



Temporally resolved ammonia emission inventories: Current estimates, evaluation tools, and measurement needs

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[1] We evaluate the suitability of a three-dimensional chemical transport model (CTM) as a tool for assessing ammonia emission inventories, calculate the improvement in CTM performance owing to recent advances in temporally varying ammonia emission estimates, and identify the observational data necessary to improve future ammonia emission estimates. We evaluate two advanced approaches to estimating the temporal variation in ammonia emissions: a process-based approach and an inverse-modeled approach. These inventories are used as inputs to a three-dimensional CTM, PMCAM_x. The model predictions of aerosol NH₄⁺ concentration, NH_x (NH_x ≡ NH₃ + NH₄⁺) concentration, wet-deposited NH₄⁺ mass flux, and NH₄⁺ precipitation concentration are compared with observations. However, it should be cautioned that errors in model inputs other than the ammonia emissions may bias such comparisons. We estimate the robustness of each of these model-measurement comparisons as the ratio of the sensitivity to changes in emissions over the sensitivity to errors in the CTM inputs other than the ammonia emission inventory. We find the NH_x concentration to be the only indicator that is sufficiently robust during all time periods. Using this as an indicator, the ammonia emission inventories with diurnal and seasonal variation improve the PMCAM_x predictions in the summer and winter. In the United States, future efforts to improve the spatial and temporal accuracy of ammonia emission inventories are limited by a lack of a long-term, widespread network of highly time-resolved NH_x measurements.

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1. Introduction

[2] Recent work has demonstrated the importance of atmospheric ammonia in contributing to fine particulate matter [West *et al.*, 1999; Vayenas *et al.*, 2005] and depositing to sensitive ecosystems [Rennenberg and Gessler, 1999; Howarth *et al.*, 2002], yet ammonia emission inventories are thought to be one of the most uncertain aspects of air quality modeling [National Academy of Sciences, 2003]. Since ammonia emissions are largely from nonpoint sources such as livestock operations and fertilized fields, all of these sources cannot be directly measured over a large domain such as the United States. These sources also have large temporal variability owing to variations in climate conditions and farming practices; hence, there is uncertainty in

both the total amount of emissions and the monthly, daily, and diurnal variation. In response to this need, the most advanced seasonally varied ammonia emission inventories have employed inverse methods [Gilliland *et al.*, 2003], process-based models [Pinder *et al.*, 2004b], and hybrid approaches [Ambelas Skjøth *et al.*, 2004]. The emissions predicted by these approaches have important differences. Inverse modeling methods generate “top-down” emission estimates that provide model predictions of a related chemical species that optimally agree with observations, while process-based models generate “bottom-up” emission estimates based on the most detailed spatial and temporal information available about the emission sources and rates. There is a pressing need for computational tools that can be used to evaluate these inventories and identify key areas for improvement.

[3] One strategy for evaluating an ammonia emission inventory is to use the emissions as input to a chemical transport model (CTM) and compare the model predictions with measurable quantities, such as wet-deposited NH₄⁺ flux, aerosol NH₄⁺ concentrations, and NH_x (NH_x ≡ NH₃ + NH₄⁺) concentrations to corresponding measurements. However, chemical transport models are imperfect, and not all of the errors in the predictions should be attributed to the ammonia emission inventory. The emission inventories of other chemical species, meteorological inputs, reaction rate constants, and deposition parameters also have errors. These

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Table 1. Summary of the Ammonia Emission Inventories Evaluated in This Study

Name	Monthly Totals	Day of Week Variation	Diurnal Variation	Total Emissions, 10 ¹² g NH ₃ yr ⁻¹
Constant inventory	CMU Inventory v. 2.0 (constant)	constant	constant	3.5
Constant with diurnal variation inventory	CMU Inventory v. 2.0 (constant)	constant	livestock: process-based [Pinder et al., 2004a, 2004b] fertilizer: process-based [Pinder et al., 2004a] mobile, industrial (NEI 1999 v. 2.0)	3.5
Process-based inventory	livestock: process-based [Pinder et al., 2004a, 2004b] fertilizer [Goebes et al., 2003] mobile, industrial (NEI 1999 v. 2.0)	constant	livestock: process-based [Pinder et al., 2004a, 2004b] fertilizer: process-based [Pinder et al., 2004a] mobile, industrial (NEI 1999 v. 2.0)	3.5
Inverse-modeled inventory	inverse-modeled (Gilliland et al. [2006])	constant	livestock: process-based [Pinder et al., 2004a, 2004b] fertilizer: process-based [Pinder et al., 2004a] mobile, industrial (NEI 1999 v. 2.0)	4.0

errors cause a bias in the model predictions that can either compensate for errors in the inventory or cause a valid inventory to appear to have errors. Furthermore, the atmospheric ammonia system is complex. The concentration of aerosol ammonium, gas-phase ammonia, and wet-deposited ammonium each have different sensitivities to changes in emissions. Therefore it is critical to select model-measurement comparisons that have high sensitivity to changes in ammonia emissions and low sensitivity to other model input biases. We refer to such comparisons as “robust.”

[4] In this research, we first develop a method that can be used to evaluate the robustness of different model-measurement comparisons as tools for evaluating ammonia emission inventories. Then, we use the most robust model-measurement comparisons to evaluate the diurnal and monthly emission estimates in seasonally resolved ammonia emission inventories derived from top-down and bottom-up approaches.

2. Methods

[5] To evaluate these ammonia emission inventories, we use the chemical transport model PMCAM_x [ENVIRON International Corporation, 2005; T. M. Gaydos et al., Development and application of a three-dimensional aerosol chemical transport model (PMCAM_x+), submitted to *Atmosphere and Environment*, 2005, hereinafter referred to as Gaydos et al., submitted manuscript, 2005] (available at http://www.camx.com/files/CAMxUsersGuide_v4_20.pdf) and observations to conduct four model-measurement comparisons frequently employed in the literature: aerosol NH₄⁺ concentration, NH_x concentration, wet-deposited NH₄⁺ mass, and NH₄⁺ precipitation concentration. Available data sources that were compared with model predictions include observations from the Speciation Trends Network (STN), the National Atmospheric Deposition Program (NADP), and the Clean Air Status and Trends Network (CASTNet). These model-measurement comparisons are used to evaluate the diurnal and monthly emission estimates from four test inventories. This section describes in further detail the different ammonia emission inventories, the chemical transport model, PMCAM_x, and the observational data. In section 3 we describe the method for

calculating the robustness of each model-measurement comparison.

2.1. Ammonia Emission Inventories

[6] Ammonia emission inventories are both uncertain in the total annual emissions and the monthly, daily, and diurnal variation. As there are thousands of nonpoint ammonia emission sources, measuring the emission rates from each source is not feasible. A scarcity of detailed data often requires simplifying assumptions at different time resolutions. In this study, we use the process-based and inverse-modeled approaches to calculate explicitly the monthly total emissions. The emissions are evenly divided for each day of the month, which is a necessary assumption as there are no data available regarding day-of-week variation in farming practices. We use a diurnal profile estimated using the process-based model to apportion the emissions to each hour of the day. Our objectives are to evaluate the monthly total emission estimates and to evaluate the importance of the diurnal profile. Table 1 summarizes the four test inventories used in this study and lists the method used to estimate the emissions at each timescale (monthly, daily, and diurnal). Each inventory is described in more detail below.

2.1.1. Constant Emission Inventory

[7] The constant inventory has the same ammonia emissions in each month and no diurnal variation in emissions. The monthly total emissions are estimated using the constant emission factors from the CMU Ammonia Emission Inventory version 2.0 [Strader et al., 2003] (available at <http://www.cmu.edu/ammonia>). The emissions are divided equally for each hour of the day. The seasonally constant inventory with diurnal variation has no monthly variation and the same total emissions as in the constant inventory, but it has the diurnal profile from the process-based inventory, described below. This inventory is used to estimate the importance of the diurnal temporal profile.

