



Project Summary

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

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

Results showed species-dependent variability in atmospheric concentrations from site to site, season to season, and day to night. In general, SO_4^{2-} , NH_4^+ , SO_2 , and HNO_3 concentrations were much higher (factor 5-10) at eastern sites than at western sites. On the other hand, NO_3^- , Na^+ , K^+ , Ca^{2+} , and Mg^{2+} concentrations were frequently comparable at eastern and western sites. Average SO_4^{2-} , NH_4^+ , and HNO_3 concentrations were typically highest during summer and lowest during fall. In contrast, SO_2 and NO_3^- were highest in winter and lowest in summer. Day/night variability was low for aerosols, but frequently pronounced for SO_2 and

HNO_3 , especially during the summer and at sites located in complex terrain. Comparison of O_3 data for 1988 and 1989 showed marked differences between years and a distinct tendency for higher concentrations in 1988. Ninety-eight exceedances of the NAAQS were observed at 18 sites in 1988, while only 15 exceedances were observed at 43 sites in 1989. Approximations of annual dry deposition rates for SO_4^{2-} , SO_2 , NO_3^- , and HNO_3 suggest that gaseous deposition greatly exceeds aerosol deposition and that dry fluxes are similar to wet deposition at numerous sites in the eastern United States. Application of site-specific dry deposition models are needed to refine these estimates.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Atmospheric deposition takes place via two pathways: wet deposition and dry deposition. Wet deposition is the result of precipitation events (rain, snow, etc.) which remove particles and gases from the atmosphere. Dry deposition is the transfer of particles and gases to the landscape in the absence of precipitation. Wet deposition rates of acidic species across the United States have been well documented



over the last 5 to 10 years; however, due to measurement difficulties, comparable information is unavailable for dry deposition rates.

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

This report describes progress on the NDDN during calendar year 1989. The purpose of this report is to familiarize the reader with the general approach of NDDN and the various types of data which are being produced and reported to EPA. It describes the network configuration and deployment schedule as well as procedures developed for field operations, laboratory operations, database management, and quality control (QC). An over-

view of air quality data for 1989, including QC results, is also presented. Finally, dry deposition rates are estimated for selected sites and compared with wet deposition rates. These estimates were prepared using literature values for deposition velocities and, therefore, are intended only to illustrate likely ranges of deposition.

Deployment of all currently planned NDDN sites was completed during 1989 (see Figure 1). Forty-one primarily rural monitoring sites were operated throughout the year in the eastern United States. In addition, nine sites in the western United States were established and operational by midyear.

Each NDDN site was equipped with sensors and sampling apparatus for continuous measurement of ozone (O_3) and meteorological variables required to estimate dry deposition. Weekly average atmospheric concentrations of particulate sulfate (SO_4^{2-}), particulate nitrate (NO_3^-), particulate ammonium (NH_4^+), SO_2 , and HNO_3 were determined throughout the year so weekly dry deposition loadings could be calculated. Particulate sodium (Na^+), particulate potassium (K^+), particulate calcium (Ca^{2+}), and particulate magnesium

(Mg^{2+}) were determined for part of the year to evaluate the presence of atmospheric base cations.

Field Operations

Each site was equipped with a shelter (complete with telephone and 100-amp electrical service), two 10-meter (m) towers, a meteorological system, an O_3 and air-quality monitoring system, and a data acquisition system (DAS). Windspeed and wind direction were measured at 10 m, temperature was measured at 9 m and 2 m, and relative humidity was measured at 9 m. Precipitation and solar radiation were measured on 1-m platforms located outside the rain and sun shadows of the shelter and towers. Surface wetness was measured at a height of approximately 3 to 6 inches above the surrounding low-lying vegetation (typically grass).

Filter pack sampling and O_3 measurements were performed at 10 m using a tilt-down aluminum tower. Filter pack flow was maintained at 1.50 liters per minute (L/min) at eastern sites and 3.00 L/min at western sites with a mass flow controller and recorded as hourly averages. O_3 was measured via ultraviolet (UV) absorbance

