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CASTNet National Dry Deposition Network 1990–1992 Status Report

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CASTNet
NATIONAL DRY DEPOSITION NETWORK
1990-1992 STATUS REPORT

by

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Foreword

In 1986, the U.S. Environmental Protection Agency (EPA) established the National Dry Deposition Network (NDDN) as a part of the Agency's support to the National Acid Precipitation Assessment Program (NAPAP). The goal of the NDDN was to provide NAPAP with estimates of dry deposition flux to use in model validation, determination of spatial patterns of dry deposition, and dry deposition flux data to relate deposition to ecological effects. NAPAP was completed in 1990 with the issuance of the Integrated Assessment.

Also, in 1990, Congress amended the Clean Air Act. These amendments require reduction in emissions of sulfur and nitrogen oxides. A national monitoring network was mandated as part of the Clean Air Act Amendments to determine the effectiveness of these future emission reductions. EPA has established the Clean Air Status and Trends Network (CASTNet) to provide data to determine relationships between emissions, air quality, deposition, and ecological effects. The basic tenets of CASTNet are to monitor sensitive ecosystems, to define the spatial distribution of pollutants, to detect and quantity trends in pollutants, to implement monitoring in cooperation with other agencies and organizations, and to implement monitoring only to fill gaps in monitoring coverage.

In 1990, the NDDN became part of CASTNet. CASTNet is the primary source for atmospheric data to estimate dry deposition and to provide data on rural ozone. The National Atmospheric Deposition Program (NADP) is the primary source for data on wet deposition. CASTNet supplements the NADP with wet deposition measurements at selected sites. The National Oceanic and Atmospheric Administration provides intensive dry and wet deposition monitoring as part of the Atmospheric and Integrated Research Monitoring Network (AIRMoN). The National Park Service operates an air quality monitoring network for ozone, sulfur dioxide, and particulate matter at a number of National Parks. Each of the above networks contributes specific data to provide a comprehensive picture of deposition and air quality in primarily rural areas of the United States.

This report is the first in a series of summaries of concentration and deposition data from the CASTNet Deposition Network. This report covers the years 1990, 1991, and 1992.

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Abstract

The National Dry Deposition Network (NDDN) was established to provide long-term estimates of dry acidic deposition across the continental United States. Fifty routine sites were operational from 1990 to 1992, 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 (O_3) and meteorological variables required for estimation of dry deposition rates. Weekly average atmospheric concentrations of particulate sulfate (SO_4^{2-}), particulate nitrate (NO_3^-), particulate ammonium (NH_4^+), sulfur dioxide (SO_2), and nitric acid (HNO_3) were measured at all sites and wet deposition of acidity and related species were measured at selected sites. Two methods development sites were installed during 1991 to evaluate: 1) comparability of United States and Canadian air quality measurements, and 2) effects of terrain on pollutant concentration and deposition. Routine application of an inferential model for calculation of deposition velocities and dry deposition fluxes was also begun.

Atmospheric concentration data show species-dependent variability in space and time. In general, the highest concentrations are observed in the northeast and midwest, and these are a factor of 5 to 10 times higher than those observed in the west. Significant concentration gradients are also observed from the northeast through upper northeast and midwest through upper midwest. Annual average concentrations of most species decreased from 1989 to 1992 in all subregions of the network.

Dry deposition calculations for 1990 and 1991 show that SO_2 and HNO_3 dominate sulfur and nitrate-nitrogen fluxes, respectively. In general, SO_2 accounts for more than 75 percent of dry sulfur deposition at eastern sites and more than 50 percent of dry sulfur deposition at western sites. HNO_3 accounts for more than 90 percent of dry nitrate-nitrogen deposition at all sites. Total deposition estimates for approximately 15 sites show that dry deposition accounts for about 20 to 50 percent of wet plus dry sulfur deposition and 30 to 60 percent of wet plus dry nitrate-nitrogen deposition.

Data from a pair of sites located in a valley and on a nearby ridge show that elevational gradients in concentration, deposition velocity, and flux can be significant. Reactive gas concentrations and fluxes are 2 to 4 times higher at the ridge than in the valley, suggesting that deposition in areas of complex terrain may be difficult to estimate.

Collocated data from the Canadian Acid Precipitation Monitoring Network (CAPMoN) and NDDN for a site in southern Ontario indicate that annual average concentrations are within ± 5 percent, except for SO_2. NDDN data for SO_2 are lower than CAPMoN by about 10 percent. These results indicate that methodological differences between networks should not interfere significantly with pattern and trend analyses across eastern North America.

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Acronyms and Abbreviations

AES	Atmospheric Environment Service
°C	degrees Celsius
Ca^{2+}	particulate calcium
CAPMoN	Canadian Acid Deposition Monitoring Network
Cl^-	chloride
cm/sec	centimeters per second
EPA	U.S. Environmental Protection Agency
ESE	Environmental Science & Engineering, Inc.
HNO_3	nitric acid
IC	ion chromatography
ICAP	inductively coupled argon plasma
ICP-AE	inductively coupled plasma-atomic emission
K^+	particulate potassium
K_2CO_3	potassium carbonate
kg-N/ha	kilogram of nitrate per hectare
kg-S/ha	kilogram of sulfate per hectare
km	kilometer
L/min	liters per minute
LAI	leaf area index
m	meter
MAD	median absolute difference
MAPD	median absolute percent difference
MFC	mass flow controller
Mg^{2+}	particulate magnesium
m/sec	meters per second
mmHg	millimeters of mercury
Na^+	particulate sodium
NAAQS	National Ambient Air Quality Standard
NADP/NTN	National Atmospheric Deposition Program/National Trends Network
NDDN	National Dry Deposition Network
NH_3	ammonia
NH_4^+	particulate ammonium
NH_4NO_3	ammonium nitrate
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
NO_x	nitrogen oxide
NO_2^-	nitrite
NO_3^-	particulate nitrate
O_3	ozone
ppb	parts per billion
RPD	relative percent difference
RTD	resistance-temperature device
SO_2	sulfur dioxide
SO_4^{2-}	particulate sulfate
tpy	tons per year
µg/L	micrograms per liter
$\mu g/m^3$	micrograms per cubic meter
µm	micrometer
USGS	U.S. Geological Survey
UV	ultraviolet
V_d	deposition velocity
W/m^2	watts per square meter

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*deceased

Chapter 1
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 10 to 15 years; however, comparable information is unavailable for dry deposition rates. This lack of information increases the uncertainty in estimates of interregional, national, and international transport and confounds efforts to determine the overall impact of atmospheric deposition.

The direct measurement of dry deposition is not straightforward, but a number of investigations have shown that it can be reasonably inferred by coupling air concentration 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 atmospheric species [including nitric acid (HNO_3)] and to use site-specific meteorological data. Similar 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 the NDDN is to obtain field data at approximately 50 sites throughout the United States to establish patterns and trends of dry deposition. The approach adopted by the NDDN is to calculate dry deposition using measured air pollutant concentrations and inferred deposition velocities (V_ds) estimated from meteorological, land use, and site characteristic data. The inferential model currently used for dry deposition calculations is a multi-layer version of the Big Leaf Model developed by Hicks et al. (1985).

This report summarizes results of NDDN monitoring activities from 1990 through 1992. Annual concentration data for atmospheric sulfur and nitrogen species are presented, and temporal variability is described. Results of dry deposition calculations for 1990, 1991, and 1992 are discussed, and the relative contribution of gases versus aerosols are evaluated. Wet deposition data for approximately 15 NDDN sites are presented and then used, along with dry deposition calculations, to estimate total depositions of sulfur and nitrate-nitrogen. The relative magnitude of wet and dry deposition are discussed. Ozone concentrations and exposure statistics are presented for 1990, 1991, and 1992.

Data are also presented from two comparability studies initiated in 1991. The first of these involves investigation of measurement biases between atmospheric sampling methods used by United States and Canadian acid deposition trends programs. Data are presented and analyzed from a collocated site in Ontario, Canada. The second study is an investigation of a terrain-induced bias in concentration measurements and dry deposition estimates. Data are presented from a pair of sites in southwestern North Carolina that are separated horizontally by about 1,000 meters (m) and in elevation by about 350 m.

Chapter 2
Summary and Conclusions

Quantitative information on dry deposition fluxes and atmospheric concentrations is needed to evaluate patterns and trends in total deposition and to support model evaluation and ecosystem effects studies. Fifty monitoring sites were operational from 1990 through 1992, including approximately 15 sites which measured wet deposition. Ozone (O_3) and meteorological data were collected continuously, and atmospheric sulfur and nitrogen species and wet deposition (if applicable) were sampled on weekly intervals. Dry deposition fluxes for 1990, 1991, and 1992 were calculated using the multi-layer model developed by the National Oceanic and Atmospheric Administration (NOAA) and data collected from the 50-site network. Studies at two non-routine sites investigated the comparability of United States and Canadian trends measurements and local variability in concentrations, V_ds, and fluxes.

Annual concentration data for sulfur and nitrogen species show fairly consistent spatial patterns from 1990 through 1992. In the eastern United States, the highest average concentrations of particulate sulfate (SO_4^{2-}) [6 to 7 micrograms per cubic meter ($\mu g/m^3$)] and SO_2 (15 to 20 $\mu g/m^3$) occur in an area surrounding the Ohio River Valley. Average SO_4^{2-} decreases gradually toward the periphery of the network to about 2.0 $\mu g/m^3$ in northern Maine and 3 to 4 $\mu g/m^3$ in Florida, Arkansas, and Wisconsin. Average SO_2 exhibits much more local variability than SO_4^{2-} and decreases more rapidly towards the periphery of the network. For western sites, SO_4^{2-} and SO_2 concentrations are generally well below 1.0 $\mu g/m^3$ and show no strong evidence of a pattern, except for somewhat elevated values at two Arizona sites.

Atmospheric concentration data for HNO_3 and particulate nitrate (NO_3^-) also show substantial variability across the network; however, differences between eastern and western sites are not as great as for SO_4^{2-} and SO_2. In general, concentration patterns for HNO_3 and NO_3^- appear to be strongly influenced by land-use and topographic features. Maximum HNO_3 concentrations (3 to 4 $\mu g/m^3$) are observed at scattered sites in New York, Pennsylvania, Virginia, and Ohio, while minimum concentrations (<1.0 $\mu g/m^3$) are observed in Maine, Arkansas, Florida, Kentucky, and North Carolina. Substantial variability in HNO_3 concentrations (factors of 2 to 3) occurs over fairly short distances in and around the southern Appalachian Mountains. Sites in this area with good fetch exhibit concentrations substantially higher than sites with limited fetch.

Annual patterns of NO_3^- aerosol show peak concentrations (3 to 4 $\mu g/m^3$) in agricultural areas of the midwest and minimum concentrations (<0.5 $\mu g/m^3$) in the forested northeast. Intermediate

concentrations occur at sites in pastured land or near limited agricultural activities. These observations suggest that land use (specifically agricultural activity) affects the partitioning of gas and aerosol nitrogen species. Two potential mechanisms for this include reaction between HNO_3 and either soil particles or ammonia (NH_3). The first mechanism would produce aerosol NO_3^- in the 1 to 5-micrometer (μm) range, and the second would produce aerosol NO_3^- in the <1-μm range. Insufficient chemical and physical data are currently available from the network to distinguish between these two formation mechanisms.

Inspection of data from 1989 through 1992 shows that atmospheric concentrations of all measured species fell by 10 to 25 percent over the 4-year period. Reductions varied from site to site but were of this magnitude for all eastern sites, as a group, all western sites, as a group, and for site groups in the midwest, northeast, and southeast. In general, SO_2 exhibited the largest change in concentration, and HNO_3 exhibited the smallest change in concentration. O_3 exhibited a decrease in the number of values above the National Ambient Air Quality Standard (NAAQS) and a decrease in annual average concentrations from 1990 and 1992.

Dry deposition calculations show that annual sulfur (S) fluxes (SO_4^{2-} plus SO_2) range from 1 kg-S/ha to about 10 kg-S/ha in the eastern United States and from 0.2 to 1.5 kg-S/ha in the western United States. Deposition of SO_2 accounts for the majority of dry sulfur flux at all NDDN sites and for at least 75 percent and 50 percent of dry sulfur deposition at eastern and western sites, respectively. Although the physical and chemical phenomena involved are complex, results suggest that the spatial pattern of SO_2 deposition is controlled primarily by variability in SO_2 concentrations, rather than variability in deposition velocity (V_ds).

Dry deposition of nitrate-nitrogen (N) dry deposition (HNO_3 plus NO_3^-) ranges from <1 to 5 kg-N/ha in the eastern United States and from 0.3 to 1.3 kg-N/ha in the western United States. Deposition of HNO_3 accounted for at least 90 percent, and usually greater than 95 percent, of dry nitrate-nitrogen fluxes at all sites. Inspection of deposition data suggests that spatial variability is a function of both concentration and deposition velocity (V_ds).

Total deposition estimates (i.e., measured wet deposition plus calculated dry deposition) for about 15 sites shows that dry deposition accounts for 20 to 50 percent and 30 to 60 percent of sulfur and nitrate-nitrogen inputs, respectively. Dry sulfur deposition appears to be roughly equivalent to wet sulfur deposition near sources of SO_2 (e.g., the midwest and northeast). Dry nitrate-nitrogen deposition appears to be roughly equivalent to wet deposition at sites located on ridges and in substantial clearings.

Inspection of data from rural sites in and around the Appalachian Mountains indicates that concentrations and fluxes of SO_2 and HNO_3 can vary by as much as factors of 2 to 5 within only a few hundred kilometers and that this variability is unlikely to be related to local sources of SO_2 and nitrogen oxides (NO_x). Data from a pair of sites located on a ridge and in a valley in the southern Appalachian Mountains may explain this phenomenon. The ridge site exhibits significantly higher concentrations and V_ds than the valley site. Together, these factors give rise to dry deposition rates that are factors of 1.6 (for SO_4^{2-}) to 4.4 (for HNO_3) higher at the ridge site than the valley site. These observations verify modeling work by McMillen (1990), which suggested that deposition rates in complex terrain could be highly variable. Ridgetop sites may provide upper limit estimates of regional deposition, while valley and intermediate elevation sites may provide reasonable estimates of average deposition to specific ecosystems. Further work has been initiated to determine if elevation is important elsewhere, and, if so, how data at a single site can be scaled over areas of interest.

Comparison of atmospheric concentration data from the United States and Canadian trends networks [NDDN and Canadian Acid Precipitation Monitoring Network (CAPMoN)] shows that annual averages of most species agree within 5 percent. Data for SO_2 differ by about 10 percent, on average, between networks, with NDDN concentrations almost invariably lower than those of CAPMoN. In general, these findings suggest that data from the two networks can be readily combined for analysis of spatial patterns and long-term trends across eastern North America. Additional work has been initiated to elucidate the disparity in SO_2 concentrations between networks and to compare United States and Canadian approaches for estimating dry deposition fluxes.

Chapter 3
Network Description and Methods

3.1 Network Description

The status of the NDDN, as of December 1992, is shown in Figure 1. Forty-one primarily rural eastern sites and nine western sites were operational from 1990 through 1992. All eastern sites, with the exception of two relocations, were installed and collecting data as of January 1989, and all western sites were collecting data as of July 1989. With few exceptions, as noted below, all sites complied with siting criteria shown in Table 1. The number of sites in the network is summarized by year in Table 2.

The current network is designed to support ecological effects research and investigation of relationships between emissions and atmospheric concentrations/depositions. Recent assessments of sensitivity to O_3 and acid deposition have shown that large areas of potentially sensitive terrestrial and aquatic ecosystems exist in the eastern United States and that limited areas of sensitive ecosystems exist in the western United States (see Figures 2 and 3). These findings, coupled with the expectation of future changes in emissions of sulfur and nitrogen oxides, underly the distribution of sites in the network.

For presentation purposes, sites in the eastern United States have been grouped into six subregions (see Figure 1). Subregional designations, with numbers of sites in parentheses, are as follows: northeast (11), upper northeast (3), midwest (9), upper midwest (3), south central (11), and southern periphery (3). Besides geographic location, site groupings were based on terrain and general spatial patterns of atmospheric concentration data. The categorization of sites also divides the Appalachian Mountains into three convenient geographic ranges. The northern Appalachians, including the Adirondack Mountains of New York, the Green Mountains of Vermont, and the White Mountains of New Hampshire fall within the upper northeast subregion. The central Appalachians, including the Catskill Mountains of New York, and the Allegheny Mountains of West Virginia, fall within the northeast subregion. Finally, the southern Appalachians, including the Great Smoky Mountains of North Carolina and Tennessee, fall within the south central subregion. Each of these subregions thus includes sites in mountainous areas, both for the purpose of monitoring deposition in sensitive areas and to elucidate variability of deposition in complex terrain.

Sites in the upper northeast subregion are exclusively rural-forested, while those in the northeast subregion exhibit a range of characteristics. Six northeastern sites are rural-forested, two are rural-agricultural (106 and 128), and three are near or within the Washington-Baltimore-Philadelphia-

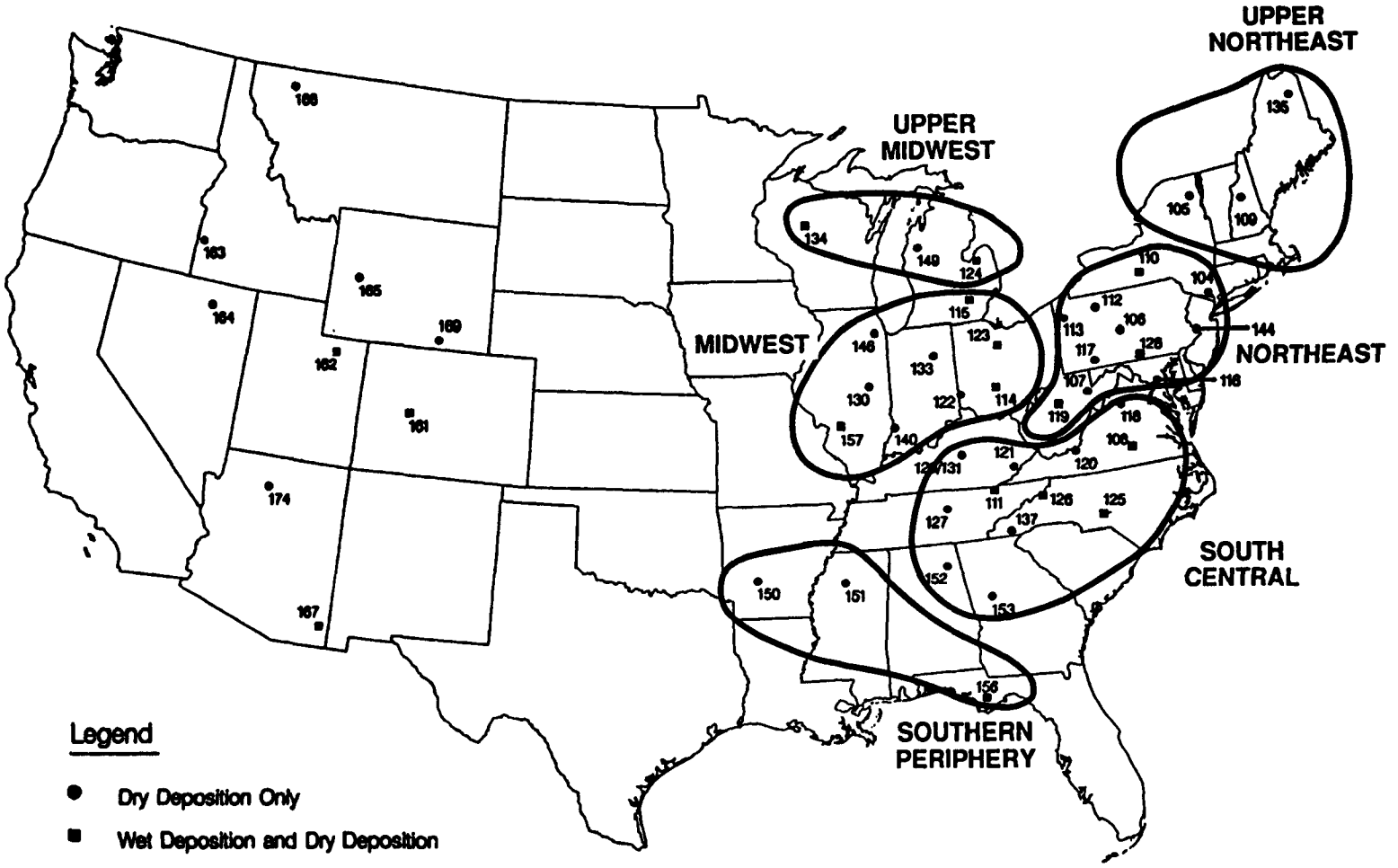


Figure 1. NDDN monitoring sites--December 1992.

Table 1. Site-Selection Criteria for CASTNet Dry Deposition Sites

Potential Interferant	Minimum Acceptable Distance (km)
SO_2 or NO_x Pt. Source >100 tpy	20
SO_2 or NO_x Pt. Source >1,000 tpy	40
Major Industrial Complex	10
Town, population 1,000 - 10,000	5
Town, population 10,000 - 25,000	10
City, population 15,000-50,000	20
City, population >50,000	40
Major highway, airport, railway	2
Secondary road, heavily traveled	0.5
Secondary road, lightly traveled	0.2
Feedlot operations	0.5
Intensive agricultural activities	0.5
Limited agricultural activities	0.1
Parking lot or large paved area	0.2
Building with fuel combustion	0.2
Sewage treatment plant	1.0
Forced main vent or lift station	0.2
Tree line	0.1
Complex terrain	variable

Note: km = kilometer.

Source: ESE.

Table 2. Deployment History of the NDDN

Year	No. of Sites*		
	Eastern	Western	Total
1988	16	0	16
1989	41	2	43
1990	41	9	50
1991	41	9	50
1992	41	9	50

*Indicates number of sites in operation as of January 1.

New York City conurbation (104, 116, and 144). The upper midwest sites are rural-agricultural or rural-forested (149). The midwest sites are rural-agricultural, except for Site 146 (suburban Chicago), which is urban-agricultural. Although rural in character, three sites (122, 140, and 157) are influenced, to a greater or lesser extent, by SO_2 emissions from nearby point sources with annual emissions in excess of 1,000 tons per year (tpy).

The south-central sites are either rural-forested or rural-agricultural but exhibit a wide range of terrain characteristics. Three sites are located above 1,000 m and form a line extending from northern Virginia to southwestern North Carolina. Site 118 is situated on a ridge of the eastern Blue Ridge Mountains, and Sites 120 and 126 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). Two sites (121 and 137) are located in hollows or valleys, and the other six sites in the subregion are in rolling terrain. The distribution of sites in this subregion provides an opportunity to investigate relationships among terrain characteristics, atmospheric concentrations, and dry deposition (see Section 4.6). Finally, all three of the southern periphery sites are rural-forested in flat or rolling terrain.

Despite apparent similarities in land use and terrain, the western sites are not homogeneous in character. For this reason, no attempt was made to group western sites. 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 semi-arid rangeland near the northern extreme of the Great Basin. Sites 165 and 169 represent the

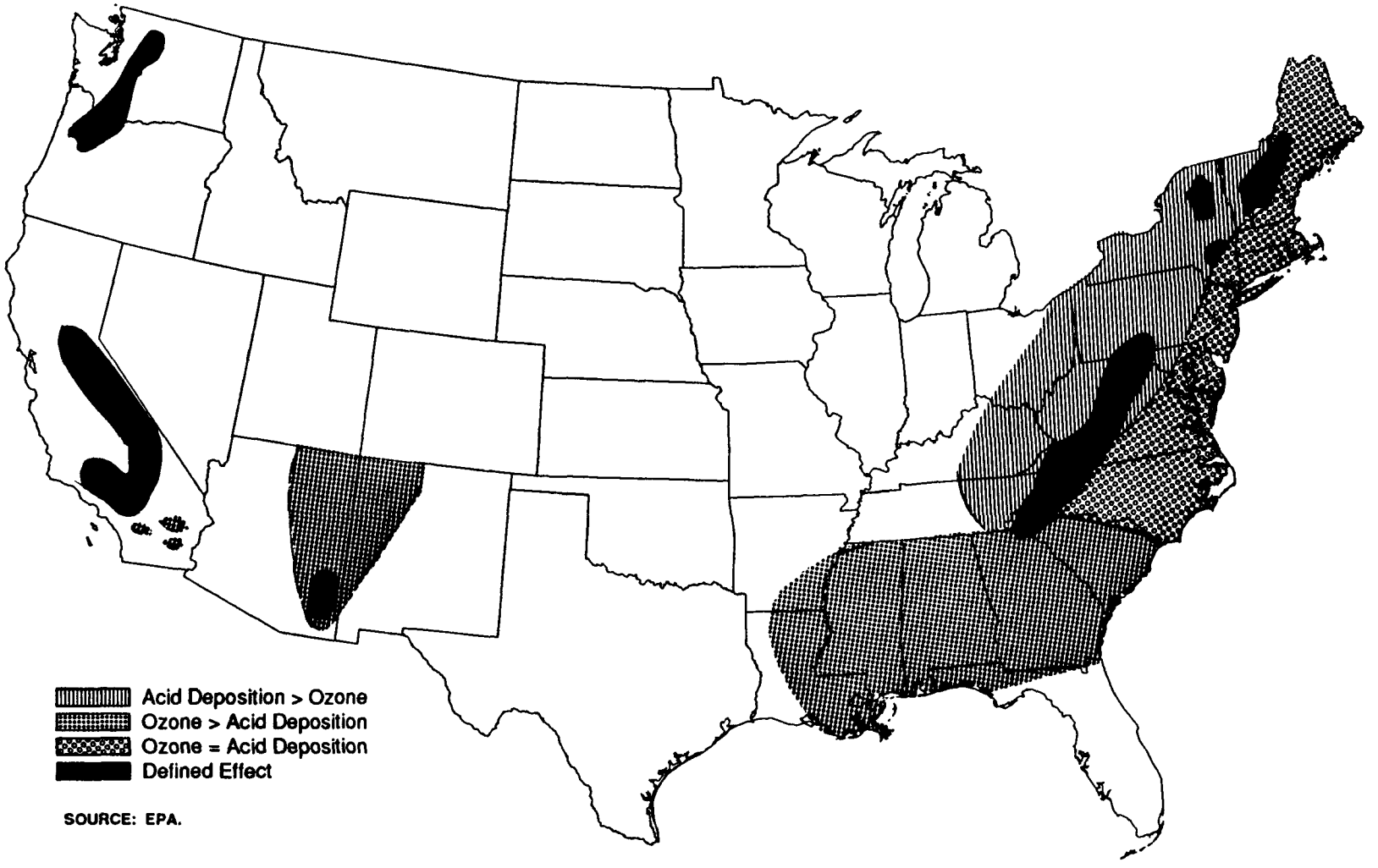


Figure 2. Sensitive terrestrial ecosystems with defined or likely effects from air pollution stress.

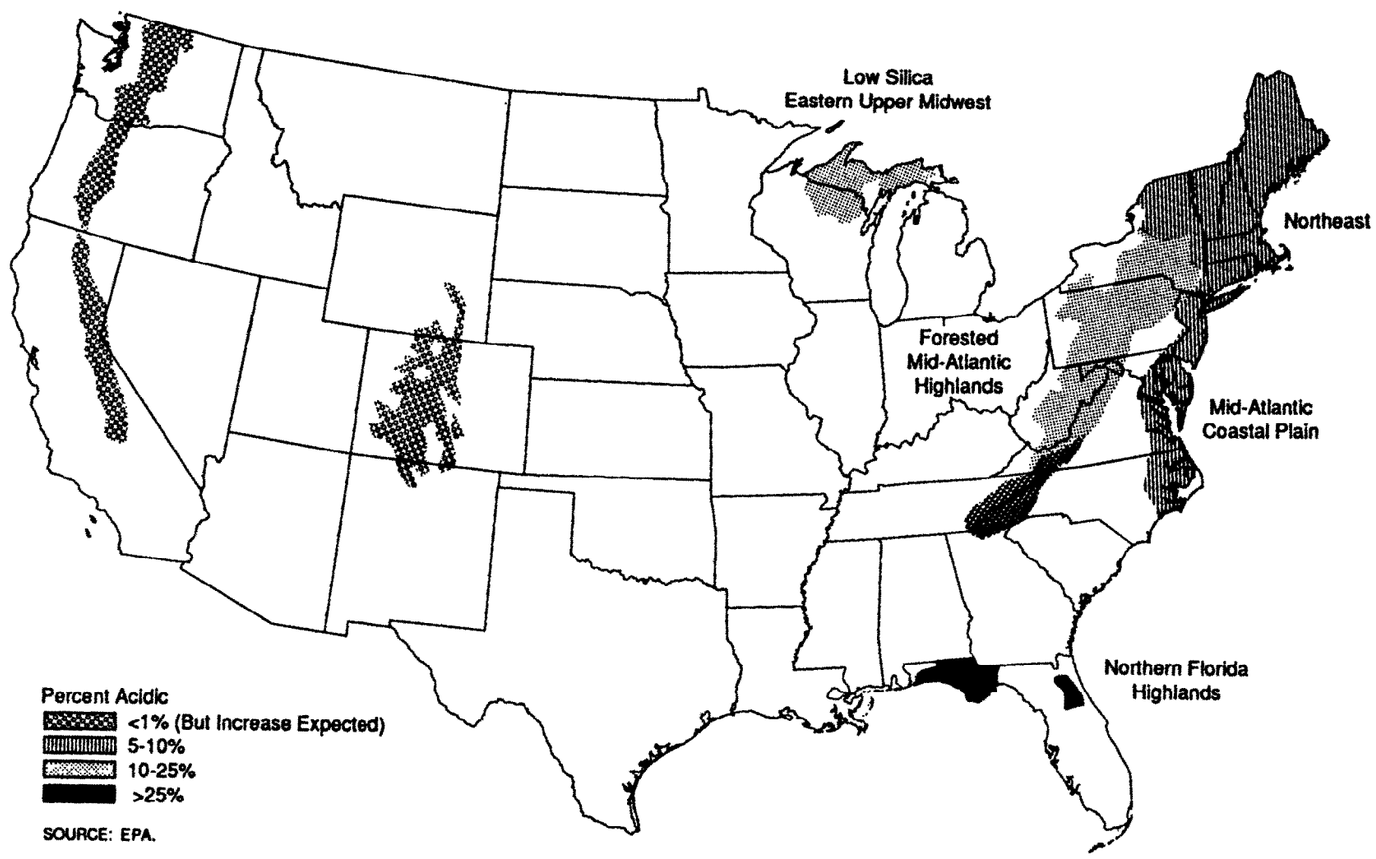


Figure 3. Acidic and susceptible aquatic ecosystems.

transition from the western Great Plains to the Rocky Mountains. Sites 167 and 174 are located in the arid southwest; 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.

Site locations and descriptive information are provided in Table 3. Terrain and land-use information refers to a 10-km radius around the site and is presented to convey a sense of the setting within which each site operates. Site numbers are used for identification purposes only and do not correlate with order of installation or operation.

3.2 Methods

This section provides a brief overview of NDDN methods. Step-by-step protocols and additional details on these activities can be found in the NDDN Field Operations Manual, Laboratory Operations Manual, and Data Management Manual (ESE, 1990a, 1990b, 1991a).

3.2.1 Field Operations

Ambient measurements for O_3, SO_2, SO_4^{2-}, NO_3^-, HNO_3, particulate ammonium (NH_4^+), and meteorological variables required for dry deposition calculations were performed at each NDDN site. Meteorological variables 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 sulfur and nitrogen species was integrated over weekly collection periods using a 3-stage filter pack. 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 to the field weekly and exchanged at each site every Tuesday. Blank filter packs were collected monthly to evaluate passive collection of particles and gases as well as contamination during shipment and handling. At 16 sites located more than 50 km from National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites (see Figure 1), wet deposition samples were collected weekly (according to NADP/NTN protocols) and shipped to ESE for chemical analysis.

Filter pack sampling and O_3 measurements were performed at 10 m using a tilt-down aluminum tower (Aluma, Inc.). 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). Wet deposition samples were collected in precleaned polyethylene buckets using an Andersen Model APS precipitation sampler. Buckets were placed on the sampler on Tuesday and removed, whether or not rainfall had

Table 3. NDDN Site Listing

Site No.	Site Name	Initial Reporting Date	Latitude	Longitude	Elevation (m)	Primary Land Use	Terrain
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	510	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	361	Agricultural	Rolling
112	Kane Experimental Forest, PA	12/31/88	41.60	78.77	622	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	615	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	920	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	303	Agricultural	Flat
124	Unionville, MI	06/30/88	43.61	83.36	201	Agricultural	Flat
125	Candor, NC	09/30/90	35.26	79.84	198	Forested	Rolling
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	77.31	269	Agricultural	Rolling
130	Bondville, IL	02/09/88	40.05	88.37	212	Agricultural	Flat
131	Mackville, KY	07/31/90	37.70	85.05	353	Agricultural	Rolling
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

Table 3. NDDN Site Listing (Continued)

Site No.	Site Name	Initial Reporting Date	Latitude	Longitude	Elevation (m)	Land Use	Terrain
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	270	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	2,500	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	Chiricahua, 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

Source: ESE.

occurred, the following Tuesday. Buckets were weighed in the field, then sealed and shipped to ESE for chemical analysis. Precipitation amount (depth) was also monitored at wet deposition sites.

O_3 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 from the 10-m air quality tower through a 3/8-inch TFE Teflon® sampling line. 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 parts per billion (ppb)], and span (400 ppb) checks of the O_3 analyzer were performed every third day using an internal O_3 generator.

In addition to the above, various observations were periodically made at the NDDN sites to support model calculations of dry deposition. Site operators recorded surface conditions (e.g., dew, frost, snow) and vegetation status weekly. Vegetation status and land-use information were used to define the

distribution and condition of plant species around each site that could influence deposition rates for gases (especially SO_2) and particles. Vegetation data were obtained to track evolution of the dominant plant canopy, from leaf emergence (or germination) to senescence (or harvesting). Once a year, site operators also provided information on major plant species and land-use classifications within 1.0 km of the site. Additional land-use data was obtained by digitization and analysis of aerial photographs obtained from the U.S. Geological Survey (USGS) National Cartographic Information Center in Reston, VA. Photographs were interpreted according to procedures described by Anderson et al. (1978).

Leaf area index (LAI) measurements were conducted at all NDDN sites during the summers of 1991 and 1992. LAI is the one-sided leaf area of the plant canopy per unit area of ground at full leaf emergence and has been shown to play an important role in atmosphere-canopy exchange processes (McMillen, 1990). LAI was measured using an LAI-2000 Plant Canopy Analyzer manufactured by Li-Cor (Lincoln, NE). The LAI-2000 makes indirect (i.e., nondestructive) estimates of LAI from simultaneous measurements of light interception by the plant canopy at five angles of inclination (Li-Cor, 1989). Initial development and testing of the LAI-2000 by the manufacturer focused on a variety of agricultural crops, such as soybeans and wheat, and similar approaches have been used to measure LAI of forest canopies (Pierce and Running, 1988; Chason et al., 1990).

All field equipment was subjected to quarterly inspections and multipoint calibrations, using standards traceable to the National Institute of Standards and Technology (NIST). In addition, independent equipment audits were performed annually by Ogden 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. Precision and accuracy criteria for NDDN field measurements are shown in Table 4.

3.2.2 Laboratory Operations

Filter pack samples were loaded, shipped, received, extracted, and analyzed by ESE personnel at the Gainesville, FL laboratory. Filter packs contained three types of filters in sequence: a Teflon® filter for collection of aerosols, a nylon filter for collection of HNO_3, and dual potassium carbonate (K_2CO_3) impregnated cellulose filters for collection of SO_2.

Following receipt from the field, exposed filters and blanks were extracted and then analyzed for SO_4^{2-} and NO_3^- by micromembrane-suppressed ion chromatography (IC). Teflon® filter extracts were also analyzed for NH_4^+ by the automated indophenol method using a Technicon II or TRAACS-800 Autoanalyzer system. All analyses were completed within 72 hours of filter extraction.

Table 4. Precision and Accuracy Objectives of NDDN Field Measurements

Measurement Parameter	Method	Objectives* Precision	Accuracy
Windspeed	Anemometer	±0.5 m/sec	the greater of ±0.2 m/sec or ±5%
Wind Direction	Wind Vane	±5°	±5°
Sigma Theta	Wind Vane	±10%	Undefined
Relative Humidity	Hygrometer	±10% (of full scale)	±10% (of full scale)
Solar Radiation	Pyranometer	±10% (of reading taken at local noon)	±10%
Precipitation	Rain Gauge	±10% (of reading)	±0.05 inch†
Ambient Temperature	Platinum RTD	±0.5°C	±0.25°C
Delta Temperature	Platinum RTD	±0.25°C	±0.25°C
O_3	UV Absorbance	±10% (of reading)	±10%
Filter Pack Flow	Mass Flow Controller	±0.15 L/min	±10%
Surface Wetness	Conductivity Bridge	Undefined	Undefined

Note: m/sec = meters per second.
RTD = resistance-temperature device.

*Precision criteria apply to collocated instruments, and accuracy criteria apply to calibration of instruments.
†For target value of 0.50 inch.

Source: ESE.

Wet deposition samples were filtered and then analyzed for pH, conductivity, acidity, sodium (Na^+), potassium (K^+), NH_4^+, calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), nitrite (NO_2^-), NO_3^-, and SO_4^{2-}. Analysis of NH_4^+ and anions was as described previously for filter pack samples. Analysis of Na^+, Mg^{2+}, and Ca^{2+} was performed with a Perkin-Elmer P-2 inductively coupled argon plasma (ICAP) emission spectrometer. Acidity was determined via titration to approximately pH 8.3, and K^+ was analyzed via atomic emission.

Results of all valid analyses were stored in the laboratory data management system. Atmospheric concentrations were calculated (based on volume of air sampled) following validation of hourly flow data. Atmospheric concentrations of particulate SO_4^{2-}, NO_3^-, and NH_4^+ 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. Precision and accuracy objectives for NDDN laboratory analyses are listed in Table 5.

3.2.3 Model Calculations

Dry deposition calculations for 1990, 1991, and 1992 were made using a multi-layer version of the NOAA inferential model, as described by Hicks *et al.* (1985). The model calculates fluxes, F, as the product of measured concentrations and inferred V_ds. Deposition velocity, in turn, is calculated as the inverse sum of three separate resistances: atmospheric resistance (R_a), boundary layer resistance (R_b), and canopy resistance (R_c), as follows:

$$F_i = C_i \times V_{di} = C_i / (R_a + R_b + R_c)$$

where: i = chemical species.

The three resistance terms are calculated for each chemical species and vegetation/surface type for every hour of available meteorological input data. Hourly values of V_d are averaged over a week and multiplied by the weekly integrated concentrations to produce weekly fluxes of HNO_3, SO_2, and particles. Ozone flux is calculated using hourly measurements of O_3 and hourly values of V_d. Weekly flux calculations for all chemical species are considered valid only if $\geq$70 percent of hourly V_d values are available for that week. Seasonal values require at least 10 of 13 weeks of data to be considered valid. Annual values are considered valid only if V_d and flux data for all four seasons are available.

Table 5. Precision and Accuracy Objectives for NDDN Laboratory Data

Analyte	Medium	Method	Objectives* Precision (RPD)	Objectives* Accuracy (%)
pH*	W	Electrometric	12	88 - 112
Conductivity	W	Electrometric	10	90 - 110
Acidity	W	Titrimetric	15	85 - 115
NH_4^+	W/F	Automated colorimetry	10	90 - 110
Na^+	W/F	ICP-AE	10	90 - 110
K^+	W/F	Flame atomic emission	10	90 - 110
Mg^{2+}	W/F	ICP-AE	10	90 - 110
Ca^{2+}	W/F	ICP-AE	10	90 - 110
Cl^-	W	IC	5	95 - 105
NO_2^-	W	IC	5	95 - 105
NO_3^-	W/F	IC	5	95 - 105
SO_4^{2-}	W/F	IC	5	95 - 105

Note: W = wet deposition samples.
F = filter pack samples.
IC = ion chromatography.
ICP-AE = inductively coupled plasma - atomic emission.
RPD = relative percent difference.

*Precision and accuracy criteria represent ±0.05 pH unit.

Source: ESE.

Chapter 4
Results and Discussion

This section presents atmospheric concentration and dry deposition flux data for NDDN. It illustrates spatial patterns and seasonal variations for 1990, 1991, and 1992, and describes inter-annual variability. The comparability of United States and Canadian atmospheric concentration sampling approaches is discussed, and sources of local variability in concentrations and fluxes are investigated.

4.1 Air Chemistry and Dry Deposition

This section presents atmospheric concentration data for SO_4^{2-}, NH_4^+, NO_3^-, SO_2, and HNO_3 derived from weekly filter pack measurements and model calculations of dry deposition for SO_4^{2-}, SO_2, HNO_3, and NO_3^-. A detailed analysis of spatial and temporal trends is beyond the scope of this report. Therefore, the emphasis of this section is on salient features of concentration patterns as well as season-to-season and year-to-year variability. Spatial correlations in the data and relationships between aerosol cations and anions are also discussed.

4.1.1 Annual Atmospheric Concentrations

Annual arithmetic mean concentrations of SO_4^{2-} for 1990, 1991, and 1992 are shown in Figures 4 through 6. Annual SO_4^{2-} concentrations in the eastern United States range from 7.0 $\mu g/m^3$ in central West Virginia (Site 119) to 2.1 $\mu g/m^3$ in northern Maine (Site 135). Mean values above 6.0 $\mu g/m^3$ cover much of the eastern United States, from Indiana, Ohio, and Pennsylvania to northern Alabama and Georgia. Averages of 5.0 to 6.0 $\mu g/m^3$ cover most of the region from southern New York to Illinois to northern Florida. Only sites from northern New York to Maine, northern Michigan, Wisconsin, and Arkansas exhibit concentrations below 4.0 $\mu g/m^3$. Strong concentration gradients (i.e., factor of 2) exist between Pennsylvania and northern New York, Ohio and Michigan, and from Illinois into Wisconsin.

Atmospheric concentrations of SO_4^{2-} across the western United States during 1990 are substantially lower than those in the east. Mean SO_4^{2-} values range from 1.40 $\mu g/m^3$ in southern Arizona (Site 167) to 0.56 $\mu g/m^3$ in northern Nevada (Site 164). Results of paired t-tests of weekly concentrations indicate that the two sites located in the Great Basin exhibit significantly ($p < 0.05$) lower concentrations than other sites. Similarly, the two Arizona sites exhibit higher concentrations than the other western sites.

Generally similar results are observed in 1991 and 1992; however, peak concentrations across the eastern United States are somewhat lower and less widespread than in 1990. For example, the

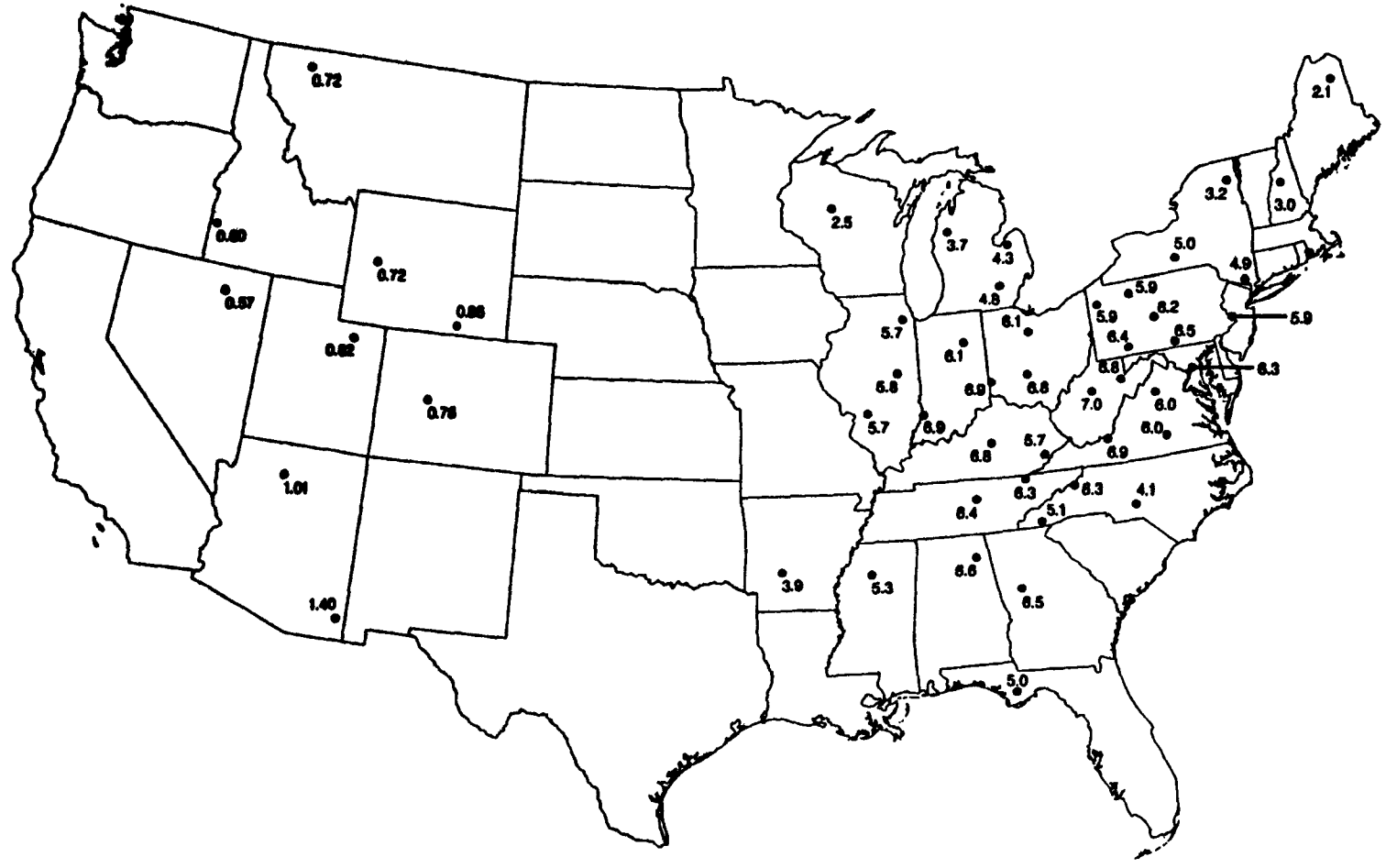


Figure 4. Mean annual SO_4^{2-} concentrations ($\mu g/m^3$) for 1990.

