

Seasonal NH₃ emission estimates for the eastern United States based on ammonium wet concentrations and an inverse modeling method

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[1] Significant uncertainty exists in the magnitude and variability of ammonia (NH₃) emissions. NH₃ emissions are needed as input for air quality modeling of aerosols and deposition of nitrogen compounds. Approximately 85% of NH₃ emissions are estimated to come from agricultural nonpoint sources, which are suspected to have a strong seasonal pattern. Because no seasonal information is available in current NH₃ emission inventories for air quality modeling, the emissions are often distributed evenly over the year by default. Doing so can adversely affect air quality model-predicted concentrations of nitrogen-containing compounds, as shown here. We apply a Kalman filter inverse modeling technique to deduce monthly 1990 NH₃ emissions for the eastern United States. The U.S. Environmental Protection Agency (USEPA) Community Multiscale Air Quality (CMAQ) model and ammonium (NH₄⁺) wet concentration data from the National Atmospheric Deposition Program network are used. The results illustrate the strong seasonal differences in NH₃ emissions that were anticipated, where NH₃ emissions are more than 75% lower during the colder seasons fall and winter as compared to peak emissions during summer. The results also suggest that the current USEPA 1990 National Emission Inventory for NH₃ is too high by at least 20%. This is supported by a recent USEPA study of emission factors that proposes lower emission factors for cattle and swine, which are two of the largest sources of NH₃ emissions in the inventory. *INDEX*

TERMS: 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); *KEYWORDS:* ammonia emissions, intra-annual or seasonal variations, inverse modeling, air quality modeling, nitrate aerosols, CMAQ

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1. Introduction and Background

[2] Air quality models rely on emission inputs, including ammonia (NH₃), to predict concentrations of fine particulate matter (PM_{2.5}) as a criteria pollutant under the National Ambient Air Quality Standard (NAAQS). The NAAQS includes both a 24-hour and an annual standard for PM_{2.5}; therefore modeling studies are needed to capture both episodic as well as annual levels of PM_{2.5}. Sulfate and nitrate aerosols are two major components of PM_{2.5}. NH₃ gas neutralizes sulfuric acid to form ammonium sulfate aerosols, and if excess NH₃ is present after reaction with sulfuric acid, NH₃ then reacts with nitric acid to form ammonium nitrate [Dentener and Crutzen, 1994]. Given this, the representation of NH₃ emissions can have a large effect on air quality model predictions of aerosol nitrate and ammonium concentrations.

Since it is necessary to consider an annual as well as a 24-hour standard for PM_{2.5}, model simulations must cover different times of the year, and NH₃ emissions under different seasonal conditions must be represented.

[3] Current NH₃ emission inventories are limited to total annual estimates with no intra-annual variability [U.S. Environmental Protection Agency (USEPA), 2000; Bouwman *et al.*, 1997] (the former is available at <http://www.epa.gov/ttn/chieftrends/trends98/>); however, we qualitatively know that NH₃ emissions should vary seasonally because of the nature of the major sources. The USEPA National Air Pollutants Emissions Trends report [USEPA, 2000] states that NH₃ emissions predominantly come from agricultural sources, primarily from livestock animal waste (Table 1). Livestock sources should vary during the year since volatilization of NH₃ from the animal waste is a function of temperature. Observations have confirmed large seasonal variations in NH₃ emissions at hog waste lagoons and swine finishing buildings [Aneja *et al.*, 2000; Heber *et al.*, 2000]. Seasonality in NH₃ emissions is also expected since field application of manure and synthetic fertilizers occurs during specific seasons [Asman *et al.*, 1998] (available at <http://www.gsf.de/>

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Table 1. National Emission Inventory (NEI) NH₃ emission estimates for 1990^a

Source Type	NH ₃ Emissions, 1000 t/yr	Percent of Total
Livestock agriculture	3,000	76%
Fertilizer application	381	10%
On-road and nonroad engines and vehicles	180	5%
Other (chemical and allied product manufacturing, waste disposal, other industrial sources, etc.)	361	9%
Total (all sources)	3922	100%

^aUSEPA [2000].

eurotrac/nl20.htm). While it is qualitatively accepted that NH₃ emissions vary substantially during a given year, limited information exists to quantitatively deduce the seasonal variability of these emissions for a regional-scale domain. In addition to the intra-annual uncertainty in NH₃ emissions, it should also be noted that many of the emission factors used to develop U.S. emission inventories are based on European studies. This adds to the uncertainty in the U.S. emission inventories because of differences in the agricultural practices between Europe and the United States.

[4] The purpose of this study is to use an inverse problem approach to quantify seasonal variations in NH₃ emission estimates on a regional scale for the eastern United States. Observed and modeled wet concentrations of NH₄⁺ are used in an optimization formula to estimate emissions. Inverse modeling techniques have been used in a variety of applications to estimate quantities that are not directly available. They have been used to estimate global-scale emissions of CFC-11 [Hartley and Prinn, 1993], CO [Bergamaschi et al., 2000], CO₂ [Bousquet et al., 1999], and CH₄ [Houweling et al., 1999; Zhang et al., 1999]. Inverse methods have also been applied to regional- and urban-scale domains to estimate air quality emissions for isoprene [Chang et al., 1996], CO [Chang et al., 1997], NO_x and VOCs [Mendoza-Dominguez and Russell, 2001a], as well as aerosol precursors SO₂ and NH₃ [Mendoza-Dominguez and Russell, 2001b]. As traditionally done in air quality modeling, these regional- and urban-scale studies focus on episodic simulations during summer conditions to estimate hourly, daily, or episodic scaling factors for the emissions.

[5] The lack of a seasonal or monthly NH₃ emission inventory is one of the larger known uncertainties in air quality modeling of the annual PM_{2.5} standard. This is the first study that has used inverse modeling to quantitatively estimate the monthly and seasonal variability in NH₃ emissions. Preliminary results for two months from this study were presented by Gilliland et al. [2001]; however, those results were limited to only January and June 1990 and relied on an older version of the National Emissions Inventory (NEI) that has since been updated. In this paper, NH₃ emission scaling factors will be presented for each season of 1990 along with air quality model results based on these estimates to provide the most comprehensive estimate of seasonal NH₃ emissions to date.

2. Methodology

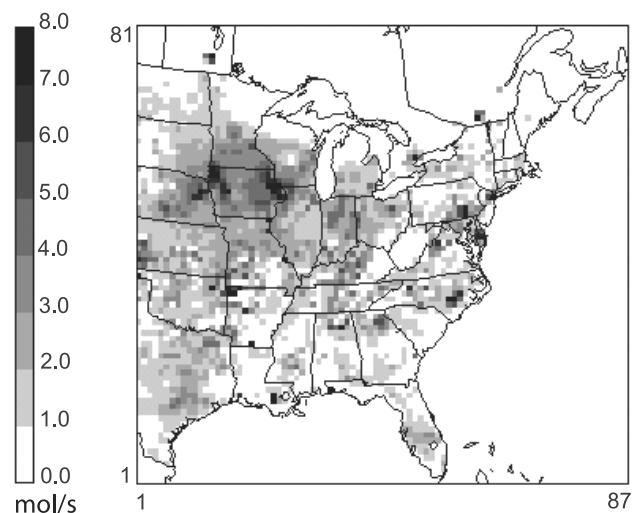
2.1. Air Quality Model and Observational Data

[6] The USEPA Models-3 Community Multiscale Air Quality (CMAQ) model [Byun and Ching, 1999; Byun,

1999] (the former is available at <http://www.epa.gov/asmdnerl/models3/doc/science/science.html>) is used in this study to generate model output. CMAQ is a Eulerian air quality model that was developed to simulate O₃, aerosol chemistry, and acidic and nutrient deposition for urban- to regional- scale domains. For this study, CMAQ is configured with 21 tropospheric layers, a horizontal grid dimension of 36 km, the RADM2 [Stockwell et al., 1990] chemical mechanism, and the AE2 aerosol module [Binkowski and Roselle, 2003; Mebust et al., 2003]. The AE2 aerosol module was derived from the Regional Particulate Matter model [Binkowski and Shankar, 1995], an extension of the Regional Acid Deposition Model (RADM) [Chang et al., 1990]. An intercomparison of equilibrium models including the one used with CMAQ's AE2 is given by Zhang et al. [2000]. The CMAQ domain for this study covers the eastern United States (Figure 1).