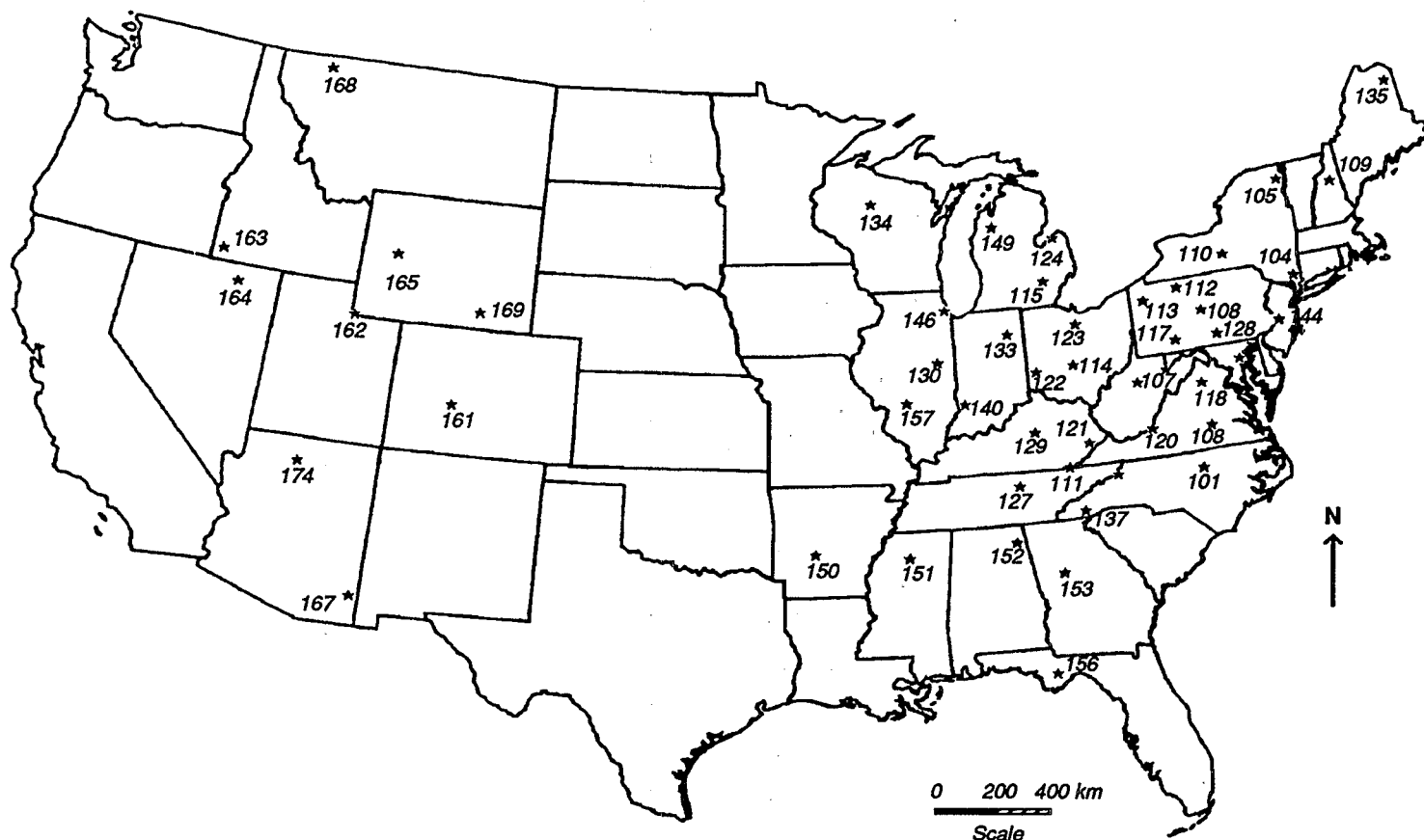


Figure 1. Status of NDDN Monitoring Sites — December 1989

using an all-Teflon® sampling line. Periodic checks indicated that line losses through the inlet system were consistently less than 3 percent.

All field equipment was subjected to inspections and multipoint calibrations by ESE personnel on a quarterly basis. In addition, independent equipment audits were performed semiannually by ERC Environmental and Energy Services, Inc., and randomly by EPA or its designee.

Laboratory Operations

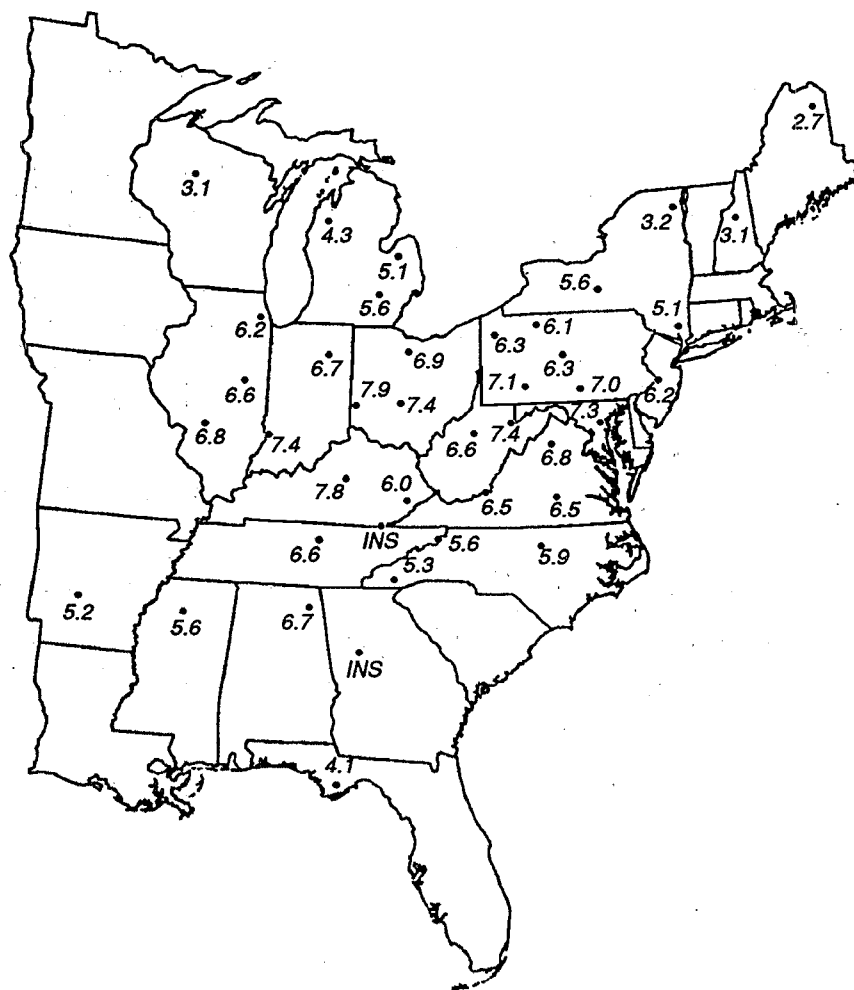
Filter pack samples were loaded, shipped, received, extracted, and analyzed by ESE personnel at the Gainesville, Florida laboratory. Filter packs contained three types of filters in sequence: a Teflon® filter for collection of aerosols, a nylon filter for collection of HNO_3 , and dual potassium carbonate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

Following receipt from the field, exposed filters and blanks were placed in color-coded bottles and extracted in 25 milliliters (mL) of deionized water (Teflon®), 25 mL of 0.003 N NaOH (nylon), or 50 mL of 0.05-percent H_2O_2 (cellulose). Extracts were then analyzed for SO_4^{2-} and NO_3^- by micromembrane suppressed ion chromatography (IC) using a Dionex Model 4000i IC equipped with an Autoion 1000 Controller. Analysis of Na^+ , Mg^{2+} , and Ca^{2+} was performed with a Perkin-Elmer P-2 inductively coupled argon plasma (ICAP) emission spectrometer. Analysis of NH_4^+ was by the automated indophenol method using a Technicon II or TRAACS-800 AutoAnalyzer system. Analysis of K^+ was via atomic emission on a Perkin-Elmer 5100 atomic absorption spectrophotometer. Various QC samples were routinely analyzed to track the accuracy and precision of laboratory data.

