



# Evaluation of a regional air-quality model with bidirectional $\text{NH}_3$ exchange coupled to an agroecosystem model

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**Abstract.** Atmospheric ammonia ( $\text{NH}_3$ ) is the primary atmospheric base and an important precursor for inorganic particulate matter and when deposited  $\text{NH}_3$  contributes to surface water eutrophication, soil acidification and decline in species biodiversity. Flux measurements indicate that the air–surface exchange of  $\text{NH}_3$  is bidirectional. However, the effects of bidirectional exchange, soil biogeochemistry and human activity are not parameterized in air quality models. The US Environmental Protection Agency’s (EPA) Community Multiscale Air-Quality (CMAQ) model with bidirectional  $\text{NH}_3$  exchange has been coupled with the United States Department of Agriculture’s (USDA) Environmental Policy Integrated Climate (EPIC) agroecosystem model. The coupled CMAQ-EPIC model relies on EPIC fertilization timing, rate and composition while CMAQ models the soil ammonium ( $\text{NH}_4^+$ ) pool by conserving the ammonium mass due to fertilization, evasion, deposition, and nitrification processes. This mechanistically coupled modeling system reduced the biases and error in  $\text{NH}_x$  ( $\text{NH}_3 + \text{NH}_4^+$ ) wet deposition and in ambient aerosol concentrations in an annual 2002 Continental US (CONUS) domain simulation when compared to a 2002 annual simulation of CMAQ without bidirectional exchange. Fertilizer emissions estimated in CMAQ 5.0 with bidirectional exchange exhibits markedly different seasonal dynamics than the US EPA’s National Emissions Inventory (NEI), with lower emissions in the spring and fall and higher emissions in July.

## 1 Introduction

Ammonia ( $\text{NH}_3$ ) is the primary atmospheric base and an aerosol precursor (Seinfeld and Pandis, 1998). Atmospheric particulate matter has been shown to have adverse effects on respiratory and cardiovascular systems (Pope, 2000) and can exacerbate preexisting respiratory and cardiovascular conditions (Pope and Dockery, 2006). The deposition of  $\text{NH}_3$  and ammonium ( $\text{NH}_4^+$ ) aerosols contributes to surface water eutrophication, soil acidification, and alters the soil nitrogen geochemistry (Galloway et al., 2003). Vegetation in ecosystems can be damaged via acute toxicity of nitrogen dioxide ( $\text{NO}_2$ ),  $\text{NH}_3$ , and  $\text{NH}_4^+$  (Sutton et al., 2011) and long term nitrogen deposition has been linked to declines in species biodiversity in nutrient-poor ecosystems (Duprè et al., 2010). The total ecosystem and human health costs of nitrogen pollution are cumulative because nitrogen cascades through the environment with multiple human health and ecosystem costs (Birch et al., 2011; Sutton et al., 2011).

$\text{NH}_3$  emissions are challenging to estimate and concentrations are difficult to measure. It is critical to understand the factors that lead to episodes of poor air quality and atmospheric deposition for the development of effective mitigation strategies. As climate change leads to increased variability in meteorology, relying on seasonal averages as the drivers of  $\text{NH}_3$  emissions estimates, as is done in most air-quality models, adds additional uncertainty to simulations. It is necessary to capture the dynamic and episodic nature of  $\text{NH}_3$  emissions, including the influences of meteorology, air–surface exchange, and human activity to reduce

uncertainty in model scenarios of NH<sub>3</sub> emissions mitigation strategies, agricultural food production and the effects of climate change.

A reduction in oxides of nitrogen (NO<sub>x</sub>) emissions in the US over the past 15 to 20 yr from power plants and mobile sources has been documented (Gilliland et al., 2008), but NH<sub>3</sub> emissions remain uncertain and are expected to increase with increased livestock production and crop cultivation (Reis et al., 2009). NH<sub>3</sub> emission inventories for regional air-quality models have been developed based on annual fertilizer sales and animal density with spatial resolution at the US county level and monthly temporal resolution (Goebes et al., 2003; Pinder et al., 2004), and from mechanistic models based on reported agricultural data and semiempirical relationships between emissions and meteorological observations with spatial resolution as fine as 50 km by 50 km and hourly temporal resolution (Skjøth et al., 2011). The improvements in spatial and temporal resolution and top down inverse modeling constraints on NH<sub>3</sub> emissions have improved air-quality models' skill regarding the estimation of NH<sub>3</sub> and aerosol NH<sub>4</sub><sup>+</sup> concentrations (Skjøth et al., 2011; Pinder et al., 2006; Gilliland et al., 2006). Despite these model improvements, a systematic difference between ambient NH<sub>3</sub> observations and model estimates on the order of 30 % persists (Erisman et al., 2007). Underestimation of emissions and/or the overestimation of dry deposition in agricultural areas have been proposed as explanations of the systematic difference between model estimates and observed NH<sub>3</sub> concentrations (Erisman et al., 2007).

Measurements have shown that the air–surface flux of NH<sub>3</sub> is bidirectional and the direction of the flux is dependent on the land use, land management, and ambient NH<sub>3</sub> concentrations (Fowler et al., 2009; Sutton et al., 1993a, b). Fertilizer application to agriculturally managed land is characterized by NH<sub>3</sub> emission peaks lasting a few days (Flechard et al., 2010). Bidirectional NH<sub>3</sub> exchange is typically observed in flux measurements, but current regional and global scale air-quality models do not include a mechanistic description of these processes. However, several recent regional scale modeling studies have included canopy compensation points used to parameterize bidirectional exchange (Wichink Kruit et al., 2010, 2012; Dennis et al., 2010). The NH<sub>3</sub> compensation point in this study is defined as a nonzero concentration in the canopy or within the mesophyll or soil air-spaces. Ambient concentrations above this concentration will result in deposition to the surface and ambient concentrations below this value will result in evasion from the surface. For the first time on a regional scale, an agroecosystem model has been coupled to a photochemical air-quality model to capture the dynamics of observed NH<sub>3</sub> fluxes from fertilized and unfertilized land where NH<sub>3</sub> emissions and deposition from seminatural vegetation and fertilizer application are modeled dynamically as a function of the soil and canopy NH<sub>4</sub><sup>+</sup> content and ambient NH<sub>3</sub> concentrations. This coupled modeling system was evaluated against observations to better un-

derstand the importance of these processes. Cultivated crops and pastures cover 22 % of the land area of the continental US (CONUS) and 38 % of Earth's ice free land (Homer et al., 2007; Foley et al., 2011). The growing of crops represents a large spatial area where the impact of agricultural management practices alters the balance of atmospheric NH<sub>3</sub> sources and sinks. This manuscript describes an analysis in which the Community Multiscale Air-Quality (CMAQ version 5.0) modeling system was modified to include bidirectional NH<sub>3</sub> exchange and coupled to a soil nitrogen model (Cooter et al., 2012) based on the routines in the United States Department of Agriculture's (USDA) Environmental Policy Integrated Climate (EPIC) agroecosystem model (Williams et al., 2008) for the US continental domain. The reduced nitrogen (NH<sub>x</sub> = NH<sub>3</sub> + NH<sub>4</sub><sup>+</sup>) wet deposition results of this coupled modeling system were evaluated against the National Atmospheric Deposition Program's (NADP) National Trends Network (NTN) NH<sub>x</sub> observations. Nitrate ambient aerosol concentration results were evaluated against observations from the Interagency Monitoring of Protected Visual Environments (IMPROVE: Malm et al., 1994) and Speciation Trends Network (STN: Chu, 2004).