[7] The Fifth Generation Penn State/NCAR Mesoscale Model (MM5) is used to generate the meteorology data fields for CMAQ [Grell et al., 1994; Dudhia et al., 1998]. In addition, the CMAQ cloud module accounts for the presence of ice and graupel. Emissions fields for all chemical species were based on the NEI inventory version 3.01a [USEPA, 2000], Mobile 5b [USEPA, 1994] for mobile emissions, and BEIS2 [Pierce et al., 1998] for biogenic emissions. The annual average gridded NH₃ emission field is presented in Figure 1 for the CMAQ domain. Since NEI NH₃ emissions data are total annual values (Table 1), the a priori NH₃ emission fields used in these simulations have no seasonality, and an inverse modeling approach (as described in the next section) will be used to estimate NH₃ emission adjustments for the specific month.

[8] Precipitation-weighted NH₄⁺ wet concentration, or wet [NH₄⁺], will be used as the primary chemical indicator for NH₃ emissions in the inverse modeling approach. Wet [NH₄⁺] data include NH₃ that entered precipitation through direct absorption into water and NH₄⁺ aerosols that have been readily scavenged. NH₃ gas reacts with sulfuric or nitric acid to form these NH₄⁺ aerosols in the atmosphere. Therefore the wet [NH₄⁺] essentially represents the full air

**Figure 1.** Average 1990 NH₃ Emissions (in gmols/s) for the eastern U.S. CMAQ domain.

concentration budget of NH₃ and NH₄⁺ (i.e., NH_x). Precipitation-weighted wet [NH₄⁺] is calculated by dividing the accumulated wet deposition of NH₄⁺ by the total precipitation, and using the appropriate conversion factors to result in units of mg/L. The National Atmospheric Deposition Program National Trends Network (NADP) [*National Atmospheric Deposition Program (NADP)*, 2001] (available at <http://nadp.sws.uiuc.edu>) has collected precipitation chemistry data for a dense network of monitors for more than twenty years. Wet concentration of NH₄⁺ was chosen over wet deposition because the wet concentration of an efficiently scavenged species like NH₃ is less sensitive to rainfall amount than wet deposition [Lindberg, 1982; Stein et al., 1993; Styer and Stein, 1992]. Predicted precipitation uncertainty is a concern because, as a process, it is difficult for mesoscale models to predict clouds and the correct amount of precipitation in the right place at the right time. Using wet concentration, rather than deposition, reduces our sensitivity to this important factor of model uncertainty.

[9] Ambient concentrations of [NH₃] + aerosol [NH₄⁺] ([NH_x]) could also be used as a chemical indicator for inverse modeling of NH₃, but there are no continuous networks collecting both NH₃ and aerosol NH₄⁺. Observational data for NH_x are available from January through May 1990 from the Eulerian Model Evaluation Field Study (EMEFS) [McNaughton and Vet, 1996], and NH_x will be used with the inverse method for these months to independently estimate NH₃ emissions adjustments as a check against the results using wet [NH₄⁺]. [NH₃] is not used in the inverse modeling application to avoid introducing model partitioning errors between [NH₃] and aerosol [NH₄⁺]. Ambient aerosol [NH₄⁺] data were found to not be suitable for inverse modeling of NH₃ emissions. Aerosol [NH₄⁺] responses to NH₃ emission changes are associated with changes in the partitioning between NO₃⁻ and HNO₃ due to the semi-volatility of ammonium nitrate, but the bulk of NH₄⁺ aerosols in the eastern United States are from ammonium sulfate which is left relatively unchanged with NH₃ emission changes. Thus the effect of NH₃ emission changes on aerosol [NH₄⁺] was shown to be dampened compared to effects on [NH_x] or wet [NH₄⁺].

[10] Observed wet [NH₄⁺] data from the NADP network have a weekly sampling frequency, and the NH₄⁺ wet deposition and precipitation data are aggregated up to monthly or 4-week values for both CMAQ and NADP to calculate precipitation-weighted mean monthly wet [NH₄⁺]. The 4-week periods that are used for monthly values coincide with the beginning and end of the NADP collection time periods. The specific dates that represent each month are listed in Table 2.

[11] Originally, we had planned to perform the inverse modeling tests for one month per season; however, the study was extended to include all months during the spring and summer seasons to capture the peak monthly emission period. Ideally, we would like to extend this study to include all months of 1990, but the time and resource requirements for running CMAQ are large and limit our ability to expand the study. These monthly simulations require about 2 weeks of runtime on a CRAY T3E system, and a minimum of 3 simulations are needed for each month, not including the resources required to develop the meteorological and emission fields.

Table 2. Dates Used to Represent Each Month

	NADP Four-Week Collection Time Periods
January	9 January to 6 February 1990
March	6 March to 3 April 1990
April	3 April to 1 May 1990
May	1–29 May 1990
June	5 June to 3 July 1990
July	3–31 July 1990
August	31 July to 28 August 1990
October	2–30 October 1990

[12] In comparing NADP weekly versus daily sampling protocols, Butler and Likens [1998] and Lamb and Comrie [1993] have shown that wet [NH₄⁺] weekly observations from the NADP network exhibit a low bias because some ammonium is removed from the sample while it remains in the field during the week because of microbial activity. For this reason, we apply a 15% upward adjustment to the NADP wet [NH₄⁺] observations based on an average bias estimate from comparisons of collocated daily versus weekly sampled data at 4 sites within the NADP network [Butler and Likens, 1998]. The variability in the bias suggests that the bias can range by about ±5% intra-annually [Gilliland et al., 2002].

[13] When reviewing observational data from the NADP monitors, sites were removed if 1 or more of the weekly samples were missing for the 4-week period. Also, data from monitors located within 9 grid cells (i.e., 324 km) of the western boundary of the model domain are not considered so that boundary conditions do not unduly influence the inverse modeling estimates of NH₃ emission adjustments.

[14] In addition to comparing NADP wet [NH₄⁺] and EMEFS [NH_x] data with CMAQ results in the inverse modeling analysis, observations of aerosol [NH₄⁺], [NO₃⁻], and [SO₄²⁻] from the Clean Air Status and Trends Network (CASTNet) [Clarke et al., 1997] will also be compared to model results before and after adjustments to the NH₃ emissions.

