

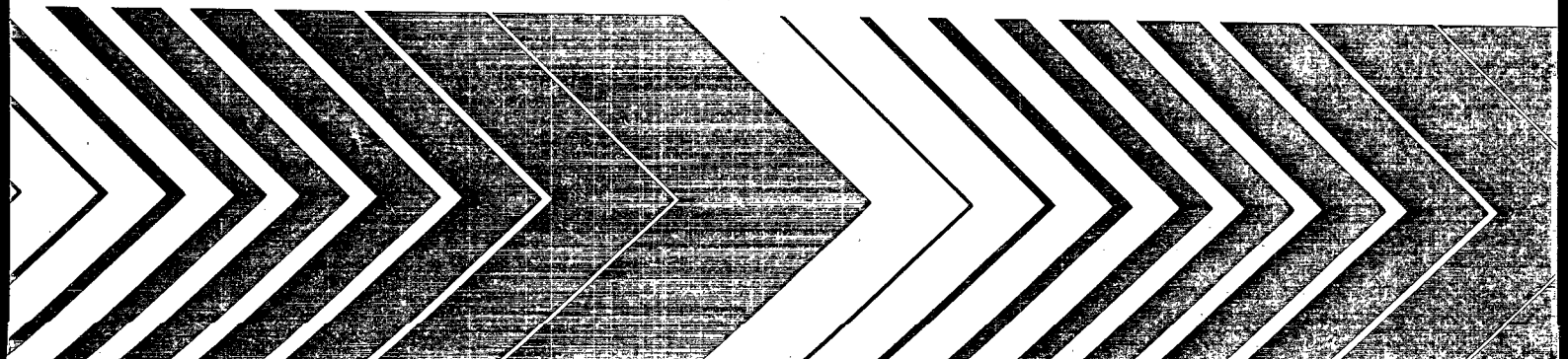
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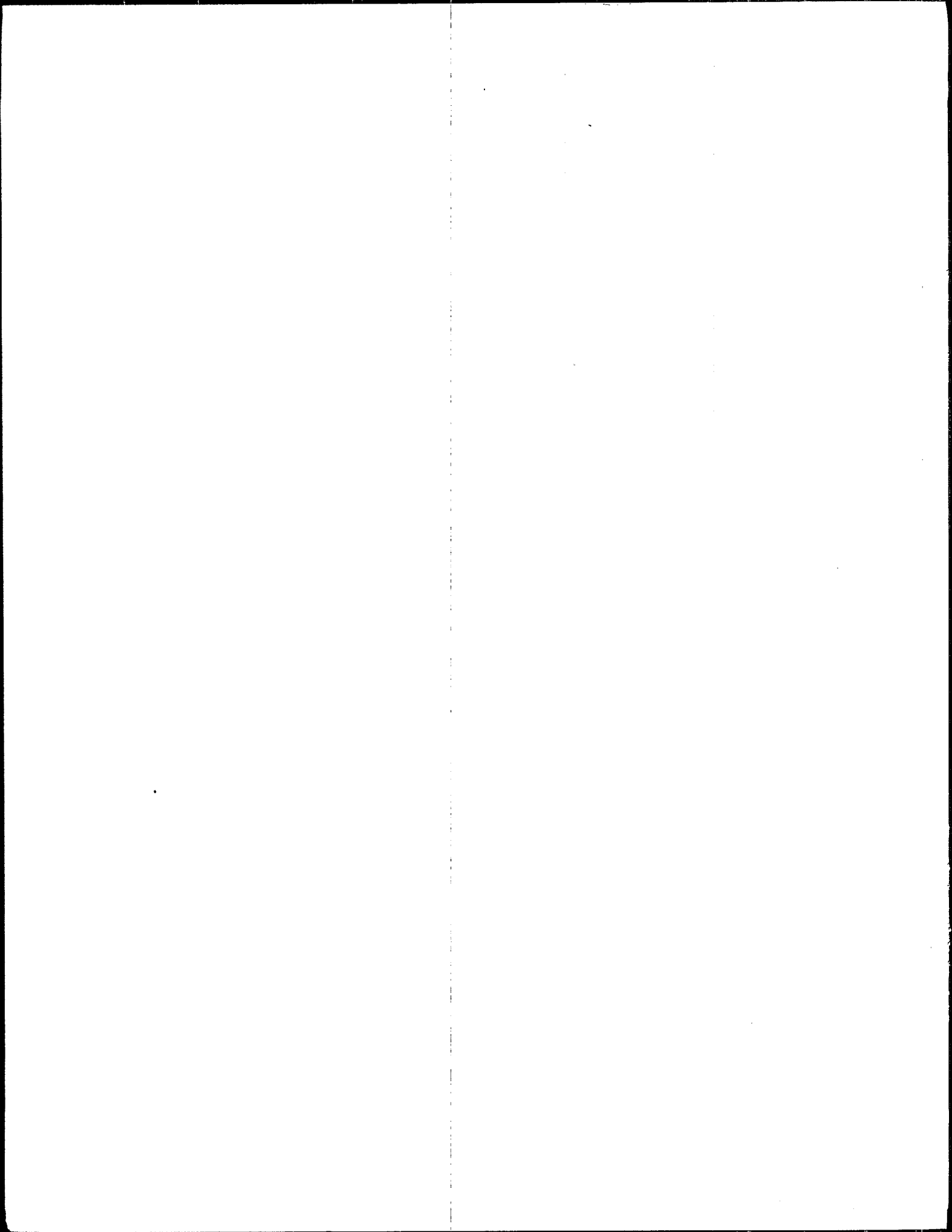
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National Dry Deposition Network: Third Annual Progress Report (1989)





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March 1991

NATIONAL DRY DEPOSITION NETWORK
THIRD ANNUAL PROGRESS REPORT (1989)

by

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FOREWORD

The Atmospheric Research and Exposure Assessment Laboratory (AREAL) is committed to performing research and development in the characterization of air pollutant sources, sinks, transport, and transformations, in the assessment and prediction of exposure of humans and ecosystems to environmental pollutants, and in the development of monitoring systems and other technologies to determine the status and trends in pollutant concentrations and the condition of the nation's ecosystems.

As national and international concern over acid deposition has grown, so has the need for information on spatial patterns and secular trends. Although wet deposition monitoring has been able to provide such information, it is realized that total acid deposition has both wet and dry components; the latter of which has not been well defined. AREAL has supported the development of a network of dry acid deposition monitoring sites to demonstrate the feasibility of operating such a network and to provide a database of atmospheric dynamics and chemical concentrations that can be transformed to dry acid deposition quantities through the application of one or more dry deposition algorithms. Applications for final data may include determination of spatial and temporal trends, evaluation of deposition models, refinement of mass balance estimates, and support to effects studies.

This report summarizes the third year's progress of the National Dry Deposition Network.

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ABSTRACT

The National Dry Deposition Network (NDDN) is designed to provide long-term estimates of dry acidic deposition across the continental United States. Fifty NDDN sites were operational during 1989, including 41 sites in the eastern United States and 9 sites in the western United States. Each site was equipped with sensors for continuous measurements of ozone and meteorological variables required for estimation of dry deposition rates. Weekly average atmospheric concentrations of SO_4^{2-} , NO_3^- , NH_4^+ , SO_2 , and HNO_3 were measured (using 3-stage filter packs) throughout the year, while Na^+ , K^+ , Ca^{2+} , and Mg^{2+} were measured from January through September. Separate day/night samples were analyzed from January through September and around-the-clock samples were analyzed for the remainder of 1989.

Results showed species-dependent variability in atmospheric concentrations from site to site, season to season, and day to night. In general, SO_4^{2-} , NH_4^+ , SO_2 , and HNO_3 concentrations were much higher (factor 5-10) at eastern sites than at western sites. On the other hand, NO_3^- , Na^+ , K^+ , Ca^{2+} , and Mg^{2+} concentrations were frequently comparable at eastern and western sites. Average SO_4^{2-} , NH_4^+ , and HNO_3 concentrations were typically highest during summer and lowest during fall. In contrast, SO_2 and NO_3^- were highest in winter and lowest in summer. Day/night variability was low for aerosols, but frequently pronounced for SO_2 and HNO_3 , especially during the summer and at sites located in complex terrain. Comparison of O_3 data for 1988 and 1989 showed marked differences between years and a distinct tendency for higher concentrations in 1988. Ninety-eight exceedances of the NAAQS were observed at 18 sites in 1988, while only 15 exceedances were observed at 43 sites in 1989. Approximations of annual dry deposition rates for SO_4^{2-} , SO_2 , NO_3^- , and HNO_3 suggest that gaseous deposition greatly exceeds aerosol deposition and that dry fluxes are similar to wet deposition at numerous sites in the eastern United States. Application of site-specific dry deposition models are needed to refine these estimates.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

cm/sec	-- centimeters per second
CVS	-- calibration verification standard
DAS	-- data acquisition system
DMC	-- data management center
EEPROM	-- electronically erasable programmable read-only memory
EPA	-- U.S. Environmental Protection Agency
eq/ha	-- equivalents per hectare
eq/ha-yr	-- equivalents per hectare per year
ESE	-- Environmental Science & Engineering, Inc.
ft	-- foot
IC	-- ion chromatography
ICAP	-- inductively coupled argon plasma
ICP-ES	-- inductively coupled plasma emission spectroscopy
km	-- kilometer
L/min	-- liters per minute
m	-- meter
m ³	-- cubic meter
MAD	-- median absolute difference
MAPD	-- median absolute percent difference
m/sec	-- meters per second
mL	-- milliliters
mmHg	-- millimeters of mercury
MFC	-- mass flow controller
NAAQS	-- National Ambient Air Quality Standard
NADP/NTN	-- National Atmospheric Deposition Program/National Trends Network
NCLAN	-- National Crop Loss Assessment Network
neq/m ³	-- nanoequivalents per cubic meter
NDDN	-- National Dry Deposition Network
NIST	-- National Institute of Standards and Technology
NOAA/ATDD	-- National Oceanic and Atmospheric Administration/Atmospheric Turbulence and Diffusion Division
PC	-- personal computer
ppb	-- parts per billion
ppm/hr	-- parts per million per hour
QA	-- quality assurance
QC	-- quality control
μL	-- microliter
μg	-- microgram
μg/filter	-- micrograms per filter

LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS, continued

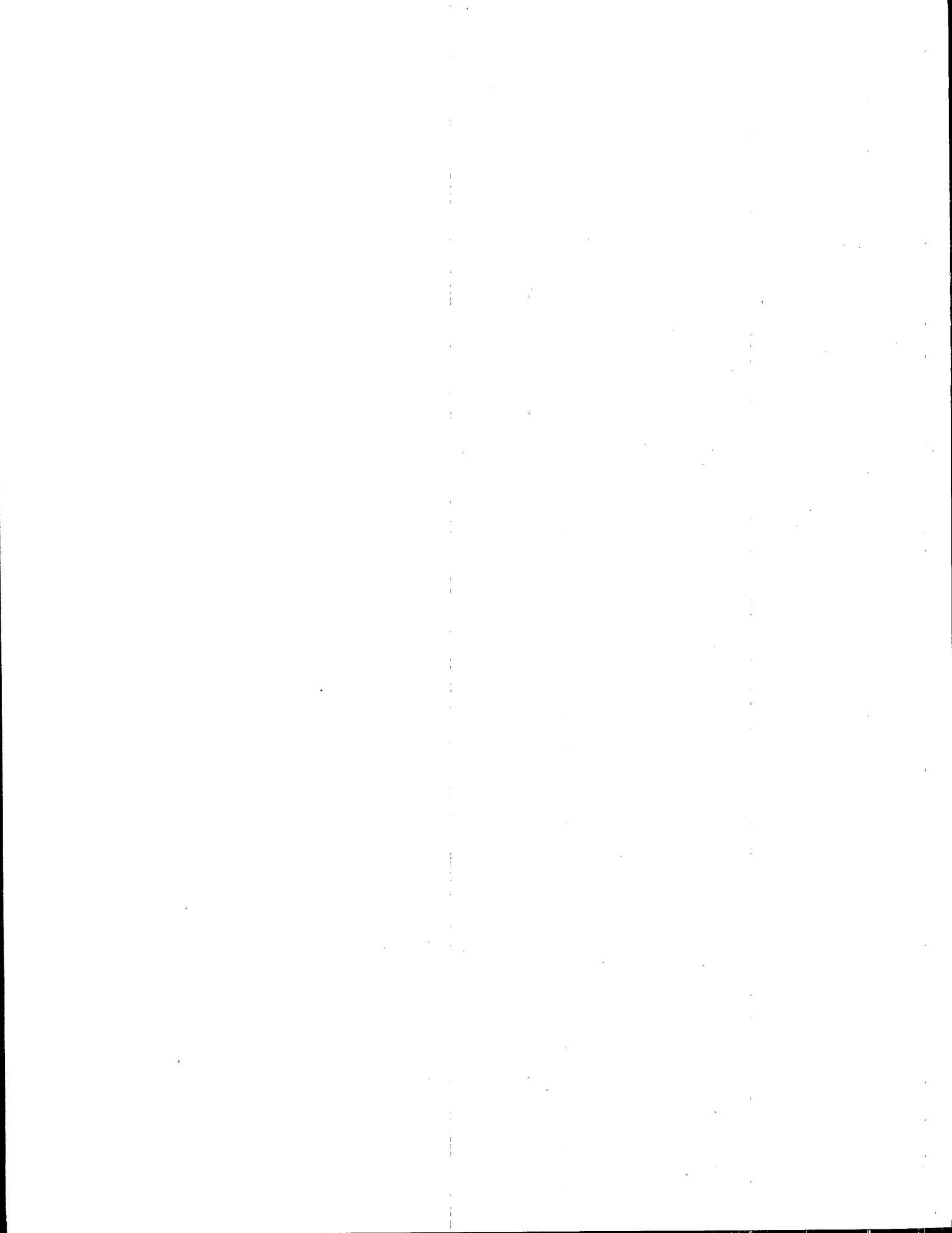
$\mu\text{g/L}$	-- micrograms per liter
μm	-- micrometer
$\mu\text{g/m}^3$	-- micrograms per cubic meter
UV	-- ultraviolet
W/m^2	-- watts per square meter

SYMBOLS

Br^-	-- bromide ion
$^{\circ}\text{C}$	-- degrees Celsius
Ca^{2+}	-- particulate calcium
HNO_3	-- nitric acid
K^+	-- particulate potassium
K_2CO_3	-- potassium carbonate
Mg^{2+}	-- particulate magnesium
Na^+	-- particulate sodium
NH_4^+	-- particulate ammonium
NH_4NO_3	-- ammonium nitrate
NO	-- nitric oxide
NO_3^-	-- particulate nitrate
O_3	-- ozone
SO_2	-- sulfur dioxide
SO_4^{2-}	-- particulate sulfate

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SECTION 1.0

INTRODUCTION

Atmospheric deposition takes place via two pathways: wet deposition and dry deposition. Wet deposition is the result of precipitation events (rain, snow, etc.) which remove particles and gases from the atmosphere. Dry deposition is the transfer of particles and gases to the landscape in the absence of precipitation. Wet deposition rates of acidic species across the United States have been well documented over the last 5 to 10 years; however, due to measurement difficulties, comparable information is unavailable for dry deposition rates.

The direct measurement of dry deposition can be extremely difficult, but a number of investigations have recently shown that it can be reasonably inferred by coupling air quality data with routine meteorological measurements (Shieh et al., 1979; Hicks et al., 1985; Meyers and Yuen, 1987; Wesely and Lesht, 1988). Using analogies with heat and momentum flux, Shieh et al. (1979) computed submicron particle and sulfur dioxide (SO_2) deposition velocities as a function of land use, season, windspeed, and meteorological stability class. Results of this calculation for the eastern United States showed that deposition rates for both species were strongly dependent on windspeed, solar radiation, and the condition and type of ground cover. For example, rapidly growing vegetation was found to experience higher deposition rates than senescent vegetation, and forests generally experienced higher rates than short grass or snow. Wesely (1988) has expanded this approach to calculate deposition rates for various additional species [including nitric acid (HNO_3)] and to use site-specific meteorological data. Seminal work on the subject of dry deposition has been performed by Hicks et al. (1985) and Hosker and Womack (1986), who developed, tested, and deployed the first field system for inferential dry deposition measurements.

In 1986, the U.S. Environmental Protection Agency (EPA) contracted with Environmental Science & Engineering, Inc. (ESE) to establish and operate the National Dry Deposition Network (NDDN). The objective of NDDN is to obtain field data at 50 to 100 sites throughout the United States to establish patterns and trends of dry deposition. Ultimately, dry deposition fluxes will be calculated using measured air pollutant concentrations and inferred deposition velocities estimated from meteorological, land use, and site characteristic data. One or more of the inferential approaches developed by Hicks et al. (1985) and Wesely (1988) will be used to estimate dry deposition velocities.

This report describes progress on the NDDN during calendar year 1989. The purpose of this report is to familiarize the reader with the general approach of NDDN and the various types of data which are being produced and reported to EPA. This report is not intended to provide a definitive analysis of the 1989 database. It describes the network configuration and deployment schedule as well as procedures developed for field operations, laboratory operations, database management, and quality control (QC). An overview of air quality data for 1989, including QC results, is also presented. Finally, dry deposition rates are estimated for selected sites and compared with wet deposition rates. These estimates were prepared using literature values for deposition velocities (not the inferential approaches cited previously) and, therefore, are intended only to illustrate likely ranges of deposition.

SECTION 2.0

CONCLUSIONS

Deployment of all currently planned NDDN sites was completed during 1989. Forty-one primarily rural monitoring sites were operated throughout the year in the eastern United States. These sites form a relatively dense sampling array, especially in the midwest and northeast, and should provide useful data for evaluation of spatial patterns east of the Mississippi River. In addition, nine sites in the western United States were established and operational by midyear. Due to the size and diversity of the western region, the sparse distribution of sites was designed to assist in the quantification of total atmospheric deposition at specific receptors, rather than to evaluate spatial patterns of dry deposition.

Each NDDN site was equipped with sensors and sampling apparatus for continuous measurement of ozone (O_3) and meteorological variables required to estimate dry deposition. Weekly average atmospheric concentrations of particulate sulfate (SO_4^{2-}), particulate nitrate (NO_3^-), particulate-ammonium (NH_4^+), SO_2 , and HNO_3 were determined throughout the year so weekly dry deposition loadings could be calculated. Particulate sodium (Na^+), particulate potassium (K^+), particulate calcium (Ca^{2+}), and particulate magnesium (Mg^{2+}) were determined for part of the year to evaluate the presence of atmospheric base cations. EPA is currently working jointly with the National Oceanic and Atmospheric Administration/Atmospheric Turbulence and Diffusion Division (NOAA/ATDD) to finalize the algorithms for dry deposition calculations.

NDDN sites were also equipped with a sophisticated data acquisition system (DAS), which permitted automated data retrieval and real-time access and review of data from a central data management center (DMC). Overall, this system has worked well; the networkwide data capture rate for 1989 was 93 percent.

The following conclusions summarize results of a preliminary analysis of the 1989 database:

1. In general, the data produced by NDDN meet quality assurance (QA) objectives established at the onset of the program. Results of equipment calibrations and audits show that NDDN meteorological and chemical sensors produce data of sufficient quality for dry deposition estimates most of the time. For example, the network-wide average accuracy for O_3 monitors was in the range of 98 to 102 percent for each calendar quarter. Individual O_3 monitors were invariably in the range of 90 to 110 percent for the entire year.

2. Operation of dual, side-by-side air samplers at four sites indicates that filter pack measurements can be very precise. For three eastern sites, analyses of SO_4^{2-} , SO_2 , and NH_4^+ exhibited precision estimates of 5 percent, or better; NO_3^- and HNO_3 exhibited precision of 10 percent, or better. For a single site in the western United States (i.e., 167), measurements of the above species uniformly exhibited precision within 5 percent. Median absolute differences between paired samples from site 167 were within 0.03 microgram per cubic meter ($\mu\text{g}/\text{m}^3$) for SO_4^{2-} , NO_3^- , NH_4^+ , SO_2 , and HNO_3 . Although the accuracy of filter pack measurement is currently unknown, this degree of precision will prove useful in the eventual determination of secular trends and spatial patterns.
3. Results of filter pack analyses throughout the year at 41 eastern sites show species-dependent variability from site to site, season to season, and day to night. Annual average concentrations of atmospheric SO_4^{2-} exhibited peak values of approximately $7.8 \mu\text{g}/\text{m}^3$ in western Ohio and central Kentucky and minimum values around 2 to $4 \mu\text{g}/\text{m}^3$ on the periphery of the network (i.e., Maine, Wisconsin, and Florida). Spatial variability for SO_4^{2-} was relatively low as compared to other species.

Data for nine western sites operated over the last half of 1989 showed appreciably lower concentrations than eastern sites (i.e., 0.7 to $1.7 \mu\text{g}/\text{m}^3$). Among western sites, the highest SO_4^{2-} concentrations were consistently observed in northern and southern Arizona.

4. Annual SO_2 concentrations for eastern sites showed a maximum of $23.2 \mu\text{g}/\text{m}^3$ in western Pennsylvania and an ellipse of values above $10 \mu\text{g}/\text{m}^3$ extending eastward from Illinois and Kentucky to the eastern seaboard. As for SO_4^{2-} , the lowest concentrations of SO_2 among eastern sites (i.e., 2.4 to $3.0 \mu\text{g}/\text{m}^3$) were observed in Maine, Wisconsin, and Florida. Western sites exhibit dramatically lower SO_2 than eastern sites (i.e., 0.4 to $1.3 \mu\text{g}/\text{m}^3$) and highest concentrations in southern Arizona.
5. Annual average HNO_3 ranges from $3.6 \mu\text{g}/\text{m}^3$ in southeastern Pennsylvania to $0.7 \mu\text{g}/\text{m}^3$ in Maine. Concentrations above $2.0 \mu\text{g}/\text{m}^3$ cover a broad region (excluding a few isolated sites) from the Great Lakes to northern Alabama and Georgia. Average HNO_3 for the western sites is typically about 50 percent of the lowest values observed in the east. Arizona sites, however, exhibit HNO_3 concentrations similar to those reported for Florida, Wisconsin, and Maine.

6. Annual NO_3^- concentrations show marked regional character, with maxima above $2.0 \mu\text{g}/\text{m}^3$ throughout the midwest and minima below $0.5 \mu\text{g}/\text{m}^3$ at scattered locations from New England to Florida. Examination of land use characteristics suggests a link between NO_3^- and land use. The highest overall concentrations correlate strongly with agricultural areas (in any region), and the lowest concentrations correlate with forested areas. Results for the western sites indicate comparable concentrations to forested areas of the eastern United States.
7. Annual average NH_4^+ data range from $3.2 \mu\text{g}/\text{m}^3$ in northern Indiana to $0.7 \mu\text{g}/\text{m}^3$ in Maine and exhibit spatial variability similar to NO_3^- . Concentrations above $2.0 \mu\text{g}/\text{m}^3$ are observed throughout the midwest and at sites near agricultural activity in the southeast and northeast. Only sites in extreme northern New York, New Hampshire, Maine, and Florida exhibit annual averages below $1.0 \mu\text{g}/\text{m}^3$. Data for western sites show the majority of NH_4^+ concentrations in the range of 0.2 to $0.4 \mu\text{g}/\text{m}^3$. Consistent with other measurements, the highest concentration among western sites occurs in southern Arizona.
8. Dry deposition rates for SO_4^{2-} , SO_2 , NO_3^- , and HNO_3 for 28 sites in the eastern United States were estimated based on annual average concentration data and literature values for deposition velocity. Results have an uncertainty of at least 50 percent. Estimated dry deposition of sulfur species (i.e., SO_4^{2-} and SO_2) range from about 100 equivalents per hectare (eq/ha) in Maine to about 750 eq/ha in western Pennsylvania.

Estimated dry deposition of nitrogen species (i.e., HNO_3 and NO_3^-) ranges from about 55 eq/ha in Maine to about 290 eq/ha in eastern Pennsylvania. Due to faster deposition velocities, the gaseous species HNO_3 and SO_2 represent a large fraction of dry nitrogen and dry sulfur deposition, respectively. Comparison of wet and dry deposition of sulfur and nitrogen at 28 eastern sites suggests that the two are of similar magnitude over large areas. However, wet deposition appears to be dominant around the periphery of the network, where atmospheric concentrations of SO_2 and HNO_3 are low.

9. Inspection of O_3 data for 1989 shows that there were relatively few episodes of elevated concentrations. Comparison of O_3 data for 1988 and 1989 shows that these two years differ significantly by virtually any measure. For example, the 18 sites operational during 1988 reported 98 exceedances of the National Ambient Air Quality Standard (NAAQS) for O_3 of 120 parts per billion (ppb), while the 43 sites operational during 1989 reported only 15. Similarly, calculations of various exposure indices show that growing season exposures

were about 25 to 100 percent higher in 1988 than in 1989, depending on the index selected. Results suggest that 1988 and 1989 represent years of extremely high and low to moderate O_3 exposure, respectively. Examination of meteorological data for the 2 years also shows that 1988 was substantially hotter and sunnier than 1989.

10. Calculations of aerosol ion balances for selected sites indicate general differences between regions and land use categories. Forested northeastern and southeastern sites exhibit an excess of measured anions (SO_4^{2-} and NO_3^-) over measured cations (NH_4^+ , Na^+ , K^+ , Ca^{2+} , and Mg^{2+}); agricultural midwestern sites exhibit a slight excess of cations over anions; and western sites exhibit a substantial excess of cations over anions. The anion/cation imbalance increases (both on relative and absolute bases) with increasing SO_4^{2-} plus NO_3^- at northeastern and western sites. Thus, the importance of an unmeasured ion (e.g., H^+ in the northeast, HCO_3^- in the west) appears to increase during periods of high concentration.

SECTION 3.0

NETWORK DESCRIPTION AND OPERATIONS

3.1 NETWORK DESCRIPTION

The status of the NDDN, as of December 1989, is shown in Figure 1. Forty-one eastern sites and two western sites were operational throughout the year. Eight additional sites (one eastern, seven western) were brought up to full operational status by July 1, 1989. The single eastern site (Site 111--Speedwell, TN) replaced another site in Tennessee (Site 102--Oak Ridge), which was demobilized due to the proximity of large point sources of SO_2 and NO_x .

The names, locations, reporting dates, elevation, terrain, and land-use classifications of all NDDN sites are listed in Table 1. Terrain and land-use information refers to a 10-kilometer (km) radius around the site and is presented to convey a sense of the setting within which each site operates. Note that site numbers are used for identification purposes only and do not correlate with order of installation or operation.

For purposes of discussion, the eastern United States sites can be divided into three regions: midwestern, northeastern, and southeastern. The midwest includes Illinois, Indiana, Kentucky, Michigan, Ohio, and Wisconsin and contains 14 NDDN sites. The southeast includes Arkansas, Alabama, Georgia, Florida, Mississippi, North Carolina, and Tennessee and contains 10 sites. The northeast includes the remaining eastern states, from Virginia to Maine, and contains 17 sites. Inspection of land-use information in Table 1 shows marked regional differences in the character of sites. Midwestern sites are predominantly agricultural, while those in the northeast and southeast are mostly forested. Terrain characteristics also differ systematically between regions. The majority of midwestern sites are located on flat countryside and only that in eastern Kentucky (Site 121--Lilley Cornett Woods) is in complex terrain. Northeastern sites, in contrast, are almost evenly divided between rolling and complex terrain, and only one site (Site 116--Beltsville, MD) is in flat terrain. Three northeastern sites are located above 1,000 meters (m) and form a line extending southward from northern Virginia to North Carolina. Site 118 (Big Meadows, VA) is situated at the crest of the Blue Ridge; Site 120 (Horton Station, VA) and Site 126 (Cranberry, NC) occupy the spine of the Appalachian Mountains. Due to the unique exposure of these sites, they have been placed in a separate terrain category (i.e., mountaintop).

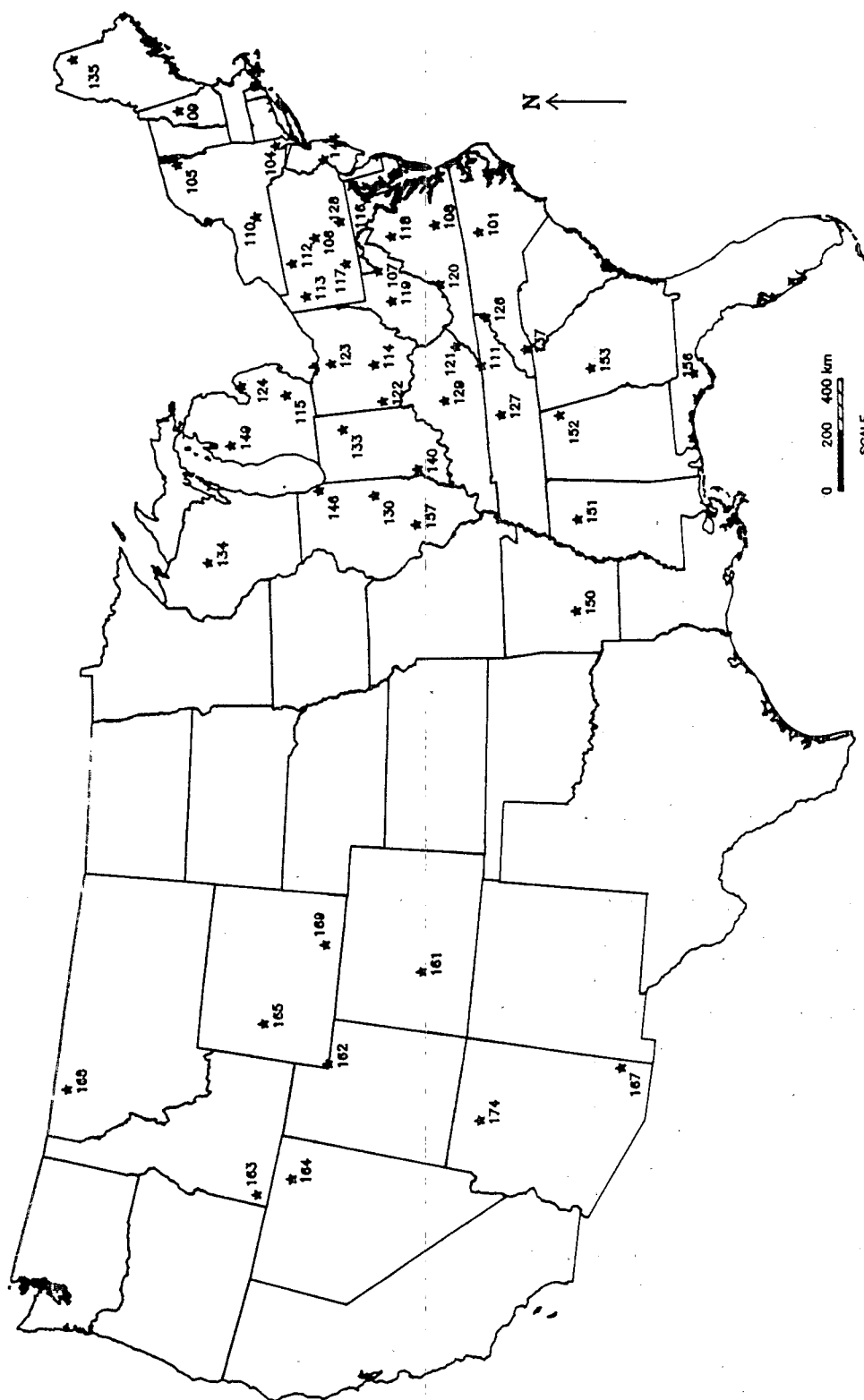


Figure 1. Status of NDDN Monitoring Sites--December 1989

TABLE 1. NDDN SITE INFORMATION

Site No.	Site Name	Initial Reporting Date	Latitude	Longitude	Elevation (m)	Land Use	Terrain
101	Research Triangle Park, NC	01/06/87	35.91	78.88	94	Forested-Urban	Rolling
102*	Oak Ridge, TN	01/06/87	35.96	84.29	341	Forested	Complex
103**	West Point, NY	01/06/87	41.35	74.05	203	Forested	Complex
104	West Point, NY	01/06/87	41.35	74.05	203	Forested	Complex
105	Whiteface Mountain, NY	01/06/87	44.39	73.86	570	Forested	Complex
106	PSU, PA	01/06/87	40.73	77.95	378	Agricultural	Rolling
107	Parsons, WV	01/14/88	39.09	79.66	505	Forested	Complex
108	Prince Edward, VA	11/01/87	37.17	78.31	146	Forested	Rolling
109	Woodstock, NH	12/31/88	43.94	71.70	258	Forested	Complex
110	Connecticut Hill, NY	09/14/87	42.40	76.65	515	Forested	Rolling
111	Speedwell, TN	07/01/89	36.47	83.83	372	Agricultural	Rolling
112	Kane Experimental Forest, PA	12/31/88	41.60	78.77	618	Forested	Rolling
113	M.K. Goddard, PA	01/08/88	41.43	80.15	384	Forested	Rolling
114	Deer Creek State Park, OH	09/30/88	39.63	83.26	265	Agricultural	Rolling
115	Ann Arbor, MI	06/30/88	42.42	83.90	267	Forested	Flat
116	Beltsville, MD	12/31/88	39.03	76.82	46	Urban-Agric.	Flat
117	Laurel Hill State Park, PA	12/10/87	40.00	79.25	616	Forested	Complex
118	Big Meadows, VA	06/30/88	38.52	78.44	1,073	Forested	Mountaintop
119	Cedar Creek State Park, WV	11/09/87	38.88	80.85	234	Forested	Complex
120	Horton Station, VA	06/03/87	37.33	80.55	972	Forested	Mountaintop
121	Lilley Cornett Woods, KY	01/19/88	37.08	82.99	335	Forested	Complex
122	Oxford, OH	08/18/87	39.53	84.72	284	Agricultural	Rolling
123	Lykens, OH	09/30/88	40.92	83.00	296	Agricultural	Flat
124	Unionville, MI	06/30/88	43.61	83.36	198	Agricultural	Flat
126	Cranberry, NC	12/31/88	36.11	82.04	1,219	Forested	Mountaintop
127	Edgar Evins State Park, TN	03/22/88	36.04	85.73	302	Forested	Rolling
128	Arendtsville, PA	06/30/88	39.92	77.30	269	Agricultural	Rolling
129	Perryville, KY	08/11/87	37.68	84.97	279	Agricultural	Rolling
130	Bondville, IL	02/09/88	40.05	88.37	212	Agricultural	Flat

TABLE 1. (continued)

Site No.	Site Name	Initial Reporting Date	Latitude	Longitude	Elevation (m)	Land Use	Terrain
133	Salamonie, IN	06/30/88	40.82	85.66	249	Agricultural	Flat
134	Perkinstown, WI	09/30/88	45.21	90.60	472	Agricultural	Rolling
135	Ashland, ME	12/31/88	46.61	68.41	235	Agricultural	Flat
137	Coweeta, NC	11/03/87	35.06	83.43	686	Forested	Complex
140	Vincennes, IN	08/05/87	38.74	87.49	134	Agricultural	Rolling
144	Washington's Crossing, NJ	12/31/88	40.30	74.87	58	Agric.-Urban	Rolling
146	Argonne National Laboratory, IL	07/01/87	41.70	87.99	229	Urban-Agric.	Flat
149	Wellston, MI	06/30/88	44.22	85.82	295	Forested	Flat
150	Caddo Valley, AR	09/30/88	34.18	93.10	71	Forested	Rolling
151	Coffeeville, MS	12/31/88	34.00	89.80	134	Forested	Rolling
152	Sand Mountain, AL	12/31/88	34.29	85.97	352	Agricultural	Rolling
153	Georgia Station, GA	06/30/88	33.18	84.41	266	Agricultural	Rolling
156	Sumatra, FL	12/31/88	30.11	84.99	14	Forested	Flat
157	Alhambra, IL	06/30/88	38.87	89.62	164	Agricultural	Flat
161	Gothic, CO	07/01/89	38.96	106.99	2,926	Range	Complex
162	Uinta, UT	07/01/89	40.55	110.32	2,377	Range	Complex
163	Reynolds Creek, ID	07/01/89	43.21	116.75	1,198	Range	Rolling
164	Saval Ranch, NV	07/01/89	41.29	115.86	1,873	Range	Rolling
165	Pinedale, WY	12/31/88	42.93	109.79	2,388	Range	Rolling
167	Chiricachua, AZ	07/01/89	32.01	109.39	1,570	Range	Complex
168	Glacier National Park, MT	12/31/88	48.51	114.00	963	Forested	Complex
169	Centennial, WY	07/01/89	41.31	106.15	2,579	Range	Complex
174	Grand Canyon, AZ	07/01/89	36.06	112.18	2,073	Forested	Complex

Note: m = meter.

*Operation terminated 12/31/88.

**Operation terminated 01/30/88.

Source: ESE, 1990.

Regional differences in terrain and land use, as reflected by the network, appear to faithfully represent actual differences between the midwest, northeast, and southeast. The midwest is largely agricultural flatland, while the northeast is largely forested. By definition, the Appalachian Mountains and foothills are almost entirely contained within the northeastern and southeastern regions. Many of the sites classified as complex are located along the eastern and western flanks of the Appalachians. As will be discussed later, these regional differences in terrain and land use appear to exert significant influences over the air quality observed across the network.

Despite apparent similarities in land use and terrain, the western sites are by no means homogeneous in character. In fact, nearly every site is located in a distinct subregion of the west. Site 161 (Gothic, CO) occupies a mountain valley within the central Rocky Mountains. Site 162 is located on the foothills of the High Uintas, the most prominent east-west mountain range in North America. Sites 163 and 164 are located in similar surroundings near the northern extreme of the Great Basin. Sites 165 and 169 represent the transition from the western Great Plains to the Rocky Mountains. Sites 167 and 174 are located in the arid southwest; however, Site 167 is in the Sonoran Desert, while Site 174 is on the extensive and forested Kaibab Plateau. Site 168 (near the Canadian border) alone represents the western boreal forest. Thus, although these sites are collectively termed the western part of the network, they represent a wide range of environments.

3.2 NETWORK OPERATIONS

This section provides an overview of the field, laboratory, and DMC operations for NDDN. Step-by-step protocols and additional details of these activities can be found in the NDDN Field Operations Manual, Laboratory Operations Manual, and Data Management Manual (ESE, 1989a, 1990a, 1990b).

Ambient measurements for O_3 , SO_2 , SO_4^{2-} , NO_3^- , HNO_3 , NH_4^+ , windspeed, wind direction, temperature, relative humidity, solar radiation, precipitation, and delta temperature were performed throughout the year at each NDDN site. In addition, atmospheric Na^+ , K^+ , Ca^{2+} , and Mg^{2+} were measured from October 1988 through September 1989, and surface wetness sensors were deployed in April 1989. Meteorological parameters and O_3 concentrations were recorded continuously and reported as hourly averages consisting of a minimum of nine valid 5-minute averages. Atmospheric sampling for particles and gases (except O_3) was integrated over weekly day and night collection periods from January through September and weekly around-the-clock collection periods from October through December, using a 3-stage filter pack (see Figure 2). In this approach, particles and selected gases are collected by passing air at a controlled flow rate through a sequence of Teflon®, nylon, and base-impregnated cellulose filters. Filter packs were prepared and shipped

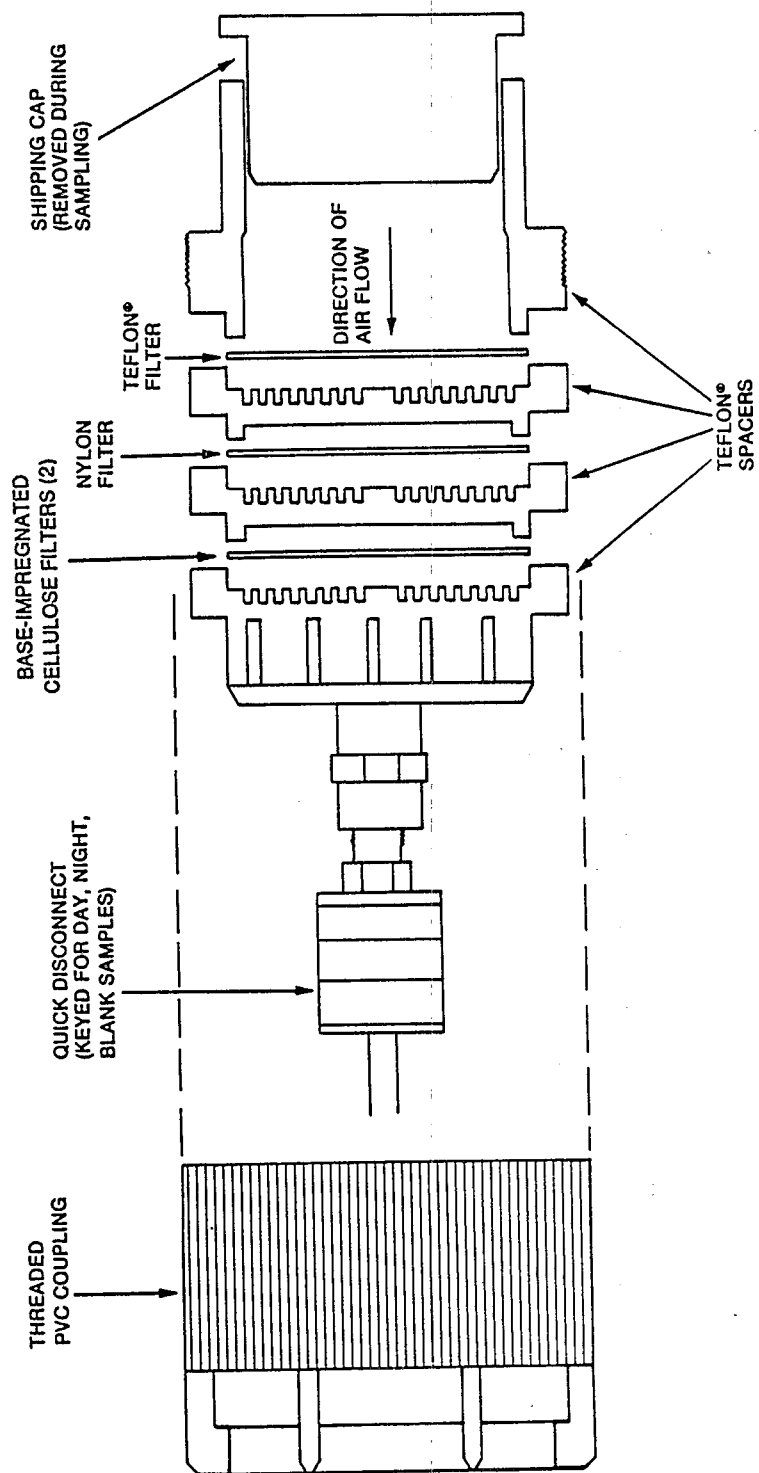


Figure 2. Filter pack assembly

to the field weekly and exchanged at each site every Tuesday. Day filter pack samples were collected over the hours of 0800 to 2000 local standard time, while night samples were collected over the remaining hours of the day. Blank filter packs were collected monthly to evaluate passive collection of particles and gases as well as contamination during shipment and handling. At 14 sites located more than 50 km from National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites, wet deposition samples were collected weekly (according to NADP/NTN protocols) and shipped to ESE for chemical analysis beginning in early 1989. Table 2 lists the equipment installed and operated at NDDN sites.

3.2.1 Field Operations

Each site was equipped with a shelter (complete with telephone and 100-amp electrical service), two 10-m towers, a meteorological system, an O₃ and air-quality monitoring system, and a DAS. One tower was used for meteorological measurements, using a Climatronics F460 system or R.M. Young AQ system. Windspeed and wind direction were measured at 10 m, temperature was measured at 9 m and 2 m, and relative humidity was measured at 9 m. Precipitation and solar radiation were measured on 1-m platforms located outside the rain and sun shadows of the shelter and towers. Surface wetness was measured at a height of approximately 3 to 6 inches above the surrounding low-lying vegetation (typically grass).

Filter pack sampling and O₃ measurements were performed at 10 m using a tilt-down aluminum tower (Aluma, Inc.). Day, night, and blank filter packs were fitted with noninterchangeable quick connects to prevent confusion and to reduce time for exchange in the field. Filter pack flow was maintained at 1.50 liters per minute (L/min) at eastern sites and 3.00 L/min at western sites [for standard conditions of 25 degrees Celsius (°C) and 760 millimeters of mercury (mmHg)] with a Teledyne-Hastings CST-10K mass flow controller (MFC) and recorded as hourly averages on the DAS. Switching from the day filter pack to the night filter pack was performed by a relay-activated solenoid controlled by the DAS.

O₃ was measured via ultraviolet (UV) absorbance with a Thermo-Environmental Model 49-103 analyzer operating on the 0- to 500-ppb range. Ambient air was drawn through an all-Teflon® sampling line upstream of the O₃ analyzer. A 3/8-inch TFE Teflon® sample line was used to sample air atop the 10-m air quality tower. Teflon® filters housed at the tower inlet and the analyzer inlet prevented particle deposition within the system. Periodic checks indicated that line losses through the inlet system were consistently less than 3 percent. Zero, precision (60 ppb), and span (400 ppb) checks of the O₃ analyzer were performed every third day using an internal O₃ generator.

TABLE 2. NDDN MONITORING EQUIPMENT

Item	Manufacturer	Model Number
Equipment Shelter [8 feet (ft) by 8 ft by 10 ft with electricity and telephone]	EKTO	8810
Ozone (O ₃) Analyzer	Thermo-Environmental	49-103
<u>Meteorological System</u>		
Windspeed	Climatronics	F460
Wind Direction	or	
Temperature	R.M. Young	AQ Series
Delta Temperature		
Relative Humidity		
Solar Radiation		
Precipitation (tipping bucket)		
Surface Wetness Sensor	Vaisala	DRD-11
10-Meter (m) Tower	Universal Mfg.	4-30
<u>Data Acquisition System (DAS)</u>		
Primary DAS	Odessa	DSM-3260
Backup DAS	Odessa	DSM-3260L
Personal Computer (PC)	Various	Various
Telecommunications Modem	Packard-Bell	2424
Printer	Star	SD-10
<u>Air Quality Monitoring System</u>		
10-m Tower	Aluma Tower	AT-048
Filter Pack	Saville	0-473-4N
Pump	Thomas	101-CA11
Flow Controller	Teledyne-Hastings	CST-10K
<u>Wet Deposition Equipment (selected sites)</u>		
Precipitation Collector	Andersen	APS
Rain Gauge (weighing)	Belfort	5915R-12
Triple-Beam Balance	Ohaus	1119-D

Source: ESE, 1990.

The onsite DAS consisted of a primary datalogger (Odessa 3260), a backup datalogger (Odessa 3260L), an IBM-compatible personal computer (PC), a printer, and a telephone modem. The primary datalogger was used to acquire, average, store, and communicate readings from all continuous sensors. It also performed a variety of control functions, such as switching the day/night filter pack relay and activating the internal O_3 generator for consistency checks. Data were stored on the primary and backup dataloggers in electronically erasable programmable read-only memory (EEPROM) cartridges, both of which were accessible through the onsite PC, or remotely, through the telephone modem. Printouts of hourly averages for the previous day were automatically generated by the onsite printer a few seconds after midnight each day.

Site operators visited each site on Tuesdays and Fridays and in response to equipment malfunctions or suspected problems. On Tuesdays, filter packs were exchanged, sample lines were leak tested, sensors were subjected to electronic and reasonableness checks, and data from the dataloggers were downloaded to diskettes. The site operator telephoned the NDDN operations center at ESE following site inspections to relay observations and problems. Data, documentation, and samples were shipped to ESE the day of collection. On Fridays, the site operator performed a limited inspection of sensors and equipment.

All field equipment was subjected to inspections and multipoint calibrations [using standards traceable to the National Institute of Standards and Technology (NIST)] by ESE personnel on a quarterly basis. In addition, independent equipment audits were performed semiannually by ERC Environmental and Energy Services, Inc., and randomly by EPA or its designee. Results of field calibrations were used to assess sensor accuracy and flag, adjust, or invalidate field data.

