

**The Effects of Changes in Sulfate, Ammonia, and Nitric Acid on Fine  
PM Composition at Monitoring Sites in Illinois, Indiana, Michigan,  
Missouri, Ohio, and Wisconsin, 2000-2002**

Final Report

Charles L. Blanchard  
Shelley Tanenbaum  
Envair  
February 20, 2004

Prepared for  
Lake Michigan Air Directors Consortium

## ACKNOWLEDGMENTS

We thank D. Kenski for helping us obtain data, A. Nenes for providing the ISORROPIA model, and J. Seinfeld for providing the SCAPE2 model. The Electric Power Research Institute granted permission to use the data from the EPRI March-Midwest study, and I. Tombach provided information about the data sets and monitoring sites.

## CONTENTS

Summary.....	4
Data and Methods .....	13
Mean Concentrations .....	16
Thermodynamic Equilibrium Modeling.....	19
Application of Equilibrium Models to Predict Changes in Nitrate Concentrations .....	27
Application of Equilibrium Models to Predict Changes in Mass Concentrations.....	41
Day-of-Week Variations of Concentrations of PM Components.....	50
Conclusion.....	58
References .....	61
Appendix A. Data Quality and Estimation Procedures.....	64

## **Summary**

Objectives. The principal objective of this report is to use ambient measurements to quantify the potential effects of SO<sub>2</sub> and NO<sub>x</sub> emission reductions on particulate nitrate concentrations and fine particle mass in the midwestern United States. A number of nonlinear reaction pathways link emissions of SO<sub>2</sub> and NO<sub>x</sub> with particle sulfate and nitrate formation (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 1986). As a result, SO<sub>2</sub> and NO<sub>x</sub> emission reductions generally do not yield proportional decreases in particulate sulfate, nitrate, and fine mass concentrations. Chemical transport models (CTMs) are typically used to study the effects of SO<sub>2</sub> and NO<sub>x</sub> emission reductions on particle composition and concentrations, as well as on deposition (NARSTO, 2003). Because of the difficulty in conducting field studies that provide sufficient data for model development and evaluation, and because many model applications are limited to one or a few episodes, complementary analyses of ambient measurements are useful for corroborating model predictions, assessing the representativeness of specific episodes, and providing independent characterizations of the responses of ambient concentrations to emission changes.

Background. Current PM management strategies in North America that focus on the reduction of SO<sub>2</sub> and NO<sub>x</sub> emissions are predicted to have a beneficial effect on reducing fine PM mass concentrations (NARSTO, 2003). Past modeling studies predicted that reductions of SO<sub>2</sub> emissions would lower average ambient particulate sulfate concentrations throughout the eastern United States, though less than proportionally to SO<sub>2</sub> emission reductions (Venkatram, 1991). For a 50 percent SO<sub>2</sub> emissions reduction, total annual sulfate deposition was predicted to decrease by 40 to 50 percent throughout eastern North America (NAPAP, 1991). Ambient air and precipitation sulfate concentrations declined between 1990 and 2000 as SO<sub>2</sub> emissions declined (NAPAP, 1998; Lynch et al., 1996; Shannon, 1999), in a way that was statistically indistinguishable from proportional. Analyses of ambient data have also shown that precipitation sulfate concentrations in North America varied geographically in proportion to SO<sub>2</sub> emissions

over semi-continental spatial scales, but not over smaller areas (Hilst, 1992). From 1988 to 1999, over 80 percent of the variation in seasonal ambient concentrations of SO<sub>2</sub> and aerosol sulfate was associated with variations in SO<sub>2</sub> emissions in over three-quarters of the areas and time periods examined for rural data from the eastern United States (Mueller, 2003). In summary, both modeling studies and data analyses have established near-proportional (i.e., ~80 percent or more) responses of ambient sulfate levels to SO<sub>2</sub> emission reductions when averaged over eastern North America, though PM sulfate responses may not be this great within smaller spatial scales in some areas.

Other important outstanding questions have to do with the responses of nitrate and fine PM mass concentrations to SO<sub>2</sub> and NO<sub>x</sub> reductions; as well, the responses of PM carbon concentrations to emission reductions are not well understood. The focus of this report is on the responses of nitrate and fine PM mass concentrations to SO<sub>2</sub> and NO<sub>x</sub> reductions.

Reductions of NO<sub>x</sub> emissions are expected to lower average ambient particulate nitrate concentrations at locations where particulate ammonium nitrate formation is not presently limited by the availability of ammonia, but the combined effects of SO<sub>2</sub> and NO<sub>x</sub> emission reductions on particulate nitrate concentrations are complex and will likely vary among locations. As ambient sulfate concentrations decline, less ammonia will be tied up as ammonium sulfates, since sulfate aerosol exists primarily as ammonium sulfates in the midwestern United States. Increased levels of ammonia could perturb the equilibrium between gas-phase nitric acid and aerosol ammonium nitrate, tending to increase the formation of ammonium nitrate, and possibly partially offsetting reductions of fine particulate matter (PM) mass associated with sulfate.

Methods. The report analyzes ambient measurements of fine particle mass and speciation from monitoring locations in the states of Illinois, Indiana, Michigan, Missouri, Ohio, and Wisconsin during the period 2000-2002 to characterize the potential responses of fine particle nitrate and mass to changes in ambient concentrations of sulfate, NO<sub>x</sub>, nitric acid (HNO<sub>3</sub>), and ammonia (NH<sub>3</sub>). Two complementary approaches are employed:

application of thermodynamic equilibrium models and analysis of differences between weekday and weekend ambient concentrations of primary and secondary pollutants.

To quantitatively evaluate potential changes in PM nitrate and fine PM mass concentrations, we used two thermodynamic equilibrium models, ISORROPIA (Nenes et al., 1998a; 1998b; Ansari and Pandis, 1999a; 1999b) and Simulating Composition of Atmospheric Particles at Equilibrium (SCAPE2) (Kim et al., 1993a; 1993b; Kim and Seinfeld, 1995; Meng et al., 1995a; 1995b). Both models use ambient data as inputs and provide predictions of changes in particulate nitrate levels that are based upon physical and chemical principles. As with all methods, thermodynamic equilibrium modeling has both strengths and limitations. Its principal strengths include a strong foundation in fundamental principles of physics and chemistry and reliance on ambient measurements. The principal limitations are that the assumption of thermodynamic equilibrium is not valid in all situations and that important aspects of gas-phase chemistry are not incorporated into the equilibrium model. As discussed in the report, the predictions of the models were compared carefully with ambient measurements to evaluate the appropriateness of the application of thermodynamic equilibrium models, and to exclude any monitoring data for which the application was inappropriate. Other limitations of the model were assessed qualitatively by bounding the possible changes that are not incorporated into the model.

The principal processes affecting the formation of particulate nitrate are illustrated schematically in Figure 1, which also indicates which compounds and processes are incorporated into the thermodynamic equilibrium models. The model simulations provide a means for calculating shifts in the equilibrium between gas-phase and condensed-phase nitrate as a result of changes in sulfate, ammonia, or nitric acid levels, accounting for the effects of temperature and relative humidity on the equilibria. Conversion of  $\text{SO}_2$  to sulfate and  $\text{NO}_2$  to  $\text{HNO}_3$  involves gas-phase or heterogeneous reactions that are not included within the models. As previously noted, the possible effects of these reactions would be to cause the ambient concentrations of sulfate and

HNO<sub>3</sub> to decrease by amounts that are less than proportional to the reductions of SO<sub>2</sub> and NO<sub>x</sub> emissions.

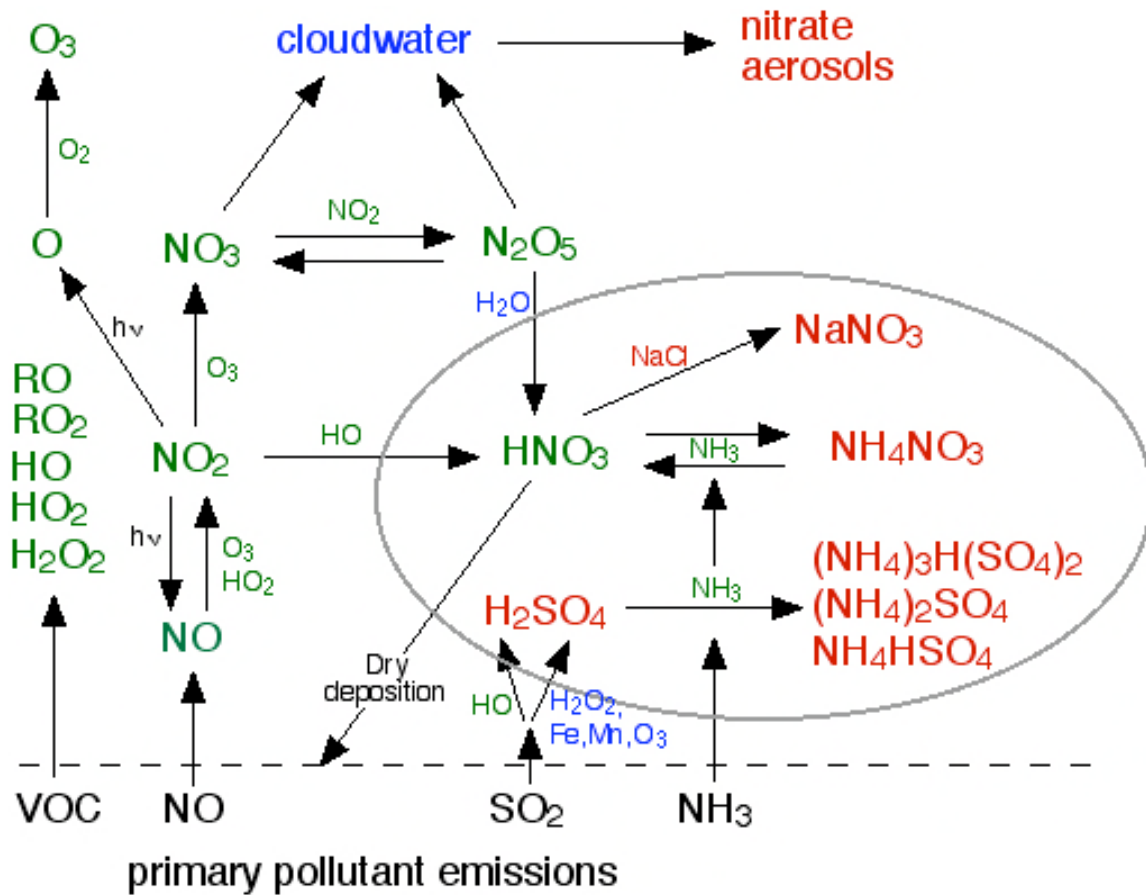


Figure 1. Schematic illustration of principal atmospheric processes affecting the formation of particulate nitrate. Processes and compounds incorporated into the thermodynamic equilibrium models are shown within the oval. Gas-phase species are shown in green. Liquid-phase is indicated by blue and aerosol species are red. While all compounds are subject to both wet and dry deposition, only dry deposition of nitric acid is illustrated to emphasize the importance of this process for the removal of nitric acid from the atmosphere.

The modeling simulations were carried out using zero, 25, 50, 75, and 90 percent reductions in ambient sulfate concentrations. The 50 percent reductions represent near-proportional reduction of sulfate to proposed reductions of SO<sub>2</sub> emissions. In 2000, the total U.S. emissions of SO<sub>2</sub> were about 17 million tons (U.S. EPA, 2003a), of which the Clean Air Act Title IV cap for electric utilities was 11.2 million tons. The utility SO<sub>2</sub> caps under the proposed Clear Skies Initiative would be 4.5 million tons per year in 2010 and 3 million tons per year in 2018, representing a reduction of 8.2 million tons from 2000 levels (73 percent of year 2000 utility emissions or about 50 percent of total SO<sub>2</sub> emissions) (US EPA, 2003b).

The effects of NO<sub>x</sub> emission reductions on ambient concentrations of HNO<sub>3</sub> are not well quantified, so the present project evaluates changes in particulate nitrate concentrations for a wide range of changes in nitric acid levels (zero to 60 percent reductions). Under the proposed Clear Skies Initiative, electric utilities in the eastern United States are to reduce NO<sub>x</sub> emissions by 73 percent from their 2002 levels by 2020 (US EPA, 2003b). Since transportation accounts for over half the total NO<sub>x</sub> emissions (US EPA, 2003a), the proposed utility NO<sub>x</sub> reduction represents a decline in total NO<sub>x</sub> emissions of about 30 to 35 percent. The U.S. EPA projects a decline of total NO<sub>x</sub> emissions from 25.9 tons in 1996 to 13.5 tons in 2020, or a reduction of somewhat under 50 percent between 2000 and 2020 (US EPA, 2002). Therefore, the range of nitric acid reductions (zero to 60 percent) used in the present study bounds the plausible changes given the projected NO<sub>x</sub> emission reductions.

A potentially important limitation of the equilibrium-model predictions is that substantial amounts of NO<sub>x</sub> reaction products are removed from the atmosphere by dry or wet deposition. Changes in deposition rates attendant upon shifting equilibria could affect ambient nitrate levels. Particulate nitrate has a much lower deposition velocity than does HNO<sub>3</sub>; nitric acid deposits readily to most surfaces, especially in moist, vegetated areas. Much of the nitric acid that forms by oxidation of NO<sub>2</sub> may be removed by deposition. Increasing rates of conversion of HNO<sub>3</sub> to particulate nitrate potentially could therefore increase concentrations of total nitrate. Quantitative evaluation of this effect requires the

application of both a gas-phase model and a deposition model. In the present study, only the shift in equilibrium between gas-phase and condensed-phase nitrate has been modeled. However, this shift is the most important first-order effect. Potentially, full consideration of changes in deposition could indicate that concentrations of particulate nitrate would increase (as sulfate levels decrease) more than has been determined in this study (due to lower deposition loss rates).

Because the equilibrium models do not incorporate gas-phase reactions (e.g., conversion of  $\text{NO}_x$  to nitric acid) or deposition, the model predictions do not describe the full set of linkages from  $\text{NO}_x$  to PM nitrate. Therefore, additional analyses were carried out to determine day-of-week variations in the concentrations of  $\text{NO}_x$  and fine PM mass and composition, providing an empirical assessment to complement the modeling. The principal advantage of the empirical day-of-week assessment is its empiricism: all changes that occur between weekdays and weekends are included in the comparisons of weekday and weekend ambient concentrations. The principal disadvantages are that the empirical assessment can only provide information on the particular types of changes that actually occur between weekdays and weekends, and it can be difficult to which specific reactions may be responsible for nonproportional weekend responses, if they occur. Coupling the equilibrium modeling results with the weekday/weekend comparisons permits some conclusions to be drawn.

Findings. The thermodynamic equilibrium models predicted that mean PM nitrate concentrations would increase by less than 0.1 to 0.4  $\mu\text{g m}^{-3}$  in response to 50 percent lower sulfate concentrations at ten sites studied. At each site, the predicted nitrate increases were offset when the modeled concentrations of  $\text{HNO}_3$  were decreased by amounts ranging from less than 10 percent to approximately 20 percent of current mean  $\text{HNO}_3$  levels.

Changes in mean PM mass concentrations were predicted from the predicted changes in sulfate, ammonium, and nitrate concentrations. Predicted fine PM mass levels were tabulated and depicted as isopleths drawn in relation to sulfate and nitric acid

concentrations. The shapes of the PM mass isopleths were the same for all sites, indicating that predicted fine mass concentrations declined as either sulfate or nitric acid concentrations declined. The PM mass decreases were typically about 2 to 3  $\mu\text{g m}^{-3}$  for a 50 percent sulfate decrease and about 1 to 1.5  $\mu\text{g m}^{-3}$  for a 50 percent nitric acid decrease, thus showing greater sensitivity to sulfate reductions. The sulfate decreases were an input to the model calculations, but their effect on fine PM mass was modified by concomitant decreases in ammonium and increases in nitrate. These concomitant changes nearly balanced each other, so that the PM mass changes in response to the assumed sulfate decreases were approximately equal in magnitude to the sulfate reductions. For the IMPROVE/CASTNet data (six of the ten sites), the predicted sensitivities of mean PM mass concentration to changes in sulfate and nitric acid concentrations should be considered preliminary because some measurements were estimated from other quantities (see appendix).

The largest predicted mean nitrate increases (0.4  $\mu\text{g m}^{-3}$ ) occurred at the Cincinnati site. At this location, approximately one-third of the samples were ammonia-limited. Once sulfate concentrations were reduced by 50 percent, particulate nitrate formation became  $\text{HNO}_3$ -limited for nearly all samples. In spite of the predicted mean nitrate increases, the predicted mean  $\text{PM}_{2.5}$  mass concentration decrease at the Cincinnati MMW site exceeded the mean sulfate decrease. This result held both when changes in water content were considered and when they were not.<sup>1</sup> The mass concentration decreases exceeded the sulfate decreases because ammonium concentrations also decreased. For the scenario with the maximum mean nitrate increase (i.e., 50 percent sulfate decrease, no  $\text{HNO}_3$  decrease), the mean sulfate decrease was 2.7  $\mu\text{g m}^{-3}$ , the mean ammonium decrease was 0.9  $\mu\text{g m}^{-3}$ , the mean nitrate increase was 0.4  $\mu\text{g m}^{-3}$ , and the mean  $\text{PM}_{2.5}$  mass concentration decrease was 3.2  $\mu\text{g m}^{-3}$ .

Further work is needed to relate the changes in model inputs (sulfate and nitric acid) to changes in emissions of  $\text{SO}_2$  and  $\text{NO}_x$ . Past modeling and empirical analyses indicate

---

<sup>1</sup> Since PM mass is measured in a laboratory under fixed temperature and RH, changes in ambient water content do not necessarily affect the reported mass concentrations. However, changes in ambient water content are of significance with respect to visibility.

that reductions of SO<sub>2</sub> emissions have led in the past to nearly proportional reductions of ambient sulfate concentrations on the semi-continental scale of eastern North America. On smaller spatial scales, including regional (e.g., the six Midwestern states studied here) and local (e.g., the Chicago CMSA), the response of ambient sulfate concentrations to SO<sub>2</sub> emission reductions may be nonproportional.

The response of ambient concentrations of nitric acid to changes in NO<sub>x</sub> emissions has not been previously well established. This report did not attempt to model the gas-phase processes linking NO<sub>x</sub> with nitric acid, nor were models used to examine the relationships between changes in NO<sub>x</sub> and PM nitrate concentrations. Instead, the links were studied empirically through quantification of the day-of-week variations in the ambient concentrations of NO<sub>x</sub> and PM nitrate.

Ambient measurements show that mean weekend NO<sub>x</sub> concentrations were lower than weekday concentrations at nearly all urban monitoring sites in the six states. Since these sites included upwind and downwind locations as well as sites closer to the urban cores, the weekend NO<sub>x</sub> reductions occurred on city-wide or possibly larger spatial scales. The median weekend NO<sub>x</sub> reductions for all monitoring sites were 12 percent on Saturdays and 30 percent on Sundays, relative to the mean 24-hour Wednesday concentrations, with 22 of 41 Wednesday-Sunday differences in mean NO<sub>x</sub> concentrations being statistically significant ( $p < 0.01$ ). Sites not located in MSAs showed a median Sunday NO<sub>x</sub> reduction of 17 percent relative to Wednesdays, and no median difference between mean Saturday and Wednesday 24-hour NO<sub>x</sub> levels. For PM nitrate, the median weekend reductions over all monitoring sites were 11 percent on both Saturdays and Sundays, relative to the mean Wednesday concentrations, with no statistically significant differences.

The comparisons of weekend changes in ambient levels of PM nitrate and NO<sub>x</sub> indicate that Sunday reductions of PM nitrate were less than urban-scale Sunday NO<sub>x</sub> reductions and therefore support the conclusion that PM nitrate concentrations display a less-than-proportional response to urban-scale changes in NO<sub>x</sub> levels. However, the regional changes in NO<sub>x</sub> were not well characterized, and neither NO<sub>x</sub> nor PM nitrate showed

statistically significant weekend changes at nonurban monitoring sites (with one exception for Sunday  $\text{NO}_x$  levels). The day-of-week variations in concentration suggest that the response of PM nitrate concentrations to changes in ambient  $\text{NO}_x$  levels may depend upon the spatial scale of the emission changes. The apparent limited response of weekend PM nitrate levels to city-wide reductions of ambient  $\text{NO}_x$  concentrations on weekends raises questions about the potential effectiveness of local PM nitrate-control strategies. Additional studies of the effects of regional  $\text{NO}_x$  emission reductions on ambient nitrate levels are therefore needed.

In summary, the equilibrium models predicted that particulate nitrate formation was not limited by the availability of ammonia for most samples at times when temperature and humidity favored the condensed phase, but weekend particulate nitrate levels did not decline in proportion to changes in weekend  $\text{NO}_x$  concentrations. Therefore, it may be concluded that important processes potentially limiting the observed responsiveness of PM nitrate to changes in  $\text{NO}_x$  emissions likely include gas-phase conversion of  $\text{NO}_x$  to nitric acid and transport. Model-predicted fine mass concentrations declined as either sulfate or nitric acid concentrations declined, with the predicted PM mass concentrations showing greater sensitivity to sulfate reductions.

## Data and Methods

Special-study measurements were obtained from the EPRI March-Midwest (MMW) study of August-September 1999 and January-February 2000 (Table 1). Species that are reported in the dataset include PM<sub>2.5</sub> mass, sulfate, ammonium, nitrate, organic carbon, elemental (black) carbon, nitric acid, and ammonia. Samples were collected daily during the study periods. The PM measurements were made with 24-hour resolution, while the gas-phase measurements were made hourly. All measurements needed as inputs to the thermodynamic models were available.

Table 1. EPRI MMW sites, co-located AIRS sites and World Meteorological Organization (WMO) sites (meteorological data).

Site	Address	AIRS co-located	Data period	WMO site
Athens OH	Close to 360 E. State Street	none	Aug-Sep 1999 Jan-Feb 2000	Lancaster/Fairfield
Chicago IL	Illinois Institute of Technology, Corner of 33 <sup>rd</sup> Street and Michigan Ave.	170310014	Aug-Sep 1999 Jan-Feb 2000	Meigs Field and Midway airports
Cincinnati OH	250 William Howard Taft Road	390610040	Aug-Sep 1999 Jan-Feb 2000	Cincinnati Municipal
Detroit MI	14700 Goddard Rd., Allen Park	261630001	Aug-Sep 1999	Detroit Metro
St Louis MO	4520 Margaretta St	295100086	Aug-Sep 1999	St. Louis Lambert
Charleston WV	312 4th Ave., South Charleston Library	540391005	Aug-Sep 1999	Charleston Yeager

At one IMPROVE location (Bondville, Illinois), a variety of special-study measurements have been made ([www.sws.uiuc.edu.atmos/bears/](http://www.sws.uiuc.edu.atmos/bears/)). The Illinois State Water Survey (ISWS) has operated a Federal Reference Method (FRM) PM<sub>2.5</sub> sampler, a dichotomous sampler, and a fine PM sampler equipped with denuders at Bondville, compiling measurements of major PM components as well as gas-phase ammonia and nitric acid. Data from March 2000 through January 2002 were available for use in the present project. Species that are reported in the dataset include PM<sub>2.5</sub> mass, sulfate, ammonium, nitrate, organic carbon, elemental (black) carbon, nitric acid, and ammonia. The PM measurements were made with 24-hour resolution. By combining these measurements with collocated 24-hour resolution measurements of sodium, chloride, calcium, potassium, and magnesium, all measurements needed as inputs to the thermodynamic models were available.

