Evaluation of a regional air-quality model with bi-directional NH_3 exchange coupled to an agro-ecosystem model

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Abstract

Atmospheric ammonia (NH_3) is the primary atmospheric base and an important precursor for inorganic particulate matter and when deposited NH_3 contributes to surface water eutrophication, soil acidification and decline in species biodiversity. Flux measurements indicate that the air-surface exchange of NH_3 is bi-directional. However, the effects of bi-directional exchange, soil biogeochemistry and human activity are not parameterized in air quality models. The U.S. Environmental Protection Agency (EPA)'s Community Multiscale Air-Quality (CMAQ) model with bi-directional NH_3 exchange has been coupled with the United States Department of Agriculture (USDA)'s Environmental Policy Integrated Climate (EPIC) agro-ecosystem model. The coupled CMAQ-EPIC model relies on EPIC fertilization timing, rate and composition while CMAQ models the soil ammonium (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 NH_x (NH_3+ NH_4^+) wet deposition and in

ambient aerosol concentrations in an annual 2002 Continental U.S. (CONUS) domain simulation when compared to a 2002 annual simulation of CMAQ without bi-directional exchange. Fertilizer emissions estimated in CMAQ 5.0 with bi-directional exchange exhibits markedly different seasonal dynamics than the U.S. EPA's National Emissions Inventory (NEI), with lower emissions in the spring and fall and higher emissions in July.

1 Introduction

Ammonia (NH_3) is the primary atmospheric base and an aerosol precursor (Seinfeld and Pandis, 1998). Atmospheric particulate matter has been shown to have adverse affects on respiratory and cardiovascular systems (Pope, 2000) and can exacerbate preexisting respiratory and cardiovascular conditions (Pope and Dockery, 2006). The deposition of NH_3 and ammonium (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 (NO_2), NH_3, and 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).

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 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 NH_3 emissions, including the influences of meteorology, air-surface exchange, and human activity to reduce uncertainty in model scenarios of NH_3 emissions mitigation strategies, agricultural food production and the effects of climate change.

A reduction in oxides of nitrogen (NO_x) emissions in the U.S. over the past 15 to 20 years from power plants and mobile sources has been documented (Gilliland et al. 2008), but NH_3 emissions remain uncertain and are expected to increase with increased livestock production and crop cultivation (Reis et al. 2009). NH_3 emission inventories for regional air-quality models have been developed based on annual fertilizer sales and animal density with spatial resolution at the U.S. county level and monthly temporal resolution (Goebes et al., 2003, Pinder et al., 2004), and from mechanistic models based on reported agricultural data and semi-empirical relationships between emissions and meteorological observations with spatial resolution as fine as 50km by 50km and hourly temporal resolution (Skjøth et al. 2011). The improvements in spatial and temporal resolution and top down inverse modeling constraints on NH_3 emissions have improved air-quality models' skill regarding the estimation of NH_3 and aerosol NH_4^+ concentrations (Skjøth et al. 2011, Pinder et al. 2006, Gilliland et al. 2006). Despite these model improvements, a systematic difference between ambient NH_3 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_3 concentrations (Erisman et al. 2007).

Measurements have shown that the air-surface flux of NH_3 is bi-directional and the direction of the flux is dependent on the land use, land management, and ambient NH_3 concentrations (Fowler et al., 2009; Sutton et al. 1993a,b). Fertilizer application to agriculturally managed land is characterized by NH_3 emission peaks lasting a few days (Flechard et al. 2010). Bi-directional NH_3 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_3 compensation point in this study is defined as a non-zero 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 agro-ecosystem model has been coupled to a photochemical air-quality model to capture the dynamics of observed NH_3 fluxes from fertilized and unfertilized land where NH_3 emissions and deposition from semi-natural vegetation and fertilizer application are modeled dynamically as a function of the soil and canopy NH_4^+ content and ambient NH_3 concentrations. This coupled modeling system was evaluated against observations to better understand the importance of these processes. Cultivated crops and pastures cover 22% of the land area of the continental U.S. (CONUS) and 38% of the

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_3 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 bi-directional NH_3 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) agro-ecosystem model (Williams et al. 2008) for the U.S. continental (CONUS) domain. The reduced nitrogen (NH_x=NH_3+NH_4^+) wet deposition results of this coupled modeling system were evaluated against the National Atmospheric Deposition Program's (NADP) National Trends Network (NTN) NH_x 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 bi-directional exchange estimates NH_3 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_4^+ content in applied fertilizers are used by CMAQ as an input to the soil NH^4_+ pool. The CMAQ soil NH_x budget follows the parameterization used in EPIC (Williams et al. 2008) and consists of solving for deposition and evasion NH_3 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_3 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, and Xiu and Pleim 2001). Soil NH_4^+ nitrification in CMAQ with bi-directional NH_3 exchange was modeled following the parameterization in EPIC (Williams et al. 2008). NH_3 fluxes and micrometeorological parameters were estimated for each sub grid cell land use category in

CMAQ with bi-directional NH_3 exchange and then aggregated up to the modeled 12 km grid cell.

2.1 Soil and vegetation emission potentials

A NH_3 bi-directional exchange model was developed for the CMAQ modeling system using field scale (~100 ha) observations taken at field sites in North Carolina, U.S.A. (Walker et al, 2012) and published NH_3 air-surface exchange parameterizations (Massad et al. 2010 and references therein). To support bi-directional exchange estimates, two soil layers and a canopy compensation point model was incorporated into CMAQ. Soil NH_4^+, pH, and the soil emission potential (Γ_g ,defined as $[NH_4^+]/[H^+]$) 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 Γ_g due to inorganic fertilization application was calculated following Massad et al. (2010).

(1)

where, N_{app} is the fertilizer application in g-N m^{-2}, θ_s is the soil volumetric water content in m^3 m^{-3}, M_N is the molar mass of nitrogen (14 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 U.S. crops were provide from a CONUS simulation of EPIC (Cooter et al. 2012). Unlike Massad et al. (2010) who used an exponential decay function to adjust Γ_g as a function of time after fertilization, the atmosphere-soil NH_4^+ budget was simulated in CMAQ as being dynamically coupled to hourly soil NH_4^+ losses due to evasion and nitrification, and increases in soil NH_3 due to deposition. The soil NH_4^+ budget was simulated in CMAQ by adding two soil layers, incorporating the EPIC nitrification routines into CMAQ, and coupling the soil NH_4^+ concentration to atmospheric reduced nitrogen deposition and evasion following Ready et al. (1979).

(2)

where, $[NH_4^+]$ is the soil NH_4^+ concentration in moles l^{-1}, $[NH_3]_{soil}$ is the soil compensation point in moles l^{-1} calculated from the solubility and Henry's Law equilibria from NH_4^+ in the soil water solution, $[NH_3]_C$ is the in-canopy concentration (modeled as the canopy compensation point) in mol l^{-1} calculated following Nemitz et al. (2001), R_{soil} is the resistance to diffusion through the soil layer s m^{-1}, and K_N is the nitrification rate in 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 $[NH_3]_{\mathrm{soil}} > [NH_3]_{\mathrm{C}}$, 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_4^+ is readily absorbed on the soil cation exchange complex and should be immobile, thus infiltration of NH_4^+ is not modeled (Sutton et al., 2011). Evasion of NH_3 from the soil NH_4^+ pool in CMAQ is modeling in parallel from both soil pools. This assumes that the rate of gaseous diffusion between soil layers is negligible compared to the evasive and nitrification losses of NH_4^+ from the soil pool.