## 2 Methods

CMAQ (Foley et al., 2010) version 5.0 with bidirectional exchange estimates NH<sub>3</sub> fluxes from agricultural cropping activities, a simple inorganic nitrogen soil geochemistry parameterization, and meteorological parameters. The agricultural cropping activity data required are fertilizer application rates, depths, and timing. These variables are provided on a daily basis from CONUS EPIC simulations (Cooter et al., 2012). EPIC estimates of the NH<sub>4</sub><sup>+</sup> content in applied fertilizers are used by CMAQ as an input to the soil NH<sub>4</sub><sup>+</sup> pool. The CMAQ soil NH<sub>x</sub> budget follows the parameterization used in EPIC (Williams et al., 2008) and consists of solving for deposition and evasion NH<sub>3</sub> fluxes and soil nitrification in CMAQ simultaneously to maintain the soil ammonium mass balance in a 0.01 m and 0.05 m soil layer to represent surface and injected fertilizer application. Evasive and deposition fluxes of NH<sub>3</sub> were modeled using a two layer (vegetation canopy and soil) resistance model similar to Nemitz et al. (2001) based on CMAQ dry deposition resistance parameterizations (Pleim and Ran, 2011) and the land surface model in the Weather Research and Forecast (WRF) model (Pleim and Xiu, 1995; Xiu and Pleim, 2001). Soil NH<sub>4</sub><sup>+</sup> nitrification in CMAQ with bidirectional NH<sub>3</sub> exchange was modeled following the parameterization in EPIC (Williams et al., 2008). NH<sub>3</sub> fluxes and micrometeorological parameters were estimated for each sub grid cell land use category in CMAQ with bidirectional NH<sub>3</sub> exchange and then aggregated up to the modeled 12 km grid cell.

## 2.1 Soil and vegetation emission potentials

A NH<sub>3</sub> bidirectional exchange model was developed for the CMAQ modeling system using field scale (~100 ha) observations taken at field sites in North Carolina, USA (Walker et al., 2013), and published NH<sub>3</sub> air–surface exchange parameterizations (Massad et al., 2010 and references therein). To support bidirectional exchange estimates, two soil layers and a canopy compensation point model was incorporated into CMAQ. Soil NH<sub>4</sub><sup>+</sup>, pH, and the soil emission potential ( $\Gamma_g$ , defined as  $[\text{NH}_4^+]/[\text{H}^+]$ ) were modeled as a function of fertilizer application rate, crop type, soil type, and meteorology. Agricultural practices including fertilizer application and timing were modeled following Cooter et al. (2012), and  $\Gamma_g$  due to inorganic fertilization application was calculated following Massad et al. (2010).

$$\Gamma_g = \frac{N_{\text{app}} / (\theta_s M_N d_s)}{10^{-\text{pH}}}, \quad (1)$$

where  $N_{\text{app}}$  is the fertilizer application in  $\text{g N m}^{-2}$ ,  $\theta_s$  is the soil volumetric water content in  $\text{m}^3 \text{m}^{-3}$ ,  $M_N$  is the molar mass of nitrogen ( $14 \text{ g mol}^{-1}$ ),  $d_s$  is the depth of the soil layer in m, and pH is the pH of the soil water solution. Fertilizer application rates, dates and methods, injected to 0.05 m or surface applied, for 21 major US crops were provided from a CONUS simulation of EPIC (Cooter et al., 2012). Unlike Massad et al. (2010), who used an exponential decay function to adjust  $\Gamma_g$  as a function of time after fertilization, the atmosphere–soil NH<sub>4</sub><sup>+</sup> budget was simulated in CMAQ as being dynamically coupled to hourly soil NH<sub>4</sub><sup>+</sup> losses due to evasion and nitrification, and increases in soil NH<sub>3</sub> due to deposition. The soil NH<sub>4</sub><sup>+</sup> budget was simulated in CMAQ by adding two soil layers, incorporating the EPIC nitrification routines into CMAQ, and coupling the soil NH<sub>4</sub><sup>+</sup> concentration to atmospheric reduced nitrogen deposition and evasion following Reddy et al. (1979).

$$\frac{d[\text{NH}_x]}{dt} = - \underbrace{\frac{1}{d_s \theta_s R_{\text{soil}}}}_1 ([\text{NH}_3]_{\text{soil}} - [\text{NH}_3]_C) - \underbrace{K_N [\text{NH}_4^+]}_2 \quad (2)$$

where  $[\text{NH}_4^+]$  is the soil NH<sub>4</sub><sup>+</sup> concentration in  $\text{mol L}^{-1}$ ,  $[\text{NH}_3]_{\text{soil}}$  is the soil compensation point in  $\text{mol L}^{-1}$  calculated from the solubility and Henry's law equilibria from NH<sub>4</sub><sup>+</sup> in the soil water solution,  $[\text{NH}_3]_C$  is the in-canopy concentration (modeled as the canopy compensation point) in  $\text{mol L}^{-1}$  calculated following Nemitz et al. (2001),  $R_{\text{soil}}$  is the resistance to diffusion through the soil layer  $\text{s m}^{-1}$ , and  $K_N$  is the nitrification rate in  $\text{s}^{-1}$  following Williams et al. (2008). Deposition and evasion from the soil is represented in part 1 of Eq. (2), with evasion occurring when  $[\text{NH}_3]_{\text{soil}} > [\text{NH}_3]_C$ , and nitrification represented according to part 2 of Eq. (2).  $K_N$  is estimated from the soil water content, soil pH, and soil temperature according to Williams et al. (2008). Note that NH<sub>4</sub><sup>+</sup> is readily absorbed on the soil

cation exchange complex and should be immobile, thus infiltration of NH<sub>4</sub><sup>+</sup> is not modeled (Sutton et al., 2011). Evasion of NH<sub>3</sub> from the soil NH<sub>4</sub><sup>+</sup> pool in CMAQ is modeled in parallel from both soil pools. This assumes that the rate of gaseous diffusion between soil layers is negligible compared to the evasion and nitrification losses of NH<sub>4</sub><sup>+</sup> from the soil pool.

