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Seasonal and annual modeling of reduced nitrogen compounds over the eastern United States: Emissions, ambient levels, and deposition amounts

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[1] Detailed description of the distributions and seasonal trends of atmospheric nitrogen compounds is of considerable interest given their role in formation of acidic substances, tropospheric ozone and particulate matter and nutrient loading effects resulting from their deposition to sensitive ecosystems. While the oxidized nitrogen species have received considerable research and regulatory attention over the past several decades, little effort has been devoted toward quantifying the atmospheric budgets of reduced nitrogen compounds (NH_x) associated with emissions of ammonia. The Regional Acid Deposition Model is enhanced to include detailed treatments of the physical and chemical processes regulating the fate of ammonia emissions and to model the interaction and chemical and thermodynamic coupling between atmospheric NO_x-SO_x-NH_x species. To account for uncertainties in magnitude and seasonal variation of ammonia emissions, regional seasonal correction factors for ammonia emissions in the eastern United States are developed through successive model applications and comparison with measurements from regional networks of ambient concentrations and deposition amounts of various species. The resulting ammonia emissions show a distinct seasonal cycle with a maximum in summer followed by spring, fall, and winter. Our calculations suggest that the range between NH_3 emissions during the cool and the warm season is a factor of 3–4. Correlations between model predicted ambient levels, gas/particle partitioning, and deposition amounts with measurements show good agreement on both an annual and seasonal basis with R^2 in the 0.4–0.7 range for most species examined. Both model calculations and measurements indicate that during winter, large portions of the eastern U.S. are characterized by aerosols that are fully neutralized. Our model calculations for emission scenarios representative of the late 1980s–early 1990s period also indicate that reduced nitrogen species contribute 47(±8)% of the total nitrogen wet deposition in the eastern U.S.; this is in good agreement with 43(±9)% inferred from deposition measurements. These comparisons suggest that the model can capture the spatial and seasonal variability in distributions of various model species, the chemical interactions between reduced and oxidized nitrogen compounds in the troposphere, and the compositional characteristics of inorganic aerosol mass in the region. *INDEX TERMS:* 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; *KEYWORDS:* ammonia, aerosols, wet deposition, atmospheric modeling, atmospheric nitrogen

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1. Introduction

[2] The fate of nitrogen-containing species in the atmosphere is of considerable interest given their role in the formation of acidic substances, particulate matter, and tropospheric ozone. Atmospheric deposition of nitrogen

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compounds can contribute significantly to eutrophication and other nutrient loading effects. Most atmospheric nitrogen compounds fall into two broad categories: oxides of nitrogen and reduced nitrogen; the reduced form of nitrogen is primarily dominated by ammonia species (NH_3 + NH_4^+, denoted NH_x). While much attention has been devoted to studying the role of oxides of nitrogen in the atmosphere and toward reducing their emissions [*National Research Council* (*NRC*), 1991], there has been little focus on the cycling of NH_x compounds in the atmosphere and their role in determining budgets of tropospheric acids and particulate matter.

[3] The role of ammonia as an alkaline component of the atmosphere has long been recognized [*Junge*, 1954]. Ammonia is the most abundant gas-phase alkaline species in the troposphere, and can neutralize a great portion of acids produced through the oxidation of SO_2 and NO_x. Emissions of NH_3 are generally associated with intensive livestock agriculture. Current estimates of NH_3 budgets in the troposphere indicate that a significant fraction of NH_3 originates from animal manure [*Dentener and Crutzen*, 1994; *Asman and Janssen*, 1987; *Warneck*, 1988]. NH_3 differs from NO_x and SO_2 in that a larger fraction of NH_3 may be deposited within a short distance of the source, because its emissions are almost entirely at ground level and its deposition velocity for most surfaces is relatively high [*Hov et al.*, 1994a]. NH_4^+ found in the atmosphere originates from the association of NH_3 with acid aerosols and plays an important role in determining the aerosol composition. Knowledge of this composition and consequently deliquescence and optical properties of the aerosols is important to determine their potential radiative effects [e.g., *Boucher and Anderson*, 1995]. NH_4^+ in aerosols can also be transported over large distances and thus may play a significant role in nitrogen budgets in remote regions. Quantification of the atmospheric deposition of both oxidized and reduced nitrogen compounds is of considerable interest because of the detrimental effects related to excess nutrient loading in sensitive ecosystems. The oxidation of NH_4^+ in soils can lead to soil acidification [e.g., *Van Breemen et al.*, 1982]. The availability of nitrogen in coastal waters also promotes production of algae. Large amounts of dead algae in turn lead to oxygen depletion in such water bodies [*Rabalais*, 2002]. *Paerl* [1997] and *Paerl et al.* [1999] suggest that reduced nitrogen species may be more biologically active compared to oxidized forms of nitrogen in such environments, so that not only is it important to quantify the total nitrogen loading, but also the form in which it is delivered.