Emission potentials from NH_4^+ in the vegetation's apoplastic solution ($\Gamma_s = [NH_4^+]/[H^+]$) and non-agricultural 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). Γ_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 Γ_s was modeled as a function of the annual N deposition field and fertilizer application. These changes increased Γ_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. in review and discussed in section 3).

2.2 Emissions and deposition estimate

The bi-directional exchange model in the regional scale air-quality model CMAQ 5.0 estimates a net NH_3 flux. However the base case of this model and most other air-quality models separates the air-surface exchange of NH_3 into emission and deposition fluxes. NH_3 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 bi-directional NH_3 exchange model, the NH_3 air-surface flux is modeled as a function of the gradient between the ambient first layer model concentration at ~20 m 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 μg m^{-3}, all fluxes are in μg m^{-2} s^{-1}, and all resistances are in s m^{-1}.

(3)

where F_t the total air-surface exchange of NH_3, R_a is the aerodynamic resistance, R_{inc} is the in-canopy aerodynamic resistance, C_c is the canopy NH_3 compensation point, and C_a is the atmospheric NH_3 concentration. C_c is a function of C_a, the stomatal compensation point, C_{st}, and the soil compensation point, C_g. All the compensation points are in the units of μg m^{-3} and all resistances are in the units of s m^{-1}.

(4)

where R_b is the quasi laminar boundary layer resistance at the leaf surface, R_{st} is the stomatal resistance, R_{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).

(5)

(6)

where M_n is the molar mass of NH_3 (1.7×10^7 μg mol^{-1}), V_m is to convert l to m^3 (1×10^{-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_4^+ comparable to the estimates used by emissions models where gradient processes are not modeled. This was done to be consistent with NH_3 emissions estimates from fertilizer application due to agricultural management practices used in most air-quality models.

(7)

where $C_c[C_a=0]$ is the compensation point calculated assuming that there is no NH_3 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.

(8)

where C_c is calculated as a function of the ambient atmospheric NH_3 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_4^+ budget.

2.3 Model simulation

Two CMAQ model cases were run to evaluate the application of this bi-directional NH_3 exchange model on a regional scale (1000-5000 km). The bi-directional case modeled dynamic NH_3 emissions and deposition depending on Γ_s and Γ_g and a base case in which NH_3 emissions and deposition were modeled separately. In the bi-directional case, NH_3 deposition increased and evasion decreased the values of Γ_g. The base case used the EPA National Emissions Inventory (NEI) fertilizer emissions estimates and CMAQ's unidirectional deposition velocity parameterization for NH_3. Annual 2002 simulations on the 12km 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_3 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_3 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 bi-directional case. The NEI fertilizer emissions were removed from the bi-directional 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 bi-directional CMAQ using EPIC (Williams, et al., 2008; Izaurralde et al., 2006) as described above and in

Cooter et al., (2012). The vegetation apoplastic emission potential, Γ_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_x wet deposition observations and $PM_{2.5}$ ammonium (NH_4^+), nitrate (NO_3^-) and sulfate (SO_4^{2-}) aerosol monitoring network observations. NH_x 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_x wet deposition fields following Appel et al., (2011).

(9)

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

Modeled inorganic NO_3^-, and SO_4^{2-} aerosol concentrations were evaluated against speciated particulate matter (PM) measurements from the mostly rural Interagency Monitoring of Protected Visual Environments (IMPROVE: Malm et al., 1994) sites and NH_4^+, NO_3^-, and SO_4^{2-} measurements from the mostly urban Speciation Trends Network (STN: Chu, 2004) sites.

3 Results and Discussion

3.1 Model Nitrogen Budget

The annual domain-wide 2002 fertilizer emissions estimated using CMAQ with bi-directional exchange and EPIC simulated fertilizer applications were lower than the totals reported in the

2002 NEI, Table 1. The bi-directional case estimated lower NH_3 emissions in the spring and fall and higher emissions in January and July (Fig. 1). Spring and fall NH_3 emissions in the NEI have a higher degree of uncertainty due to compensating errors related to a lower number of observations than other seasons and low observed precipitation in high NH_3 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 NH3 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_3 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 non-agricultural 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 bi-directional CMAQ (see Section 2.2).

The dry deposition of NH_3 was decreased by 45% across the CONUS domain in the bi-directional case. The reduced modeled NH_3 emissions from fertilized crops were more than offset by the reduction in the dry deposition sinks resulting in a net increase in atmospheric NH_3 in most areas. Overall, there was an increase in NH_x wet deposition of 14% and an increase of 10% in NH_3 and decrease of 7% in NH_4 ambient concentrations in the CONUS domain. The total NH_x deposition was reduced by 15%, total N deposition was reduced by 5% over the base case primarily due to the reduction in NH_3 dry deposition, and bi-directional total NH_3 emissions were reduced by 16%. Thus, the export of NH_x 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 bi-directional NH_3 emissions from agricultural cropping operations and a 5% increase in the domain wide total NH_3 emissions (Dennis et al, in review).

3.2 NH_x wet deposition evaluation

NH_x wet deposition estimated using the bi-directional 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 bi-directional wet deposition cases respectively. The monthly biases in the bi-directional wet deposition correlated well with the monthly meteorological precipitation biases ($r^2 = 0.581$, $p < 0.05$) while the base case NH_x 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 bias in the bi-directional 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_x wet deposition estimates by the bi-directional model parametrization is largely mitigated if one accounts for the biases in the modeled precipitation of the driving meteorological model.

Bi-directional surface exchange improved the model seasonal and spatial comparisons to NH_x wet deposition observations. The underestimation in the NH_x wet deposition in the upper Midwest was reduced in the bi-directional case (Fig. 2). Both models under estimated the wet deposition in the spring/early summer observed at NADP sites (Fig. 3). The bi-directional case NH_x 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 during these periods of 44.7%, 69.3% and 37.8% NMB, respectively. The application of bi-directional exchange in CMAQ, together with the precipitation correction, increased the bias and error in wet deposition from the Mid-Atlantic to the Northeastern U.S. states where the base case was relatively unbiased (Fig. 2). However, improvements in the domain wide model wet deposition performance with the bi-directional NH_3 parameterization offset localized degradation in the model performance and resulted in a net improvement in the regional scale simulation in NH_x wet deposition.

