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Seasonal NH$_3$ emissions for the continental united states: Inverse model estimation and evaluation

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Abstract

Significant uncertainty exists in the seasonal distribution of NH$_3$ emissions since the predominant sources are animal husbandry and fertilizer application. Previous studies that estimated bottom–up and top–down NH$_3$ emissions have provided the most comprehensive information available about the seasonality of NH$_3$ emissions. In this study, this bottom–up and top–down emission information is combined with the most recent 2001 USEPA National Emission Inventory (NEI) to construct a best prior estimate of seasonal NH$_3$ emissions. These emission estimates are then used in an annual 2001 USEPA Community Multiscale Air Quality (CMAQ) model simulation for the continental United States. A key objective of this study is to evaluate these prior NH$_3$ emission estimates and test the top–down inverse modeling method for a different year and a larger modeling domain than used previously. Based on the final posterior NH$_3$ emission estimates, the inverse modeling results suggest that the annual total NEI NH$_3$ emissions are reasonable and that a previous high bias in older USEPA emission inventories has been addressed in the updated inventory. Inverse modeling results suggest that the prior NH$_3$ emission estimates should be increased in the summer and decreased in the winter, while results for the spring and fall are questionable due to precipitation prediction biases. A final conclusion from this study is that total NH$_x$ (NH$_3$ and aerosol NH$_4^+$) air concentration data are essential for quantitative top–down analyses of NH$_3$ emissions that can extend beyond what is possible using precipitation chemistry data.
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1. Introduction and background

Emission estimates have a large influence on the air quality model's ability to predict concentrations

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of particulate matter less than 2.5 μm (PM$_{2.5}$). PM$_{2.5}$ is a criteria pollutant under the National Ambient Air Quality Standard (NAAQS) that has both episodic and annual average concentration thresholds. Sulfate and nitrate aerosols are two major components of PM$_{2.5}$, which exhibit distinctly different seasonal variations. NH$_3$ gas neutralizes sulfuric acid to form ammonium sulfate aerosols, and if excess NH$_3$ is present after reaction with sulfuric acid, NH$_3$ then reacts with nitric acid

to form ammonium nitrate (Dentener and Crutzen, 1994). The representation of NH_3 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-h standard for $PM_{2.5}$, NH_3 emissions under different seasonal conditions are needed for seasonal or annual model simulations. In addition to the impact that ammonia emission estimates can have on nitrate aerosol predictions, errors in ammonia budget can also have further impact on the total $PM_{2.5}$ response to sulfur dioxide emission reductions because of the degree of nitrate replacement of reduced sulfates (Dennis et al., 2006). Research continues to point toward the importance of the representation of ammonia emissions for air quality model predictions of $PM_{2.5}$.

Uncertainties in ammonia emissions exist both in magnitude and temporal variability. Approximately 85% of the current NH_3 emission inventory is from the animal husbandry and fertilizer application sectors. Previous studies identified NH_3 emission overestimates of approximately 25% in an earlier version of the 1990 USEPA National Emission Inventories (NEI) that largely are believed to have been caused by overestimates of the emission factors for beef cattle and swine sources (USEPA, 2002; Gilliland et al., 2003). In the newest NEI for the base year 1999, these emission factors have been updated following the USEPA (2002) recommendations. This correction is anticipated to ameliorate the high bias that was identified in the previous NEI inventories.

In addition to the uncertainty in the annual budget for ammonia emissions, the temporal variability in emissions remains relatively uncertain. Ammonia emission inventories provide annual total emission estimates based on static emission factors, but guidance is needed for distributing the emissions across the seasons. We know from the timing of fertilizer application and the meteorological dependence of NH_3 volatilization from animal waste that the NH_3 emissions should not be treated as constant across the seasons; however, process-based estimates are not yet available to derive the seasonality for all emission source types. In an effort to better understand how the emissions should be distributed, Gilliland et al. (2003) developed a top–down estimate of NH_3 emissions for the year 1990 using an inverse modeling approach. The results suggested that a strong seasonal variability should be expected in the emissions, where NH_3 emissions

should be highest in the summer and then spring and lowest in the winter and fall. Results also demonstrated that annually constant NH_3 emissions can provide substantial over-prediction of the nitrate aerosol predictions during cooler seasons that are removed when introducing the seasonality into the NH_3 emissions. Results from Gilliland et al. (2003) provided the most comprehensive estimate of the seasonal distribution of the total NH_3 emission inventory at that time; however, the results were based on an older NEI for 1990 and only a subset of winter and fall months were tested.

The purpose of this study is to evaluate prior estimates of NH_3 emission seasonality based both on these previous top–down seasonality estimates and more recent process-based seasonality estimates for fertilizer and dairy cattle emissions (Goebes et al., 2003; Pinder et al., 2004). This is the first study that has incorporated both bottom–up and top–down emission information for prior NH_3 emission estimates and that has performed NH_3 inverse modeling over an entire annual simulation. Posterior emission estimates are produced using similar inverse modeling tests as Gilliland et al. (2003) to provide seasonal estimates of the NH_3 emission variability, and in this case the entire continental United States is considered. A test case is included where inverse modeling results are generated separately for Eastern and Western United States source regions. The prior and posterior seasonal NH_3 emission estimates have been used in a series of CMAQ simulations for the year 2001 that are also presented in this special issue. Specifically, Hogrefe et al. (2005) uses the prior estimates, and Eder and Yu (2005) uses the posterior estimates of the seasonal NH_3 emissions that are presented here.

2. Methodology

2.1. Air quality model description

The USEPA Models-3 Community Multiscale Air Quality (CMAQ) model (Byun and Ching, 1999; Byun and Schere, 2006) is used in this study to generate model output. CMAQ is an Eulerian air quality model that was developed to simulate O_3, aerosol chemistry, and acidic and nutrient deposition for urban- to-regional scale domains. For this study, CMAQ is configured with 14 tropospheric layers, a horizontal grid dimension of $36 \, km \times 36 \, km$, and the CB4 chemical mechanism

(Gery et al., 1989). A pre-release version of CMAQ version 4.4 (available at http://www.cmascenter. org) is used here. The CMAQ domain for this study covers the continental United States and portions of southern Canada and northern Mexico. The Fifth Generation Penn State/NCAR Mesoscale Model (MM5) is used to generate the meteorology predictions 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 for the 2001 modeling platform (http://www.epa.gov/ttn/chief/emch/invent/index.html), the MOBILE6 model for mobile emissions (USEPA, 2003; http://www.epa.gov/otaq/m6.htm), and BEIS3.12 (Pierce et al., 1998; http://www.epa.gov/asmdnerl/biogen.html) for biogenic emissions. The annual total NH_3 emissions were based on the NEI inventory for 2001, and the prior seasonal factors for distributing these emissions were based on the approach described in the following section.

