ozone J Geophys Res [Atmos] 95 9971-9981

Leu, M -T (1988) Heterogeneous reactions of N_2O_5 with H_2O and HCl on ice surfaces implications for Antarctic ozone depletion Geophys Res Lett 15 851-854

Levander, T (1990) The relative contributions to the greenhouse effect from the use of different fuels Atmos Environ Part A 24 2707-2714

Liu, S C ; Kley, D , McFarland, M , Mahlman, J D , Levy, H , II (1980) On the origin of tropospheric ozone J Geophys Res C Oceans Atmos 85 7546-7552

Liu, S C ; Trainer, M , Fehsenfeld, F C , Parrish, D D , Williams, E J , Fahey, D W , Huebler, G , Murphy, P C (1987) Ozone production in the rural troposphere and the implications for regional and global ozone distributions J Geophys Res [Atmos] 92 4191-4207

Logan, J A. (1983) Nitrogen oxides in the troposphere global and regional budgets J Geophys Res C Oceans Atmos 88 10785-10807

Logan, J A (1985) Tropospheric ozone seasonal behavior, trends, and anthropogenic influence J Geophys Res [Atmos] 90 10463-10482

Luke, W T , Dickerson, R R (1987) The flux of reactive nitrogen compounds from eastern North America to the western Atlantic Ocean Global Biogeochem Cycles 1 329-343

Lyons, W A , Cole, H S (1976) Photochemical oxidant transport mesoscale lake breeze and synoptic-scale aspects J Appl Meteorol 15 733-743

Machta, L (1983) Effects of non-CO_2 greenhouse gases In Changing climate report of the Carbon Dioxide Assessment Committee Washington, DC National Academy Press, pp 285-291

Malko, M W , Troe, J (1982) Analysis of the unimolecular reaction $N_2O_5 + M = NO_2 + NO_3 + M$ Int J Chem Kinet 14 399-416

McCormick, M P , Steele, H M , Hamill, P , Chu, W P , Swissler, T J (1982) Polar stratospheric cloud sightings by SAM II J Atmos Sci 39 1387-1397

McElroy, M B (1980) Sources and sinks for nitrous oxide Washington, DC U S Department of Transportation, report no FAA-EE-80-20

McElroy, M B , Salawitch, R J , Wofsy, S C , Logan, J A (1986a) Reductions of Antarctic ozone due to synergistic interactions of chlorine and bromine Nature (London) 321 759-762

McElroy, M B , Salawitch, R J , Wofsy, S C (1986b) Antarctic O_3 chemical mechanisms for the spring decrease Geophys Res Lett 13(suppl) 1296-1299

McElroy, M B , Salawitch, R J (1989) Stratospheric ozone impact of human activity Planet Space Sci 37 1653-1672

Miller, D F , Alkezweeny, A J , Hales, J M , Lee, R N (1978) Ozone formation related to power plant emissions Science (Washington, DC) 202 1186-1188

Molina, L T , Molina, M J (1987) Production of chlorine oxide (Cl_2O_2) from the self-reaction of the ClO radical J Phys Chem 91 433-436

Molina, M J , Tso, T -L , Molina, L T , Wang, F C -Y (1987) Antarctic stratospheric chemistry of chlorine nitrate, hydrogen chloride, and ice release of active chlorine Science (Washington, DC) 238 1253-1257

Mosier, A R (1989) Chamber and isotope techniques In Andreae, M O , Schimel, D S , eds Exchange of trace gases between terrestrial ecosystems and the atmosphere New York, NY John Wiley & Sons, pp 175-187 (Bernhard, S , ed Life sciences research reports 47)

Muzio, L J , Kramlich, J C (1988) An artifact in the measurement of N_2O from combustion sources Geophys Res Lett 15 1369-1372

Noxon, J F , Norton, R B , Marovich, E (1980) NO_3 in the troposphere Geophys Res Lett 7 125-128

Ogren, J A , Blumenthal, D L , Vanderpol, A H (1977) Oxidant measurements in western power plant plumes Volume I technical analysis Volume II data Palo Alto, CA Electric Power Research Institute, report no EPRI EA-421 Volume II available from NTIS, Springfield, VA, DE82-901024

Oltmans, S J , Komhyr, W D (1986) Surface ozone distributions and variations from 1973-1984 measurements at the NOAA geophysical monitoring for climatic change baseline observatories J Geophys Res [Atmos] 91 5229-5236

Parrish, D D ; Fahey, D W , Williams, E J , Liu, S C , Trainer, M , Murphy, P C , Albritton, D L , Fehsenfeld, F C (1986) Background ozone and anthropogenic ozone enhancement at Niwot Ridge, Colorado. J Atmos Chem 4 63-80

Penkett, S. A (1991) Changing ozone evidence for a perturbed atmosphere Environ Sci Technol 25 631-635

Perner, D , Greenberg, J , Noxon, J F , Schmeltekopf, A , Winkler, P , Zimmerman, P (1991) The interaction of natural hydrocarbons and NO_3 above the canopy J Atmos Chem in press

Pitts, J. N , Jr (1987) Nitration of gaseous polycyclic aromatic hydrocarbons in simulated and ambient urban atmospheres· a source of mutagenic nitroarenes Atmos Environ 21 2531-2547

Pitts, J N , Jr ; Grosjean, D , Van Cauwenberghe, K , Schmid, J P , Fitz, D R (1978) Photooxidation of aliphatic amines under simulated atmospheric conditions formation of nitrosamines, nitramines, amides, and photochemical oxidant Environ Sci Technol 12 946-953

Pitts, J N , Jr , Winer, A M , Aschmann, S M , Carter, W P L , Atkinson, R (1985) Experimental protocol for determining hydroxyl radical reaction rate constants estimation of atmospheric reactivity Research Triangle Park, NC U S Environmental Protection Agency, Atmospheric Sciences Research Laboratory, EPA report no EPA-600/3-85-000 Available from NTIS, Springfield, VA, PB85-238558

Platt, U ; Perner, D., Schroeder, J , Kessler, C , Toennissen, A (1981) The diurnal variation of NO_3 J Geophys Res. C Oceans Atmos 86 11965-11970

Rodhe, H. (1990) A comparison of the contribution of various gases to the greenhouse effect Science (Washington, DC) 248· 1217-1219

Russell, A G , McRae, G J , Cass, G R (1985) The dynamics of nitric acid production and the fate of nitrogen oxides. Atmos Environ 19 893-903

Singh, H. B. (1987) Reactive nitrogen in the troposphere chemistry and transport of NO_x and PAN Environ Sci Technol 21 320-327

Singh, H B ; Hanst, P L (1981) Peroxyacetyl nitrate (PAN) in the unpolluted atmosphere an important reservoir for nitrogen oxides Geophys Res Lett 8 941-944

Singh, H B ; Salas, L J , Ridley, B A , Shetter, J D , Donahue, N M , Fehsenfeld, F C , Fahey, D W , Parrish, D D , Williams, E J , Liu, S C , Hubler, G , Murphy, P C (1985) Relationship between peroxyacetyl nitrate and nitrogen oxides in the clean troposphere Nature (London) 318 347-349

Solomon, S., Garcia, R R , Rowland, F S , Wuebbles, D J (1986) On the depletion of Antarctic ozone Nature (London) 321 755-758

Spicer, C W (1982) Nitrogen oxide reactions in the urban plume of Boston Science (Washington, DC) 215 1095-1097

Spicer, C. W., Joseph, D W , Ward, G F (1978) Investigations of nitrogen oxides within the plume of an isolated city New York, NY Coordinating Research Council, Inc , report no CRC-APRAC-CAPA-9-77 Available from NTIS, Springfield, VA, PB-290107

Spicer, C W , Joseph, D W , Sticksel, P R , Ward, G F (1979) Ozone sources and transport in the northeastern United States Environ Sci Technol 13 975-985

Spicer, C W , Sverdrup, G M (1981) Trace nitrogen chemistry during the Philadelphia oxidant data enhancement study (1979) Research Triangle Park, NC U S Environmental Protection Agency, Office of Air Quality Planning and Standards, contract no 68-02-3338

Spicer, C W , Sverdrup, G M , Kuhlman, M R (1981) Smog chamber studies of NO_x chemistry in power plant plumes Atmos Environ 15 2353-2365

Stockwell, W R , Calvert, J G (1983) The mechanism of NO_3 and HONO formation in the nighttime chemistry of the urban atmosphere J Geophys Res C Oceans Atmos 88 6673-6682

Thiemens, M H , Trogler, W C (1991) Nylon production an unknown source of atmospheric nitrous oxide Science (Washington, DC) 251 932-934

Tolbert, M A , Rossi, M J , Malhotra, R , Golden, D M (1987) Reaction of chlorine nitrate with hydrogen chloride and water at Antarctic stratospheric temperatures Science (Washington, DC) 238 1258-1260

Tolbert, M A , Rossi, M J , Golden, D M (1988a) Antarctic ozone depletion chemistry reactions of N_2O_5 with H_2O and HCl on ice surfaces Science (Washington, DC) 240 1018-1021

Tolbert, M A , Rossi, M J , Golden, D M (1988b) Heterogeneous interactions of chlorine nitrate, hydrogen chloride, and nitric acid with sulfuric acid surfaces at stratospheric temperatures Geophys Res Lett 15 847-850

Trainer, M , Williams, E J , Parrish, D D , Buhr, M P , Allwine, E J , Westberg, H H , Fehsenfeld, F C , Liu, S C (1987) Models and observations of the impact of natural hydrocarbons on rural ozone Nature (London) 329 705-707

Tuazon, E C , Atkinson, R , Plum, C N , Winer, A M , Pitts, J N , Jr (1983) The reaction of gas phase N_2O_5 with water vapor Geophys Res Lett 10 953-956

Tuazon, E C , Carter, W P L , Atkinson, R , Winer, A M , Pitts, J N , Jr (1984) Atmospheric reactions of *N*-nitrosodimethylamine and dimethylnitramine Environ Sci Technol 18 49-54

U S Environmental Protection Agency (1976) Assessment of scientific information on nitrosamines report of an ad hoc study group of the Science Advisory Board Executive Committee

U S Environmental Protection Agency (1982) Air quality criteria for oxides of nitrogen Research Triangle Park, NC Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office, EPA report no EPA-600/8-82-026 Available from NTIS, Springfield, VA, PB83-131011

Vukovich, F M , Bach, W D , Jr , Crissman, B W , King, W J (1977) On the relationship between high ozone in the rural surface layer and high pressure systems Atmos Environ 11 967-983

Wayne, R P , Barnes, I , Biggs, P , Burrows, J P , Canosa-Mas, C E , Hjorth, J , Le Bras, G , Moortgat, G K , Perner, D , Poulet, G , Restelli, G , Sidebottom, H (1991) The nitrate radical physics, chemistry, and the atmosphere Atmos Environ Part A 25 1-203

Westberg, H , Sexton, K , Roberts, E (1981) Transport of pollutants along the western shore of Lake Michigan J Air Pollut Control Assoc 31 385-388

White, W. H. (1977) NO_x-O_3 photochemistry in power plant plumes comparison of theory with observation Environ Sci Technol 11 995-1000

White, W. H , Dietz, D (1984) Does the photochemistry of the troposphere admit more than one steady state? Nature (London) 309 242-244

Winer, A M , Atkinson, R , Pitts, J N , Jr (1984) Gaseous nitrate radical possible nighttime atmospheric sink for biogenic organic compounds Science (Washington, DC) 224 156-159

Wofsy, S C ; Molina, M J , Salawitch, R J , Fox, L E , McElroy, M B (1988) Interactions between HCl, NO_x, and H_2O ice in the Antarctic stratosphere implications for ozone J Geophys Res [Atmos] 93 2442-2450.

Wolff, E. W., Mulvaney, R , Oates, K (1989) Diffusion and location of hydrochloric acid in ice implications for polar stratospheric clouds and ozone depletion Geophys Res Lett 16 487-490

World Meteorological Organization (1991) Scientific assessment of ozone depletion 1991 Geneva, Switzerland World Meteorological Organization, global ozone research monitoring project report no 25

Wuebbles, D J (1989) On the mitigation of non-CO_2 greenhouse gases Washington, DC U S Department of Energy, report no UCRL-101523 Available from NTIS, Springfield, VA, DE89016659

Wuebbles, D J , Grant, K E , Connell, P S , Penner, J E (1989) The role of atmospheric chemistry in climate change JAPCA 39 22-28

6. SAMPLING AND ANALYSIS FOR NITROGEN OXIDES AND RELATED SPECIES

6.1 INTRODUCTION

This chapter addresses various methods to measure selected airborne species containing nitrogen and oxygen The focus is on methodologies currently available or in general use for in situ monitoring of airborne concentrations in both ambient and indoor environments Methods for measuring the species of interest at their respective sources are not considered, and remote sensing technologies are mentioned in only a few cases

Although the primary focus in this document is nitrogen dioxide (NO_2), other species containing nitrogen and oxygen are also considered This chapter is organized into several sections, with each section devoted to a different species The species under consideration are nitric oxide (NO), NO_2, nitrogen oxides (NO_x), total reactive odd nitrogen oxides (NO_y), peroxyacetyl nitrate (PAN) and other organic nitrates, nitric acid (HNO_3), nitrous acid (HONO), dinitrogen pentoxide (N_2O_5), nitrate radical (NO_3), particulate nitrate ion (NO_3^-), and nitrous oxide (N_2O). In this chapter, NO_x represents the sum of NO and NO_2 (i.e., $NO_x = NO + NO_2$), whereas the term oxides of nitrogen is used as a generic name for nitroxycompounds (those compounds containing both nitrogen and oxygen)

Where possible, discussions of sampling and analysis methods for each species address pertinent characteristics for each method Topics discussed include method type (i e , in situ, remote, active, passive), description, status (i e , concept, laboratory prototype, commercially available), interferences, time resolution, sensitivity, and precision and accuracy A good overview of many of the currently available methods for measuring nitrogen-containing species is the proceedings of a recent National Aeronautics and Space Administration (NASA) workshop (National Aeronautics and Space Administration, 1983).

Methods development usually progresses through several stages concepts, laboratory prototypes, laboratory evaluations, field tests, field evaluations and comparisons against other "proven" methods, and finally, consensus acceptance by the user community At each stage, modifications may be implemented to improve or resolve weaknesses that have been revealed This is usually a winnowing process As a result of limitations discovered during

this process, many candidate methods may be abandoned in favor of other methods At some stage near the end of the process, commercialization may occur In the current document, those methods that have successfully progressed to the final stages of development are emphasized.

6.2 NITRIC OXIDE

Although NO_2, rather than NO, is the primary focus of this document, the most commonly used method of measuring NO_2 does not detect the NO_2 molecule directly Instead, the method relies on a chemiluminescent reaction of the NO molecule after NO_2 has been converted to NO Thus, to provide a background for subsequent discussions of measurement methods for NO_2 and other nitrogen-containing species, NO rather than NO_2 is the first species that is addressed Airborne concentrations of NO can be determined by various methods As noted previously, the most commonly used method is chemiluminescence (CLM). Other methods include laser-induced fluorescence (LIF), absorption spectroscopy, ionization spectroscopy, and passive collection with subsequent wet chemical analysis

6.2.1 Chemiluminescence

Chemiluminescence can be used to detect several airborne nitrogen-containing species (i.e., NO, NO_2, HONO, HNO_3, N_2O_5, PAN, NO_x, NO_y, ammonia [NH_3], and NO_3^-) Among these compounds, only NO is detected directly, whereas the other compounds must be converted in some manner to NO prior to detection

The principle is based on the detection of the light emitted following the reaction of NO with ozone (O_3) Excess O_3 is added to an air sample containing NO that is passing through a darkened reaction vessel with infrared-reflective walls and a window for viewing by a photomultiplier (PM) tube The light-emitting species is an electronically excited NO_2 radical, a product of the reaction of NO and O_3, which relaxes by photon emission that ranges in wavelength well beyond 600 nm and is centered near 1,200 nm. Light is detected by a red-sensitive PM tube fitted with optical filters to prevent interference by radiation below 600 nm produced by ozonalysis of other materials The intensity of the measured

light is proportional to the concentration of NO in the air sample, and the concentration can be determined by calibration with atmospheres of known composition

In applications to detect other airborne nitrogen-containing species, the air sample is preconditioned prior to entering the reaction vessel to convert some or all of these species to NO, and that signal is compared to the signal for an unconditioned sample The signal from the unconditioned sample represents NO, whereas that from the preconditioned sample represents the sum of the originally present NO along with the NO resulting from conversion of the other nitrogen species Signal differencing permits determination of the other nitrogen-containing species The specificity of the preconditioning process may be controversial and is discussed in subsequent sections

Chemiluminescence is designated by the U S. Environmental Protection Agency (EPA) as the Reference Method for determining NO_2 in ambient air (see Section 6.3) As a result, commercial instruments for measuring NO and NO_2 are available Detection limits of approximately 5 ppb with response times on the order of minutes are claimed by suppliers Although these performance parameters are adequate for monitoring NO and NO_2 in relatively polluted urban and suburban environments, they may be inadequate in less polluted remote areas Efforts have been reported by several researchers to improve the sensitivity and response of CLM NO measurement technology to permit deployment in remote locations both on ground-based and airborne platforms Delany et al (1982), Dickerson et al. (1984), Tanner et al (1983), and Kelly (1986) reported techniques for modifying commercially available NO_x detectors to achieve improved sensitivity and response times Modifications that can be employed include (1) operation at a low pressure, high flow rate, and increased O_3 supply, (2) addition of a prereactor where sample air and O_3 flows are mixed out of view of the PM tube to obtain a more stable background signal, (3) use of a larger, more efficient reaction vessel, with highly reflective walls, that promotes the reaction close to the PM tube, (4) use of pure oxygen as the O_3 source, (5) cooling the PM tube to reduce noise in the dark current, and (6) change of the electronics to employ photon counting techniques rather than analog signal processing

Kelly (1986) has provided instructions for application of the first three modifications to the Thermo Electron Model 14-B and the Monitor Labs Model 8840 Postmodification detection limits of 0 1 to 0 2 ppb and 90% response times of 5 to 10 s were claimed for

these instruments Dickerson et al (1984) applied modifications (1), (2), (3), and (5) noted above to a Thermo Electron Model 14 B/E and reported minimum detection limits (MDLs) for NO of 10 ppt, with a 1/e response time of 20 s

Other workers have developed highly sensitive research-grade instruments for the CLM determination of NO (Ridley and Howlett, 1974; Kley and McFarland, 1980, Helas et al , 1981; Drummond et al , 1985, Carroll et al , 1985, Torres, 1985, Kondo et al , 1987) Such devices have been used to measure NO at the earth's surface, from airborne platforms in the troposphere, and from balloon-borne platforms in the stratosphere These instruments generally employ those features listed above Minimum detection limits of 5 ppt or less, response times of 2 to 60 s, and accuracy of 10 to 20% have been claimed

Chemiluminescence NO instruments appear to be specific for NO. Water vapor may act to quench excited NO_2 efficiently (Matthews et al , 1977, Folsom and Courtney, 1979) Operation at reduced pressure reduces this problem With a commercial analyzer, a 7% reduction in the NO signal was reported for 81% relative humidity (RH) versus dry air (MacPhee et al., 1976) Recent tests of eight commercial analyzers have not shown a water vapor interference with the NO_2 signal (Michie et al , 1983) With various research-grade instruments, interference due to varying humidities has been reported to be negligible below 20 ppm water (H_2O), increase by less than 10% with RH up to 2 5%, and show no change between 2 and 100% RH (Fahey et al , 1985a, Drummond et al , 1985) Using commercial CLM instruments, no or very small (i e , less than 2%) interferences have been reported for 6 chlorine-containing species (Joshi and Bufalini, 1978), 14 sulfur-containing species (Sickles and Wright, 1979), 7 nitrogen-containing species, and 3 sulfur-containing species (Grosjean and Harrison, 1985b) Zafiriou and True (1986), however, do report interferences from hydrogen sulfide (H_2S) and from gases purged from anoxic waters that may have contained sulfur compounds Using research-grade CLM instruments, Fahey et al (1985a) found no NO interference for NO_2, HNO_3, N_2O_5, and PAN and negligible responses for NH_3, hydrogen cyanide (HCN), N_2O, methane (CH_4), and nine chlorine-containing and three sulfur-containing compounds These findings are consistent with those of Drummond et al (1985), who report no or negligible NO interferences from NO_2, HNO_3, PAN, HO_2NO_2, hydrogen peroxide (H_2O_2), propylene, H_2O, and aerosols using a research-grade instrument with a humidified O_3 source

From an operational perspective, aerosols can accumulate on the glass filter separating the reaction chamber from the PM tube, causing a reduction in sensitivity (Klapheck and Winkler, 1985) Cleaning the filter is reported to restore the original sensitivity

Whereas most of the CLM methods discussed above are continuous, CLM has also been used to analyze nitrogen species collected in integrated samples Gallagher et al (1985) have taken cryosamples (4 K) of whole stratospheric air Samples were analyzed following desorption in the laboratory for NO and NO_2 using modified commercial CLM instruments Braman et al (1986) have employed a series of hollow denuder tubes coated with chemicals chosen to preconcentrate various oxides of nitrogen The collected nitrogen species are thermally desorbed, and detected as NO with a commercial CLM instrument The coating materials used to preconcentrate the various target species in sequence are tungstic acid (removes HNO_3), potassium-iron oxide (removes HONO), copper (I) iodide (removes NO_2), and cobalt (III) oxide (removes NO) Future field testing is needed to demonstrate the adequacy of this method

6.2.2 Laser-Induced Fluorescence

Laser-induced fluorescence techniques may incorporate single-photon (SP), two-photon (TP), or photofragmentation (PF) schemes Although SP-LIF has been used to measure NO (Bradshaw et al , 1982), TP-LIF represents an advancement in the state of the art (Bradshaw et al , 1985) and is discussed here The TP-LIF detection principle requires that a molecule have more than one bonding excited state and can be sequentially pumped into the highest state If the lifetime of the excited state is short compared to collisional deactivation, the excited molecule will decay to a more stable state by a fluorescence process The fluorescence wavelength is shifted relative to that of the pumping wavelengths and thus overcomes noise problems associated with background nonresonant fluorescence For application to NO, pulsed ultraviolet (UV) and infrared (IR) laser light sources are used Ground state $X^2\Pi$ NO is excited to the $A^2\Sigma$ electronic level using UV light of 226-nm wavelength Then using IR wavelengths of 1 06 to 1 15 μm, the molecule is further pulsed to the $D^2\Sigma$ level. The fluorescence resulting from the $D^2\Sigma$ to $X^2\Pi$ transition is monitored at 187 to 220 nm By using long-wavelength blocking filters with solar-blind PM tubes, this type of detector discriminates against noise and becomes signal, rather than signal-to-noise,

limited. Photon counting and grated-charge integrators are used for signal processing The intensity of the light is related to the concentration of NO in the air sample by calibration with atmospheres of known concentration

Because the TP-LIF instrument is signal limited, the sensitivity is defined by the integration time (e g., 1 ppt for 5 min and 10 ppt for 30 s) (Davis et al , 1987) Propagation of error analysis has been used to place 90% confidence limits of $\pm 16\%$ on the accuracy of TP-LIF NO field measurements performed on an aircraft Also, the TP-LIF technique is expected to be highly specific because it has two levels of spectroscopic selectivity If some trace atmospheric compound were to produce an NO molecule by interaction with the 226-nm beam, then an opportunity for interference exists Potential interference from HNO_3, nitromethane, nitroethane, CH_3ONO_2, NO_2, PAN, HONO, sulfur dioxide (SO_2), and CH_3ONO has been evaluated Only the last compound was found to show potential interference, and arguments have been given to neglect its influence when sampling tropospheric air (Davis et al , 1987)

6.2.3 Absorption Spectroscopy

Absorption spectroscopy encompasses techniques that measure the change in radiance from a source that occurs as a result of absorption by analyte molecules over a known path length. Several techniques, including Fourier transform IR spectroscopy (FTIR), long-path absorption, and IR tunable-diode laser spectroscopy (TDLAS), have been employed for measuring the concentration of various NO_x in the atmosphere (National Aeronautics and Space Administration, 1983) Among these techniques, the TDLAS is a well-developed technique that has been applied to NO as well as NO_2 and HNO_3 Similar sensitivities have been reported for both remote sensing applications using open air path lengths and in situ application using multipass cells (Cassidy and Reid, 1982) The latter configuration has found broader application for ambient measurements of NO_x, and the use of the White cell avoids atmospheric turbulence-related errors that can affect open air application As a result, in situ TDLAS is the primary focus of this section

Tunable-diode laser spectroscopy employs a tunable-diode laser to scan over a narrow wavelength region around a particular absorption line or feature of the gas of interest High sensitivity is achieved by the high spectral radiance of the diodes and the rapid tunability of

the laser With rapid scanning back and forth across an absorption line, the absorption appears as an AC signal at twice the tuning frequency and can be sensitively detected by sychronous demodulation System sensitivities sufficient to measure signal changes of 10^{-5} permit the detection of concentrations of less than 10 ppt with a 1-km path length For analyte molecules that have resolved absorption spectra that are not coincident with other atmospheric constituents, TDLAS is highly specific Additional information on the operating principles and hardware for TDLAS is provided both by Schiff et al (1983) and by National Aeronautics and Space Administration (1983)

For optically thin systems, Beer's Law suggests that the fraction of the power transmitted through an absorbing medium is proportional to the concentration of the absorbing molecule However, because the total laser power is not measured, it is usually necessary to calibrate the TDLAS by introducing a known concentration of the target gas and determining the proportionality between signal and concentration

Using a 40-m path length near 1,850 cm^{-1}, the MDL for NO is 0 5 ppb (Schiff et al 1983) At a sampling rate giving a 4-s residence time in the White cell, stable NO signals are achieved in approximately 1 min Linearity has been demonstrated between the signal and NO concentration at levels between 7 and 175 ppb Because the NO calibration gas is introduced directly into the sampling line, surface losses are compensated for automatically As noted previously, the measurement of NO using TDLAS is highly specific

A newly developed method, two-tone frequency modulated spectroscopy (TTFMS), has shown great promise in the laboratory for the measurement of NO, NO_2, PAN, HNO_3, N_2O, and other atmospheric trace gases (Hansen, 1989) Two-tone frequency modulated spectroscopy uses a diode laser light source that is modulated simultaneously at two arbitrary, but closely spaced frequencies The beat tone between these two frequencies is monitored as the laser carrier and associated sidebands are tuned through an absorption line The method is fast, specific, and extremely sensitive Using a low pressure (20-torr) multiple-reflection optical cell with a 100-m path length and 1-min signal averaging time, the projected MDL for NO is 4 ppt, and the projected MDLs for NO_2, PAN, HNO_3, and N_2O are lower Additional development of this laboratory prototype is needed to demonstrate its performance in the field

6.2.4 Passive Samplers

Whereas the previous methods are focused primarily on low NO concentrations representative of ambient air, passive samplers are focused on atmospheres having higher concentrations, such as those found indoors or in the workplace They are used to obtain data at a large number of sites averaged over a long period of time The Palmes tube is a passive sampler that relies on diffusion of an analyte molecule through a quiescent diffusion path of known length and cross-sectional area to a reactive surface where the molecule is captured by chemical reaction (Palmes et al , 1976) After exposure durations ranging from hours to days, the reactive surface is analyzed and the integrated loading of the reaction product is used to infer the average gas concentration A quiescent diffusion path is required to ensure that sampling is diffusion controlled, and as a result, is relatively constant This permits the average ambient concentration to be related directly to the ratio of the reaction product loading to the exposure time This proportionality factor is analogous to the reciprocal of a sampling rate, where sampling rate is the product of the diffusivity of the analyte gas and the area of the opening through which the molecules diffuse divided by the distance they must travel to be collected

Palmes tubes are fabricated in a range of measurements from tubing (Palmes and Tomczyk, 1979). The dimensions are chosen to provide a ratio of sampling area to diffusion distance of 0.1 and thus ensure diffusion-controlled sampling. Reactive grids are secured and sealed at one end of the tubing segment using a plastic cap. The opposite end of the tube is sealed with a similar cap The capped sampler is stored until the sample is to be collected A sample is collected by placing the tube in the appropriate location (e g , for personal sampling the tube may be attached to a worker's lapel), removing the end cap opposite the gridded end with the open end facing down, sampling for the appropriate period, recording the time, recapping the tube, and returning the sampler to the laboratory for analysis

The Palmes tube passive sampler does not measure NO directly Two tubes are required: one has reactive grids coated with triethanolamine (TEA) to collect NO_2 The second tube is similar, but has an additional reactive surface coated with chromic acid to convert NO to NO_2, which is in turn collected by the TEA-coated grids The NO concentration is determined by subtraction after correction for differences in sampling rates caused by differences in diffusivities of the two molecules To ensure reliable results,

contact between the chromic acid coated surface and the TEA-coated grids for longer than 24 h must be avoided.

Analysis is accomplished by extracting the grids in solution and analyzing the extract for nitrite ion (NO_2^-) This analysis may be performed by adding a solution of water, sulfanilamide, and *N*-1-naphthylethylene-diamine-dihydrochloride (NEDA) reagent directly into the tube and determining the concentration using a spectrophotometer at 540 nm (Palmes et al , 1976) Increased sensitivities are claimed by analyzing the solution using ion chromatography (IC) with a concentrator column (Miller, 1984) The colorimetric analysis is calibrated by dilution of gravimetrically prepared nitrite solutions

The sampling rate (i e , 0 02 cm^3/s) for NO is reported to be independent of pressure, to increase approximately 1% for each 5 5 °C increase in temperature, and to increase by 3% for each 5 cm/s increase in wind velocity (Palmes and Tomczyk, 1979) Linear response was found for loadings between 2 and 120 ppm-h This method was proposed for sampling occupational exposures where the dosage is not to exceed 25 ppm for 8 h (i e , 200 ppm-h) This method cannot be used for sampling periods longer than 24 h. The reliability of this method in the field at both parts-per-billion and parts-per-million levels remains to be demonstrated

A badge-type sampler similar to the Palmes tube has been devised by Yanagisawa and Nishimura (1982) Their device uses a series of 12 layers of chromium trioxide (CrO_3) impregnated glass fiber to oxidize NO to NO_2 The filters also act as a diffusion barrier between the ambient air and a TEA-coated cellulose fiber filter Nitric oxide is oxidized to NO_2 on the oxidizing filters and collected along with NO_2 that has diffused from ambient air through the filters to the TEA-coated collection surface The TEA-coated filter is extracted and analyzed for NO_2^- Either a colorimetric or IC analytical finish may be employed The analytical finish is calibrated by dilution of gravimetrically prepared nitrite solutions
An effective proportionality factor (i e , calibration factor) for the badge is provided by the supplier This technique is claimed to be more sensitive than the Palmes tube and to have a lower detection limit equivalent to a dosage of 0 07 ppm-h

6.2.5 Calibration

Chemiluminescence, TP-LIF, and TDLAS NO measurement systems all employ calibration cylinders containing known concentrations of NO in molecular nitrogen (N_2) at nominal concentrations of 1 to 50 ppm (Carroll et al , 1985, Bradshaw et al , 1985, Schiff et al , 1983) Calibrations are performed using dynamic dilution with air

In the calibration procedure for the measurement of NO_2 by CLM, the EPA specifies the use of an NO concentration standard (Code of Federal Regulations, 1987a) This standard is a cylinder of compressed gas containing between 50 and 100 ppm NO in nitrogen. The concentration must be traceable according to a certification protocol to a National Institute of Standards and Technology (NIST, formerly National Bureau of Standards) Standard Reference Material (SRM) or an NIST/EPA-approved commercially available Certified Reference Material The National Institute of Standards and Technology provides 10 NO SRMs at nominal concentrations between 5 and 3,000 ppm (National Bureau of Standards, 1988) Shores and Smith (1984) have demonstrated that aluminum calibration cylinders containing 10 to 150 ppm NO in nitrogen were stable over time, and for 103 such cylinders, the average change was less than 1% over an 18-mo period Commercially supplied cylinders from 11 producers containing certified concentrations at nominal values of 70 and 400 ppm were evaluated for accuracy (Wright et al , 1987) In all cases, the certified and auditor-measured concentrations were within 5%, and in over two-thirds of the cases the agreement was within 2%

Passive NO samplers do not employ full calibration of sampling and analysis operations (Palmes et al , 1976) Only the analysis portion of the procedure is calibrated Calibration standards for colorimetric or IC determination of nitrite are prepared similarly Dilution of gravimetrically prepared liquid solutions of nitrite is used to produce calibration standards that cover the working range of analysis

6.2.6 Intercomparisons

Several intercomparisons of the performance of research-grade NO instrumentation have been conducted recently (Walega et al , 1984, Hoell et al , 1985, Hoell et al , 1987, Fehsenfeld et al., 1987). Walega et al (1984), for example, reported comparisons of NO measurements made with a highly sensitive CLM instrument and a TDLAS system

Measurements of NO-spiked synthetic air were made in the laboratory and field In addition, measurements were made of ambient and downtown Los Angeles air Good agreement was found for all test conditions

Tests to compare the performance of several instruments at measuring trace gases in the troposphere have been performed as part of NASA's Global Tropospheric Experiment/ Chemical Instrumentation Test and Evaluation 1 and 2 (GTE/CITE 1 and 2) Hoell et al (1985 and 1987) and Gregory et al (1990a) have reported comparisons of NO measurements made with two highly sensitive CLM instruments and a TP-LIF instrument The first intercomparison was a ground-based study performed at Wallops Island, VA The second intercomparison was an airborne study comprised of two missions performed on a Convair CV-990 flown out of California and Hawaii The third intercomparison involved 13 flights sampling tropical, nontropical, maritime, and continental air masses at altitudes between 150 and 5,000 m The two CLM instruments were of similar design (Kley and McFarland, 1980), with the main differences being the injection of water vapor to the airstream entering the reaction chamber of one instrument to minimize the background variability caused by changing ambient humidity and to suppress an O_3-related background signal In the first study, measurements of ambient NO concentrations ranged from 10 to 60 ppt and of NO-enriched ambient air ranged from 20 to 170 ppt Agreement among the techniques at the 95% confidence level was $\pm 30\%$, and no artifact or species interferences were identified In the second and third studies, NO concentrations ranged from below 5 ppt to above 100 ppt, with the majority below 20 ppt At NO concentrations below 20 ppt, measurements agreed to within stated instrument precision and accuracy (i e , to within 15 to 20 ppt) Good correlation was observed between CLM and TP-LIF measurements The authors concluded that equally valid measurements of ambient NO can be expected from either instrument

A field intercomparison of instruments designed to measure NO, NO_x, and NO_y was conducted near Boulder, CO (Fehsenfeld et al , 1987) The study was performed to compare the performance of instruments that employed different approaches to reduce NO_x or NO_y to NO prior to detection by CLM In several tests, both zero air and ambient air spiked with NO were measured Excellent agreement was found among the measurements of the three tested instruments These results confirm the equivalence of CLM NO detection systems

6.2.7 Sampling Considerations for Nitric Oxide and Other Nitrogen-Containing Species

Nitric oxide reacts rapidly with O_3 to form NO_2 In the presence of sunlight, NO_2 will photolyze to form NO and atomic oxygen, which will combine with atmospheric molecular oxygen to form O_3 Thus, under daylight conditions NO, O_3, and NO_2 can all exist simultaneously in ambient air in a condition known as a photostationary state, where the rate of photolysis of NO_2 is nearly equal to the rate of reaction between NO and O_3 to form NO_2. The relative amounts of the three species at any time are influenced by the intensity of the sunlight present at that moment When a sample is drawn into a dark sampling line, photolysis ceases, but NO continues to react with O_3 to form NO_2 As a result, long residence times in sampling lines must be avoided to ensure a representative sample Sampling requirements for a given error in tolerance were discussed by Butcher and Ruff (1971). Figure 6-1 shows the absolute error in NO_2 introduced for a 10-s residence time in a dark sampling line in the presence of NO and O_3 at various concentrations

In addition to sampling time considerations, sampling surfaces should be considered Oxides of nitrogen are, in general, reactive species As a result, the most nearly inert materials (i e , glass and Teflon™) are recommended for use in sampling trains If water molecules accumulate on sampling train surfaces and influence sample integrity, then species solubility may be one indicator of the susceptibility of a species to surface effects. Solubilities at 25 °C, expressed as Henry's Law coefficients (M/atm), for selected nitrogen containing species are NO, 2×10^{-3}, NO_2, 1×10^{-2}, N_2O, 3×10^{-2}, PAN, 4, HONO, 50, NH_3, 60; and HNO_3, 2×10^{5} (Schwartz, 1983) This suggests that of the NO_x species, NO may be the least susceptible to surface effects, whereas surface effects may be very important in the sampling of HNO_3

6.3 NITROGEN DIOXIDE

Among the NO_x species, NO_2 is the only criteria pollutant and the only species to have sampling and analysis methodologies specified by the EPA for determining ambient airborne concentrations. As a result, methods for sampling and analysis of NO_2 are emphasized in this document Airborne concentrations of NO_2 can be determined by several methods,

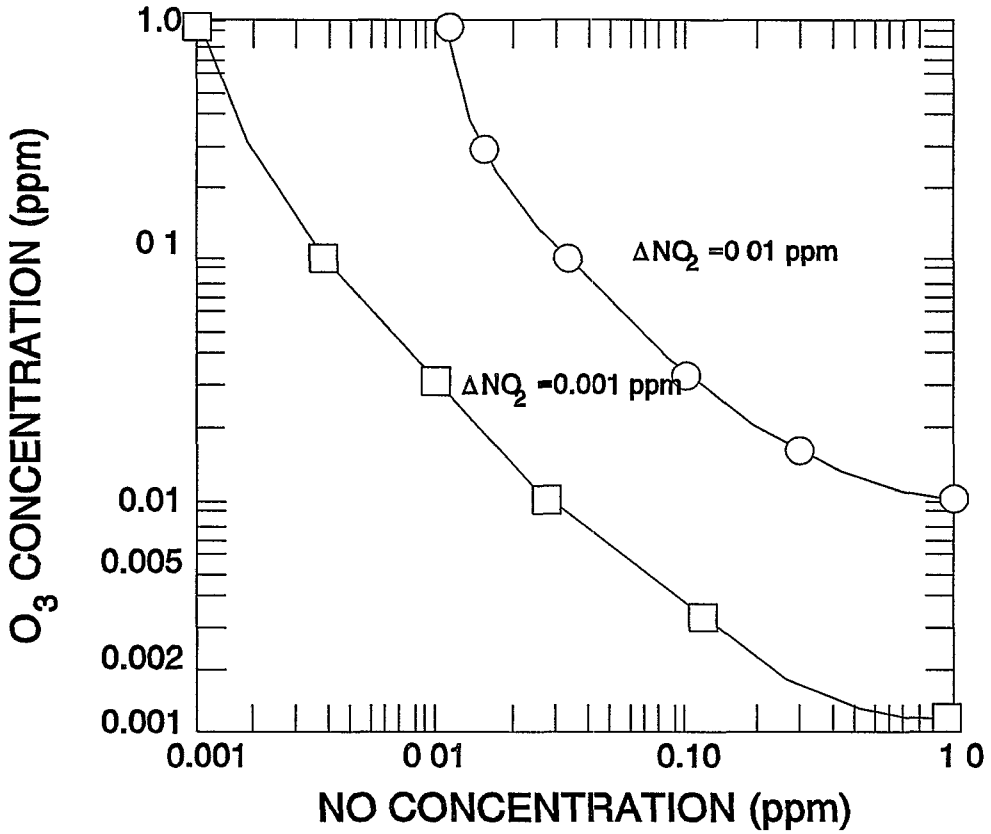


Figure 6-1. Absolute error in nitrogen dioxide (Δ NO_2) for 10 s in the dark sampling line

Source Butcher and Ruff (1971)

including CLM, LIF, absorption spectroscopy, and bubbler and passive collection with subsequent wet chemical analysis

6.3.1 Chemiluminescence, Nitric Oxide Plus Ozone

Instruments discussed in this section sample continuously and employ the CLM reaction of NO and O_3, but do not detect NO_2 directly Instead, they rely on the direct detection of NO, the conversion of some or all of the NO_2 in the air sample to NO, reaction with O_3, and the appropriate signal processing to infer the NO_2 concentration The CLM NO detection principle and hardware are described in Section 6 2 1 To measure NO_2, a CLM

NO detector, a converter, plumbing modifications, and changes in signal processing are required

Several methods have been employed to reduce NO_2 to NO (Kelly, 1986) They include catalytic reduction using heated molybdenum or stainless steel, reaction with CO over a gold catalyst surface, reaction with iron sulfate ($FeSO_4$) at room temperature, reaction with carbon at 200 °C, and photolysis of NO_2 to NO at 320 to 400 nm

Because CLM is designated by the EPA as the Reference Method for NO_2 in ambient air (Code of Federal Regulations, 1987a), CLM instruments for the determination of NO_2 are readily available commercially As noted previously, these instruments are used to measure both NO and NO_2 Nominal detection limits of approximately 5 ppb and response times on the order of minutes are claimed by suppliers Field evaluation of nine instruments has shown the MDLs to range from 5 to 13 ppb (Michie et al , 1983, Holland and McElroy, 1986). Recent field and laboratory evaluation of two commercial instruments operated on a 0.00- to 0.05-ppm range revealed detection limits of between 0 5 and 1 0 ppb and operating precision estimates of $\pm$0 3 ppb (Rickman et al , 1989) Although these performance parameters are adequate for monitoring NO and NO_2 in urban and suburban environments, they may be inadequate in less polluted remote areas As noted in Section 6 2 1, efforts have been reported by several researchers to improve the sensitivity and response of CLM NO measurement technology to permit deployment in remote locations on ground-based and airborne platforms. Because the research-grade instruments employed by these workers included NO_2-to-NO converters and were designed to measure both NO and NO_2, instrument performance for the determination of NO_2 is also improved substantially over that of commercially available instruments Typically reported performance parameters for NO_2 response using research-grade CLM instruments are MDLs of 10 to 25 ppt, response times of 1 to 100 s, and accuracy of 30 to 40% (Helas et al , 1987, Fehsenfeld et al , 1987)

Different converters may not be specific for NO_2 and may convert several nitrogen-containing compounds to NO, giving rise to artificially high values for NO_2 Early in the day, in urban areas, NO and NO_2 make up most of the airborne oxides of nitrogen As the day proceeds, these compounds are oxidized by atmospheric chemical reactions to other species (e.g , PAN, HNO_3, and other NO_y compounds [see Section 6 5]) Thus the potential for appreciable interference depends on (1) reaction time (i e , greater in the afternoon than

in the morning, and greater after days of reaction than on the day of emission), (2) sampling location and/or air mass (i e , greater in rural than in urban areas, and greater in maritime than continental air masses), and (3) the presence of a specific interferant in a freshly released plume

Using commercial instruments, Winer et al (1974) found over 90% conversion of PAN, ethyl nitrate, and ethyl nitrite to NO with a molybdenum converter and similar responses to PAN and *n*-propyl nitrate with a carbon converter With a stainless steel converter at 650 °C, Matthews et al (1977) reported 100% conversion for NO_2, 86% for NH_3, 82% for methylamine (CH_3NH_2), 68% for HCN, 1% for N_2O, and 0% for N_2 Using commercial instruments, Cox (1974) reported quantitative response to HONO, and Joseph and Spicer (1978) found quantitative conversion of HNO_3 to NO with a molybdenum converter at 350 °C Similar responses to PAN, methyl nitrate, *n*-propyl nitrate, *n*-butyl nitrate, and HNO_3, substantial response to nitrocresol, and no response to peroxybenzoyl nitrate (PBzN) were reported with a commercial instrument using a molybdenum converter at 450 °C (Grosjean and Harrison, 1985b) These results were confirmed for PAN and HNO_3 by Rickman and Wright (1986) using commercial instruments with a molybdenum converter at 375 °C and a carbon converter at 285 °C

Interferences from species that do not contain nitrogen have also been reported Joshi and Bufalini (1978), using a commercial instrument with a carbon converter, found significant apparent NO_2 responses to phosgene, trichloroacetyl chloride, chloroform, chlorine, hydrogen chloride, and photochemical reaction products of a perchloroethylene-NO_x mixture Grosjean and Harrison (1985b) reported substantial responses to photochemical reaction products of molecular chloride (Cl_2)-NO_x and Cl_2-methanethiol mixtures and small negative responses to methanethiol, methyl sulfide, and ethyl sulfide Sickles and Wright (1979), using a commercial instrument with a molybdenum converter at 450 °C, found small negative responses to 3-methylthiophene, methanethiol, ethanethiol, ethyl sulfide, ethyl disulfide, methyl disulfide, H_2S, 2,5-dimethylthiophene, methyl sulfide, methyl ethyl sulfide, and negligible responses to thiophene, 2-methylthiophene, carbonyl sulfide, and carbon disulfide

With a research-grade instrument, Bollinger et al (1983) reported that NO_2, HNO_3, *n*-propyl nitrate, and N_2O_5 are reduced to NO by a gold-catalyzed reaction with carbon

monoxide (CO). Fahey et al (1985a), using a similar instrument with 3,000 ppm CO over a gold converter at 300 °C, reported conversion efficiencies exceeding 90% for NO_2, HNO_3, N_2O_5, and PAN Although negligible response to HCN and NH_3 was found in the presence of water vapor at a converter temperature of 300 °C, complete conversion was noted at 700 °C.

A room temperature NO_2-to-NO converter using $FeSO_4$ has been suggested by Winfield (1977) and adopted in research-grade instruments by Helas et al (1981), Kondo et al (1983), and Dickerson et al (1984). A reduction in conversion efficiency has been reported under dry conditions, and conversion of PAN, HONO, and other nitrogen-containing species to NO has been noted (Fehsenfeld et al , 1987) Nonspecificity of the $FeSO_4$ converter has been observed by Fehsenfeld et al (1987) in measuring NO and NO_2 in a remote environment. At NO_x levels below 1 ppb, results from the $FeSO_4$ converter were biased high in the measurement of NO_2 (i e , a factor of 2 at 0 1 ppb) Airborne measurements of NO_2 at concentrations below 0 2 ppb showed high biases of factors of 2 to 3 for a CLM instrument with an $FeSO_4$ converter (Gregory et al , 1990b)

In another research-grade instrument, Kley and McFarland (1980) used a xenon (Xe) arc lamp to photolyze a portion of the NO_2 in sampled air to NO and determine the NO_2 concentration from the increase in NO A fractional conversion was established using a calibration source Interferences with the photolytic converter (CLM-PC) approach are expected from HONO, NO_3, HO_2NO_2, and N_2O_5, but not from HNO_3, *n*-propyl nitrate, and PAN A detailed description of the operation (including minimization of interferent decomposition and both homogeneous and heterogeneous oxidation of NO) and performance of a CLM-PC instrument is given by Ridley et al (1988) An artifact identified with this method is caused by nitrate-containing aerosols deposited on the surface of the photolysis tube that release NO and NO_2 upon irradiation (Bollinger et al , 1984) This interference is eliminated by filtering sampled air and periodic cleaning of tube surfaces

The methods discussed above employ CLM detection of NO and are continuous Other researchers have employed various methods of integrated sampling followed by a CLM instrument for measuring NO and NO_2 in the desorbed sample Gallagher et al (1985) have used cryosampling of stratospheric whole air samples, and Braman et al (1986) have used copper (I) iodide coated denuder tubes to sample NO_2 in ambient air

6.3.2 Chemiluminescence, Luminol

A method for the direct CLM determination of NO_2 was reported by Maeda et al (1980) This method is based on the CLM reaction of gaseous NO_2 with a surface wetted with an alkaline solution of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) The emission is strong at wavelengths between 380 and 520 nm. The intensity of the measured light is proportional to the NO_2 concentration in the sampled air, and the concentration can be determined by calibration with atmospheres of known concentration

Since the introduction of the luminol method by Maeda et al (1980), improvements have been made to develop an instrument suitable foi use in the field (Wendel et al , 1983), and additional modifications have recently been made to produce a continuous commercial instrument (Schiff et al , 1986) Detection limits of 5 to 30 ppt and a response time of seconds have been claimed based on laboratory tests (Wendel et al , 1983, Schiff et al , 1986) Recent laboratory evaluation of two instruments has revealed a detection limit (i e , twice the standard deviation of the clean-air response) of 5 ppt and 95% rise and fall times of 110 and 15 s (Rickman et al , 1988) Field tests of the same instruments have shown an operating precision of ± 0 6 ppb

The original method showed no interferences from NO, N_2O, NH_3, CO, propylene, and 1,2-dichloroethylene, but positive interferences from O_3 and SO_2 and a negative interference from carbon dioxide (CO_2) (Maeda et al , 1980). More recently, the luminol solution has been reformulated, containing H_2O, luminol, sodium hydroxide (NaOH), sodium sulfite, and alcohol in proportions chosen to enhance the sensitivity and minimize interferences from O_3, SO_2, and CO_2 (Wendel et al , 1983, Schiff et al , 1986)
At concentrations below 100 ppb, no interferences were reported for HNO_3, NH_3, HCN, H_2O_2, CO, CO_2, and SO_2 Negative interferences of 1 2 to 5% have been reported for NO (Schiff et al , 1986, Spicer et al , 1991) Also, the instrument has shown sensitivity to PAN (Wendel et al , 1983, Sickles, 1987), different sensitivities to HONO (Rickman et al , 1989, Spicer et al , 1991), and nonlinear response to NO_2 (Schiff et al , 1986, Kelly et al , 1990, Spicer et al , 1991) Furthermore, the method has shown appreciable sensitivity to an operating temperature that can be resolved by controlling the temperature of the reaction cell or by signal processing (Schiff et al , 1986, Bubacz et al , 1987) Recent tests of the CLM (luminol) instrument have demonstrated the need to correct results for pressure (as might be

seen in airborne applications), nonlinearity of response below 3 ppb NO_2, interferences from O_3 and PAN, and the age-dependent sensitivity of the luminol solution (Kelly et al , 1990) Lastly, a manufacturer-supplied O_3 scrubber designed to eliminate the O_3 interference was also found to remove appreciable amounts of NO_2

6.3.3 Photofragmentation/Two-Photon Laser-Induced Fluorescence

Two NO_2 sensors based on measurement of fluorescence of excited NO_2 have been reported by Fincher et al (1978) One device employs a small, high-pressure xenon arc flash lamp to excite NO_2 This device has a sensitivity of 10 ppb for an 80-s (i e , 1,024 flash-lamp pulses) integration time The other device uses a 442-nm LIF and a PM tube with photon counting of light above 600 nm The sensitivity of this device is 1 ppb for a comparable integration time A major drawback of these devices for broad ambient applications is limited sensitivity associated with background signals This has been overcome with PF/TP-LIF instrumentation

An NO_2 sensor incorporating PF/TP-LIF has recently been developed and deployed in the field (Rodgers et al., 1980, Davis, 1988) With this method, NO is measured in one cell using TP-LIF (see Section 6 2 2) A xenon fluoride excimer laser with output at 353 nm is used in a second cell to photolyze NO_2 The total NO signal in the second cell resulting from ambient and photofragment NO is measured as NO using TP-LIF The NO_2 concentration is determined from the difference in signals of the two reaction cells and the fractional photolysis of NO_2 The NO_2 fluorescence cell is calibrated using calibration sources of NO and NO_2

Because the PF/TP-LIF instrument is signal-limited, the sensitivity is defined by integration time The detection limit for NO_2 for a 2-min integration time is 12 ppt (Davis, 1988). The accuracy of PF/TP-LIF NO_2 determinations is likely to be similar to the $\pm 16\%$ reported for TP-LIF NO measurements (Davis et al , 1987) At 15 ppt NO and 50 ppt NO_2, the precision of NO_2 determinations is given as $\pm 17\%$ (Gregory et al , 1990b)

The PF/TP-LIF technique is expected to be highly specific for NO_2 In addition to those potential NO interferents with TP-LIF that are discussed in Section 6 2 2, other species that could photolyze or otherwise decompose to produce NO or NO_2 have been considered

(Davis, 1988) Arguments were given to dismiss HNO_3, HO_2NO_2, N_2O_5, CH_3ONO, and CH_3ONO_2 as possible interfering species

6.3.4 Absorption Spectroscopy

Absorption spectroscopy is discussed in a previous section for NO (Section 6 2 3) Absorption methods may measure the absorption of light in the UV, visible, or IR regions of the electromagnetic spectrum They may employ closed cells for in situ measurements (e g , TDLAS) or open paths for remote sensing Absorption methods require a source of radiation Active methods utilize artificial light from a source such as an incandescent lamp or a laser, whereas passive methods use natural light from the sun or moon Laser sources offer advantages of scanning, narrow spectral width, and high intensity, and as a result, usually provide better sensitivity than nonlaser sources In this section, several absorption techniques are addressed, including the in situ methods, TDLAS, photometry, and TTFMS, as well as remote sensors employing long-path absorption differential optical absorption spectroscopy (DOAS) and differential absorption lidar (DIAL)

Tunable-diode laser spectroscopy is a well-developed technique that has been used to measure NO_2 as well as other species in the atmosphere Descriptive information about the operating principle is given in Section 6 2 3 and the references therein With a 150-m path length near 1,600 cm^{-1}, the MDL is 0 1 ppb and the accuracy is $\pm 15\%$ (Mackay and Schiff, 1987) For a 40-m path length, the MDL for NO_2 is 0 5 ppb (Schiff et al , 1983) At a sampling rate giving a 4-s residence time in the White cell, stable NO_2 signals are achieved in approximately 1 min Linearity has been demonstrated between the signal and NO_2 concentration at levels between 35 and 175 ppb Surface losses are compensated for automatically because the NO_2 calibration gas, typically from a permeation tube, is introduced directly into the sampling line Tunable-diode laser spectroscopy is a spectroscopic technique, as a result, the measurement of NO_2 using this method is highly specific

A prototype instrument using an in situ absorption technique to measure NO_2 was recently reported (Jung and Kowalski, 1986) This technique employs a modified commercial O_3 photometric analyzer to measure the absorption of visible light by NO_2 at wavelengths longer than 400 nm The signal obtained in a 1 12-m absorption cell from

unscrubbed ambient air is compared with that from ambient air scrubbed of NO_2 A microcomputer uses Beer's Law and an absorption coefficient derived from an NO_2 calibration source to determine the NO_2 concentration Interferences from NH_3, NO, O_3, SO_2, and PAN have been shown to be negligible Comparisons with commercially available CLM analyzers monitoring smog chamber experiments and ambient air have shown good agreement when NO_2 was expected to be present The CLM signal was found to exceed that of the photometer when photochemical reaction products such as PAN were believed to be present Although noise of less than 3 ppb and linear response have been demonstrated between 100 and 700 ppb, additional development and evaluation are needed to permit routine use of this technique to ambient monitoring applications

Cryogenic sampling at 77 K combining the matrix-isolation technique (i e , solid CO_2) with FTIR spectroscopy has shown promise for the sensitive determination of NO_2, PAN, HNO_3, HONO, and N_2O_5 (Griffith and Schuster, 1987) A theoretical MDL of 5 ppt was claimed for NO_2 in 15-L integrated samples of ambient air

A laboratory prototype method, TTFMS, has been developed recently and is described in Section 6.2.3 (Hansen, 1989) This method has a projected MDL for NO_2 of 0 3 ppt

Long-path absorption is a remote sensing technique that is typically operated over open terrain with optical path lengths of up to tens of kilometers The absorption cross section for each species of interest is determined in the laboratory This information is used to convert optical densities measured in the field to concentration data For 1-h observation periods, an MDL of 20 ppt has been reported using an artificial light source and a 9 2-km path length (Johnston and McKenzie, 1984) Noxon (1978) used the sun as a light source and the structure in the NO_2 absorption spectrum near 440 nm to obtain measures of the abundance of NO_2 in both the troposphere and the stratosphere Platt and Perner (1983) have reported the application of DOAS to the determination of several nitrogen-containing species A xenon high-pressure lamp or an incandescent lamp was used with a 1- to 10-km path length Selected applicable compounds, detection limits, and target wavelengths are NO, 400 ppt, and 226 nm, NO_2, 100 ppt, and 363 nm, HONO, 20 ppt, and 354 nm, and NO_3, 0.5 ppt, and 662 nm The DOAS technique has been recently adapted to employ a 25-m multipass open reflection system with a path length of up to 2 km (Biermann et al , 1988) Using a 0.8-km path length and 12-min averaging times, MDLs and accuracies for NO_2,

HONO, and NO_3 of 4 ppb (±10%), 0 6 ppb (±30%), and 20 ppt (±15%), respectively, have been reported

Common remote sensing techniques employ light detection and ranging (lidar) Differential absorption lidar is a long-path absorption technique This method employs light of two wavelengths propagated over a given distance at a given intensity The concentration of the gas species of interest is related to the difference in intensities of the two wavelengths at the receiver Differential absorption lidar techniques have been applied to the ambient measurement of both NO (Alden et al , 1982) and NO_2 (Fredriksson and Hertz, 1984; Edner et al , 1987) Baumgartner et al (1979) reported a 5-ppb sensitivity for NO_2, and Staehr et al (1985) reported a 10-ppb sensitivity for NO_2 using a laser source and a 6-km path length Differential absorption lidar methods are in the development stages for monitoring NO_2 in ambient atmospheres

6.3.5 Wet Chemical Methods

Most wet chemical methods for measuring NO_2 involve the collection of NO_2 in solution followed by a colorimetric finish using an azo dye Many variations of this method exist, including both manual and automated versions Szonntagh (1979) traced the history of azo dye methods for NO_2 sampling and analysis Nitrogen dioxide, first collected in aqueous solution, is thought to form HONO An aromatic amine is used in the presence of an acid to react with HONO and form a diazonium salt The salt then rearranges and couples with another organic amine that has been added to form a red azo dye The intensity of the color is proportional to the NO_2 collected and is measured using a spectrophotometer A good overview of wet chemical methods for sampling and analysis of NO_2 is given by Purdue and Hauser (1980)

6.3.5.1 Griess-Saltzman Method

In this method, air is sampled for no longer than 30 min through a fritted bubbler that contains the Griess-Saltzman reagent (Saltzman, 1954) This reagent is a solution of sulfanilic acid, NEDA, and acetic acid Color development is complete within 15 min and is measured at 550 nm within an hour. Interferences from SO_2 and PAN have been noted, but are usually too low in ambient air to cause significant error Concentrations of NO_2 ranging

from 20 to 800 ppb for 30-min sampling periods may be determined using this method An MDL of 2 ppb and a precision of ±11%, as well as a positive bias of 18% for spiked ambient air, have been reported (Saltzman, 1980, Purdue and Hauser, 1980)

Calibration is usually performed statically using dilute solutions of sodium nitrite Saltzman (1954) reported that 0 72 moles of nitrite were formed for each mole of NO_2 absorbed. Values of this "stoichiometric factor" ranging from 0 5 to 1 0 have been reported (Crecelius and Forwerg, 1970). The method can, however, be calibrated dynamically using calibrated NO_2 gas standards

6.3.5.2 Continuous Saltzman Method

The measurement principle used in the Continuous Saltzman Method is based on the Griess-Saltzman reaction Ambient air is sampled continuously through a gas-liquid contactor, and NO_2 is collected on contact with an absorbing solution containing diazotizing-coupling reagents After the color has developed, the absorbance of the solution is measured continuously with a spectrophotometer Because O_3 was found to act as a negative interferent, this method was eliminated as a candidate for designation as an Equivalent Method by EPA. The MDL is 10 ppb, the bias ranges from +3 to +15% at NO_2 concentrations between 30 and 150 ppb, and the precision is approximately ±12% (Purdue and Hauser, 1980). Although calibration can be performed using nitrite solutions or calibrated NO_2 gas standards, the latter approach is recommended

6.3.5.3 Alkaline Guaiacol Method

Various alternatives to the Griess-Saltzman Method have been proposed Recently, Baveja et al. (1984) proposed a method using alkaline *o*-methoxyphenol (guaiacol) as both the absorbing medium and coupling reagent Samples are collected using fritted bubblers containing an alkaline guaiacol solution After sampling, *p*-nitroaniline is added, the pH is adjusted with hydrochloric acid (HCl) and later with NaOH, the resulting dye is extracted in amyl alcohol, and the absorbance is read at 545 nm Collection efficiency of 98% and a stoichiometric factor of 0.74 were reported

6.3.5.4 Jacobs-Hochheiser Method

This method is a modified version of the Griess-Saltzman method to permit 24-h sampling and delay in analysis times (Jacobs and Hochheiser, 1958) Samples are collected by bubbling ambient air through a 0 1 N aqueous NaOH solution using a fritted bubbler The collected nitrite is then reacted with sulfanilamide and NEDA in acid media to form an azo dye, which is measured with a spectrophotometer at 540 nm As with the Griess-Saltzman method, dilute nitrite solutions are used for calibration This method was the original Reference Method designated by the EPA for NO_2 (Purdue and Hauser, 1980) However, testing of the method showed that the originally specified NO_2 collection efficiency of 35% was not constant and that it varied nonlinearly with NO_2 concentration In addition, interferences from NO and combinations of NO and NO_2 were found As a result, this method was withdrawn in 1973 and is considered unacceptable for air sampling and analysis

6.3.5.5 Sodium Arsenite Method (Manual and Continuous)

This method has been designated by the EPA as an Equivalent Method in both the manual and continuous forms (Federal Register, 1986) The manual method is a 24-h integrated method similar to the Jacobs-Hochheiser method, except that sodium arsenite is added to the aqueous NaOH absorbing solution, and an orifice bubbler is used The nitrite is reacted with sulfanilamide and NEDA in acid media to form an azo dye, which is determined with a spectrophotometer The continuous method employs the same measurement principle, but uses hardware to permit continuous determination of NO_2 in a manner similar to that for the Continuous Saltzman Method

The overall NO_2 recovery is 82% Although NO and CO_2 may act as interferents, their impact is minimal at typical ambient levels Sulfur dioxide has not been tested as an interferent The MDL is 5 ppb, the bias is -3%, independent of concentration, and the precision at NO_2 concentrations between 30 and 150 ppb is ± 6 ppb (Purdue and Hauser, 1980) Recently, HONO was found to respond equivalently to NO_2 (Braman et al , 1986) This interference is likely to be appreciable in urban environments during nighttime hours, where concentrations above 5 ppb have been observed (Rodgers and Davis, 1989, Appel et al , 1990)

6.3.5.6 Triethanolamine-Guaiacol-Sulfite Method

This method, designated by the EPA as an Equivalent Method (Federal Register, 1986), is a manual 24-h integrated method Samples are collected using orifice bubblers and a solution of TEA, guaiacol, and sodium metabisulfite The resulting nitrite is reacted with sulfanilamide and 8-amino-1-naphthalene-sulfonic acid ammonium salt (ANSA), and the resulting azo dye is determined at 550 nm with a spectrophotometer No interferences were found in tests with NH_3, CO, formaldehyde, NO, phenol, O_3, and SO_2 The overall NO_2 recovery is 93%; the MDL is 8 ppb, the bias is −5%, independent of concentration, and the precision at NO_2 concentrations between 30 and 150 ppb is ±6 ppb (Purdue and Hauser, 1980).

6.3.5.7 Triethanolamine Method

This method is a manual 24-h integrated method (Ellis and Margeson, 1974) Samples are collected using an aqueous solution of TEA and fritted bubblers As with the Equivalent Methods, the resulting nitrite may be determined with a spectrophotometer after reaction with sulfanilamide and either NEDA or ANSA Although recoveries of 80 to 90% were found at NO_2 concentrations between 20 and 350 ppb using fritted bubblers, only 50% recovery was found using orifice bubblers. Because the requirement of a fritted rather than an orifice bubbler was considered to be a major disadvantage by the EPA, the development of this method as an Equivalent Method was terminated (Purdue and Hauser, 1980)

Triethanolamine has been used as the collection medium for many active and passive techniques to sample NO_2 Although colorimetry may be used as the analytical finish, IC recently appears to be the method of choice (Miller, 1984) Vinjamoori and Ling (1981) have used an aqueous solution of TEA, ethylene glycol, and acetone on 13X molecular sieves to sample air in the workplace for NO_2 Passive devices employing TEA have been used for industrial hygiene and indoor air quality sampling (Palmes et al , 1976, Wallace and Ott, 1982) as well as for ambient applications (Sickles and Michie, 1987, Mulik and Williams, 1987). Recently, a method using Whatman GF/B filters coated with an aqueous solution of TEA, ethylene glycol, and acetone has been developed for extended sampling of both NO_2 and SO_2 from ambient air (Sickles et al , 1990) This method, using IC to determine the collected NO_2 as nitrite and nitrate, showed no interferences from NO, NH_3, O_3, H_2S,

methanethiol (CH_3SH), and carbon disulfide (CS_2), but showed major interferences from PAN and HONO Recovery of NO_2 averaged 87% in laboratory tests at concentrations between 5 and 400 ppb Using two coated 47-mm diameter filters in series, filter temperatures above 5 °C, and flow rates below 2 L/min are required to insure good NO_2 collection efficiency This method has been incorporated into the design of a prototype sampler known as a transition flow reactor (TFR) system for measuring acidic deposition components (Knapp et al , 1986)

6.3.6 Other Active Methods

Several other methods reported for the determination of NO_2 include ionization spectroscopy, mass spectrometry, photothermal detection, denuders, and solid sorbents However, because they are in the early stages of development or are not being used widely, they are only briefly mentioned here

Ionization spectroscopy is a new and sensitive in situ laser technique that is currently under investigation for tropospheric measurements of NO and NO_2 (National Aeronautics and Space Administration, 1983). This method is in the early stages of development

Atmospheric pressure ionization mass spectrometry has been investigated for the continuous measurement of NO_2 and SO_2 in ambient air (Benoit, 1983) An MDL of approximately 0 5 ppb was reported.

Methods employing photothermal detection of NO_2 have been reported (Poizat and Atkinson, 1982, Higashi et al , 1983, Adams et al , 1986) Detection is accomplished by selectively exciting transitions of NO_2 with a chopped continuous wave or pulsed laser source At pressures near atmospheric, collisional de-excitation converts the absorbed energy into translational energy, leading to a temperature rise along the beam and expansion of the gas The resulting change in refractive index of the thermal lens can be detected by spectroscopic means (Higashi et al , 1983), or the resulting pressure change can be detected with a microphone (Poizat and Atkinson, 1982) Minimum detection limits of 2 to 5 ppb have been reported. Development of photoacoustic methods for continuous application may be limited by acoustic noise associated with vibration and flow

A denuder is a tube or channel with its walls coated with a chemical chosen to remove a gaseous species of interest from a sample drawn through the tube under laminar conditions

The concentration of the species of interest is determined by measuring the amount of the species collected on the walls or by comparing the signal strengths in the presence and absence of the denuder Possanzini et al (1984) recommended using a coating containing KI to collect NO_2. Subsequent tests showed the collection efficiency of this material to be dependent on the humidity of the sample (Sickles, 1987) An alkaline guaiacol coating on annular denuders has shown high collection efficiency for NO_2 (Buttini et al , 1987) After extraction using deionized water, IC analysis showed quantitative recovery as NO_2^- The reported MDL was 0 13 ppb for a 1-m^3 sample (i e , 16 L/min for 1 h), and the median precision for 14 paired samples was 3 9% expressed as relative standard deviation (RSD) A direct interference was noted with HONO, none was found with NO or PAN, and no humidity effects were observed between 20 and 80% RH No interference tests were performed with O_3, however, comparison of 4-h results with those of a commercial CLM (NO + O_3) instrument sampling air near Rome showed good correlation (i e , r = 0 92) Although alkaline guaiacol solutions degrade with time, no degradation effects were found for 72-h presampling or 24-h postsampling denuder storage Longer duration storage tests (e.g., 2 weeks pre- and postsampling) and additional field evaluations are needed before this method is ready for routine application

Recently, Adams et al (1986) found activated manganese dioxide to be effective under unspecified RH for removing NO_2 in denuder applications Additional tests are needed under conditions representative of the ambient environment before this approach is ready for routine application.