2.1.2. Process-Based Emission Inventory

[8] The process-based, bottom-up inventory contains monthly varied emissions from livestock operations and chemical fertilizer application. Livestock emissions are based on the temporally resolved dairy cattle inventory by Pinder et al. [2004b]. Dairy cattle emissions are calculated

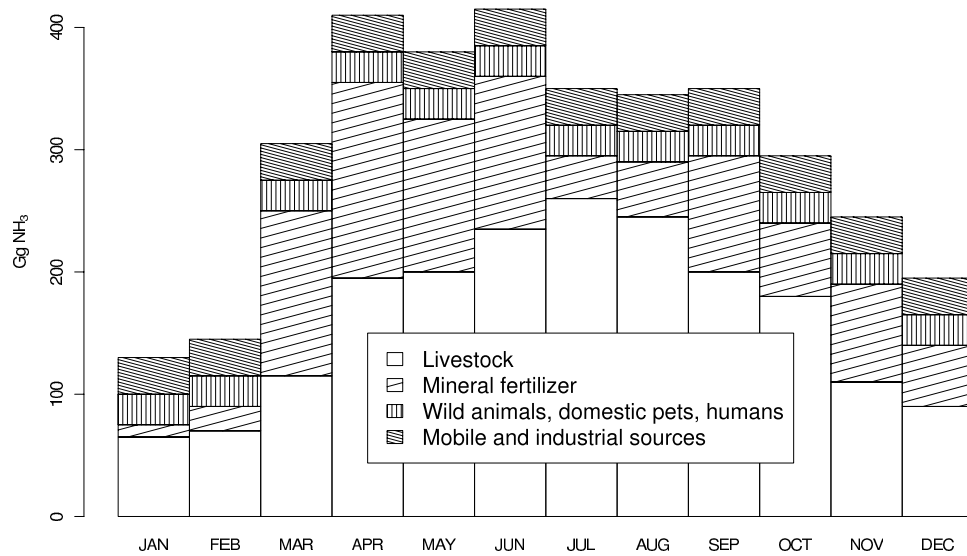


Figure 1. Monthly ammonia emissions from the process-based inventory for the continental United States.

by combining the Farm Emission Model [Pinder et al., 2004a], a mechanistic model of ammonia volatilization from a dairy farm, with a national database of farming practices and climate data. For other livestock types, a temporal profile derived using surrogate dairy farm types is applied to the annual average emission factor from the CMU Ammonia Emission Inventory. For example, the feedlot beef cattle temporal profile is derived from feedlot dairy cattle. A complete listing of the surrogate dairy types is available in Appendix A. Temporally varied chemical fertilizer emissions are from Goebes et al. [2003]. These emissions are calculated based on crop calendars and fertilizer sales data. Mobile, nonroad, and industrial stationary sources come from the U.S. EPA's National Emission Inventory (NEI) 1999 version 2.0 [U.S. Environmental Protection Agency (U.S. EPA), 2002a] (available at <http://www.epa.gov/ttl/>

<http://www.epa.gov/ttl/chieff/net/1999inventory.html>). Emissions from other sources are from the CMU Ammonia Emission Inventory with updated emission factors for domestic pets and humans [Atkins and Lee, 1993; Sutton et al., 2000]. Figure 1 is a source-resolved chart of the monthly emissions.

[9] The process-based diurnal profile is the fraction of the total emissions for that day that occurs in each hour. For livestock sources, the diurnal emissions are calculated using the Farm Emission Model executed at a 1 hour time resolution. The diurnal variation in the fertilizer is assumed to be the same as field applied manure in the Farm Emission Model. The diurnal profiles for mobile and industrial sources are from U.S. EPA's MOBILE6 and NEI 1999 database, respectively. Other sources are assumed to be diurnally constant. Figure 2 shows the source-resolved diurnal emission variation for July. This temporal profile

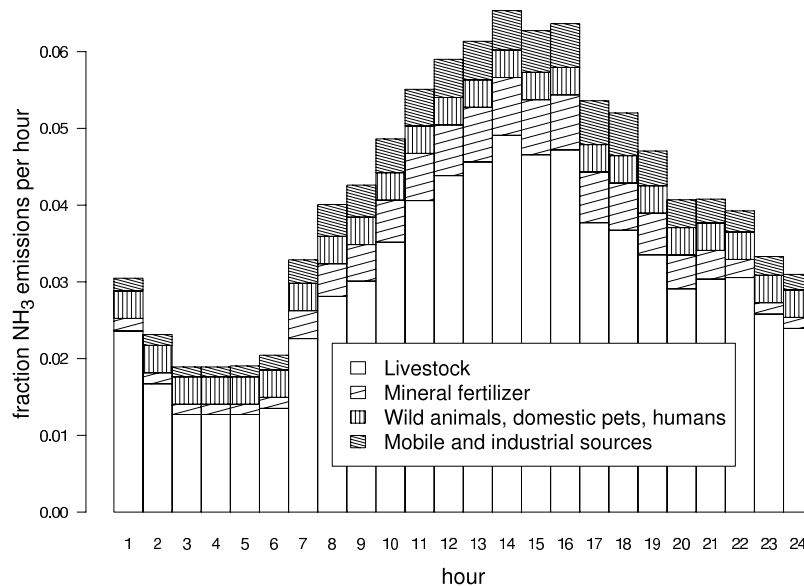


Figure 2. Source-resolved diurnal emissions profile for July 2001 derived using the process-based model.

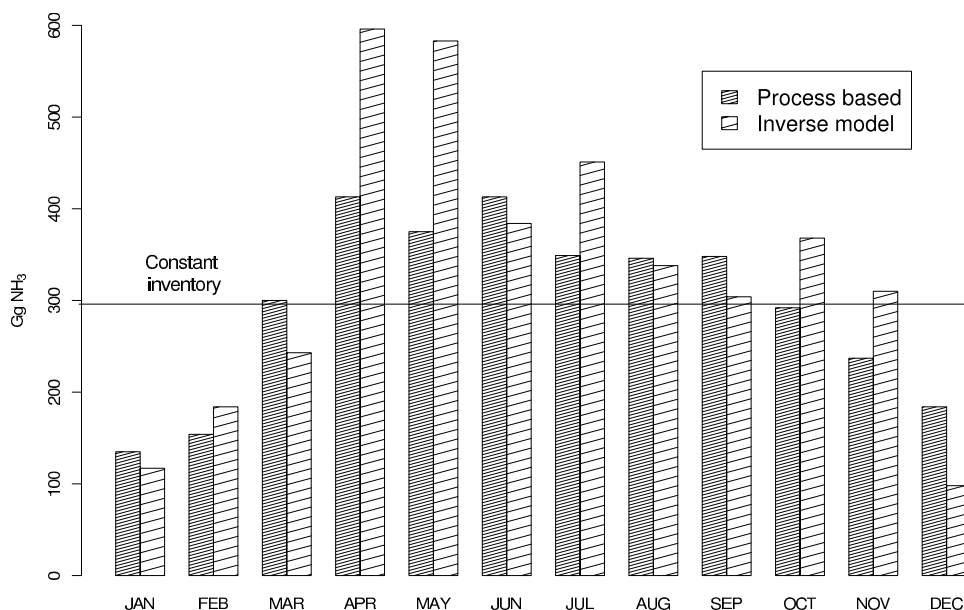


Figure 3. Comparison of the ammonia emission estimates from the process-based model [Pinder *et al.*, 2004a, 2004b] and the inverse model estimates from Gilliland *et al.* [2006]. The solid bar denotes the emissions from the “constant inventory,” which is derived from the emission factors in the CMU Ammonia Emission Inventory [Strader *et al.*, 2003] without temporal variation. The seasonally resolved inventories predict large decreases in the winter and increases in the other periods relative to the constant inventory.

and similarly derived profiles for other months are applied to the constant inventory with diurnal variation, the process-based inventory, and the inverse-modeled inventory.