[4] A detailed understanding of the distribution and fate of reduced nitrogen compounds is desirable given their role in determining tropospheric acidic substances and particulate matter budgets and potential nutrient loading effects in sensitive ecosystems resulting from their atmospheric deposition. Very little observational data on ambient NH_3 levels and deposition amounts are available to adequately quantify their atmospheric budgets. Attempts at detailed three-dimensional modeling of these compounds have also been minimal. Although some modeling efforts have characterized the atmospheric distributions of NH_x compounds over Europe [*EUROTRAC*, 1996; EMEP Programme (Cooperative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe) available at http://www.emep.int] and on global scales [*Dentener and Crutzen*, 1994; *Adams et al.*, 1999], similar studies for characterizing their regional and local distributions over the continental U.S. are lacking. The primary confounding factors limiting such investigations have been the limited understanding, and consequently the model treatment, of the sources, sinks, and chemical interactions of NH_x compounds in the atmosphere. The magnitude and temporal variability of anthropogenic and natural emissions of NH_3 are still rather poorly quantified [*Bouwman et al.*, 1997]. The atmospheric chemical and thermodynamic coupling of reduced nitrogen compounds with the oxides of sulfur and nitrogen, which is now relatively well understood [e.g., *Seinfeld and Pandis*, 1998], also dictates that the modeling framework be capable of accurately representing the oxidant chemistry related to formation of ozone and acidic substances. Further, the local to regional nature of NH_3 emission sources coupled with its atmospheric lifetime, on the order of a few hours, suggest that the modeling framework have sufficient spatial and temporal resolution. A model for atmospheric behavior of NH_x must also be able to describe both the atmospheric transport of NH_3 near a source, as well as the transport of NH_4^+ over long distances.

[5] Over the last decade, emissions of NH_3 in the eastern U.S. have increased significantly as a result of intense growth in the livestock industry. *Aneja et al.* [1998] for instance, estimate that in North Carolina, the nitrogen emitted as NH_3 is comparable to that emitted as NO_x. Current regulations under the Clean Air Act (CAA) directed toward surface O_3 control are likely to reduce NO_x emissions while emissions of NH_3 could grow further in the future. These evolving emission scenarios could potentially have significant impact on tropospheric chemical composition over North America.

[6] In the context of these needs, this study describes the development and enhancement of a comprehensive atmospheric model that is capable of representing the transport, transformation, and deposition of NH_3 and species derived from it. The model also represents in detail, the linkage of NH_3 with the chemistry of oxidant and acidic substance formation. We also present applications of the model to the eastern U.S. and the development of seasonal and annual estimates of both ambient concentrations and deposition amounts for various species and evaluate these model results against measurements from regional networks. To our knowledge, this is the first comprehensive modeling study characterizing the regional distributions of reduced nitrogen species over the eastern U.S. on a seasonal and annual basis.

2. Model Description

[7] Gaseous NH_3 does not exhibit any significant tropospheric chemistry. Its reaction with hydroxyl radical (OH) is relatively slow, with an estimated lifetime of 3–4 months [*Langford et al.*, 1992; *Warneck*, 1988]. Gaseous NH_3 in the atmosphere is incorporated into acidic aerosols and cloud droplets through association with sulfuric acid to form ammonium bisulfate (NH_4HSO_4) and ammonium sulfate ($(NH_4)_2SO_4$); this is an irreversible process [*Tang*, 1980]. NH_3 can also react with HNO_3 to form ammonium nitrate, which may dissociate to ammonia and nitric acid depending