Lipari (1984) has used a commercially available cartridge containing the sorbent Florisil (magnesium silicate) coated with diphenylamine to sample NO_2 in ambient and indoor air The NO_2 reacts with the diphenylamine to form nitro- and nitroso-derivatives, which are subsequently detected by high performance liquid chromatography (HPLC)-UV Although no interference from NO, O_3, SO_2, HNO_3, and water vapor were found, PAN produced a 50% positive interference, and HONO was expected to interfere quantitatively Sorbent temperature must be held below 32 °C to prevent volatilization of the diphenylamine and nonquantitative sampling. An MDL of 0 1 ppb for a 2 0-m^3 air sample was claimed The method shows promise for the sensitive determination of NO_2 under conditions where the noted interferents and temperature sensitivity do not pose problems

6.3.7 Passive Samplers

Passive samplers are frequently used in industrial hygiene, indoor air, and personal exposure studies, and are less frequently used in ambient air sampling Passive NO samplers were described in Section 6 2 4 Namiesnik et al (1984) have provided a good overview of passive samplers The basis for all passive samplers is the same The gaseous analyte molecule is transported from the bulk air to a reactive surface, where the molecule impinges and is captured by chemical reaction After exposure periods ranging from hours to days, the reactive surface is analyzed and the integrated loading of the reaction product is used to infer the average gas concentration present during the sampling period When the transport of analyte molecules to the reactive surface is diffusion-controlled, the average ambient concentration may be related directly to the ratio of the product loading to the sampling duration This proportionality is defined as a sampler calibration factor or alternatively as the reciprocal of the sampler sampling rate

One type of passive NO_2 sampler for ambient applications is the nitration plate It is essentially an open petri dish containing TEA-impregnated filter paper Thus, there is no diffusion barrier between the ambient air and the NO_2 collection surface Nitrogen dioxide reacts with the TEA and is retained primarily as NO_2^-, which can be extracted and determined with a spectrophotometer or by IC A single calibration factor is provided by the manufacturer A recent study indicated that the calibration factors determined experimentally for the device are extremely sensitive to wind speed, NO_2 concentration, and temperature (Sickles and Michie, 1987) Triethanolamine is expected to collect not only NO_2 but HONO, HNO_3, and PAN (Sickles, 1987) These results suggest that nitration plates may be useful only as qualitative indicators of ambient levels of NO_x

Another open-surface device has been proposed by Kosmus (1985) for ambient applications This device uses chromatographic paper in the shape of a candle that is coated with diphenylamine and is continually impregnated with a potassium thiocyanate-glycerin catalyst Nitrogen oxides, presumably NO_2 and NO to some extent, are collected by a catalyzed reaction with diphenylamine to form the nitrosamine After extraction, the nitrosamine may be determined with a spectrophotometer or by differential pulse polarigraphy Interference by iron oxide particles was noted, and interference from both PAN and HONO is expected (Lipari, 1984) Sensitivity to wind speed, as noted previously

for the nitration plate, is also expected Collocated sampling was performed using four candles and a CLM NO/NO_2 analyzer at each of 14 stations (Kosmus, 1985) The nitrosamine loadings were highly correlated, but in a nonlinear manner, with the sum of 100% NO_2 plus 90% NO from the CLM instruments These results also suggest that open-surface passive samplers may be useful as qualitative indicators of ambient levels of NO_x

Mulik and Williams (1986) have adapted the nitration plate concept by adding diffusion barriers in their design of a passive sampling device (PSD) for NO_2 in ambient and personal exposure applications The physical configuration employs a TEA-coated cellulose filter that uses two 200-mesh stainless steel diffusion screens and two stainless steel perforated plates on each side of the coated filter to act as diffusion barriers This design permits NO_2 collection on both faces of the filter After sampling, the filter is removed from the PSD, extracted in water, and analyzed for NO_2^- by IC A sensitivity of 0 03 ppm-h and a sampling rate of 2 6 cm^3/s were claimed Comparison of PSD results with CLM determinations of NO_2 in laboratory tests at concentrations between 10 and 250 ppb were linearly related and highly correlated (i e , r = 0 996) The device exhibited increased sampling rates of approximately 50% as the wind speed increased from 20 to 45 cm/s, but displayed a relatively constant sampling rate at wind speeds between 45 and 300 cm/s (Mulik and Williams, 1987) Interferences from PAN and HONO are expected (Sickles, 1987) Results of TDLAS and triplicate daily PSD NO_2 measurements in a recent 13-day field study showed good agreement between the study average values, but a correlation coefficient for daily results of only 0.47 (Mulik and Williams, 1987, Sickles et al , 1990) Further development and testing of the PSD appears warranted

The Palmes tube is a passive device that has been used to sample air in the workplace and indoor environments to assess personal exposure to NO_2 (Palmes et al , 1976, Wallace and Ott, 1982) This device and its operation were described in detail in Section 6 2 4 It consists of a tube, open at one end with a TEA-coated interior surface on the closed end Nitrogen dioxide diffuses through the 7 1-cm diffusion length, where it is captured by TEA Analysis is accomplished by extracting the TEA-coated surface and analyzing the extract for NO_2^-. This may be done directly by adding an aqueous solution of sulfanilamide and NEDA to the tube and determining the NO_2^- concentration using a spectrophotometer at 540 nm (Palmes et al., 1976) A stoichiometric factor of unity, a linear response for dosages

between 1 and 30 ppm-h, and a sampling rate of 0 02 cm^3/s are reported An improvement in sensitivity from 0 3 ppm-h to 0 03 ppm-h is claimed if the aqueous TEA extract is analyzed by IC using a concentrator column (Mulik and Williams, 1986). Absorption and desorption of NO_2 by the internal walls of the acrylic tube have been reported to limit applications to exposures of 0 1 ppm-h (Miller, 1988) This sensitivity can be improved to 0 03 ppm-h by using stainless steel rather than acrylic tubes The device exhibited sampling rates increased by up to 15% as wind speed was increased from 50 to 250 cm/s (Palmes et al., 1976) and decreased by 15% as temperature was reduced from 27 to 15 °C (Girman et al , 1984) Interferences from PAN and HONO are expected (Sickles, 1987) The calibration factor for the Palmes tube is theoretically derived, and the analytical finish is calibrated by dilution of gravimetrically prepared nitrite solutions

The performance of the Palmes tube has been compared with that of two commercially available passive personal samplers, the DuPont Pro-Tek and the MDA Chronotox System (Woebkenberg, 1982) The Palmes tube displayed greater sensitivity than either of the commercial samplers and displayed adequate precision and accuracy at loadings between 1 and 80 ppm-h Because the commercial devices may be used at only moderate to high loadings (i e , above 5 ppm-h), they are not sufficiently sensitive for most ambient or personal exposure applications They are thusly not discussed further in this document

A badge-type NO_2 personal sampler has been devised by Yanagisawa and Nishimura (1982) Their device uses a series of five layers of hydrophobic Teflon™-type filter material as a diffusion barrier between ambient air and a TEA-coated cellulose fiber filter Nitrogen dioxide diffuses through the hydrophobic filters to the TEA-coated surface, where it is collected Following extraction of the TEA-coated filter in a solution of sulfanilic acid, phosphoric acid, and NEDA, a colorimetric finish at 540 nm is employed A sensitivity of 0 07 ppm-h, a sampling rate of 1 4 cm^3/s, and an accuracy of $\pm 20\%$ are claimed The device exhibited increased sampling rates of up to 30% as the wind speed was increased from 15 to 400 cm/s Interferences from PAN and HONO are expected (Sickles, 1987) The calibration factor for the sampler is provided by the supplier, and the analytical finish is calibrated by dilution of gravimetrically prepared nitrite solutions

A variation on the above approach has been proposed by Cadoff and Hodgeson (1983) The sampler is comprised of a Nuclepore 47-mm filter holder with a capped base containing

a TEA-coated glass fiber filter and a 0 8-μm pore size polycarbonate filter The polycarbonate filter and the air space between this filter and the TEA-coated filter act as a diffusion barrier. A colorimetric analytical finish is employed The performance was tested at NO_2 loadings between 0 06 and 1 ppm-h, and a sampling rate of 1 9 cm^3/s was claimed

West and Reiszner (1978) proposed a passive NO_2 sampler using a silicone membrane as a diffusion barrier between ambient air and an alkaline thymol blue NO_2 collection solution. Collected NO_2 is converted to NO_2^- and determined colorimetrically Results of a field comparison with the EPA-designated TGS method were not favorable and showed the proposed device to yield results approximately a factor of three higher than the TGS method As a result, this method is not recommended

6.3.8 Calibration

Two methods have been designated by the EPA (Code of Federal Regulations, 1987a) as alternative calibration procedures for the measurement of NO_2 in the atmosphere These methods use permeation tubes or gas phase titration (GPT) to generate known amounts of NO_2. Calibrations are performed using dynamic dilution with air

A permeation tube is a porous, inert tube usually made of Teflon™ that has been partially filled with liquid NO_2 and sealed Permeation of NO_2 through the porous tube will occur at a constant rate if the temperature of the tube and the NO_2 concentration gradient across the tube are held constant The tube is maintained at a constant temperature ($\pm$0.1 °C), and a measured flow of a dry carrier, usually nitrogen, is passed over it The NO_2 permeating through the porous wall and entering the carrier stream is diluted with zero air to produce calibration NO_2 atmospheres of known concentrations The permeation tube is calibrated gravimetrically by measuring the weight loss of the tube over time The National Institute of Standards and Technology (NIST) provides SRM permeation tubes that emit NO_2 at a nominal rate of 1 μg/min (National Bureau of Standards, 1988) Additional information on the performance of NO_2 permeation tubes is given by Hughes et al (1977) A recent report by Braman and de la Cantera (1986) indicates that permeation sources of NO_2 can produce atmospheres that are contaminated with other oxides of nitrogen, including HNO_3, HONO, and NO Further work appears warranted to define the conditions where permeation devices may be used to provide an unambiguous source of NO_2

Gas phase titration employs the rapid, quantitative gas phase reaction between NO, usually from a standard gas cylinder, and O_3, from a stable O_3 generator, to produce one NO_2 molecule for each NO molecule consumed by reaction When O_3 is added to excess NO in a titration system, the decrease in NO (and O_3) is equivalent to the NO_2 produced Different amounts of NO_2 may be produced by adding different amounts of O_3 When the NO concentration and the flow rates entering the dynamic titration system are known accurately, the NO_2 concentration leaving the system can be determined accurately The accuracy and stability of NO standard gas cylinders are described in Section 6 2 5

A third source of NO_2 sometimes used for calibration is a cylinder of compressed gas containing NO_2, usually in N_2 (Fehsenfeld et al , 1987, Davis, 1988) Calibrations are subsequently performed using dynamic dilution with zero air These cylinders are commercially available, and the NO_2 concentration should be referenced to an accepted standard Bennett (1979) has shown that, of 26 aluminum cylinders initially containing supplier-certified concentrations of NO_2 in N_2 between 100 and 300 ppb, 10 showed modest declines in NO_2 concentration during the first 3 mo after preparation The NO_2 levels in all 26 cylinders declined substantially over the 10-mo study period Schiff et al (1983) have noted problems handling trace concentrations of NO_2 from a cylinder A cylinder containing 9 ppm NO_2 in N_2 gave 15% higher readings for NO_2 when analysis was performed by CLM than by TDLAS (Walega et al , 1984) This discrepancy may have been due to an impurity (e g , HNO_3) in the cylinder that could act as an interference with the CLM, but not the TDLAS, determination of NO_2 Davis (1988) examined a cylinder containing 44 ppm NO_2 in air at regular intervals over 3 years and observed a 16% change in concentration. In view of these findings, caution should be exercised if a cylinder containing NO_2 in N_2 or air is to be employed as a calibration source of NO_2

6.3.9 Intercomparisons

Several intercomparisons of research-grade NO_2 instrumentation have been conducted (Helas et al , 1981, Walega et al , 1984, Sickles et al , 1990, Fehsenfeld et al , 1987, 1990, Gregory et al , 1990b) and are described in this section Also, the performance of EPA-Designated Methods, based on intercomparisons and other studies, is discussed in Section 6 3 10

Helas et al (1981) report the results of a field intercomparison of several NO_2 methods conducted in April 1979 at Deuselbach, Germany Good agreement between a highly sensitive CLM instrument and long-path absorption was found over the 1- to 8 ppb range of observed NO_2 concentrations

Walega et al (1984) report comparisons of NO_2 measurements from a highly sensitive CLM instrument using a thermal NO_2 to NO converter with NO_2 measurements from a TDLAS system. Measurements of NO_2-spiked synthetic air conducted both in the laboratory and in the field showed good agreement Measurements were made of ambient and captive air in downtown Los Angeles and showed maximum respective concentrations of 100 and 600 ppb. Chemiluminescence results were appreciably higher than those of the TDLAS this difference averaged 18% in the ambient-air studies and 15% in the captive-air studies In the latter studies, the agreement was generally within 10% in the morning, but by the end of the day, could be as large as 80% This behavior was attributed to the reaction of NO_2 and the accumulation of photochemically produced CLM interferents such as PAN that occurred during the day.

Daily NO_2 concentrations determined by TDLAS, CLM (luminol), and PSDs were reported recently from a 13-day study conducted at Research Triangle Park, NC, in the fall of 1986 (Bubacz et al , 1987; Mulik and Williams, 1987, Sickles et al , 1990) Collocated sampling was performed using a TDLAS system, two CLM (luminol) instruments, and triplicate daily PSDs. Daily average results were computed for the TDLAS, each CLM (luminol) instrument, and the PSDs The 13-day average values from the CLM (luminol) instruments and the TDLAS system agreed to within 2 ppb, the average daily ratios of NO_2 by CLM (luminol) to TDLAS were 1 01 $\pm$ 0 11 (standard deviation) and 1 19 $\pm$ 0 17, the respective correlation coefficients were high, 0 94 and 0 91, and although the results of one CLM (luminol) instrument showed no bias, results of the other were biased higher than those of the TDLAS system The 13-day average values from the PSDs and TDLAS system agreed to within 1 ppb; the average daily ratio of NO_2 by PSD to TDLAS was 1 08 $\pm$ 0 32 There was no apparent bias, but the correlation coefficient was only 0 47

A field intercomparison of instruments designed to measure NO, NO_x, and NO_y was conducted near Boulder, CO (Fehsenfeld et al , 1987) In addition, an intercomparison of NO_2 measurements was performed using two different NO_2-to-NO converters prior to NO

detection by CLM. The two CLM detection systems were tested and found to be equivalent One instrument used a photolytic NO_2-to-NO converter, whereas the other employed a $FeSO_4$ $7H_2O$ surface converter In spiking tests, the instrument with the $FeSO_4$ converter responded to NO_2, PAN, and *n*-propyl nitrate, but not to HNO_3 or NH_3 The CLM-PC instrument responded to NO_2, but not significantly to HNO_3, NH_3, *n*-propyl nitrate, or PAN For measurements of NO_2 + NO in ambient air, results from the two instruments agreed at concentrations above 1 ppb However, results from the instrument with the surface converter were biased higher than those from the photolytic converter at lower NO + NO_2 concentrations This discrepancy was a factor of 2 at 0 1 ppb These results suggest that surface converters sufficiently active to convert NO_2 to NO can convert other NO_x species such as PAN to NO Although the use of CLM with surface NO_2-to-NO converters may not pose a problem in many urban and suburban areas where NO and NO_2 are expected to be the dominant NO_x, results cited here and elsewhere in this section suggest that surface converters are unsuitable for the interference-free measurement of NO_2 in ambient air containing PAN and similar compounds

Fehsenfeld et al. (1990) performed a ground-based intercomparison of NO_2 measurements using CLM-PC, CLM (luminol), and TDLAS research-grade instruments near Boulder, CO Ambient concentrations ranged from 0 02 to 4 ppb The potential interferences of H_2O_2, HNO_3, *n*-propyl nitrate, PAN, and O_3 were examined in spiking tests. Only the CLM (luminol) instrument displayed appreciable interferences, and they were with O_3 (0 6%) and PAN (24%) At ambient NO_2 concentrations above 2 ppb, all three instruments gave similar results Below 2 ppb, interferences from O_3 and PAN provided high biases to the CLM (luminol) results, but they could be corrected with measured O_3 and PAN results at NO_2 levels above 0 3 ppb An O_3 scrubber added to a second CLM (luminol) instrument removed the O_3 interference, but failed to remove PAN and appeared to remove substantial amounts (i e , 50%) of NO_2 Removal of NO_2 in the manufacturer-supplied O_3 scrubber has also been reported by Kelly et al (1990) Tunable-diode laser spectroscopy results compared favorably with CLM-PC at relatively high NO_2 levels (i e , >0 4 ppb), but displayed a high bias (i e , factor of 5) at lower NO_2 concentrations (Fehsenfeld et al , 1987) No interferences or artifacts were found for the CLM-PC results

An airborne intercomparison (i e , CITE 2) of NO_2 measurements was conducted by NASA using TDLAS, PF/TP-LIF, CLM-PC, and CLM (with $FeSO_4$ converter) research-grade instruments (Gregory et al , 1990b) Sampling flights were performed primarily in the free troposphere, and NO_2 concentrations were below 200 ppt and generally below 100 ppt High biases (i.e., factors of 2 to 3) apparently resulting from PAN interferences were present in results from the CLM instrument with the $FeSO_4$ converter, and results from this instrument were not considered in subsequent analyses At concentrations below 200 ppt, results from the remaining three instruments were highly correlated (i e , correlation coefficients ranged from 0.84 to 0 95) and displayed a general level of agreement to within 30 to 40%. The PF/TP-LIF results were higher than those of the CLM-PC, and the TDLAS results were the lowest. At concentrations below 50 ppt, the results were poorly correlated, although the PF/TP-LIF and CLM-PC results agreed to within 20 ppt Below 50 ppt, TDLAS results were much higher than those of the other two instruments. This bias, similar to that observed in the ground-based intercomparison of Fehsenfeld et al (1990), was enhanced at low NO_2 concentrations by an error in the data reduction protocol employed in both studies.

6.3.10 Designated Methods

Acceptable sampling and analysis methodologies for NO_2 have been specified by the EPA (Code of Federal Regulations, 1987b) These designated methods are termed "Reference" or "Equivalent" In 1973, the original Federal Reference Method for NO_2, the Jacobs-Hochheiser Technique, was withdrawn because of technical deficiencies (Purdue and Hauser, 1980) In 1976, the measurement principle and the associated calibration procedure on which Reference Methods for NO_2 must be based were specified The measurement principle is gas-phase chemiluminescence and the calibration procedure may employ either GPT of an NO standard with O_3 or an NO_2 permeation device (Code of Federal Regulations, 1987a). Because only the measurement principle and calibration procedures applicable to NO_2 Reference Methods were specified, different analyzers can be built and designated as Reference Methods, provided they meet the performance specifications shown in Table 6-1 (Code of Federal Regulations, 1987b)

TABLE 6-1. PERFORMANCE SPECIFICATIONS FOR NITROGEN DIOXIDE AUTOMATED METHODS[a]

Performance Parameter	Units	NO_2
Range	ppm	0-0 5
Noise		
0% upper range limit	ppm	0 005
80% upper range limit	ppm	0 005
Lower detectable limit	ppm	0 01
Interference equivalent		
Each interferant (SO_2, NO, NH_3, H_2O)	ppm	±0 02
Total interferant	ppm	≤0 04
Zero drift, 12 and 24 h	ppm	±0 02
Span drift, 24 h		
20% of upper range limit	%	±20 0
80% upper range limit	%	±5 0
Lag time	min	20
Rise time	min	15
Fall time	min	15
Precision		
20% of upper range limit	ppm	0 02
80% of upper range limit	ppm	0 03

[a]NO_2 = Nitrogen dioxide
SO_2 = Sulfur dioxide
NO = Nitric oxide
NH_3 = Ammonia
H_2O = Water

Source Code of Federal Regulations (1987b)

To be designated as an Equivalent Method, the candidate method must be based on measurement principles different from the Reference Method and meet certain performance specifications (Code of Federal Regulations, 1987b) An Equivalent Method may be either

manual or automated To be designated as Equivalent, a candidate manual method must demonstrate comparability, as shown in Table 6-2, with the Reference Method when applied simultaneously to a real atmosphere A candidate automated method must meet the performance specifications shown in Table 6-1 and demonstrate comparability as shown in Table 6-2 with the Reference Method when applied simultaneously to a real atmosphere

TABLE 6-2. COMPARABILITY TEST SPECIFICATIONS FOR NITROGEN DIOXIDE

Nitrogen Dioxide Concentration Range (ppm)		Maximum Discrepancy Specification (ppm)
Low	0.02 to 0 08	0 02
Medium	0 10 to 0 20	0 02
High	0.25 to 0 35	0 03

Source· Code of Federal Regulations (1987b)

Methods designated by the EPA as Reference and Equivalent are identified in Table 6-3 (Federal Register, 1986) Detailed descriptions of these and other methods for NO_2 are presented in previous subsections Studies were conducted to provide a basis for the designation of methods by the EPA Tests were performed to compare the performance of CLM, continuous colorimetric, manual sodium arsenite, and manual TGS methods (Purdue and Hauser, 1980). The methods were compared by measuring NO_2 in spiked and unspiked ambient air simultaneously Quadruplicate samples were taken for the two manual methods and duplicate analyzers were used for the two continuous methods The NO_2 spikes were varied randomly from day to day over the sampling schedule and ranged from 0 to 430 ppb Agreement both within and between methods was good the average difference was never greater than 4 ppb Correlation coefficients for between-method comparisons exceeded 0.985 in all cases No between-method differences could be attributed to concentrations of NO, CO_2, O_3, total sulfur, or total suspended particulate matter in the ambient air Significant negative interference in the continuous colorimetric method was found at NO_2

TABLE 6-3. REFERENCE AND EQUIVALENT METHODS FOR NITROGEN DIOXIDE DESIGNATED BY THE U.S. ENVIRONMENTAL PROTECTION AGENCY

Method	Designation Number	Method Code
Manual Methods (Equivalent Methods)		
Sodium aresnite	EQN-1277-026	026
Sodium aresnite/Technicon II	EQN-1277-027	027
TGS-ANSA	EQM-1277-028	028
Analyzers (Reference Methods)		
Beckman 952A	RFNA-0179-034	034
Bendix 8101-B	RFNA-0479-038	038
Bendix 8101-C	RFNA-0777-022	022
CSI 1600	RFNA-0977-025	025
Meloy NA53OR	RFNA-1078-031	031
Monitor Labs 844OE	RFNA-0677-021	021
Monitor Labs 8840	RFNA-0280-042	042
Philips PW9762/02	RFNA-0879-040	040
Thermo Electron 14B/E	RFNA-0179-035	035
Thermo Electron 14D/E	RFNA-0279-037	037

Source Federal Register (1986)

concentrations of 40 and 53 ppb in the presence of 180 and 340 ppb O_3 However, at O_3 concentrations of 50 ppb, no interference was detected Also, no interference was detected with the manual sodium arsenite method at NO concentrations as high as 250 ppb The performance of the CLM analyzers was judged to be superior to that of the continuous colorimetric analyzers with respect to zero drift, span drift, response times, and overall operation Of the two manual methods, the performance of the sodium arsenite method was judged superior to the TGS method

Eight of the Reference Methods have undergone extensive postdesignation testing in the laboratory and field (Michie et al , 1983) Performance test results have been reported and were found to meet the specifications shown in Table 6 1 Based on the field test results, minimum detection limits were defined as three times the precision These MDL results ranged from 5 to 13 ppb with an average of 9 ppb An independent analysis of this data by Holland and McElroy (1986) also showed similar results

Interrogation of the National Aerometric Data Bank records for 1985 revealed that NO_2 data were archived from 40 states (Hustvedt, 1987) Of the 335 data sets, CLM was employed in 291 cases, and manual methods were employed in the remainder Of the manual methods, 42 employed the sodium arsenite method with either orifice or fritted bubblers. Interrogation of the Precision Accuracy Reporting System (PARS) data base for the State and Local Air Monitoring Stations network for fourth quarter 1986 and first quarter 1987 records revealed that data were archived from tests of 114 CLM analyzers (Rhodes, 1987). Of these, 43% were Bendix 8101C, 40% were CSI 1600, 15% were Monitor Labs 8840 and 8440E, 2% were Meloy NA 530R, and 1% were Beckman 952A

To illustrate the precision and accuracy of the designated methods in field applications, PARS data were examined for 1983 through 1986 (Rhodes and Evans, 1988) The results, shown in Table 6-4 as 95% probability limits, suggest that the precision of continuous NO_2 analyzers falls in the range of ± 10 to 15%, whereas the manual methods are much worse, at ± 20 to 50%. It should be noted that the manual precision results show a recent worsening This trend may reflect the phasing out of manual methods in the network that was completed by the end of 1986

The tabulated probability limits for accuracy of continuous NO_2 analyzers are $\pm 20\%$, whereas for the manual methods, they are ± 3 to 7% (Rhodes and Evans, 1988) The accuracy results reflect audits of the analysis portion of the manual methods and audits of both sampling and analysis for the continuous methods Thus, the apparent difference in accuracy may be reflecting differences in the auditing procedures employed

6.4 NITROGEN OXIDES

For the purposes of this document, NO_x is considered to be the sum of NO and NO_2 No widely accepted methods are available for determining NO_x except by determining NO and NO_2 individually and summing, or by converting NO_2 to NO and determining NO_x as the total NO Sections 6 2 and 6 3 describe methods for the determination of NO and NO_2, respectively.

Commercial CLM NO_x analyzers catalytically convert NO_2 to NO and measure NO_x as the sum of the originally present NO and the converted NO As noted in Section 6 3.1,

TABLE 6-4. NATIONAL PRECISION AND ACCURACY PROBABILITY LIMIT VALUES EXPRESSED AS PERCENT FOR CONTINUOUS AND MANUAL METHODS FOR NITROGEN DIOXIDE

Nitrogen Dioxide Method	1983[a]	1984	1985	1986
Continuous				
Precision	−13 + 12 (9,299)[b]	−14 + 13 (8,653)[b]	−12 + 12 (7,695)[b]	−11 + 11 (6,686)[b]
Accuracy	−19 + 15 (680)[c]	−21 + 20 (613)[c]	−20 + 21 (573)[c]	−21 + 20 (529)[c]
Manual				
Precision	−19 + 21 (1,324)[d]	−21 + 27 (691)[d]	−27 + 29 (469)[d]	−48 + 45 (174)[d]
Accuracy	−5 + 6 (348)[c]	−6 + 7 (175)[c]	−3 + 5 (161)[c]	−4 + 5 (92)[c]

[a]Calculated differently for 1983 than for 1984 through 1986
[b]Number of precision checks
[c]Number of audits, manual at 0 074 to 0 083 ppm, continuous at 0 03 to 0 08 ppm
[d]Number of collocated samples

Source Rhodes and Evans (1988)

NO_2-to-NO converters used may not be specific for NO_2 Heated molybdenum converters, typically used in commercial analyzers, have been shown to convert PAN, HNO_3, and other nitroxy compounds to NO, giving rise to artificially high values for NO_2 and NO_x In research-grade CLM NO_x analyzers, $FeSO_4$ converters have been shown to overestimate NO_x by a factor of 2 to 3 at concentrations of 0 2 ppb (Fehsenfeld et al , 1987, Gregory et al , 1990b)

The catalytic conversion approach will permit an accurate measure of NO_x as long as the nitroxy compounds present in the sampled atmosphere are limited to NO and NO_2 Atmospheric concentrations of potential interferences are generally low relative to NO_2 (Code of Federal Regulations, 1987a) There are cases, however, where compounds other than NO and NO_2 contribute substantially to the atmospheric nitroxy burden Examples include urban atmospheres such as Los Angeles, where both PAN and HNO_3 levels may

reach appreciable levels (Tuazon et al , 1981), and remote environments, where PAN may comprise a significant fraction of the airborne nitroxy reservoir (Fehsenfeld et al , 1987, Gregory et al., 1990c).

A prototype method employing CLM has been suggested to measure NO_x (Fontijn et al., 1980). This method uses the reaction between atomic hydrogen and NO_2 to give NO along with the subsequent CLM reaction between atomic hydrogen and NO The emission occurs between 628 and 800 nm, and the intensity is measured by a PM tube at 640 to 740 nm At a constant atomic hydrogen concentration, the light intensity is proportional to the NO_x concentration The instrument was developed for application to automotive exhaust gas. Significant interferences were noted for O_2 and ethene, but not for H_2O, toluene, isopentane, CO, CO_2, NH_3, and HCN Response was linear within 2% from 6 to 3,000 ppm. Significant development is needed if the limit of detection for this technique is to be extended from 6 ppm to the parts-per-trillion to parts-per-billion range appropriate for ambient air monitoring applications.

6.5 TOTAL REACTIVE ODD NITROGEN OXIDES

In the present document, total reactive odd nitrogen oxides are represented by NO_y Individual components comprising NO_y are NO, NO_2, NO_3, N_2O_5, HONO, HNO_3, HO_2NO_2, PAN, other organic nitrates, and particulate NO_3^-

Although no single instrument has been devised to measure NO_y, researchers have combined highly sensitive research-grade CLM NO detectors with catalytic converters that are sufficiently active to reduce most of the important gas phase NO_y species to NO for subsequent detection (Helas et al , 1981, Dickerson, 1984, Fahey et al , 1986) Calibrations are performed using dynamic dilution with air Two standards are usually employed (1) a cylinder of compressed gas containing NO in nitrogen at an NIST-traceable concentration, and (2) an NO_2 permeation tube The NO cylinder is used to calibrate the instrument for NO, and NO_2 from the permeation tube is used as a surrogate to calibrate the instrument for NO_y

Two types of heated converters have been employed molybdenum and gold As noted in Section 6.3.1, heated molybdenum has been shown to convert NO_2, HNO_3, PAN, methyl

nitrate, ethyl nitrate and nitrite, *n*-propyl nitrate, and *n*-butyl nitrate to NO with high efficiency Dickerson (1984) also reports that NO_3 and N_2O_5 are converted to NO on heated molybdenum, whereas acetonitrile, HCN, and NH_3 are not Dickerson (1984) has coupled this converter with a sensitive CLM NO detector and reported a detection limit for NO_y of 25 ppt for a 20-s integration time and an accuracy of $\pm 40\%$ at levels well above the detection limit (Fehsenfeld et al , 1987)

A gold catalyst operated at 300 °C in the presence of 3,000 ppm CO has been reported to reduce NO_y to NO (Bollinger et al , 1983, Fahey et al , 1985a) Converter efficiencies near 100% were found for NO_2, HNO_3, N_2O_5, and PAN Interferences in the presence of water vapor were found to be negligible for O_3, NH_3, N_2O, HCN, CH_4, and various chlorine-and sulfur-containing compounds Fahey et al (1986) coupled this converter with a sensitive CLM NO detector and reported a detection limit of 10 ppt for a 10-s integration time and an accuracy of $\pm 15\%$

A field intercomparison of the two instruments described above was conducted near Boulder, CO (Fehsenfeld et al , 1987). In this study, ambient NO_y concentrations ranged from 400 ppt to over 100 ppb Both instruments gave similar estimates of NO_y concentrations under conditions that varied from representing urban to continental background air

Using the instrument described above with a gold converter, Fahey et al (1986) compared NO_y measurements with the sum of the component species measured individually The NO_y levels systematically exceeded the sum The difference was attributed to the presence of one or more unmeasured organic nitrate species that are similar to PAN and may be of photochemical origin

6.6 PEROXYACETYL NITRATE

Several methods have been used to measure the concentration of PAN in ambient air Stephens (1969) and Roberts (1990) have provided a good overview of many of these methods Peroxyacetyl nitrate was first measured by using long-path infrared spectrometry, however, insufficient sensitivity by this technique prompted the development of other methods (Darley et al , 1963) A ground-based FTIR system with a 1-km cell has reported

detection limits of 4 ppb for PAN near 790 and 1,160 cm^{-1} (Tuazon et al , 1978) The limited sensitivity and the complexity of FTIR systems have generally limited ambient applications of the FTIR to the relatively high concentrations associated with the Los Angeles basin More recently, cryogenic sampling and matrix-isolation FTIR has been used to measure PAN in 15-L integrated samples of ambient air with a theoretical MDL of 50 ppt (Griffith and Schuster, 1987) A laboratory prototype method, TTFMS, has a projected MDL for PAN of 2 ppt (Hansen, 1989) Gas chromatography with flame ionization detection (GC-FID) may be employed to measure PAN, but this method is only practical for concentrated mixtures above 10 ppm using a 1-mL sample loop (Meyrahn et al , 1987) The most common method is gas chromatography using electron capture detection (GC-ECD) (Darley et al., 1963, Smith et al , 1972, Stephens and Price, 1973, Singh and Salas, 1983)

6.6.1 Gas Chromatography-Electron Capture Detection

Both manual and automated integrated sampling methods using GC-ECD have been employed (Stephens and Price, 1973, Lonneman et al , 1976) Relatively low column and detector temperatures (below 50 and 100 °C, respectively) have been used to minimize thermal decomposition of PAN Short packed columns coated with polyethylene glycol-type stationary phases (e g , Carbowax 400) have normally been used Recently, improved precision and sensitivity have been achieved using silica capillary columns (Helmig et al , 1989; Roberts et al , 1989) Although sampling intervals are limited by the elution times of the chromatographic system, intervals of 10 to 15 min have been employed (Helmig et al , 1989; Nieboer and Van Ham, 1976) Using packed columns, detection limits of 10 ppt have been reported using direct sampling with a 20-mL sample loop (Vierkorn-Rudolph et al , 1985), and detection limits of 1 to 5 ppt have been reported using cryogenic enrichment of samples (Vierkorn-Rudolph et al , 1985, Singh and Salas, 1983) Capillary columns offer the potential for considerable (i e., factor of 20) enhancement in sensitivity (Roberts et al , 1989). Accuracy estimates of ±20 to 30% have been claimed

A comparison of two similar GC-ECD methods for airborne PAN measurements was performed (Gregory et al , 1990c) Both methods employed cryogenic enrichment of samples, used packed GC columns, and claimed detection limits below 5 ppt Results of this study showed that at PAN concentrations below 100 ppt, agreement was approximately

17 ppt, and at higher concentrations (i e , 100 to 300 ppt) the measurements agreed to within 25% (expressed as a percent difference) These findings are generally consistent with accuracy claims noted earlier

6.6.2 Alkaline Hydrolysis

Alkaline hydrolysis in 5% NaOH has been shown by Nicksic et al (1967) to convert PAN quantitatively to nitrite and acetate This permits sampling with a bubbler containing 5% NaOH and subsequent analysis for nitrite or acetate Nitrogen dioxide is usually present in ambient air with PAN It can interfere with PAN determination as nitrite because NO_2 may be collected as nitrite in alkaline solution Acetate particles or acetic acid can interfere with PAN determination as acetate A method involving alkaline hydrolysis followed by IC determination of acetate has been used to measure PAN in photochemical systems (Grosjean and Harrison, 1985a) Results compare favorably with those of a CLM method employing the difference in NO_x signals measured upstream and downstream of an alkaline bubbler In addition to NaOH, other alkaline salts (e g , potassium hydroxide and sodium carbonate [Na_2CO_3]) have been used to coat filters, cartridges, and annular denuders (Grosjean and Parmar, 1990, Williams and Grosjean, 1990) Peroxyacetyl nitrate collection efficiencies ranged from 10 to 100%, depending on the type and amount of the alkaline salt, the flow rate, and the collection device employed

6.6.3 Gas Chromatography—Alternate Detectors

As noted in Section 6 3 1, PAN is readily reduced to NO Meyrahn et al (1987) have coupled a GC to separate PAN, NO, and NO_2, a molybdenum converter, and a CLM NO analyzer to measure PAN as NO Using a 10 mL sample loop, a detection limit of 10 ppb was reported

The luminol-based detector has shown sensitivity to PAN, as discussed in Section 6 3 2 Burkhardt et al (1988) used gas chromatography and a commercially available luminol-based instrument (i e , Scintrex LMA-3 Luminox) to detect both NO_2 and PAN Using a sampling interval of 40 s, linear response was claimed from 0 2 to 170 ppb NO_2 and from 1 to 65 ppb PAN Although the PAN calibration was nonlinear below 1 ppb, an MDL of 0 12 ppb was reported Drummond et al (1989) have slightly modified the

above approach by converting the PAN from the GC column to NO_2 and measuring the resulting NO_2 with a CLM (luminol) instrument

6.6.4 Peroxyacetyl Nitrate Stability

Peroxyacetyl nitrate is an unstable gas and is subject to surface-related decomposition as well as thermal instability Peroxyacetyl nitrate exists in a temperature-sensitive equilibrium with the peroxyacetyl radical and NO_2 (Cox and Roffey, 1977) Increased temperature favors the peroxyacetyl radical and NO_2 at the expense of PAN Added NO_2 should force the equilibrium toward PAN and enhance its stability In the presence of NO, peroxyacetyl radicals react rapidly to form NO_2 and acetoxy radicals, which decompose in O_2 to radicals that also convert NO to NO_2 As a result, the presence of NO acts to reduce PAN stability and enhance its decay rate (Lonneman et al , 1982) Stephens (1969) reported that appreciable PAN loss in a metal sampling valve was traced to decomposition on a silver-soldered joint Meyrahn et al (1987) reported that PAN decayed according to first order kinetics at a rate of 2 to 4%/h in glass vessels that had been previously conditioned with PAN. They employed 200 ppm PAN in glass vessels and the noted first-order decay as the basis for one proposed method of in-field PAN calibration In contrast, Holdren and Spicer (1984) found that without NO_2 added, 20 ppb PAN decayed in Tedlar bags according to first order kinetics at a rate of 40%/h The addition of 100 ppb NO_2 acted to stabilize the PAN (20 ppb) in the Tedlar bags

A humidity-related difference in GC-ECD response has been reported (Holdren and Rasmussen, 1976) Low responses observed at humidities below 30% and PAN concentrations of 10 and 100 ppb, but not 1,000 ppb, were attributed to sample-column interactions. This effect was not observed by Lonneman (1977) Watanabe and Stephens (1978) conducted experiments at 140 ppb and did not conclude that the reduced response was from faults in the detector or the instrument They concluded that there was no column-related effect, and they observed surface-related sorption by PAN at 140 ppb in dry acid-washed glass flasks. They recommended that moist air be used to prepare PAN calibration mixtures to avoid potential surface-mediated effects

Another surface-related effect has been reported for PAN analyses of remote marine air (Singh and Viezee, 1988) Peroxyacetyl nitrate concentrations were found to increase by

20 to 170 ppt, an average factor of 3 2, when the sample was stored in a glass vessel for 1 to 2 min prior to analysis This effect remains to be explained

6.6.5 Calibration

Because PAN is unstable, the preparation of reliable calibration standards is difficult Several methods have been employed The original method used the photolysis of ethyl nitrite in pure oxygen (Stephens, 1969). When pure PAN is desired, the reaction mixture must be purified, usually by chromatography, to remove the major by-products, acetaldehyde and methyl and ethyl nitrates (Stephens et al , 1965) For GC calibration, purification is unnecessary, the PAN concentration in the reactant matrix is established from the IR absorption spectrum and subsequently diluted to the parts-per-billion working range needed for calibration purposes (Stephens and Price, 1973)

Static mixtures of molecular chlorine, acetaldehyde, and NO_2 in the ratio of 2 4 4 can be photolyzed in the presence of a slight excess NO_2 to give a near stoichiometric yield of PAN (Gay et al , 1976) This method was adapted by Singh and Salas (1983) and later by Grosjean et al (1984) using photolytic reactors to provide continuous PAN calibration units at concentrations between 2 and 400 ppb In the former approach, the PAN concentration is established by measuring the change in acetaldehyde concentration across the reactor In the latter, the PAN concentration is established by measuring the acetate in an alkaline bubbler where PAN is hydrolyzed

A static technique involving the photolysis of acetone in the presence of NO_2 and air at 250 nm has been reported to produce a constant concentration of PAN (Meyrahn et al , 1987) A Penray mercury lamp is inserted into a mixture of 10 ppm NO_2 and 1% acetone and irradiated for 3 min to yield 8 9 $\pm$ 0 3 ppm PAN

Peroxyacetyl nitrate can be synthesized in the condensed phase by the nitration of peracetic acid in hexane (Helmig et al , 1989), heptane (Nielsen et al , 1982), octane (Holdren and Spicer, 1984), or *n*-tridecane (Gaffney et al , 1984) Purification of PAN in the liquid phase is needed using the first two methods The resulting PAN-organic solution can be stored at −20 to −80 °C with losses of less than 3 6%/mo and can be injected directly into a vessel containing air to produce a calibration mixture The PAN concentration is normally established by FTIR analysis of the solution or the resulting PAN-air mixture

As noted in Section 6 3 1, PAN is readily reduced to NO, and CLM NO_x analyzers have near quantitative response to PAN Thus under some circumstances, CLM NO_x response can be used for PAN calibration One method uses the difference in NO_x signal measured upstream and downstream of an alkaline bubbler (Grosjean and Harrison, 1985a) Joos et al (1986) have coupled a CLM NO_x analyzer with a GC system to permit calibration of the ECD response by reference to the CLM NO_x analyzer that has been calibrated by traditional methods.

As noted previously, NO in the presence of PAN is converted to NO_2 Approximately four molecules of NO can react per molecule of PAN Lonneman et al (1982) have devised a PAN calibration procedure based on the reaction of PAN with NO in the presence of benzaldehyde, which is added to control unwanted radical chemistry and improve precision Using this approach and an initial NO-to-PAN ratio of between 10 and 20 to 1, the change in NO concentration is monitored with a CLM NO analyzer, the change in PAN GC-ECD response is monitored, and the resulting ratio (i e , $\Delta NO/\Delta PAN$) is divided by the stoichiometric factor of 4.7 to arrive at a calibration factor for the ECD

Peroxyacetyl nitrate and *n*-propyl nitrate (NPN) have similar ECD responses Serial dilution of the more stable compound, NPN, has been used for field operations (Vierkorn-Rudolph et al , 1985) This approach is not recommended for primary calibration, however, because it does not permit verification of quantitative delivery of PAN to the detector (Stephens and Price, 1973)

6.6.6 Other Organic Nitrates

Other organic nitrates (e g , alkyl nitrates, peroxypropionyl nitrate [PPN], and PBzN) are also present in the atmosphere, but usually at lower concentrations than PAN (Fahey et al., 1986) In general, similar methods for sampling, analysis, and calibration may be used for other organic nitrates as are used for PAN (Stephens, 1969) Both FTIR and GC-ECD may be used to measure these compounds

With MDLs of 0 1 to 0 4 ppb, inspection of 3,000 GC-ECD chromatograms recorded at five to nine sites during the 1987 Southern California Air Quality Study yielded only seven possible (but nonprobable) observations of methyl nitrate (Grosjean et al , 1990) Roberts et al. (1989) have reported separation of PAN, PPN, and C_1 to C_4 alkyl nitrates and the

potential increase in sensitivity by a factor of 20 using fused silica-coated capillary columns rather than the more conventional coated packed columns Atlas (1988) has used two 5-mg charcoal traps in series to collect C_3 to C_7 alkyl nitrates from 12- to 300-L samples at 200 to 400 mL/min in remote atmospheres The traps are extracted in small volumes of benzene and analyzed using capillary GC-ECD Concentrations as low as 1 ppt were reported Peroxybenzoyl nitrate may be collected as methyl benzoate using bubblers containing methanol-NaOH solutions (Appel, 1973) The resulting methyl benzoate is solvent extracted and analyzed by packed column GC-FID with an MDL of 70 ppt Recently, a collection method using aqueous alkaline hydrolysis of PBzN to the benzoate ion followed by IC-UV analysis was reported to have a detection limit of 30 ppt in a 60-L sample (Fung and Grosjean, 1985) Using this method, a median PBzN level of 0 32 ppb was reported for Los Angeles air samples

6.7 NITRIC ACID

Several methods are available for the determination of airborne concentrations of HNO_3 Among them are filtration (Okita et al , 1976, Spicer et al , 1978b), denuder tubes (Forrest et al , 1982, DeSantis et al , 1985, Ferm, 1986), CLM (Joseph and Spicer, 1978), absorption spectroscopy (Tuazon et al , 1978, Schiff et al , 1983, Biermann et al , 1988), and microcoulometry (Spicer et al , 1978b) Filtration and denuder techniques involve collection of HNO_3 onto a media and subsequent analytical determination As a result of its 2-ppb detection limit and long response time, microcoulometry has been largely replaced by other methods Consequently, only the first four methods listed above are described here

6.7.1 Filtration

Filtration techniques generally employ dual filters that rely on the collection of particulate NO_3^- on the first filter and gaseous HNO_3 as NO_3^- on the second filter This method is sometimes called the filter pack (FP) method Typically, filtration is used in conjunction with instrumental detection or subsequent chemical analysis of the material collected on the filter media Filter extracts are usually analyzed for NO_3^- using IC Efficient HNO_3 collection has been found with nylon filters (Spicer et al , 1978b) and with

filters impregnated with sodium chloride (NaCl) or sodium fluoride (NaF) (Okita et al , 1976; Forrest et al , 1980; Fuglsang, 1986). The HNO_3 capacity of 47-mm diameter NaCl-coated filters (500 μg/cm) far exceeds that of nylon (30 μg/cm) (Anlauf et al , 1986) This advantage may be offset because the presence of the chloride ion in the NaCl-coated filter extract may hamper IC determination of NO_3^- With a 47-mm diameter nylon filter sampling at 1 m^3/h at a nominal HNO_3 level of 5 μg/m (2 ppb), the capacity is sufficient for just over 4 days of sampling. The sensitivity of filtration and other integrative methods depends on the detection limit of the analytical finish, the variability and magnitude of the blank level, collection and extraction efficiencies, and the volume of air sampled As an example, under an assumed IC detection limit for NO_3^- of 0 05 μg/mL, a filter extraction volume of 10 mL, negligible blank, quantitative collection and extraction, and a sampled air volume of 24 m^3 (i e., flow rate 1 m^3/h for 1 day), the minimum sensitivity is 0 02 μg/m (8 ppt). A precision of $\pm 10\%$ and an accuracy of +20 to -40% are claimed for FPs containing Teflon™ and nylon filters (Fahey et al , 1986)

Although the HNO_3 determination by FP methods is desirable due to simplicity, high sensitivity, and low cost, there is great difficulty in distinguishing between gaseous and particulate forms of nitrate Errors in the measurement of gaseous HNO_3 may be in the form of positive artifacts due to volatilization of collected aerosol nitrates on the prefilter to form gaseous HNO_3 (i.e , $NH_4NO_3 \rightleftarrows NH_3 + HNO_3$) (Appel et al , 1980), reaction of collected particulate nitrates on the prefilter with strong acids, resulting in the release of HNO_3 (i e., $H_2SO_4 + 2NH_4NO_3 \rightarrow (NH_4)_2SO_4 + 2HNO_3$) (Appel and Tokiwa, 1981), or formation of HNO_3 on the collection medium by interaction with other NO_x species (e g , HONO or NO_2) (Eatough et al , 1988, Spicer and Schumacher, 1979) Negative HNO_3 artifacts may result from retention of HNO_3 by the prefilter collection medium (Appel et al , 1984), retention of HNO_3 by collected particles on the prefilter (Appel et al , 1980), a low capacity for HNO_3 on the collection medium, or losses of HNO_3 by volatilization or by displacement by other acids

Inert prefilter materials, such as Teflon™, should not collect appreciable amounts of HNO_3 (Appel et al , 1979), this, however, does not preclude the possibility of HNO_3 reaction with aerosol particles collected on Teflon™ prefilters In addition, some types of Teflon™ may sorb HNO_3 to a larger extent than others (Appel et al , 1988) This

underscores the importance of using "inert" materials for all surfaces coming into contact with HNO_3 to insure representative sampling

6.7.2 Denuders

To avoid some of the artifact problems associated with the use of filters, denuder tube samplers were introduced In general, a denuder is a tube or channel that has its walls coated with or fabricated from a substance that removes the gaseous species of interest, in this case HNO_3 (also see Section 6 3 6) The HNO_3 molecules diffuse to and impact the surface while the sample is drawn through the channel The flow conditions are usually laminar (Re < 2,000), and by taking advantage of differences in diffusivities, permit particles to pass through the denuder relatively undisturbed Using the sampled air volume, the concentration of HNO_3 is calculated from the measured amount of NO_3^- collected on the denuder walls (Ferm, 1986) or from the difference of NO_3^- collected downstream in the presence and absence of the denuder (Shaw et al., 1982, Forrest et al , 1982)

Denuder tubes have employed magnesium oxide (MgO) (Shaw et al , 1982), Na_2CO_3 (Ferm, 1986), nylon (Mulawa and Cadle, 1985), aluminum sulfate ($Al_2[SO_4]_3$) (Lindqvist, 1985), magnesium sulfate ($MgSO_4$), barium sulfate ($BaSO_4$) (Klockow, 1989), and tungstic acid (TA) (McClenny et al , 1982) to retain HNO_3 A coating of MgO is frequently used with the denuder difference (DD) approach, where one coated denuder is followed by nylon or NaCl-coated filters and a parallel arrangement uses a nylon or NaCl-coated filter The difference in NO_3^- on the two parallel filters is attributed to HNO_3 (Shaw et al , 1982) The Na_2CO_3 coating is used in methods employing the DD or direct analysis approach In the latter, the denuder is extracted, and the extract is analyzed for NO_3^-, which is attributed to HNO_3 (Ferm, 1986)

To maintain laminar flow, the flow rate through a single conventional open channel denuder of reasonable dimensions is limited to approximately 1 to 2 L/min As a result, long duration samples or numerous open channel denuders located in parallel may be required to provide sufficient analyte for quantitation A new type of denuder, the annular denuder (AD), has been developed where the same equivalent diameter permits the flow rate to be increased by a factor of 12 (Possanzini et al , 1983) In the AD, ambient air is passed through the annular space of two concentric tubes The outside of the inner tube and the

inside of the outer tube are coated with a specific gas-absorbing substance For collecting HNO_3, Na_2CO_3 has been used (DeSantis et al , 1985) In cases where appreciable HONO is present and may be cocollected on Na_2CO_3 and the resulting NO_2^- may be oxidized to NO_3^- over extended sampling periods by atmospheric oxidants (e g , O_3), two or more denuders are used to permit resolution of HNO_3 and HONO (Febo et al , 1986, Perrino et al , 1990) The first denuder is coated with NaCl or NaF to collect HNO_3 as NO_3^- and the downstream denuder(s) is coated with an aqueous solution of Na_2CO_3 and glycerol to collect HONO as the sum of NO_2^- and NO_3^- For a 1 m^3/h 1-day sample under the same assumptions given earlier for filtration, the MDL for the AD is 0 02 μg/m (8 ppt) Median precision estimates of 8 and 5% RSD have been reported for 13 22-h and 12 1-week duration samples (Sickles et al., 1989; Sickles, 1987).

Partial denuders have been fabricated of nylon filter material (Mulawa and Cadle, 1985). These denuders, operated under laminar-flow conditions, have relied on a mathematical description of molecular diffusion to a perfect wall sink along with HNO_3 deposition measured along the length of the denuder to infer the sampled, ambient HNO_3 concentration A refinement in the data treatment has been offered recently that considers interferent nitrate on nylon partial denuders (Febo et al , 1988) Although these denuders are operated under laminar-flow conditions, a recently introduced technique employs a nylon partial denuder that is operated under transition-flow conditions (Re $\approx$ 2,600) (Knapp et al , 1986). This approach, TFR, uses a piece of nylon filter material rolled into a cylindrical shape and placed in a Teflon™ tube The sample is drawn through the tube and denuder under transition-flow conditions, where a constant fraction of the HNO_3 is claimed to be collected. The tube is followed by a Teflon™ and a nylon filter The HNO_3 is calculated by analyzing the denuder extract for NO_3^- and applying the constant collection fraction The particulate NO_3^- is determined algebraically using the NO_3^- measured in the extracts of the Teflon™ and nylon filters. For 8 5% collection efficiency and 1 m^3/h 1-day sample under the same assumptions given earlier for filtration, the MDL for the TFR is 0 2 μg/m (0.1 ppb). A median precision of 7% RSD has been determined for seven 1-week duration samples (Knapp et al , 1986)

Automated systems using coated denuders with thermal desorption employ $Al_2(SO_4)_3$, $MgSO_4$, $BaSO_4$, or TA to preconcentrate HNO_3 for subsequent delivery to an instrumental

detection system In the first case, HNO_3 from a 30 L sample is collected on an $Al_2(SO_4)_3$-coated denuder, thermally desorbed, thermally converted to NO, and analyzed by gas chromatography with a photoionization detector (Lindqvist, 1985). A nominal MDL of 5 ppt and precision estimate of $\pm 10\%$ were claimed

Klockow et al (1989) have used $MgSO_4$- and $BaSO_4$-coated denuders to collect HNO_3 The sample is thermally desorbed and measured with a CLM NO_x analyzer For a 30-min sample at 5 L/min, a nominal MDL of 0 1 $\mu g/m^3$ (40 ppt) and precision estimate of $\pm 5\%$ were claimed

A TA-coated denuder has been used to collect HNO_3 for analysis on an automated basis with a 40-min cycle time (McClenny et al , 1982) The collected HNO_3 is thermally desorbed as NO_2, thermally converted to NO, and measured with a commercial CLM NO_x analyzer A nominal MDL of 70 ppt and a precision estimate of $\pm 10\%$ were claimed Recent claims for a similar device with a 20-min cycle time have included MDL of 20 ppt, accuracy of 15 to 20%, and precision of 8% (Gregory et al , 1990d) Tungstic acid-coated denuders have drawbacks they are difficult to prepare, have low capacities, and are subject to unknown atmospheric interferences (Fellin et al , 1984, Eatough et al , 1985, Roberts et al , 1987)

6.7.3 Chemiluminescence

As noted in Section 6 3 1, HNO_3 is readily reduced to NO in NO_2-to-NO converters used in commercial and many research-grade CLM NO_x analyzers (Joseph and Spicer, 1978, Bollinger et al , 1983, Fahey et al , 1985a, Grosjean and Harrison, 1985b, Rickman and Wright, 1986) Nitric acid measurements that employ CLM generally use an NO_x analyzer to measure the NO_x in a sampled air stream in the presence and absence of an HNO_3 scrubber The difference in these NO_x signals is attributed to HNO_3 Nylon filters have been used as an HNO_3 scrubber with both commercial and research-grade CLM NO_x analyzers The instrumental performance for HNO_3 is similar to that for NO_2 with the same instruments (Joseph and Spicer, 1978, Kelly et al , 1979) Losses of HNO_3 from the sampled air to the interior surfaces of the sampling line and instrument may lead to nonquantitative responses or increases in response time (Rickman and Wright, 1986, Appel et al , 1988)

In other methods employing CLM and described in Section 6 7 2, TA, $MgSO_4$, or $BaSO_4$ are used as regenerable HNO_3 scrubbers (McClenny et al , 1982, Klockow et al , 1989). With these methods, HNO_3 is collected on a coated denuder, the collected HNO_3 is thermally desorbed as NO_2 (regenerating the scrubber), the desorbed NO_2 is thermally converted to NO, and the resulting NO is measured with a commercial CLM analyzer

6.7.4 Absorption Spectroscopy

Absorption spectroscopy is discussed in Sections 6 2 3 and 6 3 4 Although FTIR, TDLAS, and, potentially, TTFMS techniques may be used to measure ambient levels of HNO_3, poor sensitivity limits ambient applications of FTIR A ground-based 23-m multipass FTIR system with a 1-km path length has reported detection limits of 4 ppb near 900 cm^{-1} (Tuazon et al , 1978; Biermann et al , 1988) A theoretical MDL for HNO_3 of 10 ppt has been claimed for 15-L integrated samples of ambient air using cryogenic sampling and matrix-isolation FTIR (Griffith and Schuster, 1987)

Cassidy and Reid (1982) report an expected MDL of 0 4 ppb using TDLAS near 1,330 cm^{-1}. For a 40-m path length near 1,720 cm^{-1}, the MDL is 0 4 ppb (Schiff et al , 1983). With a 150-m path length, Mackay and Schiff (1987) report an MDL of 0 1 ppb and an accuracy of $\pm 20\%$. Although the volumetric residence time in the White cell of the TDLAS is 4 s, sample-surface interactions limit the response time to changes in HNO_3 concentration to about 5 min As described in Section 6 2 3, a laboratory prototype method, TTFMS, has been developed (Hansen, 1989) The projected MDL for HNO_3 is 0 3 ppt

6.7.5 Calibration

Nitric acid is a highly polar material and consequently interacts readily with many surfaces (Goldan et al , 1983, Appel et al , 1988) This reactivity prevents the preparation of stable calibration mixtures in cylinders of compressed gases Two methods, permeation devices and diffusion tubes, are generally employed to generate calibration atmospheres of HNO_3 (Schiff et al , 1983; Goldan et al , 1983) Permeation tubes are described for NO_2 in Section 6 3.8 Permeation tubes for HNO_3 with various emission rates are available from commercial suppliers An alternate permeation device may be fabricated in the laboratory by

passing carrier gas through a length of Teflon™ tubing that is immersed in a reservoir of HNO_3 and sulfuric acid (H_2SO_4) (Mackay and Schiff, 1987)

Diffusion tubes are generally fabricated in the laboratory (Schiff et al , 1983) A liquid mixture of HNO_3 and H_2SO_4 is held in a reservoir that is connected to a clean air dilution manifold by a capillary tube The HNO_3 diffusion rate depends on the length and area of the capillary as well as the temperature of the reservoir

Nominal HNO_3 emission rates for permeation tubes are provided by the supplier and are calculated for diffusion tubes (Nelson, 1971) Although it is common to calibrate permeation tubes gravimetrically, it has been reported that non-HNO_3 species (i e , NO_2) are also released and may account for 10 to 15% of the observed weight loss (Goldan et al , 1983) Because the emission rate estimate for diffusion tubes is also an approximation, the independent measurement of HNO_3 emission rates from permeation and diffusion tubes is recommended

This measurement may be accomplished by pH titration or by using nylon filters, NaCl-coated filters, or caustic bubblers to collect and quantify the HNO_3 as NO_3^- Because caustic bubblers may also collect NO_2 to some extent, their use could overestimate the HNO_3 emission rate, and a filtration technique is preferred Alternative, but more elaborate, methods of confirming the HNO_3 emission rate are FTIR, TDLAS, and the CLM NO_x analysis that uses photolysis to convert NO_2 to NO

6.7.6 Intercomparisons

Several field studies have been conducted that have permitted the comparison of different techniques for the measurement of HNO_3 (Spicer et al , 1982, Walega et al , 1984, Anlauf et al , 1985, Roberts et al , 1987, Hering et al , 1988, Solomon et al , 1988, Benner et al , 1987, Tanner et al , 1989, Sickles et al , 1990, Gregory et al , 1990d, Dasch et al , 1989) Results from these studies suggest that the FP overestimates the HNO_3 concentrations and that coated denuder thermal desorption techniques in various tested configurations may not provide reliable measurements of HNO_3

An intercomparison of HNO_3 measurement methods was conducted in Claremont, CA, in August and September of 1979 (Spicer et al , 1982) Ten methods were compared

five FP, two DD, two CLM, and one FTIR The results of five methods (i e , two FP, one DD, one CLM, and one FTIR) were in excellent agreement with median results

Walega et al (1984) report comparisons of CLM and TDLAS HNO_3 measurements of ambient and captive air performed during October and November of 1981 in Los Angeles, CA The CLM gave erratic HNO_3 results for ambient air Although CLM and TDLAS measurements of HNO_3 in captive air samples were highly correlated, linear regression analysis indicated significant biases

Measurements of HNO_3 were made during June 1982 at a rural site in Ontario using FP, TDLAS, and TA techniques (Anlauf et al , 1985) For daytime measurements, the FP and TA measurements were 16% lower than the TDLAS results Nighttime TA results exceeded those from the FP by a factor of 2 Roberts et al (1987) compared FP and TA measurements of HNO_3 made at a rural site in the Colorado mountains The TA results were a factor of 3 higher than those of the FP It was concluded that there are unknown atmospheric species that interfere with TA measurements of HNO_3

Another HNO_3 intercomparison study was conducted in Claremont, CA, in September 1985 (Hering et al., 1988) The methods compared include FP, DD, AD, TFR, TA, FTIR, and TDLAS. For the whole study, comparison of method means against mean of methods showed the FP to be 36% high, the DD to be 1% low, the AD to be 21% low, and the TDLAS to be 13% low Comparison of TFR means against DD means showed the TFR to be 9% high. Tunable-diode laser spectroscopy gave lower daytime and higher nighttime readings than the DD In those few cases where the HNO_3 concentrations were sufficiently high to be detected by the FTIR, agreement within reported uncertainties was observed between the FTIR and the FP, DD, AD, and TDLAS Results from the TA technique were high at night and low during the day, and in view of large systematic differences, they were not included in many of the reported analyses

During 1986, HNO_3 data were collected using DD and FP techniques for 24-h periods every 6 days at eight sites in the Los Angeles basin and at one background site (Solomon et al., 1988). The annual average DD basin-wide estimate of HNO_3 was 4 6 μg/m The corresponding FP estimate exceeded that of the DD by 3 4 μg/m, or by approximately 80%

A study was conducted in January and February 1986 near Page, AZ (Benner et al , 1987). Twelve-hour gaseous HNO_3 concentrations were measured with FP and AD The

mean HNO_3 concentration measured with the FP, 1 1 μg/m, exceeded that measured with the AD by 10%

A study was conducted in July 1986 on Long Island, NY, to compare HNO_3 measurements resolved to a 6-h basis using high-volume FP, DD, real-time two-channel (i e , nylon filter versus no nylon filter) CLM, and $Al_2(SO_4)_3$-coated denuder thermal desorption-to-CLM (Tanner et al , 1989) The FP results were highly correlated with those of the DD The daytime real-time CLM results were correlated with those of the DD, but nighttime real-time CLM results exceeded DD results This may have been caused by the retention of nighttime HONO on the nylon filter Results with the $Al_2(SO_4)_3$-coated denuder were scattered, mostly lower, and poorly correlated with the other methods

Daily measurements of HNO_3 were made in the Research Triangle Park, NC, during 13 days in September and October 1986 (Sickles et al , 1990) Comparisons of the TDLAS results with those of the AD, FP, and TFR revealed significant differences at the 0 05 level for the comparison between the TDLAS and TFR results Significant differences were not apparent in the other two cases Comparisons of the studywide means of daily ratios of AD, FP, and TFR to TDLAS results showed the AD to be 5% low, the FP to be 8% high, and the TFR to be 36 to 76% high

6.8 NITROUS ACID

The measurement of HONO in ambient atmospheres is receiving increased recent attention Currently available techniques employ denuder (Ferm and Sjodin, 1985), AD (DeSantis et al , 1985), CLM (Cox, 1974, Braman et al , 1986), PF/LIF (Rodgers and Davis, 1989), and absorption spectroscopy (Biermann et al , 1988, Tuazon et al , 1978)

6.8.1 Denuders

See Sections 6 3 6 and 6 7 2 for additional discussions of denuders As noted in Section 6 2 1, Braman et al (1986) have employed a series of open-channel denuders coated with materials that act to preconcentrate HNO_3, HONO, NO_2, and NO from sampled ambient air Nitrous acid is collected using a potassium iron oxide coated denuder located downstream of a TA-coated denuder that removes HNO_3 The HONO is thermally desorbed

from the potassium iron oxide coated denuder and detected as NO with a CLM NO analyzer Although sub-parts-per-billion sensitivity is claimed, field testing is needed to demonstrate the adequacy of this method

Nylon filter material has also been used as an open-channel denuder to collect HONO (Benner et al., 1988) Recent studies, however, have indicated that HONO may not be retained quantitatively by nylon filters (Sickles and Hodson, 1989, Perrino et al , 1988)

Ferm and Sjodin (1985) have used two conventional open-channel Na_2CO_3-coated denuders in series for the determination of HONO in ambient air Nitrous acid is collected quantitatively on the first denuder, whereas interferent artifacts from PAN and other NO_x species (i e., NO_2) are collected in approximately equal amounts on both denuders Each denuder is extracted and the extract is analyzed for NO_2^- using spectrophometry or IC To correct for interferent artifacts, the difference in NO_2^- found on the two denuders is attributed to HONO

Annular denuders have also been used to measure HONO using a similar approach (DeSantis et al., 1985, Sickles, 1987, Sickles et al , 1988, Eatough et al , 1988, Vossler et al., 1988; Koutrakis et al., 1988, Dasch et al , 1989, Appel et al , 1990, Perrino et al , 1990). The MDL for a 1-day AD sample operating at 1 m^3/h, assuming an extract volume of 10 mL, negligible blank, and an IC detection limit of 0 05 μg NO_2^-/mL, is 0 02 μg/m (10 ppt). Estimates of precision for 1-day AD samples range from 5 to 15% (Sickles et al., 1989; Vossler et al., 1988) In those cases where denuder sampling is performed over extended periods in the presence of oxidants (i e , O_3), the collected NO_2^- may be oxidized to NO_3^- (Febo et al , 1986, Sickles et al , 1989, Sickles and Hodson, 1989, Perinno et al , 1988) To avoid this potential for sampling artifacts, an initial denuder coated with NaCl or NaF is added to collect HNO_3 as NO_3^- and pass HONO The difference in the sums of NO_2^- and NO_3^- on the two downstream Na_2CO_3-coated denuders is attributed to HONO (Febo et al., 1986, Perrino et al , 1990)

6.8.2 Chemiluminescence

It has been shown that HONO may be measured nonspecifically as NO_x with a CLM NO_x analyzer (Cox, 1974, Sickles and Hodson, 1989, Spicer et al , 1991) As a result, HONO can be determined using a CLM NO_x analyzer to measure the NO_x in a sampled air

stream in the presence and absence of a HONO scrubber by attributing the difference to HONO (Cox, 1974) Dilute aqueous NaOH solutions (Cox, 1974), filters coated with Na_2CO_3 (Sickles and Hodson, 1989, Rickman et al , 1989, Kanda and Taira, 1990), and denuders coated with Na_2CO_3 (Brauer et al , 1990) have been employed as HONO scrubbers Because these scrubbers are not specific foi HONO, this approach cannot be used to measure HONO in atmospheres containing other oxides of nitrogen that can be removed by the scrubber (e g , HNO_3) without the appropriate corrections As noted in the previous section, Braman et al (1986) have used a system of selective denuders to collect HONO as well as HNO_3, NO_2, and NO for subsequent thermal desorption and detection as NO with a CLM NO analyzer

6.8.3 Photofragmentation/Laser-Induced Fluorescence

Photofragmentation/laser-induced fluorescence is discussed in Section 6 3 3 for the measurement of NO_2. In its present application, HONO is photofragmented to NO and hydroxyl (OH) radical using radiation at 355 nm from a Nd YAG laser (Rodgers and Davis, 1989) Appreciable amounts of NO are also produced by the photolysis of NO_2, which is generally present along with HONO in ambient air As a result, the current method is based on the detection of OH radical using SP-LIF With this technique, the resulting OH radical is excited to the $A^2\Sigma^+$ state using laser radiation at 282 nm, and the fluorescence at 310 nm that accompanies the A to X transition of the excited OH radical is monitored Detection limits in the low tens of parts per trillion for 15-min integration times are claimed

6.8.4 Absorption Spectroscopy

Although HONO is potentially detectable (i e , MDL of 4 ppb) using a 23-m multipass FTIR system with a 1-km path length, FTIR has not been used to measure the concentration of HONO in ambient air (Tuazon et al , 1978) A theoretical MDL for HONO of 10 ppt has been claimed for 15-L integrated samples of ambient air using cryogenic sampling and matrix-isolation FTIR (Griffith and Schuster, 1987) Long-path UV/visible DOAS has been used to determine HONO as well as other trace atmospheric constituents (see Section 6 3 4) Using a 25-m multipass open system with a 0.8-km path length at wavelengths near 354 nm,

an MDL of 0 6 ppb is claimed (Biermann et al , 1988) Using a single-pass open system with a 10-km path length, an MDL of 20 ppt has been reported (Platt and Perner, 1983)

6.8.5 Calibration

The preparation of reliable calibration mixtures containing known concentrations of HONO is difficult Atmospheres containing HONO as well as NO_2 and NO may be produced by acidifying solutions of sodium nitrite ($NaNO_2$) with H_2SO_4 (Cox, 1974) The method of Braman and de la Cantera (1986) uses a sublimation source where HONO is produced by subliming oxalic acid onto solid $NaNO_2$ at 30 to 60% RH Small concentrations of HNO_3, NO_2, and NO may also be generated using the latter technique Both methods require independent and periodic determination of the HONO concentration because the source strengths are not necessarily constant A recent refinement in the method of Cox (1974) has employed a flow generation system to produce stable concentrations of HONO at the parts-per-billion level (Kanda and Taira, 1990)

6.8.6 Intercomparisons

Concentrations of HONO were determined in an indoor air quality study conducted in two research houses using ADs and the CLM difference method (Brauer et al , 1990) Reported concentrations (n = 60) were below 90 ppb, the results were highly correlated (r^2 = 0 86), and the slope was close to unity (CLM = 0 92 AD) In November and December 1987, an outdoor study was conducted in Long Beach, CA, where simultaneous HONO measurements were made using AD and DOAS on 6 days (Appel et al , 1990) The AD samples were integrated over 4 and 6 h, and the 15-min DOAS results were averaged to permit comparison with the AD results The HONO concentrations ranged from less than 1 to approximately 15 ppb, and the AD results were highly correlated with those of the DOAS. Except at the low HONO levels that occurred during the midday periods, where the AD results exceeded the DOAS results, the AD results were 7% lower than the DOAS results. This difference is within the ±30% uncertainty of the DOAS results in the study

6.9 DINITROGEN PENTOXIDE AND NITRATE RADICALS

The NO_3 radical photolyzes rapidly, and as a result, ambient concentrations are low during daylight hours Dinitrogen pentoxide exists in a thermally sensitive equilibrium with NO_2 and the NO_3 radical and can also react heterogeneously with water vapor to produce HNO_3 In addition, the NO_3 radical reacts rapidly with NO to produce NO_2 In spite of their low ambient concentrations, N_2O_5 and the NO_3 radical may have important roles in both tropospheric and stratospheric NO_x chemistry

Although N_2O_5 has not been measured in the troposphere, it has been observed in the stratosphere using spectroscopic methods (Roscoe, 1982) In the troposphere, nighttime N_2O_5 concentrations of up to 15 ppb have been inferred under the assumption of equilibrium using measured NO_2 and NO_3 radical concentrations (Atkinson et al , 1986)
At concentrations above 5 ppb, measurement of N_2O_5 with FTIR spectrometry appears feasible using a 1-km path length near 1,250 cm^{-1} A theoretical MDL for N_2O_5 of 20 ppt has been claimed for 15-L integrated samples of ambient air using cryogenic sampling and matrix-isolation FTIR (Griffith and Schuster, 1987)

Dinitrogen pentoxide is readily reduced to NO at temperatures above 200 °C and, as noted in Section 6 3 1, may be measured nonspecifically as NO_x with CLM NO_x analyzers (Bollinger et al , 1983, Fahey et al , 1985a) An N_2O_5 calibration system has been devised using a crystalline sample at −80 °C, thermal dissociation of gaseous N_2O_5, scavenging of the dissociation product (i e , the NO_3 radical) with added NO to produce NO_2, and a CLM NO detector (Fahey et al , 1985b) This calibration technique focuses on the loss of NO, and an accuracy of ±15% is claimed

Ambient concentrations of the NO_3 radical have been made using DOAS, and concentrations between 1 and 430 ppt have been observed (Atkinson et al , 1986) Additional information on absorption spectroscopy is given in Section 6 3 4 Using a 25-m multipass open system with 0 8-km path length, an MDL of 20 ppt is claimed (Biermann et al , 1988) Using an optical path length of 17 km and a wavelength of 662 nm, the reported detection limit for the NO_3 radical is 1 ppt (Platt et al , 1984) Noxon (1983), using a passive absorption spectroscopic method with the moon as the light source, reports an NO_3 concentration of 0 25 ppt measured at a 3-km altitude from Mauna Loa, Hawaii

6.10 PARTICULATE NITRATE

Atmospheric aerosols are chemically heterogeneous and occur in sizes ranging nominally from <0 01 to 100 μm Many methods are available for sampling ambient aerosols, including impactors, filtration, and filtration coupled with devices to remove particles larger than a specified size (e g , elutriators, impactors, and cyclones) The method of choice usually depends on the particle size range and the chemical composition of the aerosol of interest As an example, ambient concentrations of particles are subject to National Ambient Air Quality Standards (Code of Federal Regulations, 1987a) These standards focus on the concentration of particulate mass for all particles less than 10 μm in equivalent aerodynamic diameter, rather than on the individual chemical species (e g , nitrates) comprising the collected particles

The particle size distribution of ambient particulate nitrate (PN) is bimodal (Kadowaki, 1977; Wolff, 1984, Yoshizumi, 1986, Wall et al , 1988) Particulate nitrate is concentrated in the coarse size (i e , greater than 2 5 μm) in marine environments, where ambient HNO_3 reacts with the coarse suspended sea salt (i e , NaCl) to form sodium nitrate ($NaNO_3$) Under other circumstances, the size distribution of PN will be determined by environmental conditions and the relative presence of precursors, including HNO_3, NH_3, and acidic aerosols. For example, in the eastern United States, during the summer, when the concentration of acidic sulfates is high, the temperature is high, and the NH_3 emissions are low, the $NH_4NO_3 \rightleftarrows NH_3 + HNO_3$ equilibrium is shifted to the right This and metathetical reactions with acidic aerosols and gases make gaseous HNO_3 available for reaction with and retention by coarse soil-derived particles, giving rise to high concentrations of PN in the coarse size range In contrast, some western urban areas (e g , Los Angeles and Denver) have low SO_2 emissions and adequate NH_3 emissions to neutralize acidic aerosols. These conditions favor the concentration of PN in the fine size range, presumably as ammonium nitrate (NH_4NO_3)

6.10.1 Filtration

Particulate nitrates are generally collected by filtration techniques for subsequent analysis. Using ambient dust, John and Reischl (1978) found the filtration efficiencies of Nuclepore (polycarbonate, 0 8-μm pore) and Whatman 41 (cellulose) filters to be less than

90% Efficiencies exceeded 99% for Gelman GA^{-1} (cellulose acetate), Gelman Spectrograde (glass fiber), Gelman A (glass fiber), MSA (glass fiber), and EPA-grade (glass fiber) filters For polytetrafluoroethylene (Teflon™) membrane filters, the efficiencies exceeded 99% for Fluoropore 1-μm pore, Ghia 1- to 3-μm pore, and Ghia 2- to 4-μm pore filters, but did not exceed 99% for some tests with the Fluoropore 3-μm pore and Ghia 3- to 5-μm pore filters

The integrity of PN collected on filters may depend on storage conditions and other factors Highsmith et al (1986) have attributed weight loss observed on quartz high-volume and Teflon™ dichotomous filters to particle loss and volatilization during handling and shipment Smith et al (1978) report a 73% loss of NO_3^- from Gelman AE (glass fiber) high-volume filters stored for 15 mo in the open at room temperature In contrast, filters stored for 2 years in containers at −28 °C showed no loss of NO_3^- Witz et al (1990) have observed 19% loss of nitrates on PM-10 samples collected on Whatman QM-A (quartz and glass fiber) filters after 1 week of room temperature storage Nitrate losses ranged from 28 to 50% after 1 mo Dunwoody (1986), using acid-treated Whatman QM-A (quartz and glass fiber) high-volume filters, found NO_3^- losses of 86% after 6 to 8 mo of dry room temperature storage, whereas refrigerated filter extracts were stable over this period Witz et al (1990) found nitrate losses to increase with decreasing filter alkalinity, increasing acidity of the aerosol deposit, and increasing storage temperature Dunwoody (1986) found that filters spiked with solutions containing potassium nitrate and other salts showed no NO_3^- losses over 60 days of storage In contrast, filters spiked with HNO_3 lost 70 to 90% of the NO_3^- over a period of 3 days

Using filters to collect PN can also result in both positive and negative biases that occur during the sampling process Some of the difficulties encountered with filtration techniques for distinguishing between particulate and gaseous nitrate are also discussed in Section 6 7 1 Gas-filter interactions may lead to one type of positive bias Glass fiber filters have been employed to collect particles including PN from ambient air, and at one point, glass fiber filters were specified by the EPA for sampling total suspended particulate matter (Code of Federal Regulations, 1987a) Glass fiber filters can retain gaseous HNO_3 and to a lesser extent promote the oxidation of gaseous NO_2, leading to the formation of artifact nitrates and the resulting positive biases (Appel et al , 1979, Spicer and Schumacher, 1979) Substantial positive biases from HNO_3 have been reported by Appel et al (1979) for Gelman A, GA^{-1},

and Spectrograde; Whatman 41, MSA 1106 BH (glass fiber), and "EPA grade" filters, by Spicer and Schumacher (1979) for Millipore Nylon, Gelman E, A, AE, AA, and Spectrograde (glass fiber), MSA 1106 BH, Millipore (cellulose acetate), Gelman Microquartz (quartz fiber); and Pallflex E 70-2075W (quartz fiber) filters, and by Appel et al (1984) for Gelman "EPA grade", Schleicher and Schuell (glass fiber), Schleicher and Schuell 1 HV (glass fiber); Whatman EPM 2600 and EPM 1000 (glass fiber), Whatman QM-A, Pallflex 2500 QAST (quartz fiber), Gelman Microquartz, and Gelman ADL (quartz fiber) filters Witz and Wendt (1981) report that the magnitudes of artifact nitrates on high-volume sampler filters were ordered as follows Whatman EPM 1000 > Gelman AE (acid washed glass fiber) > Gelman Microquartz > Pallflex TX40H120 (Teflon™-coated glass fiber) > Pallflex 2500 QAO (quartz fiber) Artifact nitrates on Gelman A and Pallflex TX40H120 filters based on laboratory tests exceeded the amount found on Pallflex QAST filters by factors of 8.6 and 3.4, respectively (Mueller and Hidy, 1983) Substantial amounts of artifact nitrates have been reported based on field studies using Gelman A and Pallflex TX40H120 filters (Pierson et al., 1980) Higher ambient PN measurements were reported using S & S and Whatman QM-A filters than with Gelman Microquartz, Pallflex 2500 QAST, or Membrana/Ghia Zefluor (Teflon™) filters (Rehme et al , 1984) Small biases were also reported for EPA/ADL (quartz fiber) and Pallflex QAST filters (Spicer and Schumacher, 1979). Negligible artifact nitrates were reported for Fluoropore (Teflon™) (Appel et al , 1979, Mueller and Hidy, 1983) and Ghia Zefluor filters (Appel et al , 1984), and no artifact nitrates were reported for Nuclepore (0 8-μm pore) and Millipore Mitex (Teflon™) filters (Spicer and Schumacher, 1979) Good agreement was reported for PN collected on acid-treated Pallflex 2500 QAO and Fluoropore filters (Forrest et al , 1982), in contrast to tests where PN on Pallflex QAST exceeded that on Ghia Zefluor filters by 33% (Appel et al , 1984).