Data Management

Data Management Center activities consisted of three major operations: data acquisition, validation, and transmittal to EPA. The data acquisition process stressed multiple levels of redundancy to minimize data loss. The primary mode of data acquisition from the field was via telephone modem. If daily polling resulted in incomplete data capture from any site, then diskettes of data from the primary and backup DAS were read into the database management system. If the database was still incomplete, then missing data were entered manually from site printouts. Each datum was automatically given a source flag that could be used to trace its mode of entry into the system. Data validation consisted of a thorough review of

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.



INS = Insufficient Samples for the Period Covered (<75%)

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

operator logs, onsite reasonableness checks, results of field calibrations and audits, and a variety of parameter-specific range and consistency checks. Validated data were submitted to EPA on a quarterly basis.

Results And Discussion

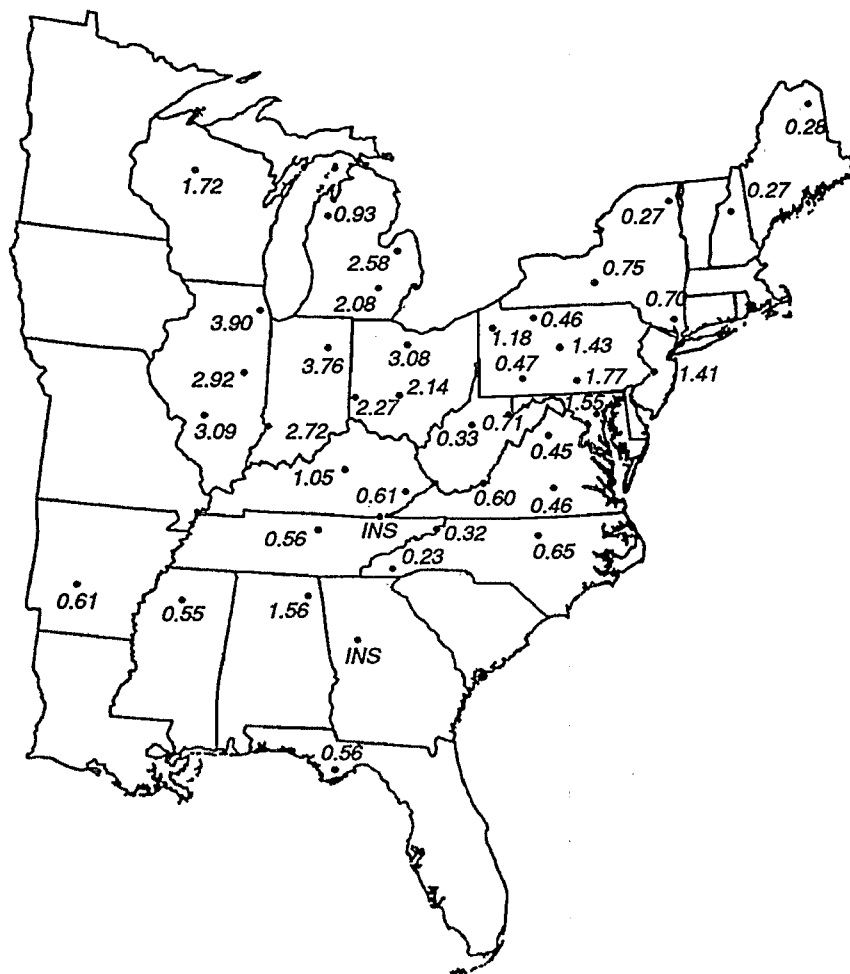
Filter Pack Measurements

Annual arithmetic mean concentrations of SO_4^{2-} for 1989 ranged from 7.9 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) in western Ohio to 2.7 $\mu\text{g}/\text{m}^3$ in northern Maine (see Figure 2). Annual averages of 5.0 $\mu\text{g}/\text{m}^3$ covered nearly the entire eastern United States, from New York and Michigan to northern Mississippi and Alabama. Only sites from northern New York to Maine, northern Michigan, Wisconsin, and Florida exhibited concentrations below 5.0 $\mu\text{g}/\text{m}^3$.

Quarterly data for SO_4^{2-} showed dramatic differences from season to season, but reasonably consistent locations of peak concentrations. The highest concentrations were observed during the third quarter (i.e., summer) and the lowest concentrations in the first quarter (i.e., winter). The seasonal progression of SO_4^{2-} concentrations, therefore, appears to follow temperature and solar radiation, which also exhibit maxima and minima in summer and winter, respectively.

Semiannual average SO_4^{2-} concentrations for the nine western sites ranged from 1.65 $\mu\text{g}/\text{m}^3$ in southern Arizona to 0.65 $\mu\text{g}/\text{m}^3$ in southern Idaho and were invariably lower than those observed across the eastern United States.