The overall precision of field measurements was evaluated by operation of collocated sets of equipment at four sites located in the northeast (Site 107), southeast (Site 153), midwest (Site 157), and southwest (Site 167). The purpose of this spatial distribution was to capture precision data across a broad range of meteorological conditions and ambient concentrations. Precision and accuracy criteria for NDDN field measurements are shown in Table 3.

3.2.2 Laboratory Operations

Filter pack samples were loaded, shipped, received, extracted, and analyzed by ESE personnel at the Gainesville, Florida laboratory. Filter packs contained three types of filters in sequence: a Teflon® filter [Gelman, Zefluor, 1.0 micrometer (μm) pore size] for collection of aerosols, a nylon filter (Gelman, 1.0 μm) for collection of HNO_3 , and dual potassium carbonate (K_2CO_3) impregnated cellulose filters (Whatman 41) for collection of SO_2 . In practice, exposed nylon filter extracts virtually always contained detectable amounts of SO_4^{2-} , which

TABLE 3. PRECISION AND ACCURACY OBJECTIVES OF FIELD MEASUREMENTS

Measurement	Reporting Units	Method	Acceptance Criteria*	
			Precision	Accuracy
Windspeed and wind velocity	m/sec	Anemometer	± 0.5 m/sec	± 0.2 m/sec
Wind direction	°	Wind vane	$\pm 5^\circ$	$\pm 2^\circ$
Standard deviation of wind direction	°	Wind vane	Undefined	Undefined
Relative humidity	%	Humidity sensor	$\pm 10\%$ (of full scale)	$\pm 10\%$
Solar radiation	W/m ²	Pyranometer	$\pm 10\%$ (of reading)	$\pm 10\%$
Precipitation	mm/hr	Rain gauge	$\pm 10\%$ (of reading)	0.10 inch [†]
Ambient temperature	°C	Thermistor	$\pm 0.5^\circ\text{C}$	$\pm 0.25^\circ\text{C}$
Delta temperature	°C	Thermistor	$\pm 0.2^\circ\text{C}$	$\pm 0.1^\circ\text{C}$
O ₃	ppb	UV absorbance	$\pm 10\%$ (of reading)	$\pm 10\%$

TABLE 3. (continued)

Measurement	Reporting Units	Method	Acceptance Criteria*	
			Precision	Accuracy
Filter pack flow	L/min	Mass flow meter	± 0.15 L/min	$\pm 10\%$
Surface wetness	hours	Wheatstone bridge	$\pm 10\%$ (of reading)	Undefined

Note:

° = degree.

°C = degrees Celsius.

L/min = liters per minute.

mm/hr = millimeters per hour.

m/sec = meters per second.

ppb = parts per billion, by volume.

% = percent.

UV = ultraviolet.

W/m² = watts per square meter.

*Field precision criteria apply to collocated instruments; accuracy criteria apply to calibrations and audits of instruments.

+For target value of 1.00 inch.

Source: ESE, 1990.

was interpreted to represent a fraction of the atmospheric SO_2 . Thus, for the purpose of this report, SO_4^{2-} data from the nylon and cellulose filters were added prior to calculation of SO_2 concentrations. Recoveries of SO_4^{2-} in nylon and cellulose extracts are reported separately to EPA to accommodate differing interpretations of SO_2 partitioning in the filter pack. All filters were subjected to acceptance tests before they were used in the network. Filters showing detectable levels of SO_4^{2-} or NO_3^- [i.e., greater than or equal to 1.0 microgram (μg) SO_4^{2-} or 0.88 μg NO_3^-] were either washed and retested or returned to the manufacturer for credit.

Following receipt from the field, exposed filters and blanks were placed in color-coded bottles and extracted in 25 milliliters (mL) of deionized water (Teflon[®]), 25 mL of 0.003 N NaOH (nylon), or 50 mL of 0.05-percent H_2O_2 (cellulose). Filters and extraction solutions were shaken for 15 minutes, sonicated for 30 minutes, and shaken again for 15 minutes to ensure complete dissolution of particles and gas reaction products. Multiple extractions of Teflon[®], nylon, and cellulose filters have repeatedly shown that greater than 95 percent of the available SO_4^{2-} and NO_3^- is recovered in the first extract. Extracts were then analyzed for SO_4^{2-} and NO_3^- by micromembrane suppressed ion chromatography (IC) using a Dionex Model 4000i IC equipped with an Autoion 1000 Controller. The instrumental configuration included a Dionex Automated Sampler, an AG4-A guard column, a AS4-A separator column, and a 25- or 50-microliter (μL) injection loop. Data acquisition, display, and analysis were accomplished with a Maxima computer integration system. The IC was calibrated prior to each analytical run with five standards plus a blank covering the typical range of sample concentrations: 35 to 9,000 micrograms per liter ($\mu\text{g}/\text{L}$) for NO_3^- and 40 to 10,000 $\mu\text{g}/\text{L}$ for SO_4^{2-} . Extraction and calibration solutions were made up with 1,000 $\mu\text{g}/\text{L}$ bromide ion (Br^-) as a check on IC column condition and to assist in detection of spurious sample injections. All IC analyses were completed within 72 hours of filter extraction.

Beginning in the third quarter of 1988 and continuing through the third quarter of 1989, Teflon[®] filter extracts were analyzed routinely for water-soluble NH_4^+ , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} . Analysis of Na^+ , Mg^{2+} , and Ca^{2+} was performed with a Perkin-Elmer P-2 inductively coupled argon plasma (ICAP) emission spectrometer. Analysis of NH_4^+ was by the automated indophenol method using a Technicon II or TRAACS-800 AutoAnalyzer system. Analysis of K^+ was via atomic emission on a Perkin-Elmer 5100 atomic absorption spectrophotometer.

Various QC samples were routinely analyzed to track the accuracy and precision of laboratory data. NIST SRM No. 2694-II (simulated rainwater) was analyzed immediately after instrument calibration and at the end of each run to monitor accuracy. Recoveries within ± 5 percent of certified values were required for analyses to continue. A midrange calibration verification standard (CVS) was analyzed after every 10 environmental samples to monitor within-run precision. For the

analytical batch to be accepted, the maximum difference between the first analysis and each subsequent analysis was limited to ± 5 percent for anions and ± 10 percent for cations. Blind replicates (10 percent of samples) were also analyzed to monitor between-run precision. Due to the potential for change in analyte concentration between analyses, replicate samples were not used as a control for acceptance of batches. Instead, replicate analyses were used to assess the stability of ions in filter extracts. Finally, one unknown sample provided by EPA was analyzed with each batch. The unknown consisted of filter media spiked with salt solutions containing SO_4^{2-} and NO_3^- . These were carried through the entire extraction and analysis procedure established for Teflon®, nylon, and cellulose filters. Precision and accuracy objectives for NDDN laboratory analyses are listed in Table 4.

Results of all valid analyses were stored in units of micrograms per filter ($\mu\text{g}/\text{filter}$) in the laboratory data management system. Concentrations of all species were then calculated (based on volume of air sampled) following validation of hourly flow data. Atmospheric concentrations of particulate SO_4^{2-} , NO_3^- , NH_4^+ , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} were calculated based on the analysis of Teflon® filter extracts; HNO_3 was calculated based on the NO_3^- found in nylon filter extracts; and SO_2 was calculated based on the sum of SO_4^{2-} found in nylon and cellulose filter extracts. Since Teflon® filters were extracted in deionized water, it should be noted that reported concentrations of particulate species refer to the water soluble component only.

3.2.3 Data Management

DMC activities consisted of three major operations: data acquisition, validation, and transmittal to EPA. The data acquisition process stressed multiple levels of redundancy to minimize data loss. The primary mode of data acquisition from the field was via telephone modem. Each site was automatically polled between 2:00 a.m. and 4:00 a.m. every day using a PC and software developed by Odessa Engineering, Inc. The polling software permits recovery of hourly data and status files, power failure logs, and automated calibration results from the previous 7 days. The program also maintains synchronization of the network by checking the clock within each DAS and correcting the time if it deviates from expectation by more than 2 minutes. If daily polling resulted in incomplete data capture from any site, then diskettes of data from the primary and backup DAS were read into the database management system. If the database was still incomplete, then missing data were entered manually from site printouts. Each datum was automatically given a source flag that could be used to trace its mode of entry into the system (i.e., modem, primary DAS, backup DAS, or printout).

Data validation consisted of a thorough review of operator logs, onsite reasonableness checks, results of field calibrations and audits,

TABLE 4. PRECISION AND ACCURACY OBJECTIVES FOR NDDN LABORATORY MEASUREMENTS

Analyte	Sample type	Method	Acceptance Criteria	
			Precision* (percent)	Accuracy+ (percent)
NH_4^+	Filter Extract	Technicon AutoAnalyzer	10	90 to 110
Ca^{2+}	Filter Extract	ICP-ES	10	90 to 110
Mg^{2+}	Filter Extract	ICP-ES	10	90 to 110
Na^+	Filter Extract	ICP-ES	10	90 to 110
K^+	Filter Extract	Atomic emission	10	90 to 110
SO_4^{2-}	Filter Extract	IC	5	95 to 105
NO_3^-	Filter Extract	IC	5	95 to 105

Note: Ca^{2+} = particulate calcium.
 K^+ = particulate potassium.
 Mg^{2+} = particulate magnesium.
 Na^+ = particulate sodium.
 NH_4^+ = particulate ammonium.
 NO_3^- = particulate nitrate.
 SO_4^{2-} = particulate sulfate.
IC = ion chromatography.
ICP-ES = inductively coupled plasma emission spectroscopy.

*Determined from midlevel standard and initial calibration curve.

+Determined from NIST SRM 2694-II.

Source: ESE, 1990.

and a variety of parameter-specific range and consistency checks. In addition, diurnal patterns for numerous parameters and a variety of interparameter relationships were examined for reasonableness. Solar radiation data, for example, were used to check for time shift errors in the database (caused by power failure), while rainfall data verified the response of relative humidity sensors (should approach 100 percent), delta temperature sensors (should approach zero), and wetness sensors (should indicate presence of surface wetness).

Following validation of data for a calendar quarter, flag counts, and parameter averages were calculated. The database, flag counts, and averages were then loaded onto a 9-track tape and submitted to the NDDN Project Officer. To verify the data transfer, flag counts and parameter averages were independently generated by EPA and repeated to ESE. Data sets were subjected to a variety of reasonableness and consistency checks by EPA before final acceptance into the EPA data archive.

SECTION 4.0

RESULTS AND DISCUSSION

4.1 OVERALL DATA QUALITY

As described in Section 3.0, extensive QC measures were undertaken to assure and document the overall quality of the NDDN database. This section summarizes NDDN QC data for 1989. Additional details on field and laboratory QC checks can be found in quarterly data reports (ESE, 1989b, 1989c, 1989d, 1990c).

4.1.1 Field Data

Results of meteorological equipment calibrations performed during 1988 are summarized by quarter in Table 5. In general, calibration data show the majority of sensors were operating within accuracy requirements for the network. Temperature and delta temperature sensors typically responded within a few tenths and a few hundredths of a degree Celsius of NIST-traceable standards. Relative humidity, solar radiation, and rainfall amount responded within a few percent of calibration standards. Windspeed and wind direction were generally within ± 0.2 meter per second (m/sec) and ± 2 degrees of target values. Inspection of quarter-to-quarter variability for calibration data shows that all sensors, except relative humidity, responded consistently throughout the year. Data quality for relative humidity improved markedly from first quarter through fourth quarter due to adoption of a new sensor (Rotronics MP100-MF) and the use of calibration salts in the field for adjustment of sensors.

Calibration data for continuous O_3 analyzers and MFC are presented in Table 6. O_3 and MFC calibrations were performed through the entire ambient air inlet to compensate for small line losses (less than or equal to 3 percent) and pressure drops within the system, respectively. In general, results for O_3 show that the instrument employed is highly stable and that it functioned with acceptable accuracy during the year. Aggregate errors for the network were within ± 2 percent during each quarter, as represented by sensor versus transfer standard slopes, and errors for individual analyzers were invariably better than ± 8 percent. Although occasional equipment failures occurred, no O_3 data were invalidated for lack of compliance with accuracy requirements.

MFCs also showed excellent stability, the errors tabulated in Table 6 indicate little instrumental drift between calibrations (i.e., from quarter to quarter). Thus, the overall impact of uncertainties in flow on concentration calculations is expected to be minimal.

TABLE 5. SUMMARY OF METEOROLOGICAL SENSOR UNADJUSTED CALIBRATIONS DURING 1989

Quarter	Parameter error (site sensor minus transfer standard)					
	Temperature (°C)	Delta temperature (°C)	Relative humidity (%)	Solar radiation (W/m ²)	Windspeed (m/sec)	Wind direction (°)
First						
Mean	0.08	-0.01	-1.6	1.4	0.02	0.2
Standard Deviation	±0.07	±0.04	±4.3	±6.9	±0.07	±0.8
Second						
Mean	-0.02	0.02	1.0	1.0	-0.01	0.4
Standard Deviation	±0.04	±0.02	±3.2	±3.2	±0.04	±2.2
Third						
Mean	0.03	0.01	0.9	0.7	-0.03	0.1
Standard Deviation	±0.10	±0.03	±4.1	±4.1	±0.09	±1.4
Fourth						
Mean	0.05	0.03	1.0	3.3	-0.02	-0.2
Standard Deviation	±0.06	±0.04	±3.6	±5.1	±0.14	±1.3

Source: ESE, 1990.

TABLE 6. SUMMARY OF 1989 O₃ AND MASS FLOW
CONTROLLER UNADJUSTED CALIBRATIONS

Quarter	O ₃		Filter pack flow (% error)*
	Slope	Intercept (ppb)	
First			
Mean	0.997	0.35	-1.5
Standard Deviation	±0.012	±1.01	±2.6
Second			
Mean	0.999	0.28	1.0
Standard Deviation	±0.009	±0.72	±3.4
Third			
Mean	1.001	0.17	-1.3
Standard Deviation	±0.014	±1.15	±4.0
Fourth			
Mean	0.996	0.08	2.2
Standard Deviation	±0.024	±1.33	±5.1

Note: Slope and intercept are regression coefficients for calibration versus a NIST-traceable O₃ transfer standard.

*Error is calculated relative to target flows of 1.50 liters per minute (L/min) for eastern sites and 3.00 L/min for western sites.

Source: ESE, 1990.

4.1.2 Laboratory Data

Laboratory accuracy and precision data from 1989 are summarized in Table 7. As described previously, an NIST reference (2694-II) is analyzed once per analytical batch, a calibration verification standard (CVS) is analyzed after every tenth environmental sample, and 10-percent blind replicates are analyzed on separate run dates. Replicate analyses for Teflon® filters were discontinued from third quarter 1988 through third quarter 1989 due to insufficient volumes after cation analyses. Replicate analyses were restarted during the fourth quarter of 1989 following removal of Ca^{2+} , Mg^{2+} , Na^+ , and K^+ from the analytical scheme.

Results for the NIST reference material and the CVS samples show that for each filter type and for each quarter instrumental error and drift was on the average less than or equal to 2.5 percent. During every quarter, all mean values were within 2.5 percent of 100 percent, while all standard deviations were less than 1.7 percent. Figure 3 depicts NIST reference sample recoveries of SO_4^{2-} and NO_3^- for all Teflon® filter batches analyzed in 1989.

Results of replicate analyses show that, on average, the between-run differences for all analytes is less than 5 percent. However, there is considerable scatter in results, as reflected in the standard deviations for each analyte. This scatter is due to a small number of outliers associated with analytical values near the detection limit.

Less than 2 percent of the replicate samples analyzed in 1989 exhibited mean percent differences greater than 20 percent (see Figure 4). For SO_4^{2-} on cellulose filters, 388 samples were replicated, and only 8 samples showed greater than ± 20 percent difference. For NO_3^- on nylon filters, 362 samples were replicated, and only 8 samples showed greater than a ± 20 percent difference. In general, mass recoveries from replicate analyses differed by $1.0 \mu\text{g}/\text{filter}$ or less for each analyte. Given a typical sample volume of 7.5 cubic meters (m^3), this translates into a mean laboratory precision of approximately $0.15 \mu\text{g}/\text{m}^3$ for SO_4^{2-} , NO_3^- , and HNO_3 and $0.2 \mu\text{g}/\text{m}^3$ for SO_2 .

Laboratory accuracy and precision should not be confused with overall sampling accuracy and precision. The accuracy of the NDDN filter pack sampling approach is unknown, and its precision should be determined based on collocated field sampling, rather than laboratory replicates. Nevertheless, the results in Table 7 show that laboratory operations conform with accuracy and precision requirements for this project.

TABLE 7. SUMMARY OF LABORATORY ACCURACY AND PRECISION DURING 1989*

Quarter	QC check	Filter type/analyte					
		Teflon®		Nylon		Cellulose	
		SO ₄ ²⁻	NO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻
First	NIST Recovery ⁺	101.9±1.0	99.8±1.2	101.1±1.0	100.6±0.7	100.6±1.4	100.9±1.3
	CVS Recovery**	98.9±1.2	99.4±0.9	98.9±1.5	100.1±0.8	99.9±1.7	101.1±1.2
	Replicates ⁺⁺	NP	NP	1.3±13.3	1.0±19.5	1.7±11.7	0.3±7.8
Second	NIST Recovery ⁺	101.5±1.1	99.2±1.0	101.1±0.6	100.8±1.5	100.7±1.2	100.5±1.0
	CVS Recovery**	99.8±0.8	99.5±0.9	98.4±1.3	98.9±1.3	100.4±1.1	100.7±1.5
	Replicates ⁺⁺	NP	NP	5.0±14.6	3.9±11.7	3.4±4.9	7.7±7.6
Third	NIST Recovery ⁺	101.4±1.1	99.7±1.0	102.0±1.4	100.6±1.0	100.9±0.9	100.9±0.9
	CVS Recovery**	99.8±0.7	100.2±0.9	97.6±1.7	98.3±1.0	100.9±1.1	100.5±1.6
	Replicates ⁺⁺	NP	NP	3.6±5.6	3.0±10.6	4.2±7.0	6.2±5.8
Fourth	NIST Recovery***	101.4±1.3	100.0±1.9	100.3±2.7	100.0±1.6	101.3±1.9	101.2±2.2
	CVS Recovery**	99.7±1.0	100.1±0.9	97.8±1.8	98.4±1.1	100.4±1.1	100.2±1.4
	Replicates ⁺⁺	1.0±0.9	3.4±3.1	2.1±2.1	2.6±11.0	2.3±4.3	5.8±7.7

Note: CVS = calibration verification standard.

NP = not performed.

QC = quality check.

*Errors are ±1 standard deviation.

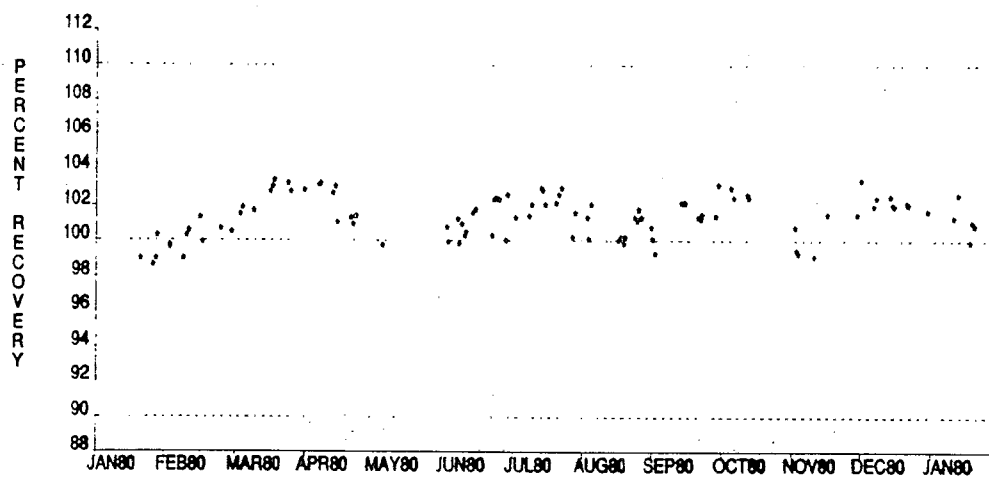
**Mean percent recovery of NIST SRM 2694-II.

***Mean percent recovery of an independent CVS analyzed after every tenth sample.

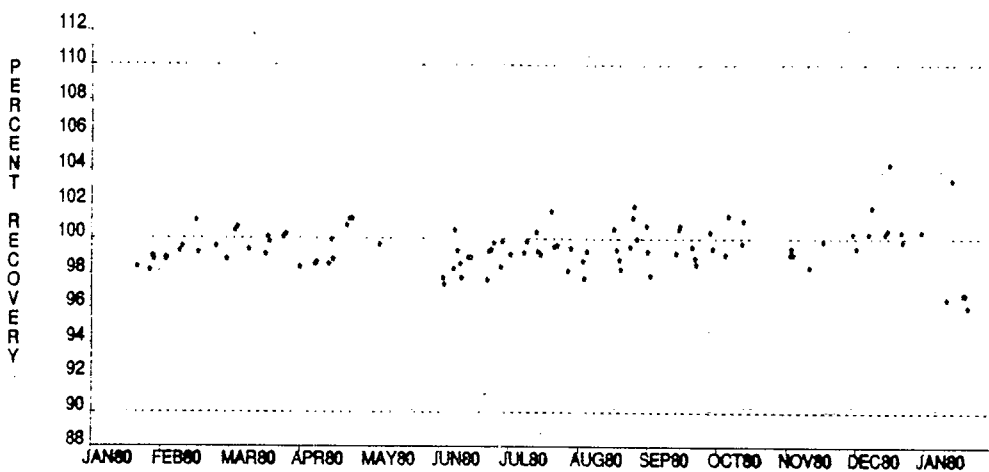
****Mean percent difference for duplicate sample analyses performed on different dates.

*****Mean percent recovery of NIST SRM 2694-II and Canadian Performance samples.

Source: ESE, 1990.



A



B

Figure 3. Recovery of SO_4^{2-} (A) and NO_3^- (B) in NIST Reference Sample 2694-II

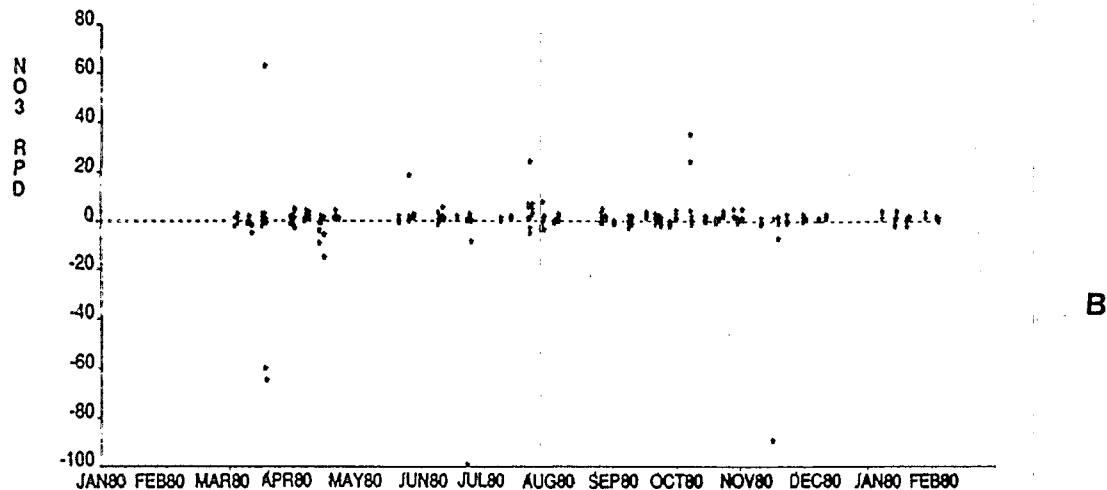
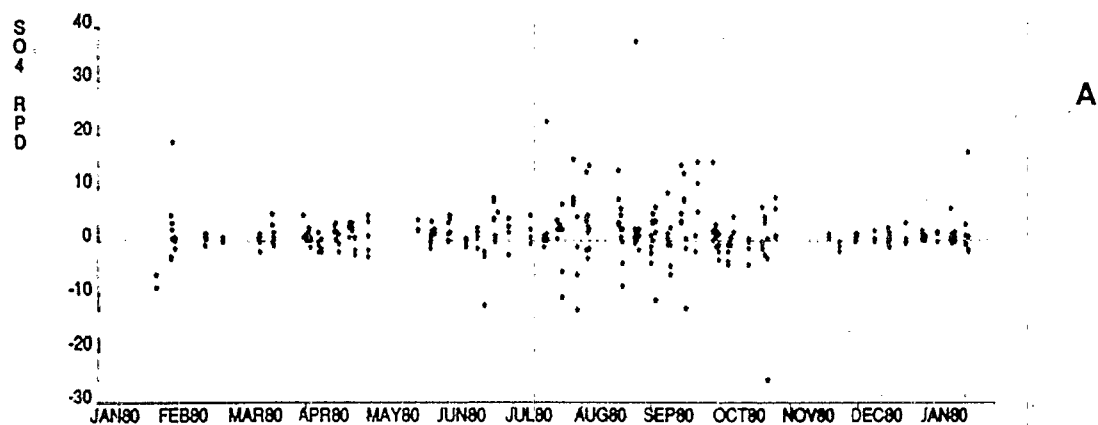


Figure 4. Relative percent difference from replicate analysis of SO_4^{2-} in cellulose filter extracts (A) and NO_3^- in nylon filter extracts (B)

4.1.3 Collocated Filter Pack Sampling

Results of collocated filter pack sampling during 1989 are shown in Table 8 and Figures 5 through 13. In general, data from the three eastern United States sites show that annual average SO_4^{2-} , SO_2 , NH_4^+ , Na^+ , and Ca^{2+} differ by less than 5 percent between collocated samplers. Annual average NO_3^- , HNO_3 , and Mg^{2+} differ by approximately 10 percent; in the case of Site 153, K^+ differs by as much as 12 percent. Inspection of median absolute differences (MADs) suggests that typical differences between paired samples are $0.2 \mu\text{g}/\text{m}^3$ (or less) for SO_4^{2-} , NO_3^- , HNO_3 , and NH_4^+ , and $0.4 \mu\text{g}/\text{m}^3$ (or less) for SO_2 .

Interestingly, the single western collocated site shows uniformly better precision than the three eastern sites. For example, MAD values for SO_4^{2-} , NO_3^- , HNO_3 , and NH_4^+ are all well below $0.05 \mu\text{g}/\text{m}^3$ and that for SO_2 is less than $0.1 \mu\text{g}/\text{m}^3$. Differences between annual means are considerably below 5 percent for all species except Ca^{2+} (6.0 percent) and K^+ (6.3 percent). This finding is somewhat surprising, given that observed concentrations at the western site are much lower than at the eastern sites.

Intuitively, one might expect that the lower the concentration the poorer the precision (on a relative basis); however, the 1989 results do not uniformly support this expectation. This is illustrated in Figures 14 through 18, which show the relationship between mean absolute percent difference (MAPD) (or MAD) and concentrations for SO_4^{2-} , NO_3^- , NH_4^+ , SO_2 , and HNO_3 . For the eastern sites, only NO_3^- and perhaps SO_4^{2-} show a clear tendency for decreasing precision with decreasing concentration. For the western collocated site, no such tendency is observed, and the overall precision (absolute or relative) is superior to the eastern sites, despite lower overall concentrations.

Two potential explanations for those differences in precision between eastern and western sites involve operating conditions and environmental conditions. The first refers to the fact that eastern sites sample air at a flow rate of 1.5 L/min, while western sites sample at 3.0 L/min. Thus, for the same concentration, the mass loading on western filter pack samples should be twice that on eastern filter packs. Atmospheric concentrations at the western collocated site are generally much less than half those at the eastern sites (at least for these major species), and, therefore, one would not expect significant overlap in mass loading. Another explanation involving flow rate could simply be that the MFCs in operation maintain flow more precisely at 3.0 L/min than at 1.5 L/min. Results of quarterly calibrations suggest that MFC drift might be slightly lower for western sites than eastern sites, but that this is unlikely, by itself, to completely explain precision differences.

TABLE 8. RESULTS OF 1989 COLLOCATED FILTER PACK SAMPLING

Statistic	SO ₄ ²⁻	NO ₃	HNO ₃	SO ₂	NH ₄ ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
<u>Parsons, WV (Site 107)</u>									
X (μg/m ³)	7.76	0.63	2.19	12.6	1.88	0.507	0.065	0.092	0.257
Y (μg/m ³)	7.78	0.59	2.00	12.4	1.88	0.490	0.060	0.095	0.234
SD	-0.3	6.6	9.1	1.6	0.3	3.4	8.0	-3.2	9.2
MAPD	1.9	14.3	8.1	4.0	2.3	5.6	7.9	6.6	24.8
MAD (μg/m ³)	0.12	0.06	0.17	0.4	0.04	0.031	0.005	0.005	0.049
n	40	40	42	42	40	27	27	27	27
<u>Georgia Station, GA (Site 153)</u>									
X (μg/m ³)	6.15	0.45	2.11	8.65	1.89	0.128	0.056	0.216	0.177
Y (μg/m ³)	6.04	0.41	2.14	8.60	1.79	0.122	0.054	0.209	0.200
SD	1.8	9.3	-2.7	0.6	5.4	4.8	3.6	3.3	12.2
MAPD	3.5	9.9	6.9	3.8	6.9	8.6	5.4	8.9	27.1
MAD (μg/m ³)	0.22	0.05	0.11	0.29	0.12	0.010	0.004	0.020	0.062
n	28	28	30	30	28	16	16	15	13
<u>Alhambra, IL (Site 157)</u>									
X (μg/m ³)	7.36	2.80	2.49	13.8	3.00	0.719	0.105	0.110	0.268
Y (μg/m ³)	7.28	2.73	2.39	13.3	2.92	0.705	0.106	0.106	0.283
SD	1.1	2.5	4.1	3.7	2.7	2.0	1.0	3.7	-5.4
MAPD	1.1	5.0	7.2	2.6	2.1	11.0	11.0	9.0	33.7
MAD (μg/m ³)	0.11	0.13	0.11	0.4	0.05	0.070	0.011	0.010	0.081
n	40	40	42	42	40	28	28	26	26

TABLE 8. (continued)

Statistic	SO ₄ ²⁻	NO ₃ ⁻	HNO ₃	SO ₂	NH ₄ ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
Chiricahua, AZ (Site 167)									
\bar{X} ($\mu\text{g}/\text{m}^3$)	1.71	0.38	0.93	1.84	0.59	0.293	0.051	0.160	0.107
\bar{Y} ($\mu\text{g}/\text{m}^3$)	1.71	0.39	0.92	1.86	0.59	0.311	0.053	0.158	0.114
%D	0.4	-2.6	1.1	-1.1	-0.3	-6.0	-3.8	1.3	-6.3
MAPD	1.4	7.7	2.5	3.8	1.6	3.3	7.7	8.0	12.6
MAD ($\mu\text{g}/\text{m}^3$)	0.02	0.03	0.03	0.06	0.01	0.008	0.003	0.010	0.014
n	29	29	29	29	29	18	18	18	18

Note:

%D = percent difference of means = $200 \times (\bar{X} - \bar{Y}) / (\bar{X} + \bar{Y})$.MAD = median absolute difference between paired weekly samples = median $(|X| - |Y|)$.MAPD = median absolute percent difference between paired weekly samples = median $\frac{200 |X - Y|}{(X + Y)}$.

n = number of valid weekly samples above detection limit for both samplers.

 \bar{X} and \bar{Y} = mean concentration for primary and secondary samplers, respectively.

Source: ESE, 1990.

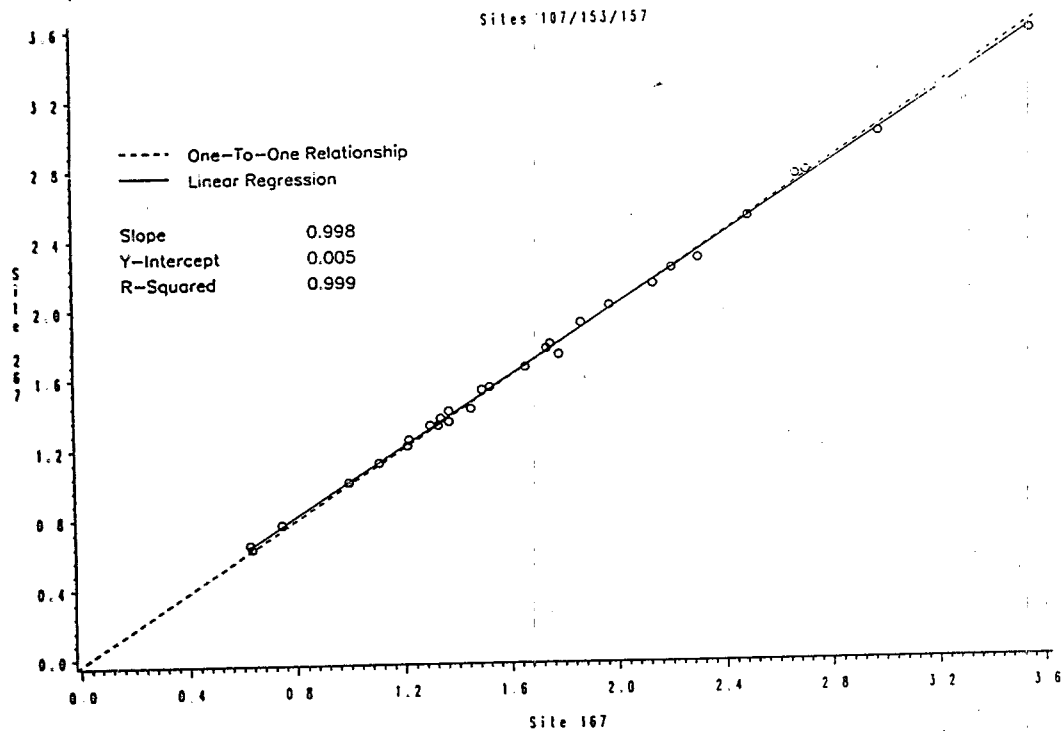
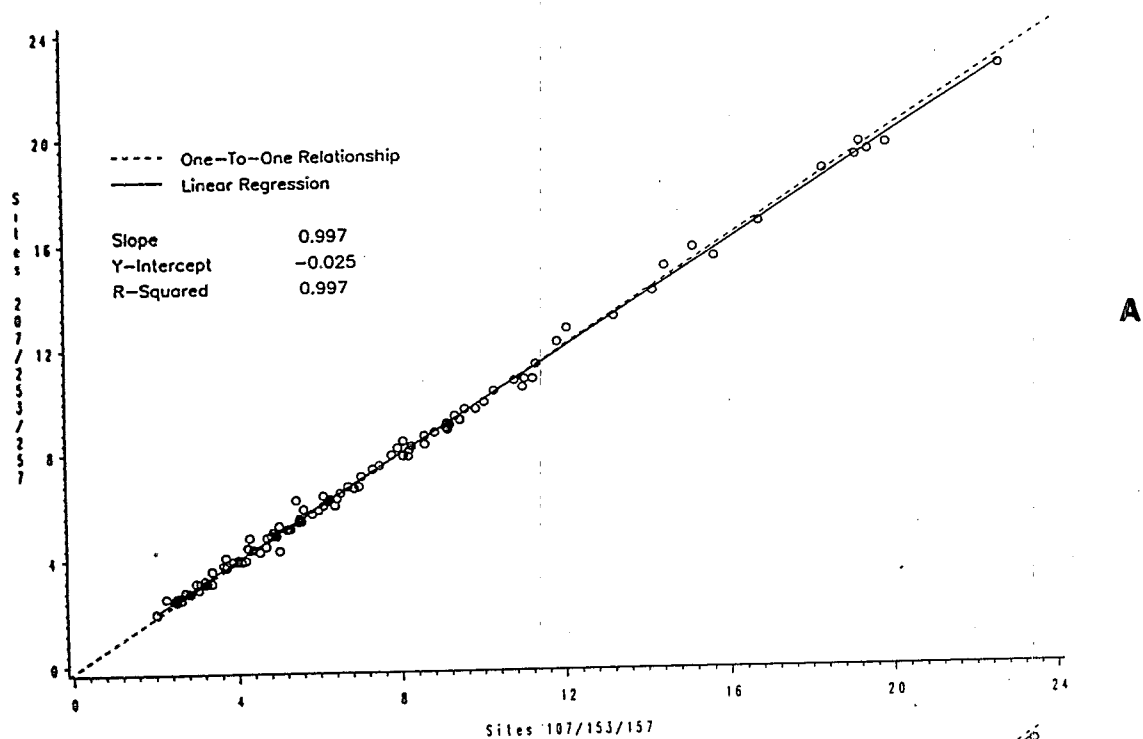


Figure 5. Scattergrams of 1989 collocated SO₄²⁻ ($\mu\text{g}/\text{m}^3$) for three eastern sites (A) and one western site (B)

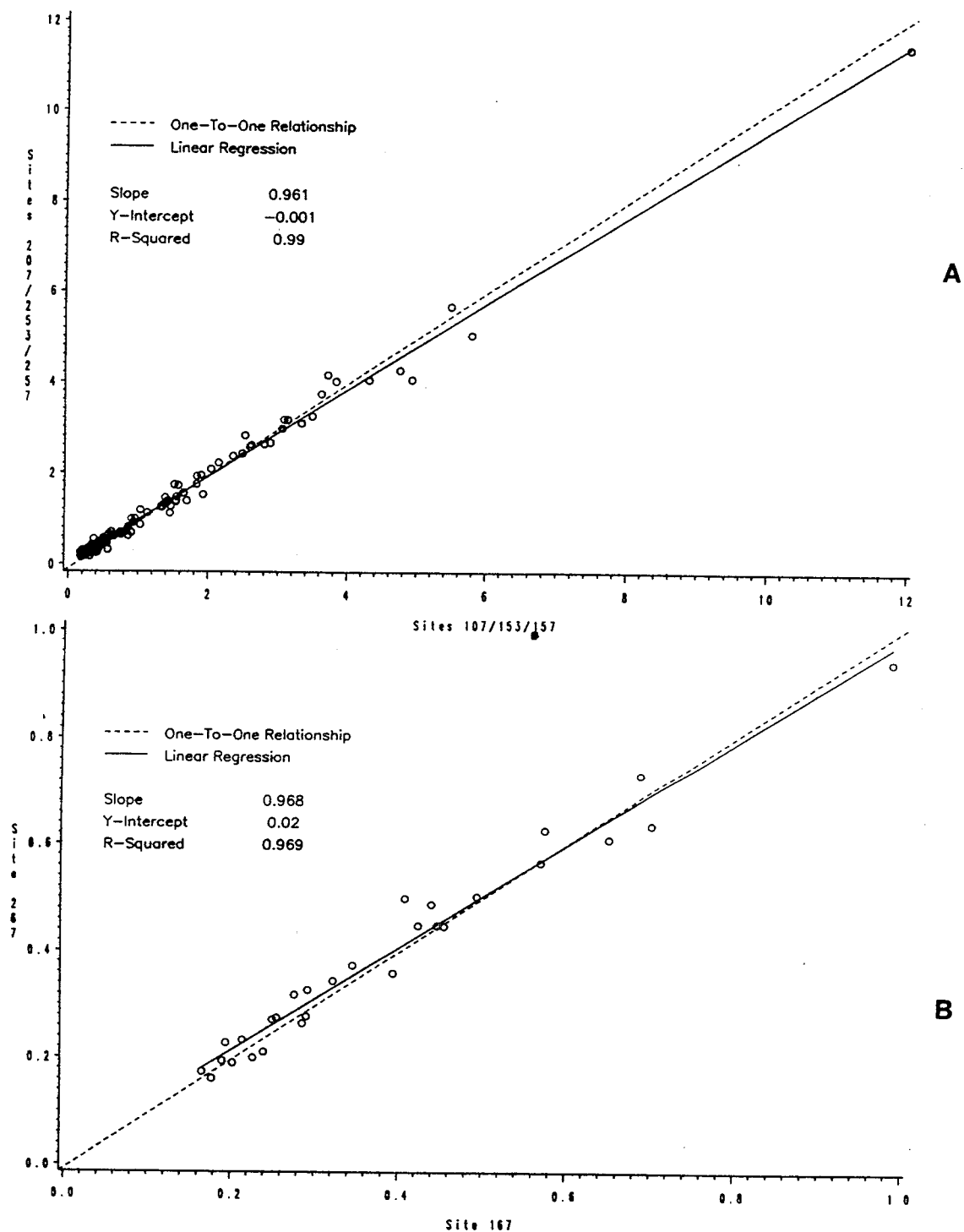
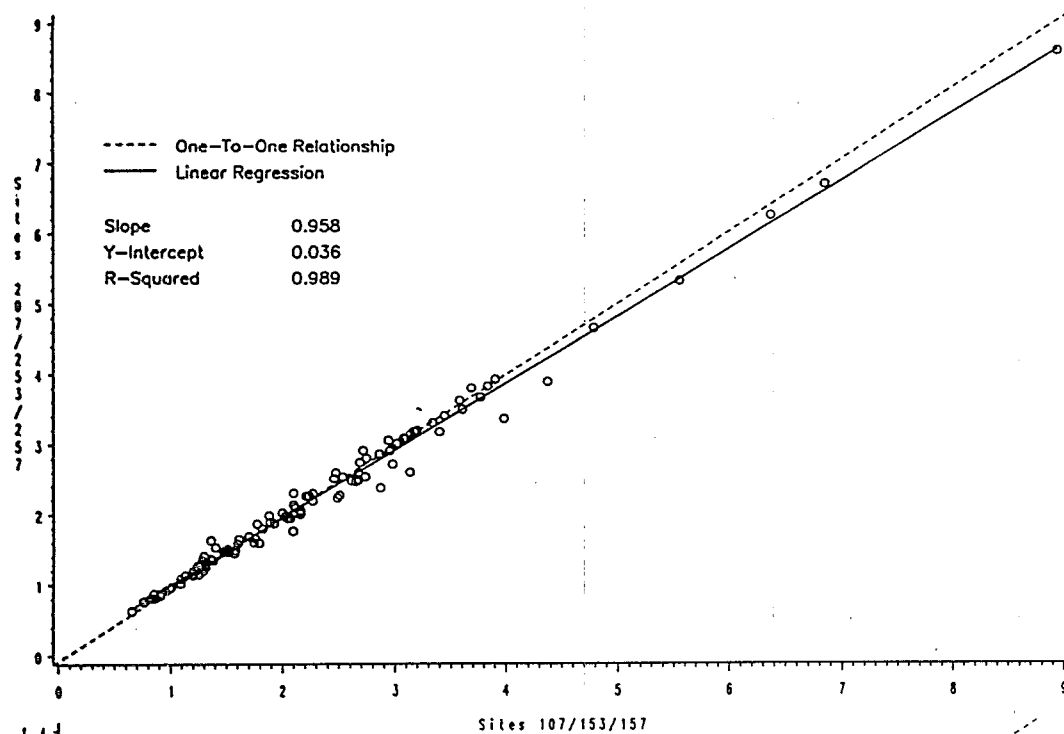
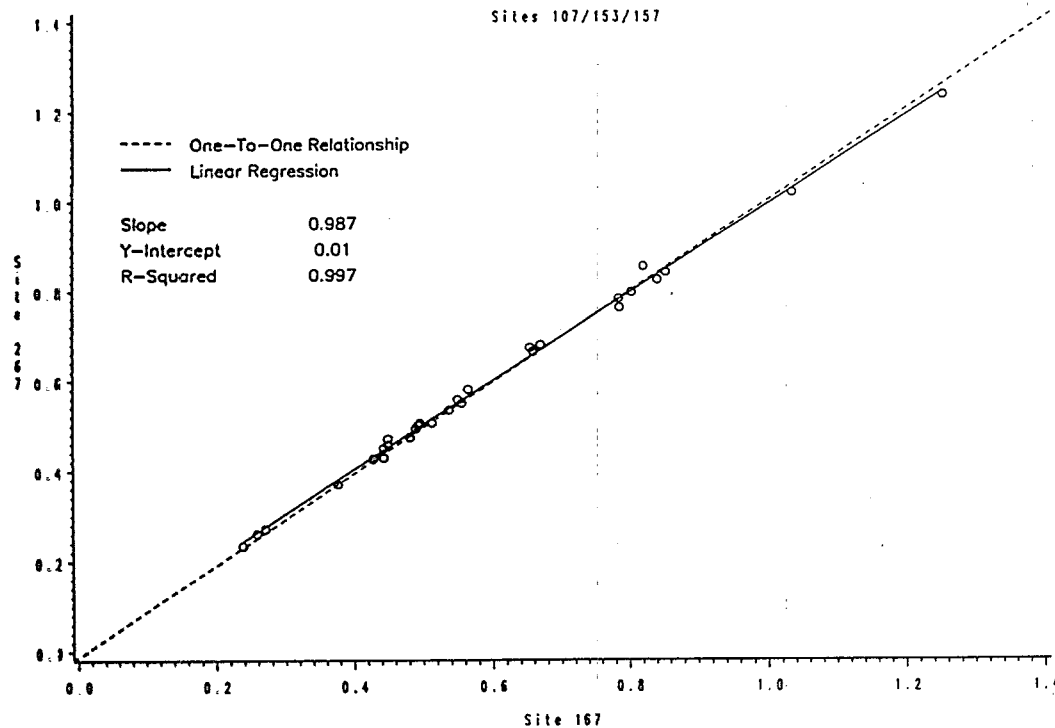


Figure 6. Scattergrams of 1989 collocated NO_3 ($\mu\text{g}/\text{m}^3$) for three eastern sites (A) and one western site (B)



A



B

Figure 7. Scattergrams of 1989 collocated NH_4^+ ($\mu\text{g}/\text{m}^3$) for three eastern sites (A) and one western site (B)