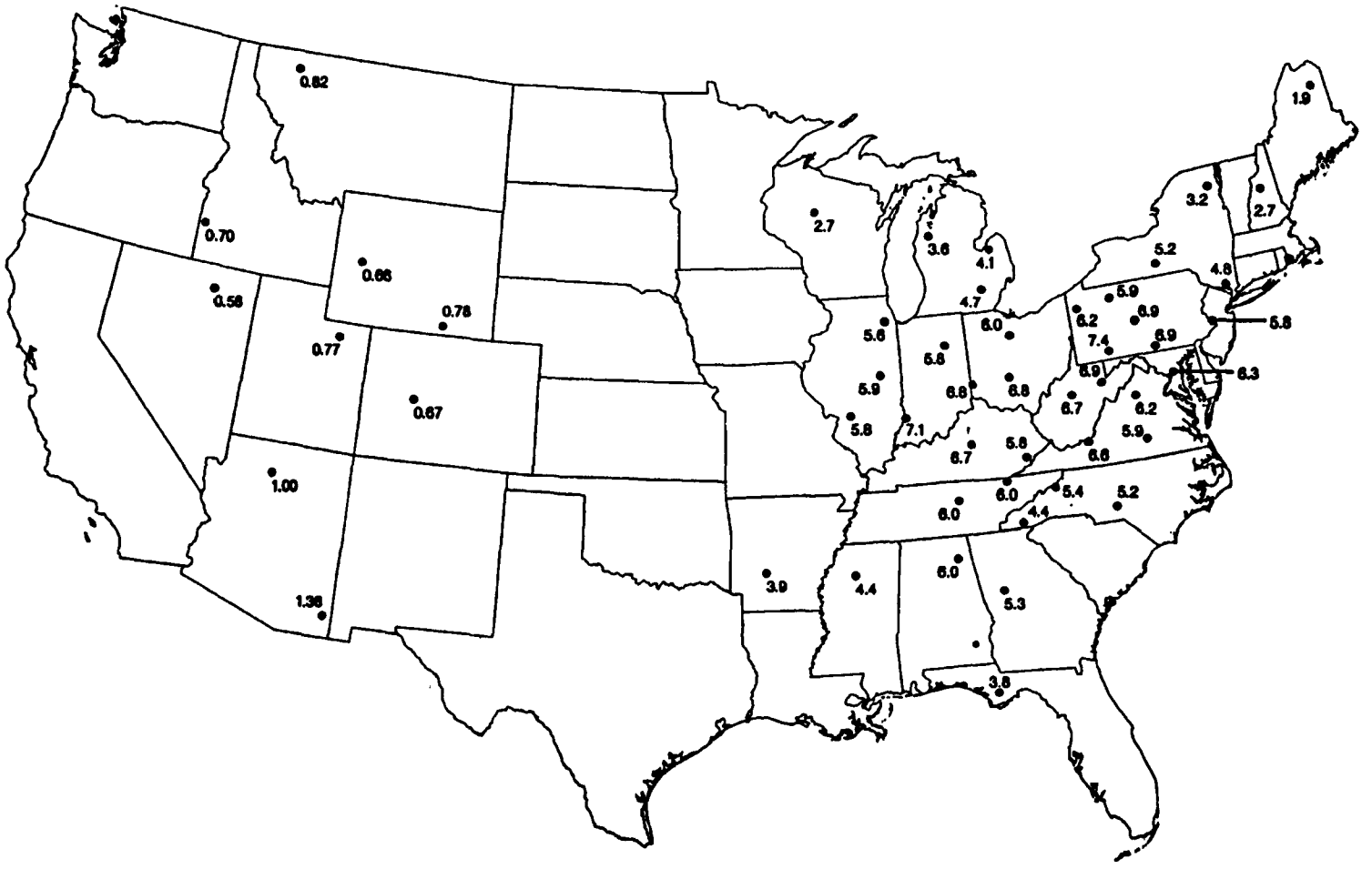


Figure 5. Mean annual SO_4^{2-} concentrations ($\mu g/m^3$) for 1991.

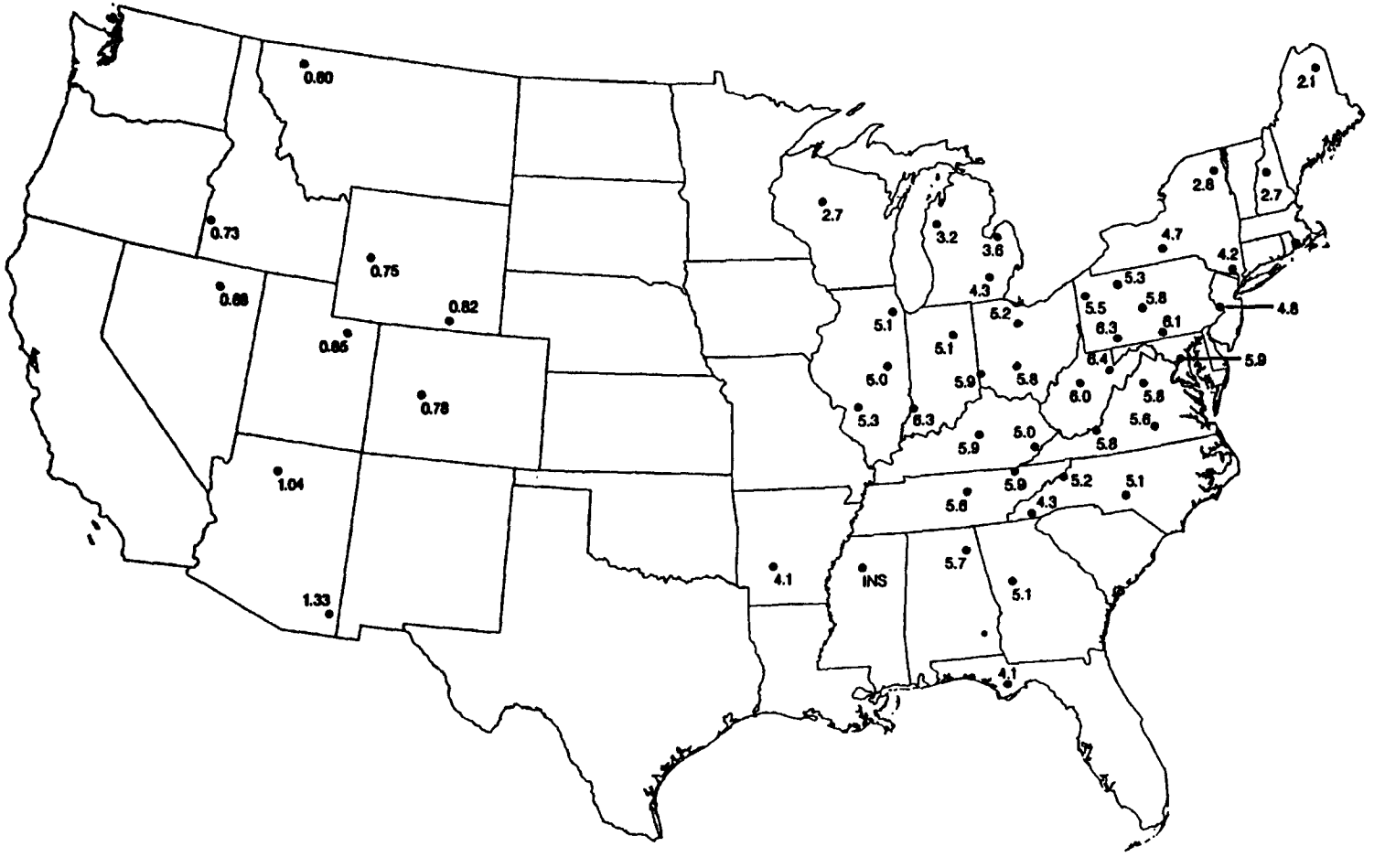


Figure 6. Mean annual SO_4^{2-} concentrations ($\mu g/m^3$) for 1992.

number of sites exhibiting mean annual concentrations $\geq$6.0 $\mu g/m^3$ was 20 in 1990, 17 in 1991, and 5 in 1992. Relatively small year-to-year changes in SO_4^{2-} were observed for most sites in the eastern and western United States.

Annual NO_3^- concentrations exhibit much more variability than SO_4^{2-} and a definite pattern of higher concentrations in the midwest than elsewhere (see Figures 7 through 9). The lowest concentrations in the eastern United States (i.e., <0.25 $\mu g/m^3$) are observed at forested sites in New England and the southern Appalachian Mountains, while the highest concentrations (i.e., 2 to 3 $\mu g/m^3$) are observed in agricultural areas of the midwest. Intermediate values (i.e., 1.0 to 2.0 $\mu g/m^3$) appear to be associated with agricultural sites anywhere in the eastern United States. 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.

Annual NO_3^- concentrations exhibit minimal variability across western sites. NO_3^- concentrations range from 0.15 $\mu g/m^3$ in the mountains of central Colorado (Site 161) to 0.41 $\mu g/m^3$ in southwestern Idaho (Site 163). The datum for Idaho may reflect agricultural activity near Boise, which is located approximately 60 km northeast of the site. Paired t-tests for NO_3^- indicate three widely spaced groups of sites in the following states: Montana, Wyoming, and Colorado (mean concentration 0.16 $\mu g/m^3$); Nevada, Utah, and southern Arizona (0.27 $\mu g/m^3$); and Idaho and northern Arizona (0.39 $\mu g/m^3$).

Annual average values for NH_4^+ range from nearly 2.7 $\mu g/m^3$ in northern Indiana (Site 133) to 0.53 $\mu g/m^3$ in Maine (Site 135) and, in general, exhibit higher values at agricultural sites than at forested sites (see Figures 10 through 12). Concentrations above 2.0 $\mu g/m^3$ are detected 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 $\mu g/m^3$ are found only in the upper northeast and northern Florida. Average concentrations for NH_4^+ range from 0.23 $\mu g/m^3$ (Site 164) to 0.45 $\mu g/m^3$ (Site 167), and only these two sites differ significantly, based on paired t-tests.

Annual values for SO_2 range during 1990 from 19.5 $\mu g/m^3$ in southwestern Indiana (Site 140) to 1.9 $\mu g/m^3$ in Maine (Site 135) (see Figures 13 through 15). Concentrations of 15 $\mu g/m^3$ or greater occur in a small area in western Pennsylvania, as well as at isolated sites in northern Illinois, southern Indiana, and western Ohio. The Pennsylvania sites are regionally representative, but the Illinois, Indiana, and Ohio sites appear to be influenced by local sources. A much larger area extending from Illinois eastward to northern Virginia and southern New York exhibits concentrations in the range of 10

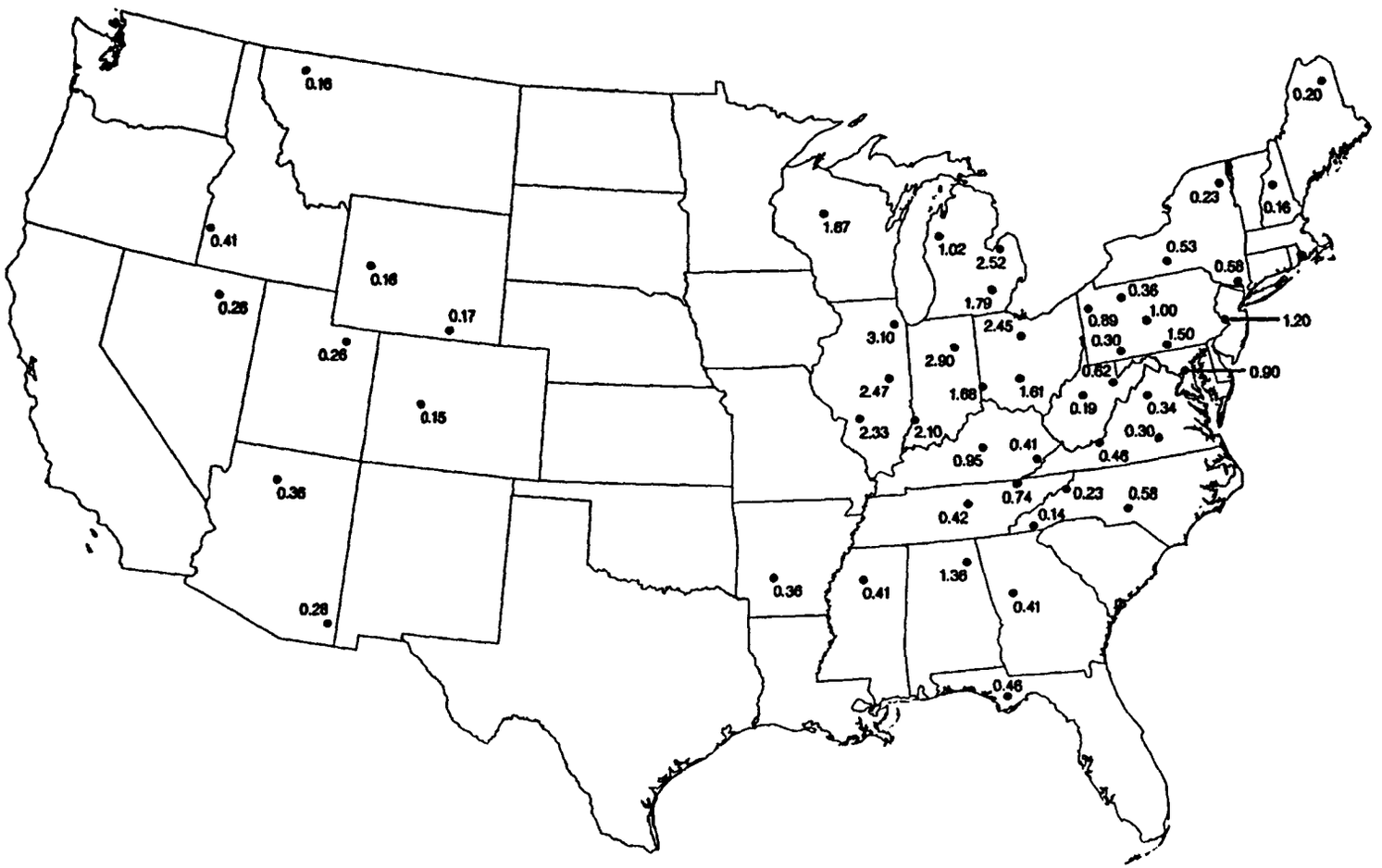


Figure 7. Mean annual NO_3^- concentrations ($\mu g/m^3$) for 1990.

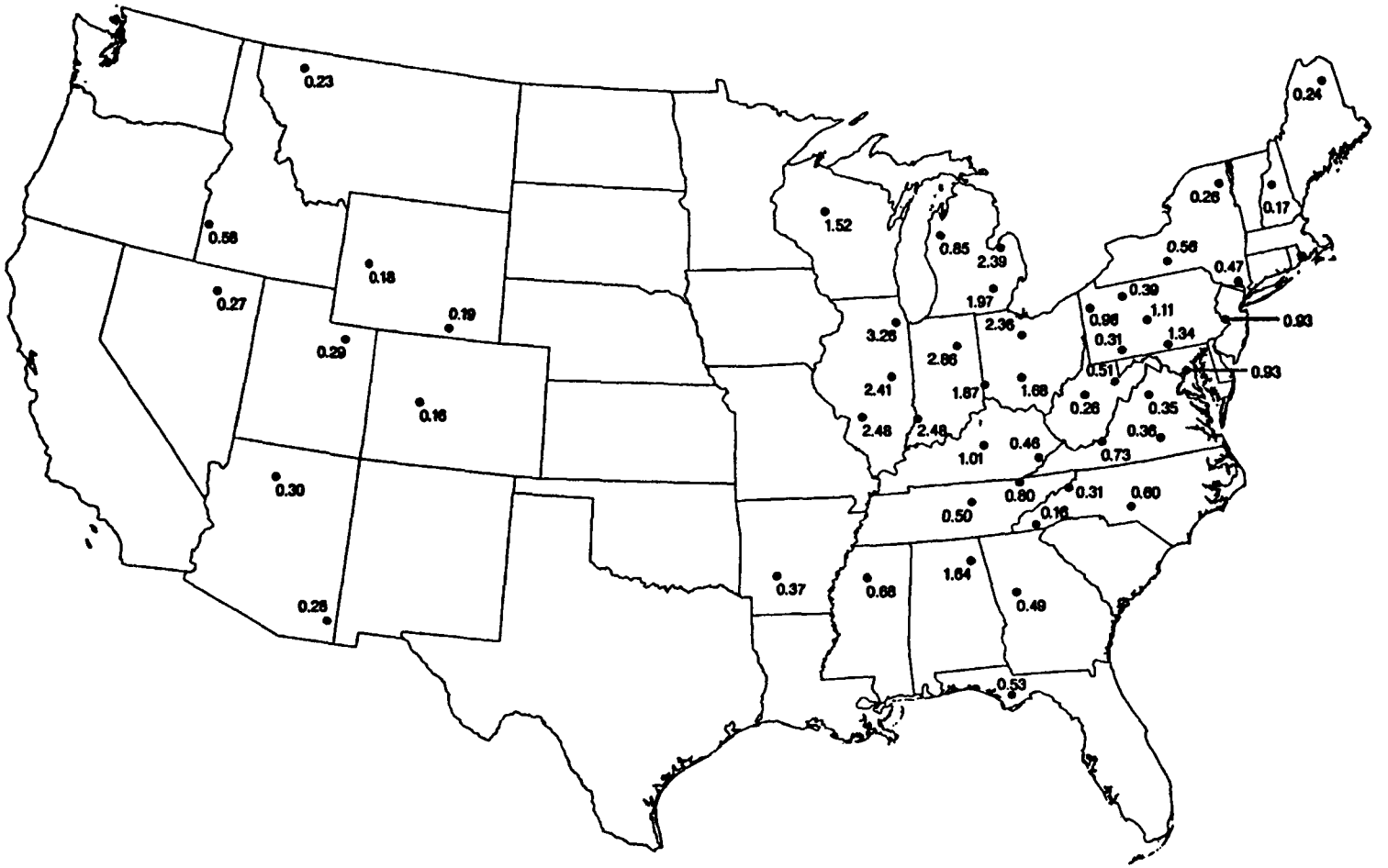


Figure 8. Mean annual NO_3^- concentrations ($\mu g/m^3$) for 1991.

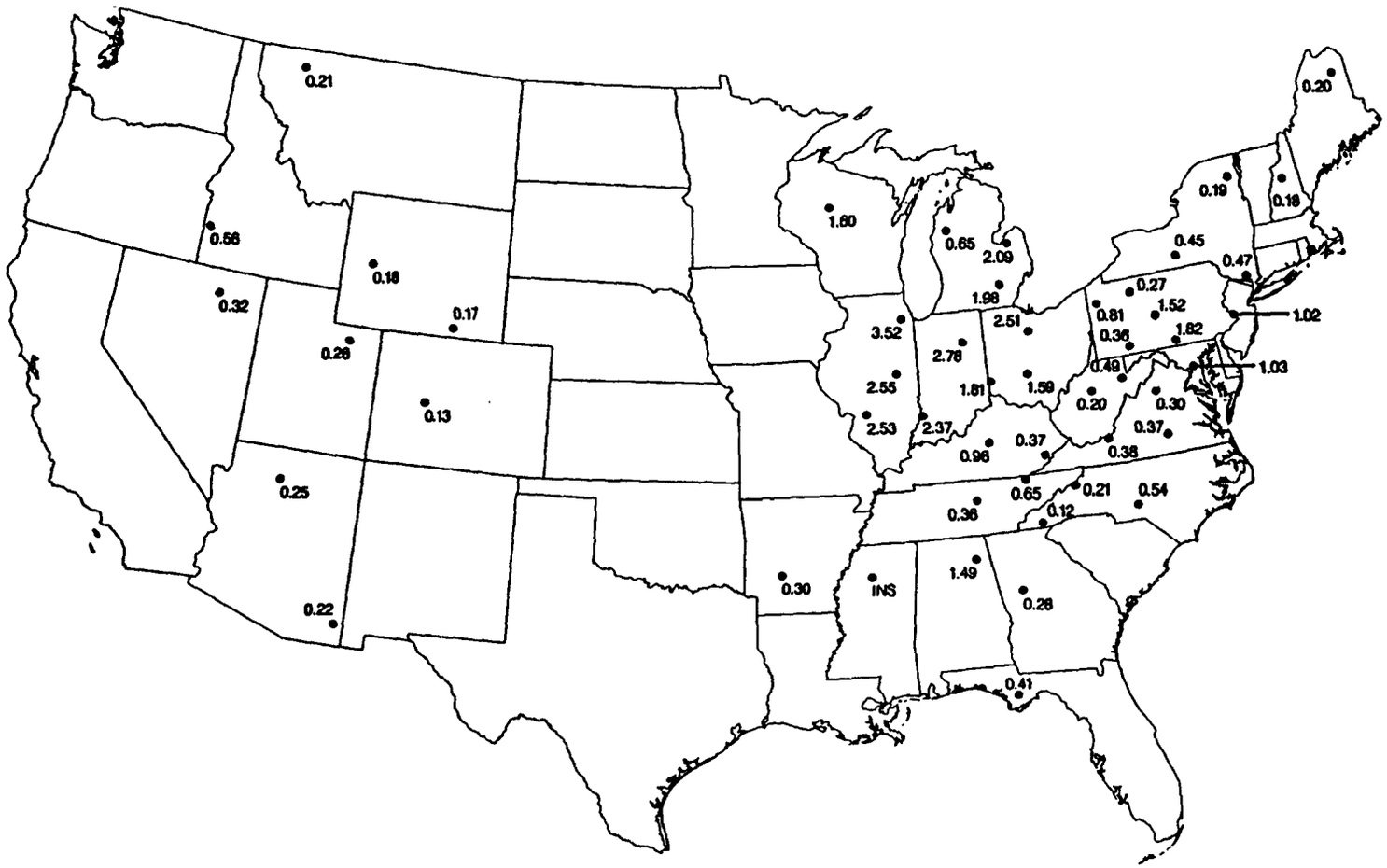


Figure 9. Mean annual NO_3^- concentrations ($\mu g/m^3$) for 1992.

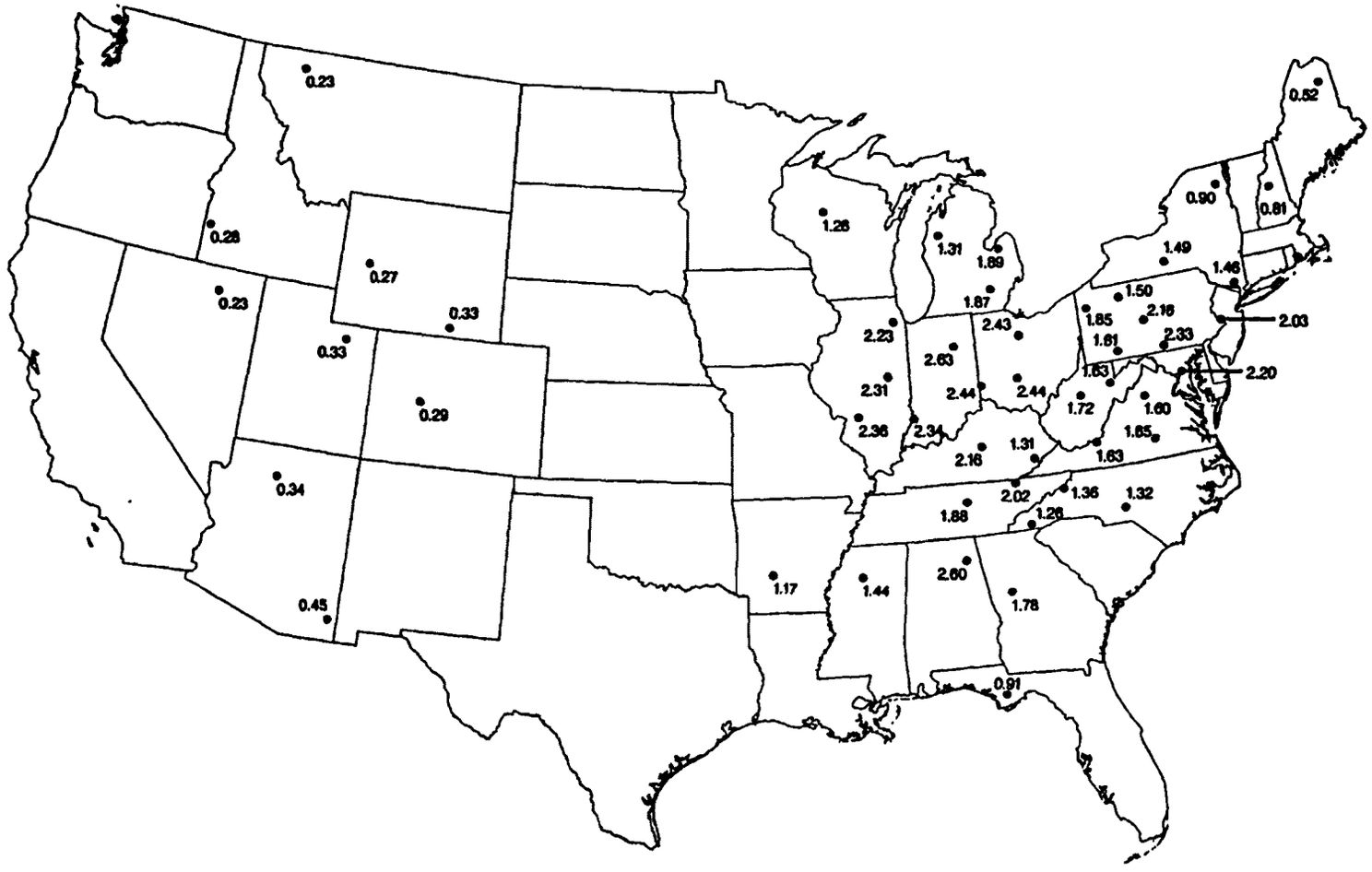


Figure 10. Mean annual NH_4^+ concentrations ($\mu g/m^3$) for 1990.

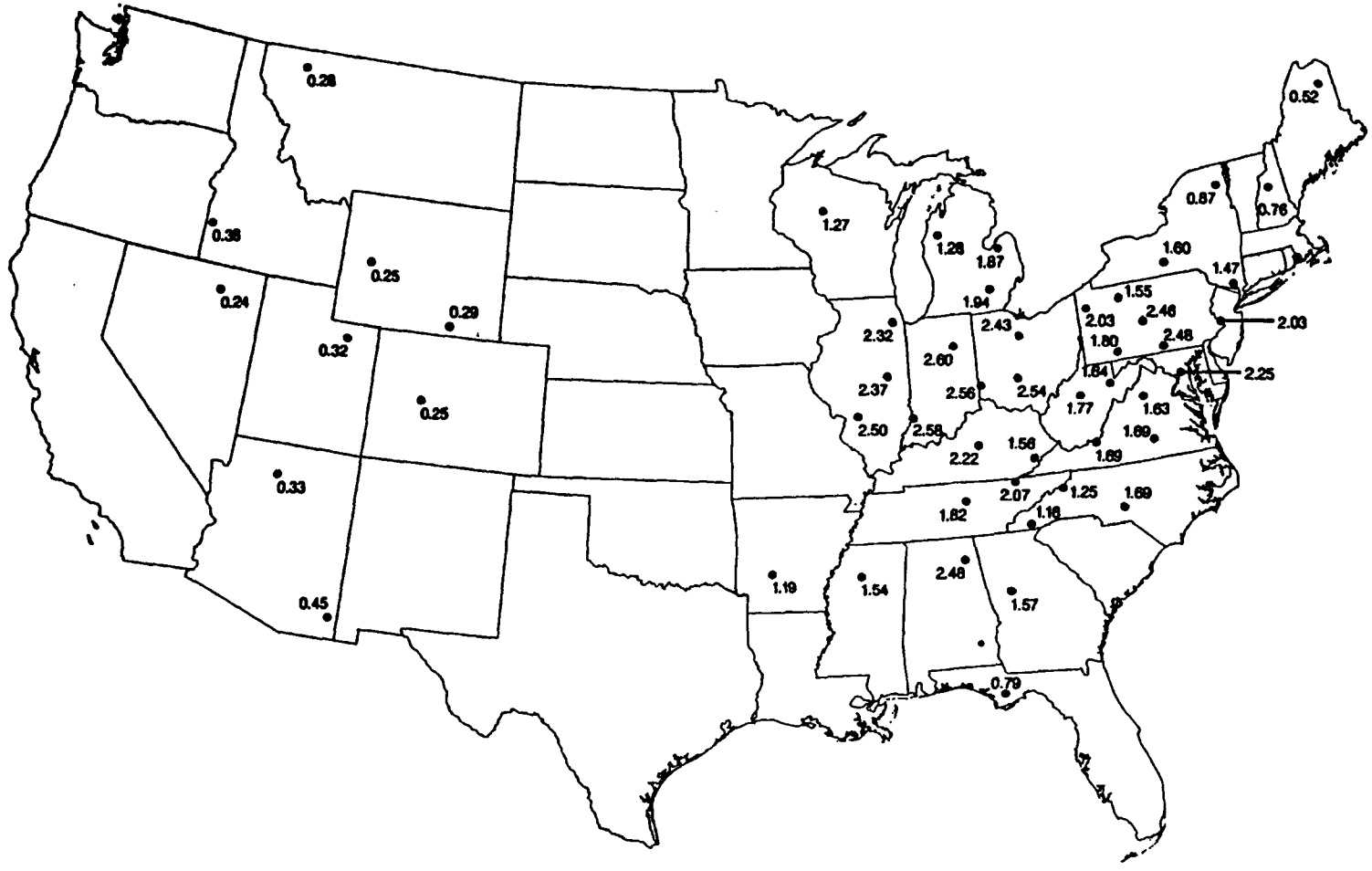


Figure 11. Mean annual NH_4^+ concentrations ($\mu g/m^3$) for 1991.

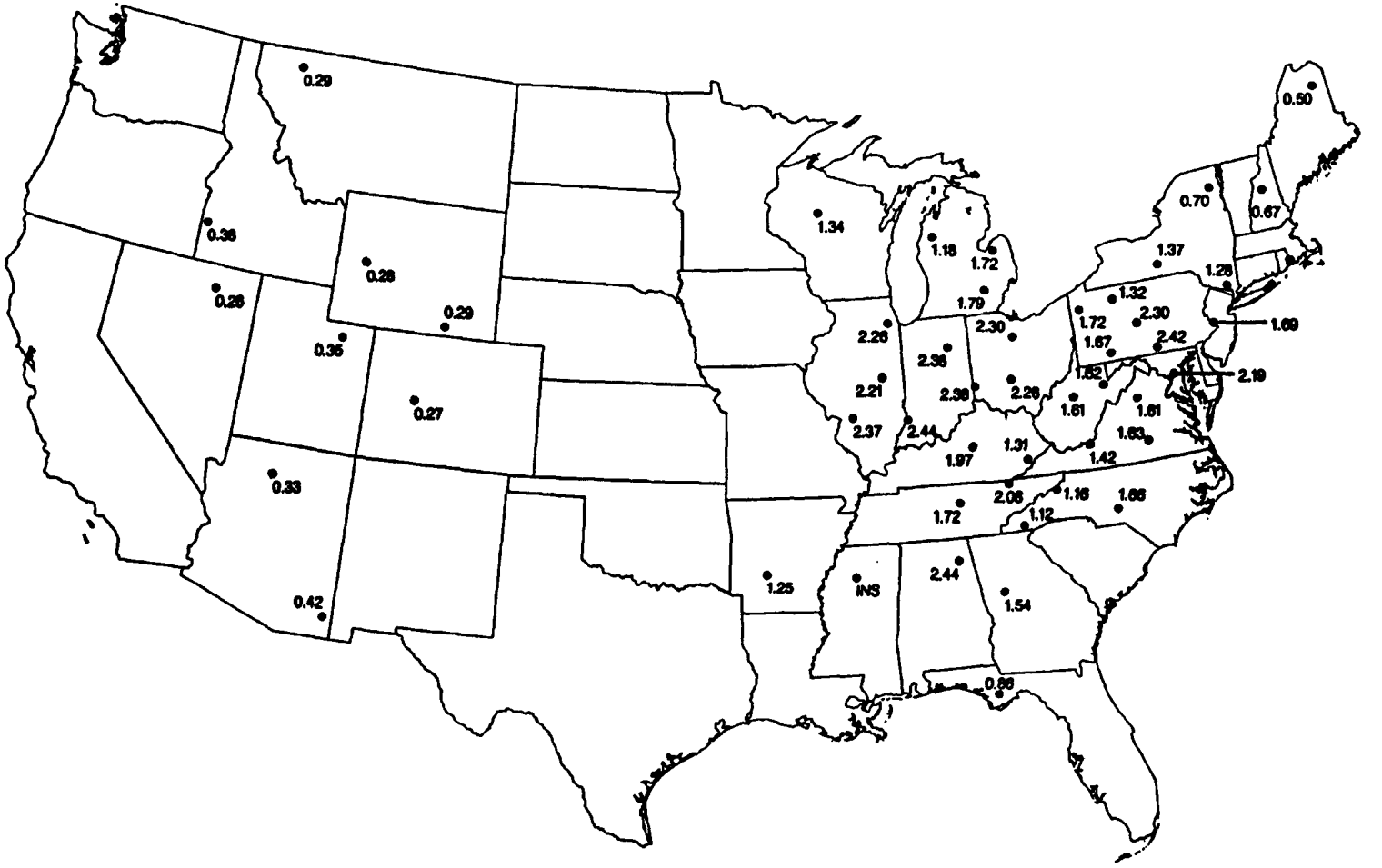


Figure 12. Mean annual NH_4^+ concentrations ($\mu g/m^3$) for 1992.

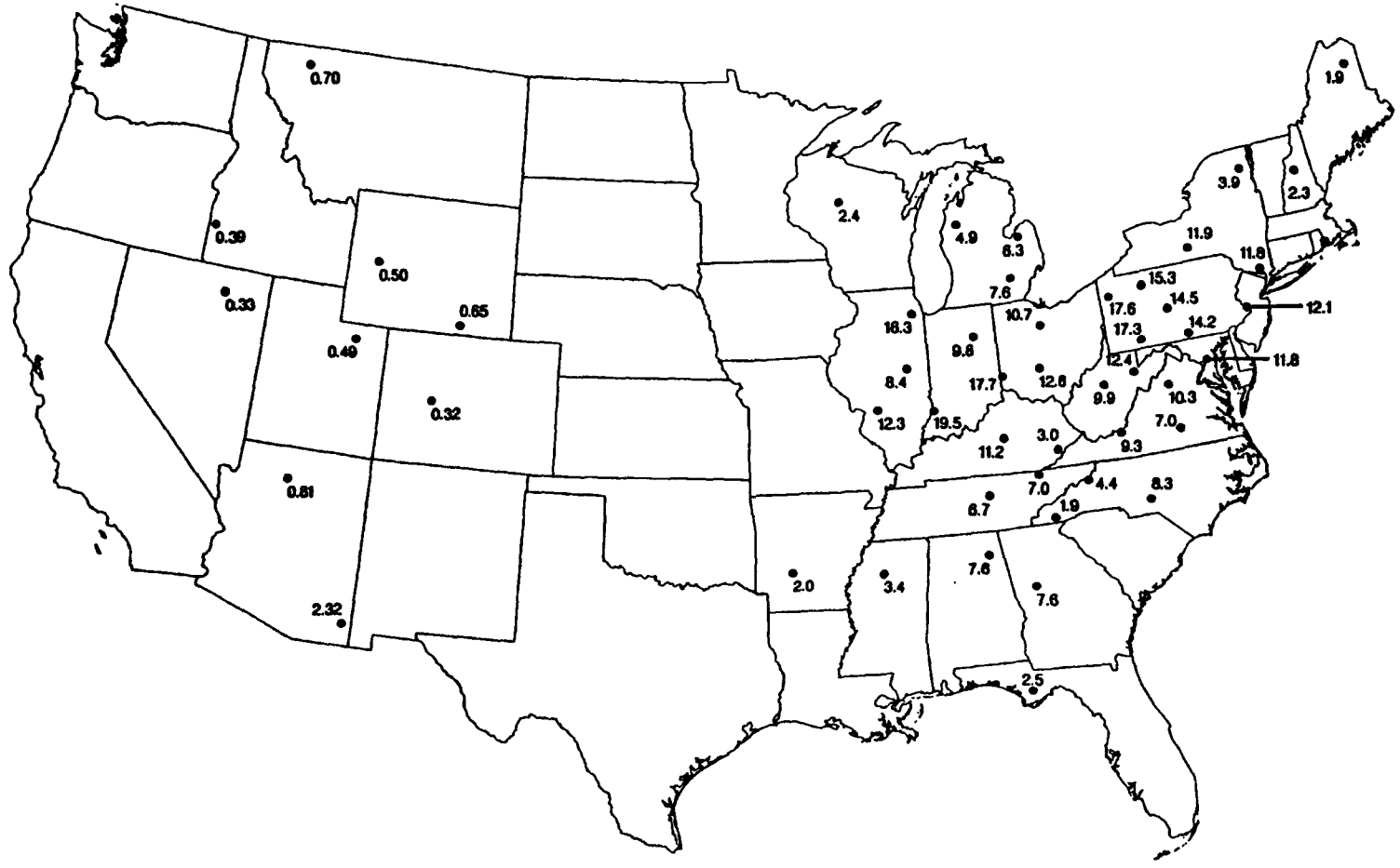


Figure 13. Mean annual SO_2 concentrations ($\mu g/m^3$) for 1990.

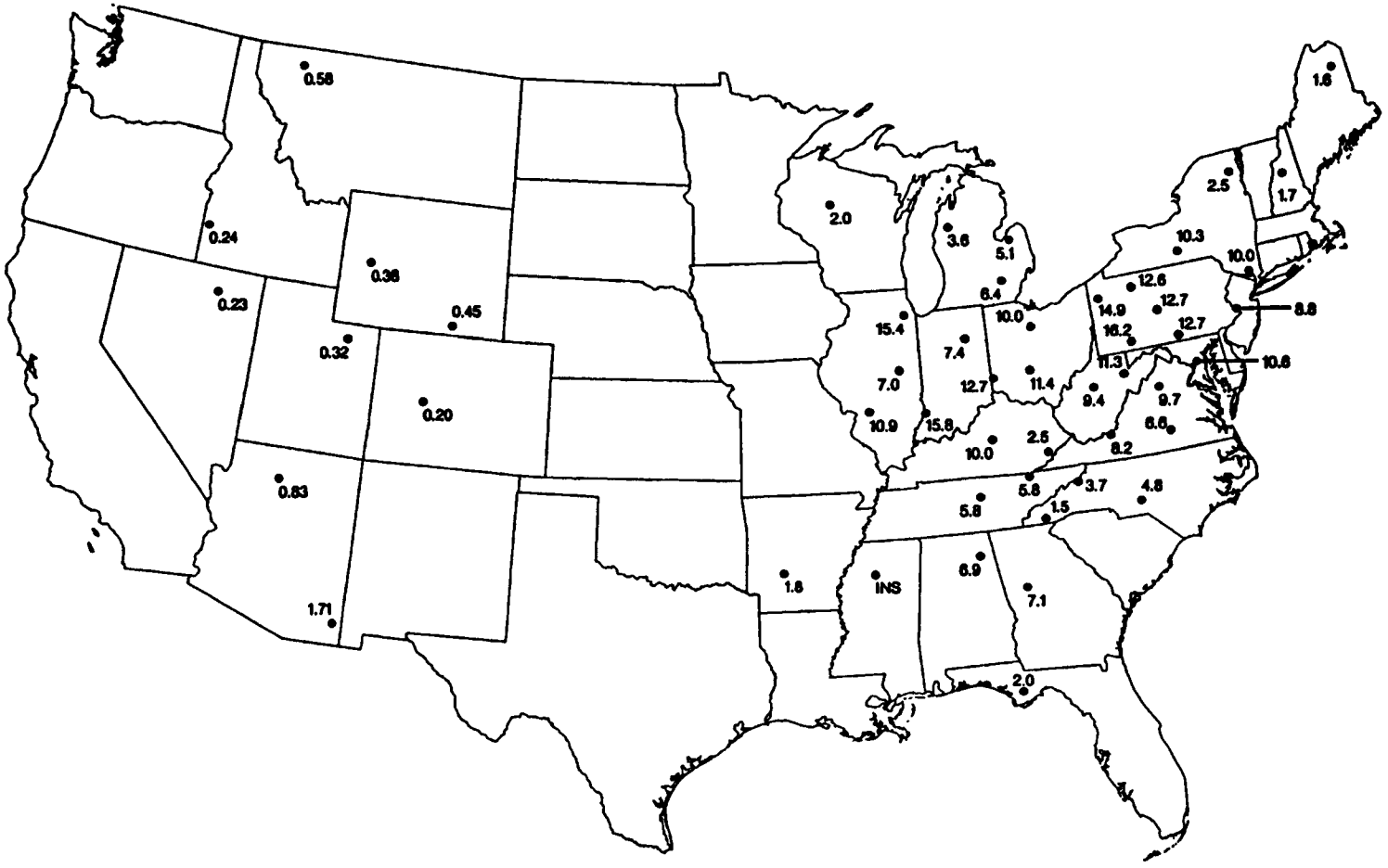


Figure 14. Mean annual SO_2 concentrations ($\mu g/m^3$) for 1991.

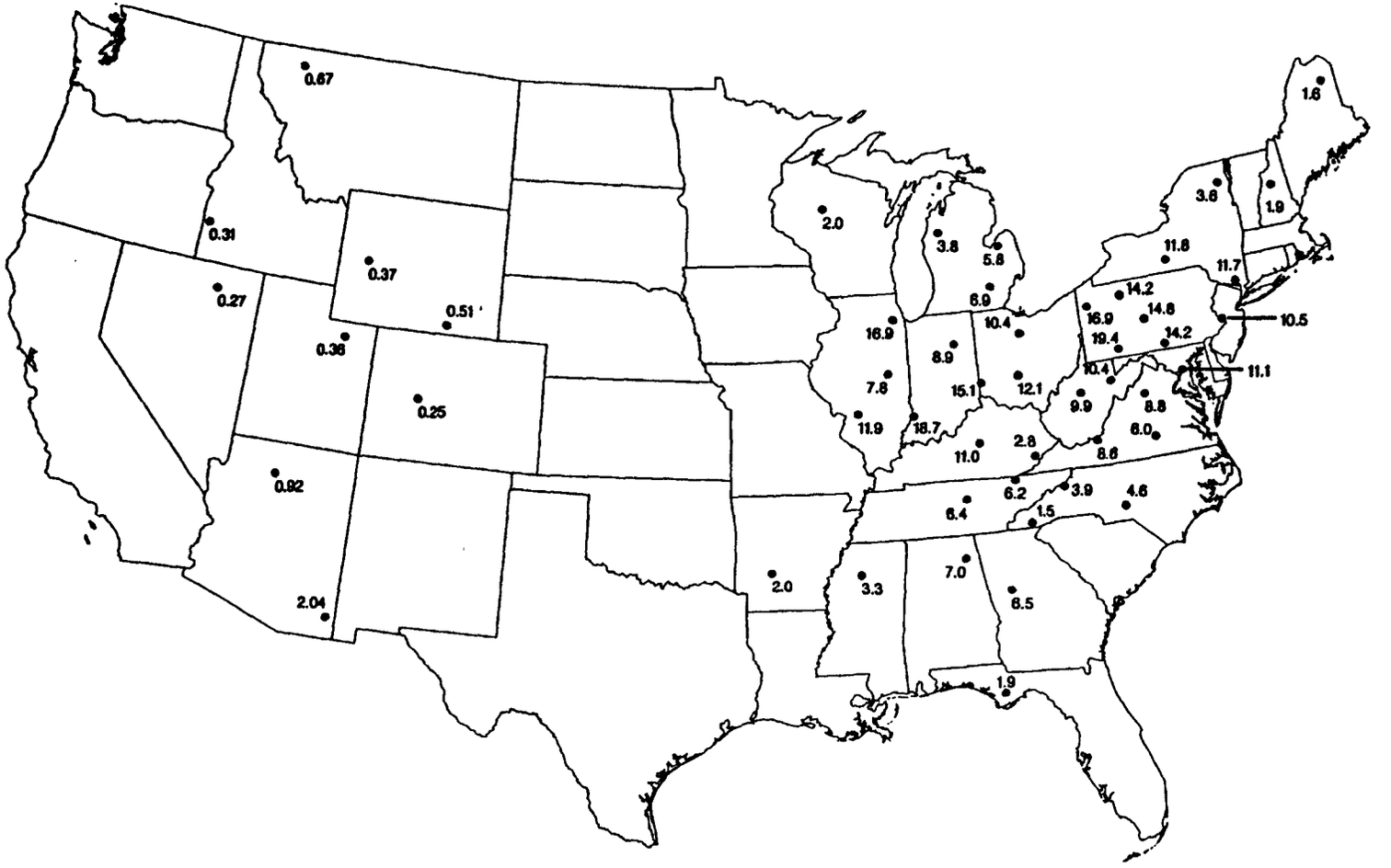


Figure 15. Mean annual SO_2 concentrations ($\mu g/m^3$) for 1992.

to 15 $\mu g/m^3$. 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. Terrain effects could account for large differences (i.e., a factor of 3) between rolling terrain sites in central Kentucky and Tennessee, and neighboring complex terrain sites in eastern Kentucky and western North Carolina.