Annual average concentrations for NO_3^- (see Figure 3) exhibited much more variability than SO_4^{2-} and a definite pattern of



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

higher concentrations in the midwest than elsewhere. The lowest concentrations were observed at forested sites in New England and the southern Appalachian Mountains, while the highest concentrations (i.e., greater than $2.0 \mu\text{g}/\text{m}^3$) were observed in agricultural areas of the midwest. Intermediate values (i.e., 1.0 to $2.0 \mu\text{g}/\text{m}^3$) appear to be associated with agricultural sites anywhere in the eastern United States. Quarterly data for NO_3^- exhibit a seasonal cycle that runs counter to that of SO_4^{2-} . That is, the highest concentrations occurred during the first quarter and the lowest in the third quarter. This cycle is consistent with the temperature-dependent equilibrium between particulate NH_4NO_3 and gaseous NH_3 and HNO_3 . Re-

sults for the western sites indicated semi-annual concentrations similar to the lowest values observed at eastern sites.

Annual average concentrations of NH_4^+ (see Figure 4) ranged from $3.2 \mu\text{g}/\text{m}^3$ in northern Indiana to $0.69 \mu\text{g}/\text{m}^3$ in Maine and, in general, exhibited higher values at agricultural sites than at forested sites. Since the midwest is primarily agricultural, this results in regional differences between the midwest, northeast, and southeast. Concentrations above $2.0 \mu\text{g}/\text{m}^3$ were found at all sites within Illinois, Indiana, and Ohio, plus the two southernmost sites in Michigan. Third and fourth quarter results for the western sites showed about a factor of 2 range in concentrations. The highest value ($0.57 \mu\text{g}/\text{m}^3$) occurred in

southern Arizona and the lowest average value ($0.28 \mu\text{g}/\text{m}^3$) occurred in Montana, Wyoming, and Nevada.

Annual averages for HNO_3 (see Figure 5) exhibited a maximum concentration of $3.6 \mu\text{g}/\text{m}^3$ in southeastern Pennsylvania and a minimum of $0.7 \mu\text{g}/\text{m}^3$ in northern Maine. Concentrations in excess of $3.0 \mu\text{g}/\text{m}^3$ occurred at six sites, while concentrations of $1.0 \mu\text{g}/\text{m}^3$ or less occurred at another six sites. The overall pattern of HNO_3 might be influenced by terrain as much or more than other factors (e.g., emissions).

Quarterly data showed that HNO_3 concentrations are relatively constant. For the 41 eastern sites, averages ranged from roughly $1.9 \mu\text{g}/\text{m}^3$ during the fourth quarter to $2.5 \mu\text{g}/\text{m}^3$ during the second quarter. Thus, seasonal variability is much less than and slightly out of phase with SO_4^{2-} (i.e., another secondary pollutant). Results for the western region indicate concentrations that are somewhat lower than the lowest values observed in the east.

Annual average data for SO_2 ranged from $23.2 \mu\text{g}/\text{m}^3$ in southwestern Pennsylvania to $2.4 \mu\text{g}/\text{m}^3$ in Maine (see Figure 6). Concentrations of $15 \mu\text{g}/\text{m}^3$ or greater occurred in a small area encompassing Pennsylvania and Maryland, as well as at isolated sites in northern Illinois, southern Indiana, and western Ohio. A much larger area extending from Kentucky and Indiana eastward to New York exhibited concentrations in the range of 10 to $15 \mu\text{g}/\text{m}^3$. Quarterly averages show dramatic changes in concentrations from season to season. Mean concentrations are nearly a factor of 3 higher in the first quarter ($16.2 \mu\text{g}/\text{m}^3$) than in the third quarter ($6.2 \mu\text{g}/\text{m}^3$). Despite large relative changes in concentrations, the locus of peak concentrations remains more or less stationary from season to season. Concentration data for the western sites ranged from $1.8 \mu\text{g}/\text{m}^3$ in southern Arizona to $0.4 \mu\text{g}/\text{m}^3$ in central Colorado and northern Nevada and southern Idaho.

Day Versus Night Concentration Data

Results for SO_4^{2-} showed appreciable seasonality in day/night concentration differences. Results for fourth quarter 1988 and first quarter 1989 showed nearly identical averages for day and night at virtually all sites. During second and third quarter 1989, differences became increasingly more pronounced and were usually statistically significant. Results for the pre-

sumptive aerosol species NO_3^- and NH_4^+ also showed similar day/night variability.

Data for HNO_3 and SO_2 showed more frequent and pronounced day/night differences than the aerosol species. Concentrations of HNO_3 were lower at night for nearly every site-season combination. This was especially apparent during summer, when all sites showed statistically significant nocturnal reductions ranging from 35 to 80 percent. The day/night behavior of SO_2 is similar to that of HNO_3 . Statistically significant differences occurred at most sites for most seasons, and the magnitude of the differences increased from winter to summer. Coupled with shallow nocturnal boundary layers, dew formation could be responsible for essentially complete depletion of SO_2 and HNO_3 at night.

Aerosol Ion Balances

Ion balances, in nanoequivalents per cubic meter (neq/m^3), from Teflon® filter extracts at three NDDN sites are illustrated in Figure 7. The sites presented appear to be representative of the eastern seaboard (Site 108), forested northeast (Site 117), and agricultural midwest (Site 133). In general, the data for these sites indicated that SO_4^{2-} and NH_4^+ are the dominant anion and cation species, respectively, at both forested and agricultural sites in the eastern United States, and that the nature of the ion balances differs between forested and agricultural sites. The forested sites exhibited fairly minor ionic contribution for NO_3^- and the base metal cations and a clear excess of anions over cations. The agricultural midwestern site, in contrast, exhibited significant ionic contributions from NO_3^- , Mg^{2+} , and Ca^{2+} and an apparent excess of cations. Results for the western sites indicated a clear excess of cations in the aerosol samples, with NH_4^+ comprising only about 50 percent of the total cations; NO_3^- is also a minor contributor to the overall ion balance.