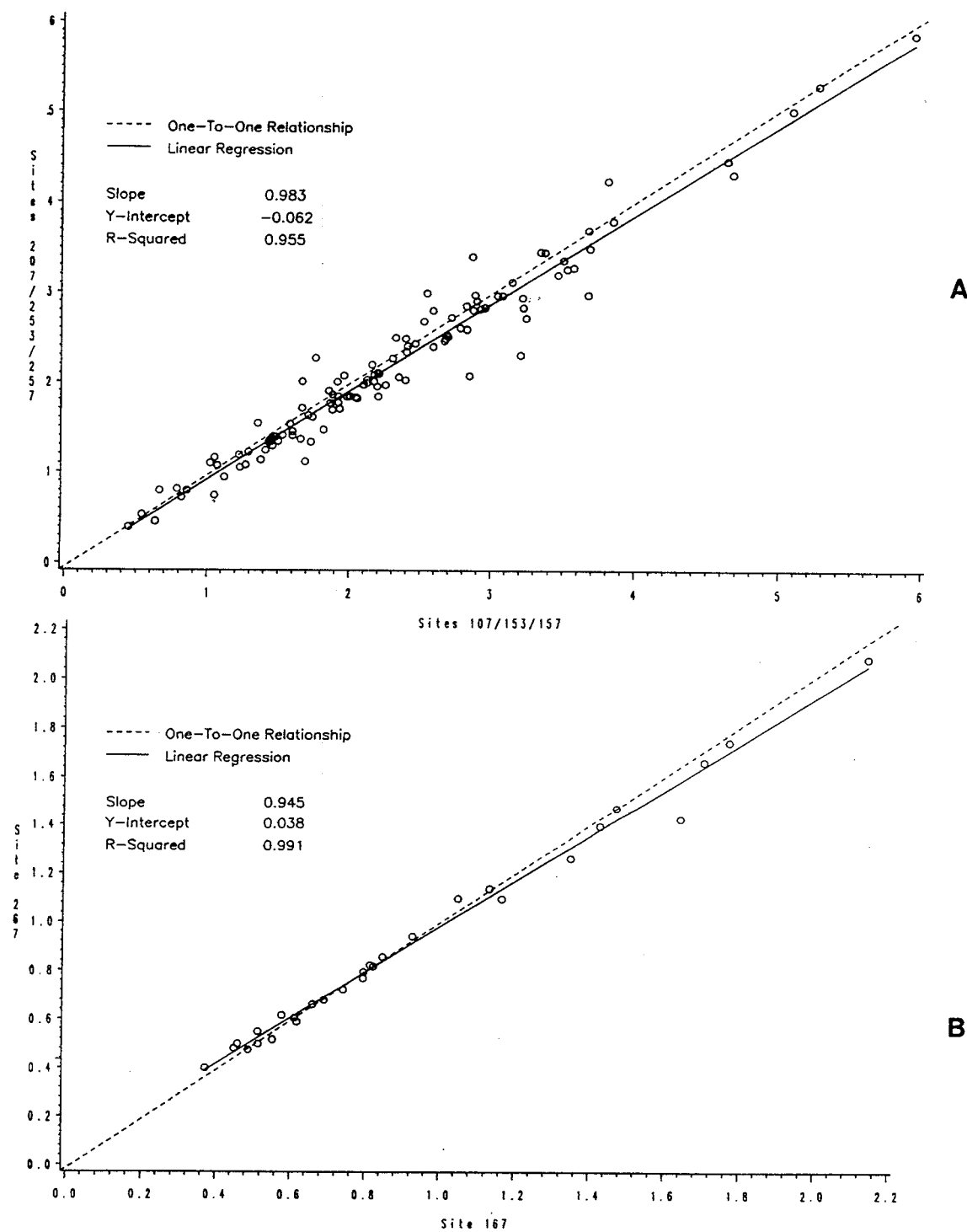
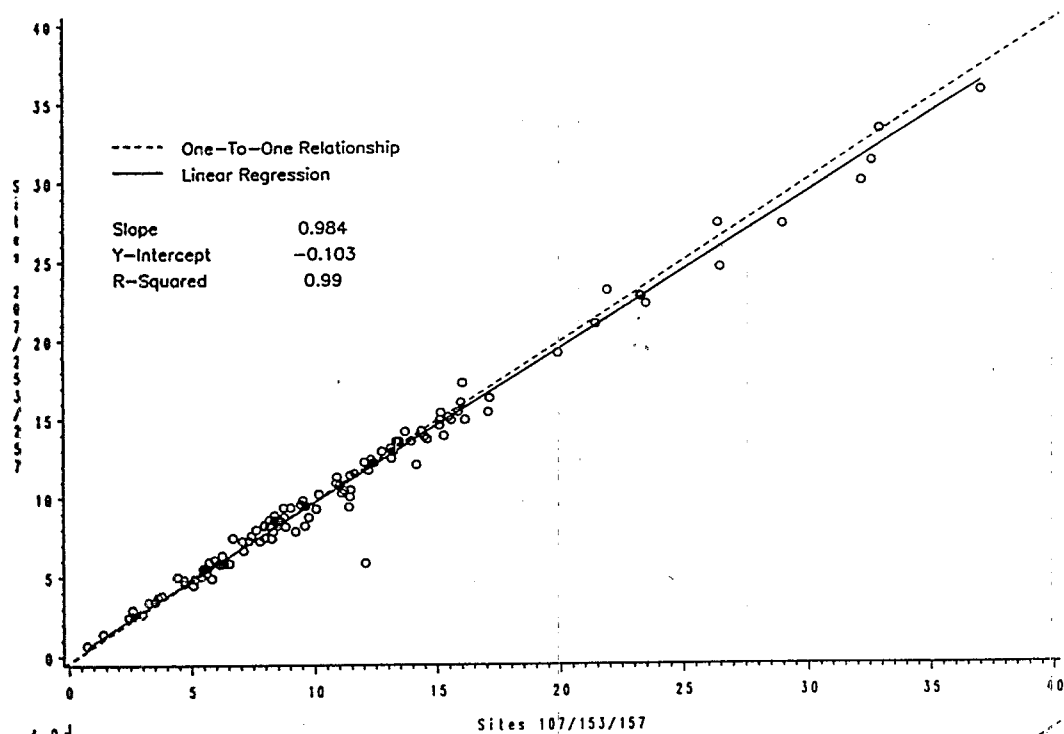
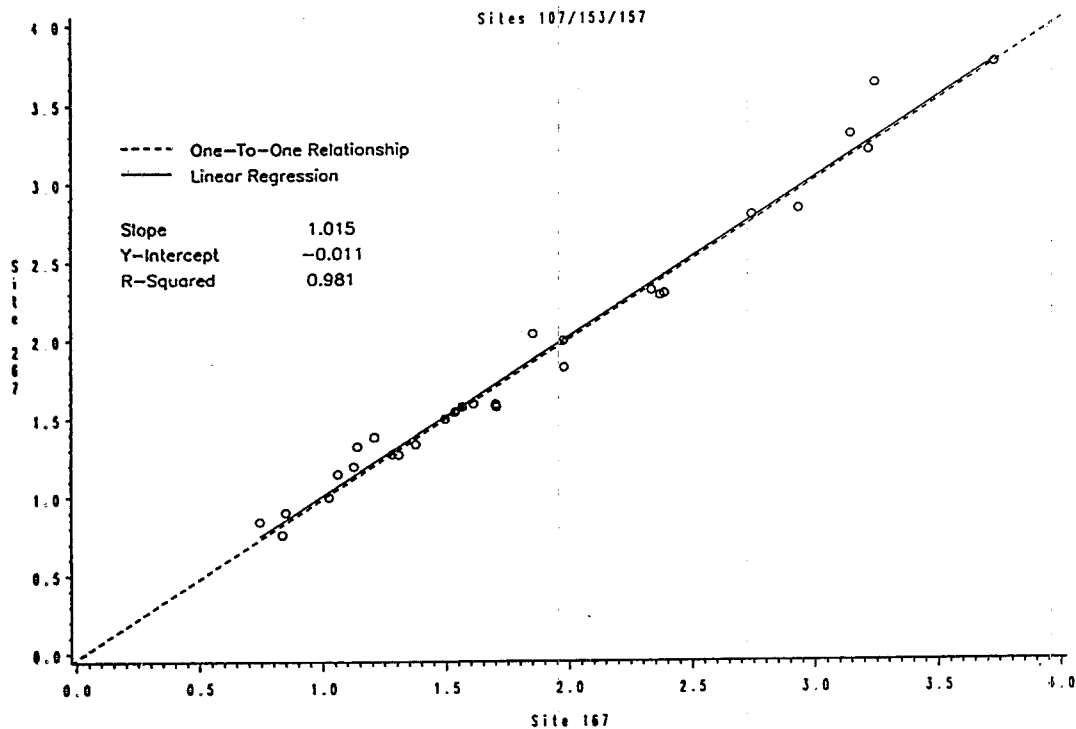


Figure 8. Scattergrams of 1989 collocated HNO_3 ($\mu\text{g}/\text{m}^3$) for three eastern sites (A) and one western site (B)



A



B

Figure 9. Scattergrams of 1989 collocated SO₂ ($\mu\text{g}/\text{m}^3$) for three eastern sites (A) and one western site (B)

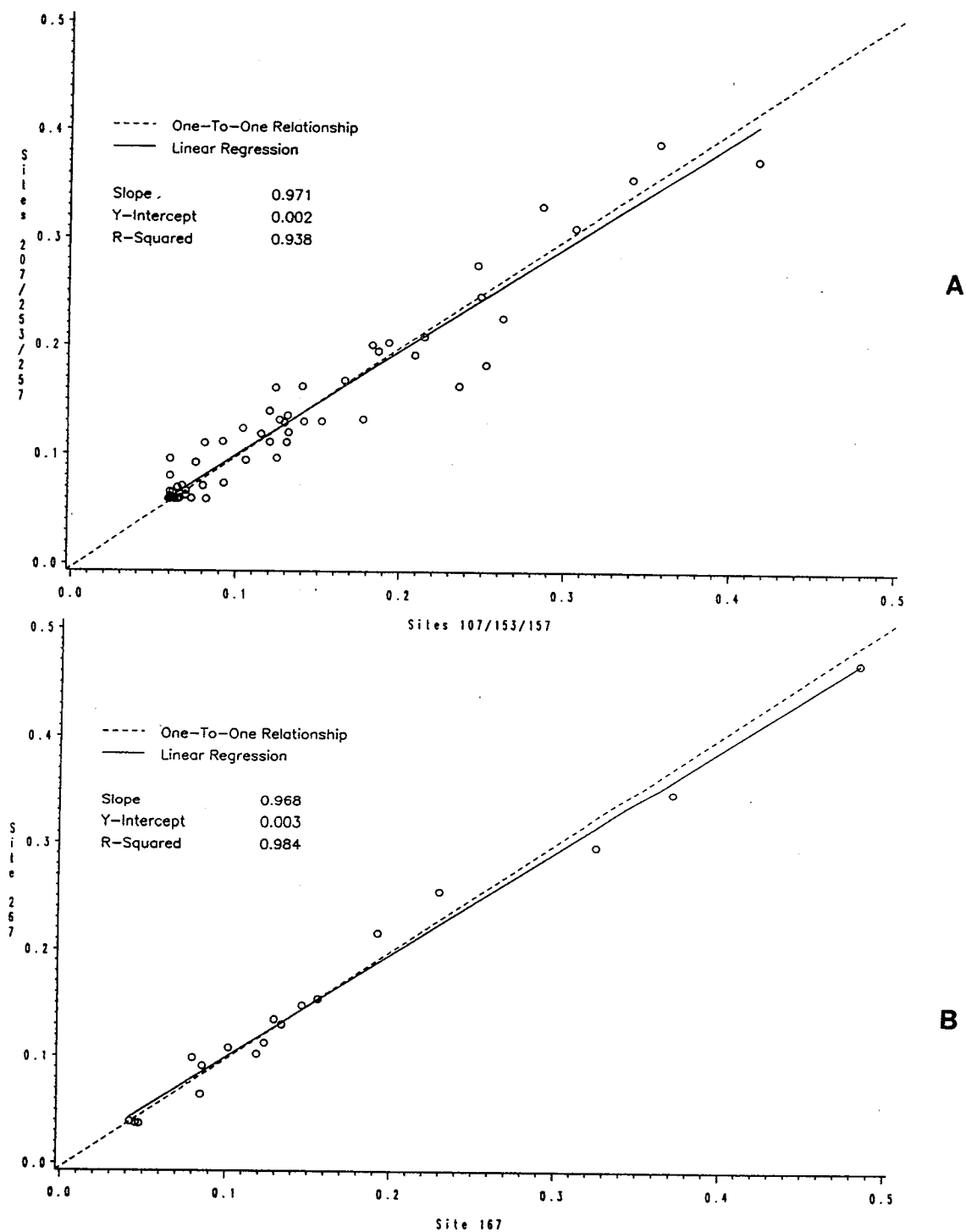


Figure 10. Scattergrams of 1989 collocated Na^+ ($\mu\text{g}/\text{m}^3$) for three eastern sites (A) and one western site (B)

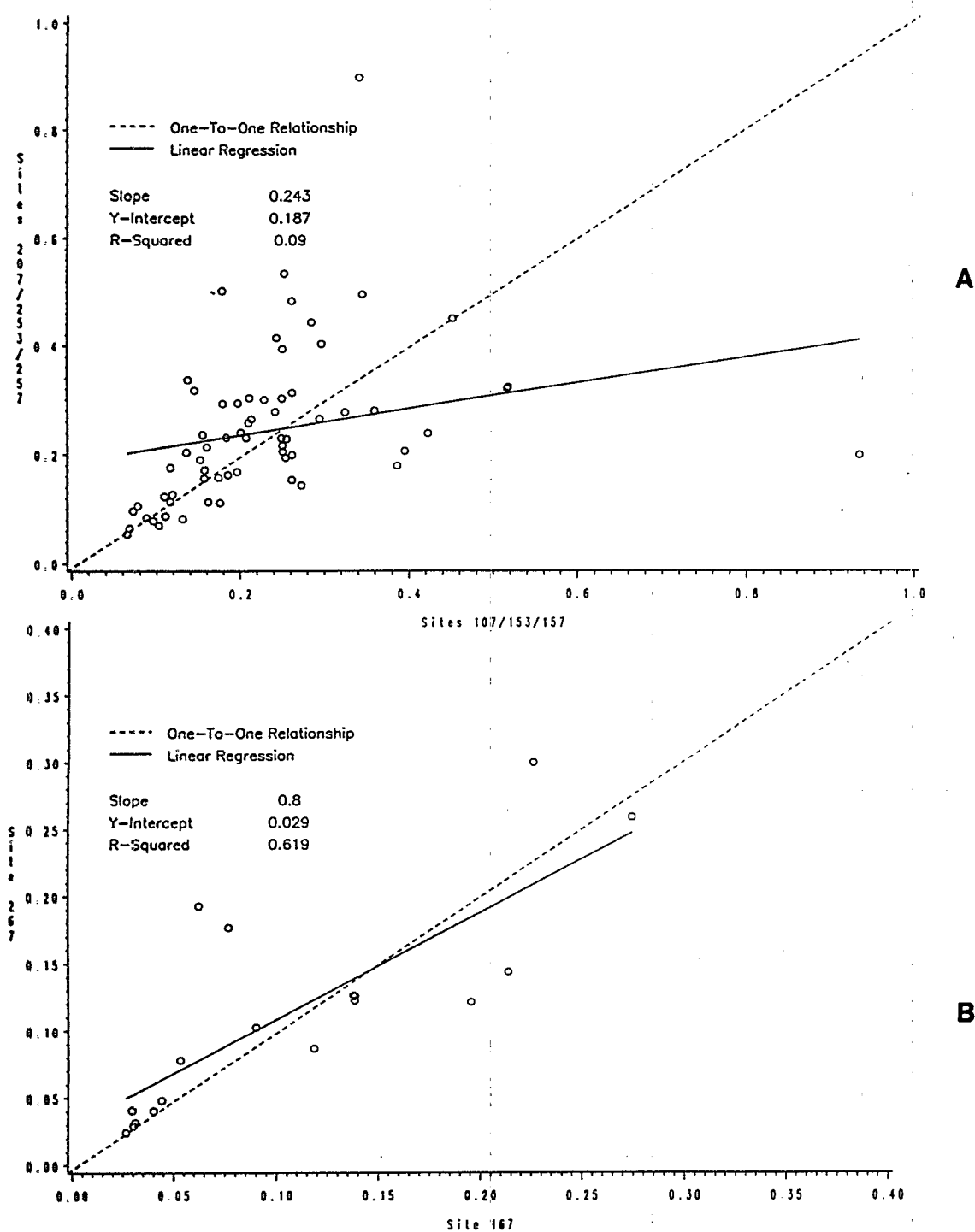


Figure 11. Scattergrams of 1989 collocated K^+ ($\mu g/m^3$) for three eastern sites (A) and one western site (B)

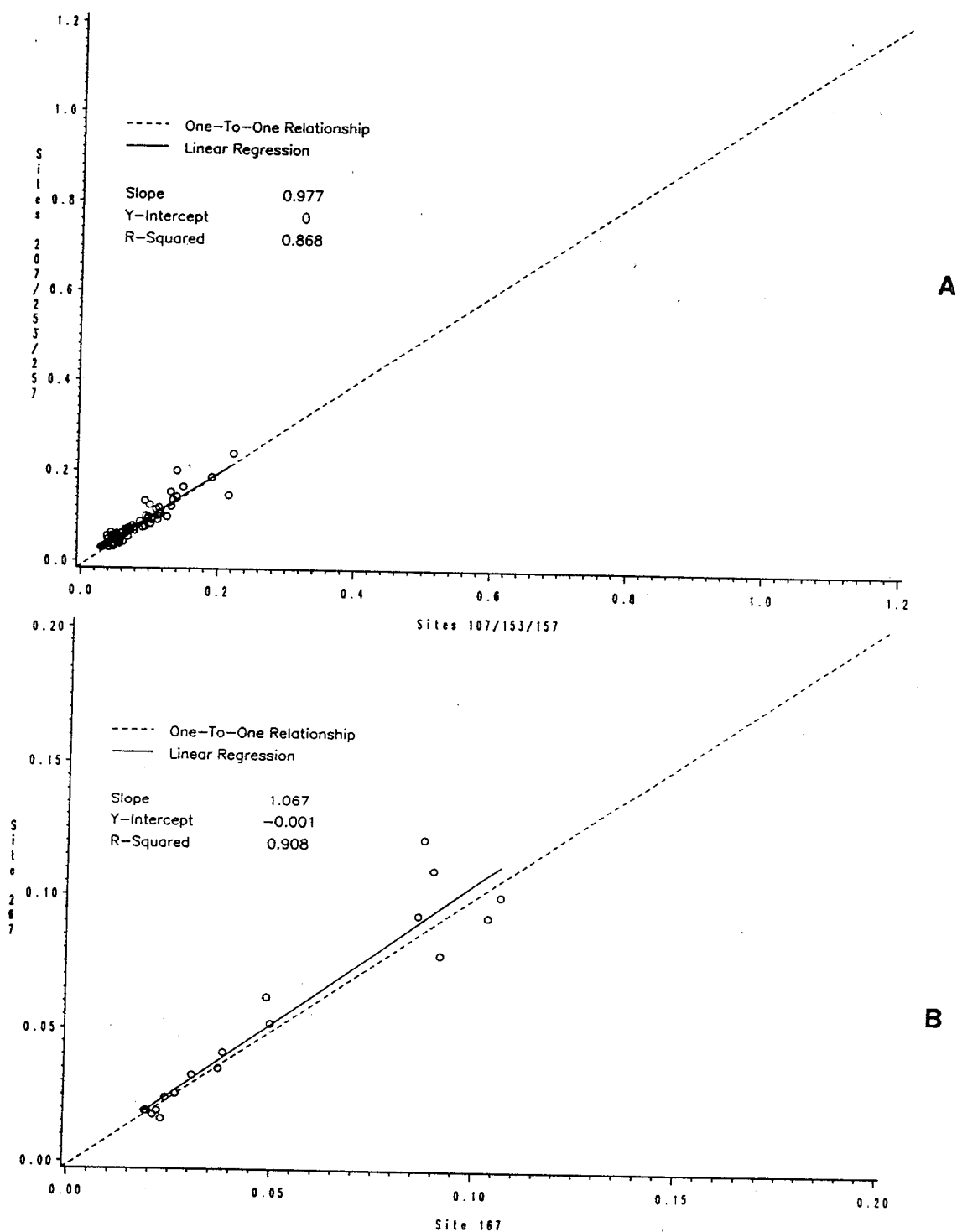
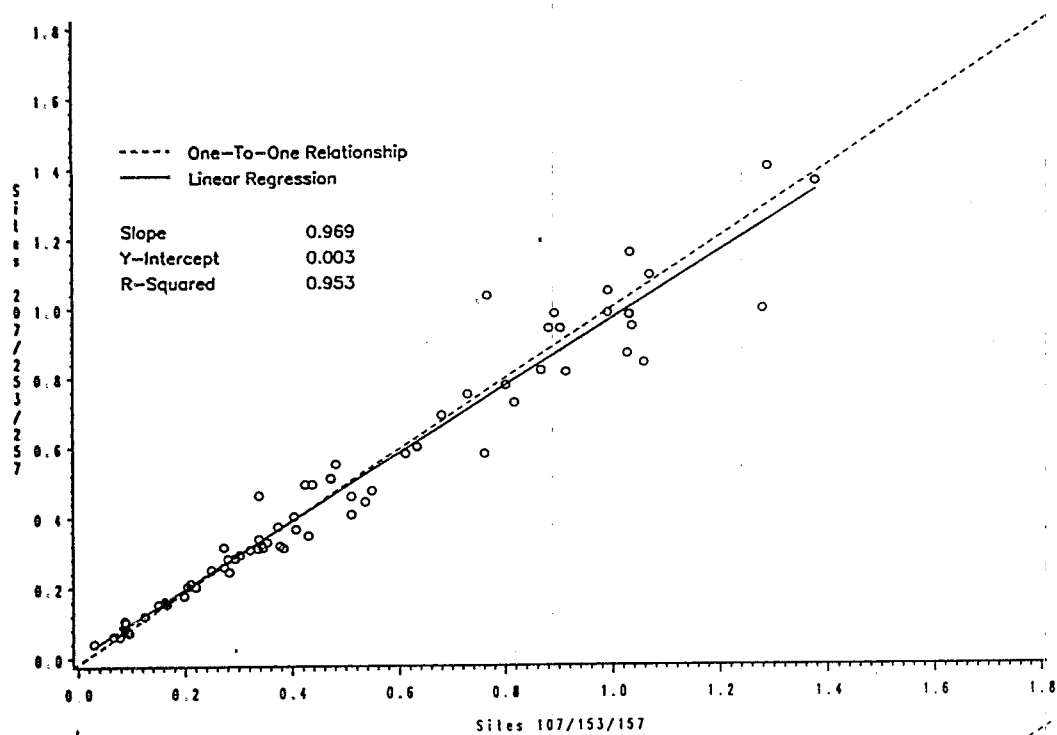
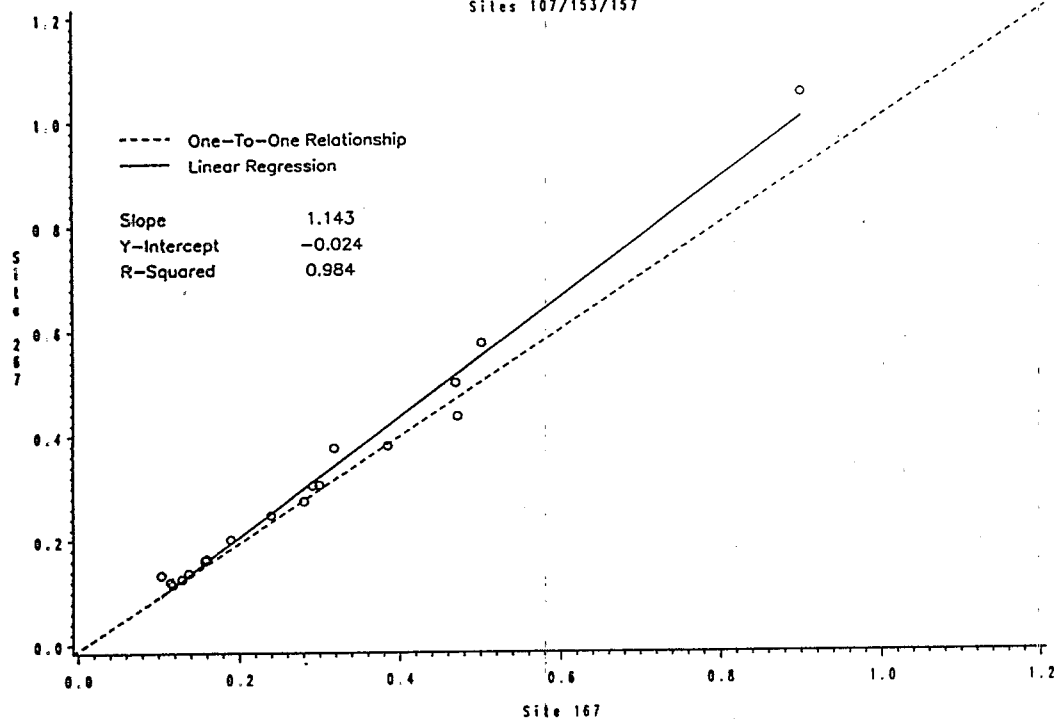


Figure 12. Scattergrams of 1989 collocated Ca^{2+} ($\mu\text{g}/\text{m}^3$) for three eastern sites (A) and one western site (B)



A



B

Figure 13. Scattergrams of 1989 collocated Mg^{2+} ($\mu g/m^3$) for three eastern sites (A) and one western site (B)

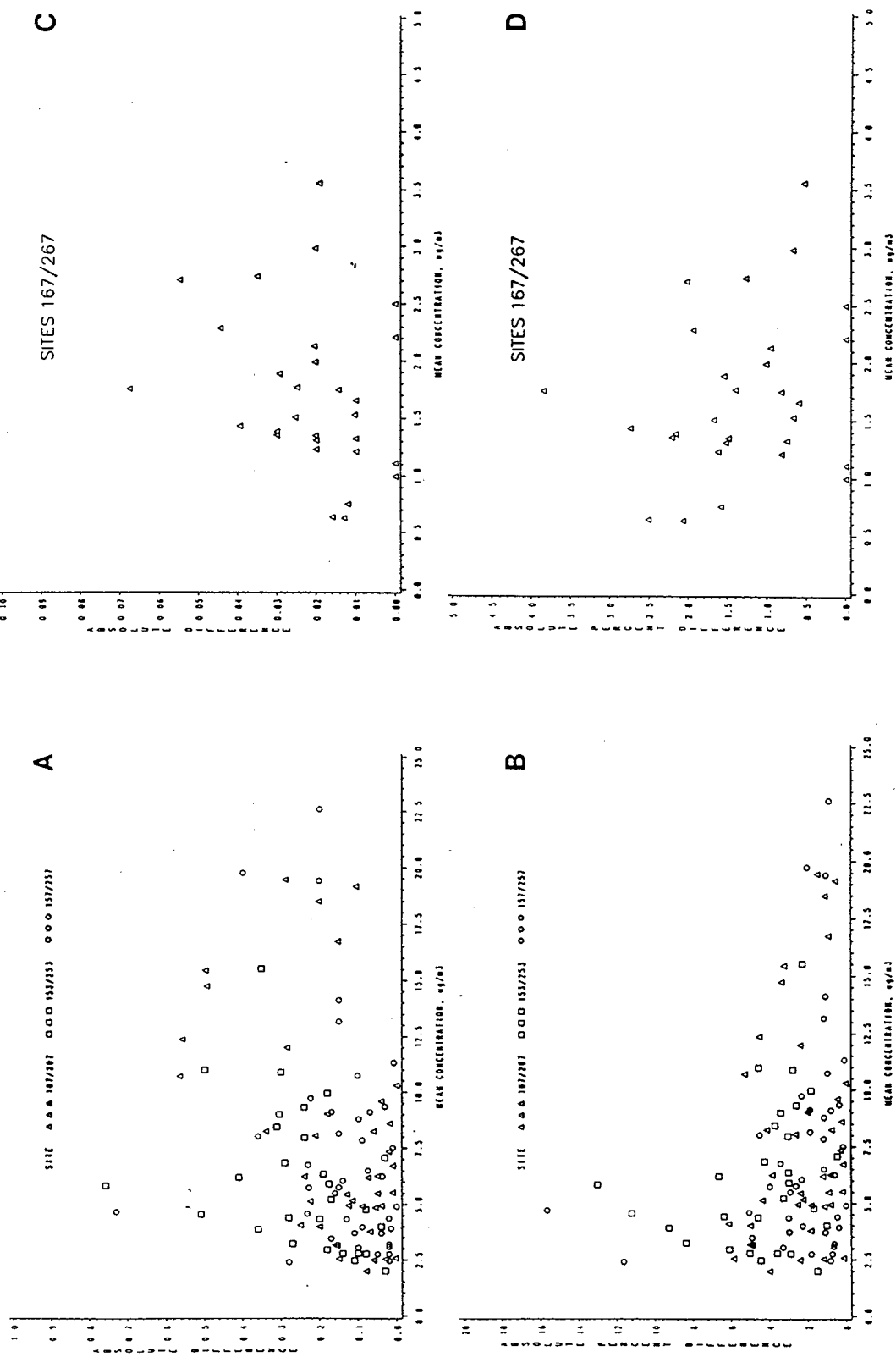


Figure 14. Absolute difference and absolute percent difference versus SO₄ concentrations for eastern (A, B) and western (C, D) collocated samples in 1989

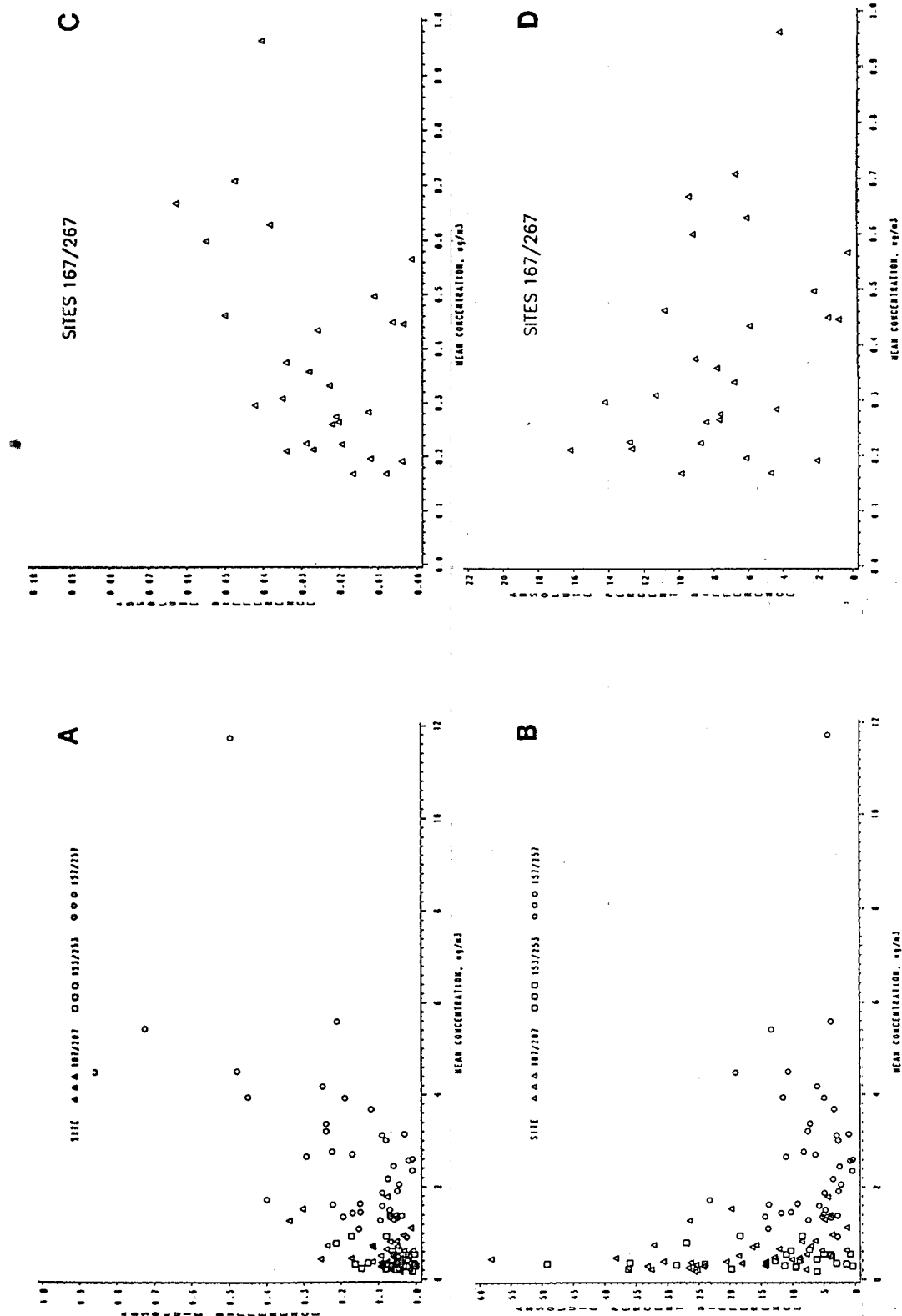


Figure 15. Absolute difference and absolute percent difference versus NO_3 concentrations for eastern (A, B) and western (C, D) collocated samples in 1989

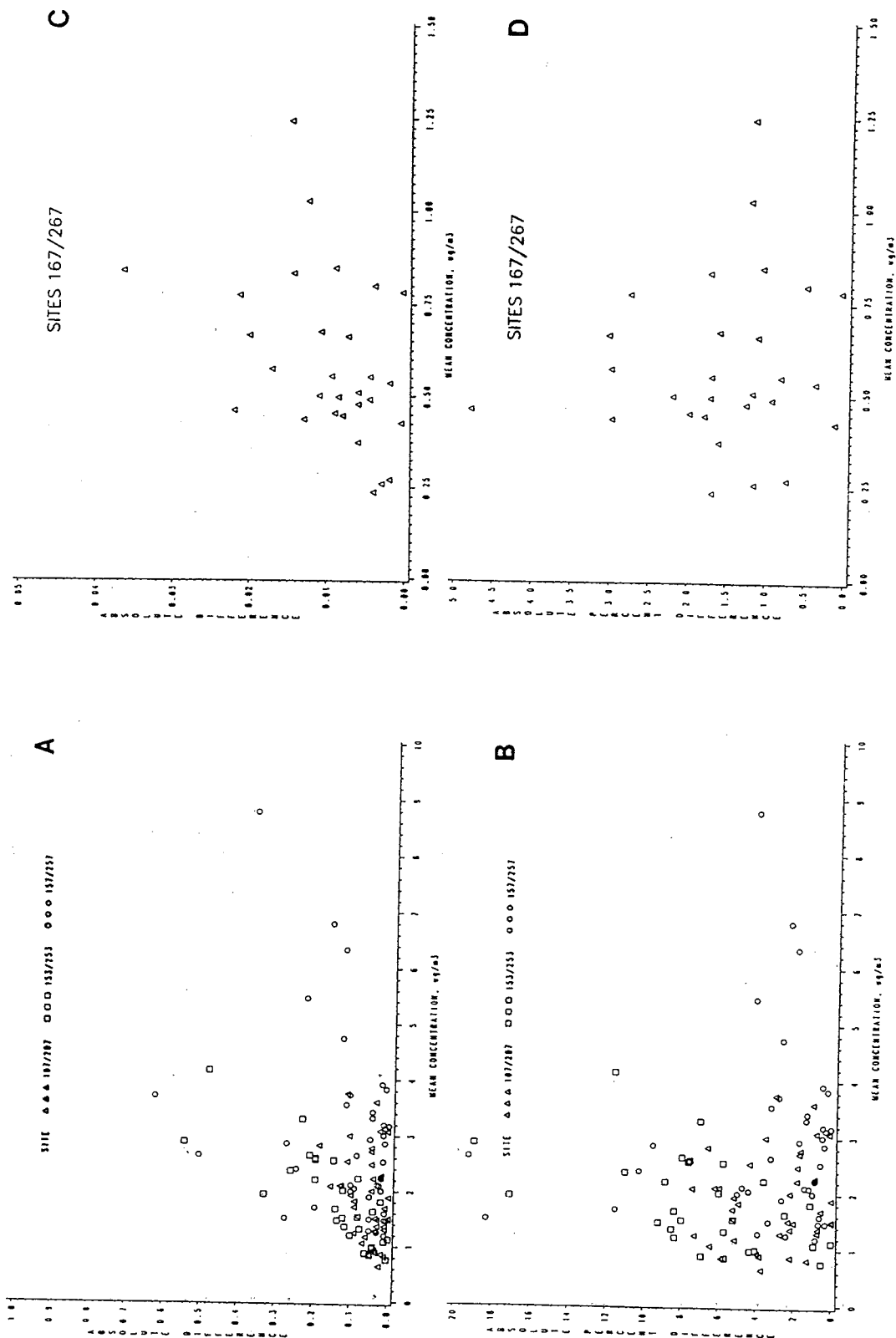


Figure 16. Absolute difference and absolute percent difference versus NH_4^+ concentrations for eastern (A, B) and western (C, D) collocated samples in 1989

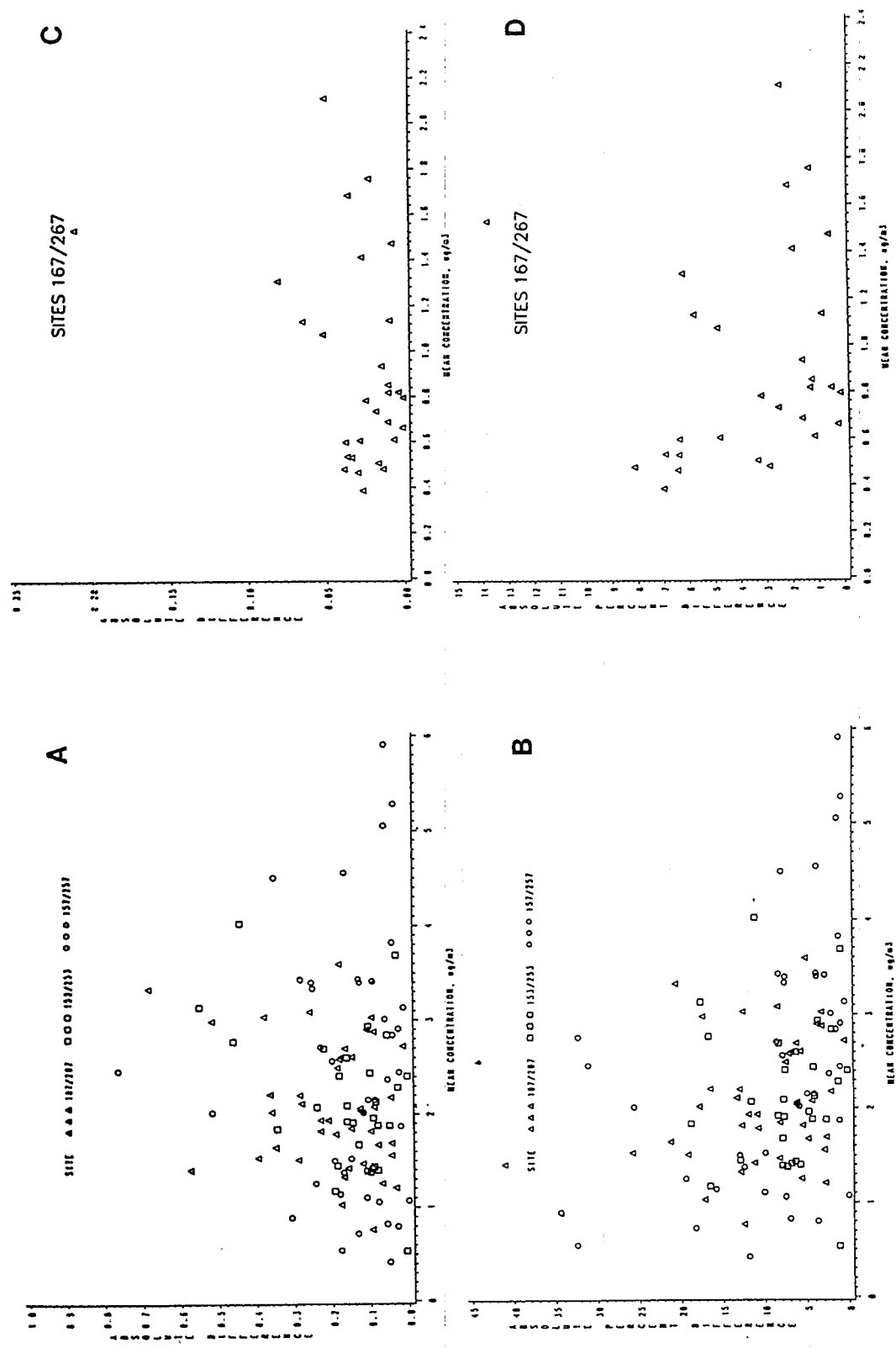


Figure 17. Absolute difference and absolute percent difference versus HNO₃ concentrations for eastern (A, B) and western (C, D) collocated samples in 1989

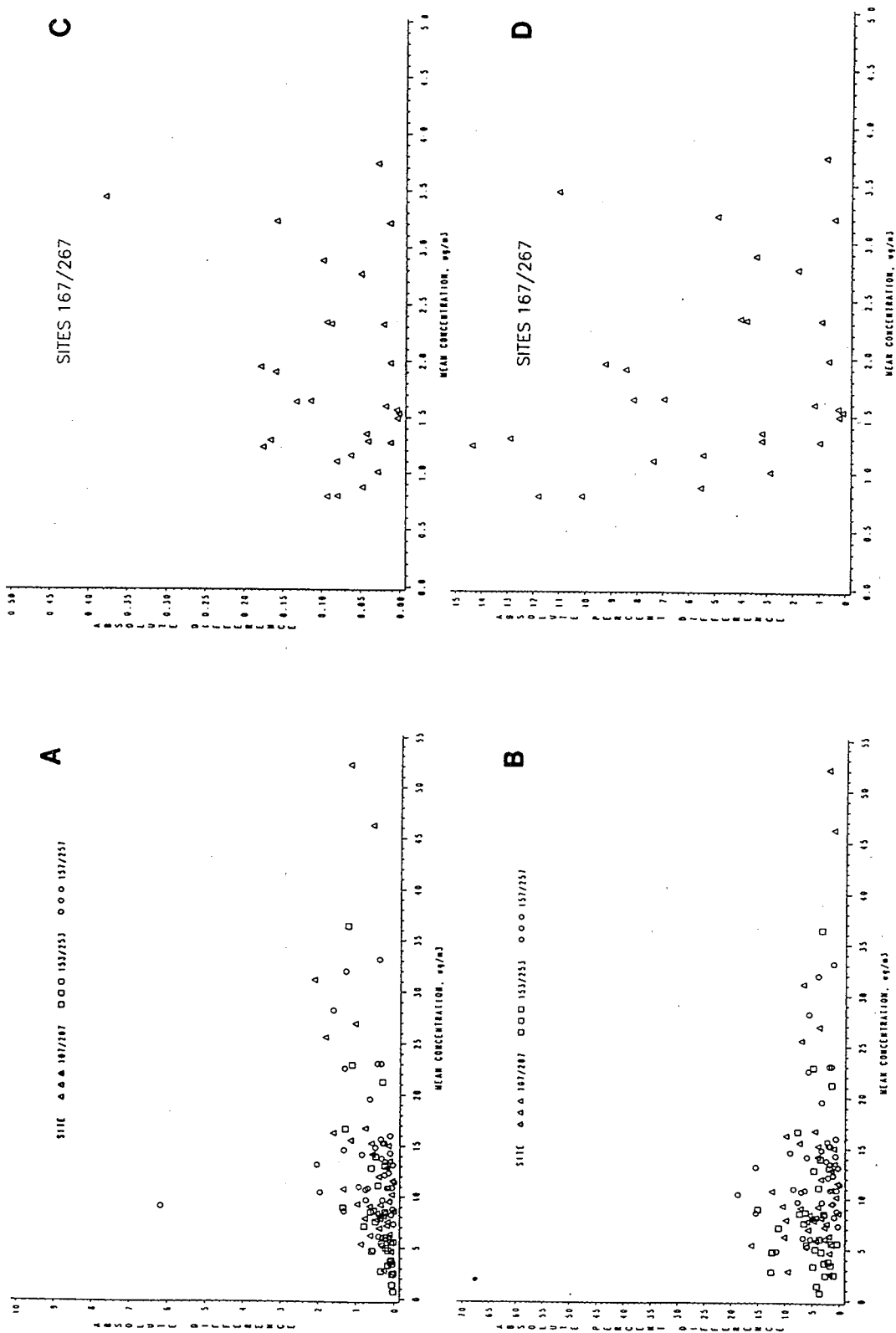


Figure 18. Absolute difference and absolute percent difference versus SO₂ concentration for eastern (A, B) and western (C, D) collocated samples in 1989

Differences in environmental conditions could conceivably give rise to precision differences between eastern and western sites. Located in southern Arizona, the western collocated site is much drier than the eastern collocated sites. Low relative humidity and infrequent rain, fog, and mist could reduce (or eliminate) interferences or loss mechanisms common to humid environments. Collocation of a site in a less arid region of the western United States could help resolve this question.

4.2 FILTER PACK MEASUREMENTS

This section summarizes results of filter pack measurements of SO_4^{2-} , NO_3^- , NH_4^+ , HNO_3 , and SO_2 during 1989. Annual and quarterly data are presented and discussed for eastern NDDN sites. Since the majority of western NDDN sites were initiated in June 1989, data are addressed as semiannual averages only. Comparisons of day versus night concentrations, aerosol cations versus aerosol anions, and 1988 versus 1989 concentrations are also presented in Sections 4.2.6 through 4.2.8.

4.2.1 SO_4^{2-}

Annual and quarterly arithmetic mean concentrations of SO_4^{2-} are shown in Figures 19 through 21. Annual concentrations range from $7.9 \mu\text{g}/\text{m}^3$ in western Ohio (Site 122) to $2.7 \mu\text{g}/\text{m}^3$ in northern Maine (Site 135). Mean values of $7.0 \mu\text{g}/\text{m}^3$, or more, extend in a narrow band from southern Indiana (Site 140) to Maryland (Site 116).

Annual averages of $5.0 \mu\text{g}/\text{m}^3$ cover nearly the entire eastern United States, from New York and Michigan to northern Mississippi and Alabama. Only sites from northern New York to Maine, northern Michigan, Wisconsin, and Florida exhibit concentrations below $5.0 \mu\text{g}/\text{m}^3$. A strong concentration gradient (i.e., greater than a factor of 2) exists between Pennsylvania and northern New York, and weak gradients extend from Ohio through Michigan and from Illinois into Wisconsin.

Quarterly data for SO_4^{2-} show dramatic differences from season to season, but reasonably consistent locations of peak concentrations (see Figures 20 and 21). Results for first quarter 1989 exhibit a narrow range from $5.2 \mu\text{g}/\text{m}^3$ in northern Alabama (Site 152) and Maryland (Site 116) to $2.4 \mu\text{g}/\text{m}^3$ in northern Maine. Mean concentrations of $4.0 \mu\text{g}/\text{m}^3$, or above, cover the region from the southern Great Lakes southward, with the exception of a small cluster of sites located in the mountains of North Carolina, Virginia, and eastern Kentucky.