2.2. Prior seasonal estimates of NH_3 emission variability

In Gilliland et al. (2003), annually constant NH_3 emission estimates were used for the prior NH_3 emission fields because of a dearth of information about the seasonality of the emissions at that time. In this study, we have developed a prior NH_3 emission estimates based on both the previous top–down estimates from Gilliland et al. (2003) and process-based estimates that are now available for fertilizer and dairy cattle from Carnegie Mellon University (CMU) NH_3 emission inventory (Goebes et al., 2003; Pinder et al., 2004). Seasonal variability for the fertilizer inventory is estimated from crop types, crop planting times, and fertilizer sales data. Seasonal variability in the dairy cattle inventory is estimated from a process-based model of ammonia emissions and a national database of farming practices. The seasonality from the CMU inventory has been applied to the NEI 2001 emissions for these two sectors. For the remainder of the agricultural emission sources, seasonal factors from Gilliland et al. (2003) were used. From the three sets of seasonal factors presented in Gilliland et al. (2003), the results that incorporated precipitation uncertainty were used. These seasonal factors were normalized so that the total annual emissions were distributed seasonally without changing the total annual emission budget. This approach was taken because, we anticipate that the previous biases identified in the 1990 NEI inventory for NH_3 have been addressed by updated emission factors. The final seasonal distribution of the prior NH_3 emissions by sector and for the total are presented in Fig. 1, and the spatial distribution of the annual NH_3 emissions from all sectors is illustrated in Fig. 2.
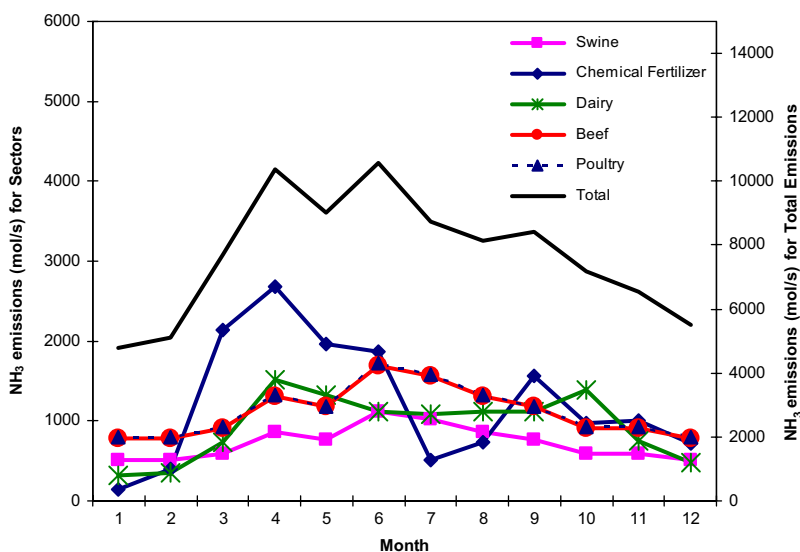

Fig. 1. Total NH_3 emissions ($mol\,s^{-1}$) for entire CMAQ domain for all sources combined and for separate agricultural sectors including dairy cattle emissions, beef cattle emissions, swine, poultry, and fertilizer. The total for all sources is plotted on the right *y*-axis, and the individual sector emissions are plotted on the left *y*-axis.
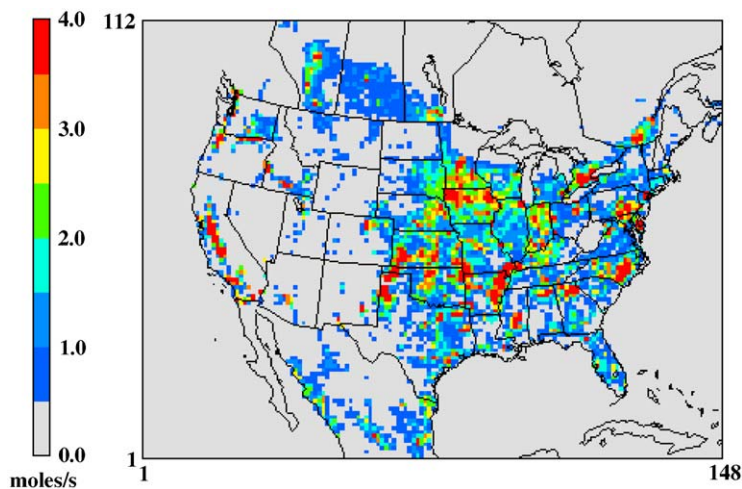
Fig. 2. Annual average NH_3 emissions for all sectors ($mol\,s^{-1}$).

For the emission sectors where the Gilliland et al. (2003) seasonal factors were used, the emissions are highest in summer and then spring. Seasonal factors for fertilizer and dairy cattle emissions, which are based on the CMU inventory, are highest in the spring and fall because fertilizer application activity peaks during those seasons. In the dairy cattle emissions model, the manure application process contributes the largest amount of NH_3 emissions in the model (Pinder et al., 2004). However, an uncertainty exists in the seasonal timing of manure application, and in most cases, very limited information was available. If county records showed that manure was applied seasonally, the current dairy cattle farm model assumes that most manure is applied in the spring and fall. The uncertainty in the dairy cattle emissions during the spring and fall is estimated to be $\pm 40\%$, while summer and winter uncertainty estimates are $\pm 30\%$ (Pinder et al., 2004).