A second source of positive bias in using filtration for the collection of PN is the retention of gaseous HNO_3 by particulate matter collected on the filter Appel et al (1980) have reported increased retention of HNO_3 with mass loading of particulate matter on Ghia Zefluor filters

Negative biases may arise from at least two sources Particulate nitrates may react with cocollected acidic aerosols or gases to release HNO_3 from the particulate catch, leading to

one type of negative bias In the laboratory, the separate introduction of H_2SO_4 aerosols and gaseous HCl each resulted in appreciable losses and downstream recovery as nitrate of preloaded NH_4NO_3 from Ghia Zefluor filters (Appel and Tokiwa, 1981) Harker et al (1977) reported that nitrates collected during chamber experiments on Gelman Spectrograde filters were displaced by sulfate-containing, and presumably acidic, aerosols according to a metathetical reaction The introduction of H_2SO_4 aerosols to ambient particles preloaded on acid-treated Pallflex 2500 QAO filters resulted in appreciable PN losses (Forrest et al , 1980) Pierson et al (1980) reported similar observations for PN on both glass and quartz filters Negative correlations have been reported between the fraction of PN measured on acid gas-denuded Teflon™ filters and both NH_3-denuded measurements of strong acid on Teflon™ filters (Appel and Tokiwa, 1981) and measurements of strong acid on acid-treated Pallflex 2500 QAO filters (Forrest et al , 1982)

A second source of a negative bias with filtration for the collection of PN is the volatilization of NH_4NO_3 Nominal 40 to 50% losses of nitrate due to volatilization have been reported where laboratory air free of HNO_3 and NH_3 was drawn through Ghia Zefluor filters preloaded with NH_4NO_3 Ambient air drawn through acid-treated Pallflex 2500 QAO filters preloaded with NH_4NO_3 has shown nitrate volatilization losses ranging between 0 and 72% (Forrest et al , 1980)

Artifact nitrate formation depends to a large extent on the composition of the filter material (e g , glass versus Teflon™) Artifact nitrate formation also increases with relative humidity and decreases with temperature (Appel et al , 1979, Forrest et al , 1980)
To insure efficient particle collection and minimize artifact nitrate formation, Teflon™ membrane or selected quartz fiber filters are preferred over glass, Teflon™-coated glass, cellulose, cellulose acetate, or polycarbonate filters Quartz fiber filters permit sampling at high flow rates with modest pressure drops, however, they are fragile, require care in handling (Rehme et al , 1984), are subject to some positive bias from artifact nitrate formation (Appel et al , 1984), and may require pretreatment to insure low blank levels (Leahy et al , 1980) Teflon™ membrane filters are the most nearly inert, but in contrast, are subject to clogging with increased mass loadings (Rehme et al , 1984)

6.10.2 Denuders/Filtration

Many of the previously mentioned biases may be eliminated by deploying a combination of denuders and filters (Appel et al , 1981) For additional information on denuders, see Section 6 7 2 Biases involving interaction of HNO_3 with the filter or collected sample have been circumvented to some degree through the use of denuders During sampling, gaseous HNO_3 diffuses to the surface of the denuder and is collected by reaction with the denuder surface, whereas particles pass through the device uncollected An inert filter material (e g., Teflon™ membrane or quartz fiber) is then used to collect the particulate matter Because the inert particulate filter is still subject to the negative biases of liberated HNO_3 and volatilized NH_4NO_3, the resulting NO_3^- must be collected on a backup filter. Nylon, Na_2CO_3-coated, NaCl-coated, or NaF-coated filters may be used as backup filters. Although pressure drop and capacity considerations favor coated filters for high flow rate applications, due to the presence of the chloride or fluoride ions, this collection method may not be compatible with an IC finish for determining NO_3^-

As noted in Section 6 7 1, a minimum sensitivity of 0 02 μg/m may be calculated under the assumptions of 0.05 μg/mL analytical detection limit, 10 mL extraction volume, negligible blank, quantitative collection and extraction, and a sampled air volume of 24 m^3 (i.e., 1 m^3/h for 1 day) Thus, for a combination of a denuder and two filters, the PN sensitivity should be approximately 0 04 μg/m Median precision estimates of 4 to 16% RSD have been reported for 22-h duration samples of fine PN (Vossler et al , 1988, Sickles, 1987), and a median precision of 4% RSD was reported for 12 1-week duration samples of fine PN (Sickles, 1987)

6.10.3 Impactors

When size-resolved samples or size distribution information are needed, impactors may be preferred over filters for sampling ambient aerosols The dichotomous sampler (Wolff, 1984, Wall et al , 1988) has employed a virtual impactor to provide individual aerosol samples of ambient aerosol above and below a given size (e g , 2 5 μm) Selected high-volume samples have employed the cascade impactor to collect ambient aerosols below a given size (e g , 10 μm) Both cyclones and impactors have been used as the initial element in AD samplers to exclude particles nominally larger than 2 5 μm from air samples

containing PN (Sickles et al , 1988, Vossler et al , 1988, Koutrakis et al , 1988) Cascade impactors have been used to obtain size distribution information on ambient PN (Kadowaki, 1977, Yoshizumi, 1986, Wall et al , 1988, Sloane et al., 1991)

Impactors may have as many as 10 stages, providing for the collection and size discrimination of aerosols with aerodynamic diameters between 0 03 and 20 μm Backup filters are usually used following the final impactor stage to collect the remaining particles Sampling artifacts using impactors include particle bounce, HNO_3 sorption, volatilization of NH_4NO_3, and changes in size distribution from RH changes in the lower stages (Wall et al , 1988, Sloane et al., 1991) In a recent study using the Berner cascade impactor, the presence of grease on impactor stages had no apparent effect, comparisons of size distributions made with and without an HNO_3 denuder preceding the impactor revealed no HNO_3 sorption effects, and PN losses from NH_4NO_3 volatilization were 8% in comparison with results from a dichotomous sampler (Wall et al., 1988) An evaluation of sampling artifacts occurring for aerosol samples collected using impactors versus filters has indicated that volatilization losses depend on several parameters, including the surface area of the aerosol deposit (Zhang, 1991) The relatively small volatilization loss with an impactor (e g , 8%) observed by Wall et al (1988), in comparison to the 50% loss with filters noted in Section 6 10 1 (Forrest et al , 1980), may be reflecting differences in the surface areas of the aerosol deposited in the two types of samples

6.10.4 Analysis

After the collection of PN by the techniques discussed in the previous sections, samples are analyzed directly or indirectly for nitrate Several methods have been used, including IC (Mulik et al , 1976), colorimetry (Mullin and Riley, 1955), derivatization/GC (Tesch et al , 1976), HPLC (Kamiura and Tanaka, 1979), voltametry (Bodini and Sawyer, 1977), ion specific electrode (Driscoll et al , 1972), FTIR (Bogard et al., 1982), and CLM (Yoshizumi et al , 1985) Ion chromatography and colorimetry are the methods most commonly used as analytical finishes for the determination of PN

Many of the methods for determining PN require the extraction of nitrates prior to analysis Extraction of nitrate spiked onto nylon filters showed quantitative recovery using IC eluent solution or basic (i e , 0 003N NaOH) solution, but not using water (Hering et al ,

1988). Similar tests with spiked Teflon™ membrane filters showed essentially quantitative recovery in each extraction medium Other tests have shown good NO_3^- recoveries from spiked and ambient nitrates on cellulose, glass fiber, and Teflon™ filters using IC eluent and ultrasonication, boiling deionized water, and sequential extraction in warm IC eluent and deionized water (Jenke, 1983)

In recent years, IC has become a method of choice for the determination of many anions and cations in solution. Ion chromatography uses conductimetric detection and a combination of resin columns to separate the ions of interest and strip or suppress the eluent from the background (Small et al , 1975, Mulik et al , 1976) The bromide and phosphate interferences noted by Mulik et al (1976) generally do not present problems with environmental samples of PN In some cases where filter or denuder extracts are analyzed by IC, to permit good resolution of various peaks, care must be taken to prevent excessive concentrations of chloride or H_2O_2 must be added to oxidize sulfite to sulfate One recent study reported a precision estimate of 1% for replicate NO_3^- measurements in extracts of ambient samples where the concentration was above 0 15 μg/mL (Sickles et al , 1988a) Detection limits for NO_3^- of 0.025 to 0 1 μg/mL have been reported using IC with a 0 5 mL sample loop (Anlauf et al , 1988, Mulik et al , 1976) As noted in Section 6 7 1, a 0.05 μg/mL analytical detection limit for NO_3^- corresponds to an ambient concentration of 0.02 μg/m on a single filter sampling at 1 m^3/h for 1 day Although nonsuppressed IC has poorer detection limits than the previously described suppressed approach, successful application to the analysis of nitrates in ambient aerosols has also been reported for nonsuppressed IC (Willison and Clark, 1984)

Various colorimetric methods for NO_3^- have been used In one widely automated method, NO_3^- in the extract is reduced to NO_2^-, which is diazotized and determined at 550 nm using the Griess-Saltzman Method (see Section 6 3 5) (Saltzman, 1954) The reduction may be accomplished using a copper-cadmium (Cu-Cd) reductor column (Technicon, 1972) or using hydrazine sulfate with copper as a catalyst under slightly basic conditions (Mullin and Riley, 1955; Kamphake et al , 1967) The detection limits of 0.001 to 0.006 μg/mL claimed with these methods are somewhat more sensitive than those previously cited for the IC method A comparison of the performance of IC with this

colorimetric method for PN collected on Fluoropore filters showed excellent agreement (Fung et al , 1979)

Another colorimetric technique, the Brucine Method, involves the reaction of NO_3^- with brucine under acidic conditions (Kothny et al , 1972) The color is measured at 410 nm, and a detection limit of 0 4 μg/mL has been reported Other colorimetric methods involve the nitration of 2,4-xylenol in the presence of H_2SO_4, followed by steam distillation and absorbance measurement at 435 nm (Saltzman et al , 1972), or the nitration of toluene in the presence of H_2SO_4, followed by extraction into toluene and absorbance measurement of the nitrotoluene-toluene complex at 284 nm (Bhatty and Townshend, 1971) The sensitivity of both methods is marginal (i e , 1 μg/mL), and they are subject to interferences (Saltzman et al , 1972, Appel et al , 1977, Norwitz and Keliher, 1978, Kamiura and Tanaka, 1979, Bhatty and Townshend, 1971)

Using reactions similar to those described above, Tesch et al (1976) have reacted NO_3^- with benzene or other aromatic compounds in the presence of H_2SO_4 and measured the resulting nitroaromatic compound using GC-ECD A sensitivity of 0 1 μg/mL and applicability to determining NO_3^- in saliva, blood, drinking water, and airborne particles were claimed The above method has been modified by Tanner et al (1979) using electron capture-sensitive fluoroaromatic derivatizing agents and a more effective catalyst (i e , trifluoromethanesulfonic acid) With a sensitivity of 0 01 μg/mL, this method has been applied to microliter-sized samples and the analysis of PN

High-performance liquid chromatography coupled with UV detection at 210 nm has been used to measure NO_3^- in the aqueous extracts of PN from glass fiber filters (Kamiura and Tanaka, 1979) No interferences were reported, and a detection limit of 0 1 μg/mL was claimed

A voltametric technique for the measurement of NO_3^- in solution has been reported by Bodini and Sawyer (1977) The technique is based on the reduction of NO_3^- by a Cu-Cd catalyst that is formed on the surface of a pyrolytic graphite electrode The detection limit is 0 06 μg/mL, but NO_2^- is a direct interferent Favorable comparison was reported between the results of this method and those of the Technicon (1972) colorimetric method for determining NO_3^- in extracts of PN

Ion specific electrodes have been used to measure NO_3^- in extracts of PN with a detection limit of 1 μg/mL (Simeonov and Puxbaum, 1977) Ion specific electrodes suffer from poor sensitivity, potential drifts caused by variable agitation speed, frequent need for restandardization, and interferences by other ions (Driscoll et al , 1972) Spicer et al (1978a) evaluated a NO gas-sensing electrode for the indirect measurement of NO_3^- in solution Because the electrode responds to NO_2^- in solution, the approach was to measure NO_2^- in solution before and after reducing the NO_3^- to NO_2^- and attribute the difference to NO_3^-. Although the gas-sensing electrode was both sensitive (i e , 0 1 μg/mL) and specific for NO_2^-, difficulties in the reduction step prevented further development

A dry technique using FTIR for measuring NO_3^- incorporated in a potassium bromide matrix from samples of ambient PN has been reported (Bogard et al , 1982) Absorbance bands for NO_3^- occur at 2,430, 1,384, and 840 cm^{-1} Using the 1,384 cm^{-1} band, a detection limit of 0 1 μg NO_3^- per sample was reported, although the nearby ammonium ion band under same circumstances may not permit distinct resolution of NO_3^- Techniques have been developed recently that permit FTIR detection of nitrates and other species in samples of ambient aerosols collected by filtration on thin Teflon™ membrane filters using direct transmission or by impaction using attenuated total internal reflection (Johnson and Kumar, 1987) This method is currently in the research prototype stage of its development

The decomposition of NO_3^- followed by the CLM detection of the resulting NO_x (see Sections 6.2.1 and 6.3 1) has been used to determine NO_3^- in PN samples Thermal decomposition can be applied to NO_3^- either on filters or in liquid extracts (Spicer et al , 1985). With this technique, NO_3^- is decomposed by rapid heating to 425 °C in an N_2 atmosphere, and the resulting NO_x (i e , NO and NO_2) is measured (i e , integrated) using a conventional CLM analyzer Particulate nitrite is a direct interferent A detection limit of 0.7 μg/mL is claimed Comparison of CLM and IC analyses of spiked and ambient samples showed good agreement, although the IC was more precise, especially at low concentration levels Yoshizumi et al (1985) have modified a method developed by Cox (1980) to reduce NO_3^- and NO_2^- in solution and measure the evolving NO using a commercially supplied CLM instrument The method of Yoshizumi et al (1985) uses a flow system and does not distinguish NO_2^- from NO_3^- (i e , NO_2^- is a direct interferent), but has a NO_3^- detection limit of 0.001 μg/mL The method of Cox (1980), although using a batch

approach, does distinguish NO_2^- from NO_3^- and has respective detection limits of 0 00005 and 0 05 μg/mL

It has been suggested that volatile and nonvolatile nitrates may be distinguished by taking advantage of their different temperatures of volatilization (Yoshizumi and Hoshi, 1985) Samples of atmospheric particles collected by filtration or impaction are heated in a furnace to the optimum volatilization temperature of NH_4NO_3 (i e , 160 °C) The volatilized nitrate is then collected in water for subsequent determination (e g , by IC) A similar principle has been used in thermal denuders (Klockow et al , 1989) In this case, HNO_3 is collected at ambient temperature on a $MgSO_4$-coated AD, and NH_4NO_3 is collected at 150 °C on a similar downstream denuder After sampling, denuders are heated in turn to 700 °C to liberate NO_x for determination by a CLM NO_x analyzer Sturges and Harrison (1988) have reported several potential interferences with the volatilization approach Nitric acid from volatilized NH_4NO_3 in the presence of NaCl, for example, will cause displacement of the chloride as HCl and formation of nonvolatile $NaNO_3$ Differences in the thermal stabilities of ammonium sulfate/nitrate double salts were also demonstrated These observations cast doubt on the feasibility of thermal speciation of PN

6.11 NITROUS OXIDE

Ambient N_2O levels have been measured by several methods These methods include infrared spectroscopy (both absorption and emissions spectra), mass spectrometry, manometry, and gas chromatography coupled with thermal conductivity, flame ionization, ultrasonic phase shift, helium ionization, and electron capture detectors (Pierotti and Rasmussen, 1977) The most commonly used method employs GC-ECD with a detection limit of 20 ppb (Thijsse, 1978) and a precision of $\pm 3\%$ at the background level of 330 ppb (Cicerone et al , 1978) Cassidy and Reid (1982) also report an expected MDL of 20 ppb for N_2O using TDLAS near 1,150 cm^{-1} (see Section 6 2 3 for more on TDLAS) As was described in Section 6 2 3, a laboratory prototype method, TTFMS, has been developed with a projected MDL for N_2O of 3 ppt (Hansen, 1989)

Calibration can be performed using commercially supplied cylinders of compressed gas (Thijsse, 1978), dilution of pure N_2O, N_2O permeation tubes (Cicerone et al , 1978), or

gravimetric preparation of calibration mixtures (Komhyr et al 1988) Standard reference material mixtures of N_2O and CO_2 in air are also available at nominal N_2O concentrations of 300 and 330 ppb (National Bureau of Standards, 1988)

6.12 SUMMARY

Since the publication in 1971 of the original version of *Air Quality Criteria for Nitrogen Oxides*, changes have occurred in the technology associated with the sampling and analysis for ambient NO_x and related species During the 1970s, roughly the period between publication of the original Criteria Document and its first update and revision, several events occurred that focused on the determination of NO_2 in ambient air In 1973, the original Reference Method was withdrawn because of unresolvable technical difficulties Major methods development efforts over the next 3 to 4 years yielded both automated and manual methods that were suitable for the determination of NO_2 in ambient air As a result, EPA designated a new Reference Method and Equivalent Methods for NO_2 The Reference Method specifies a measurement principle and calibration procedures, namely gas-phase CLM (GP-CLM) with calibration using either GPT of NO with O_3 or an NO_2 permeation device. The Sodium Arsenite Method in both the manual and continuous forms and the TGS Method were also designated as Equivalent Methods Subsequently, commercial GP-CLM instruments were designated as Reference Methods The sensitivity of these devices was in the low parts-per-billion range, and, although the GP-CLM instruments were recognized as being susceptible to interferences by other nitroxy species, it was believed that the atmospheric concentrations of these compounds were generally low relative to NO_2

In the 1980s, additional developments occurred Information from air quality monitoring networks is now readily available and has shown the GP-CLM instruments to have nominal precision and accuracy of ± 10 to 15% and 20%, respectively, and to have replaced manual methods to a large extent in network applications Heightened interest in the research community on the speciation of atmospheric trace gases and specifically nitrogen-containing species has prompted a new wave of methods development Although the basic design and performance of the commercial instruments have remained essentially unchanged, researchers have improved GP-CLM measurement technology and refined other

instrumental methods to permit the determination of NO, NO_2, and NO_y in the low parts-per-trillion range Although GP-CLM NO detectors coupled with catalytic NO_2-to-NO converters are still not specific for NO_2, they have proven useful for measuring NO_y, and GP-CLM NO detectors coupled with photolytic NO_2-to-NO converters have shown improved specificity for NO_2

A continuous liquid phase CLM device for sensitively detecting NO_2 has been developed and may be suitable to measure NO_2 if interference problems can be overcome Passive samplers for NO_2 have been used primarily for workplace and indoor applications, but hold promise for ambient measurements as well Gas chromatography with electron capture detection is useful in the determination of PAN, other organic nitrates, and N_2O.

Laser-induced fluorescence has been introduced to detect NO, NO_2, and HONO with high sensitivity and specificity Tunable-diode laser spectroscopy has been used to detect NO, NO_2, and HNO_3 Long-path spectroscopy has also been used to detect NO, NO_2, HONO, and NO_3 Two-tone frequency modulated spectroscopy holds promise for the sensitive measurement of NO, NO_2, PAN, HNO_3, and N_2O These spectroscopic methods are research tools and are not yet easily or economically suited for routine monitoring

Interest in acidification of the environment has resulted in the development of methods for HONO and HNO_3 Integrative methods using denuders have been introduced to permit sensitive determination of these and other species In recent years, the potential for artifacts in using filters for sampling particulate matter and specifically particulate nitrate has been recognized This has given rise to careful characterization of filter media for potential artifacts and the use of combinations of denuders and filters to permit more specific determination of nitrogen-containing gases and particulate nitrates in ambient air.

REFERENCES

Adams, K M , Japar, S M , Pierson, W R (1986) Development of a MnO_2-coated, cylindrical denuder for removing NO_2 from atmospheric samples Atmos Environ 20 1211-1215

Alden, M , Edner, H , Svanberg, S (1982) Laser monitoring of atmospheric NO using ultraviolet differential-absorption techniques Opt Lett 7 543-545

Anlauf, K G ; Fellin, P , Wiebe, H A , Schiff, H I , Mackay, G I , Braman, R S , Gilbert, R (1985) A comparison of three methods for measurement of atmospheric nitric acid and aerosol nitrate and ammonium Atmos Environ 19 325-333

Anlauf, K. G., Wiebe, H A , Fellin, P (1986) Characterization of several integrative sampling methods for nitric acid, sulphur dioxide and atmospheric particles J Air Pollut Control Assoc 36 715-723

Anlauf, K. G , MacTavish, D C , Wiebe, H A , Schiff, H I , Mackay, G I (1988) Measurement of atmospheric nitric acid by the filter method and comparisons with the tuneable diode laser and other methods Atmos Environ 22 1579-1586

Appel, B. (1973) A new and more sensitive procedure for analysis of peroxybenzoyl nitrate J Air Pollut Control Assoc. 23 1042-1044

Appel, B R , Tokiwa, Y (1981) Atmospheric particulate nitrate sampling errors due to reactions with particulate and gaseous strong acids Atmos Environ 15 1087-1089

Appel, B R ; Hoffer, E M , Kothny, E L , Wall, S M (1977) Interference in 2,4 xylenol procedure for nitrate determination in atmospheric aerosols Environ Sci Technol 11 189-190

Appel, B R , Wall, S M , Tokiwa, Y , Haik, M (1979) Interference effects in sampling particulate nitrate in ambient air Atmos Environ 13 319-325

Appel, B R., Wall, S M , Tokiwa, Y , Haik, M (1980) Simultaneous nitric acid, particulate nitrate and acidity measurements in ambient air Atmos Environ 14 549-554

Appel, B R.; Tokiwa, Y , Haik, M (1981) Sampling of nitrates in ambient air Atmos Environ 15 283-289

Appel, B R ; Tokiwa, Y , Haik, M , Kothny, E L (1984) Artifact particulate sulfate and nitrate formation on filter media Atmos Environ 18 409-416

Appel, B R , Povard, V , Kothny, E L (1988) Loss of nitric acid within inlet devices intended to exclude coarse particles during atmospheric sampling Atmos Environ 22 2535-2540

Appel, B. R., Winer, A M , Tokiwa, Y , Biermann, H W (1990) Comparison of atmospheric nitrous acid measurements by annular denuder and differential optical absorption systems Atmos Environ Part A 24: 611-616

Atkinson, R , Winer, A M , Pitts, J N , Jr (1986) Estimation of night-time N_2O_5 concentrations from ambient NO_2 and NO_3 radical concentrations and the role of N_2O_5 in night-time chemistry Atmos Environ 20 331-339

Atlas, E (1988) Evidence for ≥C3 alkyl nitrates in rural and remote atmospheres Nature (London) 331 426-428.

Baveja, A K , Chaube, A , Gupta, V K (1984) Extractive spectrophotometric method for the determination of atmospheric nitrogen dioxide Atmos Environ 18 989-993

Benner, C L , Eatough, D J , Eatough, N L , Bhardwaja, P (1987) Evaluation of an annular denuder method for the collection of atmospheric nitrogenous species in the southwest desert Presented at 80th annual meeting of the Air Pollution Control Association, June, New York, NY Pittsburgh, PA Air Pollution Control Association, paper no 87-63 6

Benner, C L , Eatough, N L , Lewis, E A , Eatough, D J , Huang, A A , Ellis, E C (1988) Diffusion coefficients for ambient nitric and nitrous acids from denuder experiments in the 1985 nitrogen species methods comparison study Atmos Environ 22 1669-1672

Bennett, B I (1979) Stability evaluation of ambient concentrations of sulfur dioxide, nitric oxide, and nitrogen dioxide contained in compressed gas cylinders Research Triangle Park, NC U S Environmental Protection Agency, Environmental Monitoring and Support Laboratory, EPA report no EPA 600/4-79-006 Available from NTIS, Springfield, VA, PB-292749

Benoit, F M (1983) Detection of nitrogen and sulfur dioxides in the atmosphere by atmospheric pressure ionization mass spectrometry Anal Chem 55 2097-2099

Bhatty, M K , Townshend, A (1971) Spectrophotometric determination of small amounts of nitrate and nitrite by conversion to nitrotoluene and extraction into toluene Anal Chim Acta 56 55-60

Biermann, H W , Tuazon, E C , Winer, A M , Wallington, T J , Pitts, J N , Jr (1988) Simultaneous absolute measurements of gaseous nitrogen species in urban ambient air by long pathlength infrared and ultraviolet-visible spectroscopy Atmos Environ 22 1545-1554

Bodini, M E , Sawyer, D T (1977) Voltammetric determination of nitrate ion at parts-per-billion levels Anal Chem 49 485-489

Bogard, J S , Johnson, S A , Kumar, R , Cunningham, P T (1982) Quantitative analysis of nitrate ion in ambient aerosols by Fourier-transform infrared spectroscopy Environ Sci Technol 16 136-140

Bollinger, M J , Sievers, R E , Fahey, D W , Fehsenfeld, F C (1983) Conversion of nitrogen dioxide, nitric acid, and *n*-propyl nitrate to nitric oxide by gold-catalyzed reduction with carbon monoxide Anal Chem 55 1980-1986

Bollinger, M J , Hahn, C J , Parrish, D D , Murphy, P C , Albritton, D L , Fehsenfeld, F C (1984) NO_x measurements in clean continental air and analysis of the contributing meteorology J Geophys Res [Atmos] 89 9623-9631

Bradshaw, J D , Rodgers, M O , Davis, D D (1982) Single photon laser-induced fluorescence detection of NO and SO_2 for atmospheric conditions of composition and pressure Appl Opt 21 2493-2500

Bradshaw, J D , Rodgers, M O , Sandholm, S T , KeSheng, S , Davis, D D (1985) A two-photon laser-induced fluorescence field instrument for ground-based and airborne measurements of atmospheric NO J Geophys Res [Atmos] 90 12861-12873

Braman, R S , de la Cantera, M A (1986) Sublimation sources for nitrous acid and other nitrogen compounds in air Anal Chem 58 1533-1537

Braman, R S , de la Cantera, M A , Han, Q X (1986) Sequential, selective hollow tube preconcentration and chemiluminescence analysis system for nitrogen oxide compounds in air Anal Chem 58 1537-1541

Brauer, M.; Ryan, P B , Suh, H H , Koutrakis, P , Spengler, J D , Leslie, N P , Billick, I H (1990) Measurements of nitrous acid inside two research houses Environ Sci Technol 24 1521-1527

Bubacz, D K ; Daughtrey, E H , Pleil, J D , Kronmiller, K G (1987) Luminox measurements of ambient NO_2 In· Proceedings of the 1987 EPA/APCA symposium on measurement of toxic and related air pollutants, May; Research Triangle Park, NC Pittsburgh, PA Air Pollution Control Association, pp 398-403, EPA report no EPA-600/9-87-010 Available from NTIS, Springfield, VA, PB88-113402 (APCA publication VIP-8)

Burkhardt, M R , Maniga, N I , Stedman, D H , Paur, R J (1988) Gas chromatographic method for measuring nitrogen dioxide and peroxyacetyl nitrate in air without compressed gas cylinders Anal Chem 60 816-819

Butcher, S S , Ruff, R E (1971) Effect of inlet residence time on analysis of atmospheric nitrogen oxides and ozone Anal Chem 43 1890-1892

Buttini, P , DiPalo, V., Possanzini, M (1987) Coupling of denuder and ion chromatographic techniques for NO_2 trace level determination in air Sci Total Environ 61 59-72

Cadoff, B C , Hodgeson, J (1983) Passive sampler for ambient levels of nitrogen dioxide Anal Chem 55 2083-2085

Carroll, M. A , McFarland, M , Ridley, B A , Albritton, D L (1985) Ground-based nitric oxide measurements at Wallops Island, Virginia J Geophys Res [Atmos] 90 12853-12860

Cassidy, D. T , Reid, J (1982) Atmospheric pressure monitoring of trace gases using tunable diode lasers Appl Opt 21 1185-1190

Cicerone, R J., Shetter, J D , Stedman, D H , Kelly, T J , Liu, S C (1978) Atmospheric N_2O measurements to determine its sources, sinks, and variations J Geophys Res C Oceans Atmos 83. 3042-3050

Code of Federal Regulations (1987a) National primary and secondary ambient air quality standards C F R 40· §50

Code of Federal Regulations (1987b) Ambient air monitoring reference and equivalent methods C F R 40 §53

Cox, R A (1974) The photolysis of gaseous nitrous acid J Photochem 3 175-188

Cox, R. D (1980) Determination of nitrate and nitrite at the parts per billion level by chemiluminescence Anal Chem 52 332-335

Cox, R A , Roffey, M J (1977) Thermal decomposition of peroxyacetylnitrate in the presence of nitric oxide Environ Sci Technol 11 900-906

Crecelius, H -J , Forwerg, W (1970) Investigations of the "Saltzman factor " Staub Reinhalt Luft 30 23-25

Darley, E F , Kettner, K A , Stephens, E R (1963) Analysis of peroxyacyl nitrates by gas chromatography with electron capture detection Anal Chem 35 589-591

Dasch, J M , Cadle, S H , Kennedy, K G , Mulawa, P A (1989) Comparison of annular denuders and filter packs for atmospheric sampling Atmos Environ 23 2775-2782

Davis, D D (1988) Atmospheric nitrogen oxides, their detection and chemistry In Third year report to Coordinating Research Council Atlanta, GA Georgia Institute of Technology, pp 1-13

Davis, D D , Bradshaw, J D , Rodgers, M O , Sandholm, S T , KeSheng, S (1987) Free tropospheric and boundary layer measurements of NO over the central and eastern North Pacific Ocean J Geophys Res [Atmos] 92 2049-2070

De Santis, F , Febo, A , Perrino, C , Possanzini, M , Liberti, A (1985) Simultaneous measurements of nitric acid, nitrous acid, hydrogen chloride and sulfur dioxide in air by means of high-efficiency annular denuders In Proceedings of the ECE workshop on advancements in air pollution monitoring and procedures, June, Freiburg, Federal Republic of Germany Bonn, Federal Republic of Germany Federal Ministry of the Interior, pp 68-75

Delany, A C , Dickerson, R R , Melchior, F L , Jr , Wartburg, A F (1982) Modification of a commercial NO_x detector for high sensitivity Rev Sci Instrum 53 1899-1902

Dickerson, R R (1984) Measurements of reactive nitrogen compounds in the free troposphere Atmos Environ 18 2585-2593

Dickerson, R R , Delany, A C , Wartburg, A F (1984) Further modification of a commercial NO_x detector for high sensitivity Rev Sci Instrum 55 1995-1998

Driscoll, J N , Berger, A W , Becker, J H , Funkhouser, J T , Valentine, J R (1972) Determination of oxides of nitrogen in combustion effluents with a nitrate ion selective electrode J Air Pollut Control Assoc 22 119-122

Drummond, J W , Volz, A , Ehhalt, D H (1985) An optimized chemiluminescence detector for tropospheric NO measurements J Atmos Chem 2 287-306

Drummond, J W , Schiff, H I , Karecki, D R , Mackay, G I (1989) Measurements of NO_2, NO_x, O_3, PAN, HNO_3, H_2O_2, and H_2CO during the Southern California air quality study Presented at 82nd annual meeting of the Air and Waste Management Association, June, Anaheim, CA Pittsburgh, PA Air and Waste Management Association

Dunwoody, C L (1986) Rapid nitrate loss from PM_{10} filters J Air Pollut Control Assoc 36 817-818

Eatough, D J , White, V F , Hansen, L D , Eatough, N L , Ellis, E C (1985) Hydration of nitric acid and its collection in the atmosphere by diffusion denuders Anal Chem 57 743-748

Eatough, N L , McGregor, S , Lewis, E A , Eatough, D J , Huang, A A , Ellis, E C (1988) Comparison of six denuder methods and a filter pack for the collection of ambient $HNO_3(g)$, $HNO_2(g)$, and $SO_2(g)$ in the 1985 NSMC study Atmos Environ 22 1601-1618

Edner, H , Fredriksson, K , Sunesson, A , Svanberg, S , Uneus, L , Wendt, W (1987) Mobile remote sensing system for atmospheric monitoring Appl Opt 26 4330 4338

Ellis, E C , Margeson, J H (1974) Evaluation of triethanolamine procedure for determination of nitrogen dioxide in ambient air Research Triangle Park, NC U S Environmental Protection Agency, Quality Assurance and Environmental Monitoring Laboratory, EPA report no EPA-650/4-74-031 Available from NTIS, Springfield, VA, PB-237348/8BE

Fahey, D W , Eubank, C S , Hubler, G , Fehsenfeld, F C (1985a) Evaluation of a catalytic reduction technique for the measurement of total reactive odd-nitrogen NO_y in the atmosphere J Atmos Chem 3 435-468

Fahey, D W , Eubank, C S , Huebler, G , Fehsenfeld, F C (1985b) A calibrated source of N_2O_5 Atmos Environ 19 1883-1890

Fahey, D W , Hubler, G , Parrish, D D , Williams, E J , Norton, R B , Ridley, B A , Singh, H B , Liu, S. C , Fehsenfeld, F C (1986) Reactive nitrogen species in the troposphere measurements of NO, NO_2, HNO_3, particulate nitrate, peroxyacetyl nitrate (PAN), O_3, and total reactive odd nitrogen (NO_y) at Niwot Ridge, Colorado J Geophys Res [Atmos] 91 9781-9793

Febo, A , De Santis, F , Perrino, C (1986) Measurement of atmospheric nitrous and nitric acid by means of annular denuders In Physico-chemical behavior of atmospheric pollutants proceedings of the fourth European symposium, September, Stresa, Italy Boston, MA D Reidel Publishing Company, pp 121-125.

Febo, A ; De Santis, F , Liberti, A , Perrino, C (1988) Nitric acid-nitrate aerosol measurements by a diffusion denuder· a performance evaluation Atmos Environ 22 2062-2064

Federal Register (1986) Part 58 - ambient air quality surveillance appendix A - quality assurance requirements for state and local air monitoring stations (SLAMS) F R (March 19) 51 9595

Fehsenfeld, F. C , Dickerson, R R , Hubler, G , Luke, W T , Nunnermacker, L J , Williams, E J , Roberts, J M , Calvert, J G , Curran, C M , Delany, A C , Eubank, C S , Fahey, D W , Fried, A , Gandrud, B. W , Langford, A O , Murphy, P C , Norton, R B , Pickering, K E , Ridley, B A (1987) A ground-based intercomparison of NO, NO_x, and NO_y measurement techniques J Geophys Res [Atmos] 92 14710-14722

Fehsenfeld, F C , Drummond, J W , Roychowdhury, U K , Galvin, P J , Williams, E J , Buhr, M P , Parrish, D D , Hubler, G , Langford, A O , Calvert, J G , Ridley, B A , Grahek, F , Heikes, B G , Kok, G L , Shetter, J D , Walega, J G , Elsworth, C M , Norton, R B , Fahey, D W , Murphy, P C , Hovermale, C , Mohnen, V A , Demerjian, K L , Mackay, G I , Schiff, H I (1990) Intercomparison of NO_2 measurement techniques J Geophys Res [Atmos] 95 3579-3597

Fellin, P ; Brown, P M , Caton, R B (1984) Development of a nitric acid sampler Downsview, ON, Canada Concord Scientific Corporation

Ferm, M (1986) A Na_2CO_3-coated denuder and filter for determination of gaseous HNO_3 and particulate NO_3^- in the atmosphere Atmos Environ 20 1193-1201

Ferm, M , Sjodin, A (1985) A sodium carbonate coated denuder for determination of nitrous acid in the atmosphere Atmos Environ 19 979-983

Fincher, C L , Tucker, A W , Birnbaum, M (1978) Laser and flash lamp fluorescence NO_2 monitors a comparison In Schlossberg, H , ed Laser spectroscopy applications and techniques, [proceedings], August, San Diego, CA Bellingham, WA Society of Photo-Optical Instrumentation Engineers, pp. 137-140 (Proceedings of the Society of Photo-Optical Instrumentation Engineers v 158)

Folsom, B A , Courtney, C W (1979) Accuracy of chemiluminescent analyzers measuring nitric oxide in stack gases J Air Pollut Control Assoc 29 1166-1169

Fontijn, A ; Volltrauer, H. N , Frenchu, W R (1980) NO_x (= NO + NO_2) monitor based on an H-atom direct chemiluminescence method Environ Sci Technol 14 324-328

Forrest, J , Tanner, R L , Spandau, D , D'Ottavio, T , Newman, L (1980) Determination of total inorganic nitrate utilizing collection of nitric acid on NaCl-impregnated filters Atmos Environ 14 137-144

Forrest, J , Spandau, D J , Tanner, R L , Newman, L (1982) Determination of atmospheric nitrate and nitric acid employing a diffusion denuder with a filter pack Atmos Environ 16 1473-1485

Fredriksson, K A , Hertz, H M (1984) Evaluation of the DIAL technique for studies on NO_2 using a mobile lidar system Appl Opt 23 1403-1411

Fuglsang, K (1986) A filter pack for determination of total ammonia, total nitrate, sulfur dioxide and sulfate in the atmosphere Miljoestyrelsen, Roskilde, Denmark Riso National Laboratory, report no MST-LUFT-A-103 Available from NTIS, Springfield, VA, DE87750099

Fung, K , Grosjean, D (1985) Peroxybenzoylnitrate measurements in smog chambers and in urban air Sci Total Environ 46 29-40

Fung, K K , Heisler, S L , Price, A , Nuesca, B V , Mueller, P K (1979) Comparison of ion chromatography and automated wet chemical methods for analysis of sulfate and nitrate in ambient particulate filter samples In Mulik, J D , Sawicki, E , eds Ion chromatographic analysis of environmental pollutants volume 2 Ann Arbor, MI Ann Arbor Science Publishers Inc , pp 203-209

Gaffney, J S , Fajer, R , Senum, G I (1984) An improved procedure for high purity gaseous peroxyacyl nitrate production use of heavy lipid solvents Atmos Environ 18 215-218

Gallagher, C C , Forsberg, C A , Pieri, R V , Faucher, G A , Calo, J M (1985) Nitric oxide and nitrogen dioxide content of whole air samples obtained at altitudes from 12 to 30 km J Geophys Res [Atmos] 90 7899-7912

Gay, B W , Jr , Noonan, R C , Bufalini, J J , Hanst, P L (1976) Photochemical synthesis of peroxyacyl nitrates in gas phase via chlorine-aldehyde reaction Environ Sci Technol 10 82-85

Girman, J R , Hodgson, A T , Robinson, B K , Traynor, G W (1984) Laboratory studies of the temperature dependence of the Palmes NO_2 passive sampler In Proceedings of the national symposium on recent advances in pollutant monitoring of ambient air and stationary sources, May, Raleigh, NC Research Triangle Park, NC U S Environmental Protection Agency, Environmental Monitoring Systems Laboratory, pp 152-166, EPA report no EPA-600/9-84-019 Available from NTIS, Springfield, VA, PB85-144053/REB

Goldan, P D , Kuster, W C , Albritton, D L , Fehsenfeld, F C , Connell, P S , Norton, R B , Huebert, B J (1983) Calibration and tests of the filter-collection method for measuring clean-air, ambient levels of nitric acid Atmos Environ 17 1355-1364

Gregory, G L , Hoell, J M , Jr , Torres, A L , Carroll, M A , Ridley, B A , Rodgers, M O , Bradshaw, J , Sandholm, S , Davis, D D (1990a) An intercomparison of airborne nitric oxide measurements a second opportunity J Geophys Res [Atmos] 95 10129-10138

Gregory, G L , Hoell, J M , Jr , Carroll, M A , Ridley, B A , Davis, D D , Bradshaw, J , Rodgers, M O , Sandholm, S T , Schiff, H I , Hastie, D R , Karecki, D R , Mackay, G I , Harris, G W , Torres, A L , Fried, A (1990b) An intercomparison of airborne nitrogen dioxide instruments J Geophys Res [Atmos] 95 10103-10127

Gregory, G L , Hoell, J M , Jr , Ridley, B A., Singh, H B , Gandrud, B , Salas, L J , Shetter, J (1990c) An intercomparison of airborne PAN measurements J Geophys Res [Atmos] 95 10077-10087

Gregory, G L , Hoell, J M , Jr , Huebert, B J , van Bramer, S E , LeBel, P J , Vay, S A , Marinaro, R M ; Schiff, H I ; Hastie, D R , Mackay, G I , Karecki, D R (1990d) An intercomparison of airborne nitric acid measurements J Geophys Res [Atmos] 95 10089-10102

Griffith, D W T., Schuster, G (1987) Atmospheric trace gas analysis using matrix isolation Fourier transform infrared spectroscopy J Atmos Chem 5 59-81

Grosjean, D ; Harrison, J (1985a) Peroxyacetyl nitrate comparison of alkaline hydrolysis and chemiluminescence methods Environ Sci Technol 19 749-752

Grosjean, D , Harrison, J (1985b) Response of chemiluminescence NO_x analyzers and ultraviolet ozone analyzers to organic air pollutants Environ Sci Technol 19 862-865

Grosjean, D., Parmar, S S (1990) Interferences from aldehydes and peroxyacetyl nitrate when sampling urban air organic acids on alkaline traps Environ Sci Technol 24 1021-1026

Grosjean, D , Fung, K , Collins, J , Harrison, J , Breitung, E (1984) Portable generator for on-site calibration of peroxyacetyl nitrate analyzers Anal Chem 56 569-573

Grosjean, D ; Parmar, S S , Williams, E L , II (1990) Southern California air quality study a search for methyl nitrate Atmos Environ Part A 24 1207-1210

Hansen, D A (1989) Measuring trace gases with FM spectroscopy EPRI J 14(4) 42-43

Harker, A B , Richards, L W , Clark, W E (1977) The effect of atmospheric SO_2 photochemistry upon observed nitrate concentrations in aerosols Atmos Environ 11 87-91

Helas, G ; Flanz, M , Warneck, P (1981) Improved NO_x monitor for measurements in tropospheric clean air regions Int J Environ Anal Chem 10 155-166

Helas, G ; Broll, A , Rumpel, K -J , Warneck, P (1987) On the origins of night-time NO at a rural measurement site Atmos Environ 21 2285-2295

Helmig, D , Mueller, J , Klein, W (1989) Improvements in analysis of atmospheric peroxyacetyl nitrate (PAN) Atmos Environ 23 2187-2192

Hering, S V.; Lawson, D R , Allegrini, I , Febo, A , Perrino, C , Possanzini, M , Sickles, J E , II, Anlauf, K G , Wiebe, A ; Appel, B R , John, W , Ondo, J , Wall, S , Braman, R S , Sutton, R , Cass, G R ; Solomon, P A , Eatough, D J , Eatough, N L , Ellis, E C , Grosjean, D , Hicks, B B , Womack, J D , Horrocks, J , Knapp, K T , Ellestad, T G , Paur, R J , Mitchell, W J , Pleasant, M , Peake, E , MacLean, A , Pierson, W R , Brachaczek, W , Schiff, H I , Mackay, G I , Spicer, C W , Stedman, D H , Winer, A M , Biermann, H W , Tuazon, E C (1988) The nitric acid shootout field comparison of measurement methods Atmos Environ 22 1519-1539

Higashi, T ; Imasaka, T , Ishibashi, N (1983) Thermal lens spectrophotometry with argon laser excitation source for nitrogen dioxide determination Anal Chem 55 1907-1910

Highsmith, V. R , Bond, A E , Howes, J E , Jr (1986) Particle and substrate losses from Teflon® and quartz filters Atmos Environ 20 1413-1417

Hoell, J. M , Jr , Gregory, G L , McDougal, D S , Carroll, M A , McFarland, M , Ridley, B A , Davis, D. D , Bradshaw, J , Rodgers, M O , Torres, A L (1985) An intercomparison of nitric oxide measurement techniques J Geophys Res [Atmos] 90 12843-12851

Hoell, J M , Jr , Gregory, G L , McDougal, D S , Torres, A L , Davis, D D , Bradshaw, J , Rodgers, M O ; Ridley, B A , Carroll, M A (1987) Airborne intercomparison of nitric oxide measurement techniques J Geophys Res [Atmos] 92 1995-2008

Holdren, M W , Rasmussen, R A (1976) Moisture anomaly in analysis of peroxyacetyl nitrate (PAN) Environ Sci Technol 10 185-187

Holdren, M W , Spicer, C W (1984) Field compatible calibration procedure for peroxyacetyl nitrate Environ Sci Technol 18 113-116

Holland, D M , McElroy, F F (1986) Analytical method comparisons by estimates of precision and lower detection limit Environ Sci Technol 20 1157-1161

Hughes, E E , Rook, H L , Deardorff, E R , Margeson, J H , Fuerst, R G (1977) Performance of a nitrogen dioxide permeation device Anal Chem 49 1823-1829

Hustvedt, C (1987) SAROAD quick look report [personal communication] Research Triangle Park, NC U S Environmental Protection Agency

Jacobs, M B , Hochheiser, S (1958) Continuous sampling and ultramicrodetermination of nitrogen dioxide in air Anal Chem 30 426-428

Jenke, D R (1983) Comparison of three methods for the extraction of selected anions from media used for the collection of airborne particulates J Air Pollut Control Assoc 33 765-767

John, W , Reischl, G (1978) Measurements of the filtration efficiencies of selected filter types Atmos Environ 12 2015-2019

Johnston, P V , McKenzie, R L (1984) Long-path absorption measurements of tropospheric NO_2 in rural New Zealand Geophys Res Lett 11 69-72

Joos, L F , Landolt, W F , Leuenberger, H (1986) Calibration of peroxyacetyl nitrate measurements with an NO_x analyzer Environ Sci Technol 20 1269-1273

Joseph, D W , Spicer, C W (1978) Chemiluminescence method for atmospheric monitoring of nitric acid and nitrogen oxides Anal Chem 50 1400-1403

Joshi, S B , Bufalini, J J (1978) Halocarbon interferences in chemiluminescent measurements of NO_x Environ Sci Technol 12 597-599

Jung, J , Kowalski, J (1986) Direct ambient nitrogen dioxide measurement by visible light absorption In Proceedings of the 1986 EPA/APCA symposium on measurement of toxic air pollutants, April, Raleigh, NC Pittsburgh, PA Air Pollution Control Association, pp 845-855, EPA report no EPA-600/9-86-013 Available from NTIS, Springfield, VA, PB87-182713 (APCA publication VIP-7)

Kadowaki, S (1977) Size distribution and chemical composition of atmospheric particulate nitrate in the Nagoya area Atmos Environ 11 671-675

Kamiura, T , Tanaka, M (1979) Determination of nitrate in suspended particulate matter by high-performance liquid chromatography with U V detection Anal Chim Acta 110 117-122

Kamphake, L J , Hannah, S A , Cohen, J M (1967) Automated analysis for nitrate by hydrazine reduction Water Res 1 205-216

Kanda, Y , Taira, M (1990) Chemiluminescent method for continuous monitoring of nitrous acid in ambient air Anal Chem 62 2084-2087

Kelly, T. J. (1986) Modifications of commercial oxides of nitrogen detectors for improved response Upton, NY U S Department of Energy, Brookhaven National Laboratory, report no BNL-38000 Available from NTIS, Springfield, VA, DE86010536

Kelly, T. J ; Stedman, D H , Kok, G L (1979) Measurements of H_2O_2 and HNO_3 in rural air Geophys Res Lett. 6 375-378

Kelly, T J , Spicer, C W , Ward, G F (1990) An assessment of the luminol chemiluminescence technique for measurement of NO_2 in ambient air Atmos Environ Part A 24 2397-2403

Klapheck, K., Winkler, P (1985) Sensitivity loss of a NO_x-chemiluminescence analyzer due to deposit formation Atmos Environ 19 1545-1548

Kley, D , McFarland, M (1980) Chemiluminescence detector for NO and NO_2 Atmos Technol 12 63-69

Klockow, D ; Niessner, R , Malejczyk, M , Kiendl, H , von Berg, B , Keuken, M P , Wayers-Ypelaan, A , Slanina, J (1989) Determination of nitric acid and ammonium nitrate by means of a computer-controlled thermodenuder system Atmos Environ 23 1131-1138

Knapp, K T , Durham, J L , Ellestad, T G (1986) Pollutant sampler for measurements of atmospheric acidic dry deposition Environ Sci Technol 20 633-637

Komhyr, W D., Dutton, E G , Thompson, T M (1988) A general gravimetric dilution technique for preparing trace calibration gases N_2O calibration gas preparation Environ Sci Technol 22 845-848

Kondo, Y., Iwata, A , Takagi, M (1983) A chemiluminescent NO_x-detector for the aircraft measurement J. Meteorol Soc Jpn 61 756-762

Kondo, Y , Matthews, W A , Iwata, A , Morita, Y , Takagi, M (1987) Aircraft measurements of oxides of nitrogen along the eastern rim of the Asian continent winter observations J Atmos Chem 5 37-58

Kosmus, W (1985) Summation method for monitoring nitrogen oxides Int J Environ Anal Chem 22 269-279.

Kothny, E L , Cook, W A , Dimitriades, B , Ferrand, E F , Nifong, G D , McDaniel, P W , Saltzman, B E , Weiss, F T (1972) Tentative method of analysis for nitrate in atmospheric particulate matter (brucine method) Health Lab Sci 9 324-326

Koutrakis, P , Wolfson, J M , Slater, J L , Brauer, M , Spengler, J D , Stevens, R K , Stone, C L (1988) Evaluation of an annular denuder/filter pack system to collect acidic aerosols and gases Environ Sci Technol 22 1463-1468

Leahy, D. F , Phillips, M F , Garber, R W , Tanner, R L (1980) Filter material for sampling of ambient aerosols Anal Chem 52 1779-1780

Lindqvist, F (1985) Determination of nitric acid in ambient air by gas chromatography/photoionization detection after collection in a denuder J Air Pollut Control Assoc 35 19-23

Lipari, F. (1984) New solid-sorbent method for ambient nitrogen dioxide monitoring Anal Chem 56 1820-1826

Lonneman, W A (1977) PAN measurement in dry and humid atmospheres Environ Sci Technol 11· 194-195

Lonneman, W A , Bufalini, J J , Seila, R L (1976) PAN and oxidant measurement in ambient atmospheres Environ Sci Technol 10 374-380

Lonneman, W A , Bufalini, J J , Namie, G R (1982) Calibration procedure for PAN based on its thermal decomposition in the presence of nitric oxide Environ Sci Technol 16 655-660

Mackay, G I , Schiff, H I (1987) Reference measurements of HNO_3 and NO_2 by tunable diode laser absorption spectroscopy In Proceedings of the 1987 EPA/APCA symposium on measurement of toxic and related air pollutants, May, Research Triangle Park, NC Pittsburgh, PA Air Pollution Control Association, pp 367-372, EPA report no EPA-600/9-87-010 Available from NTIS, Springfield, VA, PB88-113402 (APCA publication VIP-8)

MacPhee, R D , Higuchi, J E , Leh, F K V (1976) Comparison of oxidant measurement methods, ultraviolet photometry, and moisture effects In Speciality conference on ozone/oxidants-interactions with the total environment, March, Dallas, TX Pittsburgh, PA Air Pollution Control Association, pp 166-179

Maeda, Y , Aoki, K , Munemori, M (1980) Chemiluminescence method for the determination of nitrogen dioxide Anal Chem 52 307-311

Matthews, R D , Sawyer, R F , Schefer, R W (1977) Interferences in chemiluminescent measurement of NO and NO_2 emissions from combustion systems Environ Sci Technol 11 1092-1096

McClenny, W A , Galley, P C , Braman, R S , Shelley, T J (1982) Tungstic acid technique for monitoring nitric acid and ammonia in ambient air Anal Chem 54 365-369

Meyrahn, H , Helas, G , Warneck, P (1987) Gas chromatographic determination of peroxyacetyl nitrate two convenient calibration techniques J Atmos Chem 5 405-415

Michie, R M , Jr , Sokash, J A , Fritschel, B P , McElroy, F F , Thompson, V L (1983) Performance test results and comparative data for designated reference methods for nitrogen dioxide Research Triangle Park, NC U S Environmental Protection Agency, Environmental Monitoring Systems Laboratory, EPA report no EPA-600/4-83-019 Available from NTIS, Springfield, VA, PB83-200238

Miller, D P (1984) Ion chromatographic analysis of Palmes tubes for nitrite Atmos Environ 18 891-892

Miller, D P (1988) Low-level determination of nitrogen dioxide in ambient air using the Palmes Tube Atmos Environ 22 945-947

Mueller, P K , Hidy, G M (1983) The sulfate regional experiment (SURE) report of findings Palo Alto, CA Electric Power Research Institute, EPRI report no EA-1901 3v

Mulawa, P A , Cadle, S H (1985) A comparison of nitric acid and particulate nitrate measurements by the penetration and denuder difference methods Atmos Environ 19 1317-1324

Mulik, J D , Williams, D (1986) Passive sampling devices for NO_2 In Proceedings of the 1986 EPA/APCA symposium on measurement of toxic air pollutants, April, Raleigh, NC Pittsburgh, PA Air Pollution Control Association, pp 61-70, EPA report no EPA-600/9-86-013 Available from NTIS, Springfield, VA, PB87-182713 (APCA publication VIP-7)

Mulik, J D , Williams, D E (1987) Passive sampling device measurements of NO_2 in ambient air In Proceedings of the 1987 EPA/APCA symposium on measurement of toxic and related air pollutants, May, Research Triangle Park, NC Pittsburgh, PA Air Pollution Control Association, pp 387-397, EPA report no EPA-600/9-87-010 Available from NTIS, Springfield, VA, PB88-113402 (APCA publication VIP-8)

Mulik, J , Puckett, R , Williams, D , Sawicki, E (1976) Ion chromatographic analysis of sulfate and nitrate in ambient aerosols Anal Lett 9 653-663

Mullin, J. B., Riley, J. P (1955) The spectrophotometric determination of nitrate in natural waters, with particular reference to sea-water Anal Chim Acta 12 464-480

Namiesnik, J , Gorecki, T , Kozlowski, E , Torres, L , Mathieu, J (1984) Passive dosimeters - an approach to atmospheric pollutants analysis Sci Total Environ 38 225-258

National Aeronautics and Space Administration (1983) Assessment of techniques for measuring tropospheric N_xO_y· proceedings of a workshop, August 1982, Palo Alto, CA Hampton, VA Langley Research Center, NASA conference publication NASA-CP-2292 Available from NTIS, Springfield, VA, N84-13706

National Bureau of Standards (1988) NBS standard reference materials catalog 1988 89 Washington, DC U S Department of Commerce, Office of Standard Reference Materials, NBS special publication 260 Available from GPO, Washington, DC, S/N 003-003-02841-0

Nelson, G. O (1971) Controlled test atmospheres principles and techniques Ann Arbor, MI Ann Arbor Science Publishers, Inc , pp 126-134

Nicksic, S. W ; Harkins, J , Mueller, P K (1967) Some analyses for PAN and studies of its structure Atmos Environ 1. 11-18

Nieboer, H., Van Ham, J (1976) Peroxyacetyl nitrate (PAN) in relation to ozone and some meteorological parameters at Delft in The Netherlands Atmos Environ 10 115-120

Nielsen, T , Hansen, A M , Thomsen, E L (1982) A convenient method for preparation of pure standards of peroxyacetyl nitrate for atmospheric analyses Atmos Environ 16 2447-2450

Norwitz, G ; Keliher, P N (1978) Inorganic interferences in the 2,4-xylenol spectrophotometric method for nitrate and their elimination Anal Chim Acta 98 323-333

Noxon, J. F (1978) Tropospheric NO_2 J Geophys Res C Oceans Atmos 83 3051-3057

Noxon, J F (1983) NO_3 and NO_2 in the mid-Pacific troposphere J Geophys Res C Oceans Atmos 88. 11017-11021

Okita, T., Morimoto, S., Izawa, M , Konno, S (1976) Measurement of gaseous and particulate nitrates in the atmosphere Atmos Environ 10 1085-1089

Palmes, E D , Tomczyk, C (1979) Personal sampler for NO_x Am Ind Hyg Assoc J 40 588-591

Palmes, E D , Gunnison, A F , DiMattio, J , Tomczyk, C (1976) Personal sampler for nitrogen dioxide Am Ind Hyg Assoc J 37 570-577

Perrino, C , De Santis, F , Febo, A (1988) Uptake of nitrous acid and nitrogen oxides by nylon surfaces implications for nitric acid measurement Atmos Environ 22 1925-1930

Perrino, C , De Santis, F , Febo, A (1990) Criteria for the choice of a denuder sampling technique devoted to the measurement of atmospheric nitrous and nitric acids Atmos Environ Part A 24 617-626

Pierotti, D , Rasmussen, R A (1977) The atmospheric distribution of nitrous oxide J Geophys Res 82· 5823-5832

Pierson, W R , Brachaczek, W W , Korniski, T J , Truex, T J , Butler, J W (1980) Artifact formation of sulfate, nitrate, and hydrogen ion on backup filters Allegheny Mountain experiment J Air Pollut Control Assoc 30 30-34

Platt, U , Perner, D (1983) Measurements of atmospheric trace gases by long path differential UV/visible absorption spectroscopy In Killinger, D K , Mooradian, A , eds Optical and laser remote sensing New York, NY Springer-Verlag, pp 97-105 (Springer series in optical sciences v 39)

Platt, U F , Winer, A M , Biermann, H W , Atkinson, R , Pitts, J N , Jr (1984) Measurement of nitrate radical concentrations in continental air Environ Sci Technol 18 365-369

Poizat, O , Atkinson, G H (1982) Determination of nitrogen dioxide by visible photoacoustic spectroscopy Anal Chem 54 1485-1489

Possanzini, M , Febo, A , Liberti, A (1983) New design of a high-performance denuder for the sampling of atmospheric pollutants Atmos Environ 17 2605-2610

Possanzini, M , Febo, A , Cecchini, F (1984) Development of a KI annular denuder for NO_2 collection Anal Lett 17 887-896

Purdue, L J , Hauser, T R (1980) Review of U S Environmental Protection Agency NO_2 monitoring methodology requirements In Lee, S D , ed Nitrogen oxides and their effects on health Ann Arbor, MI Ann Arbor Science Publishers, Inc , pp 51-76

Rehme, K A , Smith, C F , Beard, M E , Fitz-Simons, T (1984) Investigation of filter media for use in the determination of mass concentrations of ambient particulate matter Research Triangle Park, NC U S Environmental Protection Agency, Environmental Monitoring Systems Laboratory, EPA report no EPA-600/4-84-048 Available from NTIS, Springfield, VA, PB84-199876

Rhodes, R C (1987) [Personal communication, interrogation of PARS database] Research Triangle Park, NC U S Environmental Protection Agency

Rhodes, R C , Evans, E G (1988) Precision and accuracy assessments for state and local air monitoring networks, 1986 Research Triangle Park, NC U S Environmental Protection Agency, Environmental Monitoring Systems Laboratory, EPA report no EPA-600/4-88-007 Available from NTIS, Springfield, VA, PB88-180138

Rickman, E E , Jr , Wright, R S (1986) Interference of nitrogenous compounds on chemiluminescent measurement of nitrogen dioxide Research Triangle Park, NC Research Triangle Institute, RTI report no RTI/3180/24-01F

Rickman, E E , Jr , Green, A H , Wright, R S , Sickles, J E , II (1988) Laboratory and field evaluations of extrasensitive sulfur dioxide and nitrogen dioxide analyzers for acid deposition monitoring Research Triangle Park, NC U S Environmental Protection Agency, Atmospheric Research and Exposure Assessment Laboratory, EPA report no EPA-600/3-90-034 Available from NTIS, Springfield, VA, PB90-201062

Rickman, E E , Jr , Green, A H , Wright, R S , Sickles, J E , II (1989) Laboratory and field evaluations of extrasensitive sulfur dioxide and nitrogen dioxide analyzers for acid deposition monitoring Research Triangle Park, NC Research Triangle Institute, RTI report no RTI/3999/18-04F

Ridley, B A , Howlett, L C (1974) An instrument for nitric oxide measurements in the stratosphere Rev Sci Instrum 45 742-746

Ridley, B A , Carroll, M A , Gregory, G L , Sachse, G W (1988) NO and NO_2 in the troposphere technique and measurements in regions of a folded tropopause J Geophys Res [Atmos] 93. 15813-15830

Roberts, J M (1990) The atmospheric chemistry of organic nitrates Atmos Environ Part A 24 243-287

Roberts, J M , Norton, R B , Goldan, P D , Fehsenfeld, F C (1987) Evaluation of the tungsten oxide denuder tube technique as a method for the measurement of low concentrations of nitric acid in the troposphere J Atmos Chem 5 217-238

Roberts, J. M ; Fajer, R W , Springston, S R (1989) Capillary gas chromatographic separation of alkyl nitrates and peroxycarboxylic nitric anhydrides Anal Chem 61 771-772

Rodgers, M O , Davis, D D (1989) A UV-photofragmentation/laser-induced fluorescence sensor for the atmospheric detection of HONO Environ Sci Technol 23 1106-1112

Rodgers, M O , Asai, K , Davis, D D (1980) Photofragmentation-laser induced fluorescence a new method for detecting atmospheric trace gases Appl Opt 19 3597-3605

Roscoe, H K (1982) Tentative observation of stratospheric N_2O_5 Geophys Res Lett 9 901-902

Saltzman, B E (1954) Colorimetric microdetermination of nitrogen dioxide in the atmosphere Anal Chem 26· 1949-1955

Saltzman, B E (1980) Critique of measurement techniques for ambient nitrogen oxides In Lee, S D , ed Nitrogen oxides and their effects on health Ann Arbor, MI Ann Arbor Science Publishers, Inc , pp 31-50

Saltzman, B E , Cook, W A , Dimitriades, B , Ferrand, E F , Kothny, E L , Levin, L , McDaniel, P W (1972) Tentative method of analysis for nitrate in atmospheric particulate matter (2,4-xylenol method (1)) In Methods of air sampling and analysis Washington, DC American Public Health Association, pp 322-324

Schiff, H I ; Hastie, D R , Mackay, G I , Iguchi, T , Ridley, B A (1983) Tunable diode laser systems for measuring trace gases in tropospheric air a discussion of their use and the sampling and calibration procedures for NO, NO_2, and HNO_3 Environ Sci Technol 17 352A-364A

Schiff, H. I , Mackay, G I , Castledine, C , Harris, G W , Tran, Q (1986) A sensitive direct measurement NO_2 instrument In Proceedings of the 1986 EPA/APCA symposium on measurement of toxic air pollutants, April, Raleigh, NC Pittsburgh, PA Air Pollution Control Association, pp 834-844, EPA report no EPA-600/9-86-013 Available from NTIS, Springfield, VA, PB87-182713 (APCA publication VIP-7)

Shaw, R W , Jr , Stevens, R K , Bowermaster, J , Tesch, J W , Tew, E (1982) Measurements of atmospheric nitrate and nitric acid the denuder difference experiment Atmos Environ 16 845-853

Sickles, J E , II, Hodson, L L (1989) Fate of nitrous acid on selected collection surfaces Atmos Environ 23 2321-2324

Sickles, J E., II, Michie, R M (1987) Evaluation of the performance of sulfation and nitration plates Atmos Environ 21 1385-1391.