2.2. Inverse Modeling Approach

[15] The inverse modeling approach chosen for this study is based on a Kalman filter approach where the filter is applied independently at each time increment. This approach is similar to the method discussed by Gilliland and Abbitt [2001] and Chang et al. [1996, 1997] except that it is not applied iteratively as in those studies because of the linear response of wet [NH₄⁺] to NH₃ emission changes. Without iterations, the approach has some similarities to that of Jacob et al. [2002]. To calculate emission adjustments, the following equation is used:

$$\hat{\mathbf{E}}_{\mathbf{t},\text{posteriori}} = \hat{\mathbf{E}}_{\mathbf{t},\text{prior}} + \mathbf{G}_{\mathbf{t}}(\chi_{\mathbf{t}}^{\text{obs}} - \chi_{\mathbf{t}}^{\text{mod}}), \quad (1)$$

$\hat{\mathbf{E}}_{\mathbf{t},\text{posteriori}}$ represents the integral of the a posteriori emissions estimate for time \mathbf{t} within the model domain. To estimate monthly NH₃ emissions, the time increment \mathbf{t} is monthly in this study. $\hat{\mathbf{E}}_{\mathbf{t},\text{prior}}$ represents the a priori integral emission estimate within the model domain. The Gain $\mathbf{G}_{\mathbf{t}}$ in equation (1) determines the sensitivity of the emission adjustment to differences between observed and modeled

concentrations, χ_t^{obs} and χ_t^{mod} , at each monitor \mathbf{n} . The optimal Gain \mathbf{G}_t is given by:

$$\mathbf{G}_t = \mathbf{C}_t \mathbf{P}_t^T (\mathbf{P}_t \mathbf{C}_t \mathbf{P}_t^T + \mathbf{N}_t)^{-1}. \quad (2)$$

\mathbf{P}_t is the Jacobian of the change in concentration with respect to emissions, ($\mathbf{P}_t = \partial \mathbf{f} / \partial \mathbf{E}_t$), and $\mathbf{f}(\cdot)$ is the function that calculates ($\chi_t^{\text{mod}} - \chi_{t-1}^{\text{mod}}$). The function $\mathbf{f}(\cdot)$ represents the chemical transport model. The approach for quantifying \mathbf{P}_t is similar to *Haas-Laursen et al.* [1996], *Chang et al.* [1996, 1997], and *Gilliland and Abbitt* [2001] where two parallel simulations are performed for the time increment t where the only difference is a 10% change in emissions. The Jacobian then reduces to $\mathbf{P}_t = \partial \mathbf{f} / \partial \mathbf{E}_t = \partial \chi_t / \partial \mathbf{E}_t$ because the lifetime of NH₃ is short relative to the month-long simulation. The variance of error \mathbf{C}_t for $\hat{\mathbf{E}}_{t,\text{prior}}$ is based on a 40% uncertainty estimate from *Asman et al.* [1998]. Following *Chang et al.* [1996, 1997], the standard approach first used to quantify the \mathbf{N}_t variance of error in concentration is based on the observations' uncertainty, $\mathbf{N}_t = [\sigma_{\text{obs}}, \sigma_{\text{obs}}]$. The analytical uncertainty in the wet [NH₄⁺] observations (σ_{obs}) is estimated to be 4% of the concentration value following *Electric Power Research Institute (EPRI)* [1994]. Because the uncertainty in the a priori emissions is much larger than \mathbf{N}_t in this approach, the a posteriori emission estimates that are generated should primarily be a result of a least squares fitting to the observations without much influence from the a priori. As a test of these results in section 3.3, a posteriori NH₃ emission adjustments are also calculated with model uncertainty included in \mathbf{N}_t so that the a priori information should play more of a role.

[16] As in previous studies using a regional- or urban-scale air quality model [*Chang et al.*, 1996, 1997; *Gilliland and Abbitt*, 2001; *Mendoza-Dominguez and Russell*, 2001a, 2001b], the entire domain is treated as one source region, so that $\hat{\mathbf{E}}_{t,\text{prior}}$ and $\hat{\mathbf{E}}_{t,\text{posterior}}$ are scalar. By treating the entire domain as one source region, the entire emission field for all sources will be adjusted by a single factor, leaving the spatial distribution of emissions (as illustrated in Figure 1) within the domain unchanged. This was taken as the first approach because we anticipated less uncertainty in the spatial distribution of emissions than the total magnitude, based on how the emissions are calculated. For animal husbandry and fertilizer emissions, the two largest sources of NH₃ emissions, a source-specific emission factor is applied to the county-level number of animals and amount of fertilizer purchased. While this county-level information should be fairly accurate, the lack of temperature dependence in the current emission factors does introduce a spatial uncertainty into the emission estimates that is not addressed in the current approach but is planned as a refinement to this study.

[17] When presenting the approach, it should be noted that equation (1) assumes that the modeled and observed concentrations at the previous time step are equal. This assumption can pose a risk if initial condition concentrations are substantially different from observed concentrations. For relatively long-lived chemical species (e.g., CO), emission adjustments can compensate for discrepancies in initial conditions, and this can subsequently affect related chemical fields and cause feedbacks [*Gilliland and Abbitt*,

2001]. However, initial condition discrepancies are inconsequential in this application because we are using monthly time increments t and the lifetime of NH₃ in the troposphere is on the order of a few days.

[18] Pseudodata tests or twin experiments [*Hartley and Prinn*, 1993; *Haas-Laursen et al.*, 1996; *Gilliland and Abbitt*, 2001] were performed to test the approach described above. Model-generated data are used as reference observations or pseudodata in equation (1). Another simulation is then performed with a perturbed emission field. If the inverse modeling technique is applied correctly, adjusted emissions should closely approximate the original emissions that were used to produce the reference observations. Pseudodata tests were successful, thus confirming that the methodology was applied correctly and that the application was suitable for the technique. Therefore we could proceed with real observational data.

3. Results and Discussion

3.1. A Posteriori NH₃ Budget

[19] The a priori and a posteriori NH₃ emission estimates are summarized in Table 3. For reference, the *Bouwman et al.* [1997] NH₃ inventory for the North American continent is approximately 4.37×10^6 tons/year as compared to the a priori NEI NH₃ emission estimates of approximately 4×10^6 tons/year for the contiguous United States. Where EMEFS data are available, a posteriori emission estimates are presented based on [NH_x] along with results based on wet [NH₄⁺]. The estimated adjustments for [NH_x] and wet [NH₄⁺] are all within 8% of each other, suggesting that wet [NH₄⁺] is behaving fairly well as an indicator for the inverse modeling application. The results in Table 3 illustrate the strong seasonal variation in the a posteriori NH₃ emission estimates, where the emissions are lowered substantially in January and October and slightly adjusted during the summer months of June and July. A less expected item of note is that the a posteriori emission estimates suggest that the annual total NEI is too high for 1990.

3.2. Comparison of Model Results Against Precipitation Chemistry and Ambient Data

[20] Scatterplots of CMAQ wet [NH₄⁺] based on a priori and a posteriori NH₃ emission estimates will first be presented for one month per season. Results for winter and fall are available for January and October. For spring, March is presented since it has the largest NH₃ emission adjustment and therefore the strongest response. For summer, the month of June is presented since June has the highest a posteriori NH₃ emissions estimates. Responses of [NH_x] and aerosol [NO₃⁻] for January will also be shown in scatterplots. Monthly median results will then be presented for wet [NH₄⁺], [NH_x] (where available) and aerosol [NO₃⁻], [SO₄⁻], and [NH₄⁺] to illustrate how well the modeled and observed seasonal variations compare when using annually constant versus inverse-adjusted NH₃ emissions. For clarification, no emissions other than NH₃ have been adjusted in these simulation results.