Ozone

Annual average O_3 concentrations at eastern sites ranged from 22.1 parts per billion (ppb) in eastern Kentucky to 45.3 ppb in northern Virginia. The highest annual averages occurred at mountaintop sites along the Blue Ridge and Appalachian Mountains, while the lowest annual averages occurred in sites located in sharp valleys and in semiurban areas. Hourly average concentrations equal to or greater than the National Ambient Air Quality Standards (NAAQS) were relatively rare during 1989. Eight sites exhibited one or more hourly values greater than or equal

to 120 ppb, and only 15 days of exceedances occurred at the 43 sites operational throughout the year.

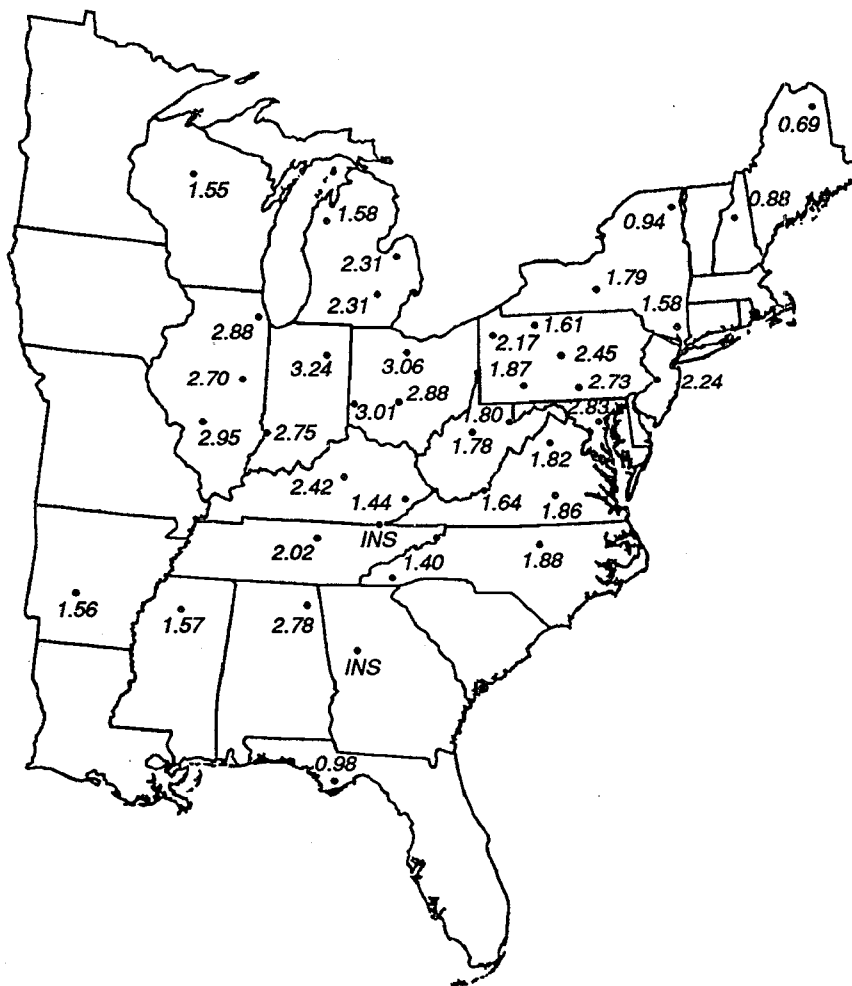
Estimated Dry Deposition

Estimated dry deposition for SO_4^{2-} plus SO_2 appeared to be highest in western Pennsylvania and lowest in southwestern North Carolina, northern Maine, and northern Florida. This pattern reflects the annual average SO_2 concentration, since it appears unlikely that SO_4^{2-} contributes more than 30 percent of the estimated dry deposition at any site. Relatively high deposition in northern Illinois, southern Indiana, and eastern Tennessee may be the result of local SO_2 emissions.

Estimated dry deposition of NO_3^- plus HNO_3 showed similar values over much of

the northeast and midwest but considerable variability in the vicinity of the Appalachian Mountains. Deposition at mountaintop site in Virginia appeared to be approximately three times that at nearby complex terrain sites in eastern Kentucky and North Carolina. The overall pattern is almost an exact transformation of annual HNO_3 concentration due to large differences in concentration and deposition velocity between HNO_3 and NO_3^- . At no site was NO_3^- responsible for more than 15 percent of the estimated dry deposition of NO_3^- plus HNO_3 .

Results for sulfur deposition suggest that wet deposition is the dominant process in northern New York, but that at most other sites wet and dry deposition could be similar, especially if the upper limit for the



deposition velocity of SO_2 is approached. Results for nitrogen suggest regional differences in the comparability of wet and dry deposition. For the northeast, dry deposition would be comparable to wet deposition only if the upper limit deposition velocity for HNO_3 is attained. Data for the midwest and parts of the southeast, in contrast, suggest that wet and dry deposition are comparable even if the lower limit deposition velocity for HNO_3 is attained.

Conclusions And Recommendations

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

1. Results of filter pack analyses throughout the year at 41 eastern sites show species-dependent variability from site to site, season to season, and day to night. Annual average concentrations of atmospheric SO_4^{2-} exhibited peak values of approximately $7.8 \mu\text{g}/\text{m}^3$ in western Ohio and central Kentucky and minimum values around 2 to $4 \mu\text{g}/\text{m}^3$ on the periphery of the network (i.e., Maine, Wisconsin, and Florida). Spatial variability for SO_4^{2-} was relatively low as compared to other species. Data for nine western sites operated over the last half of 1989 showed appreciably lower concentrations than eastern sites (i.e., 0.7 to $1.7 \mu\text{g}/\text{m}^3$). Among western sites, the highest SO_4^{2-} concentrations were consistently observed in northern and southern Arizona.