SO_2 concentrations exhibit substantial variability across the western region. Annual average concentrations range over a factor of 6 from 0.32 $\mu g/m^3$ in central Colorado (Site 161) to 2.27 $\mu g/m^3$ in southern Arizona (Site 167). Concentrations at Site 167 exceed the lowest values in the eastern region and clearly reflect local emissions on both sides of the United States/Mexico border. Similarly, SO_2 concentrations in northern Arizona (Site 174) may be influenced by southwestern sources. Results of paired t-tests on weekly concentrations suggest at least three distinct site groups: Idaho, Nevada, and Colorado (mean concentrations of 0.34 $\mu g/m^3$); northern Arizona (0.83 $\mu g/m^3$); and southeastern Arizona (2.27 $\mu g/m^3$). The remaining sites are not statistically different from either the lowest or intermediate site group.

Data for 1991 and 1992 show a very similar SO_2 pattern as for 1990. The domain for concentration $\geq$10 $\mu g/m^3$ stretches from Illinois eastward to the Atlantic seaboard. The lowest concentrations among eastern sites (i.e., $\geq$2.5 $\mu g/m^3$) routinely occur in New England, Wisconsin, Arkansas, Florida, and North Carolina.

Annual average concentrations of HNO_3 for 1990 (see Figure 16) exhibit a maximum concentration of approximately 3.5 $\mu g/m^3$ in southeastern Pennsylvania (Site 128) and a minimum of 0.6 $\mu g/m^3$ in northern Maine (Site 135). The majority of NDDN sites occupy a range from 2.0 to 3.0 $\mu g/m^3$. Only five sites exhibit average concentrations of 1.0 $\mu g/m^3$ or less. Three of these sites are located in the northern extremes of the network (i.e., Wisconsin, Maine, and New Hampshire). The other two 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 across the eastern United States might be influenced by terrain as much or more than other factors (e.g., emissions). Sites with the highest average values have good exposure (fetch), while those with the lowest values typically have poor exposure, due mainly to complex terrain. For species with significant deposition velocities (such as HNO_3), the microclimate in regions of complex terrain produces local variability in atmospheric concentrations. This could account for the highly variable concentrations in the vicinity of the Appalachian Mountains. Terrain effects are explored further in Chapter 5.

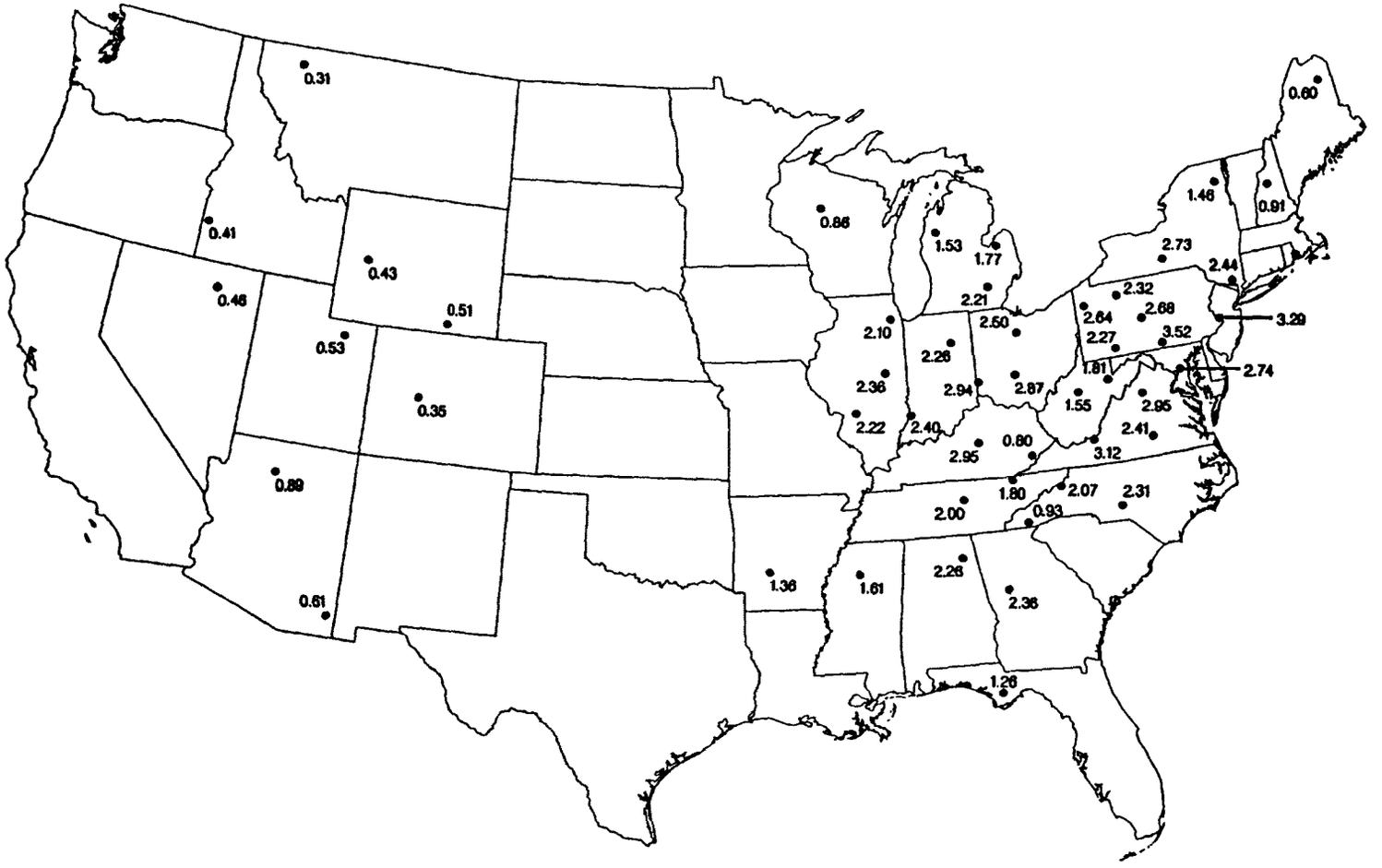


Figure 16. Mean annual HNO_3 concentrations ($\mu g/m^3$) for 1990.

Annual concentration values for HNO_3 for 1990 vary by approximately a factor of three among western sites. The lowest annual concentration occurs in Montana (Site 168), and the highest occurs in northern Arizona (Site 174). Results for northern Arizona are similar to the lowest observed values in the eastern region and may be due, in part, to the high number of visitors (during May to September only) to Grand Canyon National Park. In contrast, the low concentrations in Montana and Colorado could be due to the forested surroundings and high elevation of Sites 168 and 161, respectively.

Results for 1991 and 1992 are consistent with those for 1990 (see Figures 17 and 18). The highest annual average concentration routinely occurs in southeastern Pennsylvania (Site 128), and the lowest concentrations (<1.0 $\mu g/m^3$) occur in New England and in two complex terrain sites in Kentucky and North Carolina (121 and 137).

Results for total NO_3^- (i.e., NO_3^- plus HNO_3) for 1990 show marked variability across the eastern United States (see Figures 19 through 21). The highest concentrations (i.e., ≥ 4.0 $\mu g/m^3$) occur in the midwest, as well as in a small area from southeastern Pennsylvania to central New Jersey. The lowest concentrations (i.e., ≤ 2.0 $\mu g/m^3$) occur in the upper northeast and southern periphery, and at three complex terrain sites in North Carolina, Kentucky, and West Virginia. As for HNO_3, and to a lesser extent SO_2, spatial variability of total-NO_3^- near the Appalachian Mountains may be due to terrain influences. The peak concentrations in the midwest correspond well with peak NO_3^-, suggesting that the latter can be a significant reservoir species. Given the likely differences in deposition rates, conversion of HNO_3 to the particle phase should result in higher time-averaged concentrations.

Total NO_3^- concentrations for 1991 and 1992 are generally similar to those discussed for 1990 (see Figures 20 and 21). Average values above 4.0 $\mu g/m^3$ occur only in the midwest and at sites in New Jersey (144) and southeastern Pennsylvania (128). The lowest concentrations among eastern sites recur in New England (Sites 109 and 135), Kentucky (Site 121), and North Carolina (Site 137). Among western sites, a factor of three range in concentration persists, with the lowest annual average values in central Colorado (Site 161) and the highest in northern Arizona (Site 174).

4.1.2 Quarterly and Annual Variability of Atmospheric Concentrations

This section describes the variability of atmospheric concentrations between seasons and between years. For purposes of completeness and representativeness, a quarter/season has been treated as valid if it contains 10 valid samples, and a year has been treated as valid if it contains all four valid seasons.

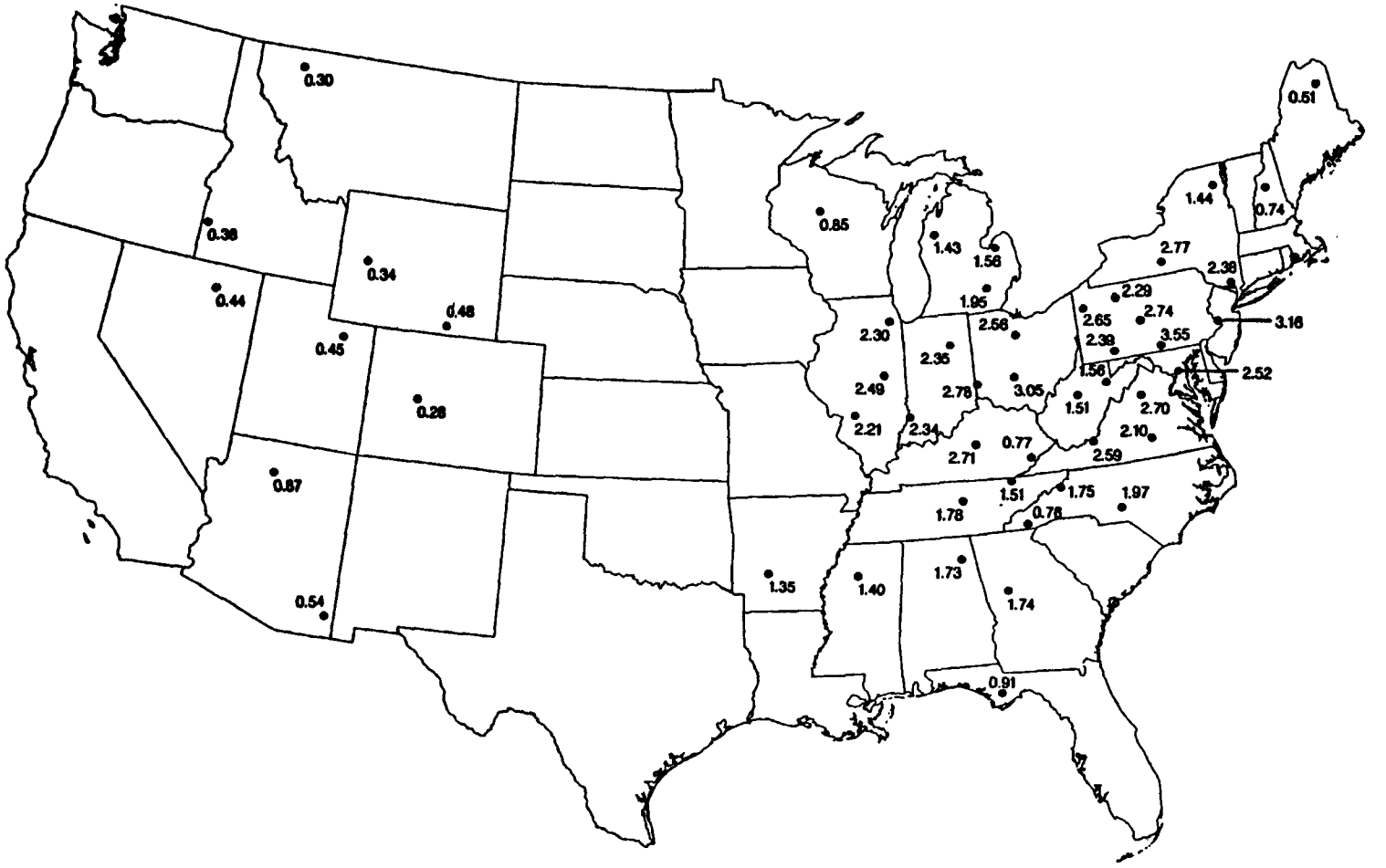


Figure 17. Mean annual HNO_3 concentrations ($\mu g/m^3$) for 1991.

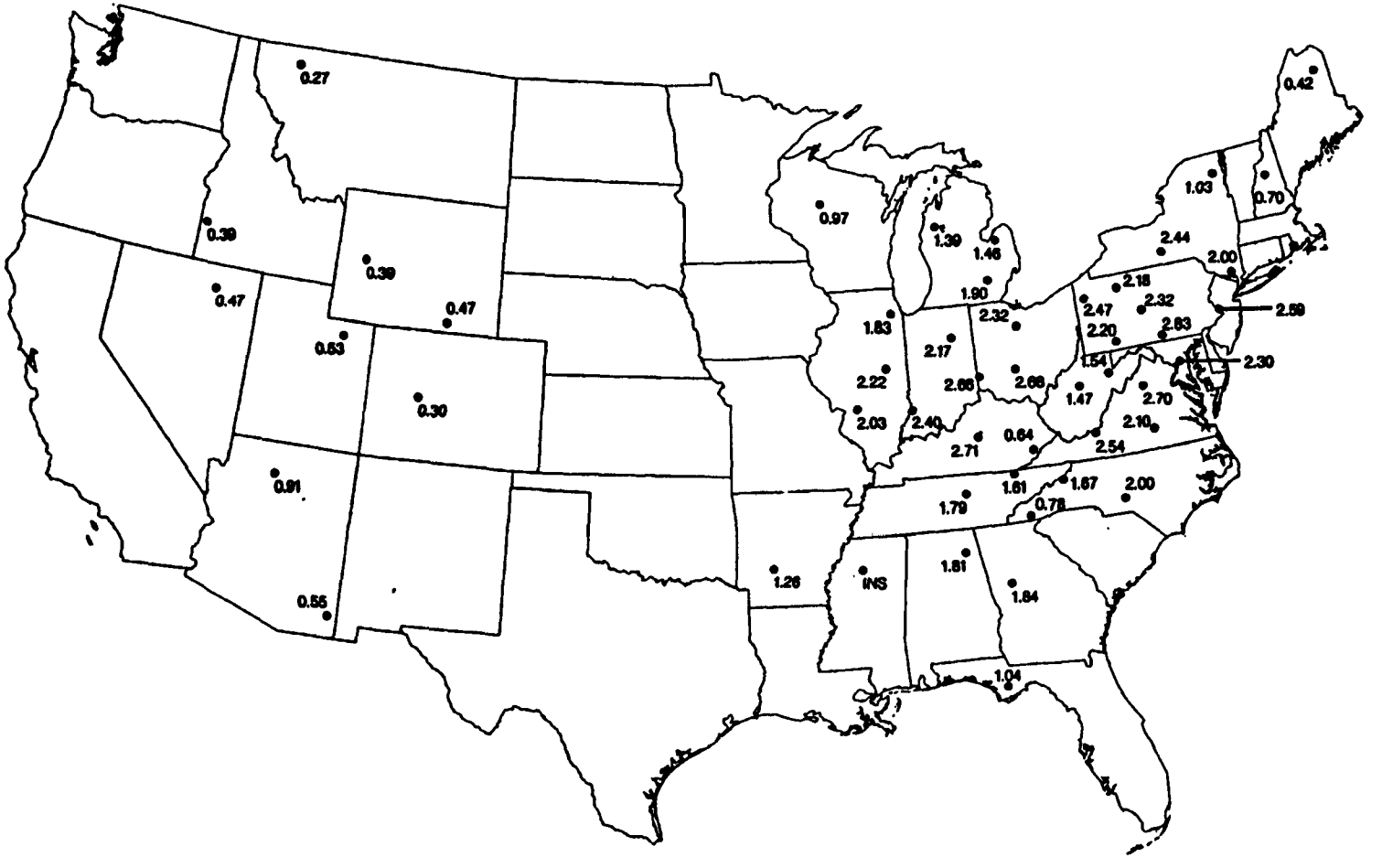


Figure 18. Mean annual HNO_3 concentrations ($\mu g/m^3$) for 1992.

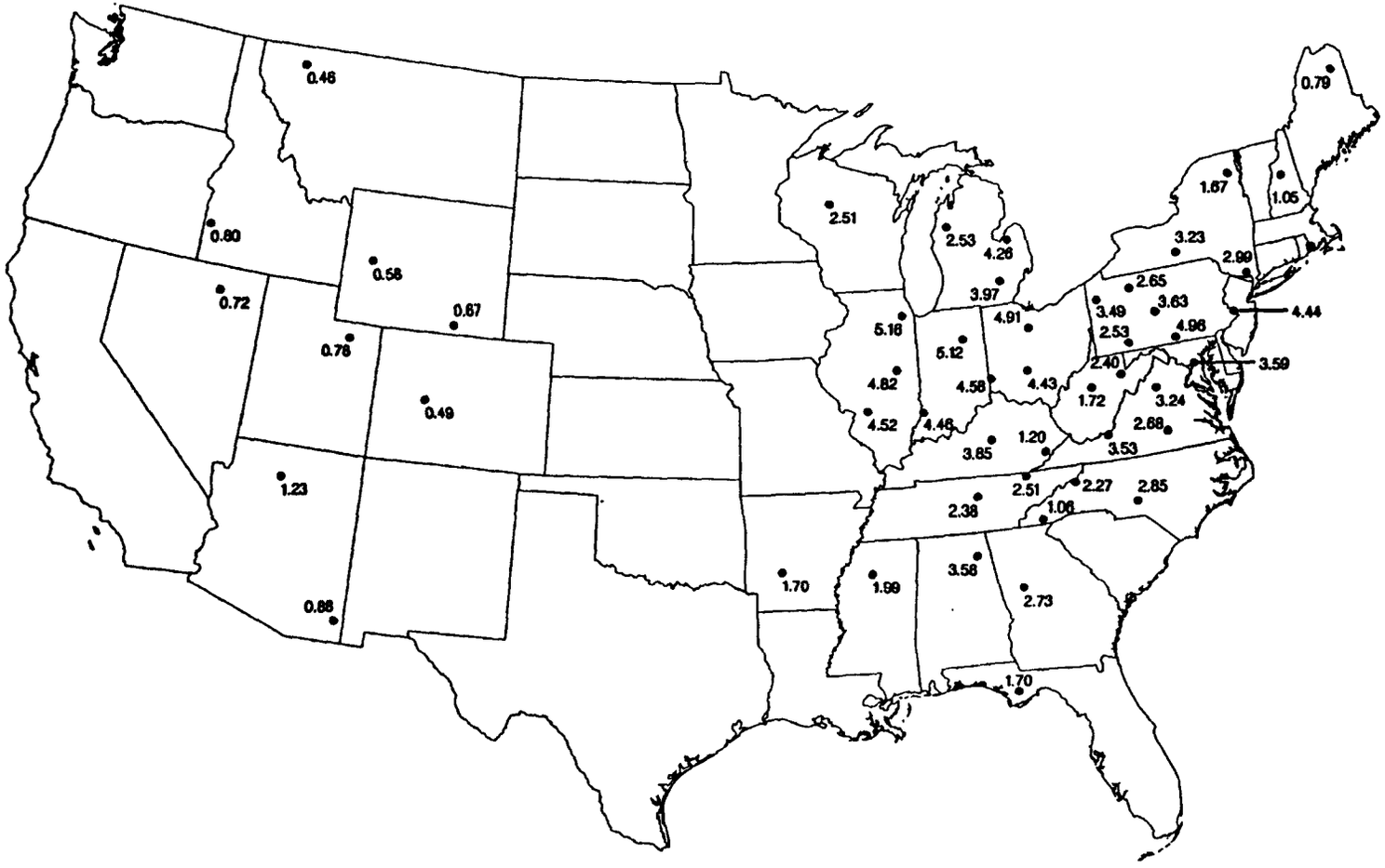


Figure 19. Mean annual total NO_3^- concentrations ($\mu g/m^3$) for 1990.

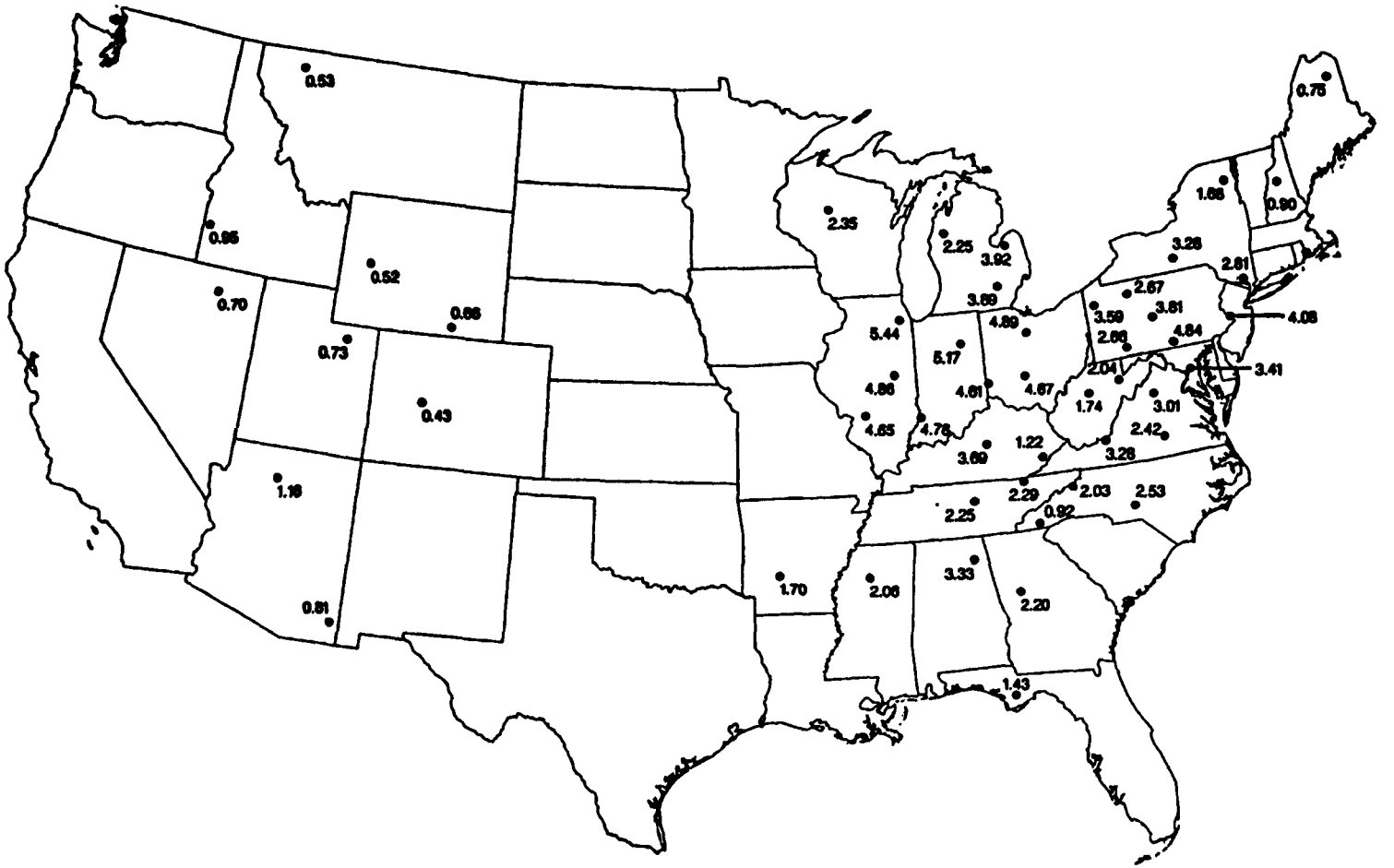


Figure 20. Mean annual total NO_3^- concentrations ($\mu g/m^3$) for 1991.

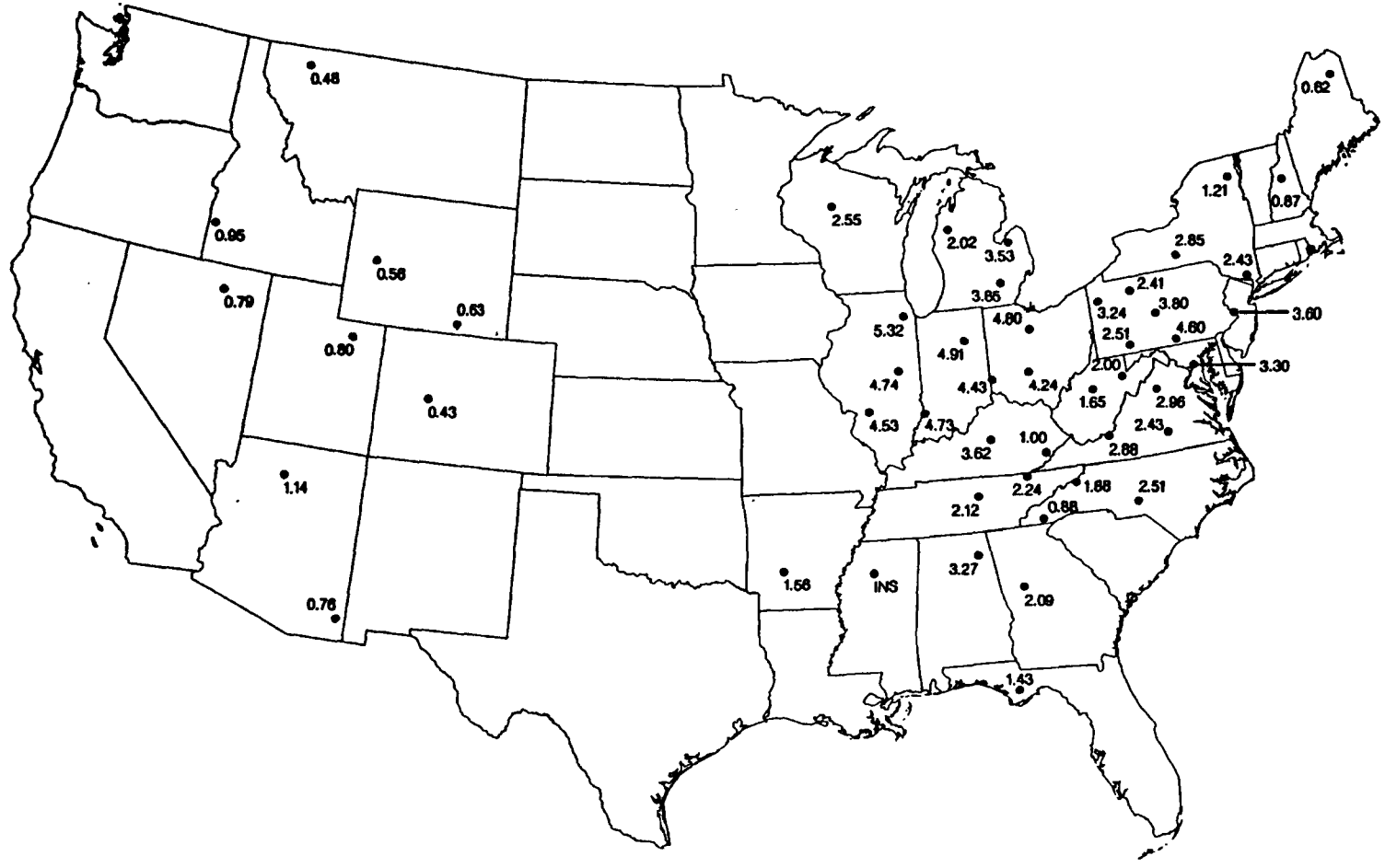


Figure 21. Mean annual total NO_3^- concentrations ($\mu g/m^3$) for 1992.

Time-series of quarterly average concentrations for five eastern sites and three western sites are shown in Figures 22 through 27. Eastern sites were selected to illustrate variability in the upper northeast (Site 105), northeast (Site 106), southeast (Sites 120 and 153), and midwest (Site 122) dating from the origin of the network. Western sites were selected to represent a transect from the United States-Canada border to the United States-Mexico border. Despite large concentration differences, seasonal patterns appear to be fairly similar among sites and reproducible between years. SO_4^{2-}, NH_4^+, and HNO_3 concentrations typically peak during the summer, and SO_2 and NO_3^- concentrations peak during the winter at all sites. For example, SO_4^{2-} data show an increase of a factor of about three from winter (first quarter) to summer (third quarter) followed by a plummet to the lowest level of the year in the fall (fourth quarter). SO_2, in contrast, exhibits peak concentrations in fall and winter and dramatically lower concentrations in spring and summer. Total-nitrate concentrations remain essentially constant from season to season at all eastern sites, due to the mirror image seasonal variations of HNO_3 and NO_3^-. Little evidence of an upward or downward trend can be seen in any of the time-series plots.

Time-series for the western sites also show pronounced seasonality. Although the data record is brief at this point, fairly reproducible year-to-year peaks and valleys in concentrations are observed. The southern Arizona site (167), which appears to be influenced by nearby SO_2 sources, exhibits significant variability, especially in SO_4^{2-} and SO_2. Sites on the periphery of the eastern United States (e.g., Maine, Arkansas, and Florida) generally show reduced seasonal variability.

Annual average concentrations for sulfur and nitrogen species are listed in Tables 6 and 7 for all eastern sites, all western sites, and groups of eastern sites from 1989 through 1992. Inspection of data shows that year-to-year variability is less than 10 percent for all site groups. Despite relatively low variability from year to year, there is evidence of a significant (10 to 20 percent) decline in concentrations for all species in all regions, except the west. The data record is obviously insufficient to tell if this is part of a secular trend or merely natural variation (e.g., meteorological variability) in annual concentrations.

Data for SO_4^{2-} show roughly a 16-percent decrease from 1989 to 1992 for 41 eastern sites and essentially no change for nine western sites. The largest regional decreases were on the order of 20 percent and occurred in the midwest and upper midwest. Results for HNO_3 and NO_3^- show year-to-year variability similar to SO_4^{2-} and apparent reductions of about 15 percent over the period of record. Similar time series for total NO_3^- concentrations show that year-to-year variability is not simply due to changes in gas-particle partitioning but to lower overall concentrations of atmospheric nitrates. The most significant change in concentration for the period occurred for SO_2. In this case, average concentrations for eastern and western sites decreased by about 25 percent from 1989 to 1991. All

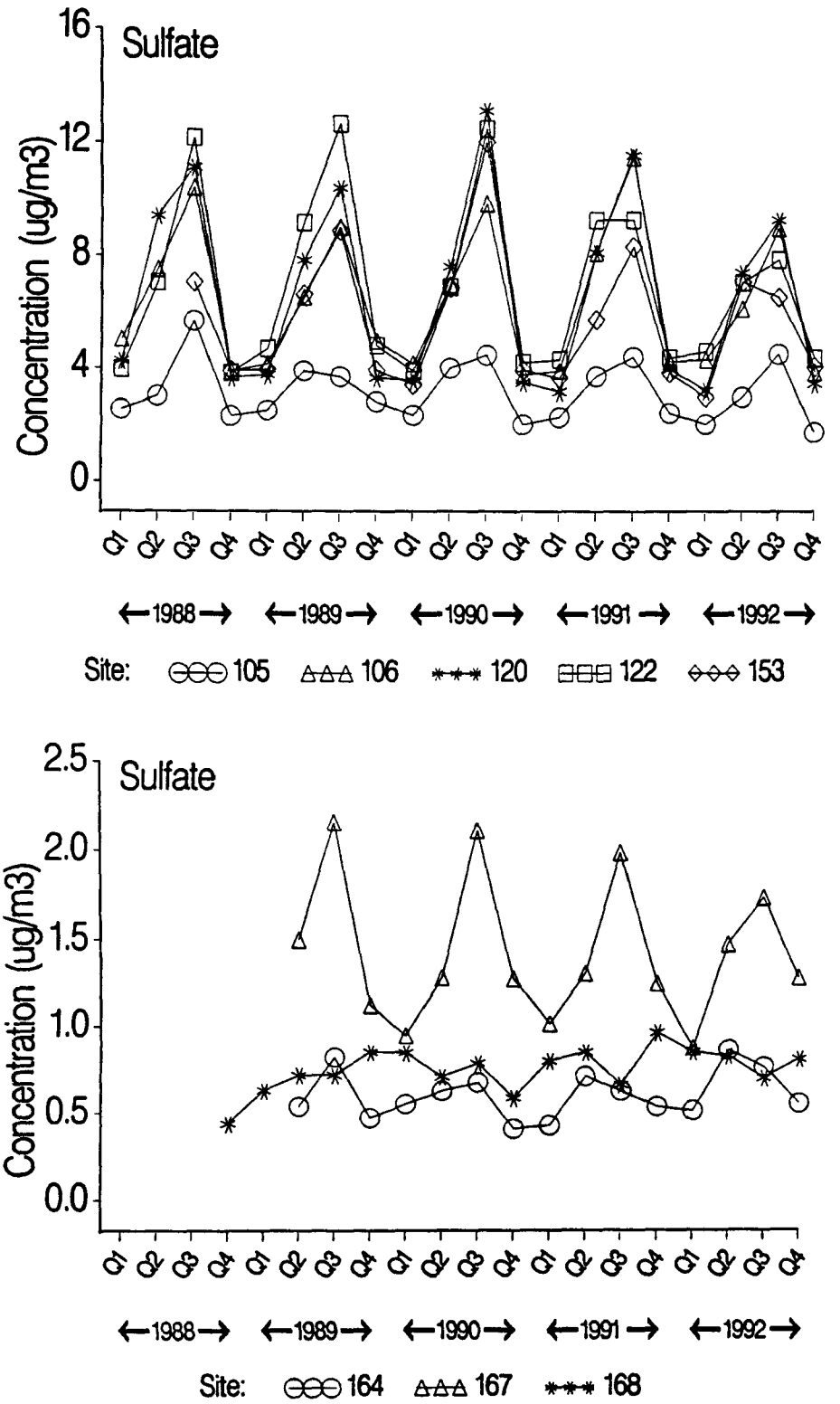


Figure 22. Seasonal variability of SO_4^{2-} ($\mu g/m^3$) for selected sites.

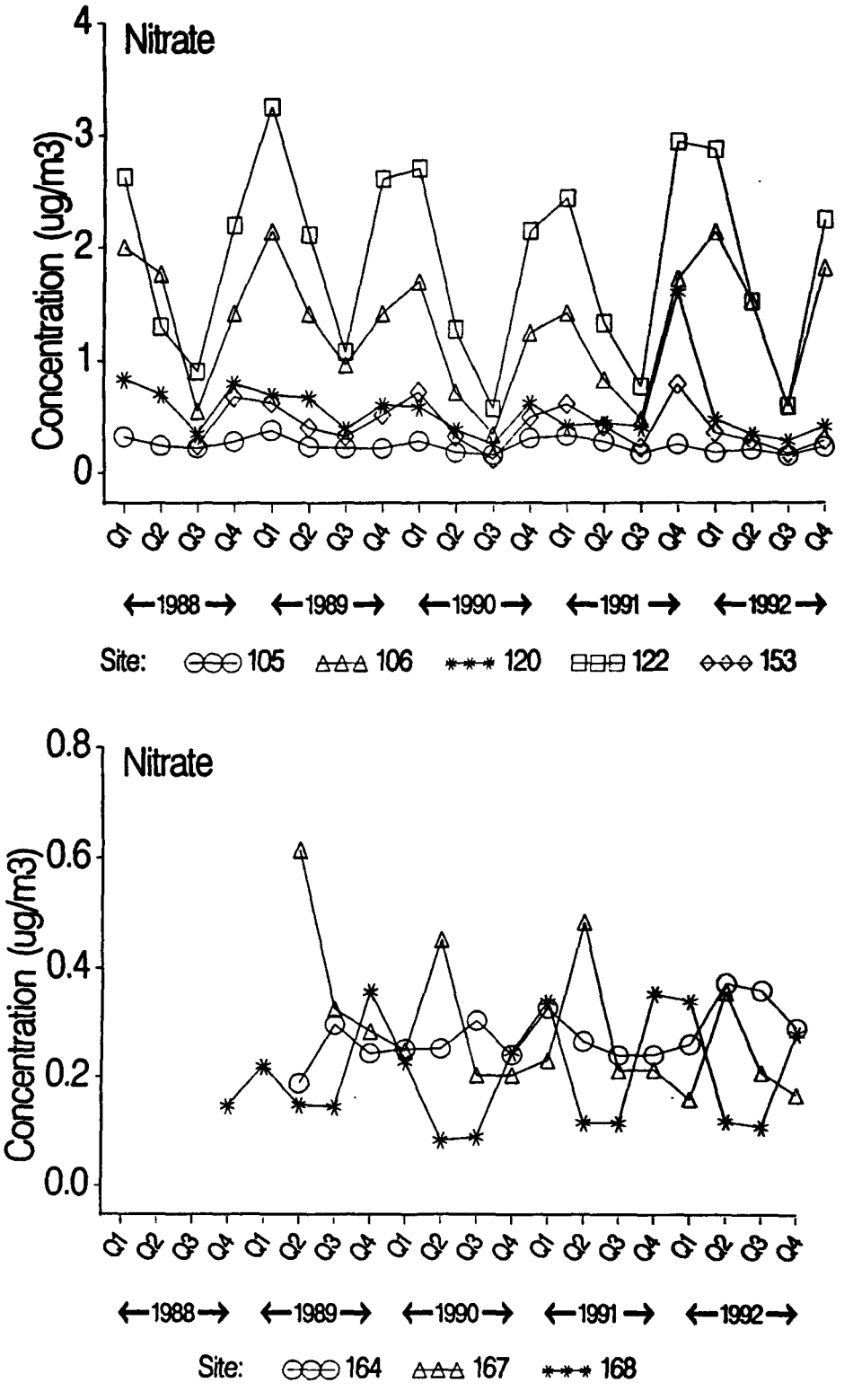


Figure 23. Seasonal variability of NO_3^- ($\mu g/m^3$) for selected sites.

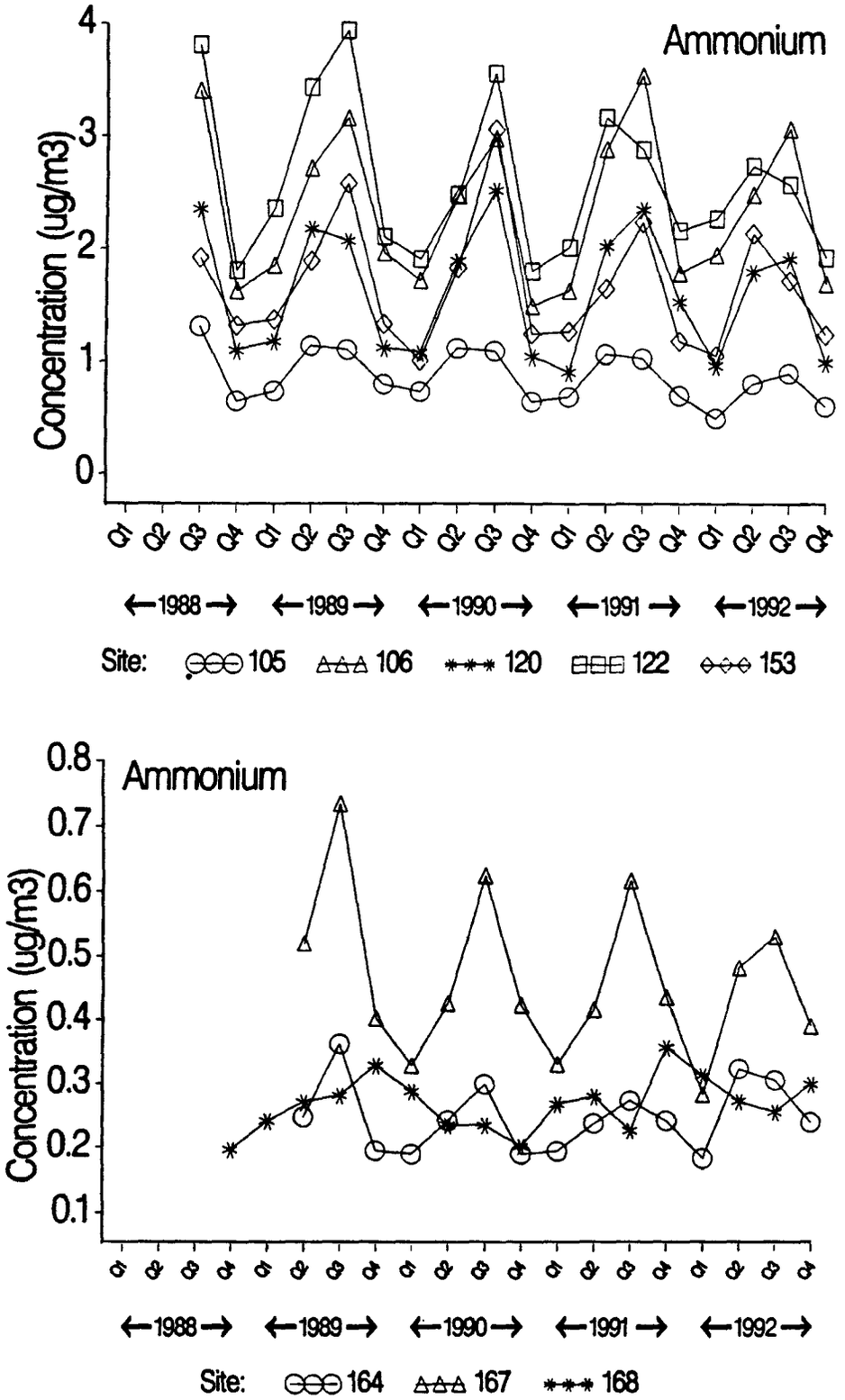


Figure 24. Seasonal variability of NH_4^+ ($\mu g/m^3$) for selected sites.