2.3. Chemical indicators of the NH_3 budget

Ambient concentrations of ($[NH_3]$ + aerosol $[NH_4^+]$), or $[NH_x]$, would be desirable to use as a chemical indicator for inverse modeling of NH_3, but there are no monitoring networks collecting both NH_3 and NH_4^+ at this time. $[NH_4^+]$ aerosol concentrations are not used as an indicator because they will suffer from partitioning errors if the model predictions of sulfate and total nitrate are biased, which would then bias the inverse modeling results. Results will be presented to illustrate this. The most comprehensive data currently available for inverse

modeling of NH_3 emissions is NH_4^+ precipitation chemistry data because it includes both NH_3 and NH_4^+ and because the National Atmospheric Deposition Program National Trends Network (NADP, 2001) network provides a relatively dense network of observations. Monthly NH_4^+ wet deposition ($kg\,ha^{-1}$) will be used here as the primary chemical indicator for NH_3 emissions to generate seasonal factor estimates using the inverse modeling approach described in Section 2.4.

NADP data have a weekly sampling frequency with collections from Tuesday to Tuesday. The NH_4^+ chemistry and precipitation data are aggregated up to monthly accumulated wet deposition for both NADP and CMAQ. Butler and Likens (1998), Lamb and Comrie (1993), and Gilliland et al. (2002) have shown that NH_4^+ weekly observations from the NADP network exhibit a negative bias because some of the sample is biologically consumed while it remains in the field during the week. Therefore, when comparing the CMAQ results to the NADP data, a 10% upward adjustment is made to the NADP NH_4^+ data to account for biases in the weekly collected data due to sample degradation. Sites were removed from the analysis if data were missing for more than 30% of the days for the monthly period. If a site has no accumulated precipitation for the entire month, these sites are also removed. For most months, approximately 70% (30%) of the available NADP data are in the East (West).

Obviously, when using precipitation chemistry data for the inverse modeling application, precipitation prediction uncertainty is an issue. In Gilliland

et al (2003), NH_4^+ wet concentration ($mg\,L^{-1}$) was selected for the inverse modeling application because the wet concentration of an efficiently scavenged species like NH_3 is less sensitive to rainfall amount than wet deposition (Lindberg, 1982; Stein et al., 1993; Styer and Stein, 1992). However, when considering the entire continental United States, a new issue arose that did not occur in Gilliland et al. (2003) where the modeling domain only covered the Eastern United States. For the continental United States, we have identified cases where the modeled NH_4^+ wet concentration predictions can be very sensitive to NH_3 emission changes at sites with extremely low precipitation. The implication is that modeled wet concentration values at these selected sites can have an amplified response to NH_3 emission changes, which is an input to the inverse modeling calculation (discussed in Section 2.4). Model tests using NH_4^+ wet deposition were stable under these same conditions.

As an independent comparison of the model results against data after the inverse modeling adjustments, observations of aerosol $[NH_4^+]$ and total nitrate from the Clean Air Status and Trends Network (CASTNet) (Clarke et al., 1997) are also compared to model results before and after adjustments to the NH_3 emissions. These comparisons to CASTNet data will show the prior and posterior model results for aerosol $[NH_4^+]$, and they will also be used to differentiate between the impact of total nitrate over-predictions and the impact of NH_3 emission biases on the model predictions of aerosol $[NH_4^+]$.

2.4. The inverse modeling approach

The inverse modeling approach used in this study is an adapted form of the Kalman filter that is applied independently at each time increment. For more detailed descriptions beyond the description provided here see Gilliland et al. (2003) and Gilliland and Abbitt (2001). To calculate emission adjustments, the following equation is used:

$$\hat{E}_{t,\text{posterior}} = \hat{E}_{t,\text{prior}} + G_t(\chi_t^{\text{obs}} - \chi_t^{\text{mod}}), \qquad (1)$$

$\hat{E}_{t,\text{posterior}}$ represents the integral or domain-wide sum of the posterior emission estimate for time t. The time increment t is monthly in this study. $\hat{E}_{t,\text{prior}}$ represents the prior integral emission estimate within the model domain. The gain G_t in Eq. (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 n. The optimal gain G_t is

$$G_t = C_{t,\text{prior}}P_t^T(P_t C_{t,\text{prior}}P_t^T + N_t)^{-1}, \qquad (2)$$

P_t is the Jacobian of the change in concentration with respect to emissions, $(P_t = \partial f/\partial E_t)$, and $f()$ is the function that calculates $(\chi_t^{\text{mod}} - \chi_{t-1}^{\text{mod}})$ (i.e., the chemical transport model). To quantify P_t, two parallel simulations are performed for the monthly time increment t where the only difference is a 10% change in emissions. The Jacobian then reduces to $P_t = \partial f/\partial E_t = \partial \chi_t/\partial E_t$ because the chemical lifetime of NH_3 is short (e.g., hours) relative to the month long simulation. The variance of error $C_{t,\text{prior}}$ for $\hat{E}_{t,\text{prior}}$ is based on a 40% uncertainty estimate for the NH_3 emission inventory for all sources from Asman et al. (1998). After Eq. (1), the variance of error $C_{t,\text{posterior}}$ for $\hat{E}_{t,\text{posterior}}$ is estimated as

$$C_{t,\text{posterior}} = C_{t,\text{prior}} - G_t P_t C_{t,\text{prior}} \qquad (3)$$

The N_t variance of error in concentration includes the observations' uncertainty and an estimate of the uncertainty in the model precipitation at each monitor. The analytical uncertainty in the wet $[NH_4^+]$ observations (σ_{obs}) is estimated to be 4% of the concentration value following EPRI (1994). The model precipitation uncertainty is estimated based on the standard error of the estimate relative to the total model precipitation, $\sigma_{\text{prec}} = \sqrt{\sum(P_{\text{daily}}^{\text{obs}} - P_{\text{daily}}^{\text{mod}})^2/N}/P_{\text{total}}^{\text{mod}}$, 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. The precipitation uncertainty was calculated separately for each monitor, and the average across all monitors was about 10% with a minimum and maximum of 1% and 100%. Uncertainties associated with the chemical transport model processes beyond the impact of precipitation uncertainty are not included in N_t. This approach for quantifying N_t is based on the final set of inverse modeling tests in Gilliland et al. (2003).