Sickles, J E , II, Wright, R S (1979) Atmospheric chemistry of selected sulfur-containing compounds outdoor smog chamber study - phase 1 Research Triangle Park, NC U S Environmental Protection Agency, Environmental Sciences Research Laboratory, pp 45-49, EPA report no EPA-600/7-79-227 Available from NTIS, Springfield, VA, PB81-141525

Sickles, J E , II, McClenny, W A , Paur, R J (1987) Sampling and analytical methods development for dry deposition monitoring Research Triangle Park, NC U S Environmental Protection Agency, Environmental Monitoring Systems Laboratory, EPA report no EPA-600/4-87-011 Available from NTIS, Springfield, VA, PB87-233318

Sickles, J E , II, Perrino, C , Allegrini, I , Febo, A , Possanzini, M , Paur, R J (1988a) Sampling and analysis of ambient air near Los Angeles using an annular denuder system Atmos Environ 22 1619-1625

Sickles, J E , II, Hodson, L L , McClenny, W A , Paur, R J , Ellestad, T G , Mulik, J D , Anlauf, K G , Wiebe, H A , Mackay, G E , Schiff, H I , Bubacz, D K (1988b) Field comparison of methods for the measurement of contributors to acidic dry deposition Atmos Environ (submitted)

Sickles, J E , II, Hodson, L L , Rickman, E E , Jr , Saeger, M L , Hardison, D L , Turner, A R , Sokol, C K , Estes, E D , Paur, R J (1989) Comparison of the annular denuder system and the transition flow reactor for measurements of selected dry deposition species JAPCA 39 1218-1224

Sickles, J E , II, Grohse, P M , Hodson, L L , Salmons, C A , Cox, K W , Turner, A R , Estes, E D (1990) Development of a method for the sampling and analysis of sulfur dioxide and nitrogen dioxide from ambient air Anal Chem 62 338-346

Simeonov, V , Puxbaum, H (1977) A comparative study on the nitrate determination in airborne dust Mikrochim Acta 2 397-403

Singh, H B , Salas, L J (1983) Methodology for the analysis of peroxyacetyl nitrate (PAN) in the unpolluted atmosphere Atmos Environ 17 1507-1516

Singh, H B , Viezee, W (1988) Enhancement of PAN abundance in the Pacific marine air upon contact with selected surfaces Atmos Environ 22 419-422

Sloane, C S , Watson, J , Chow, J , Pritchett, L , Richards, L W (1991) Size-segregated fine particle measurements by chemical species and their impact on visibility impairment in Denver Atmos Environ Part A 25 1013-1024

Small, H , Stevens, T S , Bauman, W C (1975) Novel ion exchange chromatographic method using conductimetric detection Anal Chem 47 1801-1809

Smith, R G , Bryan, R J , Feldstein, M , Levadie, B , Miller, F A , Stephens, E R (1972) Tentative method of analysis for peroxyacetyl nitrate (PAN) in the atmosphere (gas chromatographic method) In Methods of air sampling and analysis Washington, DC American Public Health Association, pp 215-219

Smith, J P , Grosjean, D , Pitts, J N , Jr (1978) Observation of significant losses of particulate nitrate and ammonium from high volume glass fiber filter samples stored at room temperature J Air Pollut Control Assoc 28 930-933

Solomon, P A , Fall, T , Salmon, L , Lin, P , Vasquez, F , Cass, G R (1988) Acquisition of acid vapor and aerosol concentration data for use in dry deposition studies in the South Coast Air Basin volume I Pasadena, CA California Institute of Technology, Environmental Quality Laboratory, EQL report 25 to CAARB

Spicer, C W ; Schumacher, P M (1979) Particulate nitrate laboratory and field studies of major sampling interferences Atmos Environ 13 543-552

Spicer, C W , Schumacher, P M , Kouyoumjian, J A , Joseph, D W (1978a) Sampling and analytical methodology for atmospheric particulate nitrates final report Research Triangle Park, NC U S Environmental Protection Agency, Environmental Sciences Research Laboratory, EPA report no EPA-600/2-78-067 Available from NTIS, Springfield, VA, PB-281933

Spicer, C. W , Ward, G F , Gay, B W , Jr (1978b) A further evaluation of microcoulometry for atmospheric nitric acid monitoring Anal Lett A11. 85-95

Spicer, C. W , Howes, J E , Jr , Bishop, T A , Arnold, L H , Stevens, R K (1982) Nitric acid measurement methods an intercomparison Atmos Environ 16 1487-1500

Spicer, C W , Joseph, D W , Schumacher, P M (1985) Determination of nitrate in atmospheric particulate matter by thermal decomposition and chemiluminescence Anal Chem 57 2338-2341

Spicer, C. W ; Ward, G F , Kenny, D V , Leslie, N P , Billick, I H (1991) Measurement of oxidized nitrogen compounds in indoor air Presented at Measurement of toxic and related air pollutants, May, Durham, NC Pittsburgh, PA Air & Waste Management Association

Staehr, W , Lahmann, W , Weitkamp, C (1985) Range-resolved differential absorption lidar optimization of range and sensitivity Appl Opt 24 1950-1956

Stephens, E R (1969) The formation, reactions, and properties of peroxyacyl nitrates (PANs) in photochemical air pollution In. Pitts, J N , Jr , Metcalf, R L , eds Advances in environmental science and technology v 1 New York, NY Wiley-Interscience, pp 119-146

Stephens, E R., Price, M A (1973) Analysis of an important air pollutant peroxyacetyl nitrate J Chem Educ 50 351-354

Stephens, E R , Burleson, F R , Cardiff, E A (1965) The production of pure peroxyacyl nitrates J Air Pollut Control Assoc 15 87-89

Sturges, W T ; Harrison, R M (1988) Thermal speciation of atmospheric nitrate and chloride a critical evaluation Environ Sci Technol 22 1305-1311

Szonntagh, E. L (1979) Colorimetric azo dye methods for the atmospheric analysis of nitrogen dioxide, historical development Period Polytech Chem Eng 23 207-215

Tanner, R. L ; Fajer, R , Gaffney, J (1979) Determination of parts-per-billion concentrations of aqueous nitrate by derivatization gas chromatography with electron capture detection Anal Chem 51 865-870

Tanner, R L , Daum, P H , Kelly, T J (1983) New instrumentation for airborne acid rain research Int J Environ Anal Chem 13 323-335

Tanner, R L ; Kelly, T J , Dezaro, D A , Forrest, J (1989) A comparison of filter, denuder, and real-time chemiluminescence techniques for nitric acid determination in ambient air Atmos Environ 23 2213-2222

Technicon. (1972) Industrial method no 158-71W/tentative nitrate and nitrite in water and seawater Tarrytown, NY: Technicon Industrial Systems

Tesch, J W , Rehg, W R , Sievers, R E (1976) Microdetermination of nitrates and nitrites in saliva, blood, water, and suspended particulates in air by gas chromatography J Chromatogr 126 743-755

Thijsse, Th R (1978) Gas chromatographic measurement of nitrous oxide and carbon dioxide in air using electron capture detection Atmos Environ 12 2001-2003

Torres, A L (1985) Nitric oxide measurements at a nonurban eastern United States site Wallops instrument results from July 1983 GTE/CITE mission J Geophys Res [Atmos] 90 12875-12880

Tuazon, E C , Graham, R A , Winer, A M , Easton, R R , Pitts, J N , Jr , Hanst, P L (1978) A kilometer pathlength Fourier-transform infrared system for the study of trace pollutants in ambient and synthetic atmospheres Atmos Environ 12 865-875

Tuazon, E C , Winer, A M , Graham, R A , Pitts, J N , Jr (1981) Atmospheric measurements of trace pollutants long path Fourier transform infrared spectroscopy Research Triangle Park, NC U S Environmental Protection Agency, Environmental Sciences Research Laboratory, EPA report no EPA-600/3-81-026 Available from NTIS, Springfield, VA, PB81-179848

Vierkorn-Rudolph, B , Rudolph, J , Diederich, S (1985) Determination of peroxyacetylnitrate (PAN) in unpolluted areas Int J Environ Anal Chem 20 131-140

Vinjamoori, D V , Ling, C -S (1981) Personal monitoring method for nitrogen dioxide and sulfur dioxide with solid sorbent sampling and ion chromatographic determination Anal Chem 53 1689-1691

Vossler, T L , Stevens, R K , Paur, R J , Baumgardner, R E , Bell, J P (1988) Evaluation of improved inlets and annular denuder systems to measure inorganic air pollutants Atmos Environ 22 1729-1736

Walega, J G , Stedman, D H , Shetter, R E , Mackay, G I , Iguchi, T , Schiff, H I (1984) Comparison of a chemiluminescent and a tunable diode laser absorption technique for the measurement of nitrogen oxide, nitrogen dioxide, and nitric acid Environ Sci Technol 18 823-826

Wall, S M , John, W , Ondo, J L (1988) Measurement of aerosol size distributions for nitrate and major ionic species Atmos Environ 22 1649-1656

Wallace, L A , Ott, W R (1982) Personal monitors a state-of-the-art survey J Air Pollut Control Assoc 32 601-610

Watanabe, I , Stephens, E R (1978) Reexamination of moisture anomaly in analysis of peroxyacetyl nitrate Environ Sci Technol 12 222-223

Wendel, G J , Stedman, D H , Cantrell, C A , Damrauer, L (1983) Luminol-based nitrogen dioxide detector Anal Chem 55 937-940

West, P W , Reiszner, K D (1978) Personal monitor for nitrogen dioxide Research Triangle Park, NC U S Environmental Protection Agency, Environmental Sciences Research Laboratory, EPA report no EPA-600/2-78-001 Available from NTIS, Springfield, VA, PB-277437

Williams, E L , II, Grosjean, D (1990) Removal of atmospheric oxidants with annular denuders Environ Sci Technol 24 811-814

Willison, M J , Clarke, A G (1984) Analysis of atmospheric aerosols by nonsuppressed ion chromatography Anal Chem 56 1037-1039

Winer, A M ; Peters, J W , Smith, J P , Pitts, J N , Jr (1974) Response of commercial chemiluminescent NO-NO_2 analyzers to other nitrogen-containing compounds Environ Sci Technol 8 1118-1121

Winfield, T W. (1977) A method for converting NO_2 to NO by ferrous sulfate prior to chemiluminescent measurements In Proceedings of the American Chemical Society 173rd national meeting, March, New Orleans, LA Washington, DC American Chemical Society, pp 372-374

Witz, S.; Wendt, J. G (1981) Artifact sulfate and nitrate formation at two sites in the South Coast Air Basin A collaborative study between the South Coast Air Quality Management District and the California Air Resources Board Environ Sci Technol 15 79-83

Witz, S.; Eden, R W , Wadley, M W , Dunwoody, C , Papa, R , Torre, K J (1990) Rapid loss of particulate nitrate, chloride and ammonium on quartz fiber filters during storage J Air Waste Manage Assoc 40. 53-61

Woebkenberg, M L (1982) A comparison of three passive personal sampling methods foi NO_2 Am Ind Hyg Assoc J 43: 553-561

Wolff, G T. (1984) On the nature of nitrate in coarse continental aerosols Atmos Environ 18 977-981

Wright, R S , Tew, E L , Decker, C E , von Lehmden, D J , Barnard, W F (1987) Performance audits of EPA protocol gases and inspection and maintenance calibration gases JAPCA 37 384-385

Yanagisawa, Y , Nishimura, H (1982) A badge-type personal sampler for measurement of peisonal exposure to NO_2 and NO in ambient air Environ Int 8 235-242

Yoshizumi, K (1986) Regional size distributions of sulfate and nitrate in the Tokyo metropolitan area in summer Atmos Environ 20 763-766

Yoshizumi, K.; Hoshi, A (1985) Size distributions of ammonium nitrate and sodium nitrate in atmospheric aerosols Environ Sci Technol 19 258-261

Yoshizumi, K , Aoki, K , Matsuoka, T , Asakura, S (1985) Determination of nitrate by a flow system with a chemiluminescent NO_x analyzer Anal Chem 57 737-740

Zafiriou, O C , True, M B (1986) Interferences in environmental analysis of NO by NO plus O_3 detectors a rapid screening technique Environ Sci Technol 20 594-596

Zhang, X (1991) Measurements of size-resolved atmospheric aerosol chemical composition with impactors data integrity and applications [Ph D dissertation] Minneapolis, MN University of Minnesota Available from· University Microfilms International, Ann Arbor, MI, order no 9116541

7. AMBIENT AND INDOOR CONCENTRATIONS OF NITROGEN OXIDES

7.1 INTRODUCTION

The preceding chapters describe the fundamental chemistry of nitrogen oxides (NO_x), the sources (ambient and indoor), the transformations to other forms that take place during transport in the atmosphere, and the methods of measurement This chapter describes the NO_x concentrations that have been measured in natural and human environments, with the major emphasis in this chapter placed on characterizing and summarizing the extensive nitrogen dioxide (NO_2) monitoring data that have been collected under ambient and indoor conditions

In the course of their daily activities, individuals spend varying amounts of time in a variety of environments (outdoors, residential, occupational, public access buildings, transportation vehicles, etc) While in these environments, exposures to NO_2 occur that can demonstrate considerable variability in magnitude, frequency, and duration In determining or assessing the potential for adverse health risks associated with exposure to NO_2, it is necessary to consider exposures that occur across all environments This chapter reviews the available data on NO_2 concentrations in two important environments that account for the major fraction of nitrogen dioxide exposures, ambient air and the indoor residential environment Little data exist for other environments

The vast majority of data on NO_2 exists for ambient air and the residential indoor environment The ambient air is important both because of exposures that occur there and because of its impact on indoor air quality. Significant ambient concentrations of nitrogen oxides are usually confined to (1) urban areas and (2) urban and rural areas near major sources of NO_x Long-term (multiple-year) patterns and trends in NO_2 concentrations are available only from stationary continuous monitors Ambient data are reviewed here for peak annual averages, trends, and seasonal, diurnal, and distributional patterns

The indoor residential environment is important because of the considerable amount of time individuals spend there (Szalai, 1972, Ott, 1989, Robinson, 1977, Wiley et al , 1991a,b) and the existence of sources of NO_2 (combustion sources) Data on indoor nitrogen

dioxide concentrations are collected predominantly in selected settings during comparatively short-term (days or weeks) studies The indoor data are reviewed within the framework of the mass balance model under equilibrium conditions Emphasis is placed on assessing the contribution of outdoor NO_2 concentrations on indoor levels and the impact of indoor concentrations, reactive decay rates for NO_2 and indoor reaction products (HONO)

Chapter 8 considers the available data on integrated NO_2 exposures that occur across different environments and are determined either by personal monitoring or through modeling

7.2 AMBIENT AIR CONCENTRATIONS OF NITROGEN OXIDES

7.2.1 Introduction

As discussed in Chapter 6, most measurements of NO_x have been made by devices that convert NO_2 to nitric oxide (NO), which is then measured by chemiluminescence (National Research Council, 1991) Comparison of these measurements with more specific techniques suggests that all surface converters that can transform NO_2 to NO also convert other reactive NO_x species, such as peroxyacetyl nitrate (PAN), to NO, thereby causing interference In urban locations, where the local NO sources are typically large, NO and NO_2 are probably the dominant constituents of the total reactive nitrogen, which comprises NO_x, nitric acid (HNO_3), nitrate radical (NO_3), dinitrogen pentoxide, nitrous acid (HONO), PAN, and other organic nitrogen compounds. Thus, interference from PAN and other NO_x species in urban areas is believed to be relatively small, in rural and remote locations, however, interferences may be substantial (National Research Council, 1991)

Nitrogen oxide concentrations have been measured in numerous U S nonurban monitoring locations (Table 7-1) Nonurban monitoring areas are not necessarily isolated from local sources of pollution (e g , Kelly et al , 1982, Lefohn et al , 1991), many of the monitoring locations listed in Table 7-1 may be affected by anthropogenic sources (National Research Council, 1991) The NO_x concentrations usually exceed 1 ppb and exhibit short-term variability. For isolated rural sites and coastal inflow areas in the United States, the NO_x concentrations generally range from a few tenths to 1 ppb (Table 7-2) The concentrations in the atmospheric boundary layer and lower free troposphere in remote

TABLE 7-1. AVERAGE NITROGEN OXIDES CONCENTRATIONS MEASURED AT U.S. NONURBAN MONITORING LOCATIONS[a]

Location	NO (ppb)	NO_2 (ppb)	NO_x (ppb)	References
Fort McHenry, MD	ND	6[b]	ND	Research Triangle Institute (1975)
Dubois, PA	ND	10[b]	ND	
McConnelsville, OH	ND	6[b]	ND	
Wilmington, OH	ND	6[b]	ND	
Wooster, OH	ND	6[b]	ND	
Bradford, PA	2	3[b]	5[b]	Decker et al (1976)
Creston, LA	4	2[b]	6[b]	
Deridder, LA	1	3[b]	4[b]	
Montague, MA	2	3[b]	5[b]	Martinez and Singh (1979)
Scranton, PA	3	11[b]	14[b]	
Indian River, DE	3	5[b]	8[b]	
Research Triangle Park, NC	10	13[b]	23[b]	
Lewisburg, WV	1	5[b]	6[b]	
Duncan Falls, OH	1	8[b]	9[b]	
Fort Wayne, IN	3	7[b]	10[b]	
Rockport, IN	3	7[b]	10[b]	
Giles County, TN	3	10[b]	13[b]	
Jetmore, KS	1	4[b]	5[b]	
Lamoure County, ND	2 4	1 7[b]	4 1[b]	Pratt et al (1983)
	4 8	1 5[b]	6 3[b]	
	3 3	2 8[b]	6 1[b]	
	2 7	2 1[b]	4 8[b]	
Wright County, MN	3 2	5 4[b]	8 6[b]	
	3 0	6 7[b]	9 7[b]	
	3 5	5 8[b]	9 3[b]	
	2 9	4 7[b]	7 6[b]	
Traverse County, MN	3 6	3 7[b]	7 3[b]	
	4 8	3 6[b]	8 4[b]	
	4 0	2 9[b]	6 9[b]	
	2 0	2 2[b]	4 2[b]	
Scotia, PA			3 0[b]	Parrish et al (1986)
Scotia, PA			3 1[b]	Parrish et al (1988)

[a]NO = Nitric oxide
NO_2 = Nitrogen dioxide
[b]Upper limit for NO_2 and NO_x
NO_x = Nitrogen oxides
ND = No data

Source National Research Council (1991)

TABLE 7-2. AVERAGE MIXING RATIOS MEASURED AT ISOLATED U.S. RURAL SITES AND COASTAL INFLOW SITES[a]

Location	NO (ppb)	NO_2 (ppb)	NO_x (ppb)	References
Niwot Ridge, CO			0-2[b]	Kelly et al (1980)
Pierre, SD[c]		1 2[b]		Kelly et al (1982)
Schaeffer Observatory, Whiteface Mountain, NY	≤0 2		1 1[b]	Kelly et al (1984)
Niwot Ridge, CO			0 80	Bollinger et al (1984)
Niwot Ridge, CO			0 56	Fehsenfeld et al (1987)
Point Arena, CA			0 37	Parrish et al (1985)

[a]NO = Nitric oxide
NO_2 = Nitrogen dioxide
NO_x = Nitrogen oxides
[b]Upper limit for NO_2 and NO_x
[c]Measurement site located 40 km WNW of Pierre

Source National Research Council (1991)

maritime locations are in the range 0 02 to 0 04 ppb, whereas concentrations of NO_x in remote tropical forests have been reported to be in the range from 0 02 to 0 08 ppb (National Research Council, 1991) The higher concentrations experienced in the remote tropical forests as compared with those observed in remote marine locations may be due to biogenic NO_x emissions from the soil (Kaplan et al , 1988, Torres and Buchan, 1988)

Elevated concentrations of NO_x occur in or near urban areas because of the dominant role of anthropogenic emissions in the budget of atmospheric NO_x and the fact that the sources of these emissions tend to be located in or near these areas (National Research Council, 1991) Concentrations of NO_x decline rapidly as pollution plumes travel away from the urban core (Kelly et al , 1986)

7.2.2 Ambient Air Concentrations of Nitric Acid and Nitrate Aerosol

Photochemically initiated reactions oxidize NO_x to HNO_3 in the atmosphere (Spicer, 1977). In addition, nitrate ion (NO_3^-) aerosols are formed as a result of reaction products of

HNO_3 Nitric acid is a major contributor to airborne strong acidity, the measurement of which is intimately related to the accurate determination of particulate nitrate, a contributor to visibility reduction. Aerosol NO_3^- is formed by the reaction of HNO_3 with alkaline aerosols (Wolff, 1984) and ammonia (NH_3) The average concentrations of HNO_3 and NO_3^- are generally in the range 0 1 to 20 ppb and 0 1 to 10 ppb, respectively (Allegrini and De Santis, 1989) The values measured at rural and urban sites, respectively, are shown in Tables 7-3 and 7-4 Because there are conflicting reports on the ability of filters to accurately separate HNO_3 from NO_3^- aerosol (Lindberg et al , 1990), in some cases, it may be more appropriate to focus on the total NO_3 (HNO_3 + NO_3^-) than on the individual components

TABLE 7-3. AVERAGE CONCENTRATIONS OF NITRIC ACID AND NITRATE IONS MEASURED AT RURAL SITES[a]

Location	HNO_3	NO_3^-	References
Bermuda	0 066 ppb	0 15 $\mu g/m^3$[b]	Wolff et al (1986a)
Berkshire Mtns , MA	—	0 10 $\mu g/m^3$[b]	Wolff and Korsog (1989)
Lewes, DE	0 52 ppb	—	Wolff et al (1986b)
Near Pierre, SD[c]	—	<0 10 $\mu g/m^3$	Kelly et al (1982)
Oak Ridge, TN	3 0 $\mu g/m^3$	0 19 $\mu g/m^3$	Lindberg et al (1990)
Smoky Mountains, NC	0 33 ppb	0 31 $\mu g/m^3$	Cadle and Mulawa (1988)
Luray, VA	0 36 ppb	0 44 $\mu g/m^3$	Cadle et al (1982)
Whiteface Mtn , NY	0 20 ppb	0 25 $\mu g/m^3$	Kelly et al (1984)
Coweeta, NC	1 8 $\mu g/m^3$	—	Hanson et al (1992)
Thompson Forest, WA	0 9 $\mu g/m^3$	—	Hanson et al (1992)
Duke Forest, NC	2 8 $\mu g/m^3$	—	Hanson et al (1992)
Huntington Forest, NY	1 8 $\mu g/m^3$	—	Hanson et al (1992)
Howland, ME	0 8 $\mu g/m^3$	—	Hanson et al (1992)
Whiteface Mtn , NY	1 2 $\mu g/m^3$	—	Hanson et al (1992)

[a]HNO_3 = Nitric acid
NO_3^- = Nitrate ion
[b]Fine particle measurement for NO_3^-
[c]Measurement site located 40 km WNW of Pierre, SD

TABLE 7-4. AVERAGE CONCENTRATIONS OF NITRIC ACID AND NITRATE IONS MEASURED AT URBAN SITES[a]

Location	HNO_3	NO_3^-	References
Claremont, CA	10 3 $\mu g/m^3$	12 4 $\mu g/m^{3b}$ 7 9 $\mu g/m^{3c}$	Wolff et al (1991)
Long Beach, CA	1.9 $\mu g/m^3$	20 2 $\mu g/m^{3b}$ 14 6 $\mu g/m^{3c}$	Wolff et al (1991)
Denver, CO		4 1 $\mu g/m^{3c}$ 0 9 $\mu g/m^{3d}$	Wolff (1984)
Warren, MI	2 69 $\mu g/m^{3e}$	3 06 $\mu g/m^{3e}$	Cadle (1985)
Warren, MI	1 24 $\mu g/m^3$	3 70 $\mu g/m^3$	Dasch et al (1989)
Warren, MI	1 14 $\mu g/m^3$	4 20 $\mu g/m^3$	Dasch and Cadle (1990)
Boston, MA	1 42 ppb[f] 0 59 ppb[g]	6 06 nmol/m^{3f} 11 76 nmol/m^{3g}	Brauer et al (1991)

[a]HNO_3 = Nitric acid
NO_3^- = Nitrate ion
[b]PM_{10} fraction
[c]Fine particle fraction
[d]Coarse particle fraction
[e]Summer seasonal ambient concentration
[f]Summer average ambient concentration
[g]Winter average ambient concentration

7.2.3 Ambient Air Concentrations of Nitric Oxide and Nitrogen Dioxide

7.2.3.1 Data Availability and Exposure Considerations

Most data on ambient concentrations of NO and NO_2 in the United States are available from a network of monitoring stations that was established to determine compliance with the National Ambient Air Quality Standard (NAAQS) for NO_2, which is 0 053 ppm or 100 $\mu g/m^3$ (annual average) Information is readily available from the data base supported by this network through the U S Environmental Protection Agency's (EPA's) computerized information system, Aerometric Information Retrieval System (AIRS) Although much of this information is closely related to compliance and enforcement, the data can also be used for determining patterns and trends and as inputs to exposure assessment (e g , Lefohn et al ,

1991) In some cases, the data can be used to augment existing epidemiological studies, where only indoor air data have been collected

The National Air Monitoring Network consists of three types of sites The National Air Monitoring Station (NAMS) sites are located in areas where the concentrations of NO_2 and subsequent potential human exposures are expected to be high Criteria for these sites have been established by regulation (Federal Register, 1979) to meet uniform standards of siting, quality assurance, equivalent analytical methodology, sampling intervals, and instrument selection to ensure consistency among the reporting agencies For NO_2, NAMS sites are located only in urban areas with populations exceeding 1 million The other two types of sites are States and Local Air Monitoring Station and Special Purpose Monitor sites, which meet the same rigid criteria for the NAMS sites but may be located in areas not necessarily directed toward high concentrations and elevated human exposure

For NO_2 and NO, the sampling interval is 1 h and the instrument method used for all stations is chemiluminescence These instruments operate continuously and produce a measurement every hour In order to produce a valid annual average, at least half the possible 8,760 hourly readings must be reported

In the following subsections, data from the AIRS network are extracted and analyzed to provide background for specific exposure issues considered in later chapters The analyses proceed from a national picture of peak annual averages in Metropolitan Statistical Areas (MSAs) through national 10- and 3-year trends to characteristic seasonal and diurnal patterns at selected stations and from a brief examination of the incidence of episodic 1-h levels and associated annual averages No attempt was made to include information on ambient air concentrations from monitoring sites other than those in the AIRS network Likewise, the major emphasis is on NO_2 information, with some discussion on NO concentrations Little information on other NO_x species is available

Hourly average concentration information (the absolute value of the highest NO_2 average concentrations, and when these concentrations occurred) is summarized for urban, rural forested, and rural agricultural areas in the United States The land use designation of "rural" does not imply that a specific location is isolated from anthropogenic influences Rather, the designation only implies the existing use of the land No attempt has been made to select isolated sites The large variation among point-source strengths (e g, electric

generating plants) makes it difficult to describe "typical" NO_2 exposures A monthly average was calculated for each hour of the day The monthly averages for each hour of the day were compared with one another to characterize the seasonal and diurnal patterns occurring at a specific site, in most cases, the increase in monthly average concentration was correlated with the occurrence of higher hourly average concentrations

7.2.3.2 Trends in Ambient Nitrogen Dioxide Concentrations

In order to be included in the 10-year trend analysis in the annual National Air Quality and Emissions Trend Report (U S Environmental Protection Agency, 1991b), a station must have reported valid data for at least 8 of the last 10 years A companion analysis of the most recent 3 years requires valid data in all 3 years Analyses in the above report cover the periods 1981 to 1990 and 1988 to 1990, respectively, 166 sites met the 10-year requirement, 211 met the 3-year requirement Of the 166 10-year sites, 42 were NAMS sites

For the period 1981 to 1990, there were indications of a downward trend for the composite annual average NO_2 concentration for both the 166 sites and the 42 NAMS sites subset (U.S. Environmental Protection Agency, 1991b) Using the full set of data, the 1990 composite NO_2 average was 8% less than the 1981 level, a statistically significant difference A similar trend was observed with the NAMS sites that, for NO_2, are located only in urban areas with populations of 1 million or greater (Figure 7-1) Using the 1980 to 1989 period, the composite annual average is strongly correlated to population size (U S Environmental Protection Agency, 1991a) When sites in MSAs with 250,000 to 500,000 population and 500,000 to 1 million people were compared to sites with more than 1 million, there was a regular pattern that persisted over the full 10 years The sites with populations over 1 million were 0 01 ppm higher than those with 250,000 to 500,000, with the mid-population sites in between, as seen in Figure 7-2

7.2.3.3 Exposure Patterns Observed for Ambient Nitrogen Dioxide and Nitric Oxide Concentrations—Urban

The NO_2 hourly average concentrations tend to be less than 0 001 ppm in remote areas, 0.001 to 0.020 ppm in rural areas, 0 02 to 0 20 ppm in moderately polluted areas, and 0 2 to 0.5 ppm in heavily polluted areas (Legge et al , 1990) Information in Tables 7-2 and 7-3

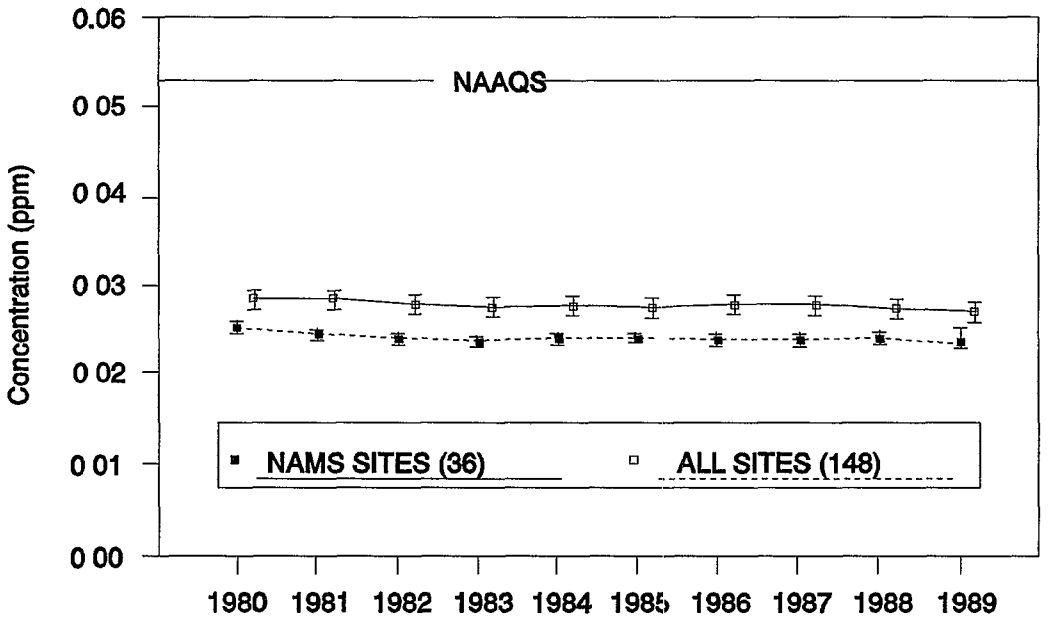


Figure 7-1. National trend in the composite annual average nitrogen dioxide concentrations at both National Air Monitoring Station sites and all sites with 95% confidence intervals, 1980 to 1989.

Source U S Environmental Protection Agency (1991a)

illustrate this observation A high-elevation site at Mt Mitchell, NC, provides an example of low NO_2 concentrations in rural areas In 1987, the maximum hourly average concentration of NO_2 was below 0 007 ppm, almost 99% of the hourly average NO_2 values were below 0 005 ppm (Lefohn, 1989) In addition, electric generating stations do provide a source of NO_2 in both rural and urban areas A summary of the hourly average NO_2 concentrations that were measured near selected electric generating stations is provided in Table 7-5 Although the hourly average NO_2 concentrations measured are a function of the emitter's source strength, as well as other considerations such as meteorological and geographic conditions, the infrequent occurrence of hourly average concentrations of NO_2 $\geq$0 10 ppm is evident In general, for the sites listed in the table, only 5% of the hourly average concentrations were $\geq$0 05 ppm For rural locations near electric generating plants, the infrequent occurrence of hourly average concentrations of NO_2 $\geq$0 05 ppm has been reported previously in the literature (Lefohn and Tingey, 1984, Lefohn et al , 1987)

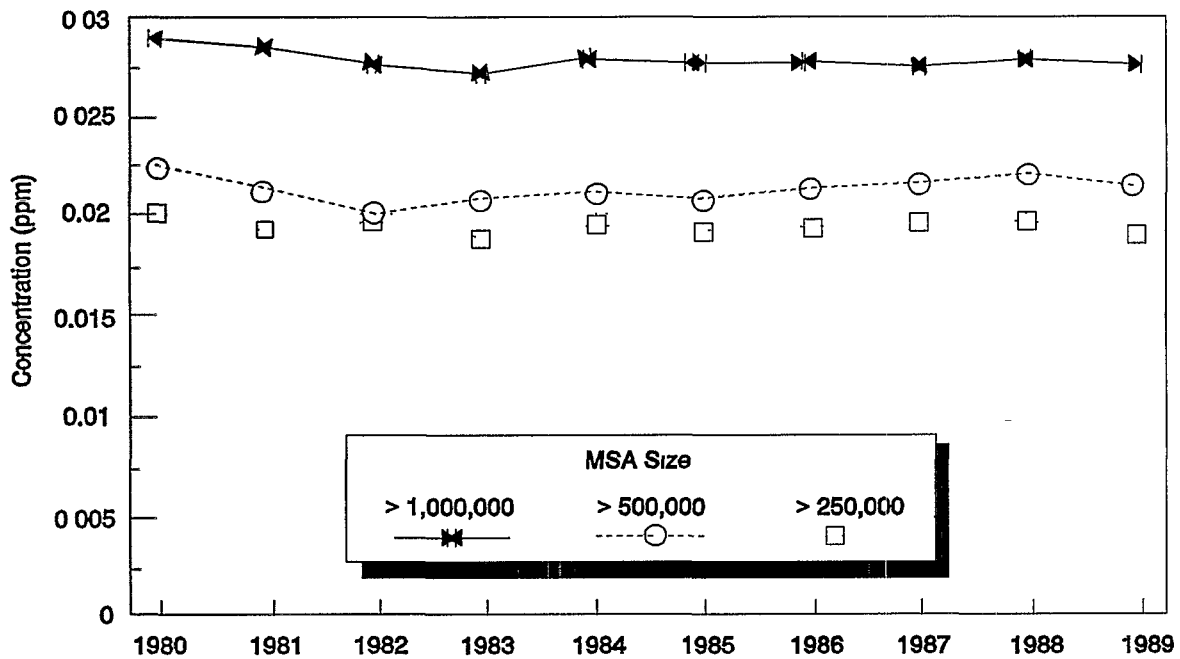


Figure 7-2. United States metropolitan area trends in the composite annual average nitrogen dioxide concentration, 1980 to 1989.

Source U S Environmental Protection Agency (1991a)

Table 7-6 lists the highest annual average for 103 MSAs reporting at least one NO_2 monitoring station with valid data in 1988, 1989, and 1990 (U S Environmental Protection Agency, 1990, 1991a, 1991b) The MSAs are listed in alphabetical order Peak annual averages in these MSAs range from 0 007 to 0 061 ppm Figure 7-3 shows that the collective mode for the peak annual average in the 1988 to 1989 period was approximately 0.02 ppm. Table 7-7 lists the highest hourly NO_2 average concentrations by MSAs reported across the United States. The highest hourly NO_2 average concentrations ranged from 0.040 to 0 540 ppm. Throughout the last 10 years, Los Angeles, CA, was the only urban area to record violations of the annual NO_2 NAAQS of 0 053 ppm (U S Environmental Protection Agency, 1991b) For the 45 sites monitoring NO_2 during the period 1980 to 1989 and experiencing at least 1 year's data capture $\geq 75\%$, nine sites exceeded the NAAQS at least 1 year during the monitoring period As expected, this area also experiences the

TABLE 7-5. CHARACTERIZATION OF HOURLY AVERAGE NITROGEN DIOXIDE CONCENTRATIONS NEAR SELECTED ELECTRICAL GENERATING PLANTS (concentrations in ppm)

				Percentiles									
Monitoring Site	Generating Plant	Year	Min	10%	30%	50%	70%	90%	95%	99%	Max	Number Obs	Annual Arith Mean
Atlanta, GA 131210048	J McDonough	1984	0 002	0 007	0 015	0 022	0 032	0 050	0 060	0 090	0 129	7,451	0 0269
		1985	0 002	0 011	0 018	0 024	0 032	0 047	0 054	0 068	0 118	8,073	0 0269
		1986	0 002	0 014	0 021	0 027	0 036	0 052	0 062	0 079	0 166	7,997	0 0306
		1987	0 003	0 012	0 018	0 025	0 034	0 049	0 058	0 073	0 125	7,163	0 0283
		1988	0 003	0 013	0 019	0 025	0 035	0 053	0 062	0 078	0 125	8,202	0 0295
		1989	0 003	0 013	0 019	0 025	0 034	0 050	0 059	0 078	0 140	7,876	0 0289
		1990	0 003	0 010	0 017	0 024	0 033	0 048	0 056	0 071	0 111	8,252	0 0270
		1991	0 003	0 009	0 016	0 022	0 031	0 045	0 054	0 072	0 127	8,110	0 0253
Indianapolis, IN 180970057	Stout	1983	0 003	0 007	0 012	0 018	0 025	0 038	0 046	0 063	0 088	8,036	0 0206
		1984	0 003	0 009	0 014	0 019	0 025	0 037	0 044	0 056	0 086	8,259	0 0212
		1985	0 003	0 009	0 013	0 018	0 024	0 037	0 045	0 058	0 087	7,681	0 0207
		1986	0 003	0 008	0 012	0 017	0 022	0 034	0 041	0 057	0 101	6,730	0 0191
		1987	0 003	0 009	0 015	0 019	0 026	0 037	0 046	0 061	0 118	6,883	0 0220
		1988	0 003	0 010	0 015	0 021	0 028	0 042	0 049	0 067	0 093	8,075	0 0238
		1989	0 003	0 009	0 015	0 019	0 025	0 036	0 044	0 060	0 088	7,772	0 0214
		1990	0 003	0 008	0 013	0 017	0 023	0 034	0 040	0 053	0 072	8,018	0 0195
Indianapolis, IN 180970073	Stout	1991	0 003	0 008	0 012	0 016	0 022	0 032	0 037	0 051	0 078	7,730	0 0183
Owensboro, KY 210590005	Elmer Smith	1979	0 002	0 002	0 006	0 010	0 014	0 025	0 031	0 047	0 080	7,396	0 0121
		1982	0 003	0 003	0 008	0 011	0 016	0 026	0 033	0 048	0 093	8,134	0 0136
		1983	0 003	0 003	0 006	0 009	0 014	0 023	0 027	0 093	0 067	8,016	0 0112
		1984	0 003	0 003	0 005	0 009	0 013	0 021	0 027	0 039	0 060	8,007	0 0106
		1985	0 003	0 003	0 007	0 010	0 014	0 022	0 027	0 039	0 068	8,079	0 0119
		1986	0 003	0 006	0 009	0 012	0 016	0 024	0 028	0 037	0 052	8,025	0 0137
		1987	0 003	0 005	0 009	0 013	0 018	0 028	0 034	0 036	0 081	7,787	0 0150
		1988	0 003	0 006	0 010	0 013	0 018	0 027	0 032	0 046	0 074	7,934	0 0153
		1989	0 003	0 005	0 009	0 012	0 016	0 024	0 030	0 044	0 090	8,234	0 0135
		1990	0 003	0 003	0 007	0 010	0 013	0 021	0 025	0 041	0 059	8,355	0 0113
		1991	0 003	0 003	0 007	0 010	0 014	0 021	0 026	0 035	0 057	8,265	0 0112

TABLE 7-5 (cont'd). CHARACTERIZATION OF HOURLY AVERAGE NITROGEN DIOXIDE CONCENTRATIONS NEAR SELECTED ELECTRICAL GENERATING PLANTS (concentrations in ppm)

				Percentiles									
Monitoring Site	Generating Plant	Year	Min	10%	30%	50%	70%	90%	95%	99%	Max	Number Obs	Annual Arith Mean
Henderson, KY	Henderson	1983	0 002	0 006	0 012	0 019	0.028	0 042	0 050	0 068	0 097	8,349	0 0220
211010013		1984	0 002	0 006	0 012	0 020	0 029	0 042	0 050	0 066	0 105	8,330	0 0225
		1985	0 002	0 002	0 012	0 020	0 029	0 044	0 052	0 068	0 103	8,230	0 0223
		1986	0 002	0 002	0 010	0 018	0 026	0 038	0 046	0 061	0 098	8,183	0 0199
		1987	0 003	0 003	0 011	0 019	0 028	0 042	0 050	0 066	0 105	8,354	0 0214
		1988	0 003	0 003	0 010	0 019	0 029	0 044	0 052	0 071	0 103	8,268	0 0219
		1989	0 003	0 003	0 010	0 017	0 026	0 043	0 051	0 070	0 102	8,259	0 0204
		1990	0 003	0 003	0 008	0 015	0 024	0 035	0 042	0 054	0 090	8,215	0 0178
		1991	0 003	0 003	0 011	0 019	0 026	0 039	0 047	0 063	0 106	7,872	0 0205
Falcon Heights, MN	High Bridge	1990	0 003	0 006	0 010	0 014	0 022	0 032	0 036	0 046	0 059	8,468	0 0168
271230864		1991	0 003	0 003	0 008	0 014	0 020	0 030	0 036	0 048	0 108	8,249	0 0157
St Charles Co , MO	Sioux	1983	0 002	0 002	0 002	0 007	0 014	0 022	0 026	0 038	0 078	8,251	0 0103
291831002		1985	0 002	0 002	0 002	0 008	0 012	0 020	0 024	0 031	0 055	7,794	0 0092
		1986	0 002	0 002	0 005	0 009	0 013	0 023	0 027	0 037	0 105	7,401	0 0107
		1987	0 003	0 003	0 007	0 012	0 016	0 028	0 032	0 045	0 078	8,127	0 0134
		1988	0 003	0 003	0 003	0 007	0 012	0 023	0 027	0 039	0 086	7,341	0 0099
		1989	0 003	0 003	0 003	0 012	0 016	0 027	0 031	0 039	0 063	8,096	0 0122
		1990	0 003	0 003	0 003	0 008	0 016	0 023	0 027	0 035	0 078	7,662	0 0106
		1991	0 003	0 003	0 003	0 007	0 012	0 022	0 028	0 038	0 077	8,200	0 0098
Monroeville, PA	Cheswick	1991	0 003	0 009	0 014	0 020	0 027	0 040	0 048	0 063	0 102	8,389	0 0228
420030003													

Source AIRS (1991, 1992)

TABLE 7-6. MAXIMUM ANNUAL AVERAGE NITROGEN DIOXIDE CONCENTRATIONS REPORTED IN U.S. METROPOLITAN STATISTICAL AREAS, 1988 TO 1990

Metropolitan Statistical Area	1988 (ppm)	1989 (ppm)	1990 (ppm)	Metropolitan Statistical Area	1988 (ppm)	1989 (ppm)	1990 (ppm)
Albuquerque, NM	0 018	0 019	0 018	Modesto, CA	0 027	0 027	0 026
Allentown-Bethlehem, PA-NJ	0 020	0 020	0 017	Nashville, TN	0 012	0 012	0 012
Anaheim-Santa Ana, CA	0 046	0 047	0 047	Nassau-Suffolk, NY	0 033	0 029	0 028
Atlanta, GA	0 030	0 029	0 027	New Haven-Meriden, CT	0 029	0 028	0 027
Austin, TX	-	0 017	0 017	New Orleans, LA	0 024	0 022	0 020
Bakersfield, CA	0 032	0 033	0 032	New York, NY	0 041	0 049	0 046
Baltimore, MD	0 034	0 035	0 034	Newark, NJ	0 040	0 038	0 035
Baton Rouge, LA	0 021	0 019	0 018	Norfolk et al , VA	0 017	0 020	0 019
Beaumont-Port Arthur, TX	-	0 007	0 013	Oakland, CA	0 026	0 025	0 023
Beaver Co , PA	0 020	0 020	0 020	Oklahoma City, OK	0 029	0 015	0 015
Bergen-Passaic, NJ	0 036	0 035	0 031	Orlando, FL	-	0 013	0 012
Boston, MA	0 033	0 032	0 032	Owensboro, KY	0 015	0 014	0 011
Bridgeport-Milford, CT	0 027	0 026	0 026	Oxnard-Ventura, CA	0 018	0 027	0 025
Buffalo, NY	0 022	0 024	0 023	Philadelphia, PA-NJ	0 039	0 040	0 035
Burlington, VT	0 019	0 019	0 018	Pittsburgh, PA	0 030	0 028	0 031
Charleston, WV	0 024	0 021	0 020	Providence, RI	-	0 024	0 024
Chicago, IL	0 032	0 034	0 031	Provo-Orem, UT	0 028	0 028	0 023
Chico, CA	0 016	0 016	0 015	Raleigh-Durham, NC	-	0 012	0 014
Cincinnati, OH-KY-IN	0 030	0 030	0 028	Reading, PA	0 024	0 023	0 022
Cleveland, OH	0 031	0 034	0 029	Redding, CA	0 013	0 014	-
Dallas, TX	0 021	0 021	0 018	Richmond-Petersburg, VA	0 026	0 025	0 023
Denver, CO	0 039	0 040	-	Riverside -San Bernardino, CA	0 047	0 045	0 041
Detroit, MI	0 023	0 026	0 024	Roanoke, VA	0 016	0 014	0 013
El Paso, TX	0 021	0 022	0 017	Sacramento, CA	0 025	0 025	0 024
Erie, PA	0 016	0 015	0 015	Saginaw-Bay City-Midland, MI	-	0 009	0 008
Evansville, IN-KY	0 022	0 020	0 018	St Louis, MO-IL	0 025	0 026	0 026
Ft Wayne, IN	0 010	0 011	0 009	Salinas-Seaside-Monterey, CA	-	0 014	0 012
Ft Worth-Arlington, TX	0 014	0 013	0 012	Salt Lake City-Ogden, UT	0 035	0 034	0 029
Fresno, CA	0 032	0 032	0 026	San Diego, CA	0 035	0 032	0 029
Greensboro et al , NC	0 018	0 016	0 017	San Francisco, CA	0 026	0 026	0 022
Harrisburg-Lebanon-Carlisle, PA	0 021	0 022	0 020	San Jose, CA	0 032	0 032	0 030
Hartford, CT	0 020	0 020	0 019	Santa Barbara et al , CA	0 017	0 027	0 022
Houston, TX	0 028	0 028	0 029	Santa Cruz, CA	0 008	0 009	0 008
Huntington-Ashland, WV-KY-OH	0 016	0 013	0 016	Santa Rosa-Petaluma, CA	0 016	0 015	0 015
Indianapolis, IN	0 024	0 023	0 020	Scranton-Wilkes-Barre, PA	0 019	0 021	0 020
Jacksonville, FL	0 019	0 015	0 015	Springfield, MO	0 010	0 010	0 008
Jersey City, NJ	0 033	0 031	0 030	Springfield, MA	-	0 029	0 026
Johnson City et al , TN-VA	-	0 019	0 019	Steubenville-Weirton, OH-WV	0 021	0 023	0,020
Johnstown, PA	0 019	0 019	0 025	Stockton, CA	0 026	0 026	0 026
Kansas City, MO-KS	0 014	0 015	0 015	Tampa et al , FL	0 021	0 022	0 013
Kenosha, WI	0 014	0 016	0 010	Tucson, AZ	0 017	0 023	0 022
Lancaster, PA	0 020	0 018	0 017	Tulsa, OK	0 017	0 020	0 015
Little Rock-N Little Rock, AR	0 010	0 009	0 009	Vallejo-Fairfield-Napa, CA	0 019	0 019	0 018
Los Angeles-Long Beach, CA	0 061	0 057	0 056	Visalia-Tulare-Porterville, CA	0 023	0 021	0 021
Louisville, KY-OH	0 023	-	0 030	Washington, DC-MD-VA	0 030	0 031	0 030
Manchester, NH	0 024	0 022	-	West Palm Beach et al , FL	0 013	0 013	0 014
Memphis, TN-AR-MS	0 034	0 026	0 023	Wheeling, WV-OH	0 018	0 019	-
Miami-Hialeah, FL	0 017	0 018	0 016	Wilmington, DE-NJ-MD	0 033	0 034	0 033
Middlesex-Somerset-Hunterdon, NJ	0 025	0 024	0 022	Worcester, MA	0 029	0 026	0 022
Milwaukee, WI	0 027	0 029	0 024	York, PA	0 023	0 022	0 022
Minneapolis-St Paul, MN-WI	0 020	0 009	0 022				

Source U S Environmental Protection Agency (1990, 1991a, 1991b)

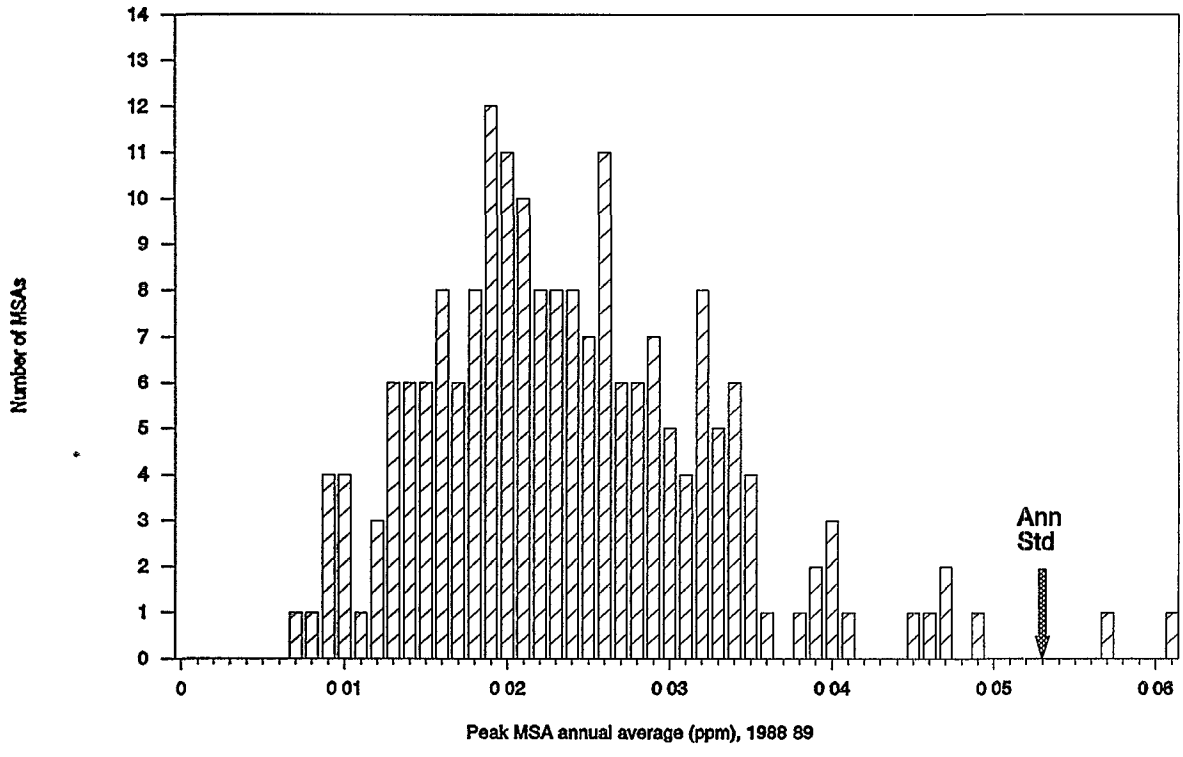


Figure 7-3. Distribution of peak annual nitrogen dioxide averages in 103 Metropolitan Statistical Areas, 1988 to 1989, as derived by the U.S. Environmental Protection Agency from AIRS (1991).

highest hourly average concentrations Although the information is limited, Table 7-8 summarizes the maximum hourly average NO concentrations reported by MSAs in the United States.

The seasonal and diurnal patterns in ambient NO_2 concentrations were explored using data from a majority of urban sites For the analysis, a subset of sites was selected from the AIRS data base. Four years of continuous data (1986 through 1989) were required, with no more than a month of incomplete data A month was considered incomplete if less than 75% of the hourly measurements were reported There were 156 sites that met these requirements, and it was observed that the vast majority of sites had at least 90% of the data present for each month The purpose of these criteria was to provide a general selection of all types of stations that could yield some information about seasonal and diurnal patterns There was no attempt to select a geographically or demographically representative set of

TABLE 7-7. MAXIMUM HOURLY AVERAGE NITROGEN DIOXIDE CONCENTRATIONS REPORTED IN U.S. METROPOLITAN STATISTICAL AREAS, 1988 TO 1990

Metropolitan Statistical Area	1988 (ppm)	1989 (ppm)	1990 (ppm)	Metropolitan Statistical Area	1988 (ppm)	1989 (ppm)	1990 (ppm)
Albuquerque, NM	0 086	0 126	0 118	Modesto, CA	0 130	0 140	0 100
Allentown-Bethlehem, PA-NJ	0 109	0 116	0 098	Nashville, TN	0 070	0 095	0 150
Anaheim-Santa Ana, CA	0 280	0 280	0 220	Nassau-Suffolk, NY	0 129	0 124	0 114
Atlanta, GA	0 125	0 140	0 111	New Haven-Meriden, CT	0 121	0 119	0 122
Austin, TX	0 080	0 080	0 080	New Orleans, LA	0 097	0 109	0 086
Bakersfield, CA	0 120	0 130	0 140	New York, NY	0 451	0 169	0 213
Baltimore, MD	0 126	0 161	0 120	Newark, NJ	0 273	0 272	0 213
Baton Rouge, LA	0 286	0 104	0 097	Norfolk et al , VA	0 088	0 098	0 083
Beaumont-Port Arthur, TX	0 050	0 060	0 060	Oakland, CA	0 140	0 150	0 130
Beaver Co , PA	0 074	0 092	0 076	Oklahoma City, OK	0 318	0 125	0 089
Bergen-Passaic, NJ	0 151	0 151	0 151	Orlando, FL	0 066	0 065	0 076
Boston, MA	0 155	0 178	0 250	Owensboro, KY	0 074	0 090	0 059
Bridgeport-Milford, CT	0 107	0 121	0 147	Oxnard-Ventura, CA	0 110	0 120	0 160
Buffalo, NY	0 096	0 149	0 107	Philadelphia, PA-NJ	0 168	0 200	0 150
Burlington, VT	0 078	0 066	0 073	Pittsburgh, PA	0 117	0 159	0 173
Charleston, WV	0 095	0 080	0 067	Providence, RI	0 112	0 111	0 097
Chicago, IL	0 200	0 380	0 150	Provo-Orem, UT	0 130	0 150	0 122
Chico, CA	0 100	0 080	0 080	Raleigh-Durham, NC	-	0 070	0 078
Cincinnati, OH-KY-IN	0 223	0 115	0 135	Reading, PA	0 118	0 117	0 096
Cleveland, OH	0 138	0 110	0 215	Redding, CA	0 100	0 080	0 070
Dallas, TX	0 110	0 140	0 090	Richmond-Petersburg, VA	0 141	0 094	0 108
Denver, CO	0 205	0 462	-	Riverside-San Bernardino, CA	0 210	0 200	0 200
Detroit, MI	0 215	0 136	0 110	Roanoke, VA	0 119	0 075	0 075
El Paso, TX	0 120	0 140	0 190	Sacramento, CA	0 180	0 270	0 160
Erie, PA	0 089	0 077	0 108	Saginaw-Bay City-Midland, MI	0 083	0 057	0 044
Evansville, IN-KY	0 312	0 102	0 118	St Louis, MO-IL	0 108	0 131	0 098
Ft Wayne, IN	0 076	0 095	0 060	Salinas-Seaside-Monterey, CA	-	0 070	0 060
Ft Worth-Arlington, TX	0 080	0 090	0 080	Salt Lake City-Ogden, UT	0 160	0 163	0 132
Fresno, CA	0 210	0 190	0 160	San Diego, CA	0 280	0 230	0 180
Greensboro et al , NC	0 206	0 113	0 075	San Francisco, CA	0 130	0 230	0 130
Harrisburg-Lebanon-Carlisle, PA	0 106	0 085	0 074	San Jose, CA	0 160	0 150	0 150
Hartford, CT	0 094	0 075	0 091	Santa Barbara et al , CA	0 160	0 120	0 110
Houston, TX	0 190	0 170	0 160	Santa Cruz, CA	0 050	0 040	0 050
Huntington-Ashland, WV-KY-OH	0 141	0 154	0 120	Santa Rosa-Petaluma, CA	0 120	0 090	0 090
Indianapolis, IN	0 096	0 091	0 072	Scranton Wilkes-Barre, PA	0 126	0 107	0 134
Jacksonville, FL	0 097	0 110	0 086	Springfield, MO	0 075	0 082	0 074
Jersey City, NJ	0 212	0 174	0 138	Springfield, MA	0 203	0 150	0 104
Johnson City et al , TN-VA	0 146	0 125	0 090	Steubenville-Weirton, OH-WV	0 117	0 167	0 128
Johnstown, PA	0 077	0 062	0 075	Stockton, CA	0 110	0 130	0 120
Kansas City, MO-KS	0 079	0 090	0 067	Tampa et al , FL	0 088	0 086	0 080
Kenosha, WI	0 058	0 082	0 061	Tucson, AZ	0 125	0 093	0 116
Lancaster, PA	0 105	0 082	0 121	Tulsa, OK	0 088	0 106	0 090
Little Rock-N Little Rock, AR	0 092	0 082	0 070	Vallejo-Fairfield-Napa, CA	0 090	0 130	0 080
Los Angeles-Long Beach, CA	0 540	0 340	0 280	Visalia-Tulare-Porterville, CA	0 170	0 210	0 120
Louisville, KY-OH	0 100	0 088	0 117	Washington, DC-MD-VA	0 155	0 158	0 149
Manchester, NH	0 239	0 178	0 115	West Palm Beach et al , FL	0 073	0 062	0 071
Memphis, TN-AR-MS	0 118	0 108	0 132	Wheeling, WV-OH	0 077	0 134	0 067
Miami-Hialeah, FL	0 092	0 096	0 088	Wilmington, DE-NJ-MD	0 110	0 130	0 290
Middlesex-Somerset-Hunterdon, NJ	0 122	0 096	0 085	Worcester, MA	0 250	0 122	0 088
Milwaukee, WI	0 113	0 117	0 094	York, PA	0 135	0 102	0 129
Minneapolis-St Paul, MN-WI	0 328	0 106	0 130				

Source AIRS (1992)

TABLE 7-8. MAXIMUM HOURLY AVERAGE NITRIC OXIDE CONCENTRATIONS (ppm) REPORTED IN U.S. METROPOLITAN STATISTICAL AREAS, 1988 TO 1990

	Hourly Average Values			Annual Average Values		
Metropolitan Statistical Area	1988	1989	1990	1988	1989	1990
Austin, TX		0 320	0 400		0 0168	0 0186
Baton Rouge, LA	0 338	0 410	0 394	0 0140	0 0120	0 0145
Beaumont-Port Arthur, TX			0 160			0 0097
Boston, MA	0 671	0 621	0 658	0 0519	0 0629	0 0665
Bridgeport-Milford, CT	0 560	0 479	0 654	0 0293	0 0245	0 0302
Charleston, WV	0 305	0 328	0 346	0 0249	0 0286	0 0351
Chicago, IL	0 868	0 899	1 078	0 0561	0 561	0 0493
Cincinnati, OH-KY-IN	0 500	0 500	0 500	0 0357	0 0439	0 0396
Cleveland, OH	0 475	0 435	0 420	0 0327	0 0359	0 0316
Dallas, TX	0 760	0 760	0 610	0 0223	0 0233	0 0205
Denver, CO	0 755			0 0517		
Evansville, IN-KY	0 466	0 476	0 346	0 0247	0 0225	0 0210
Ft. Worth-Arlington, TX	0 290	0 240	0 250	0 0112	0 0099	0 0101
Hartford, CT	0 438	0 427	0 400	0 0226	0 0204	0 0182
Houston, TX	0 850	0 640	0 840	0 0284	0 0241	0 0287
Huntington-Ashland, WV-KY-OH	0 236	0 279	0 350	0 0122	0 0120	0 0117
Indianapolis, IN	0 464	0 448		0 0148	0 0155	
Kenosha, WI	0 298		0 170	0 0082		0 0082
Milwaukee, WI	0 396	0 354	0 648	0.0196	0 0200	0 0206
Minneapolis-St Paul, MN-WI	0 463		0 404	0 0182		0 0244
Nashville, TN		0 335	0 265		0 0205	0 0196
New Haven-Meriden, CT	0 659	0 602	0 700	0 0457	0 0430	0 0441
New Orleans, LA	0 488	0 419	0 461	0 0217	0 0198	0 0198
Norfolk et al , VA		0 459	0 403		0 0130	0 0145
Oklahoma City, OK	0 438	0 416	0 348	0 0089	0 0092	0 0093
Owensboro, KY	0 173	0 144	0 170	0 0071	0 0069	0 0065
Pittsburgh, PA	0 559	0 650	0 703	0 0305	0 0400	0 0421
Raleigh-Durham, NC			0 425			0 0131
Richmond-Petersburg, VA		0 436	0 451		0 0180	0 0158
Roanoke, VA		0 203	0 248		0 0094	0 0097
St Louis, MO-IL	0 455	0 453	0 466	0 0327	0 0292	0 0291
Springfield, MA		0 475	0 512		0 0339	0 0371
Steubenville-Weirton, OH-WV	0 514			0 0145		
Washington, DC-MD-VA	0 653	0 640	0 611	0 0482	0.0318	0 0381
Wheeling, WV-OH	0 266	0 159		0 0150	0 0160	
Worcester, MA	0 549	0 694	0 648	0 0288	0 0285	0 0286

Source AIRS (1992)

sites Of the 156 sites, 70 were located in residential settings, 45 were in an industrial setting, 20 were commercial, and 20 were miscellaneous, mostly agricultural

Seasonal patterns for the 156 sites were examined by compiling monthly distributions of hourly values and plotting the 50th, 90th, and 98th percentiles over the period 1986 through 1989 The 50th percentile approximates the geometric mean In reviewing the NO_2 monitoring data, a consistent seasonal pattern was distinguishable For most of the sites, the highest monthly average concentrations occurred during the months of November, December, January, or February However, there were some exceptions The sample plots in Figure 7-4a through 7-4d illustrate the diversity of seasonal patterns that exist in the U S cities The pattern at the Long Beach site shows a broad span of winter months with elevated values—from about September into March or April The Denver site exhibits much narrower winter peaks and broader summer troughs The pattern at the Cleveland site is altogether lower, such peaks as there are occur in the spring and summer months, and are discernable only in the 90th and 98th percentiles The data for the Richmond site exhibit no discernable pattern These figures show that seasonal peaks do not occur at the same time for all sites and, indeed, there are some locations with no prominent seasonal pattern

The diurnal patterns were explored using the monthly average concentrations for each hour Generally, the highest monthly averages occur in the late afternoon and evening (1700 to 2200 hours) Because of the interest in assessing the time of day when the hourly values above a specified threshold concentration occur, an additional analysis was performed The hourly average concentration of 0.2 ppm was used as a threshold value because it is described as a possible benchmark concentration above which human physiologic responses may be detected In 1988, 216 NO_2 monitoring stations reported to EPA's data bank a "valid" year's data, that is, at least 75% of possible hourly values Figure 7-5 compares the annual averages with the second-high 1-h values Four California stations reported annual averages equaling or exceeding the annual standard of 0 053 ppm

The 18 stations reporting a second-high 1-h value greater than 0 2 ppm are identified by state in Figure 7-5. The diurnal incidences of credible 1-h NO_2 values greater than 0 2 ppm for the other 16 stations are listed in Table 7-9, late morning is when these events are most likely to occur

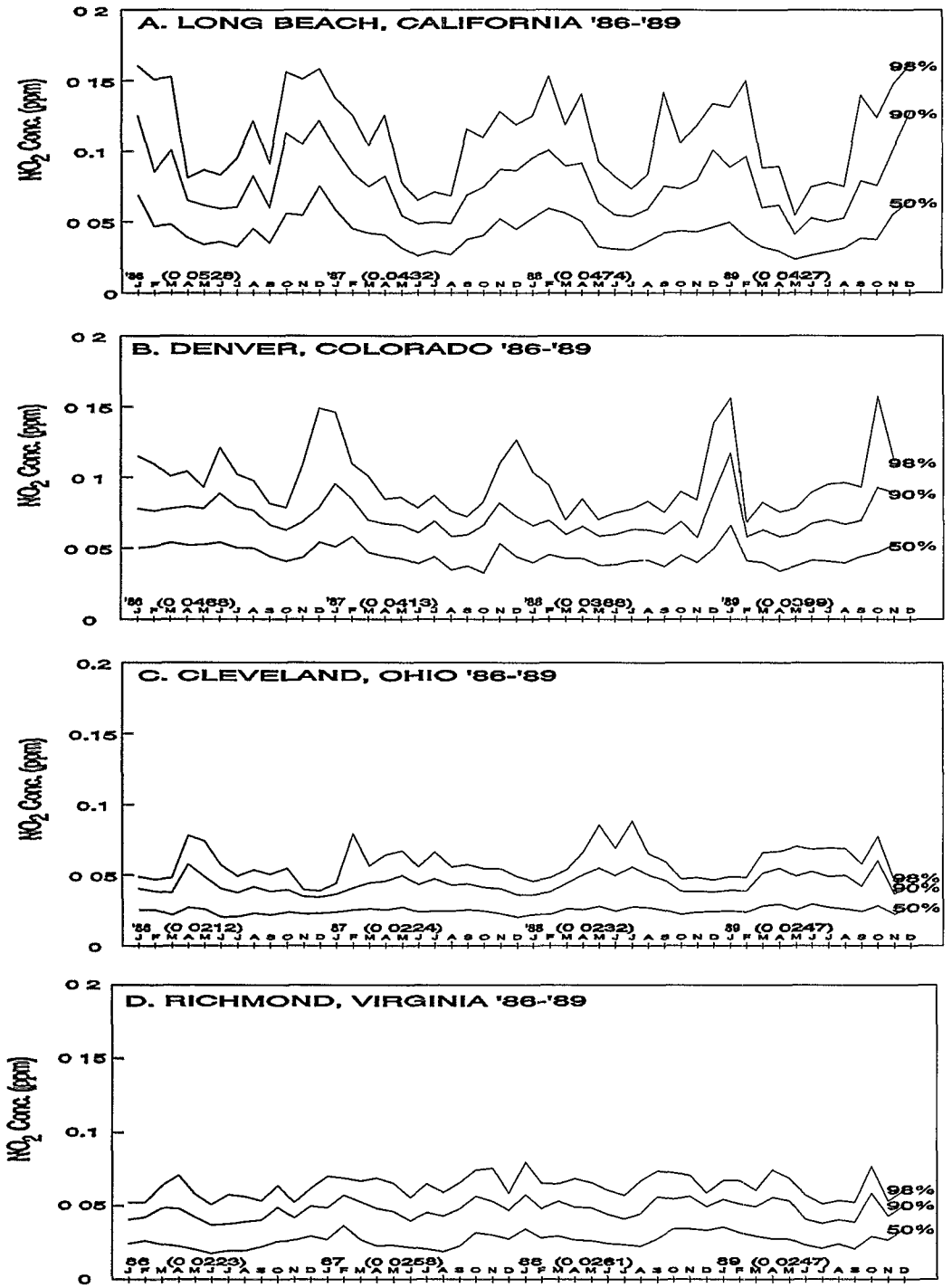


Figure 7-4. Monthly 50th, 90th, and 98th percentiles of 1-h nitrogen dioxide concentrations at selected stations, 1986 to 1989, as derived by the U.S. Environmental Protection Agency from AIRS (1991).

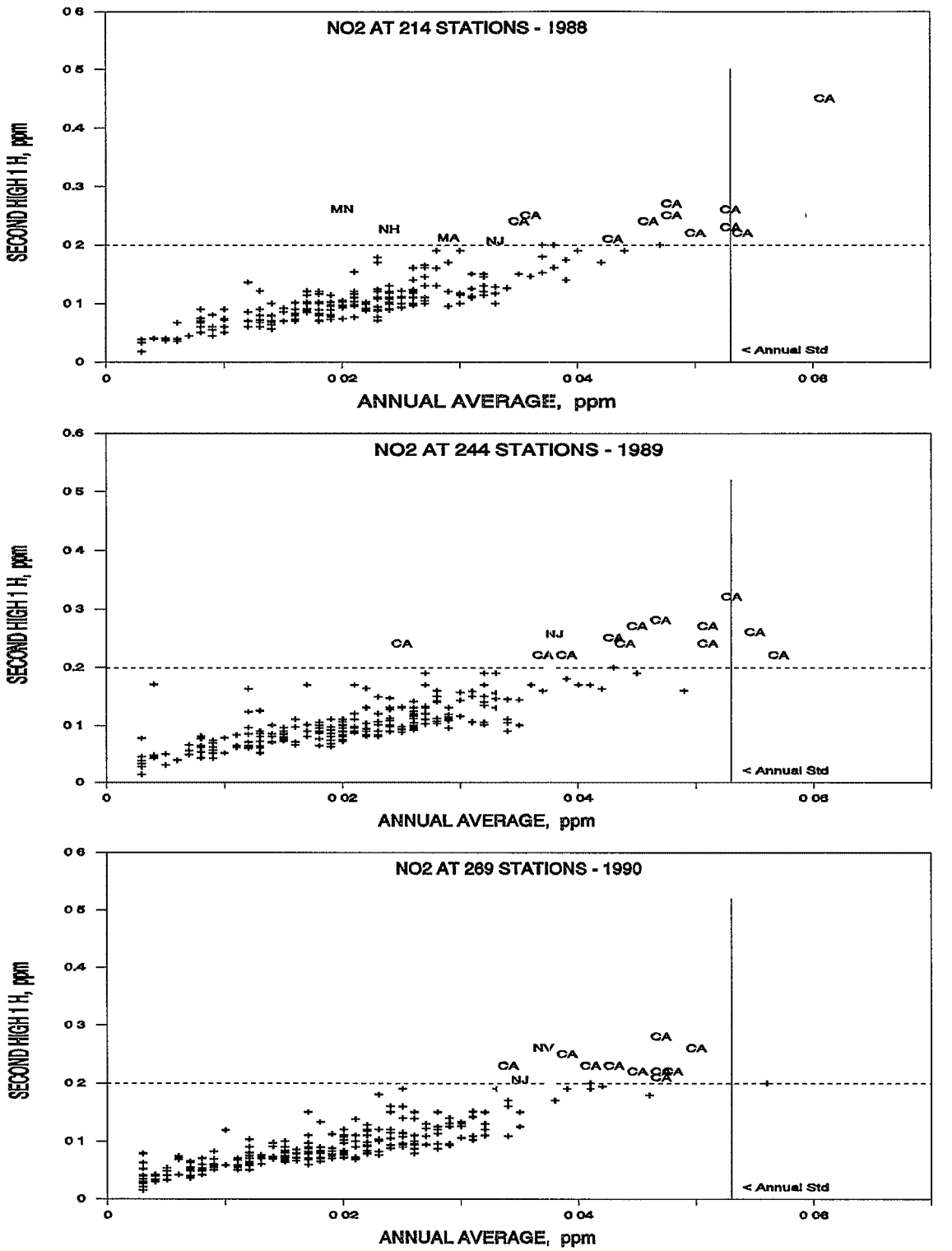


Figure 7-5. Annual average nitrogen dioxide versus second-high 1-h concentration, 1988, 1989, and 1990. (Second-high 1-h values >0.2 are identified by state, as derived by the U.S. Environmental Protection Agency from AIRS, 1991, 1992.)

TABLE 7-9. HOURLY INCIDENCE OF NITROGEN DIOXIDE CONCENTRATIONS GREATER THAN 0.2 ppm FOR STATIONS WITH MORE THAN ONE OCCURRENCE, 1988

	Clock Hour																							
1988	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Anaheim, CA											2	2	1	1										
Azusa, CA									1				1				2							
Burbank, CA											1	2		1	1	3	3	2	1	1				
Hawthorne, CA									1	2	3	1	1											
La Habra, CA											1		1											
Long Beach, CA										2	3	4	2		1									
Los Angeles (0113), CA											2	3												
Los Angeles (1103), CA									6	7	6	6	3	1	3									
Lynwood, CA									1	3	2													
Pico Rivera, CA											1	1												
San Diego, CA										2	2							1	1	1	1	1		
Whittier, CA										1	2													
Worcester, MA									1	1														
Minneapolis, MN								1	1	1														
Manchester, NH													1	1					1					
Bayonne, NJ								1			1													

Source AIRS (1991)

The 1-h data from the remaining 16 stations have been examined in detail, hour by hour, to serve two purposes to place these high values in perspective with the general distributions of 1-h values, and to show the changing shape of the general distribution of all 1-h values through the 24-h period in response to the cumulative influences of local emissions and meteorology

Figure 7-6 represents the hour-by-hour percent frequency distribution of 1-h NO_2 values for four of the stations selected from the group of 16 in Table 7-9 The San Diego, CA, location evidently often receives midday ventilation from sea breezes, causing the distributions of 1-h values to contract and shift toward lower concentrations through the early afternoon Toward sunset, the upper tails of the distributions begin to extend toward higher concentrations, but the peaks remain about 0 01 ppm After midnight, a subset of higher

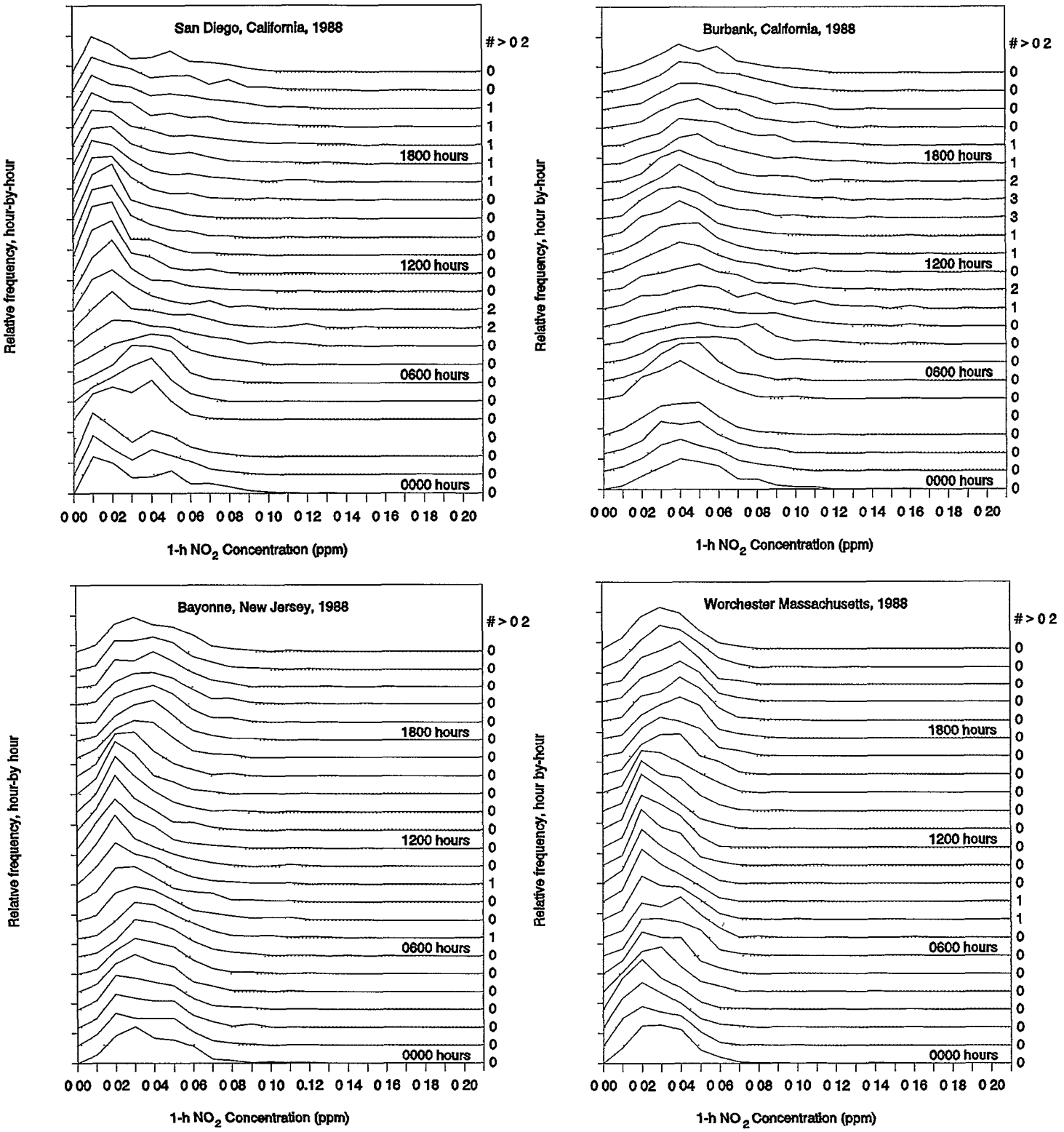


Figure 7-6. Hourly relative frequency distributions of 1-h nitrogen dioxide values at four selected stations for 1988, with numbers of values greater than 0.2 ppm, as derived by the U.S. Environmental Protection Agency from AIRS (1991).

concentrations emerges and, around sunrise, has shifted the distribution peaks to around 0.04 ppm (The 0300- or 0400-hours time slot is used for calibration checks at California stations; no data are reported)

Distributions for the Burbank, CA, station, situated along the northern edge of the valley near the mountains, are notably broader than those for the San Diego station They exhibit their narrowest spread between midnight and sunrise Morning rush-hour emissions extend the upper tail and shift the peak higher, briefly Through midday, the peaks shift somewhat lower, but the distributions remain broad From late afternoon to midnight, the peaks shift higher and the distributions broaden further

The Bayonne, NJ, and Worcester, MA, stations have similar patterns, their distributions broaden during morning rush-hour, shift toward lower peaks through early afternoon when ventilation usually improves, then broaden and shift toward higher concentrations through the evening hours when winds characteristically subside and inversion forms.