Emission potentials from NH<sub>4</sub><sup>+</sup> in the vegetation's apoplastic solution ( $\Gamma_s = [\text{NH}_4^+]/[\text{H}^+]$ ) and nonagricultural soils were modeled as a function of land cover type ranging from 10 to 160 with agricultural and heavily vegetated areas having the highest values similar to Zhang et al. (2010).  $\Gamma_s$  values used for this simulation are on the low end of the values measured in the field. To assess the models' sensitivity to these values, a simulation was run following the parameterization of Massad et al. (2010), where  $\Gamma_s$  was modeled as a function of the annual N deposition field and fertilizer application. These changes increased  $\Gamma_s$  by approximately a factor of three in background sites and by as much as a factor of 30 in agricultural regions (Dennis et al., 2013; discussed in Sect. 3).

## 2.2 Emissions and deposition estimate

The bidirectional exchange model in the regional scale air-quality model CMAQ 5.0 estimates a net NH<sub>3</sub> flux. However the base case of this model and most other air-quality models separates the air–surface exchange of NH<sub>3</sub> into emission and deposition fluxes. NH<sub>3</sub> emissions are typically based on emissions factors that can vary seasonally (Goebes et al., 2003). Atmospheric deposition is typically modeled as the product of a deposition velocity and the ambient concentration. In the CMAQ bidirectional NH<sub>3</sub> exchange model, the NH<sub>3</sub> air–surface flux is modeled as a function of the gradient between the ambient first layer model concentration at ~20 to ~40 m and the canopy compensation point modeled at 0.5 of the in-canopy resistance. Note, all ambient and compensation point concentrations in this section are in  $\mu\text{g m}^{-3}$ , all fluxes are in  $\mu\text{g m}^{-2} \text{s}^{-1}$ , and all resistances are in  $\text{s m}^{-1}$ .

$$F_t = \frac{1}{R_a + 0.5 R_{\text{inc}}} (C_c - C_a), \quad (3)$$

where  $F_t$  the total air–surface exchange of NH<sub>3</sub>,  $R_a$  is the aerodynamic resistance,  $R_{\text{inc}}$  is the in-canopy aerodynamic resistance,  $C_c$  is the canopy NH<sub>3</sub> compensation point, and  $C_a$  is the atmospheric NH<sub>3</sub> concentration.  $C_c$  is a function of  $C_a$ , the stomatal compensation point,  $C_{\text{st}}$ , and the soil compensation point,  $C_g$ .

$$C_c = \frac{\frac{C_c}{R_a + 0.5 R_{\text{inc}}} + \frac{C_{\text{st}}}{R_b + R_{\text{st}}} + \frac{C_g}{0.5 R_{\text{inc}} + R_{\text{bg}} + R_{\text{soil}}}}{(R_a + 0.5 R_{\text{inc}})^{-1} + (R_b + R_{\text{st}})^{-1} + (R_b + R_w)^{-1} + (0.5 R_{\text{inc}} + R_{\text{bg}} + R_{\text{soil}})^{-1}} \quad (4)$$

where  $R_b$  is the quasi laminar boundary layer resistance at the leaf surface,  $R_{\text{st}}$  is the stomatal resistance,  $R_{\text{bg}}$  is the quasi laminar boundary layer resistance at the ground surface, and

$R_w$  is the cuticular resistance. Note that  $R_w$  is a function of  $C_c$  similar to Jones et al. (2007), and that  $C_c$  and  $R_w$  are solved simultaneously.  $C_{st}$  and  $C_g$  are calculated following Nemitz et al. (2001).

$$C_{st} = M_n / V_m \frac{161\,500}{T_c} e^{\left(-\frac{10\,380}{T_c}\right)} \Gamma_s, \quad (5)$$

$$C_g = M_n / V_m \frac{161\,500}{T_s} e^{\left(-\frac{10\,380}{T_s}\right)} \Gamma_g, \quad (6)$$

where  $M_n$  is the molar mass of NH<sub>3</sub> ( $1.7 \times 10^7 \mu\text{g mol}^{-1}$ ),  $V_m$  is to convert L to m<sup>3</sup> ( $1 \times 10^{-3}$ ),  $T_c$  and  $T_s$  are the canopy and soil temperature in K. The following modification to Eq. (3) was used in order to estimate an emission from soil NH<sub>4</sub><sup>+</sup> comparable to the estimates used by emissions models where gradient processes are not modeled. This was done to be consistent with NH<sub>3</sub> emissions estimates from fertilizer application due to agricultural management practices used in most air-quality models.

$$F_{emis} = \frac{1}{R_a + 0.5R_{inc}} (C_c [C_a = 0]), \quad (7)$$

where  $C_c [C_a = 0]$  is the compensation point calculated assuming that there is no NH<sub>3</sub> present in the atmosphere and  $F_{emis}$  is the emission flux. Likewise, the deposition flux is estimated by modifying Eq. (3), assuming that there is no atmospheric compensation point.

$$F_{dep} = \frac{1}{R_a + 0.5R_{inc}} (C_c [\Gamma_s = 0 \text{ and } \Gamma_g = 0] - C_a) \quad (8)$$

where  $C_c$  is calculated as a function of the ambient atmospheric NH<sub>3</sub> concentration alone, the emission potentials from the soil and apoplast are set to zero and  $F_{dep}$  is the deposition component of the flux. Note, that  $F_{emis}$  and  $F_{dep}$  was used to provide for a more direct comparison with the base model and  $F_{emis} + F_{dep} = F_t$ . The net flux was used to model the soil NH<sub>4</sub><sup>+</sup> budget.

### 2.3 Model simulation

Two CMAQ model cases were run to evaluate the application of this bidirectional NH<sub>3</sub> exchange model on a regional scale (1000–5000 km). The bidirectional case modeled dynamic NH<sub>3</sub> emissions and deposition depending on  $\Gamma_s$  and  $\Gamma_g$  and a base case in which NH<sub>3</sub> emissions and deposition were modeled separately. In the bidirectional case, NH<sub>3</sub> deposition increased and evasion decreased the values of  $\Gamma_g$ . The base case used the EPA National Emissions Inventory (NEI) fertilizer emissions estimates and CMAQ's unidirectional deposition velocity parameterization for NH<sub>3</sub>. Annual 2002 simulations on the 12 km horizontal grid cell resolution CONUS domain use 2002 NEI emissions (<http://www.epa.gov/ttnchie1/net/2002inventory.html>)