[21] Figure 2 presents the [NH₄⁺] wet concentration results from CMAQ against NADP data for January 1990. The 68% reduction in NH₃ emissions in the a posteriori case reduces the Root Mean Square Error (RMSE) to less than

Table 3. Adjustments to NH₃ Emissions Based on Inverse Modeling Results

	U.S. NH ₃ Emission Inventory, 1000 t/yr		A Posteriori Scaling Factors	
	A Priori (Based on NEI)	A Posteriori	NADP [NH ₄ ⁺]	EMEFS [NH _x]
January	3,922	1,276	-68%	-73%
March	3,922	1,674	-58%	-46%
April	3,922	2,472	-38%	-33%
May	3,922	3,070	-23%	-24%
June	3,922	4,226	+6%	N/A
July	3,922	3,588	-10%	N/A
August	3,922	3,030	-24%	N/A
October	3,922	997	-75%	N/A

half of its original value. The correlation remains very similar before and after NH₃ emission adjustments, which is expected because no changes are made to the spatial distribution of the emissions. March (Figure 3) is similar to January, where the model using a priori emissions tends to substantially overpredict. The 58% a posteriori decrease in NH₃ emissions brings the results more closely in line with the observations. Again, the RMSE has improved considerably after the a posteriori decrease in emissions. Since the adjustment to NH₃ emissions was only a minimal 6% increase in NH₃ emissions during June, Figure 4 does not show any sizable changes after the emission adjustment. Similar to results for January, October results show overpredictions of wet [NH₄⁺] based on a priori annually constant NH₃ emissions (Figure 5) that are improved after the 75% a posteriori decrease in NH₃ emissions. The RMSE has also decreased to half the original value. While these results suggest that the modeled concentrations agree more closely with observations if using the a posteriori NH₃ emissions, a tendency to underpredict is apparent after the emission adjustment, and will be discussed further in section 3.3.

[22] The response of [NH_x] to the NH₃ emission adjustments is shown for January in Figure 6, where dramatic improvements in overpredictions and RMSE are evident. A

substantial response in the aerosol nitrate [NO₃⁻] is also evident with the decrease from the a priori to a posteriori NH₃ emissions for January (Figure 7). In January, large overpredictions in [NO₃⁻] are improved substantially after the decrease in a posteriori NH₃ emissions, and the RMSE improves by an order of magnitude. The NH₃ emission adjustments not only decreases the amount of particulate nitrate but also the total nitrate, which includes [NO₃⁻] and [HNO₃], because the shift from ammonium nitrate to HNO₃ has a secondary effect: HNO₃ has a much larger dry deposition velocity, so more HNO₃ is removed from the atmosphere via dry deposition. Similar responses of [NH_x] and [NO₃⁻] to the NH₃ emission reductions during other winter and fall months are also illustrated in the next series of figures.

[23] A concise picture of how well the emission adjustments capture the seasonal variability in the observed data is shown in Figures 8–12. These figures present median results from all monitors along with the 25% and 75% quartiles of NADP data and the corresponding CMAQ grid cells for each simulated month. Directly relevant to the inverse calculations themselves, Figure 8 shows the a priori and a posteriori CMAQ model results for wet [NH₄⁺] against the NADP wet [NH₄⁺]. When using the annually constant a priori NH₃ emissions, CMAQ shows large ranges of overpredictions during January, March, April, and October, and the seasonal variability evident in the observational data is poorly captured (Figure 8a). The a posteriori NH₃ emissions greatly improve the seasonal pattern in wet [NH₄⁺]

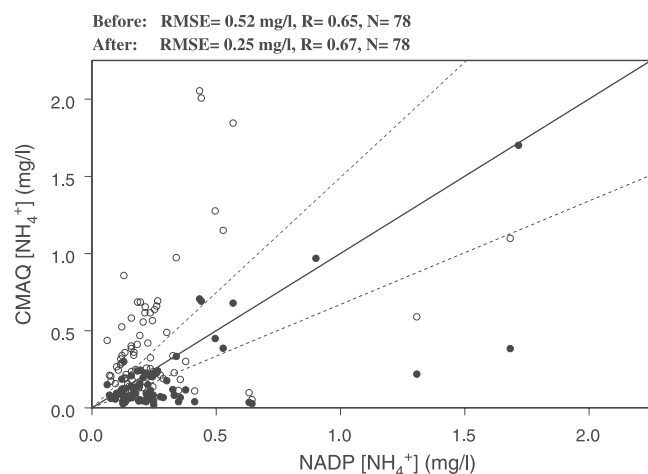


Figure 2. January 1990 NADP versus CMAQ model wet concentration of NH₄⁺ using (open circles) annually constant NH₃ emissions and (closed circles) after the NH₃ emissions were reduced 68% based on inverse results. The solid (dashed) line represents the 1:1 (factor of 2) correlation.

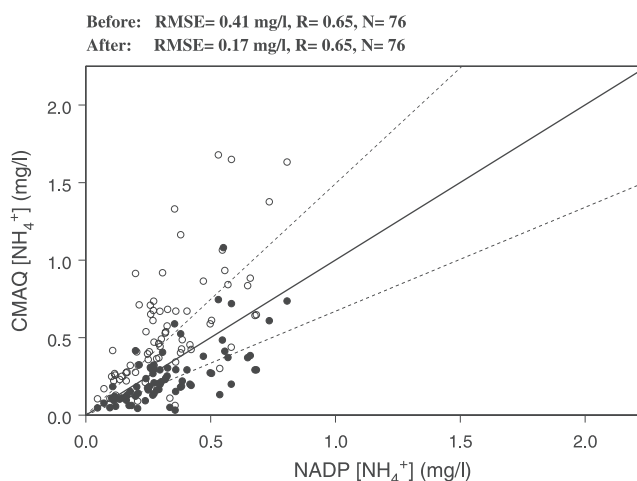


Figure 3. Same as Figure 2 but for March 1990 and 58% emissions reduction.

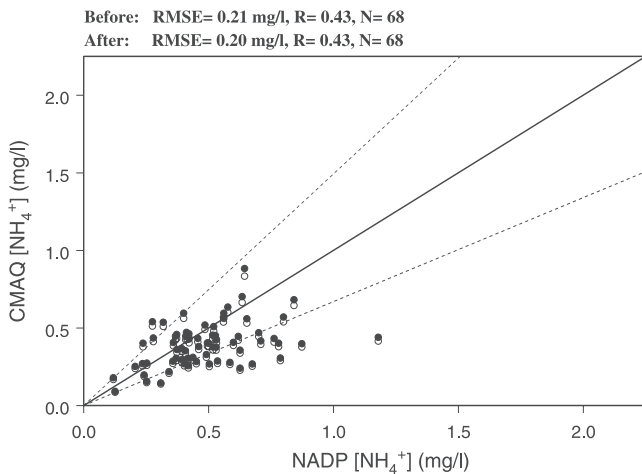


Figure 4. Same as Figure 2 but for June 1990 and a 6% emissions increase.

(Figure 8b). If the mean monthly perturbations around that annual mean are compared between CMAQ and the observational data, the annually constant a priori NH₃ emission estimates results in a correlation of $R = 0.12$, and the a posteriori NH₃ emission estimates increase the correlation to $R = 0.98$. Clearly, the adjusted NH₃ emissions better capture the seasonal variability in wet [NH₄⁺] observed in the NADP network. However, an obvious shortcoming of the results in Figure 8b is that the a posteriori model results consistently underpredict the observed values, an issue already raised in the scatterplots previously presented. The determined cause for this underprediction will be discussed in section 3.3.

[24] Figure 9 compares the [NH_x] CMAQ results based on a priori and a posteriori NH₃ emission estimates against EMEFS [NH_x]. Overpredictions are substantially corrected by the emissions adjustments for January, April, and May 1990. However, a posteriori [NH_x] results for March 1990 are noticeably lower than observed. When [NH_x] was used in equation (1), the March NH₃ emission adjustment was 8% less than the wet [NH₄⁺] results.