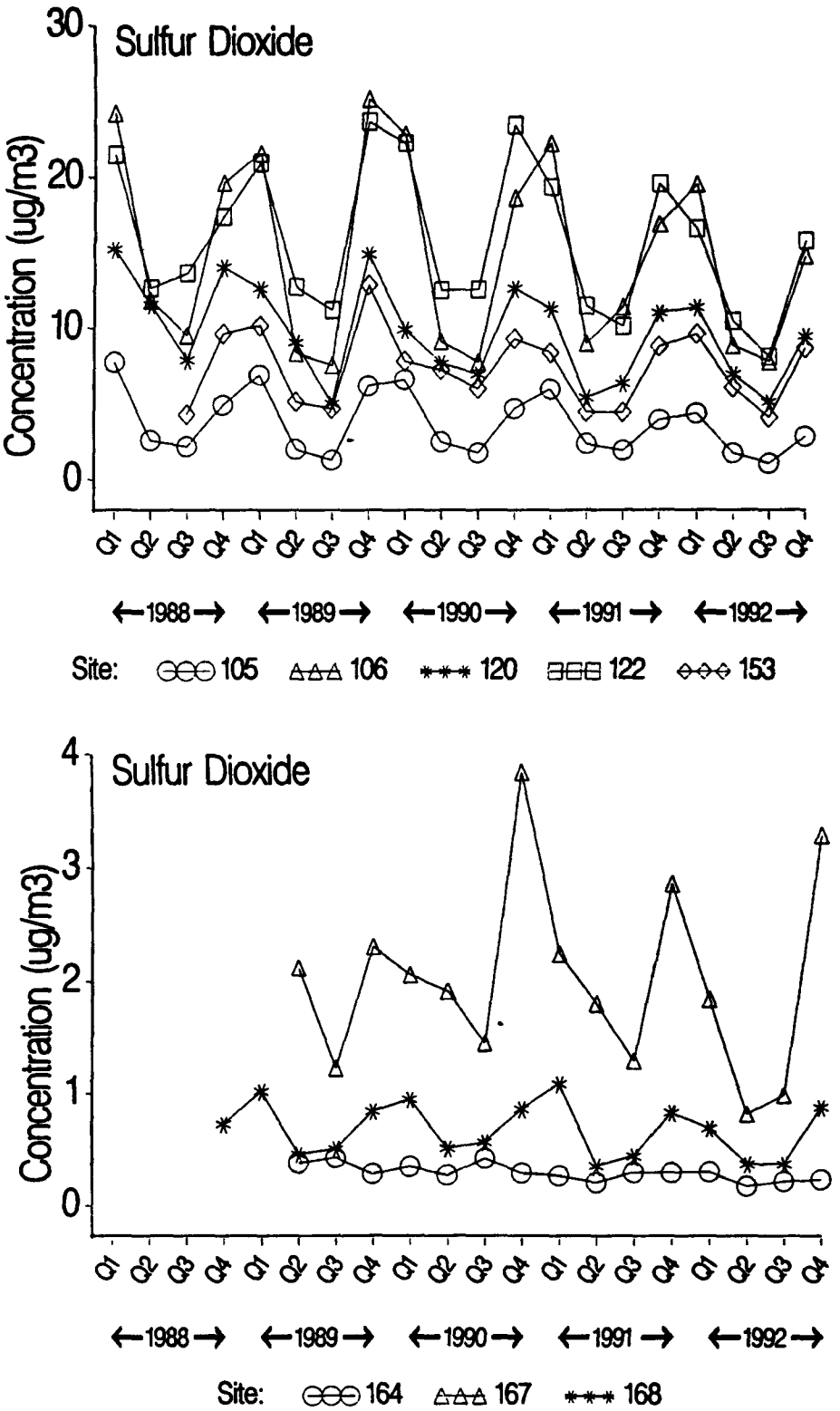
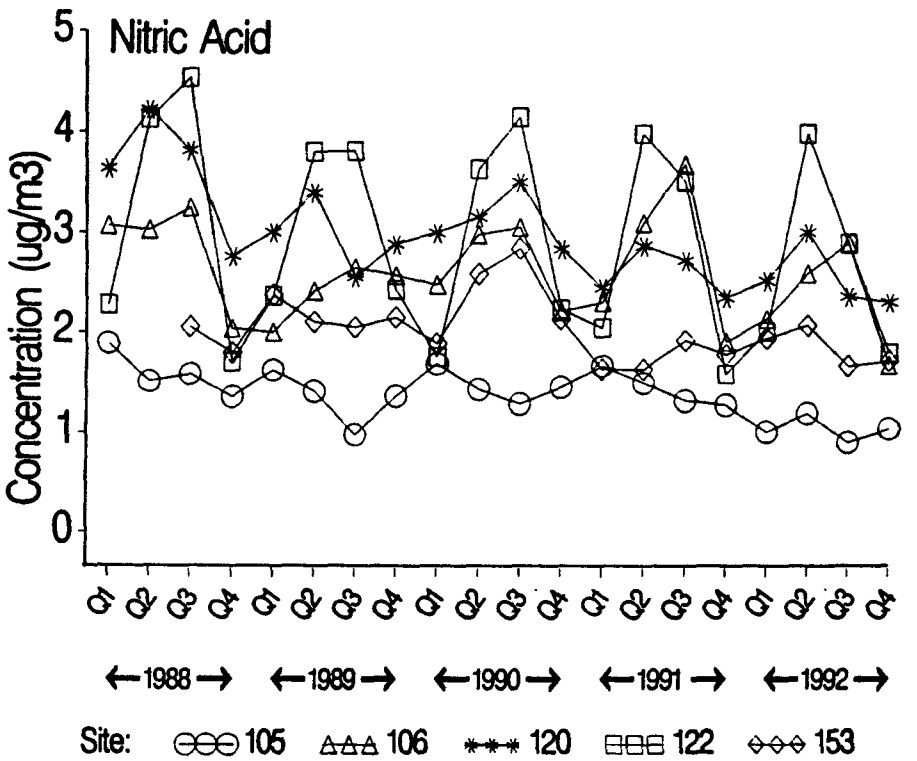


Figure 25. Seasonal variability of SO_2 ($\mu g/m^3$) for selected sites.



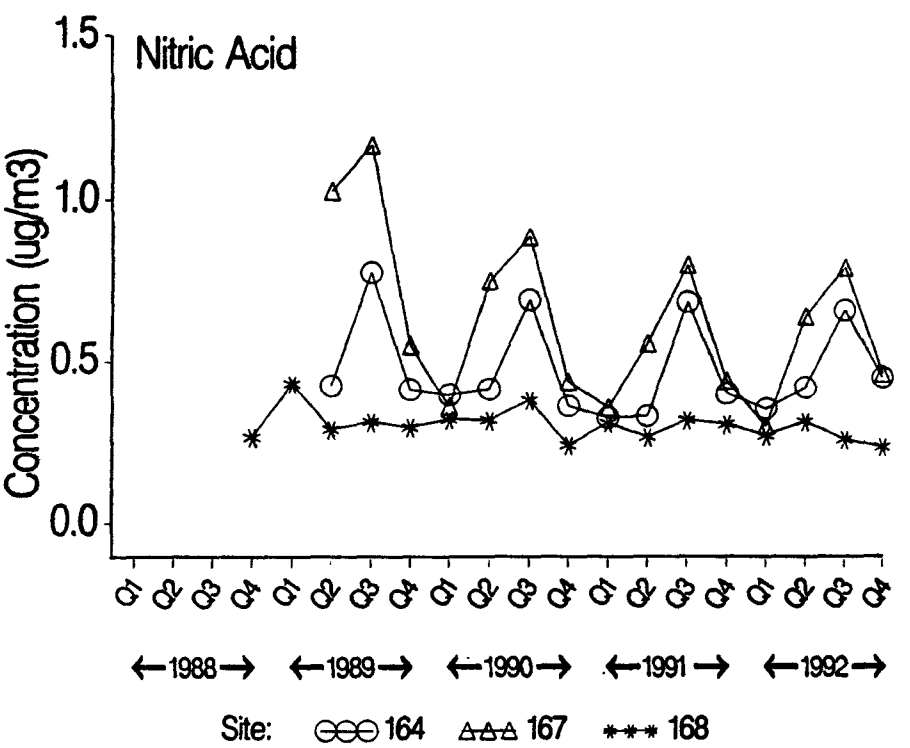


Figure 26. Seasonal variability of HNO_3 ($\mu g/m^3$) for selected sites.

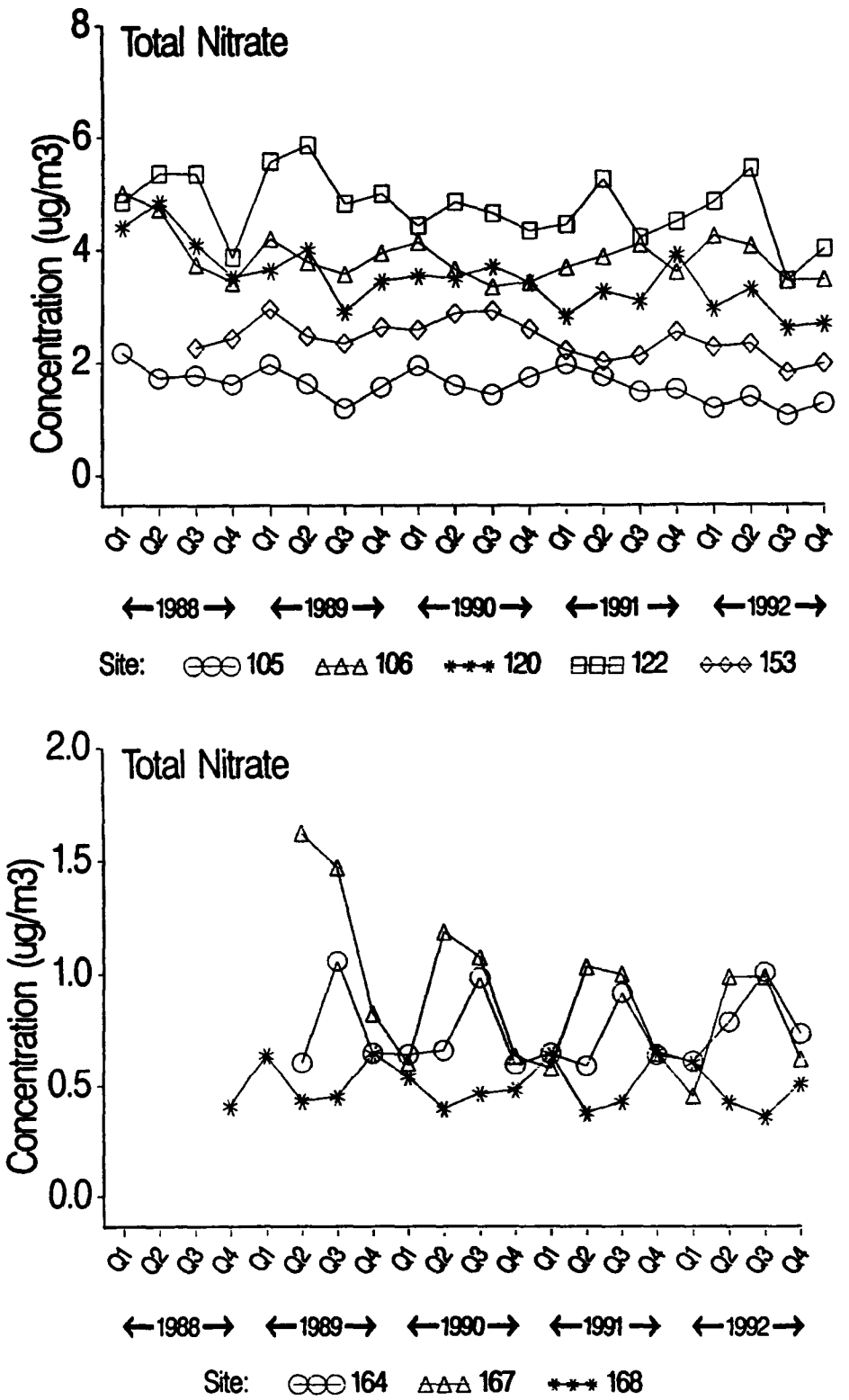


Figure 27. Seasonal variability of total NO_3^- ($\mu g/m^3$) for selected sites.

Table 6. Annual Average Concentrations ($\mu g/m^3$) of SO_4^{2-}, NO_3^-, AND NH_4^+, 1989-1992

Sub-region	No. of Sites	SO_4^{2-}				NO_3^-				NH_4^+			
		1989	1990	1991	1992	1989	1990	1991	1992	1989	1990	1991	1992
Northeast	11	6.4	6.1	6.2	5.6	1.0	0.8	0.7	0.8	2.0	1.8	1.9	1.7
Upper Northeast	3	3.0	2.8	2.6	2.5	0.3	0.2	0.2	0.2	0.8	0.8	0.7	0.6
Midwest	9	6.8	6.1	6.0	5.3	2.9	2.3	2.4	2.4	2.9	2.4	2.4	2.3
Upper Midwest	3	4.2	3.5	3.4	3.2	1.8	1.7	1.6	1.4	1.8	1.5	1.5	1.4
South Central	12	6.4	5.9	5.7	5.4	0.7	0.6	0.6	0.6	1.9	1.7	1.7	1.6
Southern Periphery	3	5.0	4.8	4.0	4.0	0.6	0.4	0.5	0.5	1.4	1.2	1.2	1.2
East	41	6.0	5.5	5.4	5.0	1.3	1.1	1.1	1.1	2.0	1.8	1.8	1.7
West	9	0.89	0.83	0.81	0.86	0.28	0.25	0.28	0.26	0.36	0.31	0.31	0.32

Source: ESE.

Table 7. Annual Average Concentrations ($\mu g/m^3$) of HNO_3, SO_2, and Total NO_3^-, 1989-1992

Sub-region	No. of Sites	HNO_3				SO_2				Total NO_3^-			
		1989	1990	1991	1992	1989	1990	1991	1992	1989	1990	1991	1992
Northeast	11	2.6	2.6	2.5	2.2	15.9	13.6	13.3	11.8	3.5	3.3	3.2	2.9
Upper Northeast	3	1.0	1.0	0.9	0.7	3.2	2.8	2.4	1.9	1.3	1.2	1.1	0.9
Midwest	9	2.6	2.4	2.4	2.2	14.0	12.7	12.3	10.8	5.4	4.7	4.7	4.6
Upper Midwest	3	1.6	1.4	1.3	1.3	5.2	4.6	3.9	3.6	3.3	3.1	2.8	2.7
South Central	12	2.2	2.1	1.8	1.9	7.8	7.4	6.1	6.0	2.8	2.6	2.4	2.3
Southern Periphery	3	1.4	1.4	1.2	1.2	3.4	2.6	2.4	2.6	1.9	1.8	1.7	1.7
East	41	2.1	2.1	1.9	1.8	10.5	9.3	8.7	7.9	3.4	3.1	3.0	2.9
West	9	0.60	0.50	0.45	0.48	0.77	0.72	0.65	0.55	0.88	0.74	0.72	0.71

Source: ESE.

regions of the network exhibited reductions in observed SO_2 ranging from 40 percent in the upper midwest to 23 percent in the midwest. Absolute changes in SO_2 concentrations averaged -2.5 $\mu g/m^3$ across all 41 eastern sites.

The observed changes in concentrations over time appear to be real and not the result of changes in field or analytical protocols. The only significant change in field sampling protocols occurred in January 1990, when sample collection intervals were modified from day/night to around the clock. This modification is not a significant factor in the apparent trend because concentration changes occur from year to year and not as a step function. The only significant change in laboratory protocols occurred in January 1991. This involved the addition of hydrogen peroxide to filter extracts to promote oxidation of residual SO_2. The expected impact of this new protocol is an increase in apparent SO_2 by $\leq$5 percent. In most cases, SO_2 values decreased by about 5 percent from 1991 to 1992. Concentration reductions thus appear to be the result of changes in emissions and/or transport and not the result in changes in sampling or analytical protocol.

4.1.3 Ammonium Versus Sulfate

Data for the 50 NDDN sites suggest regional variability in aerosol speciation as well as concentration. This is illustrated in Figure 28, which shows the relationship between NH_4^+ and SO_4^{2-} (molar basis) for each NDDN site using annual average concentrations for 1991 as an example. Similar relationships were observed for other years. Solid and dashed lines are also plotted in this figure to depict 1:1 and 2:1 ratios of NH_4^+ to SO_4^{2-}, respectively. The 2:1 line represents completely neutralized SO_4^{2-}, and the 1:1 line represents 50-percent neutralization of SO_4^{2-}, assuming that only NH_4^+ and SO_4^{2-} are present in the aerosol phase. Other aerosol species are undoubtedly present and, therefore, ratios represent only approximate levels of neutralization.

Results show that the majority of eastern sites fall between the 50-percent and 100-percent neutralization lines and that the western sites scatter around the 100-percent neutralization line. Inspection of Figure 28 also shows a small number of eastern sites on or above the 100-percent neutralization line and a small number of sites only slightly above the 50-percent neutralization line. The highest NH_4^+:SO_4^{2-} ratios all correspond to agricultural sites in the midwest and upper midwest. The lowest ratios of NH_4^+:SO_4^{2-}, in contrast, all correspond to sites in predominately forested areas of the southeast and northeast.

Although filter pack data cannot be used to quantify aerosol acidity, these results suggest broad qualitative differences in aerosol acidity. For agricultural sites in general, there appears to be sufficient NH_4^+ to completely neutralize SO_4^{2-}. For forested sites at significant distances from agricultural activity,

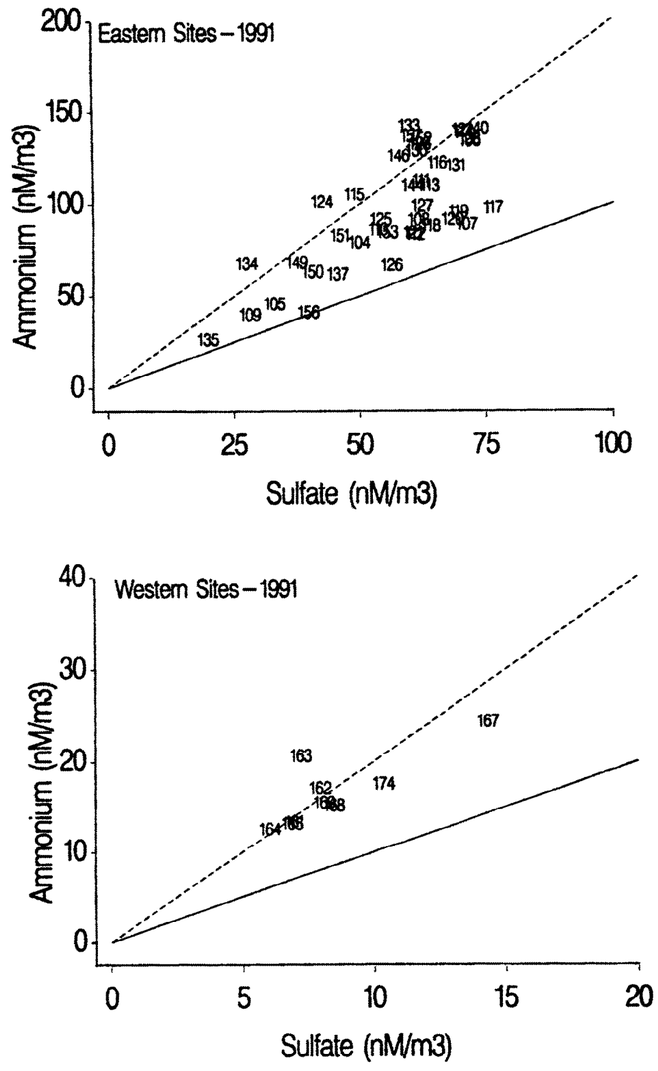


Figure 28. Scattergram of NH_4^+ versus SO_4^{2-} (molar basis) for 1991.

observed SO_4^{2-} must be balanced by other cations in addition to NH_4^+. The metal cations Na^+, K^+, Ca^{2+}, and Mg^{2+} were measured in NDDN filter pack samples during 1989 (ESE, 1990c). Results showed that Na^+, K^+, Ca^{2+}, and Mg^{2+} were minor aerosol constituents at all sites except those in the midwest or near the coast (Sites 104, 116, and 156). On the whole, these data show that aerosol composition varies from region to region and suggest that aerosol acidity may be greater at predominantly forested sites then at predominantly agricultural sites.

4.1.4 Calculated Dry Deposition

Dry deposition calculations for the NDDN sites are made using a multi-layer version of the NOAA inferential model, which has been modified to address multiple vegetation species (see Clarke and Edgerton, 1992). As described in Chapter 3, the meteorological variables necessary to determine R_a, R_b, and R_c are obtained from the 10-m meteorological tower at each of the sites, normally located in a clearing over grass or other low vegetative surface. Vegetation activity parameters (minimal stomotal resistance; light response coefficient; and optimum, minimum, and maximum growing temperatures) are assigned to each vegetation species based on published values, primarily from plant physiology studies. These data were provided by the authors of the inferential model.

The calculation procedure used for the NDDN is based on area weighting of dry deposition to the individual land-use/vegetation types. V_d and flux are calculated by species and then area-weighted within 1 km of the site to represent average values. Mixed vegetation (e.g., mixed coniferous and deciduous forest) is disaggregated into individual species prior to calculating deposition such that deposition to individual species can be calculated by the model.

The three resistance terms are calculated for each species and vegetation/surface type every hour when meteorological data are available. The inverse sum of the resistances is the V_d for the specific species and vegetation/surface type, and the site averaged V_d is the areal-weighted average V_d over all vegetation types. Hourly values of V_d are then averaged over a week and multiplied by the weekly integrated concentrations to produce weekly fluxes of HNO_3, SO_4^{2-}, NO_3^-, and SO_2.

This section presents results of dry deposition calculations for sulfur and nitrogen species for 1990, 1991, and 1992. Weekly patterns of V_ds and fluxes are also discussed to illustrate the effects of canopy condition and meteorology on atmospheric deposition. The deposition of SO_4^{2-} and SO_2 is expressed in units of kilograms sulfur per hectare (kg-S/ha) to facilitate comparison of gas and particle phase deposition and, ultimately, comparison with wet deposition.

Deposition of HNO_3 and NO_3^- is expressed in units of kilograms nitrogen per hectare (kg-N/ha), also for comparison purposes. Unlike sulfur deposition, however, HNO_3 and NO_3^- cannot be considered the primary contributors to total nitrogen. Additional potentially significant contributors include reduced nitrogen species (e.g., NH_4^+ and NH_3), organic nitrates (e.g., peroxyacetylnitrate), and other oxidized nitrogen species (e.g., nitrogen dioxide and nitrous acid). For this reason, deposition of HNO_3 and NO_3^- has been discussed in terms of nitrate-nitrogen rather than total nitrogen deposition.

4.1.4.1 Sulfur Fluxes

Calculated 1990, 1991, and 1992 fluxes of SO_2, SO_4^{2-}, and total sulfur are shown in Figures 29 through 37. Annual fluxes of SO_2 for eastern sites range from about 0.7 kg-S/ha in north Florida to approximately 9.0 kg-S/ha in northern Illinois, southern Indiana, and western Pennsylvania. The overall pattern of SO_2 deposition strongly reflects that of atmospheric concentrations. Fluxes are substantially lower for sites in complex terrain than for neighboring sites, due to a combination of low concentration and low V_d. Lindberg et al. (1988) reported similar variability in wet deposition between low- and high-elevation forests of the Southern Appalachians. McMillen (1990) showed that terrain-induced variability in meteorological parameters could have a significant impact on dry deposition estimates. Observations from the NDDN not only confirm previous studies but show that short-range variability in concentrations and meteorology complicate estimation of dry deposition in complex terrain (see Chapter 5).

Annual SO_2 fluxes for western sites are generally well below 1.0 kg-S/ha and well below minimal values observed for eastern sites. This reflects extremely low SO_2 concentrations at most western sites. The lone exception to this is the site in southern Arizona (Site 167). Deposition at this site is on the order of that observed at the more remote eastern sites and is the result of elevated local SO_2 concentrations.

Calculated dry deposition for SO_4^{2-} is shown in Figures 29 through 31. Deposition rates for eastern sites range from about 0.2 kg-S/ha in northern Maine (Site 135) to about 1.0 kg-S/ha in western North Carolina (Site 126). The three mountaintop sites in Virginia and North Carolina exhibit the highest SO_4^{2-} fluxes. This finding may be due to enhanced V_ds at high elevations, since SO_4^{2-} concentrations at mountaintop sites are not atypical of other eastern sites. Deposition among western sites ranges from 0.06 kg-S/ha in northern Montana to 0.28 kg-S/ha in southern Arizona. As noted earlier, relatively high deposition rates in southern Arizona are due to locally high concentrations of SO_4^{2-}.

Calculated dry deposition of total sulfur (i.e., SO_2 plus SO_4^{2-}) exhibits a pattern which is fairly similar to SO_2, indicating that gaseous deposition dominates the dry deposition process (see Figures 35 through 37). The dominance of SO_2 deposition is shown in Figure 38, which illustrates the percent of

Figure 29. Calculated dry deposition for SO_2 (kg-S/ha) for 1990.

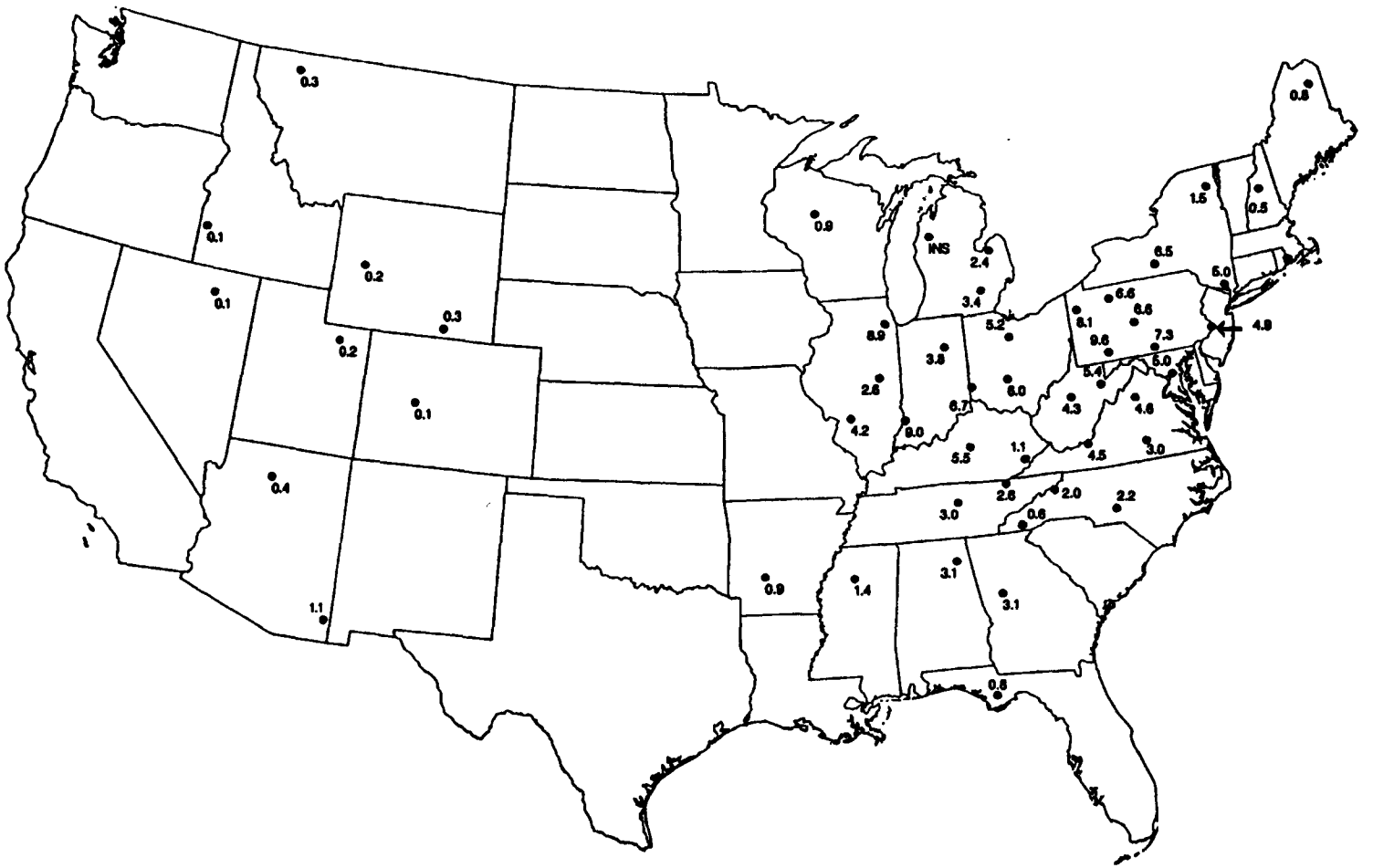


Figure 30. Calculated dry deposition for SO_2 (kg-S/ha) for 1991.

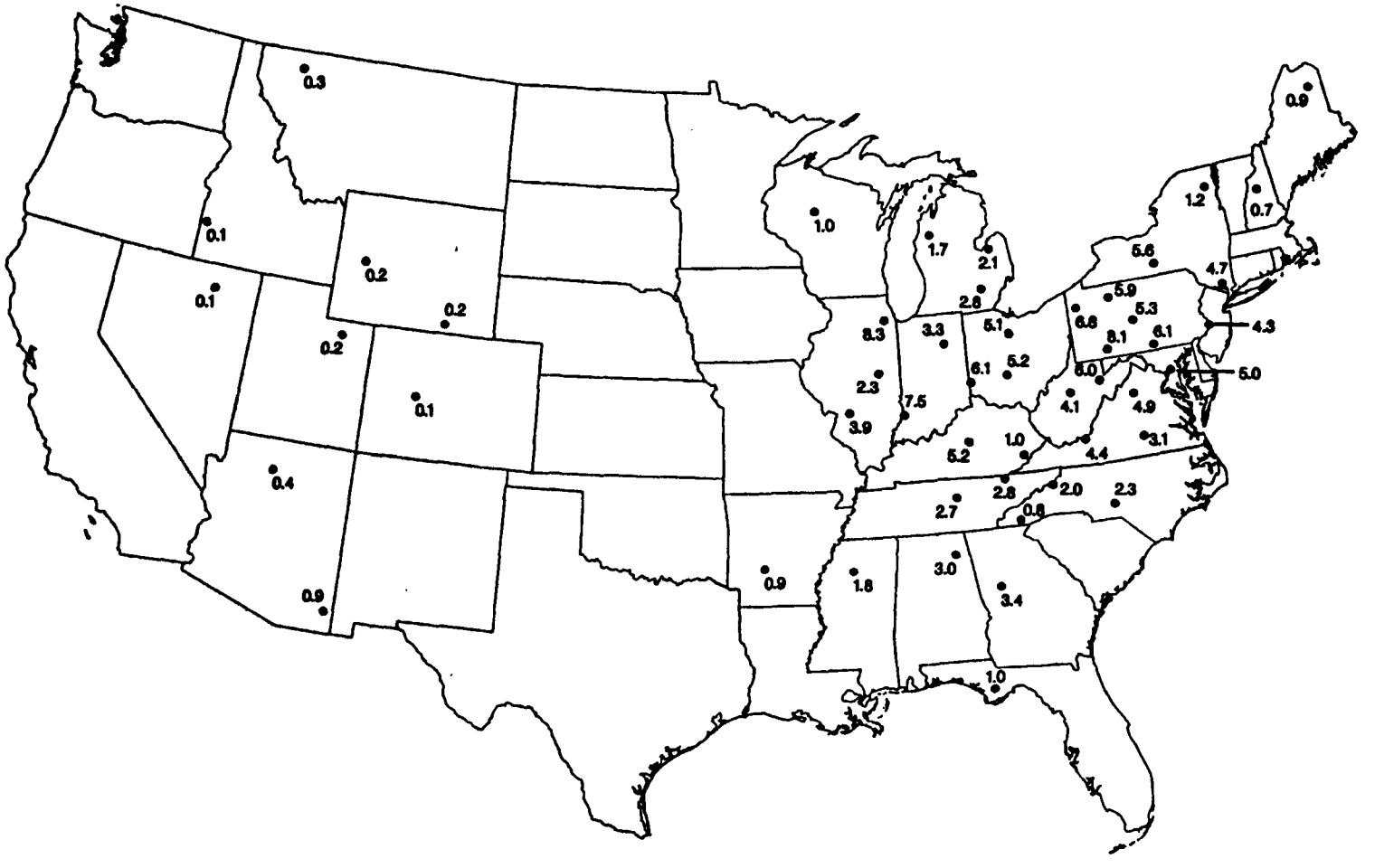


Figure 31. Calculated dry deposition for SO_2 (kg-S/ha) for 1992.

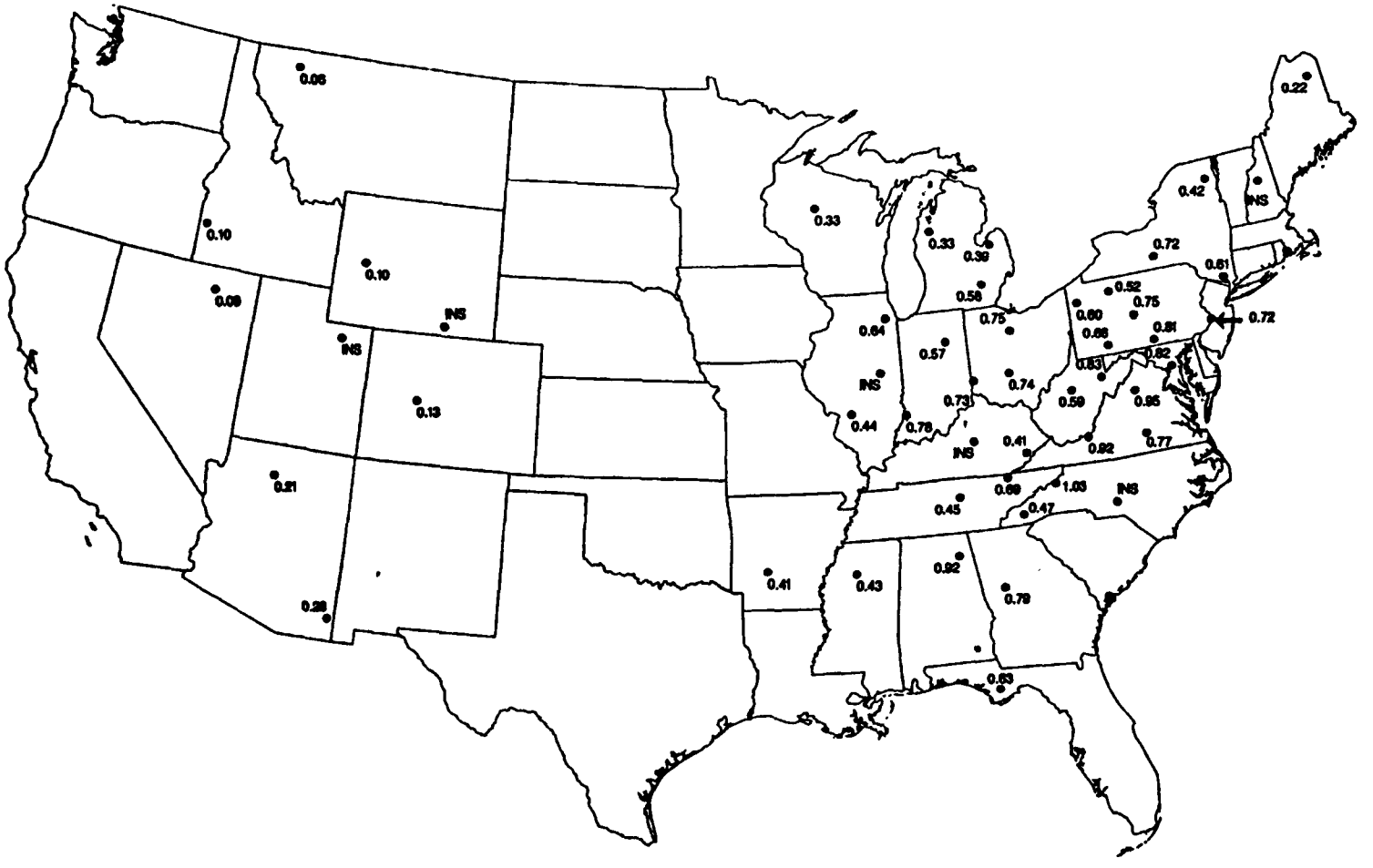


Figure 32. Calculated dry deposition for SO_4^{2-} (kg-S/ha) for 1990.

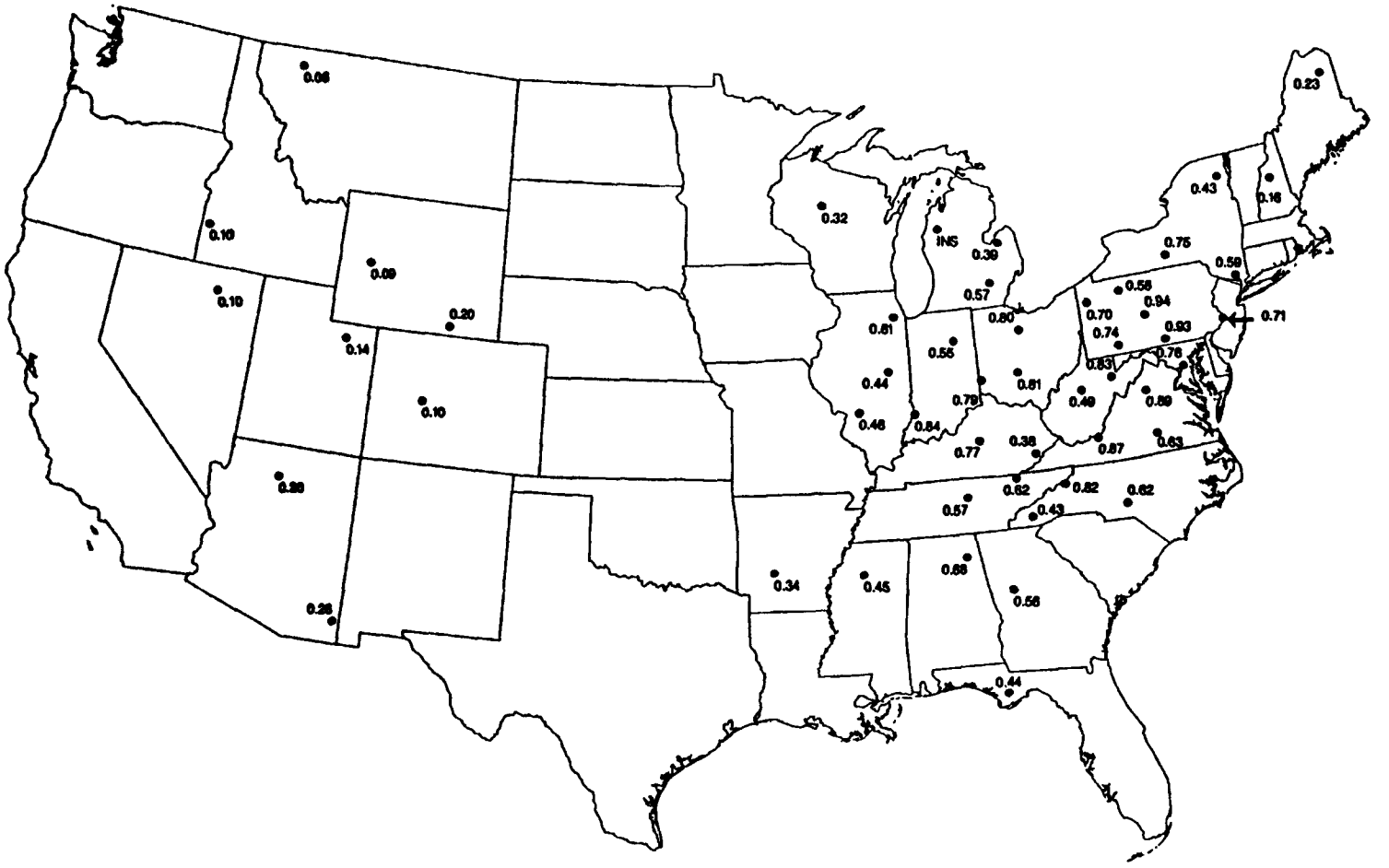


Figure 33. Calculated dry deposition for SO_4^{2-} (kg-S/ha) for 1991.

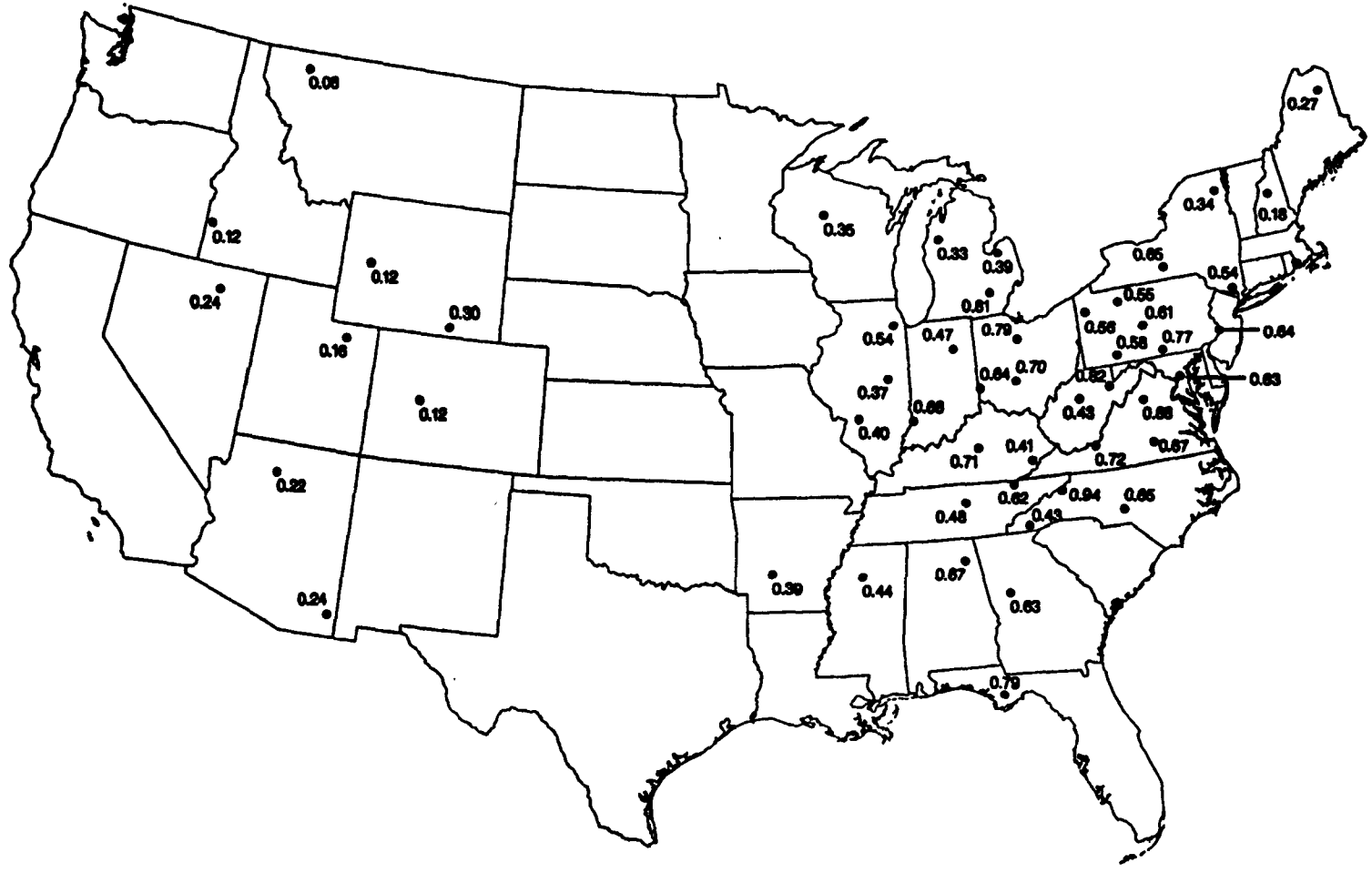


Figure 34. Calculated dry deposition for SO_4^{2-} (kg-S/ha) for 1992.

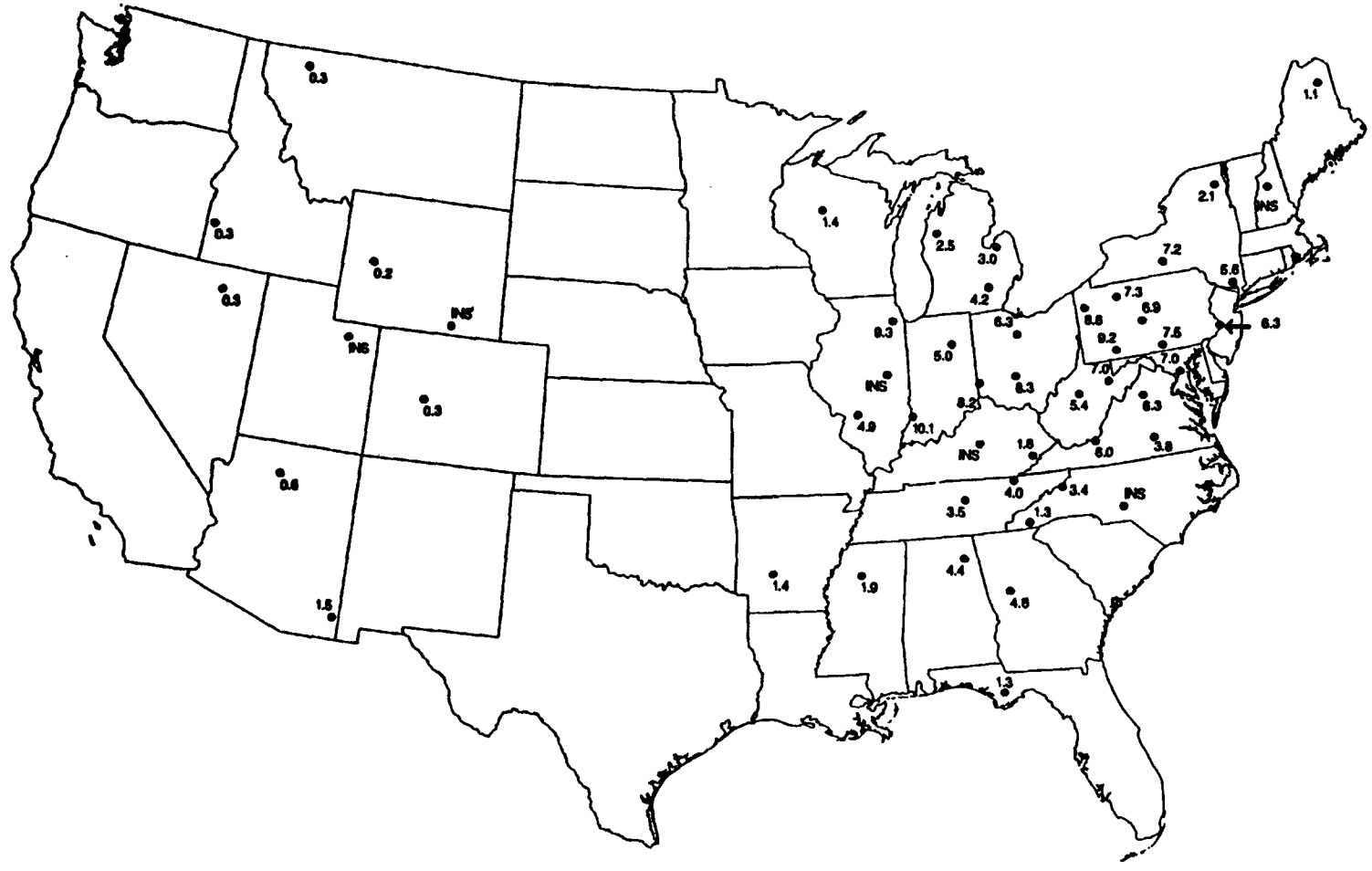


Figure 35. Calculated dry deposition for total sulfur (kg-S/ha) for 1990.