3.3 Ambient aerosol evaluation

NH_3 preferentially partitions to SO_4^{2-} aerosol and in sulfate poor conditions excess NH_3 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_3 were expected and these changes affected the modeled NO_3^- aerosol concentrations. CMAQ NO_3^- $PM_{2.5}$ aerosol estimates were compared to STN $PM_{2.5}$ observations located primarily in urban sites and IMPROVE observations $PM_{2.5}$ located primarily in rural sites. At STN sites the mean annual domain base case $PM_{2.5}$ NO_3^- concentration was nearly unbiased (0.2% NMB) while the bi-directional case introduced a -10.5% negative bias (under prediction). 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 bi-directional case. The over prediction in $PM_{2.5}$ NO_3^- aerosol concentrations in Ohio Valley and Midwest in the base case is reduced in the bi-directional case (Fig. 4). Incorporation of the bi-directional exchange model in CMAQ improved the annual mean $PM_{2.5}$ NO_3^- concentrations at almost all IMPROVE sites, but both model cases still underestimated annual mean $PM_{2.5}$ NO_3^- concentrations at many Western U.S. STN sites (Fig. 4). The positive bias in modeled $PM_{2.5}$ NO_3^- concentrations at IMPROVE sites was reduced in the bi-directional case for almost the entire distribution of the observed concentrations, while the bi-directional case reduced the over prediction in $PM_{2.5}$ NO_3^- aerosol concentrations at STN sites for observed concentrations below approximately 3 $\mu g\ m^{-3}$ and both models under estimated observations with concentrations above 5 $\mu g\ m^{-3}$ (Fig. 5). Both model cases overestimated the $PM_{2.5}$ NO_3^- concentrations in the Mid Atlantic region of the U.S. The bi-directional case underestimate of $PM_{2.5}$ NO_3^- aerosol concentrations at STN sites was due to an over-reduction of the winter (7.2% base and -10.2% bi-directional NMB) and fall (7.2% base and -3.9% bi-directional NMB) base case concentrations. On the other hand, the bi-directional case reduced the summertime base case under prediction (-15.1% base and -4.5% bi-directional NMB) in $PM_{2.5}$ NO_3^- aerosol concentrations (Fig. 6). The bi-directional case reduced the over estimation of $PM_{2.5}$ 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 under prediction of the nitrate aerosol by 15.8% percentage points (from a NMB of 29.2% to 13.4%). At both STN and

IMPROVE sites, the under prediction of $PM_{2.5}$ NO_3^- aerosol during the spring was increased in the bi-directional case (from -7.2% to -23.7% and -6.6% to -23.5% respectively).

These results show that ambient $PM_{2.5}$ NO_3^- aerosol concentrations are sensitive to NH_3 emissions and that the reduction in the seasonal aerosol biases (Fig. 6), have similar patterns as the change in 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 under estimation of the NH_3 emission, or due to the bi-directional exchange parameterization. To evaluate this question, March 2002 was rerun with the bi-directional exchange model with approximately a seven fold increase in fertilizer application. This introduced a positive bias in the $PM_{2.5}$ NO_3^- aerosol evaluation in these bi-directional simulations, but this bias was still approximately half of the bias in the base (82.0% NBM at IMPROVE sites and 35.2% NMB at STN sites) case for March 2002. The increase in NH_3 evasion in March 2002 was not as sensitive to increases in fertilizer applications as the June 2006 simulations reported in Dennis et al. (in review). Thus it appears that the reduction in the NH_3 emissions and, therefore, the bias in the winter aerosol observations were likely due to the parameterization of NH_3 bi-directional exchange and the exponential temperature function of the NH_3 compensation point (Eq. 6).

The gap in observed and modeled $PM_{2.5}$ NO_3^- 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 $PM_{2.5}$ NO_3^- aerosol concentrations than resulted from increases in modeled fertilization rates (Dennis et al. in review). The increase in the $PM_{2.5}$ NO_3^- aerosol concentrations using the Massad et al. (2010) compensation point model may be from the parameterization of Γ_s as a function of the annual total N deposition field. This increased the apoplastic compensation point and atmospheric NH_3 in urban areas where there was often abundant ambient NO_x, sufficient HNO_3 for $PM_{2.5}$ NO_3^- aerosol formation, and higher oxidized N deposition rates relative to the total N deposition budget resulting in an increased Γ_s. The Ammonia Monitoring Network (AMoN; Purchalski et al. 2011) began sampling in the continental U.S. in the fall of 2007, thus long term monitoring data of NH_3 was not available to compare against these 2002 annual simulations. However, simulations are planned to evaluate CMAQ modeled NH_3 concentrations to AMoN observations as well as satellite derived and aircraft observations.

Additionally, multiyear simulations are planned to evaluate how NH_3 bi-directional exchange may alter estimated trends in total N deposition to sensitive ecosystems.

4 Conclusions

A photochemical air-quality model has been coupled with an agro-ecosystem model in CMAQ version 5.0 to simulate the bi-directional exchange of NH_3. This allows for the direct estimation of NH_3 emissions, transport and deposition from agricultural practices from the parameterizations of soil geochemistry, transport and dynamic NH_3 compensation point processes. This coupled modeling system improved the simulations of NH_x 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 bi-directional model can likely be improved with additional soil and vegetation geochemical and ambient NH_3 concentration and flux data to enhance and evaluate these parameterizations. The coupled CMAQ-EPIC model estimates dynamic bi-directional NH_3 fluxes from semi-natural and agricultural ecosystems connecting air-quality and nitrogen deposition to agricultural management practices and variability in meteorology and climate.

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Table 1, Annual 2002 NEI and bi-directional NH_3 emissions estimated for the CONUS domain

	Fertilizer Emissions 10^{12} g NH_3 year^{-1}	% Change from NEI	Total Emissions 10^{12} g NH_3 year^{-1}	% Change from NEI	% of emissions from fertilizer
NEI	1.0	0%	3.5	0	30%
Bi-directional	0.4	-66%	2.8	-20%	13%

Table 2, Annual base and bi-directional Pearson's correlation coefficient, NMB and NME compared to annual NADP observations

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

Figure Captions:

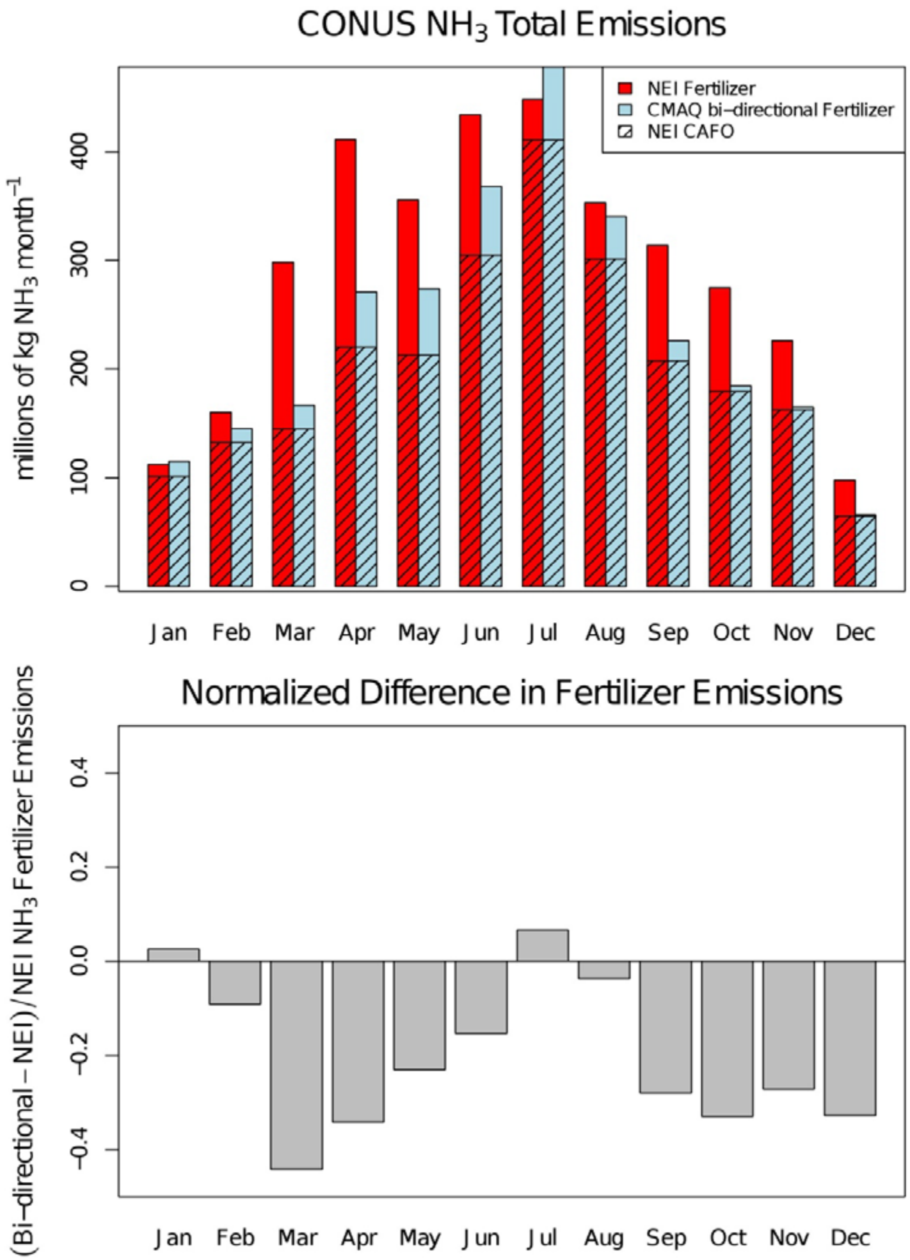
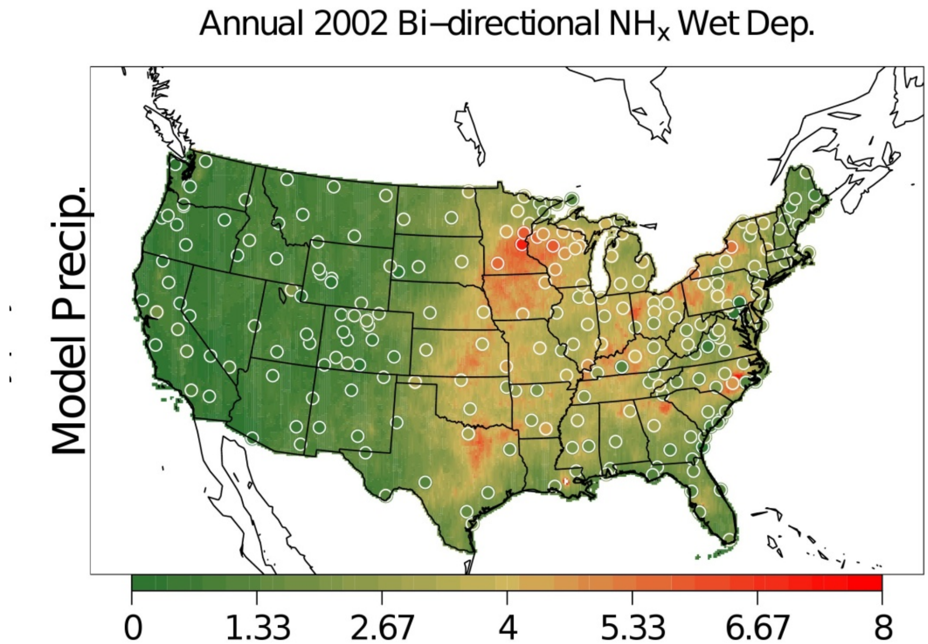
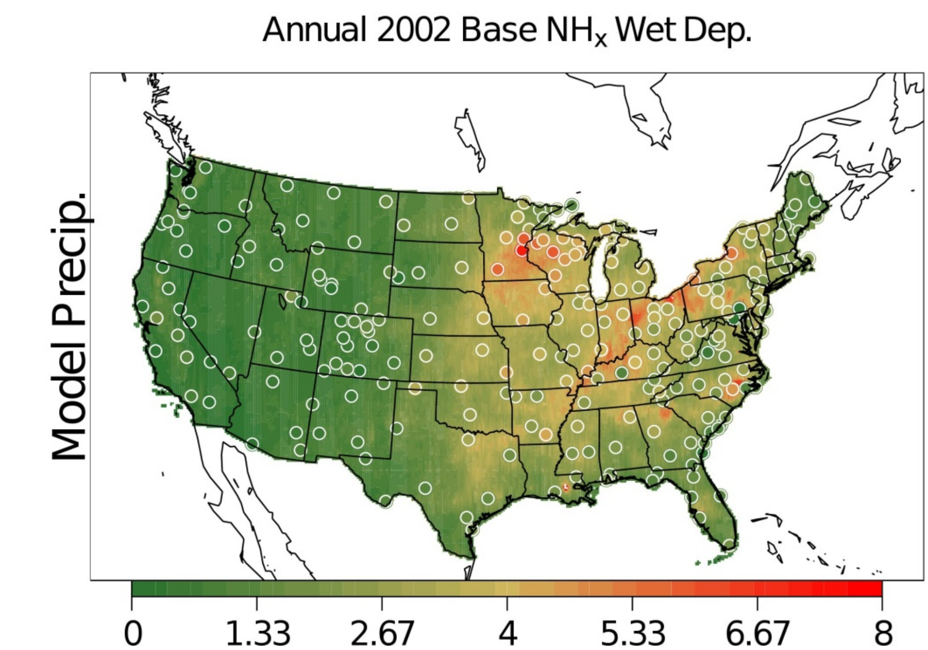


Figure 1, Total domain wide NH_3 emissions estimated by the NEI and CMAQ with bi-directional exchange coupled to the EPIC agro-ecosystem model (top panel) and the fractional difference in the NH_3 fertilizer emissions (bottom panel) on the CONUS domain from the NEI estimated in CMAQ 5.0 with bi-directional exchange.


