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Research and Development

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Project Summary

Clean Air Status and Trends Network Deposition Summary Report (1987-1995)

The National Dry Deposition Network (NDDN) was established in 1986 to provide long-term estimates of dry acidic deposition across the continental U.S. In 1990, NDDN was incorporated into the Clean Air Status and Trends Network (CASTNet) which was created to address the requirements of the Clean Air Act Amendments (CAAA). Approximately 50 standard sites were operational from 1989 through 1995 with the majority of the sites located in the rural eastern U.S. Each site is 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. Precipitation samples were collected at selected sites and analyzed for acidity and related species in order to estimate wet deposition. Under CASTNet, a visibility monitoring network and a Mountain Acid Deposition Program (MADPro) were established. A micrometeorological model has been applied to calculate deposition velocities and dry deposition fluxes.

Atmospheric concentration data showed species-dependent variability in space and time. In general, the highest annual concentrations [>6.0 micrograms per cubic meter ($\mu g/m^3$) for SO_4^{2-}] were observed along the Ohio River valley, and these were a factor of 5 to 10 times higher than concentrations observed in the west. Significant concentration gradients were observed between the northeast and upper northeast, and the Midwest and upper Midwest. A comparison of 1989 and 1995 annual concentrations show SO_2 concentrations averaged over all eastern sites decreased by 43%. Sulfate concentrations decreased by 23%. Annual average concentrations of nitrogen species showed little change between 1989 and 1995. These results do not account for the yearly variability in concentrations.

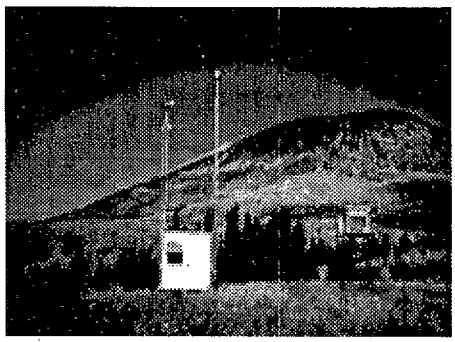


Figure 1. A typical CASTNet monitoring station (Site 161, Gothic, CO).

Dry deposition calculations for 1987 through 1995 showed that SO_2 accounts for more than 70% of dry sulfur deposition at eastern sites and more than 55% of dry sulfur deposition at western sites. HNO_3 accounts for more than 65% of dry nitrogen deposition at all sites. Data for all eastern sites showed a 29% reduction in SO_2 deposition and a 6% reduction in SO_4^{2-} deposition from 1989 to 1995. There is no apparent trend for western sites. The dry deposition calculations represent lower bound estimates of actual fluxes and do not account for quantified uncertainties of the model.

Annual precipitation concentrations of SO_4^{2-} from 1989 to 1995 declined significantly only in certain parts of the eastern region. There were no statistically significant trends in precipitation concentrations of NO_3^-. Wet depositions

from 1989 to 1995 showed statistically significant reductions of sulfur species for the eastern region. No statistically significant reductions were observed for nitrogen species.

Total (wet plus dry) deposition estimates from 1989 to 1995 showed that dry deposition accounts for about 15 to 45% of total sulfur deposition, and 20 to 60% of total nitrogen deposition. The total deposition data showed a 32% reduction in atmospheric sulfur and no trend in nitrogen from 1987 through 1995.

Ozone data indicated considerable geographic variability in annual averages, but little yearly variability at individual stations. There was no discernible trend in annual averages. Hourly concentrations above the 1-hour National Ambient Air Quality Standard (NAAQS) were limited to sites in the Washington-New York corridor. Ozone measurements show that about 80% of the eastern sites would have recorded violations of the new 8-hour O_3 standard.

Data from MADPro for 1994 to 1996 showed that cloudwater can be the primary pathway for deposition of pollutants to high elevation ecosystems.

An initial analysis of visual air quality measurements taken in 1994 shows a strong relationship among atmospheric light scattering, fine particle concentrations, and visual quality. Fine particle concentrations peaked in the summer and were highly correlated with fine SO_4^{2-}, which is declining in the eastern U.S. Fine particle mass concentrations were below the proposed national standards of 15 μg/m³ annual average and 65 μg/m³ 24-hour average.

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

In 1986, the EPA contracted with Environmental Science and Engineering, Inc. (ESE) [now QST Environmental Inc. (QST)] to establish and operate the National Dry Deposition Network (NDDN). The objective of the NDDN was to obtain field data at approximately 50 sites throughout the U.S. to establish patterns and trends of dry deposition. The approach adopted by the NDDN was to estimate dry deposition using measured air pollutant concentrations and modeled deposition velocities estimated from meteorological, land use, and site characteristic data. The model currently used for dry deposition calculations is a multi-layer version of the Big Leaf Model.