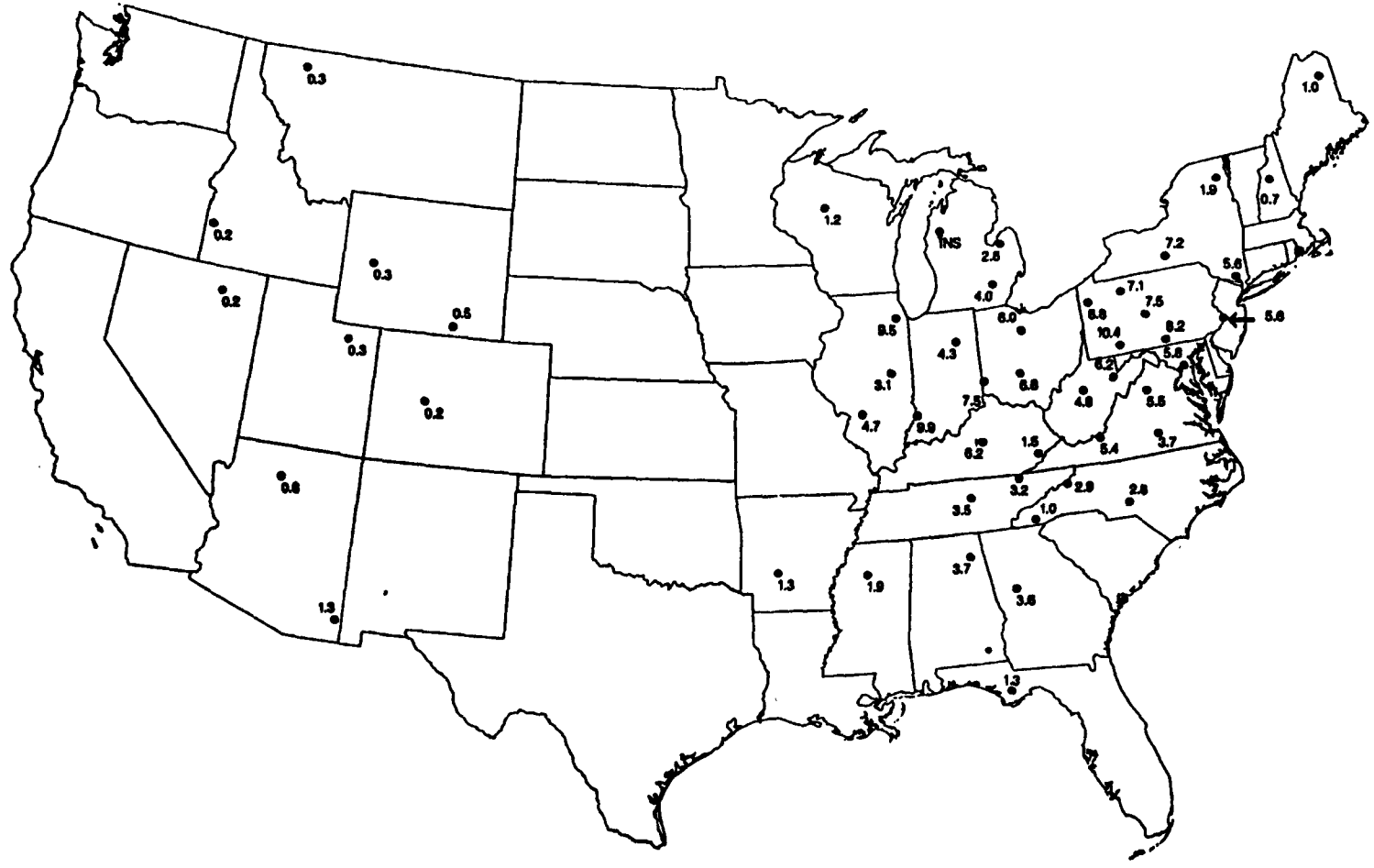


Figure 36. Calculated dry deposition for total sulfur (kg-S/ha) for 1991.

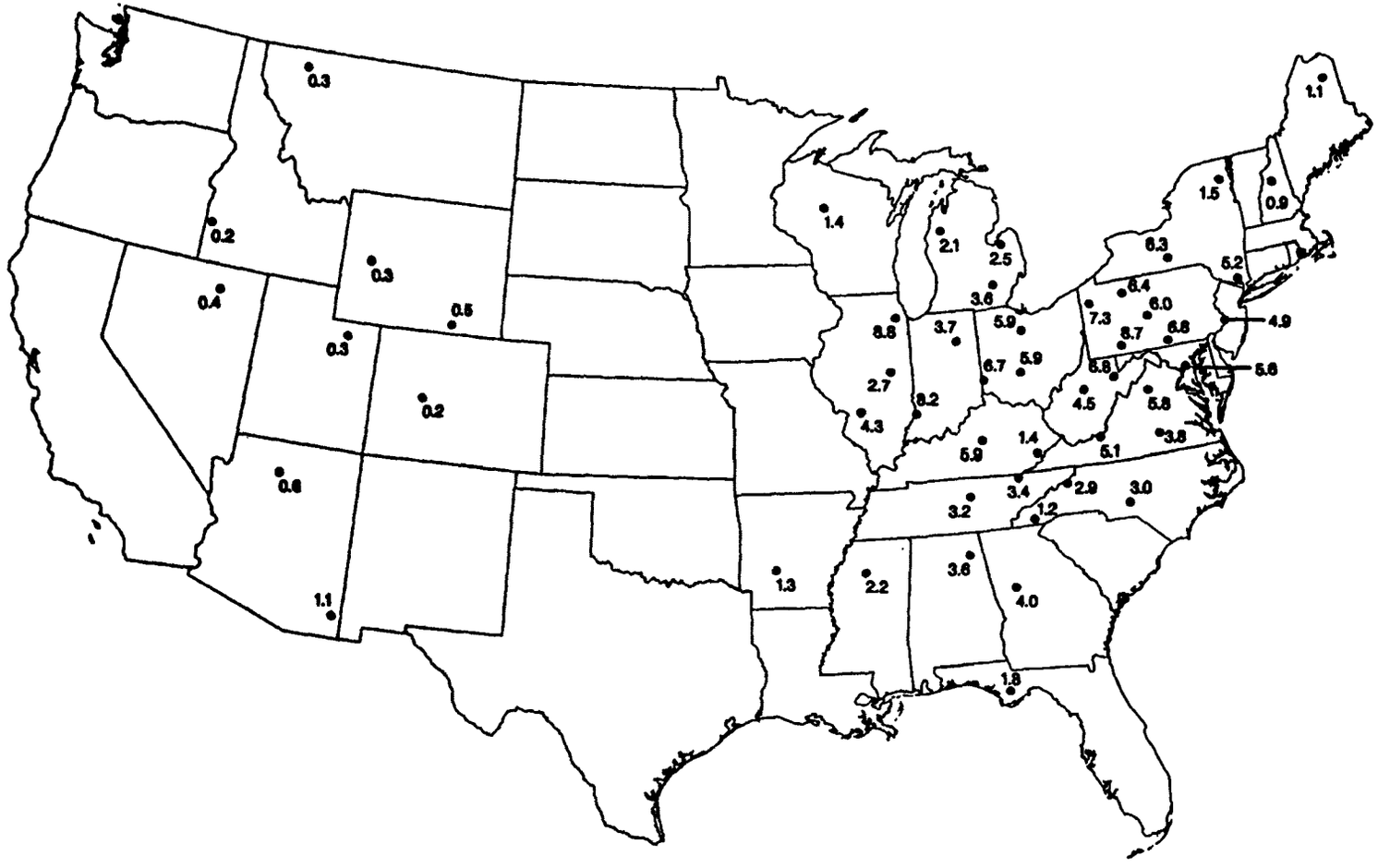


Figure 37. Calculated dry deposition for total sulfur (kg-S/ha) for 1992.

Figure 38. Percent gaseous sulfur deposition for 1991.

total dry sulfur deposition attributable to SO_2, using 1991 data as an example. Data for eastern sites show that SO_2 accounts for 59 to 93 percent of dry sulfur deposition. In general, the highest percentages (i.e., >85 percent) occur in an area extending from Illinois to southern New York. Not suprisingly, the lowest percentages occur around the network periphery, where SO_2 concentrations are low. Data for western sites show lower percentages of SO_2 deposition, reflecting low SO_2 concentrations throughout the region. At no site, however, does SO_2 account for less than 50 percent of dry sulfur deposition.

The week-to-week variability of SO_2 V_ds and fluxes are shown for three sites in Figures 39 and 40. These three sites represent a range in land-use characteristics and terrain in Indiana, Pennsylvania, and North Carolina. The Indiana site is surrounded by mixed grass and crops in flat terrain. The Pennsylvania site is agricultural in rolling terrain and the North Carolina site is in forested complex terrain. Weekly deposition velocities exhibit a pronounced summertime peak at all three sites, with the highest V_ds ranging from 0.4 to 0.5 centimeters per second (cm/sec). The period of peak V_d is considerably shorter at the agricultural site in Pennsylvania than the other sites, presumably due to the short growing season for corn and soybeans relative to native grasses (Indiana) and trees (North Carolina). V_ds are a factor of 3 to 5 lower in winter and fall than summer but still show appreciable differences between sites. In this case, low V_ds for the Pennsylvania site reflect large surface resistances of bare soil. Relatively high V_ds for the Indiana site are the consequence of high windspeeds and low atmospheric resistance.

Weekly flux data for the three sites show a summertime peak for the Indiana and Pennsylvania sites but little weekly variability for North Carolina site (Figure 40). The seasonal pattern of SO_2 concentrations runs counter to that of V_d, and, therefore, the product of the two exhibits much less seasonality than either one by itself.

4.1.4.2 HNO_3 and NO_3^- Fluxes

Calculated annual fluxes of HNO_3 for 1990, 1991, and 1992 range from 0.7 to 5.0 kg-N/ha for eastern sites and 0.4 to 1.3 kg-N/ha for western sites (see Figures 41 through 43). Spatial variability is high across the United States, reflecting large ranges in V_d and concentration. As noted for SO_2, sites in valleys experience more frequent and persistent nocturnal inversions than sites in rolling terrain or on ridges. The overall effect of such inversions is to suppress vertical exchange and thus to reduce fluxes of gases and particles to the surface. Inversions may also reduce frequency of plume impaction at sites located in valleys.

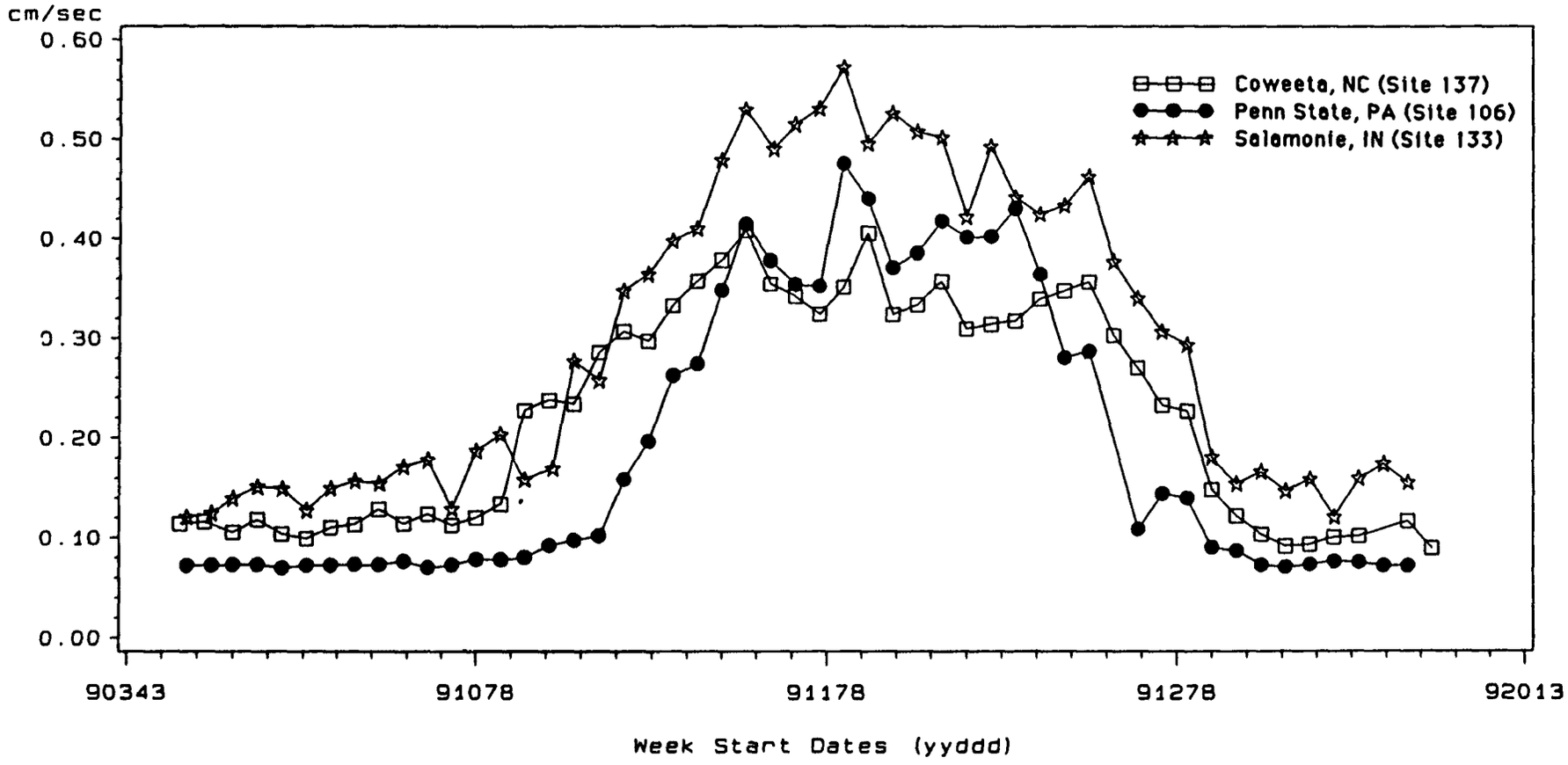


Figure 39. Weekly deposition velocities for SO_2 for selected sites.

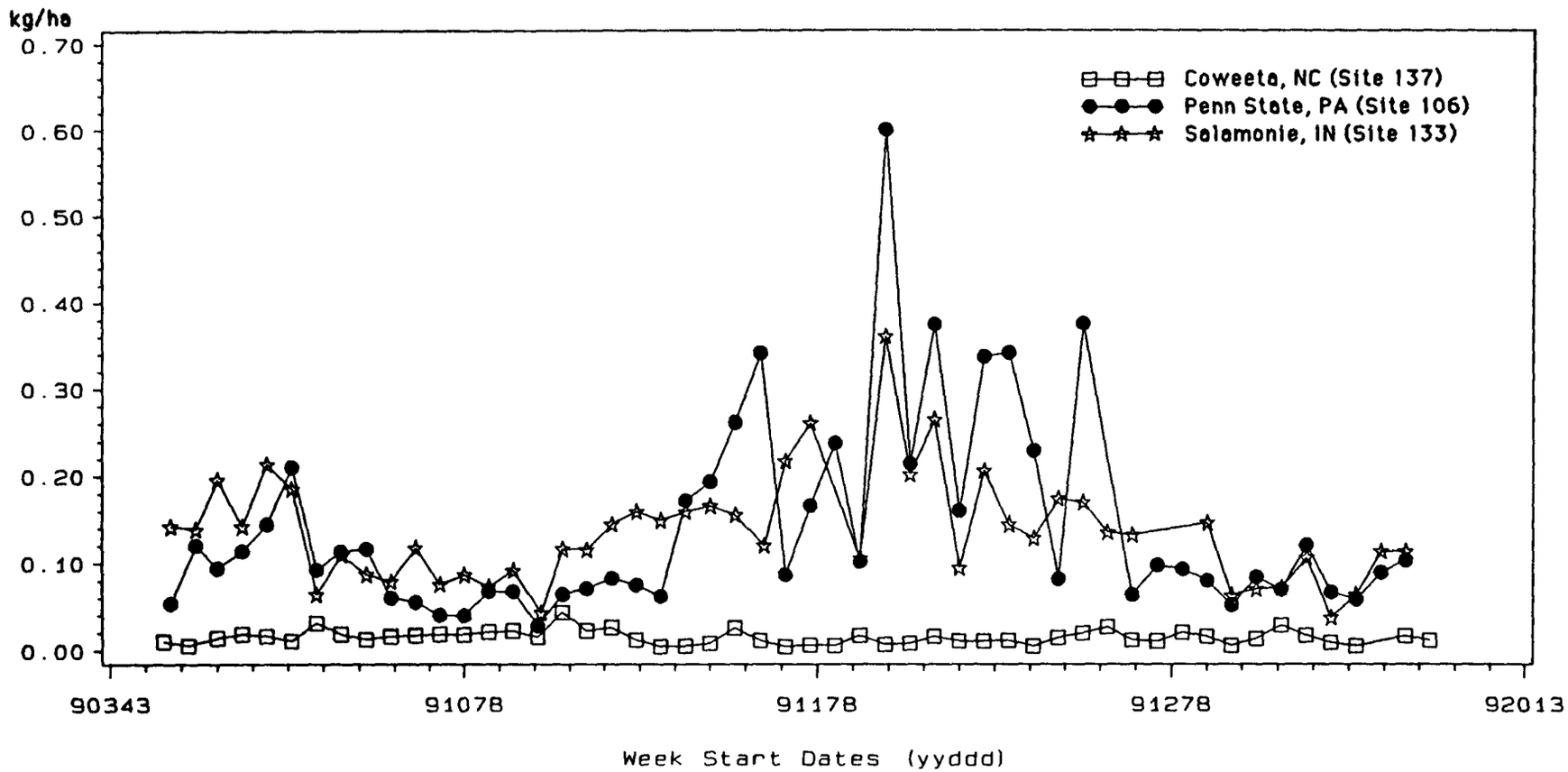


Figure 40. Weekly SO_2 fluxes for selected sites.

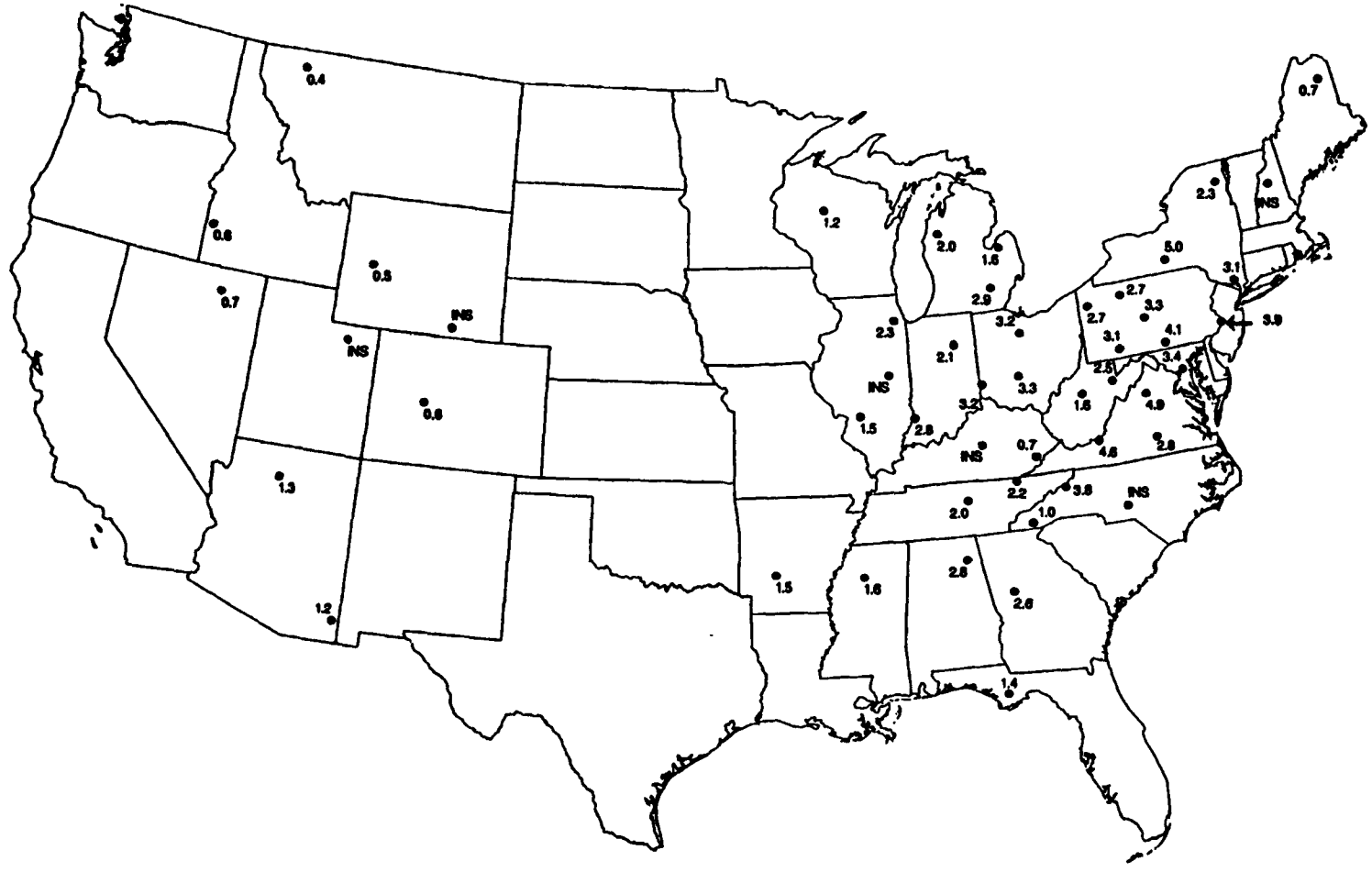


Figure 41. Calculated dry deposition of HNO_3 (kg-N/ha) for 1990.

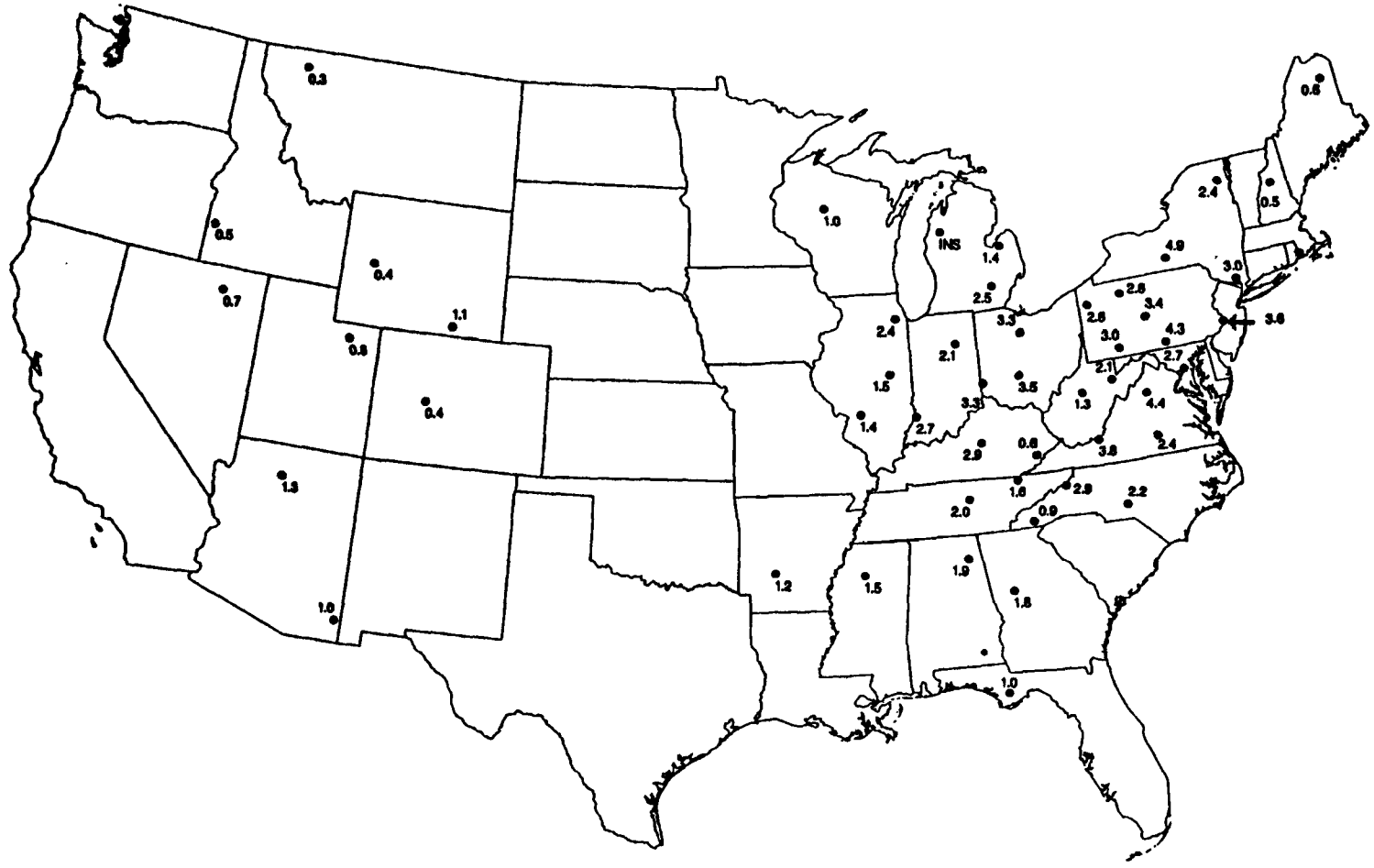


Figure 42. Calculated dry deposition of HNO_3 (kg-N/ha) for 1991.

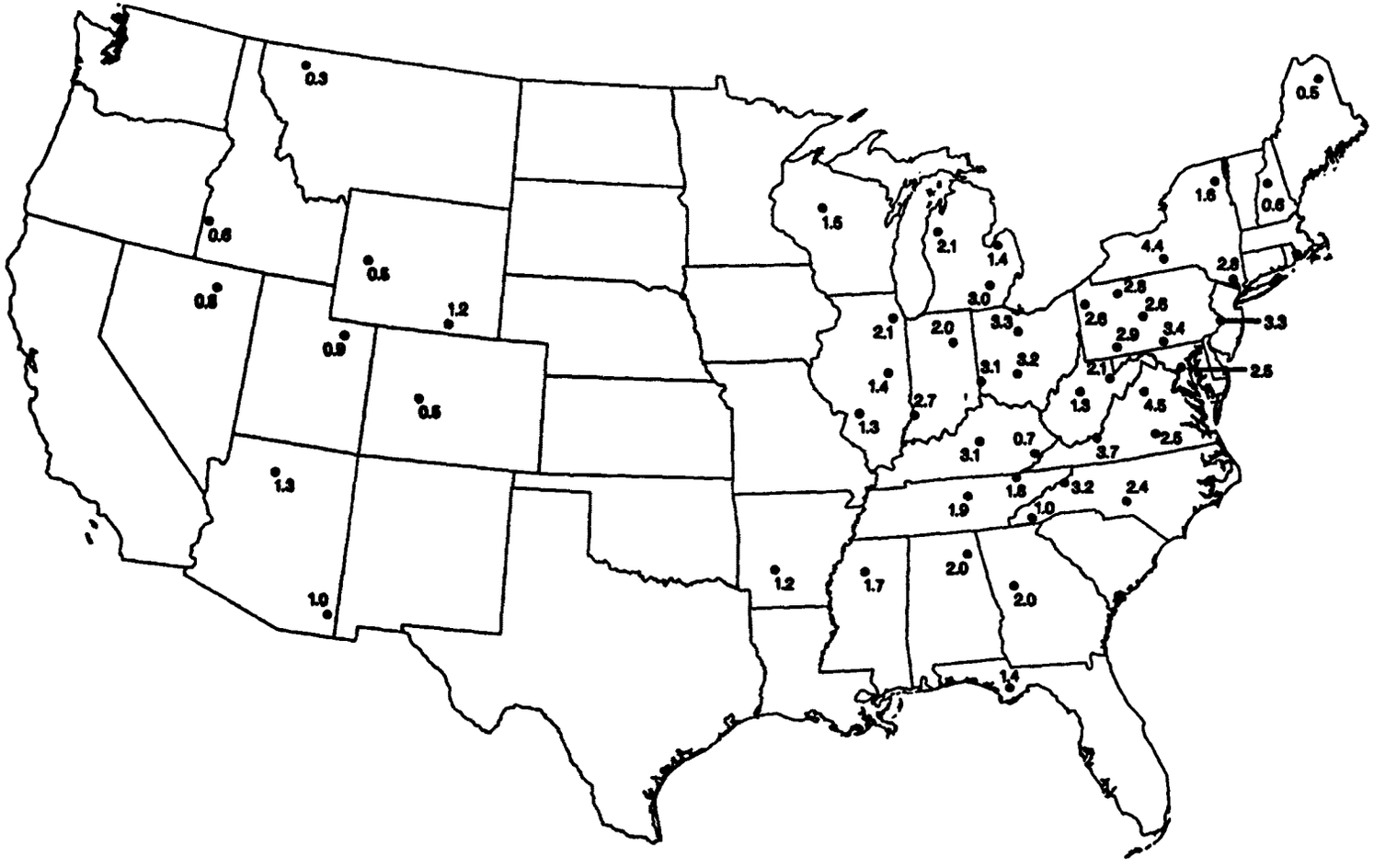


Figure 43. Calculated dry deposition of HNO_3 (kg-N/ha) for 1992.

Annual fluxes for NO_3^- (Figures 44 through 46) range from 0.01 kg-N/ha in northern Maine and northern Montana (Sites 135 and 168) to 0.2 kg-N/ha in northern Illinois and northern Indiana (Sites 133 and 146). In general, NO_3^- deposition is similar between eastern and western sites and, provided the former are not located near intensive agricultural activities, and is inconsequential relative to HNO_3 deposition. This is illustrated in Figures 47 through 49, which show total nitrate-nitrogen dry deposition, and Figure 50, which shows the percentage contribution of HNO_3 to dry nitrate-nitrogen deposition. Gaseous deposition accounts for at least 91 percent, and usually more than 95 percent, of nitrate-nitrogen dry deposition at NDDN sites. Unlike sulfur deposition, the percentage of nitrate-nitrogen does not appear to differ between eastern and western sites.

Weekly HNO_3 V_d and flux data for three sites in Indiana, Pennsylvania, and North Carolina are shown in Figures 51 and 52. Deposition velocities exhibit only moderate seasonality, but were generally highest during spring and winter (i.e., periods of highest winds). The presence of actively growing vegetation appears to exert little influence over V_ds for HNO_3. Fluxes of HNO_3 were generally similar at Pennsylvania and Indiana sites but much lower at the North Carolina site. This is the result of very low concentrations and low V_d in complex terrain.

The relationship between atmospheric concentration and dry deposition of SO_2 and HNO_3 is illustrated in Figure 53. Each data point represents the intersection of annual average concentration and annual deposition for a site, using data for 1991. Despite the complexity of the dry deposition process, data for SO_2 are fairly consistent from site to site. This, in turn, suggests that variability in deposition is largely driven by variability in concentration. This appears to hold for western and eastern sites.

Data for HNO_3 exhibit markedly greater scatter from site to site. For example, a large range in deposition is calculated for sites with annual average concentrations of 2 to 3 $\mu g/m^3$ of HNO_3. This can only occur due to variability in both V_d and concentration. Closer inspection of data in Figure 53 shows some evidence of geographical clustering of sites. Three sites in flat terrain (i.e., 133, 130, and 157) fall significantly below and three mountaintop sites fall significantly above the general flux-concentration relationship. The three sites in flat terrain are located in extensive cropland areas of Illinois and Indiana while the three mountaintop sites are in forested ecosystems of Virginia and North Carolina. This contrast in terrain and vegetation suggests that differences in atmospheric turbulence controls much of the site-to-site variation of HNO_3 deposition.

Clarke and Edgerton (1992) assessed the overall uncertainty of dry deposition calculations using the inferential model. Seasonal and annual values of calculated fluxes for sites located in flat terrain with uniform vegetation and not influenced by nearby sources are probably accurate within about 25 to

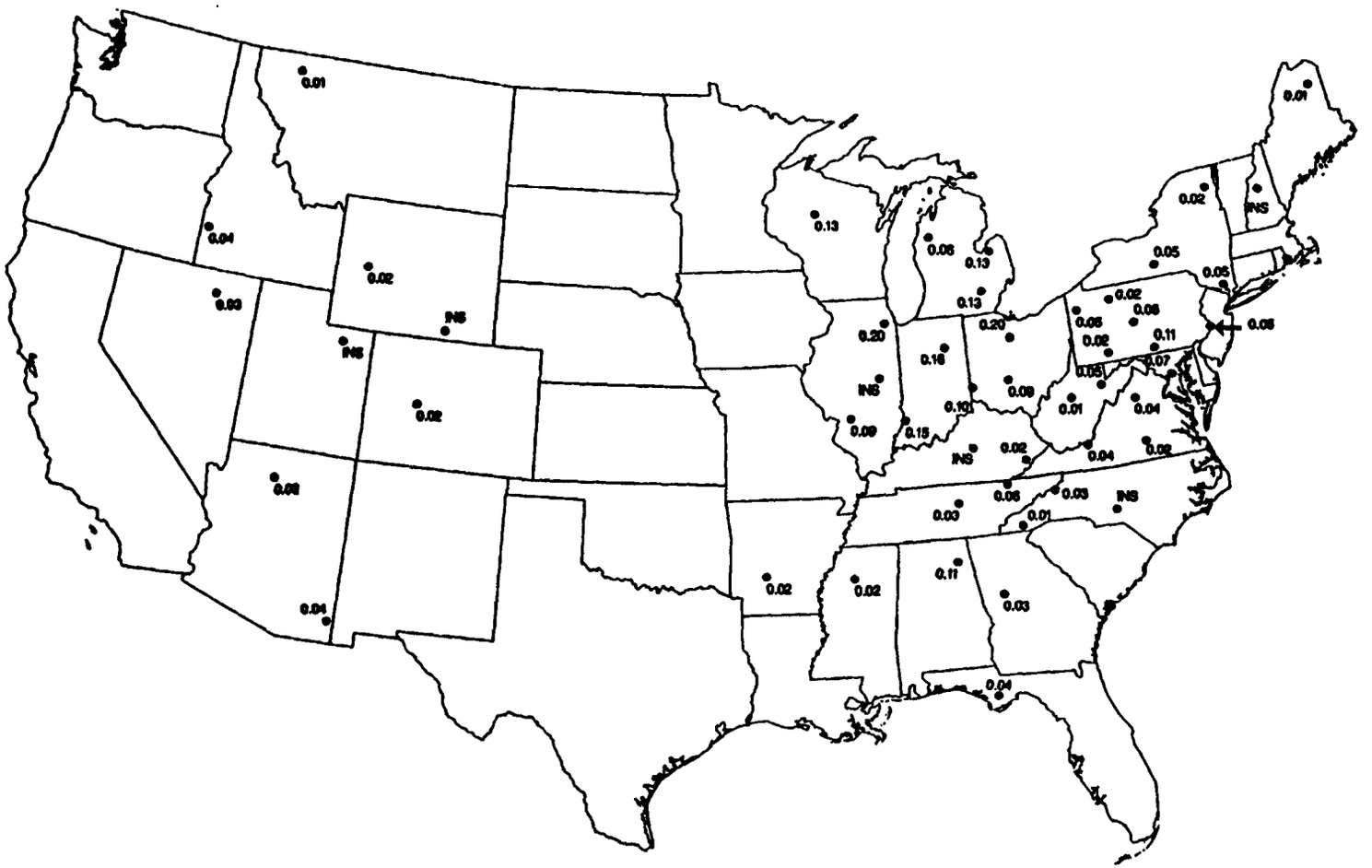


Figure 44. Calculated dry deposition of NO_3^- (kg-N/ha) for 1990.

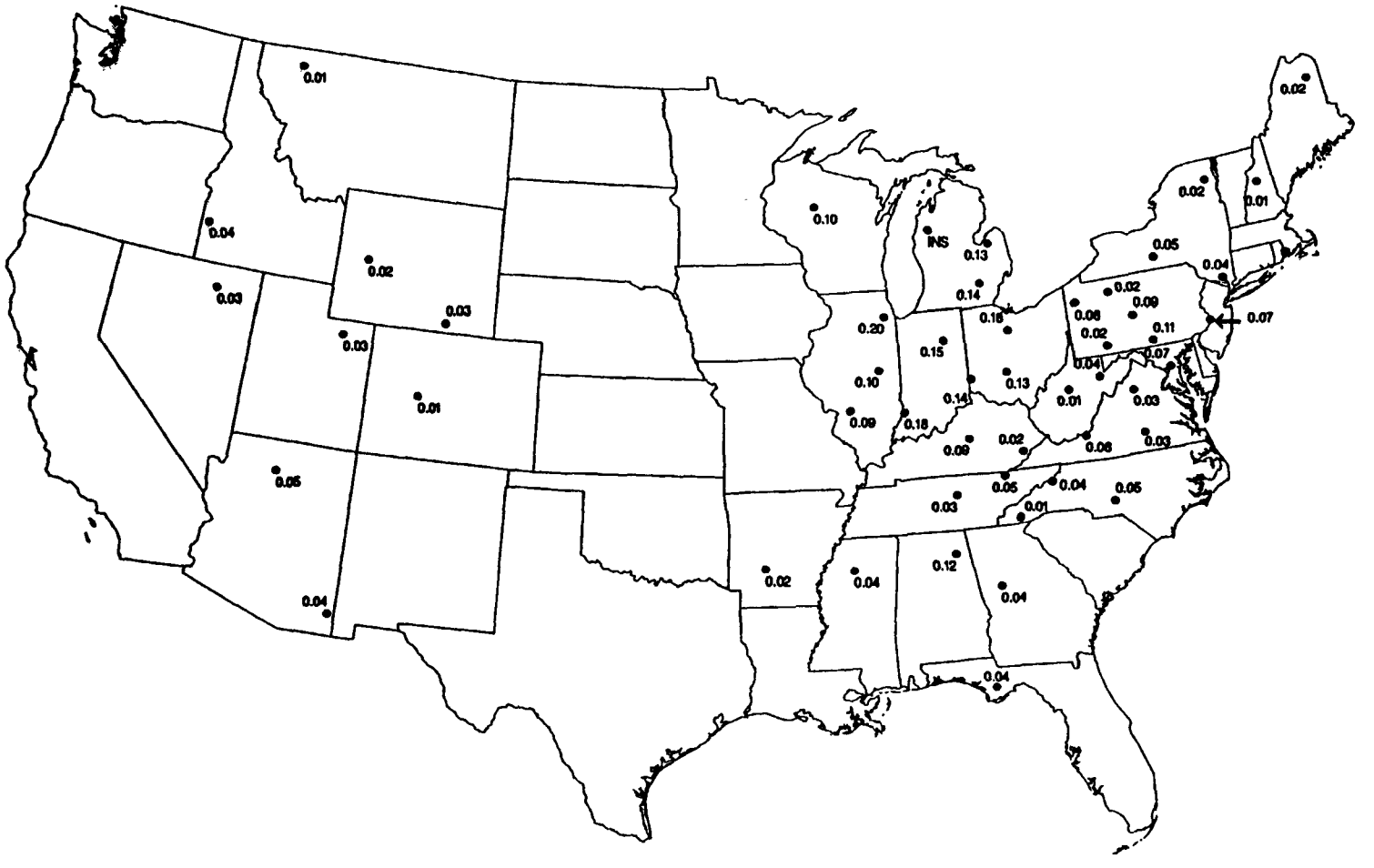


Figure 45. Calculated dry deposition of NO_3^- (kg-N/ha) for 1991.

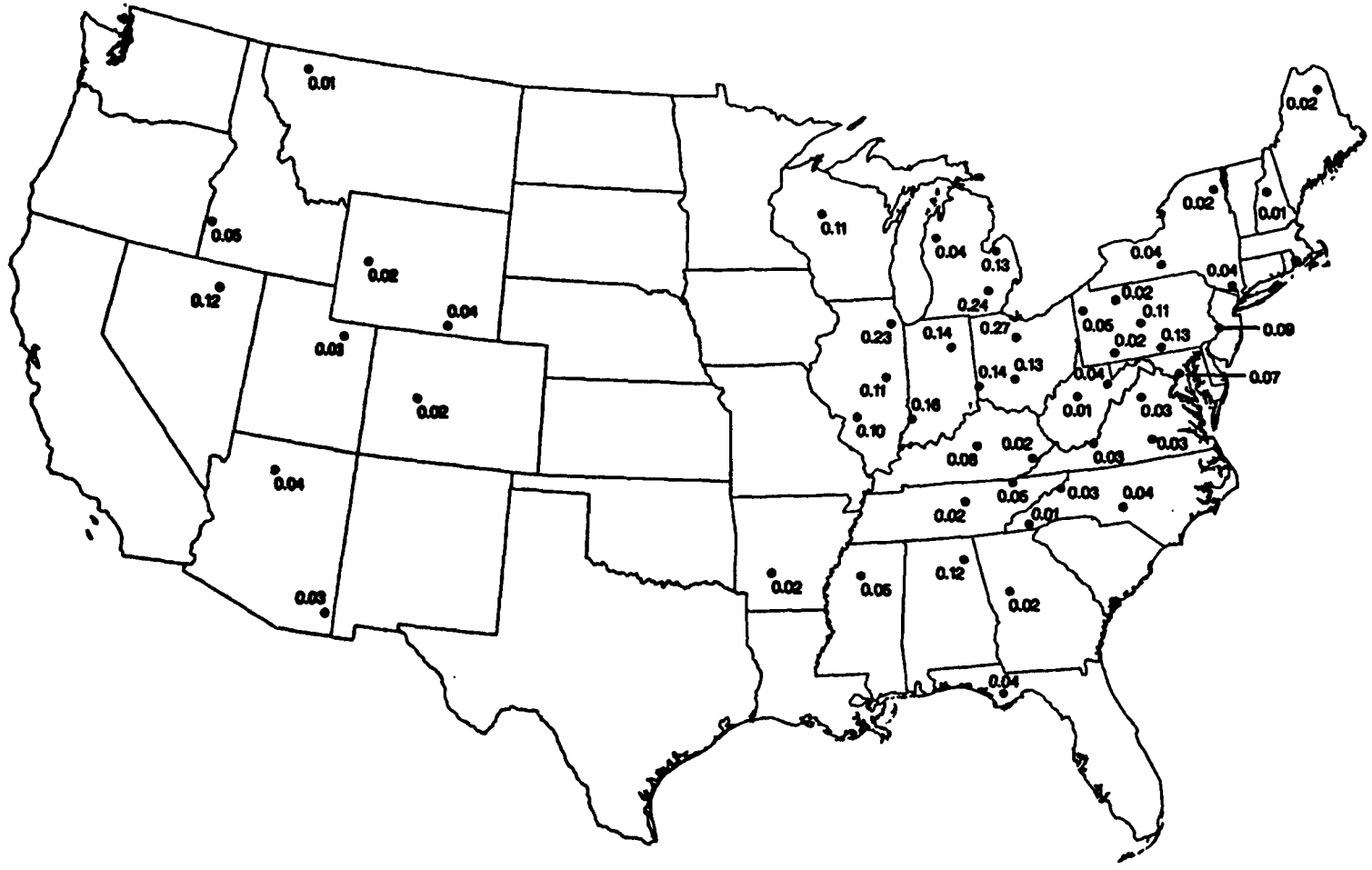


Figure 46. Calculated dry deposition of NO_3^- (kg-N/ha) for 1992.