Annual 2002 Bi–directional NH_x Wet Dep.
Model Precip.
0
1.33
2.67
4
5.33
6.67
8


Annual 2002 Base NH_x Wet Dep.
Model Precip.
0
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4
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6.67
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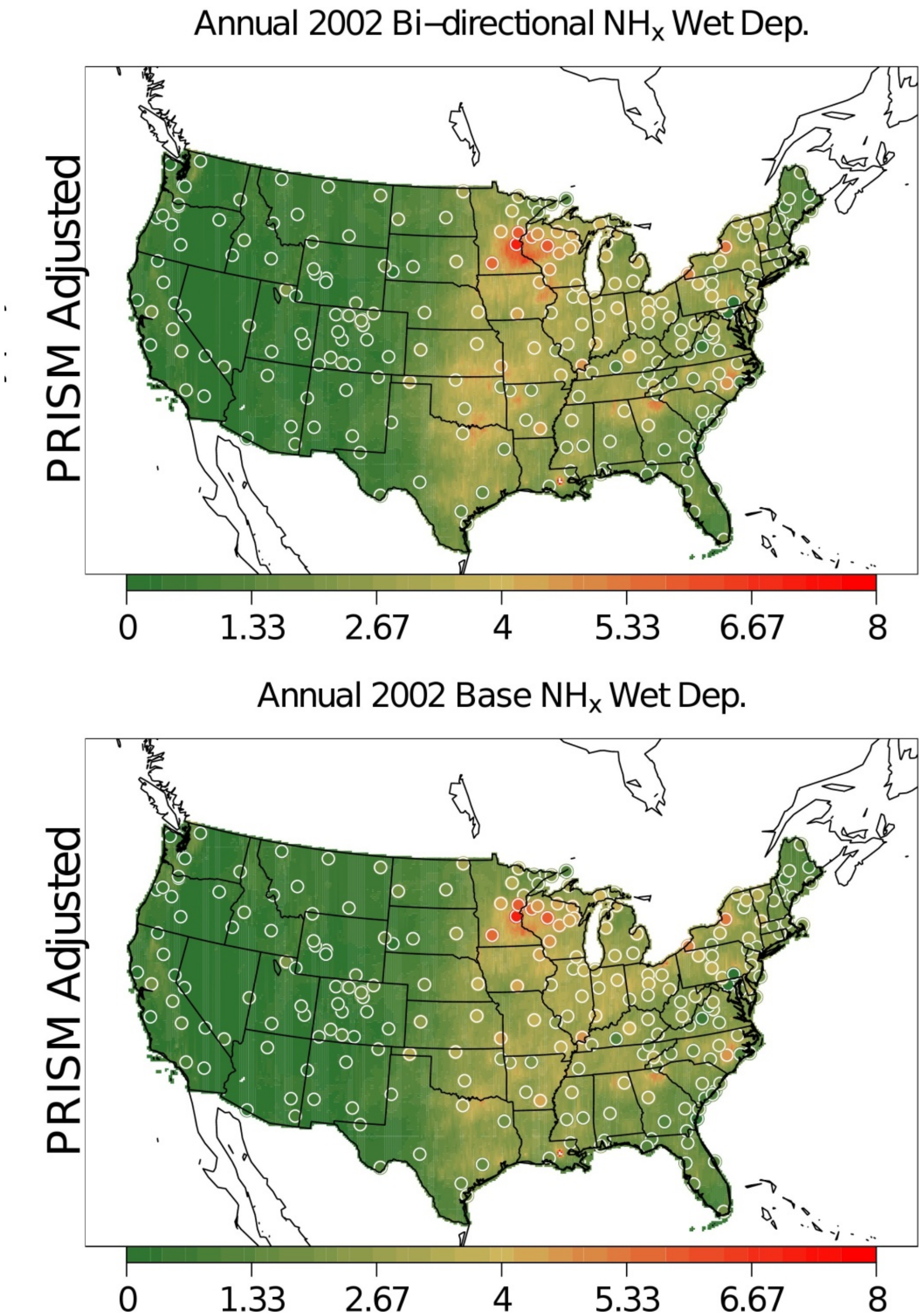
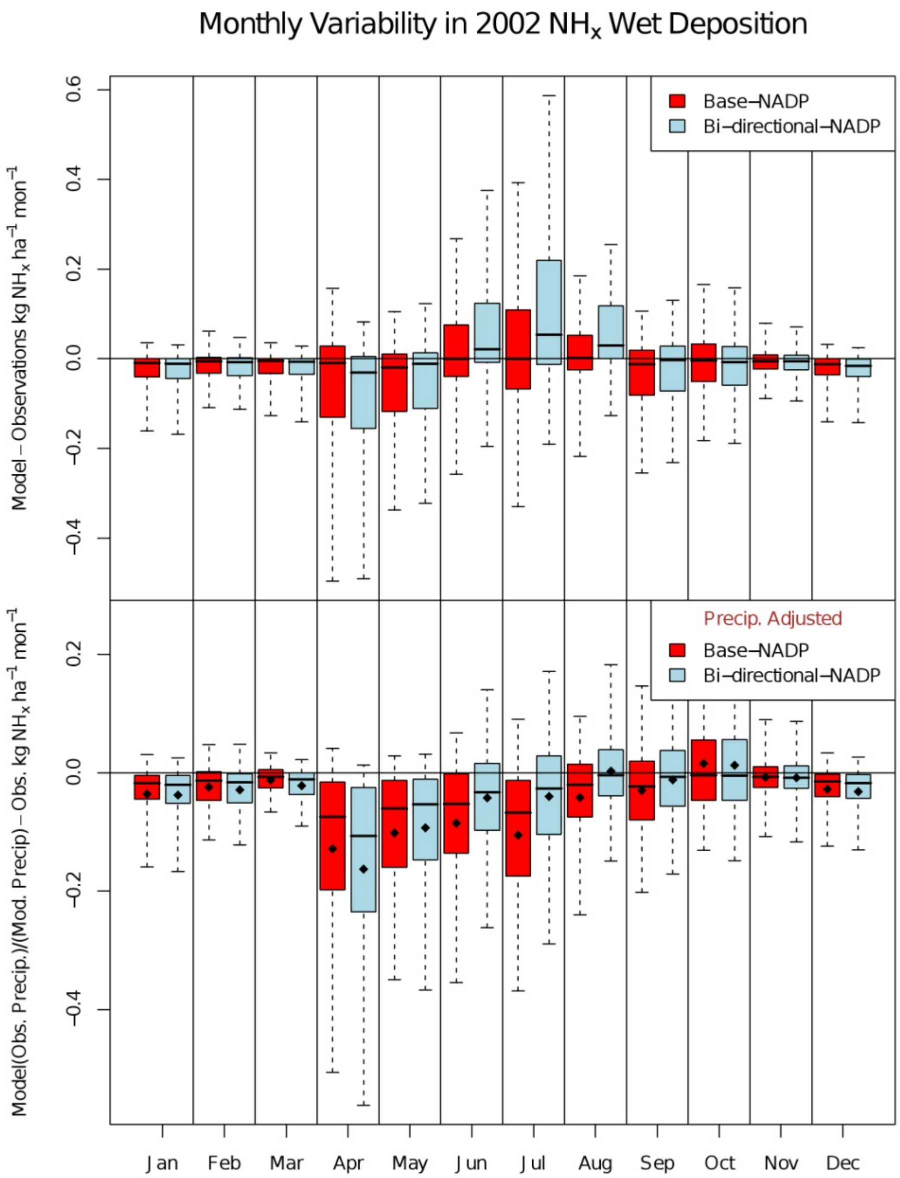


Figure 2, Maps of bi-directional and base annual NH_x wet deposition fields top two panels respectively, annual NH_x deposition maps scaled by annual 2002 PRISM precipitation fields for bi-directional and base cases bottom two panels respectively. Mean annual NADP observations at each measurement site (N = 243) are plotted in the same color scales over the modeled results.