A substantial difference in this application over Gilliland et al. (2003) is that the modeling domain includes the entire continental United States, while the previous study covers only the Eastern United States. Following the previous NH_3 top–down study, the entire domain is first treated as one source region, so that $\hat{E}_{t,\text{prior}}$ and $\hat{E}_{t,\text{posterior}}$ are scalar. Since approximately 70% of the available monitors are in the East for most months, we anticipate that the inverse results will be dominated by the model performance in the East. To test this,

we also calculate and compare the emission adjustments only considering the Eastern sites and Western sites in two separate inverse calculations to test the robustness of the results using one source region for the entire United States.

3. Results and discussion

3.1. Posterior NH$_3$ budget

Table 1 and Fig. 3 present the monthly NH$_3$ emission factors produced using the inverse meth-

odology described in Section 2, where NH$_4^+$ wet deposition data from NADP are used for model optimization in the inverse modeling application. Adjustment factors were also calculated separately for the eastern versus the western modeling domain based on a division at $-100\,^\circ$W (Table 1) for comparison. For most months, the emission adjustment factors for the eastern portion of the domain do not differ largely from the posterior results for the entire domain as one source region. Since approximately 70% of the NADP monitors are within the Eastern domain, it was anticipated that the inverse modeling results would be more directly related to the emissions in the East.

When comparing the total sum of emissions for the modeling domain after inverse modeling adjustments, the posterior results for the domain as one source region versus separate treatment of the eastern and western regions do not differ by more than 10% for all months except for March ($+19\%$), May (-20%), and July ($+16\%$) 2001. In all three of these exception cases, there are larger NH$_3$ emission increases in the West when the western domain is analyzed separately. Tests were also performed using NH$_4^+$ wet concentration data as the inverse modeling indicator for this application, where the total sum of emissions for the modeling domain showed much larger differences greater than 50% for three of the months when treating the eastern and western portions of the domain separately (not shown). The cause of these amplified results was

Table 1
Monthly adjustments factors applied to annually constant NH$_3$ emission rates

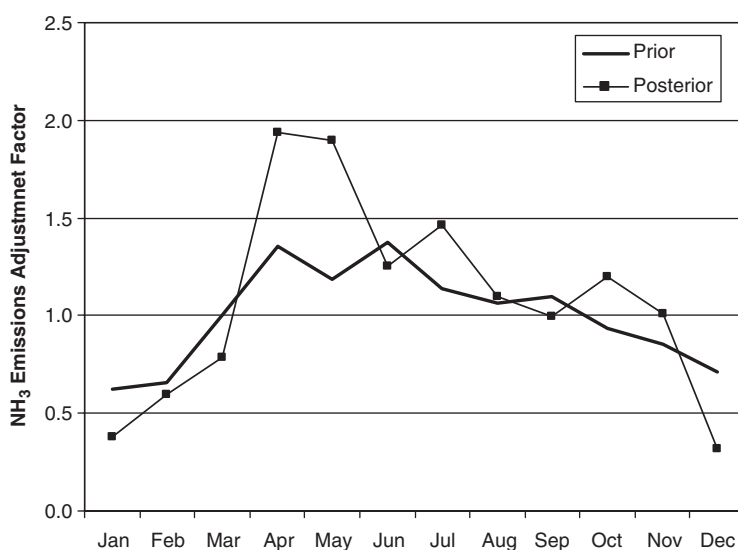|	Prior	Posterior	Posterior	
			East	West
Jan.	0.62	0.38	0.38	0.47
Feb.	0.66	0.60	0.60	0.75
Mar.	1.00	0.79	0.95	0.91
Apr.	1.35	1.94	2.01	1.39
May	1.19	1.90	1.35	2.12
Jun.	1.38	1.25	1.30	1.49
Jul.	1.14	1.47	1.45	2.60
Aug.	1.06	1.10	1.05	1.70
Sep.	1.10	0.99	1.05	1.09
Oct.	0.94	1.20	1.16	1.30
Nov.	0.85	1.01	0.99	1.11
Dec.	0.71	0.32	0.35	0.19

Fig. 3. Monthly scaling factors (dimensionless) that were applied to the annual average NH$_3$ emissions for the prior and posterior simulations.

attributed to unstable responses to P_t values that are over-sensitive at sites with extremely low precipitation. The posterior results presented here using NH_4^+ wet deposition data as the inverse modeling chemical indicator show much less sensitivity to the treatment of the modeling domain as one or two separate source regions.

The comparison of separate Eastern and Western sources regions is included as a sensitivity test, but results for the domain-wide seasonal adjustments are used for the posterior model simulations and comparisons against data. The seasonal NH_3 factors developed in this study have been used in other applications where it would not be acceptable to spatially shift the net annual NH_3 emissions. Therefore, the intent is to provide seasonal characterization estimates of NH_3 emissions that can be used for the entire domain. As an extension to this study, testing of multiple sources regions would be warranted where we could more thoroughly test the Western United States NH_3 emission biases that are suggested by the sensitivity test results shown in Table 1.

The posterior inverse modeling results for the one source region domain suggest that NH_3 emissions are highest in the spring, next highest in the summer, slightly lower in the fall than summer, and lowest in the winter. In the following section, we will explain why we doubt the NH_3 emission increases suggested for April, May, October, and November based on additional analysis and sensitivity tests. If precipitation uncertainty had not been accounted for in the analysis, the posterior results suggest an increase in emissions in the spring and summer that would have been at least 10% higher. The largest difference is for July, where a 26% higher adjustment factor would have been imposed if precipitation uncertainty had been taken into account. By including the precipitation uncertainty in the inverse calculation, the amount of emission adjustments are more constrained because of larger uncertainty bounds for the wet deposition predictions. Results in the next section will also show that noticeable under-predictions still exist in the posterior NH_4^+ wet deposition results for July because of this constraint on the emission adjustments. On an annual basis, the posterior results only suggest a relatively nominal increase to the total annual NH_3 emissions of $+8\%$, that is in the same order of magnitude as the uncertainty for the posterior estimates based on $C_{t,posterior}$.