The complete report summarizes results of NDDN and CASTNet monitoring activities from 1987 through 1995. Concentration and deposition data for atmospheric sulfur and nitrogen species are presented and analyzed. Annual and seasonal averages for each year are discussed regionally. Relative contribution of gases versus aerosols are evaluated. Wet deposition data for 21 CASTNet and 38 National Atmospheric Deposition Program (NADP) sites are presented and then used, along with dry deposition calculations, to estimate total depositions of sulfur and nitrogen. The relative magnitude of wet and dry deposition is discussed. Ozone concentrations and exposure statistics are analyzed and discussed in terms of existing and proposed national air quality standards.

Data and results from the visibility and mountain acid deposition programs are briefly discussed. A mobile system for the direct measurement of dry deposition is described along with field studies in which the system was successfully utilized. Initial results of the comparison between filter packs and annular denuders are also given.

Procedures

Measurements of ambient O_3, SO_2, SO_4^{2-}, NO_3^-, HNO_3, NH_4^+, and meteorological variables required for dry deposition calculations are taken at each CASTNet site. Meteorological variables and O_3 concentrations are recorded continuously and reported as hourly averages consisting of a minimum of nine valid 5-minute averages. Atmospheric sampling for sulfur and nitrogen species is 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 (Whatman) filters. The Teflon® filter removes particulate SO_4^{2-}, NO_3^-, and NH_4^+; the nylon filter removes HNO_3; and the cellulose filter, which is impregnated by potassium carbonate (K_2CO_3), is used for removal of SO_2. In practice, a fraction (usually <20%) of ambient SO_2 is captured on the nylon filter. The nylon filter SO_2 and Whatman filter SO_2 are therefore summed to provide weekly average concentrations. The nylon filter HNO_3 is converted to NO_3^- and added to the Teflon® filter NO_3^- to provide weekly total NO_3^- concentrations.

Filter packs are prepared and shipped to the field weekly and exchanged at each site every Tuesday. Blank filter packs are collected monthly to evaluate passive collection of particles and gases as well as contamination during shipment and handling. At 21 sites located more than 50 kilometers (km) from NADP sites, precipitation samples are collected weekly (according to NADP protocols) and shipped to QST for chemical analysis.

Filter pack samples and O_3 measurements are taken at 10 meters (m) using a tilt-down aluminum tower (Aluma, Inc.). Filter pack flow is maintained at 1.50 liters per minute (Lpm) at eastern sites and 3.00 Lpm at western sites, for standard conditions of 25 degrees Celsius (°C) and 760 millimeters of mercury (mmHg) with a mass flow controller (MFC). Precipitation samples are collected in precleaned polyethylene buckets using an Andersen Model APS precipitation sampler. Buckets are placed on the sampler on Tuesday and removed, whether or not rainfall has occurred, the following Tuesday. Buckets are weighed in the field, decanted to a 1-liter (L) polyethylene bottle, sealed, and shipped to QST for chemical analysis. Precipitation amount (depth) is also monitored at wet deposition sites.

O_3 is measured via ultraviolet (UV) absorbance with a Thermo-Environmental Model 49-103 analyzer operating on the 0- to 500-part per billion (ppb) range. Ambient air is 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 prevent particle deposition within the system. Periodic checks indicate that online losses through the inlet system are consistently less than 3%. Zero, precision (60 ppb),