Monthly Variability in 2002 NH_x Wet Deposition
Model – Observations kg NH_x ha^{-1} mon^{-1}
Base–NADP
Bi–directional–NADP
Model(Obs. Precip.)/(Mod. Precip) – Obs. kg NH_x ha^{-1} mon^{-1}
Precip. Adjusted
Base–NADP
Bi–directional–NADP
0.6
0.4
0.2
0.0
−0.2
−0.4
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec

567

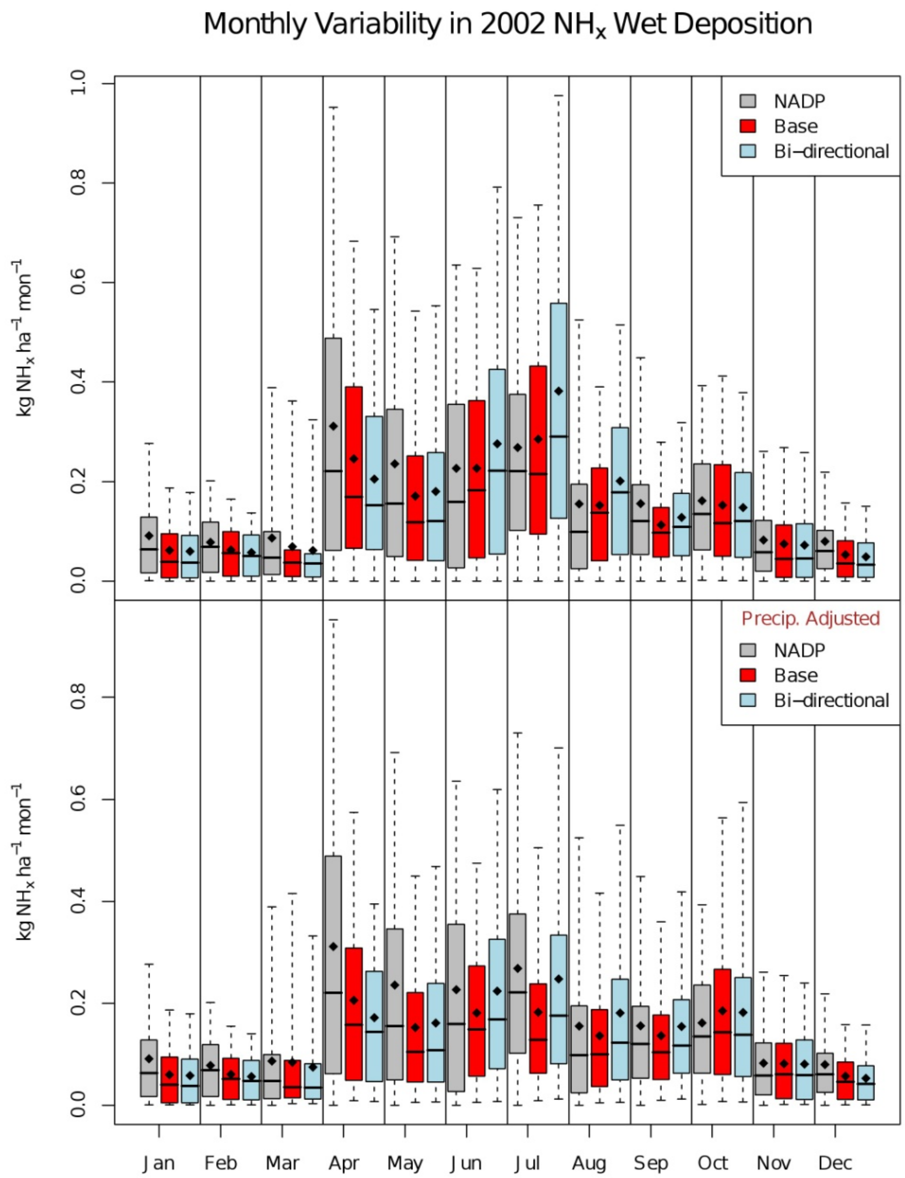


Figure 3, Box plots of NH_x wet deposition monthly model bias (top two panels) and total simulated wet deposition (bottom two panels) paired in space and time with NADP observations (N = 560 to 863 per month) for the CMAQ base case estimates (red) and CMAQ with bi-directional case (blue). Monthly biases 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 precentiles, the horizontal bar represents the median, and the black diamond represents the mean.