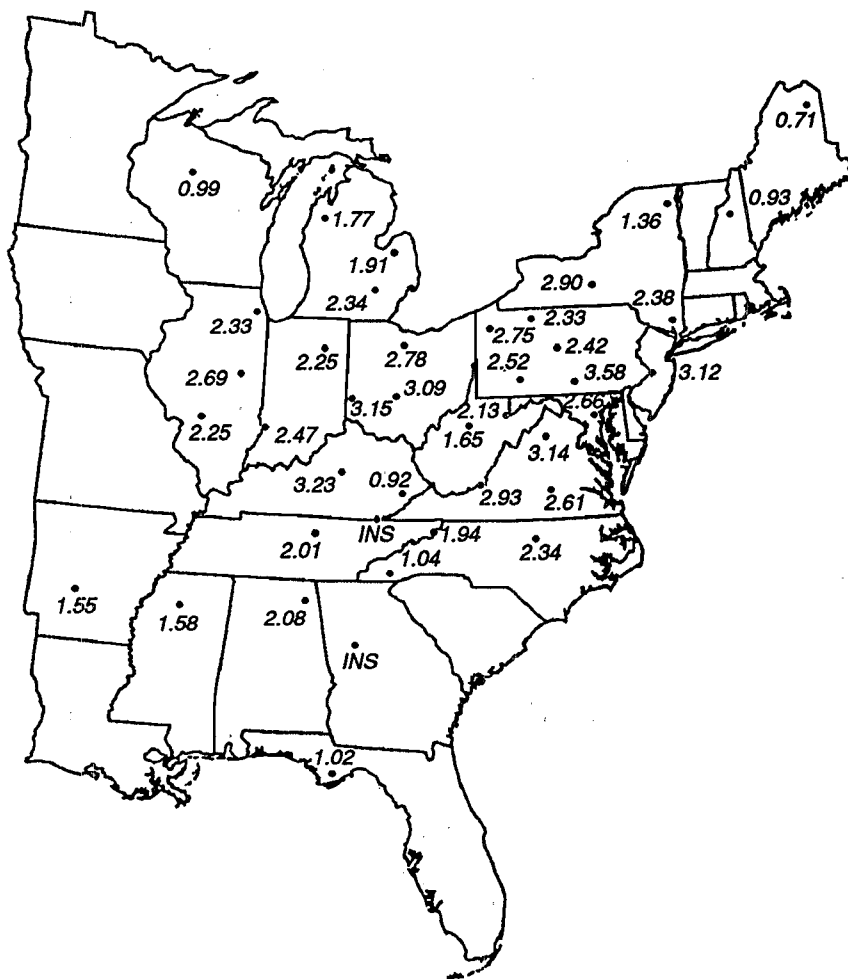
2. Annual SO_2 concentrations for eastern sites showed a maximum of $23.2 \mu\text{g}/\text{m}^3$ in western Pennsylvania and an ellipse of values above $10 \mu\text{g}/\text{m}^3$ extending eastward from Illinois and Kentucky to the eastern seaboard. As for SO_4^{2-} , the lowest concentrations of SO_2 among eastern sites (i.e., 2.4 to $3.0 \mu\text{g}/\text{m}^3$) were observed in Maine, Wisconsin, and Florida. Western sites exhibited dramatically lower SO_2 than eastern sites (i.e., 0.4 to $1.3 \mu\text{g}/\text{m}^3$) and highest concentrations in southern Arizona.

3. Annual average HNO_3 ranged from $3.6 \mu\text{g}/\text{m}^3$ in southeastern Pennsylvania to $0.7 \mu\text{g}/\text{m}^3$ in Maine. Concentrations above $2.0 \mu\text{g}/\text{m}^3$ covered a broad region (excluding a few isolated sites) from the Great Lakes to northern Alabama and Georgia. Average HNO_3 for the western sites is typically about 50 percent of the lowest values observed in the east. Arizona sites, however, exhibited HNO_3 concentrations similar to those reported for Florida, Wisconsin, and Maine.

4. Annual NO_3^- concentrations showed marked regional character, with maxima above $2.0 \mu\text{g}/\text{m}^3$ throughout the midwest and minima below $0.5 \mu\text{g}/\text{m}^3$ at scattered locations from New England to Florida. Examination of land use characteristics suggests a link between NO_3^- and land use. The highest overall concentrations correlate strongly with agricultural areas (in any region), and the lowest concentrations correlate with forested areas. Results for the western sites indicate comparable concentrations to forested areas of the eastern United States.

5. Annual average NH_4^+ data ranged from $3.2 \mu\text{g}/\text{m}^3$ in northern Indiana to $0.7 \mu\text{g}/\text{m}^3$ in Maine and exhibited spatial variability similar to NO_3^- . Concentrations above $2.0 \mu\text{g}/\text{m}^3$ were observed throughout the midwest and at sites near agricultural activity in the southeast and northeast. Only sites in extreme northern New York, New Hampshire, Maine, and Florida exhibited annual averages below $1.0 \mu\text{g}/\text{m}^3$. Data for western sites showed the majority of NH_4^+ concentrations in the range of 0.2 to $0.4 \mu\text{g}/\text{m}^3$. Consistent with other measurements, the highest concentration among western sites occurred in southern Arizona.