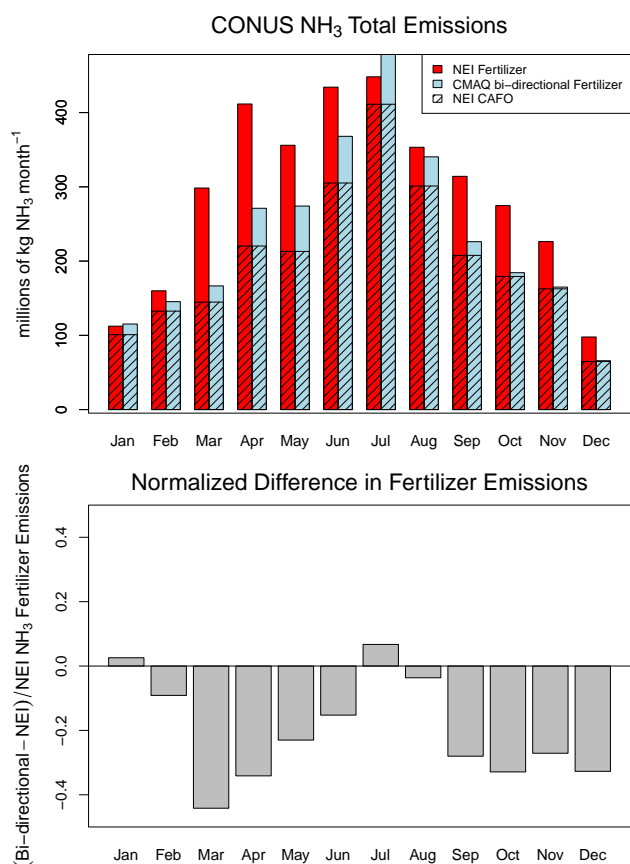
and Weather Research Forecasting (WRF v3.1, Skamarock et al., 2008) meteorology using the Pleim-Xiu land surface scheme (Pleim and Xiu, 1995) and Asymmetric Convective Model version 2 (Pleim, 2007). CMAQ was run with 24 vertical layers using terrain following coordinates with a surface layer thickness of approximately 40 m. The upper most layer was located at 7500 Pa.

Emissions were identical between the two cases except for NH<sub>3</sub> emissions from agricultural fertilizer application. Agricultural fertilizer emissions in the base case are the product of annual fertilizer activity (applications) following the Carnegie Mellon University (CMU) emissions model (Goebes et al., 2003) and fixed emission factors. The total annual NH<sub>3</sub> emissions (fertilizer emissions plus animal husbandry) were seasonally allocated using inverse modeling techniques that relied on wet deposition (Gilliland et al., 2006). The seasonally adjusted animal operation emissions were kept the same in the base case and the bidirectional case. The NEI fertilizer emissions were removed from the bidirectional case and fertilizer emissions were estimated dynamically within CMAQ using the EPIC agricultural management output. Information regarding inorganic fertilizer application amounts and timing were simulated for bidirectional CMAQ using EPIC (Williams, et al., 2008; Izaurrealde et al., 2006) as described above and in Cooter et al. (2012). The vegetation apoplastic emission potential,  $\Gamma_s$ , was parameterized as a function of the land cover type.

The model simulations were evaluated on a domain-wide basis for the CONUS on annual and monthly time frames against NH<sub>x</sub> wet deposition observations and PM<sub>2.5</sub> ammonium (NH<sub>4</sub><sup>+</sup>), nitrate (NO<sub>3</sub><sup>-</sup>) and sulfate (SO<sub>4</sub><sup>2-</sup>) aerosol monitoring network observations. NH<sub>x</sub> wet deposition and precipitation were measured by the National Acid Deposition Program's (NADP) National Trends Network (NTN). CMAQ modeled deposition and WRF modeled precipitation were evaluated against the NTN wet deposition and precipitation observations to quantify the precipitation biases as part of the wet deposition evaluation at NTN sites. Spatially interpolated Parameter-elevation Regression on Independent Slopes Model (PRISM, Daly et al., 1994) gridded data are available for the entire CONUS domain on a monthly frequency and compare quite well with the NADP precipitation site data. Assuming that the errors in precipitation and deposition are linear, an adjustment of the observed to estimated precipitation was applied to the CMAQ wet deposition fields to evaluate precipitation biases on a monthly deposition basis using PRISM interpolated observations (Eq. 9) to generate CONUS NH<sub>x</sub> wet deposition fields following Appel et al. (2011).

$$F_{ba, WD} = \frac{\sum P_{PRISM}}{\sum P_{Model}} \sum F_{WD}, \quad (9)$$

where  $F_{ba, WD}$  is the bias adjusted wet deposition,  $P_{PRISM}$  is the monthly total PRISM precipitation,  $P_{Model}$  is the monthly



**Fig. 1.** Total domain wide NH<sub>3</sub> emissions estimated by the NEI and CMAQ with bidirectional exchange coupled to the EPIC agroecosystem model (top panel) and the fractional difference in the NH<sub>3</sub> fertilizer emissions (bottom panel) on the CONUS domain from the NEI estimated in CMAQ 5.0 with bidirectional exchange.

total WRF precipitation, and  $F_{WD}$  is the monthly model wet deposition.

Modeled inorganic NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> aerosol concentrations were evaluated against speciated particulate matter (PM) measurements from the mostly rural IMPROVE sites and NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> measurements from the mostly urban STN sites.

### 3 Results and discussion

#### 3.1 Model nitrogen budget

The annual domain-wide 2002 fertilizer emissions estimated using CMAQ with bidirectional exchange and EPIC simulated fertilizer applications were lower than the totals reported in the 2002 NEI, Table 1. The bidirectional case estimated lower NH<sub>3</sub> emissions in the spring and fall and higher emissions in January and July (Fig. 1). Spring and fall NH<sub>3</sub> emissions in the NEI have a higher degree of uncertainty due to compensating errors related to a lower number of obser-

vations than other seasons and low observed precipitation in high NH<sub>3</sub> emission regions when inverse modeling techniques were used to determine the seasonal emissions based on wet deposition observations used in the NEI fertilizer and CAFO emissions (Gilliland et al., 2006). Inverse modeling of NH<sub>3</sub> emissions was sensitive to the lack of observations in these agricultural regions and resulted in a likely overestimation of emissions in the spring and fall (Gilliland et al., 2006). The total NH<sub>3</sub> emissions were lowered by as much as 45 % in March and increased by as much as 7 % in July. A portion of these emission differences stems from the EPIC simulated cropland fertilization rates being ~ 12 % lower than total agricultural and nonagricultural inorganic fertilizer sales-based activity values used by the NEI (Cooter et al., 2012). A much larger portion of these differences likely relates to the dynamic emissions response to local temperature conditions present in bidirectional CMAQ (see Sect. 2.2).