Concentrations during second quarter 1989 exhibit a substantial increase (50 to 75 percent) at most sites relative to first quarter 1989. Average values range from $8.8 \mu\text{g}/\text{m}^3$ in western Ohio to $2.8 \mu\text{g}/\text{m}^3$ in Maine and Wisconsin (Site 134). Concentrations above $8.0 \mu\text{g}/\text{m}^3$ occur at



INS = Insufficient samples for the period covered (<75%)

Figure 19. Annual average SO_4^{2-} concentrations ($\mu\text{g}/\text{m}^3$) for the eastern United States during 1989

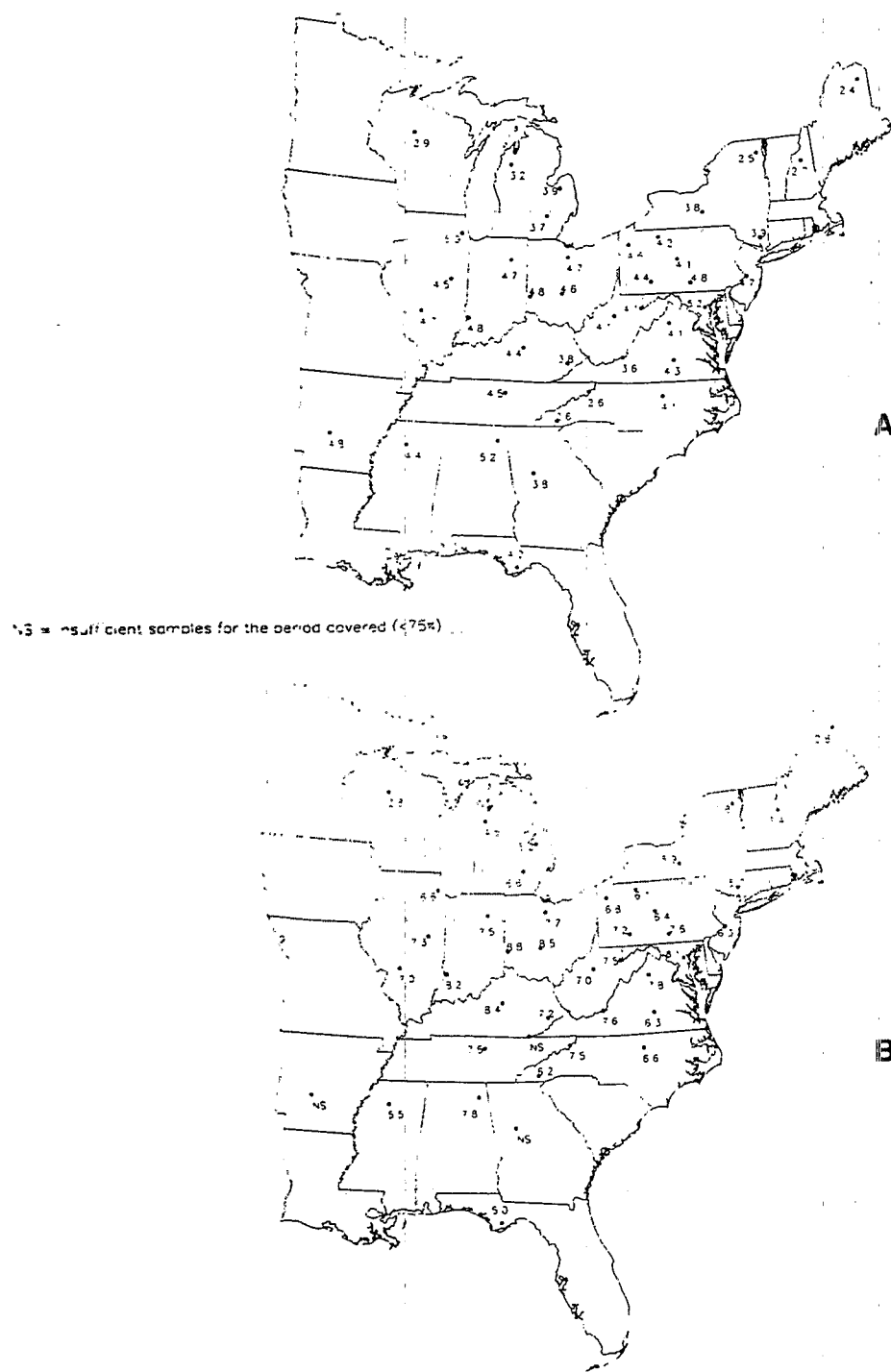


Figure 20. Average SO_4^{2-} concentrations ($\mu\text{g}/\text{m}^3$) for the first (A) and second (B) quarter 1989

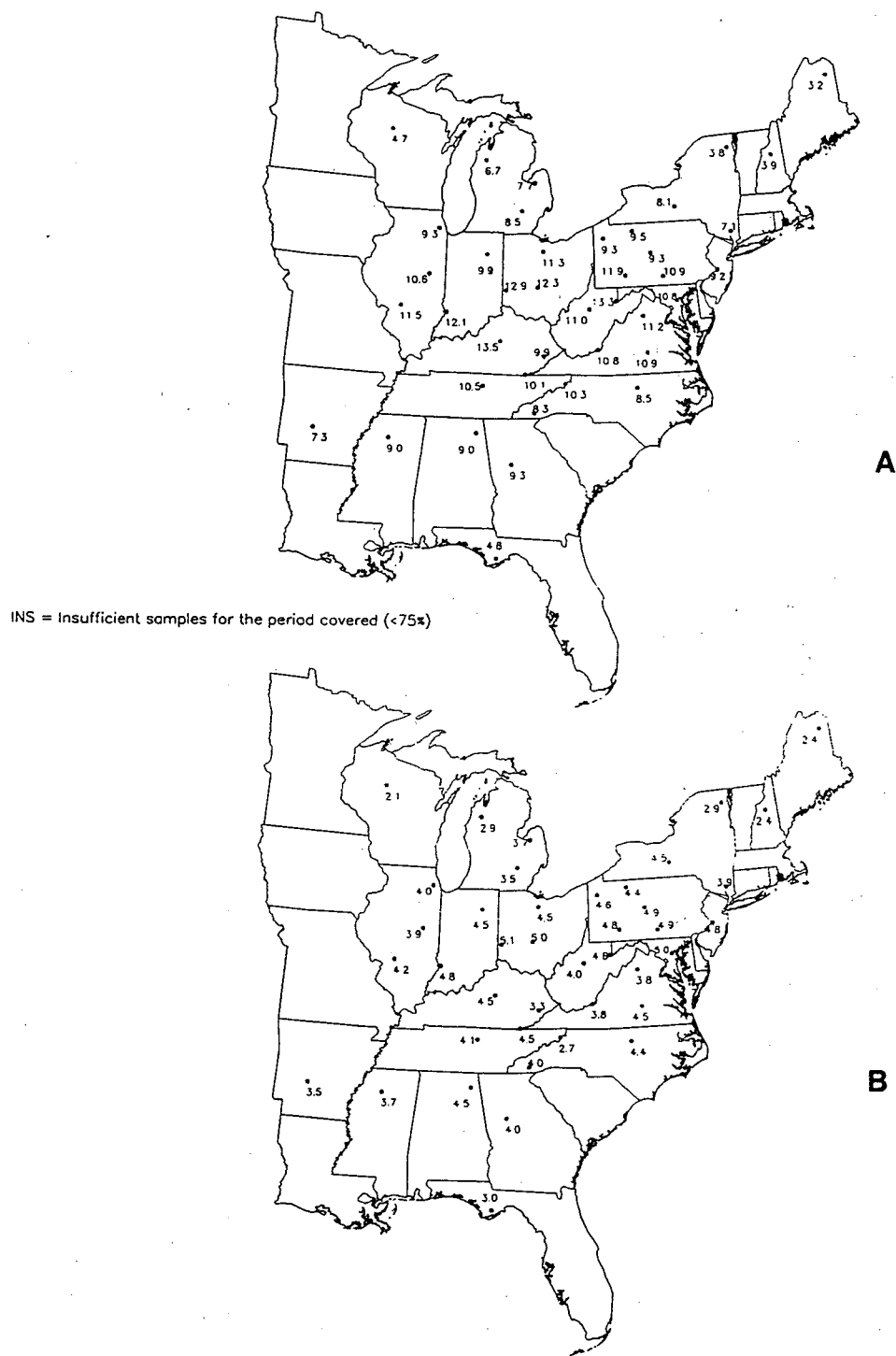


Figure 21. Average SO_4^{2-} concentrations ($\mu\text{g}/\text{m}^3$) for the third (A) and fourth (B) quarter 1989

a ring of sites in Indiana, Ohio, and Kentucky, while concentrations below $5.0 \mu\text{g}/\text{m}^3$ occur only in New England and the upper midwest.

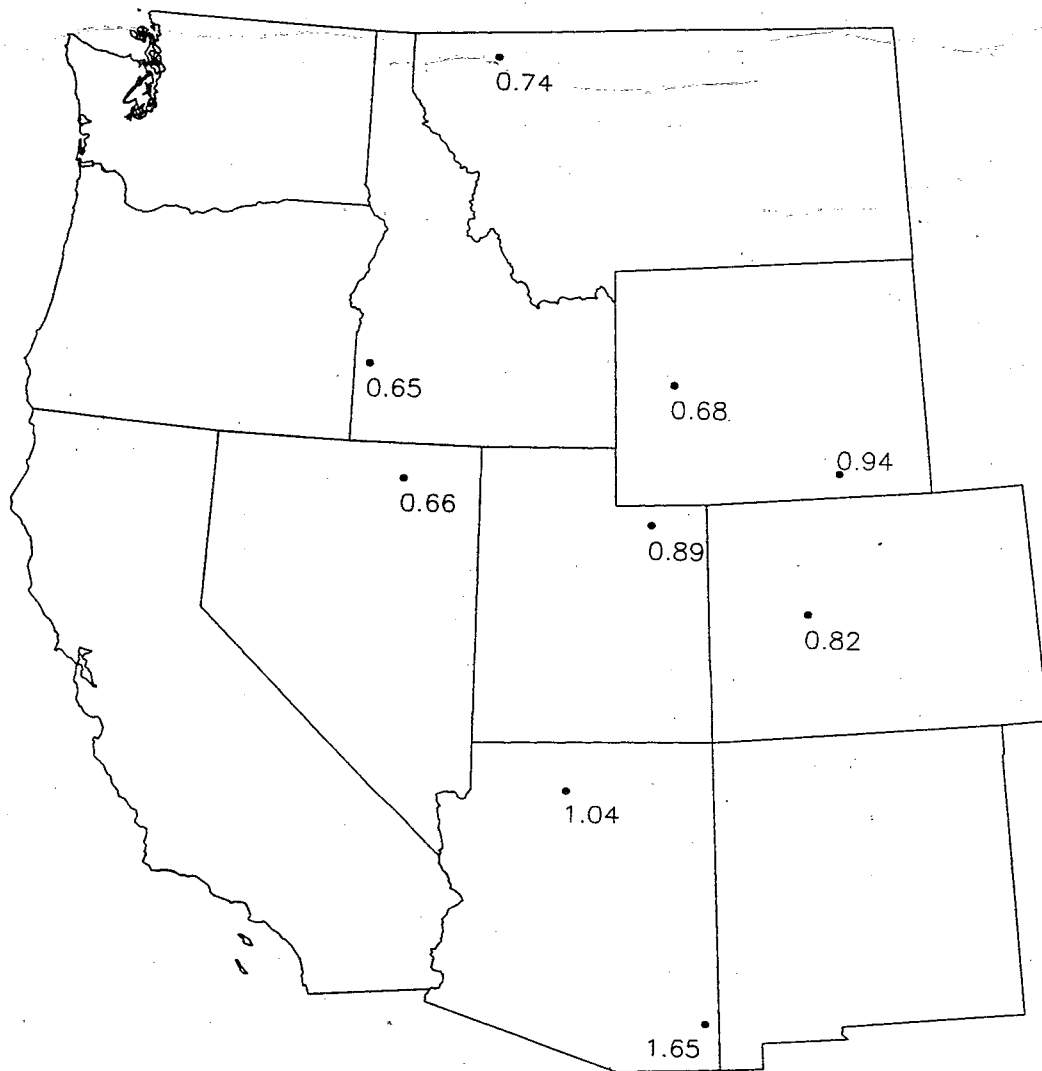
Results for third and fourth quarter 1989 show another large increase in concentrations, followed by a dramatic decline to the lowest levels of the year. For third quarter 1989, mean SO_4^{2-} ranges from $13.5 \mu\text{g}/\text{m}^3$ in central Kentucky (Site 129) to $3.2 \mu\text{g}/\text{m}^3$ in Maine. Values above $12.0 \mu\text{g}/\text{m}^3$ occur at a small number of sites in Indiana, Kentucky, Ohio, and West Virginia, while values above $8.0 \mu\text{g}/\text{m}^3$ extend from the southern Great Lakes into northern Mississippi, Alabama, and Georgia. Fourth quarter concentrations range from $5.1 \mu\text{g}/\text{m}^3$ in western Ohio, to $2.1 \mu\text{g}/\text{m}^3$ in Wisconsin and are generally similar to those observed during the first quarter.

The seasonal progression of SO_4^{2-} concentrations, therefore, appear to follow temperature and solar radiation, which also exhibit maxima and minima in summer and winter, respectively. Seasonal variability for individual sites, however, is much lower around the periphery of the network than near its center. For example, quarterly average concentrations for the site in Maine (Site 135) fell within a narrow range of 2.4 to $3.2 \mu\text{g}/\text{m}^3$. In contrast, quarterly averages in western Ohio (i.e., those sites with the highest annual averages) ranged from 4.8 to $12.9 \mu\text{g}/\text{m}^3$.

Semiannual average SO_4^{2-} concentrations for the nine western sites (see Figure 22) range from $1.65 \mu\text{g}/\text{m}^3$ in southern Arizona (Site 167) to $0.65 \mu\text{g}/\text{m}^3$ in southern Idaho (Site 163). Results are invariably lower than those observed across the eastern United States. For example, the range of semiannual concentrations was only 27 to 69 percent of the lowest quarterly average reported for the site in northern Maine.

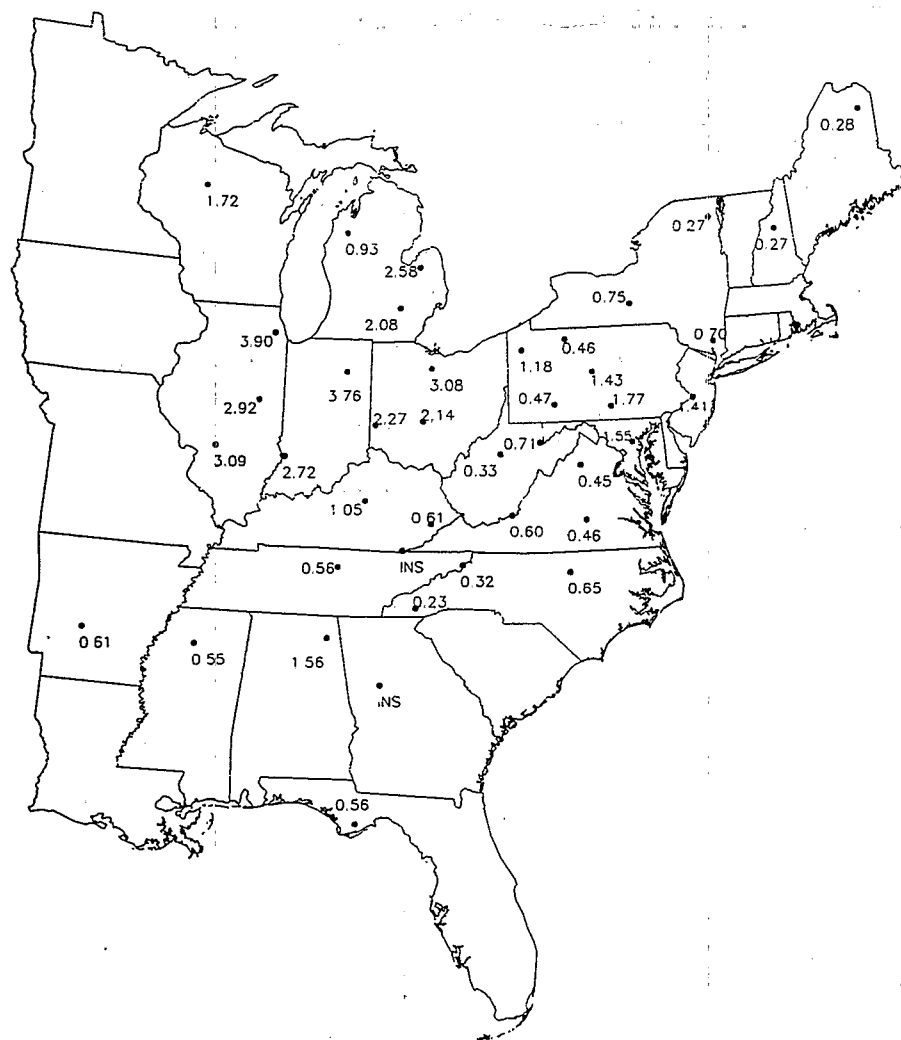
4.2.2 NO_3

Annual average concentrations for NO_3 exhibit much more variability than SO_4^{2-} and a definite pattern of higher concentrations in the midwest than elsewhere (see Figure 23). The lowest concentrations are observed at forested sites in New England and the southern Appalachian Mountains, while the highest concentrations (i.e., greater than $2.0 \mu\text{g}/\text{m}^3$) are observed in agricultural areas of the midwest. Intermediate values (i.e., 1.0 to $2.0 \mu\text{g}/\text{m}^3$) appear to be associated with agricultural sites anywhere in the eastern United States. This finding supports the idea of a link between agricultural activity and NO_3 concentrations. Two potential mechanisms for NO_3 production include gas-phase reaction between HNO_3 and NH_3 and gas-particle reaction of HNO_3 with soil particles. Although both of these reactions are likely to be enhanced in agricultural areas, the spatial correlation of NH_4^+ and NO_3 concentrations suggests that the former may be more important.



INS = Insufficient samples for the period covered (<75%)

Figure 22. Average SO_4^{2-} concentrations ($\mu\text{g}/\text{m}^3$) for western NDDN sites, combined third and fourth quarters 1989



INS = Insufficient samples for the period covered (<75%)

Figure 23. Annual average NO_3 concentrations ($\mu\text{g}/\text{m}^3$) for the eastern United States during 1989

Quarterly data for NO_3^- (see Figures 24 and 25) exhibit a seasonal cycle that runs counter to that of SO_4^{2-} and NH_4^+ . That is, the highest concentrations occur during the first quarter, and the lowest occur in the third quarter. This cycle is consistent with the temperature-dependent equilibrium between particulate NH_4NO_3 and gaseous NH_3 and HNO_3 .

The highest quarterly concentrations invariably occur at sites located in the midwest. These sites also undergo the greatest seasonal excursions, with typical concentrations decreasing by factors of 2 to 3 from winter to summer. The lowest concentrations occur at forested sites remote from any agricultural activity. This distinction often results in fairly sharp concentration gradients. For example, the forested site in central West Virginia (Site 119) typically exhibits seasonal concentrations that are lower by a factor of 5 than an adjacent site in Ohio (Site 114). A gradient of this magnitude suggests that NO_3^- aerosol either deposits rapidly or, more likely, changes phases readily outside of the region of peak concentration.

Results for the western sites (see Figure 26) indicate semiannual concentrations similar to the lowest values observed at eastern sites. As with other variables, the overall range of concentrations is on the order of 2 (i.e., much narrower than for eastern sites), and the sites in Arizona (along with that in Idaho) represent the highest average concentrations.

4.2.3 NH_4^+

Annual and quarterly average concentrations of NH_4^+ are illustrated in Figures 27 through 29. Annual average values range from $3.2 \mu\text{g}/\text{m}^3$ in northern Indiana (Site 133) to $0.69 \mu\text{g}/\text{m}^3$ in Maine and, in general, exhibit higher values at agricultural sites than at forested sites. Since the midwest is primarily agricultural, this results in regional differences between the midwest, northeast, and southeast. Concentrations above $2.0 \mu\text{g}/\text{m}^3$ are found at all sites within Illinois, Indiana, and Ohio, plus the two southernmost sites in Michigan. Additional concentrations in this range also are found in northern Alabama, eastern Pennsylvania, and Maryland. Average values below $1.0 \mu\text{g}/\text{m}^3$ are found only in New England. Seasonal concentration data follow a similar, but not as pronounced, pattern as those for SO_4^{2-} . Summertime (i.e., third quarter) averages are the highest of any season, with concentrations above $2.0 \mu\text{g}/\text{m}^3$ encompassing all states from Michigan to Georgia. Similarly, sites on the periphery of the network (e.g., Maine) exhibit both the lowest concentrations and the lowest quarter-to-quarter variability.

Results for the third and fourth quarters for the western sites show about a factor of 2 range in concentrations (see Figure 30). The highest value ($0.57 \mu\text{g}/\text{m}^3$) occurs in southern Arizona and the lowest

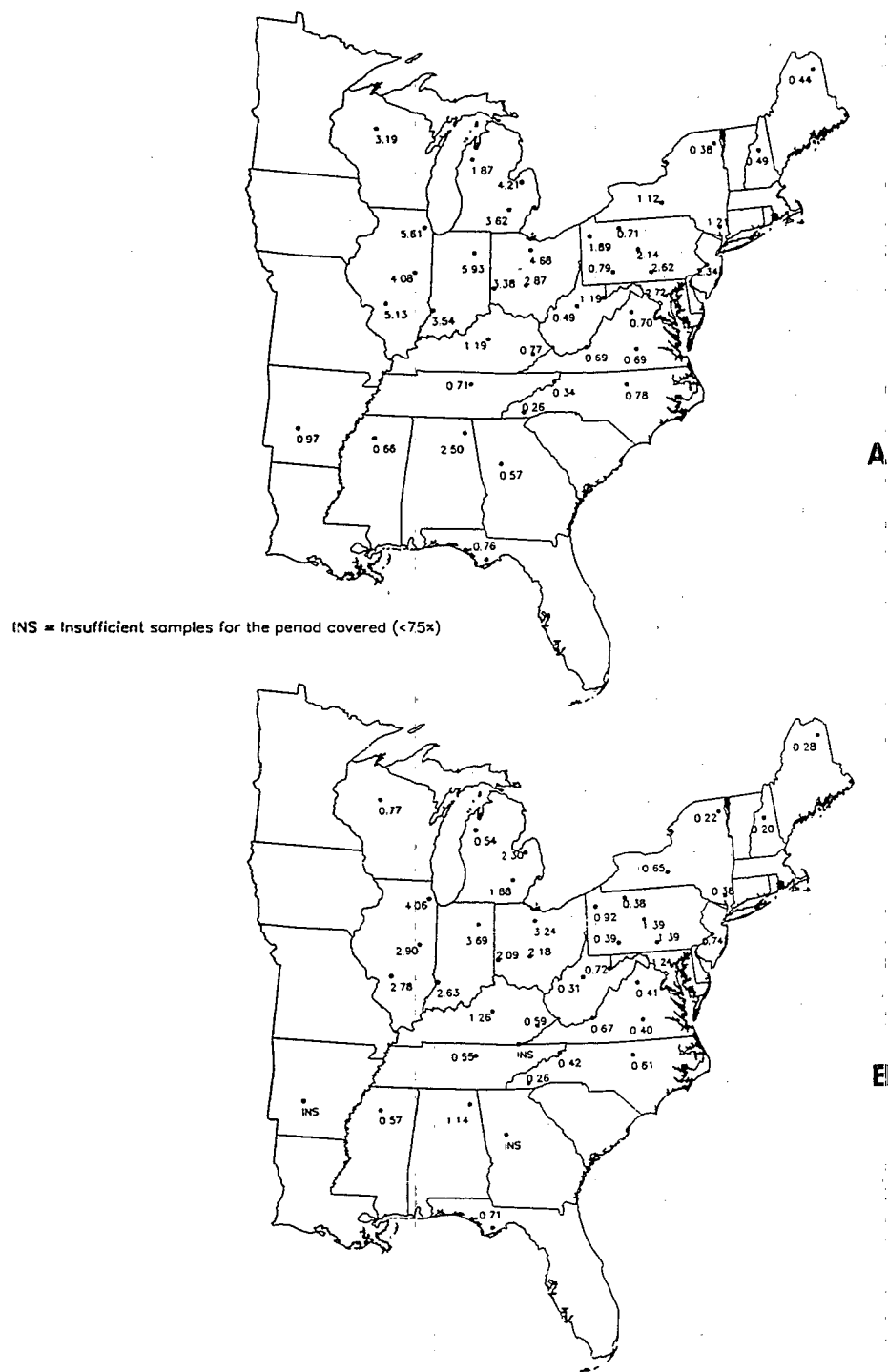


Figure 24. Average NO₃ concentrations (μg/m³) for the first (A) and second (B) quarter 1989

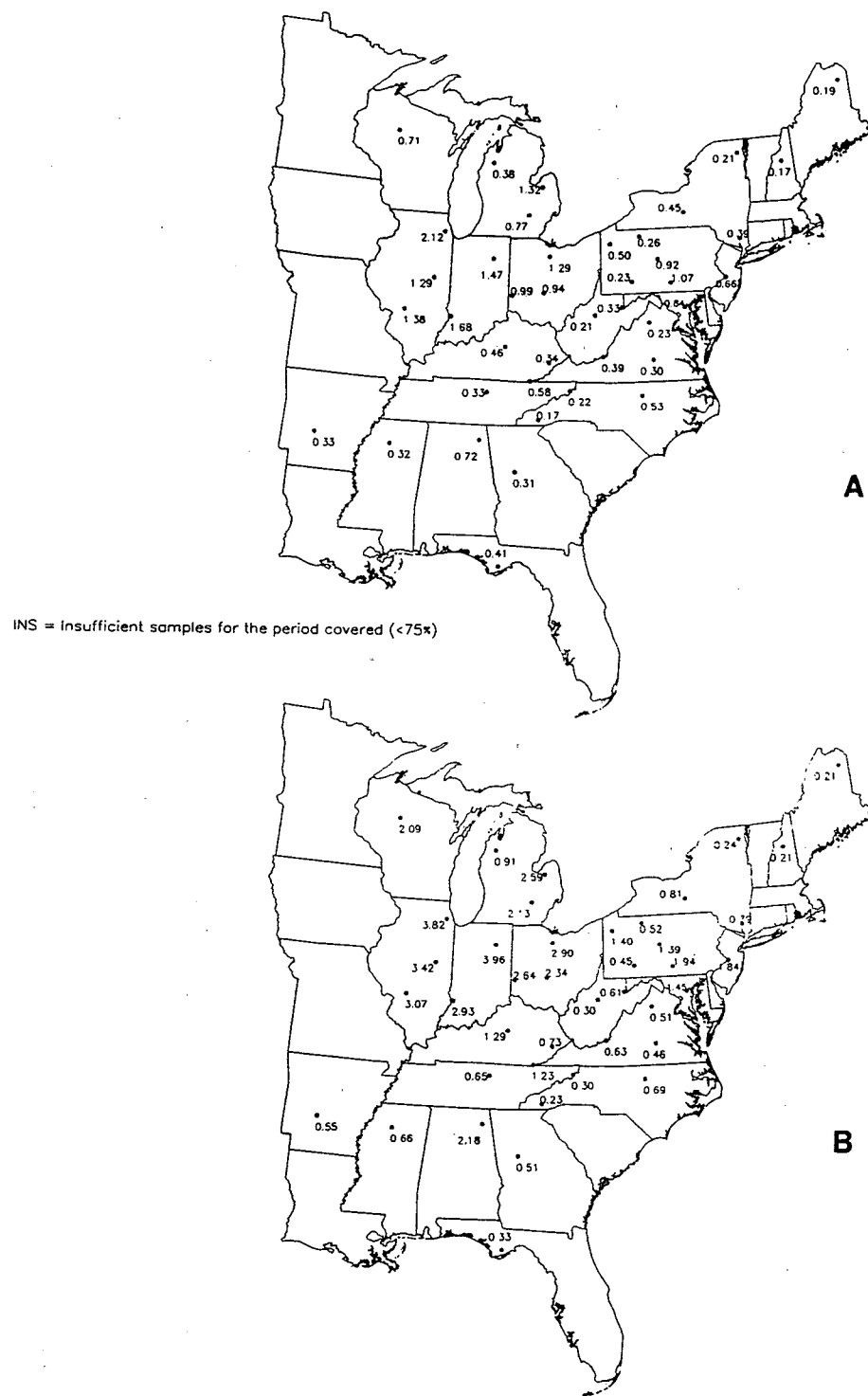
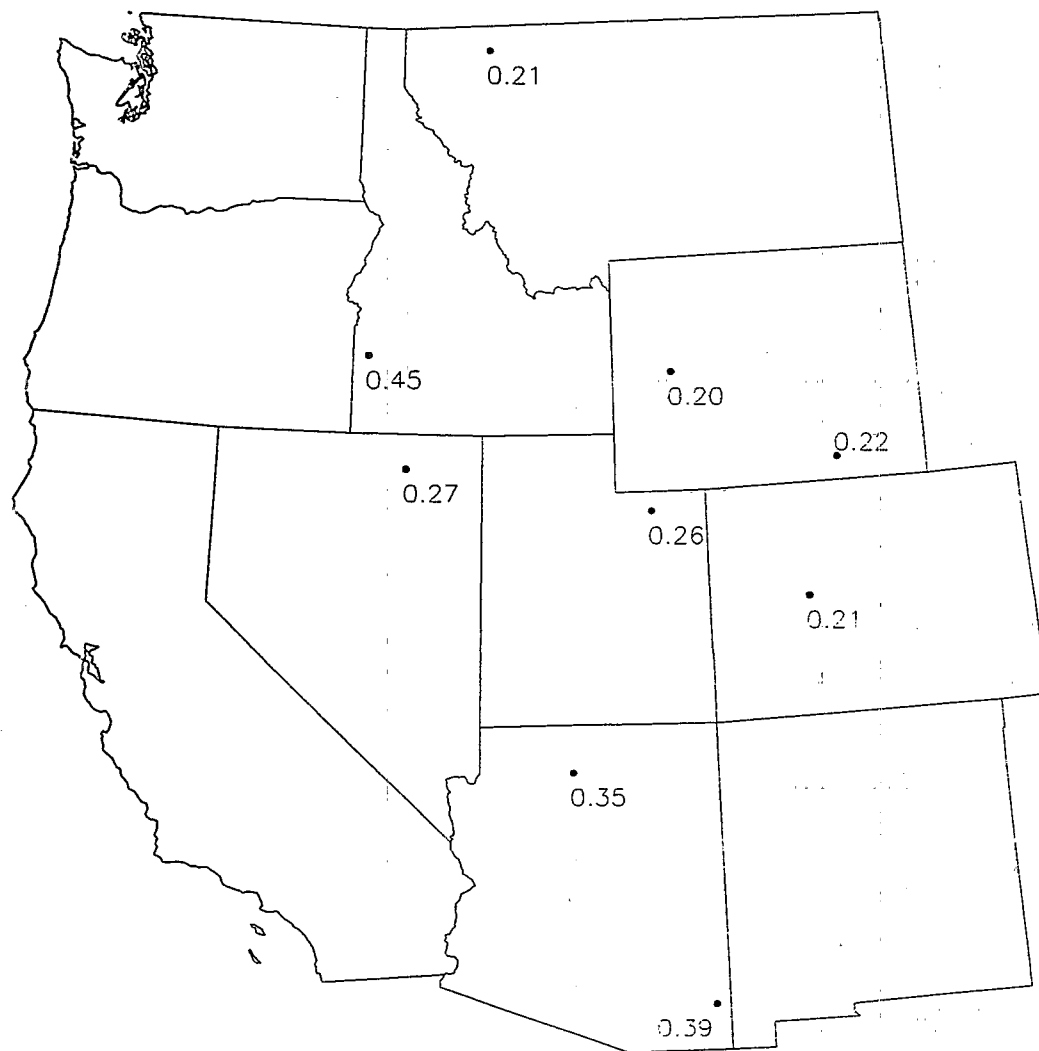
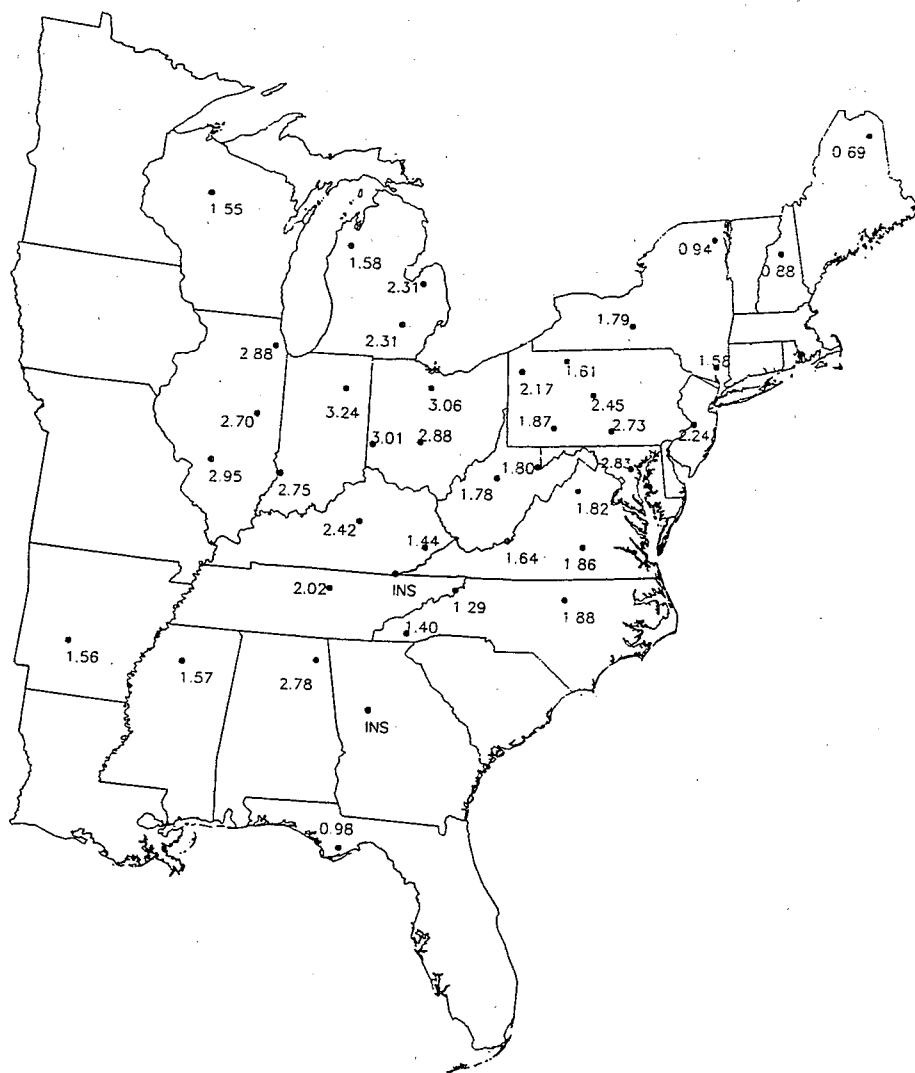


Figure 25. Average NO_3 concentrations ($\mu\text{g}/\text{m}^3$) for the third (A) and fourth (B) quarter 1989



NS = insufficient samples for the period covered (<75%)

Figure 26. Average NO_3 concentrations ($\mu\text{g}/\text{m}^3$) for western NDDN sites, combined third and fourth quarters 1989



INS = Insufficient samples for the period covered (<75%)

Figure 27. Annual average NH_4^+ concentrations ($\mu\text{g}/\text{m}^3$) for the eastern United States during 1989*

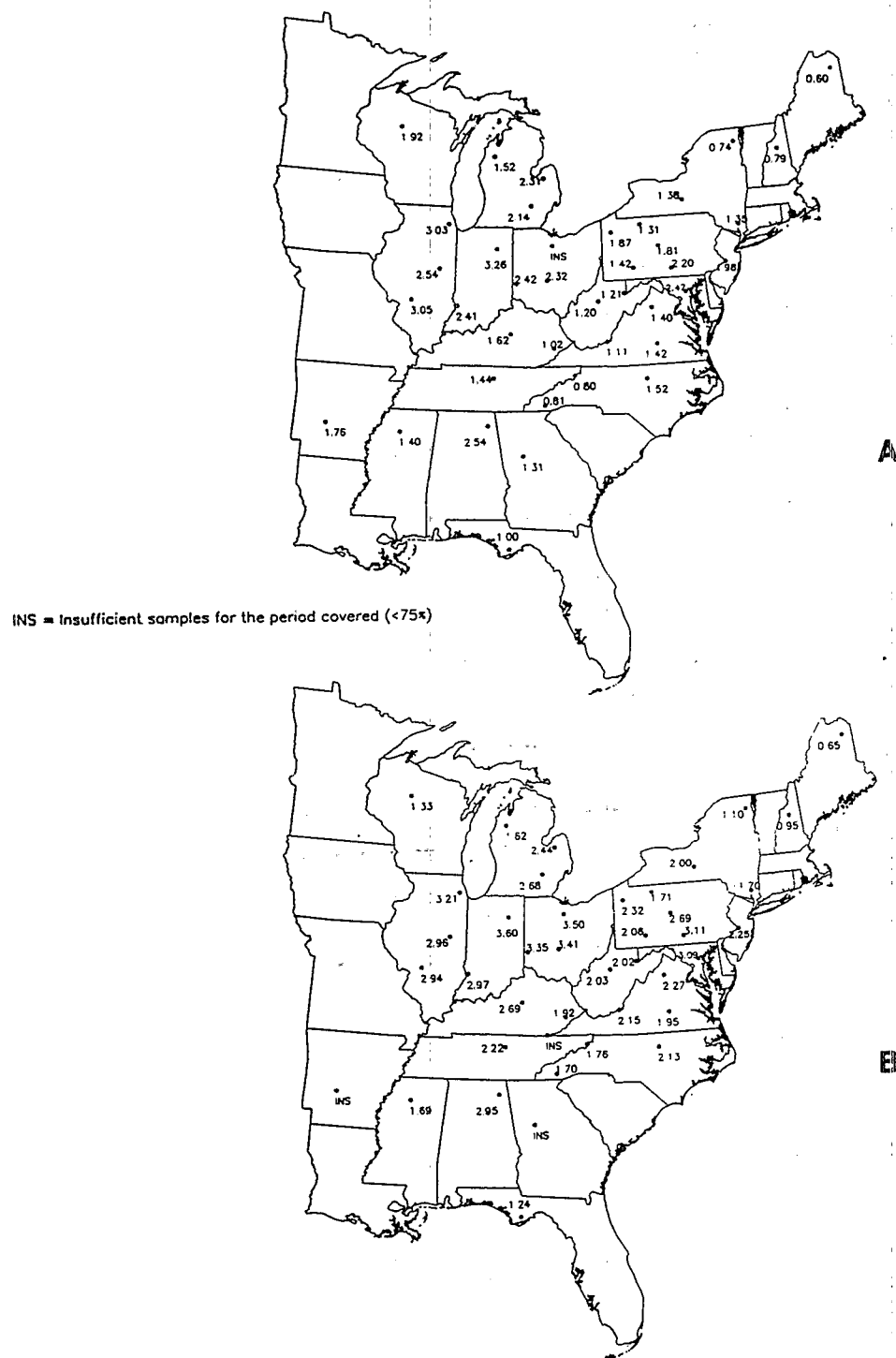
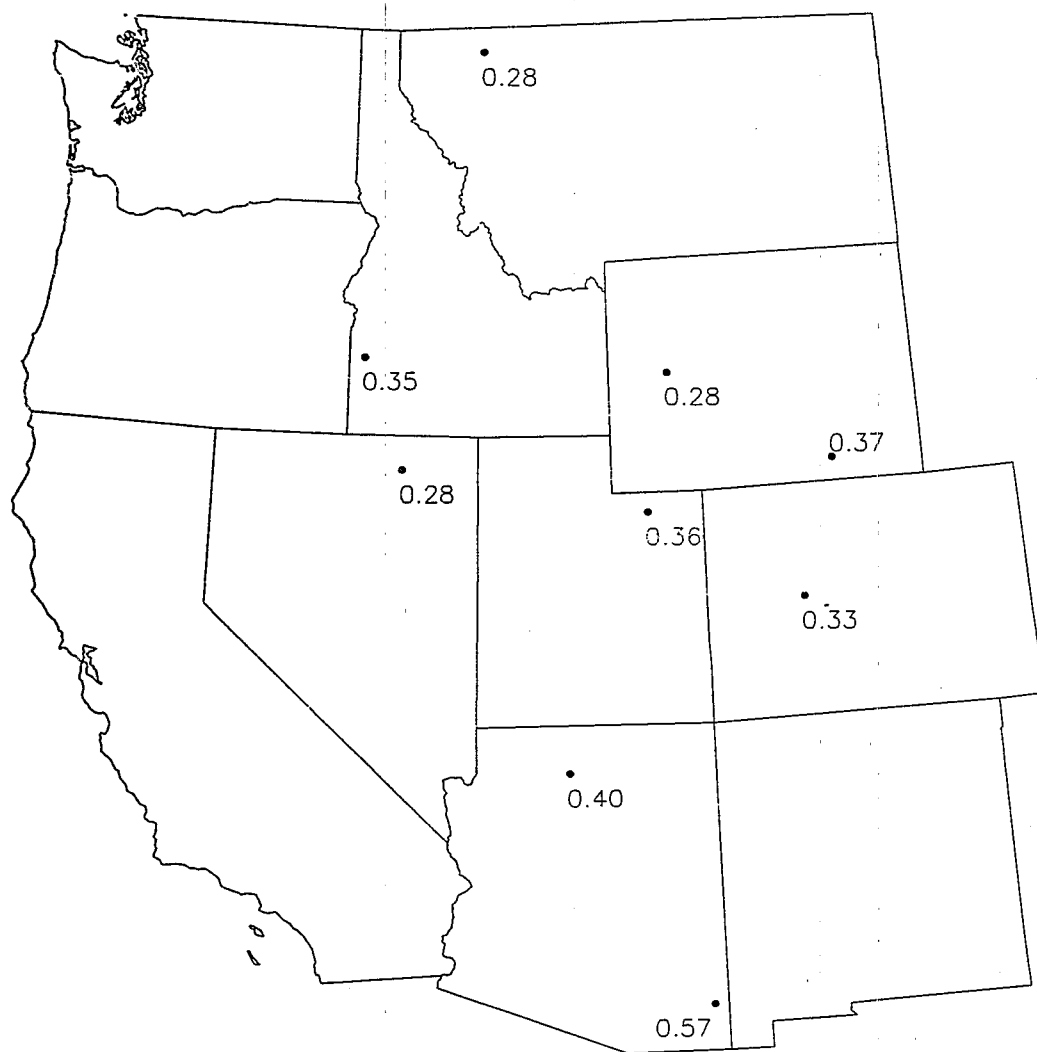


Figure 28. Average NH_4^+ concentrations ($\mu\text{g}/\text{m}^3$) for the first (A) and second (B) quarter 1989



INS = Insufficient samples for the period covered (<75%)

Figure 30. Average NH_4^+ concentrations ($\mu\text{g}/\text{m}^3$) for western NDDN sites, combined third and fourth quarters 1989

average value ($0.28 \mu\text{g}/\text{m}^3$) occurs in Montana, Wyoming, and Nevada. The overall pattern suggests a weak north-south gradient for the reporting period. Since none of the western sites is agricultural in nature, the apparent gradient could be a reflection of temperature-dependent emission rates of NH_3 . Alternatively, it could simply be due to chemical association with SO_4^{2-} aerosols.

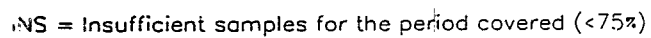
4.2.4 HNO_3

Annual averages for HNO_3 (Figure 31) exhibit a maximum concentration of approximately $3.6 \mu\text{g}/\text{m}^3$ in southeastern Pennsylvania (Site 128) and a minimum of $0.7 \mu\text{g}/\text{m}^3$ in northern Maine (Site 135). Concentrations in excess of $3.0 \mu\text{g}/\text{m}^3$ occur in two groups of three sites. The first group is located in central Kentucky (Site 129) and Ohio (Sites 114 and 122); the other group is located in an arc extending from northern Virginia (Site 118) through Pennsylvania and into New Jersey (Site 144). The majority of NDDN sites fall in the range of 2.0 to $3.0 \mu\text{g}/\text{m}^3$. Only six sites exhibit average concentrations of $1.0 \mu\text{g}/\text{m}^3$ or less. Four of these sites are located in the northern and southern extremes of the network (i.e., Wisconsin, Maine, New Hampshire, and Florida). In contrast, two of the sites with lowest concentrations are located near the geographic center of the network in eastern Kentucky (Site 121) and southwestern North Carolina (Site 137).

The overall pattern of HNO_3 might be influenced by terrain as much or more than other factors (e.g., emissions). Sites with the highest average values have good exposure to wind flow (fetch), while those sites with the lowest values typically have poor exposure, due mainly to complex terrain. For a species with a large deposition velocity (such as HNO_3), the microclimate in regions of complex terrain could produce local variability in atmospheric concentrations.

Quarterly data show that HNO_3 concentrations are relatively constant from season to season (see Figures 32 and 33). For example, quarterly averages in southeastern Pennsylvania, the site with the highest annual average, vary only over a range of $1.2 \mu\text{g}/\text{m}^3$. The majority of sites exhibit an even narrower range. For the 41 eastern sites, averages range from roughly $1.9 \mu\text{g}/\text{m}^3$ during the fourth quarter to $2.5 \mu\text{g}/\text{m}^3$ during the second quarter. Thus, seasonal variability is much less than and slightly out of phase with SO_4^{2-} (i.e., another secondary pollutant).

Results for the western region indicate concentrations that are somewhat lower than the lowest values observed in the east (see Figure 34). Exceptions to this are the two Arizona sites (Sites 167 and 174), which exhibit semiannual averages similar to those in New England, Florida, and Wisconsin. In conjunction with data for other species, these observations suggest the Arizona sites may be influenced by local emissions and/or long-range transport from neighboring California and Mexico.