on ambient temperature and relative humidity [*Stelson and Seinfeld*, 1982; *Hildemann et al.*, 1984]. Consequently, the transformation of ammonia to ammonium is closely coupled with emissions of NO_x and SO_2. More importantly, the atmospheric fate of NH_3 emissions depends on the chemical form in which it exists, since the removal processes for each form is significantly different. Gaseous NH_3 has a relatively high dry deposition velocity compared to NH_4^+ aerosol, and consequently has relatively short transport distances. NH_4^+ in aerosols exist primarily in accumulation mode, where the particle deposition velocity is relatively low. Since the primary atmospheric sink is wet scavenging, NH_4^+ aerosol can be transported over relatively large distances under dry conditions. The differences in dry removal rates of ammonium aerosols and NH_3 thus influence the transport distances of airborne NH_x, which in turn is linked to the distribution of NO_x and SO_2 emissions [*Hov and Hjøllo*, 1994b]. Similarly, through its association with HNO_3, NH_3 exerts a direct influence on the lifetime of atmospheric nitrate and, consequently, the total inorganic nitrogen budget in the atmosphere.

2.1. Extended RADM: Process Considerations and Formulation

[8] The Regional Acid Deposition Model (RADM) [*Chang et al.*, 1987] was used as the base model in this study. The RADM is an Eulerian model that was developed under the National Acidic Precipitation Assessment Program (NAPAP) to address regional photochemistry, aqueous chemistry, cloud processes, transport and wet and dry deposition. A primary deficiency in the use of RADM to study NH_x, however, is the lack of representation of the relative roles of two primary atmospheric sinks of NH_3, deposition and conversion to aerosol NH_4^+, which are central in describing the fate of NH_3 emissions. In order to synthesize the current knowledge of the processes governing the fate of inorganic nitrogen in a consistent modeling framework, the RADM was enhanced, by adding several additional modules to represent the various atmospheric physical and chemical pathways governing the fate of emitted NH_3. These processes, their model representation, and assumptions in their formulation are described subsequently.

[9] Compared to several atmospheric species (e.g., O_3, SO_2, NO_2), the dry deposition of NH_3 to most surfaces is a relatively efficient removal process [*Sutton et al.*, 1994]. In conditions of large ambient concentrations, NH_3 is taken up rapidly by moist surfaces that do not have a high pH and through leaf stomata [*Wesley and Hicks*, 2000]. Current estimates of the dry deposition velocity of NH_3 (V_d) are quite uncertain. In recent years, however, significant effort has been devoted to quantify and parameterize the dry deposition velocity of NH_3 for a variety of surface conditions in Europe [*Sutton et al.*, 1993; *Duyzer*, 1994; *Erisman et al.*, 1994; *Fletchard et al.*, 1999, and references therein]. *Sutton et al.* [1994] summarize several observation studies and report typical V_d values in the range of 0.5–5 cm s^{-1} for a variety of natural and forested ecosystems. *Duyzer* [1994] reports an observed average daytime V_d of 1.9 cm s^{-1} over heathland. *Asman* [2001] estimated an average V_d of 1.2 cm s^{-1} for low vegetation landscapes typical in Netherlands and Denmark, and suggests that for regions covered mainly by forests, the V_d could be of the order of 2.5 cm s^{-1}. *Wyers et al.* [1992] and *Duyzer et al.* [1992] estimated NH_3 dry deposition velocities over forests in the range of 3.2–3.6 cm s^{-1}.