Data were also obtained from portions of the period 1998-2002 from monitoring sites in Illinois, Indiana, Michigan, Missouri, Ohio and Wisconsin that are part of the Interagency Monitoring of Protected Visual Environments (IMPROVE) network, the Clean Air Status and Trends Network (CASTNet), and the PM<sub>2.5</sub> Speciated Trends Network (STN). These networks provide a longer monitoring record than the EPRI MMW and Bondville studies, though fewer parameters were measured. The IMPROVE sites included: Cadiz KY, Bondville IL, Seney MI, MK Goddard PA, Livonia IN, Isle Royale MI, and Quaker City OH (the Kentucky and Pennsylvania sites were included because of their proximity to the study area). These 24-hour resolution samples were collected on a once-in-3-day schedule commencing in early 2001; species that are reported in the dataset include PM<sub>2.5</sub> mass, ammonium sulfate, ammonium nitrate, organic carbon, and elemental (black) carbon. Sulfate, nitrate, and ammonium concentrations were calculated from the stoichiometry of ammonium sulfate and ammonium nitrate.

Prior to 2001, Cadiz, Bondville, MK Goddard, Livonia IN, and Quaker City were part of the CASTNet, operating under the IMPROVE protocol and collocated with monitors that collected weekly-average samples under the CASTNet dry-deposition sampling

protocol.<sup>2</sup> The weekly CASTNet HNO<sub>3</sub> measurements were used as estimates of daily HNO<sub>3</sub> levels for each sampling day within a week (see Appendix).

For 2002, there were 24 sites in the STN dataset within this region providing data for 75 percent of the period. Data are collected on either a 3-day or 6-day schedule, depending on the site and year. Species that were obtained directly from the STN dataset include PM<sub>2.5</sub> mass, ammonium, organic carbon, nitrate, elemental carbon, and sulfate.

Appendix A provides further discussion of the comparability of measurements made by different networks. The appendix also describes the procedures that we used for estimating missing data.

---

<sup>2</sup> The collocated sites are Bondville, Cadiz, Quaker City, and MK Goddard. The CASTNet sampler at Vincennes IN is closest to the IMPROVE sampler at Livonia IN. For this project, CASTNet weekly data from Voyageur National Park were matched with the IMPROVE and IMPROVE-protocol data from Isle Royale and Seney MI.

## Mean Concentrations

The annual means for 2002 were calculated from IMPROVE and STN data (Table 2). Data were included if at least 75 percent of expected measurements were present in each month, at least two months for each quarter had data, and all four quarters of the year were present. The data are grouped geographically in Table 2 by area, with the southern area including all sites at or south of the latitude of Indianapolis, the middle including all sites between the latitudes of Indianapolis and Grand Rapids MI, and the northern area including all sites north of the latitude of Grand Rapids. Sites are listed within each area from west to east.

The mean concentrations exhibit several characteristics:

- $PM_{2.5}$  mass and species concentrations are generally lower in the northern tier of sites than in the middle and southern sections.
- $PM_{2.5}$  mass, nitrate, and total carbon (OC + BC) concentrations are generally lower at the IMPROVE sites (which are rural) than at the STN sites (most of which are urban); mean sulfate concentrations are similar at IMPROVE and STN sites within a given tier of sites.

These differences among monitoring sites imply that data from many sites should be used for evaluating predicted responses of PM concentrations to changes in sulfate, ammonia, and nitric acid. In particular, the differences between more northerly and more southerly sites, and between urban and rural sites, should be represented.

Table 2 does not include mean ammonia concentrations. Ammonia data were obtained from the EPA national ammonia survey. Data were available from different time periods and for varying lengths of time from 6 sites in Iowa (300-1400 hourly values in 2003), 2 in Missouri (2200-8600 hourly values for each site and year 2001-03), 3 in Kentucky (2-14 observations, 1996-99), 5 in North Carolina (1400-7500 hourly values 3-4 years each from 1998-2003), and 1 in North Dakota (1000-8600 hourly values, 2000-2003). Mean concentrations varied by up to a factor of five at two closely located sites in Missouri and

also at two closely located sites in North Carolina. Given the sparse sampling and variability among locations, the applicability of any of the ammonia measurements to the monitoring sites listed in Table 2 could not be established.

Table 2. Annual (2002) means for STN and IMPROVE sites. Means were constructed for each month with 75 percent sampling completeness. Quarterly means were constructed for each quarter with at least two months data. The annual means were determined as the arithmetic average of four quarters. Rural sites (IMPROVE sites and STN sites classified as rural by EPA) are highlighted in green. Units of measurement are  $\mu\text{g m}^{-3}$ .

SITE	AIRS	STATE	MASS	SO <sub>4</sub>	NO <sub>3</sub>	NH <sub>4</sub>	HNO <sub>3</sub>	OC	BC
<b>Southern Area (listed from west to east)</b>									
STODDARD CTY	292070001	MISSOURI	13.9	3.9	1.4	1.5		3.3	0.3
CLAY CTY	290470005	MISSOURI	13.6	3.2	2.9	1.8		3.0	0.3
JEFFERSON CTY	290990012	MISSOURI	16.0	4.2	2.3	1.8		4.9	0.6
ST LOUIS	295100085	MISSOURI	16.4	4.3	2.9	2.1		4.6	0.8
ALTON	171192009	ILLINOIS	14.4	3.8	2.6	1.9		3.2	0.4
CADIZ	IMPROVE	KENTUCKY	12.0	4.3	1.2	2.0	2.1	2.1	0.4
LIVONIA	IMPROVE	INDIANA	12.4	4.8	1.5	2.3	2.2	1.6	0.4
INDIANAPOLIS	180970078	INDIANA	16.7	4.9	2.9	2.3		4.6	0.6
MIDDLETOWN	390171004	OHIO	14.1	4.3	2.1	1.8		4.0	0.5
DAYTON	391130031	OHIO	14.4	4.6	2.6	2.1		4.0	0.5
<b>Middle (listed from west to east)</b>									
DODGE CTY	550270007	WISCONSIN	11.3	2.6	3.0	1.6		3.2	0.3
BONDVILLE	IMPROVE	ILLINOIS	11.4	3.7	2.3	2.0	2.1	1.5	0.4
MILWAUKEE	550790026	WISCONSIN	13.5	3.0	3.0	1.7		4.1	0.6
PLEASANT PRAIRIE	550590019	WISCONSIN	11.5					3.3	0.4
CHICAGO	170310057	ILLINOIS	15.2	3.5	3.4	2.0		4.4	0.7
CHICAGO	170310076	ILLINOIS	15.1	3.8	2.4	1.9		3.1	0.6
MIDDLETOWN	180650003	INDIANA	13.2	4.0	2.6	2.0		3.1	0.4
TOLEDO	390950026	OHIO	13.2	3.3	2.6	1.8		3.9	0.6
ALLEN PARK (DETROIT)	261630001	MICHIGAN	16.6	4.4	3.3	2.3		4.5	0.9
CLEVELAND	390350038	OHIO	15.8	4.2	2.3	2.2		4.4	0.8
CLEVELAND	390350060	OHIO	17.9	4.5	3.0	2.4		4.7	1.1
CLEVELAND	390350060	OHIO	17.7	4.6	3.1	2.4		4.9	1.1
QUAKER CITY	IMPROVE	OHIO	11.8	4.9	0.8	2.1	3.5*	1.6	0.4
MK GODDARD	IMPROVE	PENNSYLVANIA	11.0	4.0	1.1	1.8	2.3	1.9	0.5
<b>Northern Area (listed from west to east)</b>									
TAYLOR CTY	551198001	WISCONSIN	8.8	2.0	1.8	1.0		3.0	0.3
ISLE ROYALE	IMPROVE	MICHIGAN	5.1	1.5	0.5	0.7	0.5^	1.1	0.2
TWO RIVERS	550710007	WISCONSIN	9.7	2.5	2.4	1.4		3.1	0.3
MANISTIQUE	261530001	MICHIGAN	6.0	1.9	0.8	0.6		2.4	0.2
SENEY	IMPROVE	MICHIGAN	5.3	2.0	0.7	1.0	0.5^	1.1	0.2
MISSAUKEE	261130001	MICHIGAN	9.2	2.4	1.4	1.0		2.8	0.3
SAULT ST MARIE	260330901	MICHIGAN	7.4	1.7	1.0	0.6		3.0	0.3

\* Did not meet 75 percent completeness

^ HNO<sub>3</sub> measurements from Voyageur National Park

## **Thermodynamic Equilibrium Modeling**

Two thermodynamic equilibrium models were used to evaluate the effects of changes in sulfate, nitric acid, and ammonia on particulate nitrate concentrations: ISORROPIA (Nenes et al., 1998a; 1998b; Ansari and Pandis, 1999a; 1999b) and Simulating Composition of Atmospheric Particles at Equilibrium (SCAPE2) (Kim et al., 1993a; 1993b; Kin and Seinfeld, 1995; Meng et al., 1995a; 1995b). Both models partition ammonia and nitrate between condensed and gas phases, based upon specification of total (gas plus condensed) concentrations of sulfate, nitrate, ammonia, chloride, and sodium plus temperature and relative humidity (RH); SCAPE2 also incorporates carbonate chemistry and uses inputs of calcium, magnesium, potassium, and total carbonate.

The EPRI MMW data included all measurements needed as inputs to ISORROPIA or to SCAPE2 (input concentrations of calcium, magnesium, sodium, and potassium for SCAPE2 were estimated from the reported crustal mass, which was small). The models were applied to each 24-hour sample. The agreement between model predictions and measurements supported the applicability of the model (Figures 2 and 3). Similarly, the Bondville special-study data also included all measurements needed as inputs to ISORROPIA or to SCAPE2 (input concentrations of chloride, calcium, magnesium, sodium, and potassium were obtained from the collocated CASTNet and IMPROVE samplers). Again, the models were applied to each 24-hour sample and the agreement between model predictions and measurements supported the applicability of the model (Figure 4). While some measurements of nitric acid were substantially lower than predicted by the model, the concentrations were low (Figure 4). However, the differences between predicted and measured nitric acid correlated with weekly-average nitric acid levels from the collocated CASTNet dry-deposition sampler (Figure 4). Because of this correlation, and because of the results of comparisons described in the Appendix, it is possible that some of the nitric acid measurements from Bondville were lower than the true levels. We did not exclude such samples from further analysis, though, as no definitive evidence exists for a bias in the nitric acid measurements, and the number of samples affected was small.

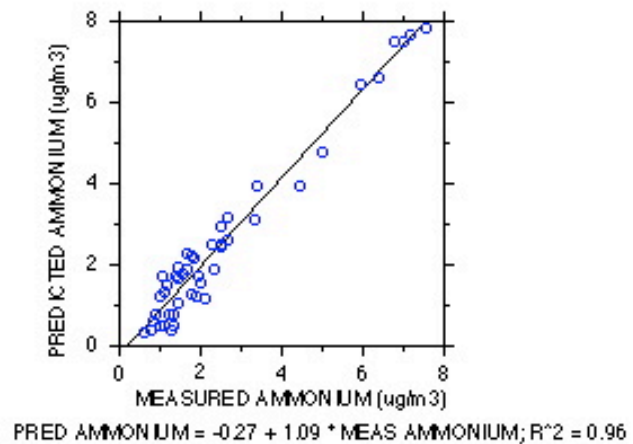
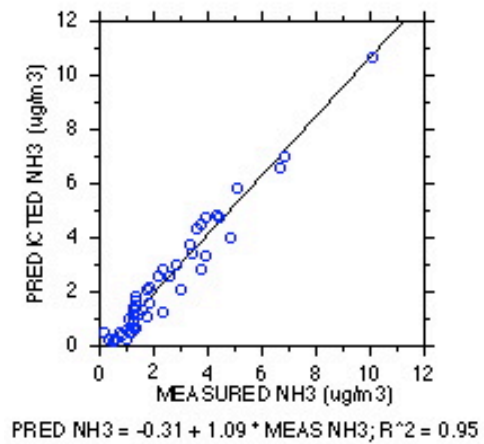
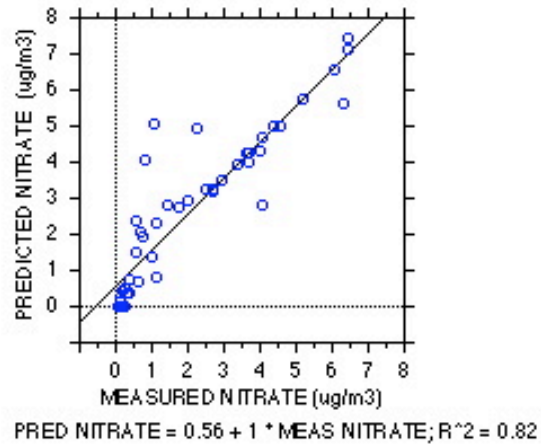
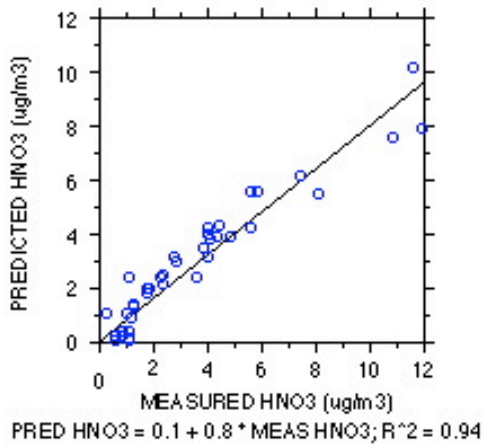


Figure 2. Comparison of measured HNO<sub>3</sub>, NO<sub>3</sub>, NH<sub>3</sub>, and NH<sub>4</sub> with predictions from ISORROPIA, using data from the MMW Chicago site, 1999-2000. Each data point represents one 24-hour sample.

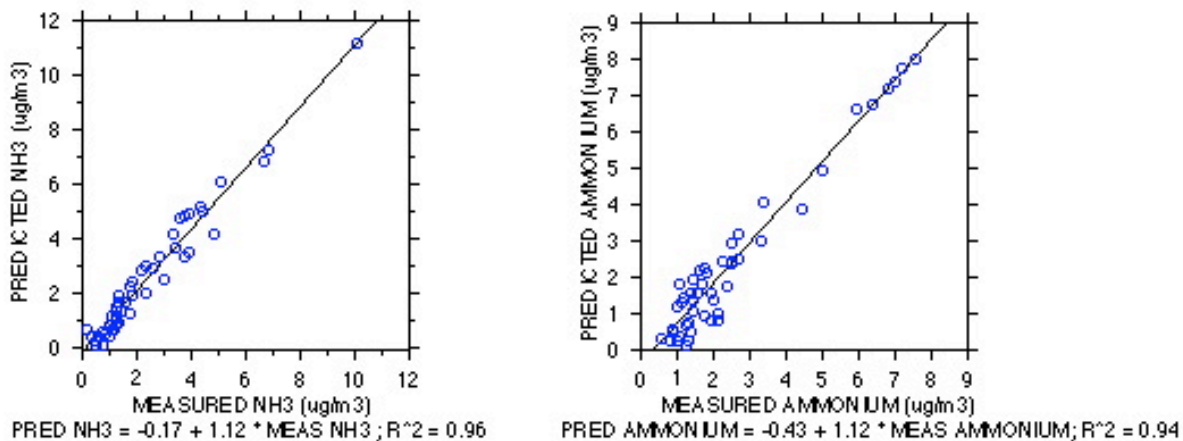
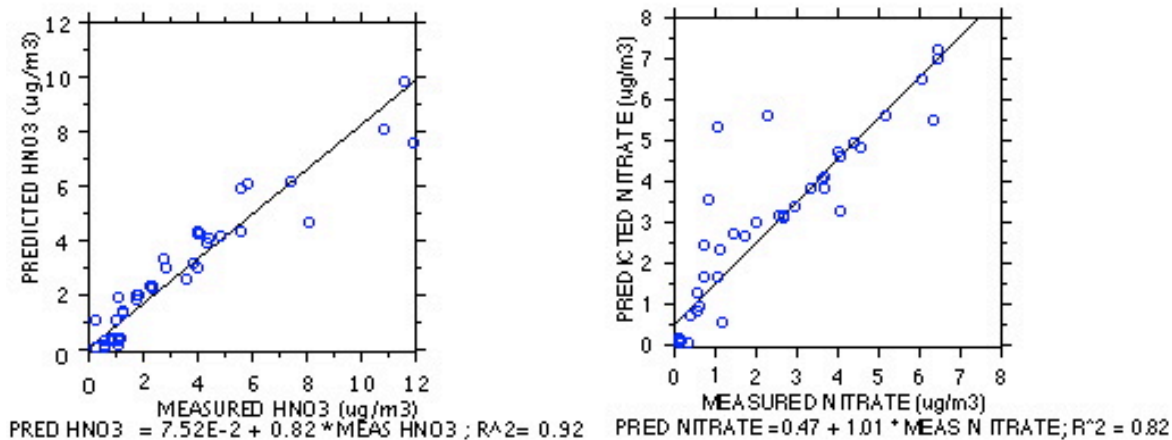


Figure 3. Comparison of measured HNO<sub>3</sub>, NO<sub>3</sub>, NH<sub>3</sub>, and NH<sub>4</sub> with predictions from SCAPE2, using data from the MMW Chicago site, 1999-2000. Each data point represents one 24-hour sample.

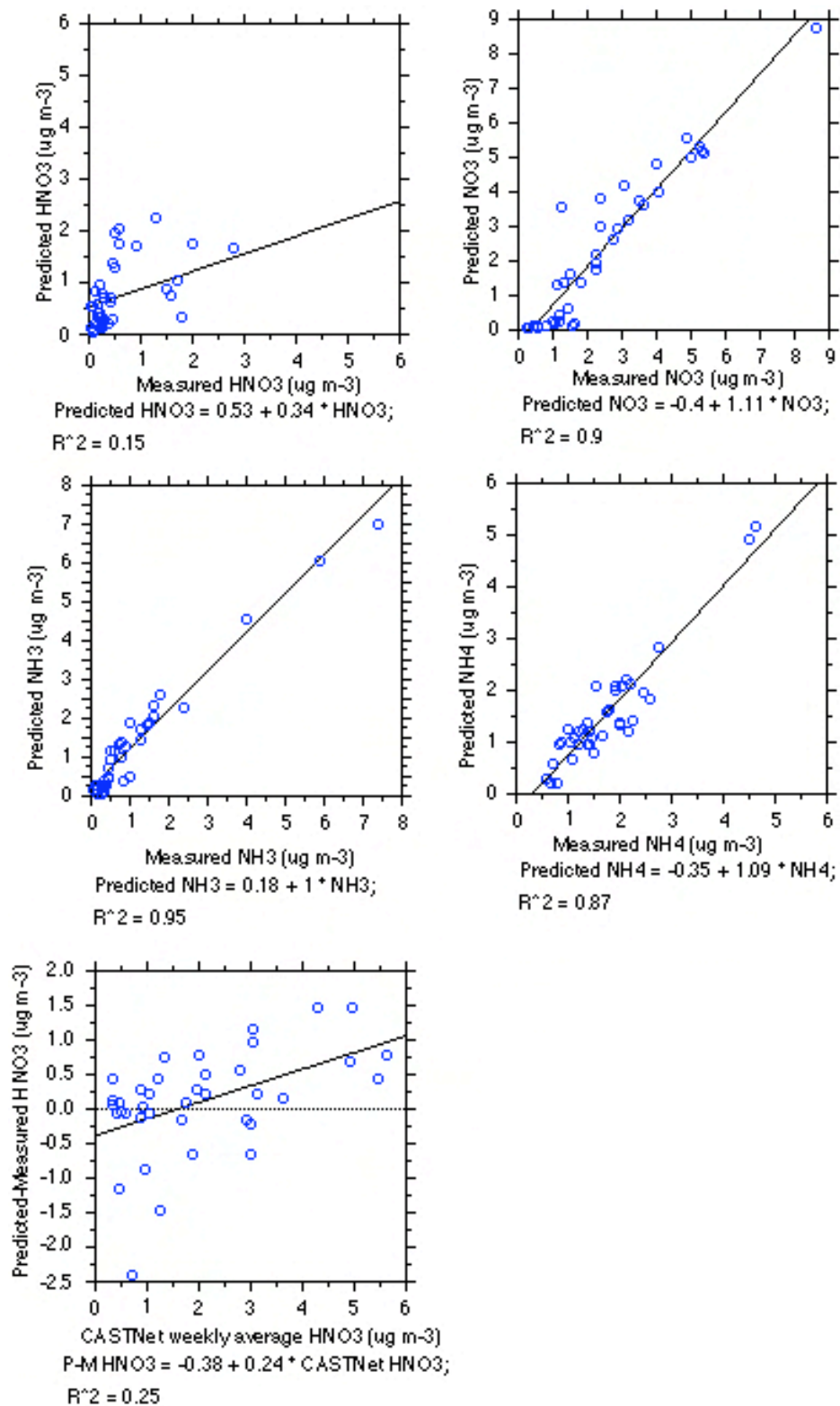


Figure 4. Comparison of measured HNO<sub>3</sub>, NO<sub>3</sub>, NH<sub>3</sub>, and NH<sub>4</sub> with predictions from SCAPE2, using data from the BEARS (Bondville) site, 2000-2002. Each data point represents one 24-hour sample.

Neither the IMPROVE/CASTNet nor the STN databases provide all the measurements required for input to ISORROPIA and SCAPE2. The missing measurements are gas-phase ammonia (for both IMPROVE/CASTNet and STN) and nitric acid (for STN). As noted previously, the IMPROVE/CASTNet measurements of particulate ammonium are calculated from particulate sulfate and nitrate concentrations. To use the IMPROVE/CASTNet data as inputs to ISORROPIA and SCAPE2, surrogate measurements or estimates were substituted for missing data. First, as previously noted, the weekly CASTNet HNO<sub>3</sub> measurements were substituted for daily HNO<sub>3</sub> levels. Second, for each 24-hour sample, ISORROPIA was used to estimate ambient concentration of ammonia that would be in thermodynamic equilibrium with the measured sulfate, nitrate, ammonium, and nitric acid at each of the IMPROVE/CASTNet sites (see Appendix A). An iterative procedure was followed until the predicted concentrations of nitric acid and particulate nitrate were each within ten percent of the measured values, on average, as determined from the slopes of the regressions of predicted against measured values. The ISORROPIA 24-hour model predictions are compared with measured nitric acid, nitrate and ammonium in Figure 5. The plots show a nearly one-to-one fit for ammonium.<sup>3</sup> The predictions for nitric acid show more scatter around the regression line than do the nitrate and ammonium predictions, but this difference is due in part to the scale differences in the plots.

The agreement between model predictions and measurements support the applicability of the model (Figure 5). However, because ammonia concentrations were estimated and weekly averages were used for nitric acid (there being no other measurements), we believe that conclusions drawn from these model simulations should be considered preliminary. They will be compared with conclusions drawn from the monitoring locations where complete measurements were available. In the future, additional simulations should be carried out using actual measurements of ammonia and nitric acid at the IMPROVE sites.