From this review of NO_2 data, it is concluded that 1-h concentrations greater than 0.2 ppm are infrequent events that lie well above the general distribution of 1-h values These excursions presumably are produced by the rare coincidence of emissions and meteorological conditions, a distal rather than a proximal feature on the very attenuated tail of a station's main data distribution

From the group of 216 stations with valid data for 1988, discussed previously, the subset of 43 stations with annual averages $\geq$0 03 ppm are examined next Twenty-three stations are located in California, the other 20 are located in 13 other states For this group of stations with annual averages above this concentration of potential interest, this question is posed: What is the relationship between the annual average and incidence of 1-h values above selected thresholds? In Figure 7-7, the percentages of 1-h values greater than 0 03 ppm and 0.05 ppm are plotted versus the annual averages for these 43 stations For this subset of stations in the upper portion of the distribution, the percentages of 1-h values above the chosen thresholds bear a reasonably linear relationship to the stations' annual averages for the 0 03-ppm group, R^2= 0 805, and for the 0 05-ppm group, R^2 = 0 924

Complete distributions of a year's 1-h values for four stations are compared in Figure 7-8. Two stations were selected from the California basin area and two were selected

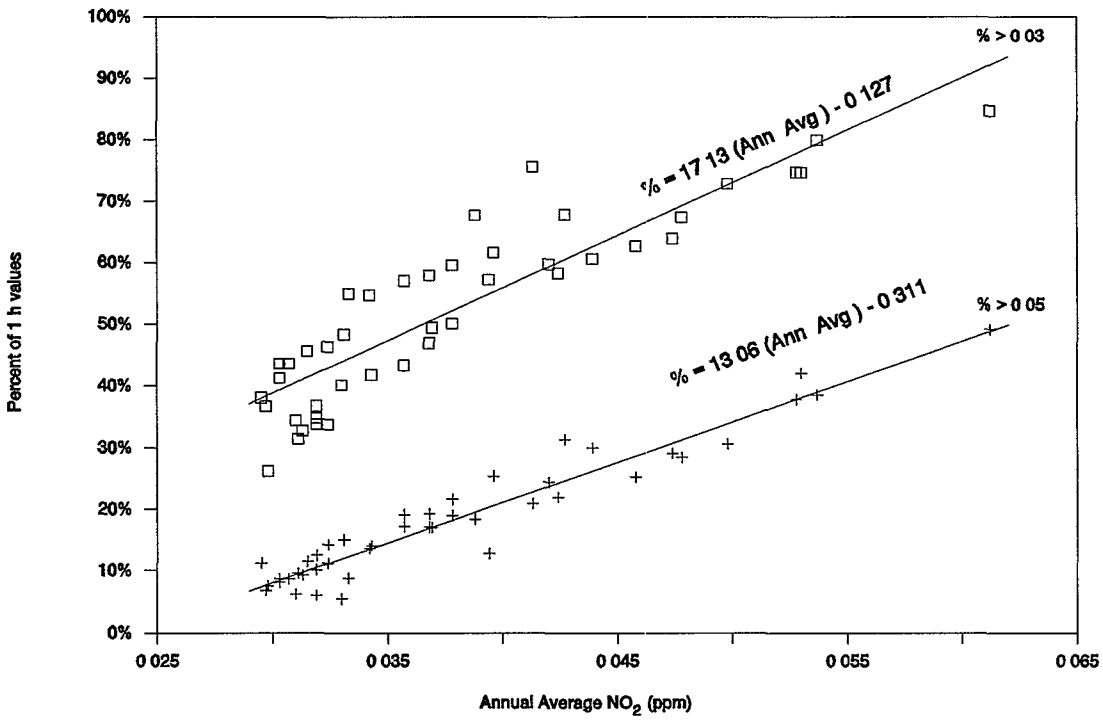


Figure 7-7. Percent of 1-h nitrogen dioxide values above 0.03 and 0.05 ppm versus annual averages >0.03 ppm, 1988, as derived by the U.S. Environmental Protection Agency from AIRS (1991).

from the east coast, with annual averages approximately in the middle of the annual average range depicted in Figure 7-7 Although the Los Angeles and Baltimore stations have similar annual averages, the Baltimore station has a higher percentage of values around 0 04 ppm, and its distribution slides under the Los Angeles distribution at around 0 07 ppm Likewise, the Anaheim and New York City annual averages are similar, but the New York City station has a higher percentage of 0 05-ppm values, then drops under the Anaheim distribution at 0 07 ppm

This very limited comparison suggests that, at fixed-site ambient monitoring locations with annual averages above the national average (see Figure 7-2), percentages of values in the middle of the 1-h distribution are rather consistently related to the annual average However, as discussed earlier in this chapter, the NO_2 elevated concentrations in the California basin area are not experienced in most of the rest of the country The California exposures are a result of a unique combination of sources and meteorology

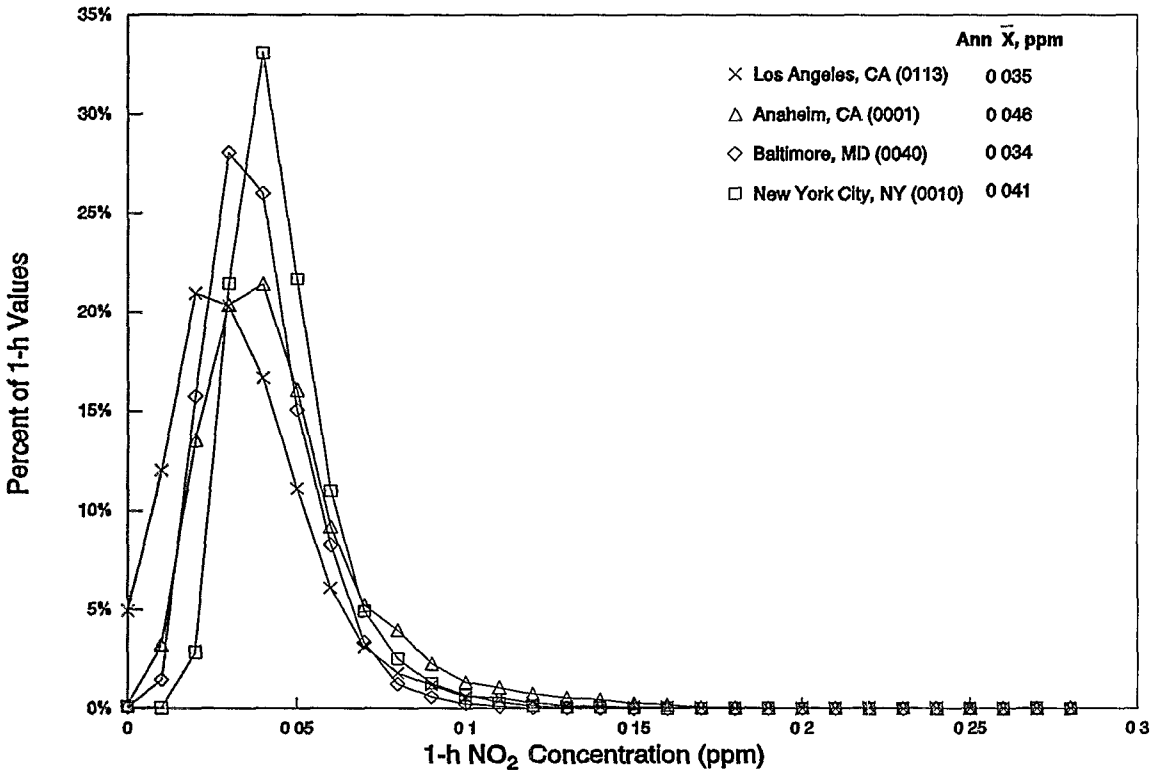


Figure 7-8. Relative distributions of 1-h nitrogen dioxide values at selected stations, 1988, as derived by the U.S. Environmental Protection Agency from AIRS (1991).

7.2.3.4 Exposure Patterns Observed for Ambient Nitrogen Dioxide and Nitric Oxide Concentrations—Rural Forest and Agriculture Areas

Because of the interest in assessing the potential effects of NO_2 and NO exposures on vegetation, monitoring data from rural forested and agricultural stations are characterized Because of the paucity of information, the main focus is on NO_2 hourly average concentration data. To be selected, a station that measured NO_2 had to (1) be designated rural forested or agricultural, (2) have collected data at least during the period 1990 to 1991, and (3) have experienced data capture of at least 75% or greater for the hourly average values over an annual period Eight stations at rural forested sites, which measured hourly average values of NO_2, were selected for analysis Thirty-three site-years of data were used in the analysis, where a site-year is defined as one year of data for a specific site For example, for the Perry County station in Pennsylvania, 1983-1991 data were used in the

analysis, thus, 9 site-years of information were used For the rural agricultural sites, data from 25 stations were used in the analysis, for a total of 142 site-years of information

For the period 1979 to 1991, the hourly average NO_2 concentrations for selected forest and agricultural sites were <0 10 ppm in most cases Table 7-10 summarizes the maximum hourly average concentrations for the eight rural forested sites used in the analysis An example of the percentile distribution information for the 1-h values, as well as the annual arithmetic average concentration, for a specific year is provided in Table 7-11 Table 7-12 lists the maximum hourly average concentrations for the 25 rural agricultural sites, Table 7-13 shows the percentile distributions and annual arithmetic means for some of these sites Agricultural sites that were not located near major metropolitan areas experienced few hourly average maximum concentrations >0 10 ppm

As observed for urban locations, a consistent seasonal pattern for NO_2 was distinguishable for both the rural forested and the rural agricultural sites In general, the NO_2 monthly average values decreased during the spring, were at their lowest levels during the summer, then rose during the fall and winter The months of November, December, January, or February contained the highest monthly average concentrations (Figure 7-9)

A consistent NO_2 diurnal pattern was observed for the rural forested and agricultural sites The late afternoon and evening hours (approximately 1700 to 2200 hours) contained the highest NO_2 monthly average concentrations (Figure 7-10) After 2200 hours, the NO_2 levels dropped until approximately 0600 hours The levels began to rise for a few hours until approximately 0900 to 1000 hours After 1000 hours, levels began to drop again and continued to drop throughout the afternoon The NO_2 monthly average concentrations decreased to their lowest levels between the hours of 1000 and 1700 hours Figures 7-11 and 7-12 illustrate the typical patterns observed for selected rural forested and agricultural sites Upon reviewing the individual hourly average concentrations, the same pattern became apparent

For the data set used, the seasonal and diurnal patterns were consistent across all sites, with the exception of five sites in Montana and two in California Some of the Montana data sets contained monthly average NO_2 values so low that it was difficult to distinguish any pattern However, the data for some of the site-years showed a slight increase in the average

TABLE 7-10. MAXIMUM HOURLY AVERAGE NITROGEN DIOXIDE CONCENTRATIONS FOR SELECTED U.S. RURAL FORESTED SITES (concentrations in ppm)

AIRS ID[a]	Site Name	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991
051191002	North Little Rock, AR	0 039	0 075	0 141	0 055	0 062	0 102	0 080	0 071	0 074	0 092	0.082	0 070	0 090
181090004	Morgan Co , IN													0.060
250154002	Ware Co , MA								0 095	0 064	0 082	0 091	0 086	0 081
300870761	Rosebud Co , MT												0 032	
300870762	Rosebud Co , MT												0 041	
350281002	Los Alamos Co , NM													0 010
420990301	Perry Co , PA					0 160	0 060	0 065	0 051	0 044	0 072	0 055	0 041	0 045
450190046	Mount Pleasant, SC													0 031

[a]AIRS ID = Aerometric Information Retrieval System identification number

Source AIRS (1992)

TABLE 7-11. CHARACTERIZATION OF HOURLY AVERAGE NITROGEN DIOXIDE CONCENTRATIONS FOR SELECTED U.S. FOREST SITES (concentrations in ppm)

AIRS ID[a]	Monitoring Site	Year	Min	10%	30%	50%	70%	90%	95%	99%	Max	Number Obs	Annual Arith Mean
				Percentiles									
051191002	N Little Rock, AR	1990	0 003	0 003	0 005	0 007	0 011	0 020	0 025	0 038	0 070	8,240	0 0094
181090004	Morgan Co , IN	1991	0 003	0 003	0 006	0 007	0 010	0 015	0 019	0 026	0 060	7,239	0 0086
250154002	Ware, MA	1990	0 003	0 003	0 003	0 005	0 009	0 022	0 031	0 048	0 086	7,848	0 0090
300870761	Rosebud Co , MT	1990	0 003	0 003	0 003	0 003	0 003	0 003	0 003	0 010	0 032	8,359	0 0027
300870762	Rosebud Co , MT	1990	0 003	0 003	0 003	0 003	0 003	0 003	0 003	0 010	0 041	8,299	0 0027
350281002	Los Alamos Co , NM	1991	0 003	0 003	0 003	0 003	0 003	0 005	0 005	0 007	0 010	8,677	0 0030
420990301	Perry Co , PA	1989	0 003	0 003	0 003	0 005	0 008	0 015	0 020	0 031	0 055	7,068	0 0069
450190046	Mount Pleasant, SC	1991	0 002	0 002	0 002	0 002	0 002	0 005	0 010	0 010	0 031	6,147	0 0027

[a]AIRS ID = Aerometric Information Retrieval System identification number

Source AIRS (1992)

TABLE 7-12. MAXIMUM HOURLY AVERAGE NITROGEN DIOXIDE CONCENTRATIONS FOR SELECTED U.S. RURAL AGRICULTURAL SITES (concentrations in ppm)

AIRS ID[a]	Site Name	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991
060295001	Kern Co , CA												0 070	
061110005	Ventura Co , CA						0 060	0 050	0 080	0 040	0 080	0 060	0 050	
061113001	Oxnard, CA						0 110		0 130	0 080	0 110	0 110	0 100	
080013001	Welby, CO		0 224	0 190		0 300	0 203	0 305	0 199	0 217	0 205			
181470002	Spencer Co , IN	0 054		0 059	0 049	0 042	0 046	0 049	0 047	0 357	0 076		0 035	0 048
181470006	Spencer Co , IN	0 065		0 049	0 089	0 040	0 046	0 038	0 045	0 239	0 118		0 045	0 185
181550001	Switzerland, IN													0 045
260430901	Dickinson Co , MI							0 044	0 046	0 039	0 045	0 049	0 049	0 042
260430902	Dickinson Co , MI							0 037	0 050	0 063	0 035	0 039	0 035	0 034
270176316	Carlton Co , MN											0 035	0 052	
271710007	Wright Co , MN											0 075	0 061	
290470005	Clay Co , MO				0 197	0 081	0 120	0 057	0 080	0 156	0 079	0 076	0 054	0 072
291831002	St Charles Co , MO					0 078		0 055	0 105	0 078	0 086	0 063	0 078	0 077
300870701	Rosebud Co , MT							0 054	0 038	0 039	0 040	0 044	0 035	0 113
300870702	Rosebud Co , MT							0 042	0 033	0 030	0 033	0 142	0 039	0 029
300870704	Rosebud Co , MT							0 045	0 038	0 029	0 041	0 054	0 045	0 054
340273001	Morris Co , NJ						0 108	0 118	0 098	0 081	0 103	0 076	0 094	0 082
350450014	San Juan Co , NM											0 070	0 063	0 071
360010012	Albany Co , NY												0 192	
380130001	Burke Co , ND											0 017	0 026	
380650002	Oliver Co , ND											0 037		
401430174	Tulsa Co , OK				0 062	0 080	0 060	0 111	0 079	0 059	0 076	0 090	0 053	0 083
471190106	Maury Co , TN												0 041	0 044
540250001	Greenbrier Co , WV								0 083		0 037	0 038	0 038	0 044
550210008	Columbia Co., WI		0 047	0 048	0 046	0 060	0 037	0 047	0 047	0 052	0 040			

[a]AIRS ID = Aerometric Information Retrieval System identification number

Source AIRS (1992)

TABLE 7-13. CHARACTERIZATION OF HOURLY AVERAGE NITROGEN DIOXIDE CONCENTRATIONS FOR SELECTED U.S. AGRICULTURAL SITES (concentrations in ppm)

			Percentiles										
AIRS ID[a]	Monitoring Site	Year	Min	10%	30%	50%	70%	90%	95%	99%	Max	Number Obs	Annual Arith Mean
060295001	Kern Co , CA	1990	0 003	0 010	0 010	0 010	0 010	0 020	0 030	0 030	0 070	7,928	0 0134
061110005	Ventura CO , CA	1989	0 003	0 003	0 010	0 010	0 010	0 010	0 020	0 020	0 060	7,614	0 0086
061113001	Oxnard, CA	1989	0 003	0 010	0 010	0 020	0 020	0 030	0 040	0 050	0 110	7,811	0 0180
080013001	Welby, CO	1987	0 003	0 003	0 010	0 021	0 035	0 053	0 063	0 097	0 217	8,136	0 0257
181470002	Spencer CO , IN	1985	0 003	0 003	0 006	0 008	0 011	0 016	0 020	0 026	0 049	7,429	0 0091
181470006	Spencer CO , IN	1985	0 003	0 005	0 007	0 009	0 012	0 017	0 021	0 027	0 038	8,191	0 0103
181550001	Switzerland, IN	1991	0 003	0 006	0 008	0 011	0 014	0 019	0 023	0 029	0 045	7,922	0 0117
260430901	Dickinson Co , MI	1990	0 003	0 003	0 003	0 003	0 008	0 016	0 021	0 030	0 049	8,651	0 0070
260430902	Dickinson Co , MI	1990	0 003	0 003	0 003	0 005	0 006	0 010	0 013	0 020	0 035	8,491	0 0054
270176316	Carlton Co , MN	1990	0 003	0 003	0 003	0 003	0 005	0 009	0 012	0 020	0 052	7,417	0 0044
271710007	Wright Co , MN	1989	0 003	0 003	0 003	0 006	0 010	0 019	0 025	0 036	0 075	7,917	0 0086
290470005	Clay Co , MO	1990	0 003	0 003	0 003	0 007	0 011	0 020	0 027	0 039	0 054	7,981	0 0088
291831002	St Charles Co , MO	1990	0 003	0 003	0 003	0 008	0 016	0 023	0 027	0 035	0 078	7,662	0 0106
300870701	Rosebud Co , MT	1988	0 003	0 003	0 003	0 003	0 003	0 011	0 016	0 027	0 040	7,093	0 0048
300870702	Rosebud Co , MT	1988	0 003	0 003	0 003	0 003	0 003	0 005	0 008	0 016	0 033	6,888	0 0033
300870704	Rosebud Co , MT	1988	0 003	0 003	0 003	0 003	0 003	0 006	0 009	0 017	0 041	8,003	0 0034
340273001	Morris Co , NJ	1990	0 003	0 003	0 007	0 011	0 016	0 029	0 035	0 047	0 094	8,260	0 0138
350450014	San Juan Co , NM	1990	0 003	0 003	0 003	0 003	0 008	0 018	0 025	0 041	0 063	8,548	0 0076
360010012	Albany Co , NY	1990	0 003	0 005	0 009	0 015	0 024	0 036	0 041	0 054	0 192	8,499	0 0182
380130001	Burke Co , ND	1990	0 003	0 003	0 003	0 003	0 003	0 003	0 003	0 005	0 026	8,361	0 0026
380650002	Oliver Co , ND	1989	0 003	0 003	0 003	0 003	0 003	0 003	0 005	0 013	0 037	8,701	0 0029
401430174	Tulsa Co , OK	1989	0 003	0 003	0 003	0 003	0 009	0 019	0 024	0 038	0 090	8,259	0 0077
471190106	Maury Co , TN	1990	0 003	0 003	0 003	0 005	0 008	0 012	0 015	0 023	0 041	7,271	0 0064
540250001	Greenbrier Co , WV	1989	0 003	0 003	0 003	0 003	0 003	0 007	0 009	0 018	0 038	7,501	0 0037
550210008	Columbia Co , WI	1988	0 002	0 002	0 002	0 002	0 006	0 013	0 017	0 027	0 040	7,963	0 0056

[a]AIRS ID = Aerometric Information Retrieval System identification number

Source AIRS (1992)

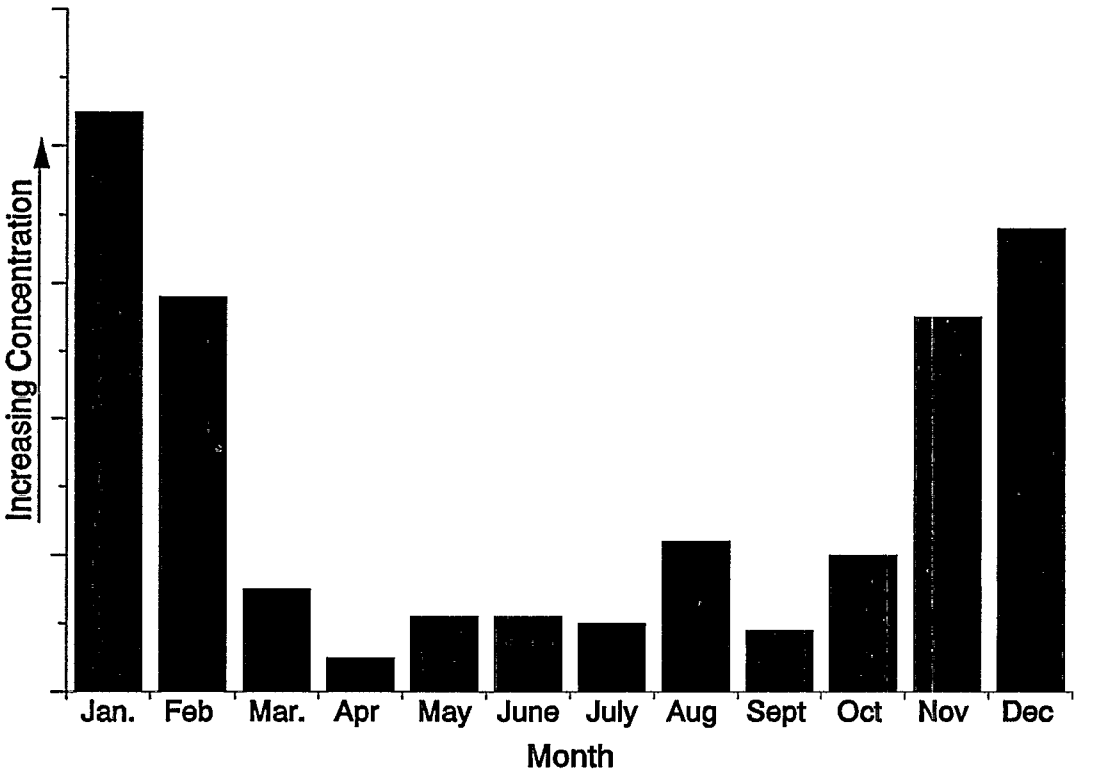


Figure 7-9. Seasonal pattern for nitrogen dioxide concentrations at rural and forested Aerometric Information Retrieval System monitoring sites.

Source: AIRS (1992)

values during the summer months There was no clear or consistent pattern in the California data sets

Studies of the joint occurrence of gaseous NO_2/sulfur dioxide (SO_2) and NO_2/ozone (O_3) have concluded that (1) the co-occurrence of two-pollutant mixtures lasted only a few hours per episode, and (2) the time between episodes is generally large (i e , weeks, sometimes months) (Lefohn and Tingey, 1984, Lane and Bell, 1984, Jacobson and McManus, 1985, Lefohn et al , 1987) Lefohn et al (1987), using hourly averaged data collected at rural sites, reported that the periods of co-occurrence represent a small portion of the potential plant growing period For human ambient exposure considerations, Lefohn and Tingey (1984) noted that, in most cases, the simultaneous co-occurrence of NO_2/O_3 was infrequent. However, for several sites located in the southern California South Coast Air Basin, the authors reported more than 450 simultaneous co-occurrences of each pollutant at

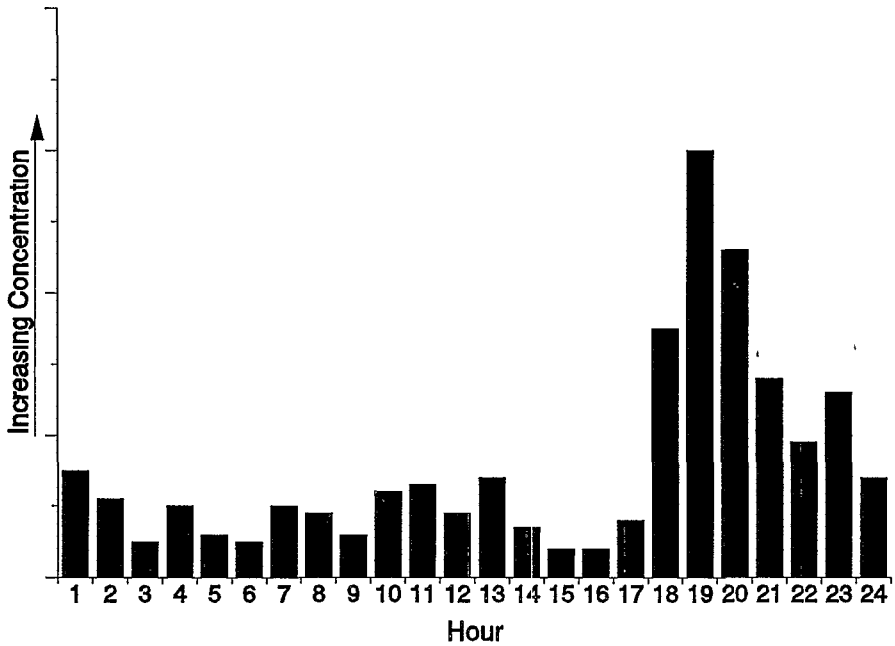


Figure 7-10. Diurnal pattern for nitrogen dioxide at rural and forested Aerometric Information Retrieval System monitoring sites.

Source AIRS (1992)

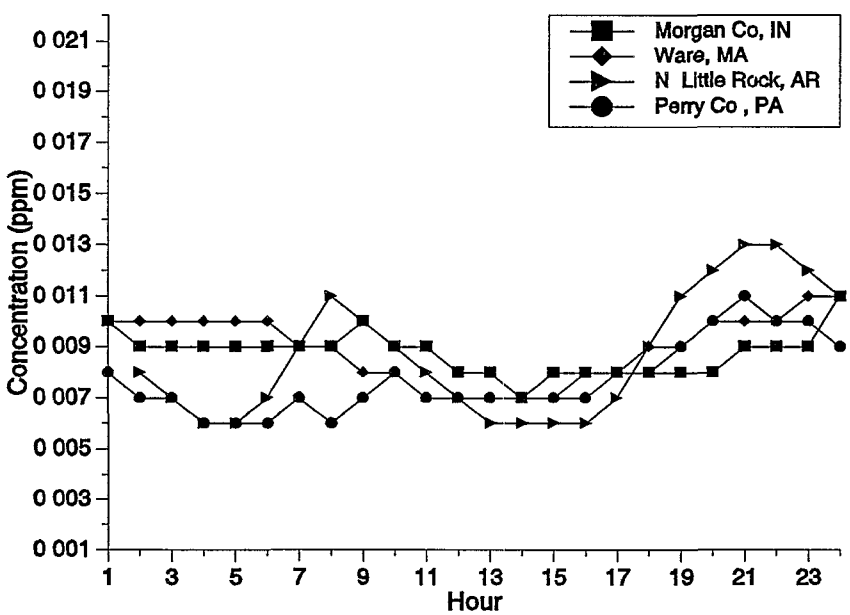


Figure 7-11. Diurnal patterns for nitrogen dioxide monthly average concentrations at selected rural forested Aerometric Information Retrieval System monitoring sites.

Source AIRS (1992)

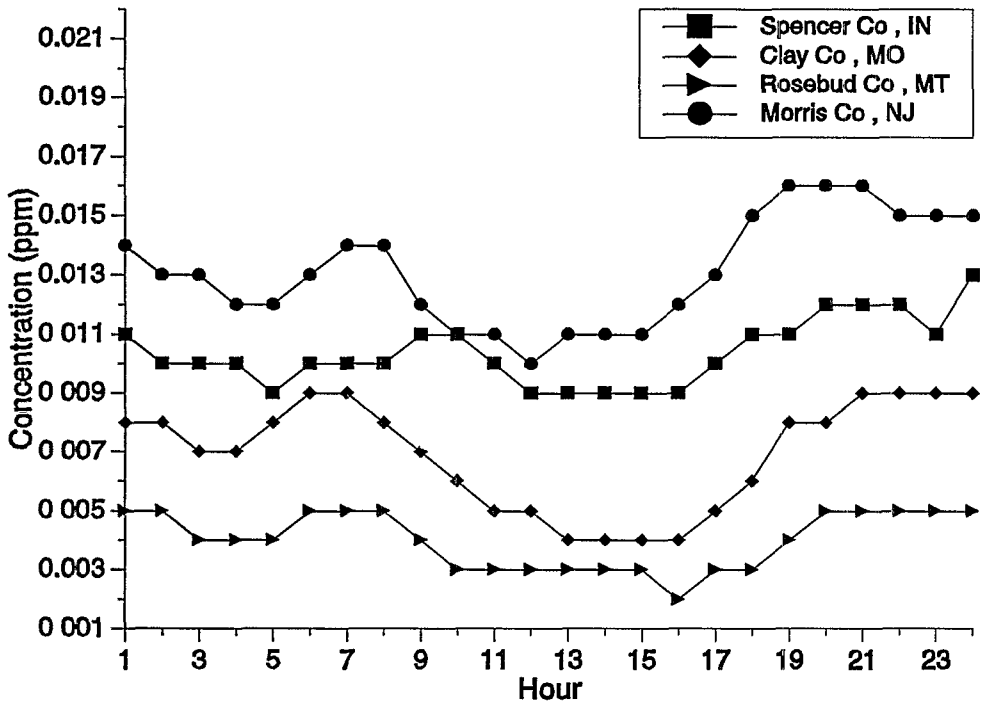


Figure 7-12. Diurnal patterns for nitrogen dioxide monthly average concentrations at selected rural agricultural Aerometric Information Retrieval System monitoring sites.

Source AIRS (1992)

hourly average concentrations equal to or greater than 0 05 ppm For Denver, CO, and San Jose, CA, more than 100 co-occurrences were reported

Table 7-14 summarizes the maximum hourly average NO concentrations reported in rural areas for the period 1988 to 1990

7.3 INDOOR AIR CONCENTRATIONS OF NITROGEN OXIDES

7.3.1 Background

Exposures to air contaminants occur across a number of microenvironments (residences, industrial and nonindustrial workplaces, community air, automobiles, public access buildings, etc.) in which people spend their time A major portion of their time is spent in the residential indoor environment (Szalai, 1972) A microenvironment is a three-dimensional

TABLE 7-14. MAXIMUM HOURLY AVERAGE NITRIC OXIDE CONCENTRATIONS (ppm) REPORTED IN RURAL AREAS, 1988 TO 1990

	Hourly Average Values			Annual Average Values		
	1988	1989	1990	1988	1989	1990
North Little Rock, AR	0 138	0 128	0 163	0 0062	0 0058	0 0056
Santa Maria, CA			0 143			0 0065
Jalama, CA			0 015			0 0050
Lompoc, CA			0 005			0 0050
Los Padres NF, CA			0 005			0 0050
Gaviota, CA			0 053			0 0059
Isla Vista, CA			0 220			0 0094
Vandenberg AFB, CA			0 014			0 0051
Adams Co , CO	0 574			0 0346		
Ware, MA	0 064	0 067	0 059	0 0060	0 0055	0 0061
Clay Co , MO	0 506	0 428	0 375	0 0130	0 0071	0 0088
St Charles Co , MO	0 370	0 348	0 444	0 0137	0 0158	0 0093
St Louis Co , MO	0 210	0 269	0 225	0 0092	0 0097	0 0089
Morris Co , NJ	0 148	0 108	0 140	0 0070	0 0077	0 0066
Burke Co , ND		0 013	0 017		0 0050	0 0050
Dunn Co , ND	0 066			0 0051		
Mercer Co , ND	0 058	0 438	0 083	0 0052	0 0056	0 0052
Oliver Co , ND	0 265	0 061		0 0052	0 0051	
Maury Co , TN			0 085			0 0064
Greenbrier Co , TN	0 027	0 053		0 0050	0 0050	
Ft Winnebago, WI		0 041			0 0052	

Source AIRS (1992)

space having a volume such that the pollutant concentration during some specific time interval is considered to be spatially defined, and usually is assumed to be spatially uniform (National Research Council, 1981) Ideally, the total exposure to a given air contaminant or category of air contaminants should be assessed over all microenvironments in evaluating adverse health or comfort effects and in formulating cost-effective mitigation efforts to reduce or minimize the risks associated with exposure

The indoor residential environment is particularly important in assessing total air contaminant exposure because (1) individuals spend the major portion of their time indoors (Szalai, 1972), (2) the highest concentrations of several important air contaminants occur indoors (National Research Council, 1981), and (3) the most susceptible segments of the population (the old, the young, and the infirm) are indoors for long periods of time In addition, weatherization programs and the use of supplemental space heaters may have

resulted in increased indoor levels of potentially hazardous air contaminants, further highlighting the relative importance of the nonindustrial indoor settings

Nitrogen oxides are introduced to indoor environments through emissions from a variety of combustion sources and through the infiltration or ventilation of air from outdoors The resulting indoor concentration, both long- and short-term averages (averaging times of seconds to weeks), is dependent on a complex interaction of several interrelated factors affecting the introduction, dispersion, and removal of NO_x These factors include, for example, such variables as (1) the type, nature (factors affecting the generating rate of NO_2), and number of sources, (2) source use characteristics, (3) building characteristics, (4) infiltration or ventilation rates, (5) air mixing between and within compartments in an indoor space; (6) removal rates and potential remission or generation by indoor surfaces and chemical transformations, (7) existence and effectiveness of air contaminant removal systems, and (8) outdoor concentrations

The above factors interact to produce a range of indoor concentrations of NO_2 The variability of NO_2 levels in residences is demonstrated in Figure 7-13 (Drye et al , 1989) This figure summarizes data collected in five areas located in four distinct geographical regions in the United States (Boston and Watertown, MA, Southern California, Portage, WI, and St. Louis, MO) during the winter for 978 residences Nitrogen dioxide levels were measured for 1-week periods using Palmes passive samplers (Palmes et al , 1976) in three locations (outdoors, kitchen, and bedroom) over a summer (not shown here) and a winter period The relationship between the means by sampling location is similar across all sites, with kitchen means higher than bedroom means and ambient means lower than bedroom means. The exception to this is Southern California, where the bedroom mean is slightly lower than the ambient mean Indoor levels of NO_2, particularly in the kitchen, exhibited considerably more variability than outdoor levels, except in Southern California The data collected for the summer period exhibited the same trends as shown for the winter data in Figure 7-13. The data in Figure 7-13 highlight not only the variability in indoor NO_2 concentrations, but also the importance of considering residential NO_2 concentrations in assessing exposures. The interaction of the factors to produce the resulting indoor concentrations shown in Figure 7-13 is usually considered within the framework of the mass-balance principle.

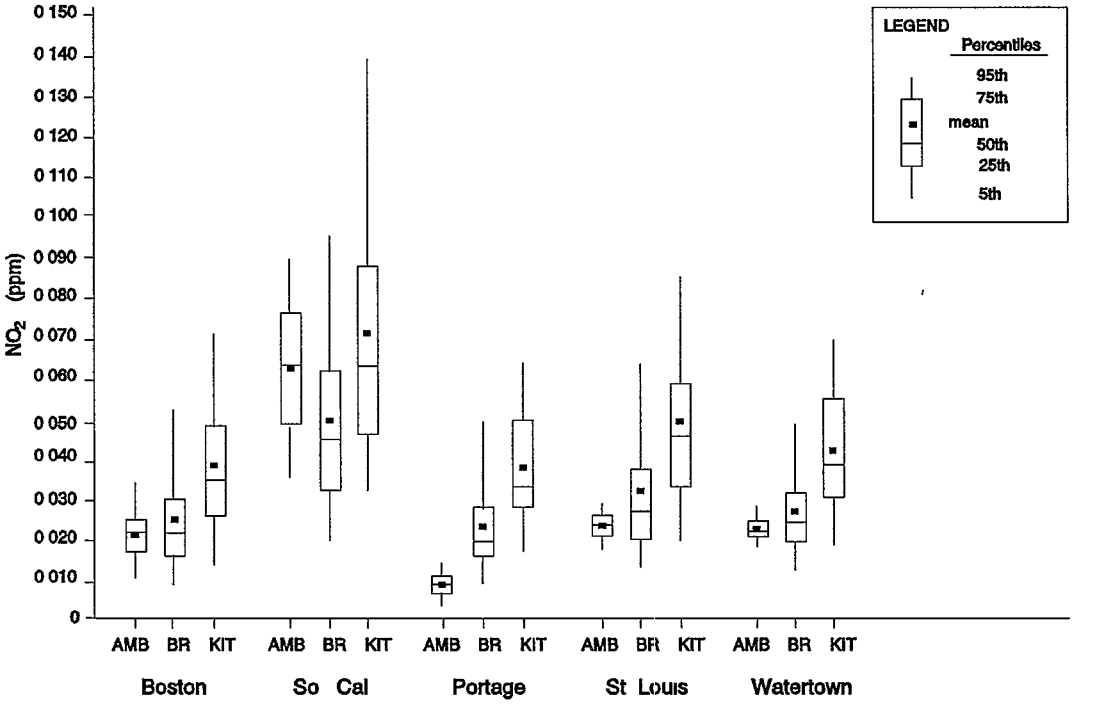


Figure 7-13. Winter nitrogen dioxide concentrations by site and sampling location.

Abbreviations
AMB = Outdoor
BR = Bedroom
KIT = Kitchen

Source Drye et al (1989)

In its simplest form, where equilibrium conditions are assumed for a single compartment with complete mixing and no air cleaner, the mass-balance model can be represented by the following equation

$$C_i = C_1 + C_2, \tag{7-1}$$

where

$$C_1 = \frac{PAC_o}{A+K} = \text{Outdoor Air Contribution}, \tag{7-2}$$

$$C_2 = \frac{S/V}{A+K} = \text{Indoor Source Contribution}, \tag{7-3}$$

and where C_1 = steady-state indoor concentration of NO_2 ($\mu g/m^3$)
C_1 = contribution to indoor NO_2 from outdoor air ($\mu g/m^3$)
C_2 = contribution to indoor NO_2 from indoor sources ($\mu g/m^3$)
P = fraction of outdoor NO_2 that penetrates the building shell
A = air exchange rate in air changes per hour—ACH (h^{-1})
C_o = outdoor NO_2 ($\mu g/m^3$)
K = removal rate of NO_2 by indoor chemicals transformations—equivalent ACH (h^{-1})
S = generation rate or source strength of NO_2 ($\mu g/h$)
V = volume of the indoor space (m^3)

This simplified form of the model could be used to evaluate NO_2 levels indoors In actuality, however, indoor spaces are often multicompartments with incomplete mixing where the source generation and contaminant removal rates and air contaminant concentrations vary considerably in time Equation 7-1 is particularly useful for determining the impact on indoor air contaminant concentrations from sources that are used over relatively long periods of time (e g , unvented kerosene or gas space heaters) where steady-state or equilibrium conditions are approximated (on the order of hours) When applied to sources that are intermittent in their use (e g , gas range or tobacco combustion), Equation 7-1 averages over the off/on periods of the sources to determine average input parameters for the model Short-term indoor concentrations (on the order of seconds or minutes) of air contaminants associated with sources whose use varies considerably with time can be modeled with the differential version of Equation 7-1 (National Research Council, 1981) when detailed information is available on the time variability of the source use, mixing, and removal terms Field data on short-term variability of contaminant concentrations and associated variables regulating the introduction, dispersal, and removal of NO_2 exist for small numbers of "test-house" studies where test conditions were partially controlled, but have not typically been collected for homes under normal occupancy use conditions The test-house data, nevertheless, do provide insights into the dynamics of the generation, dispersal, and removal of contaminants in homes

Outdoor levels of NO_2 play an important role in determining indoor levels The available ambient NO_2 data recorded by stationary monitors are reviewed in Section 7 2 Penetration of NO_2 through the building envelope (P) and removal by indoor surfaces or chemical transformations (K) are related to its chemical reactivity and to the building

construction materials and furnishings and other factors No direct measurements of the penetration factor for NO_2 through building shells are available The removal rate, K, can vary from less than 0 1 to longer than 2 0 h^{-1} The factors influencing the removal rate of NO_2 are discussed in Section 7 3 8 Infiltration rates (A) and house volumes (V) can vary by an order of magnitude or more Infiltration rates from 0 1 to 2 0 h^{-1} and house volumes from 100 to more than 700 m^3 are within the range encountered (Grimsrud et al , 1982, Grot and Clark, 1979, Billick, 1991, Koutrakis et al , 1992) Factors impacting the source strengths for NO_2 emissions from indoor source are reviewed in Chapter 4

Section 7 3 summarizes the available data on the levels of NO_2 indoors, C_1, largely within the framework of the simplified mass-balance model shown in Equation 7-1 Nitrogen dioxide concentrations measured indoors in homes with no known sources, C_1, are compared to outdoor levels as a function of season of the year, housing type, and region Data on average and peak NO_2 levels indoors as a function of individual and combinations of indoor sources, C_2, are reviewed with an emphasis on attempting to approximate the average contribution to indoor levels as a function of source type, housing type, and region Data on the spatial distribution of NO_2 between and within rooms indoors as a function of source type are reviewed, as are recent data on the removal of NO_2 by indoor surfaces A gaseous product of NO_2 reactivity, HONO, has recently been identified as a potentially important indoor air contaminant Section 7 4 reviews the recent data on indoor levels of HONO and the variables related to its formation Available results on efforts to model (both empirical and physical/chemical models) indoor NO_2 levels are presented and discussed, as are efforts to use chamber-generated emission factors for major indoor sources to predict levels in homes under actual use conditions The impact of infiltration rates, air exchange rates between rooms, and house volumes are not addressed

Nitrogen dioxide is the major NO_x species considered in this chapter because a considerable amount of indoor sampling data exists for it and exposure to it is of health importance Indoor concentrations of HONO (Section 7 4) are also considered because of speculation that it may be of health interest The residential indoor environment has been the major indoor microenvironment for which NO_2 levels have been measured There are few data available on NO_2 levels in other indoor microenvironments Section 7 3 focuses primarily on findings of major field studies that have evaluated NO_2 levels in residential

indoor microenvironments in order to approximate the range of concentrations indoors associated with indoor sources Data collected in test-house studies are drawn upon to highlight various aspects of the dispersal and removal of NO_2 indoors

7.3.2 Residences Without Indoor Sources

In the absence of any indoor source of NO_2, indoor NO_2 concentrations are a function of the building envelope penetration factor (P), the air exchange rate (A), the reactivity rate (K), and the outdoor concentration (C_o) This condition is represented in Equation 7-1 for steady-state conditions when S/V is set to zero as

$$C_i = \frac{PAC_o}{A+K} \tag{7-4}$$

There are no chamber or field studies that have measured the penetration factoi (P) for NO_2 or field studies that have separate measures of both ventilation and the reactivity rate for NO_2. Indirect estimates of K from field ventilation data have been made (Wilson et al , 1986). Limited field data for ventilation rates in residences exist (e g , Grimsrud et al , 1982; Grot and Clark, 1979, Wilson et al , 1986, Sheldon et al , 1989, New York State Department of Health, 1989, Koutrakis et al , 1992) There have, however, been several field studies that have investigated levels of NO_2 in residences As part of these study designs, indoor and outdoor levels of NO_2 were monitored in subsamples of homes that had no known indoor sources of NO_2 The indoor/outdoor ratios of NO_2 measured in these studies provide general information on the role of the penetration factor, the air exchange rate, and the reactivity rate ($PA/[A+K]$) in impacting indoor NO_2 concentrations in residences without known NO_2 sources

Table 7-15 presents the average outdoor NO_2 concentrations measured in several large field studies and the corresponding average NO_2 indoor/outdoor ratios by location in the residences without indoor NO_2 sources The table also presents a breakdown (when available) of the data by geographical location, housing type, and season of the year

The average indoor/outdoor ratios for all the studies in Table 7-15 are less than 1, as would be predicted by Equation 7-2 when indoor sources are not present The exceptions are the winter Kingston, TN, ratio for the kitchen and bedroom and the kitchen summer ratio for

TABLE 7-15. AVERAGE OUTDOOR CONCENTRATIONS OF NITROGEN DIOXIDE AND AVERAGE INDOOR/OUTDOOR RATIOS IN HOMES WITHOUT KNOWN INDOOR SOURCES FROM FIELD STUDIES OF PRIVATE RESIDENCES[a]

Location	Housing Type	Averaging Time	Seasons	Number of Homes	Average NO_2 Outdoors (ppm)	Indoor/Outdoor Ratios		Reference
						Kitchen	Bedroom	
Southern California	Mixed	7 days	Summer	70	0 0381	0 80	0 75	Wilson et al (1986)
			Spring	100	0 0231	0 72	0 60	
			Winter	69	0 0483	0 56	0 47	
New Haven, CT	Single-family unattached	14 days	Winter	60	0 0070	0 56	0 55	Leaderer et al (1986a)
Albuquerque, NM	Mixed	14 days	Winter 1	60	0 0141	--	0 50	Marbury et al (1988)
			Winter 2	56	0 0195	0	0 32	
California	Mobile homes	7 days	Summer	46	0 0137	0 61	0 54	Petreas et al (1988)
			Winter	23	0 0236	0 27	0 26	
Portage, WI	Mixed	7 days	Summer	47	0 0081	0 91	0 72	Quackenboss et al (1986)
			Winter	47	0 0091	0 65	0 45	
Tucson, AZ	Mixed	14 days	Summer	56	0 0106	0 86	0 76	Quackenboss et al (1987)
			Spring/Fall	41	0 0136	0 71	0 55	
			Winter	23	0 0195	0 64	0 52	
Boston, MA	Mixed	14 days	Summer	117	0 0168	0 76	0 75	Ryan et al (1988)
			Fall	117	0 0200	0 43	0 40	
			Winter/Spring	124	0 0178	0 53	0 47	
Northern Central Texas	Single-family unattached	5 days	Winter	9	0 0285			Koontz et al (1986)
Suffolk County, NY	Single-family unattached	7 days	Winter	49	0 0188	0 47	--	Research Triangle Institute (1990)
Onondago County, NY	Single-family unattached	7 days	Winter	66	0 0115	0 70	--	
Portage, WI	Single-family unattached	7 days	Average over all seasons	25	0 0068	0 65	0 51	Spengler et al (1983)
Watertown, MA	Not given	3-4 days	November	18	0 0196	0 65	0 51	Clausing et al (1984)
			December	10	0 0244	0 39	0 30	

TABLE 7-15 (cont'd). AVERAGE OUTDOOR CONCENTRATIONS OF NITROGEN DIOXIDE AND AVERAGE INDOOR/OUTDOOR RATIOS IN HOMES WITHOUT KNOWN INDOOR SOURCES FROM FIELD STUDIES OF PRIVATE RESIDENCES[a]

Location	Housing Type	Averaging Time	Seasons	Number of Homes	Average NO_2 Outdoors (ppm)	Indoor/Outdoor Ratios		Reference
						Kitchen	Bedroom	
Middlesbrough	Not given	7 days	Winter	87	0 0186	0 97	0 75	Goldstein et al (1979)
Middlesbrough	Not given	7 days	Winter	15	0 0184	--	0 75	Melia et al (1982)
Los Angeles	Mixed	2 days	Winter	47	0 0442	--	0 51	Spengler et al (1992a,b)
			Not Winter	124	0 0305	--	0 57	
Portage, WI	Mixed	7 days	Summer	176	0 0069	0 91	0 82	Butler et al (1990)
			Winter	205	0 0085	0 73	0 65	
Kingston, TN	Mixed	7 days	Summer	291	0 0093	0 7	0 63	
			Winter	306	0 0121	1 15	1 01	
Steubenville, OH	Mixed	7 days	Summer	53	0 0256	0 74	0 68	
			Winter	71	0 0212	0 66	0 58	
Topeka, KS	Mixed	7 days	Summer	171	0 0081	1 0	0 88	
			Winter	208	0 0109	0 81	0 79	
Watertown, MA	Mixed	7 days	Summer	70	0 0212	0 77	0 71	
			Winter	77	0 0204	0 52	0 40	
St Louis, MO	Mixed	7 days	Summer	176	0 0140	0 92	0 83	
			Winter	202	0 0167	0 84	0 79	

[a]NO_2 = Nitrogen dioxide
Mixed = Single-family attached, single-family unattached, condominium apartment

Topeka, KS The high ratios in these locations suggest that significant indoor sources existed in some of the houses thought not to have sources Exceptionally high standard deviations were reported in indoor concentrations for these studies (Butler et al , 1990) relative to the outdoor levels observed

The indoor/outdoor ratios reported for the studies in Table 7-15 show general trends related to season and location in the residence Average ratios are highest in the summer and lowest in the winter, with the ratios in the spring and fall period falling between the winter and summer values The highest ratios are found for the kitchen and lowest for the bedroom, with the living room values in between There are not enough data to determine if the average ratios exhibit any differences as a function of housing type or geographical location, although these studies were conducted in widely different climate regions with different housing and demographic characteristics

The ratios listed in Table 7-15 are calculated from the average indoor and outdoor concentrations reported for each study listed. These studies typically did not report the standard deviations or standard errors of the average indoor/outdoor ratios from which the above observations are drawn, thus not allowing a test for statistical significance of the trends The distributions of the ratios by season and location in the residence were also not reported Some studies have reported on the distribution of the indoor/outdoor ratios for residences without sources

Leaderer et al (1986a) reported an overall house NO_2 indoor/outdoor ratio of 0 58 ± 0 31 (n = 123) for the winter sample period in the New Haven, CT, area, demonstrating the variability of the ratio The distributions of 2-week indoor to ambient NO_2 ratios for homes without known indoor sources in three U S cities (Portage, WI, Kingston/Harriman, TN, and Steubenville, OH) were recently reported (Spengler et al , 1992b) A box plot of the data is presented in Figure 7-14 The figure demonstrates the lack of normality in the ratios and considerable variability in the ratios The variability could be due to several factors, including failure to account for existence of indoor sources (attached garages, backdrafting and faulty or disconnected flues, cigarette smoking, unvented combustion sources, etc), variations in infiltration rates, and differences in removal rates related to interior furnishings

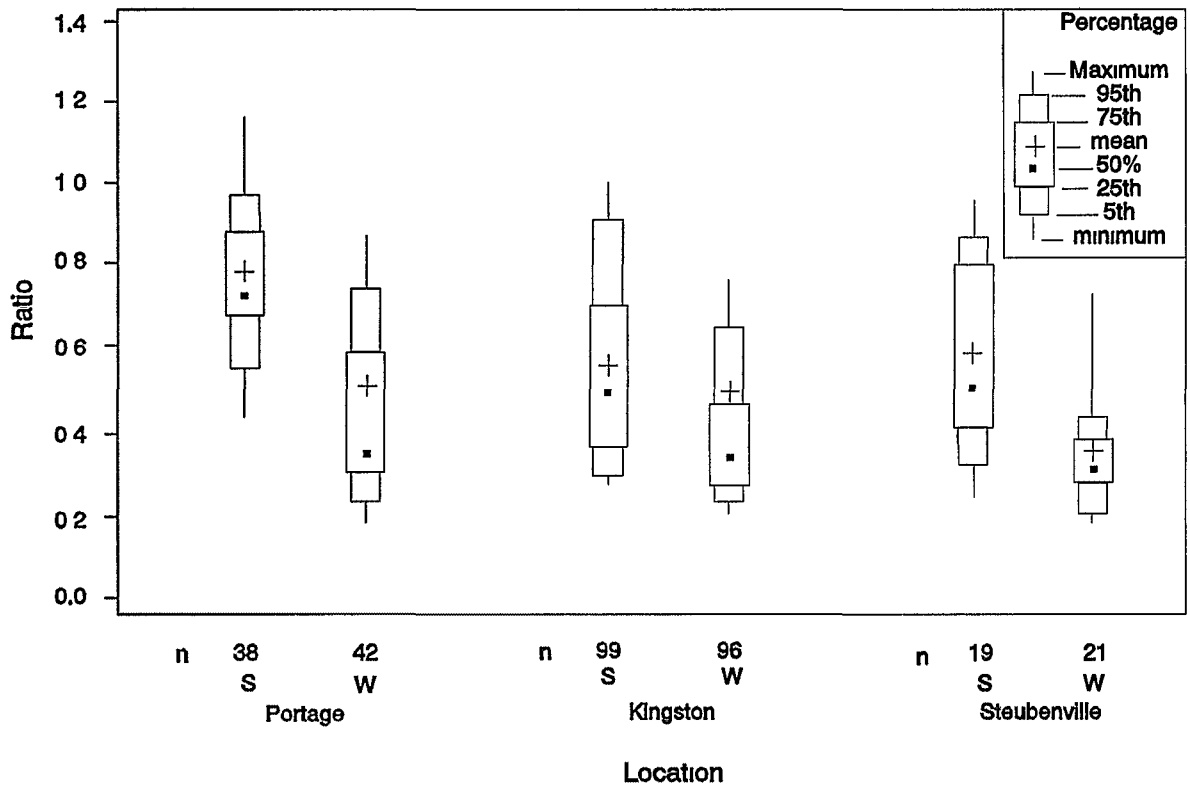


Figure 7-14. Ratio of average indoor nitrogen dioxide to ambient nitrogen dioxide concentrations by season and location in homes without a nitrogen dioxide source.

Abbreviations
S = Summer
W = Winter
n = Number of homes observed

Source. Spengler et al (1992a)

Distributions of indoor and outdoor concentrations by season have been reported for two large field studies These data can be evaluated for indoor and outdoor concentrations for residences without known indoor NO_2 sources The cumulative frequency distributions of concentrations of NO_2 for residences without known indoor sources by location in the residence and for outdoors for two different geographic areas (Southern California and New Haven, CT) during the winter season are shown in Figures 7-15 and 7-16 A similar

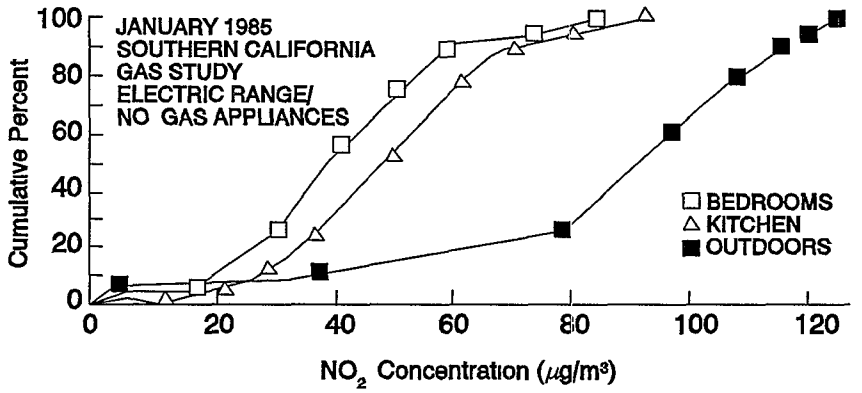


Figure 7-15. Cumulative frequency distribution of nitrogen dioxide concentrations (1-week sampling period) by location for homes with no known gas appliances for a winter period in Southern California.

Source Wilson et al (1986)

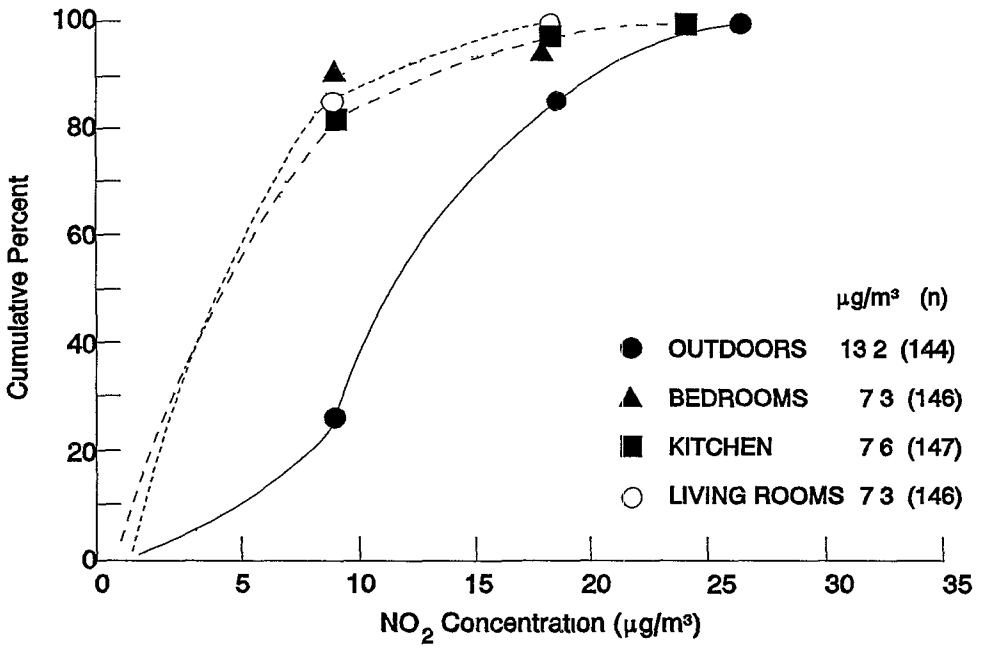


Figure 7-16. Cumulative frequency distribution and arithmetic means of nitrogen dioxide concentrations (2-week sampling period) by location for homes with no kerosene heater and no gas range for a winter period in the New Haven, CT, area.

Source Leaderer et al (1984)

cumulative frequency distribution for the summer period for homes monitored in the Southern California Gas Company study is shown in Figure 7-17 The winter distributions for the two studies (Figures 7-15 and 7-16) are similar despite the large differences in outdoor concentrations Figures 7-15 and 7-16 highlight the substantial differences in indoor and outdoor concentrations during the winter period Figures 7-15 and 7-17, for the same population of homes in the Southern California Gas Company study, highlight the differences in the distributions of NO_2 concentrations indoors relative to the outdoor levels as a function of season (winter versus summer) The distributions are different, with indoor levels much closer in concentration to outdoor levels in the summer period

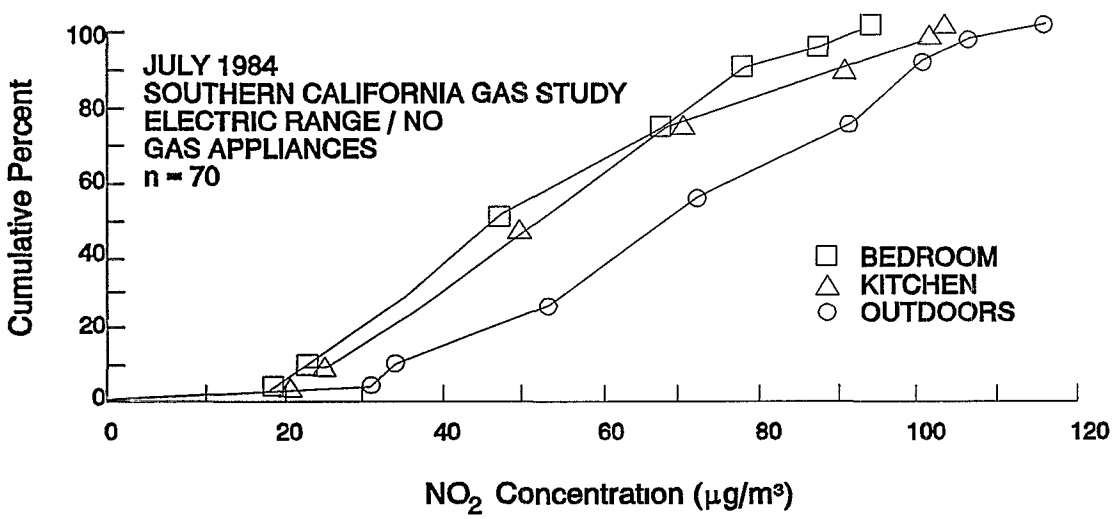


Figure 7-17. Cumulative frequency distribution of nitrogen dioxide concentrations (1-week sampling period) by location for homes with no gas appliances for a summer period in Southern California.

Source: Wilson et al (1986)

The variability of the indoor/outdoor ratio by season observed in Table 7-15 is clearly demonstrated in a study in the United Kingdom by Atkins and Law (1987) In this study, measurements of 2-week NO_2 concentrations indoors and outdoors over a 12-mo period were made in three houses without any known indoor source of NO_2 The results, Figure 7-18, show a pronounced temporal trend The seasonal variability in the ratio is in part due to

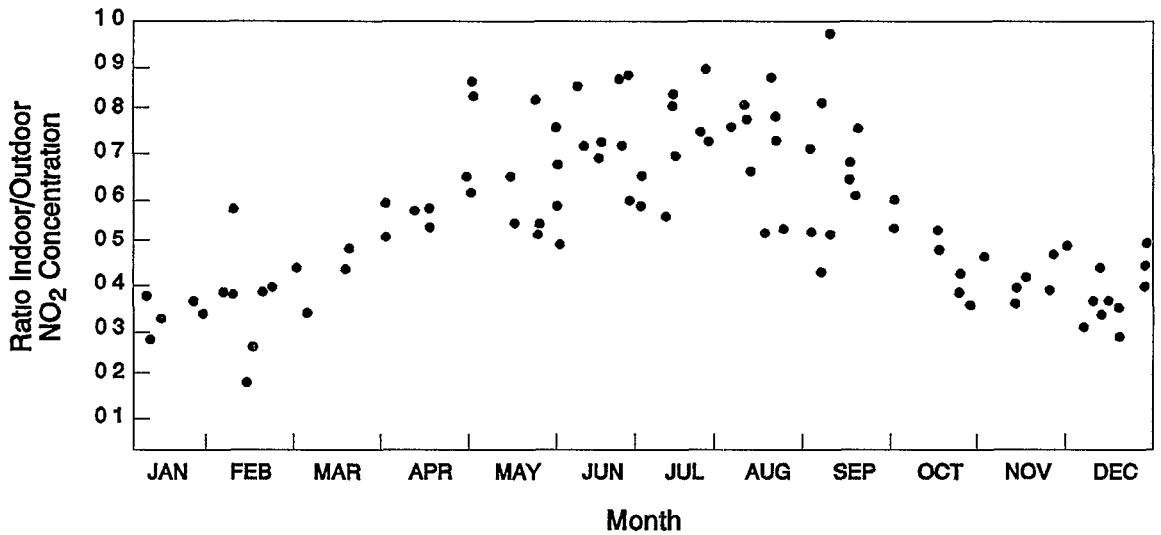


Figure 7-18. Indoor/outdoor nitrogen dioxide concentration ratios (2-week sampling periods) as a function of time for three homes in the United Kingdom without indoor nitrogen dioxide sources.

Source Atkins and Law (1987)

seasonal variability in the airtightness of the residences. In the winter months, outside doors, windows, and other openings are closed and air entering the residences infiltrates through the building envelope, with more effective removal of outdoor NO_2 With lower air exchange rates in the winter, the $A/(A+K)$ term in Equation 7-2 is smaller, this term approaches 1 in summer conditions with higher air exchange rates During the summer period, windows and doors are more typically open, minimizing removal by the building envelope
No information is available on the impact on the summer ratio for homes with air conditioning Seasonal differences in the ratio and variability in the ratio within a season from residence to residence are also likely due to variations in the penetration factor and reactivity rate for NO_2 Variations in the penetration factor and reactivity rate, like ventilation, can have a substantial impact on the indoor/outdoor ratios of NO_2 There is, however, little information on the variability of these two additional factors

Indoor concentrations of NO_2 in residences without known indoor sources of NO_2 are typically dominated by outdoor levels Indoor levels are usually below outdoor levels in such homes, thus providing some degree of protection from outdoor concentrations. The

indoor/outdoor NO_2 ratios in these homes are typically lower in the winter than in the summer and lower in the bedroom than in the kitchen The ratios by season and location in a residence show considerable variability The factors impacting this variability are not well characterized.

7.3.3 Residences with Gas Appliances

In the 1980 census, it was estimated that gas (natural gas and liquid propane) was used for cooking, heating water, or drying clothes in approximately 45 1% of all homes in the United States (U S Bureau of the Census, 1982) The 1990 U S census asked the more general question of what fuel is used most for heating without the specific inquiry for fuel used for water heating and for cooking Thus the results for 1990 of 56 7% using natural gas or liquid propane may not be directly comparable to the earlier result (U S Bureau of the Census, 1989, 1992). In some other countries (e g , the Netherlands), nearly 100% of the homes may have gas appliances Unvented, partially vented, and improperly vented gas appliances, particularly the gas cooking range and oven, represent an important source category of NO_2 emissions into the indoor residential environment Emissions of NO_2 from these gas appliances (the source term, S, in Equation 7-1) are a function of a number of variables related to source type (range top or oven, water heater, dryer, number of pilot lights, burner design, etc.), source condition (age, maintenance, combustion efficiency, etc.), source use (number of burners used, frequency of use, fuel consumption rate, length of use, improper use, etc), and venting of emissions (existence and use of outside vents over ranges, efficiency of vents, venting of gas dryers, etc) The available data on emissions rates from gas appliances and other indoor sources are presented in Section 4 3

The factors that affect NO_2 emissions from gas appliances into residences in combination with the residence factors (house volume, number of rooms, infiltration rate, room and whole-house mixing rate, pollutant decay rate, etc) result in indoor residential NO_2 concentrations associated with gas appliance use The contribution of NO_2 emissions from gas appliances to indoor concentrations in simple terms can be represented by the source contribution term of Equation 7-1

$$C_2 = \frac{S/V}{A + K} = \text{Indoor Source Contribution} \quad (7\text{-}3)$$

This assumes complete mixing in and between rooms and representation of a highly time-varying source as an equivalent constant source When the contribution of the outdoor NO_2 levels is added (Equation 7-2), the resultant indoor concentration is determined (Equation 7-1)

7.3.3.1 Average Indoor Concentrations and Estimated Source Contributions

The presence and use of a gas range in a residence result in higher indoor levels of NO_2 than in homes with electric cooking ranges This is clearly demonstrated in data collected as part of a study of respiratory illnesses in infants and NO_2 exposure (Samet et al , 1992) In this study, NO_2 concentrations were obtained over 2-week periods outdoors and in infants' bedrooms using Palmes passive samplers for a sample of approximately 700 homes with and approximately 315 homes without gas appliances The summary results averaged across seasons are shown in Figure 7-19 Nitrogen dioxide concentrations in homes with gas stoves are higher than those found outdoors and considerably higher than levels found in homes with electric stoves Levels in homes with gas stoves are higher in the kitchen than in the bedroom Bedroom concentrations in homes with electric stoves are less than outdoor levels. Bedroom levels in homes with gas stoves are higher than those in homes with electric stoves and are higher than outdoor concentrations Concentrations of NO_2 in homes with gas stoves also demonstrated more variability than levels in homes with electric stoves

The importance of presence and use of gas appliances on indoor NO_2 concentrations is also demonstrated in a study conducted Chattanooga, TN (Parkhurst et al , 1988) In this study, weekly NO_2 concentrations were measured over four periods during a 10-week sampling period for 235 residences in five housing developments Four of the developments were served by natural gas heating (vented) and appliances, and one development was served by all electric heating and cooking Measured average indoor and outdoor concentrations by development are shown in Figure 7-20 Houses in the development served by electric heating and cooking had indoor levels that were 80% of the outdoor levels On the other hand, NO_2 concentrations in homes in the developments served by natural gas for cooking and heating were 2 6 to 5 8 times the outdoor levels In these homes, kitchen levels were

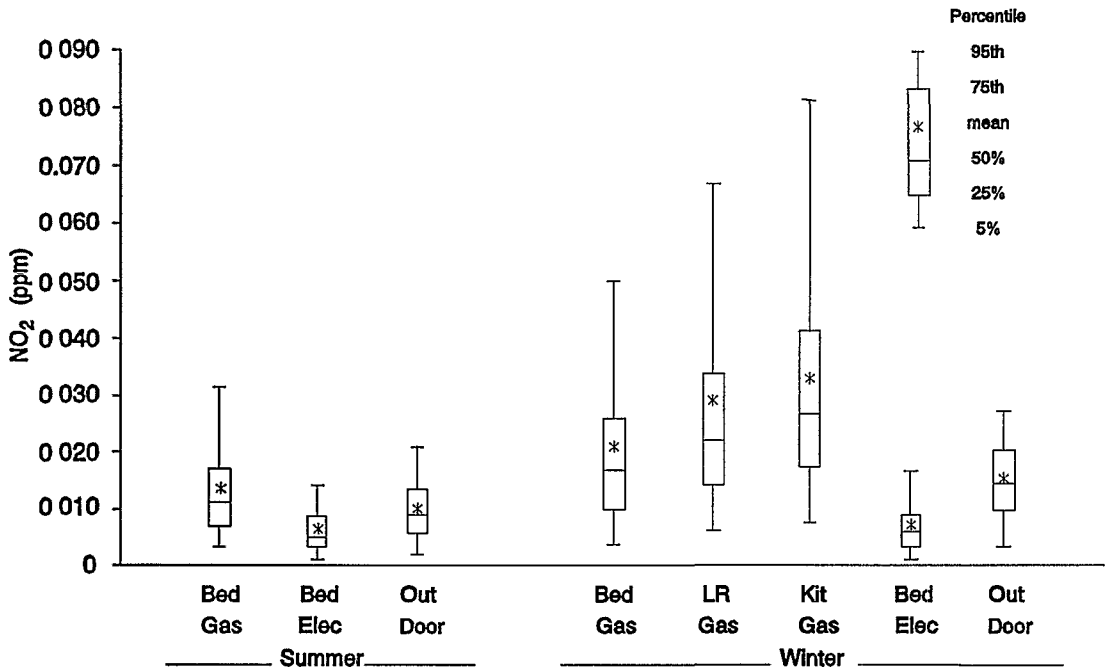


Figure 7-19. Concentrations of nitrogen dioxide (ppm) from October through March during 1988 and 1989, Albuquerque, NM. Concentrations are provided for infants' bedrooms in homes with gas and electric stoves, outdoors, and for the kitchen and living room for homes with gas stoves, by season.