[10] The RADM parameterization of dry deposition velocities for various gaseous species, including NH_3, is based on the resistance analog method of *Wesley* [1989] and is detailed in *Chang et al.* [1990] and *Wamsley and Wesley* [1996]. The value of V_d is dependent on three terms representing the bulk properties of the lower atmosphere and the underlying surface: the aerodynamic resistance (r_a), the laminar sub-layer resistance (r_b), and the canopy resistance (r_c). For the various cases considered in this study, over most of the continental eastern U.S. we found the mean daytime values of V_d computed using this approach to be about 0.5–0.7 cm s^{-1}. These estimates are considerably lower than those reported in the measurements discussed earlier, but cannot be verified given the lack of comprehensive observational data on NH_3 deposition velocity over the eastern U.S. These lower estimates of V_d could be related to the computed canopy resistance (r_c) in the model. The r_a and r_b are dependent on prevalent meteorological conditions and standard methods for their estimation are widely used [*Wesley and Hicks*, 2000]. The canopy or surface resistance describes the uptake process at the surface and in turn is dependent on the vegetative characteristics of the underlying surface, with smaller r_c for surfaces with stronger uptake. The r_c paramterization in the RADM was inferred from limited deposition measurements for other species (e.g., SO_2) since reliable measurements of atmospheric NH_3 were lacking. It appears that this approach results in modeled r_c values which are overestimated. To account for this overestimation and to be more consistent with the European measurements, we modified the calculation of the NH_3 deposition velocity through reducing the computed canopy resistance for NH_3, by one-third. Though somewhat approximate, this simplistic approach yields V_d values in the upper range of 1–1.25 cm s^{-1}, while retaining the regional spatial heterogeneity in its distribution due to variations in micrometeorology, land-use, and surface wetness [*Wamsley and Wesley*, 1996].

[11] The thickness of the lowest model layer used in this study was 75 m. In Eulerian model calculations, inadequate resolution of the lowest model layer thickness can potentially create a bias in the estimated dry deposition. The RADM uses a constant flux regime computation to deal with estimation of the surface aerodynamic resistance, r_a, and takes the surface layer thickness into account [*Byun*, 1990, 1991]. The turbulent flux is integrated over the thickness of the lowest cell to compute r_a. During day time conditions when the PBL height is high relative to the height of the lowest layer the constant flux concept is valid (the eddy diffusivity, K_z, near the surface monotonically increases with height) and the bias in V_d is small and typically of the order of ±20% [*Byun and Dennis*, 1995]. Under these conditions ambient concentrations are relatively well mixed in the vertical; thus, the bias in deposition due to layer thickness is small. At night, under stable conditions, the constant flux concept may not be entirely valid, leading to r_a being a factor of 2–4 too high. However, the RADM has been shown to systematically over-predict nighttime surface-level concentrations by fac-

tors of 2 and larger [*Dennis et al.*, 1990a]. For nighttime calculations of deposition these two biases are in opposite directions and to a large degree cancel each other out. Because the nighttime V_d is typically much smaller than the daytime V_d, the overall deposition bias is estimated to be the order of +20% to −50%. Given the large uncertainty in deposition velocity estimates, this degree of bias is considered acceptable.

[12] Unlike most gas phase pollutants, which are consistently deposited, NH_3 is both emitted from and deposited to land and water surfaces [*Quinn et al.*, 1988; *Asman et al.*, 1994]. In characterizing the air-surface exchange of NH_3, several measurement studies point toward the existence of a "compensation point" [e.g., *Farquhar et al.*, 1979; *Lemon and Van Houte*, 1980]. These studies report that, depending on whether the difference between NH_3 concentrations in the air and those in the depositing surface is positive or negative, either dry deposition or emission from the surface could occur. This could imply that there may be no NH_3 dry deposition to surfaces that contain a substantial amount of NH_3, such as fields within a few weeks of spreading of manure or cattle-grazing meadows [*Asman and van Jaarsveld*, 1992]. *Asman and Janssen* [1987] estimated averaged annual reductions in NH_3 deposition on the order of 20% for such fields. Measurements from *Langford and Fehsenfeld* [1992] demonstrated that under circumstances of high NH_3 concentrations, a pine forest acted as a sink, but it acted as a source at low NH_3 concentrations. These studies imply that natural vegetation may be a net sink in the vicinity of the source regions but a net source of NH_3 in regions where un-neutralized acidic aerosols could depress gaseous NH_3 concentrations below the compensation point. The representation of this bi-directional air-surface exchange in regional models employing relatively coarse grid resolution is, however, challenging since detailed information on the land management practices employed for the mosaic of land-use categories represented within each coarse model grid cell is currently lacking. Further, the characterization of this net NH_3 emission from surfaces such as intensively grazed pastures and fertilized croplands require detailed information on the local surface environmental conditions such as form of nitrogen input, NH_x status in the plant leaves, nitrogen status in the soil, plant growth stage, and micrometeorology. Since these conditions vary considerably spatially and temporally, are not typically available, are subject to significant uncertainty, are not likely to be resolved by model grid resolution typical of regional scale models, and since our initial intent is to characterize the mean seasonal and annual features of the distribution of NH_x compounds, in this study we ignore the explicit treatment of such NH_3 emission sources, except where they are already accounted for in the base inventory (e.g., fertilized croplands).