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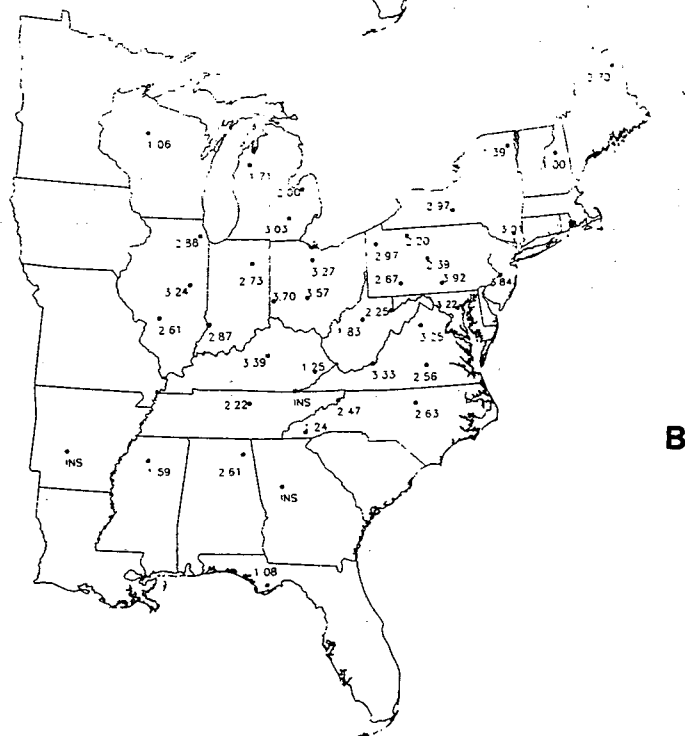
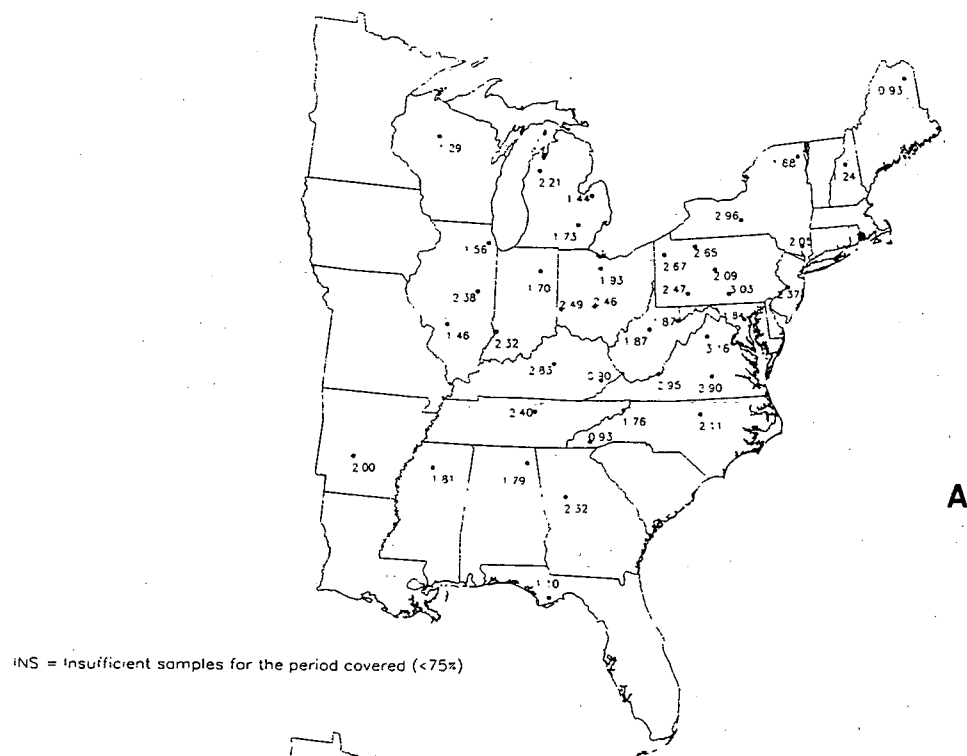
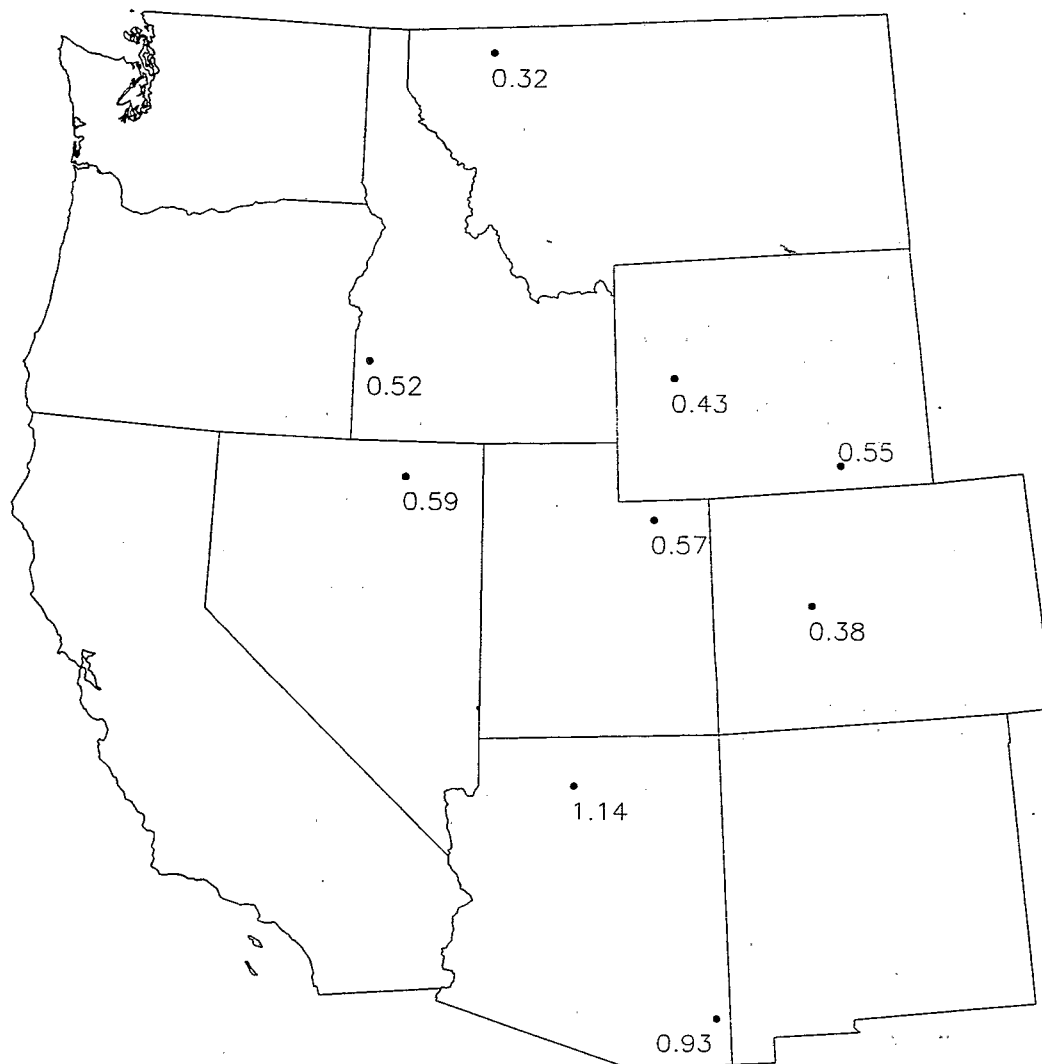


Figure 32. Average HNO₃ concentrations (μg/m³) for the first (A) and second (B) quarter 1989



INS = Insufficient samples for the period covered (<75%)

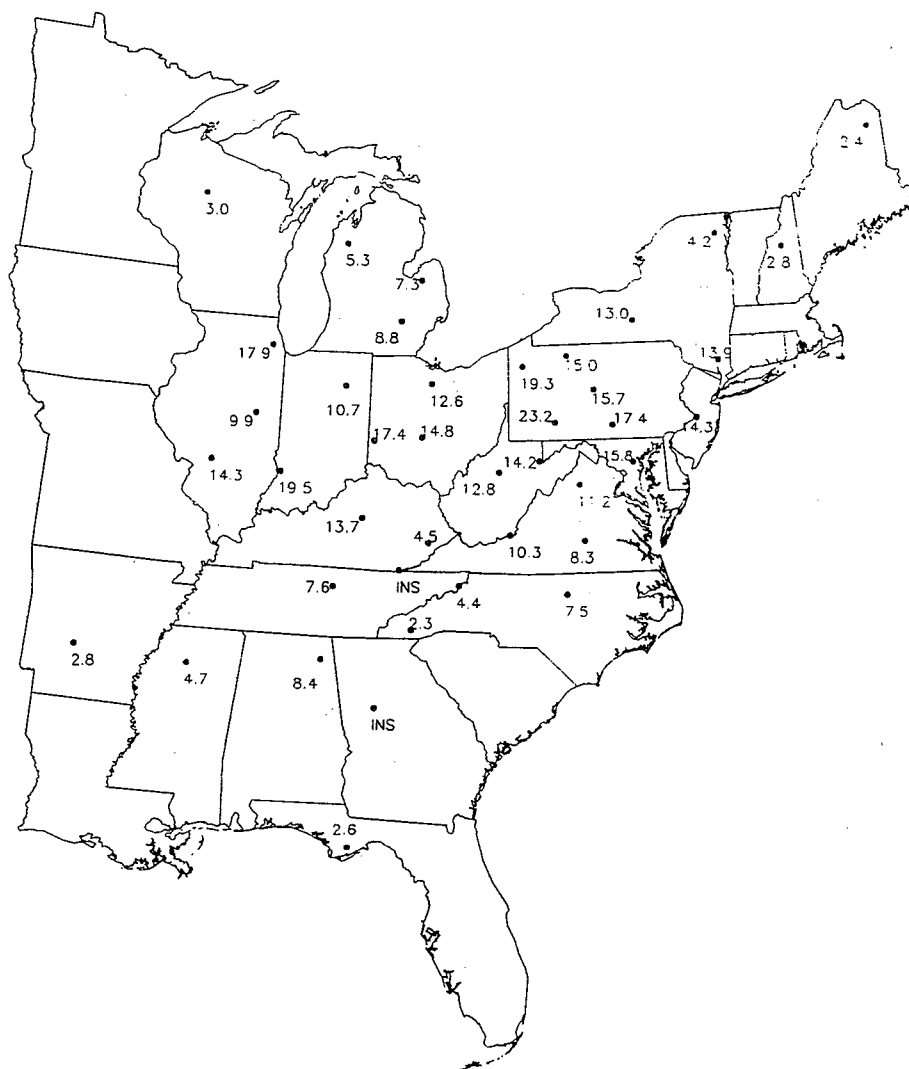
Figure 34. Average HNO_3 concentrations ($\mu\text{g}/\text{m}^3$) for western NDDN sites, combined third and fourth quarters 1989

4.2.5 SO_2

Annual average data for SO_2 range from $23.2 \mu\text{g}/\text{m}^3$ in southwestern Pennsylvania (Site 117) to $2.4 \mu\text{g}/\text{m}^3$ in Maine (Site 135) (see Figure 35). Concentrations of $15 \mu\text{g}/\text{m}^3$ or greater occur in a small area encompassing Pennsylvania and Maryland, as well as at isolated sites in northern Illinois, southern Indiana, and western Ohio. A much larger area extending from Kentucky and Indiana eastward to New York exhibits concentrations in the range of 10 to $15 \mu\text{g}/\text{m}^3$. Sharp concentration gradients occur from Pennsylvania to northern New York, from the lower midwest to upper midwest, and around isolated sites in Kentucky and North Carolina. As suggested earlier for HNO_3 , relatively rapid dry deposition of SO_2 could account for large differences (i.e., a factor of 3) between rolling terrain sites in central Kentucky, central Tennessee, central North Carolina, and neighboring complex terrain sites in eastern Kentucky and western North Carolina. Relatively low emission densities for SO_2 in the central Appalachian Mountains also might account for low SO_2 concentrations in Kentucky and North Carolina.

Inspection of quarterly averages shows dramatic changes in concentrations from season to season (see Figures 36 and 37). Domainwide mean concentrations are nearly a factor of 3 higher in the first quarter ($16.2 \mu\text{g}/\text{m}^3$) than in the third quarter ($6.2 \mu\text{g}/\text{m}^3$). Despite large relative changes in concentrations, the locus of peak concentrations remains more or less stationary from season to season. In general, the highest values occur in western Pennsylvania (Sites 113 and 117) and at source-influenced sites in Illinois and Indiana. Another persistent feature of the SO_2 field is marked depressions at complex terrain sites in Kentucky and North Carolina. As suggested previously, this appears to be the result of meteorological isolation of these sites.

Concentration data for the western sites range from $1.8 \mu\text{g}/\text{m}^3$ in southern Arizona (Site 167) to $0.4 \mu\text{g}/\text{m}^3$ in central Colorado (Site 161) and northern Nevada (Site 164) and southern Idaho (Site 163) (see Figure 38). Consistent with the other species measured, relatively high concentrations at the Arizona site appear to be attributable to large point sources in the southwest or Mexico. Despite the absence of point sources within 50 km of NDDN sites, intermediate SO_2 concentrations in Montana and eastern Wyoming appear to reflect small-scale industrial activities within their respective airsheds. Low SO_2 concentrations in Nevada (Site 164) and Colorado (Site 161), in turn, suggest that sites in the Great Basin and central Rocky Mountains are isolated from local or regional emissions.



INS = Insufficient samples for the period covered (<75%)

Figure 35. Annual average SO_2 concentrations ($\mu\text{g}/\text{m}^3$) for the eastern United States during 1989

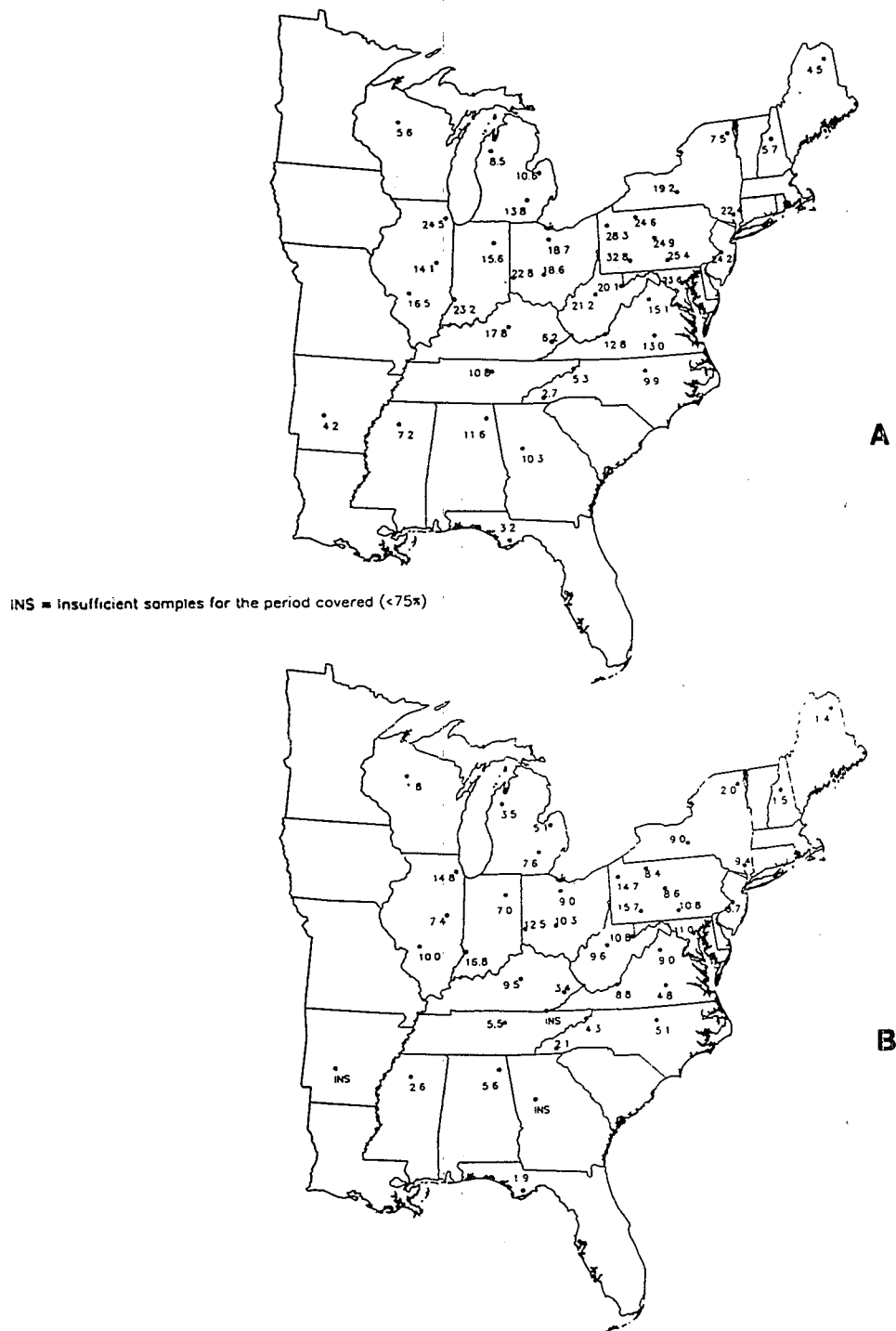
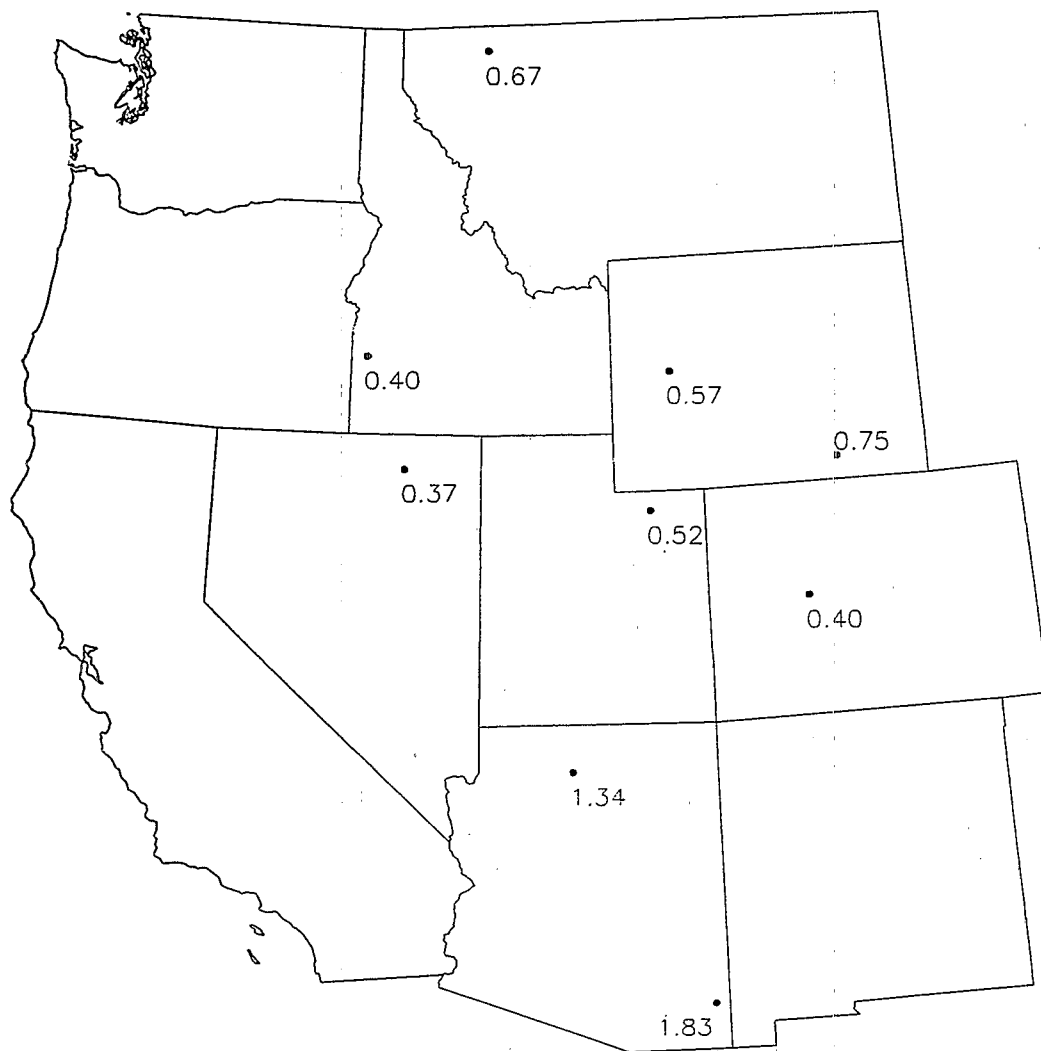


Figure 36. Average SO_2 concentrations ($\mu\text{g}/\text{m}^3$) for the first (A) and second (B) quarter 1989



NS = insufficient samples for the period covered (<75%)

Figure 38. Average SO₂ concentrations ($\mu\text{g}/\text{m}^3$) for western NDDN sites, combined third and fourth quarters 1989

4.2.6 Day Versus Night Concentration Data

Day/night filter pack samples were collected at NDDN sites through September 1989 to determine whether diurnal variations could affect the uncertainty of dry deposition estimates. Results are summarized in this section for the period October 1988 through September 1989 for selected sites that exemplify the day/night variability observed throughout the network.

Day/night concentration data for SO_4^{2-} , NO_3^- , NH_4^+ , HNO_3 , total NO_3^- (i.e., NO_3^- plus HNO_3), and SO_2 are tabulated, by quarter, for 19 NDDN sites in Tables 9 through 14. Data for SO_4^{2-} show appreciable seasonality in day/night concentration differences. Results for fourth quarter 1988 and first quarter 1989 (approximately equivalent to fall and winter, respectively) show nearly identical averages for day and night at virtually all sites. During this period, only two sites exhibited statistically significant day/night differences. In both cases, differences were detected during the fall, and day values were higher than night values by $0.3 \mu\text{g}/\text{m}^3$, or about 10 percent.

During second and third quarter 1989 (spring and summer, respectively), differences become increasingly more pronounced. Daytime concentrations during the summer, for example, are typically $2.0 \mu\text{g}/\text{m}^3$ greater than those at night and are, with only two exceptions, statistically significant.

Results for the presumptive aerosol species NO_3^- and NH_4^+ also show relatively low day/night variability. For NO_3^- , day/night excursions occur primarily during winter and spring at a few midwestern sites. In this case, concentrations at night are typically greater than those during the day, frequently by $1.0 \mu\text{g}/\text{m}^3$ or more. This behavior is not unexpected, based on the temperature dependence of the NH_4NO_3 equilibrium with NH_3 and HNO_3 . If NH_4NO_3 is forming at night, it is not clear why the behavior of NH_4^+ does not follow that of NO_3^- more closely. One explanation for this behavior is that variability in ammonium sulfate (or bisulfate) concentrations obscures any day/night variability in NH_4NO_3 .

Data for HNO_3 and SO_2 show more frequent and pronounced day/night differences than the aerosol species. Concentrations of HNO_3 are lower at night for nearly every site-season combination. This is especially apparent during summer, when all sites show statistically significant nocturnal reductions ranging from 35 to 80 percent. Given the high affinity of HNO_3 for virtually any surface, nocturnal depletion is not surprising. However, day/night differences of this magnitude imply a shallow nocturnal boundary layer or minimal nocturnal production rates of HNO_3 (e.g., from N_2O_5) or both.

TABLE 9. DAY (D) VERSUS NIGHT (N) CONCENTRATIONS OF PARTICULATE SO_4^{2-}
FOR SELECTED SITES

Region	State	Site	Quarter							
			04/88		01/89		02/89		03/89	
			D	N	D	N	D	N	D	N
Northeast	ME	135	N/O	N/O	2.4	2.4	2.9	2.6	3.4	3.0
	NY	104	3.4	3.4	3.8	4.0	5.9*	5.1	8.1 ⁺	6.1
	PA	106	3.9	3.7	4.2	4.3	7.0*	5.9	10.5 ⁺	8.2
	PA	117	3.8	3.5	4.4	4.4	7.4	7.1	13.8 ⁺	10.1
	PA	128	3.8*	3.5	4.9	4.7	8.3*	7.2	11.7*	10.0
	VA	108	3.1	2.9	4.3	4.3	6.8*	5.7	12.2 ⁺	9.6
	VA	120	3.7	3.7	3.5	3.7	7.4	7.8	11.4*	10.3
	WV	119	3.2	3.2	4.1	4.2	7.6	7.0	13.1 ⁺	8.9
Midwest	IL	130	3.6	3.3	4.5	4.5	7.3	7.3	11.4 ⁺	9.8
	IN	133	3.6	3.7	4.7	4.7	7.8	7.3	10.6 ⁺	9.1
	KY	121	3.0*	2.7	3.8	3.8	7.7*	6.7	11.2 ⁺	8.6
	KY	129	3.5	3.5	4.6	4.2	8.7*	8.1	14.4 ⁺	12.5
	MI	115	2.8	2.7	3.7	4.0	7.0*	6.1	8.9*	8.1
	OH	114	3.6	3.5	4.7	4.6	8.8	8.2	13.6 ⁺	11.3
Southeast	GA	153	4.2	3.8	3.9	3.7	7.5*	6.3	10.0 ⁺	8.4
	NC	101	3.8	3.6	3.9	4.0	7.2 ⁺	6.1	9.5 ⁺	7.4
	NC	137	2.8	2.8	2.5	2.6	6.2	6.2	9.0 ⁺	7.6
West	MT	168	N/O	N/O	0.59	0.65	0.74	0.74	0.73	0.69
	WY	165	N/O	N/O	0.42	0.42	0.70	0.67	0.95*	0.89

Note: N/O = not operational.

*Day greater than night at the 95-percent confidence level.

⁺Day greater than night at the 99-percent confidence level.

Source: ESE, 1990.

TABLE 10. DAY (D) VERSUS NIGHT (N) CONCENTRATIONS OF PARTICULATE NH_4^+
FOR SELECTED SITES

Region	State	Site	Quarter							
			04/88		01/89		02/89		03/89	
			D	N	D	N	D	N	D	N
Northeast	ME	135	N/O	N/O	0.6	0.6	0.7	0.6	0.9	0.8
	NY	104	1.1	1.1	1.3	1.4**	1.7	1.6	2.0	1.8
	PA	106	1.6	1.7	1.7	2.0	2.7	2.7	3.3	3.4
	PA	117	1.2	1.2	1.3	1.5**	1.9	2.2	2.5	2.7
	PA	128	1.6	1.5	2.2	2.2	3.3	3.0	3.8	3.5
	VA	108	1.1	1.0	1.4	1.5**	2.0	1.9	2.6	2.7
	VA	120	1.1	1.1	1.1	1.2	2.2	2.1	2.2 ⁺	2.0
	WV	119	1.0	1.1**	1.2	1.2	2.0	2.2**	2.7	2.5
Midwest	IL	130	1.6	1.8	2.4	2.7**	2.7	3.2**	3.4	3.6
	IN	133	1.9	2.2**	3.1	3.5**	3.4	3.8**	3.9	3.6
	KY	121	0.9*	0.8	1.0	1.0	1.9	1.9	2.1	2.1
	KY	129	1.4	1.5	1.6	1.7	2.7	2.8	3.5	3.4
	MI	115	1.5	1.5	2.0	2.4**	2.6	2.7	2.9	2.9
	OH	114	1.5	1.8**	2.1	2.5**	3.2	3.7	3.6	4.0
Southeast	GA	153	1.4	1.3	1.3	1.4	1.9	1.9	2.7	2.6
	NC	101	1.3	1.3	1.4	1.5	2.2	2.1	2.3	2.3
	NC	137	0.8	0.8	0.8	0.8	1.6	1.8	1.9	1.9
West	MT	168	N/O	N/O	0.24	0.23	0.27	0.28	0.28	0.30
	WY	165	N/O	N/O	0.15	0.16	0.28	0.30	0.38	0.39

Note: N/O = not operational.

*Day greater than night at the 95-percent confidence level.

⁺Day greater than night at the 99-percent confidence level.

**Night greater than day at the 95-percent confidence level.

Source: ESE, 1990.

TABLE 11. DAY (D) VERSUS NIGHT (N) CONCENTRATIONS OF PARTICULATE NO₃⁻
FOR SELECTED SITES

Region	State	Site	Quarter							
			04/88		01/89		02/89		03/89	
			D	N	D	N	D	N	D	N
Northeast	NE	135	N/O	N/O	0.4	0.4	0.3	0.3	0.2	0.2
	NY	104	0.6	0.5	1.1	1.3 ⁺	0.4	0.4	0.5*	0.3
	PA	106	1.4	1.6	2.0	2.2	0.9	1.9 ⁺	0.8	1.0
	PA	117	0.6	0.7	0.7	0.8	0.4	0.4	0.3*	0.2
	PA	128	1.7	1.8	2.6	2.6	1.4	1.4	0.9	1.2
	VA	108	0.5	0.7	0.6	0.8	0.4	0.4	0.4	0.2
	VA	120	0.7	0.9 ⁺	0.6	0.8	0.6	0.7	0.4	0.3
	WV	119	0.4	0.5	0.5	0.4	0.3	0.3	0.2	0.2
Midwest	IL	130	2.4	3.4 ⁺	3.5	4.6 ⁺	2.2	3.6 ⁺	1.1	1.5 ⁺
	IN	133	2.8	3.9 ⁺	5.5	6.7	2.7	4.7 ⁺	1.1	1.8 ⁺
	KY	121	0.8*	0.6	0.9*	0.7	0.6	0.6	0.4*	0.2
	KY	129	1.4	1.5	1.1	1.4 ⁺	1.1	1.4 ⁺	0.4	0.5
	MI	115	2.1	2.3	3.3	4.0 ⁺	1.5	2.3 ⁺	0.8	0.8
	OH	114	1.8	2.3 ⁺	2.4	3.3 ⁺	1.4	3.0 ⁺	0.7	1.2 ⁺
Southeast	GA	153	0.6	0.7 ⁺	0.6	0.6	N/O	N/O	0.4*	0.2
	NC	101	0.9	0.8	0.7	0.9 ⁺	0.6	0.6	0.6*	0.4
	NC	137	0.3	0.2	0.3	0.2	0.3*	0.2	0.2*	0.1
West	MT	168	N/O	N/O	0.19	0.26 ⁺	0.15	0.13	0.15	0.13
	WY	165	N/O	N/O	0.16	0.17	0.27	0.22	0.25*	0.22

Note: N/O = not operational.

*Day greater than night at the 95-percent confidence level.

⁺Night greater than day at the 95-percent confidence level.

Source: ESE, 1990.

TABLE 12. DAY (D) VERSUS NIGHT (N) CONCENTRATIONS OF
HNO₃ (μg/m³) FOR SELECTED SITES

Region	State	Site	Quarter							
			04/88		01/89		02/89		03/89	
			D	N	D	N	D	N	D	N
Northeast	NE	135	N/O	N/O	1.0	1.0	0.8 ⁺	0.5	0.7 ⁺	0.5
	NY	104	2.1*	1.5	2.3*	1.8	3.8 ⁺	2.2	3.4 ⁺	1.5
	PA	106	2.1	1.8	2.2	2.0	3.3 ⁺	1.5	3.6 ⁺	1.8
	PA	117	2.2*	1.4	2.9 ⁺	2.0	3.6 ⁺	1.8	4.1 ⁺	1.3
	PA	128	2.5	2.2	3.0	3.1	4.7 ⁺	3.3	5.3 ⁺	3.2
	VA	108	2.3	2.0	3.0	2.8	3.4 ⁺	1.8	3.5 ⁺	1.5
	VA	120	2.6	3.0**	2.5	3.4**	3.2	3.5**	2.9 ⁺	2.3
	WV	119	1.5 ⁺	0.7	2.5 ⁺	1.3	2.8 ⁺	1.0	2.2 ⁺	0.5
Midwest	IL	130	1.3*	0.7	2.9*	1.7	4.3 ⁺	2.2	5.2 ⁺	2.3
	IN	133	1.2	0.8	2.1	1.3	3.9 ⁺	1.6	4.4 ⁺	1.5
	KY	121	0.8 ⁺	0.4	1.2 ⁺	0.6	1.9 ⁺	0.6	1.4 ⁺	0.3
	KY	129	2.1	1.6	3.2*	2.6	4.3 ⁺	2.5	5.1 ⁺	2.2
	MI	115	1.2	1.0	1.9	1.6	4.0 ⁺	2.0	4.4 ⁺	1.6
	OH	114	2.0*	1.3	2.9*	2.0	4.8 ⁺	2.4	5.4 ⁺	2.5
Southeast	GA	153	2.4 ⁺	1.3	2.4	2.2	N/O	N/O	3.1 ⁺	1.2
	NC	101	2.4 ⁺	1.3	2.4 ⁺	1.4	3.7 ⁺	1.6	3.6 ⁺	1.4
	NC	137	1.1 ⁺	0.6	1.2 ⁺	0.7	1.7 ⁺	0.8	1.3 ⁺	0.3
West	MT	168	N/O	N/O	0.41	0.46	0.39 ⁺	0.21	0.46 ⁺	0.18
	WY	165	N/O	N/O	0.33 ⁺	0.24	0.41 ⁺	0.27	0.95 ⁺	0.52

Note: N/O = not operational.

*Day greater than night at the 95-percent confidence level.

⁺Day greater than night at the 99-percent confidence level.

**Night greater than day at the 95-percent confidence level.

Source: ESE, 1990.

TABLE 13. DAY (D) VERSUS NIGHT (N) CONCENTRATIONS OF TOTAL NO₃
FOR SELECTED SITES

Region	State	Site	Quarter							
			04/88		01/89		02/89		03/89	
			D	N	D	N	D	N	D	N
Northeast	NE	135	N/O	N/O	1.4	1.4	1.1*	0.8	0.9*	0.6
	NY	104	2.7	2.2	3.3	3.2	4.1 ⁺	2.6	3.8 ⁺	1.8
	PA	106	3.5	3.3	4.1	4.3	4.2 ⁺	3.3	4.4 ⁺	2.8
	PA	117	2.8	2.1	3.6*	2.9	4.0 ⁺	2.2	4.3 ⁺	1.4
	PA	128	4.2	4.0	5.6	5.6	6.0 ⁺	4.6	6.1 ⁺	4.4
	VA	108	2.8	2.7	3.5	3.5	3.8 ⁺	2.2	3.8 ⁺	1.7
	VA	120	3.3	3.9	3.1	4.1**	3.8	4.1	3.3 ⁺	2.6
	WV	119	2.0	1.3	2.9 ⁺	1.7	3.0 ⁺	1.2	2.4 ⁺	0.7
Midwest	IL	130	3.6	4.1	6.4	6.1	6.4	5.8	6.3 ⁺	3.8
	IN	133	3.9	4.7	7.5	8.0	6.5	6.2	5.4 ⁺	3.3
	KY	121	1.6	1.0	2.0 ⁺	1.3	2.5 ⁺	1.1	1.8 ⁺	0.6
	KY	129	3.5	3.1	4.2	3.9	5.4 ⁺	3.8	5.4 ⁺	2.7
	MI	115	3.3	3.3	5.1	5.6	5.4*	4.3	5.2 ⁺	2.3
	OH	114	3.8	3.6	5.3	5.3	6.1	5.3	6.0 ⁺	3.6
Southeast	GA	153	3.0	2.0	3.0	2.8	N/O	N/O	3.4 ⁺	1.4
	NC	101	3.2*	2.2	3.1*	2.3	4.2 ⁺	2.2	4.2 ⁺	1.8
	NC	137	1.4	0.8	1.4 ⁺	0.9	2.0 ⁺	0.9	1.5 ⁺	0.5
West	MT	168	N/O	N/O	0.60	0.70	0.54 ⁺	0.34	0.60 ⁺	0.30
	WY	165	N/O	N/O	0.48	0.41	0.67 ⁺	0.49	1.18 ⁺	0.73

Note: N/O = not operational.

*Day greater than night at the 95-percent confidence level.

⁺Day greater than night at the 99-percent confidence level.

**Night greater than day at the 95-percent confidence level.

Source: ESE, 1990.

TABLE 14. DAY (D) VERSUS NIGHT (N) CONCENTRATIONS OF SO₂
($\mu\text{g}/\text{m}^3$) FOR SELECTED SITES

Region	State	Site	Quarter							
			04/88		01/89		02/89		03/89	
			D	N	D	N	D	N	D	N
Northeast	NE	135	N/O	N/O	4.7	4.5	1.8 ⁺	0.9	1.0 ⁺	0.8
	NY	104	16.5 ⁺	11.7	24.8*	19.6	12.4 ⁺	7.0	10.9 ⁺	4.3
	PA	106	19.5*	15.8	28.1	21.1	10.4 ⁺	6.9	9.1 ⁺	5.6
	PA	117	28.1 ⁺	18.8	35.7*	30.0	21.0 ⁺	11.4	16.1 ⁺	7.0
	PA	128	16.7	17.3	26.8*	24.1	10.7	10.9	9.3	8.3
	VA	108	14.0 ⁺	10.8	14.6*	11.5	6.3 ⁺	3.5	4.6 ⁺	2.4
	VA	120	14.2	14.7	12.7	13.0	7.6	9.9**	4.7	5.1
	WV	119	16.1 ⁺	7.1	26.8 ⁺	15.7	13.4 ⁺	5.5	9.0 ⁺	1.3
Midwest	IL	130	9.6*	6.2	15.1	12.8	8.5 ⁺	6.3	10.1 ⁺	6.4
	IN	133	11.3	10.5	17.3	15.1	7.7	6.3	7.5 ⁺	4.2
	KY	121	5.2 ⁺	2.5	8.3 ⁺	4.1	5.5 ⁺	1.3	2.5 ⁺	0.5
	KY	129	13.7*	10.8	19.1	16.4	11.0 ⁺	8.0	14.3 ⁺	6.8
	MI	115	8.0	7.4	15.0	12.6	8.2	6.9	6.6 ⁺	3.5
	OH	114	16.7*	12.6	21.1*	16.1	12.7 ⁺	8.0	15.0 ⁺	6.6
Southeast	GA	153	13.3*	6.6	10.8	9.8	N/O	N/O	7.4 ⁺	2.5
	NC	101	11.9 ⁺	9.0	11.2 ⁺	8.4	6.4 ⁺	3.9	4.6 ⁺	2.8
	NC	137	3.6*	2.2	3.3	2.2	2.9*	1.3	1.0 ⁺	0.4
West	MT	168	N/O	N/O	1.1	1.0	0.49	0.42	0.68 ⁺	0.33
	WY	165	N/O	N/O	0.41	0.36	0.46	0.47	0.87 ⁺	0.65

Note: N/O = not operational.

*Day greater than night at the 95-percent confidence level.

⁺Day greater than night at the 99-percent confidence level.

**Night greater than day at the 95-percent confidence level.

Source: ESE, 1990.

The day/night behavior of SO_2 is similar to that of HNO_3 . Statistically significant differences occur at most sites for most seasons, and the magnitude of the differences increases from winter to summer. Site 120, in southwestern Virginia, represents one exception to the previous pattern. In this case, day/night concentrations differ significantly only in the summer, with night averages greater than those during the day. As will be discussed later for O_3 , this phenomenon appears to be related to the unique circulation patterns around the mountaintop NDDN sites.

The fractional depletion of SO_2 at night frequently equals that of HNO_3 . This is especially apparent at complex terrain sites (such as Site 119), where day/night ratios are greater than 5.0 during the summer. One explanation for this behavior involves surface wetness via condensation. Although long-term average deposition velocities of HNO_3 are likely to be much greater than SO_2 , short-term deposition velocities are thought to be similar, if the surface is wet with dew. Inspection of limited surface wetness data from NDDN sites for the summer of 1989 suggests that dew occurs almost every night. The frequency of dew occurrences also appears to increase from flat and rolling terrain sites to sites in isolated valleys or hollows. Coupled with shallow nocturnal boundary layers, dew formation could be responsible for essentially complete depletion of SO_2 at night. Figure 39 illustrates weekly day/night concentrations of SO_2 at a complex terrain site (Site 119), a rolling terrain site (Site 129), and a mountaintop site (Site 120). Although day/night differences are apparent for the rolling terrain and mountaintop sites, nighttime SO_2 varies appreciably from week to week. In contrast, nighttime concentrations at the complex terrain site exhibit minimal week-to-week variability, especially during the summer months. An alternative explanation for the observed SO_2 could involve plume-like behavior. An unknown fraction of the long-term average SO_2 concentration could be due to brief concentration spikes. If this fraction is large, and if it occurs primarily during the day, then day/night concentration differences would occur in the absence of dry deposition. In this case, a stable nocturnal boundary layer would isolate the monitoring site from plumes aloft.

4.2.7 Aerosol Ion Balances

The analysis of NH_4^+ and base metal cations on Teflon® filters permits evaluation of various ionic relationships in aerosol samples. This section presents data comparing total measured cations (i.e., NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+}) with total measured anions (i.e., NO_3^- and SO_4^{2-}) and NH_4^+ with SO_4^{2-} . The first of these relationships is designed to evaluate whether there are significant unmeasured species in the samples collected and to provide insight into what those species, if any, might be. The second comparison (i.e., NH_4^+ versus SO_4^{2-}) focuses on the simultaneous behavior of what appear to be the dominant anionic and cationic species throughout NDDN. As a cautionary note, it should be

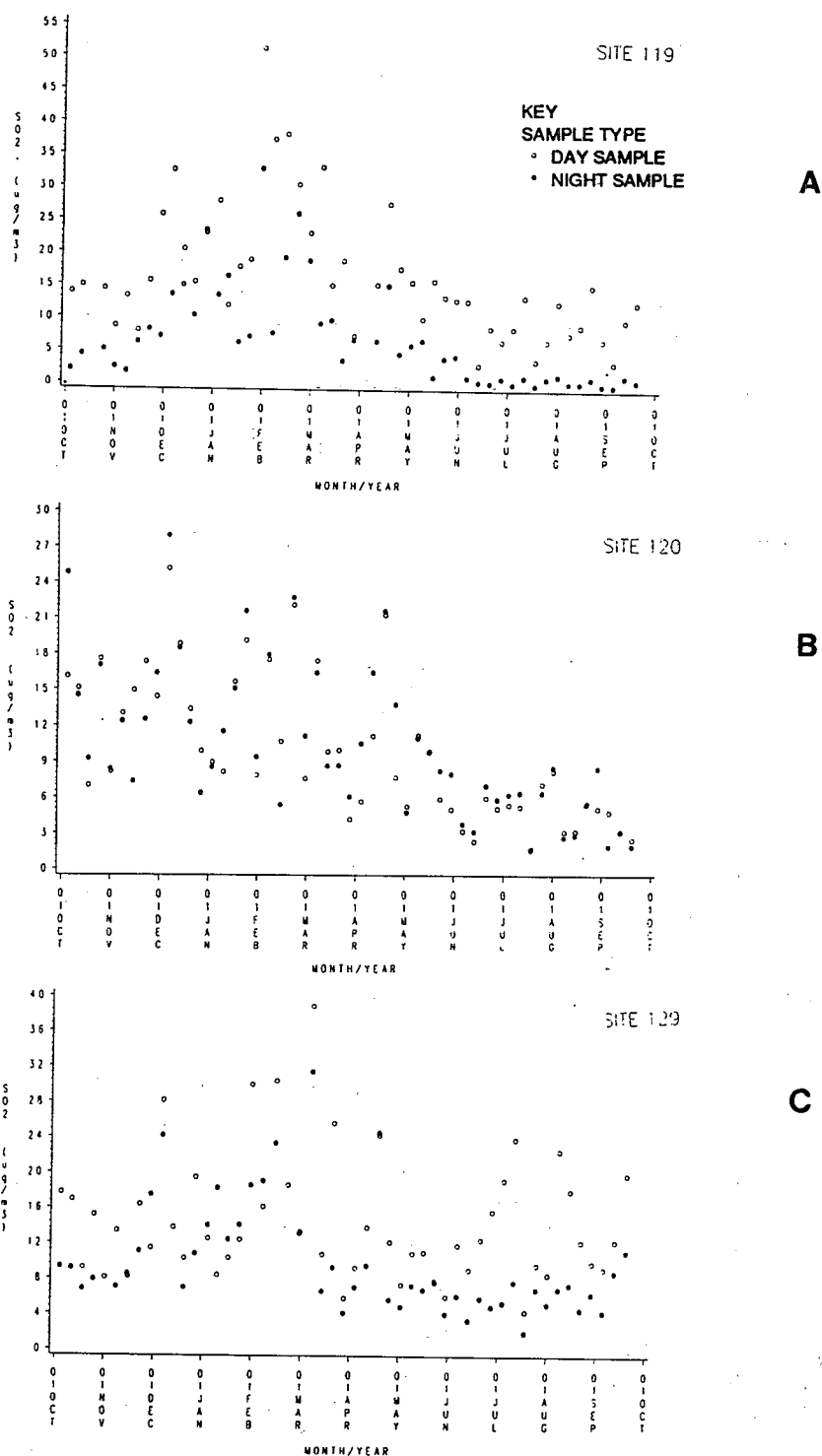


Figure 39. Weekly day/night SO₂ concentrations for sites in complex terrain (A), mountaintop (B), and rolling terrain (C), October 1988 through September 1989

recalled that the filter pack sampling approach used for NDDN does not unambiguously separate particles and gases and does not have a well characterized cutpoint for aerosol size. Thus, gas/aerosol interactions could be important and a wide range of aerosol sizes with widely differing chemical composition could be sampled by the current filter pack samples. Results should therefore be interpreted to reflect the chemical makeup of the filter extract, rather than as a definitive indication of aerosol chemistry at NDDN sites.

Ion balances, in nanoequivalents per cubic meter (neq/m^3), from Teflon® filter extracts at nine NDDN sites are illustrated in Figures 40 through 42. The sites presented in Figure 40 appear to be representative of the eastern seaboard (Site 108), forested northeast (Site 117), and agricultural midwest (Site 133). In general, the data for these sites indicate that SO_4^{2-} and NH_4^+ are the dominant anion and cation species, respectively, at both forested and agricultural sites in the eastern United States, and that the nature of the ion balances differs between forested and agricultural sites. The forested sites exhibit fairly minor ionic contribution for NO_3^- and the base metal cations and a clear excess of anions over cations. The agricultural midwestern site, in contrast, exhibits significant ionic contributions from NO_3^- , Mg^{2+} , and Ca^{2+} and an apparent excess of cations.

Results shown in Figure 41 suggest that similar relationships hold for forested sites in complex terrain (Site 119) and at high elevation (Site 120). Data for the urban-agricultural site in Maryland (Site 116) and the midwestern agricultural site exhibit similar relationships between cations and anions. Figure 42 shows ionic balances for relatively pristine sites in the northeast (Site 135) and the southeast (Site 156), as well as a typical western site (Site 165). Results for the eastern sites indicate nearly identical concentrations of anions and cations and, on a percentage basis, reduced dominance of NH_4^+ as the primary cation relative to other sites. For the western site, there is a clear excess of cations in the aerosol samples, with NH_4^+ comprising only about 50 percent of the total cations. Results from all three sites suggest that NO_3^- is a minor contributor to the overall ion balance.