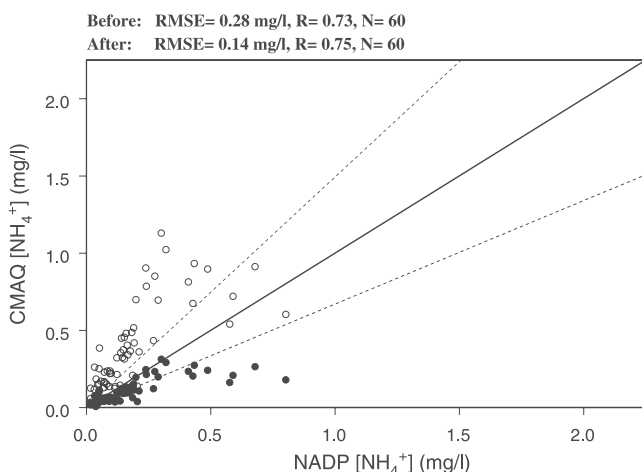


Figure 5. Same as Figure 2 but for October 1990 and for 75% emissions reduction.

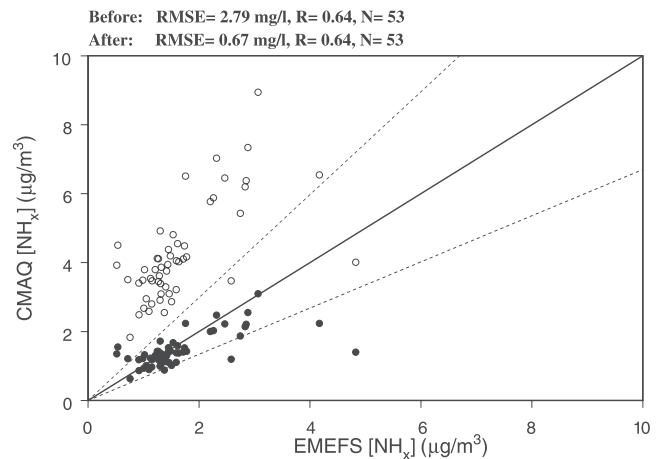


Figure 6. January 1990 EMEFS versus CMAQ model ambient concentration of NH_x (NH₃ + NH₄) using (open circles) annually constant NH₃ emissions and (closed circles) after the NH₃ emissions were reduced 68% based on inverse results from [NH₄⁺]. The solid (dashed) line represents the 1:1 (factor of 2) correlation.

[25] The effects of the NH₃ emissions adjustments on aerosol [NH₄⁺] in CMAQ are presented in Figure 10. Substantial improvements are evident in the winter, spring, and fall months. During summer months in the eastern United States, most of the aerosol [NH₄⁺] is in the form of ammonium sulfate, and sulfate aerosols are not affected to a noticeable extent by the modifications in NH₃ emissions (Figure 11).

[26] Improvements in the a posteriori aerosol [NO₃⁻] results are dramatic during the winter, spring, and fall periods (Figure 12b). These improvements in [NO₃⁻] are related to the improvements seen in aerosol [NH₄⁺] predictions during winter, spring, and fall in Figure 10b (as compared to Figure 10a). The dramatic improvements to

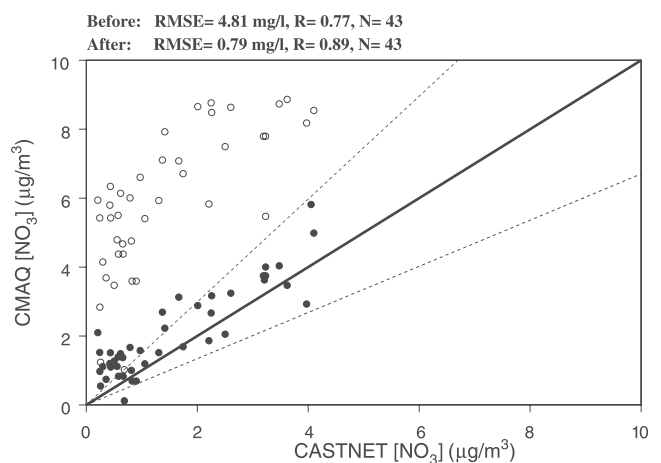


Figure 7. January 1990 CASTNET versus CMAQ model ambient concentration of NO₃ using (open circles) annually constant NH₃ emissions and (closed circles) after the NH₃ emissions were reduced 68% based on inverse results. The solid (dashed) line represents the 1:1 (factor of 2) correlation.

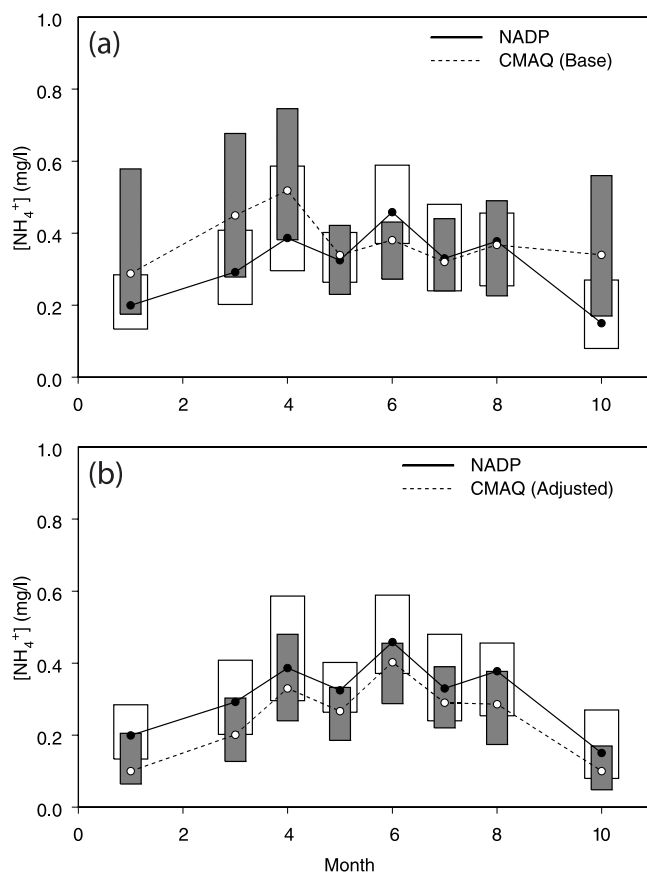


Figure 8. $[\text{NH}_4^+]$ wet concentrations from NADP, (a) CMAQ results based on annually constant NH_3 emissions, and (b) CMAQ results using inverse-adjusted NH_3 emissions. The median monthly value is denoted by the lines, and the boxes outline the 25% and 75% quartile for the NADP (open) and CMAQ (shaded) data.

$[\text{NO}_3^-]$ result from less NH_3 gas being available to form ammonium nitrate, so more remains as HNO_3 and is removed via dry deposition. When performing annual or seasonal model simulations to evaluate model predicted concentrations of nitrate aerosols, the need for seasonal NH_3 emissions is obvious from these results.

3.3. Biases and Uncertainties in a Posteriori NH_3 Emission Estimates

[27] As previously mentioned, the CMAQ results with inverse-adjusted NH_3 emissions impose an underprediction in wet $[\text{NH}_4^+]$ during most months (Figure 8). Since the intention with the inverse modeling methodology is to optimize the modeled wet $[\text{NH}_4^+]$ against observed values, the underprediction of the directly compared indicator is troubling. Based on tests shown here, we have determined that the underprediction is caused by the uniform relative error used when quantifying the Noise N_t , where the same 4% uncertainty value is used at all monitors. We test this by calculating the emission adjustments using a uniform absolute error for N_t , based on the average wet $[\text{NH}_4^+]$ value from all monitors multiplied by the same 4% analytical error. Because of resource constraints, no additional simulations were made here, but we compare the adjustment estimates

themselves. As presented in Figure 13, the adjustments based on a uniform absolute error are clearly higher in the spring, summer, and fall, with June having the largest difference of a 24% increase versus the previous 6% increase.