The comparison of the prior and posterior estimates of monthly NH_3 emissions suggest that the prior estimates were reasonable for much of the year and that the NH_3 emission inventory no longer shows a substantial bias on an annual basis, unlike the earlier 1990 inventory (Gilliland et al., 2003). Results do suggest that the NH_3 emissions during the summer should be higher than in the prior estimates. With much uncertainty in the timing of manure fertilizer application for dairy cattle, this suggests that more of those emissions should perhaps have been distributed into the summer months.

A comparison of these posterior NH_3 emission adjustments and the previous 1990 NH_3 emission adjustments over the Eastern domain shows differences in the spring and fall but quite similar in the summer and winter. The differences in spring and fall could be due to issues in the new posterior estimates for those seasons. Differences could also be caused by interannual meteorological influences on the NH_3 emission rates or by emission trends over time. An in-depth analysis of emission source trends and modeling studies over additional years would be helpful in diagnosing the key factors that may be influencing NH_3 emission variability on that time scale.

3.2. Comparison of model results against precipitation chemistry and ambient data

Fig. 4 presents time series plots of the NH_4^+ wet deposition and wet concentration results for the prior and posterior simulations. Since posterior results are based on inverse modeling to optimize NH_4^+ wet deposition predictions, the posterior NH_4^+ wet deposition time series generally shows improvement over the prior simulation when comparing against the NADP observations, as anticipated. Fig. 4d also suggest some improvements in the posterior NH_4^+ wet concentration results, except in the fall where an increased high bias is introduced. Minimal improvements in summer for both NH_4^+ wet deposition and wet concentration are influenced by MM5 precipitation prediction issues including over-prediction of precipitation in July and August and high precipitation prediction uncertainty values. For the summer, spring, and fall months, improvements are evident when comparing the normalized mean bias (NMB), but the NMB values do not suggest improvements in months including January, February or March (Table 2). In some cases, the amount of adjustment is relatively small, such that we do not see noticeable
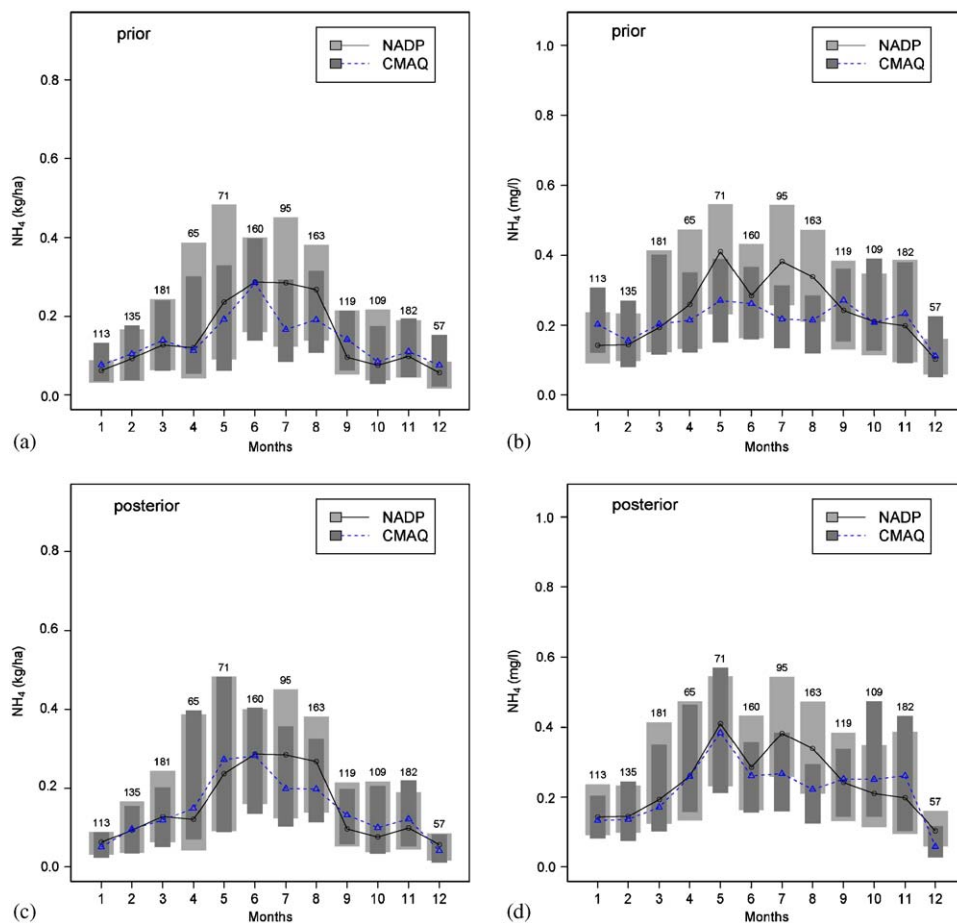
Fig. 4. NH_4^+ wet deposition (left column) and wet concentration (right column) from the NADP network and the CMAQ posterior simulations. The lines and boxes represent the median and 25–75% quartiles. The numbers above the quartiles represent the total number of sites.

differences in the prior and posterior statistics. In this case, a null result is a positive confirmation that our prior estimate of the monthly NH_3 emission factor was reasonable according to the NH_4^+ wet deposition and that additional modifications may not provide substantial improvements.

In the previous section, the posterior emission adjustments for April and May were noted because we believe they are too high and because there were substantially fewer observational data than other months. In both April and May, spatial plots of NH_4^+ wet deposition show a large cluster of high NADP deposition values in western Great Lakes area in Minnesota and Wisconsin (see April as an example in Fig. 5). The meteorology model underpredicted the observed NADP precipitation in the same area during these months. Concurrently, very low amounts of precipitation are both observed and

predicted in the Southeast and Midwest, both of which have a high density of the NH_3 emissions due to cattle, swine, and poultry farming. An independent comparison of NH_4^+ concentrations to CAST-Net observations shows large over-prediction in the Midwest and Eastern United States (Fig. 6). We have concluded that the precipitation biases and patterns during these 2 months are leading to increases in the posterior NH_3 emission adjustments. Specifically, with model underpredicted precipitation west of the Great Lakes, compensating increases in the NH_3 emissions are needed to reach similar NH_4^+ wet deposition values in this area as observed. While high NH_3 emissions exist in the Southeast and Midwest, they only provide a small contribution to the NH_4^+ wet deposition amounts observed and modeled in these areas because of low precipitation during April and May. However,