Source· Samet et al (1992)

higher than activity room levels, and levels in homes that reported the use of their gas stove for heating were about 85 ug/m^3 (0 045 ppm) higher than in those that did not

There have been a large number of field studies, both in the United States and in Europe, that have sought to determine the levels (averaged over several days or more) of NO_2 in residences associated with the use of gas appliances and, more specifically, gas ranges and ovens. These field studies have been directed toward both assessing exposures to complement epidemiologic studies and to determine the range and distribution of indoor NO_2 levels in homes with gas cooking A summary of the findings of the major field studies (those with large sample sizes) directed toward assessing residential indoor NO_2 levels in homes with gas appliances is shown in Table 7-16 The results of 18 such studies (15 U S studies, 2 British studies, and a summary of several studies conducted in the Netherlands) are

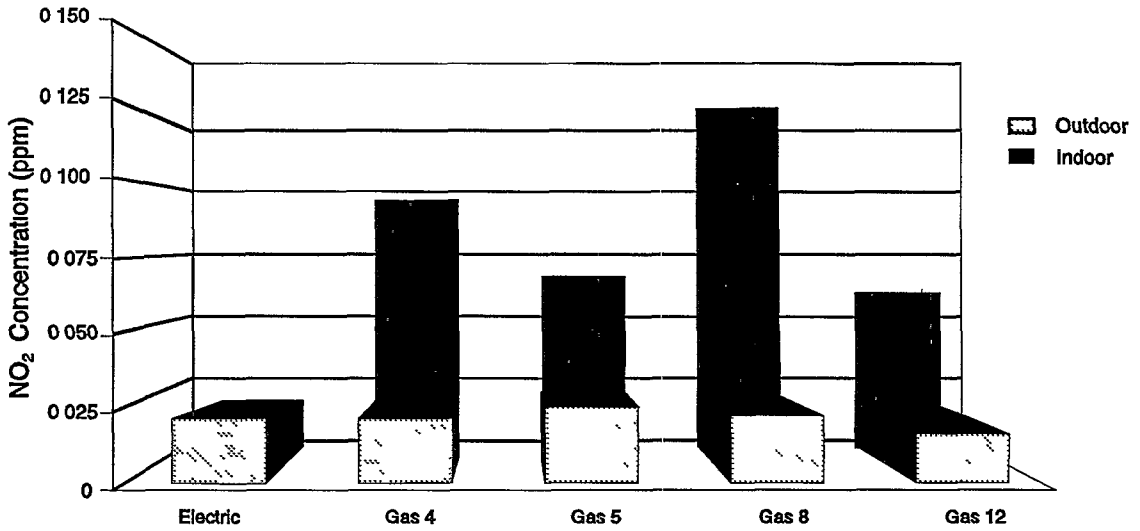


Figure 7-20. Indoor versus outdoor nitrogen dioxide in five housing developments in Chattanooga, TN. One development was all electric and four had gas heating and appliances (Numbers 4, 5, 8, and 12).

Source Parkhurst et al (1988)

presented as the average NO_2 concentrations measured outdoors and at various locations indoors by geographic location, housing type, sampling time, and the type of cooking device present Butler et al (1990) and Neas et al (1991) report data from six locations

Many of the homes included in Table 7-16 may have had other gas appliances, which may or may not have been explicitly described or analyzed, or other sources (attached garages, leaky flues, etc) The presence of kerosene heaters was noted in varying percentages of the residences sampled in the six locations reported by Butler et al (1990) and Neas et al (1991). It should be emphasized that only the average NO_2 concentrations measured in each study are presented and that there was a broad variation of concentrations associated with each mean The distributions are not normal This variation can be seen in Figure 7-14

All measurements in Table 7-16 employed passive NO_2 monitors (Palmes et al , 1976) except for the Spengler et al (1992b) study in California, which used passive badges (Yanagisawa and Nishimura, 1982, Lee et al , 1992) Table 7-16 also presents estimates of

TABLE 7-16. INDOOR AND OUTDOOR CONCENTRATIONS OF NITROGEN DIOXIDE IN HOMES WITH GAS APPLIANCES, AND THE CALCULATED AVERAGE CONTRIBUTION OF THOSE APPLIANCES TO INDOOR RESIDENTIAL NITROGEN DIOXIDE LEVELS[a]

						Average Measured NO_2 (ppm)				Indoor NO_2 Due to Source (ppm)				
Location	Housing Type	Averaging Time	Gas Appliances Furnace	Season	Number of Homes	Outdoors	Kitchen	Bedroom	Other	Kitchen	Bedroom	Other	Comment[b]	Reference
Southern California	Mixed	7 days	Oven/range w/wo pilot lights	Summer	147	0 040	0 049	0 036	—	0 016	0 006	—	1,2	Wilson et al (1986)
				Spring	202	0 026	0 042	0 027	—	0 019	0 012	—	1,2	
				Winter	141	0 055	0 054	0 037	—	0 025	0 011	—	1,2	
			Oven/range pilots	Winter	98	0 057	0 060	0 040	—	0 028	0 014	—	1,2	
			Oven/range no pilots	Winter	38	0 051	0 039	0 028	—	0 011	0 004	—	1,2	
			Water heater in home	Winter	21	0 049	0 031	0 027	—	0 006	0 006	—	1,2,3	
			Wall furnace	Winter	90	0 069	0 085	0 060	—	0 026	0 020	—	1,4	
			Floor furnace	Winter	42	0 063	0 094	0 067	—	0 035	0 023	—	1,4	
New Haven, CT	Single family unattached	14 days	Oven/range w/wo pilot	Winter	42	0 008	0 024	0 015	0 016	0 020	0 011	0 012	1,5	Leaderer et al (1986a)
Albuquerque, NM	Mixed	14 days	Oven/range w/wo pilot	Winter	82	0 019	—	0 036	0 041	—	0 024	0 031	1,5,6	Marbury et al (1988)
				Winter	75	0 020	—	0 020	0 039	—	0 024	0 032		
California	Mobile homes	7 days	Oven/range w/wo pilot	Summer	265	0 011	0 023	0 016	—	0 016	0 010	—		Petreas et al (1988)
				Winter	231	0 022	0 028	0 020	—	0 022	0 014	—	1,7	
Portage, WI	Mixed	7 days	Oven/range w/wo pilot	Summer	36	0 006	0 021	0 011	0 016	0 015	0 007	0 011		Quackenboss et al (1986)
				Winter	34	0 008	0 037	0 017	0 027	0 032	0 008	0 022	1,8	
Tucson, AZ	Mixed	14 days	Oven/range w/wo pilot	Summer	13	0 012	0 021	0 014	0 016	0 010	0 004	0 006		Quackenboss et al (1987)
				Spring/Fall	11	0 019	0 024	0 017	0 022	0 011	0 006	0 004		
				Winter	10	0 024	0 032	0 023	0 027	0 017	0 011	0 013	1,9	
Boston, MA	Mixed	14 days	Oven/range w/wo pilot	Summer	301	0 022	0 035	0 024	0 027	0 018	0 008	0 010		Ryan et al (1988), Ryan and Spengler (1992)
				Fall	277	0 023	0 039	0 025	0 028	0 030	0 016	0 018		
				Wint /Sprg	298	0 021	0 039	0 026	0 029	0 028	0 016	0 018	1,9	

TABLE 7-16 (cont'd). INDOOR AND OUTDOOR CONCENTRATIONS OF NITROGEN DIOXIDE IN HOMES WITH GAS APPLIANCES, AND THE CALCULATED AVERAGE CONTRIBUTION OF THOSE APPLIANCES TO INDOOR RESIDENTIAL NITROGEN DIOXIDE LEVELS[a]

						Average Measured NO_2 (ppm)				Indoor NO_2 Due to Source (ppm)				
Location	Housing Type	Averaging Time	Gas Appliances Furnace	Season	Number of Homes	Outdoors	Kitchen	Bedroom	Other	Kitchen	Bedroom	Other	Comment[b]	Reference
Northern Central Texas	Single family unattached	5 days	Oven/range w/wo pilot	Winter	22	0 018	---	---	0 029	---	---	0 020	1,10	Koontz et al (1986)
Suffolk Co , NY	Single-family unattached	7 days	Oven/range w/wo pilot	Winter	42	0 020	0 041	---	0 028	0 032	---	0 020		Research Triangle Institute (1990)
Onondago Co , NY	Single-family unattached	7 days	Oven/range w/wo pilot	Winter	56	0 016	0 033	0	0 027	0 022	---	0 014	1,9	
New York, NY	Apartments	2 days	Oven/range	Summer	14	0 058	0 065	0 052	0 056	0 016	0 003	0 007		Goldstein et al (1985)
				Fall 1	15	0 032	0 051	0 034	0 038	0 028	0 012	0 015		
				Fall 2	9	0 039	0 057	0 035	0 040	0 024	0 008	0 013		
			w/wo pilot	Winter 1	8	0 053	0 064	0 040	0 050	0 032	0 008	0 019	9,11,12	
				Winter 2	18	0 040	0 067	0 033	0 043	0 043	0 010	0 020		
				Spring	13	0 050	0 064	0 043	0 052	0 029	0 008	0 018		
Portage, WI	Single-family unattached	7 days	Natural gas oven/range w/o pilots	All seasons	36	0 008	0 035	0 019	---	0 029	0 015	---		Spengler et al (1983)
			LP gas oven/range w/o pilots	All seasons	76	0 006	0 035	0 020	---	0 031	0 016	---	1,13	
Watertown, MA	Not given	3-4 days	Gas cooking	November	60	0 020	0 039	0 024	0 027	0 027	0 014	0 018		Clausing et al (1984)
				December	51	0 024	0 046	0 024	0 032	0 036	0 017	0 023	1,9,14	
Middlesbrough, UK	Not given	7 days	Gas cooking w/o pilots	Winter	428	0 019	0 113	0 031	---	0 095	0 013	---	1,15	Goldstein et al (1979)
Middlesbrough, UK	Not given	7 days	Gas cooking	Winter	183	0 018	---	0 032	0 044	---	0 021	0 032	1,16	Melia et al (1982)
Arnet Enschede	Not given	7 days	Gas cooking w/o pilots Water heaters	Fall/Winter	294	0 019	0 063	--	0 051	0 051	--	0 020		Noy et al (1984)
Ede	Not given	7 days	""	""	173	0 023	0 060	0 023	0 027	0 047	0 009	0 015		
Vlagttwedde	Rural area	7 days	""	""	162	0 015	0 057	0 013	0 027	0 048	0 004	0 018		
Rotterdam I	Inner City	7 days	""	""	228	0 024	0 076	0 027	0 042	0 062	0 013	0 028		
Rotterdam II	Inner City	7 days	""	""	102	0 024	0 076	0 034	0 039	0 062	0 020	0 024	9,17	

TABLE 7-16 (cont'd) . INDOOR AND OUTDOOR CONCENTRATIONS OF NITROGEN DIOXIDE IN HOMES WITH GAS APPLIANCES, AND THE CALCULATED AVERAGE CONTRIBUTION OF THOSE APPLIANCES TO INDOOR RESIDENTIAL NITROGEN DIOXIDE LEVELS[a]

						Average Measured NO_2 (ppm)				Indoor NO_2 Due to Source (ppm)				
Location	Housing Type	Averaging Time	Gas Appliances Furnace	Season	Number of Homes	Outdoors	Kitchen	Bedroom	Other	Kitchen	Bedroom	Other	Comment[b]	Reference
Watertown, MA	Mixed	7 days	Oven/range w/wo pilot	Summer	162	0 021	0 030	0 023	--	0 014	0 007	--	1	Butler et al (1990), Neas et al (1991)
				Winter		0 022	0 041	0 025	--	0 030	0 017	--		
Kingston, TN	Mixed	7 days	Oven/range w/wo pilot	Summer	91	0 015	0 018	0 015	--				1,18	
				Winter		0 015	0 055	0 043	--					
St Louis, MO	Mixed	7 days	Oven/range w/wo pilot	Summer	208	0 017	0 032	0 020	--	0 016	0 006		1,19	
				Winter		0 019	0 045	0 033	--	0 029	0 018			
Steubenville, OH	Mixed	7 days	Oven/range w/wo pilot	Summer	93	0 025	0 036	0 026	--	0 017	0 008		1,20	
				Winter		0 023	0 048	0 031	--	0 033	0 017			
Portage, WI	Mixed	7 days	Oven/range w/wo pilot	Summer	110	0 008	0 019	0 012	--	0 012	0 006		1,21	
				Winter		0 009	0 027	0 016	--	0 020	0 010			
Topeka, KS	Mixed	7 days	Oven/range w/wo pilot	Summer	87	0 010	0 023	0 014	--	0 013	0 005		1,22	
				Winter		0 013	0 039	0 027	--	0 029	0 017			
Southern California	Mixed	2 days	Gas/oven w pilot	Not Winter	221	0 039	--	0 034	--	--	0 011		1	Spengler et al (1992b)
				Winter	93	0 049	--	0 034	--	--	0 004			
			Gas/oven wo pilot	Not Winter	115	0 032	--	0 023	--	--	0 005		1	
				Winter	34	0 043	--	0 023	--	--	0 001			
Chattanooga, TN	Apartments in a development	7 days	Oven/range w/wo pilots	Winter	--	0 021	--	--	0 075	--	--	0 058	1,23	Parkhurst et al (1988)
			Oven/range used for heating	Winter	--	0 021	--	--	0 120	--	--	0 103		

[a]NO_2 = Nitrogen dioxide
Mixed = Single-family attached, single-family unattached, condominium apartment
LP = Liquified petroleum
[b]The comment codes are as follows

1 Background correction determined by multiplying the indoor/outdoor ratio for homes in the study with no indoor NO_2 sources for a given season times the outdoor NO_2 concentration measured for the home with sources and subtracting the product from the indoor level measured in the house
2 Homes contain forced-air gas furnace These homes are thought not to contribute significantly to indoor levels for this sample
3 Homes with electric range/oven, forced-air gas furnace, and gas water heater in home Comparison is made with electric range/oven, forced-air gas furnace, and gas water heater located outside home
4 Homes have gas range/oven with source contribution calculated after correction of a gas range/oven Values are background corrected with gas stove
5 Living room or activity room
6 Sampling was done over two different periods for the same houses within the same winter period

7 Outdoor values were obtained from five locations, housing types, mobile home
8 Other location is home average, bedroom refers to average of levels in one or more bedrooms in house
9 Other location is the main living room
10 Other location is point nearest center of home
11 48-h samples over 30 consecutive days
12 Indoor/outdoor (I/O) ratio is assessed to be 0 6, 0 7, and 0 85 for the Winter, Spring/Fall, and Summer periods, respectively, for all locations because no control home (no gas appliances) measurements were available Using these I/O ratios, the impact of sources was calculated as in footnote #1
13 Each home was sampled six times over a 1-year period
14 Outdoor levels are average for homes with and without gas appliances
15 Outdoor levels were recorded at 75 locations in the general sampling area and are not home-specific Bedroom levels were obtained for 107 of the 428 homes
16 Outdoor levels were recorded at 82 locations in the general sampling areas and are not home-specific Outdoor levels were recorded at the beginning and end of the study
17 Indoor/outdoor (I/O) ratio is assumed to be 0 6 for all locations because no control home (no gas appliances) measurements were available Using I/O ratio of 0 6, the impact of sources was calculated as in footnote #1
18 90 of the 91 homes had kerosene heaters, thus contribution of gas stove cannot be estimated
19 13 of the 208 homes had kerosene heaters
20 29 of the 93 homes had kerosene heaters
21 10 of the 110 homes had kerosene heaters
22 13 of the 87 homes had kerosene heaters
23 The total number of houses sampled in four developments with gas stoves was approximately 188 No breakdown was given for the number of apartments in which the gas stove was or was not used for heating The other location here is the whole-house average

contributions of the various apparent indoor sources for all gas appliances to the average indoor NO_2 levels measured, in Equation 7-3 This was done by applying a background correction factor (subtracting the contribution of outdoor concentrations) to the measured indoor levels. The correction factor was determined by multiplying the mean indoor/outdoor ratio for homes in the study with no indoor NO_2 sources (Table 7-15) for a given season by the mean outdoor NO_2 concentration measured for the homes with sources and then subtracting the product from the mean indoor levels Indoor/outdoor ratios of 0 6 for the winter, 0.85 for the summer, and 0 7 for the fall and spring were assumed for those studies that did not have a sample of homes without indoor sources

Although only average concentrations are presented in Table 7-16, they do allow for a number of general observations to be made regarding both the measured levels of NO_2 in homes with gas appliances and the calculated contributions of the gas appliances to those levels.

(1) There is considerable variation in the reported average indoor concentrations among the U S and European studies (see Table 7-16) The Parkhurst et al (1988) study and the European studies indicate that there may be housing groups with gas stoves that have elevated indoor levels of NO_2 These variations are no doubt related to variations in a number of factors, including outdoor concentrations, cooking patterns, source characteristics, unreported sources, existence of different gas appliances (in the Dutch homes, gas-fired, water tap heaters [geysers]), house infiltration rates, use of local exhaust fans, house volumes, and differences in removal rates by internal surfaces

(2) Both indoor and outdoor concentrations are generally higher in the winter than in the summer The higher indoor levels in the winter are reflected in the calculated contribution by gas stoves shown below The higher indoor levels during the winter may be due to lower ventilation rates, increased source use, and possible seasonal differences in removal rates

(3) Within a typical house with an unvented gas cooking range in the kitchen, a concentration gradient within a residence and between seasons exists. The concentration is highest in the kitchen and lowest in the bedroom, with other rooms (e g , living room) between the two Bedroom levels can typically range from 50 to 75% of those measured in the kitchen This gradient is reflected in the calculated contribution of gas cooking ranges and ovens to the average concentrations of NO_2 in the kitchen, bedroom, and other rooms among the U S studies

(excluding the Parkhurst et al [1988] study) The contribution of gas cooking ranges and ovens to the average concentrations, by room, by season, is very consistent, varying by about a factor of 2 Winter contributions to the kitchen, bedroom, and other locations across all studies averaged 52, 28, and 39 $\mu g/m^3$ (0 028, 0 015, and 0 021 ppm), respectively, whereas summer contributions averaged 28, 13, and 16 $\mu g/m^3$ (0 015, 0 007, and 0 008 ppm), respectively The contribution during the fall/spring period lies between the summer and winter periods Although the contribution to the kitchen in the European studies is higher than the U S studies, the contribution of gas stoves to the other areas in the home is similar for the European and U.S. studies It should be noted that these are only approximations and that the variation associated with them is large The seasonal differences may be related to seasonal differences in source use, infiltration, and removal by interior surfaces and furnishings The gradient may be due to differences in air mixing within and between rooms in residences

(4) Indoor concentrations are higher in homes that have gas cooking ranges with pilot lights than those without pilot lights The extensive Wilson et al (1986) data indicate that pilot lights in the gas cooking range add about 20 $\mu g/m^3$ (0 011 ppm) to the kitchen levels in the winter and less to the other rooms Data from the Boston study (Ryan and Spengler, 1992) indicate that the presence of a continuously burning pilot light in a gas range home increases the indoor NO_2 concentration by approximately 0 010 ppm above that which it would be if the gas range used an alternative ignition system The water heater was found on average to add approximately 12 $\mu g/m^3$ (0 006 ppm) to the kitchen during the winter and less to the rest of the house This result, however, was not found to be statistically significant due to high variability in the measurements Also, no data examine peak concentrations in homes with gas range with and without pilot lights

(5) The presence of wall or floor furnaces with gas appliances is more associated with higher concentrations than just gas appliances Indoor NO_2 levels associated with wall or floor furnaces were thought to be due to leaky flues (Wilson et al , 1986) In a follow-up study (Beals et al , 1987), the homes with high levels of NO_2 were investigated for the source of high levels and to determine the role of leaky flues The results of the follow-up study indicated that there was not a generic problem with this system However, this system is more likely to have an undetected leaky flue or unvented pilot light

(6) Elevated NO_2 levels in apartments associated with the use of gas ranges for space heating were observed in one study (Parkhurst et al , 1988) and suspected in another (Beals et al , 1987) In the Parkhurst et al (1988) study, NO_2 levels were found to increase approximately

85 $\mu g/m^3$ (0 045 ppm) due to stove use for space heating The Beals et al (1987) study found that 20% of all residences with gas ranges use the ranges as supplemental heat sources, 28% of those residences with wall or floor furnaces reported occasional use of the gas range for space heating The impact on residential levels, however, was not estimated In a recent study conducted in Albuquerque, NM (Spengler and Samet, 1992), it was estimated that approximately 10% of the homes with gas stoves reported using them for space heating Figure 7-21 compares NO_2 levels across several seasons for residences with gas stoves that do and do not use the stove for space heating This study estimated that during the heating season, the use of gas stoves for space heating added approximately 0 038 ppm to the bedroom Spengler et al (1992b) report use of stove to heat on the average of 13% but ranging from 3.8 to 33 3% across U S and Canadian communities Koontz et al (1992) report a relatively small fraction of households, about 6% in the United States use a range for residential heating It is used during winter for 1 5 to 2 0 days

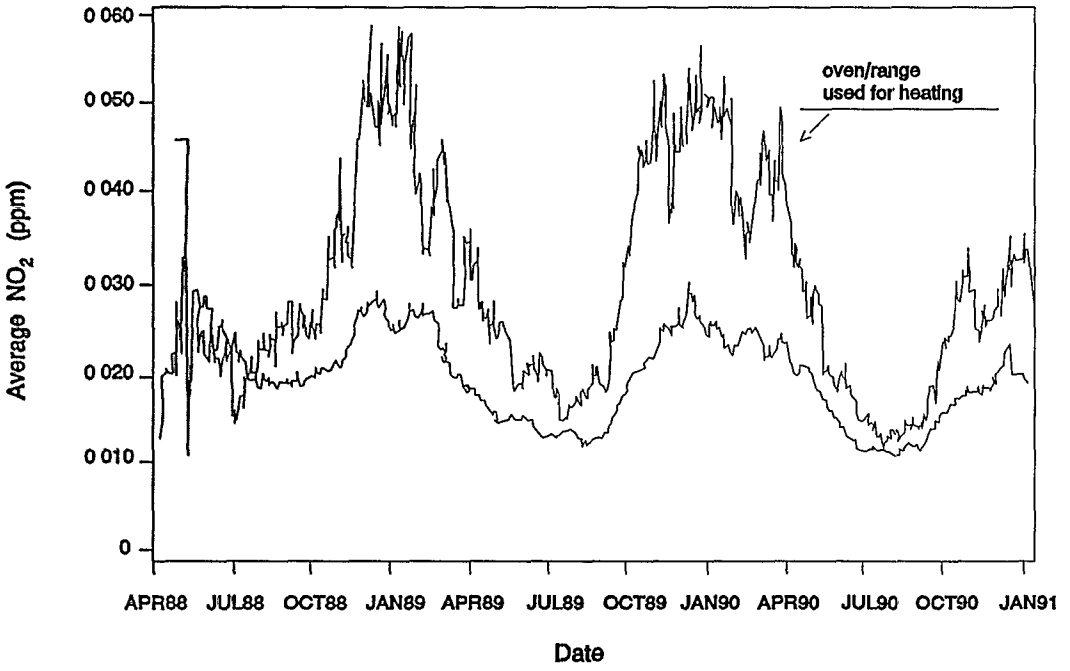


Figure 7-21. Nitrogen dioxide concentrations across seasons in Albuquerque, NM; bedrooms that do and do not use the gas stove for space heating.

Source: Spengler and Samet (1992)

It is remarkable that the contribution of gas cooking to indoor NO_2 levels is as consistent as it is among studies for locations in the residences and by season, given the great variability of the factors that govern the emissions (source type, source condition, source use, and source venting) and dilution and removal of NO_2 indoors (house volume, infiltration, mixing within and between rooms, decay rates, etc) This consistency is not observed until the impact of outdoor concentrations is corrected for These background levels can vary considerably over time and geographic area The impact of gas cooking and possibly other unvented or improperly vented combustion sources on indoor NO_2 levels is superimposed upon the indoor background level resulting from outdoor levels In areas where outdoor levels are low, concentrations indoors from gas appliances will be higher than (and in many cases, much higher than) outdoor levels (e g , Marbury et al , 1988, Quackenboss et al , 1987, 1988, Spengler et al , 1983, Leaderer et al , 1986a, Ryan et al , 1988, Ryan and Spengler, 1992) If outdoor concentrations are high, then indoor levels in homes with gas appliances will be closer to and even lower than the outdoor levels (Wilson et al , 1986) In the Los Angeles study (Colome et al , 1992), exposures to NO_2 away from home on average exceed personal exposures encountered while at home due to higher outdoor NO_2 concentrations In Los Angeles (Spengler et al , 1992a,b), outdoor concentrations are strong predictors of personal exposure

Ryan et al (1992) observes that bedroom concentrations have a strong influence on personal exposures in both Boston and Los Angeles A salient difference between Boston and Los Angeles is that, in Los Angeles, the outdoor concentration appeared to play a dominant role in influencing indoor concentrations, whereas in Boston this is not the case

The contributions of gas appliances to indoor levels of NO_2 shown in Table 7-16 are average concentrations calculated from the average levels reported by the investigators for each field study It is important to note that the variability around the calculated contributions in Table 7-16 is generally large

Koontz et al (1992) report the results of 1985 and 1991 surveys of type of cooking facilities and frequency of cooking in the United States The frequency distribution for type of range is shown in Table 7-17, which shows a 2 6% decrease in gas ranges with pilot lights The statistical variation of these results is not reported The average amount of time in minutes spent using the range to cook by income is shown in Table 7-18 Changes in

TABLE 7-17. FREQUENCY DISTRIBUTION FOR TYPE OF RANGE FROM 1985 AND 1991 SURVEYS

	Percent Frequency for	
Type of Range	1985 Survey	1991 Survey
Gas, with pilot light	29 3	26 7
Gas, pilotless	7 4	9 9
Gas, not sure	0 2	0 7
Electric	61 0	60 8
Gas and electric	1 9	1 9
None	0 1	0 1

Source. Koontz et al (1992)

TABLE 7-18. AVERAGE NUMBER OF DAYS OF RANGE USE PER WEEK FOR COOKING, BY INCOME

Characteristic	Days for Breakfast	Days for Lunch	Days for Dinner
Income of Respondent			
Less than $12,500	2 8	2 6	4 6
$12,500 to $22,499	2 8	2 4	4 8
$22,500 to $34,999	2 4	2 2	4 9
$35,000 to $49,999	1 9	1 6	5 1
$50,000 or more	2 2	1 8	5 1

Source Koontz et al (1992)

reported range/oven cooking frequency in 1985 and 1991 related to microwave use is shown in Table 7-19. Use of gas ranges without pilot lights and changes in cooking practices, such as increased use of microwave ranges, could result in lower NO_2 levels in such homes

The Koontz et al. (1992) survey examines the change from 1985 to 1991 but provides no data for earlier use of cooking stoves with and without pilot lights or the use of microwave ranges The trend in this data suggests that, in the period before 1985, homes with pilot lights would be more common than after 1985, and other cooking choices, such as microwave, were used less frequently Thus, in epidemiology studies (see Chapter 14)

TABLE 7-19. REPORTED RANGE/OVEN COOKING FREQUENCY IN 1985 AND 1991, BY TYPE OF OTHER COOKING APPLIANCE

Type of Other Cooking Appliance	Average Cooking Days per Week	
	1985 Survey	1991 Survey
	Breakfast	
Microwave oven only	3 5	2 3
None	3 7	3 3
	Lunch	
Microwave oven only	2 9	2 2
None	2 9	3 2
	Dinner	
Microwave oven only	5 5	4 9
None	5 5	5 8

Source Koontz et al (1992)

conducted before 1985 that did not directly measure NO_2 levels, NO_2 estimates based on average differences between homes with gas ranges with pilot lights and homes with electric stoves may reflect gas stove type and other cooking practices in use at that time

7.3.3.2 Spatial Distributions

As demonstrated in Table 7-16, NO_2 concentrations in residences with gas appliances exhibit a pronounced variation by season and by location in a residence The calculated contribution of gas appliances to indoor levels of NO_2 (corrected for outdoor contributions—Table 7-16) is highest in the winter and lowest in the summer, with the largest differences seen in the kitchen The calculated total seasonal differences are on the order of a factor of 2 (e g , Quackenboss et al , 1986, 1987, Ryan et al , 1988, Ryan and Spengler, 1992, Wilson et al , 1986, Spengler et al , 1983, Goldstein et al , 1985) The seasonal effect is related to variations in outdoor NO_2 levels, source use, infiltration, and removal by interior surfaces

Spatial distributions of NO_2 within and among rooms in a house where a gas range or oven is used are a function of mixing in the space Goldstein et al (1985) reported the vertical distributions of NO_2 levels in nine apartments in New York City where gas ranges were used. The concentrations were 48-h average values (Palmes tubes) measured at five elevations in the kitchens and living rooms of each apartment Figure 7-22 shows the result of that study. A pronounced vertical gradient was observed in the kitchen, with the highest levels observed at the ceiling and lowest at the floor A similar, but less pronounced, gradient was observed for the living area Wilson et al (1986) investigated the vertical distribution of NO_2 levels in gas-cooking homes The results showed a vertical gradient in the kitchen for some, but not all, of the homes The potential for a strong spatial NO_2 gradient in kitchens with gas ranges suggests that placement of monitors in the kitchen during field studies could result in a larger standard deviation in kitchen concentrations than for other rooms. In considering the results from such studies, the monitor placement issue has to be considered in interpreting the results

All studies investigating NO_2 concentrations in homes with gas appliances have found a concentration gradient between rooms (Table 7-16), with the kitchen being highest and the bedroom being lowest This gradient is highlighted in Figure 7-23 Figure 7-23 also highlights the seasonal differences in indoor NO_2 levels in homes with gas appliances In this study (Spengler et al , 1983), season and location in the house were found to be statistically significant predictors of NO_2 levels in homes with gas appliances The within-home spatial variations are related to such variables as air exchange rates among rooms, air mixing within a room, volume of a house, location of the air sampler, and the frequency and length of gas appliance use

7.3.3.3 Short-Term Indoor Concentrations

The majority of data on indoor NO_2 levels associated with gas stove use is from integrated monitors, sampling over periods of days The recorded NO_2 values are averaged over several on/off periods of gas stove use, and as such, do not directly measure short-term indoor NO_2 levels (levels on a time frame of minutes or hours) in homes, which occur during source use. The short-term concentrations are associated with length of source use, number of sources (e g., number of gas burners used), and location at which the

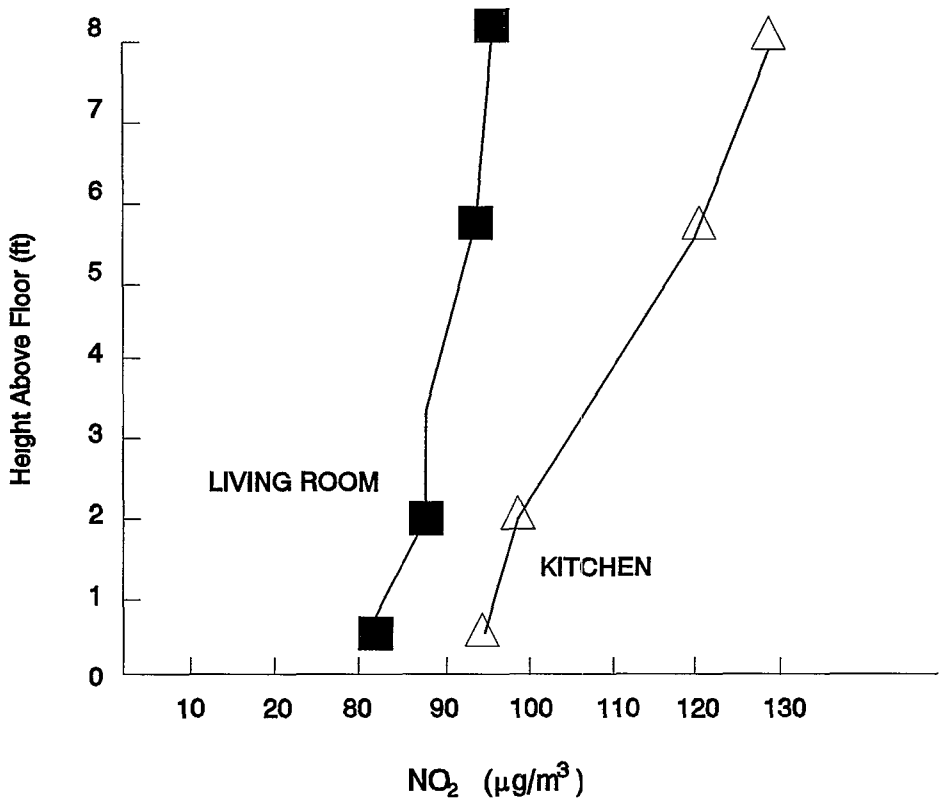


Figure 7-22. Verticle distribution of average nitrogen dioxide concentrations (48-h sampling periods) measured in nine New York City apartments. Plotted from data by Goldstein et al. (1985).

measurement is taken relative to the source (e g , immediately over the source or several feet away) Few studies have measured short-term NO_2 levels in residences with gas appliances

In a study of the incidence of respiratory illness in households using gas and electricity for cooking, Keller et al (1979) used continuous chemiluminescence monitoring over 3-day periods in 46 homes in the Columbus, OH, area to measure continuous variations in indoor NO_2 and NO levels in relation to cooking times The study found that variations in instantaneous peak NO_2 levels (highest concentrations measured with a continuous monitor) in gas-cooking households reached as high as eight times the 24-h average values In several households, instantaneous peak NO_2 concentrations exceeded 1,900 $\mu g/m^3$ (1 ppm) The study did not report the location of the sampler relative to the source, the number of sources, length of source use, or sample averaging time As part of a study of respiratory disease

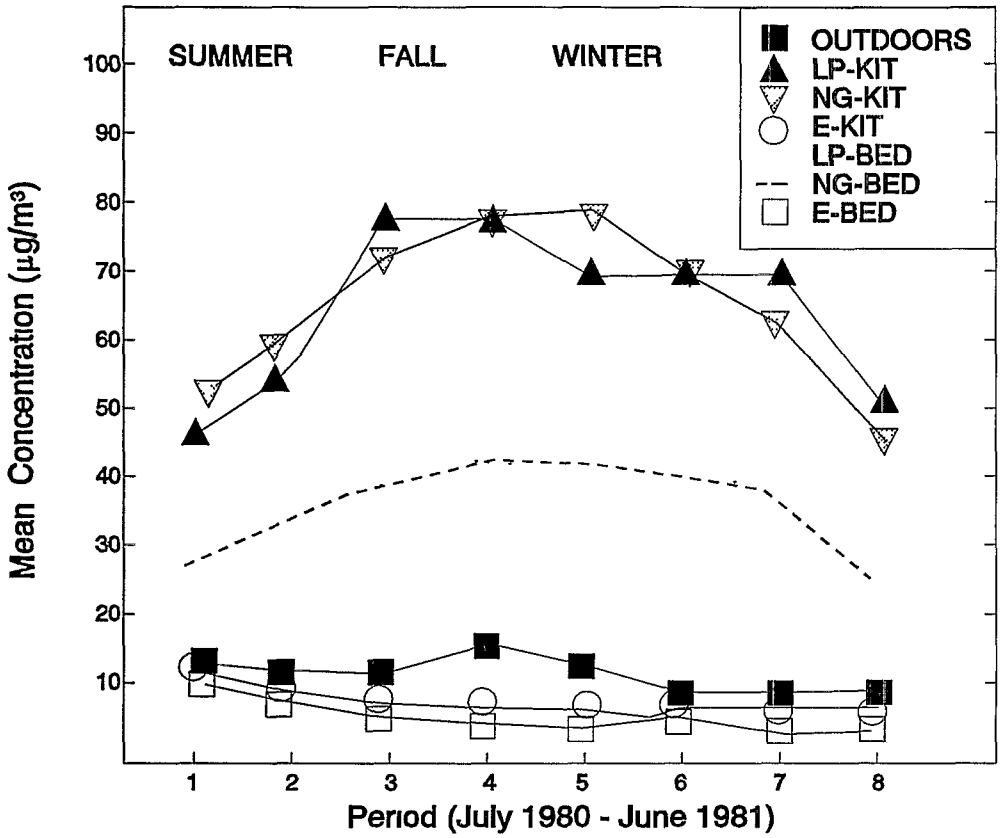


Figure 7-23. Mean nitrogen dioxide concentrations (1-week sampling periods) for eight sampling periods by location in the home and type of cooking fuel.

Source Spengler et al (1983)

rates and pulmonary function in children associated with NO_2 exposure, Speizer et al (1980) reported instantaneous peak NO_2 exposures, measured by a continuous chemiluminescence monitor, in excess of 1,100 $\mu g/m^3$ (0 583 ppm) in a kitchen within 3 ft of a gas range/oven (gas oven on), with 1-h average peak exposure at approximately 665 $\mu g/m^3$ (0 352 ppm) The peak 1-h average level associated with a range-top gas burner was 428 $\mu g/m^3$ (0.227 ppm). Concentrations were monitored continuously by chemiluminescence in only one house. Hosein and Bouhuys (1979), using monitoring by chemiluminescence, reported peak 2-h NO_2 levels of over 3,000 $\mu g/m^3$ (1 59 ppm) 3 ft from the source in a kitchen during use of a gas range

In one of the first studies of the impact of gas ranges on indoor air quality, Wade et al (1975) reported continuous NO_2 measurements (chemiluminescence) in three locations in four

houses with gas ranges Measurements were spread over all four seasons and outdoor levels were recorded Nitrogen dioxide levels in the kitchen responded rapidly to gas range use, with less rapid response in other locations in the house Peak 5-min concentrations 1 m from the gas range exceeded 100 $\mu g/m^3$ (0 053 ppm) over 50% of the time in two of the houses and 20% of the time in one house The data were not sufficient to construct cumulative frequency distributions for the fourth house measured Peak levels were considerably lower in other locations in the houses The NO_2 frequency distributions for longer averaging times (e g , 1 h) for other locations in the houses were not reported

The most extensive data collected to date on peak indoor levels of NO_2 associated with gas appliance use are reported by Harlos et al (1987) In this study, an electrochemical-cell NO_2 monitor was used to record time-averaged NO_2 levels of 5 s and longer during cooking for personal exposure for over 18 volunteers Subjects wore the electrochemical monitor during their cooking activities and the sample was drawn at the breathing zone Table 7-20 shows the summary statistics reported from the study for personal exposures over averaging times from 0 6 seconds to 1 h Peak 1-min concentrations reached as high as 1,880 $\mu g/m^3$ (1 ppm) The considerable variability in recorded exposures is due to source, source use, subjects' activities, and air-mixing characteristics in the kitchen

Lebret et al (1987) conducted real-time NO_2 concentration measurements at three locations (kitchen, living room, and bedroom) and outdoors for 12 Dutch homes using a chemiluminescence monitor Measurements were conducted over periods of 135 to 273 h The homes sampled had gas ranges and geysers (demand gas water heaters) Maximum 1-min average concentrations in the kitchens ranged from 400 to 3,808 $\mu g/m^3$ (0 21 to 2 02 ppm) in the kitchen, whereas the living room and bedroom levels were typically on the order of 30 and 18%, respectively, of the kitchen levels Maximum 1-h average concentrations in the kitchen ranged from 230 to 2,055 $\mu g/m^3$ (0 12 to 1 09 ppm), whereas living room levels were typically 50% of the kitchen levels and bedroom levels were about 30% of the kitchen levels The relative contribution to peak levels from gas range use verses geyser use was not determined

Using a chemiluminescent analyzer, Tikalsky et al (1987) measured NO_2 levels continuously in three locations (kitchen, main activity room, and outside) in 10 homes for two 3- to 6-day sampling periods The sampling probes were placed 4 to 6 ft above the

TABLE 7-20. SUMMARY STATISTICS FOR GAS RANGE NITROGEN DIOXIDE MAXIMA (ppm) OVER SEVERAL AVERAGING TIMES

	Time					
Gas Cooking (n = 18)	5 s	15 s	1 min	3 min	30 min	1 h
Mean Maxima	0 52	0 44	0 38	0 34	0 22	0 18
Standard Error	0.24	0 23	0 215	0 22	0 13	0 09
Maximum	1.20	1 13	1 0	0 98	0 60	0 42
Minimum	0 196	0 175	0 13	0 11	0 07	0 06

Source Harlos et al (1987)

ground and, in the kitchen, 6 to 10 ft from the gas stove The homes had gas appliances The continuously monitored NO_2 concentrations were averaged over 1-, 3-, and 24-h periods. Data were also gathered on source use One-hour average NO_2 levels in the kitchens and activity rooms as high as 1,000 and 750 $\mu g/m^3$ (0 53 and 0 40 ppm), respectively, were recorded Hourly NO_2 monitoring data covering one 24-h period for one home are shown in Figure 7-24 Baseline levels in the home without oven and stove top use are above outdoor levels and are related to pilot light and water heater use The highest 1-h average concentrations occurred in the late morning and late afternoon and were associated with oven use (morning peak) and stove-top use (late afternoon) Time plots of NO_2 for the other homes sampled demonstrate considerable variability within the course of a day, with NO_2 levels in the homes varying with gas appliance use and, in some cases, with furnace use.

There is only a very limited data base available on short-term indoor concentrations of NO_2 associated with gas appliance use In the absence of adequate field study data, it is difficult to assess the short-term average levels indoors associated with gas appliances The existing data, however, suggest that short-term indoor NO_2 concentrations of concern may be higher than those recorded for outdoors

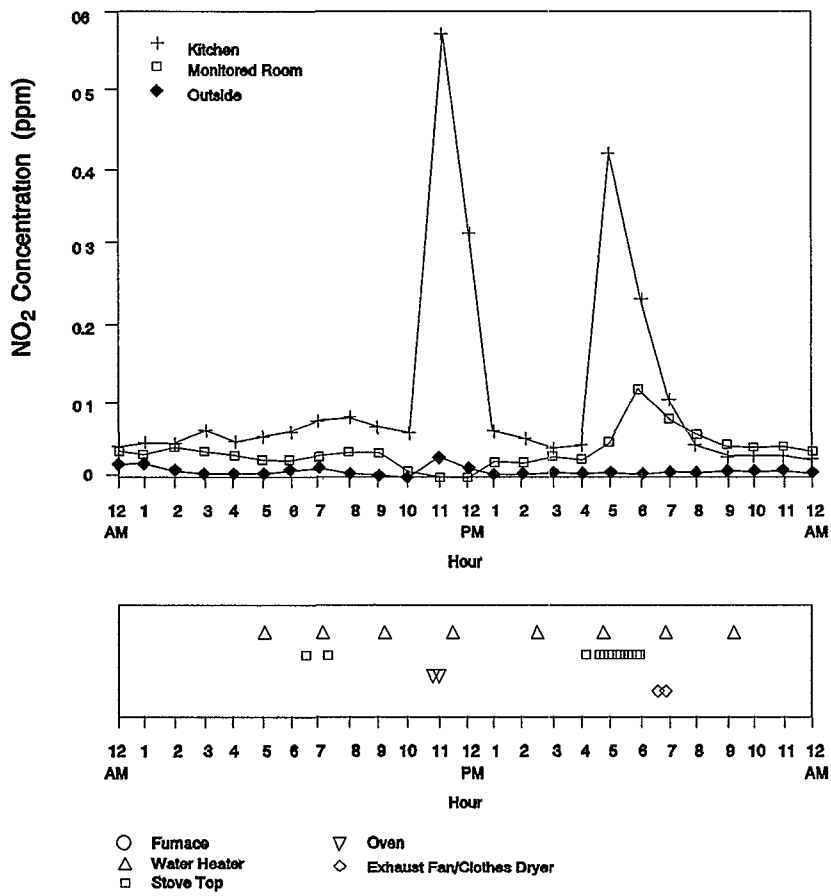


Figure 7-24. Nitrogen dioxide hourly levels in one home with gas appliances.

Source Tikalsky et al (1987)

7.3.4 Unvented Space Heaters

Unvented space heaters are used in the colder climates to supplement central heating systems or in more moderate climates as the primary source of heat During the heating season, space heaters will generally be used for a number of hours during the day, resulting in emissions over a relatively long period of time

The actual number of unvented space heaters in use in residential and commercial settings in the United States and their use patterns is not known In many countries, kerosene heaters are an important heating source (Middle East, Japan, Korea, etc) As many as 17 million such heaters have been sold through 1987, with current yearly estimated sales of 1 million A residential energy survey conducted by the U S Bureau of

Census (1982) estimated that 3 million residences use unvented gas space heaters (fueled by natural gas or propane) The heaters are used in 3 to 4% of the houses in the United States, with their use being more prevalent in the South Census region of the United States, where they are the main heating system in about 10% of the housing units In recent years, the numbers of new unvented kerosene and gas space heaters sold have declined The large number of unvented space heaters sold in the United States and the potential for their use, particularly during periods when energy costs rise quickly, make them an important source of NO_2 indoors.

As discussed in Chapter 4, NO_2 emissions from unvented kerosene and gas space heaters can vary considerably and are a function of heater design (convective, radiant, combination burner designs, etc) and condition of heater and manner of operation (e g , flame setting) Levels of NO_2 indoors resulting from heater use are a function of the heater emission variables, along with heater use variables (number of hours of use, volume of house heated, etc) and the variables governing the dispersal and elimination of the NO_2 emissions indoors (infiltration, mixing, etc) The contribution of NO_2 emissions from unvented kerosene and gas space heaters to indoor concentrations in simple terms is given in the source contribution term in Equation 7-3 Because kerosene and gas space heaters, unlike other gas appliances, are typically used for several hours at a time, they approach being a continuous source and hence their contribution to indoor concentrations is probably reasonably represented by the steady state model in Equation 7-3

7.3.4.1 Unvented Kerosene Space Heaters

Average Indoor Concentrations

The most extensive data collected to date on residential levels of NO_2 associated with the use of unvented kerosene space heaters are reported by Leaderer et al (1986a) This field study of 333 homes in the New Haven, CT, area was conducted during the 1982-1983 heating season to assess the range and distribution of air contaminants associated with residential unvented combustion sources, with particular emphasis on NO_2 levels related to kerosene heaters, and to assess exposures to complement an epidemiologic study of the health impact of heater use The study employed a nested design for exposure assessment that utilized questionnaires and several levels of air monitoring Two-week average NO_2 levels

were recorded in three locations in each house (kitchen, living room, and bedroom) and outdoors using Palmes tubes (Palmes et al , 1977)

The measured 2-week NO_2 concentrations by location in the homes for six general source categories are shown in Table 7-21 Also shown in Table 7-21 are the percent of homes in which NO_2 levels exceeded the primary ambient air quality standard The findings indicate that the greater the number of sources, the higher the average concentrations of NO_2 Homes with one kerosene heater and no gas range/oven had NO_2 levels four to five times higher than the levels in homes without a heater or a gas range/oven Nitrogen dioxide levels in homes with a kerosene heater but no gas range/oven were roughly comparable to homes with a gas range/oven only The study also showed that homes with convective heaters had higher NO_2 levels than homes with radiant heaters It was noted that the average concentrations measured may have been lower than would have been expected due to the particularly mild winter encountered during the study—the median of daily hours of kerosene heater use was only 6 h/day

The data in Table 7-21 represent the average levels over a 2-week period and do not reflect the actual concentrations in the homes during heater use Using the measured concentrations and questionnaire data on heater use during air sampling and correcting for outdoor levels, the authors calculated the indoor NO_2 levels that may have existed during actual heater use The resultant calculated cumulative frequency distribution of NO_2 levels by location in the homes during heater use for homes with one kerosene heater and no gas range/oven is shown in Figure 7-25 The adjusted data show that over 49% of the residences with one kerosene heater had average NO_2 concentrations in the house in excess of 100 $\mu g/m^3$ (0.053 ppm), with 8 4% in excess of 480 $\mu g/m^3$ (0 254 ppm) The levels would be higher in homes with more than one kerosene heater and/or a gas range

In a study of two Vermont homes in which kerosene space heaters were used, Ryan et al (1983) found average NO_2 concentrations indoors (Palmes tubes) to range from 19 to 304 $\mu g/m^3$ (0 01 to 0 16 ppm) over two sampling periods from 81 to 174 h Nitrogen dioxide levels were highest in the house that used two kerosene heaters as a primary heat source Traynor et al (1984), in a field study of indoor air pollutants in residences with suspected combustion-related sources, reported 1-week average NO_2 levels in three homes with kerosene heaters and five homes with a kerosene heater and gas range Nitrogen

TABLE 7-21. TWO-WEEK AVERAGE NITROGEN DIOXIDE LEVELS BY LOCATION FOR HOMES IN SIX PRINCIPLE SOURCE CATEGORIES,[a] NEW HAVEN, CONNECTICUT, AREA STUDY, WINTER, 1983

Source Category, Location	Nitrogen Dioxide (ppm)			
	n	Mean	SD[b]	% >0 053 ppm
No Kerosene Heater or Gas Stove				
Outdoors	144	0 007	0 003	0
House Average	145	0 004	0 002	0
Kitchen	147	0 004	0 002	0
Living Room	146	0 004	0 002	0
Bedroom	145	0 004	0 005	0
One Kerosene Heater, No Gas Stove				
Outdoors	95	0 007	0 002	0
House Average	95	0 020	0 017	2 1
Kitchen	96	0 021	0 019	4 2
Living Room	96	0 020	0 019	5 2
Bedroom	95	0 017	0 016	5 3
No Kerosene Heater, Gas Stove				
Outdoors	42	0 008	0 002	0
House Average	42	0 018	0 014	4 8
Kitchen	42	0 024	0 017	4 8
Living Room	42	0 016	0 013	4 8
Bedroom	42	0 015	0 013	4 8
One Kerosene Heater, Gas Stove				
Outdoors	18	0 008	0 003	0
House Average	18	0 035	0 023	16 7
Kitchen	18	0 040	0 028	22 2
Living Room	18	0 030	0 020	11 1
Bedroom	18	0 036	0 030	16 7

TABLE 7-21 (cont'd). TWO-WEEK AVERAGE NITROGEN DIOXIDE LEVELS BY LOCATION FOR HOMES IN SIX PRINCIPLE SOURCE CATEGORIES,[a] NEW HAVEN, CONNECTICUT, AREA STUDY, WINTER, 1983

Source Category, Location	Nitrogen Dioxide (ppm)			
	n	Mean	SD[b]	% >0 053 ppm
Two Kerosene Heaters, No Gas Stove				
Outdoors	13	0 009	0 005	0
House Average	13	0 037	0 020	23 0
Kitchen	13	0 038	0 017	23 0
Living Room	13	0 039	0 023	38 5
Bedroom	13	0 036	0 024	23 1
Two Kerosene Heaters, Gas Stove				
Outdoors	3	0 012	0 003	0
House Average	3	0 045	0 013	33 3
Kitchen	3	0 050	0 012	66 6
Living Room	3	0 041	0 020	33 3
Bedroom	3	0 045	0 010	33 3

[a] Repeat monitoring data (n = 19) are included Samples were lost for two homes in one home, the monitors were capped early by the residents, and in the second home, repeated efforts by the interviewers to retrieve the monitors failed

[b] SD = Standard deviation

Source Leaderer et al (1986a)

dioxide levels in the homes with kerosene heaters ranged from 48 to 222 $\mu g/m^3$ (0 025 to 0 118 ppm) The differences in concentrations reflected differences in usage

Spatial Distributions

As shown in Table 7-21, NO_2 levels in homes with a kerosene heater only do not exhibit a pronounced concentration gradient among rooms in a house Leaderer et al (1984) found no strong spatial gradient among rooms, which contrasted with the strong gradient

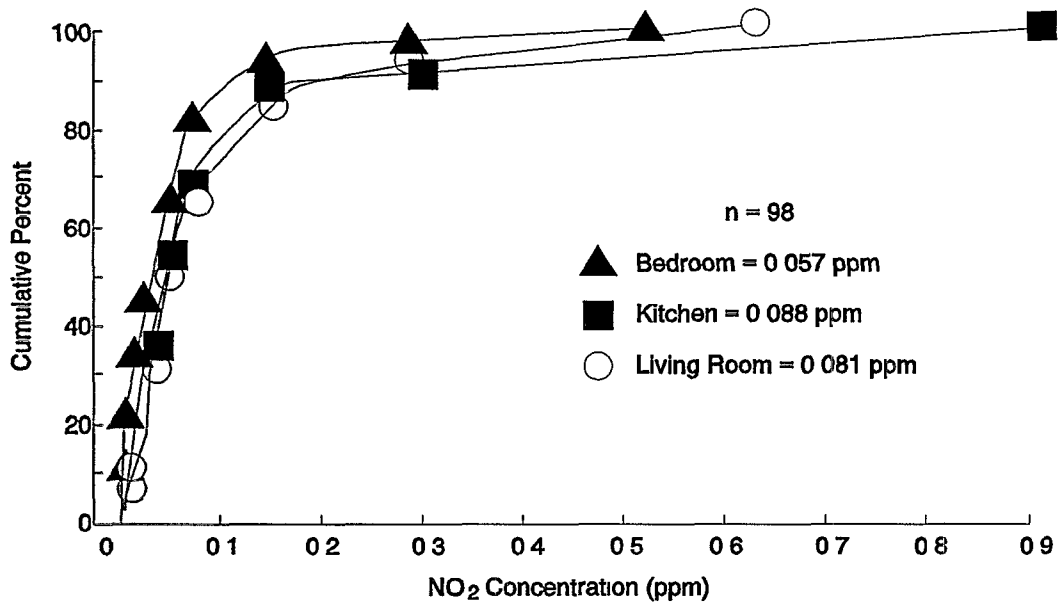


Figure 7-25. Cumulative frequency distribution and arithmetic means by location, of average nitrogen dioxide levels (2-week sampling periods) during kerosene heater use for residences with one kerosene heater and no gas range, New Haven, CT, area study, winter 1983.

Source Leaderer et al (1986a)

observed for homes with gas ranges The relatively long operating periods for the heater, on the order of several hours, and the strong convective heat output evidently foster rapid mixing within the homes where they are used

Concentrations During Heater Use

Because the heaters are used for several hours at a time, unlike gas appliances, equilibrium concentrations are more likely to be achieved, resulting in sustained high NO_2 concentrations over periods of several hours rather than seconds or minutes as with gas appliances. The variability in these equilibrium levels from heater use period to heater use period for a given heater will be driven by variations in infiltration rates, NO_2 deposition rates and the volume of the house heated (e g , one room or several rooms)

As part of the nested air sampling design protocol used by Leaderer et al (1987), 14 residences were monitored for periods of 43 to 209 h for NO_2 levels in two locations in the home (room with heater and a bedroom) and outdoors using a continuous chemiluminescence monitor (Leaderer et al , 1984) Thirteen had kerosene heaters, of which four had a gas range, whereas one house had a gas range but no kerosene heater Equilibrium levels in the homes associated with kerosene heater use ranged from 19 3 to 847 $\mu g/m^3$ (0 010 to 0 45 ppm), and levels typically exceeded 100 $\mu g/m^3$ (0 053 ppm) In this set of houses, levels were generally higher in the room where the heater was used These levels were typically sustained over periods of several hours (outdoor levels subtracted) and were sustained for a 24-h period in one of the houses monitored (Leaderer et al , 1986a)

7.3.4.2 Unvented Gas Space Heaters

Average Indoor Concentrations

The most comprehensive study on indoor levels of NO_2 associated with the use of unvented gas space heaters (UVGSHs) was reported by Koontz et al 1986 and 1988 In this study, 157 residences in four Texas cities were monitored for NO_2 concentrations and frequency of UVGSH and gas range use from January to March 1985 Nitrogen dioxide was monitored in two locations in all homes (central location and remote or peripheral location) using Palmes tubes over sampling periods of approximately 5 days In a subsample of 16 homes, NO_2 was measured continuously by chemiluminescence

The cumulative percent distributions of 5-day average NO_2 levels measured in all homes in both locations are shown in Figure 7-26 Approximately 70% of the homes exceeded 100 $\mu g/m^3$ (0 053 ppm), and 20% exceeded 480 $\mu g/m^3$ (0 25 ppm) The cumulative frequency distributions for average NO_2 by three categories of homes (primary UVGSH, secondary UVGSH, and non-UVGSH) are shown in Figure 7-27 The highest concentrations were measured in homes where the UVGSH was the primary source of heat (average of 472 $\mu g/m^3$ [0 25 ppm]) and lowest for non-UVGSH (average of 56 $\mu g/m^3$ [0 03 ppm])

Table 7-22 presents a more detailed breakdown of the average levels recorded as a function of source categories Gas stove use alone contributed 57 $\mu g/m^3$ (0 03 ppm) on

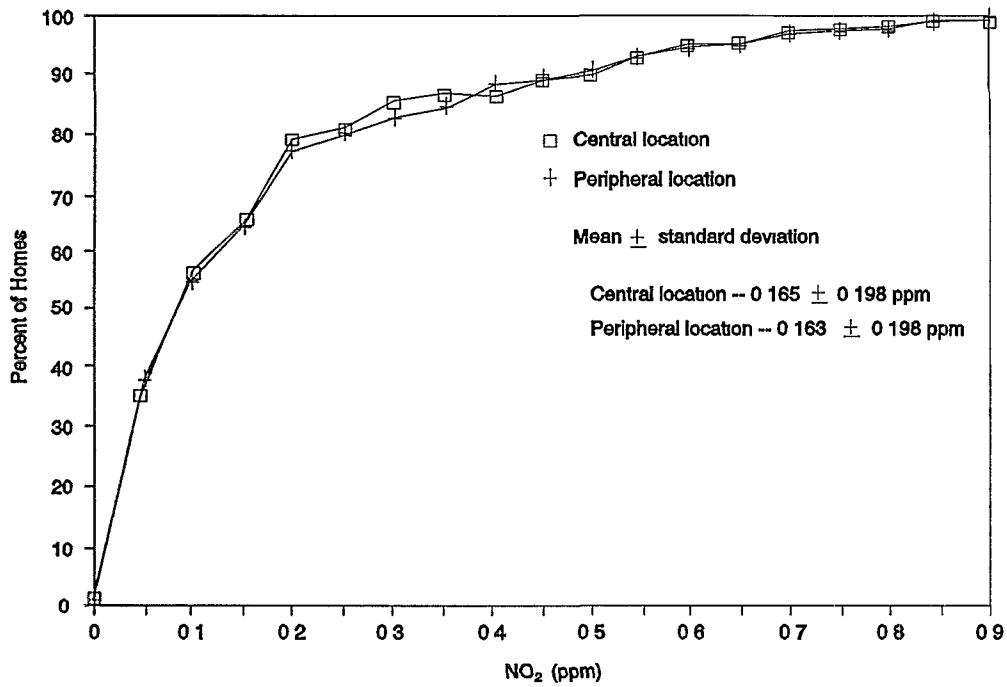


Figure 7-26. Cumulative frequency distributions and summary statistics for integrated nitrogen dioxide measurements in two locations (152 study homes).

Source Koontz et al (1986)

average to residential levels The use of UVGSHs in homes either as a primary or secondary heat source results in high levels of NO_2 in those homes In this study, associations between indoor concentrations of NO_2 and variables derived from questionnaires, activity logs, and other recorded information (indoor and indoor temperatures, gas-meter readings, etc) were examined. The single most important variable accounting for variations in indoor NO_2 levels in homes using UVGSHs was the difference between indoor and outdoor temperatures In homes using the heaters as a primary heat source, variations in indoor/outdoor temperature differences accounted for 64% of the variation in NO_2 levels and 33% of the variation for homes where the heaters are used as a supplemental heat source

In a study of 14 homes with one or more UVGSHs (primary source of heat) in the Atlanta, GA, area, McCarthy et al (1987) measured NO_2 levels by both chemiluminescence and passive monitors in two locations in the homes (room with the heater and a remote room in the house) and outdoors Chemiluminescence measurements were taken over 5-min

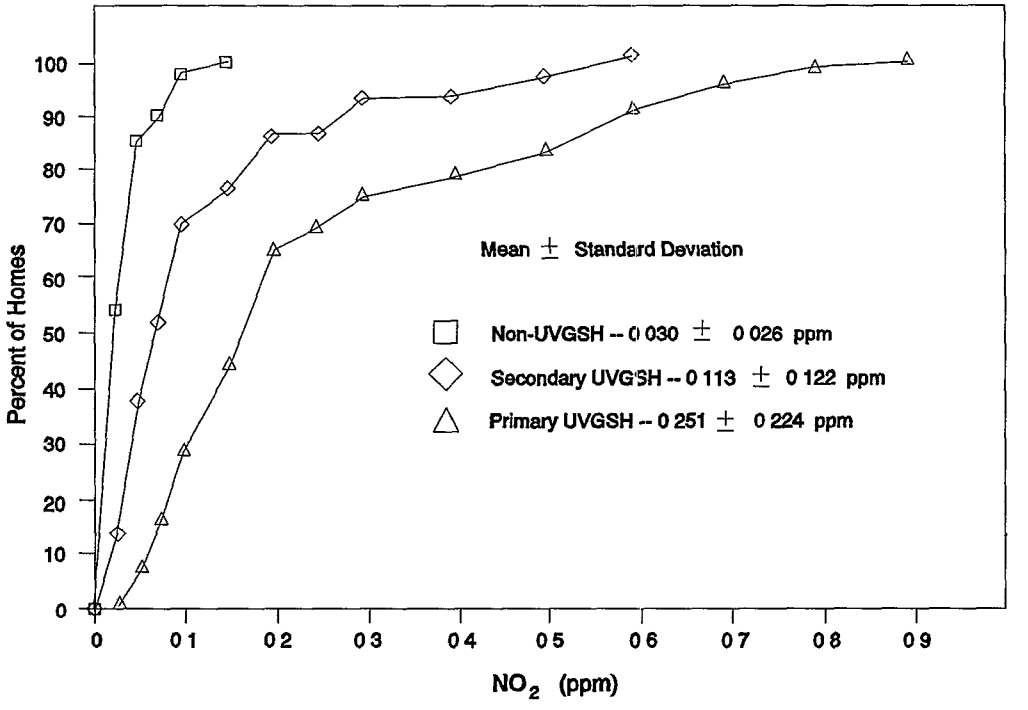


Figure 7-27. Cumulative frequency distributions and summary statistics for indoor nitrogen dioxide concentrations in three groups of monitored homes.

Source Koontz et al (1988)

periods in turn from each of the three sampling points for each house over a 96-h sampling period The authors reported only the summary statistics for NO_2 based on the continuously collected data Eleven of the 14 UVGSH homes exceeded 100 $\mu g/m^3$ (0 053 ppm) during the sampling period Mean values ranged from 40 to 1,460 $\mu g/m^3$ (0 02 to 0 77 ppm) and varied as a function of the use pattern of the heater Only one of the homes used more than one heater during air sampling

The highest residential average NO_2 concentrations observed for homes are associated with UVGSHs Unvented gas space heaters are a major source of NO_2 in residences The reported average concentrations covered periods when the heaters were used as well as not used Unless the gas heaters were in continuous operation during the air sampling period, actual NO_2 levels during heater use will be higher than the average values reported

TABLE 7-22. ONE-WEEK AVERAGE NITROGEN DIOXIDE LEVELS IN HOMES IN NORTH CENTRAL TEXAS BY SOURCE CATEGORY, WITH AND WITHOUT UNVENTED GAS SPACE HEATER[a]

	NO_2 (ppm)		
Source Category.	N	Mean	SD
No UVGSH, Gas Stove	22	0 030	0 019
UVGSH as Secondary Heat Source, No Gas Stove	9	0 068	0 075
UVGSH as Secondary Heat Source, Gas Stove	29	0 099	0 094
UVGSH as Primary Heat Source, No Gas Stove	5	0 098	0 053
UVGSH as Primary Heat Source, Gas Stove	73	0 280	0 235

[a]NO_2 = Nitrogen dioxide
N = Number
SD = Standard deviation
UVGSH = Unvented gas space heater

Source Koontz et al (1986)

Concentrations During Heater Use and Spatial Variations

Results from the two field studies on indoor NO_2 concentrations in residences with UVGSHs (Koontz et al., 1986, 1988, McCarthy et al , 1987) indicate that there are no significant differences in NO_2 levels between the room with the heater and remote rooms in the houses monitored Koontz et al (1986, 1988) demonstrated there was not a strong spatial NO_2 gradient in homes using UVGSHs Concentrations were highly correlated between the two locations (r = 0 89), with a difference of less than 20% in more than half the homes. This finding is similar to that for unvented kerosene space heaters and is in contrast to the pronounced spatial gradient for NO_2 observed for homes with gas ranges The high convective heat output of the heaters and relatively long heater use times apparently foster rapid and complete mixing in houses

Although both field studies collected data on short term indoor concentrations of NO_2 associated with UVGSH use, only Koontz et al (1988) have reported the results of those measurements Of the 16 houses monitored continuously for NO_2, 12 reported use of their UVGSH during the monitoring period A box plot of the monitoring results (15-min averages) for these 12 houses is shown in Figure 7-28 The wide variation in concentrations is evident with a highest 15-min concentration of 2,716 $\mu g/m^3$ (1 44 ppm) recorded in house A The higher concentrations may be the levels encountered for sustained periods of time (e g , hours) because they may approximate the equilibrium levels under periods of heater use

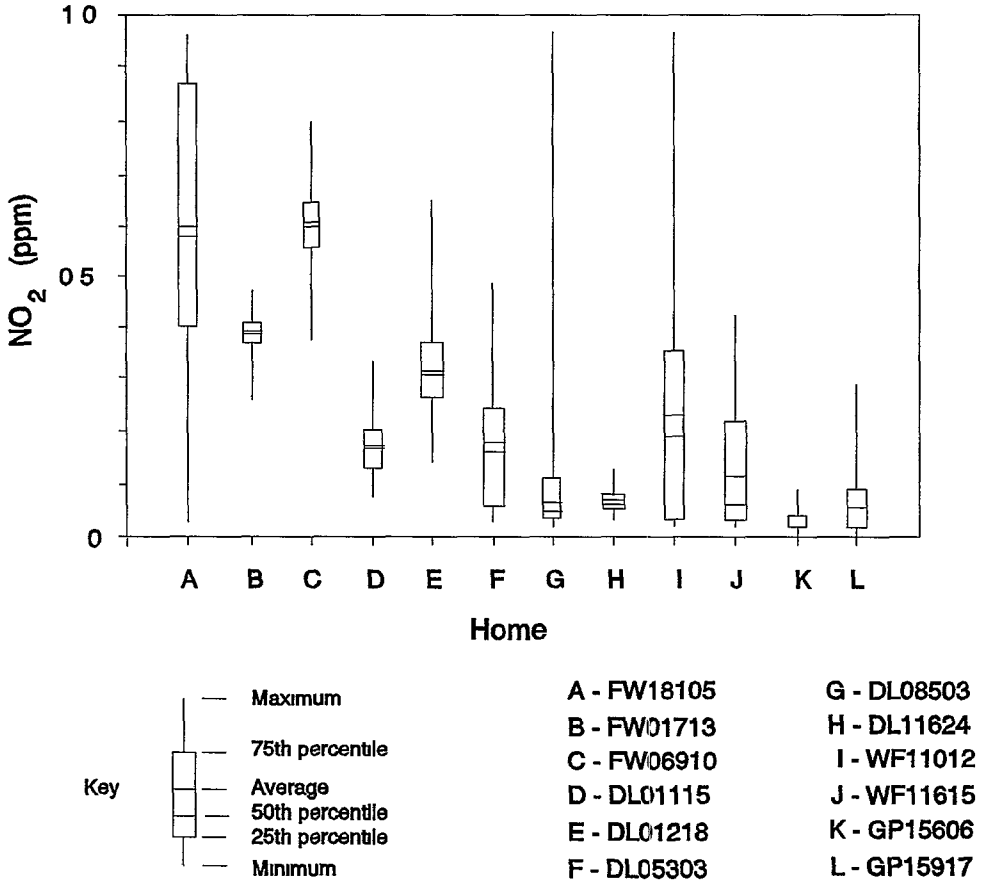


Figure 7-28. Nitrogen dioxide box plots for 12 continuously monitored homes.

Source Koontz et al (1988)

7.3.5 Other Sources

The major sources of NO_2 in residences are unvented gas and kerosene space heaters, gas appliances, and outdoor NO_2 levels Improper use of gas appliances (e g , using a gas stove to heat living space) and improper operation of vented gas appliances (e g , improper use or malfunctioning gas appliances) can be important contributors to NO_2 concentrations measured indoors. Beals et al (1987) provides some data on the contribution to indoor NO_2 levels from improper use of gas appliances The highest NO_2 concentrations in the homes studied were associated with the use of a gas range/oven as a supplemental heat source The impact of improperly operating wall or floor furnaces (spilling a portion of the exhaust fumes into the home) on indoor NO_2 levels has not been assessed

The contribution of wood or coal burning stoves or fireplaces to indoor NO_2 levels has not yet been assessed To the extent that there is leakage of the exhaust gas into the living space during stoking the fire or through spilling of a portion of the exhaust gas into the living space, these sources will contribute to indoor levels of NO_2

Using Palmes tubes, Good et al (1982) compared 7-day average NO_2 levels in homes with and without smokers and without gas ranges Concentrations were measured in three locations in each home (living room, bedroom, and kitchen) and outdoors There were a total of 79 homes monitored (no gas range) over two seasons (winter and summer) Analysis of the data indicates that the contribution to residential NO_2 levels from cigarette smoking was 4 and 3 $\mu g/m^3$ (0 0021 and 0 0016 ppm) in the summer and winter, respectively In another field study (Leaderer et al , 1986a), 14-day average NO_2 levels were monitored using Palmes tubes in homes with no known sources of NO_2 ($n = 69$) and homes having smokers only ($n = 61$) Homes with smokers showed significantly higher levels of NO_2 only in the living room ($t = 2\ 09$, $p = 0\ 038$) The mean NO_2 level in the smokers' living rooms was 1.1 $\mu g/m^3$ (0 0006 ppm) higher than in the unexposed homes Other studies, however, have found no impact on indoor residential NO_2 levels from cigarette smoking (e.g., Wilson et al., 1986)

7.3.6 Modeling of Indoor Concentrations

Predictive or exploratory models for indoor concentrations of indoor air contaminants generally take two basic forms The first is a physical/chemical model that usually follows

some form of the general mass balance equation (e g , Equation 7-1) The physical/chemical modeling approach requires detailed information on the input parameters (source strengths, infiltration rates, mixing, reaction rates, etc) to predict the indoor concentrations The input parameters are either measured in chamber studies and in homes or are estimated The second modeling approach is statistical in nature based upon empirical measurements These models make simple assumptions with little or no transformations of the independent variables that are input to the model The statistical models utilize as input parameters data obtained in large field studies through both measurement and estimation (questionnaires) The statistical models are typically simple linear models where the independent variables are used as they are recorded from the questionnaires to explain variations in the concentrations of the air contaminants measured Both modeling approaches have been utilized in evaluating indoor concentrations of NO_2

7.3.6.1 Physical/Chemical Models

The physical/chemical modeling approach has been used by a number of investigators in chamber, test-house, and small field studies (involving a small number of homes) to estimate emission rates of NO_2 from combustion sources (e g , Traynor et al , 1982, Moschandreas et al , 1984, Leaderer, 1982, Brauer et al , 1990), to estimate reactive decay rates (e g , Yamanaka, 1984, Borrazzo et al , 1987a,b, Leaderer et al , 1986a,b, Spicer et al , 1986, 1989, Ozkaynak et al , 1982), to estimate the impact of ventilation and mixing on the spatial and temporal distribution of NO_2 (e g , Borrazzo et al , 1987a; Ozkaynak et al , 1982, Traynor et al , 1982), and to evaluate the applicability of emission rates determined under controlled conditions in estimating indoor concentrations of NO_2 (e g , Traynor et al , 1982, Borrazzo et al , 1987a) The physical/chemical approach is the bases for a number of models or subcomponents of larger exposure models that calculate the air concentrations of a single- or multiroom building (e g , Austin et al , 1988, Hayes, 1989, Sparks, 1988, Nazaroff and Cass, 1986) More recently, three studies have been reported that utilize distributions of the input variables to the mass balance equation (emission rates, source use, decay rates, ventilation rates, etc) determined from the published literature to estimate the distributions of NO_2 levels indoors for specific sources and combinations of sources (Traynor et al , 1987, Hemphill et al , 1987, Drye et al , 1989) Use of the

physical/chemical models to evaluate model input parameters (e g , source strength) in explaining measured indoor levels of NO_2, user-friendly computer models for predicting NO_2 for specific indoor settings and conditions, and efforts to use physical/chemical models to estimate concentration distributions will be touched upon here Emphasis is placed upon physical/chemical models that are used to predict population distributions of NO_2

Borrazzo et al (1987a) applied a mass-balance model to NO_2 levels measured in a town house with gas appliances Nitrogen dioxide emission rates were determined from a portable sampling hood, reactive decay rates were determined from a comparison of NO_2 and sulfur hexafluoride (SF_6), and infiltration rates were determined from SF_6 decay rates Comparing model predictions with measured concentrations yielded a difference of 28% for NO_2 Differences in NO_2 emission rates over time of use of gas appliances and breakdown of the well-mixed single-compartment model assumption were thought to account for the discrepancies in the predicted versus measured concentrations In a study of the effects of ventilation on residential air pollution from a gas-fired range (Traynor et al , 1982), a gas range tested in a series of chamber studies was used in a test house and measured NO_x levels were compared to those predicted by a mass-balance model In this study, infiltration, gas consumption, and NO_2 reactivity rates were measured The results indicated good overall agreement between the measured and predicted NO_x levels over the full test periods, although discrepancies in predicited and measuied concentration were observed in the start-up phase of the sources The authors note that the main deficiency in the model is the assumption that the house is a single cell and, as such, does not address the spatial variation in concentrations.