---

<sup>3</sup> Since ammonia concentrations were estimated by iteratively comparing model predictions with measured ammonium and adjusting total ammonia by the residuals, the predicted versus measured ammonium fits are not an independent measure of model performance.

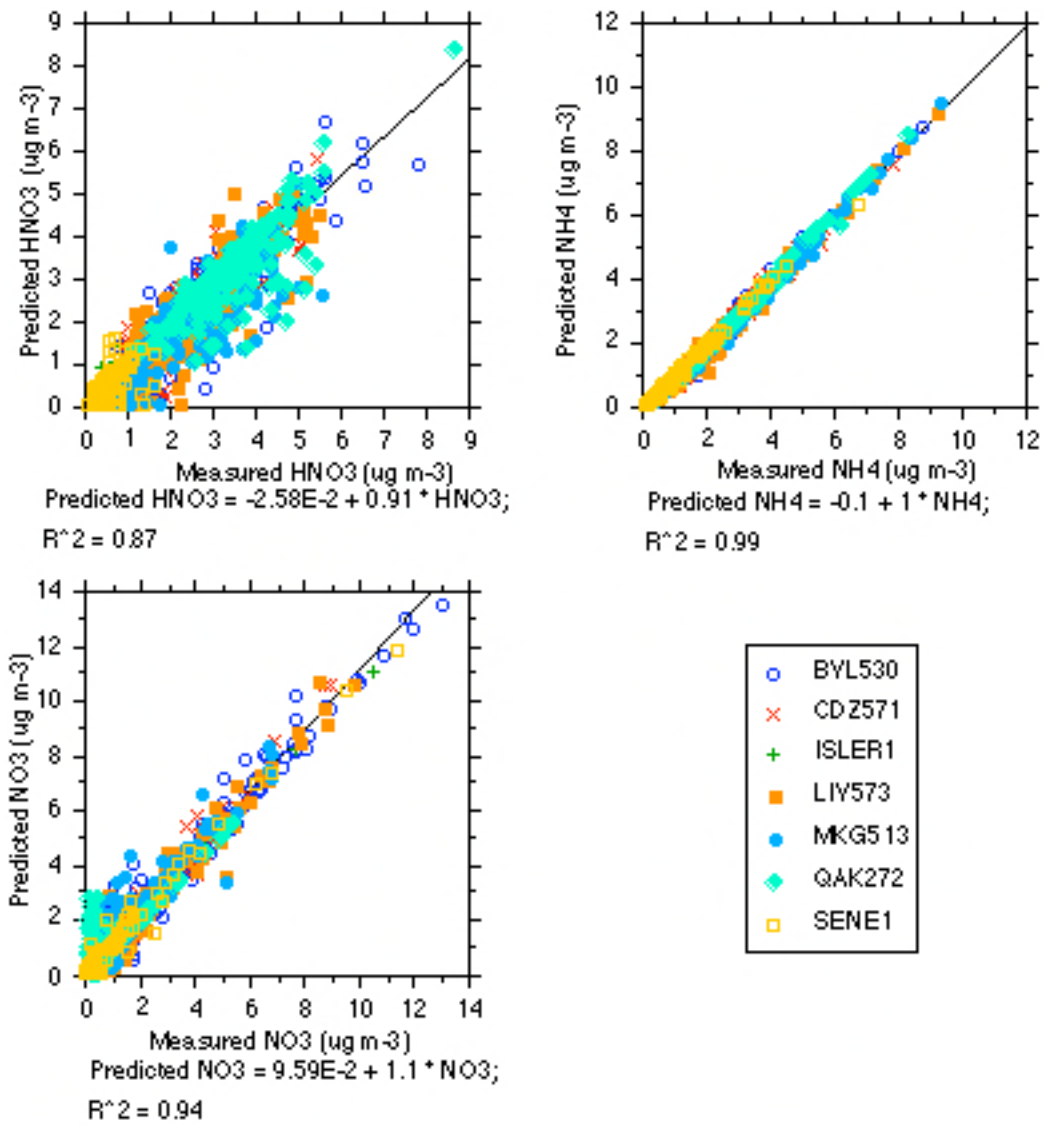


Figure 5. Comparison of measured HNO<sub>3</sub>, NO<sub>3</sub>, and NH<sub>4</sub> with predictions from ISORROPIA, using data from CASTNet/IMPROVE sites, 1998-2002. Each data point represents one 24-hour sample.

The 24-hour IMPROVE/CASTNet data were also used as inputs to SCAPE2 (using the ISORROPIA predictions of gas-phase ammonia). The SCAPE2 model predictions were similar to those obtained with ISORROPIA:  $r^2$  values were nearly the same for the SCAPE2 and ISORROPIA fits, and the SCAPE2 plots also show a nearly one-to-one fit for ammonium (regression slope of 1.02,  $r^2 = 0.94$ ). Like ISORROPIA, SCAPE2 slightly under-predicted nitric acid (regression slope of 0.85,  $r^2 = 0.81$ ) and over-predicted nitrate (regression slope of 1.08,  $r^2 = 0.92$ ).

The representativeness of the days that were modeled was assessed by comparison with the full data sets. Days were selected for modeling if all measurements were available, precipitation was less than 0.254 mm (0.01 in), and 24-hour RH was less than 95 percent. Table 3 compares the mean values of the IMPROVE data selected for modeling with the means from the full data sets for 2000-2002 and with the annual 2002 mean (calculated from Nov-Dec, 2001 and Jan-Oct, 2002). For each location, the 2002 annual mean was based on months with at least 75% of the possible data present, at least two out of three months per quarter present, and all four quarters of the year present to determine completeness. The table shows that the means for RH, temperature, mass, sulfate, ammonium, nitrate and nitric acid are comparable for the model data input, the larger 3-year data sample, and the annual 2002 mean with completeness criteria applied.

Table 3. Comparison of species means for model days, years 2000-2002, and 2002 annual average (see text). Locations are IMPROVE monitoring sites.

LOCATION	SPECIES	Model Days	2000-2002	2002 Average
<b>BONDVILLE IL</b>	HNO3 ( $\mu\text{g m}^{-3}$ )	2.3	2.2	2.1
	MASS ( $\mu\text{g m}^{-3}$ )	11.8	11.3	11.4
	NH4 ( $\mu\text{g m}^{-3}$ )	2.1	2	2
	NO3 ( $\mu\text{g m}^{-3}$ )	2.3	2	2.3
	SO4 ( $\mu\text{g m}^{-3}$ )	3.8	3.8	3.7
	Sample size	124	203	
	RH (%)	68.2	71.5	
<b>CADIZ KY</b>	TEMPERATURE (K)	284.9	286.4	
	HNO3 ( $\mu\text{g m}^{-3}$ )	2.2	2	2.1
	MASS ( $\mu\text{g m}^{-3}$ )	12.3	12.4	12
	NH4 ( $\mu\text{g m}^{-3}$ )	2	2	2
	NO3 ( $\mu\text{g m}^{-3}$ )	1.2	1.1	1.2
	SO4 ( $\mu\text{g m}^{-3}$ )	4.5	4.6	4.3
	Sample size	115	204	
<b>ISLE ROYALE MI</b>	RH (%)	67.3	72.1	
	TEMPERATURE (K)	287.9	289.6	
	HNO3 ( $\mu\text{g m}^{-3}$ )	0.6	0.5	0.5
	MASS ( $\mu\text{g m}^{-3}$ )	4	4.7	5.1
	NH4 ( $\mu\text{g m}^{-3}$ )	0.6	0.7	0.7
	NO3 ( $\mu\text{g m}^{-3}$ )	0.6	0.5	0.5
	SO4 ( $\mu\text{g m}^{-3}$ )	1.2	1.4	1.5
<b>LIVONIA IN</b>	Sample size	185	342	
	RH (%)	68.7	72	
	TEMPERATURE (K)	274.3	278.2	
	HNO3 ( $\mu\text{g m}^{-3}$ )	2.2	2.1	2.2
	MASS ( $\mu\text{g m}^{-3}$ )	13.5	13	12.4
	NH4 ( $\mu\text{g m}^{-3}$ )	2.4	2.3	2.3
	NO3 ( $\mu\text{g m}^{-3}$ )	1.5	1.4	1.5
<b>MK GODDARD PA</b>	SO4 ( $\mu\text{g m}^{-3}$ )	5.2	5.1	4.8
	Sample size	123	202	
	RH (%)	70.3	73.4	
	TEMPERATURE (K)	288	288.5	
	HNO3 ( $\mu\text{g m}^{-3}$ )	2.4	2.4	2.3
	MASS ( $\mu\text{g m}^{-3}$ )	12.2	12	11
	NH4 ( $\mu\text{g m}^{-3}$ )	1.9	1.9	1.8
<b>QUAKER CITY OH</b>	NO3 ( $\mu\text{g m}^{-3}$ )	0.9	0.9	1.1
	SO4 ( $\mu\text{g m}^{-3}$ )	4.3	4.4	4
	Sample size	140	193	
	RH (%)	69.4	71.6	
	TEMPERATURE (K)	285	285.4	
	HNO3 ( $\mu\text{g m}^{-3}$ )	3.2	3.2	
	MASS ( $\mu\text{g m}^{-3}$ )	13.2	12.7	11.8
<b>SENEY MI</b>	NH4 ( $\mu\text{g m}^{-3}$ )	2.2	2.2	2.1
	NO3 ( $\mu\text{g m}^{-3}$ )	0.9	0.6	0.8
	SO4 ( $\mu\text{g m}^{-3}$ )	5.1	5.3	4.9
	Sample size	59	192	
	RH (%)	68.3	69.4	
	TEMPERATURE (K)	284	287.3	
	HNO3 ( $\mu\text{g m}^{-3}$ )	0.6	0.5	0.5
<b>SENEY MI</b>	MASS ( $\mu\text{g m}^{-3}$ )	4.3	5.1	5.3
	NH4 ( $\mu\text{g m}^{-3}$ )	0.8	0.9	1
	NO3 ( $\mu\text{g m}^{-3}$ )	0.7	0.7	0.7
	SO4 ( $\mu\text{g m}^{-3}$ )	1.5	1.8	2
	Sample size	198	341	
	RH (%)	69	72	
	TEMPERATURE (K)	275.4	278.2	

### **Application of Equilibrium Models to Predict Changes in Nitrate Concentrations**

Since the two equilibrium models provided comparable predictions, either could be used to evaluate changes in particulate nitrate concentrations. For the EPRI MMW data, we used both models to evaluate the effects of a 50 percent reduction in sulfate combined with HNO<sub>3</sub> reductions ranging from zero to 60 percent (Figures 6 and 7). The results were similar, with both models indicating that particulate nitrate levels would increase in Athens, Chicago and Cincinnati if sulfate concentrations were reduced by 50 percent, but would decrease as HNO<sub>3</sub> concentrations decreased (since only summer measurements were available from Detroit, St. Louis, and Charleston, predictions were not made for those sites).

For Bondville, two data sets were used: the special study data from 2000-02 and CASNet/IMPROVE data from 1998-2002 (Figure 8). Both showed declining PM nitrate levels as HNO<sub>3</sub> concentrations decreased. Both data sets also indicated that particulate nitrate levels would increase if sulfate concentrations were reduced by 50 percent but no changes occurred in nitric acid levels, though the specific quantitative changes differed.

For the remaining IMPROVE/CASTNet data, we used SCAPE2 to evaluate the effects of a 50 percent reduction in sulfate combined with HNO<sub>3</sub> reductions ranging from zero to 60 percent (Figures 9,10, and 11). At the two southernmost sites (Cadiz and Livonia), results were comparable to those from Bondville: they exhibited relatively small changes in their distributions of particulate nitrate concentrations when sulfate levels were reduced by 50 percent (Figure 9). At the easternmost sites (Quaker City and MK Goddard), the median nitrate levels increased by somewhat larger amounts when sulfate levels decreased by 50 percent (Figure 10). The northern sites (Seney and Isle Royale) showed low nitrate levels for all simulations (Figure 11). All sites showed declining particulate nitrate levels as HNO<sub>3</sub> concentrations were decreased (Figures 9 through 11).

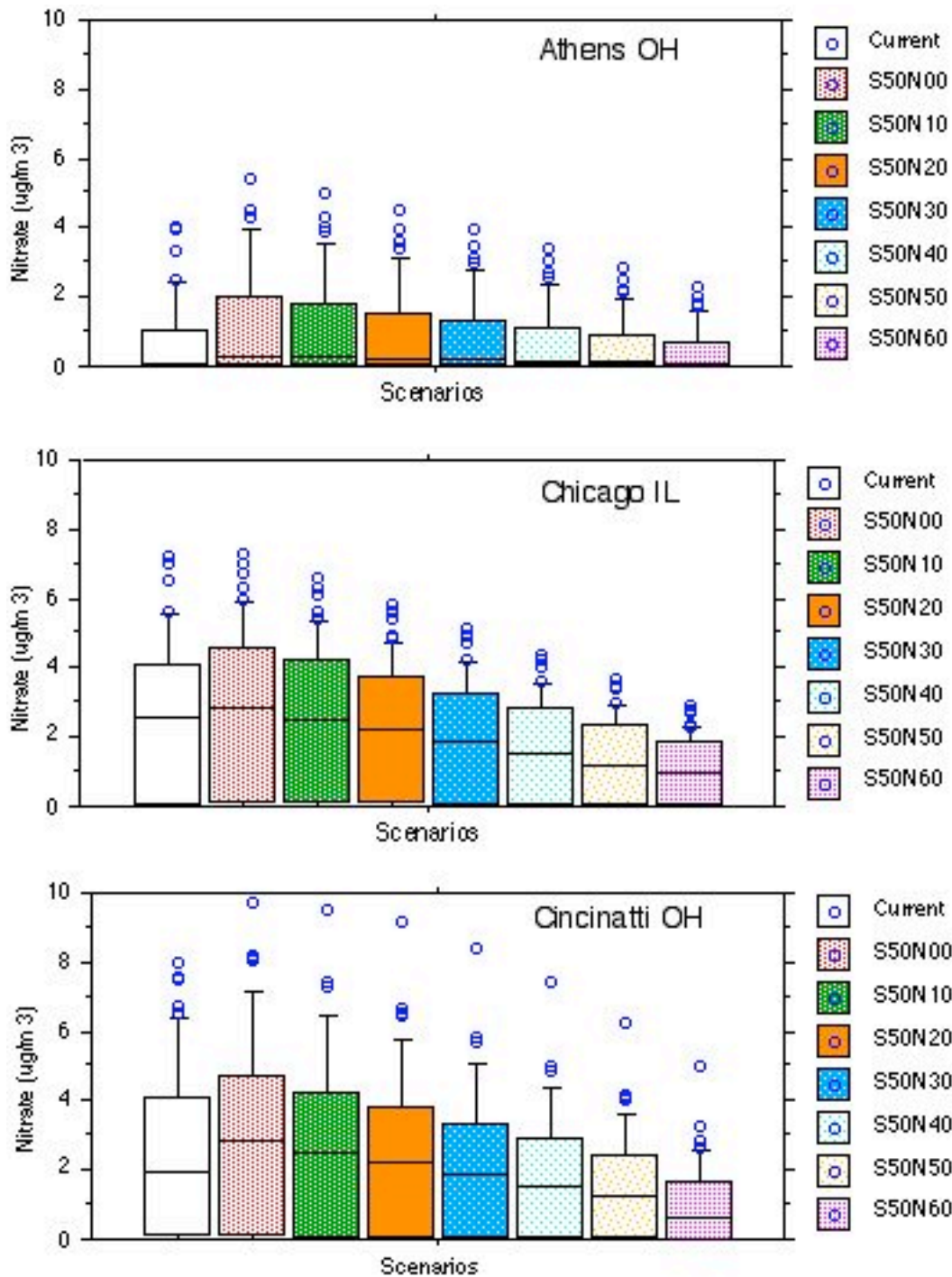


Figure 6. SCAPE2-predicted particulate nitrate concentrations for current conditions and for scenarios with a 50 percent reduction in sulfate and with nitric acid reductions ranging from 0 to 60 percent. The box plots show the 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles. Predictions made for the period Aug-Sept 1999 and Jan-Feb 2000.

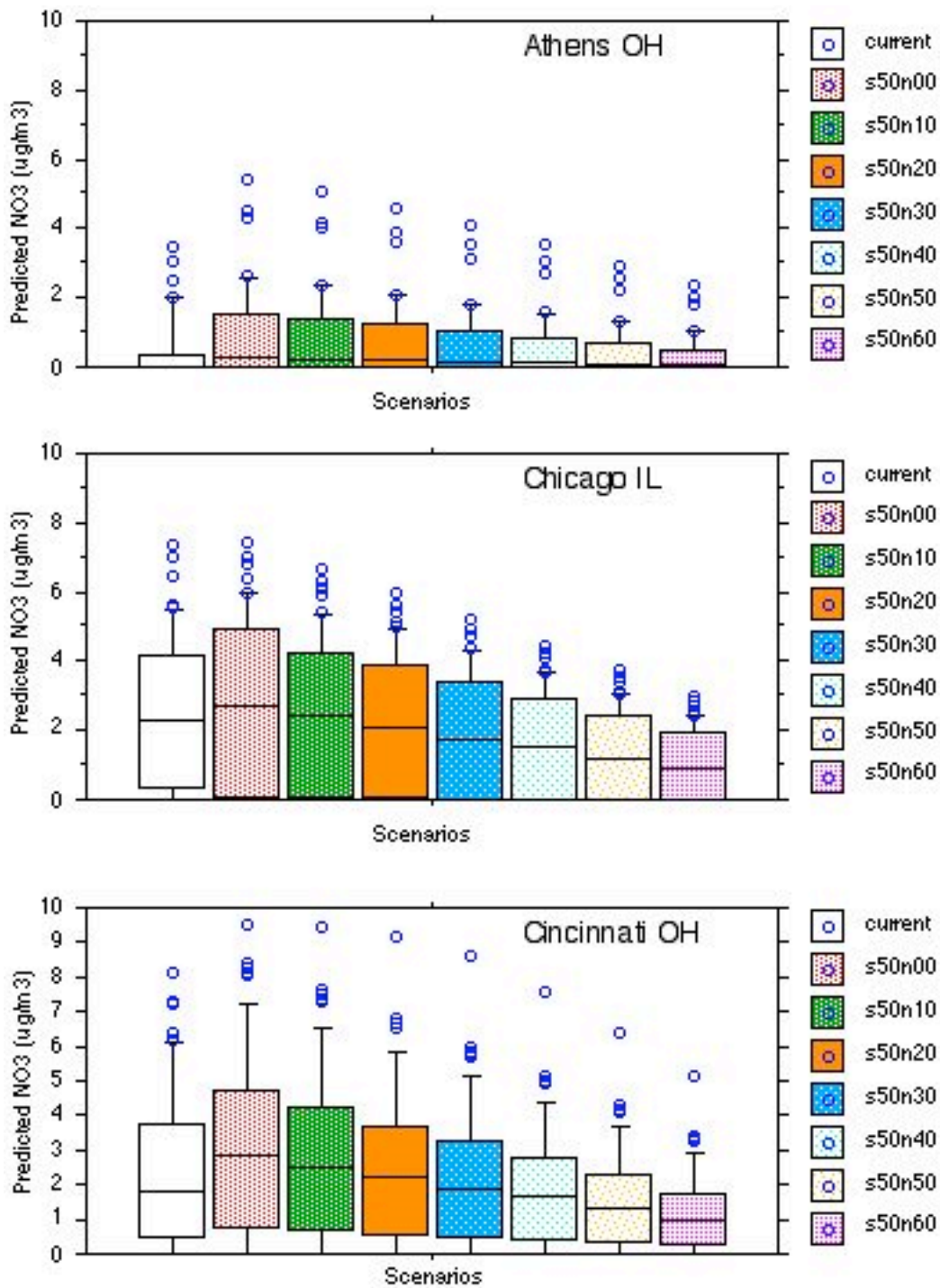


Figure 7. ISORROPIA-predicted particulate nitrate concentrations for current conditions and for scenarios with a 50 percent reduction in sulfate and with nitric acid reductions ranging from 0 to 60 percent. The box plots show the 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles. Predictions made for the period Aug-Sept 1999 and Jan-Feb 2000.

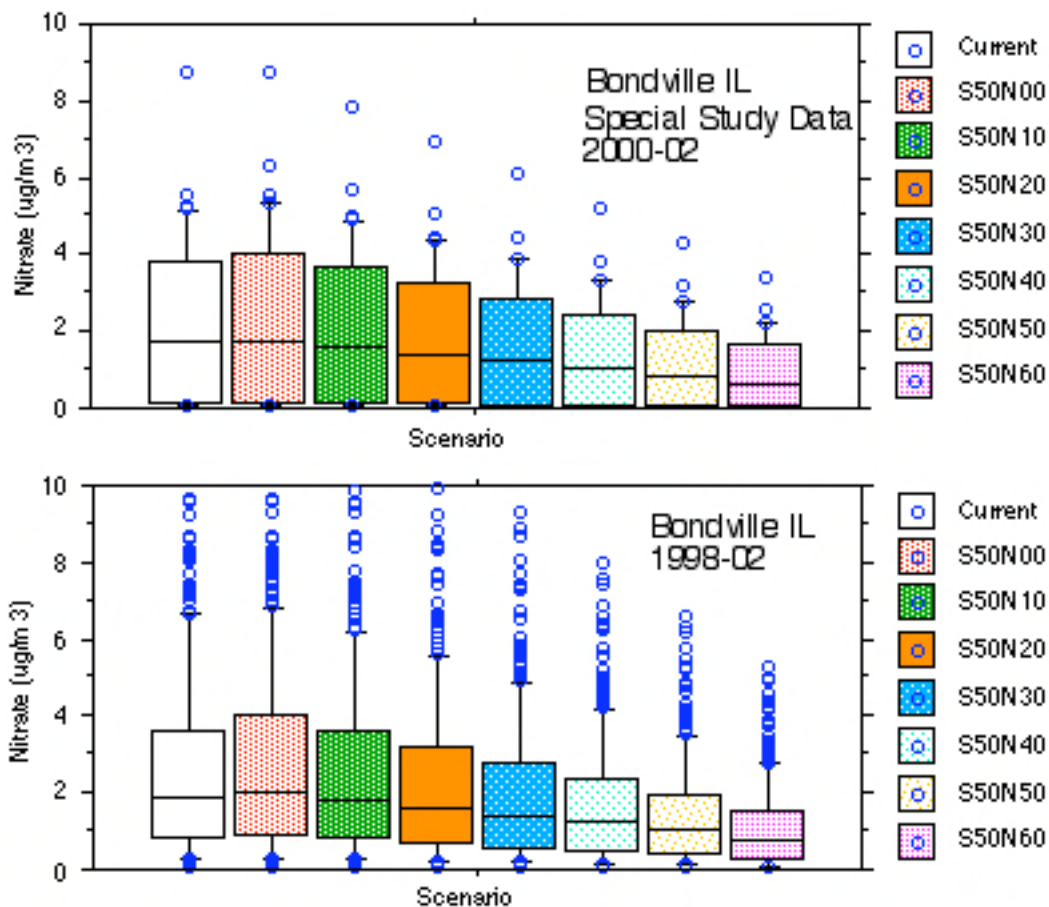


Figure 8. SCAPE2-predicted particulate nitrate concentrations at Bondville IL for current conditions and for scenarios with a 50 percent reduction in sulfate and with nitric acid reductions ranging from 0 to 60 percent. The box plots show the 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles. Two data sets were used; special study data from 2000-02 (top) and CASNet/IMPROVE data from 1998-2002 (bottom).