The spatial variability of aerosol ion ratios is illustrated in Figure 43. Note that data for the eastern United States represent the period October 1988 through September 1989, while those for the western sites represent the period June through September 1989. Results indicate a general dichotomy between midwestern sites and the majority of northeastern and southeastern sites that apparently is related to agricultural activity. With only one exception, midwestern sites exhibit cation/anion ratios above unity; and with only six exceptions, northeastern and southeastern sites exhibit ratios below unity. Five of the six sites are located in agricultural or urban-agricultural areas, and the sixth (Site 121 in eastern Kentucky) is apparently influenced by

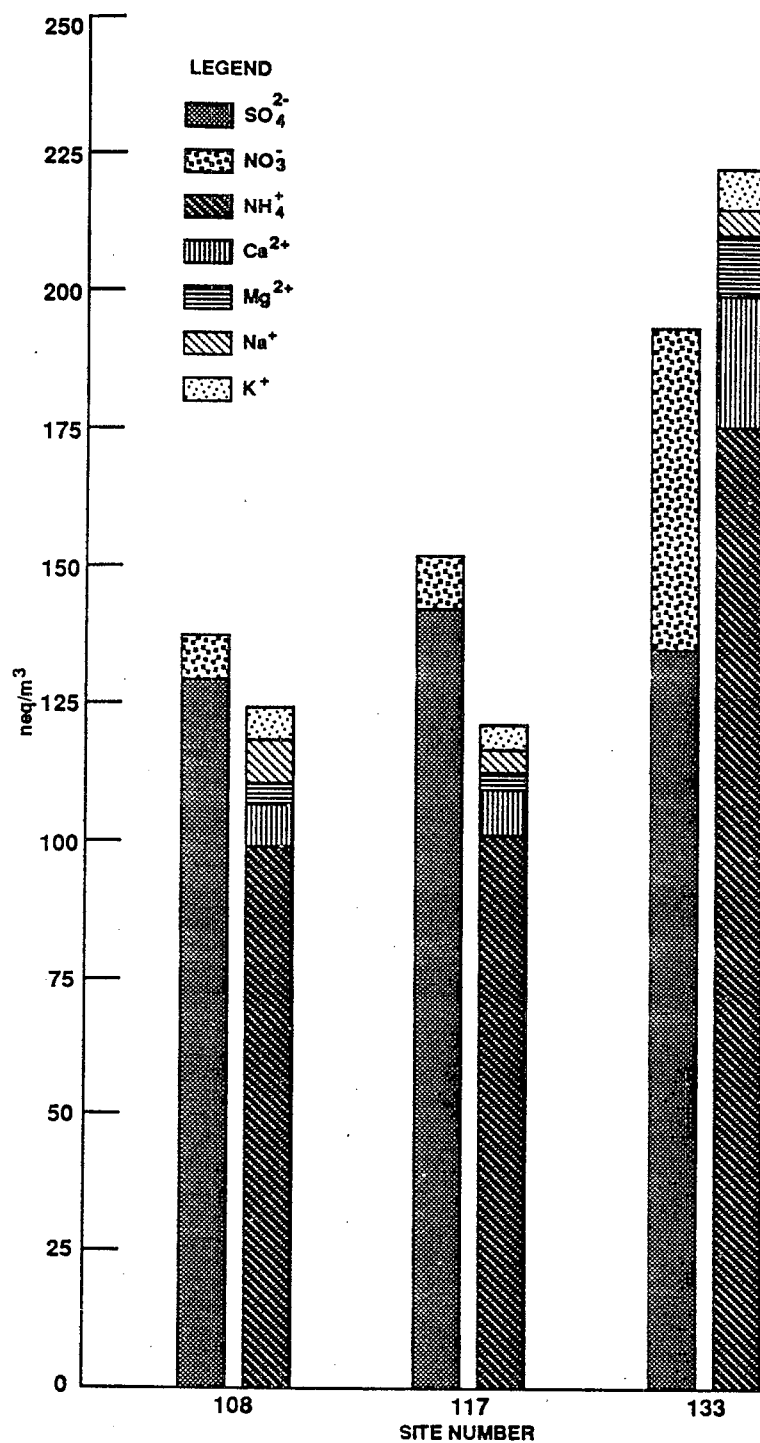


Figure 40. Aerosol ion balances for Sites 108, 117, and 133

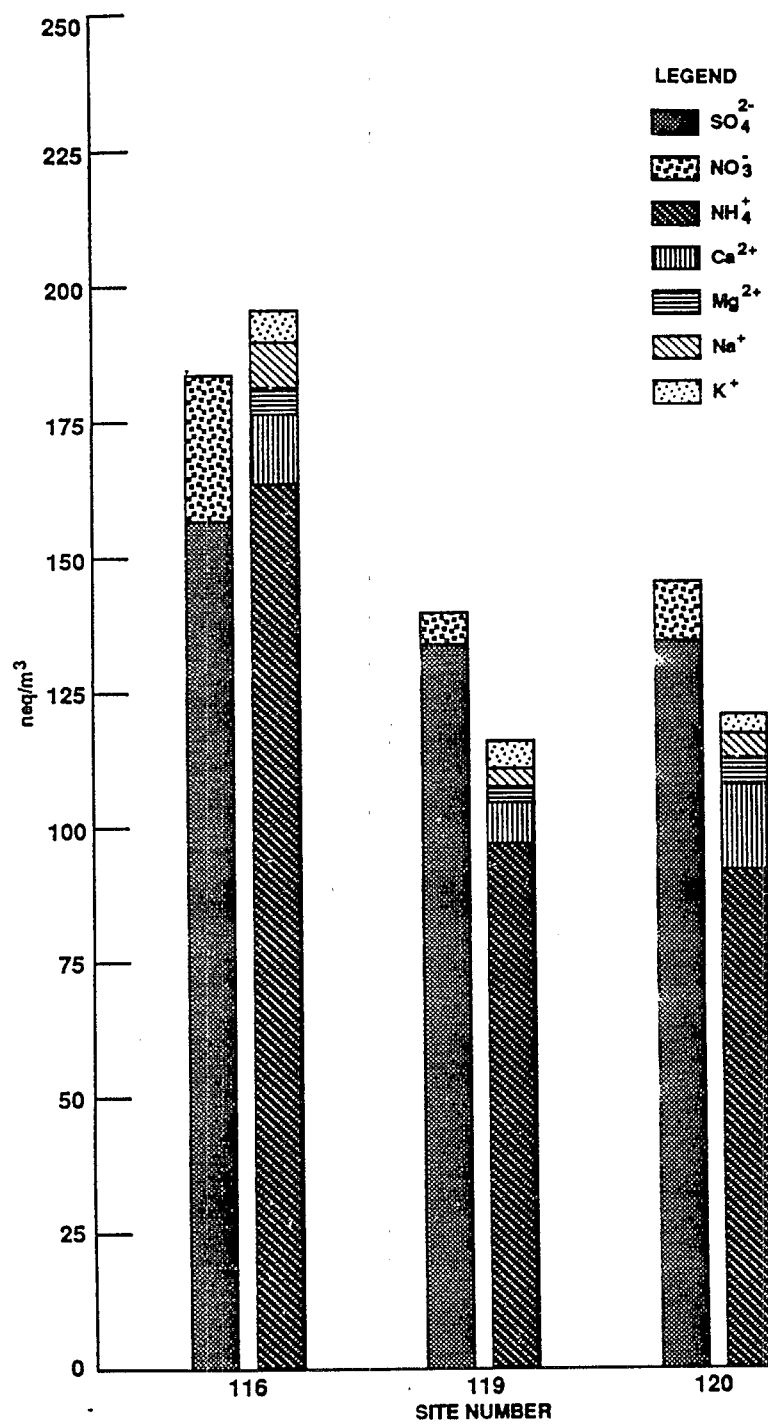


Figure 41. Aerosol ion balances for Sites 116, 119, and 120

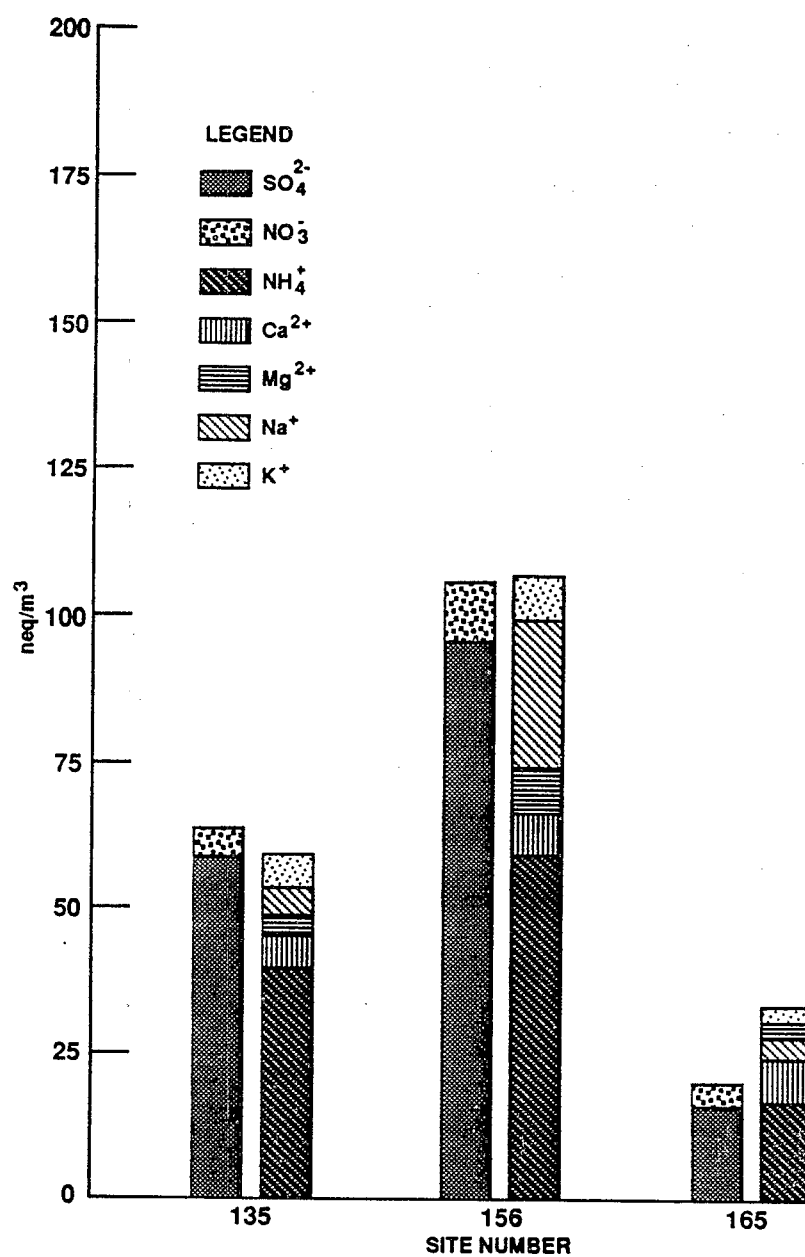


Figure 42. Aerosol ion balances for Sites 135, 156, and 165

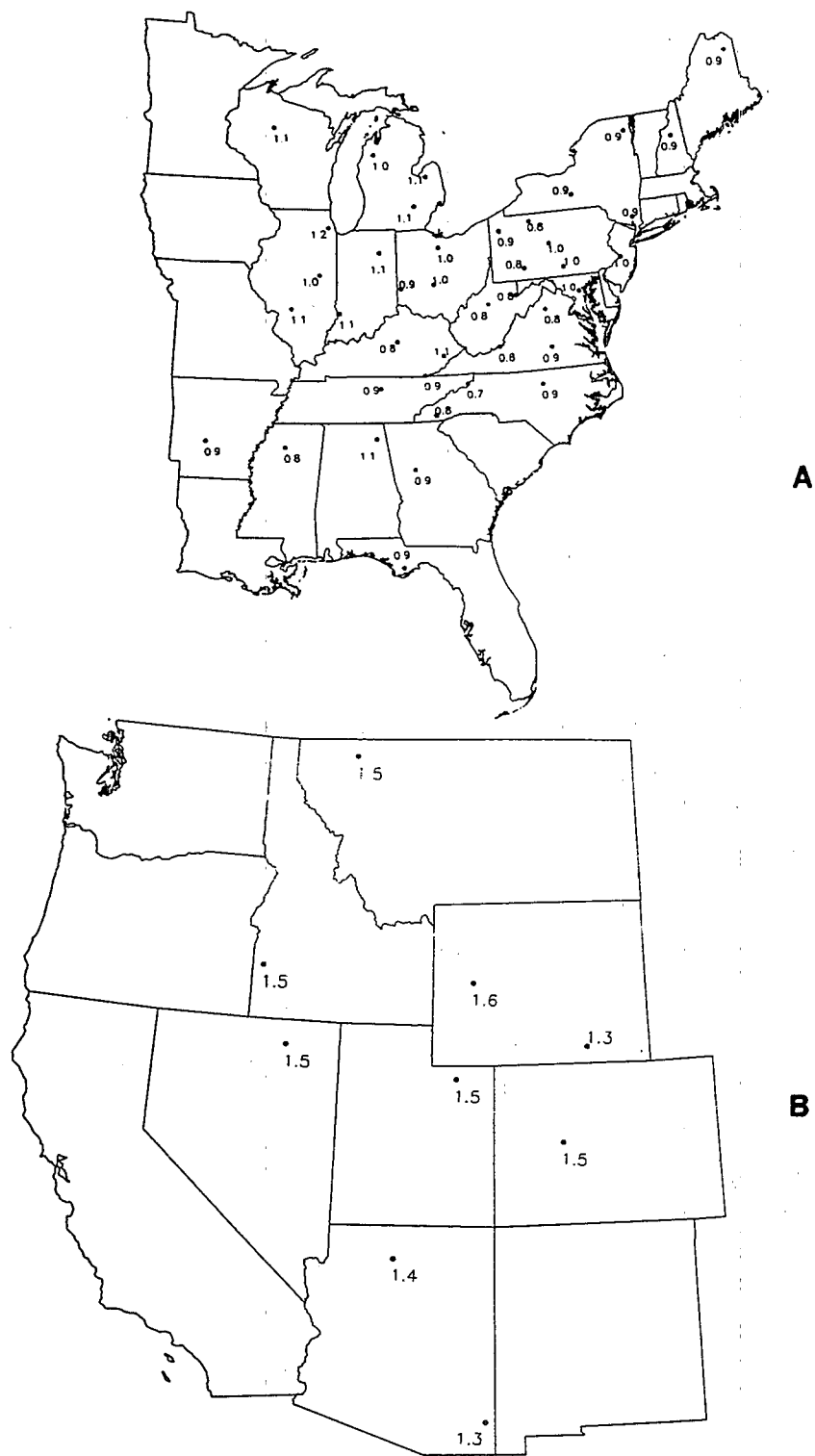


Figure 43. Aerosol cation/anion ratios for eastern (A) and western (B) NDDN sites

road dust from a coal mining operation. Western sites invariably show a substantial excess of cations over anions.

Although the previous relationships refer to average values taken over a year or a quarter, they are generally adhered to on a sample-by-sample basis. Figure 44 shows scattergrams of total anions versus total cations for weekly day, night, or composite samples taken at a northeastern site (Site 117), midwestern site (Site 133), and western site (Site 165). With few exceptions, samples from the midwestern and western sites exhibit ion ratios of 1.0 or greater. The northeastern site shows considerable scatter around a 1:1 relationship, but a clear tendency for ratios to fall below unity with increasing total anions. Periods of high concentration, therefore, appear to drive ion balances below unity at northeastern sites.

Ratios of NH_4^+ to SO_4^{2-} in aerosol samples are shown for all NDDN sites in Figure 45. Results show very similar spatial variability to those for the cation/anion ratios. This is not surprising, since NH_4^+ and SO_4^{2-} are the dominant cation and anion, respectively, at all NDDN sites. However, the similarity of ratios strongly suggests that the chemical composition of aerosols containing SO_4^{2-} control ion balances and ratios.

In the majority of northeastern sites, ion balances and $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios fall below unity, and an unmeasured cation (possibly H^+) must be present to satisfy electroneutrality conditions. For midwestern and western sites, cations are in excess, and one or more unmeasured anions (possibly HCO_3^- or CO_3^{2-}) must therefore be present. Unfortunately, the NDDN filter pack cannot definitively quantify certain atmospheric species (including H^+ and HCO_3^-) due to the potential for gas-particle interactions within the sampler itself.

4.2.8 1988 Versus 1989 Concentration Data

One of the principal objectives of the NDDN is to evaluate long-term trends in dry deposition rates and atmospheric concentrations. Since the network has recently been fully deployed, little historical data are available to evaluate trends. This section compares annual concentration data from 1988 and 1989 and determines whether interannual differences are statistically significant, or merely random fluctuations in observations.

Annual average concentrations of SO_4^{2-} and NO_3^- for 1988 and 1989 are shown in Figure 46. Results for SO_4^{2-} indicate what appear to be distinct regional patterns. In general, annual averages for the 2 years are within ± 0.2 to $0.3 \mu\text{g}/\text{m}^3$ for the easternmost sites in the network, from North Carolina to New York. The midwestern sites from central Kentucky to northern Illinois invariably exhibit higher (i.e., greater than or equal to $0.5 \mu\text{g}/\text{m}^3$) concentrations in 1989, while two sites in

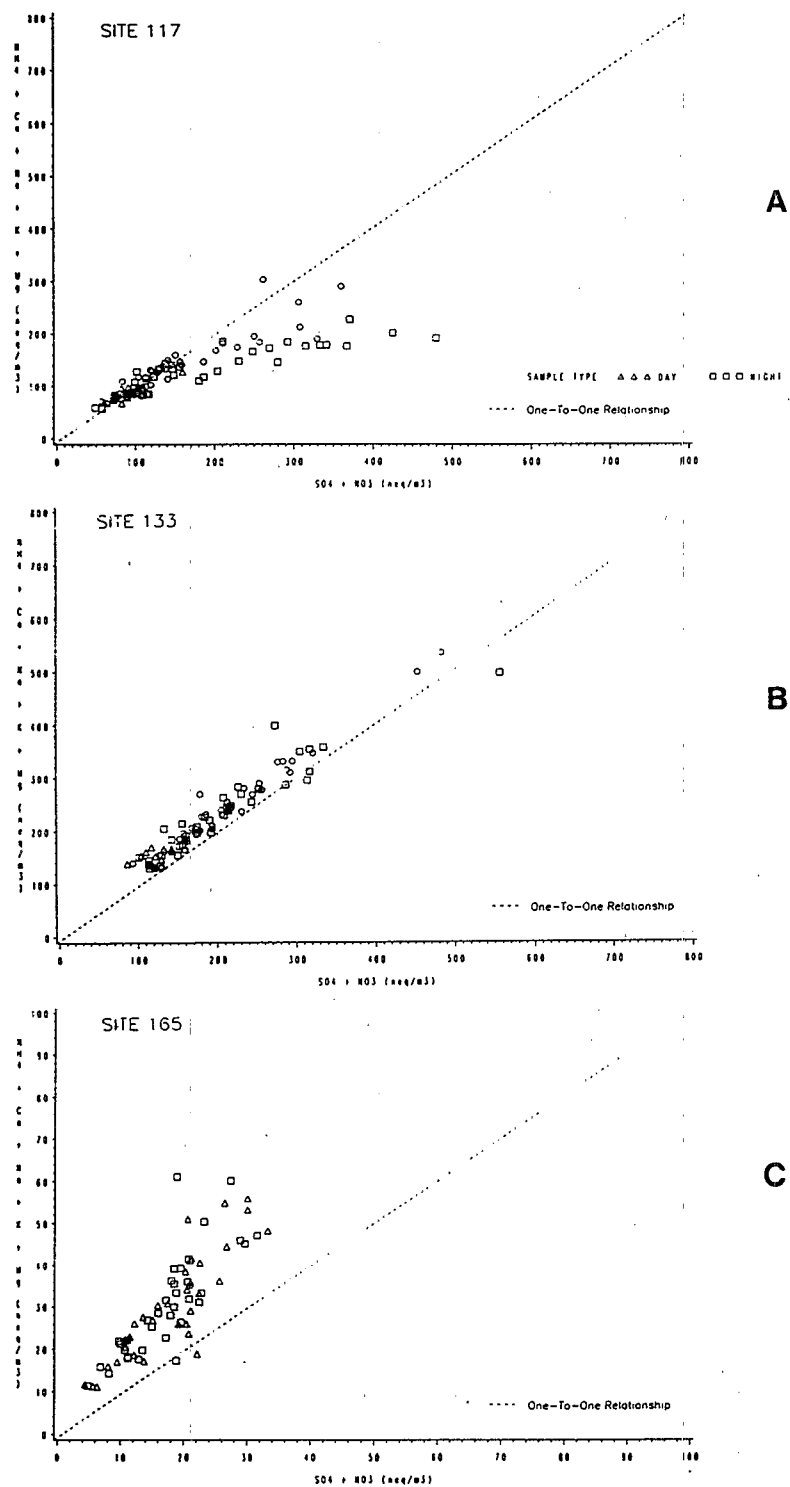


Figure 44. Total cations versus total anions for a northeastern site (A), a midwestern site (B), and a western site (C), October 1988 through September 1989

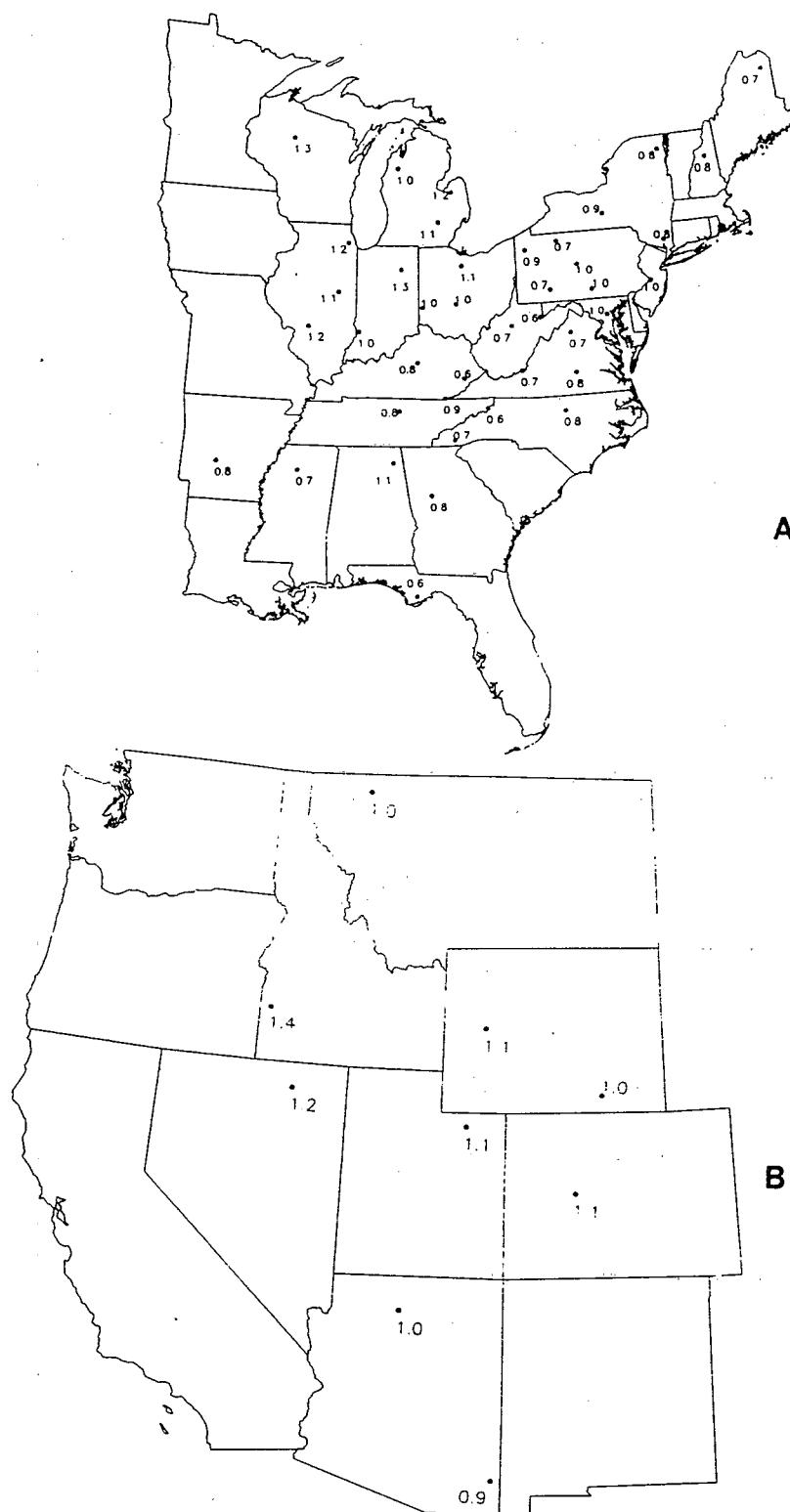


Figure 45. $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios for eastern (A) and western (B) NDDN sites

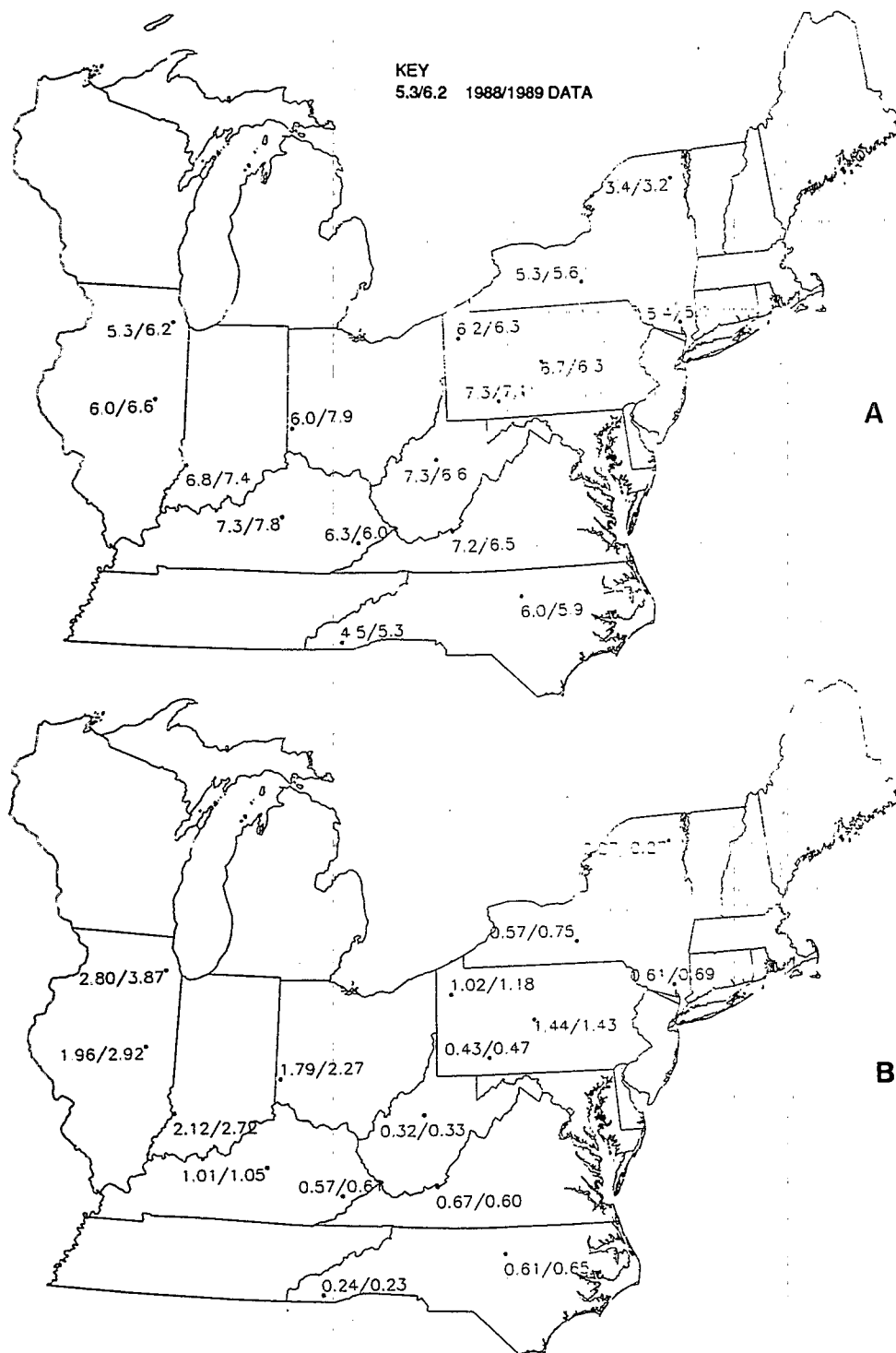


Figure 46. Annual average concentrations ($\mu\text{g}/\text{m}^3$) of SO_4^{2-} (A) and NO_3^- (B) for 1988/1989

West Virginia and Virginia exhibit somewhat higher values in 1988. Only the largest interannual difference of $1.9 \mu\text{g}/\text{m}^3$ (in western Ohio) is statistically significant at the 95-percent confidence level. The inherent noise in observed concentrations thus appears to prevent statistical discrimination between successive years of concentration differences on the order of $1.0 \mu\text{g}/\text{m}^3$ or less.

Combination of data across sites (within regions), adjusting for seasonal variability or relaxation of statistical confidence levels, may be necessary for detection of statistically significant interannual differences.

Results for NO_3 show, if anything, a more dramatic contrast between the northeast and midwest. Northeast data for 1988/1989 show remarkable temporal stability across a broad range of concentrations. Midwestern data show not only higher concentrations, but larger differences between years. As with SO_4^{2-} , the higher concentrations were associated with 1989. Relative differences at midwestern sites ranged from 27 percent in western Ohio (Site 122) to 49 percent in central Illinois (Site 130). Differences between years were significant for all midwestern sites except Site 122.

Annual average concentrations of HNO_3 (see Figure 47) show higher values in 1988 than 1989 for all sites, except Site 122. However, differences exceeded 15 percent only at a cluster of three sites in eastern Kentucky, West Virginia, and Virginia, and at a single site in central Pennsylvania. Absolute differences for these sites ranged from $0.17 \mu\text{g}/\text{m}^3$ to $0.70 \mu\text{g}/\text{m}^3$ and in all cases were statistically significant.

Results for SO_2 show small differences between years and no evidence of a consistent regional pattern. Data for eastern Pennsylvania and New York show essentially no detectable differences between years. Sites in western Pennsylvania, Ohio, Virginia, and North Carolina exhibit annual differences of 10 to 20 percent. Sites in Ohio and Pennsylvania suggest an increase in concentrations from 1988 to 1989, while those in Virginia and North Carolina suggest the opposite. Despite interannual differences of 2 to $3 \mu\text{g}/\text{m}^3$ at some sites, no site exhibited a statistically significant difference between years. As for SO_4^{2-} , it appears that variability in concentrations, rather than measurement uncertainty, can mask statistical detection of relatively large year-to-year variations.

4.3 OZONE

As described in Section 3.0, continuous O_3 concentrations were monitored throughout the year at a height of 10 m at all NDDN sites. Annual averages, valid observations, and peak observed concentrations for 1989 are summarized in Table 15. Annual averages among eastern

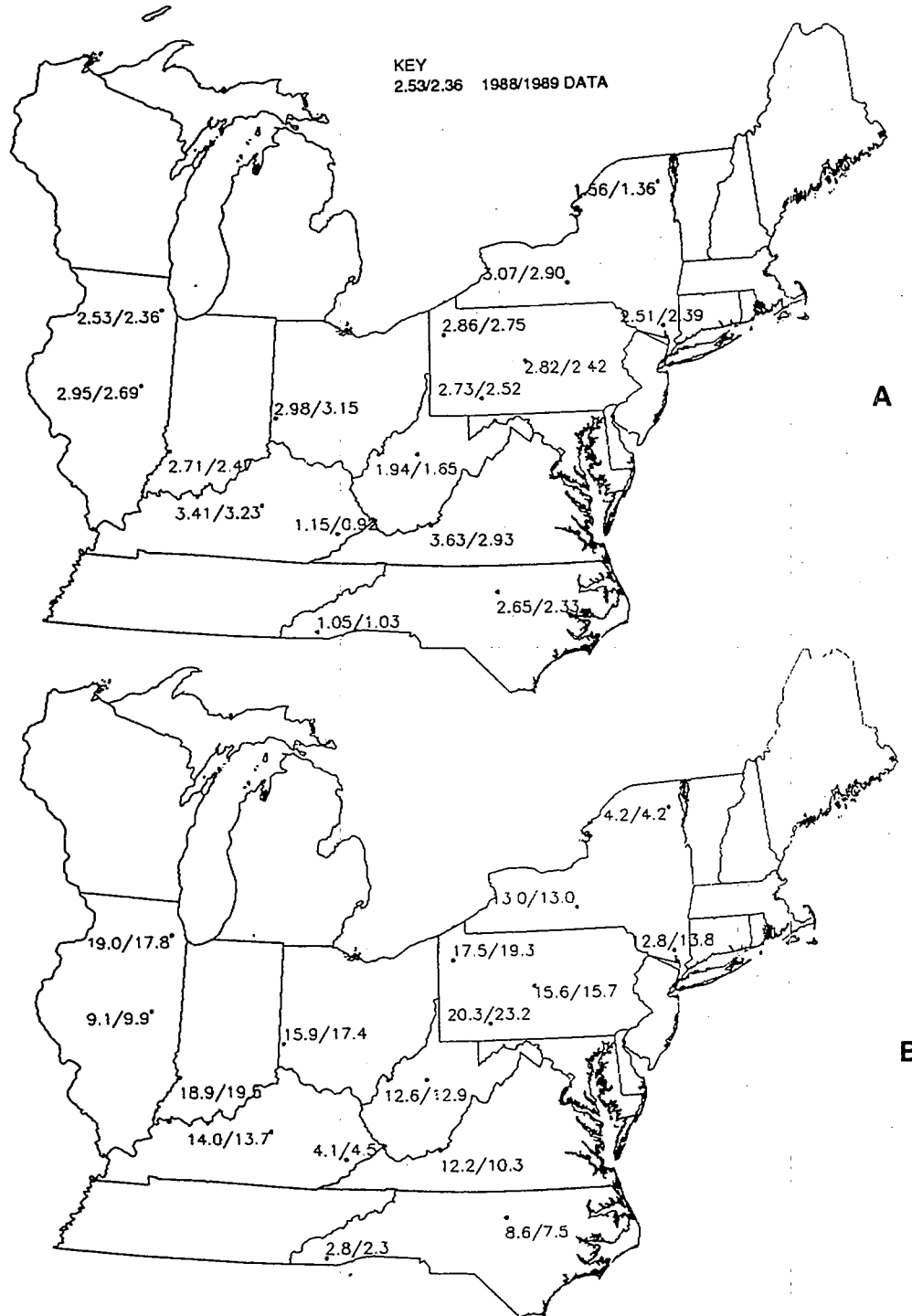


Figure 47. Annual average concentrations ($\mu\text{g}/\text{m}^3$) of HNO_3 (A) and SO_2 for 1988/1989

TABLE 15. SUMMARY OF NDDN O₃ MEASUREMENTS DURING 1989

Site no.	Valid. n	Percent valid	Annual average (ppb)	Highest		Second highest		Third highest	
				Value (ppb)	Date	Value (ppb)	Date	Value (ppb)	Date
101	8499	97	26.6	121	8/4	115	6/2	104	7/10
104	8552	98	29.1	125	7/3	115	5/20	106	7/18
105	7485	85	38.1	93	7/19	91	3/27	91	7/2
106	8673	99	29.1	104	7/2	101	7/25	95	8/3
107	8609	98	30.0	107	6/27	103	8/3	101	6/25
108	8433	96	33.0	105	9/11	99	5/25	97	5/30
109	8100	92	32.2	91	5/19	87	5/20	85	5/1
110	8503	97	38.5	101	7/2	91	6/20	89	3/27
111*	4007	46	26.9	95	7/26	93	7/18	90	7/4
112	8124	93	37.4	102	8/3	98	7/3	96	7/2
113	8610	98	32.0	117	7/1	104	7/7	104	8/3
114	8228	94	31.4	157	6/26	109	8/15	107	7/7
115	8464	97	32.5	109	6/8	103	7/2	101	6/23
116	8606	98	25.8	131	7/1	126	6/27	120	7/25
117	8241	94	28.4	110	6/26	104	6/27	101	7/25
118	8334	95	45.3	97	6/14	97	6/24	95	4/15
119	8609	98	24.5	112	7/17	109	6/24	105	7/18
120	8553	98	43.6	103	5/22	98	6/27	98	7/7
121	8589	98	22.1	98	6/24	88	5/18	87	4/27
122	8650	99	33.3	109	6/7	108	6/23	108	7/7
123	8507	97	34.4	110	7/7	104	8/2	100	8/11
124	8639	99	35.2	113	7/2	103	6/26	100	7/1

TABLE 15. (continued)

Site no.	Valid n	Percent valid	Annual			Highest			Second highest			Third highest		
			Value (ppb)	Date	Hour	Value (ppb)	Date	Hour	Value (ppb)	Date	Hour			
126	8140	93	45.2	103	7/26	20	98	5/8	16	95	7/11	01		
127	8529	97	34.2	90	7/13	17	88	5/29	13	83	4/22	17		
128	8635	99	35.9	112	5/19	21	108	6/19	16	108	6/27	17		
129	8328	95	36.3	102	6/25	12	101	4/27	18	99	6/24	16		
130	8602	98	33.3	104	7/1	15	101	7/6	17	100	10/13	15		
133	8360	95	35.0	109	6/26	15	109	7/7	15	106	7/1	18		
134	8020	92	35.4	85	5/18	12	81	10/1	13	79	6/21	16		
135	8568	98	32.4	103	5/26	14	80	5/20	13	72	7/18	16		
137	7752	88	28.4	94	4/14	19	86	5/6	16	79	4/28	14		
140	8650	99	30.4	112	6/25	15	100	7/8	15	98	7/7	13		
144	8622	98	29.0	159	7/1	18	141	7/3	16	138	6/19	15		
146	8610	98	25.8	126	6/25	17	114	7/6	16	111	7/8	14		
149	8668	99	37.3	107	7/2	12	107	7/9	21	104	5/24	24		
150	8592	98	28.4	102	10/12	15	87	4/22	16	87	10/11	15		
151	8230	94	36.5	149**	3/17	15	103**	3/11	20	97	6/13	12		
152	8072	92	36.4	97	6/25	18	92	6/10	17	92	7/15	13		
153	6049	69	33.8	118	8/3	15	105	8/11	18	104	7/28	18		
156	7590	87	31.6	98	5/3	15	88	6/20	14	87	5/6	22		
157	8615	98	33.4	133	7/8	16	121	6/2	16	111	10/12	17		
161*	4160	47	42.7	72	11/8	17	70	7/3	13	70	7/18	18		
162*	4274	49	42.6	75	7/26	15	72	7/2	11	70	7/3	13		
163*	2755	31	32.4	78	8/30	17	73	8/24	19	66	9/16	18		
164*	4314	49	43.3	88	9/3	23	83	9/21	23	80	9/7	09		

TABLE 15. (continued)

Site no.	Valid n	Percent valid	Annual average (ppb)	Highest		Second highest		Third highest	
				Value (ppb)	Date	Value (ppb)	Date	Value (ppb)	Date
165	8036	92	46.2	89	4/24	84	4/20	84	5/18
167*	5760	66	42.6	89	12/7	88	7/9	79	7/19
168	8051	92	31.2	67	4/7	67	4/30	65	5/11
169*	4260	49	43.2	88	7/27	83	7/26	80	7/23
174*	4205	48	48.9	80	8/15	77	9/10	74	7/15

*Initiated July 1989.

*Initiated April 1989.

**Impacted by local forest fires.

Source: ESE, 1990.

sites range from 22.1 ppb in eastern Kentucky (Site 121) to 45.3 ppb in northern Virginia (Site 118). The highest annual averages (i.e., 43 to 45 ppb) occur at mountaintop sites along the Blue Ridge and Appalachian Mountains, while the lowest annual averages occur in sites located in sharp valleys (e.g., Sites 119 and 121) and in semiurban areas (e.g., Sites 101, 116, and 146).

Hourly average concentrations equal to or greater than the NAAQS were relatively rare during 1989. Eight sites exhibited one or more hourly values greater than or equal to 120 ppb, and only 15 days of exceedances occurred at the 43 sites operational throughout the year.

Results for western sites, which were typically operational for half of 1989, showed average O_3 concentrations ranging from 31.2 ppb in northern Montana (Site 168) to 48.9 ppb in northern Arizona (Site 174). In general, average concentrations exceeded those in the east. Peak concentrations, in contrast, were almost invariably less than those observed across the eastern part of the network. The average elevation for the western sites is well above the highest elevation of any eastern site. Thus, relatively high annual averages among western sites are consistent with similarly high averages for the eastern sites located on mountaintops.

Daily average and daily maximum O_3 concentrations for selected pairs of northeastern, midwestern, southeastern, and western sites are shown in Figures 48 through 51. Each figure also shows a horizontal line at 120 ppb, which represents the NAAQS for O_3 . The NAAQS for O_3 is violated if four or more daily maxima greater than or equal to 120 ppb are observed during a 3-year period. In general, results for the majority of sites reflect the classical seasonal cycle of O_3 production. Maximum concentrations are usually observed during the period June through September, and minimum concentrations are observed in November, December, and January. Seasonal variability of this nature has been observed previously over widespread areas of the eastern United States (Altshuller, 1987; Meagher *et al.*, 1987). Results for the two western sites, in contrast, show limited seasonal variability in both daily average and maximum O_3 concentrations.

Inspection of daily O_3 averages for 1989 shows considerable fine structure in the overall annual pattern. O_3 concentrations at nearly all sites rise and decay with a period of approximately 5 to 10 days, which is probably meteorologically driven. For example, examination of daily maxima listed in Table 15 shows that greater than 50 percent of the first, second, and third highest hourly observations occurred during two episodes (i.e., June 23 through June 27 and July 1 through July 4) within a 2-week period.

As mentioned previously, annual average O_3 values appear to show deterministic differences between mountaintop sites and valley sites and

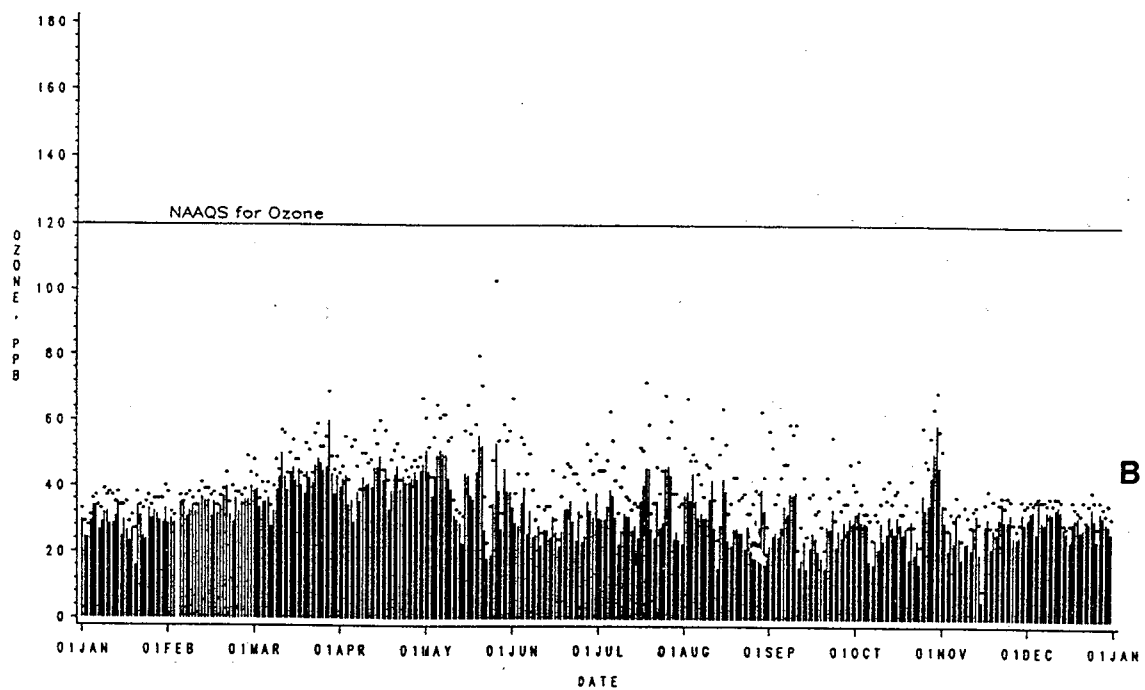
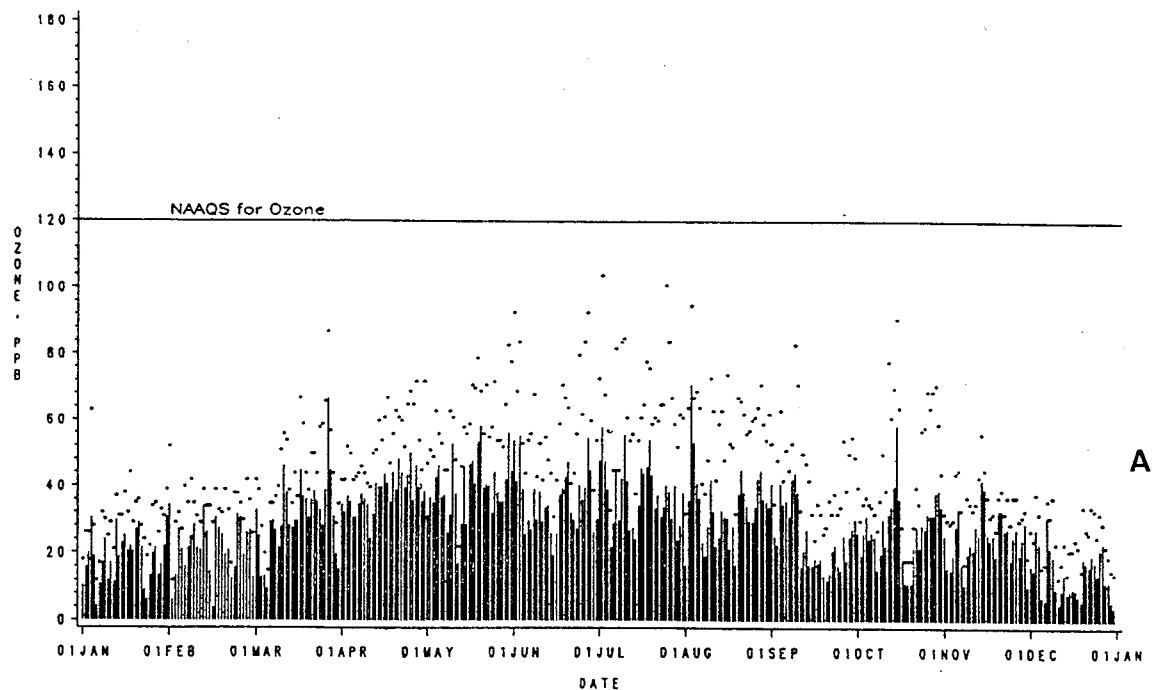


Figure 48. O₃ daily averages and maxima for two northeastern sites:
Site 106 (A) and Site 135 (B)--1989

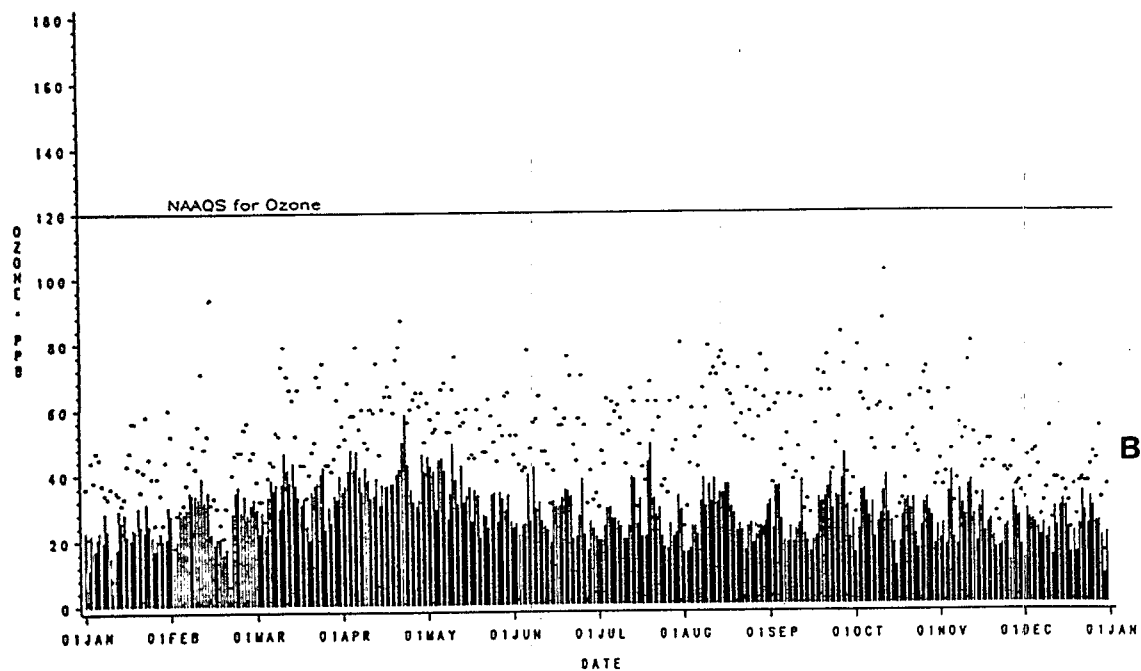
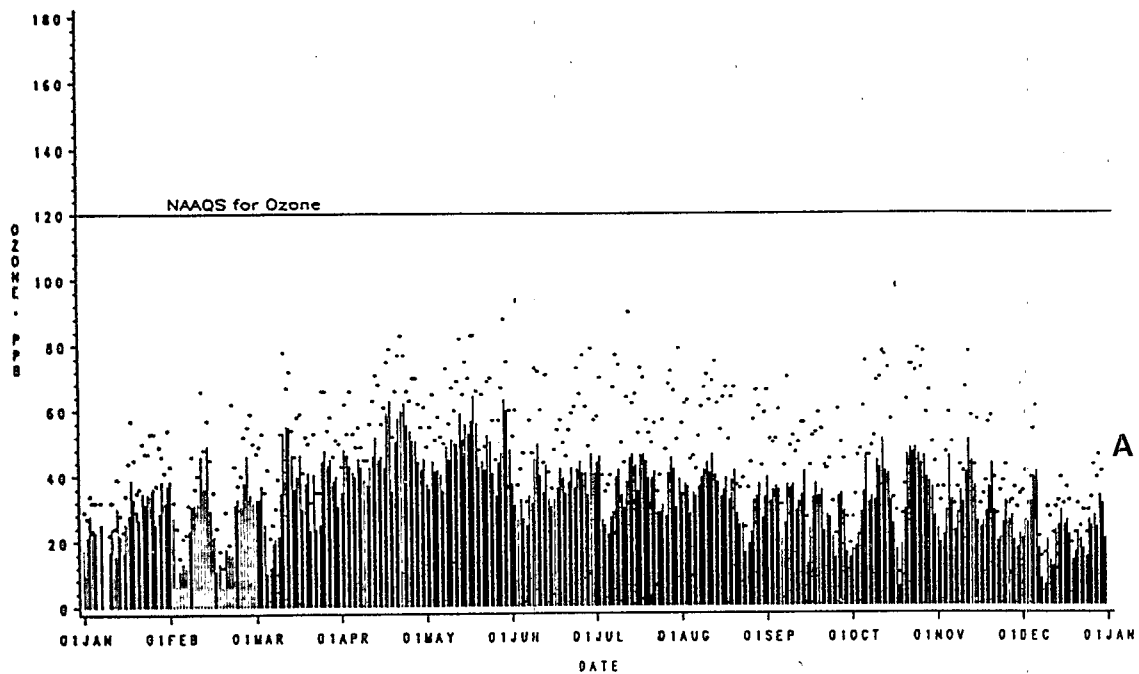


Figure 49. O₃ daily averages and maxima for two southeastern sites:
Site 127 (A) and Site 150 (B)--1989