In recent years a number of user-friendly indoor air quality models, based upon physical/chemical approaches, have been developed (e g , SHAPE, PAQM) to evaluate the impact of indoor sources and outdoor contaminant levels on air contaminant levels in single rooms or multiple rooms (e g., Austin et al , 1988, Hayes, 1989, Sparks, 1988, Nazaroff and Cass, 1986) These models are frequently a component of a larger model used to predict personal exposure A brief review of these models is provided by Weii et al (1990) The models utilize estimated or measured values for whole-house air exchange rates, mixing within and between rooms, source strengths and use patterns, and contaminant removal and/or chemical transformations to predict indoor concentrations over varying time frames

The uncertainty associated with the input parameters and the use of these models to predict indoor NO_2 concentrations in single residences is not known No systematic effort has been made to validate these models for predicting NO_2 levels in single residences

Traynor et al (1987) have reported on efforts to develop a macromodel for assessing indoor concentrations of combustion-generated pollutants The model is a single-chamber, well-mixed, mass-balance model (Equation 7-1) that utilizes experimentally derived estimates of emission factors, building penetration factors, and reactivity rates in combination with existing regional and national data (e g , house volumes, market penetration of unvented combustion sources) and source usage and infiltration models to estimate indoor pollutant concentration distributions Deterministic and Monte Carlo simulation techniques are used to combine all of the inputs to yield the concentration distributions The macro model will be used to estimate the distribution of NO_2 concentrations indoors In a parallel development of a statistical and physical/chemical model, Hemphill et al (1987) developed a stochastic model based on the physical model to predict indoor NO_2 concentration distributions in homes using UVGSHs as the primary source of heat

Billick et al (1988) used a macro modeling approach similar to that used by Traynor et al (1987) This simulation model used parameters measured in field and laboratory studies as inputs to construct distributions of air exchange rates, reactive decay rates, outdoor NO_2 levels, gas range NO_2 emission rates, and gas range useage The model was used to generate indoor distributions of NO_2 for homes with gas or electric ranges for winter and summer The computed distributions were then compared to measured concentrations in a sample of over 600 homes in Southern California The measured and estimated NO_2 means differed by 5% for the summer For the winter,, modeled values of the means were 10% lower than the measured values for gas range homes and 25% lower for electric range homes

An extensive data base on indoor levels of NO_2 associated with unvented gas space heating was reported by Koontz et al ,(1986, 1988) (see Section 7 3 4 2) The authors utilized the physical/chemical model to predict indoor NO_2 levels and to compare the results to indoor levels predicted from a regression analysis of the measured data The physical/chemical model was used to predict steady-state concentrations for four cases (no indoor sources, pilot lights only, pilot lights plus cooking, and pilot lights plus cooking

and heating) The authors incorporated into the model a term for heat demand for a UVGSH to maintain a given indoor/outdoor temperature differential Emission rates were derived from the literature, source use and house volumes were measured, air exchange rates were estimated, and a constant decay rate was assumed The model predicts a broad distribution of indoor NO_2 concentrations associated with use of UVGSHs where indoor/outdoor temperature differentials are the best predictors This study also found good agreement between the mass-balance model and a regression model developed from the collected data The authors concluded that the steady-state physical/chemical model provides reliable estimates for annual average NO_2, but may underestimate the frequency of occurrence of peak concentrations Statistical results to assess the accuracy of the model were not presented.

The use of physical/chemical (mass-balance) models (single compartment) to predict indoor concentrations of NO_2 indoors or distributions of concentrations in homes with combustion sources requires accurate information on the input parameters Although data are available for some of the input parameters under controlled experimental conditions (e g , emission rates), there are very limited data available on the variability of the input parameters in actual homes or the factors that control the variability of those inputs (e g , variability of emission or decay rates) Obtaining field measurements or estimates of the inputs in large numbers of homes would be expensive and time consuming. Such modeling efforts, however, do help to identify the potential range of indoor NO_2 concentrations and factors that may result in high levels and the potential effectiveness of mitigation efforts

7.3.6.2 Statistical/Empirical Models

Field studies that have measured NO_2 concentrations in residences and associated outdoor levels for time periods of a week or more have typically obtained questionnaire information on sources in the residences, source use, building characteristics (house volume, number of rooms, etc), building use, and meteorological conditions In some cases, additional measurements such as temperatures have been recorded Several investigators have attempted to fit simple regression models to their field-study data bases in an effort to determine if the variations in NO_2 levels seen among houses can be explained by variations in the questionnaire responses and any additional measurements that may have been taken

The goal has been to see how well questionnaire information or easily available information (meteorological data) can predict indoor NO_2 levels In most cases, a linear model has been used, but several investigators have used log transformations of variables Table 7-23 presents a summary of the regression models that have been fitted to large field-study data bases The independent variables entered into the analysis ($p < 0\ 05$), the R^2, and standard error of the estimate reported by the investigators are shown in the table No standard errors were reported for a number of the models, although several investigators reported standard errors for the independent variables in their models Linear regression models, with the exception of the Petreas et al (1988) model, explain from 40 to 70% of the variations in residential NO_2 levels and typically have large standard errors associated with their estimates Although the log transformations of variables have always produced a higher percent of explained variation due to the skewed distribution of the original variables, interpretation of the coefficients in a nonlinear model can require special attention

The independent variables reported as being significant in each model are broken down into four general categories in Table 7-23 (1) sources, (2) source use, (3) removal/dilution, and (4) interactive terms The only independent variables that are common to all models are those that deal with the identification of sources in the residences and outdoor concentrations The identification of the sources accounted for the major portion of the explained variation in indoor NO_2 levels for all models Those models that incorporate source-use information or proxies for source-use generally produce better fitting models Only one model, developed from an extensive data base (Wilson et al , 1986), found a number of variables related to the removal or dilution of NO_2 indoors Three models found independent variable interactive terms to be significant

Butler et al (1990) reported on the regression model developed from the most extensive data base (up to 1,952 observations) It is an extension of a previous effort (Drye et al , 1989), but differs from it in that a larger data base is used, data from electric ranges are also factored in, and additional independent variables are considered The data used are from eight different locations and are drawn from several studies the Beals et al (1987) study, the Indoor Air Quality Characterization Study (Wilson et al , 1986), the Boston Residential NO_2 Characterization Study (Ryan et al , 1988), and the Harvard Six City Study (Ferris et al , 1979) The authors reported conducting a verification test (results not shown) of the

TABLE 7-23. EMPIRICAL STATISTICAL MODELS (REGRESSION) FOR RESIDENTIAL NITROGEN DIOXIDE CONCENTRATIONS REPORTED FROM FIELD STUDIES OF INDOOR LEVELS[a]

House Location	Number of Observations	R^2	SE (ppm)	Sources	Source Use	Removal/Dilution	Interactive Terms	Reference
Bedroom Kitchen	400 to 578	0 45 to 0 63	(0 012 to 0 022)	Outdoor NO_2 Gas range/oven Gas floor furnace Range pilots Oven pilots Gas water heater Age of gas oven	Oven use Number of occupants Oven cleaning Max temp	Total house volume Air exchange rate Open windows Bedroom area House age Number of bedrooms Gas range hood use	Pilot lights, ventilation volume, outdoor NO_2	Wilson et al (1986)
Bedroom Kitchen Living room	318	0 57 to 0 66	(0 010 to 0 011)	Outdoor NO_2 Convect /radiant kerosene heater Gas range/oven Other gas appl Cig smoking	Outdoor temp Convect /radiant kero heater use Gas/oven use Number of cigarettes	Number of fireplaces	Convective kerosene heater use squared	Leaderer et al (1987)
Activity room	114	0 69	(0 075)	Outdoor NO_2 Gas stove with pilot light Gas stove w/o pilot light Gas dryer Floor/wall furnace Use of toaster/microwave in gas stove house	Income level			Marbury et al (1988)
Kitchen Bedroom	215 to 262	0 31 to 0 39	—	Gas/cooking fuel Location variable Cigarette smoking		House volume Bedroom window open		Petreas et al (1988)
Center of house	29 to 82	0 40 to 0 69	—	Unvented gas space heater Condition of furnace Number of pilot lights Outdoor NO_2	Difference between indoor/outdoor temp Exposure to high wind Use of gas range for heat	Gas range exhaust fan		Koontz et al (1986)
Kitchen Living room	173	0 59 to 0 68	—	Outdoor NO_2 Presence of gas geyser Cooking fuel Type of space heating Log of NO_2 in rooms		Kitchen volume Number of doors		Noy et al (1984)
Kitchen Bedroom	1782 to 1952	0 40 to 0 76	— —	Outdoor NO_2 Gas range pilot lights Microwave oven	Presence or absence	House volume Multifamily		Butler et al (1990)

[a]SE = Standard error NO_2 = Nitrogen dioxide

model by comparing modeled results to values measured in Watertown, MA, and reported that in general, there was good correspondence between the modeled and observed values Tests of the earlier version of this model (Drye et al , 1989) indicated good model performance

The model developed from the second most extensive data base on NO_2 levels indoors associated with gas appliances (Beals et al , 1987) only explained approximately 60% of the variation in indoor levels, with standard errors in the range of 40 $\mu g/m^3$ (0 021 ppm) There is little uniformity among the models in the form of the source use and removal/dilution terms or their significance in the models

Regression models developed from field studies employing questionnaires to explain variations in indoor levels of NO_2 have met with only moderate success Better information through additional measurements and better questionnaire design, is needed on source type and condition, source use, contaminant removal (infiltration and reactive decay), and between- and among-room mixing if the statistical/empirical models are to be used to estimate indoor concentrations of NO_2 in homes without measurements The unexplained variance may be a function of factors that are difficult to address by questionnaire, such as actual reactive decay in a home

7.3.7 Reactive Decay Rate of Nitrogen Dioxide Indoors

A number of field studies of NO_2 levels in residences have reported that NO_2 is removed more rapidly than can be accounted for by infiltration alone (Wade et al , 1975, Macriss and Elkins, 1977, Ozkaynak et al , 1982, Ryan et al , 1983, Traynor et al , 1982, Leaderer et al , 1986a) Nitrogen dioxide indoors is removed by infiltration/ventilation and by interior surfaces and furnishings The removal of NO_2 by interior surfaces and furnishings and reactions occurring in air is often referred to as the reactive decay rate of NO_2 Failure to account for the reactive decay rate (K in Equations 7-2 and 7-3) can (1) lead to a serious underestimation of emission rate measurements in chamber and test-house studies and a serious overestimate of indoor concentrations when using emission rates to model indoor levels and (2) be a significant factor in the actual NO_2 levels measured in residences The NO_2 reactive decay rate is typically determined by comparing the decay of NO_2, after a source is shut off, to that of a relatively nonreactive gas (e g , carbon monoxide

[CO], carbon dioxide [CO_2], SF_6) The measured reactive decay rates in the above-mentioned field studies typically ranged from 0 1 to 1 6 air changes per hour All studies noted that the reactive decay of NO_2 is as important and in some cases, more important than infiltration in removing NO_2 indoors Leaderer et al (1986a), in the continuous monitoring of NO_2, NO, CO, and CO_2 in seven houses over periods ranging from 2 to 8 days, reported that the NO_2 decay rate was always greater than that due to infiltration alone and was highly variable among houses and among time periods within a house

In an effort to identify the factors that control the NO_2 reactive decay rate, a number of small chamber (Miyazaki, 1984, Spicer et al , 1986), large chamber (Moschandreas et al , 1985; Leaderer et al , 1986b), and test-house studies (Yamanaka, 1984, Borrazzo et al , 1987a,b; Fortmann et al , 1987) have been conducted The most extensive small chamber work is reported by Spicer et al (1986), in which 35 residential materials were screened for NO_2 reactivity in a 1 64-m^3 chamber, and in which a limited number of the materials were tested for the impact of relative humidity on the reactivity rate Figure 7-29 shows the relative rates of NO_2 removal for the materials screened The figure indicates that many of the materials used for building construction and furnishings are significant sinks for NO_2 and that their removal rate is highly variable Many of the materials were found to reduce a significant fraction of the removed NO_2 to NO In no cases was NO_2 remitted, although some materials emitted NO The authors noted that the materials that removed NO_2 most rapidly fall in two categories porous mineral materials of high surface area and cellulosic material derived from vegetable matter Higher relative humidities were found to enhance the removal rate for some materials (e g , wool carpet), reduce the removal rate for some (e.g., cement block), and have little effect on others (e g , wallboard) In a subset of experiments (Spicer et al , 1989), the mechanisms by which selected materials removed NO_2 were investigated In these experiments, known amounts of NO_2 were passed over a packed bed of granular or shredded materials Nitrogen dioxide and NO_2 reaction products were measured and mass balances calculated The results indicated different removal mechanisms for NO_2, including removal and retention by materials, reactions with adsorbed water producing NO and HONO, and chemical reactions with organic constituents of the test material

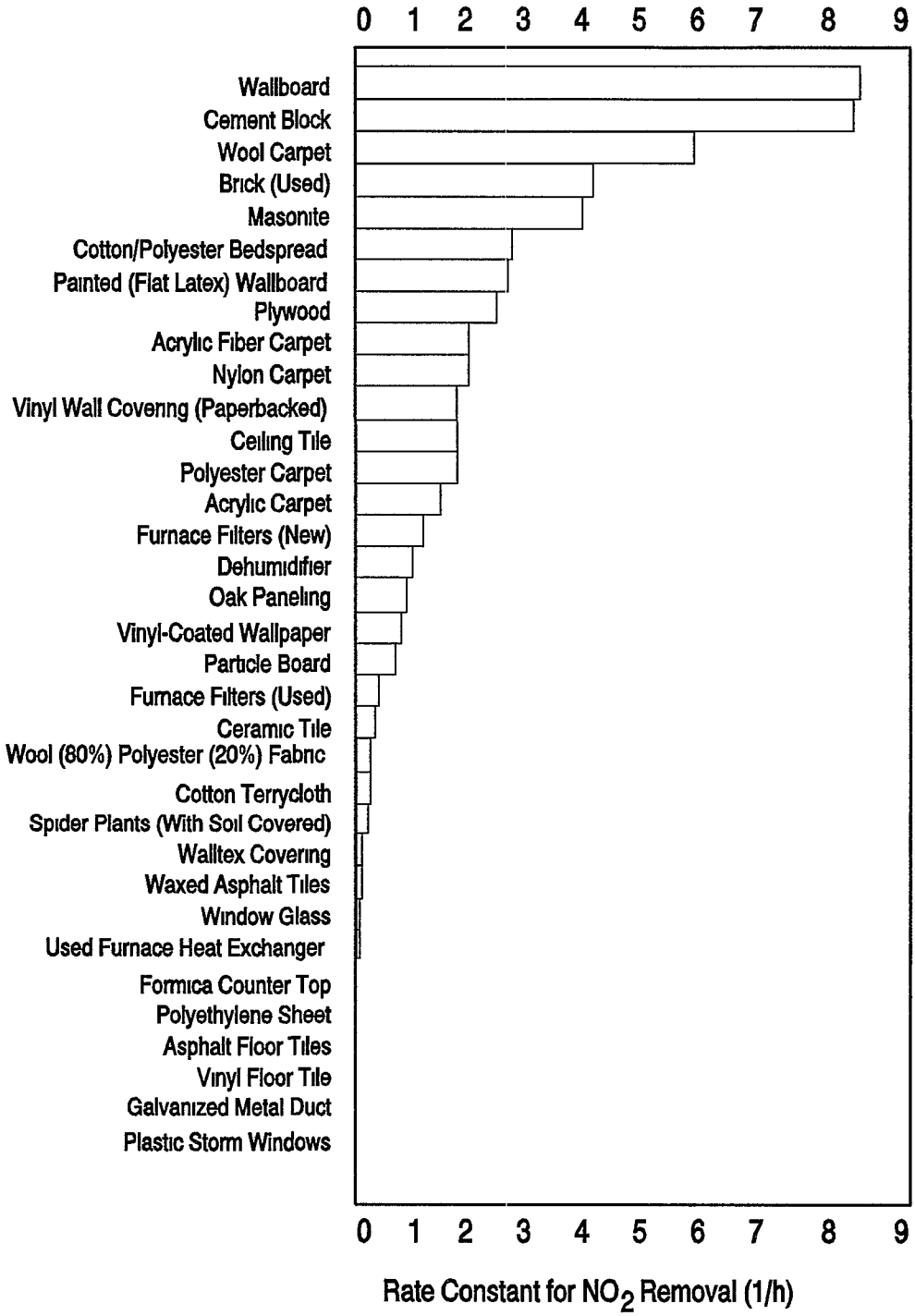


Figure 7-29. Bar graph of nitrogen dioxide removal rate for various materials evaluated in a 1.64-m^3 test chamber at 50% relative humidity.

Source Spicer et al (1986)

In a series of small (0 69-m^3) chamber studies (Miyazaki, 1984), reactive decay rates for NO_2 were found to vary as a function of material type and to increase with increasing surface area of the material, degree of stirring in the chamber, temperature, and relative humidity A saturation effect was noted on some of the carpets tested

In a series of large (34-m^3) chamber studies, Leaderer et al (1986b) evaluated the reactive decay rate of NO_2 as a function of material type, surface area of material, relative humidity, and air mixing (Figure 7-30) The reactive decay rate was found to vary as a function of material surface roughness and surface area Carpeting was found to be most effective in removing NO_2, and painted wallboard was least effective Increases in relative humidity were associated with increases in removal rates for all materials tested, but the slope was a shallow one Of particular interest is the finding in this study that the degree of air mixing and turbulence was a dominant variable in determining the reactive decay rate for NO_2. Moschandreas et al (1985) evaluated six materials in a 14 5-m^3 chamber and found variations in decay rates by material types and a positive impact on NO_2 decay rates in an empty chamber by relative humidity

Yamanaka (1984) assessed NO_2 reactive decay rates in a Japanese living room and found the decay to be comprised of both homogeneous and heterogeneous processes The rates were found to vary as a function of surface property and sharply as a function of relative humidity. During the decay, NO production was noted In a test-house study, Fortmann et al (1987) noted that the NO_2 decay rate tends to decrease as the concentration increases It is not clear whether this is due to surface saturation or second-order kinetics This study also noted a sharp increase in NO levels during the NO_2 decay, indicating NO production as a result of the NO_2 decay In a test-house study conducted over a 7-mo period, Borrazzo et al (1987a) found that reaction rates for NO_2 in the test house were sensitive to the location in the house where they were measured This indicates that reaction losses during transport of NO_2 from room to room in a house may be important

The reactive decay of NO_2 in residences associated with interior surface materials and furnishings is an important mechanism for removing NO_2 in residences Nitrogen dioxide reactive decay rates vary as a function of the type of material and surface area of the material The impact of relative humidity on the decay rate is unclear, with some studies showing a pronounced impact (Yamanaka, 1984) and others showing moderate or little

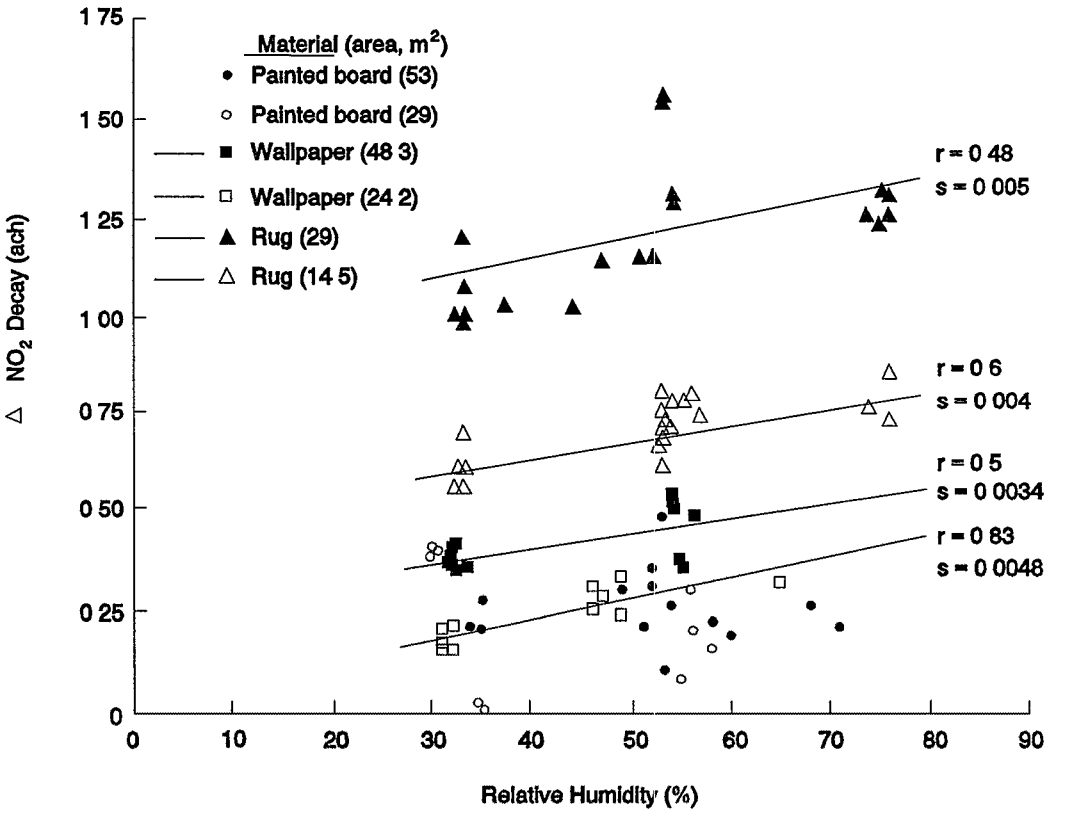


Figure 7-30. The deposition rates in air changes per hour for nitrogen as a function of percent relative humidity for two surface areas of three materials.

Source Leaderer et al (1986b)

impact (e g , Spicer et al , 1986, Leaderer et al , 1986b) The degree of air mixing or turbulence can have an important effect on the reactive decay rate A by-product of NO_2 removal by materials is NO production and a saturation effect may occur for some materials Reactive decay of NO_2 in residences is highly variable between residences, within rooms in a residence, and on a temporal basis within a residence The large number of variables controlling the reactive decay rate makes it very difficult to assess in large field studies through questionnaire or integrated air sampling

7.4 NITRIC AND NITROUS ACIDS CONCENTRATIONS

Nitric acid and HONO may be formed in the gas phase during combustion and by heterogenous hydrolysis of NO_2 The rate of formation of nitrogen acids, particularly HONO, is expected to vary with the NO_2 concentration, humidity and temperature, light intensity, and the various surfaces present in a home (Spengler et al , 1993)

Brauer et al (1991) used annular denuder filter pack sampling systems to measure the gaseous pollutants HNO_3, HONO, NO_2, and NH_3 during summer and winter periods in Boston, MA Five homes were sampled during the winter period and six were sampled during the summer. All homes in the winter period had gas ranges During the summer period, four of the six homes had no unvented gas appliances Indoor samples were placed in a room adjacent to the kitchen and at a height of approximately 1 5 m above the floor Outdoor samples were placed 3 to 5 m from the home Outdoor levels of HNO_3 exceeded indoor concentrations during both seasons (Figure 7-16b) Lower indoor concentrations are due to the lack of measurable indoor production and the high surface reactivity of HNO_3 The authors attribute the higher indoor levels in the summer to higher outdoor summer levels of HNO_3 and higher infiltration rates in the summer The authors conclude that the major source of HNO_3 indoors is outdoor concentrations In a recent paper, Weschler et al (1992) argue that in the summer an indoor reaction between O_3 and NO_2 can be a significant source of HNO_3 and peroxy radicals High air-exchange rates could produce levels of O_3 and NO_2 high enough for such a reaction to be significant The major pathway for formation of HNO_3 indoors may be the NO_3 abstracting a hydrogen atom from vapor-phase organic compounds. A review of data collected by Brauer et al (1991) and Weschler et al (1992) supports this conclusion

It is not known whether exposure to gaseous HONO is associated with health effects An effective nitrosating agent, HONO may react with gaseous secondary amines in air to form nitrosamines, which have been shown to be carcinogenic in animals (Pitts et al , 1978, Magee, 1982). In Brauer et al (1991), indoor levels of HONO were higher indoors than outdoors for both winter and summer for all of the homes (Figure 7-31), even those without unvented gas appliances where indoor levels of NO_2 were lower than outdoor levels Indoor and outdoor levels of HONO were found to be correlated with NO_2 concentrations Winer and Bierman (1991) report ambient short-term (15-min) HONO levels of 7 ppb in Claremont,

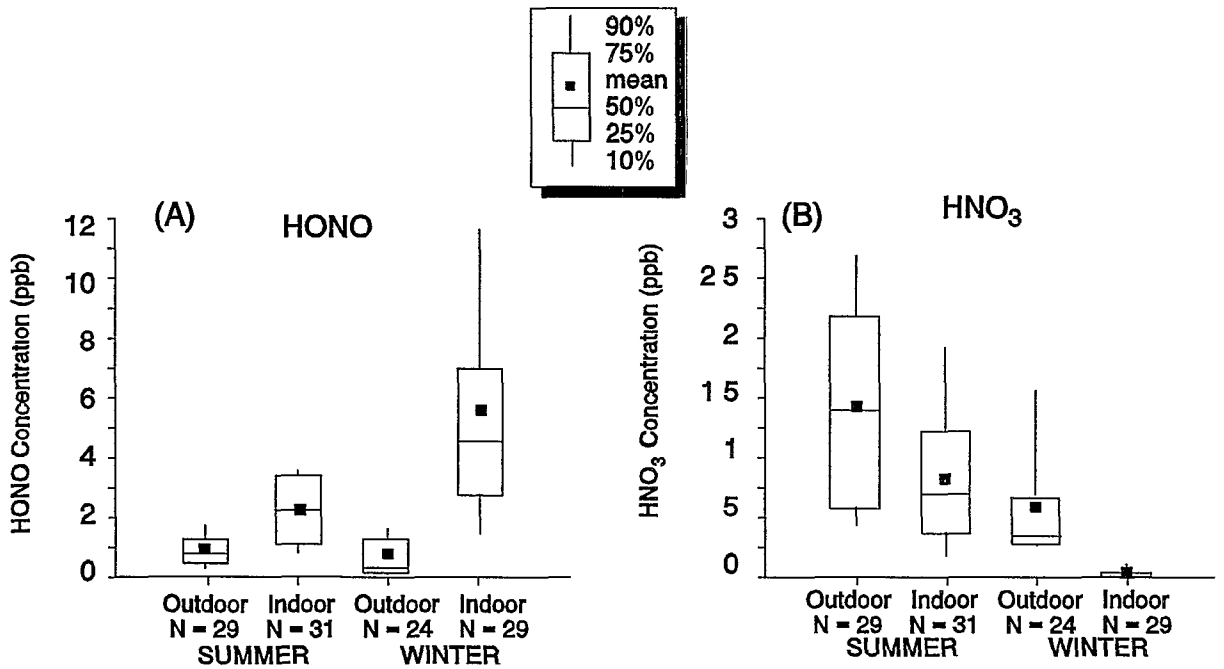


Figure 7-31. Concentration distributions (in ppb) for gas-phase species in Boston: (A) nitrous acid and (B) nitric acid (N = number of valid observations).

Source Brauer et al (1991)

CA, and 16 ppb in Long Beach, CA The highest levels occurred just before sunrise Nighttime concentrations between 2 and 4 ppb were not uncommon in Los Angeles Spengler et al (1993) studied levels of NO_2 and HONO indoors in 10 homes in Albuquerque, NM The indoor 24-h mean HONO concentration ranged from 2 to 8 ppb Indoor HONO concentrations were found to be well correlated with indoor NO_2 levels, HONO concentrations ranged from 5% to 15% of the measured NO_2 concentrations

Indoor concentrations of HONO appear to be higher indoors than outdoors, even when indoor concentrations of NO_2 are do not exceed outdoor levels A possible mechanism for this is the heterogeneous reaction of NO_2 with water (Sakamaki et al , 1983, Pitts et al , 1984, Svensson et al , 1987; Jenkin et al , 1988, Brauer et al , 1990, 1991). In homes where unvented combustion sources are used, elevated HONO levels may be associated with direct emission of HONO from the flame as well as with heterogeneous reactions with water of the produced NO_2 (Pitts et al , 1989, Brauer et al , 1990, 1991)

7.5 SUMMARY

7.5.1 Ambient Nitrogen Dioxide Levels

Nitrogen oxides concentrations in isolated rural sites and coastal inflow areas in the United States generally range from a few tenths to 1 ppb The concentrations in the atmospheric boundary layer and lower free troposphere in remote maritime locations are in the range 0 02 to 0.04 ppb, and concentrations of NO_x in remote tropical forests have been reported to range from 0 02 to 0 08 ppb (Kelly et al , 1982, Lefohn et al , 1991, National Research Council, 1991)

Analysis of NO_2 data in the AIRS data base for the period 1981 to 1990 indicates a downward trend for the composite United States annual average NO_2 concentration The 1990 composite NO_2 average was 8% less than the 1981 average, and the difference was statistically significant (AIRS, 1992)

The highest hourly and annual ambient NO_2 levels are reported from stations in Southern California, where the current annual standard of 0 053 ppm has been exceeded The seasonal patterns at California stations are usually quite marked and reach their highest levels during the fall and winter months For most of the other urban sites characterized, the highest monthly average NO_2 concentrations also were obtained in the fall or winter months (U.S. Environmental Protection Agency, 1991a,b)

The diurnal patterns of NO_2 for the urban sites showed that, on the average, the highest concentrations occur in the late afternoon and evening hours (1700 to 2200 hours) For those urban areas experiencing hourly NO_2 concentrations >0 2 ppm, the episodic occurrences are experienced usually in the midmorning and afternoon/evening hours (AIRS, 1991)

Based on data collected at rural locations for the period 1979 to 1991, the hourly average NO_2 concentrations for selected U S forest and agricultural sites were <0 10 ppm in most cases. As observed for urban locations, a consistent seasonal pattern was distinguishable for both the rural forested and agricultural sites In general, the NO_2 monthly average values were at their highest during the fall and winter months A consistent diurnal pattern was also observed for the rural forested and agricultural sites, late afternoon and evening hours (approximately 1700 to 2200 hours) contained the highest NO_2 concentrations There were some exceptions to these patterns (AIRS, 1992)

Studies characterizing the joint occurrence of gaseous NO_2/SO_2 and NO_2/O_3 have demonstrated that (1) the co-occurrence of two-pollutant mixtures lasted only a few hours per episode, and (2) the time between episodes is generally long (i e, weeks, sometimes months) (Lefohn and Tingey, 1984) The periods of co-occurrence represent a small portion of the potential plant growing period For human ambient exposure considerations, in most cases, the simultaneous co-occurrence of NO_2/O_3 was infrequent However, for several sites located in the Southern California South Coast Air Basin, more than 450 simultaneous co-occurrences of each pollutant at hourly average concentrations equal to or greater than 0 05 ppm have been reported Besides considering the joint occurrence of gaseous pollutants, it may be advisable to consider the joint occurrence of O_3 with nitrogen via dry deposition in forested landscapes (Taylor et al , 1992)

The average concentrations of HNO_3 and NO_3^- are generally in the range 0 1 to 20 ppb and 0 1 to 10 ppb, respectively (Allegrini and De Santis, 1989, Wolff et al , 1986a,b, 1991, Kelly et al , 1982, 1984) Because there are conflicting reports on the ability of filters to accurately separate HNO_3 from NO_3^- aerosol, it may be more appropriate in some cases to focus on the total NO_3 (HNO_3 + NO_3^-) than on the individual components

7.5.2 Indoor Nitrogen Dioxide Levels

Indoor concentrations of NO_2 are a function of outdoor concentrations, indoor sources (source type, condition of source, source use, etc), infiltration/ventilation, air mixing within and between rooms, reactive decay by interior surfaces, and air cleaning or source venting In homes without indoor sources of NO_2, concentrations are lower than outdoor levels due to removal by the building envelope and interior surfaces, thus providing some degree of protection from outdoor concentrations Indoor/outdoor ratios for homes without sources vary considerably by season of the year, with the lowest ratios occurring in the winter and the highest occurring during the summer Considerable variability in the ratios within a season exists The differences are probably due to seasonal differences in infiltration rates, NO_2 reactivity rates, penetration factors, and outdoor concentrations (Leaderer et al , 1986a)

Gas appliances (gas range/oven, water heater, etc) are the major indoor source category for indoor residential NO_2 by virtue of the number of homes with such sources (approximately 45% of all homes in the United States) (U S Bureau of the Census, 1982)

Nitrogen dioxide levels in homes with gas appliances are higher than those without such appliances and are often higher than levels encountered outdoors Within this category, the gas range/oven is a major contributor, especially when used as a supplemental heat source Average indoor concentrations in bedrooms (over a 1- to 2-week measurement period) range from 20 to 120 $\mu g/m^3$ (0 010 to 0 064 ppm) in some homes with gas ranges Homes with gas ranges with pilot lights have higher NO_2 levels than homes that have gas ranges without pilot lights (Wilson et al , 1986, Quackenboss et al , 1986, Leaderer et al , 1986a, Melia et al., 1982; Butler et al , 1990, Neas et al , 1991)

Average NO_2 concentrations in homes with gas ranges/ovens exhibit a spatial gradient within and between rooms Kitchen levels are higher than other rooms and a pronounced vertical concentration gradient in the kitchen has been observed in some homes, with concentrations being highest nearest the ceiling (Goldstein et al , 1985, Wilson et al , 1986) Average NO_2 concentrations are highest during the winter months and lowest during the summer months This seasonal temporal gradient is probably related to seasonal differences in infiltration, source use, NO_2 reactivity rates indoors, and outdoor concentrations (Spengler et al., 1983; Wilson et al , 1986) The impact of gas appliance use on indoor NO_2 levels may be superimposed upon the background level resulting from outdoor concentrations The results of field studies of the impact of gas ranges on indoor NO_2 are fairly consistent Once corrected for the contribution of outdoor concentrations, the average contribution of gas ranges to NO_2 levels indoors is similar by locations within homes and by season across the studies There is, however, considerable variability associated with these averages

Very limited data exist on short-term (3-h or less) average indoor concentrations of NO_2 associated with gas appliance use Harlos et al. (1987) reported a 1-h mean maximum of 346 $\mu g/m^3$ (0.18 ppm) in a study of 18 volunteers The limited data suggest that short-term indoor averages of NO_2 are higher than those recorded for outdoors

Unvented kerosene and gas space heaters are important sources of NO_2 in homes both because of the NO_2 production rate of the heaters and the length of time they are used Field studies indicate that average residential concentrations (1- or 2-week average levels) exhibit a wide distribution, varying primarily with the amount of heater use and type of heater. Average concentrations in homes using unvented kerosene heaters have been measured well in excess of 100 $\mu g/m^3$ (0.053 ppm) In one study, calculations of NO_2

residential levels during heater use (in homes without gas appliances) indicate that approximately 50% of the homes had concentrations above 100 $\mu g/m^3$ (0 053 ppm) and 8% had concentrations above 480 $\mu g/m^3$ (0 25 ppm) (Leaderer et al , 1986a) Nitrogen dioxide levels of 847 $\mu g/m^3$ (0 45 ppm) over a 1-h period in a home during use of a kerosene heater have been measured A large field study of indoor NO_2 concentrations in homes using UVGSHs (most also had gas ranges) found that approximately 70% of the homes had average concentrations in excess of 100 $\mu g/m^3$ (0 053 ppm) and 20% had levels in excess of 480 $\mu g/m^3$ (0 025 ppm) (Koontz et al , 1986, 1988) This study found that the indoor/outdoor temperature difference was the best indicator of indoor NO_2 levels during the colder winter periods when heating demands are greatest The highest concentration recorded for a home with a UVGSH was 2,716 ug/m^3 (1 44 ppm) (15-min averaging period) (Koontz et al , 1988) The higher concentrations may be the levels encountered for sustained periods of time (e g , hours) because they may approximate the equilibrium levels under periods of heater use No pronounced spatial gradient of NO_2 was found in homes with unvented kerosene space heaters, contrary to the strong spatial gradient noted for homes with gas appliances. This is probably due to the strong convective heat output and the long operating hours of the heaters, which result in rapid mixing within the homes

Improper use of gas appliances (e g , using a gas range to heat a living space) and improperly operating gas appliances or vented heating systems (e g , out of repair gas range or improper operation of a gas wall or floor furnace) can be important contributors to indoor NO_2 concentrations, but little data are available to assess the extent of that contribution (Beals et al , 1987) Data have not been reported that would allow for an assessment of the contributions of wood- or coal-burning stoves or fireplaces to indoor NO_2 concentrations, but such a contribution would be expected to be small Cigarette smoking is expected to add little NO_2 to homes (Wilson et al , 1986, Leaderer et al , 1986a, Good et al , 1982)

Efforts to model indoor NO_2 levels have employed both (1) physical/chemical and (2) empirical/statistical models Physical/chemical models have largely been applied to test-house data or to small samples of homes where detailed data on the factors impacting the concentrations have been measured These models have been used, with varying success in explaining measured indoor levels of NO_2, in user-friendly computer models (Weir et al , 1990) for predicting NO_2 for specific indoor settings, and to estimate indoor concentration

distributions (Traynor et al , 1987, Hemphill et al , 1987, Billick et al , 1989) Various empirical/statistical models have also been developed from large field-study data bases These employ questionnaire responses and measured physical data (house volume, etc) as key independent variables and have met with moderate success (Butler et al , 1990, Drye et al., 1989; Wilson et al , 1986).

The removal of NO_2 indoors by surfaces (reactive decay) is often equal to or greater than infiltration in removing NO_2. Nitrogen dioxide reactive decay rates vary as a function of the type of material and surface area of the material The degree of mixing or turbulence in a space is also important, as is relative humidity A by-product of NO_2 removal by materials is NO production and a saturation effect may occur for some materials Reactive decay of NO_2 in residences is highly variable between residences, within rooms in a residence, and on a temporal basis within a residence (Spicer et al , 1986, Leaderer et al , 1986b; Borrazzo et al , 1987b).

Indoor concentrations of HONO appear to be higher than outdoors, even when indoor NO_2 concentrations do not exceed outdoor levels A possible mechanism for this is the heterogeneous reaction of NO_2 with water In homes where unvented combustion sources are used, elevated HONO levels may be associated with direct emissions of HONO from the flame as well as with heterogeneous reactions of the produced NO_2 with water Nitric acid has been measured indoors during a summer period at concentrations lower than ambient levels Indoor production of HNO_3 has been postulated (Brauer et al , 1991)

REFERENCES

AIRS, Aerometric Information Retrieval System [database] (1991) [Data on NO_x] Research Triangle Park, NC U S Environmental Protection Agency, Office of Air Quality Planning and Standards Disc, IBM 3090

AIRS, Aerometric Information Retrieval System [database] (1992) [Data on NO_x] Research Triangle Park, NC U S Environmental Protection Agency, Office of Air Quality Planning and Standards

Allegrini, I , De Santis, F (1989) Measurement of atmospheric pollutants relevant to dry acid deposition Crit Rev Anal Chem 21 237-255

Atkins, D H F , Law, D V (1987) Indoor-outdoor nitrogen dioxide concentration ratios for homes with gas and electric cooking In Seifert, B , Esdorn, H , Fischer, M , Rueden, H , Wegner, J , eds Indoor air '87 proceedings of the 4th international conference on indoor air quality and climate, v 1, volatile organic compounds, combustion gases, particles and fibres, microbiological agents, August, Berlin, Federal Republic of Germany Berlin, Federal Republic of Germany Institute for Water, Soil and Air Hygiene, pp 383-389

Austin, B S , Rosenbaum, A S , Hayes, S R (1988) User's guide to the NEM/SAI exposure model San Rafael, CA Systems Applications, Inc , SYSAPP-88/051

Beals, S A , Holiman, J C , Kubo, R , Rubio, S A , Stanford, R , Colome, S D , Wilson, A L (1987) Residential indoor air quality characterization study of nitrogen dioxide Phase II final report the wall and floor furnace inspection study Los Angeles, CA Southern California Gas Company

Billick, I H (1991) An update of the natural gas industry's research related to indoor air quality Presented at American Gas Association 1991 distribution/transmission conference, April-May, Nashville, TN

Billick, I H , Baker, P E , Colome, S D (1989) Simulation of indoor nitrogen dioxide concentrations In Harper, J P , ed Combustion processes and the quality of the indoor environment transactions of an international specialty conference, September 1988, Niagara Falls, NY Pittsburgh, PA Air & Waste Management Association, pp 151-172 (A&WMA transactions series TR-15)

Bollinger, M J , Hahn, C J , Parrish, D D , Murphy, P C , Albritton, D L , Fehsenfeld, F C (1984) NO_x measurements in clean continental air and analysis of the contributing meteorology J Geophys Res [Atmos] 89 9623-9631

Borrazzo, J E , Osborn, J F , Fortmann, R C , Keefer, R L , Davidson, C I (1987a) Modeling and monitoring of CO, NO and NO_2 in a modern townhouse Atmos Environ 21 299-311

Borrazzo, J E , Peters, C , Peck, S , Davidson, C I (1987b) Determination of NO_2 loss rates from concentration measurements in an occupied urban residence In Seifert, B , Esdorn, H , Fischer, M , Rueden, H , Wegner, J , eds Indoor air '87 proceedings of the 4th international conference on indoor air quality and climate, v 1, volatile organic compounds, combustion gases, particles and fibres, microbiological agents, August, Berlin, Federal Republic of Germany Berlin, Federal Republic of Germany Institute for Water, Soil and Air Hygiene, pp 321-325

Brauer, M , Ryan, P B , Suh, H H , Koutrakis, P , Spengler, J D , Leslie, N P , Billick, I H (1990) Measurements of nitrous acid inside two research houses Environ Sci Technol 24 1521-1527

Brauer, M , Koutrakis, P , Keeler, G J , Spengler, J D (1991) Indoor and outdoor concentrations of inorganic acidic aerosols and gases J Air Waste Manage Assoc 41 171-181

Butler, D A , Ozkaynak, H , Billick, I H , Spengler, J D (1990) Predicting indoor NO_2 concentrations as a function of home characteristics and ambient NO_2 levels In Indoor air '90 precedings of the 5th international conference on indoor air quality and climate, volume 2, characteristics of indoor air, July-August; Toronto, ON, Canada Ottawa, ON, Canada International Conference on Indoor Air Quality and Climate, Inc , pp 519-524

Cadle, S H (1985) Seasonal variations in nitric acid, nitrate, strong aerosol acidity, and ammonia in an urban area. Atmos. Environ 19 181-188

Cadle, S H , Mulawa, P A (1988) Atmospheric summertime concentrations and estimated dry deposition rates of nitrogen and sulfur species at a Smoky Mountain site in North Carolina Presented at 81st annual meeting of the Air Pollution Control Association, June, Dallas, TX Pittsburgh, PA Air Pollution Control Association, paper no 88-119 3

Cadle, S H.; Countess, R J , Kelly, N A (1982) Nitric acid and ammonia in urban and rural locations Atmos Environ 16 2501-2506

Clausing, P , Mak, J. K., Spengler, J D , Letz, R (1984) Personal NO_2 exposures of high school students In Berglund, B , Lindvall, T , Sundell, J , eds Indoor air proceedings of the 3rd international conference on indoor air quality and climate, v 4, chemical characterization and personal exposure, August, Stockholm, Sweden Stockholm, Sweden Swedish Council for Building Research, pp 135-139 Available from NTIS, Springfield, VA, PB85-104214

Colome, S D., Wilson, A L , Spengler, J D (1992) Nitrogen dioxide exposure studies volume V, personal exposure to nitrogen dioxide in the Los Angeles basin a microenvironmental approach Chicago, IL Gas Research Institute, report no GRI-92/0427

Dasch, J. M , Cadle, S H (1990) The removal of nitric acid to atmospheric particles during a wintertime field study Atmos Environ Part A 24 2557-2562

Dasch, J M , Cadle, S H , Kennedy, K G , Mulawa, P A (1989) Comparison of annular denuders and filter packs for atmospheric sampling Atmos Environ 23 2775-2782

Decker, C E , Ripperton, L A , Worth, J J B , Vukovich, F M , Bach, W D , Tommerdahl, J B , Smith, F , Wagoner, D E (1976) Formation and transport of oxidants along Gulf Coast and in northern U S. Research Triangle Park, NC U S Environmental Protection Agency, Office of Air Quality Planning and Standards, EPA report no EPA-450/3-76-033 Available from NTIS, Springfield, VA, PB-260384

Drye, E. E., Ozkaynak, H , Burbank, B , Billick, I H , Baker, P E , Spengler, J D , Ryan, P B , Colome, S D (1989) Development of models for predicting the distribution of indoor nitrogen dioxide concentrations JAPCA 39 1169-1177

Federal Register (1979) Air programs, ambient air quality monitoring, data reporting, and surveillance provisions. F R (May 10) 44 27558-27604

Fehsenfeld, F C ; Dickerson, R R , Hubler, G , Luke, W T , Nunnermacker, L J , Williams, E J , Roberts, J M ; Calvert, J G , Curran, C M , Delany, A C , Eubank, C S , Fahey, D W , Fried, A , Gandrud, B W , Langford, A O , Murphy, P C , Norton, R B , Pickering, K E , Ridley, B A (1987) A ground-based intercomparison of NO, NO_x, and NO_y measurement techniques J Geophys Res [Atmos] 92 14710-14722

Ferris, B G , Jr , Speizer, F E , spengler, J D , Dockery, D , Bishop, Y M M , Wolfson, M , Humble, C (1979) Effects of sulfur oxides and respirable particles on human health Methodology and demography of populations in study Am Rev Respir Dis 120 767-779

Fortmann, R C , Nagda, N L , Harper, J P (1987) Radon mitigation through residential pressurization control strategy In Seifert, B , Esdorn, H , Fischer, M , Rueden, H , Wegner, J , eds Indoor air '87 proceedings of the 4th international conference on indoor air quality and climate, v 2, environmental tobacco smoke, multicomponent studies, radon, sick buildings, odours and irritants, hyperreactivities and allergies, August, Berlin, Federal Republic of Germany Berlin, Federal Republic of Germany Institute for Water, Soil and Air Hygiene, pp 300-304

Fugas, M (1976) Assessment of total exposure to an air pollutant In International conference on environmental sensing and assessment, v 2, September, Las Vegas, NV New York, NY Institute of Electrical and Electronic Engineers, paper no 38-5

Goldstein, B D , Melia, R J W , Chinn, S , Florey, C du V , Clark, D , John, H H (1979) The relation between respiratory illness in primary schoolchildren and the use of gas for cooking II Factors affecting nitrogen dioxide levels in the home Int J Epidemiol 8 339-345

Goldstein, I F , Hartel, D , Andrews, L R (1985) Monitoring personal exposure to nitrogen dioxide Presented at 78th annual meeting of the Air Pollution Control Association, June, Detroit, MI Pittsburgh, PA Air Pollution Control Association, paper no 85-85 7

Good, B W , Vilcins, G , Harvey, W R , Clabo, D A , Jr , Lewis, A L (1982) Effect of cigarette smoking on residential NO_2 levels Environ Int 8 167-175

Grimsrud, D T , Sherman, M H , Sonderegger, R C (1982) Calculating infiltration implications for a construction quality standard In Proceedings of the ASHRAE-EOE conference on the thermal performance of the exterior envelope of buildings II, December, Las Vegas, NV New York, NY American Society of Heating, Refrigerating and Air-Conditioning Engineers, pp 422-452

Grot, R A , Clark, R E (1979) Air leakage characteristics and weatherization techniques for low-income housing In Proceedings of the ASHRAE-DOE conference on the thermal performance of the exterior envelope of buildings, December, Orlando, FL New York, NY American Society of Heating, Refrigerating and Air-Conditioning Engineers, pp 178-194

Hanson, P J , Taylor, G E , Jr , Vose, J (1992) Experimental laboratory measurements of reactive N gas deposition to forest landscape surfaces biological and environmental controls In Johnson, D W , Lindberg, S E , eds Atmospheric deposition and forest nutrient cycling a synthesis of the integrated forest study New York, NY Springer-Verlag, pp 166-177 (Ecological studies 91)

Harlos, D P , Spengler, J D , Billick, I (1987) Continuous nitrogen dioxide monitoring during cooking and commuting personal and stationary exposures In Seifert, B , Esdorn, H , Fischer, M , Rueden, H , Wegner, J , eds Indoor air '87 proceedings of the 4th international conference on indoor air quality and climate, v 1, volatile organic compounds, combustion gases, particles and fibres, microbiological agents, August, Berlin, Federal Republic of Germany Berlin, Federal Republic of Germany Institute for Water, Soil and Air Hygiene, pp 278-282

Hayes, S R (1989) Estimating the effect of being indoors on total personal exposure to outdoor air pollution JAPCA 39 1453-1461

Hemphill, C P , Ryan, P B , Billick, I H , Nagda, N L , Koontz, M D , Fortmann, R C (1987) Estimation of nitrogen dioxide concentrations in homes equipped with unvented gas space heaters In Seifert, B , Esdorn, H , Fischer, M , Rueden, H , Wegner, J , eds Indoor air '87 proceedings of the 4th international conference on indoor air quality and climate, v 1, volatile organic compounds, combustion gases, particles and fibres, microbiological agents, August, Berlin, Federal Republic of Germany Berlin, Federal Republic of Germany Institute for Water, Soil and Air Hygiene, pp 420-424

Hosein, H R , Bouhuys, A (1979) Possible environmental hazards of gas cooking [letter] Br Med J (6156) 125.

Jacobson, J S , McManus, J M (1985) Pattern of atmospheric sulphur dioxide occurrence an important criterion in vegetation effects assessment Atmos Environ 19 501-506

Jenkin, M E , Cox, R A , Williams, D J (1988) Laboratory studies of the kinetics of formation of nitrous acid from the thermal reaction of nitrogen dioxide and water vapour Atmos Environ 22 487-498

Kaplan, W A., Wofsy, S C , Keller, M , Da Costa, J M (1988) Emission of NO and deposition of O_3 in a tropical forest system J Geophys Res 93 1389-1395

Keller, M D , Lanese, R R , Mitchell, R I , Cote, R W (1979) Respiratory illness in households using gas and electricity for cooking I survey of incidence Environ Res 19 495-503

Kelly, T. J ; Stedman, D H , Ritter, J A , Harvey, R B (1980) Measurements of oxides of nitrogen and nitric acid in clean air J Geophys Res 85 7417-7425

Kelly, N. A , Wolff, G T , Ferman, M A (1982) Background pollutant measurements in air masses affecting the eastern half of the United States—I air masses arriving from the northwest Atmos Environ 16· 1077-1088

Kelly, T J ; Tanner, R L , Newman, L , Galvin, P J , Kadlecek, J A (1984) Trace gas and aerosol measurements at a remote site in the northeast U S Atmos Environ 18 2565-2576

Kelly, N A ; Ferman, M A , Wolff, G T (1986) The chemical and meteorological conditions associated with high and low ozone concentrations in southeastern Michigan and nearby areas of Ontario J Air Pollut Control Assoc 36 150-158

Koontz, M D , Fortmann, R C , Nagda, N L , Billick, I H (1986) Protocol for an indoor air quality monitoring survey conducted in Texas Presented at 79th annual meeting of the Air Pollution Control Association, June, Minneapolis, MN Pittsburgh, PA Air Pollution Control Association, paper no 86-6 3

Koontz, M D , Fortmann, R C , Nagda, N L (1988) A topical report on a field monitoring study of homes with unvented gas space heaters v IV—quality assurance/control procedures and results [final report (January 1985-June 1987)] Chicago, IL Gas Research Institute, report no GRI-87/0044 3

Koontz, M D , Mehegan, L L , Nagda, N L (1992) Distribution and use of cooking appliances that can affect indoor air quality topical report (November 1985—December 1991) Chicago, IL Gas Research Institute, report no GRI-93/0013 Available from NTIS, Springfield, VA, PB93-185452/XAB

Koutrakis, P , Briggs, S L K , Leaderer, B P (1992) Source apportionment of indoor aerosols in Suffolk and Onandaga Counties, New York Environ Sci Technol 26 521-527

Lambert, W E (1991) [Letter to Dr Dennis Kotchmar concerning nitrogen dioxide measurements for a sample of 100 homes participating in the UNM study of infant respiratory illness] Albuquerque, NM The University of New Mexico, New Mexico Tumor Registry Medical Center, July 10

Lane, P I , Bell, J N B (1984) The effects of simulated urban air pollution on grass yield part I—description and simulation of ambient pollution Environ Pollut Ser B 8 245-263

Leaderer, B P (1982) Air pollutant emissions from kerosene space heaters Science (Washington, DC) 218 1113-1115

Leaderer, B P , Stolwijk, J A J , Zagraniski, R T , Qing-Shan, M (1984) A field study of indoor air contaminant levels associated with unvented combustion sources Presented at 77th annual meeting of the Air Pollution Control Association, June, San Francisco, CA Pittsburgh, PA Air Pollution Control Association, paper no 84-33 3

Leaderer, B P , Zagraniski, R T , Berwick, M , Stolwijk, J A J (1986a) Assessment of exposure to indoor air contaminants from combustion sources methodology and application Am J Epidemiol 124 275-289

Leaderer, B P , Renes, S , Bluyssen, P , Van De Loo, H (1986b) Chamber studies of NO_2, SO2 and RSP deposition rates indoors Presented at 79th annual meeting of the Air Pollution Control Association, June, Minneapolis, MN Pittsburgh, PA Air Pollution Control Association, paper no 86-38 3

Leaderer, B P , Zagraniski, R T , Berwick, M , Stolwijk, J A J (1987) Predicting NO_2 levels in residences based upon sources and source use a multivariate model Atmos Environ 21 361-368

Lebret, E , Noy, D , Boley, J , Brunekreef, B (1987) Real-time concentration measurements of CO and NO_2 in twelve homes In Seifert, B , Esdorn, H , Fischer, M , Rueden, H , Wegner, J , eds Indoor air '87 proceedings of the 4th international conference on indoor air quality and climate, v 1, volatile organic compounds, combustion gases, particles and fibres, microbiological agents, August, Berlin, Federal Republic of Germany Berlin, Federal Republic of Germany Institute for Water, Soil and Air Hygiene, pp 435-439

Lee, K , Yanagisaswa, Y , Spengler, J D , Ozkaynak, H (1992) Nitrogen dioxide exposure studies volume VI, the NO_2 badge Chicago, IL Gas Research Institute, report no GRI-92/0428

Lefohn, A S (1989) The characterization of sulfur dioxide, nitrogen dioxide, and ozone gaseous concentrations at Mountain Cloud Chemistry Program monitoring sites in the United States Research Triangle Park, NC U S Environmental Protection Agency, Atmospheric Research and Exposure Assessment Laboratory

Lefohn, A S , Tingey, D T (1984) The co-occurrence of potentially phytotoxic concentrations of various gaseous air pollutants Atmos Environ 18 2521-2526

Lefohn, A S , Davis, C E , Jones, C K , Tingey, D T , Hogsett, W E (1987) Co-occurrence patterns of gaseous air pollutant pairs at different minimum concentrations in the United States Atmos Environ 21 2435-2444

Lefohn, A S , Benkovitz, C M , Tanner, R L , Smith, L A , Shadwick, D S (1991) Air quality measurements and characterizations for terrestrial effects research In Irving, P M , ed Acidic deposition state of science and technology, volume I, emissions, atmospheric processes, and deposition Washington, DC The U S National Acid Precipitation Assessment Program (State of science and technology report no 7)

Legge, A H , Peake, E , Strosher, M , Nosal, M , McVehil, G E , Hansen, M (1990) Characteristics of the background air quality In Legge, A H , Krupa, S V , eds Acidic deposition sulphur and nitrogen oxides Chelsea, MI Lewis Publishers, pp 129-248

Lindberg, S E ; Bredemeier, M , Schaefer, D A , Qi, L (1990) Atmospheric concentrations and deposition of nitrogen and major ions in conifer forests in the United States and Federal Republic of Germany Atmos Environ Part A 24 2207-2220

Macriss, R A , Elkins, R H (1977) Control of the level of NO_x in the indoor environment In Kasuga, S , Suzuki, N , Yamada, T , Kimura, G , Inagaki, K , Onoe, K , eds Proceedings of the fourth international clean air congress, May, Tokyo, Japan Tokyo, Japan Japanese Union of Air Pollution Prevention Associations, pp 510-514

Magee, P N , ed (1982) Nitrosamines and human cancer Cold Spring Harbor, NY Cold Spring Harbor Laboratory (Banbury report 12)

Marbury, M C , Harlos, D P , Samet, J M , Spengler, J D (1988) Indoor residential NO_2 concentrations in Albuquerque, New Mexico JAPCA 38 392-398

Martinez, J. R , Singh, H B (1979) Survey of the role of NO_x in nonurban ozone formation Research Triangle Park, NC U.S Environmental Protection Agency, Office of Air Quality Planning and Standards, EPA report no EPA-450/4-79-035 Available from NTIS, Springfield, VA, PB80-122815

McCarthy, S M , Yarmac, R F , Yocom, J E (1987) Indoor nitrogen dioxide exposure the contribution from unvented gas space heaters In Seifert, B , Esdorn, H , Fischer, M , Rueden, H , Wegner, J , eds Indoor air '87 proceedings of the 4th international conference on indoor air quality and climate, v 1, volatile organic compounds, combustion gases, particles and fibres, microbiological agents, August, Berlin, Federal Republic of Germany Berlin, Federal Republic of Germany Institute for Water, Soil and Air Hygiene, pp 478-482

Melia, R J. W ; Florey, C du V , Morris, R W , Goldstein, B D , Clark, D , John, H H (1982) Childhood respiratory illness and the home environment I Relations between nitrogen dioxide, temperature and relative humidity Int J Epidemiol 11 155-163

Miyazaki, T (1984) Adsorption characteristics of NO_x by several kinds of interior materials In Berglund, B , Lindvall, T , Sundell, J , eds Indoor air proceedings of the 3rd international conference on indoor air quality and climate, v 4, chemical characterization and personal exposure, August, Stockholm, Sweden Stockholm, Sweden Swedish Council for Building Research, pp 103-110 Available from NTIS, Springfield, VA, PB85-104214

Moschandreas, D J , Relwani, S M , Macriss, R A , Cole, J T (1984) Differences and similarities of two techniques used to measure emission rates from unvented gas appliances In Berglund, B , Lindvall, T , Sundell, J , eds Indoor air proceedings of the 3rd international conference on indoor air quality and climate, v 4, chemical characterization and personal exposure, August, Stockholm, Sweden Stockholm, Sweden Swedish Council for Building Research, pp 375-379 Available from NTIS, Springfield, VA, PB85-104214.

Moschandreas, D J ; Relwani, S M , O'Neill, H J , Cole, J T , Elkins, R H , Macriss, R A (1985) Characterization of emission rates from indoor combustion sources Chicago, IL Gas Research Institute, report no GRI 85/0075 Available from NTIS, Springfield, VA, PB86-103900

National Research Council (1981) Indoor pollutants Washington, DC National Academy Press

National Research Council (1991) Rethinking the ozone problem in urban and regional air pollution Washington, DC National Academy Press

Nazaroff, W W , Cass, G R (1986) Mathematical modeling of chemically reactive pollutants in indoor air Environ Sci Technol 20 924-934

Neas, L M , Dockery, D W , Ware, J H , Spengler, J D , Speizer, F E , Ferris, B G , Jr (1991) Association of indoor nitrogen dioxide with respiratory symptoms and pulmonary function in children Am J Epidemiol 134 204-219

New York State Department of Health (1989) Influence of surficial soil and bedrock on indoor radon in New York state homes task II, subtask of an investigation of infiltration and indoor air quality in New York state homes Albany, NY New York State Energy Research and Development Authority, energy authority report no 89-14

Noy, D , Lebret, E , Boleij, J , Brunekreef, B (1984) Integrated NO_2 exposure estimates In Berglund, B , Lindvall, T , Sundell, J , eds Indoor air proceedings of the 3rd international conference on indoor air quality and climate, v 4, chemical characterization and personal exposure, August, Stockholm, Sweden Stockholm, Sweden Swedish Council for Building Research, pp 37-42 Available from NTIS, Springfield, VA, PB85-104214

Ott, W (1989) Human activity patterns a review of the literature for estimating time spent indoors, outdoors, and in-transit In Starks, T H , ed Proceedings of the research planning conference on human activity patterns Las Vegas, NV U S Environmental Protection Agency, Environmental Monitoring Systems Laboratory, chapter 3, EPA report no EPA-600/4-89-004 Available from NTIS, Springfield, VA, PB89-166599

Ozkaynak, H , Ryan, P B , Allen, G A , Turner, W A (1982) Indoor air quality modeling compartmental approach with reactive chemistry Environ Int 8 461-471

Palmes, E D , Gunnison, A F , DiMattio, J , Tomczyk, C (1976) Personal sampler for nitrogen dioxide Am Ind Hyg Assoc J 37 570-577

Palmes, E D , Tomczyk, C , DiMattio, J (1977) Average NO_2 concentrations in dwellings with gas or electric stoves Atmos Environ 11 869-872

Parkhurst, W J , Humphreys, M P , Harper, J P , Spengler, J D (1988) Influence of indoor combustion sources on indoor air quality Environ Prog 7 257-261

Parrish, D D , Williams, E , Norton, R B , Fehsenfeld, F C (1985) Measurement of odd-nitrogen species and O_3 at Point Arena, California EOS Trans Am Geophys Union 66 820

Parrish, D D , Trainer, M , Williams, E J , Fahey, D W , Huebler, G , Eubank, C S , Liu, S C , Murphy, P C , Albritton, D L , Fehsenfeld, F C (1986) Measurements of the NO_x-O_3 photostationary state at Niwot Ridge, Colorado J Geophys Res [Atmos] 91 5361-5370

Parrish, D D , Buhr, M , Norton, R , Fehsenfeld, F (1988) Study of atmospheric oxidation processes at a rural, eastern U S site EOS Trans Am Geophys Union 69 1056

Petreas, M , Liu, K -S , Chang, B -H , Hayward, S B , Sexton, K (1988) A survey of nitrogen dioxide levels measured inside mobile homes JAPCA 38 647-651

Pitts, J N., Jr , Grosjean, D , Van Cauwenberghe, K , Schmid, J P , Fitz, D R (1978) Photooxidation of aliphatic amines under simulated atmospheric conditions formation of nitrosamines, nitramines, amides, and photochemical oxidant Environ Sci Technol 12 946-953

Pitts, J. N , Jr , Sanhueza, E , Atkinson, R , Carter, W P L , Winer, A M , Harris, G W , Plum, C N (1984) An investigation of the dark formation of nitrous acid in environmental chambers Int J Chem Kinet. 16 919-939

Pitts, J. N , Jr , Biermann, H W , Tuazon, E C , Green, M , Long, W D , Winer, A M (1989) Time-resolved identification and measurement of indoor air pollutants by spectroscopic techniques gaseous nitrous acid, methanol, formaldehyde and formic acid J Air Waste Manage Assoc 39. 1344-1347

Pratt, G C , Hendrickson, R C , Chevone, B I , Christopherson, D A , O'Brien, M V , Krupa, S V (1983) Ozone and oxides of nitrogen in the rural upper-midwestern U S A Atmos Environ 17 2013-2023

Quackenboss, J J , Spengler, J D , Kanarek, M S , Letz, R , Duffy, C P (1986) Personal exposure to nitrogen dioxide relationship to indoor/outdoor air quality and activity patterns Environ Sci Technol 20 775-783

Quackenboss, J J , Lebowitz, M D , Hayes, C (1987) Epidemiological study of respiratory responses to indoor-outdoor air quality In Seifert, B , Esdorn, H , Fischer, M , Rueden, H , Wegner, J , eds Indoor air '87. proceedings of the 4th international conference on indoor air quality and climate, v 2, environmental tobacco smoke, multicomponent studies, radon, sick buildings, odours and irritants, hyperreactivities and allergies, August, Berlin, Federal Republic of Germany Berlin, Federal Republic of Germany Institute for Water, Soil and Air Hygiene, pp 198-202

Quackenboss, J J , Bronnimann, D , Camilli, A E , Lebowitz, M D (1988) Bronchial responsiveness in children and adults in association with formaldehyde, particulate matter, and environmental tobacco smoke exposures Am Rev Respir Dis 137(suppl) 253

Research Triangle Institute (1975) Investigation of rural oxidant levels as related to urban hydrocarbon control strategies Research Triangle Park, NC U S Environmental Protection Agency, Office of Air Quality Planning and Standards, EPA report no EPA-450/3-75-036 Available from NTIS, Springfield, VA, PB-242299.