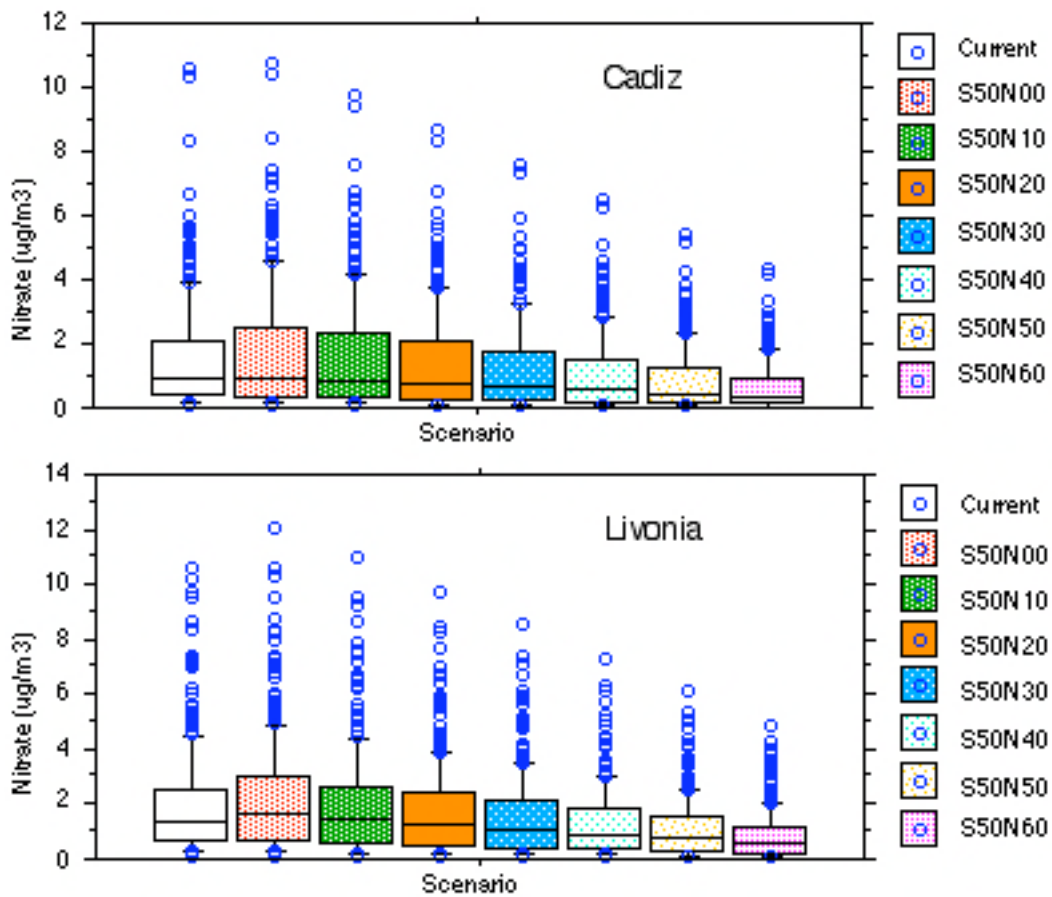


Figure 9. SCAPE2-predicted particulate nitrate concentrations at Cadiz and Livonia for current conditions and for scenarios with a 50 percent reduction in sulfate and with nitric acid reductions ranging from 0 to 60 percent. The box plots show the 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles.

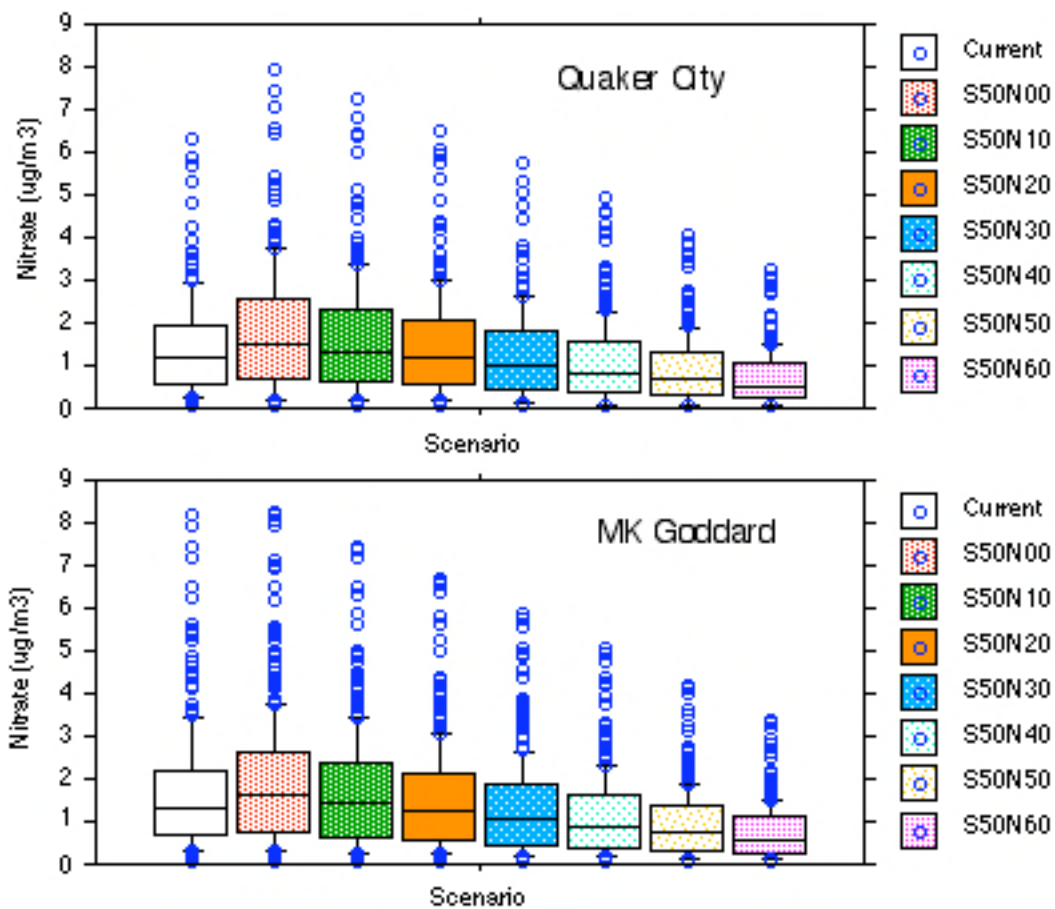


Figure 10. SCAPE2-predicted particulate nitrate concentrations at Quaker City and MK Goddard for current conditions and for scenarios with a 50 percent reduction in sulfate and with nitric acid reductions ranging from 0 to 60 percent. The box plots show the 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles.

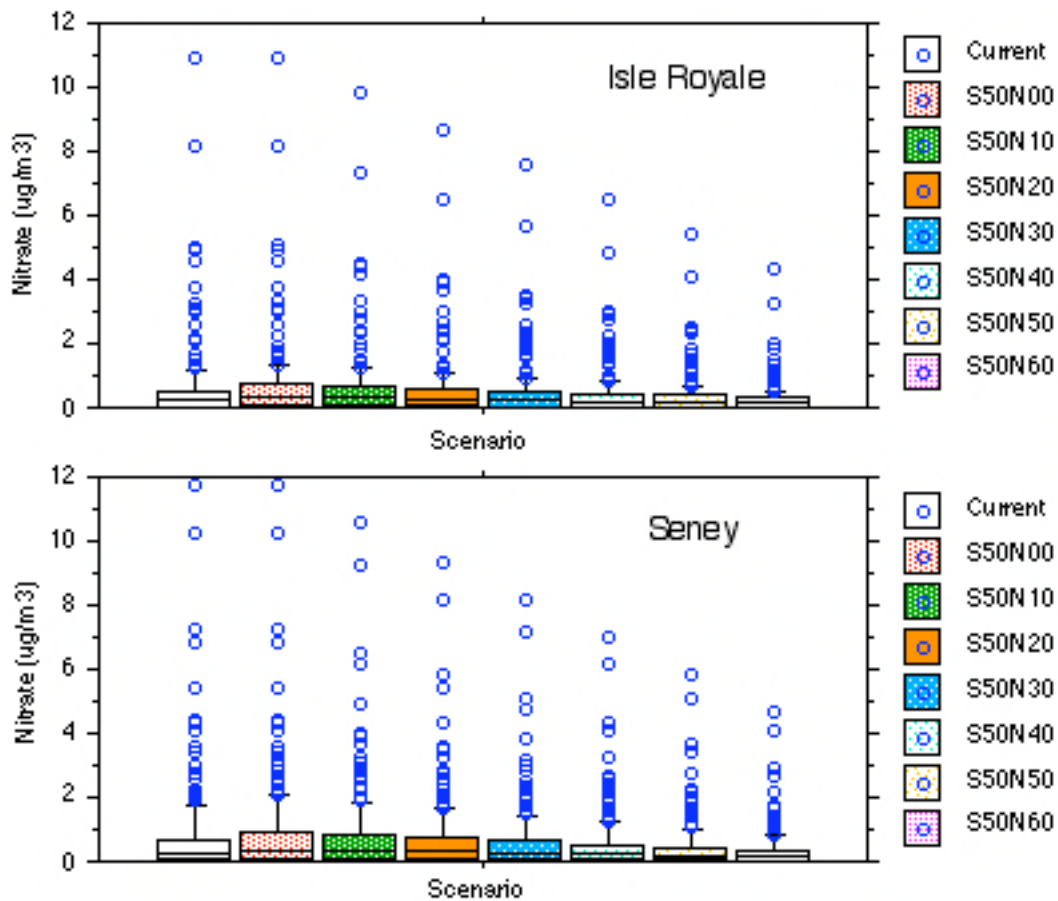


Figure 11. SCAPE2-predicted particulate nitrate concentrations at Seney and Isle Royale for current conditions and for scenarios with a 50 percent reduction in sulfate and with nitric acid reductions ranging from 0 to 60 percent. The box plots show the 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles.

Once the sulfate levels were reduced by 50 percent, decreases in HNO<sub>3</sub> concentrations produced essentially proportional decreases in mean particulate nitrate concentrations (Figures 13 and 14). ISORROPIA and SCAPE provided similar predictions for the MMW sites (Figure 13). The mean concentrations at the three MMW sites during the four months when measurements were made are compared to 2002 annual-average concentrations from collocated or nearby PM STN sites in Table 4. The means from the MMW monitoring period are higher for sulfate and lower for nitrate than are the 2002 annual means, suggesting that the predicted nitrate changes at the MMW sites might be somewhat different than would occur for complete annual averages.

Table 4. Mean concentrations from MMW sites for the samples used in the thermodynamic equilibrium model predictions compared with 2002 annual mean concentrations at nearby PM monitoring sites (from Table 1). Units are  $\mu\text{g m}^{-3}$ .

SITE	AIRS	STATE	MASS	SO <sub>4</sub>	NO <sub>3</sub>	NH <sub>4</sub>	HNO <sub>3</sub>	NH <sub>3</sub>	OC	BC
CHICAGO MMW	170310014	IL	19.7	5.1	1.9	2.5	3.3	2.4	7.6	2.2
CHICAGO	170310057	IL	15.2	3.5	3.4	2.0			4.4	0.7
CHICAGO	170310076	IL	15.1	3.8	2.4	1.9			3.1	0.6
CINCINNATI MMW	390610040	OH	20.5	5.4	1.9	2.4	4.2	1.4	6.8	1.6
DAYTON	391130031	OH	14.4	4.6	2.6	2.1			4.0	0.5
ATHENS MMW	none	OH	14.3	6.0	0.5	2.0	2.2	0.4	3.3	0.5
QUAKER CITY	IMPROVE	OH	11.8	4.9	0.8	2.1	3.5*		1.6	0.4

\* Did not meet 75 percent completeness

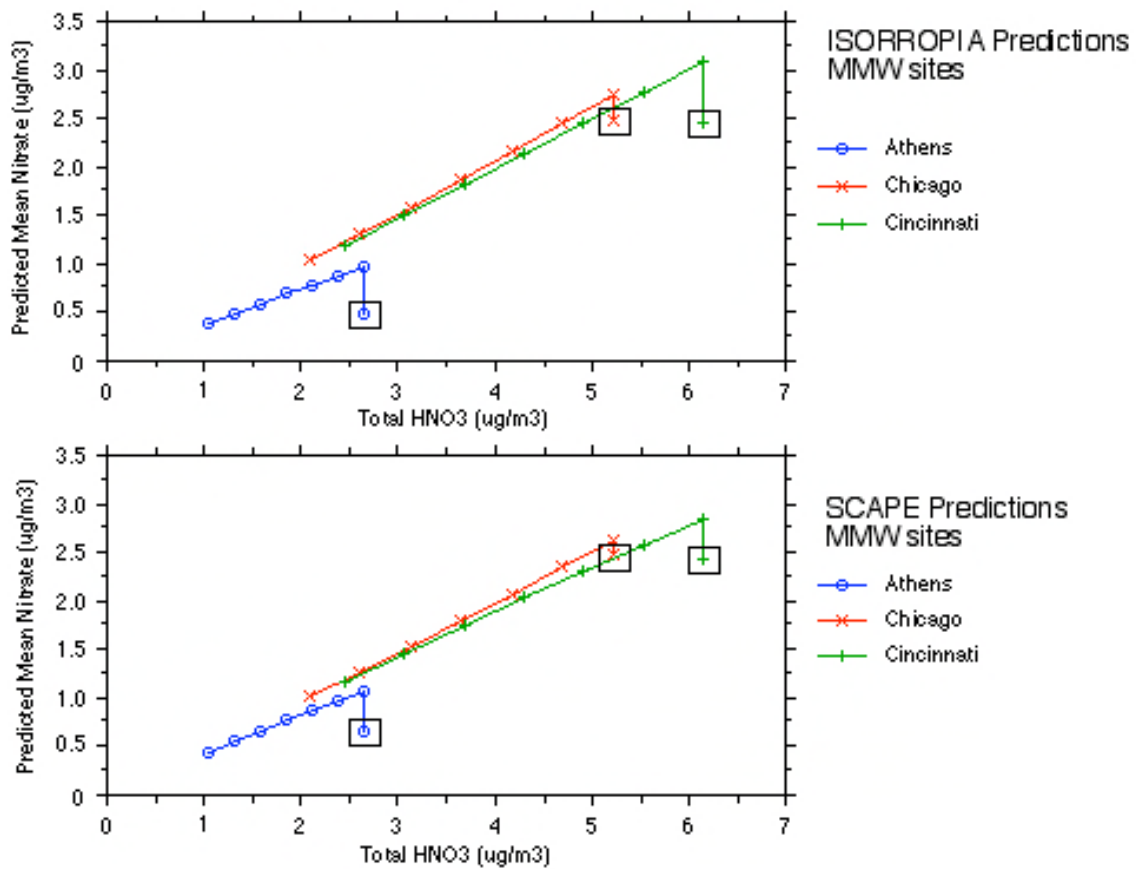


Figure 12. Mean predicted particulate nitrate concentrations versus total mean HNO<sub>3</sub> at IMPROVE sites and MMW sites. Current conditions are marked by boxes. Modeled predictions include 50 percent reductions of sulfate and 10, 20, 30, 40, 50, and 60 percent reductions in HNO<sub>3</sub>.

The SCAPE predictions differ quantitatively for the two sets of data from Bondville, though they are qualitatively similar (Figure 13). As previously noted, the Bondville special-study data exhibit lower mean nitric acid and sulfate concentrations than is true for the longer period of record of the CASTNet/IMPROVE data; both factors contribute to the differences shown in Figure 13.

For all sites, the PM nitrate increases that are predicted to occur in response to lowered sulfate concentrations would be offset by decreases in ambient concentrations of  $\text{HNO}_3$  ranging from less than 10 percent to approximately 20 percent of current mean levels (Figures 12 and 13).

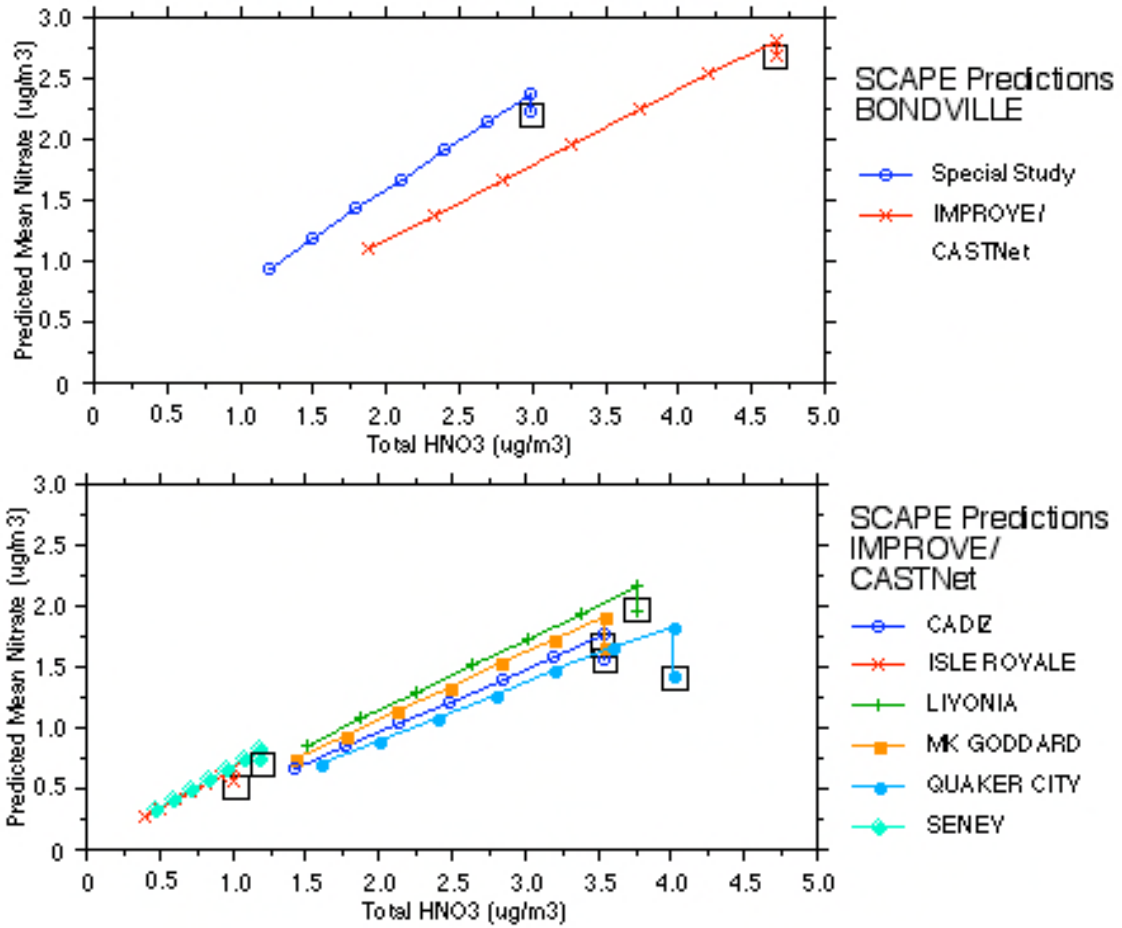


Figure 13. Mean predicted particulate nitrate concentrations versus total mean HNO<sub>3</sub> at IMPROVE sites. Current conditions are marked by boxes. Modeled predictions include 50 percent reductions of sulfate and 10, 20, 30, 40, 50, and 60 percent reductions in HNO<sub>3</sub>.

The largest predicted mean nitrate increases occurred at the Cincinnati site. At this location, approximately one-third of the samples were ammonia-limited (Figure 14). Once sulfate concentrations were reduced by 50 percent, predicted particulate nitrate formation became HNO<sub>3</sub>-limited for nearly all samples. The mean nitrate increases predicted by the models as a result of lowering sulfate concentrations were strongly influenced by those samples that are presently ammonia limited.

In spite of the mean nitrate increases, the median (and mean) PM<sub>2.5</sub> mass concentration decreases at the Cincinnati MMW site exceeded the median (and mean) sulfate decreases for all scenarios (Figure 15). This result held both when changes in water content were considered and when they were not.<sup>4</sup> The mass concentration decreases exceeded the sulfate decreases because ammonium concentrations also decreased. For the scenario with the maximum mean nitrate increase (i.e., 50 percent sulfate decrease, no HNO<sub>3</sub> decrease), the mean sulfate decrease was 2.7  $\mu\text{g m}^{-3}$ , the mean ammonium decrease was 0.9  $\mu\text{g m}^{-3}$ , the mean nitrate increase was 0.4  $\mu\text{g m}^{-3}$ , and the mean PM<sub>2.5</sub> mass concentration decrease was 3.2  $\mu\text{g m}^{-3}$ . Expressed in percentages, the mean sulfate concentration decreased by 50 percent, leading to a 17 percent increase in the mean nitrate concentration, a 38 percent decrease in mean ammonium, and a 16 percent decrease in the mean PM<sub>2.5</sub> mass concentration.

---

<sup>4</sup> Since PM mass is measured under fixed temperature and RH in a laboratory, changes in ambient water content do not necessarily affect the reported mass concentrations. However, changes in ambient water content are of significance with respect to visibility.