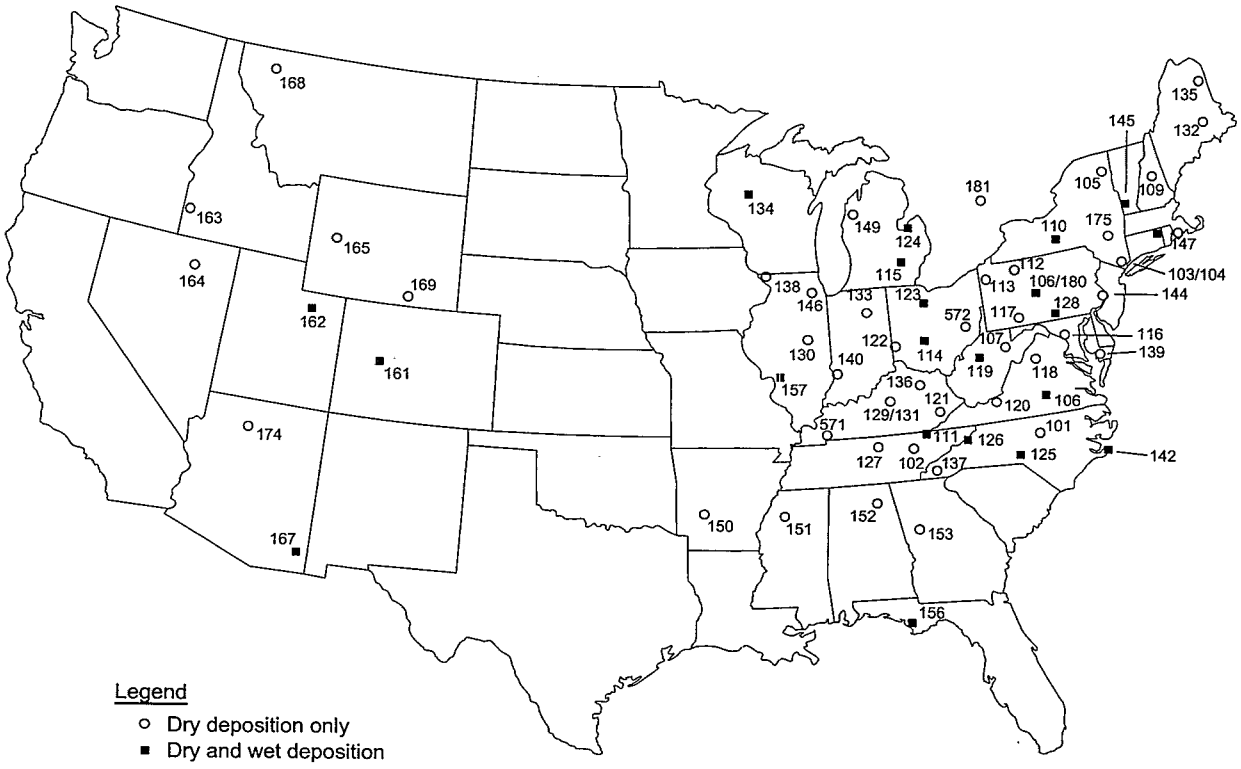


Figure 2. CASTNet monitoring sites (Source: QST).

and span (400 ppb) checks of the O_3 analyzer are performed every third day using an internal O_3 generator.

In addition, various observations are periodically made at the CASTNet sites to support model calculations of dry deposition. Site operators record surface conditions (e.g., dew, frost, snow) and vegetation status weekly. Vegetation data are obtained to track evolution of the dominant plant canopy, from leaf emergence (or germination) to senescence (or harvesting). Once a year, site operators also provide information on major plant species and land-use classifications within 1.0 km of the site. Additional land-use data were 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 taken at all CASTNet sites during the summers of 1991 and 1992. LAI was measured using an LAI-2000 Plant Canopy Analyzer manufactured by Li-Cor (Lincoln, NE).

All field equipment is 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. (Ogden), and randomly by EPA or its designee. Results of field calibrations are used to assess sensor accuracy and flag, adjust, or invalidate field data.

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

Wet deposition samples are 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-}.

A micrometeorological model called the multilayer model (MLM) was used to simulate deposition velocities for the measured ambient species as the inverse sum of three separate resistances: atmospheric resistance (Ra), boundary layer resistance (Rb), and canopy resistance (Rc). Dry depositions were then calculated as the product of concentrations and deposition velocities. An analysis of the uncertainties in simulated deposition velocities suggest that the MLM underestimates observed deposition velocities and consequently dry depositions. Since the uncertainties in the model have not been quantified, calculated dry depositions represent lower bound estimates only.

Results and Discussion

The CASTNet measurements show statistically significant reductions in annual ambient SO_2, SO_4^{2-}, and HNO_3 concentrations averaged over all eastern sites. The data for the eastern sites combined show a 23% reduction in SO_4^{2-} and a 43% reduction in SO_2 between 1989 and 1995 annual concentrations. Changes in sulfur species are more pronounced in the northeast and smaller, but still substantial, in the southeast. There is no apparent trend in the data from the western sites. The eastern data indicate about 70% of ambient sulfur is in the form of SO_2. These comparisons do not account for year-to-year variations in concentrations. Analyses that address these variations may yield slightly different results.

SO_2 concentrations show significant reductions in summer and winter, even though concentrations are much lower in summer when SO_2 emissions are involved in photochemical reactions.

A slight reduction in HNO_3 concentrations results from the decline in summer averages. The downward trend is observed in most of the network, except for the southern peripheral sites and the western sites. No trends are observed in annual concentrations of NO_3^- aerosol and total NO_3^-.