[13] The partitioning of reduced and oxidized nitrogen forms between the gas and the aerosol phases is governed by thermodynamic equilibrium [*Seinfeld and Pandis*, 1998]. To model this partitioning, an additional process module representing aerosol equilibrium was added to the RADM framework. This module calculates equilibrium chemical composition of the sulfate-nitrate-ammonium-water aerosol, and is based on the work of *Saxena et al.* [1986] with further modifications described in *Binkowski and Shankar* [1995] and *Binkowski* [1999]. *Zhang et al.* [2000] have compared the performance of this thermodynamic module with other more comprehensive approaches and found its results to be comparable for the sulfate-nitrate-ammonium-water system.

[14] Two additional species representing particulate NH_4^+ and particulate NO_3^- were also added to RADM. Existing transport modules were modified to account for advective and turbulent transport, and dry deposition of these additional particulate species. The dry deposition velocities for particulate NH_4^+ and NO_3^- were set to be the same as that of SO_4^{2-} already computed in RADM, and is based on the assumption of an internally mixed aerosol. Further, no distinction of aerosol size was retained since inorganic particles over the continental region are primarily in the fine aerosol size fraction. The representation of aqueous chemistry was modified to include the participation of particulate nitrate and ammonium. Further, the cloud transport and cloud scavenging portions of the model were modified to include the impact of these important processes in the representation of particulate ammonium and nitrate and to include their contribution to the eventual ammonium and nitrate wet deposition amounts. This enhanced version of the model is termed the Extended-RADM.

2.2. NH_3 Emission Inventories

[15] It is well recognized that errors in emission inventories can be a source of significant uncertainty in atmospheric chemistry-transport modeling. Approximately 90% of NH_3 emissions in the United States come from animal husbandry and agricultural related sources [*Battye et al.*, 1994]. *Galloway et al.* [1996] estimate that fertilizers contribute 0.5 Tg N/year and animal husbandry contribute 3 Tg N/year to the U.S. emissions while contributions from other sources (e.g., combustion, industry, refrigeration, and human contributions) are relatively small. However, current estimates of the sources (and their strengths) of NH_3 emissions in the United States have significant uncertainty. Uncertainties in estimates of NH_3 emissions are related to the intrinsically local nature of NH_3 sources, making it difficult to construct regional estimates. Another source of uncertainty in regional NH_3 emissions for the U.S. relates to the fact that almost all available NH_3 inventories are based on annual estimates and ignore its intrinsic seasonal variability. This seasonal character of NH_3 emissions results from changes in livestock housing, time of fertilizer application, the growing season, and dependence of NH_3 volatilization on meteorological conditions, especially temperature [e.g., *Aneja et al.*, 2000]. Thus, even if the annual NH_3 estimates are accurate, its uniform application across different seasons in the model, could result in positive/negative bias in the model predictions across different seasons.

[16] In this study, the emissions for NO_x, SO_2 and VOCs are based on the EPA 1990 National Emissions Inventory (NEI) [*Environmental Protection Agency* (*EPA*), 2002]. The estimates for NO_x, SO_2 and VOC emissions in the 1990 NEI evolved from the 1985 NAPAP inventory and were consistent with the changes in emission patterns for these compounds during this period. Initial estimates for NH_3 emissions in this study were based on the 1985 NAPAP inventory since (1) the 1990 NEI NH_3 estimates are largely