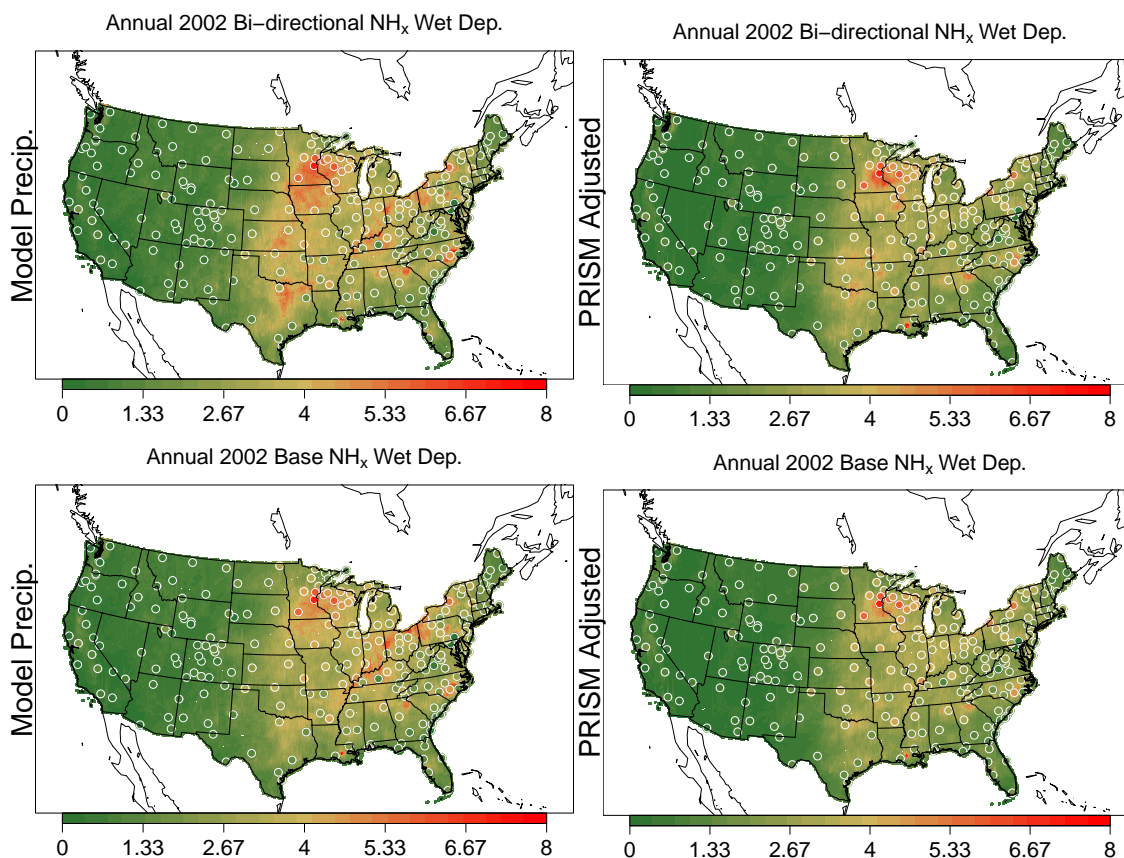
The dry deposition of NH<sub>3</sub> was decreased by 45 % across the CONUS domain in the bidirectional case. The reduced modeled NH<sub>3</sub> emissions from fertilized crops were more than offset by the reduction in the dry deposition sinks resulting in a net increase in atmospheric NH<sub>3</sub> in most areas. Overall, there was an increase in NH<sub>x</sub> wet deposition of 14 % and an increase of 10 % in NH<sub>3</sub> and decrease of 7 % in NH<sub>4</sub> ambient concentrations in the CONUS domain. The total NH<sub>x</sub> deposition was reduced by 15 %, total N deposition was reduced by 5 % over the base case primarily due to the reduction in NH<sub>3</sub> dry deposition, and bidirectional total NH<sub>3</sub> emissions were reduced by 16 %. Thus, the export of NH<sub>x</sub> off the continent was increased by 2 %. A June 2006 sensitivity run using the apoplast compensation point of Massad et al. (2010) resulted in a 17 % increase in June bidirectional NH<sub>3</sub> emissions from agricultural cropping operations and a 5 % increase in the domain wide total NH<sub>3</sub> emissions (Dennis et al., 2013).

#### 3.2 NH<sub>x</sub> wet deposition evaluation

NH<sub>x</sub> wet deposition estimated using the bidirectional exchange parameterization increased the model bias over the base case by 8 % at NADP sites on an annual bases (Table 2). However the 2002 modeled precipitation was biased by 18.1 %. The precipitation biases were highest in the summer when convective precipitation was highest with a peak mean bias in the precipitation of 49.8 % at NADP sites during July resulting in a July correction factor of -36.0 % and -35.1 % in the modeled base and bidirectional wet deposition cases, respectively. The monthly biases in the bidirectional wet deposition correlated well with the monthly meteorological precipitation biases ( $r^2 = 0.581$ ,  $p < 0.05$ ) while the base case NH<sub>x</sub> wet deposition biases did not significantly correlate with precipitation biases ( $r^2 = 0.08$ ,  $p = 0.373$ ). When the annual wet deposition is corrected for precipitation using PRISM interpolated precipitation data following Appel et al. (2011), the absolute magnitude of the normalized

**Table 1.** Annual 2002 NEI and bidirectional NH<sub>3</sub> emissions estimated for the CONUS domain.

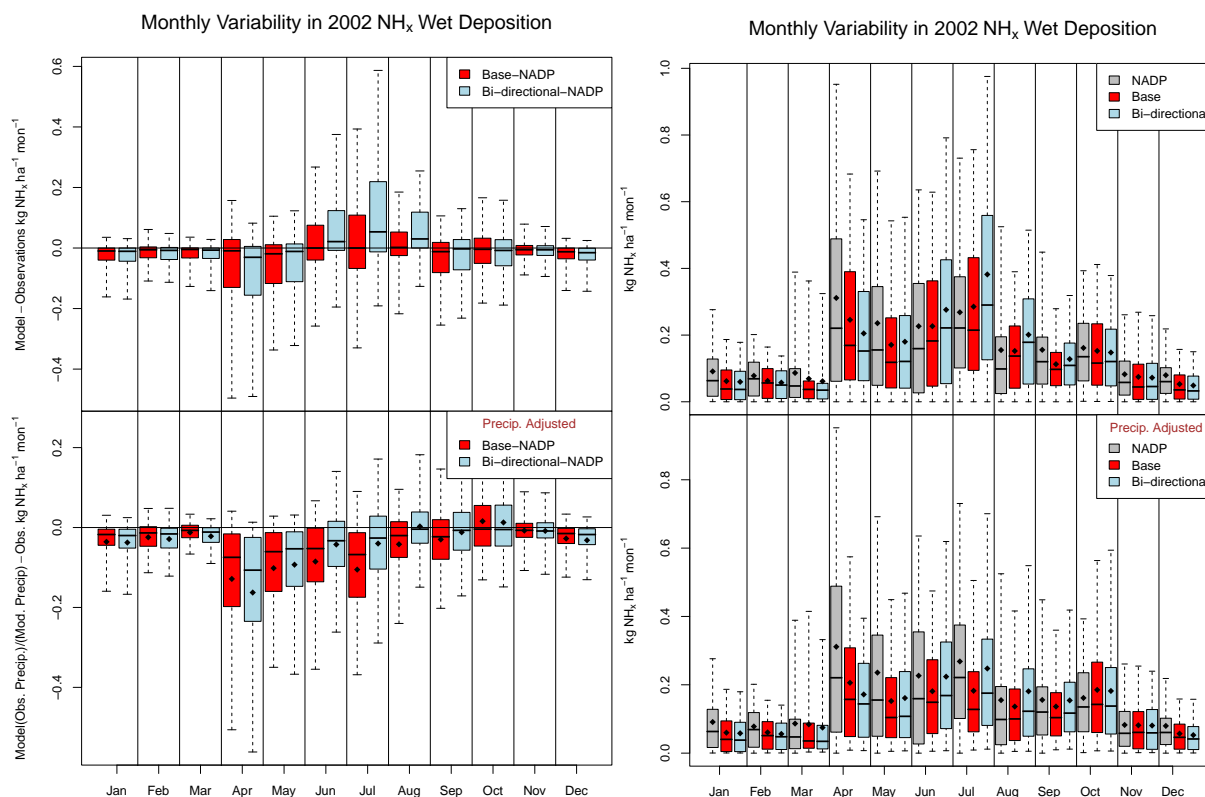
	Fertilizer emissions 10 <sup>12</sup> g NH <sub>3</sub> yr <sup>-1</sup>	% change from NEI	Total emissions 10 <sup>12</sup> g NH <sub>3</sub> yr <sup>-1</sup>	% change from NEI	% of emissions from fertilizer
NEI	1.0	0 %	3.5	0	30 %
Bidirectional	0.4	-66 %	2.8	-20 %	13 %