2.1.3. Inverse-Modeled Inventory

[10] The monthly emission estimates for the inverse-modeled inventory are calculated using wet deposition inverse-modeled estimates by Gilliland *et al.* [2006]. The prior estimate for ammonia emissions in the inverse modeling uses an inventory based on NEI 2001. The seasonal profile from Pinder *et al.* [2004b] is applied to dairy cattle sources; the seasonal profile from Goebes *et al.* [2003] is applied to the chemical fertilizer sources. All other source categories use the seasonal profile derived using an inverse modeling study for 1990 [Gilliland *et al.*, 2003]. Then the chemical transport model CMAQ was used to calculate the change in emissions necessary to minimize the difference between model predictions and measured NH_4^+ wet concentration at NADP monitoring locations. Model prediction uncertainties were accounted for in these inverse modeling estimates based on daily observed precipitation at the NADP monitors. These monthly estimates were applied to all emission sectors. The inverse model posterior monthly totals are then scaled to match the modeling domain used in this study. We then apply the same diurnal temporal profile used in the process-based inventory described above.

2.1.4. Comparison of Ammonia Emission Inventories

[11] A comparison of the monthly ammonia emissions from the constant, process-based, and inverse-modeled inventories is displayed in Figure 3. Compared to the constant inventory, both the process-based and inverse-modeled inventories show lower emissions in the winter and higher emissions in the summer. However, there are larger differences between the inventories in the spring and

fall, which are also the months where the two approaches have the greatest uncertainty. Uncertainties in the process-based emission inventory are largely from uncertainty in the national distribution of farming practices, especially the monthly calendar of manure application at livestock operations. These uncertainties are largest in the spring and fall and are estimated as $\pm 40\%$ [Pinder *et al.*, 2004b]. Uncertainty in the inverse modeling approach is due to sparser measurement data sets during spring months and possible compensating errors from precipitation biases in the fall months.

2.1.5. Emissions for Species Other Than Ammonia

[12] For species other than ammonia, we use the LADCO BaseE inventory, generated using EMS-2003 [LADCO, 2003] (available at <http://www.ladco.org/tech/emis/>). Emissions are derived primarily from the U.S. EPA's NEI 1999 version 2.0 [U.S. EPA, 2002a]. On-road transportation sources are from U.S. EPA's MOBILE6 [U.S. EPA, 2002b] (available at <http://www.epa.gov/otaq/m6.htm>), non-road sources are from U.S. EPA's NONROAD [U.S. EPA, 2002c] (available at <http://www.epa.gov/oms/nonrmdl.htm>). The temporal profiles for electric power utility point sources are from an analysis of Continuous Emission Monitors [Janssen, 2003]. Biogenic emissions are from BIOME3 [Wilkinson and Janssen, 2001].

2.2. PMCAM_x

[13] PMCAM_x is an Eulerian ozone and aerosol chemical transport model of regional air quality. PMCAM_x models the change in species concentration due to emission, advection, dispersion, gas-phase chemistry, aerosol processes (coagulation, condensation, and nucleation), aqueous chemistry, and wet and dry deposition. For gas-phase chemistry,

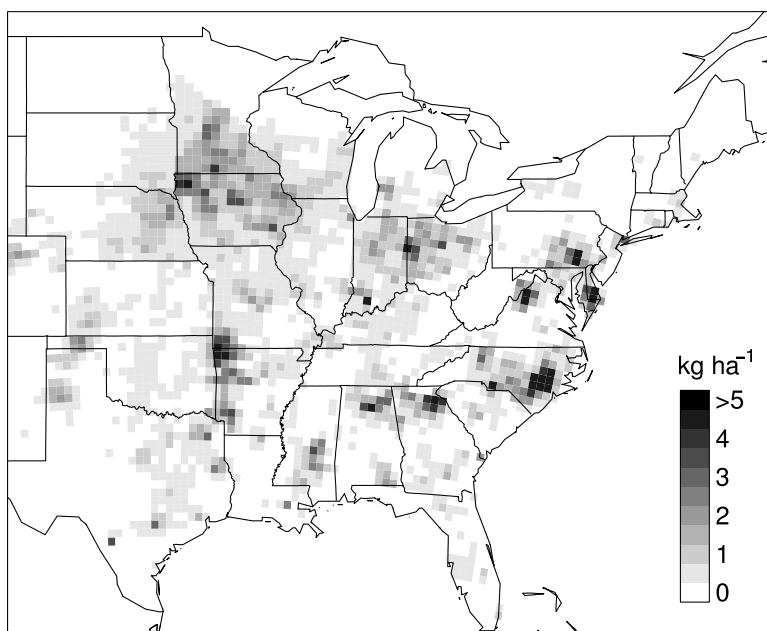


Figure 4. NH_3 emission fluxes estimated by the process-based inventory for the eastern and Midwestern United States in kg ha^{-1} for the month of July 2001. The spatial variation is identical for all test inventories, but the monthly emissions are different as in Figure 3.

we use the Carbon Bond IV chemical mechanism [Gery *et al.*, 1989]. The inorganic aerosol evaporation/condensation equations employ a bulk equilibrium approach [Capaldo *et al.*, 2000; Gaydos *et al.*, 2003], and the aerosol thermodynamics model ISORROPIA [Nenes *et al.*, 1998] is used to predict the gas-aerosol partitioning. Temperature, wind fields, rainfall and other meteorological inputs are from the MM5 meteorological model [Grell *et al.*, 1995] (available at <http://www.mmm.ucar.edu/mm5/documents/>). The model domain is discretized into a 36 km^2 horizontal grid with 16 vertical layers between the surface and 14 km. The lowest model layer is slightly less than 30 m thick vertically. A more detailed description of the model and its evaluation can be found in Gaydos *et al.* (submitted manuscript, 2005) and the CAM_x User's Guide [ENVIRON International Corporation, 2005].

[14] The removal of gases and aerosols by precipitation is modeled as both in-cloud and below-cloud processes. All in-cloud aerosols are contained in cloud droplets and interstitial gases are in equilibrium with the cloud droplet water according to their Henry's law constant. Species dissolved in cloud droplets are scavenged as precipitation is formed. The removal of below-cloud pollutants is calculated using an explicit scavenging rate, which is a function of the size distribution for aerosols and a function of the mass transfer rate for gases. The details of these calculations are described by Seinfeld and Pandis [1998] and ENVIRON International Corporation [2005].

2.3. Description of Inorganic Aerosol in the Model Domain

[15] For this study, we have chosen a model domain consisting of the eastern and Midwestern United States, shown in Figure 4. This domain includes the large ammonia

source regions of the agricultural Midwest and Southeast, as well as the large combustion sources of SO_2 and NO_x present in the industrial Midwest and Northeast. In the summer, the inorganic aerosol is dominated by sulfate; in the winter, sulfate and nitrate can be found in approximately equal proportions [U.S. EPA, 1996]. Since the aerosol lifetimes are on the order of 7–10 days [Seinfeld and Pandis, 1998], the inorganic aerosol concentration has little variability on a regional (100 km) scale [Rao *et al.*, 2002; Tang *et al.*, 2004]. In many locations and seasons, the NH_x concentrations exceed what is necessary for neutralizing the anions. Under these conditions, the aerosol ammonium concentration is more sensitive to the sulfate and nitrate concentrations than the ammonia emissions.

2.4. Observational Data

[16] Model predictions are compared to observations from measurement networks to form four model-measurement comparisons: aerosol ammonium concentration, NH_x concentration, wet-deposited ammonium mass flux, and ammonium precipitation concentration. The locations of the monitoring sites are shown in Figure 5. Monitoring stations are sited away from local plumes in order to best estimate the regional average.