untested and inconsistent with the 1985 NAPAP inventory estimates, (2) the 1990 NEI does not partition NH_3 emissions seasonally, and (3) to provide a consistent starting point with previous deposition studies conducted during the NAPAP study, as discussed subsequently. It should however be noted that the 1985 NAPAP NH_3 emissions have been previously found to be biased low. *Chang et al.* [1990] note that the NH_3 emission estimates from the 1985 NAPAP inventory could differ by a factor of 2 to perhaps as much as 5. To account for such uncertainties in NH_3 emissions, *McHenry and Dennis* [1994] developed seasonal correction factors to be applied to in-cloud NH_3 partial pressures in RADM to improve the model's predictions of NH_4^+ wet deposition. While these uncertainties do limit the usefulness of this NH_3 emissions inventory, it does provide a staring point for our modeling analysis. Since these emissions estimates have been previously used in several evaluation studies of RADM predictions of acid deposition [e.g., *Dennis et al.*, 1990a, 1990b], it also provides a basis for benchmarking the Extended-RADM predictions of sulfur and oxidized nitrogen against previous results. Further, it allows for a systematic investigation of development of seasonal correction factors for NH_3 emissions as will be discussed later.

2.3. Aggregation of Seasonal and Annual Estimates

[17] The application of regional atmospheric chemistry transport models that predict photochemistry and deposition on an hourly and finer timescales, to determine long-term relationships between emissions and air quality is severely limited by the computational burden associated with such simulations. While recent advances in computational technology and computer code optimization have enabled the application of regional models over monthly to seasonal scales, their applications to study long-term pollutant behavior and deposition patterns over several seasonal and annual cycles challenge the practical limits of current computer resources. Aggregation techniques that combine a limited number of episodic estimates representing a variety of meteorological cases from such models, into seasonal and annual totals have emerged as useful practical methods to model the long-term relationships between changing emission patterns and regional air quality and atmospheric deposition. These techniques are based on the concept that the atmospheric chemistry, transport, and deposition at a given location is governed by a number of different recurring weather patterns that can be combined to produce a realistic estimate of annual and seasonal synoptic and chemical climatology [*Brook et al.*, 1995a].

[18] The aggregation technique used here has been previously used during the NAPAP study to develop climatological seasonal and annual estimates of acid deposition totals [*Dennis et al.*, 1990b]. The approach involves the selection of a set of events for model simulations that are representative of the cross section of synoptic conditions occurring on a climatological annual cycle. Meteorological cases of 5-day durations during the 1979–1983 period were grouped by wind flow patterns through cluster analysis and sampled proportionate to their frequency of occurrence as detailed in *Brook et al.* [1995a, 1995b]. The model predictions from these are then aggregated using weighted averages to derive the seasonal and annual average estimates.

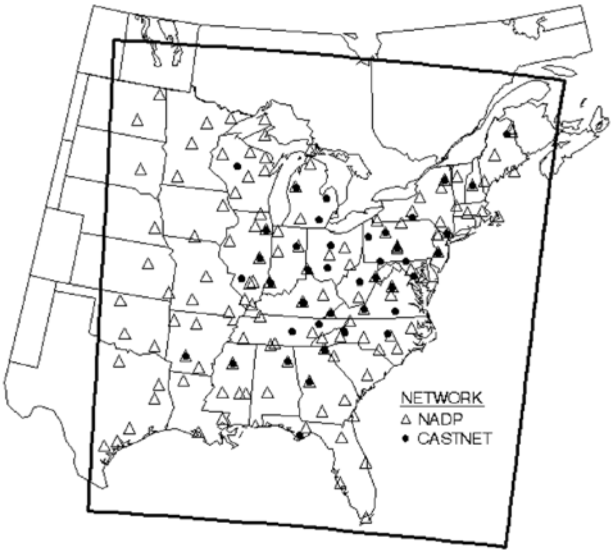


Figure 1. The modeling domain (2560 km and 2800 km in the east-west and north-south directions, respectively) and location of measurement sites in the CASTNet (filled circles) and NADP (open triangles) networks.

3. Results and Discussion

[19] Regional simulations with the Extended-RADM were conducted over the eastern United States to estimate the ambient distributions and deposition amounts of reduced and oxidized nitrogen. The horizontal model domain (shown in Figure 1) was discretized using grids with an 80 km resolution, while the vertical domain from the surface to 100 mb was discretized using 15 layers of variable thickness. The meteorological inputs were derived using the MM4/MM5 modeling system [*Grell et al.*, 1994]. A total of 30 cases, each of 5-day duration, were simulated over this region and constituted the aggregation set; the specific dates for each of these cases can be found in *Dennis et al.* [1990b] and *Brook et al.* [1995a, 1995b]. These were then aggregated to construct seasonal and annual model estimates of both ambient concentrations and deposition amounts.