Research Triangle Institute (1990) An investigation of infiltration and indoor air quality Albany, NY New York State Energy Research and Development Authority, report no NYERDA 90-11 Available from NTIS, Springfield, VA, PB91-119156

Robinson, J. P (1977) How Americans use their time a social psychological analysis of everyday behavior New York, NY Praeger Publishers

Ryan, P. B , Spengler, J D (1992) Nitrogen dioxide exposure studies volume II, the Boston residential home characterization study Chicago, IL Gas Research Institute, report no GRI-92/0424

Ryan, P. B ; Spengler, J D., Letz, R (1983) The effects of kerosene heaters on indoor pollutant concentrations a monitoring and modeling study Atmos Environ 17 1339-1345

Ryan, P. B ; Soczek, M L , Treitman, R D , Spengler, J D , Billick, I H (1988) The Boston residential NO_2 characterization study—II survey methodology and population concentration estimates Atmos Environ 22 2115-2125

Ryan, P B , Schwab, M , Spengler, J D , Colome, S D , Wilson, A L (1992) Nitrogen dioxide exposure studies, volume IV human exposure to nitrogen dioxide in the Los Angeles basin Chicago, IL Gas Research Institute and Los Angeles, CA Southern California Gas Company

Sakamaki, F , Hatakeyama, S , Akimoto, H (1983) Formation of nitrous acid and nitric oxide in the heterogeneous dark reaction of nitrogen dioxide and water vapor in a smog chamber Int J Chem Kinet 15 1013-1029

Samet, J M , Lambert, W E , Skipper, B J , Cushing, A H , McLaren, L C , Schwab, M , Spengler, J D (1992) A study of respiratory illnesses in infants and nitrogen dioxide exposure Arch Environ Health 47 57-63

Sheldon, L S , Hartwell, T D , Cox, B G , Sickles, J E , II, Pellizzari, E D , Smith, M L , Perritt, R L , Jones, S M (1989) An investigation of infiltration and indoor air quality final report Albany, NY New York State Energy Research and Development Authority, New York State ERDA contract no 736-CON-BCS-85

Sparks, L E (1988) Indoor air—sources indoor air quality model version 1 0 Research Triangle Park, NC U S Environmental Protection Agency, Air and Energy Engineering Research Laboratory, EPA report no EPA-600/8-88-097

Speizer, F E , Ferris, B , Jr , Bishop, Y M M , Spengler, J (1980) Respiratory disease rates and pulmonary function in children associated with NO_2 exposure Am Rev Respir Dis 121 3-10

Spengler, J , Samet, J (1992) NO_2 concentrations in a subsample of Albuquerque NM homes participating in the infant respiratory health study conducted by J Samet, University of New Mexico, New Mexico Tumor Registry Medical Center Personal communication February

Spengler, J D , Duffy, C P , Letz, R , Tibbitts, T W , Ferris, B G , Jr (1983) Nitrogen dioxide inside and outside 137 homes and implications for ambient air quality standards and health effects research Environ Sci Technol 17 164-168

Spengler, J D , Ozkaynak, H , McDermott, A , Brauer, M (1992a) Review of the draft air quality criteria for oxides of nitrogen (EPA/600/8-91/049) Boston, MA Harvard School of Public Health, Department of Environmental Health

Spengler, J D , Ryan, P B , Schwab, M , Colome, S D , Wilson, A L (1992b) Nitrogen dioxide exposure studies volume IV, personal exposure to nitrogen dioxide in the Los Angeles basin Chicago, IL Gas Research Institute, report no GRI-92/0426

Spengler, J D , Brauer, M , Samet, J M , Lambert, W E (1993) Nitrous acid in Albuquerque, New Mexico, homes Environ Sci Technol 27 841-845

Spicer, C W (1977) The fate of nitrogen oxides in the atmosphere In Pitts, J N , Jr , Metcalf, R L , Lloyd, A C , eds Advances in environmental science and technology v 4 New York, NY John Wiley and Sons, Inc , pp 163-261

Spicer, C W , Coutant, R W , Ward, G F (1986) Investigation of nitrogen dioxide removal from indoor air [final report (December 1984—September 1986)] Chicago, IL Gas Research Institute, report no GRI-86/0303 Available from NTIS, Springfield, VA, PB87-185971

Spicer, C W , Coutant, R W , Ward, G F , Joseph, D W , Gaynor, A J , Billick, I H (1989) Rates and mechanisms of NO_2 removal from indoor air by residential materials Environ Int 15 643-654

Svensson, R , Ljungstroem, E , Lindqvist, O (1987) Kinetics of the reaction between nitrogen dioxide and water vapour Atmos Environ 21 1529-1539

Szalai, A , ed (1972) The use of time daily activities of urban and suburban populations in 12 countries The Hague, The Netherlands Mouton and Co

Taylor, G E , Ross-Todd, B M , Allen, E , Conklin, P , Edmonds, R , Joranger, E , Miller, E , Ragsdale, L, Shepard, J.; Silsbee, D , Swank, W (1992) Patterns of tropospehric ozone in forested landscapes of the Integrated Forest Study In Johnson, D W , Lindberg, S E , eds Atmospheric deposition and forest nutrient cycling—a synthesis of the Integrated Forest Study New York, NY Springer-Verlag, pp 50-71

Tikalsky, S , Reisdorf, K , Flickinger, J , Totzke, D , Haywood, J , Annen, L , Kanarek, M , Kaarakka, P , Prins, E (1987) Gas range/oven emissions impact analysis [final report (July 1985-December 1987)] Chicago, IL Gas Research Institute, report no GRI-87/0119 Available from NTIS, Springfield, VA, PB88-232756

Torres, A. L , Buchan, H (1988) Tropospheric nitric oxide measurements over the Amazon Basin J Geophys Res 93 1396-1406

Traynor, G W , Anthon, D W , Hollowell, C D (1982) Technique for determining pollutant emissions from a gas-fired range Atmos Environ 16 2979-2987

Traynor, G W , Apte, M G , Carruthers, A R , Dillworth, J F , Grimsrud, D T , Thompson, W T (1984) Indoor air pollution and interroom pollutant transport due to unvented kerosene-fired space heaters Berkeley, CA Lawrence Berkeley Laboratory, report no LBL-17600 Available from NTIS, Springfield, VA, DE84015949

Traynor, G W ; Aceti, J C , Apte, M G , Smith, B V , Green, L L , Smith-Reiser, A , Novak, K M , Moses, D O (1987) Macromodel for assessing indoor exposures to combustion-generated pollutants In Seifert, B , Esdorn, H , Fischer, M , Rueden, H , Wegner, J , eds Indoor air '87 proceedings of the 4th international conference on indoor air quality and climate, v 1, volatile organic compounds, combustion gases, particles and fibres, microbiological agents, August, Berlin, Federal Republic of Germany. Berlin, Federal Republic of Germany Institute for Water, Soil and Air Hygiene, pp 273-277

U S Bureau of the Census (1982) 1980 census of population and housing supplementary report provisional estimates of social, economic, and housing characteristics states and selected standard metropolitan statistical areas Washington, DC U S Department of Commerce, report no PHC 80-S1-1 Available from GPO, Washington, DC

U S. Bureau of the Census (1989) 1990 Census of population and housing—content determination reports Housing plumbing, equipment, and fuels Washington, DC U S Department of Commerce, report no 1990 CDR-12 Available from GPO, Washington, DC

U.S Bureau of the Census (1992) 1990 Census of population and housing summary social, economic, and housing characteristics—United States Washington, DC U S Department of Commerce, report no 1990 CPH-5-1 Available from GPO, Washington, DC

U.S. Environmental Protection Agency (1990) National air quality and emissions trends report, 1988 Research Triangle Park, NC Office of Air Quality Planning and Standards, EPA report no EPA/450/4-90/002 Available from NTIS, Springfield, VA, PB90-200114/XAB

U.S. Environmental Protection Agency (1991a) National air quality and emissions trends report, 1989 Research Triangle Park, NC Office of Air Quality Planning and Standards, EPA report no EPA/450/4-91/003 Available from NTIS, Springfield, VA, PB91-172247/XAB

U S Environmental Protection Agency (1991b) National air quality and emissions trends report, 1990 Research Triangle Park, NC Office of Air Quality Planning and Standards, EPA report no EPA-450/4-91-023 Available from NTIS, Springfield, VA, PB92-141555/XAB

Wade, W A , III, Cote, W A , Yocom, J E (1975) A study of indoor air quality J Air Pollut Control Assoc 25 933-939

Weir, B R , Anderson, G E , Hayes, S R , Greenfield, S M (1990) Specification of indoor air model characteristics In Indoor air '90 precedings of the 5th international conference on indoor air quality and climate, volume 4, building and system assessments and solutions, July-August, Toronto, ON, Canada Ottawa, ON, Canada International Conference on Indoor Air Quality and Climate, Inc , pp 231-236

Weschler, C J , Brauer, M , Koutrakis, P (1992) Indoor ozone and nitrogen dioxide a potential pathway to the generation of nitrate radicals, dinitrogen pentaoxide, and nitric acid indoors Environ Sci Technol 26 179-184

Wiley, J A , Robinson, J P , Piazza, T , Garrett, K , Cirksena, K , Cheng, Y -T , Martin, G (1991a) Activity patterns of California residents Sacramento, CA California Air Resources Board, contract no A6-177-33

Wiley, J A , Robinson, J P , Piazza, T , Garrett, T , Cirksena, K , Cheng, Y -T , Martin, G (1991b) Study of children's activity patterns final report Sacramento, CA California Air Resources Board, contract no A-733-149

Wilson, A L , Colome, S D , Baker, P E , Becker, E W (1986) Residential indoor air quality characterization study of nitrogen dioxide Phase I Volumes 1, 2 and 3 Southern California Gas Company, October

Winer, A M , Biermann, H W (1991) Measurements of nitrous acid, nitrate radicals, formaldehyde and nitrogen dioxide for the Southern California Air Quality Study by differential optical absorption spectroscopy In Conference on chemical sensing of the environment measurement of atmospheric gases, January, Los Angeles, CA Proc SPIE-Int Soc Opt Eng (1433) 44-55

Wolff, G T (1984) On the nature of nitrate in coarse continental aerosols Atmos Environ 18 977-981

Wolff, G T , Korsog, P E (1989) Atmospheric concentrations and regional source apportionments of sulfate, nitrate and sulfur dioxide in the Berkshire Mountains in western Massachusetts Atmos Environ 23 55-65

Wolff, G T , Ruthkosky, M S , Stroup, D P , Korsog, P E , Ferman, M A , Wendel, G J , Stedman, D H (1986a) Measurements of SO_x, NO_x and aerosol species on Bermuda Atmos Environ 20 1229-1239

Wolff, G T , Kelly, N A , Ferman, M A , Ruthkosky, M S , Stroup, D P , Korsog, P E (1986b) Measurements of sulfur oxides, nitrogen oxides, haze and fine particles at a rural site on the Atlantic coast J Air Pollut Control Assoc 36 585-591

Wolff, G T , Ruthkosky, M S , Stroup, D P , Korsog, P E (1991) A characterization of the principal PM-10 species in Claremont (summer) and Long Beach (fall) during SCAQS Atmos Environ Part A 25 2173-2186

Yamanaka, S (1984) Decay rates of nitrogen oxides in a typical Japanese living room Environ Sci Technol 18 566-570

Yanagisawa, Y.; Nishimura, H (1982) A badge-type personal sampler for measurement of personal exposure to NO_2 and NO in ambient air Environ Int 8 235-242

8. ASSESSING TOTAL HUMAN EXPOSURE TO NITROGEN DIOXIDE

8.1 INTRODUCTION

In the course of their daily activities, humans are exposed to nitrogen dioxide (NO_2) in a number of settings or environments (residential, industrial, nonindustrial occupational, transportation, outdoors, etc) Human exposure to NO_2 consists of contact at the air boundary layer between the human and the environment at a specific concentration for a specified period of time The integrated NO_2 exposure is the sum of the individual NO_2 exposures over all possible time intervals for all settings or environments Thus, the units of exposure are concentration multiplied by time

The assessment of human exposures to NO_2 can be represented by the following simplified basic model that was first proposed by Fugas (1976) and used by a number of other researchers (e g , Duan, 1981, Sexton and Ryan, 1988)

$$E = \sum_i E_i = \sum_i f_i c_i, \tag{8-1}$$

where E is the total or integrated exposure to NO_2 for an individual expressed as an average concentration over a specified period of time across all microenvironments, E_i is the average NO_2 exposure in the ith microenvironment, f_i is the fraction (percentage) of time spent in the ith microenvironment, and c_i is the NO_2 concentration in the ith microenvironment This model essentially represents exposures as a linear combination of the average concentration in each microenvironment, weighted by an individual's time in a microenvironment type A microenvironment is defined as a three-dimensional space having a volume in which the pollutant concentration is considered or assumed to be spatially uniform In theory, there can be a large number of microenvironments, in practice, however, microenvironments are aggregated into a reduced number for air monitoring and modeling applications (outdoors, public transportation, indoor residential, nonindustrial occupational, industrial, public access buildings, etc) The NO_2 concentration in each microenvironment can show substantial spatial and temporal variability and is a complex function of the sources, source use, and

dispersal and removal mechanisms A more detailed discussion of the general theoretical concepts in assessing exposure to air contaminants can be found in a recent report prepared by the National Research Council (1991)

Until recently, efforts to assess adverse health and comfort effects associated with NO_2 and subsequent efforts to mitigate or reduce exposures have focused on measurements of ambient air quality obtained from fixed-location monitoring sites Numerous studies on indoor concentrations of NO_2 (see Chapter 7) combined with studies on human activity patterns (e.g., Szalai, 1972, Chapin, 1974, Robinson, 1977, Ott, 1989, Schwab et al , 1990, Wiley et al., 1991a,b) clearly underscore the need to consider contributions of individual microenvironments in assessing NO_2 exposures Outdoor NO_2 levels also impact indoor concentrations, and they can dominate indoor concentrations when there are no indoor sources or when outdoor concentrations are elevated (Chapter 7) The magnitude of that impact is determined by outdoor levels, temporal variability in outdoor levels, and building characteristics (infiltration/ventilation and indoor decay rates) In contrast, outdoor levels do not well represent indoor concentrations where there are indoor NO_2 sources, particularly when outdoor levels are low and show little variability Direct individual exposure to outdoor concentrations accounts on average for a small portion of a person's total exposure because of the small amount of time typically spent outdoors It is important to note, however, that for some significant segments of the population (e g , police, other outdoor workers, etc.), outdoor exposures can account for a high fraction of their total exposure Total personal exposure to NO_2 and a consideration of the microenvironments in which those exposures take place is essential in assessing the potential risk for associated health effects and in developing effective mitigation measures

Central to the design of a human exposure assessment effort is the identification of the health or comfort effect under study, ascertainment of the individual contaminant thought to be associated with that effect, and specification of the contaminant exposure on a time scale corresponding to the effect It is in fact the biological response time that is central to the development of the exposure assessment methodology The principal biological response of human exposures to NO_2 known at this time is respiratory disease Given that the current air quality health standard (primary NAAQS) for NO_2 reflects a long-term average concentration, emphasis is placed here on assessing long-term exposures to NO_2 on the order

of days or weeks It is important to note, however, that short-term high episodes can elevate total exposures (concentration × time) and may be of importance in impacting health (Chapter 13) Also, other exposure measures may be appropriate

In developing and conducting an exposure assessment protocol, the application of the acquired data must be considered The three principal applications for NO_2 exposure assessment efforts are environmental epidemiology, risk assessment, and risk management In environmental epidemiology, misclassifications and the influence of confounders can be minimized when NO_2 exposures of the study population are adequately assessed In addition, the application of an appropriate NO_2 exposure assessment methodology will reduce the error or uncertainty in calculating risks associated with NO_2 exposure, aid in formulating cost effective mitigation efforts to minimize risk, and permit the monitoring of progress in reducing the risk

Adequate exposure assessment for NO_2 is particularly critical in conducting and evaluating epidemiological studies As discussed in more detail in Chapter 13, failure to measure or estimate exposures adequately and to address the uncertainty in the measured exposures can lead to misclassification errors (Shy et al , 1978, Gladen and Rogan, 1979, Ozkaynak et al , 1986, Willet, 1989, Dosemeci et al , 1990, Lebret, 1990) Early epidemiological studies comparing incidence of respiratory illness in children living in homes with and without gas stoves used the presence of a gas cooker as a simple categorical variable of NO_2 exposure Such a dichotomous grouping can result in a severe nondifferential misclassification error in assigning exposure categories This type of error is likely to underestimate the true relationship and could possibly result in a null finding Where categories of exposure are assigned based upon measured or estimated concentrations, the intermediate categories of exposure may be biased either away from or towards the null In support of epidemiologic studies of NO_2, it is important to employ an exposure assessment protocol that will minimize the misclassification and characterize the uncertainty associated with assessed exposures (Lambert et al , 1990)

Exposures to NO_2 can be assessed by either direct or indirect methods Direct methods include biomarkers and personal monitoring (breathing zone measurements) Indirect methods refer to the coupling of measurements of NO_2 concentrations in various settings or environments with models to estimate exposure In this chapter, the available data on human

exposure to NO_2 will be reviewed within the context of the direct and indirect methods of exposure assessment

8.2 DIRECT METHODS

8.2.1 Biomarkers

Biological markers are cellular, biochemical, or molecular measures that are obtained in biological media such as human tissues, cells, or fluids and are indicative of exposure to environmental chemicals (National Research Council, 1989) Biomarkers of exposure can theoretically integrate total intake to the body from multiple sources of exposure to environmental contaminants If they are stable over time, they can be used to integrate exposure over time. They can be useful tools in elucidating mechanisms of disease or in extrapolations between internal doses, routes of exposure, and species or tissues, but do not necessarily provide the direct link between environmental exposure and disease Biomarkers may be measures of the contaminant or its metabolites that are directly related to the specific contaminant associated with the effect outcome (e g , lead) or may only be a surrogate for exposure to a complex source of environmental contaminants (e g , cotinine)

The relationship between the biological marker and the air contaminant concentration and length of exposure is typically poorly understood Biomarkers are indicators that an exposure has taken place, but are not necessarily a measure of exposure Biomarkers by themselves do not provide information on the environment or setting in which the exposure takes place and hence on the factors that control the exposure

Hydroxyproline excretion, an indicator of increased collagen catabolism or connective tissue injury, has been proposed as a biomarker for exposure to NO_2 Yanagisawa et al (1986, 1988) found an association between the hydroxyproline to creatinine ratio and daily average personal NO_2 levels in a sample of 800 women in two communities near Tokyo Hydroxyproline, however, was found to be significantly correlated with passive and active smoking. In chamber studies of normal males exposed to 0 6 ppm NO_2 for 3 consecutive days for 4 h/day, Muelenaer et al (1988) saw no significant changes in hydroxyproline excretion More recently, Maples et al (1991) have studied the potential for the

nitric oxide/heme protein complex to serve as a useful biologic marker for NO_2 exposure The impact on hydroxyproline excretion of diet is not well characterized

8.2.2 Personal Monitoring

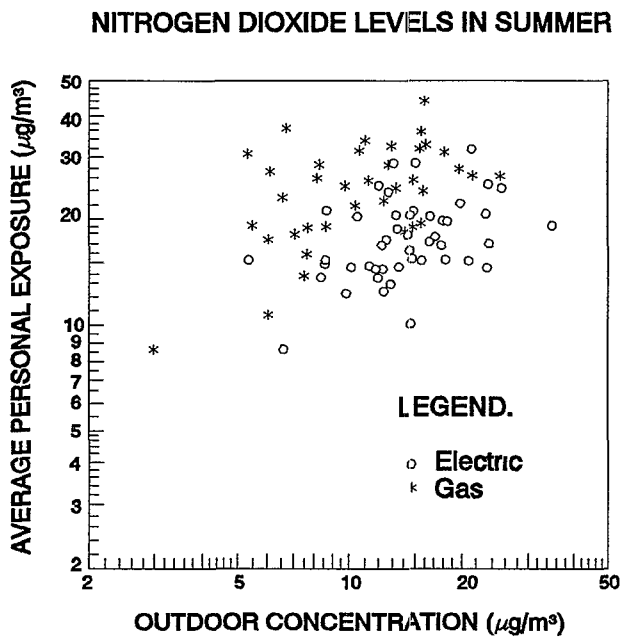
Personal air monitoring provides a direct measurement of the concentrations of air contaminants in the immediate breathing zone of an individual as a measure of personal exposure It provides a measure of exposure across the microenvironments or settings in which individuals spend their time Personal monitoring employs samplers (worn by subjects) that record pollutant concentrations that individuals are exposed to in the course of their normal activity for periods of seconds to several days These monitors can be (a) passive dosimeters (e g , Palmes tubes or Yanagisawa badges), that provide an integrated measure of exposure, or (b) portable monitors with data loggers, which can provide a nearly continuous measure of exposure Little personal NO_2 exposure data have been reported using portable monitors The vast majority of personal NO_2 exposure data have been gathered using passive dosimeters Measures of integrated personal exposure (passive dosimetry) by themselves are not adequate to determine the major sources of exposure and the settings in which the exposures take place Personal integrated measures of exposure need to be supplemented by personal activity diaries and measures of the factors affecting those exposures if effective mitigation measures are to be developed and instituted A direct measure of personal exposure (integrated or continuous) in epidemiologic studies of NO_2 health effects, however, is highly desirable to minimize misclassification and to uncover exposure-response relationships Personal exposures on whole study populations or selected subsamples are not easy to obtain and can be expensive

The ability to obtain measures of personal exposure is in large part controlled by the availability of accurate, small, easy to use, and inexpensive personal monitors The Palmes tube (Palmes et al , 1976) and the NO_2 badge (Yanagisawa and Nishimura, 1982) have provided the sensitivity and specificity necessary to conduct personal NO_2 air monitoring at a reasonable cost These monitors are passive samplers that utilize diffusion to control delivery of gases to the collection medium The samples are then returned to a laboratory for subsequent laboratory analysis These passive samplers have been used extensively in the

monitoring of various microenvironments (Chapter 7) and to a lesser extent in personal exposure monitoring.

There are relatively few studies reported where subjects wore passive NO_2 monitors in the course of their daily activities to assess personal NO_2 exposure In such studies, personal exposures were typically compared to NO_2 measurements made in the various microenvironments in which they spent their time Frequently, these studies obtained supplemental information, through time activity diaries, on the time subjects spent in various microenvironments in which NO_2 measurements were made. When microenvironmental measurements and time activity diaries are obtained, the personal exposure measurements are compared to the microenvironmental data, and personal exposure models are developed using both the microenvironmental measurements and time activity diaries Many of the personal monitoring studies have in fact resulted in the development and testing of indirect methods of assessing personal NO_2 exposures

An extensive study on personal NO_2 exposures as a function of outdoor and indoor concentrations, indoor sources and time/activity patterns was reported by Quackenboss et al (1986). In this study, 1-week NO_2 samples were obtained during both a winter and summer period using Palmes tubes for 350 volunteers residing in 82 homes in the rural Portage, WI, area. The personal samples were supplemented with household measurements made outside and in the kitchen and bedroom of each house, time spent in various microenvironments (inside of home, outside, inside a motor vehicle, inside at work or school, and at other indoor locations) and information on household characteristics (i e , existence of gas or electric stove) Average NO_2 personal exposures were weakly correlated to outdoor NO_2 concentrations in the winter and moderately correlated in the summer (Figure 8-1) Personal exposures were strongly correlated to home average (average of the bedroom and kitchen) concentrations for homes with and without gas cooking ranges (Figure 8-2) Outdoor concentrations were considerably lower than personal exposures for individuals in homes with gas cooking ranges and higher than personal exposures for individuals in homes with electric stoves A comparison of the indoor and outdoor NO_2 concentrations for this study as a function of season and use of a gas or electric cooking range is discussed in Chapter 7 The low explained variability in personal exposures by outdoor levels in this study may be



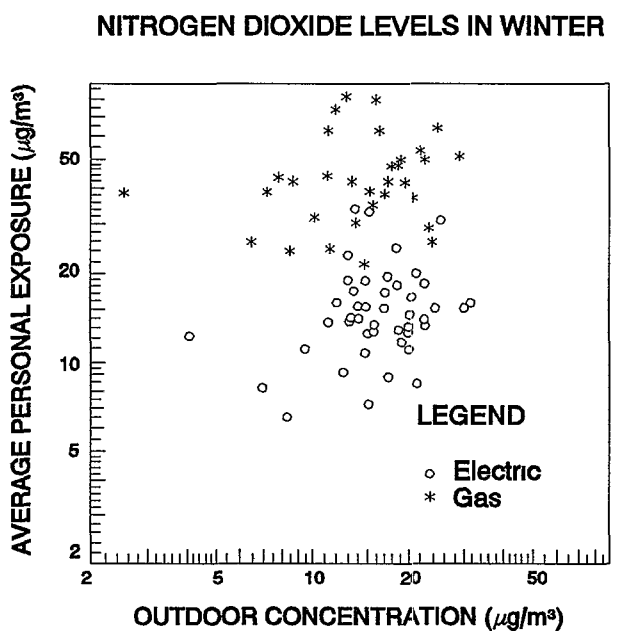
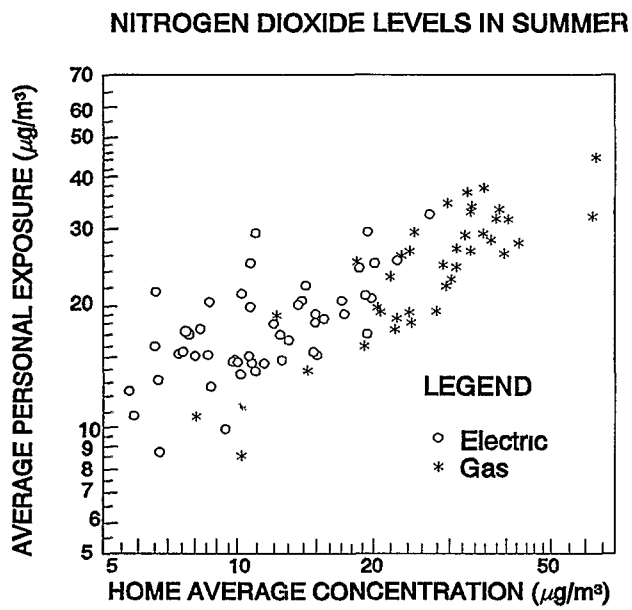


Figure 8-1. Average personal nitrogen dioxide exposure for each household compared with outdoor concentrations for summer and winter.

Source Quackenboss et al (1986)



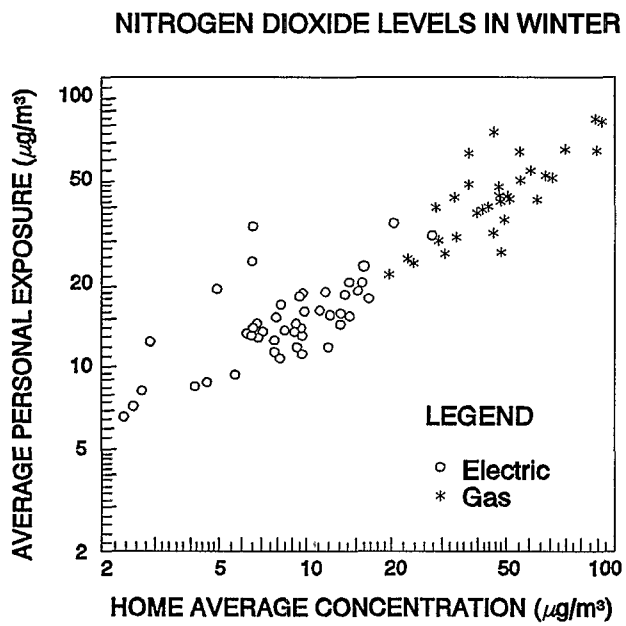


Figure 8-2. Average personal nitrogen dioxide exposure for each home compared with average indoor concentrations for summer and winter.

Source Quackenboss et al (1986)

due in part to the low outdoor levels measured in Portage, WI, during the study (typically less than 20 $\mu g/m^3$ [see Table 7-4])

The time/activity diary results reported by Quackenboss et al (1986) showed that the subjects spent more than 65% of their time at home, whereas about 15% of their time was spent outdoors in the summer and 5% in the winter Approximately 4% of the time was spent in motor vehicles, up to 15% at work or school, and approximately 8% in other indoor environments The study estimated personal exposures from home and average indoor and outdoor levels weighted by the proportion of time spent there for three categories of people (student, worker, and other) by season and stove type The estimated exposures were then compared to the measured personal exposures The explained variance ranged from 3 to 71% The measured exposures were generally not well predicted by the estimated exposures

In an earlier study (a pilot for the one discussed above), Quackenboss et al (1982) measured personal NO_2 exposures (from 5 to 7 days) of 66 family members in 19 homes in Portage, WI, and NO_2 concentrations in a bedroom, kitchen, and outdoors for each residence Time budgets were obtained for each subject and information on cooking fuel was obtained for each house Personal exposures were found to be strongly associated with bedroom ($r = 0\ 84$, gas, $r = 0\ 63$, electric) and kitchen ($r = 0\ 71$, gas, $r = 0\ 6$, electric) concentrations for both the gas and electric cooking homes, but poorly associated with outdoor concentrations ($r = 0\ 4$) Several models using microenvironment monitoring, time budgets, and household characteristics were applied to the data to relate average personal NO_2 exposures to indoor concentrations The models explained as much as 90% of the variation in personal exposures

As part of an epidemiological study of the impact of kerosene heaters on health, Leaderer et al (1986) compared personal 1-week NO_2 measurements on 23 adult subjects with 1-week NO_2 measurements made in three locations in the subjects' homes (kitchen, living room, and bedroom) and outdoors The homes monitored had a mix of NO_2 sources (gas stove, kerosene heater, gas stove and kerosene heater, and no known source) Eighty percent of the variation in total personal NO_2 exposures were accounted for by variations in indoor average NO_2 concentrations for homes with the mix of sources (Figure 8-3) Total personal NO_2 exposures were found to be 90% of the house average concentration When

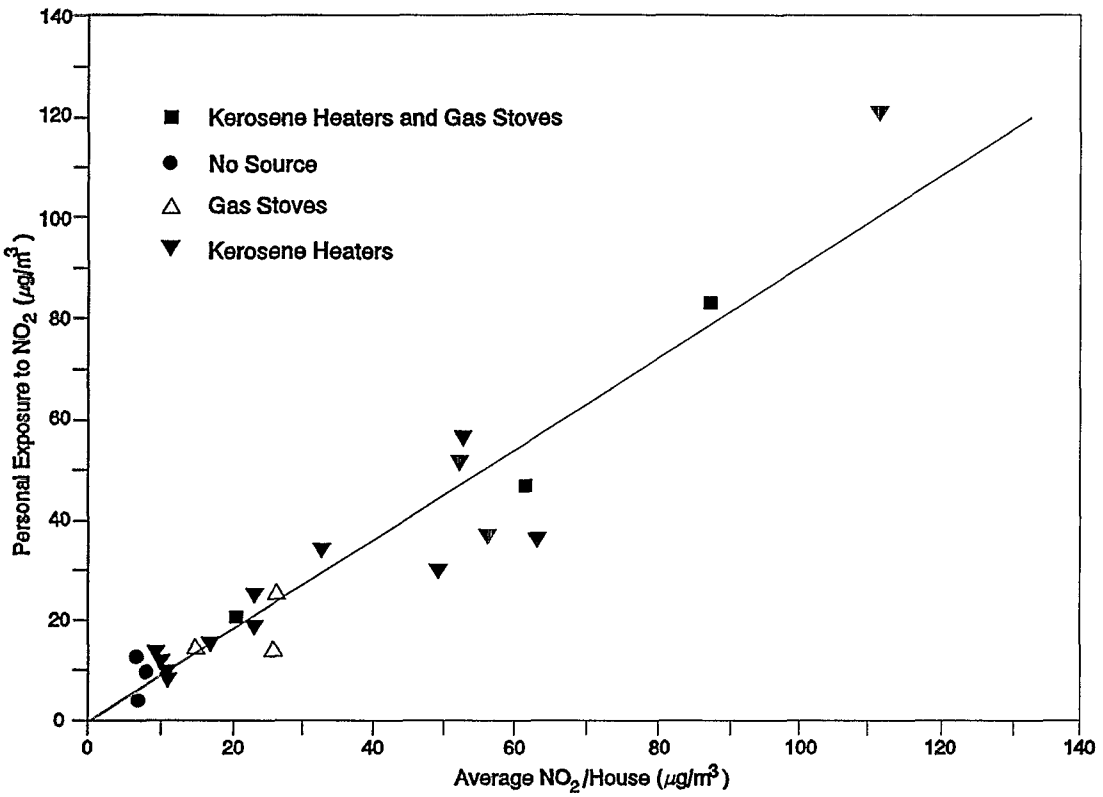


Figure 8-3. Comparison of the house average 2-week nitrogen dioxide concentrations with the total personal nitrogen dioxide levels measured over the same time period for one adult resident in each house, New Haven, CT, area, winter 1983. Each house is identified by the type of sources in the house and the fitted regression line is presented.

Source: Leaderer et al (1986)

compared to concentrations measured in different locations in the house, the bedroom concentration was the best predictor (R^2 = 0 88) Total personal exposures to NO_2 were not found to be related to outdoor concentrations of NO_2 measured at each residence

In a recent study, Harlos et al (1987) obtained 1-day personal NO_2 measurements for 15 infants in homes with gas ranges Corresponding NO_2 measurements were made in the infants' bedrooms and in the living room and kitchen of each house As might be expected, the measured personal exposure correlated well with the bedroom concentrations (r = 0 78) An effort to model the infants' personal exposure based upon the infants' activity patterns

and room concentrations resulted in a slightly stronger relationship with measured personal exposure (r = 0 82)

In a study of 500 junior high students in Watertown, MA (Clausing et al , 1986), personal NO_2 concentrations were measured over a 3- to 4-day period between November and December of 1982 Nitrogen dioxide measurements were made in the bedroom, living room, kitchen, and outside for 200 of the homes of the students on a time scale that corresponded to the personal monitoring Time/activity diaries were kept by the subjects and a questionnaire was utilized to obtain information on home characteristics, particularly sources of NO_2 and their use A variety of models utilizing indoor and outdoor measured NO_2 concentrations, time activity information, and home characteristics were explored to explain variations in measured personal NO_2 exposure The correlation between personal exposure and outdoor concentrations was not significant at the 0 05 level Models that included indoor NO_2 concentrations explained from 60 to 90% of the variation in personal NO_2 exposures Excluding indoor concentrations and using cooking range characteristics (gas range, presence of pilot lights, etc) explained only 40% of the variation in personal NO_2 exposures

As part of a large study on indoor air pollution in the Netherlands (a sample of over 900 homes), a small study was conducted on a subsample of 14 families (11 mothers, 11 school children, and 8 preschool children) to determine relationships between measured indoor NO_2 concentrations and personal exposures (Hoek et al , 1984) Weekly average personal exposures were measured for mothers and for primary (mean age = 7 8 years) and preschool (mean age = 3 4 years) children, and weekly NO_2 concentrations were monitored in several locations A self-administered questionnaire was used to obtain time/activity patterns Measured and calculated (from microenvironment measurements and time/activity data) personal exposures were highly correlated (R^2 from 82% for the whole group to 92% for the preschool children), but the calculated levels were on average 20% lower than the measured personal exposures The mothers' exposure was found to be a good predictor of the primary and preschool children (R^2 of 91% and 93%, respectively), but overestimated the children's exposure by approximately 20%

One-day personal exposures and corresponding microenvironment NO_2 concentrations (home, workplace, and outdoors) were measured for 20 housewives and 44 office workers

(same office building) in Tokyo (Nitta and Maeda, 1982) Activity diaries were obtained during the sampling period. Repeat sampling during a different season was conducted on a subsample of the population Outdoor concentrations were found to be weak predictors of personal exposures, with correlation coefficients no higher than 0 33 for all comparisons by group (housewife or worker) and season Housewife personal exposures compared well with both modeled personal exposures (from microenvironmental measurements and activity diaries) for winter (r = 0 88 and 0 89) and moderately for the summer (r = 0 62 and 0 57) Results for the office workers were similar

In another study, daily averages of personal NO_2 exposures and indoor and outdoor NO_2 concentrations were measured for 40 housewives and their preschool children (subsample) living in and near Tokyo for a winter, spring, and summer period (Yanagisawa et al., 1984) An additional nine housewives were monitored for seven 1-day periods each month for a year. Gas ranges were used for cooking in almost all houses Activity diaries and information on home characteristics were obtained Outdoor concentrations were not significantly related to personal exposures Indoor levels were above outdoor levels, with the living room and bedroom concentration averages close to the personal exposures of the housewives and preschool children for the different locations and seasons Kitchen concentrations were on average higher than personal exposures Measured and calculated personal exposures for the nine housewives agreed well

Hoek et al (1984) monitored 12 primary school children for a 1-week period for NO_2 exposures as part of a study of indoor air quality and respiratory symptoms Time/activity patterns and NO_2 concentrations in the bedroom, living room, and kitchen of the homes of the subjects were also obtained Outdoor NO_2 concentrations were obtained from a central monitoring site The homes contained geysers (unvented, gas-fired, hot water sources at the water tap), an important source of NO_2 Living room and bedroom concentrations best predicted personal exposures (R^2 of 0 64 and 0 63), whereas the kitchen concentrations explained 35% of the variation of personal exposures Overall, 84% of the variation in personal NO_2 exposure was explained by variations in the modeled exposure, using time/activity and microenvironment measurements

Dockery et al. (1981) measured 1-week personal NO_2 exposures along with bedroom, kitchen, and outdoor concentrations for nine families in Topeka, KS, during a summer

period The homes had a mix of electric and gas cooking ranges, and activity diaries were obtained Mean personal exposures were similar to the bedroom means Measured and calculated personal exposures agreed well, with 86% of the variation being explained

As part of an epidemiologic study of an association between personal exposure to NO_2 and respiratory illness in Hong Kong (Koo et al , 1990), 24-h personal measurements of NO_2 using passive badges (Yanagisawa and Nishimura, 1982) were acquired on 362 children age 13 and under and attending the same school, and 319 of their mothers The passive badges were also hung in the school classrooms and school playground A questionnaire was used to obtain data on indoor sources of air pollution (e g , smoking habits of family members, types of heating and cooking fuels, frequency of cooking, ventilation patterns, burning of incense and mosquito coils, and mother's exposure to dust or fumes in the workplace) The sampling was conducted during warm weather (average ambient temperature of 27 °C) Ventilation was supplied to the school through open windows Variations in classroom NO_2 concentrations explained 56% of the variation in personal exposure levels of the children Personal NO_2 exposures of the mothers was not significantly correlated with the personal exposures of their children ($p > 0\ 05$) Neither the children's nor the mothers' personal NO_2 exposure related to number of cigarettes smoked in the home or the number of hours of exposure to cigarette smoke The children's exposure was not related to cooking and heating habits, whereas the mothers' level was highest for liquified petroleum gas and kerosene users and lowest for piped gas users Increases in mothers' personal NO_2 levels were also seen when kitchens did not have ventilating fans (11%), when incense was burned in the home (10%), and when the mother reported dust exposure in the workplace (21%)

The largest field study of personal exposures reported to date was conducted in the Los Angles Basin (Schwab et al , 1990, Spengler et al , 1992, Colome et al , 1992) In this study, 700 individuals from 500 households were monitored for two consecutive 24-h periods for their integrated NO_2 exposure using Yanagisawa filter-badge monitors In addition, NO_2 concentrations were monitored in both the bedroom and outside the home of each participant over the 48-h period that they were monitored for personal exposures Data were collected on housing units (including indoor sources), personal characteristics, and time/activity patterns The objective of the study was to investigate the seasonal, spatial, and

demographic trends in personal NO_2 exposure and the influence of indoor and outdoor NO_2 concentrations and activity patterns on NO_2 exposure Seasonal variations in outdoor, indoor, and personal exposures were apparent Concentrations away from home averaged 0.007 to 0 030 ppm, depending on the cycle, higher than the at-home concentrations Personal exposures of participants who cooked with gas averaged 0 010 ppm to 0 028 ppm higher than those without gas

Several analysis techniques (stepwise regression, analysis of variance, and path analysis) were applied to the collected data to determine the relative contribution to personal NO_2 exposures of factors hypothesized to influence those exposures The factors considered in the analysis included indoor and outdoor concentrations of NO_2, activity patterns of the subjects; type of cooking range (electric, gas without pilot lights, and gas with pilot lights), season (winter versus summer), location (potential high, medium, and low ambient NO_2 levels); and six population subgroups defined by age, sex, and employment status In the analysis, the two consecutive 24-h personal NO_2 measurements were averaged, with the resultant variable used as the dependent variable in the analysis

The analysis indicated that the time spent in each of the microenvironments considered was a poor predictor of personal exposure (R^2 typically less than 0 10) The explained variation in personal exposures increased to 55% when the bedroom concentration was included in the model and decreased to 42% when only outdoor concentrations were considered. Only small differences in the time/microenvironment relationships were observed between groups defined by range-type or population subgroups (explained variation changes of 1 to 10% were observed) Analysis of variance showed that cooking range type, season, and geographic location explained 30% of the personal NO_2 exposure and the addition of outdoor NO_2 levels increased the explained variation to 54% Inclusion of bedroom concentration increased the explained variation to 62% The model with outdoor levels alone produced an R^2 of 0.48, whereas using bedroom concentrations alone resulted in an R^2 of 0 59.

Colome et al (1992) indicate that in the higher ambient NO_2 levels, observed in Los Angeles, personal concentrations measured outside the home were generally higher than personal concentrations encountered while at home, reinforcing the importance of outdoor concentrations of NO_2 Models developed for each of the population subgroups using

bedroom and outdoor NO_2 concentrations and range type resulted in explained variations in personal NO_2 levels ranging from 60 to 78% The study estimates that in the Los Angeles Basin, 68% of the variation in personal NO_2 exposures is explained by measured outdoor and indoor concentrations and that 32% of the variation is unexplained by the parameters measured The authors noted that time/activity measures by themselves are weak predictors of exposure, whereas surrogates of exposure such as cooking range type and location are relatively good predictors Outdoor NO_2 concentrations in the Los Angeles Basin are considerably higher than in most other locations in the United States and show more variability in time than most locations in the United States, and as such, aspects of the results of this study may not be applicable to other regions, especially those with lower ambient NO_2 levels Following the discussion of a similar study in Boston, discussed next, is a presentation of comparisons between the Boston and Los Angeles results

One additional large field study of personal exposure to NO_2 was conducted in the Boston area (Ryan et al , 1988, Ryan and Spengler, 1992, Ryan et al , 1992) This study of approximately 400 homes was conducted during 1985 and 1986 by the same research group using the same protocols as discussed above in the Los Angeles study Ryan and Spengler (1992) state that the response rate of approximately 60% was comparable to other exposure studies In Boston, outdoor NO_2 contributes to indoor NO_2 levels, but the outdoor levels explain less than 10% of the variation in indoor levels in the gas range homes The important sources of indoor NO_2 are gas range use and the presence of a continuously lit pilot light Levels in the kitchen are about twice those experienced in other rooms of the house Other sources and home factors are relatively minor modifiers of indoor concentrations

Ryan and Spengler (1992) report that, in Boston, the homes with gas ranges that have pilot lights show consistently 0 010 to 0 015 ppm higher NO_2 concentrations across the distribution than for homes with a gas range without pilot lights For homes with gas cooking, the indoor concentrations always exceeded outdoor concentrations for those with pilot lights The highest NO_2 concentrations for gas cooking homes were measured in the kitchen, followed by the living room, then the bedroom Kitchen concentrations exceeded ambient levels by 0 014 to 0 015 ppm Exploring other nongas combustion variables, including wood burning stove, smoking, air-conditioning, and fireplace, adds little intuitive

or quantitative understanding The most consistent influence is seen in lower indoor NO_2 levels with the presence of a wood stove It is believed that this variable is a surrogate for other factors not immediately apparent The ratio of indoor to outdoor NO_2 concentrations reveals the presence or absence of sources For electric range homes, the geometric mean indoor/outdoor (I/O) ratio is approximately 0 4 in the fall, 0 75 in the summer, and 0 5 in the winter sampling periods The I/O ratio is clearly higher for the homes with gas pilot lights. But the overall geometric mean is approximately 1 25, 1 20, and 1 50 for the fall, summer, and winter sampling periods, respectively For the Boston Standard Metropolitan Statistical Area, presence of gas range results in an effective increase in NO_2 concentration of 0.010 to 0 020 ppm depending on season The variability in this effective source is large with a coefficient of variation of approximately 100% The source of this variability includes home characteristics such as presence of pilot lights or other unvented appliances, and use patterns

Ryan et al (1992) indicate that, in Boston, bedroom NO_2 concentrations were significantly related to personal NO_2 exposures Personal exposures of individuals living in homes with gas ranges with pilot lights were 0.015 ppm greater, on average, than the NO_2 exposures of those with electric ranges The difference between NO_2 exposures of participants living in homes with electric appliances versus those living in homes with ranges with no pilot lights was less, about 0 011 ppm

Ryan et al. (1992) provide comparisons between the Boston and Los Angeles results There are several similarities between the results of the analysis of the Boston Personal Monitoring Study and the results of the Los Angeles Personal Exposure Study Specifically, no strong correlations between personal exposure and the amount of time individuals spent in each activity category were found in either study Also, bedroom concentrations have a strong influence on personal exposure in both cities In Boston, 48% of the variation in personal NO_2 exposure is explained by variations in bedroom concentrations, whereas the figure is 53% in Los Angeles

There are also some salient differences in the multivariate analysis results between Boston and Los Angeles Specifically, in Los Angeles, the outdoor concentration appeared to play a dominant role in influencing indoor concentrations, 40% of the variation in bedroom concentrations is explained by variations in outdoor concentrations The outdoor

concentrations also played a strong influence on personal exposure (R^2 is 41) In Boston, however, this is not the case, only 9% of the variation in bedroom concentrations is explained by outdoor concentrations The correlation between personal exposure and outdoor concentrations is even weaker (R^2 = 0 05) A portion of this reduced explanatory power may be due to the use of previous-year data, rather than concurrent ambient data

Additionally, although in both cities those who have a gas range have personal exposure levels that are 0 010 ppm higher than the personal exposure levels of individuals with electric ranges, the entire scale is 0 010 ppm higher in Los Angeles

The measured data on personal NO_2 exposures indicate that outdoor measurements of NO_2 (measured in the vicinity of residences) by themselves only explain typically less than 50% of the variations in personal exposure, primarily because of the small amount of time individuals spend outdoors, the impact of buildings on removing outdoor NO_2, and the important contribution from indoor sources Outdoor NO_2 concentrations, however, dominate indoor levels when there are no indoor sources and when outdoor concentrations are high (e g , in Los Angeles) No studies have been reported that examine the relationship between NO_2 concentrations measured at central outdoor sites and personal NO_2 exposures It is likely, however, given the outdoor spatial variability of NO_2, that in general NO_2 levels measured at central sites may be poor predictors of personal NO_2 exposures In some specific outdoor locations, central sites may be better than others Nitrogen dioxide concentrations measured in the living room or bedroom of a house or whole-house average measurements are better predictors of personal exposure than outdoor measurements for the population as a whole It is important to note that there may be significant segments of the population (e g , infants, police, etc) for which indoor NO_2 levels may not be good predictors of their exposure Calculated exposures from microenvironmental measurements and activity diaries are good indicators of personal exposure

8.3 INDIRECT METHODS

Indirect methods employ various degrees of microenvironmental monitoring and questionnaires to estimate an individual's or population's total NO_2 exposure They attempt to measure and understand the underlying relationships between personal exposure and the

variables causing exposure so that NO_2 exposures in other populations in other locations can be estimated Such models can provide exposure frequency distributions for the entire population or segments of the population

Estimates of NO_2 concentrations in various microenvironments (microenvironmental monitoring) can provide information on the spatial and temporal distribution of such concentrations in those environments and the factors (sources, emission rates, removal and dispersal mechanisms, etc) affecting them Estimates of microenvironmental NO_2 concentrations combined with time/activity patterns can be used to estimate or model total NO_2 exposure (i.e , Equation 8-1) Questionnaires are used to gather information on microenvironmental factors (sources, source use, volume, etc), human activities, or time budgets or for the simple categorization of an individual's exposure status

Physical/chemical, empirical/statistical, or hybrid models have been used to estimate NO_2 concentrations in various microenvironments These models utilize inputs on sources and emissions, air contaminant dispersal, contaminant reactions, removal mechanisms, and responses to questionnaires Several attempts to model indoor concentrations of NO_2 were reviewed in Chapter 7 Section 7 3 should be referred to for a detailed discussion of efforts to model indoor NO_2 concentrations The indoor modeling approaches have been very limited in applications because of the lack of data on the variability of the input parameters (e.g , emission rates, source use, mixing, reactive decay rates, etc) in actual indoor environments and the lack of adequate questionnaires for obtaining information on building or household characteristics Efforts are under way to attempt to standardize questionnaires for use in indoor air quality studies (i e , Lebowitz et al , 1989a,b) Such efforts will provide better input data to models for predicting indoor NO_2 concentrations Ambient models do not provide spatial and temporal NO_2 concentrations on a scale needed to assess concentrations outside of various microenvironments or at the interface between the outdoor air and an individual No models exist for transit microenvironments

The primary method for determining exposures in epidemiologic studies of the effects of NO_2 has been the use of questionnaires (e g , Melia et al , 1977, 1979) Typically, the questionnaires determined such information as the geographic location of a respondent's residence, type of occupation, and whether a source exists in a house (gas cooking stove, kerosene heater, etc) Reliance on this type of data for exposure, as discussed earlier

(Section 8 2), can result in serious misclassification errors due to faulty exposure specifications and failure to adequately account for confounding factors These errors result in the increased probability of masking or misrepresenting any exposure-effect relationships that may exist It is not enough, for example, to determine a respondent's exposure status based upon their response to the question of existence of a gas cooking range in their home Chapter 7 indicates that there is a wide distribution of indoor NO_2 levels in homes with gas cooking ranges related to outdoor levels, indoor sources, indoor source use, condition of the source, season of the year, indoor mixing, infiltration, and indoor building materials and furnishings

Total personal exposures to NO_2 are assessed indirectly by using a surrogate microenvironmental measurement or by combining modeled microenvironmental concentrations with time/activity patterns Section 8 2 2 indicates that a whole-house NO_2 measurement or a bedroom NO_2 measurement is highly correlated with total personal NO_2 exposure The good agreement is in large part due to the time spent in the residential environment by individuals Presumably, a model that predicts whole-house NO_2 levels could be used to represent personal exposures Combining microenvironmental monitoring data or modeled concentrations with time/activity patterns (Equation 8-1) for an individual has been used in a number of the studies discussed in Section 8 2 2 The results indicated good agreement between measured personal exposures and those calculated from time/activity patterns and microenvironmental monitoring Due to the potential for higher levels indoors and the high level of time spent indoors, outdoor levels by themselves are typically only weak predictors of total exposure, although they can contribute substantially to indoor levels where people spend their time In areas with high ambient NO_2 levels, such as the Los Angeles Basin, the influence of outdoor levels is greater than in areas where outdoor levels are low and show little variability The time/activity portions of these studies and the extensive review of time/activity studies conducted by Ott (1989) clearly demonstrate the importance of the home environment in terms of a time budget Figures 8-4a and 8-4b (Ott, 1989) highlight the portion of time spent in the home by individuals employed outside the home and by full-time homemakers It should be emphasized again, however, that Figures 8-4a and 8-4b represent average time budgets and that segments of the population can deviate significantly from those averages

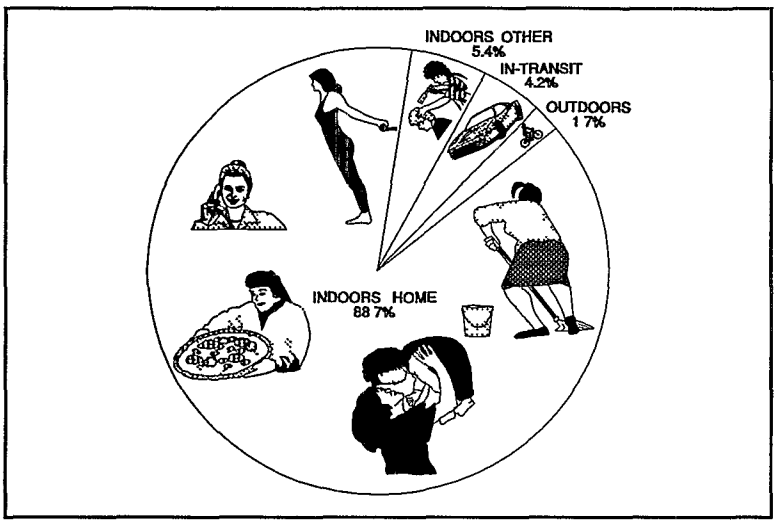


Figure 8-4a. Proportion of time spent by women who are full-time homemakers in indoor, outdoor, and in-transit microenvironments.

Source· Data from time budget studies in 44 U S cities (Szalai, 1972, Robinson, 1977), additional interpretation and analyses appear in Ott (1989)

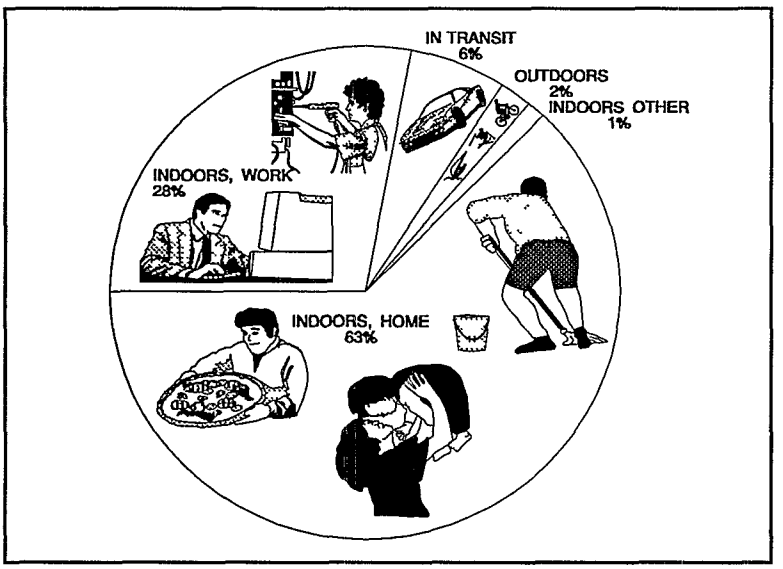


Figure 8-4b. Proportion of time spent by employed persons in indoor, outdoor, and in-transit microenvironments.

Source: Data from time budget studies in 44 U S cities (Szalai, 1972, Robinson, 1977), additional interpretation and analyses appear in Ott (1989)

8.3.1 Personal Exposure Models

Billick et al (1991) report an effort to develop a model predictive of personal NO_2 exposure based upon microenvironmental measurements and time/activity patterns Data used to develop the model come from eight different sites in the United States and were obtained from three different studies (Wilson et al , 1986, Ryan et al , 1988, Spengler et al , 1987) The data base, reviewed all or in part in earlier publications (e g , Butler et al , 1990, Drye et al , 1989, Spengler et al , 1989), contains over 6,400 measurements of NO_2 (Palmes tubes) in over 1,700 households and represents a range of exposure levels over a diverse set of geographic and climatic conditions in the U S The model was developed in two steps The first step was to develop a model predictive of indoor/outdoor and of in-vehicle/outdoor levels of NO_2 The second step involved the integration of time/activity data with the models developed in the first step

The indoor/outdoor residential model was developed from a simplified version of the general mass-balance equation (see Equations 7-1, 7-2, and 7-3) The model (Sexton et al , 1983, Drye et al , 1989) is given below

$$C_{in} = mC_{out} + b, \tag{8-2}$$

where C_{in} is the indoor concentration (micrograms per cubic meter), m is the penetration coefficient for outdoor NO_2, C_{out} is the outdoor concentration (micrograms per cubic meter), and b is the concentration contribution by indoor sources (micrograms per cubic meter) In the above model, m and b are estimated from a multivariate analysis of data collected in the eight studies The model was estimated for NO_2 concentrations separately for indoor location (e g , bedroom, kitchen, in-vehicle), season (winter, summer), and for cooking range type (gas versus electric) All the models used measured outdoor NO_2 levels and the models for gas versus electric ranges used the inverse volume of the dwelling The model for electric range contained a dichotomous independent variable for the presence of a gas furnace, whereas the model for gas cooking range dwellings was characterized by whether the appliance employs a continuously burning pilot light and whether a microwave oven is present An earlier version of this model (Drye et al , 1989), based on a more limited data set, is discussed in Chapter 7

The model for in-vehicle/outdoor relationships uses data obtained in a study of NO_2 concentration measured inside and outside vehicles (Chan et al , 1990) The predictive models fitted from the data for dwellings are shown in Tables 8-1 and 8-2 The in-vehicle/outdoor model uses a range of indoor/outdoor ratios from 0 2 to 3 32 The fitted models resulted in R^2 values ranging from 0 12 to 0 64, indicating that from 36 to 82% of the variation in indoor variations in NO_2 levels remained unexplained

TABLE 8-1. ELECTRIC-RANGE HOME LEAST SQUARES REGRESSION COEFFICIENTS AND T-STATISTICS (IN PARENTHESES)[a]

	Kitchen				Bedroom			
Variable	Summer		Winter		Summer		Winter	
Ambient NO_2 (ppb)	0 61	(28 44)	0 52	(15 27)	0 58	(32 15)	0 43	(11 23)
1/(Home Volume)[b]	-2 52	(0 59)	42 22	(5 39)	-2 87	(0 81)	41 81	(4 65)
Furnace Fuel (gas = 1)	4 50	(8 16)	-0 43	(0.44)	3 64	(7 87)	-0 01	(0 01)
R^2	0 58		0 21		0 64		0 12	
Observations	646		754		641		736	

Regression Equation· Indoor NO_2 = $\beta 1$ (ambient NO_2 level) + $\beta 2$ (1/home volume) + $\beta 3$ (gas furnace present)

[a]Shaded t-statistics values are nonsignificant at the 95% confidence level NO_2 = Nitrogen dioxide
[b]Units. 1/thousands of cubic feet

Source Billick et al (1991)

The model used to estimate the time-weighted average NO_2 exposure was presented simply as the sum of the products of the time spent in each of the three environments (in dwellings, outdoors, and in vehicles) multiplied by the predicted concentration in each environment, divided by the sum of the time spent in each environment (Equation 8-1) The concentrations in each environment were determined from the above model (Equation 8-2), whereas the time in each environment is developed from simulations formed by taking random draws from distributions of observed amounts of time spent outdoors and in vehicles (e.g., Schwab et al., 1990) The utility of the model stems from its capacity to estimate a

TABLE 8-2. GAS-RANGE HOME LEAST SQUARES REGRESSION COEFFICIENTS AND T-STATISTICS (IN PARENTHESES)[a]

Variable	Kitchen				Bedroom			
	Summer		Winter		Summer		Winter	
Ambient NO_2 (ppb)	0 85	(29 08)	0 70	(20 50)	0 70	(34 42)	0 53	(16 60)
No Pilot/Microwave	2 51	(1.69)	7 48	(3 06)	1 22	(1.17)	2 14	(0.93)
No Pilot/No Microwave	4 05	(1 96)	7 39	(2.06)	2 56	(1.77)	-0 34	(0.10)
Pilot/Microwave	14 30	(11 10)	26 11	(12 69)	6 85	(7 55)	11 92	(6 10)
Pilot/No Microwave	16 66	(10 17)	28 96	(10 47)	7 60	(6 62)	13 06	(5 04)
1/(Home Volume)[b]	28 21	(3 31)	37 85	(2 59)	28 04	(4 55)	56 20	(3 94)
R^2	0 58		0 41		0 63		0 29	
Observations	876		952		868		947	

Regression Equation Indoor NO_2 = $\beta 1$ (ambient NO_2 level) + $\beta 2$ (no pilot/microwave) + $\beta 3$ (no pilot/no microwave) + $\beta 4$ (pilot/microwave) + $\beta 5$ (pilot/no microwave) + $\beta 6$ (1/home volume)

[a]Shaded t-statistics values are nonsignificant at the 95% confidence level NO_2 = Nitrogen dioxide
[b]Units 1/thousands of cubic feet

Source Billick et al (1991)

personal NO_2 exposure profile for an area based on a limited set of relative easily obtainable data on microenvironmental concentrations and household characteristics The model is a potentially useful tool with which to develop and test the impact of mitigation measures The utility of the model was demonstrated by the authors in using it to estimate population-based exposure profiles in Los Angeles (utilizing readily available data on outdoor concentrations, housing characteristics, and time/activity patterns) and in demonstrating the impact on exposure distributions of various exposure reduction scenarios Billick (1990) discusses methods to estimate population NO_2 exposure in general The overall model has not yet been validated and the uncertainty associated with modeled personal NO_2 exposures has not been determined Such information will be needed before the overall utility of the model in NO_2 risk management applications can be assessed

8.4 SUMMARY

Exposure to NO_2 occurs across a number of microenvironments or settings An individual's integrated exposure is the sum of all of the individual NO_2 exposures over all time intervals for all microenvironments, weighted by the time in each microenvironment (Fugas, 1976, Sexton and Ryan, 1988, National Research Council, 1991) The assessment of human exposures to NO_2 can be represented by the following simplified basic model

$$E = \sum_i E_i = \sum_i f_i c_i \tag{8-1}$$

Accurate assessments of total NO_2 exposure and the environments in which exposures take place are essential to minimize misclassification errors in epidemiologic studies (Shy et al , 1978), in defining population exposure distributions in risk assessment, and in developing effective mitigation measures in risk management

Personal NO_2 exposures can be assessed by direct and indirect measures Direct measures include biomarkers and use of personal monitors (Yanagisawa et al , 1986, 1988, Maples et al., 1991). No validated biomarkers for exposure are presently available for NO_2 A limited number of studies have been conducted in which personal exposures to NO_2 were measured using passive monitors (Quackenboss et al , 1986, Leaderer et al , 1986, Harlos et al., 1987). These studies generally indicate that outdoor levels of NO_2, although related to and contributing substantially to both personal levels and indoor concentrations, are by themselves poor predictors of personal exposures for most populations Average indoor residential concentrations (e g , whole-house average or bedroom level) tend to be the best predictor of personal exposure, typically explaining 50 to 60% of the variation in personal exposures. In selected populations, the indoor residential environment may not be a good predictor of total exposure because of the higher percentages of time spent in different environments and/or the potential for unusual NO_2 concentrations

Indirect estimations of personal exposure to NO_2 employ various degrees of both microenvironmental monitoring and questionnaires to estimate an individual's or population's total exposure. One such model, developed from an extensive monitoring and questionnaire data base, can estimate population exposure distributions from easily obtained data on outdoor NO_2 concentrations, housing characteristics, and time/activity patterns (Billick et al ,

1991) This indoor/outdoor residential model (Sexton et al , 1983; Drye et al , 1989), developed from a simplified version of the general mass-balance equation (see Equations 7-1, 7-2, and 7-3), is given below

$$C_{in} = mC_{out} + b, \tag{8-2}$$

where C_{in} is the indoor concentration (micrograms per cubic meter), m is the penetration coefficient for outdoor NO_2, C_{out} is the outdoor concentration (micrograms per cubic meter), and b is the concentration contribution by indoor sources (micrograms per cubic meter) The model used to estimate the time-weighted average NO_2 exposure was presented simply as the sum of the products of the time spent in each of the three environments (in dwellings, outdoors, and in vehicles) multiplied by the predicted concentration in each environment, divided by the sum of the time spent in each environment (Equation 8-1) This model is proposed for use in evaluating the impact of various NO_2 mitigation measures The model is promising, but it has not yet been validated and the uncertainty associated with it has not been characterized

REFERENCES

Billick, I. H (1990) Estimation of population exposure to nitrogen dioxide Toxicol Ind Health 6 325-335

Billick, I H , Ozkaynak, H , Butler, D A , Spengler, J D (1991) Predicting personal exposures to NO_2 for population-based exposure and risk evaluations Presented at 84th annual meeting of the Air and Waste Management Association, June, Vancouver, BC, Canada Pittsburgh, PA Air and Waste Management Association, paper no 91-172 9

Butler, D A , Ozkaynak, H , Billick, I H , Spengler, J D (1990) Predicting indoor NO_2 concentrations as a function of home characteristics and ambient NO_2 levels In Indoor air '90 precedings of the 5th international conference on indoor air quality and climate, volume 2, characteristics of indoor air, July-August, Toronto, ON, Canada Ottawa, ON, Canada International Conference on Indoor Air Quality and Climate, Inc , pp 519-524

Chan, C (1990) Commuter exposures to volatile organic compounds [Ph D dissertation] Boston, MA Harvard School of Public Health

Chapin, F. S , Jr (1974) Human activity patterns in the city New York, NY John Wiley & Sons (Clark, T. N , ed Wiley series in urban research)

Clausing, P , Mak, J K , Spengler, J D , Letz, R (1986) Personal NO_2 exposures of high school students Environ Int 12 413-417

Colome, S D , Wilson, A L , Spengler, J D (1992) Nitrogen dioxide exposure studies—volume V, personal exposure to nitrogen dioxide in the Los Angeles basin a microenvironmental approach Chicago, IL Gas Research Institute, report no GRI-92/0427

Dockery, D W.; Spengler, J D , Reed, M P , Ware, J (1981) Relationships among personal, indoor and outdoor NO_2 measurements Environ Int 5 101-107

Dosemeci, M , Wacholder, S , Lubin, J H (1990) Does nondifferential misclassification of exposure always bias a true effect toward the null value? Am J Epidemiol 132 746-748

Drye, E E., Ozkaynak, H , Burbank, B , Billick, I H , Baker, P E , Spengler, J D , Ryan, P B , Colome, S D (1989) Development of models for predicting the distribution of indoor nitrogen dioxide concentrations JAPCA 39 1169-1177

Duan, N (1981) Microenvironment types a model for human exposure to air pollution Stanford, CA Stanford University, Dept of Statistics, SIMS technical report no 47

Fugas, M (1976) Assessment of total exposure to an air pollutant In International conference on environmental sensing and assessment, v 2, September, Las Vegas, NV New York, NY Institute of Electrical and Electronic Engineers, paper no 38-5

Gladen, B , Rogan, W J (1979) Misclassification and the design of environmental studies Am J Epidemiol 109 607-616

Harlos, D P , Marbury, M , Samet, J , Spengler, J D (1987) Relating indoor NO_2 levels to infant personal exposures Atmos Environ 21 369-376

Hoek, G., Brunekreef, B , Meijer, R , Scholten, A , Boleij, J (1984) Indoor nitrogen dioxide pollution and respiratory symptoms of schoolchildren Int Arch Occup Environ Health 55 79-86

Koo, L C , Ho, J H-C , Ho, C -Y , Matsuki, H , Shimizu, H , Mori, T , Tominaga, S (1990) Personal exposure to nitrogen dioxide and its association with respiratory illness in Hong Kong Am Rev Respir Dis 141 1119-1126

Lambert, W E , Samet, J M , Stidley, C A , Spengler, J D (1990) Classification of chronic exposure to nitrogen dioxide In Indoor air '90 precedings of the 5th international conference on indoor air quality and climate, volume 2, characteristics of indoor air, July-August, Toronto, ON, Canada Ottawa, ON, Canada International Conference on Indoor Air Quality and Climate, Inc , pp 537-542

Leaderer, B P , Zagraniski, R T , Berwick, M , Stolwijk, J A J (1986) Assessment of exposure to indoor air contaminants from combustion sources methodology and application Am J Epidemiol 124 275-289

Lebowitz, M D , Quackenboss, J J , Soczek, M L , Kollander, M , Colome, S (1989a) The new standard environmental inventory questionnaire for estimation of indoor concentrations JAPCA 39 1411-1419

Lebowitz, M D , Quackenboss, J J , Soczek, M L , Colome, S D , Lioy, P J (1989b) Workshop development of questionnaires and survey instruments In Nagda, N L , Harper, J P , eds Design and protocol for monitoring indoor air quality Philadelphia, PA American Society for Testing and Materials, pp 203-216 (ASTM special technical publication 1002

Lebret, E (1990) Errors in exposure measures Toxicol Ind Health 6 147-156

Maples, K R , Sandstrom, T , Su, Y -F , Henderson, R F (1991) The nitric oxide/heme protein complex as a biologic marker of exposure to nitrogen dioxide in humans, rats, and in vitro models Am J Respir Cell Mol Biol 4 538-543

Melia, R J W , Florey, C du V , Altman, D G , Swan, A V (1977) Association between gas cooking and respiratory disease in children Br Med J 2 149-152

Melia, R J W , Florey, C du V , Chinn, S (1979) The relation between respiratory illness in primary schoolchildren and the use of gas for cooking I—results from a national survey Int J Epidemiol 8 333-338

Muelenaer, P , Reid, H , Morris, R , Saltzman, L , Horstman, D , Collier, A , Henderson, F (1987) Urinary hydroxyproline excretion in young males exposed experimentally to nitrogen dioxide In Seifert, B , Esdorn, H , Fischer, M , Rueden, H , Wegner, J , eds Indoor air '87 proceedings of the 4th international conference on indoor air quality and climate, v 2, environmental tobacco smoke, multicomponent studies, radon, sick buildings, odours and irritants, hyperreactivities and allergies, August, Berlin, Federal Republic of Germany Berlin, Federal Republic of Germany Institute for Water, Soil and Air Hygiene, pp 97-103

National Research Council (1989) Biologic markers of pulmonary toxicology Washington, DC National Academy Press

National Research Council (1991) Human exposure assessment for airborne pollutants advances and opportunities Washington, DC National Academy of Sciences

Nitta, H , Maeda, K (1982) Personal exposure monitoring to nitrogen dioxide Environ Int 8 243-248

Ott, W (1989) Human activity patterns a review of the literature for estimating time spent indoors, outdoors, and in-transit In Starks, T H , ed Proceedings of the research planning conference on human activity patterns Las Vegas, NV U S Environmental Protection Agency, Environmental Monitoring Systems Laboratory, chapter 3, EPA report no EPA-600/4-89-004 Available from NTIS, Springfield, VA, PB89-166599

Ozkaynak, H , Ryan, P. B , Spengler, J D , Laird, N M (1986) Bias due to misclassification of personal exposures in epidemiologic studies of indoor and outdoor air pollution In Berglund, B , Berglund, U., Lindvall, T , Spengler, J , Sundell, J , eds Indoor air quality papers from the third international conference on indoor air quality and climate, August 1984, Stockholm, Sweden Environ Int 12· 389-393

Palmes, E D., Gunnison, A F , DiMattio, J , Tomczyk, C (1976) Personal samplei for nitrogen dioxide Am Ind Hyg Assoc J 37 570-577

Quackenboss, J J , Kanarek, M S , Spengler, J D , Letz, R (1982) Personal monitoring for nitrogen dioxide exposure. methodological considerations for a community study Environ Int 8 249-258

Quackenboss, J J , Spengler, J D , Kanarek, M S , Letz, R , Duffy, C P (1986) Personal exposure to nitrogen dioxide relationship to indoor/outdoor air quality and activity patterns Environ Sci Technol 20 775-783.

Robinson, J. P. (1977) How Americans use their time a social psychological analysis of everyday behavior New York, NY Praeger Publishers

Ryan, P. B , Koutrakis, P (1990) Indoor air chemistry an emerging field In Indoor air '90 precedings of the 5th international conference on indoor air quality and climate, volume 2, characteristics of indoor air, July-August, Toronto, ON, Canada Ottawa, ON, Canada International Conference on Indoor Air Quality and Climate, Inc , pp 489-494

Ryan, P B ; Spengler, J D (1992) Nitrogen dioxide exposure studies—volume II, the Boston residential home characterization study Chicago, IL Gas Research Institute, report no GRI-92/0424

Ryan, P B , Soczek, M L , Treitman, R D , Spengler, J D , Billick, I H (1988) The Boston residential NO_2 characterization study—II survey methodology and population concentration estimates Atmos Environ 22 2115-2125

Ryan, P B , Schwab, M , Spengler, J D (1992) Nitrogen dioxide exposure studies—volume III, personal exposure to nitrogen dioxide in Boston a microenvironmental approach Chicago, IL Gas Research Institute, report no GRI-92/0425 2

Schwab, M , Colome, S D , Spengler, J D , Ryan, P B , Billick, I H (1990) Activity patterns applied to pollutant exposure assessment data from a personal monitoring study in Los Angeles Toxicol Ind Health 6 517-532

Sexton, K ; Ryan, P B (1988) Assessment of human exposure to air pollution methods, measurements, and models. In Watson, A Y , Bates, R R , Kennedy, D , eds Air pollution, the automobile, and public health Washington, DC National Academy Press, pp 207-238

Sexton, K., Letz, R , Spengler, J D (1983) Estimating human exposure to nitrogen dioxide an indoor/outdoor modeling approach Environ Res 32 151-166

Shy, C. M , Kleinbaum, D G , Morgenstern, H (1978) The effect of misclassification of exposure status in epidemiological studies of air pollution health effects Bull N Y Acad Med 54 1155-1165

Spengler, J D , Ware, J , Speizer, F , Ferris, B , Dockery, D , Lebret, E , Brunnekreef, B (1987) Harvard's indoor air quality respiratory health study In Seifert, B , Esdorn, H , Fischer, M , Rueden, H , Wegner, J , eds Indoor air '87 proceedings of the 4th international conference on indoor air quality and climate, v 2, environmental tobacco smoke, multicomponent studies, radon, sick buildings, odours and irritants, hyperreactivities and allergies, August, Berlin, Federal Republic of Germany Berlin, Federal Republic of Germany Institute for Water, Soil and Air Hygiene, pp 218-223

Spengler, J , Ryan, P B , Schwab, M , Colome, S , Wilson, A L , Billick, I , Becker, E (1989) An overview of the Los Angeles personal monitoring study Presented at First international symposium on total exposure assessment methodology a new horizon Las Vegas, NV, pp 66-85

Spengler, J D , Ryan, P B , Schwab, M , Colome, S D , Wilson, A L (1992) Nitrogen dioxide exposure studies—volume IV, personal exposure to nitrogen dioxide in the Los Angeles basin Chicago, IL Gas Research Institute, report no GRI-92/0426

Szalai, A , ed (1972) The use of time daily activities of urban and suburban populations in 12 countries The Hague, The Netherlands Mouton and Co

Wiley, J A , Robinson, J P , Piazza, T , Garrett, K , Cirksena, K , Cheng, Y -T , Martin, G (1991a) Activity patterns of California residents Sacramento, CA California Air Resources Board, contract no A6-177-33

Wiley, J A , Robinson, J P , Piazza, T , Garrett, T , Cirksena, K , Cheng, Y -T , Martin, G (1991b) Study of children's activity patterns final report Sacramento, CA California Air Resources Board, contract no A-733-149

Willett, W. (1989) An overview of issues related to the correction of non-differential exposure measurement error in epidemiologic studies Stat Med 8 1031-1040, 1071-1073

Wilson, A L , Colome, S D , Baker, P E , Becker, E W (1986) Residential indoor air quality characterization study of nitrogen dioxide Phase I Volumes 1, 2 and 3 Southern California Gas Company, October

Yanagisawa, Y , Nishimura, H (1982) A badge-type personal sampler for measurement of personal exposure to NO_2 and NO in ambient air Environ Int 8 235-242

Yanagisawa, Y , Matsuki, H , Osaka, F , Kasuga, H , Nishimura, H (1984) Annual variation of personal exposure to nitrogen dioxide In Berglund, B , Lindvall, T , Sundell, J , eds Indoor air proceedings of the 3rd international conference on indoor air quality and climate, v 4, chemical characterization and personal exposure, August, Stockholm, Sweden Stockholm, Sweden Swedish Council for Building Research, pp 33-36 Available from NTIS, Springfield, VA, PB85-104214

Yanagisawa, Y , Nishimura, H , Matsuki, H , Osaka, F , Kasuga, H (1986) Personal exposure and health effect relationship for NO_2 with urinary hydroxyproline to creatinine ratio as indicator Arch Environ Health 41· 41-48

Yanagisawa, Y , Nishimura, H , Matsuki, H , Osaka, F , Kasuga, H (1988) Urinary hydroxyproline to creatinine ratio as a biological effect marker for exposure to NO_2 and tobacco smoke Atmos Environ 22 2195-2203

☆U S GOVERNMENT PRINTING OFFICE 1993-550-001/80323

United States
Environmental Protection Agency
Center for Environmental Research Information
Cincinnati, OH 45268

Official Business
Penalty for Private Use
$300

EPA/600/8-91/049aF

Please make all necessary changes on the below label, detach or copy and return to the address in the upper left hand corner

If you do not wish to receive these reports CHECK HERE ☐, detach, or copy this cover, and return to the address in the upper left hand corner