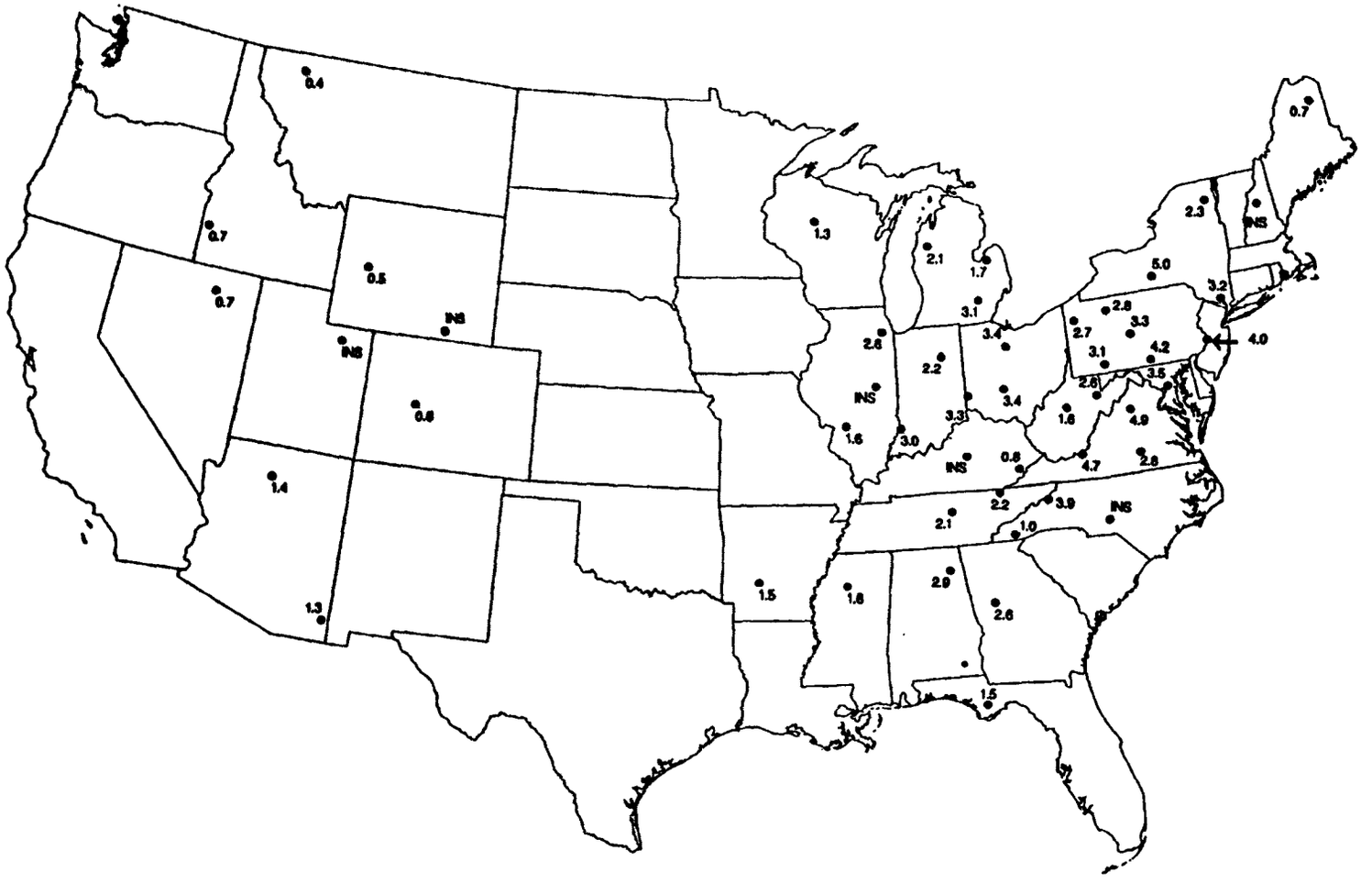


Figure 47. Calculated dry deposition of total NO_3^- (kg-N/ha) for 1990.

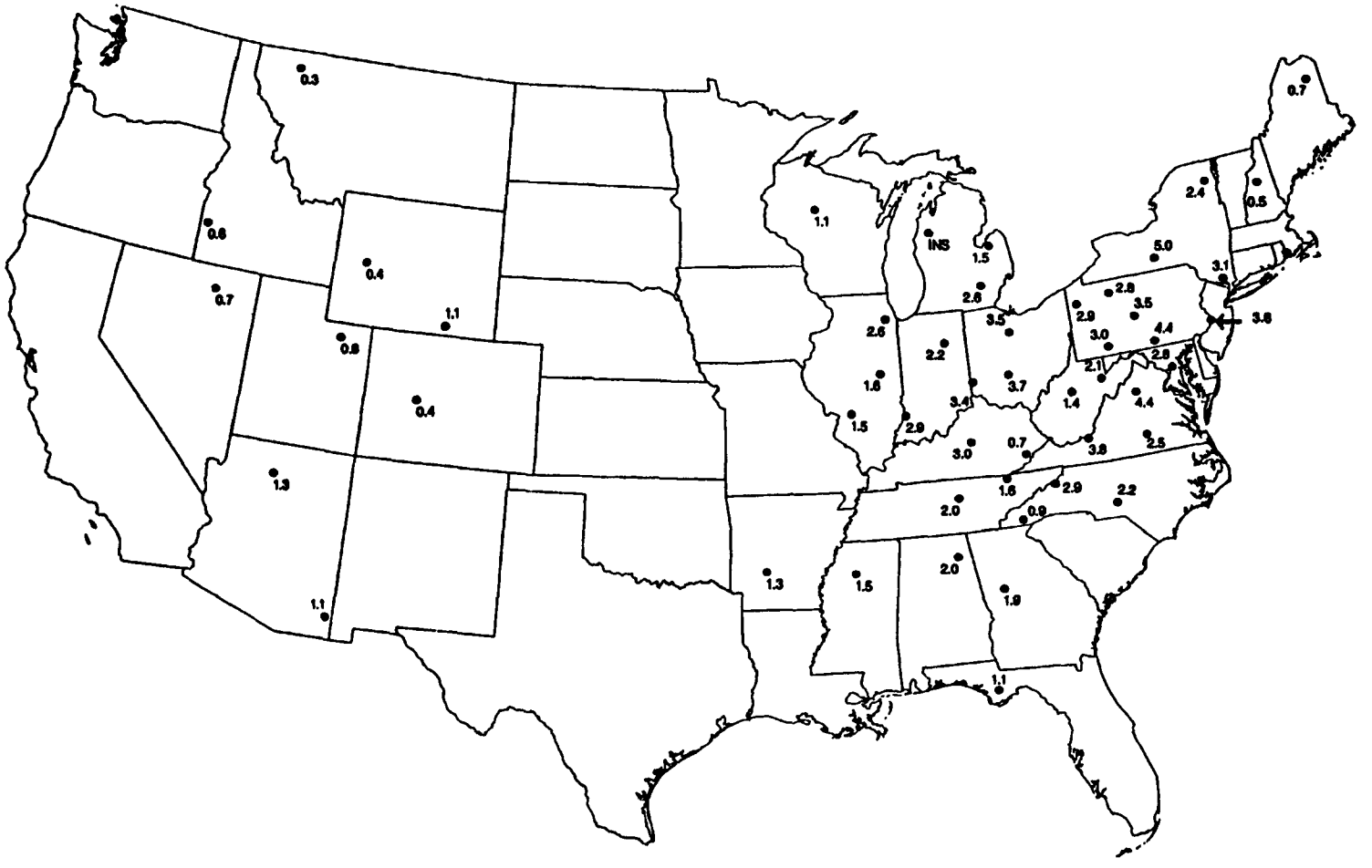


Figure 48. Calculated dry deposition of total NO_3^- (kg-N/ha) for 1991.

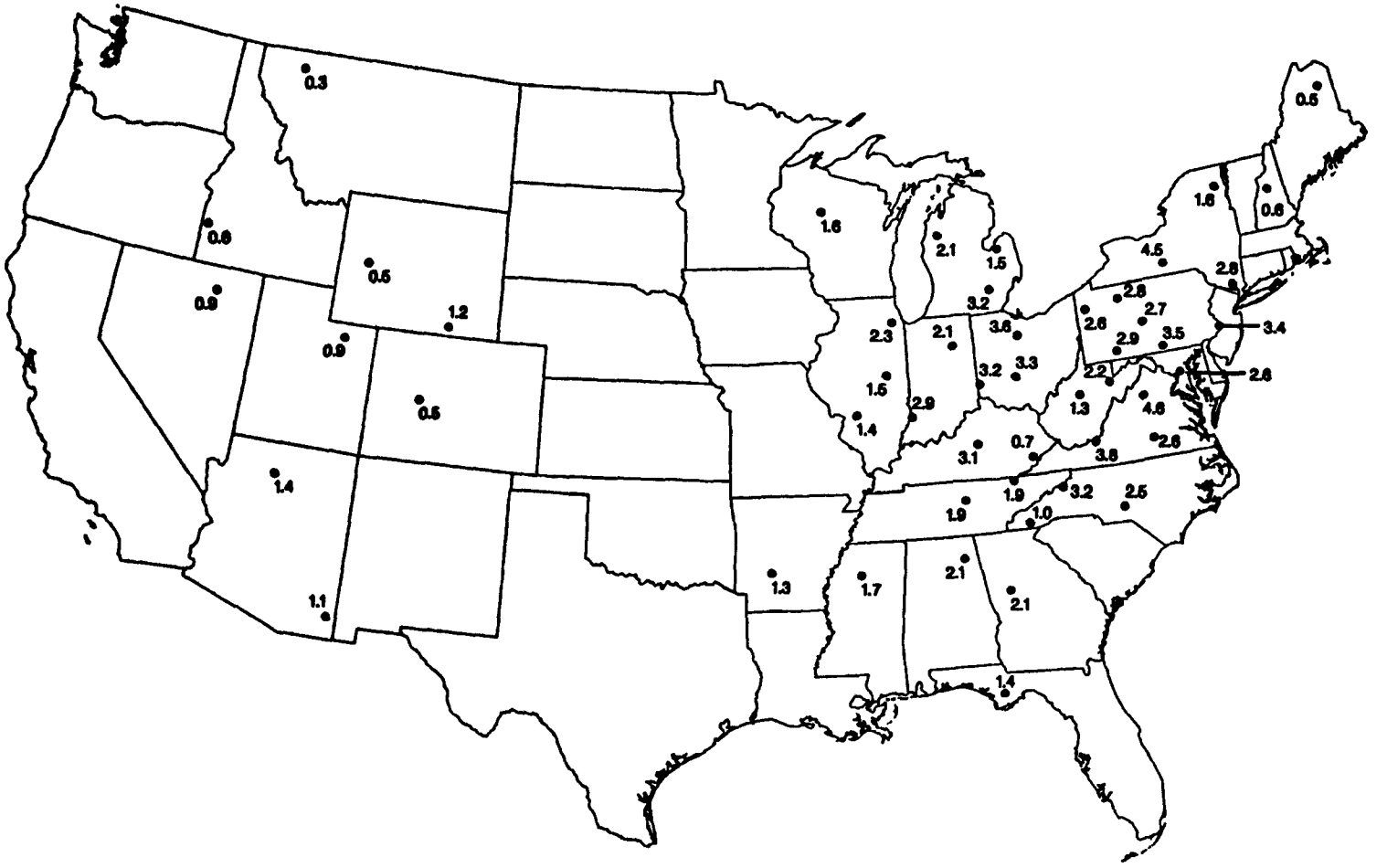


Figure 49. Calculated dry deposition of total NO_3^- (kg-N/ha) for 1992.

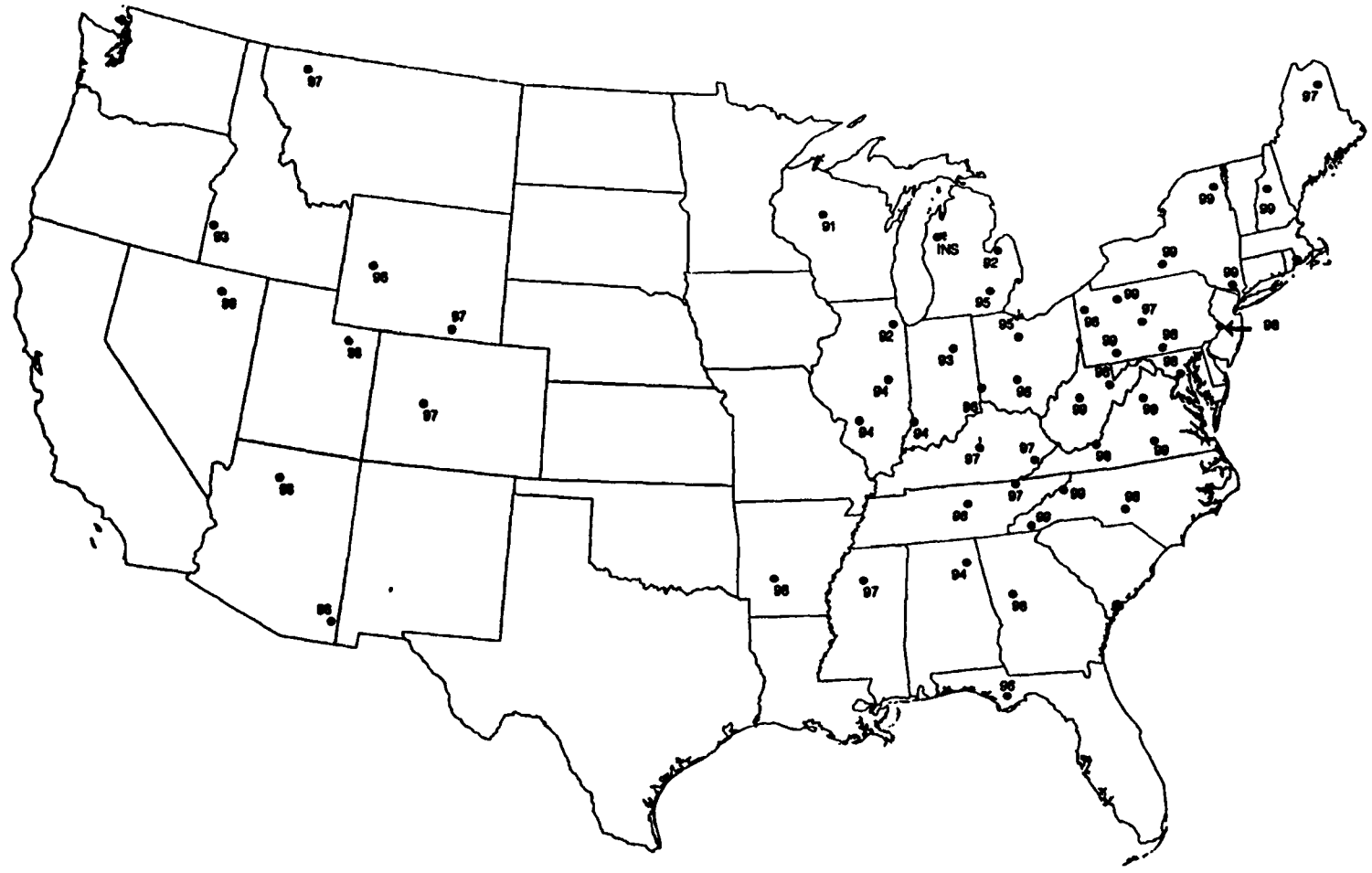


Figure 50. Percent gaseous NO_3^- deposition for 1991.

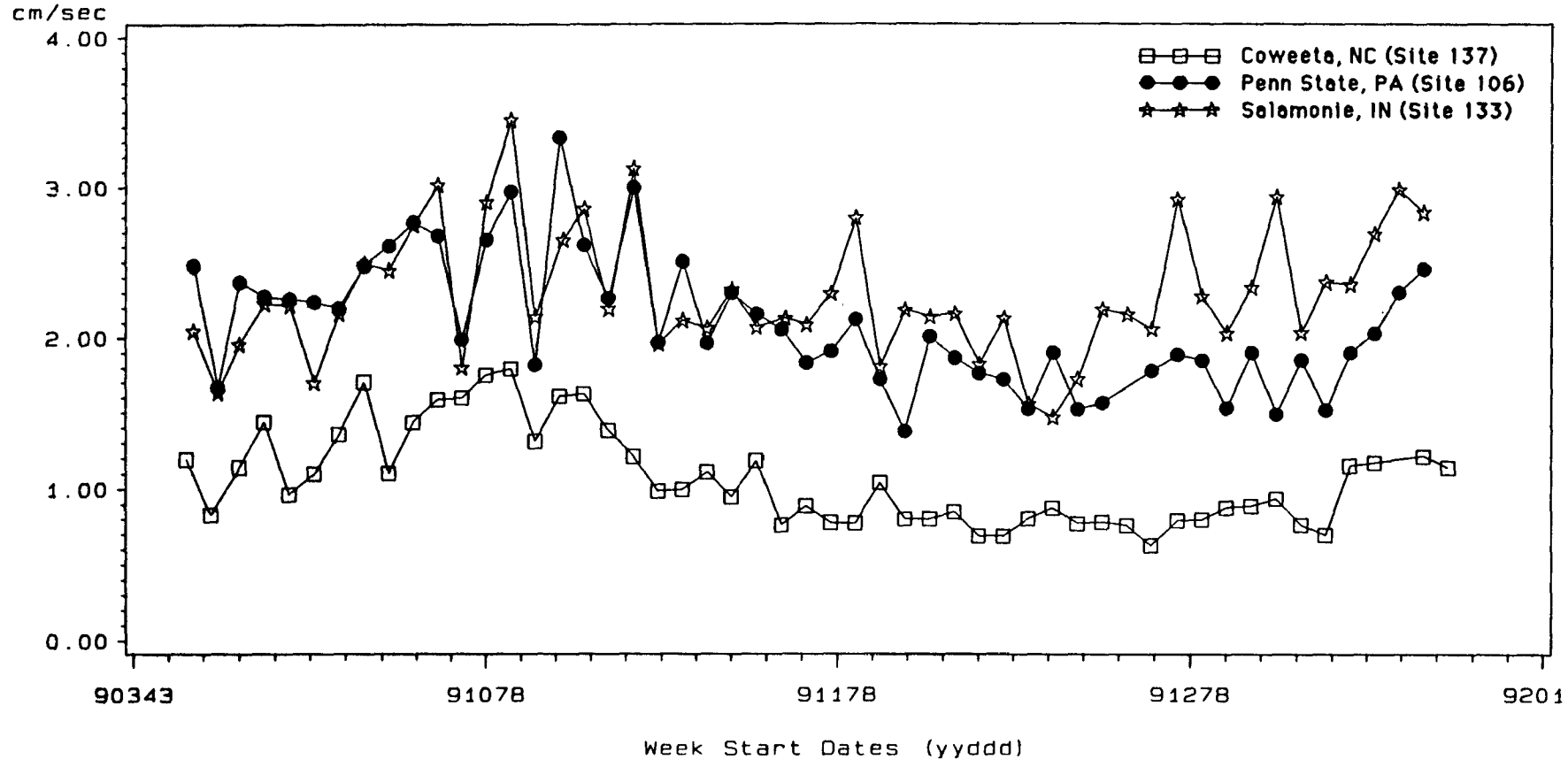


Figure 51. Weekly deposition velocities for HNO_3 (cm/sec) for selected sites.

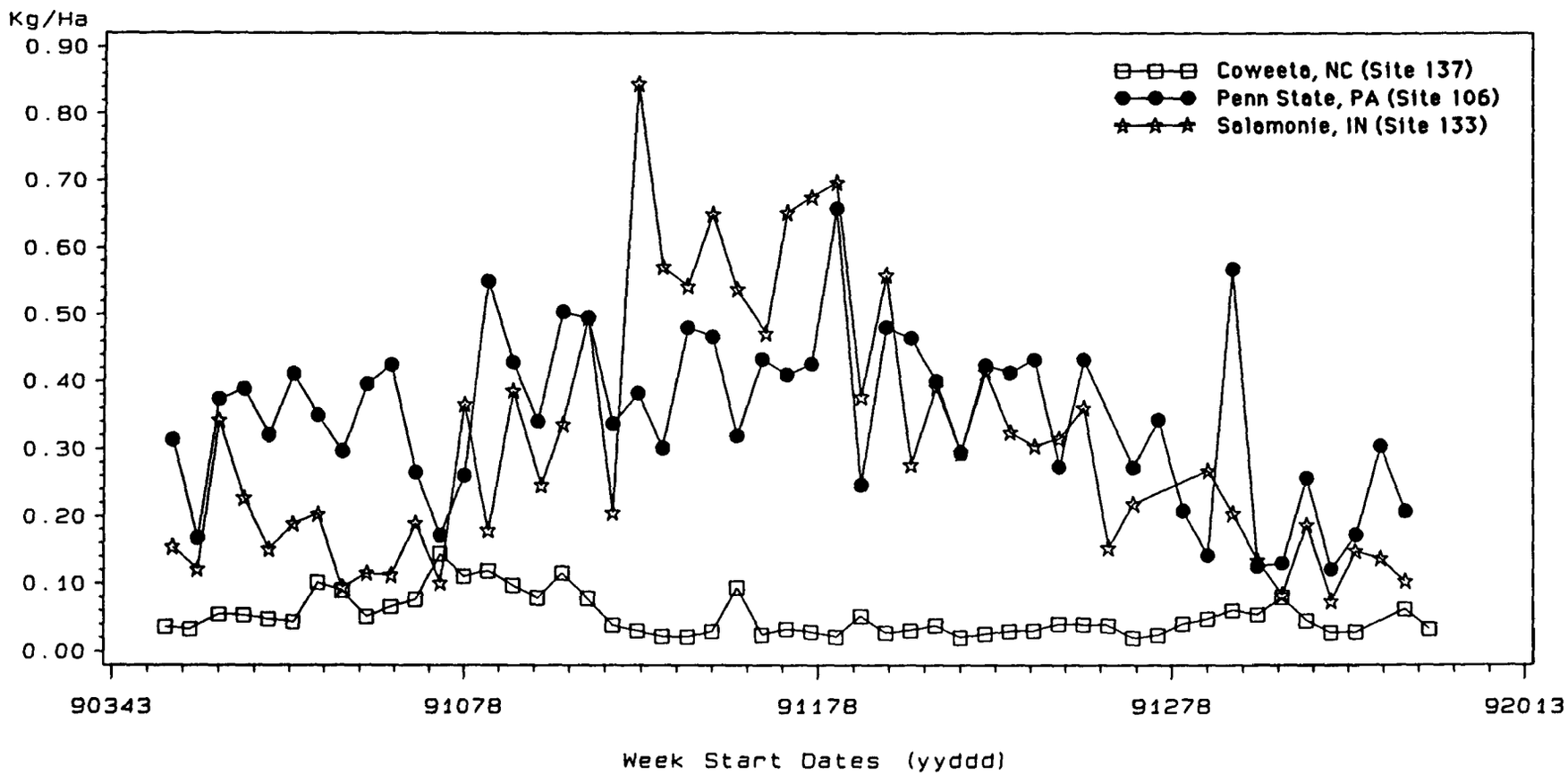
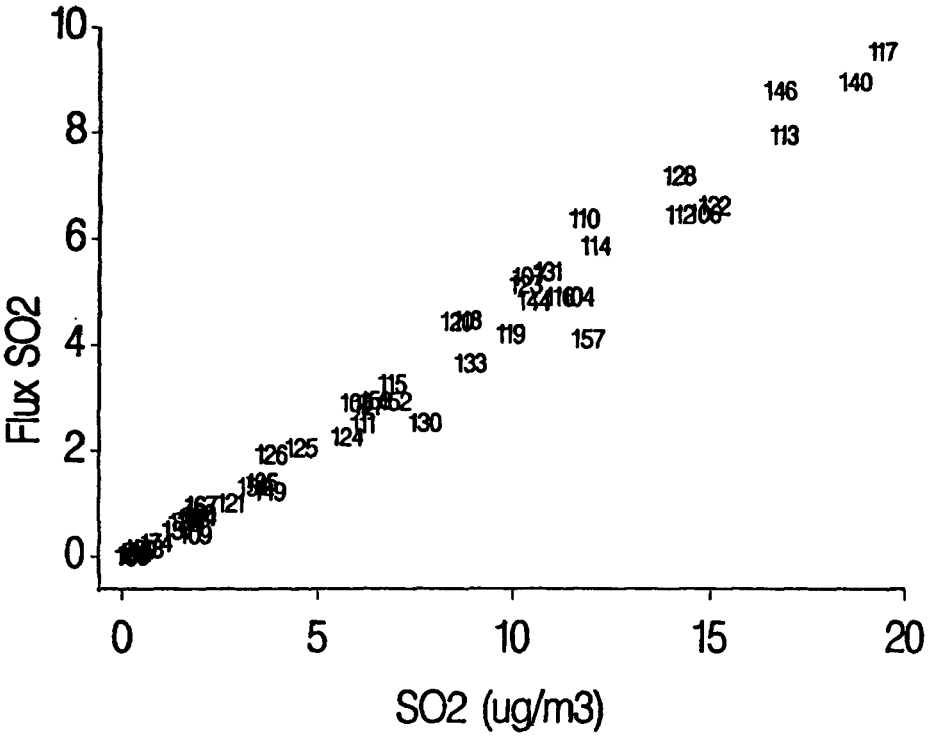


Figure 52. Weekly HNO_3 fluxes for selected sites.



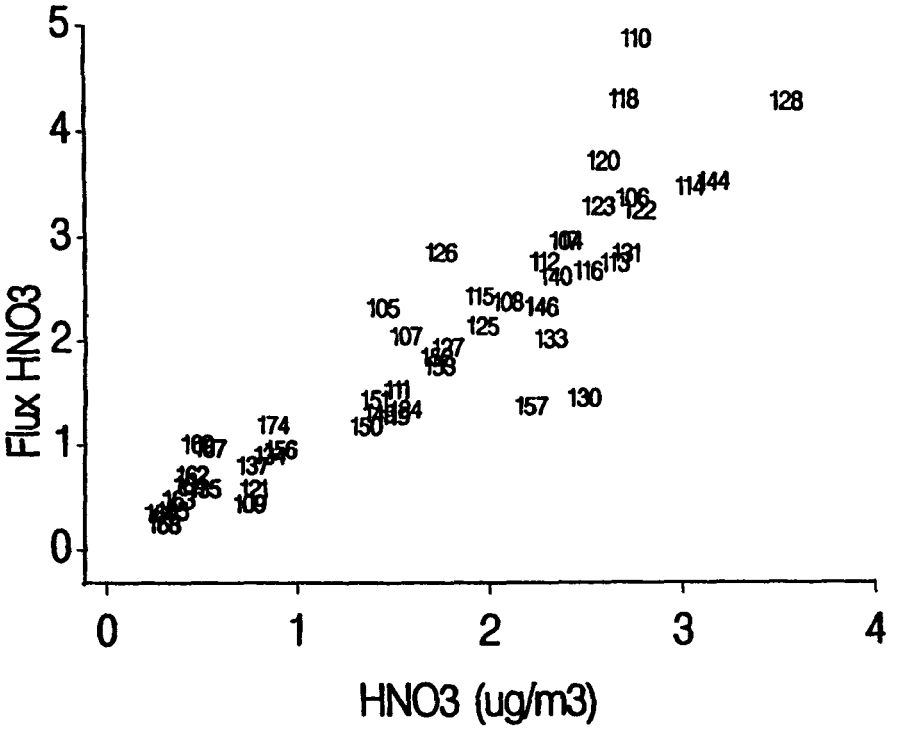


Figure 53. Scattergrams of SO_2 flux (kg-S/ha) versus concentration and HNO_3 flux (kg-N/ha) versus concentration for 1991.

40 percent, depending on the chemical species. Dry deposition fluxes for SO_2 are likely to be more accurate than those for HNO_3 and particulates which are strongly dependent on atmospheric turbulence. As terrain and vegetation complexity increases, uncertainty also increases, and fluxes, especially those for HNO_3 and particulates, are likely to be undercalculated.

Inferential model flux calculations for the NDDN were generally biased low due to the weekly integrated sampling protocol, especially for SO_2 and HNO_3 during the summer season. The bias appeared to be site specific and caused by a correlation between V_d and concentration on hourly and diurnal time scales. Sulfur dioxide concentrations from the network may be biased low (10 to 15 percent), which will also contribute to an undercalculation of flux for that species. Duplicate NDDN sites showed good precision. Deposition fluxes from duplicate sets of NDDN equipment (i.e., located side by side) were typically within 5 to 10 percent for the major species.

4.2 Wet Deposition

The primary objective of the NDDN is the calculation of dry deposition rates for various sulfur and nitrogen species. This will permit (1) examination of patterns and trends of dry deposition over space and time, (2) comparison with wet deposition rates, (3) calculation of total deposition rates, and (4) estimation of mass budgets for various regions and subregions of the United States and North America. This section presents wet deposition observations for SO_4^{2-} and NO_3^- for 16 NDDN sites in the eastern and western United States. Ultimately, these data should be combined with other networks (e.g., NADP/NTN and CAPMoN) to develop continental-scale patterns of wet deposition and total deposition.

Annual wet deposition of SO_4^{2-} and NO_3^- for the eastern NDDN sites is illustrated in Figures 54 through 59. Data are expressed in units of kg-S/ha or kg-N/ha to permit straightforward comparison between wet and dry deposition. Although a convenient bookkeeping approach, these units may or may not be appropriate for determining ecological effects of deposited species.

Wet deposition of SO_4^{2-} at NDDN sites varied by more than an order of magnitude during all 3 years. The highest deposition (>10 kg-S/ha) occurred in Ohio and West Virginia, and the lowest (about 1.0 kg-S/ha) occurred in northern Utah and central Colorado. Average depositions across the upper midwest, upper northeast, south central, and southern periphery subregions are approximately one-half to two-thirds of peak values. The overall deposition pattern is strongly reminiscent of atmospheric SO_4^{2-} concentrations.

Wet NO_3^- deposition for 1990 to 1992 ranged from about 4 kg-N/ha in central Ohio and West Virginia to less than 1 kg-N/ha for the three western sites. Although deposition amounts for NO_3^- are

Figure 54. Wet deposition of SO_4^{2-} (kg-S/ha) for 1990.

Figure 55. Wet deposition of SO_4^{2-} (kg-S/ha) for 1991.

Figure 56. Wet deposition of SO_4^{2-} (kg-S/ha) for 1992.

Figure 57. Wet deposition of NO_3^- (kg-N/ha) for 1990.

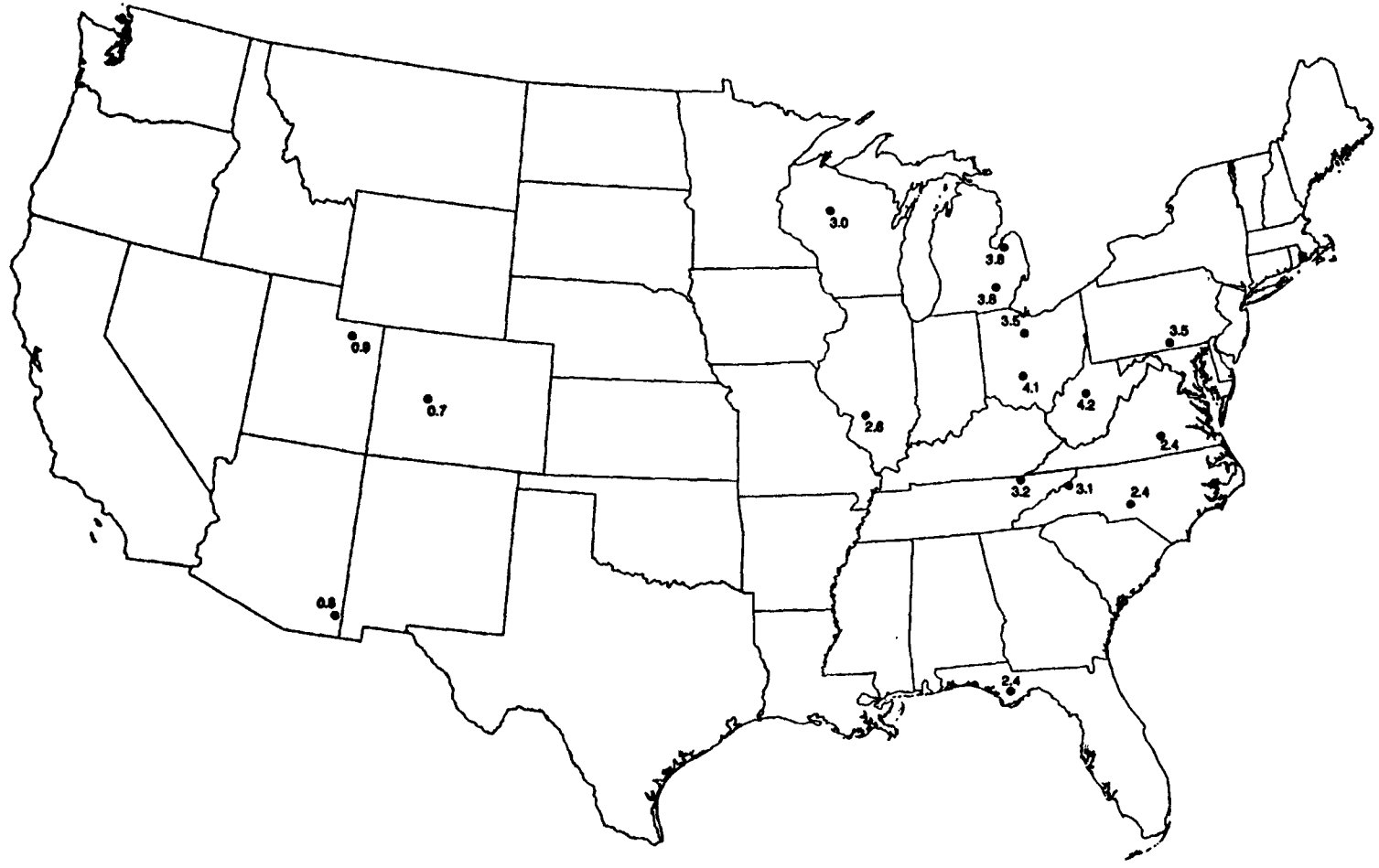


Figure 58. Wet deposition of NO_3^- (kg-N/ha) for 1991.

Figure 59. Wet deposition of NO_3^- (kg-N/ha) for 1992.

only about half those for SO_4^{2-}, they exhibit similar spatial distributions. Deposition amounts in excess of 3 kg-N/ha cover a large area from northern Wisconsin to southwestern North Carolina. Inclusion of all wet deposition sites in the eastern United States (and Canada) could modify deposition patterns somewhat. By the same token, overall deposition patterns may differ from year to year, due to precipitation variability and other factors.

4.3 Total Deposition

This section provides estimates of wet plus dry deposition (i.e., total deposition) and the percentage as dry deposition at NDDN sites which collect both wet and dry deposition data. Total sulfur deposition is defined as the sum of wet SO_4^{2-} deposition plus dry SO_2 and SO_4^{2-} deposition, expressed in units of kg-S/ha. Total nitrate-nitrogen deposition is defined as wet NO_3^- deposition plus dry HNO_3 and NO_3^- deposition, expressed as units of kg-N/ha. As discussed earlier, estimates of dry deposition are uncertain by about ±30 to 50 percent and biased low by 5 to 20 percent, depending on chemical species and site characteristics (Clarke and Edgerton, 1992). These uncertainties propagate directly into total deposition estimates. The uncertainty of wet deposition data is probably on the order of 10 to 20 percent (James, 1993). It is also worth noting that total deposition, as defined above, does not include other deposition processes, such as cloud and fog deposition. These processes are not likely to be important at existing NDDN sites but could be significant at high elevations and in areas of frequent or persistent fog. Caution is therefore advised in extrapolating total deposition data to locations not represented by the NDDN.

Estimates of total sulfur deposition and total nitrate-nitrogen deposition for 1990, 1991, and 1992 are shown in Tables 8 through 10 for 16 NDDN sites. Results show that total deposition of sulfur ranges from about 1 kg-S/ha in central Colorado (Site 161) to 20 kg-S/ha in central Ohio (Site 114). Both eastern and western regions exhibit substantial ranges in depositions which is largely due to variability in SO_2 concentrations (see Section 4.1.4). The contribution of dry sulfur deposition to total sulfur deposition ranges from less than 25 percent for sites in Wisconsin (134), northern Florida (156), and central Colorado (161) to more than 40 percent for sites in Virginia (108), Ohio (114), and Pennsylvania (128).

Among eastern sites, it appears that the percentage of dry sulfur deposition decreases from the center of the region to the periphery (e.g., Florida and Wisconsin).

Estimates of total nitrate-nitrogen deposition range from about 1 kg-N/ha in central Colorado (Site 161) to about 8 kg-N/ha in northern Ohio (Site 123) and eastern Pennsylvania (Site 128) and are fairly consistent from 1990 to 1991. As a rule, differences between eastern and western sites are not as

Table 8. Total Sulfur and Nitrate-Nitrogen Deposition for NDDN Sites Measuring Wet and Dry Deposition for 1990

Site	Total Sulfur (S)		Nitrate-Nitrogen (N)	
	kg/ha	%Dry	kg/ha	%Dry
108	8.3	46	4.6	60
111	13.5	29	5.2	43
114	19.7	42	7.7	45
115	11.4	37	6.6	46
119	17.3	31	6.1	27
123	17.6	36	8.0	43
124	9.1	33	4.5	38
125	INS	INS	INS	INS
126	11.9	29	6.9	56
128	17.2	44	8.5	50
134	6.9	21	4.3	31
156	5.4	24	3.0	48
157	12.5	39	4.6	35
161	1.4	20	1.4	41
162	INS	INS	INS	INS
167	3.5	43	2.3	55

Note: INS = insufficient data.
Total sulfur deposition = wet SO_4^{2-}-S + dry SO_4^{2-}-S + dry SO_2-S.
Nitrate-nitrogen deposition = wet NO_3^--N + dry NO_3^--N + dry HNO_3-N.

Source: ESE.

Table 9. Total Sulfur and Nitrate-Nitrogen Deposition for NDDN Sites Measuring Wet and Dry Deposition for 1991

Site	Total Sulfur (S)		Nitrate-Nitrogen (N)	
	kg/ha	%Dry	kg/ha	%Dry
108	9.5	39	4.9	50
111	13.0	25	4.9	34
114	15.8	43	7.8	47
115	11.3	35	6.4	41
119	15.3	31	5.6	24
123	13.0	46	7.0	51
124	10.0	28	5.4	28
125	7.9	35	4.7	48
126	11.5	25	6.1	49
128	16.1	51	8.0	56
134	6.4	18	4.1	26
156	6.8	19	3.5	30
157	11.8	40	4.1	38
161	1.0	21	1.1	39
162	1.3	25	1.7	48
167	3.1	43	1.9	57

Note: Total sulfur deposition = wet SO_4^{2-}-S + dry SO_4^{2-}-S + dry SO_2-S.
Nitrate-nitrogen deposition = wet NO_3^--N + dry NO_3^--N + dry HNO_3-N.

Source: ESE.

Table 10. Total Sulfur and Nitrate-Nitrogen Deposition for NDDN Sites Measuring Wet and Dry Deposition for 1992

Site	Total Sulfur (S)		Nitrate-Nitrogen (N)	
	kg/ha	%Dry	kg/ha	%Dry
108	9.2	41	4.7	55
110	15.7	40	8.7	51
111	9.7	35	4.0	47
114	14.3	41	6.7	48
115	10.7	34	6.7	48
119	15.3	31	5.4	24
123	16.0	37	7.5	48
124	9.6	26	5.0	30
125	8.7	34	4.8	52
126	12.8	23	6.3	51
128	15.5	44	7.2	48
134	6.2	22	3.9	40
156	7.3	25	3.3	43
157	11.1	39	3.5	41
161	1.0	23	1.0	49
162	1.2	27	1.6	57
167	2.8	40	1.8	60

Note: Total sulfur deposition = wet SO_4^{2-}-S + dry SO_4^{2-}-S + dry SO_2-S.
Nitrate-nitrogen deposition = wet NO_3^--N + dry NO_3^--N + dry HNO_3-N.

Source: ESE.

great as for sulfur deposition. Dry deposition of nitrate-nitrogen ranges from approximately 30 percent, or less, of total deposition in central West Virginia (Site 119) to 50 percent, or more, in central Virginia (Site 108), eastern Pennsylvania (Site 128), and southern Arizona (Site 167). As discussed earlier, much of the variability in nitrate-nitrogen deposition appears to be due to the effects of complex terrain in and around the Appalachian Mountains. Terrain effects are discussed further in Chapter 5.

Comparison of results for sulfur and nitrate-nitrogen show that dry deposition generally contributes a greater percentage of the latter. This may be explained, in part, by substantially higher (factor of 4) V_d for HNO_3 than for SO_2. Another reason for this could involve network design and site selection. The network is designed to provide regionally representative deposition data, and, therefore, sites are selected which are outside the immediate influence of pollution sources, including sources of SO_2. The total sulfur deposition and the percentage dry deposition are likely to decrease with increasing distance from sources of SO_2. As a secondary pollutant, HNO_3 is much less sensitive to proximity of precursors than SO_2.

4.4 Ozone

As described in Section 3.0, continuous O_3 concentrations were monitored throughout the period at a height of 10 m at all NDDN sites. Annual averages, valid observations, and peak observed concentrations for 1990, 1991, and 1992 are summarized in Tables 11 through 13. Annual averages among eastern sites ranged from about 25 to 50 ppb for all three years. The highest annual averages (i.e., 45 to 50 ppb) occur at mountaintop sites along the Blue Ridge and Appalachian Mountains, while the lowest annual averages (i.e., 20 to 25 ppb) occur in sites located in sharp valleys (e.g., Sites 119 and 121) and in semiurban areas (e.g., Sites 116 and 146). Hourly average concentrations equal to or greater than the NAAQS were relatively rare for all years. In 1990, eight sites exhibited one or more hourly values $\geq$120 ppb, and only 15 days of exceedances occurred at the 48 sites operational throughout the year. During 1991 and 1992, 9 sites and 5 sites recorded O_3 values $\geq$120 ppb, respectively, and there were a total of 14 days and 7 days with exceedances, respectively.

For the 3-year period, as a whole, average O_3 concentrations fell by approximately 3 ppb over the eastern United States. Reductions were not consistent from site to site or year to year. Southeastern sites exhibited about a 2-ppb change from 1990 to 1991 and again for 1991 to 1992. Northeastern sites exhibited a 2-ppb increase from 1990 to 1991 and then a 7-ppb decrease from 1991 to 1992. This year-to-year variability is similar to that reported earlier for SO_4^{2-}, SO_2, and HNO_3; however, insufficient data are available to determine whether the similarity is simply fortuitous or the result of linkage between chemical and meteorological processes.

Table 11. Summary of NDDN Ozone Maxima for 1990

Site No.	Valid (n)	Percent valid	Annual Average (ppb)	Highest Value (ppb)	Highest Date	Highest Hour	Second Highest Value (ppb)	Second Highest Date	Second Highest Hour	Third Highest Value (ppb)	Third Highest Date	Third Highest Hour
104	8440	96	27.3	150	06/17	16	113	07/04	16	108	04/28	15
105	8508	97	36.5	115	07/04	16	102	07/03	22	102	07/17	24
106	8625	98	32.9	120	07/20	16	113	07/18	16	107	07/17	17
107	8640	99	30.2	123	07/04	18	102	07/19	16	94	06/14	14
108	8251	94	33.9	107	07/26	20	103	08/04	15	102	08/08	17
109	8582	98	29.8	86	06/15	20	83	05/09	18	83	06/02	15
110	8349	95	36.5	93	04/28	20	91	06/14	11	89	08/18	12
111	8275	94	30.5	117	09/07	17	108	06/26	17	106	08/12	17
112	7637	87	35.3	101	07/04	20	100	06/13	18	99	08/04	16
113	8086	92	30.7	105	07/04	20	103	08/17	15	101	06/13	15
114	8577	98	32.8	115	08/28	15	112	07/04	15	111	06/13	14
115	8666	99	31.0	111-	06/16	17	108	07/04	21	106	07/28	18
116	8171	93	24.8	137	06/28	17	136	07/19	16	121	07/09	15
117	8612	98	28.8	109	07/04	18	98	06/14	15	97	06/13	17
118	8011	91	45.7	103	08/26	18	97	07/04	19	97	07/05	13
119	8588	98	25.1	116	07/04	14	108	08/28	16	107	06/29	16
120	8585	98	45.1	97	06/28	16	96	04/27	20	92	09/03	02
121	8552	98	22.1	85	11/03	14	84	04/27	11	84	05/08	12
122	8664	99	32.1	116	07/08	20	110	06/16	17	108	06/28	18
123	8000	91	32.6	103	07/08	22	97	06/13	20	94	07/17	16
124	8643	99	34.3	105	07/28	17	100	06/13	17	100	09/13	17
125	2049	93	30.0	85	10/03	17	73	11/02	13	70	11/16	16
126	8337	95	47.6	110	09/07	17	108	06/29	18	102	07/09	23
127	8617	98	37.5	109	08/18	16	99	08/19	15	93	08/29	14
128	8653	99	35.6	124	06/14	19	113	08/17	16	107	08/04	19
129/131	7845	90	37.8	108	08/03	17	107	08/04	03	103	09/02	17
130	8217	94	30.8	106	06/16	13	104	08/26	12	102	07/27	13
133	8491	97	32.9	110	06/13	19	104	06/28	18	104	07/29	14
134	8523	97	32.3	74	05/31	20	73	07/03	15	70	05/25	16
135	8684	99	30.5	88	06/02	12	80	07/19	04	78	06/03	15
137	8548	98	30.0	85	05/15	18	85	07/06	15	84	06/29	14
140	8650	99	30.5	110	08/27	16	109	07/28	16	108	06/27	16
144	8354	95	28.9	148	08/17	17	144	07/18	16	128	08/18	16
146	8560	98	24.2	97	09/05	14	96	08/11	16	90	07/27	15
149	8609	98	32.3	98	07/03	20	96	05/08	17	96	07/17	18
150	8646	99	27.4	94	06/20	13	90	08/31	17	90	09/06	12
151	8488	97	39.0	100	09/07	14	87	09/06	14	87	09/18	14
152	8628	98	39.7	117	06/20	15	116	07/08	13	116	07/26	17
153	8319	95	40.5	144	08/17	17	127	08/03	16	122	07/02	19
156	7630	87	32.3	93	07/27	17	84	04/05	17	81	09/07	17
157	8516	97	32.5	148	08/28	13	126	09/06	16	116	09/05	18
161	8138	93	44.3	88	05/18	16	84	08/30	09	80	05/21	10
162	8600	98	45.0	74	02/23	17	74	05/18	09	73	06/29	17
163	8225	94	39.0	80	08/09	19	68	01/08	20	68	06/26	18
164	7261	83	42.5	78	08/01	06	77	09/13	14	76	06/07	23
165	8621	98	42.7	74	06/23	18	72	06/18	20	70	07/25	19
167	8342	95	41.3	138	05/09	05	85	07/11	16	80	06/27	16
168	8549	98	25.4	66	05/06	13	60	03/27	17	58	03/30	16
169	8433	96	46.4	78	04/22	16	77	06/24	01	76	07/29	10
174	8645	99	47.1	92	07/23	07	82	07/13	15	80	06/05	10

Source: ESE.