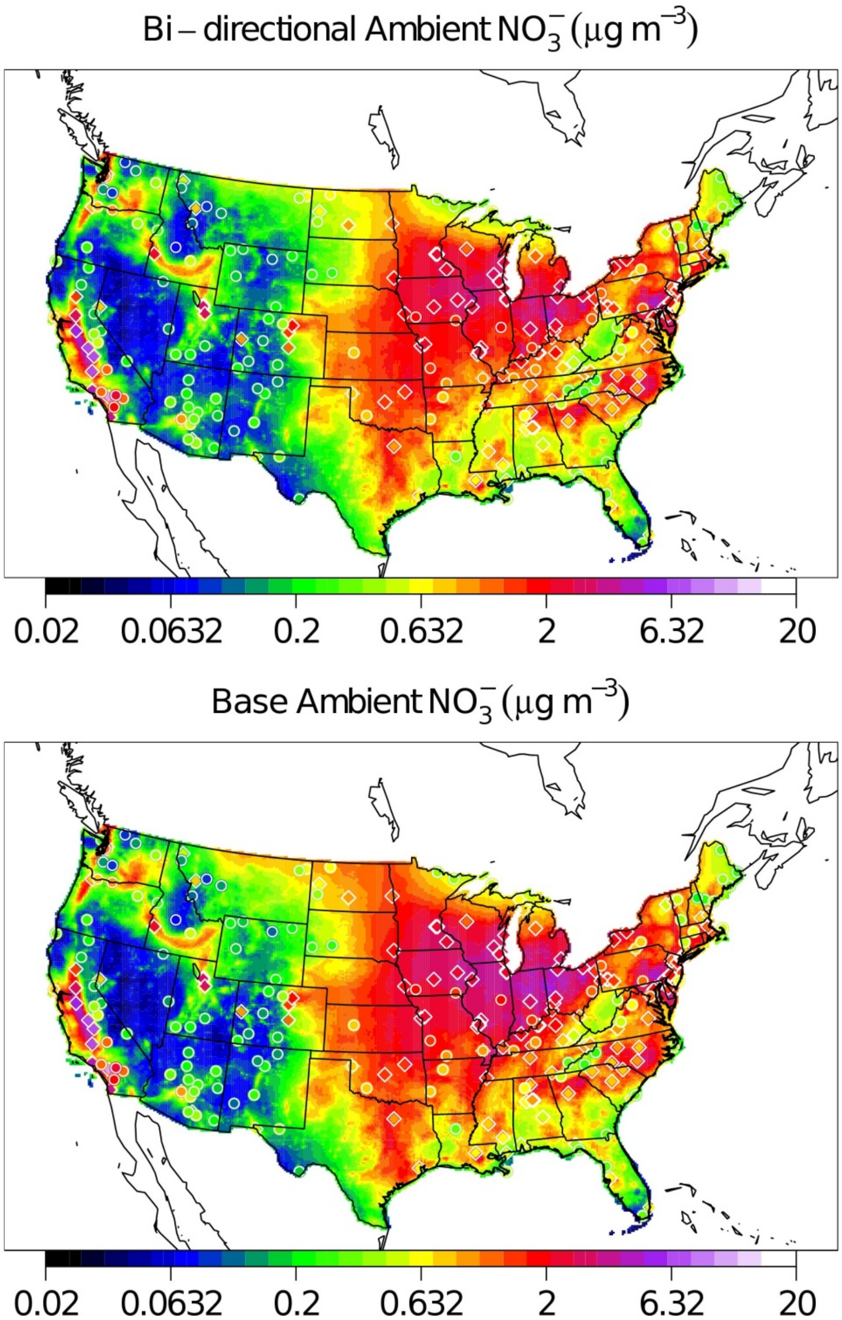


Figure 4, 2002 annual mean NO_3^- aerosol concentration in the bi-directional (top panel) and base case (bottom panel). Mean annual STN observations (N = 208) are plotted over the map as diamonds and IMPROVE observations (N = 156) for each measurement site are plotted over the map as circles. Note that the color scale has been plotted on a log axis.

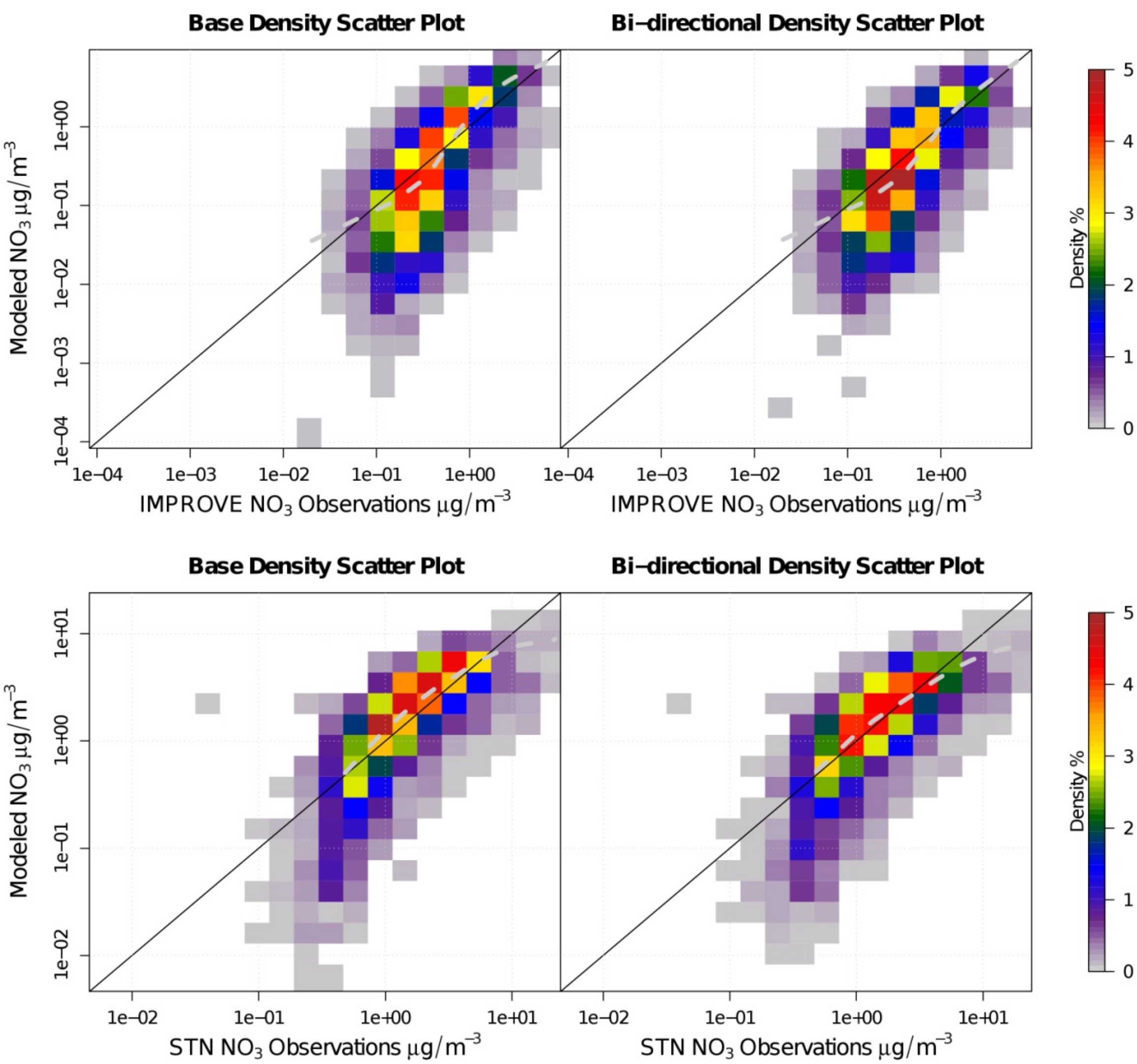
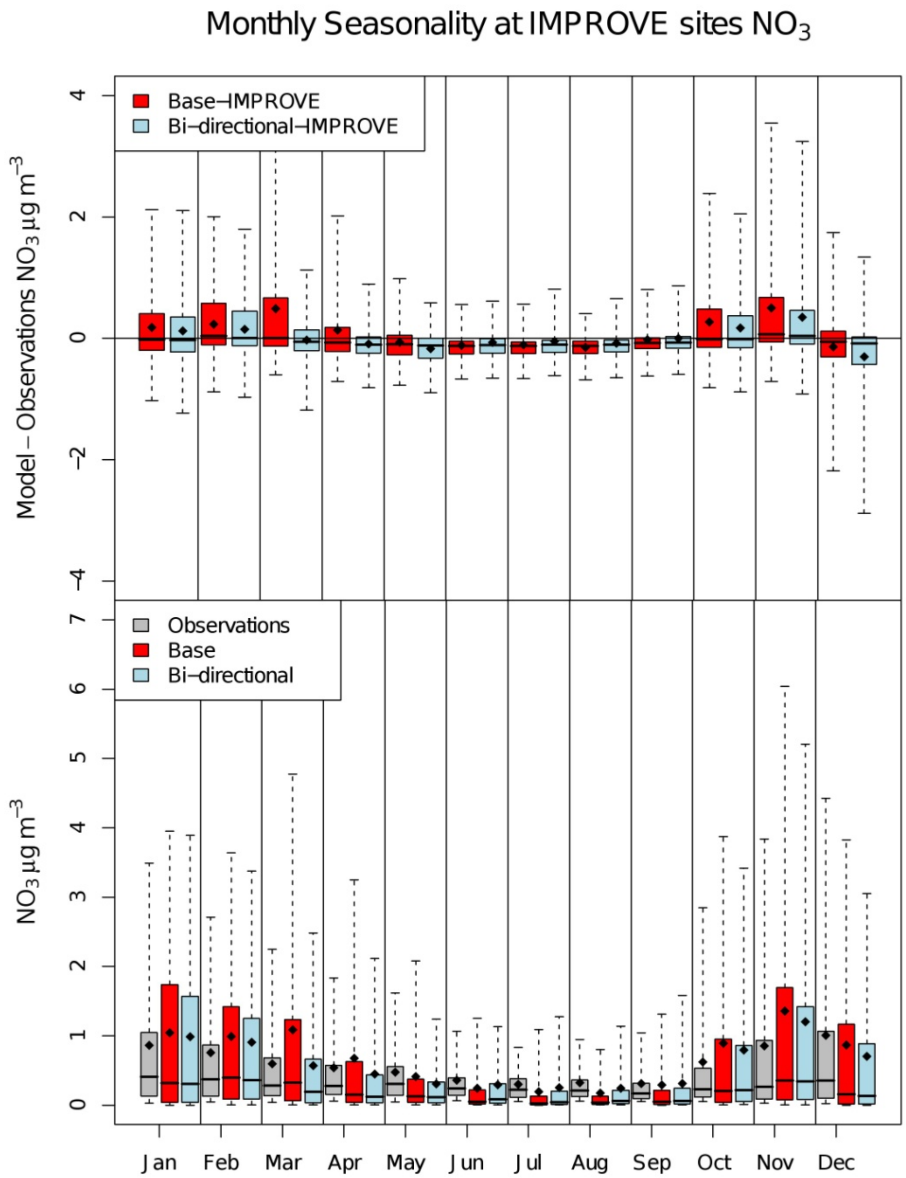