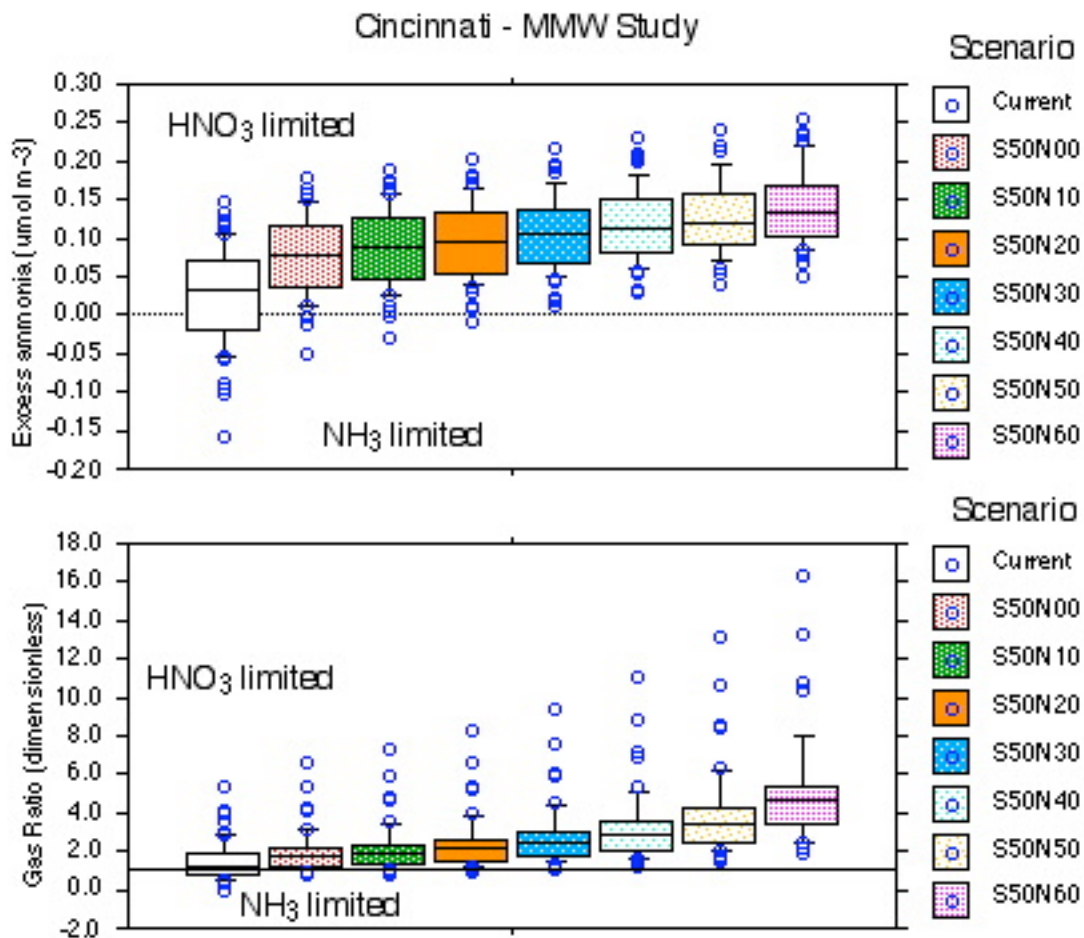


Figure 14. Estimates of ammonia limitation for current conditions and hypothetical reductions of sulfate and nitric acid. The top panel shows excess ammonia (Blanchard et al., 2000) and the bottom panel shows the gas ratio (Ansari and Pandis, 1998). Particulate nitrate formation is not limited by the availability of ammonia for samples having excess ammonia exceeding zero or a gas ratio exceeding one.

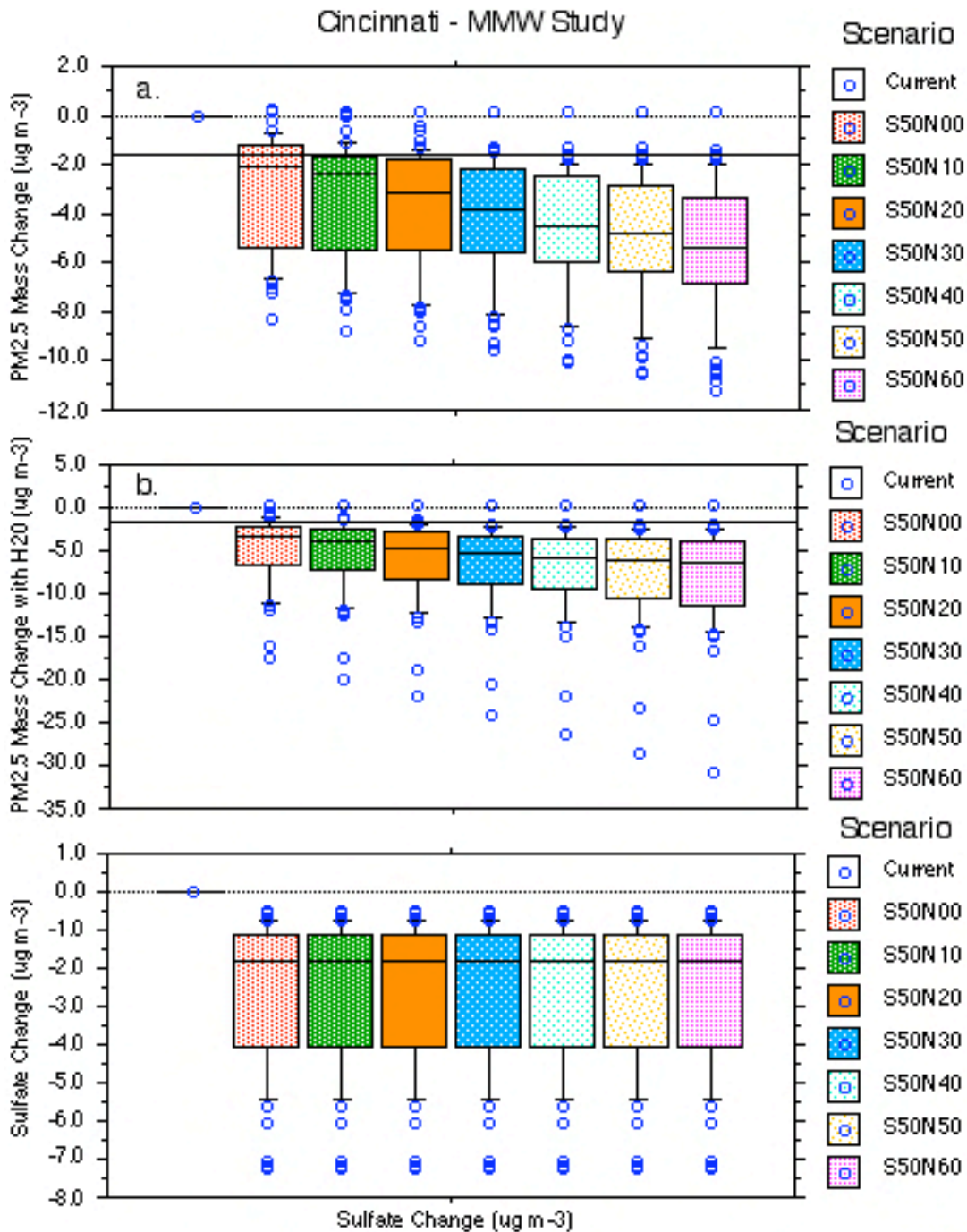


Figure 15. Predicted changes in (a) PM<sub>2.5</sub> mass, (b) PM<sub>2.5</sub> mass including changes in water content, and (c) sulfate following an assumed 50 percent decrease in sulfate concentrations and zero to 60 percent decreases in HNO<sub>3</sub> concentrations at the Cincinnati MMW site. The median sulfate decrease of 1.7 mg m<sup>-3</sup> is marked by horizontal lines in panels (a) and (b).

### **Application of Equilibrium Models to Predict Changes in Mass Concentrations**

Changes in PM mass concentrations resulting from changes in sulfate and nitric acid levels were estimated for all monitoring locations. The simulations with 50 percent reductions of sulfate were augmented with simulations in which sulfate levels were reduced by zero, 25, 75, or 90 percent. PM mass changes were estimated as:

PM mass change = Measured fine mass – change in sum of sulfate, nitrate, ammonium

We also calculated changes in water content, though we did not include these changes in estimating the changes in mass concentrations. Since PM mass is measured under fixed temperature and RH in a laboratory, changes in ambient water content do not necessarily affect the reported mass concentrations. However, changes in ambient water content are of significance with respect to visibility.

The change in the sum of sulfate, nitrate, and ammonium was calculated as:

Change in sum = current predicted sum – future predicted sum

The current model predictions were used rather than the current measured sulfate, nitrate, and ammonium so that the estimated change would not be a function of the lack of fit between measured and predicted values. The agreement between predicted and measured concentrations is discussed in previous sections and in Appendix A.

The changes in mean mass are listed in Tables 5 through 7 and depicted as isopleths in Figures 16 through 18. Each set of isopleths was drawn from 35 sets of simulations, each set representing the means from 40 to 288 individual 24-hour samples. The tables list results for 12 of the 35 sets (three levels of sulfate reduction times four levels of nitric acid reduction).

Table 5. Predicted mean PM<sub>2.5</sub> mass concentrations with sulfate reduction of 25 percent and three levels of reduction of HNO<sub>3</sub>, mean measured PM<sub>2.5</sub> mass concentration determined from all sampling days during 1998-2002, and mean measured PM<sub>2.5</sub> mass, sulfate, and nitrate concentrations determined from modeling days only.

LOCATION	MEAN (all days)	MEAN (modeling days)			Predicted PM <sub>2.5</sub> Mass After Specified Precursor Reductions			
	PM <sub>2.5</sub> Mass	PM <sub>2.5</sub> Mass	Sulfate	Nitrate	Sulfate 25%	Sulfate 25% HNO <sub>3</sub> 20%	Sulfate 25% HNO <sub>3</sub> 40%	Sulfate 25% HNO <sub>3</sub> 60%
Athens <sup>4</sup>	13.68	14.35	5.95	0.49	12.73	12.55	12.33	12.09
Chicago <sup>4</sup>	19.69	19.68	5.01	1.99	18.08	17.40	16.72	16.04
Cincinnati <sup>4</sup>	20.06	20.54	5.45	1.87	19.02	18.40	17.71	16.96
Bondville <sup>5</sup>	11.96	12.95	2.86	2.35	12.09	11.56	10.96	10.34
Bondville <sup>6</sup>	11.49	11.86	3.89	2.39	10.58	9.85	9.08	8.32
Cadiz <sup>6</sup>	12.59	13.03	4.70	1.26	11.55	11.13	10.67	10.20
Isle Royale <sup>6</sup>	4.69	4.27	1.43	0.47	3.93	3.75	3.56	3.36
Livonia <sup>6</sup>	13.34	13.11	5.07	1.60	11.49	10.95	10.4	9.84
MK Goddard <sup>6</sup>	13.83	14.30	4.72	1.14	12.88	12.43	11.93	11.43
Quaker City <sup>6</sup>	12.76	12.87	5.46	0.72	11.58	11.12	10.58	10.00
Seney <sup>6</sup>	5.08	4.37	1.84	0.64	3.94	3.70	3.46	3.22

1. EPRI MMW
2. BEARS
3. CASTNet visibility network (IMPROVE protocol) 1998-2001; IMPROVE 2001-02

Table 6. Predicted mean PM<sub>2.5</sub> mass concentrations with sulfate reduction of 50 percent and three levels of reduction of HNO<sub>3</sub>, mean measured PM<sub>2.5</sub> mass concentration determined from all sampling days during 1998-2002, and mean measured PM<sub>2.5</sub> mass, sulfate, and nitrate concentrations determined from modeling days only.

LOCATION	MEAN (all days)	MEAN (modeling days)			Predicted PM <sub>2.5</sub> Mass After Specified Precursor Reductions			
	PM <sub>2.5</sub> Mass	PM <sub>2.5</sub> Mass	Sulfate	Nitrate	Sulfate 50%	Sulfate 50% HNO <sub>3</sub> 20%	Sulfate 50% HNO <sub>3</sub> 40%	Sulfate 50% HNO <sub>3</sub> 60%
Athens <sup>1</sup>	13.68	14.35	5.95	0.49	10.95	10.69	10.41	10.12
Chicago <sup>1</sup>	19.69	19.68	5.01	1.99	16.38	15.67	14.97	14.30
Cincinnati <sup>1</sup>	20.06	20.54	5.45	1.87	17.29	16.61	15.87	15.12
Bondville <sup>2</sup>	11.96	12.95	2.86	2.35	11.17	10.58	9.96	9.34
Bondville <sup>3</sup>	11.49	11.86	3.89	2.39	9.26	8.50	7.71	6.95
Cadiz <sup>3</sup>	12.59	13.03	4.70	1.26	9.97	9.50	9.02	8.55
Isle Royale <sup>3</sup>	4.69	4.27	1.43	0.47	3.57	3.37	3.16	2.95
Livonia <sup>3</sup>	13.34	13.11	5.07	1.60	9.86	9.29	8.71	8.15
MK Goddard <sup>3</sup>	13.83	14.30	4.72	1.14	11.35	10.84	10.32	9.80
Quaker City <sup>3</sup>	12.76	12.87	5.46	0.72	10.09	9.53	8.91	8.29
Seney <sup>3</sup>	5.08	4.37	1.84	0.64	3.48	3.24	2.98	2.73

1. EPRI MMW
2. BEARS
3. CASTNet visibility network (IMPROVE protocol) 1998-2001; IMPROVE 2001-02

Table 7. Predicted mean PM<sub>2.5</sub> mass concentrations with sulfate reduction of 75 percent and three levels of reduction of HNO<sub>3</sub>, mean measured PM<sub>2.5</sub> mass concentration determined from all sampling days during 1998-2002, and mean measured PM<sub>2.5</sub> mass, sulfate, and nitrate concentrations determined from modeling days only.

LOCATION	MEAN (all days)	MEAN (modeling days)			Predicted PM <sub>2.5</sub> Mass After Specified Precursor Reductions			
	PM <sub>2.5</sub> Mass	PM <sub>2.5</sub> Mass	Sulfate	Nitrate	Sulfate 75%	Sulfate 75% HNO <sub>3</sub> 20%	Sulfate 75% HNO <sub>3</sub> 40%	Sulfate 75% HNO <sub>3</sub> 60%
Athens <sup>7</sup>	13.68	14.35	5.95	0.49	8.96	8.66	8.36	8.06
Chicago <sup>7</sup>	19.69	19.68	5.01	1.99	14.52	13.84	13.19	12.55
Cincinnati <sup>7</sup>	20.06	20.54	5.45	1.87	15.46	14.72	13.98	13.23
Bondville <sup>8</sup>	11.96	12.95	2.86	2.35	10.22	9.61	8.98	8.36
Bondville <sup>9</sup>	11.49	11.86	3.89	2.39	7.98	7.19	6.40	5.63
Cadiz <sup>9</sup>	12.59	13.03	4.70	1.26	8.34	7.86	7.39	6.93
Isle Royale <sup>9</sup>	4.69	4.27	1.43	0.47	3.21	3.00	2.79	2.57
Livonia <sup>9</sup>	13.34	13.11	5.07	1.60	8.29	7.69	7.10	6.51
MK Goddard <sup>9</sup>	13.83	14.30	4.72	1.14	9.73	9.19	8.66	8.16
Quaker City <sup>9</sup>	12.76	12.87	5.46	0.72	8.49	7.87	7.24	6.60
Seney <sup>9</sup>	5.08	4.37	1.84	0.64	3.02	2.76	2.51	2.24

1. EPRI MMW
2. BEARS
3. CASTNet visibility network (IMPROVE protocol) 1998-2001; IMPROVE 2001-02

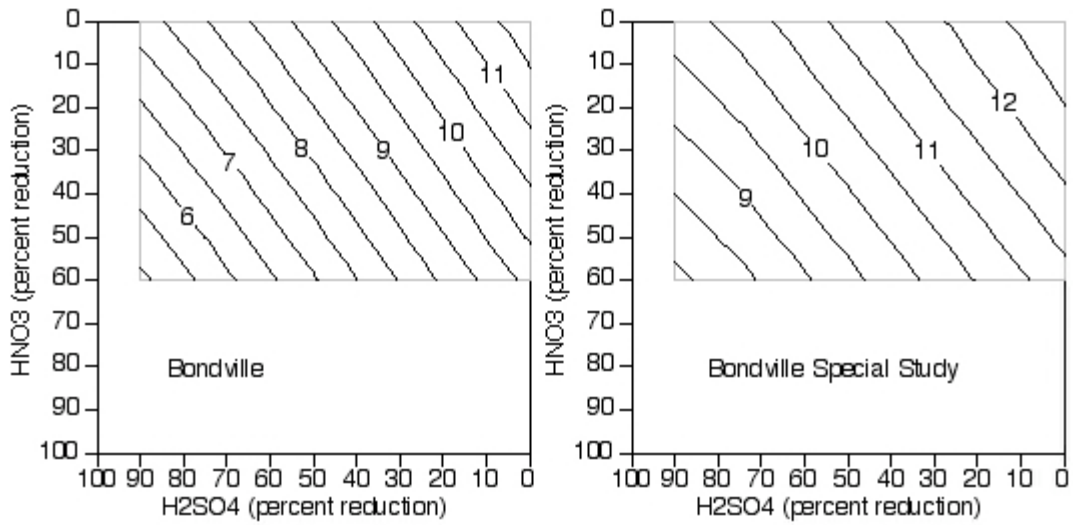


Figure 16. Predicted mean  $PM_{2.5}$  mass concentrations as a function of reductions of sulfate (0 to 90 percent) and  $HNO_3$  (0 to 60 percent) at Bondville IL. The predictions were determined using SCAPE2 applied to CASTNet/IMPROVE data from 1998-2002 (left) and the special-study measurements from 2000-2001 (right). There are differences in the mean measured concentrations between these two time periods and data sets (Table 5).

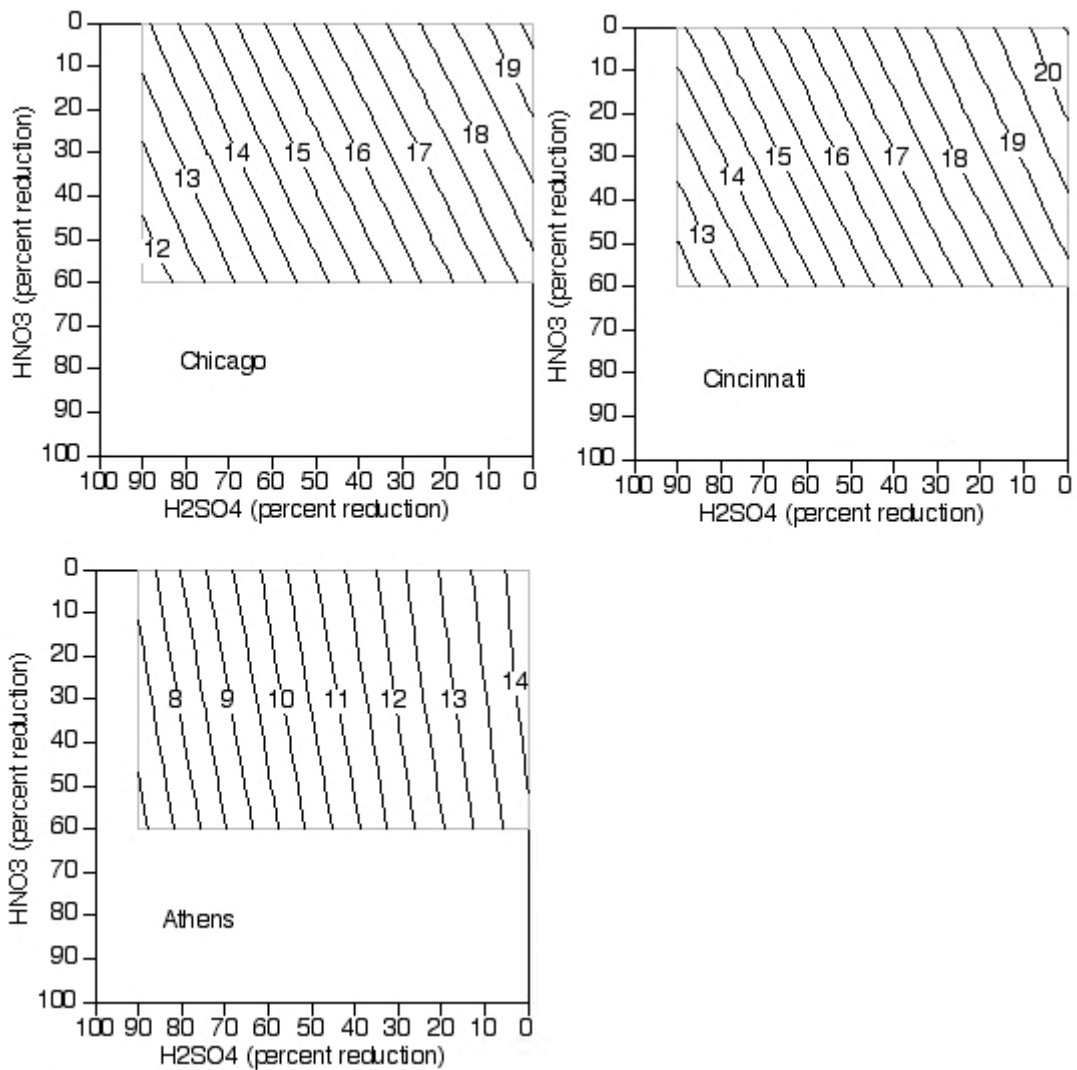


Figure 17. Predicted mean  $PM_{2.5}$  mass concentrations as a function of reductions of sulfate (0 to 90 percent) and  $HNO_3$  (0 to 60 percent) at three locations. The predictions were determined using SCAPE2 applied to EPRI MMW study data from August-September 1999 and January-February 2000. The winter measurements at the rural site (Athens) were underrepresented (11 of 37 samples), so the results may not represent the full sensitivity of mean PM mass concentration to changes in nitric acid concentrations.

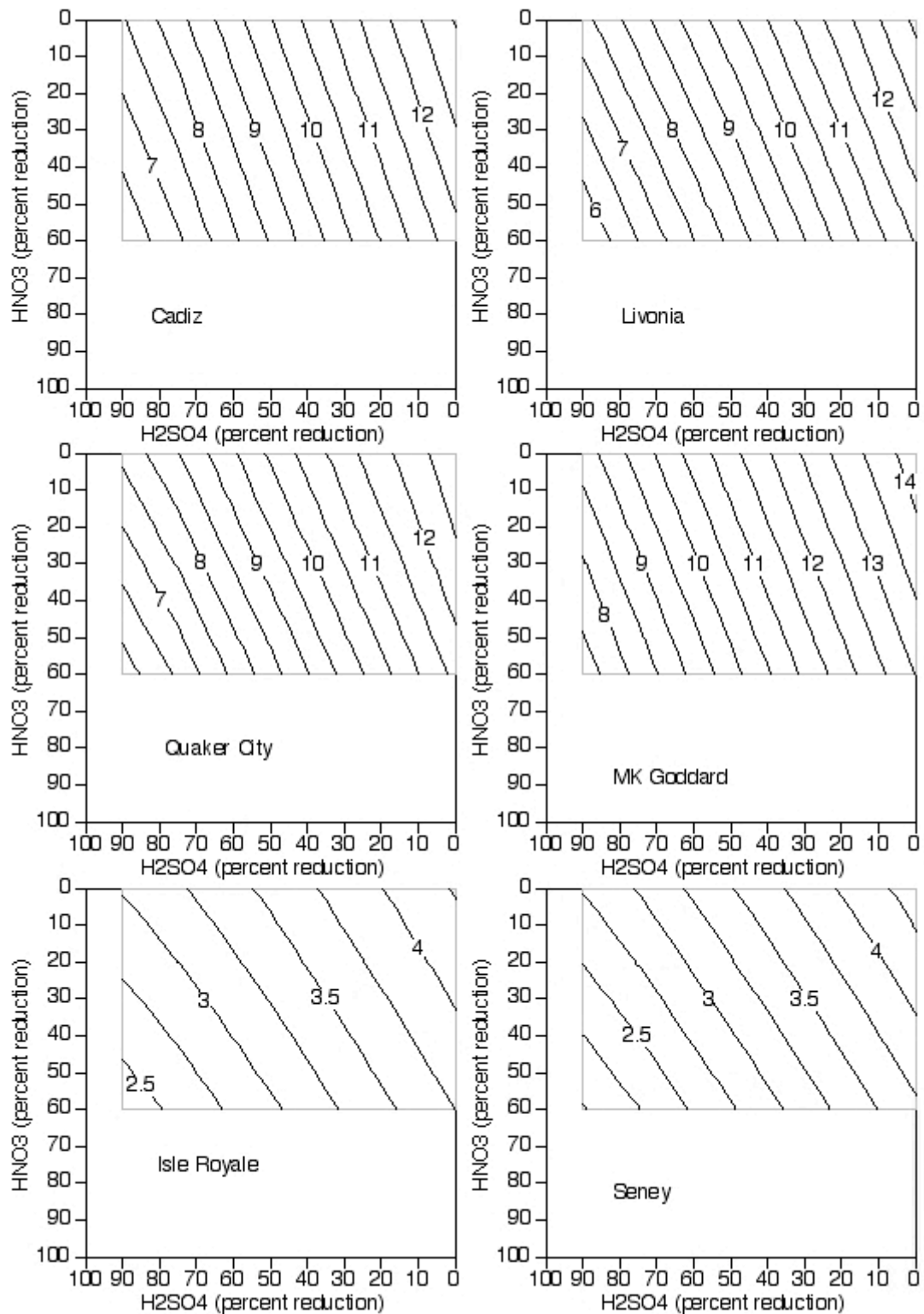


Figure 18. Predicted mean PM<sub>2.5</sub> mass concentrations as a function of reductions of sulfate (0 to 90 percent) and HNO<sub>3</sub> (0 to 60 percent) at six sites. The predictions were determined using SCAPE2 applied to CASTNet/IMPROVE data from 1998-2002.