The geographic distributions of annual dry sulfur depositions (fluxes) are similar from year to year and correspond well with distributions of SO_2 and SO_4^{2-} concentrations and reflect the locations of SO_x sources. Annual fluxes of total nitrogen show a fairly uniform pattern of depositions above 2.0 kg/ha (as N) from year to year. Lower depositions were calculated for the CASTNet sites in the Appalachian chain, similar to the results for HNO_3 concentrations.

Time series of weekly fluxes show considerable site-by-site and weekly variability. The seasonal cycles of fluxes of individual species are similar to the seasonal behavior of concentrations. Scattergrams and correlation statistics show a strong relationship between concentrations and depositions of SO_2, SO_4^{2-}, and HNO_3.

Results of linear regressions of dry depositions versus year for all eastern sites combined show downward trends for the sulfur species although the trend lines are not considered statistically significant. The downward slopes for SO_2 and total sulfur are greater than for SO_4^{2-}, consistent with the results for concentrations. The data show a 29% reduction in dry deposition of SO_2 (as S) and only a 6% reduction in deposition of SO_4^{2-} aerosol. These percentage reductions in depositions are lower than the comparable reductions in concentrations. The linear regressions show no significant trends in depositions of the nitrogen species. Depositions of sulfur and nitrogen species calculated for the western sites exhibit no trends.

Concentrations of anions and cations measured in precipitation samples collected at CASTNet sites and concentrations measured at those NADP sites approximately collocated with CASTNet sites that do not collect precipitation samples were combined to form one concentration and wet deposition database. Annual SO_4^{2-} concentrations exhibited statistically significant downward trends for the northeastern and southern peripheral sites. Although the eastern region did not exhibit a statistically significant reduction, a downward trend is indicated by the data and analyses.

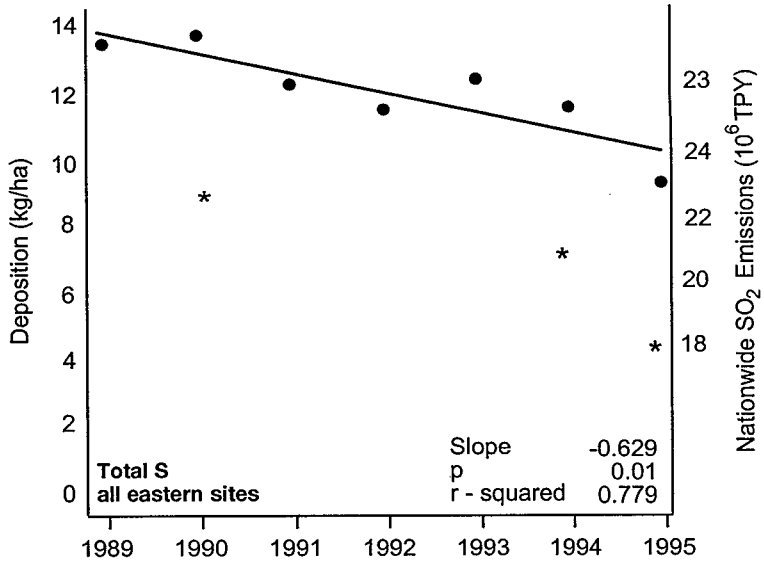
Linear regressions of annual wet depositions of SO_4^{2-} (as S) show statistically significant downward trends for all the eastern sites combined. The results show an overall decrease in wet SO_4^{2-} deposition of approximately 35% over the period 1989 to 1995. No significant trends were indicated for wet NO_3^- depositions. However, the measurements still show a reduction of about 20% for the eastern data combined over the 7-year period.

Dry and wet depositions were summed to obtain total depositions of sulfur and nitrogen species. A preliminary trends analysis of total deposition data, which does not correct for meteorological variations or model uncertainties, shows statistically significant reductions in annual deposition of sulfur over the period 1989 through 1995. The downward trends are considered significant throughout the eastern network. Figure 3 depicts the linear regression analysis of total sulfur deposition versus year. The figure also shows nationwide annual SO_2 emissions. No trend is apparent in the western data. Estimates of total deposition of nitrogen species exhibit no trend.