6. Estimated dry deposition of sulfur species (i.e., SO_4^{2-} and SO_2) ranged

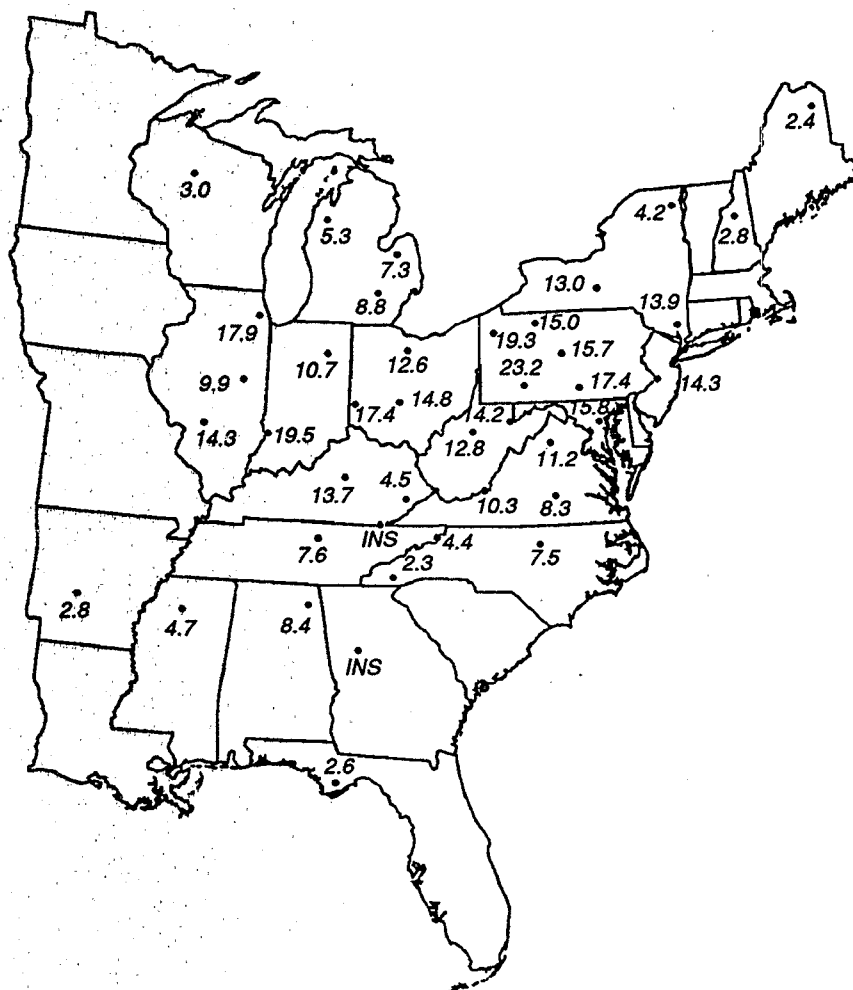


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Figure 5. Annual average HNO_3 concentrations ($\mu\text{g}/\text{m}^3$) for the eastern United States during 1989.

from about 100 equivalents per hectare (eq/ha) in Maine to about 750 eq/ha in western Pennsylvania. Estimated dry deposition of nitrogen species (i.e., HNO_3 and NO_3^-) ranged from about 55 eq/ha in Maine to about 290 eq/ha in eastern Pennsylvania. Due to faster deposition velocities, the gaseous species HNO_3 and SO_2 represent a large fraction of dry nitrogen and dry sulfur deposition, respectively. Comparison of wet and dry deposition of sulfur and nitrogen at 28 eastern sites suggests that the two are of similar magnitude over large areas.

7. Inspection of O_3 data for 1989 shows that there were relatively few episodes of elevated concentrations. Comparison of O_3 data for 1988 and 1989 shows that these two years differ significantly by virtually any measure. For example, the 18 sites operational during 1988 reported 98 exceedances of NAAQS for O_3 of 120 ppb, while the 43 sites operational during 1989 reported only 15.
8. Calculations of aerosol ion balances for selected sites indicate general differences between regions and land use categories. Forested northeastern and southeastern sites exhibited an excess of measured anions (SO_4^{2-} and NO_3^-) over measured cations (NH_4^+ , Na^+ , K^+ , Ca^{2+} , and Mg^{2+}); agricultural midwestern sites exhibited a slight excess of cations over anions; and western sites exhibited a substantial excess of cations over anions.
9. Operation of dual, side-by-side air samplers at four sites indicates that filter pack measurements can be very precise. For three eastern sites, analyses of SO_4^{2-} , SO_2 , and NH_4^+ exhibited precision estimates of 5 percent, or better; NO_3^- and HNO_3 exhibited precision of 10 percent, or better. For a single site in the western United States (i.e., 167), measurements of the above species uniformly exhibited precision within 5 percent.



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Figure 6. Annual average SO_2 concentrations ($\mu\text{g}/\text{m}^3$) for the eastern United States during 1989.