The shapes of the isopleths were the same for all sites, indicating that predicted fine mass concentrations declined as either sulfate or nitric acid concentrations declined (Figures 16 to 18). Also, the rates of mass decrease were typically about 2 to 3  $\mu\text{g m}^{-3}$  for a 50 percent sulfate decrease and about 1 to 1.5  $\mu\text{g m}^{-3}$  for a 50 percent nitric acid decrease, thus showing greater sensitivity to sulfate reductions. The sulfate decreases were an input to the model calculations, but their effect on fine PM mass was modified by concomitant decreases in ammonium and increases in nitrate. These concomitant changes nearly balanced each other, so that the PM mass changes in response to the assumed sulfate decreases were approximately equal in magnitude to the sulfate reductions (Tables 5 through 7). For the IMPROVE/CASTNet data (six of the ten sites), the predicted sensitivities of mean PM mass concentration to changes in sulfate and nitric acid concentrations should be considered preliminary because some measurements were estimated from other quantities (see appendix).

Isopleths were also computed separately for summer and winter samples (Figure 19). They show that PM mass concentrations are predicted to decrease in response to sulfate decreases during summer but to  $\text{HNO}_3$  decreases during winter.

Further work is needed to relate the changes in model inputs (sulfate and nitric acid) to changes in emissions of  $\text{SO}_2$  and  $\text{NO}_x$ . As previously discussed, past modeling and empirical analyses indicate that reductions of  $\text{SO}_2$  emissions have led in the past to nearly proportional reductions of ambient sulfate concentrations on the semi-continental scale of eastern North America. On smaller spatial scales, including regional (e.g., the six Midwestern states studied here) and local (e.g., the Chicago CMSA), the response of ambient sulfate concentrations to  $\text{SO}_2$  emission reductions may be nonproportional. Also as noted earlier, the response of ambient concentrations of nitric acid to changes in  $\text{NO}_x$  emissions has not been previously well established. This report does not attempt to model the gas-phase processes linking  $\text{NO}_x$  with nitric acid. Instead, the next section examines the links empirically through quantification of the day-of-week variations in the ambient concentrations of  $\text{NO}_x$  and PM nitrate.

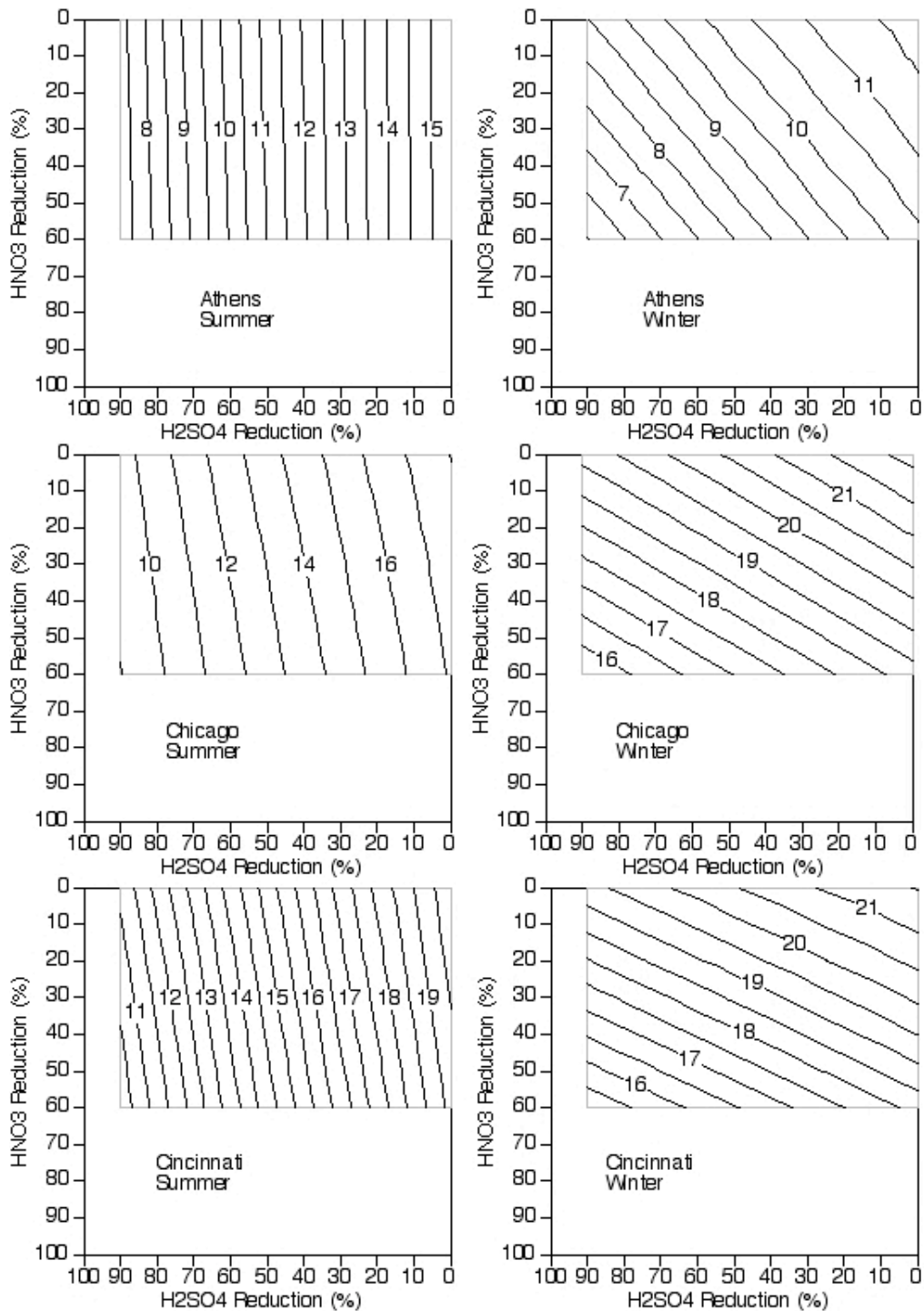


Figure 19. Predicted seasonal mean PM<sub>2.5</sub> mass concentrations as a function of reductions of sulfate (0 to 90 percent) and HNO<sub>3</sub> (0 to 60 percent) at three locations. The predictions were determined using SCAPE2 applied to EPRI MMW study data from August-September 1999 (summer) and January-February 2000 (winter).

### **Day-of-Week Variations of Concentrations of PM Components**

Mean concentrations of PM components were computed by the day of the week and were examined graphically (Figures 20 and 21). Because the periods of monitoring are not yet long enough to minimize the standard errors of the means, few day-of-week differences are statistically significant (Table 8). Nonetheless, some day-of-week variations appear to exist. Mean sulfate concentrations vary by day of week, sometimes being highest on Wednesdays and lowest on Fridays. Black carbon (BC) concentrations tend to show lower weekend than weekday mean concentrations at urban but not rural (e.g., Bondville and Livonia) sites. Ten of 52 weekend-Wednesday BC comparisons were statistically significant, all at urban sites, and the median BC reductions were substantially greater at urban than rural sites (Table 8). BC is a primary pollutant deriving substantially from diesel motor vehicle emissions, so these day-of-week variations are potentially indicative of local day-of-week changes in emissions. Mean nitrate concentrations tend to show higher mid-week than weekend levels at many of the sites, with median changes of about 11 percent from Wednesday to Saturday and Sunday. However, none of the weekend-Wednesday mean nitrate differences are statistically significant and they are not large relative to the typical standard errors of approximately  $0.5 \mu\text{g m}^{-3}$ . The weekend nitrate reductions at urban sites tended to be larger than at rural sites, but the differences were not prominent (e.g., median 8 percent lower at rural sites and 11 percent lower at urban sites on Saturdays compared with Wednesdays).

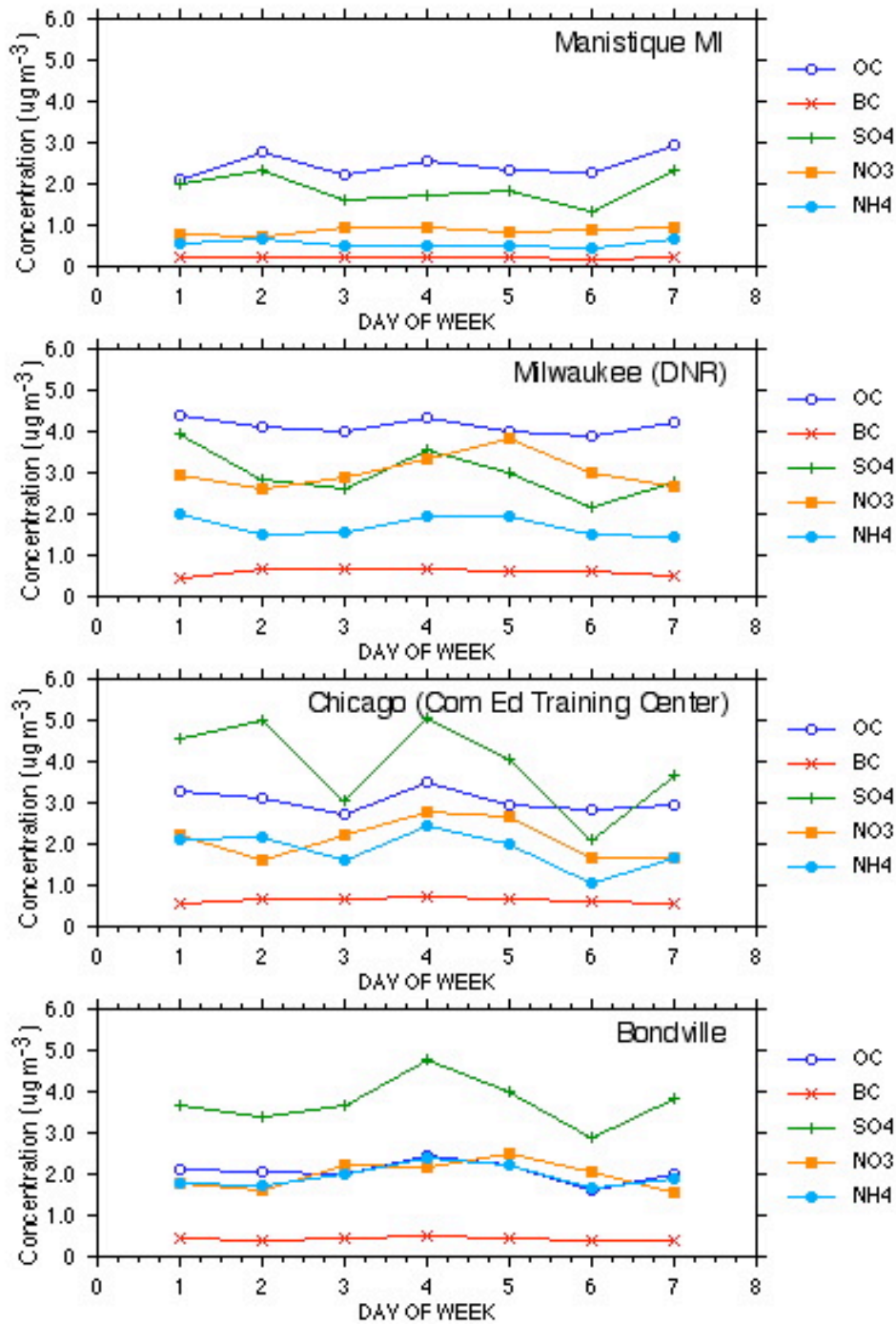


Figure 20. Mean concentrations of PM components by day of week at Manistique MI, Milwaukee WI, Chicago IL, and Bondville IL. Sites were selected so that each mean consisted of 25 to 40 daily measurements. The average standard errors of the means ranged from less than  $0.1 \mu\text{g m}^{-3}$  for BC to  $0.9 \mu\text{g m}^{-3}$  for sulfate.

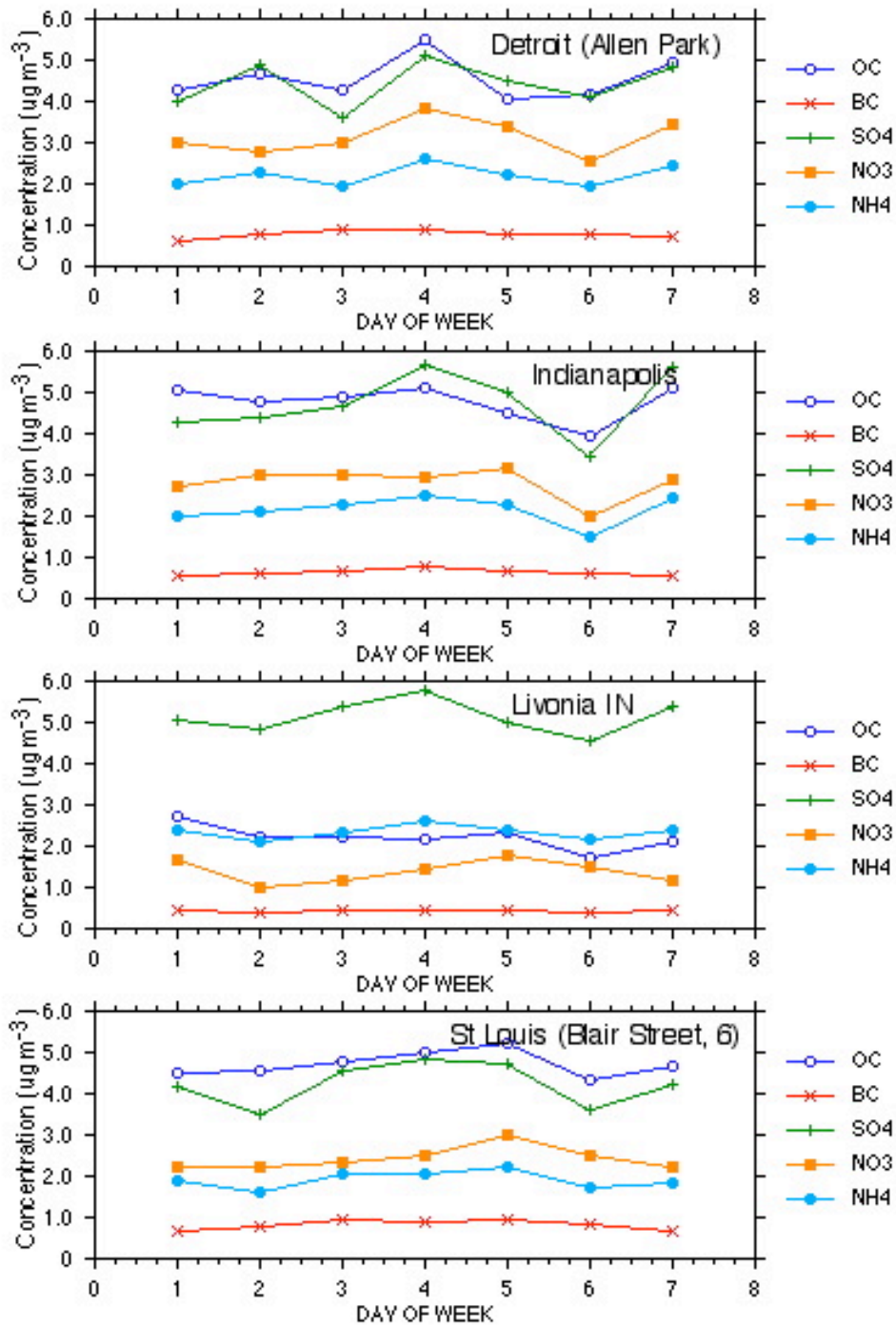


Figure 21. Mean concentrations of PM components by day of week at Detroit MI, Livonia IN, Indianapolis IN, and St. Louis MO. Sites were selected so that each mean consisted of 25 to 40 daily measurements. The average standard errors of the means ranged from less than  $0.1 \mu\text{g m}^{-3}$  for BC to  $0.9 \mu\text{g m}^{-3}$  for sulfate.

Table 8. Changes in mean BC and nitrate concentrations from Wednesdays to Saturdays and Sundays, expressed as percentage differences relative to mean Wednesday levels. Negative values indicate weekend decreases. Statistically significant ( $p < 0.01$ ) differences are marked in boldface type. Rural sites are shown in italics.

LOCATION	AIRS	Wed Mass $\mu\text{g m}^{-3}$	Wed Nitrate $\mu\text{g m}^{-3}$	Sun-Wed Nitrate % of Wed	Sun-Wed BC % of Wed	Sat-Wed Nitrate % of Wed	Sat-Wed BC % of Wed
ALLEN PA	261630001	21.5	3.8	-22.0	<b>-34.6</b>	-9.8	-22.8
ALTON	171192009	13.4	2.9	-36.6	-4.5	-18.4	-1.8
<i>BONDVILLE</i>	IMPROVE	13.8	2.1	-17.0	-15.5	-28.4	-21.0
<i>CADIZ</i>	IMPROVE	13.5	1.0	17.1	-8.7	-14.4	-15.3
CHICAGO	170310057	17.8	3.4	1.8	-27.4	-43.9	<b>-44.1</b>
CHICAGO	170310076	17.8	2.8	-20.1	-19.3	-39.7	-20.3
<i>CLAY CO</i>	290470005	11.3	2.3	-11.6	-36.5	22.9	-20.7
CLEVELAND	390350060	19.6	3.1	-25.7	<b>-55.4</b>	-14.6	<b>-43.9</b>
CLEVELAND	390350060	18.9	3.2	-27.0	<b>-58.9</b>	-4.3	<b>-42.8</b>
DETROIT	261630019	15.4	2.4	32.1	-34.5	23.5	-22.2
<i>DODGE CO</i>	550270007	11.0	2.9	8.7	-1.2	-6.1	2.1
INDIANAPOLIS	180970078	19.4	3.0	-8.2	-25.4	-2.2	<b>-27.9</b>
<i>ISLE ROYALE</i>	IMPROVE	5.4	0.8	-44.6	-12.5	-31.3	-3.6
<i>JEFFERSON CO</i>	290990012	15.3	1.9	-29.3	-13.2	-8.9	0.2
<i>LIVONIA</i>	IMPROVE	13.8	1.5	15.6	5.3	-18.8	1.0
<i>MANISTIQUE</i>	261530001	6.4	1.0	-18.8	-11.7	-3.6	-0.6
MILWAUKEE	550790026	15.5	3.3	-11.6	<b>-34.5</b>	-19.8	<b>-28.9</b>
<i>MISSAUKE</i>	261130001	7.8	1.0	34.3	0.7	18.9	0.8
<i>MKGODDARD</i>	IMPROVE	14.4	0.9	40.8	-8.3	8.9	-13.5
<i>QUAKER CITY</i>	IMPROVE	15.2	0.8	4.4	-13.9	-5.5	-24.5
SAULT ST MARIE	260330901	7.2	0.5	39.3	-32.1	-0.7	-17.0
<i>SENEY WILDLIFE</i>	IMPROVE	5.7	0.9	3.7	-0.1	-18.6	-7.1
ST LOUIS	295100085	17.8	2.5	-9.6	<b>-27.8</b>	-11.2	-25.1
ST LOUIS	295100089	18.2	2.3	-10.5	-27.7	-14.8	10.7
<i>STODDARD CO</i>	292070001	13.8	1.3	-24.9	0.6	-37.2	-21.0
<i>TAYLOR CO</i>	551198001	8.8	2.1	-24.1	-3.8	3.8	1.6
MEDIAN RURAL		12.4	1.2	-3.9	-8.5	-7.5	-5.3
MEDIAN URBAN		17.8	2.9	-11.1	-29.9	-12.9	-23.9
MEDIAN		14.1	2.2	-11.0	-14.7	-10.5	-18.6

Even though statistically significant day-of-week PM nitrate differences were not evident, it is still of interest to compare them with changes in ambient NO<sub>x</sub> concentrations. Mean weekend ambient NO<sub>x</sub> concentrations were lower than weekday concentrations at nearly all urban monitoring sites (Table 9). Of 41 sites, 22 showed statistically-significant ( $p < 0.01$ ) NO<sub>x</sub> reductions on Sundays and two on Saturdays. The median weekend reductions over all monitoring sites were 12 percent on Saturdays and 30 percent on Sundays, relative to the mean Wednesday concentrations. These median weekend reductions of ambient NO<sub>x</sub> concentrations exceed the 11 percent weekend reductions of PM nitrate, thus suggesting that PM nitrate concentrations exhibited a nonproportional response to NO<sub>x</sub> changes. The spatial scales of the NO<sub>x</sub> reductions require consideration, however.

The weekend NO<sub>x</sub> reductions occurred in all MSAs. The Chicago-Gary CMSA and St. Louis MSA include 12 and 8 NO<sub>x</sub> monitors, respectively, and all showed lower weekend NO<sub>x</sub> levels. Since these sites included upwind and downwind locations as well as sites closer to the urban cores, the weekend NO<sub>x</sub> reductions occurred on city-wide or possibly larger spatial scales. The comparisons of weekend changes in ambient levels of PM nitrate and NO<sub>x</sub> indicate that Sunday reductions of PM nitrate were less than urban-scale Sunday NO<sub>x</sub> reductions and therefore support the conclusion that PM nitrate concentrations display a less-than-proportional response to urban-scale changes in NO<sub>x</sub> levels.

Sites not located in MSAs showed a median Sunday NO<sub>x</sub> reduction of 17 percent relative to Wednesdays, and no difference between mean Saturday and Wednesday NO<sub>x</sub> levels. Therefore, the regional weekend NO<sub>x</sub> reductions were less than the city-wide reductions. However, the regional changes in NO<sub>x</sub> are not well characterized, and neither NO<sub>x</sub> nor PM nitrate shows statistically significant weekend changes at nonurban monitoring sites (with one exception for Sunday NO<sub>x</sub> levels). Further analyses, including modeling studies, are therefore needed to establish more definitive linkages between regional NO<sub>x</sub> emission changes and PM nitrate concentrations.