Table 12. Summary of NDDN Ozone Maxima for 1991

Site No.	Valid (n)	Percent valid	Annual Average (ppb)	Highest Value (ppb)	Highest Date	Highest Hour	Second Highest Value (ppb)	Second Highest Date	Second Highest Hour	Third Highest Value (ppb)	Third Highest Date	Third Highest Hour
104	8638	99	29.3	149	07/19	16	114	06/15	16	113	07/17	18
105	8605	98	37.0	122	06/27	01	111	06/10	20	109	07/19	23
106	8518	97	33.4	117	07/18	15	116	07/17	17	110	07/19	12
107	8663	99	30.4	99	08/03	13	98	06/09	18	95	06/27	18
108	8244	94	33.2	108	06/15	17	103	08/17	15	99	09/16	16
109	8632	99	30.7	98	05/24	16	88	06/26	15	86	06/27	14
110	8685	99	39.5	109	06/28	03	105	06/27	15	99	07/17	11
111	8550	98	28.6	108	08/03	14	100	08/17	16	96	07/23	14
112	8624	98	37.6	112	06/27	16	108	05/16	19	105	06/28	02
113	8524	97	34.0	116	07/18	12	115	07/17	14	113	06/27	16
114	8399	96	32.4	107	06/10	16	106	06/21	15	104	08/07	16
115	8297	95	31.5	101	05/16	17	101	05/20	18	101	06/25	15
116	8288	95	26.6	156	07/20	16	137	07/19	16	132	06/21	14
117	8483	97	31.0	118	08/30	17	110	06/10	16	106	07/18	14
118	8345	95	46.0	114	06/21	21	100	05/16	20	98	06/10	13
119	8614	98	26.0	111	07/22	14	111	08/08	15	106	06/10	12
120	8563	98	44.0	108	10/30	20	99	05/16	01	97	05/15	24
121	8595	98	21.7	96	08/03	14	90	05/15	14	88	10/31	16
122	8636	99	32.9	113	06/21	15	113	07/18	17	112	07/20	20
123	8532	97	34.2	120	06/14	15	115	06/03	19	113	05/15	19
124	8314	95	33.7	111	06/14	19	103	05/22	18	101	05/21	17
125	8599	98	35.6	118	10/31	16	102	07/22	17	86	08/08	16
126	8576	98	44.9	95	04/18	20	92	03/21	14	90	11/01	11
127	8503	97	35.6	98	06/03	15	93	09/14	16	89	08/04	14
128	8604	98	38.3	122	07/19	17	121	06/28	15	117	06/21	17
130	7916	90	31.0	145	06/14	13	116	07/01	23	116	07/02	02
131	8319	95	36.4	109	08/03	15	100	08/01	14	95	08/02	13
133	8627	98	33.3	107	06/20	17	106	08/16	16	99	07/18	18
134	8594	98	33.4	79	05/10	19	79	08/27	16	74	05/14	18
135	8602	98	31.6	99	08/17	23	90	08/18	01	88	06/11	03
137	8569	98	26.5	86	04/18	17	86	05/03	18	82	03/26	17
140	8664	99	30.0	112	06/19	16	111	08/24	17	104	06/09	17
144	8634	99	30.5	143	07/19	15	141	05/23	16	135	08/08	18
146	8338	95	24.5	132	06/01	16	118	06/20	18	117	06/18	17
149	8545	98	33.6	106	07/20	14	105	05/15	19	105	07/19	21
150	8641	99	24.7	87	08/01	15	86	06/18	15	85	08/24	17
151	8226	94	35.7	110	07/27	15	101	08/12	18	88	08/14	15
152	8301	95	33.6	99	07/15	16	95	06/05	17	92	09/15	14
153	8643	99	34.7	123	09/13	17	118	08/05	18	115	06/29	16
156	7837	89	30.4	90	05/09	12	85	08/21	14	83	10/12	15
157	8606	98	30.6	117	08/03	13	112	08/16	14	110	09/12	17
161	8317	95	45.3	86	05/15	18	83	05/02	19	78	05/13	11
162	8390	96	46.2	88	05/18	18	82	05/15	10	78	06/11	18
163	8386	96	38.1	73	06/06	07	73	08/22	18	67	05/23	19
164	7852	90	43.1	91	07/19	17	88	08/05	06	86	08/04	23
165	7768	89	47.0	76	05/09	24	74	05/19	10	74	05/20	14
167	7878	90	41.9	83	05/23	20	82	05/24	09	79	05/04	17
168	8642	99	23.9	62	05/23	13	61	05/20	15	61	06/03	19
169	7605	87	48.0	81	05/20	14	79	06/14	15	78	07/14	19
174	8566	98	45.9	81	05/18	16	79	05/10	14	79	09/07	14

Source: ESE.

Table 13. Summary of NDDN Ozone Maxima for 1992

Site No.	Valid (n)	Percent valid	Annual Average (ppb)	Highest Value (ppb)	Highest Date	Highest Hour	Second Highest Value (ppb)	Second Highest Date	Second Highest Hour	Third Highest Value (ppb)	Third Highest Date	Third Highest Hour
104	8304	95	25.0	144	05/23	18	112	08/27	15	107	08/24	15
105	8595	98	34.1	115	05/23	03	111	05/22	22	109	06/13	24
106	8675	99	30.4	104	06/30	16	102	05/23	13	98	06/13	16
107	8405	96	27.4	89	05/23	14	81	05/13	14	79	07/30	13
108	8509	97	30.9	123	07/14	18	97	07/21	16	93	05/23	17
109	8536	97	29.7	100	05/23	10	94	06/14	13	89	05/30	16
110	8715	99	35.5	102	05/22	23	98	05/23	01	98	06/30	11
111	8543	97	26.7	96	05/12	14	90	05/11	18	90	06/23	16
112	8635	98	32.8	106	06/29	19	97	06/30	11	92	05/23	17
113	8538	97	28.5	110	06/30	20	101	06/29	18	101	07/01	14
114	8553	97	29.0	98	05/12	16	97	06/06	17	94	06/15	15
115	8383	95	27.9	126	05/21	17	116	06/30	18	110	07/01	17
116	8043	92	23.7	118	07/12	15	117	07/20	16	113	07/01	15
117	8658	99	26.6	96	05/23	16	93	05/22	17	92	05/13	15
118	8056	92	39.5	99	05/23	14	96	05/22	14	95	07/02	22
119	8604	98	22.6	91	05/23	15	90	07/29	16	85	06/15	14
120	8631	98	40.3	92	05/23	17	85	05/12	13	82	05/22	17
121	8503	97	19.4	100	05/12	13	87	05/11	12	85	05/10	16
122	8687	99	29.1	100	06/16	19	98	05/16	15	98	06/29	19
123	8666	99	31.5	104	05/22	17	103	06/12	18	99	05/11	19
124	8549	97	30.1	98	08/23	17	97	06/17	16	96	05/11	18
125	8602	98	35.8	102	07/09	16	102	07/13	16	101	05/23	15
126	8638	98	42.7	97	05/23	19	87	05/10	17	85	06/24	08
127	8655	99	30.7	99	05/09	17	88	05/10	15	88	06/19	20
128	8566	98	32.0	105	05/23	18	95	07/20	17	94	05/11	17
130	8503	97	26.3	98	06/30	13	90	06/29	13	89	05/09	14
131	8595	98	35.3	97	05/10	15	87	08/10	15	86	05/23	15
133	8695	99	29.9	103	06/30	17	100	06/16	17	95	06/12	17
134	8351	95	32.3	95	06/04	13	89	06/13	14	83	05/10	18
135	8642	98	31.5	93	05/23	16	89	05/21	24	87	05/22	01
137	8592	98	26.9	93	05/10	13	85	05/12	12	83	04/09	18
140	8614	98	27.3	103	06/29	18	99	05/16	15	96	06/30	16
144	8486	97	26.1	139	08/24	16	125	06/30	16	122	06/29	16
146	8631	98	21.5	131	06/13	16	99	06/29	14	99	07/01	13
149	8608	98	31.3	96	05/22	22	92	05/20	18	92	06/03	17
150	8604	98	24.2	88	04/09	14	88	10/05	15	84	05/09	13
151	8608	98	34.2	90	05/30	18	88	05/09	17	84	05/31	14
152	8365	95	32.5	101	05/11	16	97	05/15	18	97	06/29	14
153	8687	99	32.9	117	05/23	17	107	05/24	16	106	06/24	14
156	8480	97	30.8	88	03/27	20	84	06/22	18	82	03/01	18
157	8471	96	29.7	106	08/18	16	104	06/30	13	97	06/29	16
161	8250	94	43.5	73	04/30	14	72	05/11	16	71	04/29	16
162	8569	98	45.2	78	05/27	15	76	06/05	17	75	04/27	19
163	8425	96	37.8	73	05/05	20	72	05/16	18	71	07/04	18
164	7592	86	42.1	79	12/06	07	74	07/16	23	72	06/09	13
165	8360	95	46.0	72	04/30	10	72	05/06	13	70	08/21	17
167	8101	92	40.1	76	05/18	15	76	06/03	24	71	04/29	15
168	8498	97	20.9	77	05/17	16	76	05/22	16	69	04/11	16
169	8139	93	47.2	74	04/30	16	73	10/02	22	71	08/20	17
174	8144	93	46.0	81	04/28	04	79	06/28	08	78	06/26	11

Source: ESE.

Data for western sites showed average O_3 concentrations ranging from 25 ppb in northern Montana (Site 168) to 47 ppb in northern Arizona (Site 174). In general, while average concentrations exceeded those in the east, peak concentrations 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. Relatively high annual averages among western sites are consistent with similarly high averages for the eastern sites located on mountaintops.

Differences in diurnal O_3 cycles appear to offer partial explanation for the differences in concentrations between sites on mountaintops, in valleys, and near urban areas. Hour-by-hour average O_3 concentrations for 1990, for a rolling terrain site (108), a complex terrain site (119), a mountaintop site (120), a semiurban site (116), and two western sites (168 and 164) are plotted in Figure 60. Results are typical of all 3 years and show generally consistent differences between types of sites for the annual period. The rolling terrain site exhibits moderate day/night variability, with nocturnal minima typically on the order of 50 to 60 percent of the day maxima. Day maxima show a fairly broad plateau between the hours of 1400 through 1700. Hourly averages for the complex terrain site shows markedly different behavior. In this case, nocturnal minima are much less than half the daily maxima. In addition, periods of maximum concentration are appreciably shorter than at rolling terrain sites, and average maximum concentrations are slightly lower than at rolling terrain sites. The mountaintop site exhibits a unique diurnal pattern, or lack of one. For this, and other mountaintop 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. Results for the semiurban site show markedly depressed nocturnal values and slightly depressed daytime values, relative to rolling terrain sites.

One explanation for the observed behavior involves the relationship between sampler location and the nocturnal inversion layer. The mountaintop sites presumably sit above the nocturnal 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. The result of this day/night variability is a gradient in average concentrations from mountaintop to rolling terrain to complex terrain. 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 the 3-year period. Other measures of integrated O_3 exposure or concentration, however,

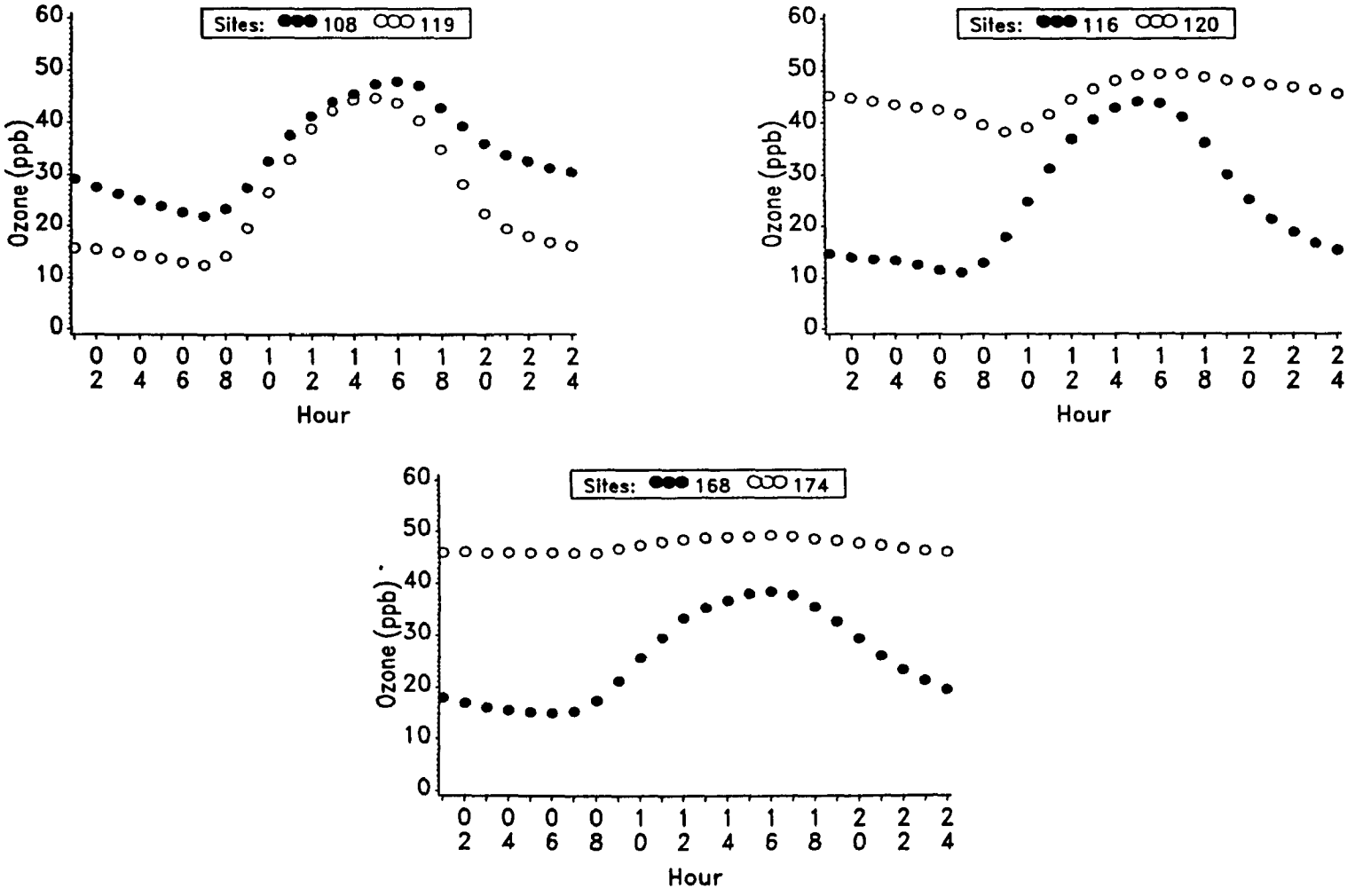


Figure 60. Hourly average O_3 concentrations for typical rolling terrain (Site 108), complex terrain (Site 119), mountaintop (Site 120), semi-urban (Site 116), and western (Sites 168 and 174) sites.

suggest marked differences from year to year. The sigmoidally weighted O_3 concentration (W126) is a statistic proposed by Lefohn and Runeckles (1987) as a tool for examining O_3 damage to forests and crops. This S-shaped function weights O_3 concentrations in a manner that emphasizes high values (e.g., $\geq$80 ppb) and deemphasizes low values (e.g., $\leq$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 1990 through 1992 are presented in Figures 61 through 63.

Calculated W126 values for 1990 range from less than 20 ppm-hr in northern Maine and Wisconsin to approximately 100 ppm-hr in northern Virginia. Not suprisingly, sites with the highest values include mountaintop locations along the spine of the central and southern Appalachian Mountains. These sites exhibit limited diurnal variations and would be expected to experience among the highest O_3 exposures among rural sites. Typical values elsewhere are on the order of 50 to 70 ppm-hr, except for two sites in northern Alabama and northern Georgia, which exceeded 90 ppm-hr. Reasons for these isolated high values are unknown.

W126 data for 1991 are generally similar to 1990, except for slightly higher values in Pennsylvania and New York and dramatically lower (50 percent) values at the two sites in Georgia and Alabama. Data for 1992 show substantially lower W126 values for a large number of sites compared to 1990 and 1991. Peak values in 1992 were on the order of 60 ppm-hr for the three mountaintop sites in Virginia and North Carolina. These findings show that year-to-year variability in exposure statistics can be substantial, even where measures of central tendency (e.g., averages) and extremes (e.g., concentrations $\geq$120 ppb) show limited variability.

Similar variability is observed in other statistics used to estimate O_3 exposure. The SUM60 statistic, for example, has been related to O_3 damage in agricultural crops and has been suggested as a potential model for a secondary O_3 standard (Lefohn et al., 1988). By definition, SUM60 is the sum of all O_3 concentrations $\geq$60 ppb over a 3-month period (typically June through August) which is equated to the growing season for many crops. SUM60 calculations for eastern NDDN sites for 1990 through 1992 are displayed in Figures 64 through 66. The overall pattern of SUM60 for 1990 is very similar to that for W126. The highest exposures occur along the Appalachian Mountains from Pennsylvania to Georgia. The lowest exposures occur in Maine, Wisconsin, and eastern Kentucky. Generally similar patterns and somewhat to significantly lower values are observed in 1991 and 1992.

Figure 61. W126 (ppm-hr) for eastern sites for 1990.

Figure 62. W126 (ppm-hr) for eastern sites for 1991.

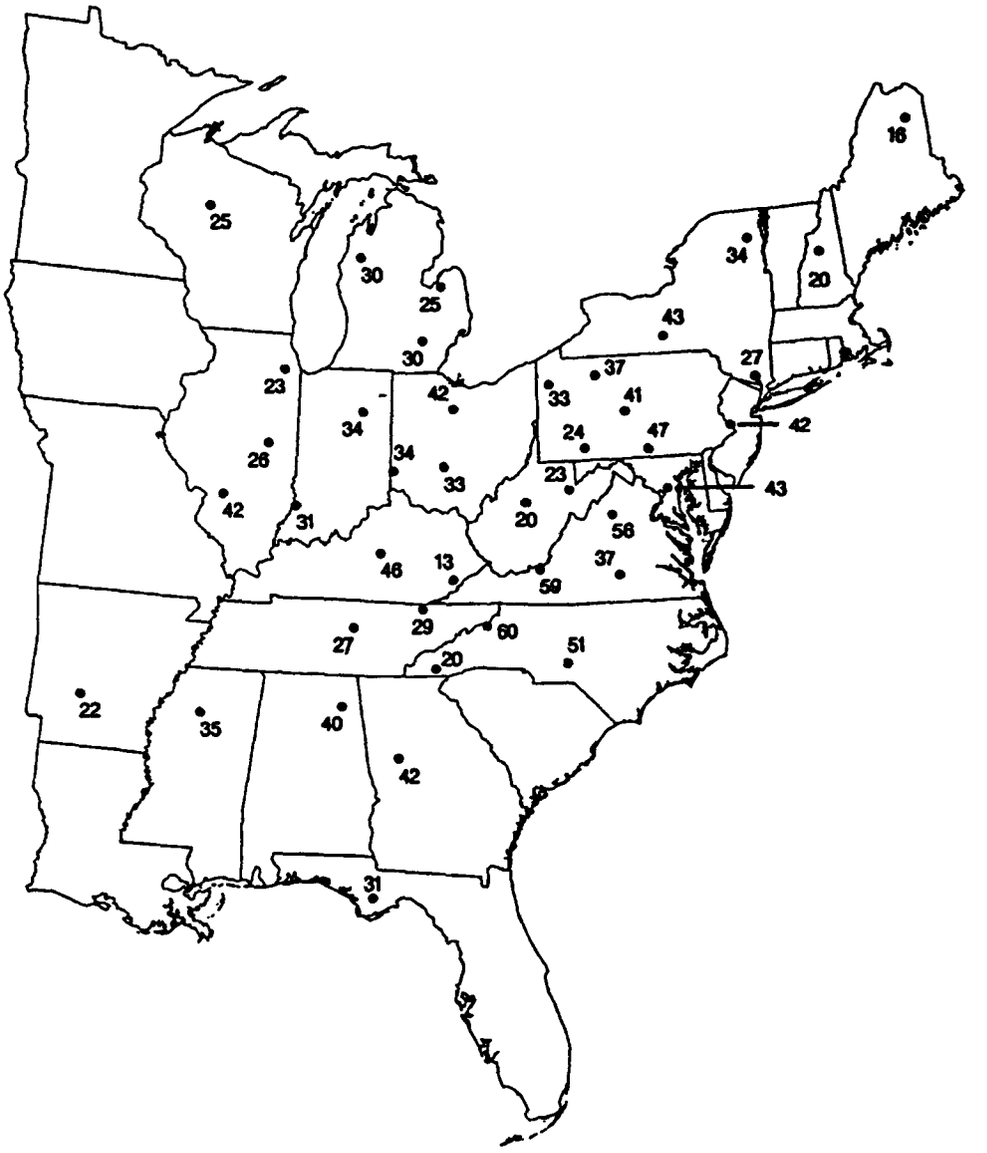


Figure 63. W126 (ppm-hr) for eastern sites for 1992.

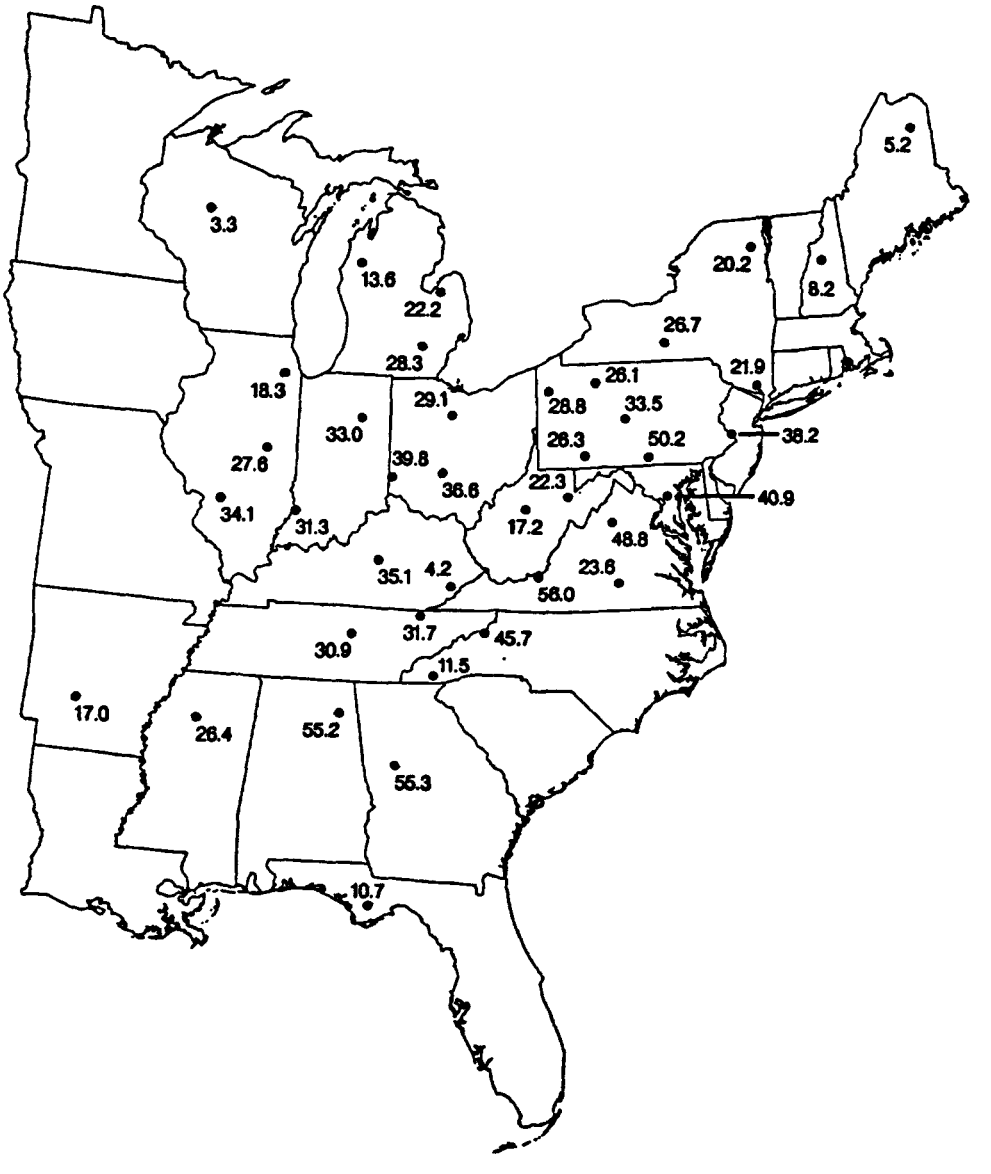


Figure 64. SUM60 (ppm-hr) for eastern sites for 1990.

Figure 65. SUM60 (ppm-hr) for eastern sites for 1991.

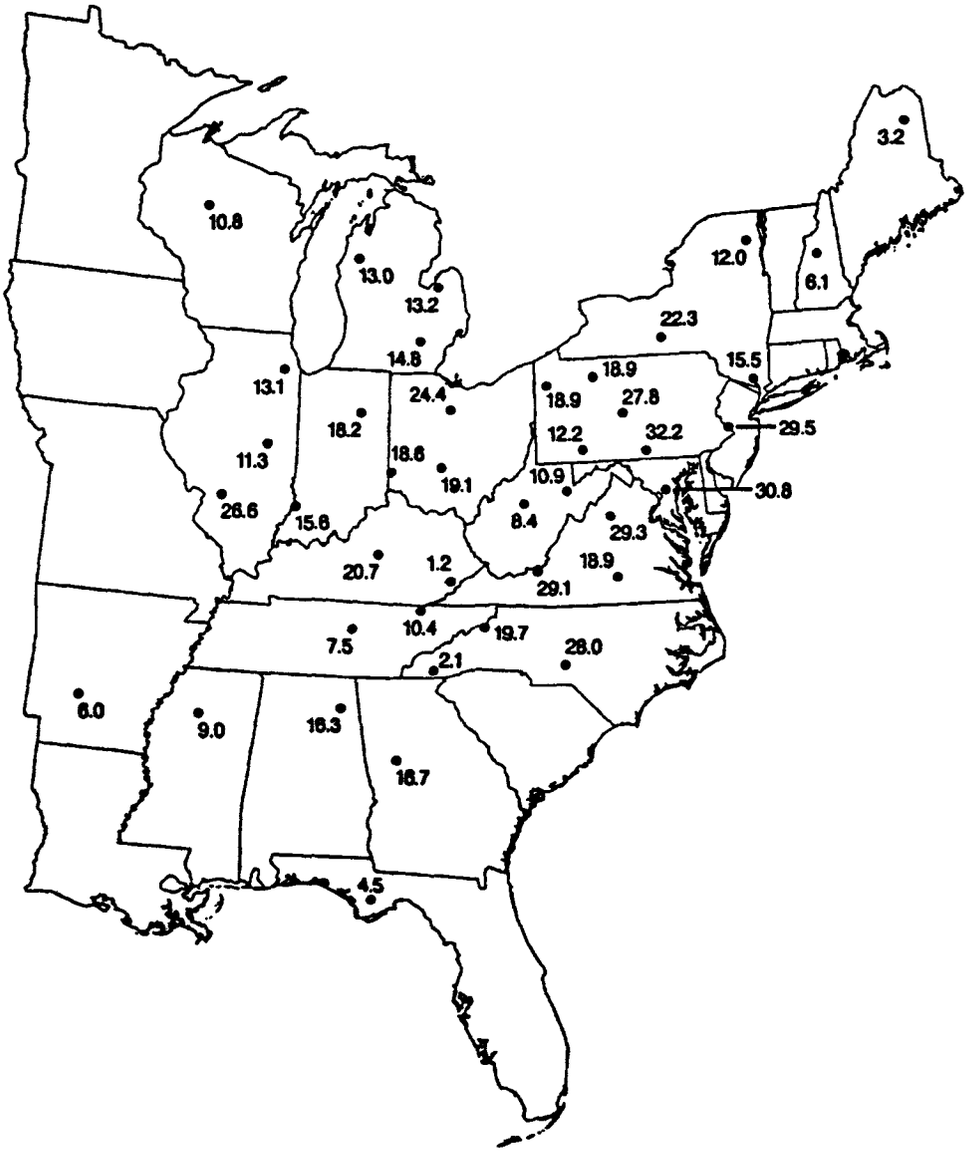


Figure 66. SUM60 (ppm-hr) for eastern sites for 1992.

Chapter 5
Special Studies

Two special studies were conducted during 1990 to 1992 to provide information on the comparability and representativeness of NDDN atmospheric concentration data. The first of these studies involved side-by-side collection of air samples using the NDDN and CAPMoN filter pack systems. The purpose of this experiment was to provide data on the comparability of United States and Canadian air quality trends databases. Information of this nature will prove useful in establishing uncertainty limits for spatial patterns across eastern North America.

The second study involved simultaneous collection of filter pack and meteorological data at two closely spaced sites in the southern Appalachians. One site was located on a mid-elevation ridge and the other (Site 137) was located about 1.0 km away in a valley approximately 300 m below the ridge. The objective of this study was to determine if concentrations and deposition velocities of acidic species were affected by complex terrain. This chapter presents initial findings from these two studies.

5.1 Comparability of United States and Canadian Atmospheric Concentration Data

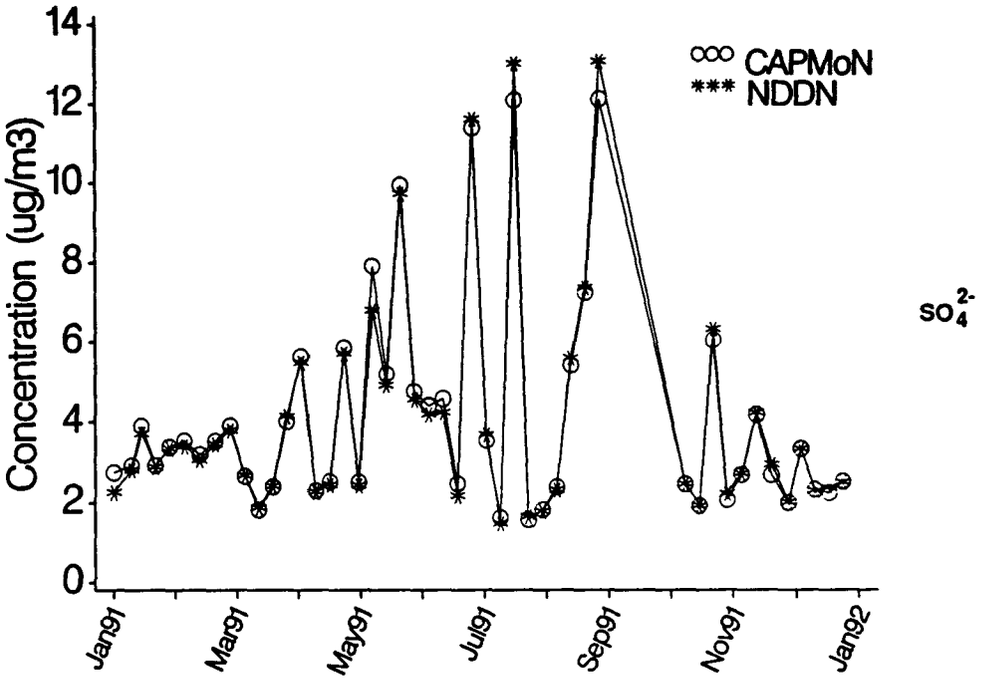
Late in 1990, NDDN filter pack sampling was initiated at Egbert, Ontario, a Canadian acid deposition trends site. The objective of this sampling effort was to establish a database for tracking the comparability of data that will be used by the two countries to evaluate trends in atmospheric concentration and dry deposition. Although both NDDN and CAPMoN use filter pack approaches for measuring atmospheric concentrations, several notable differences exist between programs. First, NDDN samples weekly, and CAPMoN samples daily. NDDN samples are thus exposed to a broader range of environmental conditions (e.g., temperature and relative humidity) over the 7-day sampling interval and may, therefore, be more susceptible to various artifact reactions. Second, NDDN and CAPMoN samples operate at substantially different flow rates (i.e., 1.5 L/min versus 25 L/min). Despite a shorter collection interval, the CAPMoN filter pack samples about 2.5 times the amount of air than the NDDN filter pack. This difference raises the question of gas-particle interactions, due to build-up of material on filters and other effects. Finally, differences exist in laboratory and data management operations. Both laboratories use IC for analysis of filter extracts; however, quality control protocols differ, and analytical accuracy is traceable to different standards. Data management procedures mandate slightly different approaches for calculating sample volume and, in the case of CAPMoN, blank correction of filter loadings prior to calculation of atmospheric concentrations.

Validated 1991 CAPMoN data for Egbert were received from Mr. Robert Vet of the Canadian Atmospheric Environment Service (AES) in the form of daily concentrations referenced to 273 degrees Kelvin (K) and 1 atmosphere pressure. These data were aggregated into weekly composite concentrations, corresponding to the start/end dates of NDDN samples, and then scaled to a reference temperature of 298 K (i.e., the NDDN reference temperature). The weekly aggregated CAPMoN data were then used, for purposes of this comparison, only if seven valid daily samples were available to be composited. In all, 47 pairs of valid weekly samples met selection criteria.

Results of side-by-side collection of CAPMoN and NDDN samples are shown in Figures 67 through 69 and summarized in Table 14. Data for SO_4^{2-} exhibit a very high correlation coefficient ($r^2 = 0.99$) and show no evidence of bias, either for the year as a whole or for extended periods (i.e., about 3 months) between equipment calibrations. Over all samples, mean concentrations differ by less than 1 percent. Median absolute differences (MADs) and median absolute percent differences (MAPDs) are 0.1 $\mu g/m^3$ and 2.7 percent, respectively. These data indicate that no substantial biases occur in the collection and analysis of samples and manipulation of data by the two networks. This is not surprising since atmospheric SO_4^{2-} is relatively straightforward to measure; however, it shows that the two networks were in good control of measurement systems during 1991.

Results for NH_4^+ are generally similar to SO_4^{2-}, while those for NO_3^- and HNO_3 exhibit considerable scatter. Annual average concentrations of NO_3^- and HNO_3 are well within 5 percent, but correlation coefficients are only 0.86 and 0.90, respectively. Inspection of time series shows extended periods during which one sampler is higher than the other. In most cases, the pattern for NO_3^- runs counter to that for HNO_3. For example, the NDDN appears to underestimate HNO_3 and overestimate NO_3^- during the spring and summer months. The opposite is true during the fall and winter. Large MAPDs compared to overall percent differences for NO_3^- and HNO_3 suggest that there may be compensating effects which cancel out if averaging periods are sufficiently long. This is supported, to some extent, by total NO_3^- data. In general, results for total NO_3^- show that the two samplers collect the essentially same amount of material, even though they may partition the particle and gas phases somewhat differently.

Data for SO_2 exhibit a distinct and persistent bias between samplers. The overall mean concentrations differ by 10 percent and the MAPD (a measure of the typical difference between samples) is nearly 15 percent. Differences cannot be explained by errors in sample flow rates or analytical biases because these would also be evident for SO_4^{2-} and perhaps other species. McNaughton and Bowne (1993) recently reviewed numerous intercomparisons of atmospheric sampling methods. In general, results showed that filter pack methods were biased low relative to annular denuder and continuous



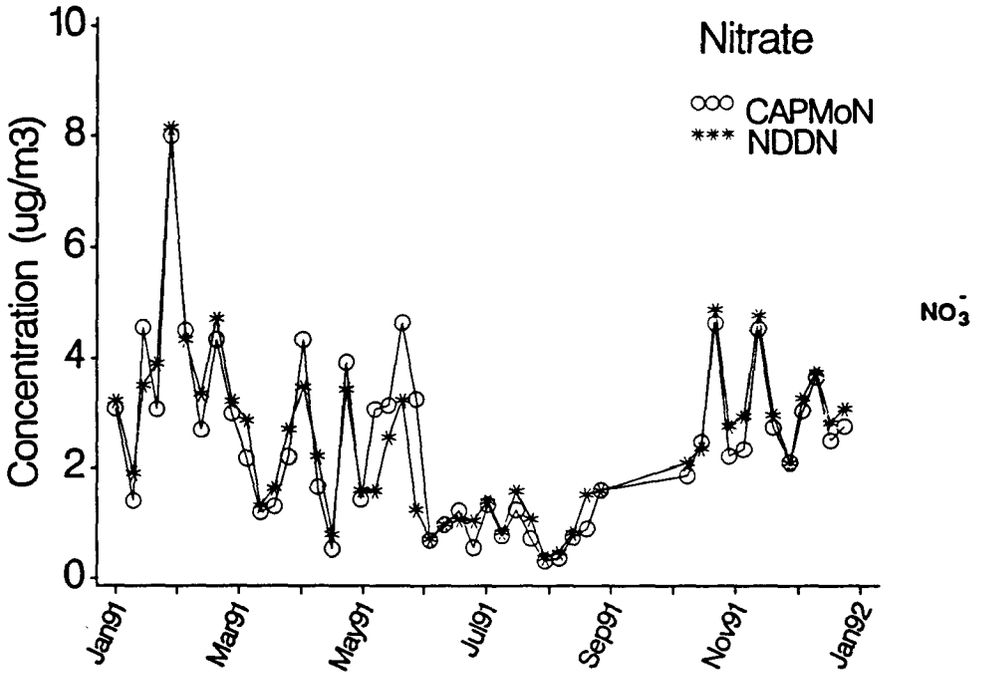


Figure 67. Time series of SO_4^{2-} and NO_3^- concentrations ($\mu g/m^3$) collected by CAPMoN and NDDN at Egbert, Ontario.

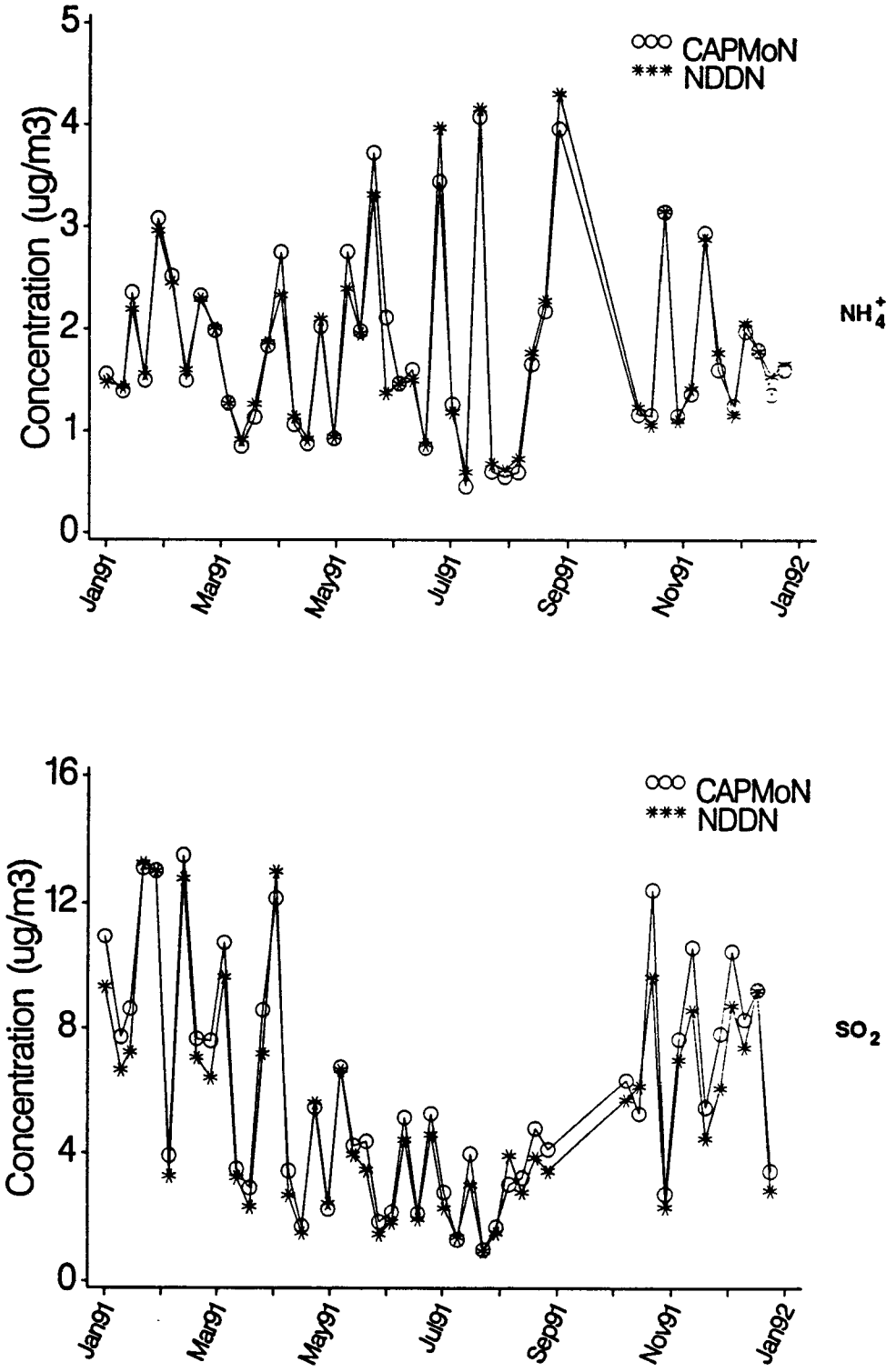


Figure 68. Time series of NH_4^+ and SO_2 concentrations ($\mu g/m^3$) collected by CAPMoN and NDDN at Egbert, Ontario.

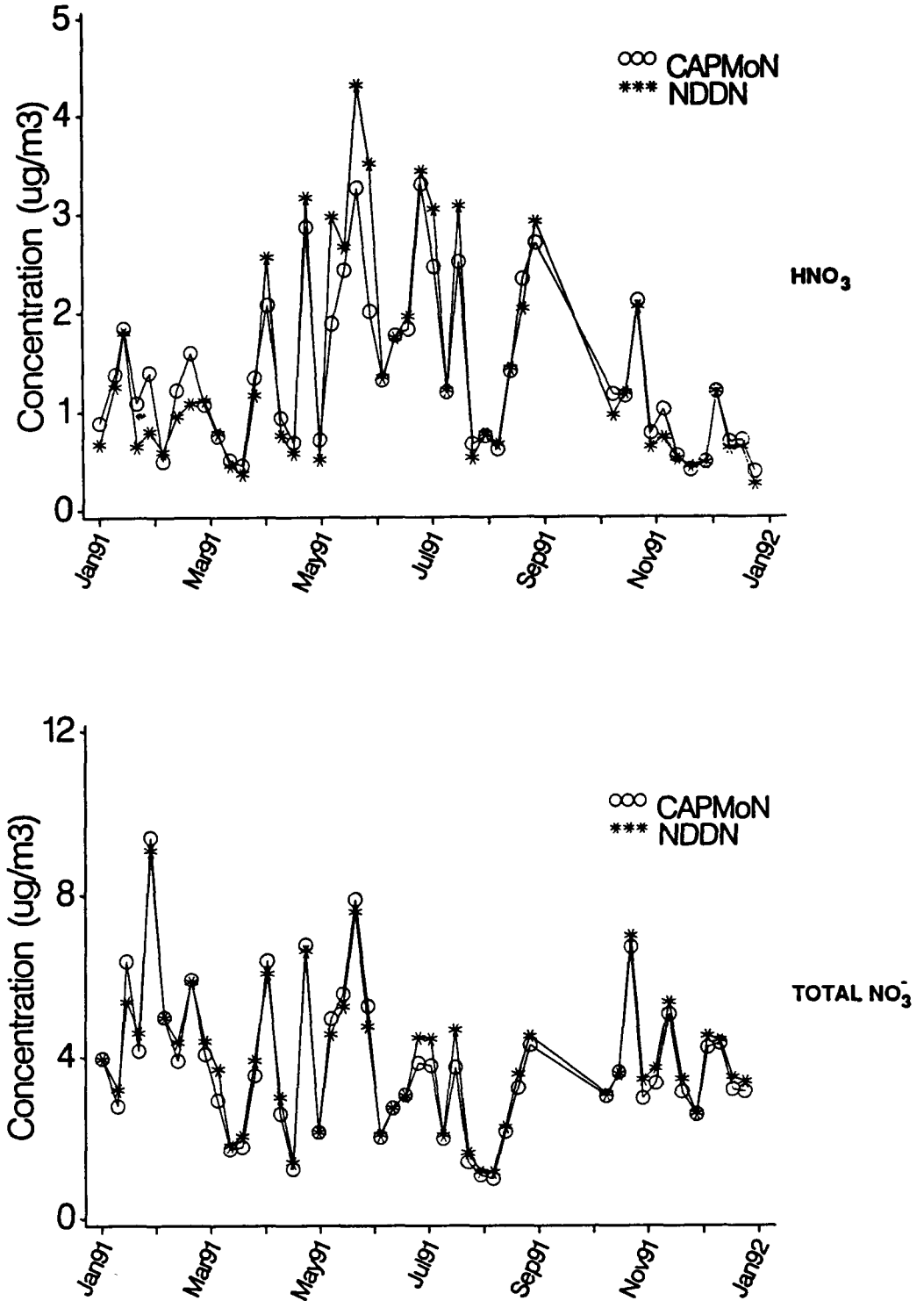


Figure 69. Time series of HNO_3 and total NO_3^- concentrations ($\mu g/m^3$) collected by CAPMoN and NDDN at Egbert, Ontario.