Table 2
Comparison of NADP and CMAQ predicted NH_4^+ wet deposition and CASTNet and CMAQ predicted NH_4^+ aerosols

Month	NH_4^+ wet deposition (kg ha^{-1})			CASTNet NH_4^+ (µg m^{-3})		
	R	NMB (%)	RMSE (kg ha^{-1})	R	NMB (%)	RMSE (µg m^{-3})
Prior						
Jan.	0.40	14.22	0.10	0.91	15.0	0.21
Feb.	0.67	0.21	0.08	0.88	19.0	0.16
Mar.	0.51	−3.24	0.15	0.90	18.6	0.18
Apr.	0.89	−21.63	0.15	0.91	27.8	0.20
May	0.73	−34.18	0.23	0.88	−6.2	0.12
Jun.	0.56	−1.66	0.21	0.93	−4.9	0.12
Jul.	0.60	−30.80	0.20	0.89	−18.6	0.21
Aug.	0.46	−21.20	0.19	0.89	−24.8	0.40
Sep.	0.68	1.62	0.10	0.91	0.5	0.09
Oct.	0.85	−12.20	0.08	0.87	47.6	0.28
Nov.	0.80	−7.68	0.08	0.91	36.1	0.26
Dec.	0.70	47.66	0.07	0.87	17.7	0.12
Posterior						
Jan.	0.41	−23.99	0.09	0.91	−18.9	0.21
Feb.	0.69	−10.50	0.08	0.89	9.6	0.16
Mar.	0.51	−18.02	0.14	0.90	4.9	0.18
Apr.	0.88	2.47	0.13	0.91	47.1	0.20
May	0.72	−5.44	0.20	0.91	13.6	0.12
Jun.	0.53	−2.52	0.21	0.93	−6.8	0.12
Jul.	0.57	−16.13	0.19	0.91	−6.7	0.21
Aug.	0.40	−19.60	0.19	0.89	−23.0	0.40
Sep.	0.67	−6.68	0.10	0.90	−3.8	0.09
Oct.	0.85	4.45	0.08	0.88	66.1	0.28
Nov.	0.80	4.28	0.08	0.90	45.6	0.26
Dec.	0.72	−19.93	0.04	0.84	−30.6	0.12

R is the correlation coefficient, NMB is the normalized mean bias, and RMSE is the root mean square error.

overpredictions in NH_4^+ aerosol concentrations are evident in these same areas as compared to the CASTNet network (Fig. 6).

Originally, the substantial amount of missing data during April and May also raised concerns about the validity of the posterior NH_3 emission adjustments for these months. For this application, a site was excluded from the analysis if more than 30% of the days were missing from the monthly data samples. When this criteria is lessened to exclude a site if more than 35% if the days were missing from the monthly samples, a substantial number of sites were gained for some months including April and May. The posterior adjustments were recalculated based on the 35% criterion. For 4 of the 12 months, including April, the posterior adjustments would have changed by 10–15%. All

other months had smaller or no change in their posterior NH_3 emission adjustments. An NH_3 emission change on the order of 10–15% would lead to only a small incremental change and would not change the overall conclusions here that April and May posterior emission adjustments are being influenced by compensating errors related to precipitation underpredictions near the Great Lakes and because other areas with a high density of NH_3 emissions are not well represented during these months due to small amounts of observed and predicted wet deposition and precipitation.

For all months of 2001, NH_4^+ aerosol predictions for the prior and posterior simulations are compared against CASTNet data in a time series format (Figs. 7(a) and (b), respectively). Statistical comparisons are also shown in Table 2. NH_4^+ concentration over-predictions in the winter months appear reduced after applying posterior adjustments, with a slight under-prediction introduced. Under-predictions in July are only slightly improved. Large NH_4^+ aerosol over-predictions in the spring and fall are exacerbated in the posterior results. Spatial comparisons against CASTNet NH_4^+, which are not shown for brevity, support these findings. The NH_4^+ aerosol concentrations can be affected by the NH_x budget and the total nitrate budget, so we must consider that either can be the cause of these over-predictions in NH_4^+ aerosols. Sulfate predictions were quite good and are not affecting these high biases. Fig. 7(d) shows substantial over-prediction of total nitrate in the posterior simulation.

Much uncertainty exists in the heterogeneous reaction rate to produce nitric acid, which plays a key role in the total nitrate over-predictions during cooler months (Dennis et al., 2006). A sensitivity simulation was conducted where this heterogeneous reaction rate was reduced by a factor of ten to decrease the amount of total nitrate over-prediction (Fig. 7(e)). With this test correction to the total nitrate budget, NH_4^+ concentration predictions are still too high in the spring and fall (Fig. 7(c)), which suggests NH_3 emissions are the culprit. We have already discredited the spring posterior results based on compensating errors related to precipitation, but these results question whether the fall emission factors are too high as well. Comparison of precipitation shows that MM5 precipitation predictions had a low bias during October and November, so the wet deposition-based inverse modeling results may also be introducing compensating errors here to account for a lower precipitation volume in the
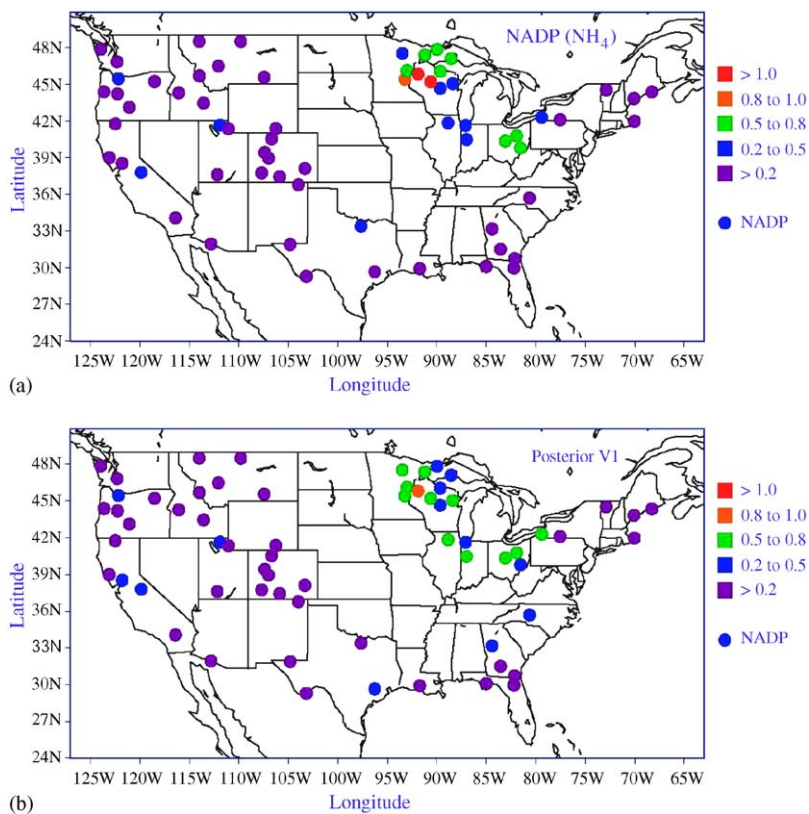
Fig. 5. (a) NADP and (b) posterior CMAQ NH_4^+ wet deposition ($kg\,ha^{-1}$) for April 2001.