[17] The aerosol ammonium observations are from STN monitoring stations that record 24 hour, filter-based measurements taken at 3 day and 6 day intervals [U.S. EPA, 2001]. While other monitoring networks also measure NH_4^+ , the 24 hour duration of the STN measurements decreases opportunities for measurement bias. Most monitors are located in or around urban centers, and there are 44 monitoring locations in the domain. Note that, while STN sites measure NH_4^+ , they do not provide simultaneous

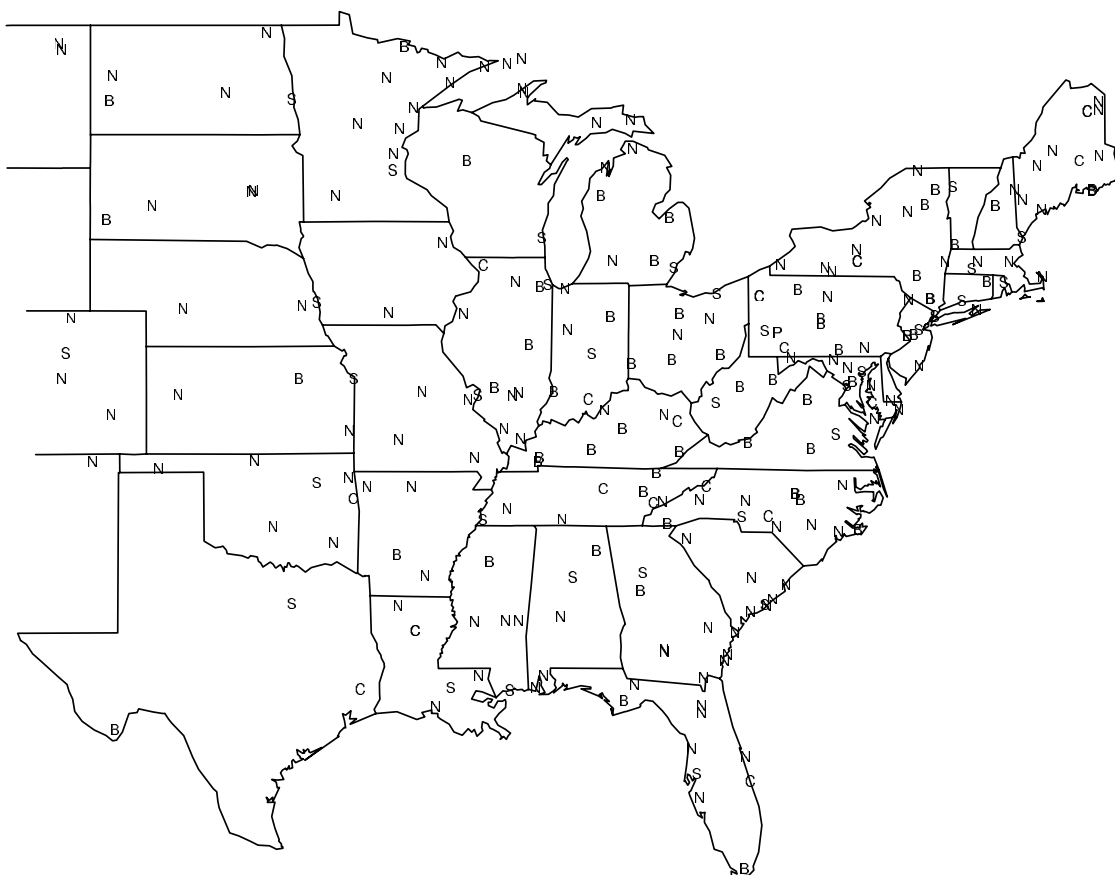


Figure 5. Monitoring sites in the model domain: S denotes STN sites, N denotes NADP sites, C denotes CASTNET, B denotes collocated CASTNET and NADP sites, and P denotes the location of the Pittsburgh Air Quality Study.

measurement of NH_3 or NH_x , a limitation we will discuss further below.

[18] Observations of NH_x are from the Pittsburgh Air Quality Study (PAQS) [Wittig *et al.*, 2004]. The PAQS site is located approximately 6 km east of downtown Pittsburgh and data were collected from July 2001 to July 2002.

[19] NH_x is measured using the steam sampler of Khlystov *et al.* [1995] and reported as 1 hour or 2 hour averages. Precipitation chemistry measurements are from NADP [National Atmospheric Deposition Program, 2005]. The precipitation concentration measurements are reported at weekly intervals at 96 sites in the modeling domain. Wet deposition values are then calculated by multiplying the precipitation concentration values in mg L^{-1} by the weekly precipitation at that site and applying conversions to achieve the appropriate units kg ha^{-1} . Locations are excluded from the analysis if 25% or more of the weeks are missing, flagged as compromised, or where the precipitation was snow rather than rain.

[20] Additionally, observations of aerosol sulfate from STN, filter-based total nitrate measurements (sum of gas-phase nitric acid and aerosol nitrate) from CASTNet [Clarke *et al.*, 1997; MACTEC, Inc., 2004], and precipitation volume from NADP are compared with model predictions to characterize biases in other modeled quantities that affect our ammonia model-measurement comparisons (see

section 3.1 below). The CASTNet observations are weekly average samples from rural locations; there are 55 monitoring stations in the modeling domain. The STN network is selected for estimating the bias in sulfate since the STN network is also used for the NH_4^+ measurements, such that the sulfate bias is calculated at the same locations as the ammonia model-measurement comparisons. Observations from CASTNet are used to calculate the total nitrate bias since total nitrate is not measured by any other regional network. The aerosol nitrate can be biased by the sulfate and ammonia; therefore the total nitrate is necessary to determine associated model input biases. While some spatial discrepancies in the bias may result from using two different networks, we expect these discrepancies to be small since both networks have a large number of locations and the aerosol tends to be regionally distributed.

2.5. Evaluating the Ammonia Emission Inventory Using PMCAM_x

[21] Each of the four ammonia emission inventories described in section 2.1 is used as input to PMCAM_x and is tested for four 1 month periods: July 2001, October 2001, January 2002, and April 2002. These time periods represent each of the seasons and are selected to overlap with the Pittsburgh Air Quality Study. The PMCAM_x predictions are compared with wet deposition measurements from NADP,

speciated aerosol measurements from STN, and NH_x measured during PAQS.

3. Estimating the Robustness of Each Model-Measurement Comparison

[22] The chemical transport model can be used as a tool to evaluate the ammonia emission inventories; however, it is first necessary to characterize the robustness of the various metrics that can be used for the evaluation. In principle, one can evaluate an ammonia emission inventory simply by comparing model predictions to measurements. However, the atmospheric ammonia system is complex. The CTM is an imperfect representation, and there are errors in the meteorological inputs and the emissions of other species. An ammonia emission inventory that has large errors may have good model-measurement agreement, if errors in ammonia emissions are mitigated by compensating errors in the other CTM inputs or processes. Before using the CTM as a tool for ammonia emission inventory evaluation, it is necessary to characterize the magnitude of the bias. We use the bias as a statistical metric, rather than the root mean squared error, because it provides a measure of the direction of the error (over or under prediction). This is essential to differentiate errors in the ammonia emission inventory from errors in other model inputs.

[23] Here it is necessary to introduce three metrics which are useful for evaluating the CTM predictions: the model input bias sensitivity, the monthly emission sensitivity, and the robustness. These metrics are discussed in the following sections.

3.1. Model Input Bias Sensitivity

[24] The model input bias refers to all biases in the model inputs and parameterizations other than the ammonia emissions. Qualitatively, we define the model input bias sensitivity (MIBS) as the change in the CTM predictions that results from the model input bias. The MIBS is used to differentiate between the change in model performance owing to the ammonia emissions and the change in the model performance owing to bias in the other CTM inputs and parameterizations. Formally, the model input bias sensitivity is calculated as

$$\text{MIBS}_i = \frac{1}{N} \sum_{j=1}^N \frac{P_{ij} - P_{ij}^{\text{MIB}}}{P_{ij}}, \quad (1)$$

where P_{ij} is the model prediction for parameter i with the contributing bias, P_{ij}^{MIB} is the model prediction for parameter i without the model input bias, and the subscript i refers to either the aerosol NH_4^+ , NH_x , wet-deposited NH_4^+ mass, or NH_4^+ precipitation concentration, and N is the number comparisons. This section describes our methodology for determining P_{ij}^{MIB} and therefore the model input bias sensitivity.