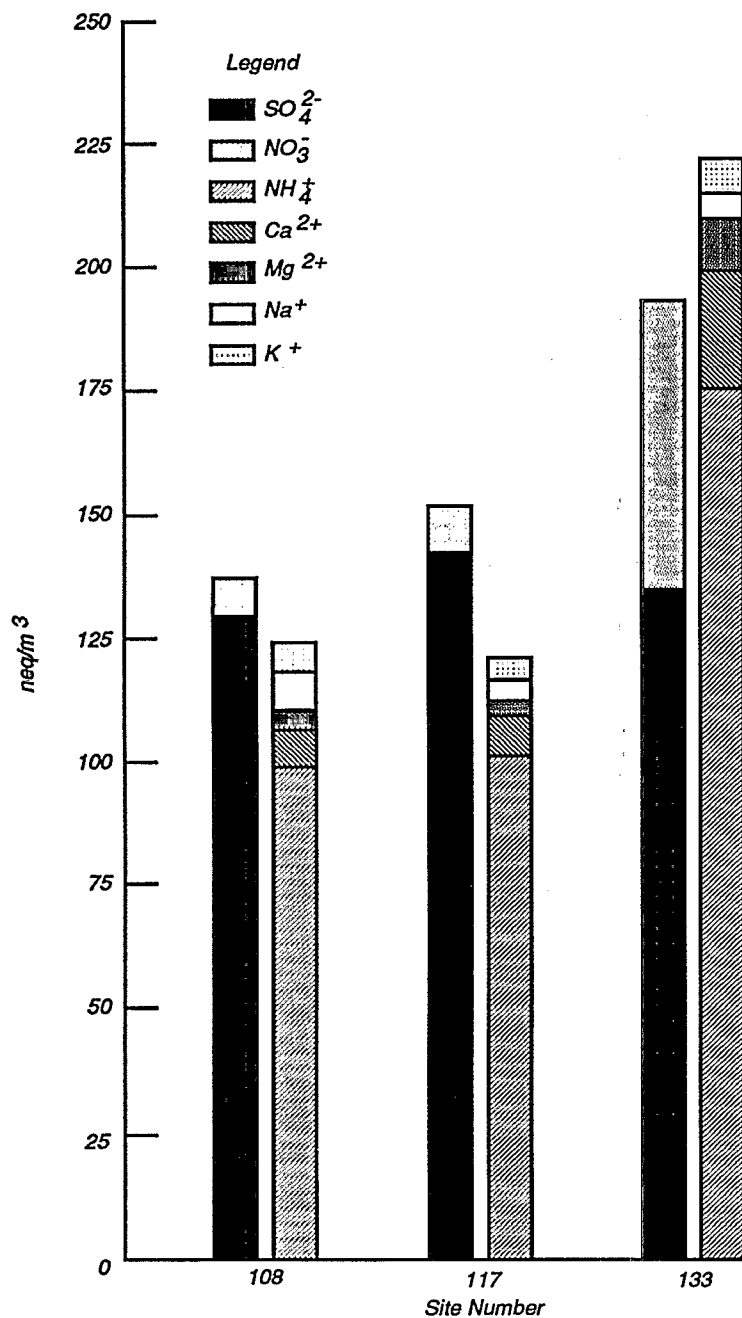
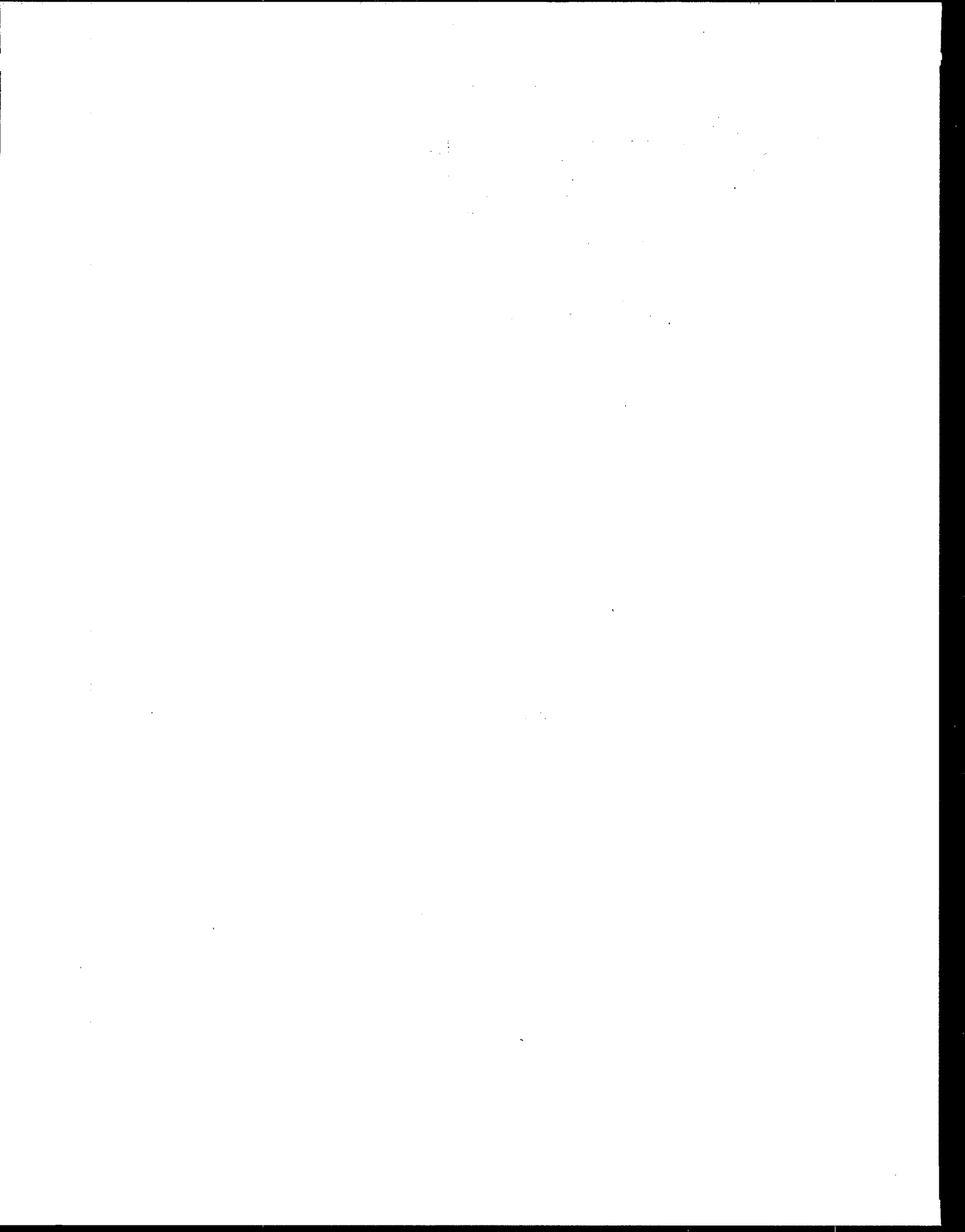


Figure 7. Aerosol ion balances for Sites 108, 117, and 133.



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The complete report, entitled "National Dry Deposition Network: Third Annual Progress Report (1989)," (Order No. PB91-181784; Cost: \$23.00, subject to change) will be available only from:

*National Technical Information Service
5285 Port Royal Road
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Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:
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