model. Unlike April and May, the precipitation biases in October and November are quite homogeneous across the modeling domain, so that the posterior NH_3 emission adjustments are not being driven by local NH_3 source areas but a rather consistent underprediction of NH_4^+ over the domain.

4. Summary

For an annual 2001 CMAQ simulation, a prior estimate of NH_3 emission seasonality was estimated for the most recent USEPA NEI inventory. This prior estimate of seasonality integrated the best information that we have available from recent studies. This information included both bottom–up, process-based estimates of seasonality for chemical fertilizer and dairy cattle emissions and top–down estimates of NH_3 seasonality (Pinder et al., 2004; Goebes et al., 2003; Gilliland et al., 2003). Since these seasonal NH_3 emission estimates would be used for several studies, including several in this issue, a top–down analysis was conducted to

evaluate the prior inventory and potentially improve upon it.

To produce top–down estimates of the monthly NH_3 emissions, an inverse modeling method was used to estimate monthly variations in the NH_3 emission fields. Currently, NH_4^+ precipitation chemistry data is the best indicator to use for this application because it provides a budget for NH_x. It has been demonstrated here that NH_4^+ aerosol concentrations are not a good chemical species indicator for the inverse modeling of NH_3 emissions unless the total nitrate budget and sulfate are in good agreement, because the partitioning between NH_4^+ and NH_3 is affected. To account for precipitation prediction issues, precipitation uncertainty is accounted for in the inverse modeling calculations on a site-by-site basis; however, precipitation issues can still impact the results in other ways. For example, it was found in this study that sites with very low precipitation can have too much influence on the inverse modeling results if wet concentration values are used in the inverse calculations, as opposed to wet deposition. Thus,
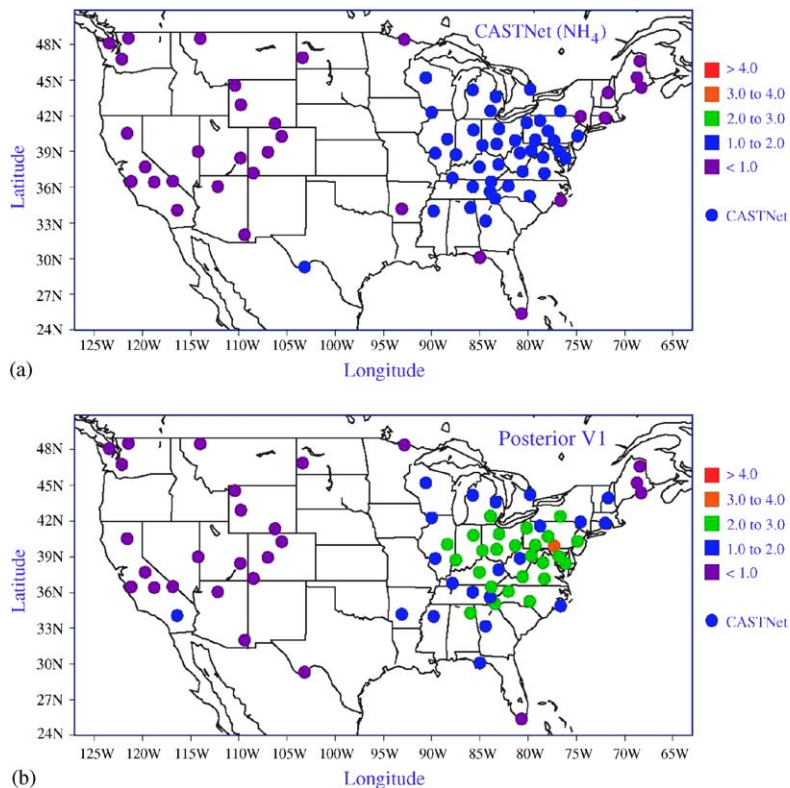
Fig. 6. (a) CASTNet and (b) posterior CMAQ NH_4^+ ($\mu g\,m^{-3}$) for April 2001.

we conclude that wet deposition was a safer indicator for this analysis.

The posterior emission estimates suggested that our prior NH_3 emission seasonality needs to be increased in the summer period and decreased in the winter. Comparisons to CASTNet NH_4^+ concentrations support the need for higher summer and lower winter NH_3 emissions than in the prior estimates. Increases were also suggested in the spring and fall periods, but they are discounted based on precipitation bias issues that were identified, cross-comparisons to CASTNet NH_4^+ concentrations, and a model sensitivity test where total nitrate over-predictions were corrected. Therefore, we conclude that our prior emission estimates for the spring and fall months should be retained, but our prior seasonal factors for NH_3 emissions should be increased during the summer period and decreased in the winter to be more similar to our previous inverse modeling results. When the bottom–up seasonal estimates for chemical fertilizer and dairy cattle emissions were integrated with the previous top–down estimates, the resulting prior emission estimated seasonality had a dampened amplitude of

the minimum and maximum NH_3 emissions as compared to Gilliland et al.'s (2003) results. This is influenced by the spring and fall peak emissions in the fertilizer application (both chemical and manure from dairy cattle) in the bottom–up inventory estimates. Limited information existed about the timing of the fertilizer application, and these results suggest that the estimated timing of the application may need to be refined in the bottom–up inventory.