The CASTNet O_3 data provide estimates of exposure statistics and allow gauging compliance with the existing and proposed NAAQS for O_3. After 1988, violations of the 1-hour standard were limited to suburban sites in the Washington-New York corridor. Concentrations above the proposed 8-hour standard of 85 ppb were measured throughout the midwest and northeast subregions. The measure SUM06 has been suggested as a secondary standard for O_3. From 1989 through 1995, many CASTNet sites show SUM06 values above 25 ppm-hr, the proposed numerical limit. Measurements from the CASTNet visibility network for 1994 show a strong relationship between fine particle mass (FPM) and fine SO_4^{2-} concentrations. Fine SO_4^{2-} contributes more than 85% of the mass of total particulate SO_4^{2-}. The rural CASTNet measurements show compliance with the proposed 24-hour and annual FPM standards of 65 $\mu g/m^3$ 24-hour average and 15 $\mu g/m^3$ annual average. Furthermore, the CASTNet data show a downward trend in ambient SO_4^{2-}, which is a major contributor to FPM in the east.

MADPro is a component of CASTNet designed to study the deposition of air pollutants to high elevation forests. MADPro objectives are to measure cloud chemistry, determine total deposition and define source regions which impact high elevation ecosystems in the eastern U.S. The results to date show that cloudwater can be the primary pathway for deposition of air pollutants.

A mobile system to measure direct dry deposition fluxes via eddy correlation has been in operation since 1994. The system has been deployed at several sites with



Note: Emissions are indicated by a *.

Figure 3. Linear regressions of total sulfur depositions versus year for all eastern sites combined (Source: QST).

varying terrain settings and land uses to better understand deposition processes and to improve the MLM and other models.

Preliminary results of the CASTNet intercomparison study between annular denuders and filter packs show a high correlation between SO_4^{2-} measurements using the two different methods, and similar results for SO_2. Filter pack HNO_3 measurements were higher than denuder measurements.

Conclusions and Recommendations

The CASTNet database presents the opportunity for the first time to investigate trends in total (wet plus dry) deposition of sulfur and nitrogen species and contrast the results with trends in emissions. Total deposition of atmospheric sulfur (Figure 3) averaged over all CASTNet eastern sites has decreased by 32% over the period 1989 through 1995. Nationwide SO_2 emissions have declined by 22% over the period 1985 through 1995. Electric utility SO_2 emissions have dropped by 24% over that same period. A dramatic drop in SO_2 emissions has been reported from 1994 to 1995. Nationwide SO_2 emissions have dropped 13% and utility emissions 17% in one year. NO_x emissions have been relatively flat since 1970. However, an 8% reduction in overall NO_x emissions and 21% reduction in electric utility NO_x emissions was reported between 1994 and 1995. Despite these reported recent NO_x emission reductions, the CASTNet data show no change in total deposition of nitrogen over the period 1989 through 1995.

Advanced statistical analyses, beyond the scope of this report, are performed independently on the CASTNet data to further elucidate the apparent trends, and to decipher trends not detectable by simple linear regressions. Statistical analyses should investigate trends at individual sites as well as subregional averages to better understand the response to changes in emissions and meteorological fluctuations.

The full report presents quantitative information on dry deposition fluxes and atmospheric concentrations for the network from 1987 through 1995. A description of the network's quality assurance/quality control (QA/QC) program and key indicators of data quality such as precision and accuracy statistics are presented as well. The results of the QA/QC program demonstrate conclusively that the observed changes in concentrations and depositions are real and not the result of network modifications or of data imprecision or inaccuracy.

Concentration and deposition changes are the result of changes in emissions and of meteorological fluctuations. In short, the CASTNet data constitute an exceptional database for the purpose of discerning status and trends in air quality and of supporting other scientific activities. To preserve the integrity of and to continue building upon the existing database, CASTNet should be operated with minimum disruptions. The number of sites and locations should be reviewed to optimize site locations for improvement in the detection of trends. Evaluation of the MLM should continue in order to reduce the uncertainties of the accuracy and precision of deposition estimates. Model acceptance criteria should be fine-tuned. Therefore, the mobile dry deposition field studies should continue until the MLM is fully evaluated and flux calculations are representative of a wide variety of land use and terrain settings.

The visibility network should be continued and perhaps expanded to better detect trends in visibility related air quality parameters and fine particle concentrations. The MADPro sites should also be continued so that investigation of the impact of cloud deposition to sensitive ecosystems may continue.

CASTNet has produced an exceptional database that satisfies many of the requirements of the CAAA of 1990. The network will help assess compliance with the proposed NAAQS for O_3 and fine particles. It will continue to measure improvements in air quality and depositions associated with CAAA-mandated reductions in SO_x, NO_x, and VOC emissions over the next 10 years.

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

The complete report, entitled "Clean Air Status and Trends Network Deposition Summary Report (1987-1995)," (Order No. PB98-150097; Cost: $71.50, subject to change) will be available only from:

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