[28] With a uniform relative error, model discrepancies have more influence on the emission adjustment when the observed concentrations are low. This is because the low concentrations result in smaller error values (and larger Gain G_t values). If the modeled concentrations had a similar spatial pattern as the observed concentrations, the uniform relative error approach would not create a noticeable bias in the results because there would not be sporadic locations with large model overpredictions and low observed concentrations. This is why the problem was not detected in the pseudodata tests, where the spatial pattern of the emissions was not perturbed. However, in reality, the model does not consistently overpredict or underpredict at all monitors. Figure 14 shows the most extreme example, June 1990. G_t is much smaller in areas where the observed concentrations are high, but the model substantially underpredicts wet $[\text{NH}_4^+]$ in these areas. On the other hand, there are five NADP monitors (AL99, MN18, TN11, MI99, and PA42) where the model overpredicts wet $[\text{NH}_4^+]$ and the G_t weighting is quite high.

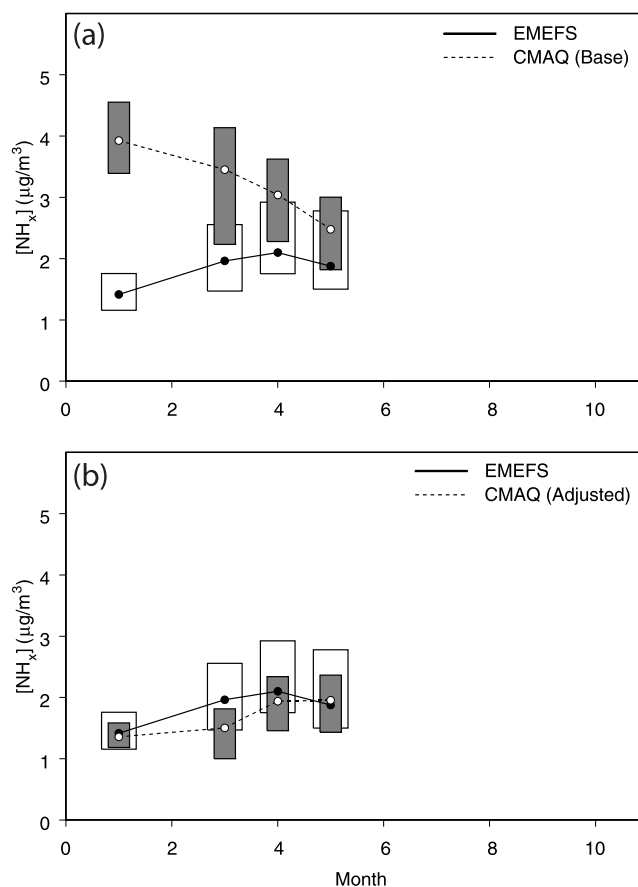


Figure 9. $[\text{NH}_x]$ ambient concentrations from EMEFS, (a) CMAQ results based on annually constant NH_3 emissions, and (b) CMAQ results using inverse-adjusted NH_3 emissions. The median monthly value is denoted by the lines, and the boxes outline the 25% and 75% quartile for the EMEFS (open) and CMAQ (shaded) data.

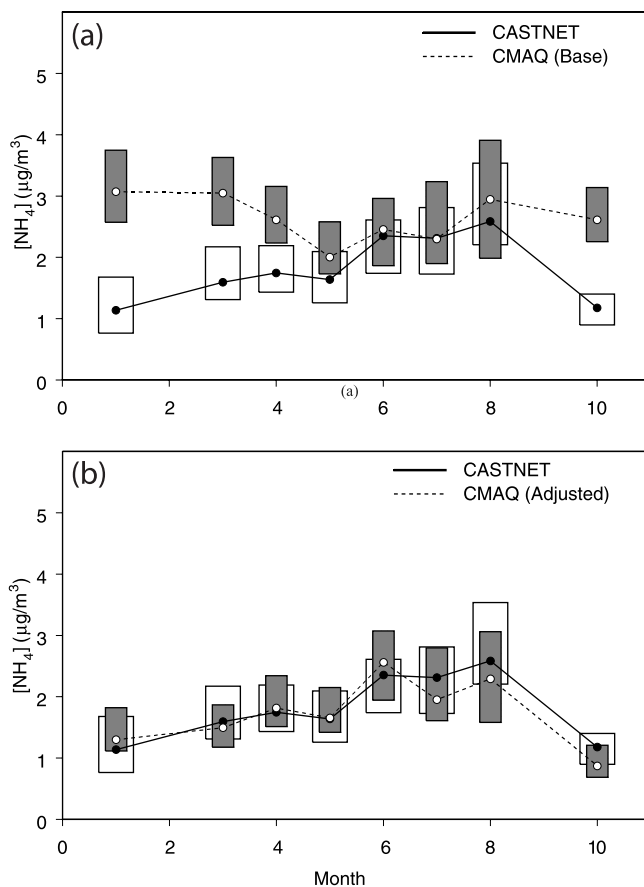


Figure 10. [NH₄] ambient aerosol concentrations from CASTNET, (a) CMAQ results based on annually constant NH₃ emissions, and (b) CMAQ results using inverse-adjusted NH₃ emissions. The median monthly value is denoted by the lines, and the boxes outline the 25% and 75% quartile for the CASTNET (open) and CMAQ (shaded) data.

[29] Analytical precision tests in the NADP 2000 Quality Assurance Report show that the uncertainty is indeed higher for [NH₄⁺] at low concentrations [NADP, 2002] (available at <http://nadp.sws.uiuc.edu/lib/qa/qa2000.pdf>), which suggests that a uniform relative error is not a correct representation of the uncertainty for these data. These test results show that the representation of error throughout the range of concentrations should be carefully considered where dense networks of observed data are used within much coarser source regions.

[30] Going back to a point made in the previous section, the emission adjustments estimated here by the inverse modeling approach suggest that the current NEI's annual NH₃ emissions are too high. Seasonally weighted a posteriori NH₃ emissions based on wet [NH₄⁺] and the initial inverse modeling approach (Table 3) suggest that the NEI annual NH₃ emissions should be 47% lower to optimize modeled wet [NH₄⁺] against observations. The low bias that has been detected in the a posteriori model results in Figure 8 suggests that this decrease may be too large. We have also shown that a uniform relative error does not correctly represent the uncertainty at lower concentrations and puts too much weight on model performance at lower concen-

trations. Based on the results using a uniform absolute error for the observed data, the NEI annual NH₃ emissions should be approximately 37% lower to optimize modeled wet [NH₄⁺] against observations. This may be a more reasonable estimate, but it is still based on an air quality model that has its own uncertainties. Two areas of model uncertainty are considered here, precipitation and the dry deposition of NH₃.