**Fig. 2.** Maps of bidirectional and base annual NH<sub>x</sub> wet deposition fields, top two panels respectively, annual NH<sub>x</sub> deposition maps scaled by annual 2002 PRISM precipitation fields for bidirectional and base cases, bottom two panels respectively. Mean annual NADP observations at each measurement site ( $N = 243$ ) are plotted in the same color scales over the modeled results.

bias in the bidirectional case is slightly reduced from 10.2 to -9.8% and the absolute magnitude of the normalized bias in the base case increases from 1.9 to -16% (Table 2). This indicates that the relatively unbiased wet deposition in the base case was likely due to meteorological model precipitation errors. The model precipitation biases are greatest during periods of summertime convective precipitation. These precipitation biases are well documented and will be difficult to resolve in mesoscale models due to the localized/small scale nature of convective precipitation (Tost et al., 2010). Precipitation post processing techniques are necessary to account for potential precipitation biases in chemical transport models to illuminate the differences between biases propagated from errors in the simulated precipitation field and errors in

the emissions, transport and fate in the chemical transport model (Appel et al., 2011). The bias introduced in NH<sub>x</sub> wet deposition estimates by the bidirectional model parametrization is largely mitigated if one accounts for the biases in the modeled precipitation of the driving meteorological model.

Bidirectional surface exchange improved the model seasonal and spatial comparisons to NH<sub>x</sub> wet deposition observations. The underestimation in the NH<sub>x</sub> wet deposition in the upper Midwest was reduced in the bidirectional case (Fig. 2). Both models underestimated the wet deposition in the spring/early summer observed at NADP sites (Fig. 3). The bidirectional case NH<sub>x</sub> wet deposition in June, July and August was biased high by 21.8, 42.3 and 29.6% respectively (Fig. 3) as a result of model biases in the precipitation



**Fig. 3.** Box plots of NH<sub>x</sub> wet deposition monthly model bias (top two panels) and total simulated wet deposition (bottom two panels) paired in space and time with NADP observations ( $N = 560$  to  $863$  per month) for the CMAQ base case estimates (red) and CMAQ with bidirectional case (blue). Monthly biases and total deposition for the raw model output are presented in the top panel of each set and precipitation corrected biases are presented in the bottom panel of each set. The boxes enclose the 25th to 75th percentiles, the whiskers represent the 5th and 95th percentiles, the horizontal bar represents the median, and the black diamond represents the mean.

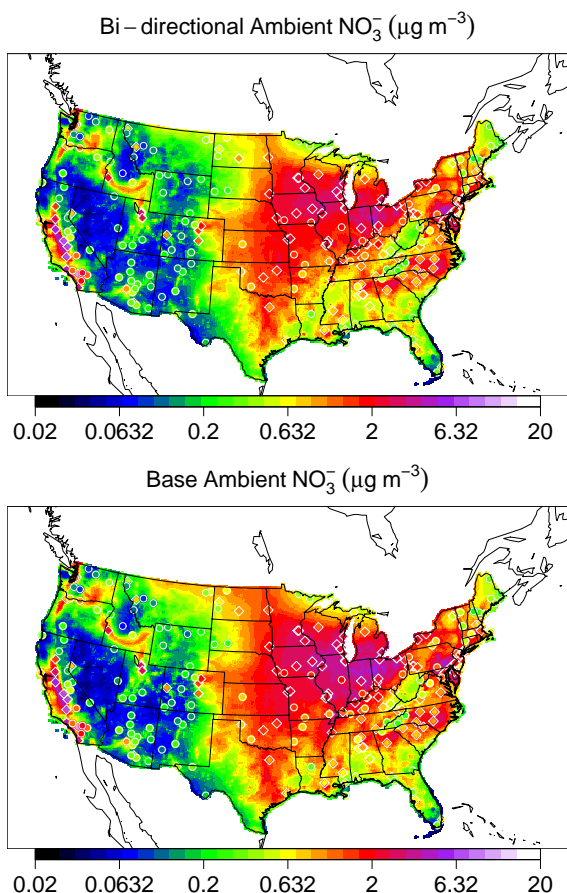
**Table 2.** Annual base and bidirectional Pearson’s correlation coefficient, NMB and NME compared to annual NADP observations.

	Correlation ( $r$ )	NMB	NME
Base	0.766	1.9 %	30.6 %
Bidirectional	0.791	10.2 %	30.3 %
Base PRISM	0.750	-16 %	33.8 %
Bidirectional PRISM	0.777	-9.8 %	31.3 %
WRF vs. PRISM precipitation	0.851	18.1 %	25.5 %

during these periods of 44.7, 69.3 and 37.8 % NMB, respectively. The application of bidirectional exchange in CMAQ, together with the precipitation correction, increased the bias and error in wet deposition from the mid-Atlantic to the northeastern US states where the base case was relatively unbiased (Fig. 2). However, improvements in the domain wide model wet deposition performance with the bidirectional NH<sub>3</sub> parameterization offset localized degradation in the model performance and resulted in a net improvement in the regional scale simulation in NH<sub>x</sub> wet deposition.