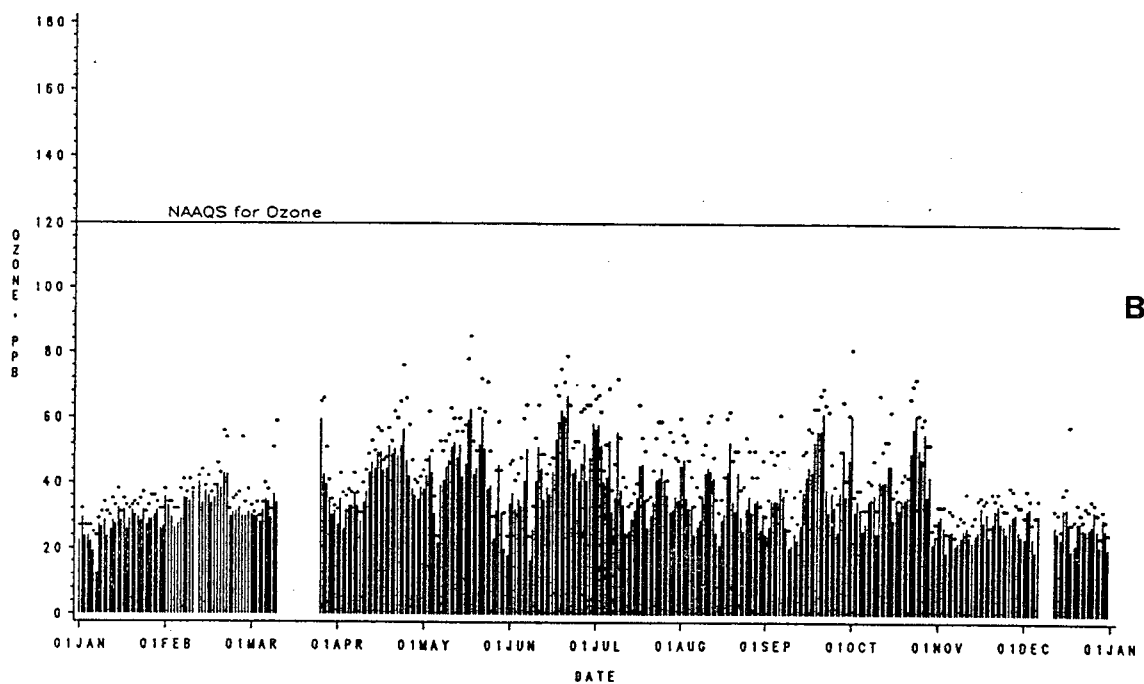
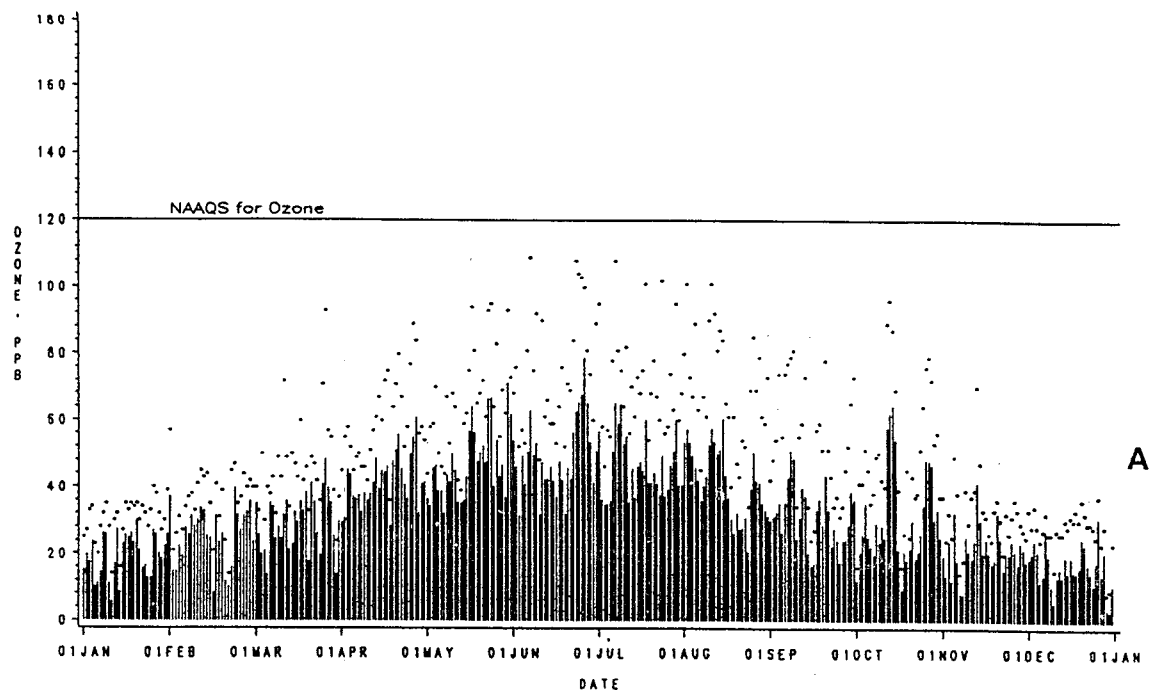


Figure 50. O_3 daily averages and maxima for two midwestern sites:
Site 122 (A) and Site 134 (B)--1989

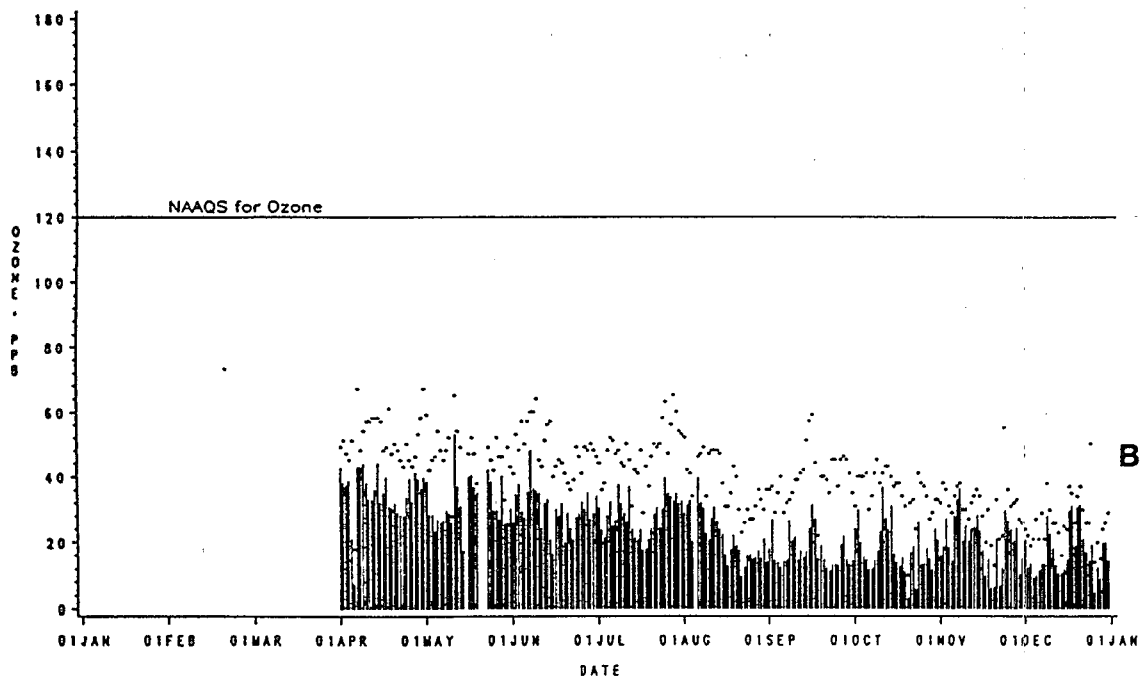
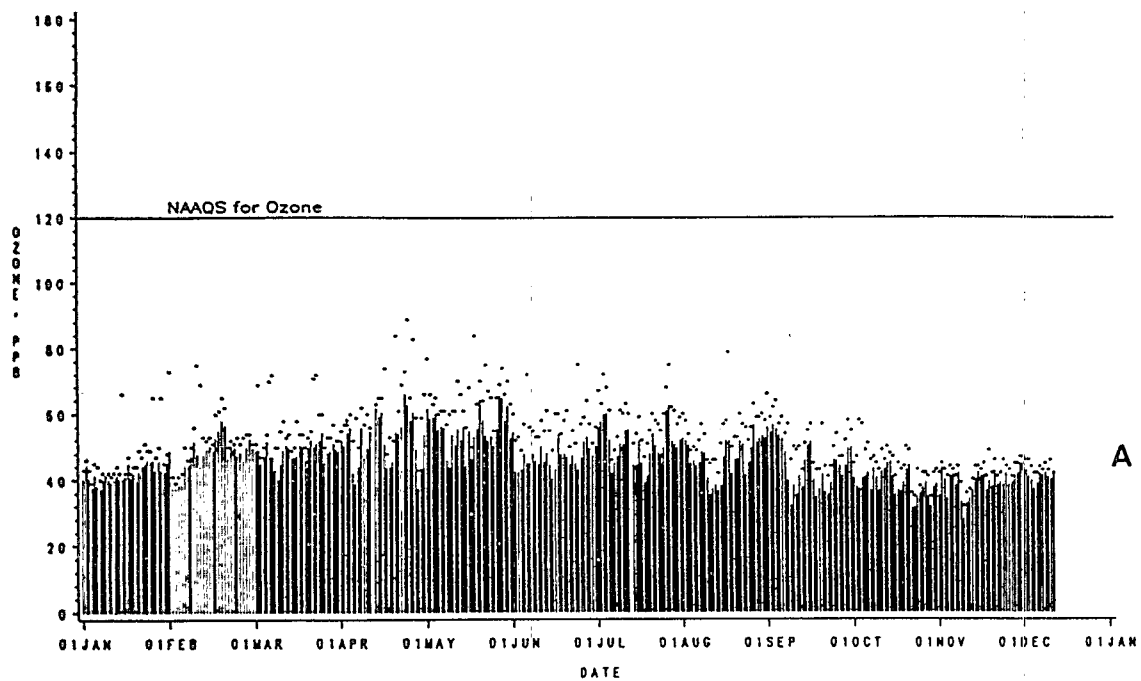


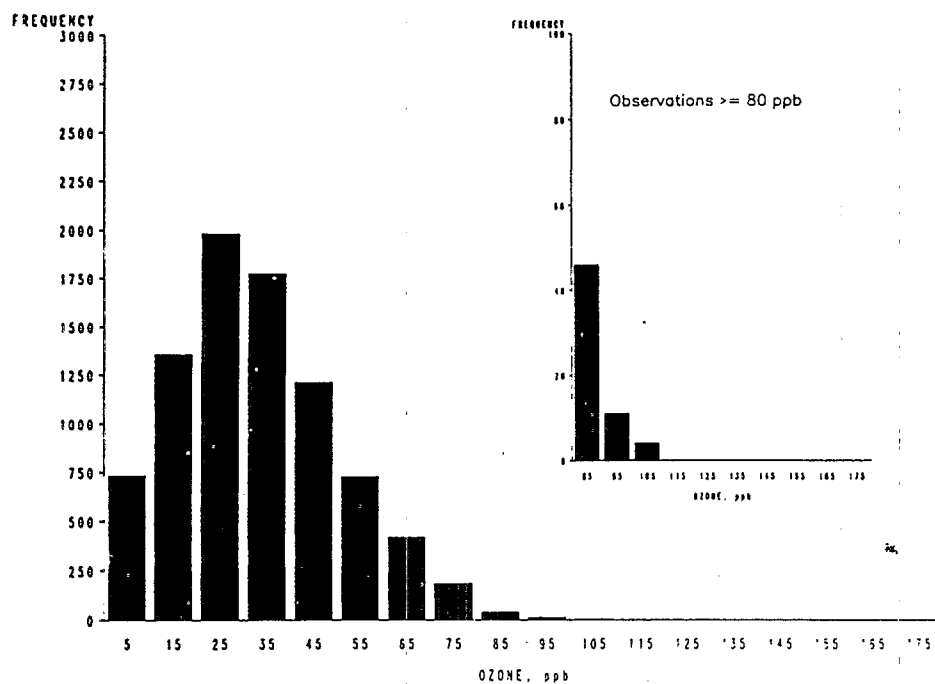
Figure 51. O₃ daily averages and maxima for two western sites: Site 165 (A) and Site 168 (B)--1989

between semiurban sites and nearby rural sites. These relationships are exhibited in Figures 52 and 53, which present frequency distributions for a rolling terrain site (Site 108 in south-central Virginia), a complex terrain site (Site 119 in West Virginia), a mountaintop site (Site 118 in northern Virginia), and a semiurban site (Site 116 in the Baltimore-Washington corridor). Results for these sites are typical of the majority of NDDN sites located in similar settings.

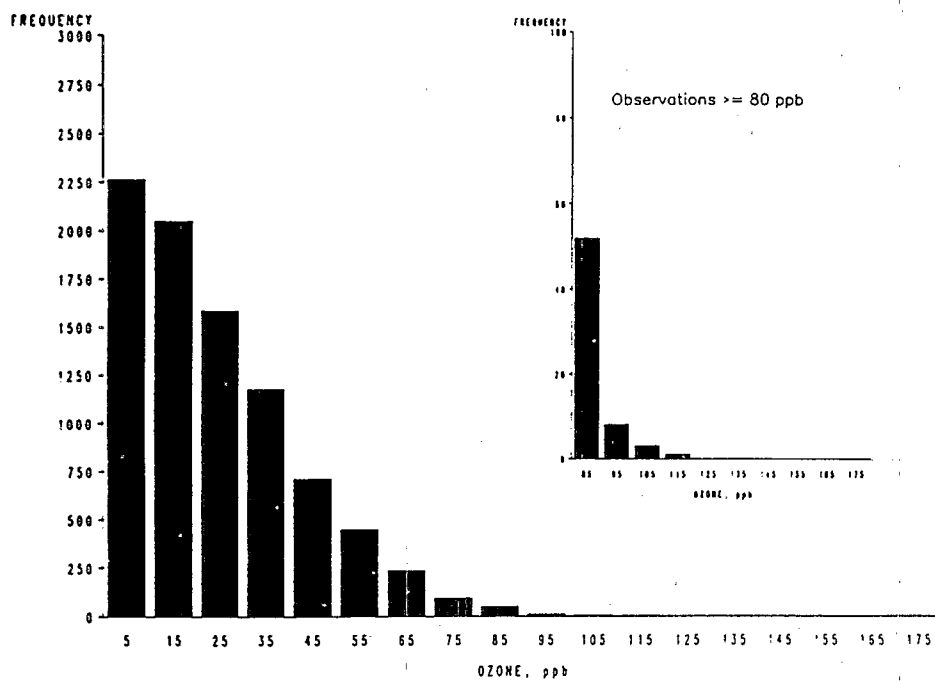
Results for Site 108 show a peak in the frequency distribution around 20 to 30 ppb and approximately equal numbers of observations in the 0- to 10-ppb and 50- to 60-ppb ranges. Hourly values greater than or equal to 80 ppb (see inset in Figures 52 and 53) represent less than 5 percent of total observations. Results for Site 119, a typical valley site, show a peak in the frequency distribution in the 0- to 10-ppb range and a monotonic decrease at successively higher concentration levels. Interestingly, the frequency of observations greater than or equal to 80 ppb is nearly identical to that at the rolling terrain site.

Data for the mountaintop site in northern Virginia show a peak in the frequency distribution in the 30- to 40-ppb range and very few observations (i.e., less than 5 percent) below 20 ppb. The number of hourly values greater than or equal to 80 ppb exceeds that at the rolling terrain and valley sites by approximately a factor of 3. Urban NDDN sites, in general, show a unique distribution of O_3 observations. In this case, a pronounced peak in the frequency distribution is observed in the 0- to 10-ppb range, but a secondary peak also occurs in the 20- to 30-ppb range. The distribution also exhibits a much longer tail than other classes of sites and a much higher frequency of values greater than or equal to 80 ppb than even the mountaintop site.

Differences in diurnal O_3 cycles appear to offer partial explanation for the different frequency distributions previously described. Hour-by-hour average O_3 concentrations for January, July, and calendar year 1989 for two rolling terrain sites, two complex terrain sites, two mountaintop sites, and two urban or semiurban sites in the eastern United States are plotted in Figures 54 through 57. Results show generally consistent differences between types of sites, both for the summer and winter months and the entire annual period. The rolling terrain sites exhibit moderate day/night variability, with night minima typically on the order of 50 to 60 percent of the day maxima. Day maxima during the summer period of maximum photochemical activity show a fairly broad plateau between the hours of 1200 through 1800. Hourly averages for the complex terrain sites show markedly different behavior. In this case, nocturnal minima (especially during July) are much less than half the daily maxima. In addition, periods of minimum and maximum concentrations last appreciably longer and shorter, respectively, than at rolling terrain sites. However, maximum concentrations are similar at the two types of sites.

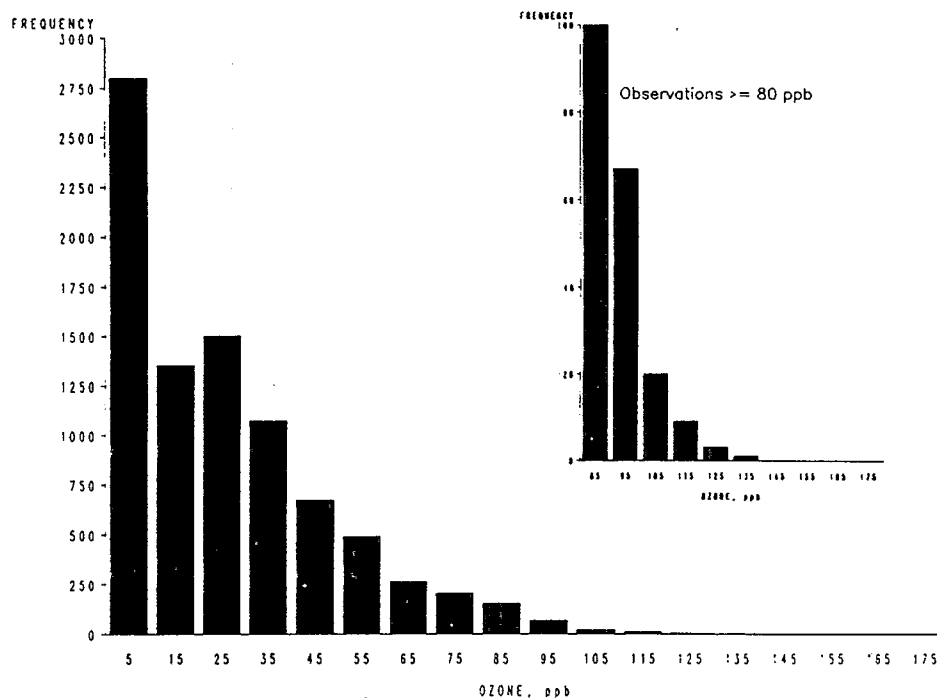


A

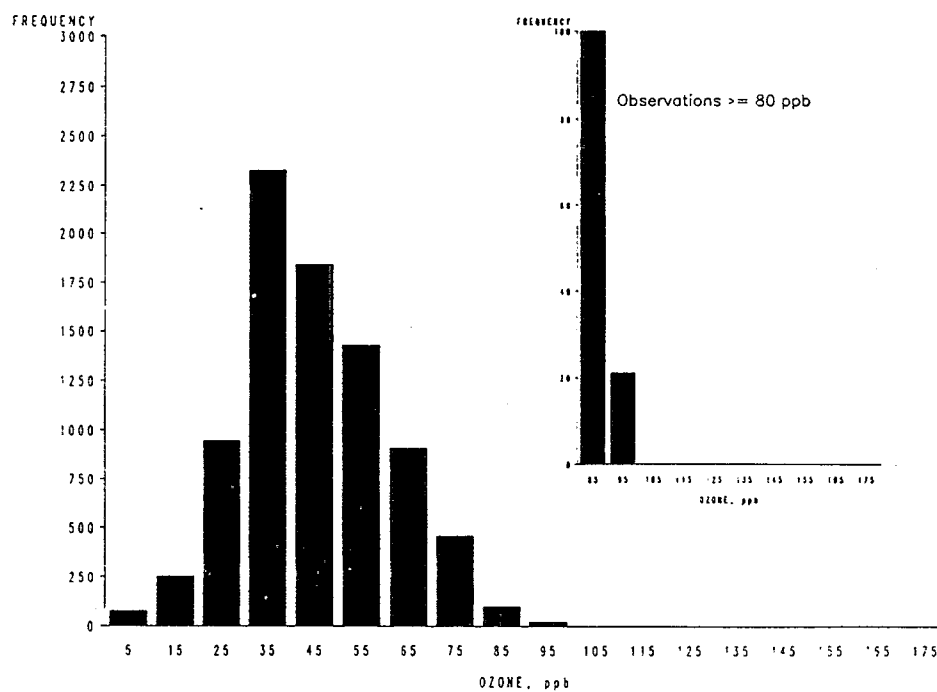


B

Figure 52. O₃ frequency distribution for Sites 108 (A) and 119 (B) during 1989

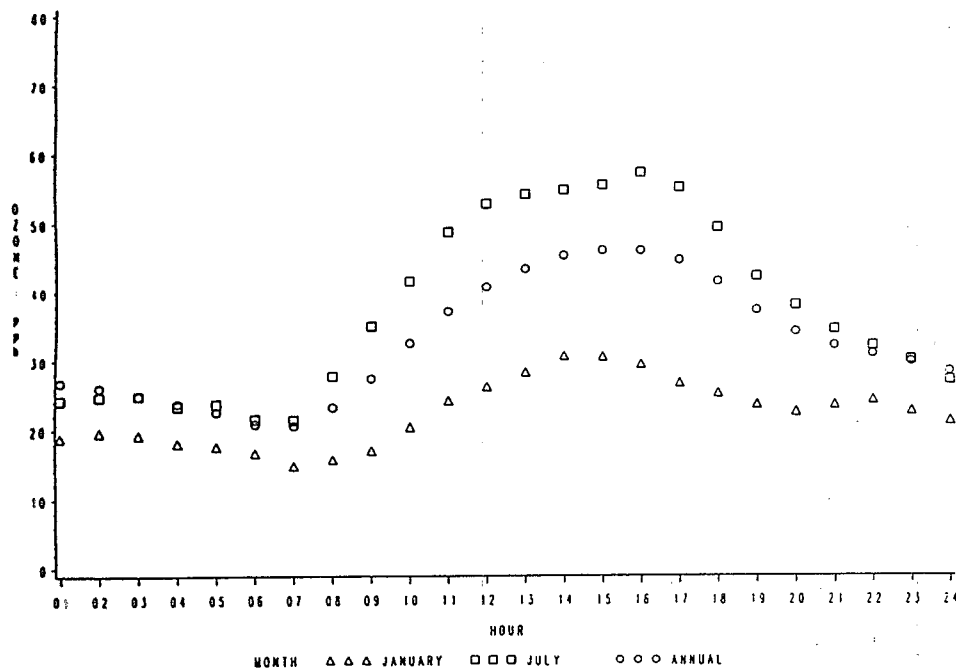


A

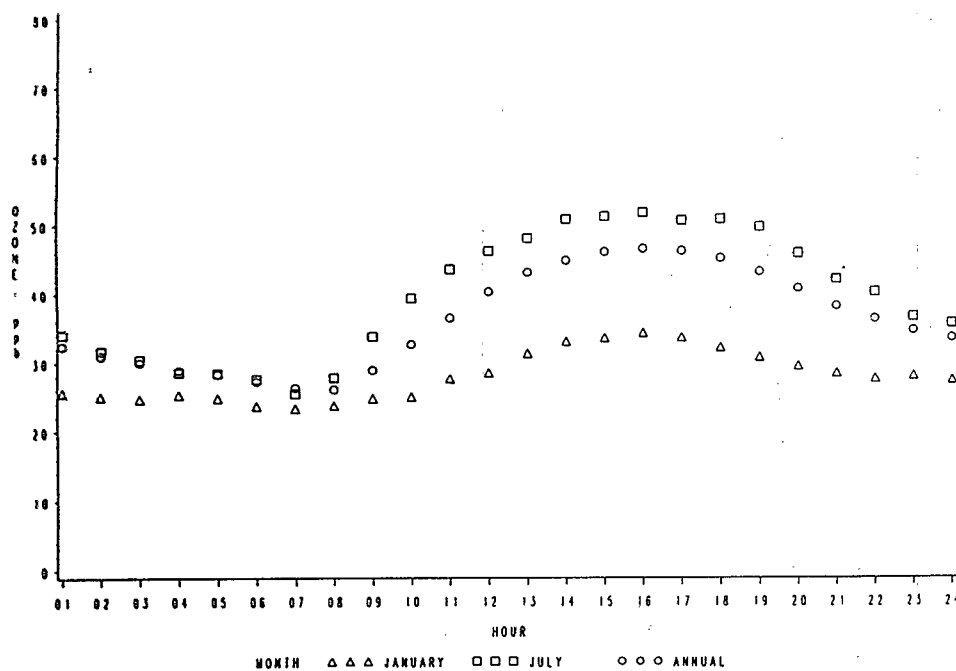


B

Figure 53. O₃ frequency distribution for Sites 116 (A) and 118 (B) during 1989



A



B

Figure 54. Hourly average O₃ concentrations for typical sites in rolling terrain: Site 108 (A) and Site 129 (B)

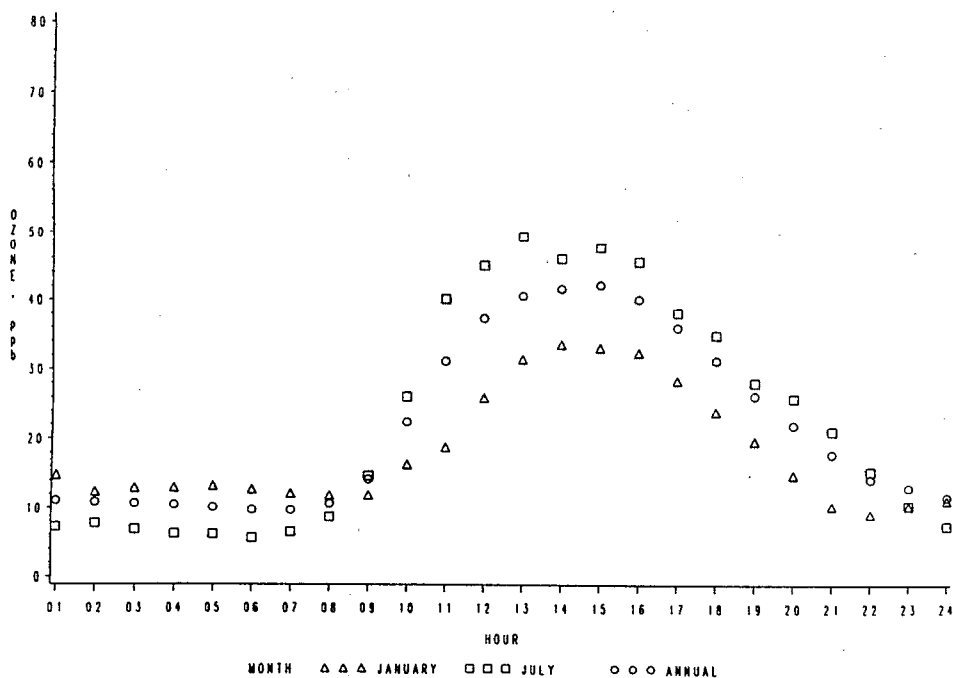
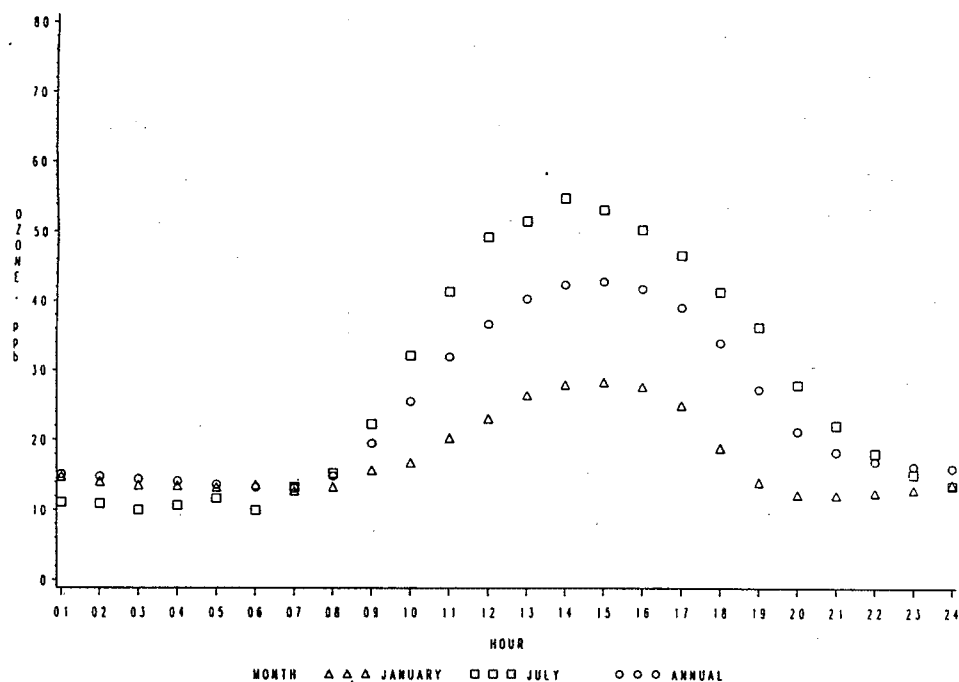
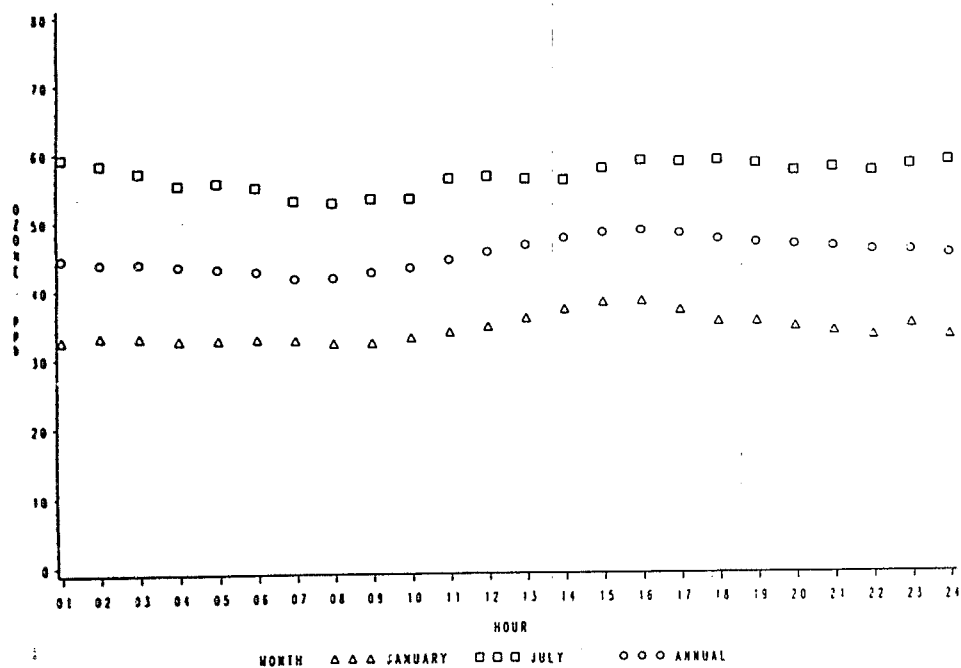
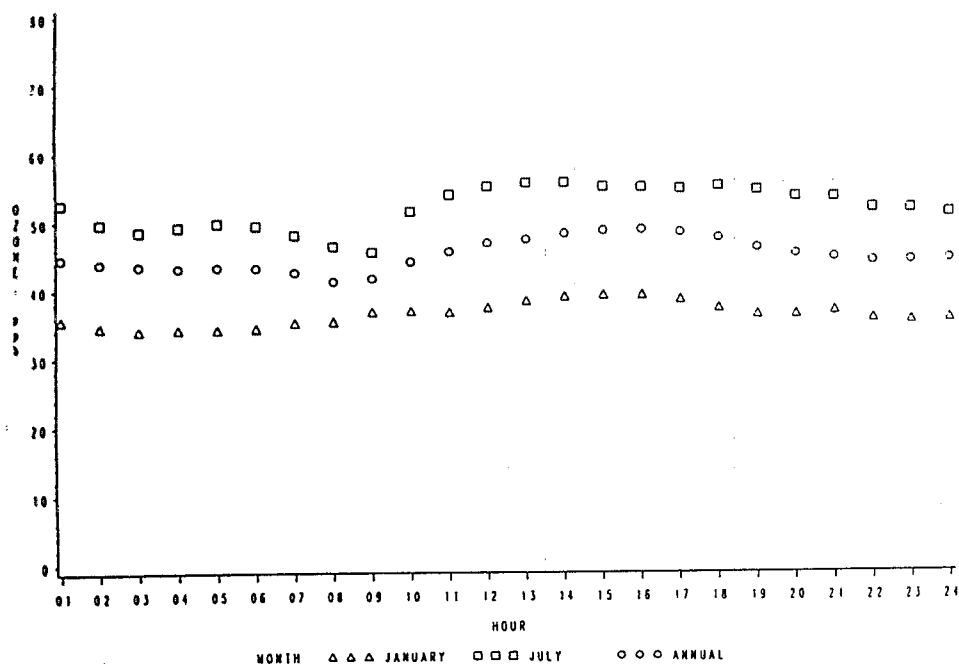


Figure 55. Hourly average O_3 concentrations for typical sites in complex terrain:
Site 119 (A) and Site 121 (B)



A



B

Figure 56. Hourly average O_3 concentrations for typical mountaintop sites:
Site 118 (A) and Site 126 (B)

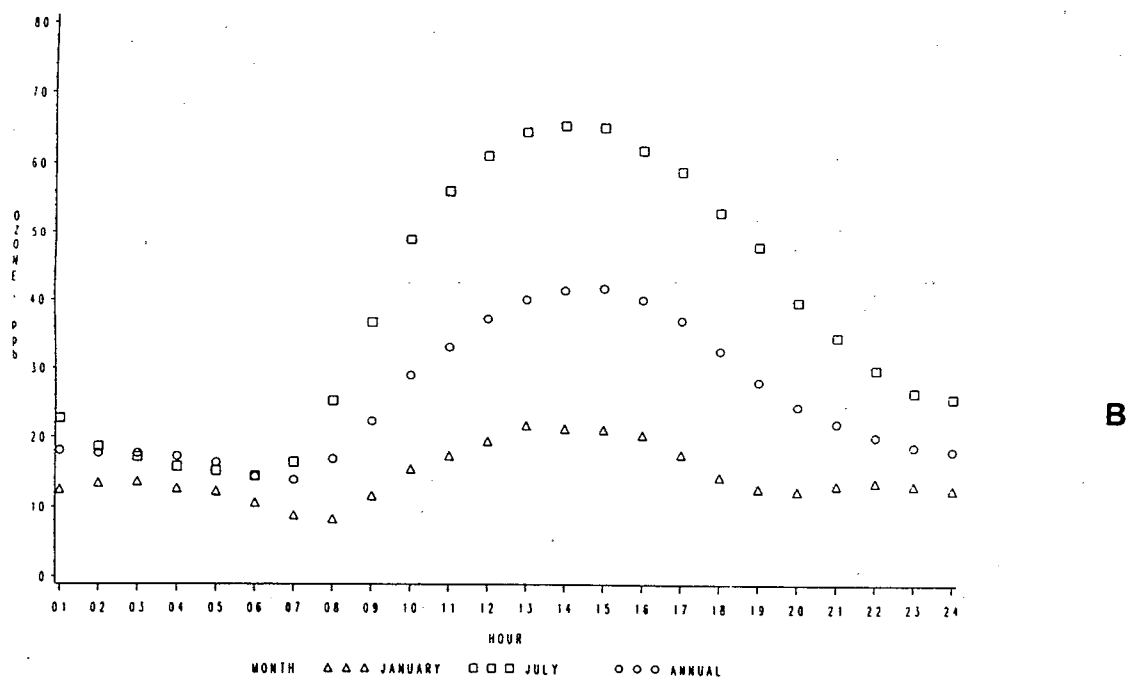
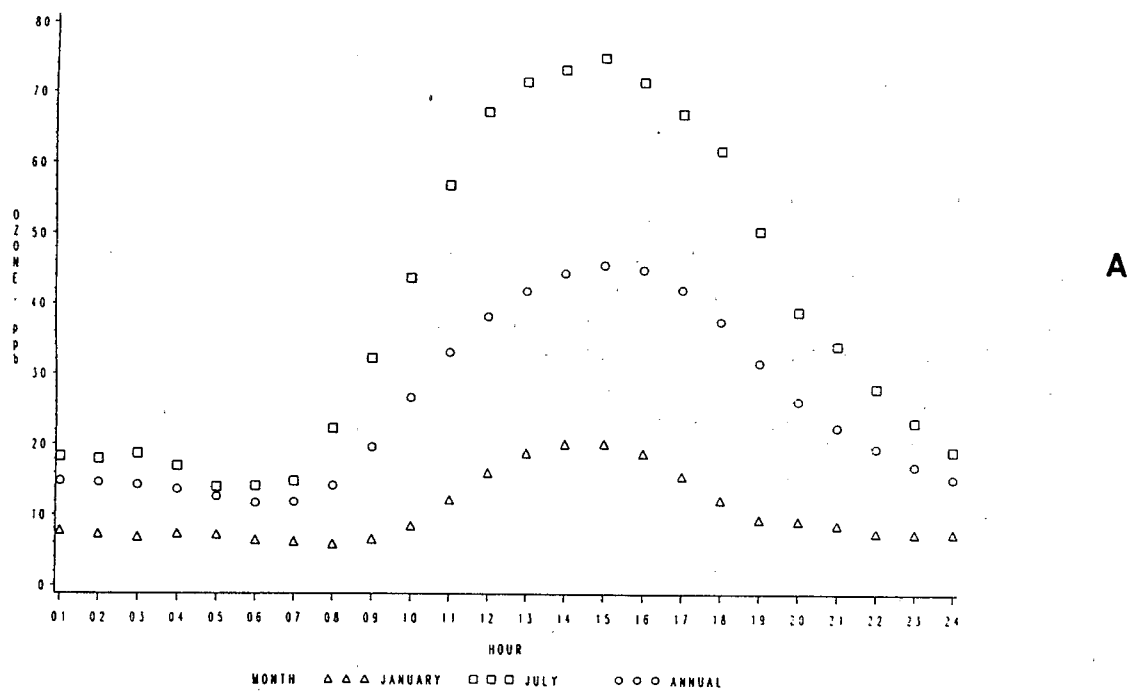
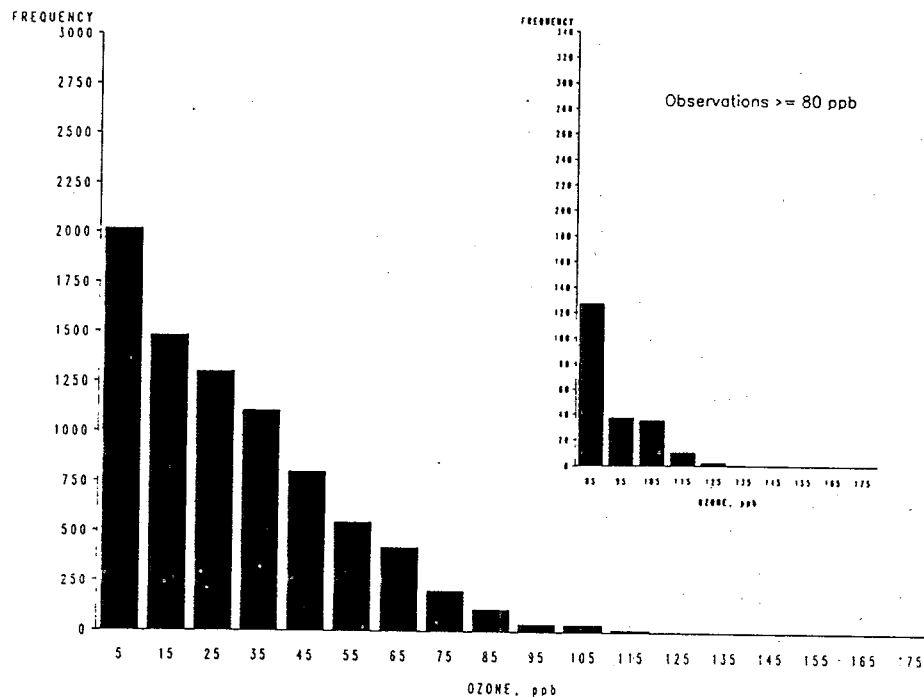


Figure 57. Hourly average O_3 concentrations for typical urban or semi-urban sites: Site 116 (A) and Site 146 (B)

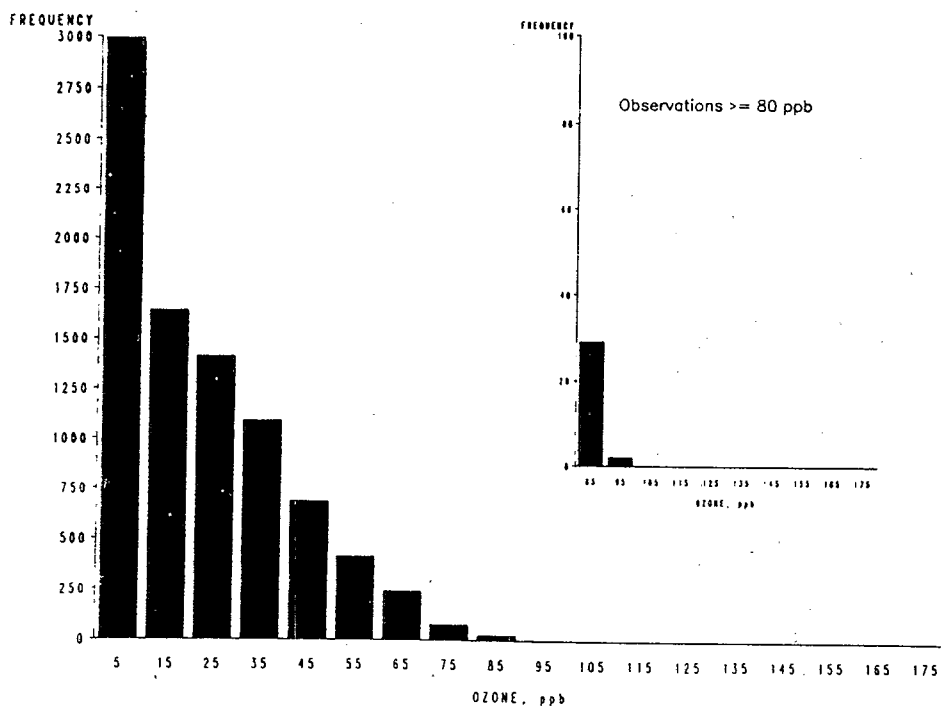
Mountaintop sites exhibit a unique diurnal pattern, or lack of one. For these sites, there is no distinct period of maximum or minimum concentration. Rather, hourly average values consistently remain within a few parts per billion of hourly maxima observed at the other sites. July and January hourly averages differ dramatically (approximately a factor of 2) over the entire 24-hour cycle. Finally, results for the semiurban sites show depressed nocturnal values (especially during winter) and pronounced day maxima during the summer. In general, day maxima are 5 to 10 ppb higher than at the other sites but similar in duration to the complex terrain sites. Both of these semiurban sites are located in rolling terrain. Thus, similarities between semiurban and complex terrain sites could have distinctly different explanations.

One explanation for the observed behavior involves the relationship between sampler location and the nocturnal inversion layer. The mountaintop sites presumably sit above the inversion layer and, therefore, are always in contact with a large reservoir for O_3 . The rolling terrain and complex terrain sites are situated below the inversion layer, within which O_3 is subject to a variety of depletion processes. Longer lasting and/or shallower inversions could result in rapid decay of O_3 in complex terrain than in rolling terrain. The end result of this day/night variability is a gradient in integrated exposure (i.e., average concentrations) from mountaintop to rolling terrain to complex terrain. Although no continuous data support this, the same terrain effect might also account for the SO_2 and HNO_3 pattern described previously for these sites. For the semiurban sites, broad nocturnal minima could be the result of destruction by nitric oxide (NO), while sharp day maxima could be due to enhanced photochemical production in the presence of NO_x and natural or manmade volatile organic gases.

As mentioned previously, relatively few O_3 concentrations greater than or equal to 120 ppb were observed during 1989 (i.e., 15 exceedances from 43 sites). This contrasts sharply with data from 1988, which showed 98 exceedances from only 18 sites. Differences between 1988 and 1989 are clearly illustrated on examination of frequency distributions for the 2 years. Frequency distributions for a rolling terrain site in central Kentucky (Site 129), a complex terrain site in eastern Kentucky (Site 121), and a mountaintop site in southwestern Virginia (Site 120) are shown in Figures 58 through 60. As a rule, the differences between terrain types previously discussed appear to hold for both years. However, the frequency distribution for each site is skewed toward higher concentrations in 1988 than in 1989. In addition, Site 121 exhibits a dramatic increase in frequency of observations in the 0- to 10-ppb interval from 1988 to 1989, while Sites 120 and 129 show only modest changes in this range.