[31] To test the sensitivity of the emission adjustment factors to model uncertainty, we calculate the standard error of the estimate relative to the total model precipitation,

$$\sigma_{\text{prec}} = \frac{\sqrt{\frac{\sum (P_{\text{daily}}^{\text{obs}} - P_{\text{daily}}^{\text{mod}})^2}{N}}}{P_{\text{total}}^{\text{mod}}},$$

where $P_{\text{daily}}^{\text{obs}}$ is the daily precipitation value from the NADP monitors and $P_{\text{daily}}^{\text{mod}}$ is the same from MM5. At monitors with many days of no precipitation, extremely large relative error values resulted if the error was calculated relative to the mean precipitation. For the purpose of a sensitivity test, using the total accumulated model precipitation for the

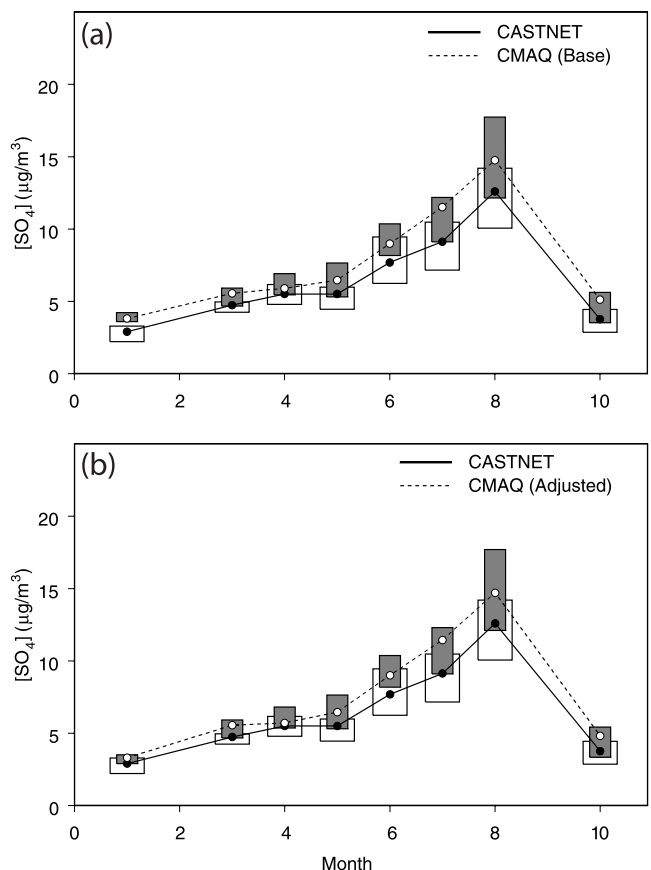


Figure 11. [SO₄] ambient aerosol concentrations from CASTNET, (a) CMAQ results based on annually constant NH₃ emissions, and (b) CMAQ results using inverse-adjusted NH₃ emissions. The median monthly value is denoted by the lines, and the boxes outline the 25% and 75% quartile for the CASTNET (open) and CMAQ (shaded) data.

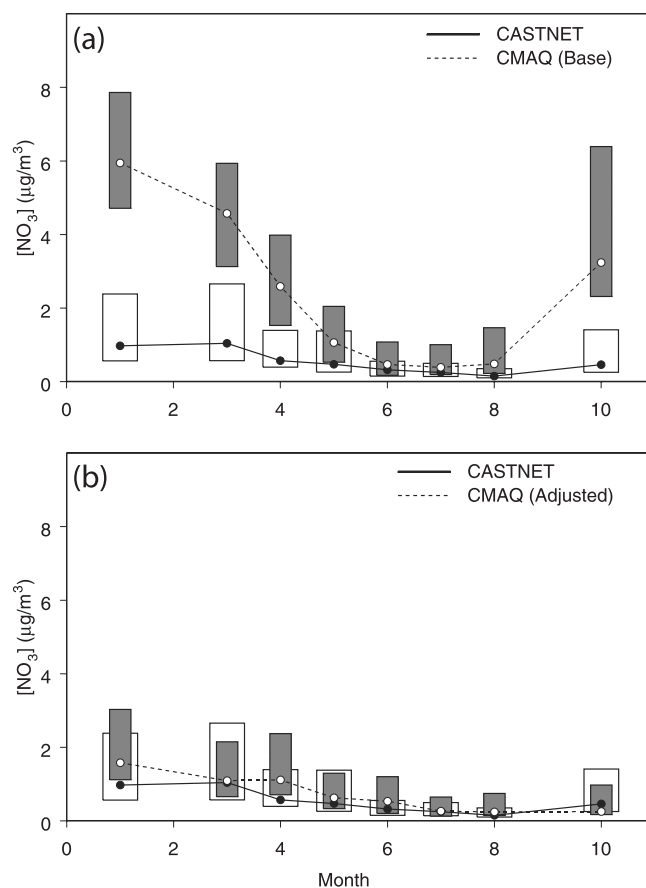


Figure 12. [NO₃] ambient aerosol concentrations from CASTNET, (a) CMAQ results based on annually constant NH₃ emissions, and (b) CMAQ results using inverse-adjusted NH₃ emissions. The median monthly value is denoted by the lines, and the boxes outline the 25% and 75% quartile for the CASTNET (open) and CMAQ (shaded) data.

month $P_{\text{total}}^{\text{mod}}$ was chosen as a practical solution around this problem. The precipitation uncertainty was calculated separately for each monitor, and the average across all monitors was about 15% and ranged between about 5% and 100%. The precipitation uncertainty must then be translated into an uncertainty in the wet [NH₄⁺]. To do so, we use a uniform absolute error approach by multiplying the precipitation uncertainty at each monitor against an average wet [NH₄⁺] for the domain. This way, the model uncertainty parameter and N_t values were weighted primarily by the model's ability to predict precipitation, and the same relative uncertainty is not assumed throughout the concentration range. The resulting NH₃ emission adjustment factors for most months are approximately 5 to 10% higher than results based only on a uniform absolute error for the observed concentrations (Figure 13). The results from this test including model uncertainty suggest approximately a 30% decrease in the annual total NEI NH₃ emissions based on a seasonally weighted average of the emission adjustment factors.

[32] Another area of model uncertainty that could affect the CMAQ predicted wet [NH₄⁺] is NH₃ dry deposition. A review of published field data [Y. Wu, personal communication, 2002; Poor *et al.*, 2001; Pryor *et al.*, 2001; Hansen *et al.*, 1998] indicates that the NH₃ dry deposition velocity, v_d , is too low in the standard dry deposition model used in CMAQ [Wesely, 1989]. To test the sensitivity of the inverse results to this discrepancy, we performed CMAQ simulations for January and June 1990 by doubling the NH₃ v_d . This change resulted in about a 10% higher adjustment in the computed emission adjustment factors. Further research is needed in the area of NH₃ dry deposition modeling before a more conclusive impact could be assessed for these results; however, at a minimum, we believe that our a posteriori adjustments to NH₃ emissions may be compensating for an underprediction of NH₃ dry deposition removal in the model.

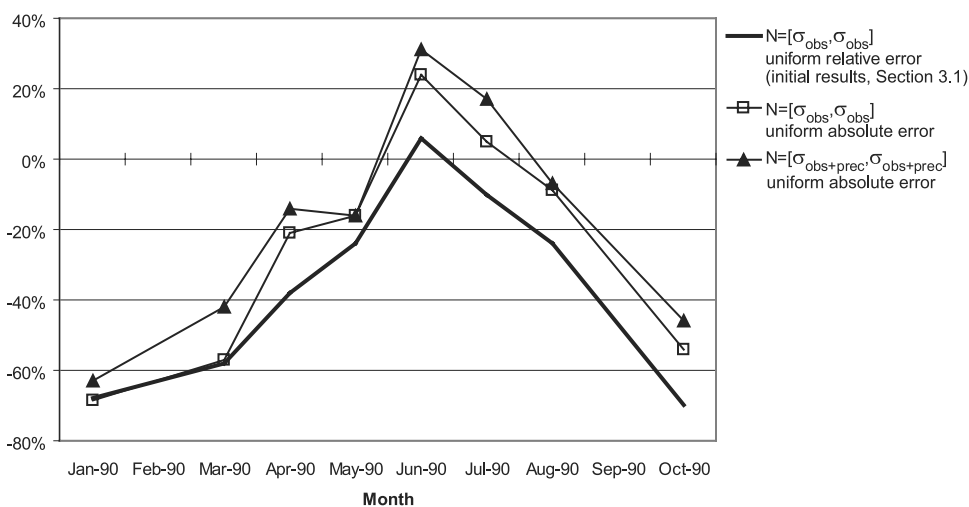


Figure 13. Adjustments to NH₃ emissions as estimated by three approaches: (1) the standard approach presented in Table 3 and Figure 1 that relies on a uniform relative error for observed concentrations (solid line), (2) if a uniform absolute error is used for N_t (open squares), and (3) if model precipitation and observational uncertainty is considered in the calculation (solid triangles). These estimates were based on comparisons of model and observed wet [NH₄⁺].