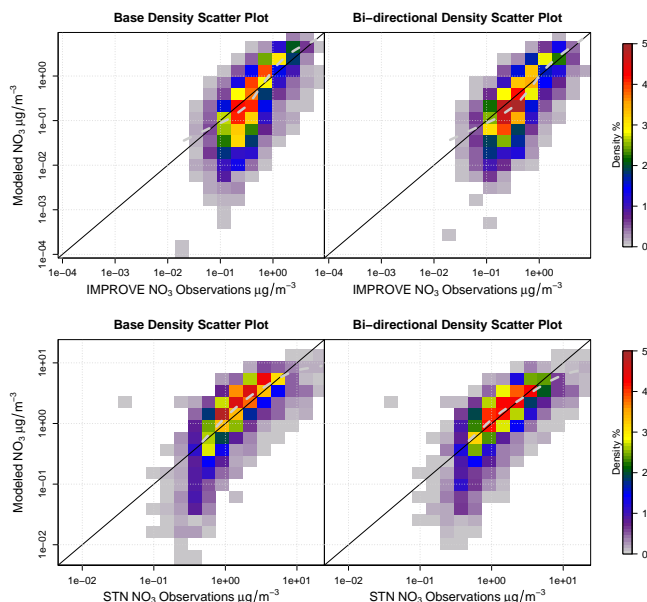
### 3.3 Ambient aerosol evaluation

NH<sub>3</sub> preferentially partitions to SO<sub>4</sub><sup>2-</sup> aerosol, and in sulfate poor conditions excess NH<sub>3</sub> will react with other species (Nenes et al., 1998). Thus, large differences in the total sulfate aerosol were not observed nor expected. However, changes in the ambient NH<sub>3</sub> were expected and these changes affected the modeled NO<sub>3</sub><sup>-</sup> aerosol concentrations. CMAQ NO<sub>3</sub><sup>-</sup> PM<sub>2.5</sub> aerosol estimates were compared to STN PM<sub>2.5</sub> observations located primarily in urban sites and IMPROVE observations PM<sub>2.5</sub> located primarily in rural sites. At STN sites the mean annual domain base case PM<sub>2.5</sub> NO<sub>3</sub><sup>-</sup> concentration was nearly unbiased (0.2 % NMB) while the bidirectional case introduced a -10.5 % negative bias (underprediction). At the more rural IMPROVE monitoring sites, the normalized mean annual bias was reduced from 18.2 % in base case to 0.6 % in the bidirectional case. The overprediction in PM<sub>2.5</sub> NO<sub>3</sub><sup>-</sup> aerosol concentrations in the Ohio Valley and Midwest in the base case is reduced in the bidirectional case (Fig. 4). Incorporation of the bidirectional exchange model in CMAQ improved the annual mean PM<sub>2.5</sub> NO<sub>3</sub><sup>-</sup> concentrations at almost all IMPROVE sites, but both



**Fig. 4.** 2002 annual mean  $\text{NO}_3^-$  aerosol concentration in the bidirectional (top panel) and base case (bottom panel). Mean annual STN observations ( $N = 208$ ) are plotted over the map as diamonds and IMPROVE observations ( $N = 156$ ) for each measurement site are plotted over the map as circles. Note that the color scale has been plotted on a log axis.

model cases still underestimated annual mean  $\text{PM}_{2.5} \text{NO}_3^-$  concentrations at many Western US STN sites (Fig. 4). The positive bias in modeled  $\text{PM}_{2.5} \text{NO}_3^-$  concentrations at IMPROVE sites was reduced in the bidirectional case for almost the entire distribution of the observed concentrations, while the bidirectional case reduced the over prediction in  $\text{PM}_{2.5} \text{NO}_3^-$  aerosol concentrations at STN sites for observed concentrations below approximately  $3 \mu\text{g m}^{-3}$  and both models underestimated observations with concentrations above  $5 \mu\text{g m}^{-3}$  (Fig. 5). Both model cases overestimated the  $\text{PM}_{2.5} \text{NO}_3^-$  concentrations in the mid-Atlantic region of the US. The bidirectional case underestimate of  $\text{PM}_{2.5} \text{NO}_3^-$  aerosol concentrations at STN sites was due to an over-reduction of the winter (7.2 % base and  $-10.2$  % bidirectional NMB) and fall (7.2 % base and  $-3.9$  % bidirectional NMB) base case concentrations. On the other hand, the bidirectional case reduced the summertime base case underprediction ( $-15.1$  % base and  $-4.5$  % bidirectional NMB) in  $\text{PM}_{2.5} \text{NO}_3^-$  aerosol