Table 9. Differences between mean NO<sub>x</sub> concentrations on Wednesdays compared with Saturdays and Sundays. The data are from all days during 2001 and 2002. The hourly NO<sub>x</sub> measurements were averaged over 24 hours and day-of-week averages were computed from the 24-hour averages. The difference between Wednesday means and Saturday and Sunday means is shown as a percent of the Wednesday means (positive differences indicate higher mean concentrations on Wednesdays). Statistical significance (p<0.01) is indicated by bold type. The statistical test was a t-test of the difference of two means.

AIRS	MSA	Difference Wed-Sun (%)	Difference Wed-Sat (%)
170310063	CHICAGO-GARY	<b>51.2</b>	8.1
170310072	CHICAGO-GARY	2.4	4.6
170310075	CHICAGO-GARY	14.7	14.1
170310076	CHICAGO-GARY	<b>42.0</b>	19.8
170313103	CHICAGO-GARY	<b>44.4</b>	13.0
170314002	CHICAGO-GARY	<b>27.0</b>	14.5
170314201	CHICAGO-GARY	22.4	9.7
170314201	CHICAGO-GARY	18.5	6.3
170318003	CHICAGO-GARY	<b>29.8</b>	4.5
170971007	CHICAGO-GARY	7.2	-1.9
171971011	CHICAGO-GARY	<b>31.1</b>	1.9
180890022	CHICAGO-GARY	26.2	15.3
Area Median		26.6	8.9
181630012	EVANSVILLE	<b>25.5</b>	9.1
180970073	INDIANAPOLIS	<b>35.2</b>	19.4
181411008	SOUTH BEND	<b>37.3</b>	7.3
Area Median		35.2	9.1
261630016	DETROIT	<b>37.4</b>	24.2
261630019	DETROIT	36.7	<b>36.6</b>
261630019	DETROIT	24.9	20.0
260810020	GRAND RAPIDS	<b>49.7</b>	17.3
260650012	LANSING	22.9	9.6
Area Median		36.7	20.0
290470005	KANSAS CITY	21.6	-8.9
171630010	ST. LOUIS	16.3	3.1
291831002	ST. LOUIS	26.9	14.3
291890004	ST. LOUIS	<b>42.6</b>	14.1
291890006	ST. LOUIS	<b>30.7</b>	7.6
291893001	ST. LOUIS	<b>33.1</b>	7.3
291895001	ST. LOUIS	<b>30.3</b>	11.9
291897002	ST. LOUIS	24.3	23.8
291897003	ST. LOUIS	<b>30.6</b>	1.1
Area Median		30.3	7.6
390610040	CINCINNATI	<b>30.5</b>	12.3

AIRS	MSA	Difference Wed-Sun (%)	Difference Wed-Sat (%)
390614002	CINCINNATI	<b>37.2</b>	17.1
390350060	CLEVELAND	<b>51.6</b>	15.3
390350066	CLEVELAND	<b>28.7</b>	14.1
Area Median		33.9	14.7
550790007	MILWAUKEE	29.8	11.7
550790041	MILWAUKEE	<b>32.5</b>	19.0
Area Median		31.2	15.3
180510010	NOT IN MSA	<b>43.3</b>	4.6
181470008	NOT IN MSA	17.0	-2.0
290390001	NOT IN MSA	14.6	-18.1
291290001	NOT IN MSA	15.3	-1.0
291290001	NOT IN MSA	17.5	12.0
291860005	NOT IN MSA	25.0	1.0
Area Median		17.3	0.0
Median all sites		29.8	11.7

At monitoring sites where PM nitrate and NO<sub>x</sub> measurements were both made, lower weekend levels of NO<sub>x</sub> were not matched by lower weekend levels of PM nitrate (Figure 22). The number of sites with adequate data for comparison was limited, and better comparisons will be possible as more PM measurements are made. Nonetheless, the three sites shown in Figure 22 exhibit no correlations that would suggest that local NO<sub>x</sub> levels control PM nitrate concentrations. The PM nitrate levels were an order of magnitude lower than NO concentrations at the Chicago (PAMS Type 1, upwind) and Cleveland (urban center) sites, and a factor of five less than the ambient NO<sub>x</sub> concentrations at the Clay County MO (nonurban Kansas City MSA) site. These concentration differences between PM nitrate and its gas-phase precursors indicate that the rate of conversion of NO<sub>x</sub> to nitrate is determined by factors other than the local concentrations of NO<sub>x</sub>.

The apparent lack of response of weekend PM nitrate levels to city-wide reductions of ambient NO<sub>x</sub> concentrations on weekends raises questions about the potential effectiveness of local PM nitrate-control strategies. Additional studies of the effects of regional NO<sub>x</sub> emission reductions on ambient nitrate levels are therefore needed.

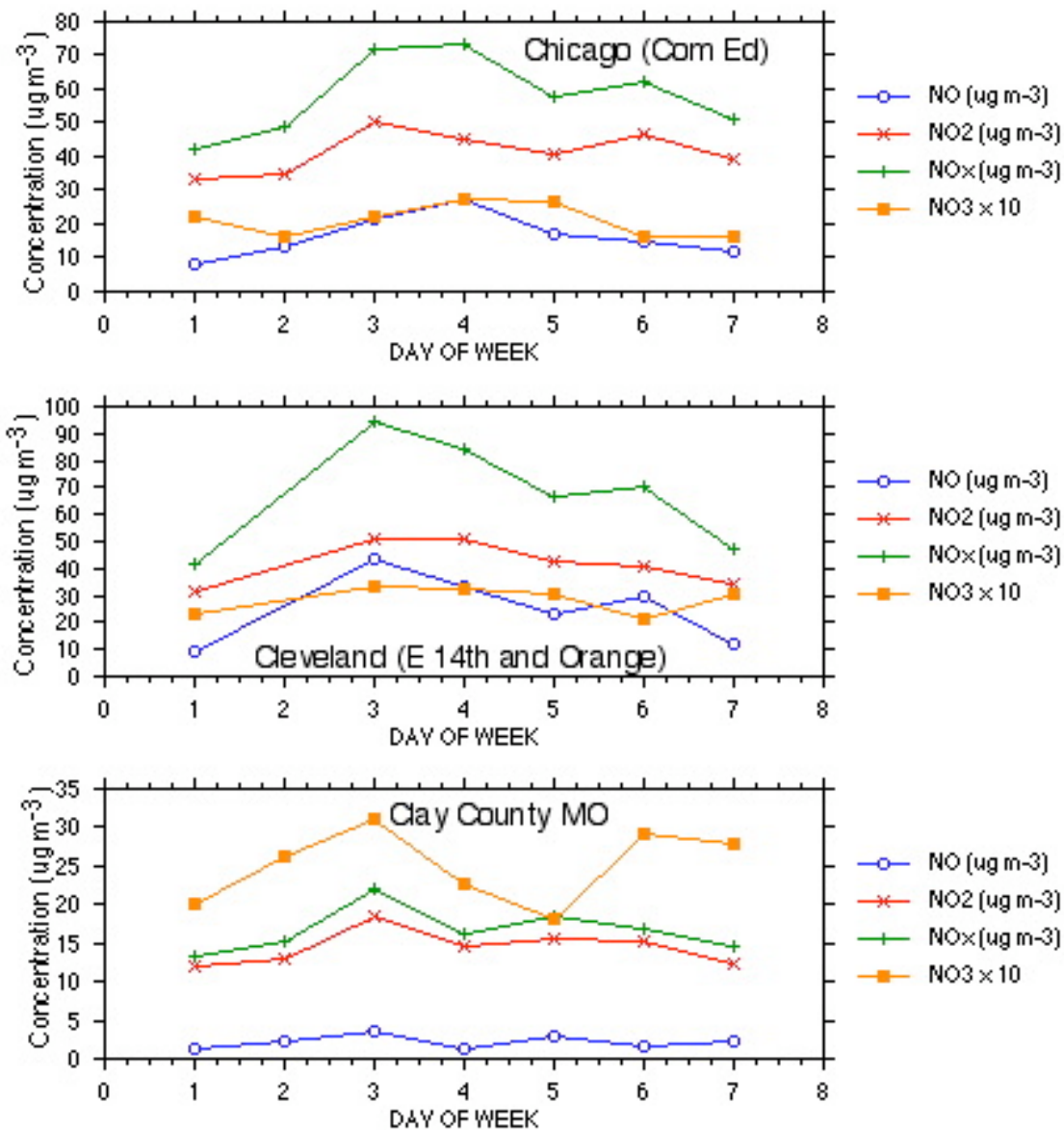


Figure 22. Day-of-week mean concentrations of NO, NO<sub>2</sub>, NO<sub>x</sub>, and PM nitrate at three monitoring sites. Chicago (Com Ed Training Center) is the PAMS Type 1 (upwind) site for Chicago. Cleveland (East 14<sup>th</sup> and Orange) is located on the edge of downtown near industrial manufacturing sites. Clay County MO is a nonurban (downwind) site within the Kansas City MSA. Daily-average concentrations of NO, NO<sub>2</sub>, and NO<sub>x</sub> were computed from hourly averages and then matched by date with PM nitrate measurements from 2001 and 2002. The selected sites had sufficient data to provide about 15 measurements for each mean. Nitrate has been scaled by a factor of ten. The averages for the gas-phase species were converted to  $\mu\text{g m}^{-3}$  assuming one atmosphere and 25 degrees C.

## Conclusion

The thermodynamic equilibrium models predicted that mean PM nitrate concentrations would increase by less than 0.1 to 0.4  $\mu\text{g m}^{-3}$  in response to 50 percent lower sulfate concentrations at ten sites studied. At each site, the predicted nitrate increases were offset when the modeled concentrations of  $\text{HNO}_3$  were decreased by amounts ranging from less than 10 percent to approximately 20 percent of current mean  $\text{HNO}_3$  levels.

Changes in mean PM mass concentrations were predicted from the predicted changes in sulfate, ammonium, and nitrate concentrations. Predicted fine PM mass levels were tabulated and depicted as isopleths drawn in relation to sulfate and nitric acid concentrations. The shapes of the PM mass isopleths were the same for all sites, indicating that predicted fine mass concentrations declined as either sulfate or nitric acid concentrations declined. The PM mass decreases were typically about 2 to 3  $\mu\text{g m}^{-3}$  for a 50 percent sulfate decrease and about 1 to 1.5  $\mu\text{g m}^{-3}$  for a 50 percent nitric acid decrease, thus showing greater sensitivity to sulfate reductions. The sulfate decreases were an input to the model calculations, but their effect on fine PM mass was modified by concomitant decreases in ammonium and increases in nitrate. These concomitant changes nearly balanced each other, so that the PM mass changes in response to the assumed sulfate decreases were approximately equal in magnitude to the sulfate reductions. For the IMPROVE/CASTNet data (six of ten sites), the predicted sensitivities of mean PM mass concentration to changes in sulfate and nitric acid concentrations should be considered preliminary because some measurements were estimated from other quantities (see appendix).

The largest predicted mean nitrate increases (0.4  $\mu\text{g m}^{-3}$ ) occurred at the Cincinnati site. At this location, approximately one-third of the samples were ammonia-limited. Once sulfate concentrations were reduced by 50 percent, particulate nitrate formation became  $\text{HNO}_3$ -limited for nearly all samples. In spite of the predicted mean nitrate increases, the predicted mean  $\text{PM}_{2.5}$  mass concentration decrease at the Cincinnati MMW site exceeded the mean sulfate decrease. This result held both when changes in water content were

considered and when they were not.<sup>5</sup> The mass concentration decreases exceeded the sulfate decreases because ammonium concentrations also decreased. For the scenario with the maximum mean nitrate increase (i.e., 50 percent sulfate decrease, no HNO<sub>3</sub> decrease), the mean sulfate decrease was 2.7  $\mu\text{g m}^{-3}$ , the mean ammonium decrease was 0.9  $\mu\text{g m}^{-3}$ , the mean nitrate increase was 0.4  $\mu\text{g m}^{-3}$ , and the mean PM<sub>2.5</sub> mass concentration decrease was 3.2  $\mu\text{g m}^{-3}$ .

Further work is needed to relate the changes in model inputs (sulfate and nitric acid) to changes in emissions of SO<sub>2</sub> and NO<sub>x</sub>. Past modeling and empirical analyses indicate that reductions of SO<sub>2</sub> emissions have led in the past to nearly proportional reductions of ambient sulfate concentrations on the semi-continental scale of eastern North America. On smaller spatial scales, including regional (e.g., the six Midwestern states studied here) and local (e.g., the Chicago CMSA), the response of ambient sulfate concentrations to SO<sub>2</sub> emission reductions may be nonproportional.

The response of ambient concentrations of nitric acid to changes in NO<sub>x</sub> emissions has not been previously well established. This report did not attempt to model the gas-phase processes linking NO<sub>x</sub> with nitric acid, nor were models used to examine the relationships between changes in NO<sub>x</sub> and PM nitrate concentrations. Instead, the links were studied empirically through quantification of the day-of-week variations in the ambient concentrations of NO<sub>x</sub> and PM nitrate.

Ambient measurements show that mean weekend NO<sub>x</sub> concentrations were lower than weekday concentrations at nearly all urban monitoring sites in the six states. Since these sites included upwind and downwind locations as well as sites closer to the urban cores, the weekend NO<sub>x</sub> reductions occurred on city-wide or possibly larger spatial scales. The median weekend NO<sub>x</sub> reductions for all monitoring sites were 12 percent on Saturdays and 30 percent on Sundays, relative to the mean 24-hour Wednesday concentrations, with 22 of 41 Wednesday-Sunday differences in mean NO<sub>x</sub> concentrations being statistically

---

<sup>5</sup> Since PM mass is measured in a laboratory under fixed temperature and RH, changes in ambient water content do not necessarily affect the reported mass concentrations. However, changes in ambient water content are of significance with respect to visibility.

significant ( $p < 0.01$ ). Sites not located in MSAs showed a median Sunday  $\text{NO}_x$  reduction of 17 percent relative to Wednesdays, and no median difference between mean Saturday and Wednesday 24-hour  $\text{NO}_x$  levels. For PM nitrate, the median weekend reductions over all monitoring sites were 11 percent on both Saturdays and Sundays, relative to the mean Wednesday concentrations, with no statistically significant differences.

The comparisons of weekend changes in ambient levels of PM nitrate and  $\text{NO}_x$  indicate that Sunday reductions of PM nitrate were less than urban-scale Sunday  $\text{NO}_x$  reductions and therefore support the conclusion that PM nitrate concentrations display a less-than-proportional response to urban-scale changes in  $\text{NO}_x$  levels. However, the regional changes in  $\text{NO}_x$  were not well characterized, and neither  $\text{NO}_x$  nor PM nitrate showed statistically significant weekend changes at nonurban monitoring sites (with one exception for Sunday  $\text{NO}_x$  levels). The day-of-week variations in concentration suggest that the response of PM nitrate concentrations to changes in ambient  $\text{NO}_x$  levels may depend upon the spatial scale of the emission changes. The apparent limited response of weekend PM nitrate levels to city-wide reductions of ambient  $\text{NO}_x$  concentrations on weekends raises questions about the potential effectiveness of local PM nitrate-control strategies. Additional studies of the effects of regional  $\text{NO}_x$  emission reductions on ambient nitrate levels are therefore needed.

In summary, the equilibrium models predicted that particulate nitrate formation was not limited by the availability of ammonia for most samples at times when temperature and humidity favored the condensed phase, but weekend particulate nitrate levels did not decline in proportion to changes in weekend  $\text{NO}_x$  concentrations. Therefore, it may be concluded that important processes potentially limiting the observed responsiveness of PM nitrate to changes in  $\text{NO}_x$  emissions likely include gas-phase conversion of  $\text{NO}_x$  to nitric acid and transport. Model-predicted fine mass concentrations declined as either sulfate or nitric acid concentrations declined, with the predicted PM mass concentrations showing greater sensitivity to sulfate reductions.

## References

- Ansari AS and Pandis SN. 1998. Response of inorganic PM to precursor concentrations. Environ. Sci. Tech. 32: 2706-2714.
- Ansari AS and Pandis SN. 1999a. An analysis of four models predicting the partitioning of semivolatile inorganic aerosol components. Aeros.Sci.Tech. 31: 129-153
- Ansari AS and Pandis SN. 1999b. Prediction of multicomponent inorganic atmospheric aerosol behavior. Atmos.Env. 33: 745-757.
- Blanchard CL, Roth PM, Tanenbaum SJ, Ziman SD, and Seinfeld JH. 2000. The use of ambient measurements to identify which precursor species limit aerosol nitrate formation. J. Air Waste Manage. Assoc. 50: 2073-2084.
- Finlayson-Pitts B. and Pitts J. 1986. Atmospheric Chemistry: Fundamentals and Experimental Techniques. New York: Wiley & Sons. 1098 pp.
- Hilst GR. 1992. Proportionality between SO<sub>2</sub> emissions and wet SO<sub>4</sub><sup>2-</sup> concentrations: the effect of area of averaging. Atmos. Environ. 26A: 1413-1420.
- Kim YP, Seinfeld JH, and Saxena P. 1993a. Atmospheric gas-aerosol equilibrium I. Thermodynamic model. Aerosol Sci. Technol. 19: 157-181.
- Kim YP, Seinfeld JH, and Saxena P. 1993b. Atmospheric gas-aerosol equilibrium II. Analysis of common approximations and activity coefficient calculation methods. Aerosol Sci. Technol. 19: 182-198.
- Kim YP and Seinfeld JH. 1995. Atmospheric gas-aerosol equilibrium III. Thermodynamics of crustal elements Ca<sup>2+</sup>; K<sup>+</sup>; Mg<sup>2+</sup>. Aerosol Sci. Technol. 22: 93-110.
- Lynch JA, Bowersox VC, and Grimm JW. 1996. Trends in Precipitation Chemistry in the United States, 1983-1994: An Analysis of the Effects in 1995 of Phase I of the Clean Air Act Amendments of 1990, Title IV. US Geol. Surv. 96-0346. US Geol. Survey, Washington DC. <http://water.usgs.gov/public/pubs/acidrain>.
- Makar PA, Bouchet VS, and Nenes A. 2003. Inorganic chemistry calculations using HETV x2013; a vectorized solver for the SO<sub>4</sub>-NO<sub>3</sub>-NH<sub>4</sub> system based on the ISORROPIA algorithms. Atmos.Env. 37: 2279-2294.
- Malm WC. 2000. Spatial and Seasonal Patterns and Temporal Variability of Haze and its constituents in the United States. National Park Service.

- Meng Z, Seinfeld JH, Saxena P, and Kim YP. 1995a. Atmospheric gas-aerosol equilibrium IV. Thermodynamics of carbonates. Aerosol Sci. Technol. 23: 131-154.
- Meng Z, Seinfeld JH, Saxena P, and Kim YP. 1995b. Contribution of water to particulate mass in the South Coast Air Basin. Aerosol Sci. Technol. 22: 111-123.
- Mueller SF. 2003. Seasonal aerosol sulfate trends for selected regions of the United States. J. Air Waste Manage. Assoc. 53: 168-184.
- NAPAP. 1991. National Acid Precipitation Assessment Program 1990 Integrated Assessment Report. The NAPAP Office of the Director, 722 Jackson Place NW, Washington DC 20503. 520 pp.
- NAPAP. 1998. NAPAP Biennial Report to Congress: An Integrated Assessment. National Science and Technology Council, Committee on Environment and Resources, Silver Spring MD. 118 pp.
- NARSTO. 2003. Particulate Matter Science for Policy Makers: A NARSTO Assessment. EPRI Report 1007735. [www.cgenv.com/Narsto](http://www.cgenv.com/Narsto)
- Nenes A, Pandis SN, and Pilinis C. 1998a. ISORROPIA: A new thermodynamic equilibrium model for multiphase multicomponent inorganic aerosols. Aquat. Geoch. 4: 123-152.
- Nenes A, Pilinis C, and Pandis SN. 1998b. Continued development and testing of a new thermodynamic aerosol module for urban and regional air quality models. Atmos. Env. 33: 1553-1560.
- Pilinis C, Capaldo KP, Nenes A, and Pandis, S.N. 2000. MADM - a new multicomponent aerosol dynamics model. Aerosol Sci. Tech. 32(5): 482-502.
- Seinfeld S. and Pandis S. 1998. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. New York: Wiley & Sons. 1326 pp.
- Shannon J. 1999. Regional trends in wet deposition of sulfate in the United States and SO<sub>2</sub> emissions from 1980 through 1995. Atmos. Environ. 35: 807-816.
- Sickles JE, Hodson LL, and Vorburger LM. 1999. Evaluation of the filter pack for long-duration sampling. Atmos. Environ. 33: 2187-2202.
- Sickles JE and Shadwick DS. 2002a. Biases in CASTNet filter pack results associated with sampling protocol. Atmos. Environ. 36: 4687-4698.
- Sickles JE and Shadwick DS. 2002b. Precision of atmospheric dry deposition data from the Clean Air Status and Trends Network (CASTNet). Atmos. Environ. 36: 5671-5686.

U.S. EPA 2002. [ftp.epa.gov/pub/modelingcenter/Clear\\_Skies\\_Initiative/Emissions](ftp.epa.gov/pub/modelingcenter/Clear_Skies_Initiative/Emissions)

U.S. EPA 2003a. Latest Findings on National Air Quality: 2002 Status and Trends. EPA 454/K-03-001. US EPA, Office of Air Quality Planning and Standards, Research Triangle Park NC.

U.S. EPA 2003b. [www.epa.gov/clearskies](http://www.epa.gov/clearskies)

Venkatram A. 1991. Relationships between atmospheric emissions and deposition/air quality. In: PM Irving, ed. Acidic Deposition: State of Science and Technology. Summary Report of the U.S. National Acid Precipitation Assessment Program. The NAPAP Office of the Director, 722 Jackson Place NW, Washington DC 20503. 265 pp.

## **Appendix A. Data Quality and Estimation Procedures**

### Data Documentation and QA/QC Issues

As of mid-2003, the IMPROVE data for 2001 and 2002 had passed level 0 and level 1 data validation, but had not been validated through level 3

(<http://vista.cira.colostate.edu/improve/Data>). Therefore, we consulted the data documentation and compared species measurements. In addition, comparisons were made of IMPROVE with collocated data (see next subsection).

The IMPROVE measurements of sodium and chloride exhibited several unusual features. The majority of the chloride measurements were flagged as being below detection limits. Many (1455 of 1645) of the chloride values were recorded as zeroes. In contrast, sodium values were typically nonzero; site means ranged from 0.03 to 0.1  $\mu\text{g m}^{-3}$ . However, for some samples collected during June and July of 2002, sodium concentrations ranged up to 2.5  $\mu\text{g m}^{-3}$ ; sodium maxima during the previous four-year record of CASTNet (IMPROVE-protocol) monitoring at these same sites never exceeded 0.5  $\mu\text{g m}^{-3}$ .

Samples having high sodium concentrations during 2002 did not have high chloride concentrations. The IMPROVE monitoring history that was included with the data files indicated that the measurement methods for elements having atomic weights from Na through Mn were changed from PIXE to XRF as of December 2001. Sodium is the lowest atomic weight measured, and the accuracy of the measurement is less than the accuracy of the measurements of elements having greater atomic weights ([http://vista.cira.colostate.edu/improve/Publications/GrayLit/NA\\_factor\\_eldred/Na\\_Factor\\_3\\_8\\_01.htm](http://vista.cira.colostate.edu/improve/Publications/GrayLit/NA_factor_eldred/Na_Factor_3_8_01.htm)). Therefore, we treated the IMPROVE 2002 sodium measurements as suspect data, and substituted sodium data from the collocated CASTNet weekly samplers. With this step, the IMPROVE sodium maxima ranged from 0.2 to 0.9  $\mu\text{g m}^{-3}$ . When the equilibrium models were applied to samples having high ( $> 2 \mu\text{g m}^{-3}$ ) sodium concentrations, they predicted the presence of particulate nitrate that was not in fact measured; the discrepancies did not occur after substitutions were made for the suspect sodium measurements.