With some confidence in the prior seasonal emission estimates based on Gilliland et al. (2003) and newer bottom–up inventory estimates of the seasonality of the NH_3 emissions (Pinder et al., 2004; Goebes et al., 2003), we have followed our previous inverse modeling protocol to test our prior seasonal NH_3 emissions estimates and potentially gain new insights into the seasonal NH_3 emissions. With respect for the inherent uncertainties, we have focused on qualitative results to constrain our confidence in the seasonal characterizations in the NH_3 emissions. The results demonstrate that top-down approaches can be extremely valuable as tools for evaluating, testing, and refining emission estimates. However, this study also highlights that an
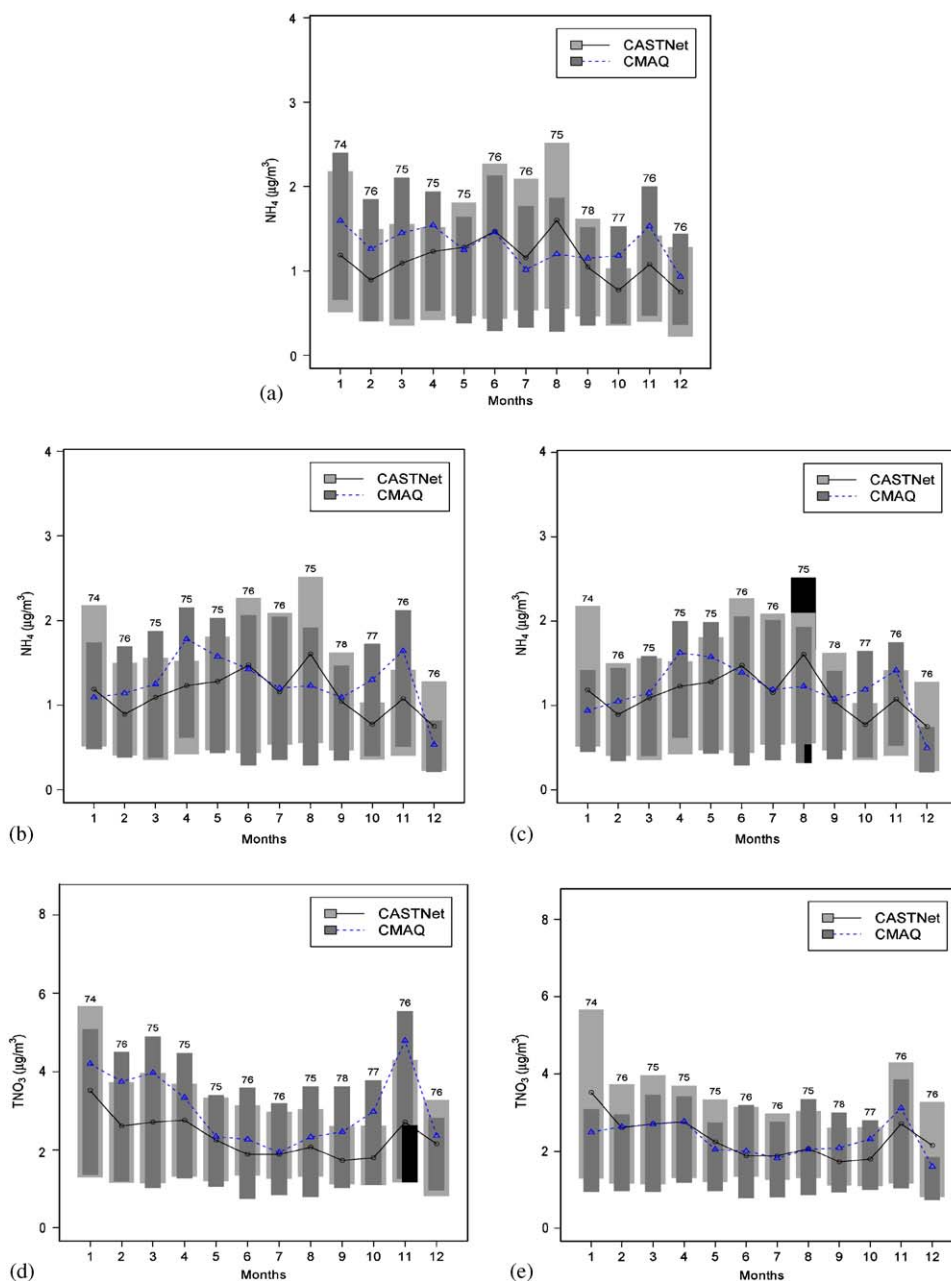
Fig. 7. Model predictions versus CASTNet ($\mu g\,m^{-3}$) for (a) prior NH_4^+ aerosols, (b) posterior NH_4^+ aerosols, and (c) posterior NH_4^+ aerosols results when the heterogeneous reaction rate for nitric acid is reduced by a factor of 10. The posterior model predictions versus CASTNet ($\mu g\,m^{-3}$) for total nitrate (TNO_3) (d) before and (e) after the decreased heterogeneous nitric acid reaction rate is also shown. The lines and boxes represent the median and 25–75% quartiles. The numbers represent the total number of sites.

independent comparison against NH_x air concentration data is needed to cross-check the results. While the results from this study build confidence in our understanding of NH_3 emission seasonality, the importance of interannual variations in the seasonality is unknown. Comparisons against our previous

1990 NH_3 emission estimates suggest that the posterior NH_3 emissions in the Eastern Unites States were very similar for the winter and summer, with substantial differences in the spring and fall. Future plans should include the continued analysis of NH_3 emissions and inverse modeling analyses for

additional years to better understand the degree of interannual differences that exist in NH_3 emission inventories. As new bottom–up, process-based NH_3 emission inventories continue to advance, inverse methods will also be used to support the new inventories as a complementary evaluation tool.

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