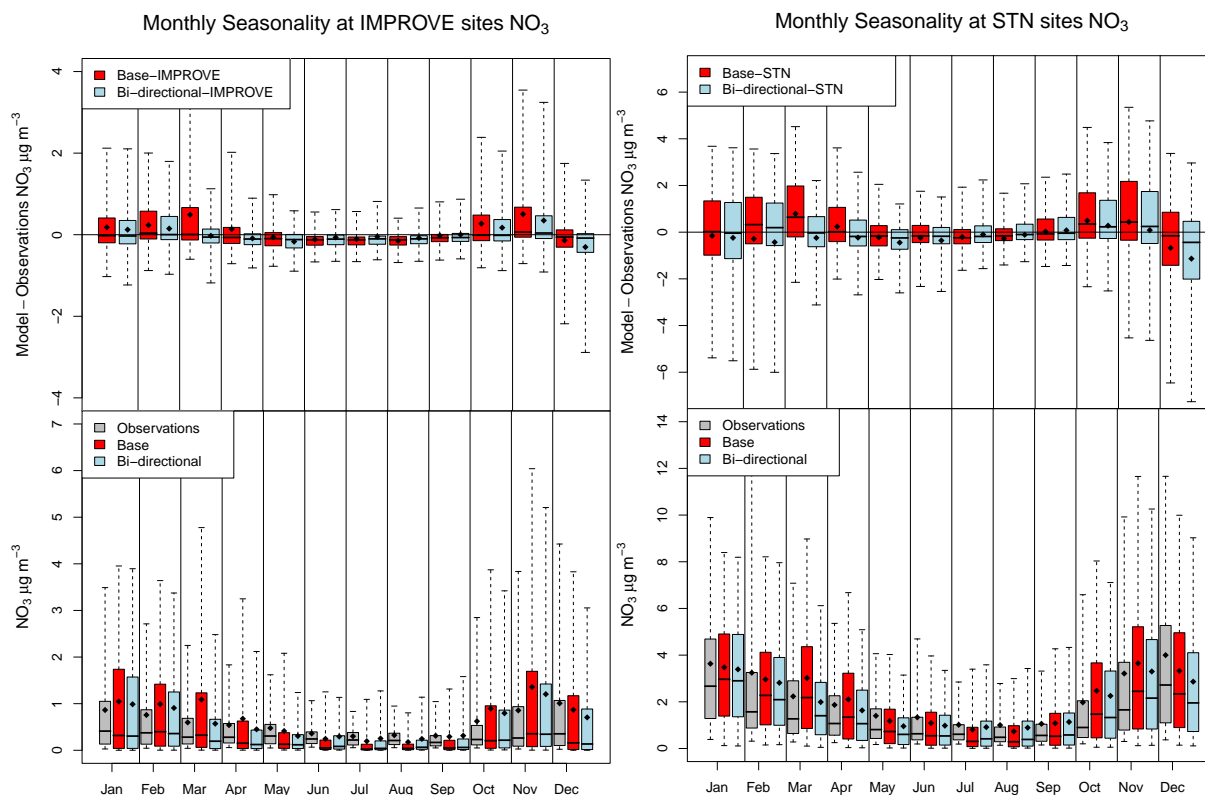


**Fig. 5.** Density scatter plots of monthly mean  $\text{NO}_3^-$  aerosol observations paired with base and bidirectional CMAQ modeled values at IMPROVE sites,  $N = 1745$  (top panels), and STN sites,  $N = 2320$  (Bottom panels). Annual data were aggregated into 20 bins on a  $\log_{10}$  scale spanning the range of the observations and model results, from  $1 \times 10^{-4}$  to  $10 \mu\text{g m}^{-3}$  for the IMPROVE data and a  $5 \times 10^{-3}$  to  $25 \mu\text{g m}^{-3}$  for the STN data. The dashed line represents a least squares local polynomial regression fit of the model data to the observations.

concentrations (Fig. 6). The bidirectional case reduced the overestimation of  $\text{PM}_{2.5} \text{NO}_3^-$  aerosol observations at rural IMPROVE sites during the winter and fall (from 44.6 to 9.9 % NMB and 29.5 to 12.8 % NMB respectively) and reduced the summertime underprediction of the nitrate aerosol by 15.8 % (from a NMB of 29.2 to 13.4 %). At both STN and IMPROVE sites, the underprediction of  $\text{PM}_{2.5} \text{NO}_3^-$  aerosol during the spring was increased in the bidirectional case (from  $-7.2$  to  $-23.7$  % and  $-6.6$  to  $-23.5$  % respectively).

These results show that ambient  $\text{PM}_{2.5} \text{NO}_3^-$  aerosol concentrations are sensitive to  $\text{NH}_3$  emissions and that the reduction in the seasonal aerosol biases (Fig. 6) have similar patterns as the change in  $\text{NH}_3$  emissions, Fig. 1. However, it is not clear if the reduction in the bias was due to an underestimation of the fertilizer application and, subsequently, an underestimation of the  $\text{NH}_3$  emission, or due to the bidirectional exchange parameterization. To evaluate this question, March 2002 was rerun with the bidirectional exchange model with approximately a seven fold increase in fertilizer application. This introduced a positive bias in the  $\text{PM}_{2.5} \text{NO}_3^-$  aerosol evaluation in these bidirectional simulations, but this bias was still approximately half of the bias in the base (82.0 % NMB at IMPROVE sites and 35.2 % NMB at STN sites) case for March 2002. The increase in  $\text{NH}_3$  evasion in March 2002 was not as sensitive to increases in





**Fig. 6.** Box plots of modeled monthly ambient NO<sub>3</sub><sup>-</sup> aerosol biases and concentrations at STN (top two panels;  $N = 871$  to 1236 per month) and IMPROVE sites (bottom two panels;  $N = 691$  to 1135 per month). The base case is in red, the bidirectional case is in blue and STN and IMPROVE observations are in grey. The boxes enclose the 25th to 75th percentile, the whiskers represent the 5th and 95th percentiles, the horizontal bar represents the median, and the black diamond represents the mean.

fertilizer applications as the June 2006 simulations reported in Dennis et al. (2013). Thus it appears that the reduction in the NH<sub>3</sub> emissions and, therefore, the bias in the winter aerosol observations were likely due to the parameterization of NH<sub>3</sub> bidirectional exchange and the exponential temperature function of the NH<sub>3</sub> compensation point (Eq. 6).

The gap in observed and modeled PM<sub>2.5</sub> NO<sub>3</sub><sup>-</sup> aerosol concentrations at STN sites may be partially closed by adopting the Massad et al. (2010) apoplast compensation point model. The June 2006 simulation with this parameterization resulted in proportionally (relative to the change in emissions) higher PM<sub>2.5</sub> NO<sub>3</sub><sup>-</sup> aerosol concentrations than resulted from increases in modeled fertilization rates (Dennis et al., 2013). The increase in the PM<sub>2.5</sub> NO<sub>3</sub><sup>-</sup> aerosol concentrations using the Massad et al. (2010) compensation point model may be from the parameterization of  $\Gamma_s$  as a function of the annual total N deposition field. This increased the apoplastic compensation point and atmospheric NH<sub>3</sub> in urban areas where there was often abundant ambient NO<sub>x</sub>, sufficient HNO<sub>3</sub> for PM<sub>2.5</sub> NO<sub>3</sub><sup>-</sup> aerosol formation, and higher oxidized N deposition rates relative to the total N deposition budget resulting in an increased  $\Gamma_s$ . The Ammonia Monitoring Network (AMoN; Purchalski et al., 2011) began sampling in the conti-

mental US in the fall of 2007, thus long term monitoring data of NH<sub>3</sub> was not available to compare against these 2002 annual simulations. However, simulations are planned to evaluate CMAQ modeled NH<sub>3</sub> concentrations to AMoN observations as well as satellite derived and aircraft observations. Additionally, multiyear simulations are planned to evaluate how NH<sub>3</sub> bidirectional exchange may alter estimated trends in total N deposition to sensitive ecosystems.

#### 4 Conclusions

A photochemical air-quality model has been coupled with an agroecosystem model in CMAQ version 5.0 to simulate the bidirectional exchange of NH<sub>3</sub>. This allows for the direct estimation of NH<sub>3</sub> emissions, transport and deposition from agricultural practices from the parameterizations of soil geochemistry, transport and dynamic NH<sub>3</sub> compensation point processes. This coupled modeling system improved the simulations of NH<sub>x</sub> wet deposition (when compensating precipitation biases were accounted for) and improved the simulation of ambient nitrate aerosol concentrations. The largest improvements in the aerosol simulations were during the spring and fall. NEI estimates at these times

are particularly uncertain since significant precipitation prediction biases were incorporated in the inverse modeling adjustments to the seasonality (Gilliland et al., 2006; Pinder et al., 2006; Henze et al., 2009). The CMAQ bidirectional model can likely be improved with additional soil and vegetation geochemical and ambient NH<sub>3</sub> concentration and flux data to enhance and evaluate these parameterizations. The coupled CMAQ-EPIC model estimates dynamic bidirectional NH<sub>3</sub> fluxes from seminatural and agricultural ecosystems connecting air-quality and nitrogen deposition to agricultural management practices and variability in meteorology and climate.

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