[25] The MIBS can arise from several sources; Figure 6 illustrates the processes that regulate the atmospheric ammonia system and are relevant to the model-measurement comparisons of interest in this study. Sources of ammonia include transport into the model domain and emissions. The total reduced-form nitrogen (NH_x) is partitioned between

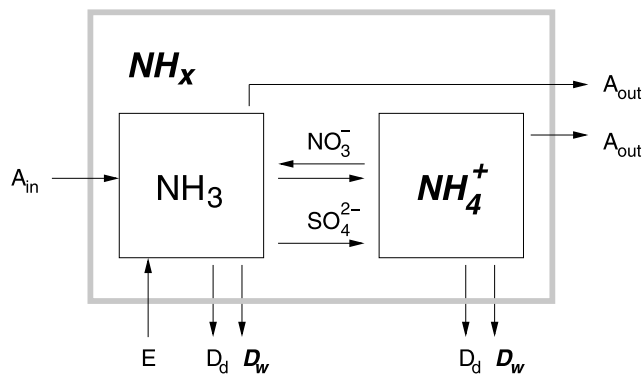


Figure 6. Atmospheric ammonia system including the gas-aerosol phase partitioning, which depends on the concentrations of nitrate and sulfate. Inputs include emissions (E) and mass advected into the domain (A_{in}). Removal processes are dry deposition (D_d), wet deposition (D_w), and mass advected out of the domain (A_{out}). The gray box indicates the total reduced-form nitrogen (NH_x), which is less sensitive than aerosol ammonium to changes in the nitrate and sulfate concentrations. Bold italic terms are measured quantities.

gas-phase ammonia and aerosol ammonium, depending on the temperature, relative humidity, and the concentrations of total nitrate and sulfate. Ammonia and ammonium are subject to removal by dry deposition, wet deposition, and transport out of the model domain. Quantities measured by atmospheric monitors are shown in bold italics and include the wet-deposited NH_4^+ mass, precipitation NH_4^+ concentration, aerosol NH_4^+ concentration, and NH_x concentration.

[26] Within this system, there are many opportunities for model input bias. The prediction of aerosol ammonium is sensitive to the concentration of total nitrate, sulfate, rate of deposition, temperature, and relative humidity. *Yu et al.* [2005] found that a large fraction of the error in CTM aerosol nitrate predictions can be attributed to errors in the sulfate and NH_x concentrations. Similarly, where NH_x concentrations are sufficient to neutralize aerosol anions as is common in the eastern United States, errors in the sulfate and total nitrate concentration bias the aerosol ammonium predictions. The wet-deposited NH_4^+ is sensitive to errors in the precipitation amount and the scavenging parameterization. *Metcalfe et al.* [2005] have noted difficulties in evaluating deposition models due to variability in precipitation rates. The potential for model input bias is less for NH_x , but it is still sensitive as its atmospheric lifetime and the deposition rate are dependent on gas-aerosol partitioning and the rate of wet deposition.

[27] The inputs and model-predicted values that control the processes in Figure 6 are the sulfate concentration, total nitrate concentration, temperature, relative humidity, precipitation volume, the wet deposition scavenging rate, and the ammonia dry deposition rate. We refer to the bias in these predicted values as the contributing biases.

[28] A conventional method for calculating the contributing biases would be to calculate the error in the model inputs, alter the model inputs by that amount, reexecute the CTM, and calculate the change in model predictions. However, these processes are controlled by thousands of

Table 2. Normalized Bias (NB) Calculated From the Comparisons of PMCAM_x and MM5 Results and Observations From Monitoring Networks^a

Month	STN PM _{2.5} SO ₄ ²⁻ , %	CASTNET Total Nitrate, %	NADP Precipitation Volume, %
Jan 2002	-19 (338)	37 (232)	32 (201)
Apr 2002	-29 (282)	10 (240)	13 (284)
Jul 2001	-30 (297)	-21 (220)	-43 (384)
Oct 2001	38 (258)	10 (220)	30 (244)

^aThe size of the comparison data set is shown in parentheses. Positive values denote model overprediction.

nonlinearly related model inputs and parameters. Systematically estimating the error in all of these values is not possible. Instead, we employ a more direct approach, where we calculate the normalized bias (NB) in the model predictions of each contributing bias by comparing them to observed values:

$$\text{NB} = \frac{1}{N} \sum_{i=1}^N \frac{C_i - O_i}{O_i}, \quad (2)$$

where C is the model prediction of either the PM_{2.5} sulfate concentration, total nitrate concentration, or precipitation volume, O is the corresponding observed value, and N is the number of model-measurement pairs. Table 2 shows the normalized biases when the PMCAM_x predicted PM_{2.5} sulfate, total nitrate, and precipitation volume are compared with STN sulfate concentrations, CASTNet total nitrate concentration, and NADP precipitation amount. Not shown in Table 2 are the biases in temperature and relative humidity, which are less than 0.5°C and less than 2%, respectively, for all months when compared with meteorology measurements from the CASTNet monitoring locations. These biases are sufficiently small that they are not included in the calculation of the MIBS.

[29] However, the scavenging rate and the dry deposition flux are not measured by monitoring networks. To estimate the bias in the scavenging rate, we examine the PAQS data and the literature. We observed that during precipitation events in Pittsburgh, when the model precipitation is approximately equal to the measured precipitation, the rate of decrease in the ambient NH_x concentration as predicted by PMCAM_x is less than the rate of decline in the hourly PAQS observations. This suggests that the PMCAM_x scavenging rate is biased low, but a more exact calculation is precluded by a lack of data. Previous studies have found a large uncertainty in the magnitude of the scavenging rate. *Scott and Luecken* [1992] estimated the uncertainty in wet deposition to range from 30 to 60% owing to conservative assumptions about variation of cloud properties and precipitation characteristics across a modeled grid cell. A literature survey by *Kasper-Giebl et al.* [1999] of NH_x scavenging ratios calculated over 3 month periods found that these values differed by 55% at different locations. Given these uncertainties, we use a conservative estimate of a -10% bias in the scavenging rate. While a larger scavenging rate bias may be justified by the literature, we find that even with a small scavenging rate bias, the wet deposition mass flux and wet deposition concentration model-measurement concentrations are not sufficiently robust for all time periods. A larger scavenging rate bias would strengthen this result, as discussed later in section 4.1.

[30] The ammonia dry deposition rate is not routinely measured, and therefore it is not possible to differentiate between an increase in dry deposition and a decrease in emissions. Since they cannot be separated, the results of the present work are not strictly for the ammonia emission inventory, but more precisely for the net flux of emissions minus dry deposition.

[31] We calculate the model prediction without the contributing bias (P_i^{MIB}) by iteratively perturbing selected model parameters until the model predicted sulfate, total nitrate, and precipitation has approximately zero bias in their respective values. For the sulfate concentration, total nitrate concentration, and precipitation amount contributing biases, the parameters in PMCAM_x are adjusted to remove the biases in Table 2. The adjusted parameters include the reaction rate constants for the gas-phase and aqueous-phase sulfate production reactions, the reaction rate constants for nitric acid production for the day and night reactions, and the precipitation rate. We perturb the reaction rate constants rather than the emissions or other parameters because the reaction rate constants introduce the model perturbation with the least impact on the other model processes.

[32] To remove the model input bias, these parameters are scaled by a single factor which is constant across the domain and for the entire model time period. These factors are iteratively adjusted until the absolute value of normalized bias is less than 0.5%. The scavenging rate is increased by 10%. PMCAM_x is then reexecuted with these altered parameters, and the resulting predictions (P_i^{MIB}) are without the contributing bias. The model in this perturbed state is only used for calculating the MIBS; it is not used for the ammonia model-measurement comparisons themselves, which are based on PMCAM_x in its default biased state.

