



# Project Summary

## CASTNet National Dry Deposition Network 1990-1992 Status Report

The National Dry Deposition Network (NDDN) was established to provide longterm 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 ( $SO_4^-$ ), 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, 1991, and 1992 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  $\pm 5$  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.

*This Project Summary was developed by the U.S. Environmental Protection Agency's (EPA's) National Environmental Research 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).**

## Background

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.

In 1986, EPA contracted with Environmental Science & Engineering, Inc. (ESE) to establish and operate the 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 ( $V_d$ s) 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).

The full 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 through 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 mea-

surement 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.

## Procedures

Ambient measurements for  $O_3$ ,  $SO_2$ ,  $SO$ ,  $NO$ ,  $HNO_3$ ,  $NH$ , 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, 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 ( $^{\circ}C$ ) 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 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.

Ozone 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. Surface information was collected to determine the frequency of conditions 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. Leaf area index (LAI) measurements were conducted at all NDDN sites during the summers of 1991 and 1992. LAI was measured using an LAI-2000 Plant Canopy Analyzer manufactured by Li-Cor (Lincoln, NE).

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  $SO$  and  $NO$  by micromembrane-suppressed ion chromatography (IC). Teflon® filter extracts were also analyzed for  $NH$  by the automated indophenol method. Wet deposition samples were filtered and then analyzed for pH, conductivity, acidity, sodium ( $Na^+$ ), potassium ( $K^+$ ),  $NH$ , calcium ( $Ca^{2+}$ ), magnesium ( $Mg^{2+}$ ), chloride ( $Cl^-$ ), nitrite ( $NO_2^-$ ),  $NO$ , and  $SO$ .

Atmospheric concentrations of particulate  $SO$ ,  $NO$ , and  $NH$  were calculated based on the analysis of Teflon® filter extracts;  $HNO_3$  was calculated based on

the NO found in nylon filter extracts; and SO<sub>2</sub> was calculated based on the sum of SO<sub>4</sub><sup>-</sup> found in nylon and cellulose filter extracts.

Dry deposition calculations for 1990 through 1992 were made using the multi-layer version of the National Oceanic and Atmospheric Administration (NOAA) inferential model. The model calculates fluxes, F, as the product of measured concentrations and inferred V<sub>d</sub>s. Deposition velocity, in turn, is calculated as the inverse sum of three separate resistances: atmospheric resistance (R<sub>a</sub>), boundary layer resistance (R<sub>b</sub>), and canopy resistance (R<sub>c</sub>).

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<sub>d</sub> are averaged over a week and multiplied by the weekly integrated concentrations to produce weekly fluxes of HNO<sub>3</sub>, SO<sub>2</sub>, and particles. Ozone flux is calculated using hourly measurements of O<sub>3</sub> and hourly values of V<sub>d</sub>. Weekly flux calculations for all chemical species are considered valid only if ≥70 percent of hourly V<sub>d</sub> values are available for that week. Annual values are considered valid only if V<sub>d</sub> and flux data for all four seasons are available.

## Conclusions

The full report presents quantitative information on dry deposition fluxes and atmospheric concentrations for the network from 1990 through 1992. Annual concentration data for sulfur and nitrogen species show fairly consistent spatial patterns. In the eastern United States, the highest average concentrations of SO<sub>4</sub><sup>-</sup> [6 to 7 micrograms per cubic meter (μg/m<sup>3</sup>)] and SO<sub>2</sub> (15 to 20 μg/m<sup>3</sup>) occur in an area surrounding the Ohio River Valley. Average SO<sub>4</sub><sup>-</sup> decreases gradually toward the periphery of the network to about 2.0 μg/m<sup>3</sup> in northern Maine and 3 to 4 μg/m<sup>3</sup> in Florida, Arkansas, and Wisconsin. Average SO<sub>2</sub> exhibits much more local variability than SO<sub>4</sub><sup>-</sup> and decreases more rapidly towards the periphery of the network. For western sites, SO<sub>4</sub><sup>-</sup> and SO<sub>2</sub> concentrations are generally well below 1.0 μg/m<sup>3</sup> and show no strong evidence of a pattern, except for somewhat elevated values at two Arizona sites.

Atmospheric concentration data for HNO<sub>3</sub> and NO also show substantial variability across the network; however, differences between eastern and western sites are not as great as for SO<sub>4</sub><sup>-</sup> and SO<sub>2</sub>. In general, concentration patterns for HNO<sub>3</sub> and NO appear to be strongly influenced by land-use and topographic features. Maximum HNO<sub>3</sub> concentrations (3 to 4 μg/m<sup>3</sup>) are observed at scattered sites in New York, Pennsylvania, Virginia, and Ohio, while minimum concentrations (<1.0 μg/m<sup>3</sup>) are observed in Maine, Arkansas, Florida, Kentucky, and North Carolina. Substantial variability in HNO<sub>3</sub> concentrations (factors of 2 to 3) occurs over fairly short distances in and around the southern Appalachian Mountains.

Annual patterns of NO aerosol show peak concentrations (3 to 4 μg/m<sup>3</sup>) in agricultural areas of the midwest and minimum concentrations (<0.5 μg/m<sup>3</sup>) 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.

Dry deposition calculations show that annual sulfur (S) fluxes (SO<sub>4</sub><sup>-</sup> plus SO<sub>2</sub>) range from 1 kg-S/ha to about 10 kg-S/ha in the eastern United States and from 0.2 kg-S/ha to 1.5 kg-S/ha in the western United States. Deposition of SO<sub>2</sub> 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<sub>2</sub> deposition is controlled primarily by variability in SO<sub>2</sub> concentrations, rather than variability in deposition velocity.

Dry deposition of nitrate-nitrogen (HNO<sub>3</sub> plus NO) ranges from <1 kg-N/ha to 5 kg-N/ha in the eastern United States and from 0.3 kg-N/ha to 1.3 kg-N/ha in the western United States. Deposition of HNO<sub>3</sub> 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<sub>d</sub>s). These results are uncertain by ±20 percent to

±40 percent and are biased low for a number of reasons.

Total deposition estimates (i.e., measured wet deposition plus calculated dry deposition) for 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<sub>2</sub> (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.

Data from sites in and around the Appalachian Mountains indicate that concentrations and fluxes of SO<sub>2</sub> and HNO<sub>3</sub> can vary by as much as factors of 2 to 5 within only a few hundred kilometers. Data from two closely spaced 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<sub>d</sub>s than the valley site. Together, these factors give rise to dry deposition rates that are factors of 1.6 (for SO<sub>4</sub><sup>-</sup>) to 4.4 (for HNO<sub>3</sub>) higher at the ridge site than the valley site. 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, 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<sub>2</sub> concentrations between networks and to compare United States and Canadian approaches for estimating dry deposition fluxes.

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**Ralph Baumgardner** is the EPA Project Officer (see below).

The complete report, entitled "CASTNet National Dry Deposition Program 1990-1992 Status Report," (Order No. PB95-234506; Cost: \$27.00, subject to change) will be available only from:

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