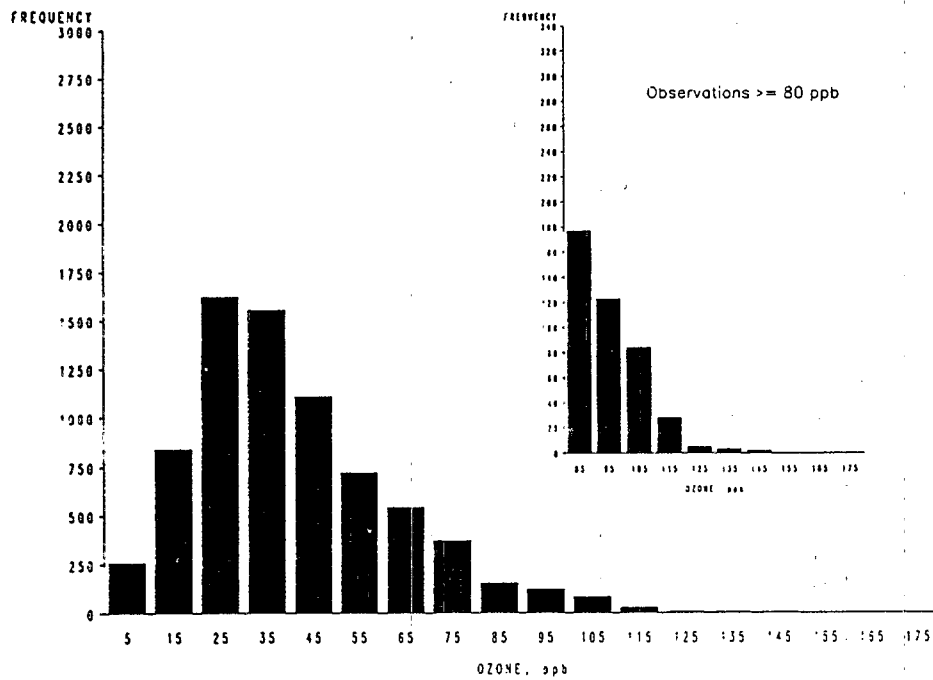


A

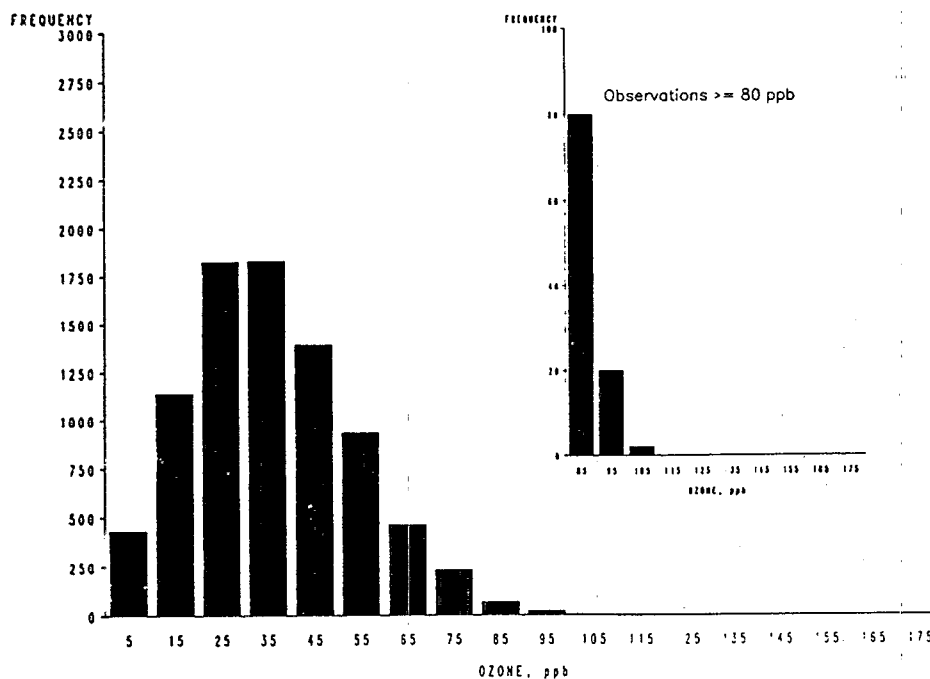


B

Figure 58. 1988 (A) versus 1989 (B) O₃ frequency distribution for Site 121

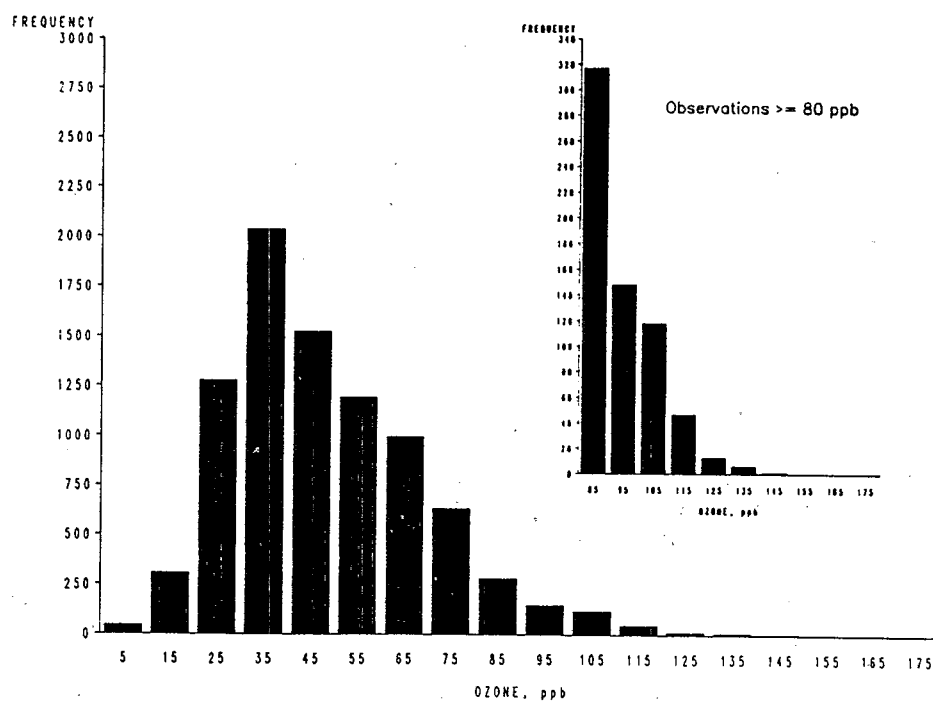


A

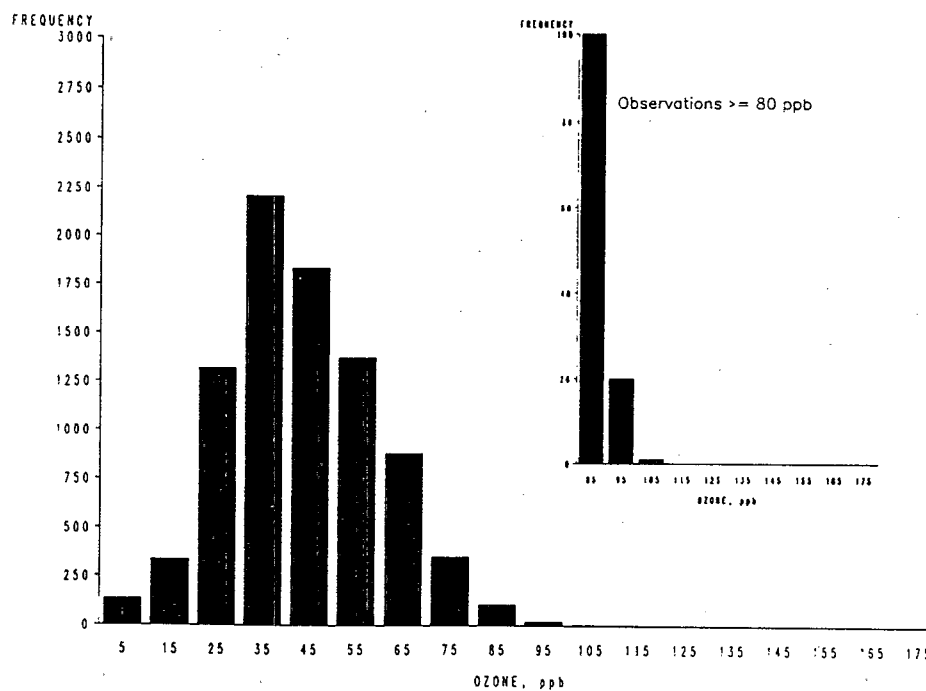


B

Figure 59. 1988 (A) versus 1989 (B) O₃ frequency distribution for Site 129



A



B

Figure 60. 1988 (A) versus 1989 (B) O₃ frequency distribution for Site 120

Differences in annual frequency distributions are most obvious in the concentration range above 80 ppb (see insets). For all three sites, the number of observations greater than or equal to 80 ppb is at least a factor of 5 higher in 1988 than in 1989. This phenomenon was generally observed across the midwestern and northeastern United States, as shown in Figure 61.

Other measures of integrated O₃ exposure or concentration also suggest that 1988 and 1989 were markedly different years. One such measure is the 7-hour growing season average, which has been used by the National Crop Loss Assessment Network (NCLAN) to assess O₃ effects on various agricultural crops (Heck *et al.*, 1982). This measure represents an arithmetic average of observations taken during the period 0900 to 1559 during the relevant growing season for a particular location. The 7-hour growing season averages for 1988 and 1989 are shown in Figure 62 for the 16 sites completely operational during both years. Since growing season varies over the NDDN domain, May through September was selected as a likely period of biological activity at all sites. Results show a fairly consistent 10- to 20-percent difference between 1988 and 1989. The only significant exception to this occurred in extreme northern New York (Site 105), which showed essentially no difference between years.

The sigmoidally weighted O₃ concentration (W126) is a statistic recently proposed by Lefohn and Runeckles (1987) as a tool for examining O₃ damage to forests and crops. This function weights each O₃ concentration in a manner that emphasizes high values (e.g., greater than or equal to 80 ppb) and deemphasizes low values (e.g., less than or equal to 30 ppb). Thus, concentrations believed to be more harmful to crops are given greater weight in the averaging scheme than low concentrations. Calculations of W126 for 1988 and 1989 (see Figure 63) uniformly show higher values for the earlier year. In fact, differences are generally on the order of a factor of 2, suggesting that, by at least one measure, O₃ exposure in 1988 was twice that in 1989.

The underlying reasons for differences between 1988 and 1989 are undoubtedly complex; however, various observations at NDDN sites suggest a meteorological link. Solar radiation and surface temperature (9 m) are routinely measured by NDDN. Growing season data for 1988 and 1989 for these variables are compared in Figure 64. Results for solar radiation show that, on average, 20 percent more sunlight was received at the surface in 1988 than in 1989. The same may not be exactly the case for the more important UV radiation, which drives atmospheric photochemical cycles, but it should have been at least a few percent greater in 1988 than 1989. The only site that does not show an appreciable difference in solar radiation was the one exhibiting the smallest differences in exposure statistics between years (i.e., Site 105).

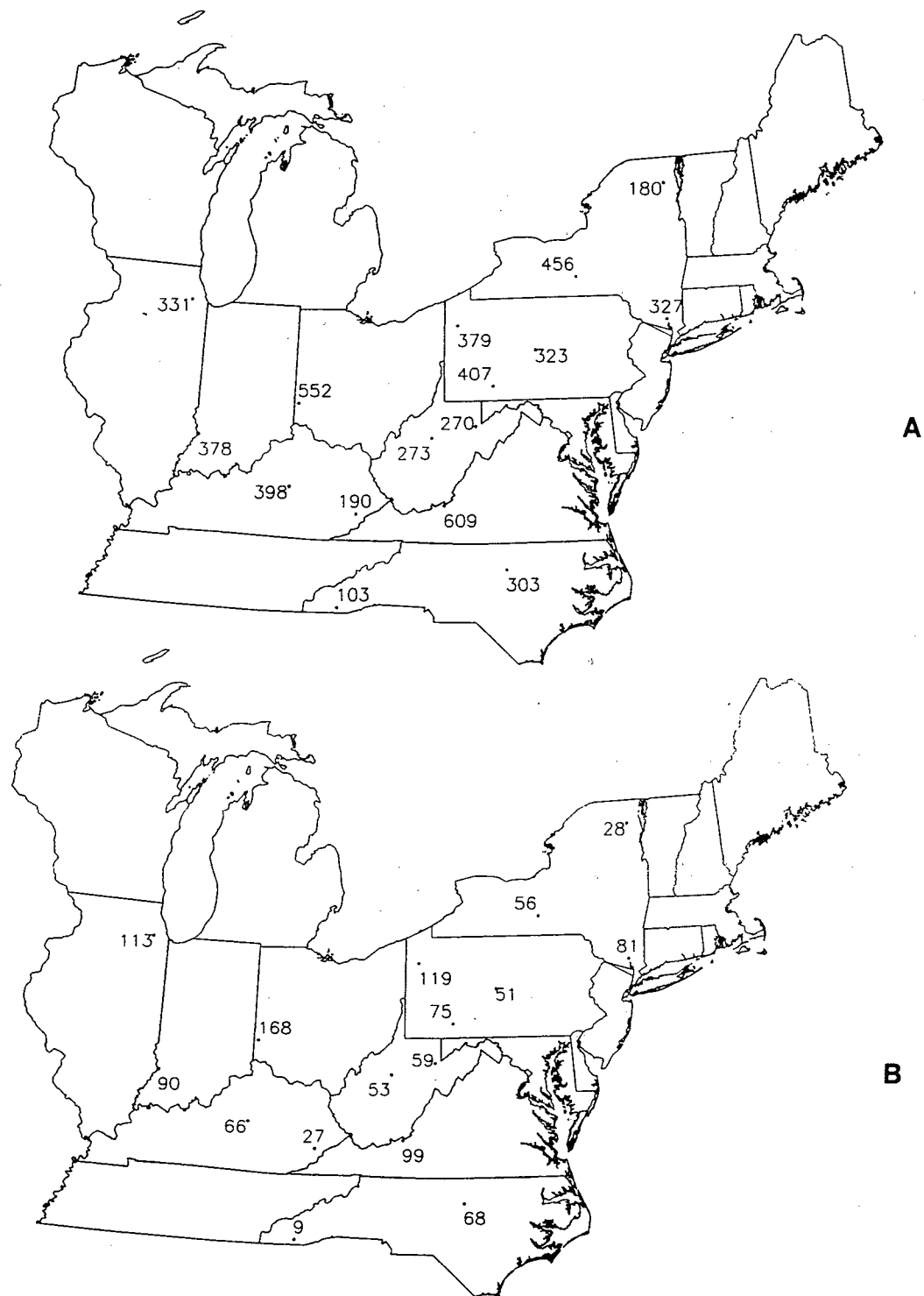


Figure 61. Number of hourly observations greater than or equal to 80 ppb, 1988 (A) versus 1989 (B)

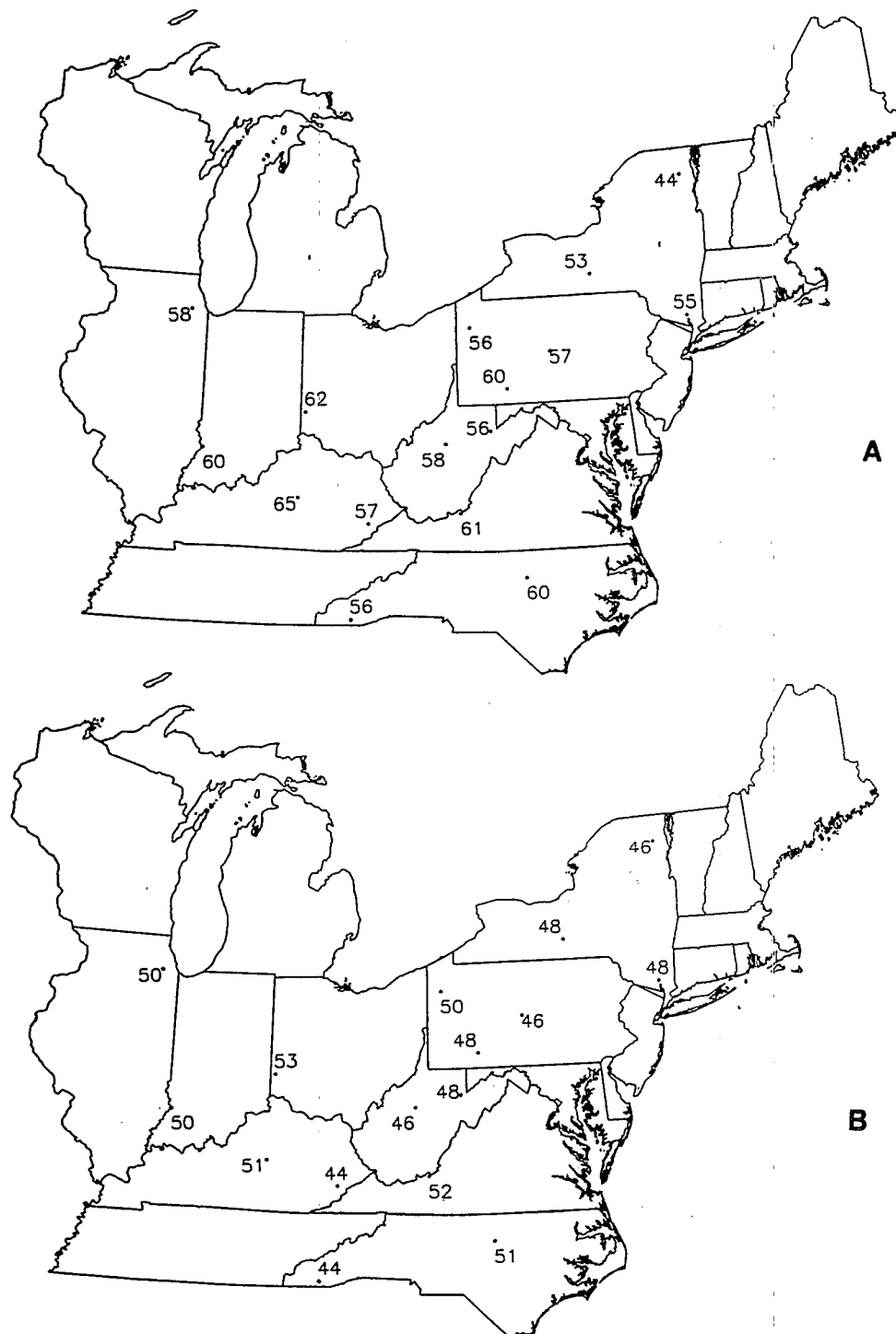


Figure 62. Seven-hour growing season averages (ppb), 1988 (A) versus 1989 (B)

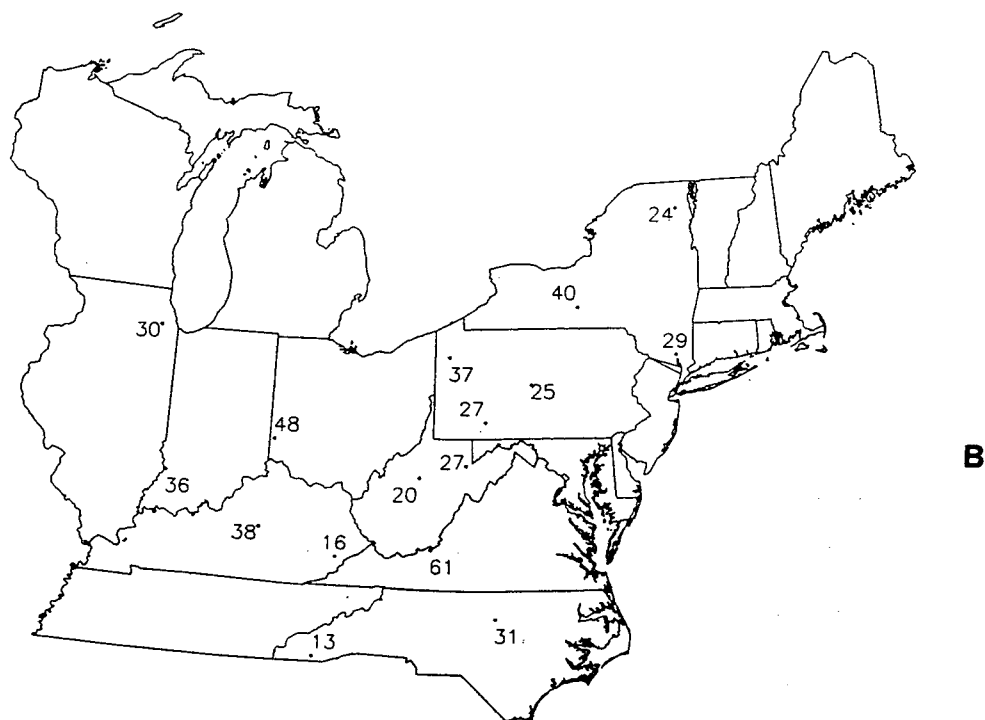
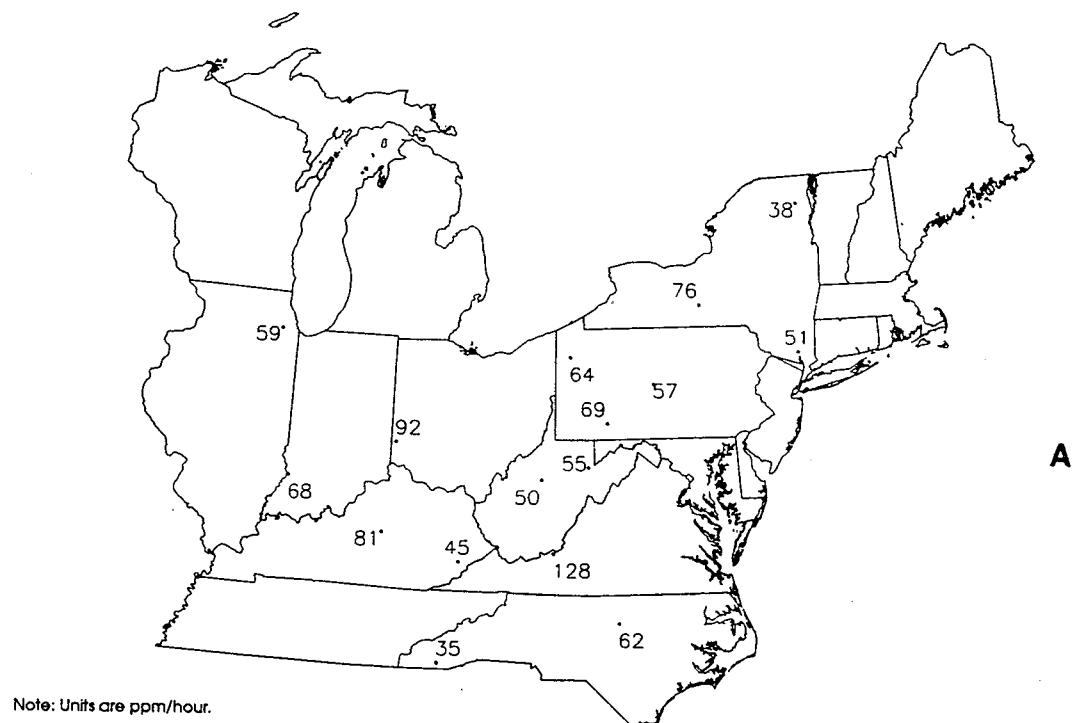


Figure 63. Integrated O₃ exposure indices (W126) for 1988 (A) and 1989 (B)

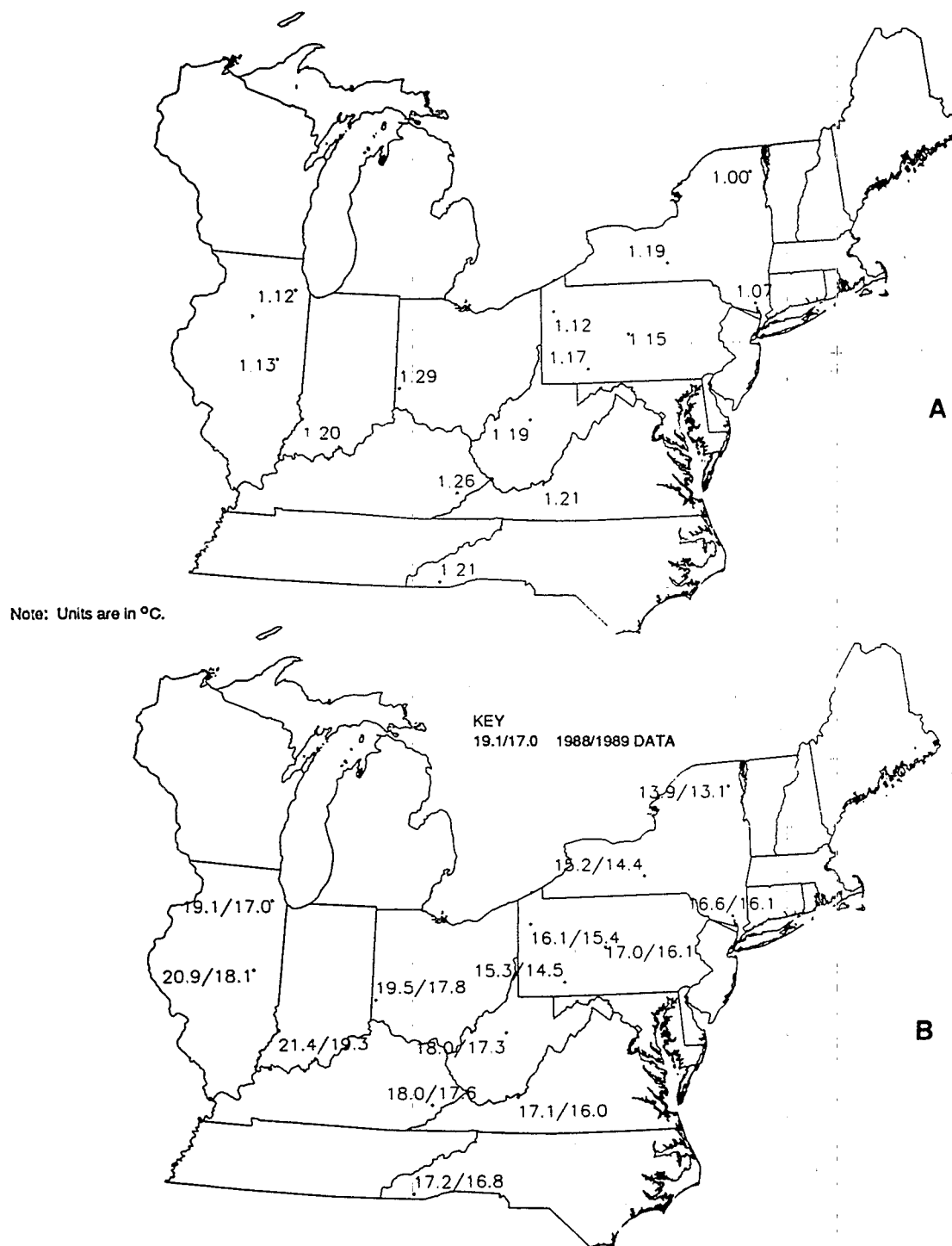


Figure 64. Ratios of 1988 versus 1989 growing season solar radiation (A) and 1988/1989 growing season temperatures (B)

Growing season temperatures also showed marked differences between years, with higher temperatures in 1988 than 1989. This is especially apparent in the midwest, where growing season averages differ by as much as 2 percent or more. This difference between years is many times the uncertainty of the measurement. The 1988 growing season appears to have been significantly hotter, drier, and sunnier than 1989. Although these results do not prove cause and effect, they reinforce the notion of meteorology as an important forcing function to O_3 exposure.

4.4 ESTIMATED DRY DEPOSITION

Another NDDN objective is to produce long-term data on patterns and trends of dry deposition across the continental United States. Ultimately, dry deposition rates will be calculated using one or more algorithms that couple land use or vegetation data, meteorological data, and air-quality data to produce weekly, seasonal, and annual fluxes. This section presents estimates of dry deposition rates for 1989 using assumed values for annual average deposition velocities taken from the literature and annual average concentration data from 28 NDDN sites in the eastern United States that were operational throughout 1989. They are specifically not intended to be an approximation of, or substitute for, deposition estimates based on the inferential approaches described by Hicks *et al.* (1985) and Wesely (1988). Calculated dry deposition rates are then compared with average wet deposition rates obtained by NADP and other precipitation chemistry networks in the vicinity of NDDN sites. The wet deposition sites used in this comparison, and distances to neighboring NDDN sites, are listed in Table 16. Results are intended only to illustrate a possible range of dry deposition rates across the network.

The estimated deposition velocities used in these calculations are listed in Table 17. Tabulated values reflect a variety of theoretical estimates, experimental tests, and modeling results. Wu and Davidson (1988) used the resistance model of Hicks *et al.* (1985) to estimate weekly and annual deposition velocities of SO_2 , SO_4^{2-} , and HNO_3 for three sites during 1986. Ranges of annual average deposition velocity for Oak Ridge, TN, Penn State University, PA, and Whiteface Mountain, NY (all current or former NDDN sites), were 0.07 to 0.13 centimeter per second (cm/sec) for SO_4^{2-} , 0.18 to 0.33 cm/sec for SO_2 , and 0.96 to 1.9 cm/sec for HNO_3 . Sheih *et al.* (1979) and Wesely and Lesht (1988) have developed computer routines for estimating deposition velocity as a function of land use, season, and meteorological stability class. Wesely and Lesht (1988) recently compared their model with a site-specific inferential technique similar to that which may be used for the NDDN (Hicks *et al.*, 1988). Calculated deposition velocities were consistent with data shown in Table 17 and, on average, within ± 30 to 40 percent of deposition velocities provided by the inferential technique. Little information is available on the deposition velocity for atmospheric NO_3^- . Since, by definition, both NO_3^- and SO_4^{2-} occur in

TABLE 16. WET DEPOSITION SITES USED TO EVALUATE WET VERSUS DRY DEPOSITION RATES

NDDN site	Wet deposition site		Distance between wet/dry sites (km)
	Network	Site identifier Averaging period	
101	NADP	NC41	1984-1988
104	NADP	NY99	1984-1988
105	NADP	NY98	1985-1988
106	NADP	PA55	1984-1988
107	NADP	WV18	1984-1988
109	NADP	NH02	1984-1988
110	MAP3S	Ithaca, NY	1983-1987
112	NADP	PA29	1984-1988
113	PADMP	M.K. Goddard, PA	1984-1988
117	PADMP	Laurel Hill, PA	1984-1988
118	NADP	VA28	1984-1988
120	NADP	VA13	1984-1988
121	NADP	KY22	1984-1988
122	MAP35	Oxford, OH	1983-1987
128	PADMP	Gettysburg, PA	1984-1988
129	NADP	KY03	1984-1988
130	NADP	IL11	1984-1988
133	NADP	IN20	1984-1988
135	NADP	ME00	1984-1988
137	NADP	NC25	1984-1988
140	NADP	IN22	1985-1988
144	NADP	NJ99	1984-1988
146	NADP	IL19	1984-1988
149	NADP	MI53	1984-1988
150	NADP	AR03	1985-1988
151	NADP	MS30	1985-1988
152	NADP	AL99	1985-1988
153	NADP	GA41	1985-1988

Source: ESE, 1990.

TABLE 17. ESTIMATED DEPOSITION VELOCITIES FOR AEROSOLS AND GASES

Species	Vd (cm/sec)	Reference
SO ₄ ²⁻	0.1 - 0.2	Sehmel, 1980; Sheih <u>et al.</u> , 1979; Voldner <u>et al.</u> , 1986; Wesely and Lesht, 1988; Wu and Davidson, 1988
NO ₃	0.1 - 0.2	Assumed to be the same as SO ₄ ²⁻
SO ₂	0.2 - 0.4	Sehmel, 1980; Sheih <u>et al.</u> , 1979; Cadle <u>et al.</u> , 1987; Wesely and Lesht, 1988; Wu and Davidson, 1988
HNO ₃	1.0 - 2.0	Heubert, 1983; Wesely and Lesht, 1988; Wu and Davidson, 1988

Note: cm/sec = centimeter per second.

Vd = deposition velocity.

Source: ESE, 1990.

the particulate phase, the same range of deposition velocities was used for these species. However, differences in particle size and reactivity could result in substantial differences in deposition velocities for NO_3 and SO_4^{2-} .

Estimates of annual dry deposition for SO_4^{2-} , SO_2 , NO_3 , and HNO_3 are listed in Table 18. Estimated dry deposition for SO_4^{2-} plus SO_2 appears to be highest in western Pennsylvania (Site 117) and lowest in southwestern North Carolina (Site 137), northern Maine (Site 135), and northern Florida (Site 156). This pattern reflects the annual average SO_2 concentration, since it appears unlikely that SO_4^{2-} contributes more than 30 percent of the estimated dry deposition at any site. Relatively high deposition in northern Illinois, southern Indiana, and eastern Tennessee may be the result of local SO_2 emissions. Similarly high values in western Pennsylvania and West Virginia seem to reflect more widespread sources.

Estimated dry deposition of NO_3 plus HNO_3 shows similar values over much of the northeast and midwest but considerable variability in the vicinity of the Appalachian Mountains. Deposition at the mountaintop site in Virginia (Site 120) appears to be approximately three times that at complex terrain sites in eastern Kentucky and North Carolina (Site 121 and Site 137). The overall pattern is almost an exact transformation of annual HNO_3 concentration due to large differences in concentration and deposition velocity (assumed) between HNO_3 and NO_3 . At no site was NO_3 responsible for more than 15 percent of the estimated dry deposition of NO_3 plus HNO_3 . As stated previously, NO_3 deposition could be significantly greater if it exists in large particles with appreciable settling velocities.

Wet and dry deposition data from a variety of NDDN sites are compared in Figures 65 and 66. The data shown for dry deposition reflect the midpoint of the SO_4^{2-} plus SO_2 fluxes listed in Table 17 and, therefore, are uncertain by at least ± 50 percent. In addition, estimated dry deposition rates refer to calendar year 1989, while wet deposition rates are averaged over the period 1984 through 1988 (or 1983 through 1987). Thus, the data illustrate possible, rather than actual, relationships between wet and dry deposition. Results for sulfur deposition suggest that wet deposition is the dominant process in northern New York (Site 105), but that at most other sites wet and dry deposition could be similar, especially if the upper limit for the deposition velocity of SO_2 is approached. Results for nitrogen suggest regional differences in the comparability of wet and dry deposition. For the northeast, dry deposition would be comparable to wet deposition only if the upper limit deposition velocity for HNO_3 is attained. Data for the midwest and parts of the southeast, in contrast, suggest that wet and dry deposition are comparable even if the lower limit deposition velocity for HNO_3 is attained.

TABLE 18. ESTIMATED DRY DEPOSITION OF SO_2 , SO_4^{2-} , HNO_3 , AND NO_3^- DURING 1989

Site	SO_2 (eq/ha)	SO_4^{2-} (eq/ha)	Percent SO_4^{2-}	HNO_3 (eq/ha)	NO_3^- (eq/ha)	Percent HNO_3^*
101	150-300	40-80	79	120-240	3-7	96
104	270-550	35-70	89	120-240	3-7	96
105	80-170	20-40	80	70-140	1-3	97
106	310-620	40-80	89	120-240	7-14	92
107	280-560	50-100	90	105-210	3-7	95
109	60-110	20-40	75	45-90	1-3	98
110	260-510	40-80	87	145-290	4-8	97
112	300-600	40-80	88	120-240	2-5	98
113	380-760	40-80	90	140-275	6-12	96
117	460-910	45-90	92	130-250	3-5	98
118	220-440	45-90	83	160-310	3-5	97
120	200-400	40-80	83	145-290	3-6	97
121	90-180	40-80	69	45-90	3-6	94
122	340-690	50-100	87	155-310	11-23	93
128	340-690	45-90	89	180-360	8-18	96
129	270-540	50-100	84	160-320	5-10	97
130	200-390	45-90	82	135-270	15-30	90
133	210-420	45-90	82	110-225	18-37	86
135	50-100	20-35	71	35-70	1-3	97
137	50-90	35-70	59	50-100	1-2	98
140	380-770	50-100	88	120-245	13-27	90
144	280-560	40-80	88	155-310	7-14	96
146	350-700	40-80	90	115-230	20-39	85

TABLE 18. (continued)

Site	SO ₂ (eq/ha)	SO ₄ ²⁻ (eq/ha)	Percent SO ₂ *	HNO ₃ (eq/ha)	NO ₃ ⁻ (eq/ha)	Percent HNO ₃ *
149	100-210	30-55	77	90-180	5-10	95
150	60-110	35-70	63	75-150	3-6	96
151	90-180	35-75	72	80-160	3-6	96
152	170-330	45-90	76	105-210	8-16	93
153	170-340	40-85	81	105-210	2-5	98
156	50-100	30-55	63	50-100	3-6	94

*Assuming midpoint of deposition range.

Source: ESE, 1990.

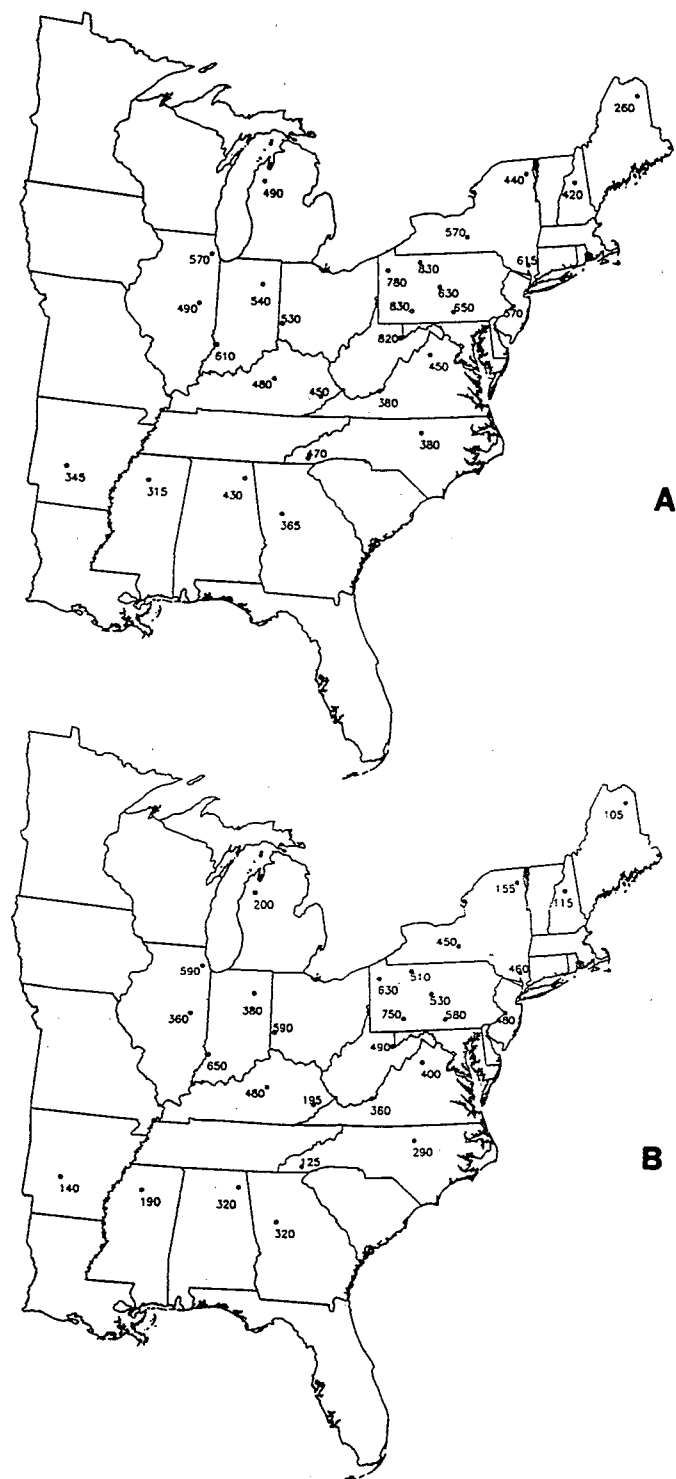


Figure 65. Observed wet (A) and estimated dry (B) deposition (eq/ha-yr) of SO_4^{2-} at selected sites

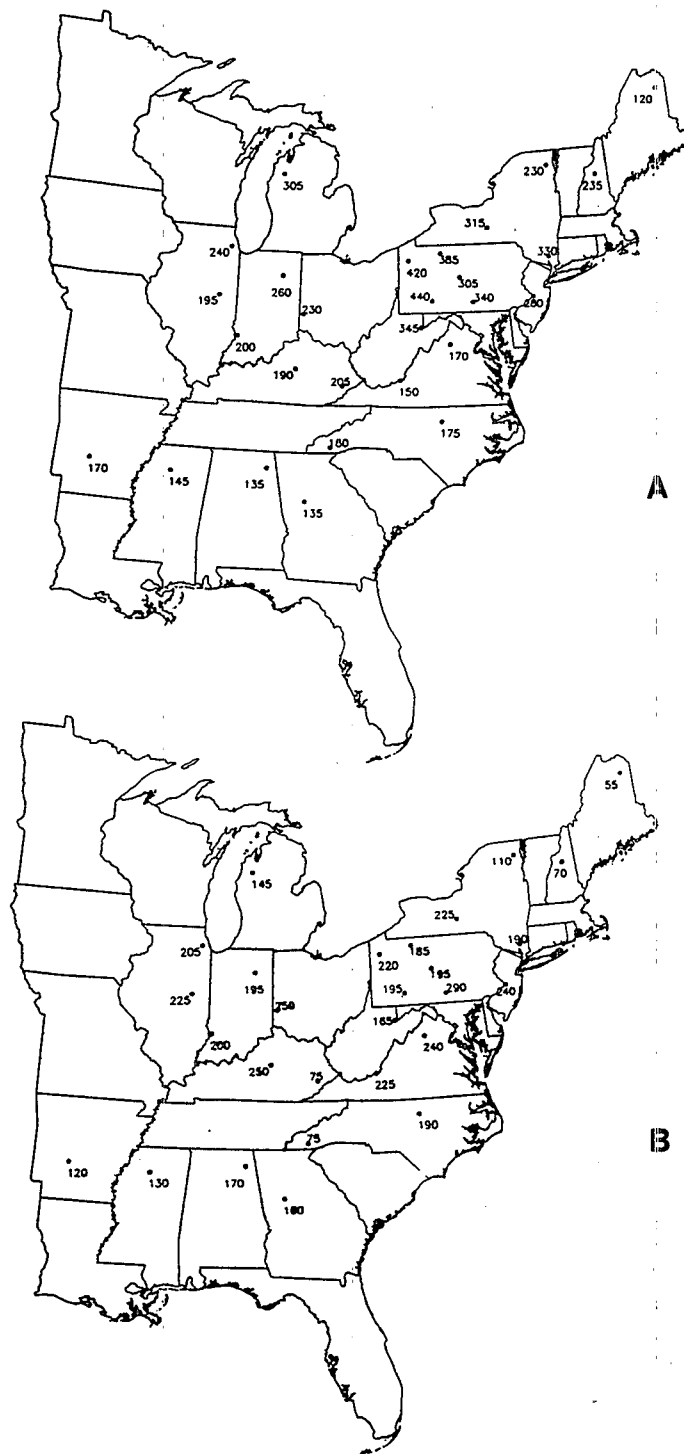


Figure 66. Observed wet (A) and estimated dry (B) deposition (eq/ha-yr) of NO_3 at selected sites

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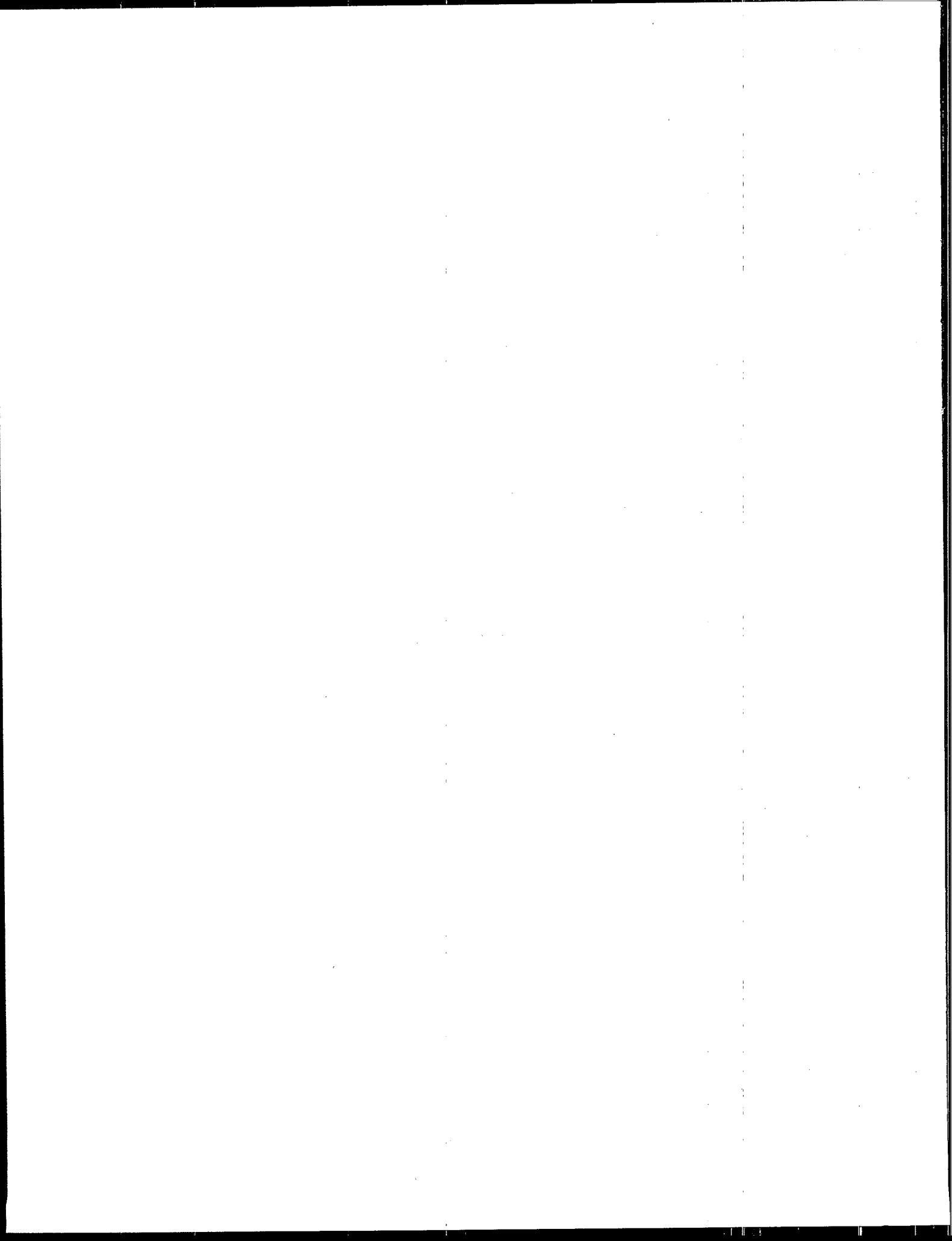
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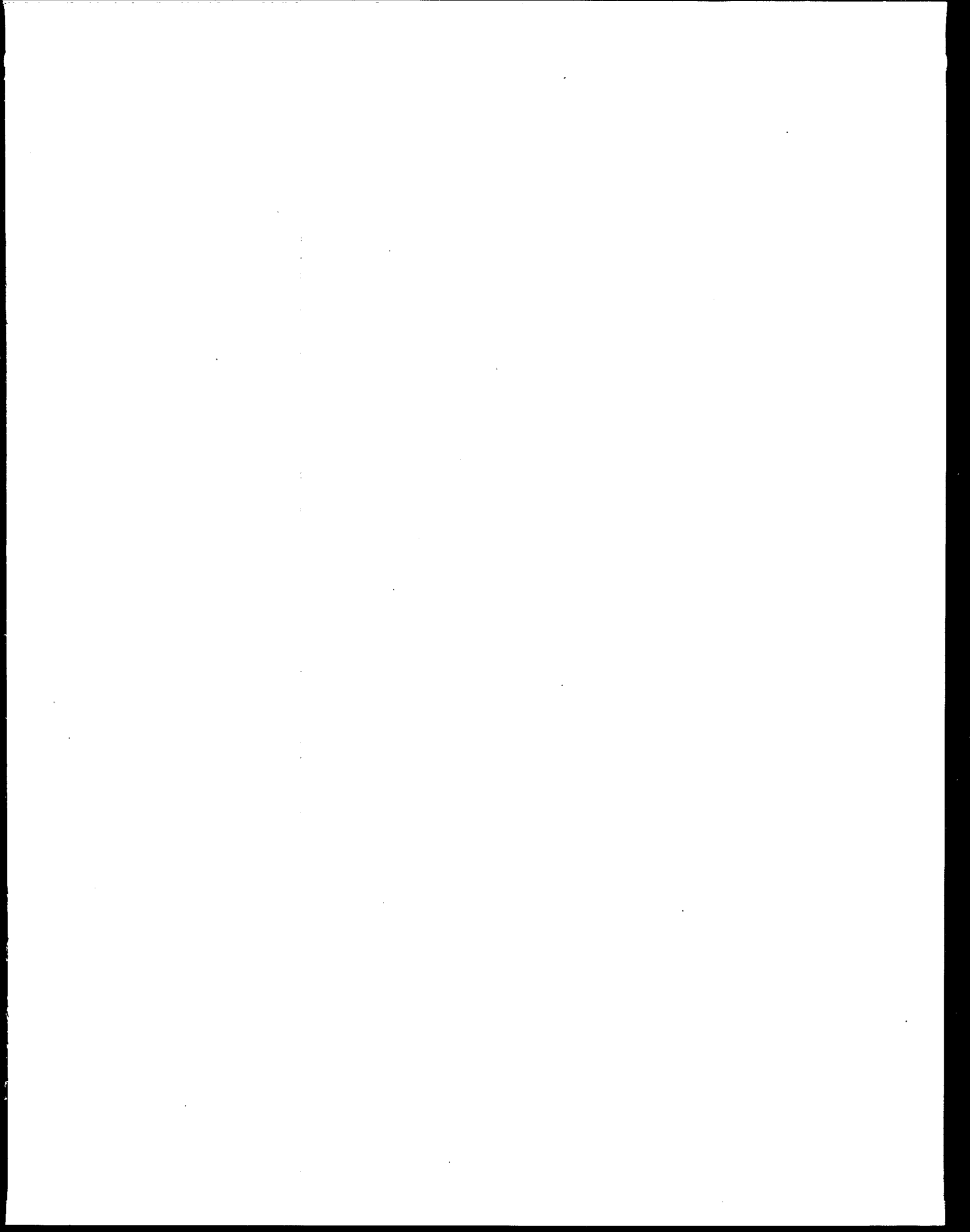
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