[33] As an example of this process, consider July, for which according to Table 2, the sulfate, total nitrate, and precipitation amount are underpredicted. To calculate P_i^{MIB} , the production rates for sulfate and nitrate and the precipitation rate are first increased to match the observations with a minimized normalized bias, and the scavenging rate is increased by 10%. The MIBS (equation (1)) for aerosol NH₄⁺, NH_x, wet-deposited NH₄⁺ mass, or NH₄⁺ precipitation concentration is then calculated as the average percent change in the model predictions after these influencing factors have been optimally adjusted (Table 3). Since the sulfate and nitrate are underpredicted in July, the MIBS_{NH4+} is negative. In other words, the underprediction in sulfate and total nitrate leads to an underprediction in aerosol ammonium. The underpredicted precipitation causes the MIBS for the wet deposition metrics to be negative also.

[34] After repeating this process for each season and candidate model-measurement comparison, the values of

Table 3. Model Input Bias Sensitivity (MIBS)^a

Month	Aerosol NH ₄ ⁺ , %	Total Ammonia (NH _x), %	Wet Deposition Mass Flux, %	Wet Deposition Concentration, %
Jan 2002	46 (338)	13 (298)	15 (201)	39 (201)
Apr 2002	-38 (282)	-6.8 (195)	17 (284)	21 (284)
Jul 2001	-36 (297)	-4.2 (348)	-21 (384)	-39 (384)
Oct 2001	3.9 (258)	3.5 (219)	13 (244)	40 (244)

^aThe size of the comparison data set is shown in parentheses. Positive values denote overprediction.

MIBS that result from equation (1) are shown in Table 3. For all of the months, we find that the NH_x concentration is the least susceptible to model input bias, followed by the wet deposition mass flux. This is not surprising since the NH_x captures the total budget of NH₃ and NH₄⁺, so that partitioning errors are not as relevant for that metric. Mass deposition and precipitation concentrations of NH₄⁺ also account for NH_x, since both NH₃ and NH₄⁺ are simultaneously scavenged by precipitation. Therefore these results suggest that model wet deposition calculations are either sensitive to gas-phase/aerosol partitioning of NH₃ or the precipitation biases have a substantial effect on the model predicted mass deposition and an even larger effect on precipitation concentration budget of NH_x.

3.2. Monthly Emission Sensitivity

[35] The monthly emission sensitivity (MES) is the normalized change in the model prediction due to a change in emissions relative to the constant inventory for a specific month:

$$\text{MES}_i = \frac{1}{N} \sum_{j=1}^N \frac{P_{ij} - P_{ij}^E}{P_{ij}}, \quad (3)$$

where i is either the aerosol NH₄⁺, NH_x, wet-deposited NH₄⁺ flux, or NH₄⁺ precipitation concentration, P is the model prediction using the constant inventory, P^E is the model prediction using a test inventory, N is the number of comparisons. The monthly emission sensitivity is small if the predicted value is not sensitive to changes in ammonia emissions or if the magnitude of the emission change is not small.

[36] Table 4 lists the calculated MES where P^E are the predictions when using the process-based emission inventory. The magnitude of the emission change is different for each month (see Figure 3) and should not be compared across months; for example, the MES is low in October for all metrics, because the difference in emissions between the process-based and seasonally constant inventories in October is small. For all four simulated time periods, the NH_x is more sensitive to emission changes than NH₄⁺. This result is reasonable given that the temperature, relative humidity, or

sulfate and nitrate concentrations may not always be favorable for ammonium formation. However, these differences are small compared to the differences in the model input bias. The MES for the wet deposition mass flux and concentration vary each month such that neither of the precipitation metrics have greater sensitivity for all time periods. This variability can be attributed to different precipitation characteristics in each season and the importance of when and where the precipitation occurs.

3.3. Robustness

[37] The robustness (R) of each model-measurement comparison is defined as the absolute value of the ratio of the monthly emission sensitivity to the model input bias sensitivity:

$$R = \left| \frac{\text{MES}}{\text{MIBS}} \right|. \quad (4)$$

This ratio is large for model-measurement comparisons that are not susceptible to model input bias and have high sensitivity to emission changes. At a minimum, this ratio must exceed one for a valid comparison. If the MIBS exceeds the MES, then for the emission change in that month, it is not possible to differentiate the change in model performance owing to the ammonia emissions from the bias in the other CTM inputs and parameterizations. We repeat the robustness calculation for each model-measurement comparison, and retain those model-measurement comparisons that are greater than one for all time periods.

3.4. Model-Measurement Comparison

[38] The MIBS is used to determine if the differences in the model predictions and the observations can be explained by other model errors or should be attributed to inaccurate ammonia emissions. Only when discrepancies between CTM predictions using a given inventory and measurements exceed a carefully characterized MIBS can one conclude that the inventory is not consistent with the observations. The range from the CTM prediction (P) to the prediction without contributing bias (P^B) specifies the range of model predictions that can be attributed to model input errors. If this range overlaps the uncertainty range of the observa-

Table 4. Monthly Emission Sensitivity Calculated as the Percent Difference in Each Model-Measurement Comparison Due to Changes in Emissions From the Seasonally Constant Ammonia Emission Inventory to the Process-Based Ammonia Emission Inventory^a

Month	Aerosol NH ₄ ⁺ , %	Total Ammonia (NH _x), %	Wet Deposition Mass Flux, %	Wet Deposition Concentration, %
Jan 2002	-38 (338)	-52 (298)	-60 (201)	-69 (201)
Apr 2002	8.6 (282)	34 (195)	29 (284)	28 (284)
Jul 2001	9.7 (297)	21 (348)	19 (384)	12 (384)
Oct 2001	-4.1 (258)	-4.4 (219)	-4.8 (244)	-4.0 (244)

^aSee Figure 3 for emission differences. The size of the comparison data set is shown in parentheses.

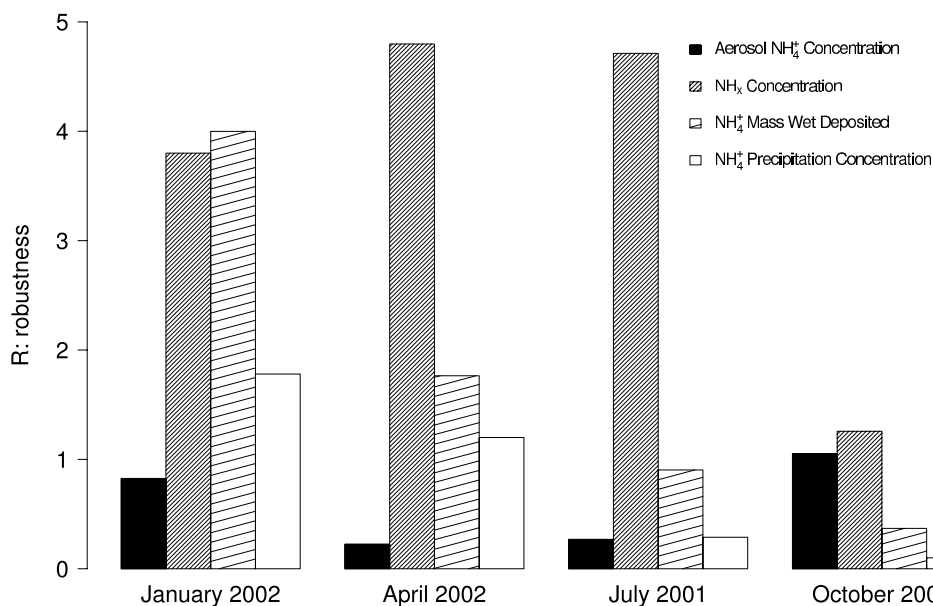


Figure 7. Robustness ratio for each model-measurement comparison for each month. A value greater than 1 denotes that the model prediction of that quantity is a robust indicator and should be used to evaluate the ammonia emission inventory. The NH₄⁺ mass wet deposited is a robust indicator for some months, but total ammonia (NH_x) is robust for all months.

tions, then the given inventory is accepted. If this range does not overlap, then even accounting for the model input bias, the model predictions using a given inventory do not fall within the range of the observations, and the inventory should be rejected.