The CASTNet IMPROVE-protocol and weekly data had been documented and validated. One QA/QC issue of concern has to do with the accuracy of the CASTNet weekly-average measurements of nitric acid. Potentially, two positive artifacts could exist in the CASTNet nitric acid data. The first is that dissociation of ammonium nitrate on the front Teflon filter and retention of the resulting nitric acid on the backup nylon filter could occur over the one-week sampling interval. This artifact would affect the apparent split between the gas and condensed phases, though not the total nitrate. However, the CASTNet sample is not size-selective, so that it would collect coarse as well as fine PM nitrate, thus possibly also biasing the total nitrate in comparison with measures of fine particulate nitrate. Previous comparisons of IMPROVE with CASTNet weekly measurements have shown that the sulfate data agreed well, but the PM nitrate concentrations did not (Malm, 2000). The differences in nitrate concentrations were thought to stem from the presence of coarse particle nitrate and nitrate volatilization in the CASTNet samples (Malm, 2000).

Prior to April, 1997, CASTNet samples were collected as a weekly daytime and a weekly nighttime sample; after that date, a single weekly sample was collected. The nitric acid concentrations were lower during winter (median 10 percent) and higher during summer (median 7 percent) on the single weekly samples compared to the combined day/night weekly samples (Sickles and Shadwick, 2002a). This result is consistent with volatilization of particulate ammonium nitrate during the warmer months. The comparisons demonstrate the differences between two sampling protocols, but do not establish absolute biases. CASTNet sampling and laboratory precision for nitrate and nitric acid is better than 10 percent (Sickles and Shadwick, 2002b).

A second potential positive artifact in the CASTNet nitric acid concentrations could occur if nitrous acid was collected and converted on the sample filters. During a 14-week period from August 9 to November 15, 1988, CASTNet weekly-average measurements were compared with collocated 24-hour average measurements from an annular denuder system and filter-pack sampling, with the CASTNet samples averaging three percent greater than the former and five percent greater than the latter (Sickles et al, 1999). Two

of the 14 weekly CASTNet samples were thought to be biased high due to the presence of nitrous acid (Sickles et al., 1999). During periods of high photochemical activity, nitrous acid levels may be comparable to the concentrations of nitric acid, as is the case for the summer EPRI MMW data.

In summary, existing evidence indicates that the CASTNet nitric acid concentrations may be subject to positive artifacts on occasion. However, the magnitudes of the artifacts are not uniform and appear to affect a limited number of samples. Published estimates indicate that sampling and analytical precision is better than ten percent for the overall data set. For the comparisons that have been done, the accuracy of nitric acid measurements also averages better than ten percent, but larger biases may sometimes exist for individual samples.

Ongoing air-quality studies at Bondville (Bondville Environmental and Atmospheric Research Site, BEARS) are described at [www.sws.uiuc.edu/atmos/bears/](http://www.sws.uiuc.edu/atmos/bears/). The specific aerosol data set that we were provided (March 2000 – January 2002) did not include supporting QA/QC reports.

#### Comparability of Measurements From Different Data Bases

At the IMPROVE Bondville site, the Illinois State Water Survey (ISWS) measurements of sulfate, nitrate, and ammonium compare well with data from the IMPROVE sampler, with the ISWS measurements averaging approximately 10 to 20 percent lower than the IMPROVE values (Figure A1).

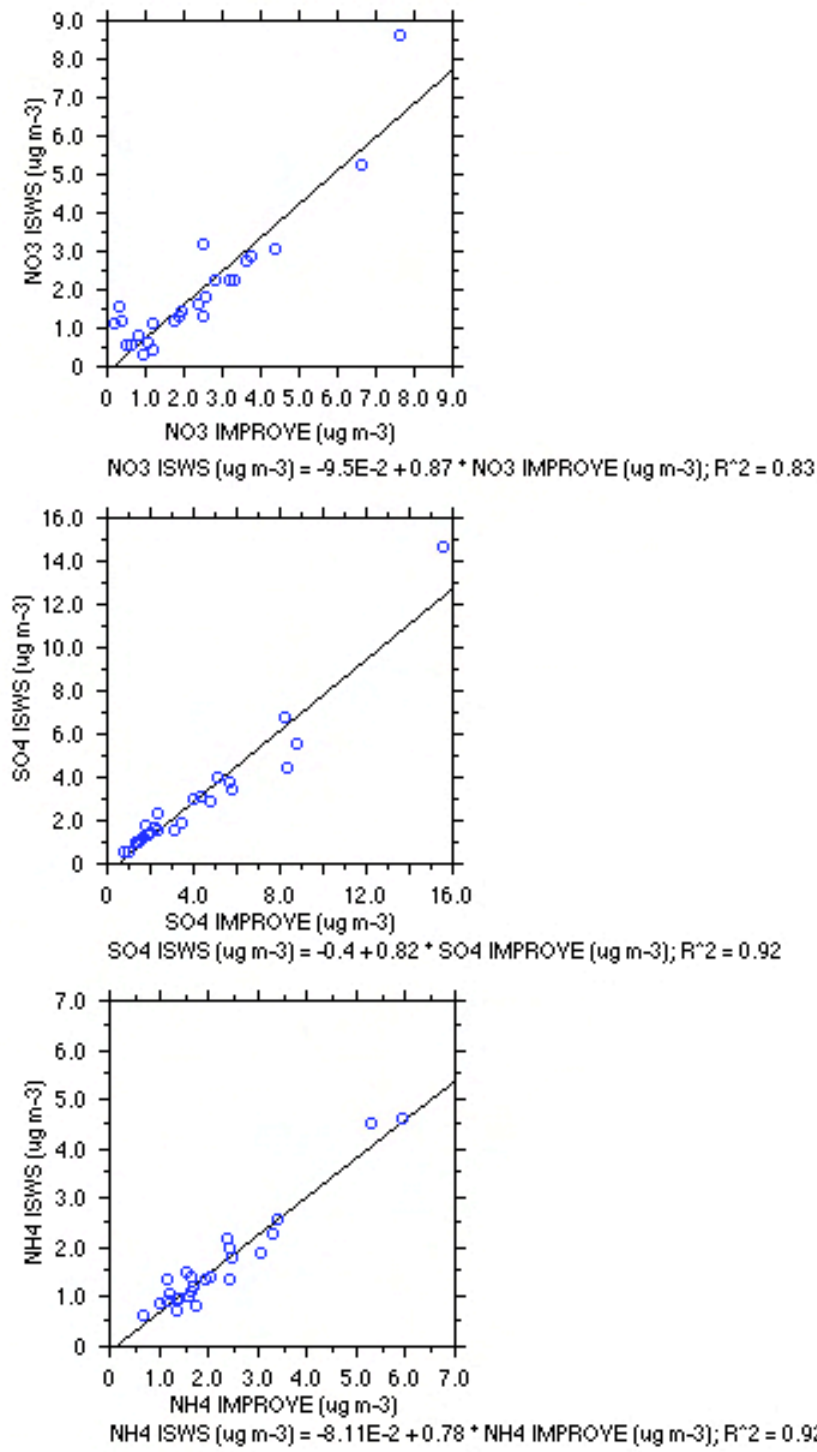


Figure A1. Comparisons of 24-hour average nitrate, sulfate, and ammonium concentrations from the ISWS and IMPROVE monitors at Bondville (March 2001 through January 2002).

The seasonal patterns exhibited by monthly-average nitric acid concentrations were similar for the EPRI MMW and the CASTNet sites (Tables A1 and A2). The urban sites showed higher summer monthly-average nitric acid levels than did the rural sites, consistent with the differences to be expected from emissions densities and photochemical production of nitric acid from NO<sub>x</sub> emissions. The CASTNet means at Quaker City for the months of August and September were higher than the corresponding means from the EPRI MMW site at Athens, Ohio, possibly indicating the existence of positive artifacts in the summer CASTNet values for nitric acid, as previously discussed. Definitive conclusions cannot be drawn, however, as the samples were collected during different time periods and the sites were not collocated. The CASTNet Quaker City means for August and September were comparable to, or less than, the corresponding means from the five urban EPRI MMW sites (Tables A1 and A2). The monthly-average nitric acid concentrations from the Bondville special studies did not exhibit the same seasonal pattern as did other sites, and were much lower than other rural locations during the months of June through October. Again, definitive conclusions cannot be drawn, though these differences suggest the need to verify the special-study measurements of nitric acid. The daily-average Bondville nitric acid concentrations showed no correlation with, and were substantially lower than, paired weekly-average CASTNet HNO<sub>3</sub> measurements from Bondville (Figure A2). The CASTNet weekly-average nitric acid concentrations were correlated with daily-average ozone levels<sup>6</sup>, but the daily-average special-study nitric acid concentrations did not correlate with paired daily-average ozone levels (Figure A2).

---

<sup>6</sup> Each day was paired with the week in which it occurred.

Table A1. Monthly-average nitric acid concentrations measured at urban and rural sites.

MONTH	W.VA/PA		OHIO/KY		MO/IN		MI/MN	
	Charleston EPRI MMW 99-00	MK Goddard CASTNet 98-02	Cincinnati EPRI MMW 99-00	Cadiz CASTNet 98-02	St. Louis EPRI MMW 99-00	Vincennes CASTNet 98-02	Detroit EPRI MMW 99-00	Voyageurs CASTNet 98-02
1		1.63	1.46	1.93		1.24		0.60
2		1.87	1.94	1.90		1.22		0.55
3		2.13		2.20		1.70		0.50
4		2.03		1.94		2.06		0.62
5		2.86		2.07		2.25		0.41
6		3.20		2.40		3.19		0.60
7		3.18		2.40		3.15		0.64
8	3.94	2.95	5.40	3.04	5.06	2.95	2.74	0.57
9	3.10	2.44	6.56	2.88	5.99	2.30	4.48	0.58
10		1.97		2.09		1.49		0.30
11		1.56		2.60		1.48		0.57
12		1.29		1.71		1.15		0.42

Table A2. Monthly-average nitric acid concentrations measured at urban and rural sites in Ohio and Illinois.

MONTH	OHIO		ILLINOIS		
	Athens EPRI MMW 99-00	Quaker City CASTNet 98-02	Bondville Special studies 00-02	Bondville CASTNet 98-02	Chicago EPRI MMW 99-00
1	2.28	2.50	0.39	0.83	0.87
2	2.63	2.59	1.45	0.88	0.99
3		3.18	1.29	1.54	
4		2.86		2.11	
5		3.75		2.86	
6		3.92	0.62	4.16	
7		3.66		3.84	
8	2.39	3.68	0.46	3.22	3.46
9	1.58	3.70	0.18	2.86	6.30
10		2.56	0.16	1.65	
11		3.23	0.22	0.75	
12		2.36	0.75	0.83	

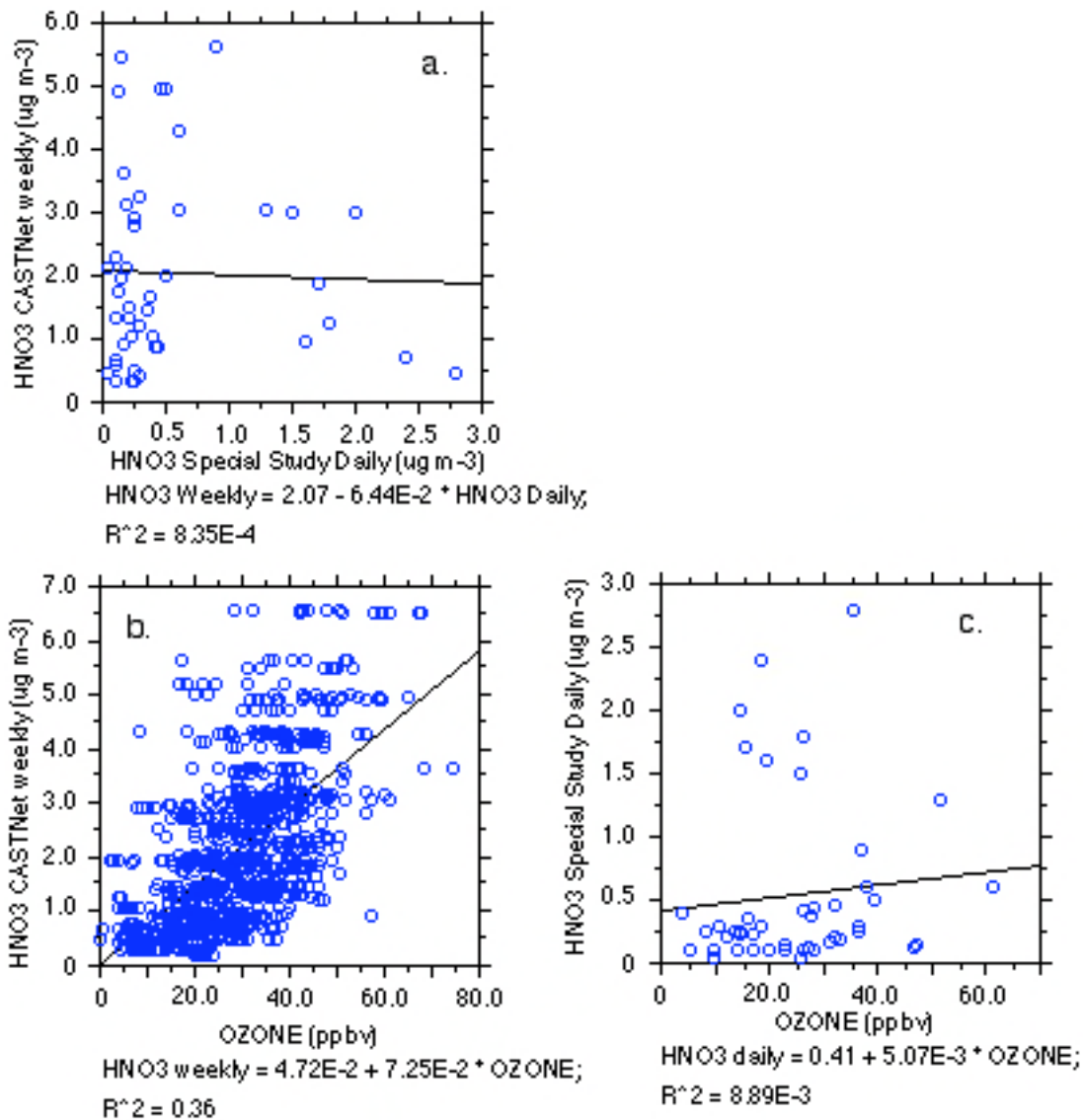


Figure A2. Comparisons of (a) weekly-average nitric acid concentrations from the CASTNet monitor at Bondville with 24-hour average nitric acid concentrations from the special-study monitor (April 2000 through January 2002), (b) weekly-average CASTNet nitric-acid concentrations with daily-average ozone levels, and (c) daily-average special-study nitric acid concentrations with daily-average ozone concentrations.

### Weekly and Daily-Average Concentrations

Daily-average concentrations of sulfate, nitrate, and ammonium were statistically significantly correlated with weekly-average concentrations (Figure A3). The regression slopes did not differ from unity, though the individual daily averages varied by approximately a factor of two from their corresponding weekly-average concentrations. These comparisons suggest that substitution of the weekly-average CASTNet nitric acid concentrations for daily averages is likely to provide surrogate values that are accurate on average, though subject to considerable variation from sample to sample.

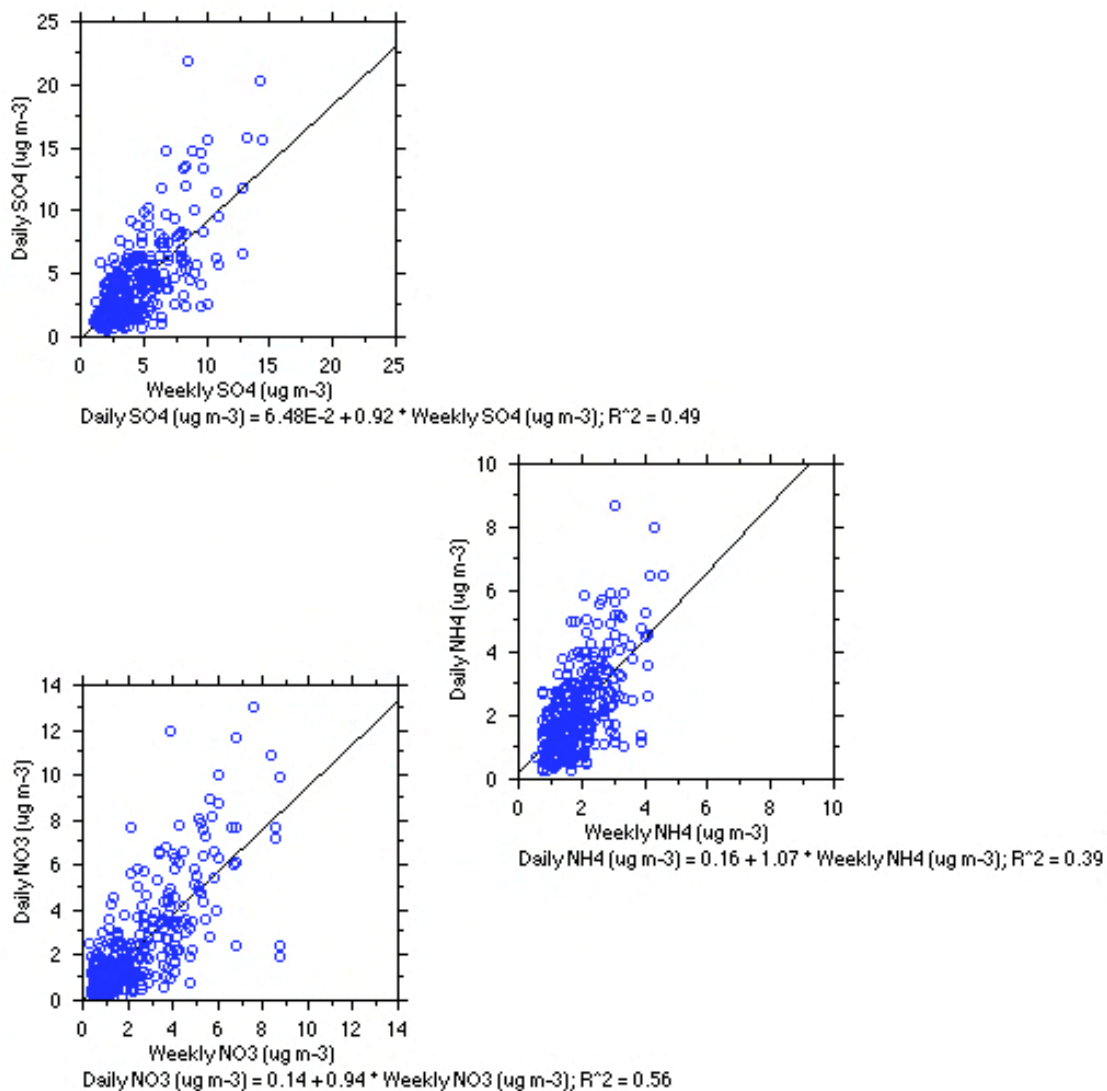


Figure A3. Comparisons of daily-average with weekly-average concentrations of sulfate, nitrate, and ammonium. The data are from the CASTNet sites at Bondville, Cadiz, Quaker City, MK Goddard, Vincennes IN, and Voyageur National Park. Each daily-average measurements was paired with the weekly-average from the week in which the daily sample occurred.

### Estimation of Ammonia Concentrations

Since ammonia was not measured at the IMPROVE/CASTNet sites, the thermodynamic equilibrium models were used to estimate the ammonia levels that would be in equilibrium with the measured sulfate, nitrate, ammonium, and nitric acid concentrations for each sample, at the measured temperatures and relative humidities. The inputs to ISORROPIA include total ammonia, which is the sum of gas-phase ammonia and particulate ammonium. For the initial iteration, this total was specified as twice the measured ammonium for each 24-hour sample (this being the approximate relation occurring in the EPRI MMW measurements). Predictions were obtained for each 24-hour sample, and compared with the actual observations. For each sample, the total ammonia was then adjusted by the molar equivalent of the difference between the predicted and observed concentrations of particulate nitrate (molar units):

New total ammonia = old total ammonia – (predicted nitrate – measured nitrate)

In the preceding equation, overprediction of particulate nitrate implies overestimation of total ammonia. Seven iterations of ISORROPIA yielded predicted concentrations of nitric acid and particulate nitrate that were each with ten percent of the measured values, on average, as determined from the slopes of the regressions of predicted against measured values (Figure 5). The resulting monthly mean predicted concentrations of ammonia exhibited seasonality (higher summer levels) and were comparable in magnitude to the mean monthly measured concentrations at Bondville and the EPRI MMW sites (Tables A3 and A4).

Table A3. Comparison of mean monthly concentrations of ammonia measured at urban EPRI MMW sites in Charleston, Cincinnati, St. Louis and Detroit with values predicted by ISORROPIA for rural CASTNet sites.

MONTH	W.VA/PA		OHIO/KY		MO/IN		MI/MN	
	Charleston measured 99-00	MKGoddard predicted 98-02	Cincinnati measured 99-00	Cadiz predicted 98-02	St. Louis measured 99-00	Vincennes predicted 98-02	Detroit measured 99-00	Voyageur predicted 98-02
1		0.32	0.79	0.11		0.76		0.24
2		0.26	0.71	0.19		0.25		0.12
3		0.50		0.83		1.00		0.17
4		0.70		1.85		1.37		0.64
5		1.57		1.74		2.15		0.70
6		1.50		1.87		2.16		0.99
7		1.83		2.10		2.14		0.90
8	4.81	1.61	1.72	2.51	1.84	2.17	2.15	0.82
9	3.53	1.26	1.77	1.87	1.89	1.71	2.10	0.72
10		0.76		1.61		1.42		0.44
11		0.49		1.06		1.25		0.97
12		0.32		0.37		0.62		0.43

Table A4. Comparison of mean monthly concentrations of ammonia measured at sites in Athens and Chicago (EPRI MMW) and Bondville (special studies) with values predicted by ISORROPIA for rural sites in Quaker City and Bondville.

MONTH	OHIO			ILLINOIS		
	Athens Measured 99-00	Quaker City Predicted 98-02	Bondville Measured 00-02	Bondville Predicted 98-02	Chicago Measured 99-00	
1	0.22	0.12		0.18	1.46	0.99
2	0.17	0.07		0.60	0.68	1.00
3		0.25		0.88	0.84	
4		0.86		1.19	1.20	
5		1.63		1.30	1.65	
6		1.40		1.40	1.72	
7		1.36		1.36	2.05	
8	0.42	1.77		1.09	1.86	2.87
9	0.35	1.21		1.50	1.77	3.64
10		0.79		1.01	1.63	
11		0.76		2.45	1.72	
12		0.10		0.19	0.82	