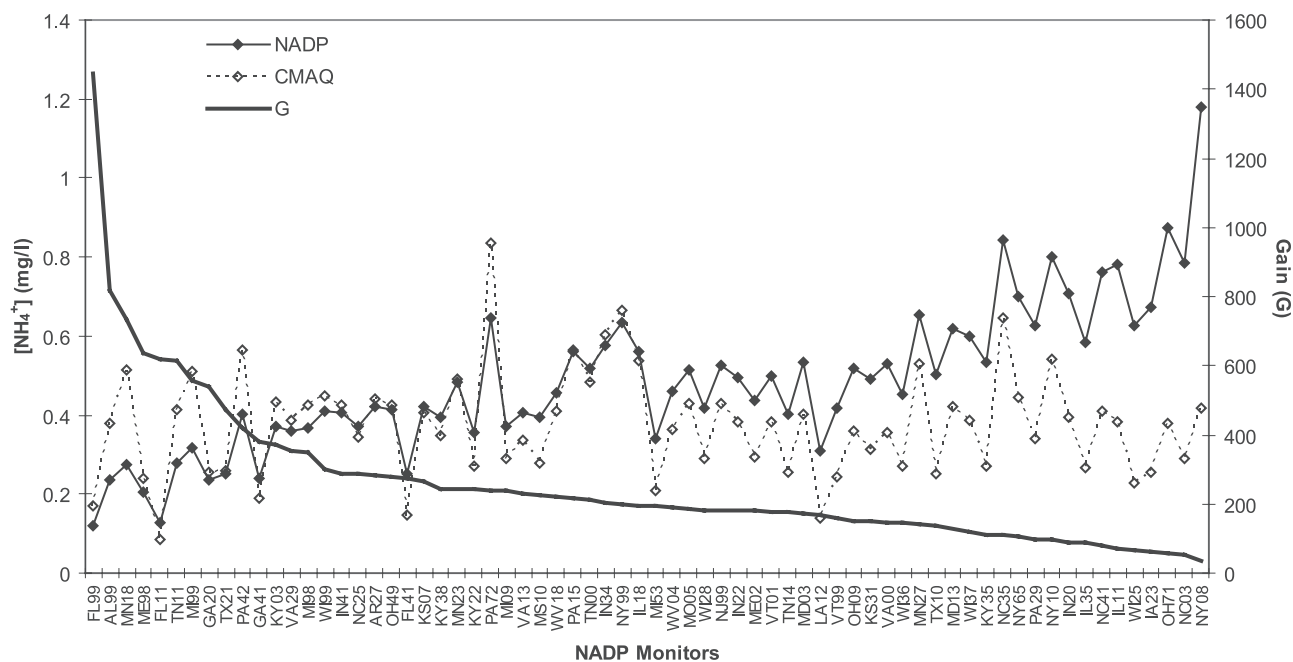


Figure 14. Observed and a priori Modeled $[\text{NH}_4^+]$ are paired and sorted by the Gain values. NADP monitors are labeled on the x axis.

[33] If modeled precipitation uncertainty and potential biases in the NH_3 dry deposition velocity are considered, the NH_3 emission adjustments suggest that as an upper bound, the annual NEI inventory is potentially about 20% too high. This is supported by the *USEPA* [2002] report that proposed modifications to the NH_3 emission factors currently used in the NEI. The proposed modification that has the largest impact is the emission factor for nondairy cattle. Cattle are the largest source of NH_3 in the inventory, and the NEI currently uses the same emission factor for both dairy and nondairy cattle. The report suggests that the emission factor for nondairy cattle should be decreased by approximately 50%. This change, along with a proposed decrease of 24% in the NH_3 emission factor for swine, would result in a total 23% decrease to the NEI NH_3 emission inventory. This 23% decrease provides some grounding for the decrease in emissions that is suggested based on these inverse modeling tests.

4. Summary

[34] Monthly NH_3 emissions are estimated using an inverse modeling approach that compares wet $[\text{NH}_4^+]$ data from NADP network against USEPA CMAQ model results. The motivation is that the EPA NEI inventory for NH_3 emissions currently provides NH_3 emission estimates only on an annual timescale, but we suspect seasonal variability in these emissions. The a posteriori NH_3 estimates presented here suggest a strong seasonal variation in the NH_3 emissions where emissions are approximately 70% higher in June as compared to fall and winter months. Similarly, NH_3 flux observations from two swine finishing buildings were about 75% higher during summer as compared to early spring conditions [Heber *et al.*, 2000], and fluxes observed from a hog waste lagoon were approximately 80–90%

higher during summer as compared to winter and fall conditions [Aneja *et al.*, 2000]. The only other inverse modeling study that has considered NH_3 emissions focused on May and July 1995 episodes [Mendoza-Dominguez and Russell, 2001b], but a different emission inventory was used for that study so that a direct comparison with their results cannot be made here.

[35] The results presented include independent comparisons of modeled data against observations for related chemical species including $[\text{NH}_x]$, aerosol $[\text{NH}_4^+]$ and $[\text{NO}_3^-]$, as well as the wet $[\text{NH}_4^+]$ used in the inverse applications. These comparisons suggest that the a posteriori NH_3 emission adjustments provide considerable improvements in the CMAQ model results over using the annually constant a priori NH_3 emissions, particularly during the fall and winter periods. As no official seasonal distribution is currently available for the NEI NH_3 inventory, a default approach has been to distribute the emissions evenly throughout the year. The results presented here elucidate the large biases that can be introduced into the air quality modeling results if constant NH_3 emissions are applied. Annual simulations of $\text{PM}_{2.5}$ should carefully consider the temporal allocation of NH_3 emissions as annually constant emissions are inadequate for winter, early spring, or fall conditions.

[36] In addition, the resulting NH_3 emission adjustment presented here suggests that the annual 1990 NEI NH_3 emissions could be too high. This is supported by the *USEPA* [2002] report that proposed modifications to the NEI NH_3 emission factors for nondairy cattle and swine, which would result in a total 23% decrease to the NEI NH_3 emission inventory. Considering the results of this study along with the *USEPA* [2002] report, we believe that it is plausible to consider as a bounding estimate that the 1990 NEI NH_3 inventory could be at least 20% too high on an annual basis.

[37] While quantitative results are presented, emphasis should be placed on the qualitative conclusions from this study regarding the seasonal variations in the emissions and the over-estimate of NH₃ emissions in the NEI. The uncertainties within the air quality model can influence the results, and not all model uncertainties are or can be included when estimating a posteriori NH₃ emissions. Furthermore, these results are specific to the domain and time period considered. Other aspects that will be considered as extensions of this study include larger (e.g., national) domains, individual source regions, interannual variability, and additional testing of model uncertainties. Field measurements linking environmental conditions to different livestock categories should also provide improvements to a national emission inventory and hopefully help to develop emission models that relate emission fluxes to climatic conditions. In the meantime, this study provides the most rigorous seasonal NH₃ emission estimates to date for urban and regional air quality modeling.

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