4. Results

4.1. NH_x as a Robust Indicator of Ammonia Emissions

[39] A robust model-measurement comparison has high sensitivity to the MES and low sensitivity to the MIBS. In Figure 7, the chart shows the robustness ratio for each time period and model-measurement comparison. The MIBS is listed in Table 3; the MES is calculated in Table 4.

[40] NH_x concentrations are the most robust indicator and should be used for evaluating the inventory. Owing to errors in the modeled sulfate or nitrate concentrations, aerosol ammonium is a poor indicator for the performance of the ammonia emission inventory for all time periods. The mass deposition and precipitation concentration are robust model-measurement comparisons for some months but not for others. We selected a conservative scavenging rate bias; the mass deposition and precipitation concentration indicators would have an even lower robustness had we accounted for the larger scavenging rate bias. Since NH_x is the only model-measurement comparison that is robust during all time periods, we restrict the remainder of our analysis to NH_x model-measurement comparisons.

4.2. Importance of Diurnal Variation in Ammonia Emissions

[41] The diurnal pattern of the emissions is as important as the total emissions. During the night, vertical mixing is weak, and emitted pollutants remain closer to the surface; during the day, the mixing height is often much higher. As a

result, the surface-level concentration at night is more sensitive to the emissions than the daytime concentration. Figure 8 compares the model predicted NH_x concentration for the ammonia emissions without diurnal variation and ammonia emissions with diurnal variation derived from the process-based model. Both models have the same total daily emissions, but since the constant inventory has greater emissions at night, more ammonia accumulates near the surface. During the day, the difference between the two inventories is smaller, as the increased vertical mixing decreases the sensitivity to the emission differences. Since excluding the diurnal profile can significantly change the daily average concentration, the remaining comparisons use the seasonally constant inventory with the diurnal profile to isolate the effect of seasonal emissions variability.

4.3. Seasonally Varied Ammonia Emissions Significantly Improve Model Performance in Winter and Summer

[42] Figure 9 shows selected time series plots of NH_x for each season. The seasonally varied ammonia emission inventories significantly improve model performance in the winter and summer, although they do not improve the model performance in spring and fall. The annually constant and seasonally varying process-based NH₃ emission inventories are very similar in July and August, so very little difference is anticipated in these cases. To determine if these differences are significant relative to the MIBS, Figure 10 compares the monthly mean NH_x and model input bias sensitivity listed in Table 3 for each month with PAQS observations. The arrows for the observational data denote $\pm 15\%$ measurement errors [Takahama *et al.*, 2004]. The arrows for the model predictions are the estimated MIBS. If the arrows from

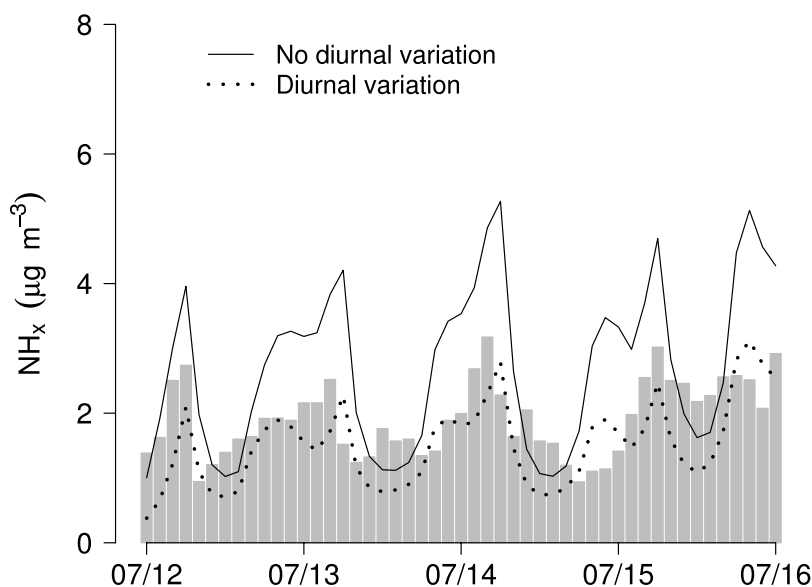


Figure 8. Comparison of PMCAM_x predicted NH_x for the constant ammonia emission inventory with and without diurnal variation for July 2001. The solid line denotes the constant ammonia emission inventory; the dotted line has the same total emissions but uses the diurnal profile derived using the process-based model [Pinder *et al.*, 2004a, 2004b]. Vertical bars denote 2 hour averaged observations from PAQS. The vertical bars immediately above the date labels correspond to the midnight and 0200 LT time period.

the observations and predictions overlap, the emission inventory is consistent with observations.

[43] The magnitude of the MIBS for NH_x is a lower bound. As described in section 3.1, these calculations do not include error in the NH₃ dry deposition, and the estimate of the error in the scavenging rate is conservative. If a more realistic estimate of these two errors were included, we would expect the MIBS to be larger. Unfortunately, this estimate is not possible without measurements of NH₃ dry deposition and more highly time-resolved measurements of NH_x wet deposition.

[44] In January, the constant inventory overestimates the total emissions. The reductions estimated by the process-based model improve the performance, and the further reductions in the inverse-modeled inventory move the predictions closer to the observations. While none of the inventories strictly overlap with the error range of the measurements, the model predictions are substantially closer to observations using the seasonally resolved inventory. In July, the seasonally varied inventories are more consistent with the observations, and the further emission increases in the inverse-modeled estimates cause the model predictions to overlap with the range of the observations.

[45] For April and October, the measured NH_x is lower than the other seasons, while the seasonally resolved emissions are higher. This causes a decrease in the model performance for these months. To explain this difference, it is important to examine the details of the process-based and inverse-modeled approaches. Inaccuracies in the seasonally varied inventories can be explained by a scarcity of temporal data in the case of the process-based model, and compensating errors in the inverse-modeled inventory. Owing to a scarcity of data, the process-based approach makes

assumptions regarding the seasonal calendar of manure application. These assumptions have been found to be one of the most significant drivers of the uncertainty in the emissions estimates, especially in the spring and fall [Pinder *et al.*, 2004b]. The results of this study further emphasize the importance of better data regarding temporal variation in manure management practices. The inverse-modeled approach is susceptible to model input bias, and adjusts the emission inventory to compensate for those biases or for the specific conditions of the modeled time period. Gilliland *et al.* [2006] have shown that large amounts of missing data and compensating errors in the precipitation predictions are influencing the inverse-modeled results during the spring and fall, respectively.