Table 14. Comparison of 1991 Atmospheric Concentration Data for CAPMoN and NDDN at Egbert, Ontario

Statistic	Species					
	SO_4^{2-}	NO_3^-	NH_4^+	SO_2	HNO_3	Total NO_3^-
Mean NDDN ($\mu g/m^3$)	4.08	2.47	1.80	5.46	1.43	3.94
Mean CAPMoN ($\mu g/m^3$)	4.09	2.42	1.80	6.05	1.38	3.79
MAD ($\mu g/m^3$)	0.12	0.26	0.08	0.65	0.12	0.29
MAPD (%)	2.7	13.2	5.4	14.8	10.1	7.8
% D	< 1	2.0	< 1	10.3	3.6	3.9
Slope	0.96	0.98	0.98	1.04	0.72	1.06
Intercept ($\mu g/m^3$)	0.19	0.00	0.03	0.38	0.35	-0.36
r^2	0.99	0.86	0.96	0.96	0.90	0.97

Note: MAD = median absolute difference between sample pairs.
MAPD = median absolute percent difference between sample pairs.
% D = percent difference between mean concentrations.

methods and that the magnitude of the bias varied inversely to flow rate through the filter pack. Further studies are needed to elucidate the mechanism for such biases.

In summary, results for 1991 show excellent comparability between NDDN and CAPMoN for all species, except SO_2, when averaged over the year. Seasonal and possibly temperature-dependent biases occur for NO_3^- and HNO_3, but not for total NO_3^-, suggesting that the two samplers observe slightly different phase distributions for certain species. Based on these results, CAPMoN and NDDN data are generally comparable, except for SO_2, and it would appear that data sets can be merged for analysis of annual concentration patterns across eastern North America. For SO_2, it may be necessary to adjust results for the observed bias to avoid a transboundary step function.

5.2 Elevational Gradients in Concentration and Fluxes

Data presented earlier show that spatial variability of concentrations and deposition is relatively high in and around the Appalachian Mountains, especially for the reactive gases SO_2 and HNO_3. This

variability is of concern because it complicates estimation of deposition to sensitive and protected ecosystems as well as to mountainous areas in general.

In mid-1991, an auxiliary monitoring site was established at the Coweeta Hydrologic Laboratory in southwestern North Carolina. The purpose of this site was to examine short-range variations in concentration and dry deposition, specifically, the effect of elevation. Coweeta Hydrologic Laboratory was selected for this study because of its remoteness from pollutant sources and because of the accessibility to a ridgetop site.

Equipment was installed at an elevation of 850 m on a ridge located about 1.5 km northwest of the routine NDDN site (elevation 550 m). Weekly filter packs and hourly meteorological data were collected from mid-June through the end of the year. An ozone monitor was not installed because an environmentally controlled shelter was not available.

Results of the 1991 study are shown in Figures 70 through 72 and summarized in Table 15. Weekly concentration data for SO_4^{2-} exhibit a very strong correlation between the ridge and valley sites, with a definite tendency for higher concentrations at the ridge site. The strong correlation between sites suggests that the two are generally exposed to the same air mass. The time series of SO_4^{2-} concentrations also shows some evidence of seasonality. Differences between ridge and valley are pronounced through October, after which they agree essentially within the precision of the measurements. The transition coincides with leaf senescence and leaf drop at Coweeta, suggesting that ridge/valley differences may be the result of canopy interactions.

Data for SO_2 and HNO_3 also show substantial ridge/valley differences. For these species, ridgetop concentrations are frequently 2 to 3 times higher than valley concentrations. Correlations between the two sites are lower than for SO_4^{2-} but still highly significant. Differences between ridge and valley concentrations also persist through the end of the year (i.e., beyond leaf drop).

Ratios of ridge/valley concentrations of SO_4^{2-}, SO_2, and HNO_3 over the 6½-month study were 1.3, 2.4, and 2.6, respectively (see Table 15), and, in general, increase in order of calculated V_d. This behavior may indicate that a variety of factors, including dry deposition, contribute to ridge/valley differences.

Calculated V_ds for the two sites show moderate enhancements for SO_4^{2-} and SO_2 and a dramatic enhancement for HNO_3 at the ridgetop. This observation reflects species-dependent sensitivity to windspeed, since this is the only model input variable to differ significantly from valley to ridge. As

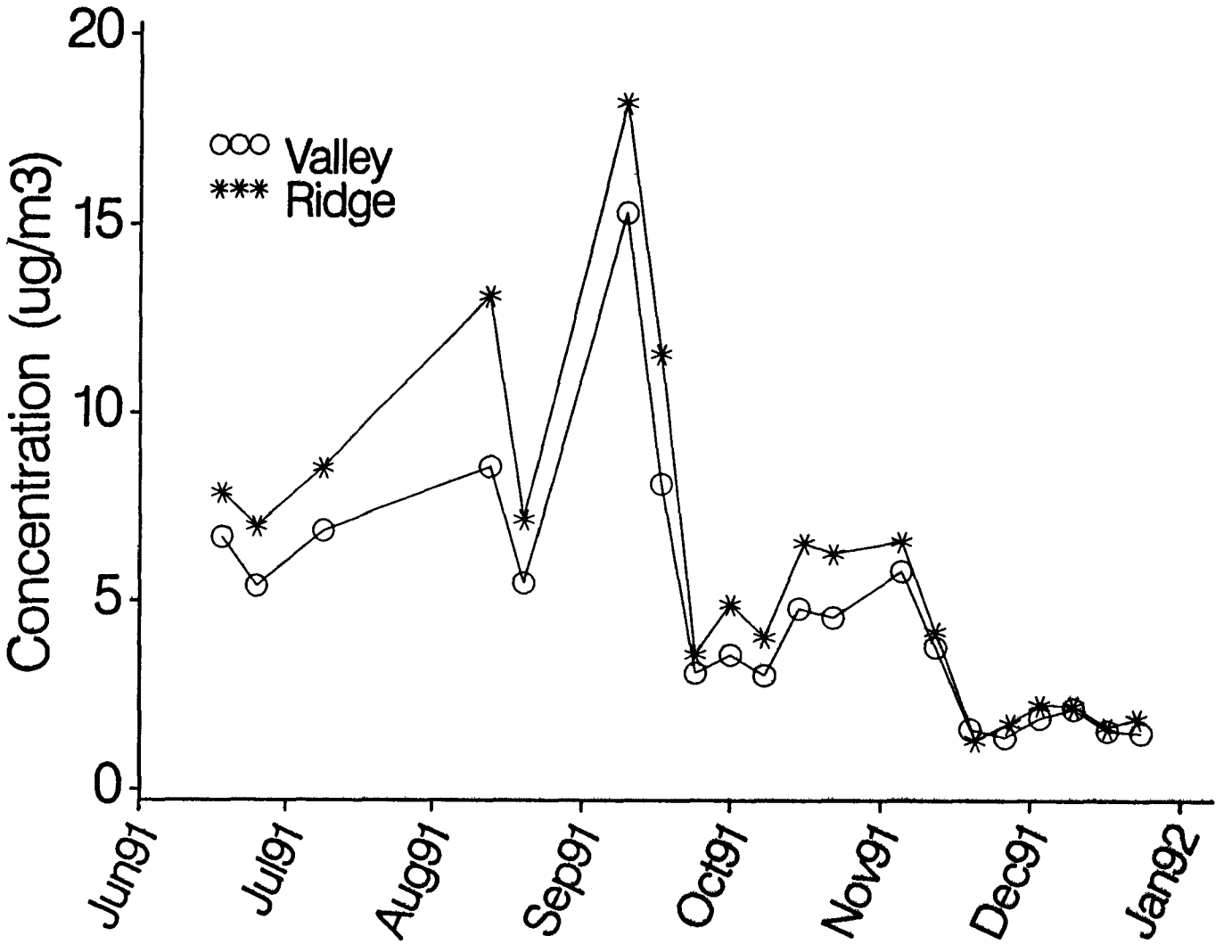


Figure 70. Time series of SO_4^{2-} concentrations ($\mu g/m^3$) for ridge and valley sites at Coweeta Hydrologic Laboratory (Site 137)

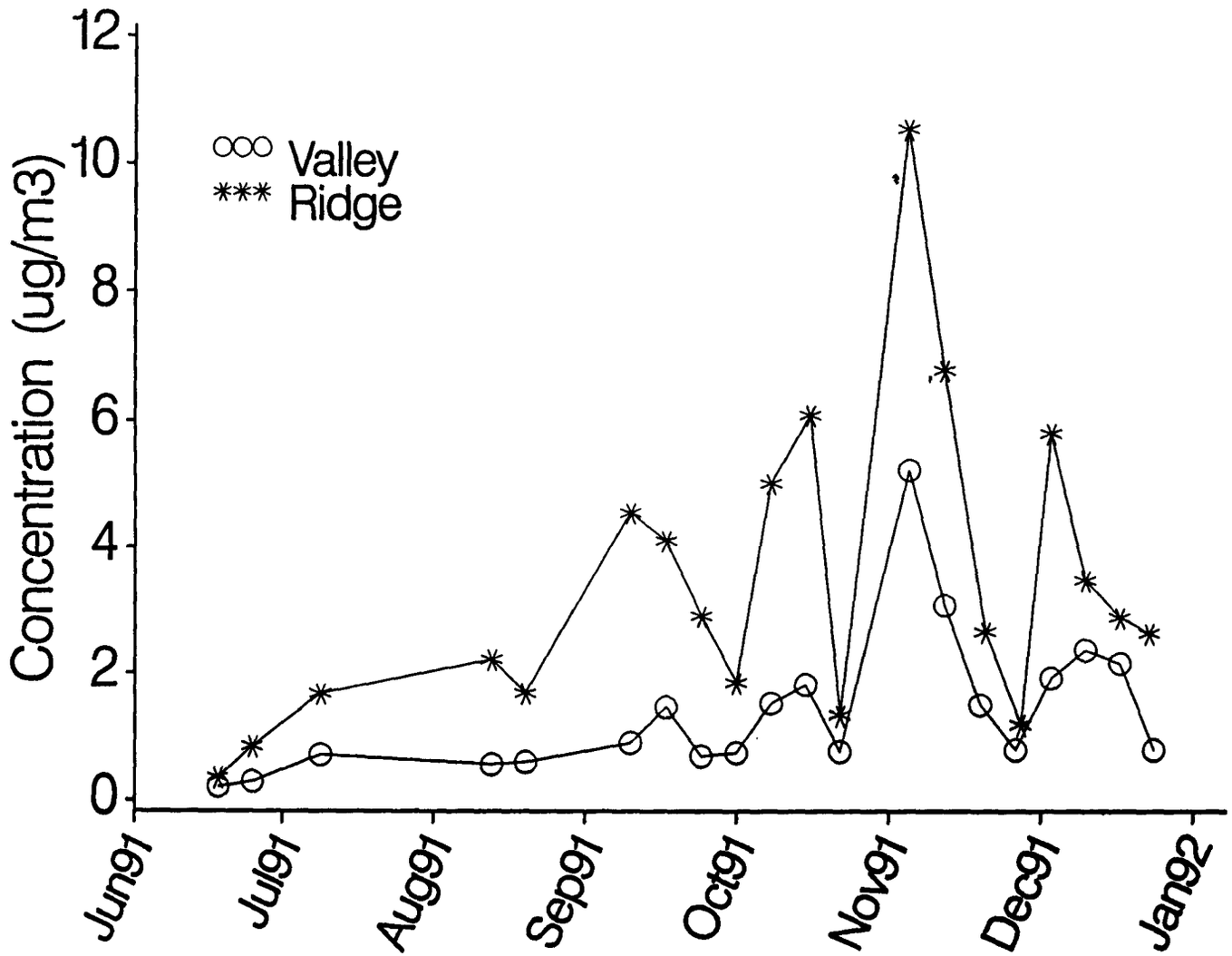


Figure 71. Time series of SO_2 concentrations ($\mu g/m^3$) for ridge and valley sites at Coweeta Hydrologic Laboratory (Site 137).

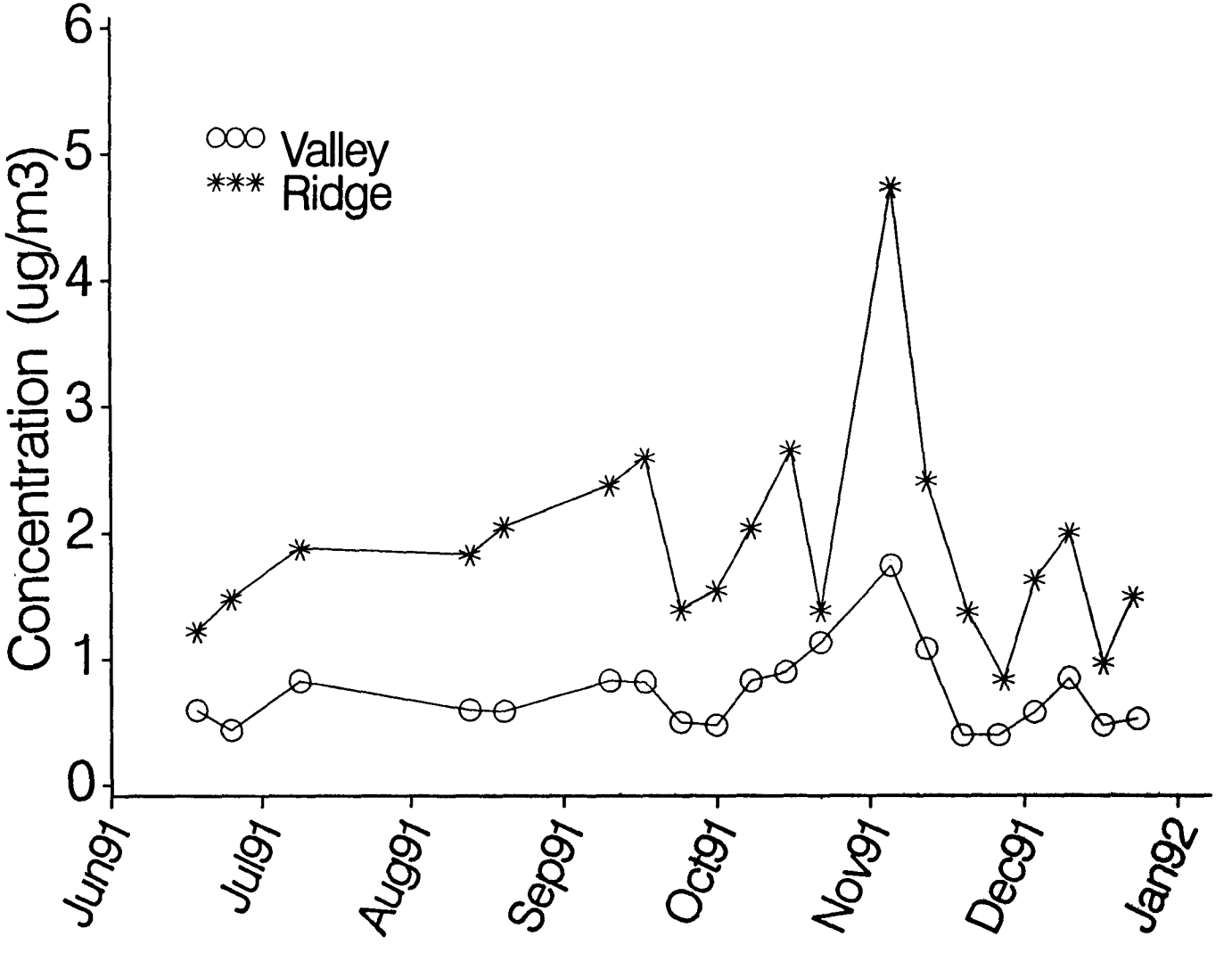


Figure 72. Time series of HNO_3 concentrations ($\mu g/m^3$) for ridge and valley sites at Coweeta Hydrologic Laboratory (Site 137).

Table 15. Comparison of Ridge (R) and Valley (V) Data for Coweeta Hydrologic Laboratory, July through December 1991

	Species		
	SO_4^{2-}	SO_2	HNO_3
Concentration ($\mu g/m^3$)			
R	6.04	3.44	1.90
V	4.75	1.41	0.73
R/V	1.3	2.4	2.6
Deposition Velocity (cm/sec)			
R	0.08	0.37	1.49
V	0.07	0.31	0.89
R/V	1.1	1.2	1.7
Flux (kg/ha) as S or N			
R	0.25	1.00	1.96
V	0.17	0.34	0.45
R/V	1.4	2.9	4.4

discussed previously, V_d for HNO_3 is very sensitive to windspeed because surface resistances are assumed to be negligible. Other species, such as SO_4^{2-} and SO_2, have significant surface resistances and, therefore, are much less sensitive to windspeed effects.

Estimated fluxes for SO_4^{2-}, SO_2, and HNO_3 exhibit ridge/valley ratios of 1.4, 2.9, and 4.4, respectively, indicating that strong deposition gradients occur over short distances in areas of complex terrain. These findings support recent investigations by Lovett and Likens (1991), who have compared several approaches for estimating atmospheric fluxes of sulfur and nitrogen to the Hubbard Brook Experimental Forest. Results of these studies indicate that estimates of dry sulfur deposition can vary widely. For example, flux estimates based on watershed mass balances were 2 to 3 times higher than estimates based on model calculations. Input for the model calculations came from NDDN measurements at a valley site, similar to Coweeta, located at the base of the watershed. Model output for the NDDN site was then assumed to represent the entire watershed. Although much less direct than the observations

at Coweeta, these findings suggest that elevational gradients might be widespread phenomena. If so, the issue of site representativeness should include some consideration for terrain complexity. Additional work is needed to determine scaling factors, so measurements at individual sites can be applied to large areas of complex terrain. Certain aspects of this work are currently under development in the Large Area Deposition model (McMillen, 1990).

Chapter 6
Quality Assurance Summary

As described in Chapter 3, extensive quality control checks have been implemented, both in the field and the laboratory, to ensure that data quality consistently meets program requirements. These checks include frequent calibration of equipment with NIST-traceable standards (when available) to determine accuracy and collocation of equipment at numerous sites to determine overall measurement precision. This chapter summarizes accuracy and precision data for the CASTNet deposition network. Results are presented for 1992 (a typical year) to exemplify data quality routinely provided by the network or an annual timeframe. Readers interested in quality control data for different years, or for time periods of less than 1 year, are referred to periodic data reports and summaries provide to EPA (e.g., ESE, 1990).

6.1 Laboratory Accuracy and Precision

The accuracy of laboratory measurements is determined by frequent analysis of independent standards of known concentration. These standards are typically obtained directly from NIST or another authoritative source (e.g., EPA). In practice, standards are analyzed by ESE at the beginning and end of every laboratory batch (roughly 50 to 100 samples). The initial analysis is used to verify the analytical calibration curve, while the final analysis is used to check for instrumental drift. Both results must be within a specified range for the analytical batch to be accepted.

Laboratory precision is determined by the replicate analysis of at least one sample per laboratory batch. In this case, a sample is randomly selected and re-analyzed at the end of the batch. With this approach, precision data incorporate sample-to-sample variability and instrumental drift across the observed range of sample concentrations.

It should be noted that laboratory accuracy represents only a portion (and frequently a small portion) of the total uncertainty surrounding precipitation chemistry and air quality measurements. Currently, no standard exists for directly assessing the accuracy of filter pack data and precipitation chemistry data. Rather, accuracy must be inferred on the basis of standard laboratory measurements, round-robin measurements of split samples and/or direct comparison with methods of known accuracy. Results presented in this section represent only the first of these approaches. Work has been initiated to obtain accuracy information with the other two approaches.

As with accuracy, laboratory precision represents only part of the overall precision of environmental measurements. Unlike accuracy, however, there is an authoritative, or at least consensus, approach for

determining the overall precision of precipitation chemistry and air quality data. This approach (typically referred to as collocation) involves side-by-side collection of samples with independent systems. Results of collocated sampling at a number of sites are presented in Section 6.2.

6.1.1 Laboratory QC for Filter Pack Measurements

Laboratory accuracy and precision data for 1992 filter pack measurements (filter extracts) are shown in Table 16. In general, accuracies are well within the ±5 percent criterion established for filter pack data. Concentrations of NO_3^- ion exhibit a slight (about 1 percent) negative bias in both Teflon® and nylon analyses, while SO_4^{2-} ion exhibits a slight (2 percent) positive bias in nylon and Whatman analyses. These biases are unlikely to have a major effect on analysis of spatial patterns.

Precision data for filter pack analyses easily meet acceptance criteria for the program. Mean replicate differences for all analytes were less than 2 percent and for Teflon-SO_4^{2-} and nylon-NO_3^- were less than 1 percent.

6.1.2 Laboratory QC for Precipitation Chemistry Measurements

Precision and accuracy data for laboratory analyses of ionic species in precipitation are summarized in Table 17. As for filter pack measurements, results easily fall within acceptable ranges for most analytes. Average recovery of anions (SO_4^{2-}, NO_3^-, and Cl^-) was within ±2 percent. Interestingly, NO_3^- ion exhibits a similar negative bias as was observed in filter pack measurements. This likely reflects a small, but persistent, systematic difference between calibration standards used in the ESE laboratory and NIST references used to determine accuracy.

Cation measurements generally show a wider range of recoveries than anion measurements, but still fall within the acceptance range of ±10 percent. Unfortunately, the species with the lowest overall accuracy (i.e., largest absolute departure from 100 percent recovery) is the most important cation, H^+ In this case, there is a positive bias of about 7 percent. This corresponds to a measurement error of about 0.03 pH unit, which is only slightly larger than the uncertainty in the standards used to calibrate the instrument.

Precision data for precipitation chemistry measurements also meet acceptance criteria for all species. The precision of anion measurements (especially SO_4^{2-} and NO_3^-) is generally greater than that for cation measurements because anion concentrations are rarely, if ever, near the analytical detection limit. Cation concentrations, except for H^+ and NH_4^+, are frequently within a factor of two of analytical detection limits.

Table 16. Summary of Laboratory Accuracy and Precision Data for Filter Pack Measurements, 1992

Filter		Parameter	Accuracy (% Recovery)*		Precision (% Difference)+	
			Mean	Std. Dev.	Mean	Std. Dev.
Teflon®	SO_4^{2-}	SO_4^{2-}	100.1	1.2	0.4	0.7
		NO_3^-	98.6	1.3	1.4	2.8
		NH_4^+	100.7	2.1	1.6	3.2
Nylon			101.4	1.7	1.4	2.4
		NO_3^-	98.8	1.6	0.8	1.0
Whatman		SO_4^{2-}	102.2	1.0	1.7	3.7

*Accuracy based on analyses of NIST reference solutions.
+Precision based on within-run replicate analyses of filter extracts.

Source: ESE.

Table 17. Summary of Laboratory Accuracy and Precision Data for Precipitation Chemistry Measurements, 1992

Parameter	Accuracy (% Recovery)*		Precision (% Difference)+	
	Mean	Std. Dev.	Mean	Std. Dev.
SO_4^{2-}	100.5	1.0	0.6	0.6
NO_3^-	98.2	0.9	0.5	0.4
Cl^-	101.0	2.0	3.1	4.5
H^+	107.1	3.0	3.8	5.2
NH_4^+	100.2	2.0	2.8	2.8
Na^+	97.8	3.7	5.3	7.1
K^+	103.2	3.6	3.6	4.4
Ca^{2+}	103.6	4.2	2.0	2.6
Mg^{2+}	103.3	3.4	1.7	2.6

*Accuracy based on analysis of NIST simulated rainwater.
+Precision based on within-run replicate analyses of rainwater samples.

6.2 Results of Collocated Measurements

As mentioned previously, collocated measurements are a broadly accepted approach for determining the overall precision of atmospheric measurements. Collocated filter pack measurements and continuous ozone and meteorology measurements were conducted at a number of sites from 1990 through 1992. This section presents results for filter pack sampling at two sites (one eastern and one western) and continuous measurements for one site. Collocated precipitation chemistry measurements were not conducted during the reporting period, but have been subsequently initiated.

6.2.1 Filter Pack Data

Collocated filter pack data for 1992 are summarized in Table 18 and displayed in Figures 73 and 74. Inspection of summary statistics shows that annual average concentrations are nearly identical for all species. For the eastern United States sites, average SO_4^{2-}, NO_3^-, NH_4^+, and SO_2 agree within ±2 percent, while HNO_3 and total NO_3^- agree within about ±6 percent. Median absolute differences (MADs) reflect typical differences between a pair of samples and are less than 0.1 $\mu g/m^3$ for SO_4^{2-}, NO_3^-, and NH_4^+ and less than 0.5 $\mu g/m^3$ for HNO_3 and total NO_3^-. In general, the collocated precision for sulfur species (i.e., SO_4^{2-} and SO_2) and NH_4^+ is better than that for the nitrate-nitrogen species, when expressed on a percentage basis (i.e., MAPD). This observation may reflect artifact reactions and interconversions of NO_3^- and HNO_3 in the filter pack.

Data for Site 163, located in the western United States, also show good precision, despite very low concentrations of all species. Median absolute differences between samples are ≤ 0.02 $\mu g/m^3$, and median absolute percent differences (MAPDs) are less than 8 percent for all species. These findings show that overall measurement precision does not vary greatly over the observed range of concentrations in the eastern and western United States. As expected, they also show that laboratory precision is typically a small component of the overall precision of atmospheric measurements.

Scattergrams and regression statistics for individual sample pairs show that agreement between samplers is generally acceptable. Linear regression statistics indicate essentially 1:1 agreement for most species and equally good agreement across the entire range of measurements. One exception to this is HNO_3 for Site 128 (Arendtsville, PA), which shows a definite bias of about 0.2 $\mu g/m^3$ between samplers. This cannot be attributed to flow differences, since other species (especially SO_4^{2-}) do not show the same effect. Work is underway to investigate reasons for this behavior.

Table 18. Summary of Collocated Filter Pack Data for 1992

Statistic	Parameter					
	SO_4^{2-}	NO_3^-	NH_4^+	SO_2	HNO_3	Total NO_3^-
Site 128 (n = 52)						
$\bar{X}$ ($\mu g/m^3$)	6.07	1.81	2.42	12.7	2.83	4.60
$\bar{Y}$ ($\mu g/m^3$)	6.12	1.83	2.42	12.9	3.01	4.79
D (%)	-0.8	-1.1	0.6	-2.0	-6.2	-4.1
MAD ($\mu g/m^3$)	0.06	0.08	0.04	0.43	0.21	0.22
MAPD (%)	1.3	6.2	1.7	4.6	8.1	5.6
Site 163 (n = 47)						
$\bar{X}$ ($\mu g/m^3$)	0.72	0.57	0.36	0.24	0.39	0.96
$\bar{Y}$ ($\mu g/m^3$)	0.74	0.61	0.38	0.24	0.39	0.99
D (%)	-2.7	-6.8	-5.4	-3.2	-1.6	-3.1
MAD ($\mu g/m^3$)	0.01	0.02	0.01	0.01	0.02	0.02
MAPD (%)	1.6	7.3	2.8	6.9	5.0	3.4

Note: D = percent difference of quarterly means = 200 x $(\bar{X} - \bar{Y})/(\bar{X} + \bar{Y})$.
MAD = median absolute difference.
MAPD = median absolute percent difference.
$\bar{X}$ = quarterly mean for primary sampler.
$\bar{Y}$ = quarterly mean for collocated sampler.

Source: ESE.

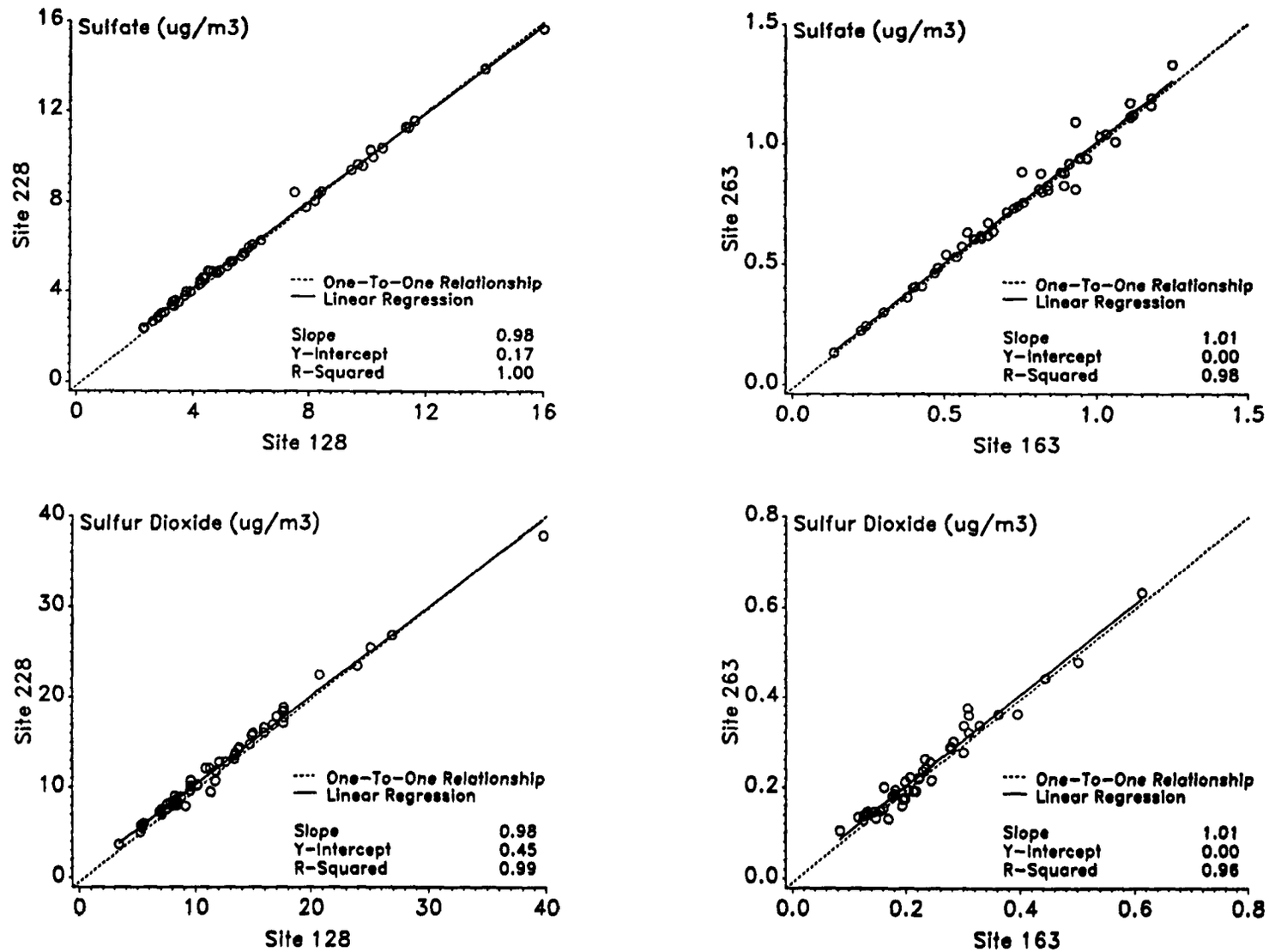


Figure 73. Scattergrams of collocated filter pack data for SO_4^{2-} and SO_2 for one eastern site (128) and one western site (163)

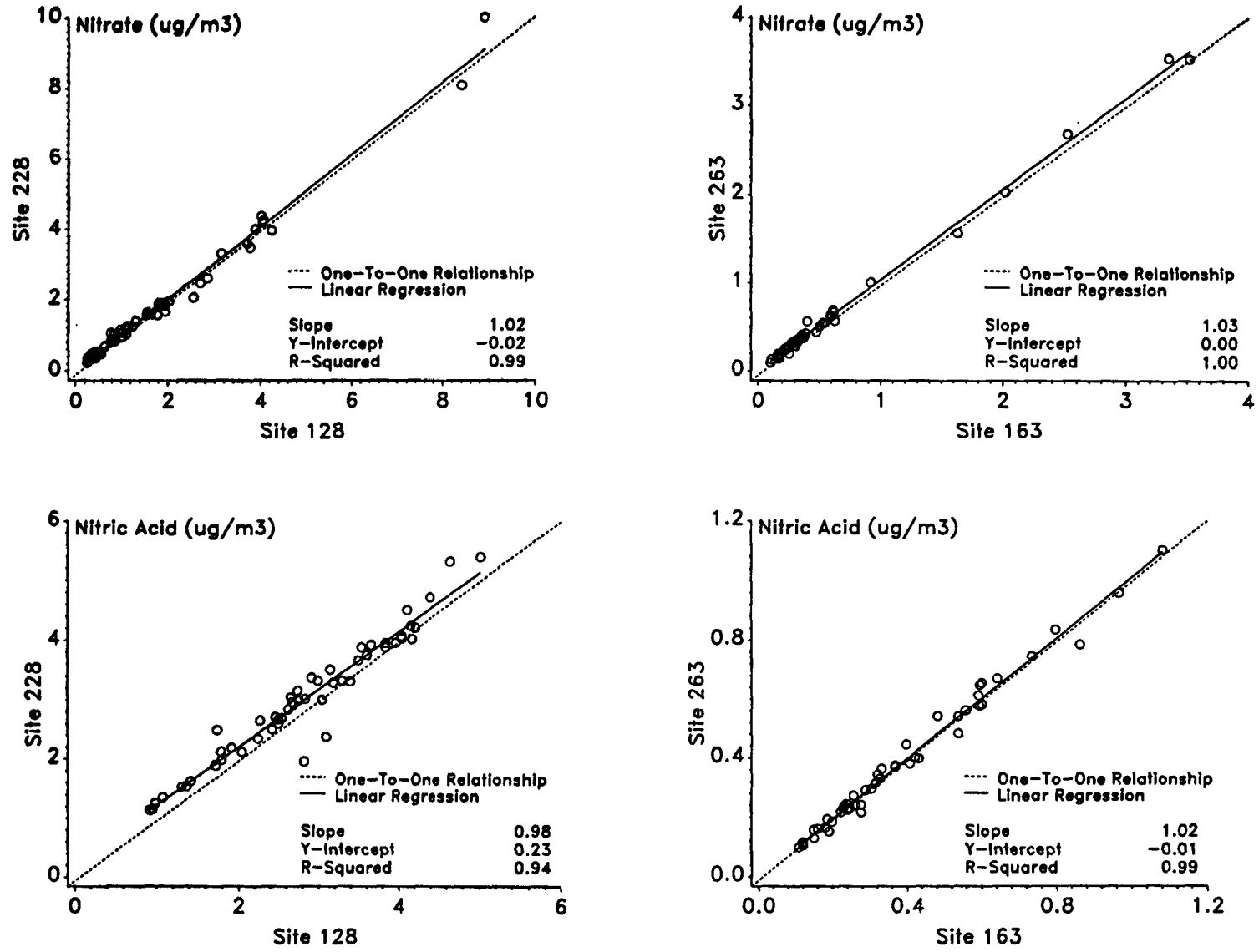


Figure 74. Scattergrams of collocated filter pack data for NO_3^- and HNO_3 for one eastern site (128) and one western site (163)

6.2.2 Continuous Measurements

Results of continuous (i.e., hourly) collocated measurements for O_3, temperature, solar radiation, and windspeed are illustrated in Figure 75. Data displayed in Figure 75 represent maxima daily values for each day during 1992. Maximum values were chosen because these are typically of greatest importance in determining ecological effects and deposition rates. As for filter pack data, these results indicate overall precision which is well within CASTNet requirements. Results also show that well-maintained instruments exhibit very little drift between periodic calibrations.

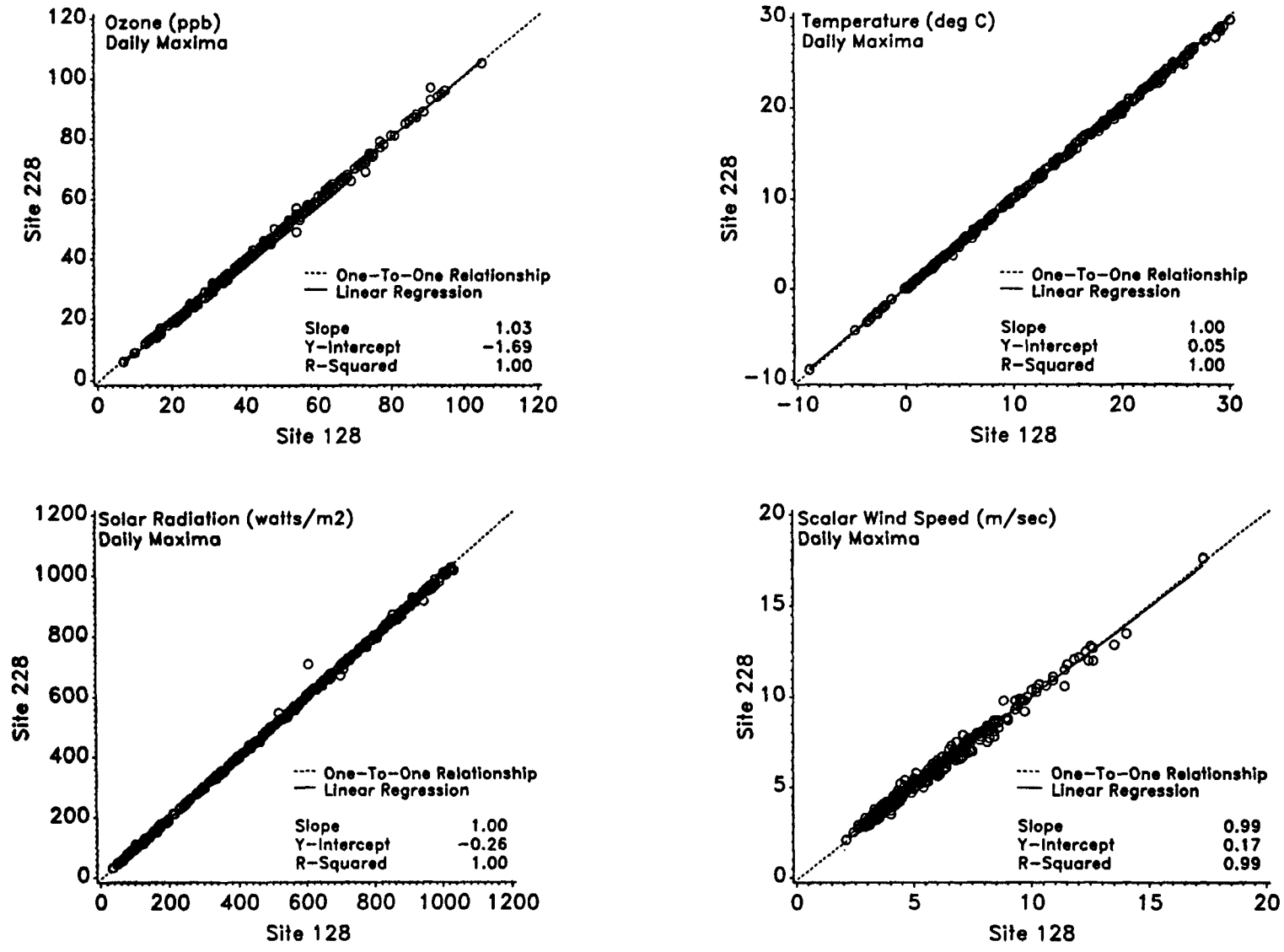


Figure 75. Scattergrams of collocated continuous data for O_3, temperature, solar radiation, and windspeed.

References

Anderson, J.R., Hardy, E.E., Roach, J.T., and Witmer, R.E. 1978. A Land Use and Land Cover Classification System for Use with Remote Sensor Data. U.S. Geological Survey Circular 671. Geological Survey Professional Paper 964.

Chason, J., Huston, M., and Baldocchi, D. 1990. A Comparison of Direct and Indirect Methods for Estimating Forest Canopy Leaf Area. Environmental Sciences Division. Oak Ridge National Laboratory. Oak Ridge, TN.

Clark, J.F., and Edgerton, E.S. 1992. Dry Deposition Flux Calculations for the National Dry Deposition Network. Prepared for the U.S. Environmental Protection Agency, Atmospheric Research and Exposure Assessment Laboratory. Research Triangle Park, NC.

Environmental Science & Engineering, Inc. (ESE). 1990a. National Dry Deposition Network (NDDN) Field Operations Manual. Prepared for U.S. Environmental Protection Agency (EPA). Contract No. 68-02-4451. Gainesville, FL.

Environmental Science & Engineering, Inc. (ESE). 1990b. National Dry Deposition Network (NDDN) Laboratory Operations Manual. Prepared for U.S. Environmental Protection Agency (EPA). Contract No. 68-02-4451. Gainesville, FL.

Environmental Science & Engineering, Inc. (ESE). 1991a. National Dry Deposition Network (NDDN) Data Management Manual. Prepared for U.S. Environmental Protection Agency (EPA). Contract No. 68-02-4451. Gainesville, FL.

Hicks, B.B., Baldocchi, D.D., Hosker, R,P., Jr., Hutchison, B.A., McMillen, R.T., and Satterfield, L.C. 1985. On the Use of Monitored Air Concentrations to Infer Dry Deposition (1985), NOAA Technical Memorandum ERL ARL-141. 66 pp.

Hosker, R.P., Jr. and Womack, J.D. 1986. Simple Meteorological and Chemical Filter Pack Monitoring System for Estimating Dry Deposition of Gaseous Pollutants. In: Proceedings of the 5th Annual National Symposium on Recent Advances in the Measurement of Air Pollutants, Raleigh, NC, 14-16 May 1985, EPA/600/8-85/029 (available from NTIS, Springfield, VA), pp. 23-29.

James, K.O.W. 1993. 1991 Quality Assurance Report, NADP/NTN Deposition Monitoring. Office of Atmospheric Chemistry. Illinois State Water Survey. Champaign, IL.

Lefohn, A.S. and Runeckles, V.C. 1987. Establishing a Standard to Protect Vegetation-Ozone Exposure/Dose Considerations. Atmos. Environ., 21:561-568.

Lefohn, A.S., Laurence, J.A., and Kohut, R.J. 1988. A Comparison of Indices that Describe the Relation Between Exposure to Ozone and reduction in the Yield of Agricultural Crops. Atmos. Environ., 22:1229-1240.

Li-Cor, Inc. 1989. LAI-2000 Plant Canopy Analyzer--Technical Information. LI-COR, Inc., 4421 Superior Street, Lincoln, NE.

Lindberg, S.E., Silsbee, D., Schaefer, D.A., Owens, J.G., and Petty, W. 1988. A Comparison of Atmospheric Exposure Conditions at Low- and High-Elevation Forests in Southern Appalachian Mountain Range, pp. 321-344. In: M.H. Unsworth and D. Fowler, eds. Acid deposition at High Elevation Sites, NATO ASI Series C:Vol.252, Klumer Publ., Boston.

References (Continued)

McMillen, R.T. 1990. Estimating the Spatial Variability of Trace Gas Deposition Velocities. NOAA Tech. Memo. ERL ARL-181, 37 pp.

Meyers, T.P. and Yuen, T.S. 1987. An Assessment of Averaging Strategies Associated with Day/Night Sampling of Dry-Deposition Fluxes of SO_2 and O_3. J. Geophysic Res., 92, 6705-6712.

Pierce, L.L. and Running, S.W. 1988. Rapid Estimation of Coniferous Forest Leaf Area Index Using a Portable Integrating Radiometer. Ecology 69(6) 1762-1767.

Sheih, C.M., Wesely, M.L., and Hicks, B.B. 1979. Estimated Dry Deposition Velocities of Sulfur Over the Eastern United States and Surrounding Waters. Atmos. Envir., 13:1361-1368.

Wesely, M.L. and Lesht, B.M. 1988. Comparison of RADM Dry Deposition Algorithm with a Site-Specific Method for Inferring Dry Deposition. Water, Air, and Soil Pollution, 44, 273-293.

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