Figure 5, density scatter plots of monthly mean NO3 aerosol observations paired with base and bi-directional CMAQ modeled values at IMPROVE sites, N = 1745 (top panels), and STN sites, N = 2320 (Bottom panels). Annual data were aggregated into 20 bins on a $\log_{10}$ scale spanning the range of the observations and model results, from $1x10^{-4}$ to 10 μg m^{-3} for the IMPROVE data and a $5x10^{-3}$ to 25 μg m^{-3} for the STN data. The dashed line represents a least squares local polynomial regression fit of the model data to the observations.



Monthly Seasonality at IMPROVE sites NO3
Base−IMPROVE
Bi−directional−IMPROVE
Model − Observations NO3 µg m−3
Observations
Base
Bi−directional
NO3 µg m−3
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec

595

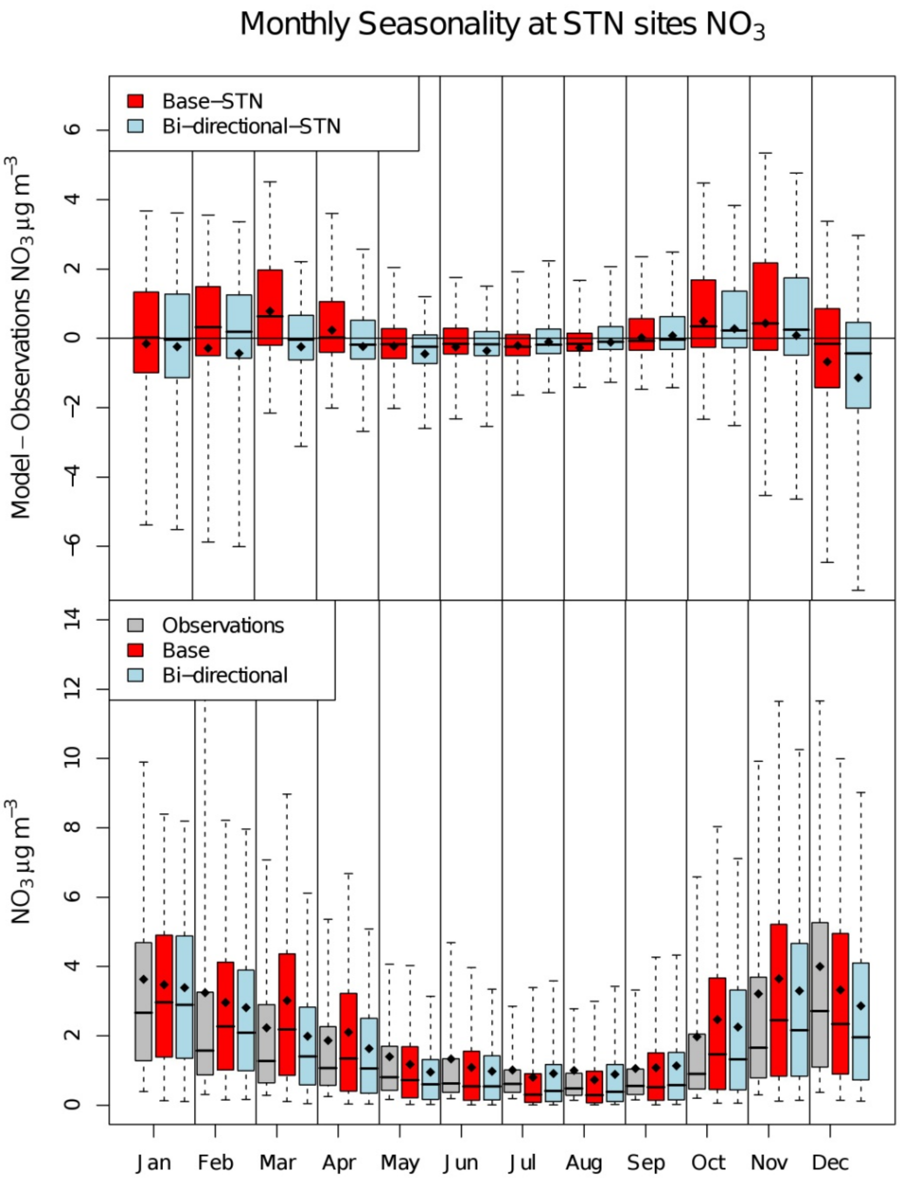


Figure 6, Box plots of modeled monthly ambient NO_3^- aerosol biases and concentrations at STN (top two panels; N = 871 to 1236 per month) and IMPROVE sties (bottom two panels; N = 691 to 1135 per month). The base case is in red, the bi-directional case is in blue and STN and IMPROVE observations is 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 filled diamond represents the mean.