5. Discussion and Conclusions

[46] In this study, we began by assessing systematically the robustness of four quantities as possible indicators of ammonia emission inventory performance: aerosol NH₄⁺ concentration, NH_x concentration, wet-deposited NH₄⁺ mass flux, and precipitation NH₄⁺ concentration. We first calculate the model input bias sensitivity as the change in model prediction due to the bias in the input values other than the ammonia emission inventory. We also calculate the monthly emission sensitivity, as the change in model predictions for a given change in emissions relative to the constant ammonia emission inventory for that month. A robust indicator has monthly emission sensitivity which exceeds the model input bias sensitivity. We find the NH_x concentration to be the only robust indicator for all simulated time periods throughout the year. As an indicator of NH₃ emissions, The NH₄⁺ concentrations are sensitive to errors in the

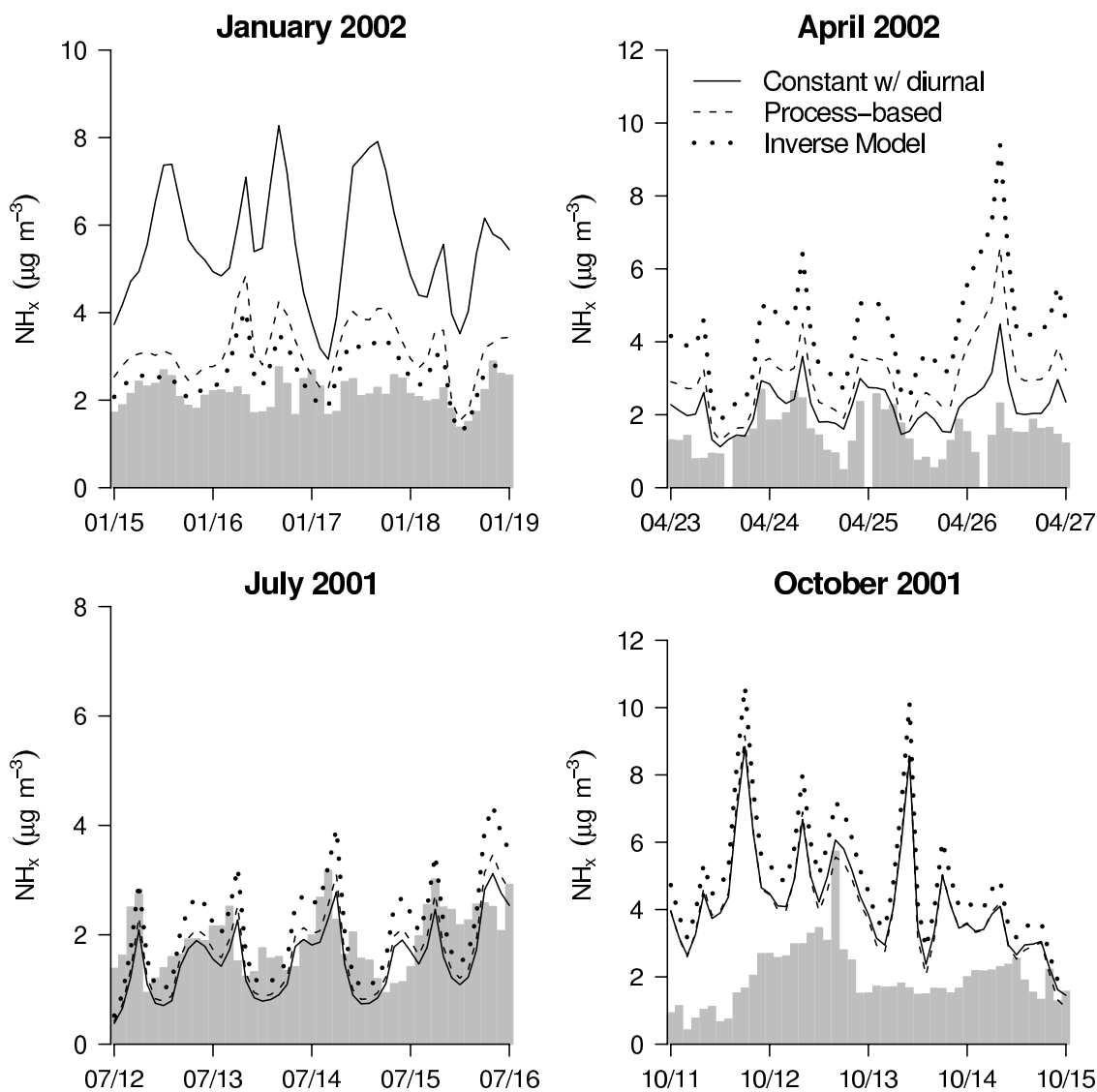


Figure 9. Time series plots of PMCAM_x predicted NH_x concentrations using inverse-modeled inventory, process-based inventory, and the constant with diurnal variation inventory. Each ammonia emission inventory has the same diurnal variation derived using the process-based model. Vertical bars denote 2 hour averaged observations from PAQS.

concentrations of sulfate and total nitrate. While the precipitation indicators have similar monthly emission sensitivity as the NH_x concentration, they are susceptible to errors in the precipitation volume and the scavenging rate.

[47] We find that accurate diurnal variation in emissions is very important for predicting both the time-varying and daily average NH_x concentrations. The diurnal profile is especially important for accurately predicting the concentration at night, since the decreased atmospheric mixing makes the night especially sensitive to emission changes. Without diurnal variation in the emissions, PMCAM_x overestimates the concentrations at night, which biases both the hourly and daily average NH_x concentrations.

[48] Using NH_x measurements from the Pittsburgh Air Quality Study, we find that in January and July, the seasonally varied inventories significantly improve the chemical transport model NH_x predictions. The larger changes in the inverse-modeled inventory further im-

proved the model performance over the process-based inventory.

[49] For the spring and fall, the increased emissions in the seasonally varied inventories relative to the seasonally constant inventory were not consistent with the NH_x concentrations in the observations at the PAQS site, which suggests that the constant inventory already overpredicted ammonia emissions during these seasons. For the process-based model, this can be attributed to a scarcity of important temporal data, especially knowledge of the monthly schedule of manure and fertilizer application. The inverse-modeled approach is susceptible to model input bias. An inverse-modeled result derived using NH_x would be less subject to model input bias.

[50] Unfortunately, there are few NH_x measurements. Measurements of NH₃ or NH₄⁺ alone do not sufficiently constrain the evaluation of ammonia emission inventories. Future improvements to ammonia emission inventories,



Figure 10. Comparison of monthly average model-predicted NH_x concentrations with measurements at Pittsburgh, Pennsylvania. PAQS observations are marked with “O,” and PMCAM_x model results with process-based inventory, inverse-modeled inventory, and seasonally constant inventory are marked with “P,” “I,” and “C,” respectively. The double arrows around the observed values denote ±15% measurement error. The single arrows for the model predictions denote the magnitude and direction of MIBS. If the arrows for the observations overlap with the arrow for the model prediction, then the emission inventory is consistent with the measurements. If the arrows do not overlap, then the difference between the model prediction and the observations cannot be explained by the errors in the CTM sulfate, total nitrate, precipitation, and scavenging rate alone.

and hence regional air quality modeling, depend on a network of monitors measuring NH₃ and NH₄⁺ with hourly time resolution.

Appendix A

[51] To derive the seasonal profile of emissions for livestock types other than dairy cows, surrogate dairy farm types were used. We retain the same annual total emissions for each livestock group as in the constant inventory, but

apply the fraction of monthly emissions predicted by the diary model to get a new seasonal distribution. For each surrogate farm, the fraction of annual emissions is calculated for each month. These fractions are multiplied by the total for the other livestock group to derive the monthly distribution. Surrogate dairy farms are selected to most closely match the manure characteristics of the other livestock group. For example, for feedlot beef cattle, we use the monthly profile from the feedlot dairy cattle. Table A1

Table A1. Analogous Dairy Model Used to Derive the Seasonal Cycle for Other Livestock Groups

Animal Group	Description	Analogous Dairy Model Farm Type	Livestock Types in CMU Ammonia Model
Beef cow/calf operations	This is the early stage of beef production. Young animals are fed on pasture or rangeland.	grazing dairy cows (no confinement)	heifers, steers
Beef feedlot/finisher operations	Animals are fed specially optimized rations for weight gain on dense feedlots. Manure collected in solid form; runoff captured in lagoons.	dairy cows confined on feedlots, solid and liquid manure, seasonal application	beef cattle
Hogs and swine	Animals densely confined in buildings, manure stored in lagoons; 90% off arms report manure application in spring and fall, 50% in summer and winter.	confined dairy cows, liquid manure stored in lagoons, seasonal application	hogs and swine
Poultry	Manure excreted as liquid but absorbed by bedding. Bedding and manure removed after flock is slaughtered. Four to six flocks are raised per year.	confined dairy cows, solid manure applied monthly	broilers, pullets, layers, turkeys

describes each of the surrogate farms applied to each of the nondairy livestock groups.

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