3.1. Corrections to Regional NH_3 Emissions

[20] To account for the low bias in the NH_3 emission estimates for the U.S. from the 1985 NAPAP inventory, we developed seasonal correction factors for NH_3 emissions through successive applications of the Extended-RADM and systematic comparisons with observed data. This simple "brute-force" inversion analysis allows us to develop a seasonal modeling inventory for NH_3 that, as will be discussed subsequently, provides model results that are consistent with observed values for both ambient concentrations and wet deposition amounts. On the basis of their comparison of RADM predicted NH_4^+ wet deposition with measurements, *McHenry and Dennis* [1994] developed seasonal scaling factors for each 80 km grid cell using a kriging technique. Since their study did not explicitly treat the atmospheric NH_3 pathways, their factors do not accu-

rately represent the bias in the emissions. In contrast to their approach wherein they applied these factors to adjust modeled in-cloud NH_3 levels, as an initial approximation we directly applied their factors to the NH_3 emission fields input to the Extended-RADM, and then refined them through successive model application and comparison with a suite of ambient and wet measurements. In these analyses, we included comparisons of model results against measurements of ambient levels of HNO_3, SO_4^{2-}, NO_3^-, and NH_4^+ and wet deposition amounts of SO_4^{2-}, NO_3^-, and NH_4^+, but gave more weight toward satisfying three specific criteria: (1) the adjustment in NH_3 emissions should not disturb the modeled ambient and wet deposition for sulfate through perturbations in cloud pH related oxidation pathways, such as through ozone oxidation, (2) since NH_3 provides a pathway for formation of particulate NO_3^- the predicted ambient $NO_3^-/(HNO_3 + NO_3^-)$ ratio should retain the spatial regional signature indicated by measurements, and (3) any bias structure in modeled NH_4^+ wet deposition should be similar to that for SO_4^{2-} and NO_3^- wet deposition. This approach provides a physically based, self-consistent constraint for potential growth in NH_3 emissions as opposed to a purely empirically based one in which NH_3 increases are dictated solely by discrepancies between model and observed ambient NH_x levels without accounting for other modeled species.

[21] Table 1 presents the resulting estimated domain mean seasonal adjustment factors for NH_3 emissions in the NAPAP inventory. These results suggest that on an annual basis, the 1985 NAPAP NH_3 emission inventory is a factor of 2.75 too low, confirming suspicions of previous studies [e.g., *Chang et al.*, 1990]. Additionally, the adjustment factors show a pronounced seasonal variation and yield maximum NH_3 emissions during summer, followed by spring, fall and winter. These trends are in agreement with recent NH_3 flux measurements reported by *Aneja et al.* [2000], who observed similar seasonal variation in NH_3 emissions from waste storage and treatment lagoons. It should however be noted that since the ambient and wet deposition measurements used in our simple inversion analysis are for the late 1980s to early 1990s period, the magnitude of regional NH_3 emissions estimated should be taken as representative emissions only for that period. Also, since the method only scales the emissions based on a fixed inventory, growth in local NH_3 emissions are only captured to the extent that they are detailed in the base inventory. The seasonally adjusted NH_3 emissions are used in the model simulations and analysis presented in subsequent sections.

Table 1. Seasonal Correction Factors for the 1985 NAPAP NH_3 Emission Inventory[a]

Season	Factor
Summer	4.9
Fall	1.32
Winter	1.31
Spring	3.5

[a] Estimates representative of late 1980s-early 1990s period.

3.2. Comparison of Model Predictions With Measurements

[22] To assess the performance of the Extended-RADM, model predicted climatological annual and seasonal predictions of both ambient concentrations and wet deposition amounts were compared against measurements from the Clean Air Status Trends Network (CASTNet) (available at http://www.epa.gov/castnet) and precipitation chemistry data from the National Atmospheric Deposition Program (NADP) (available at http://nadp.sws.uiuc.edu), respectively. To develop climatologically representative measurements to compare against the aggregated model results, we used several years of measurements from the CASTNet (1988–1992) and NADP (1984–1993) networks. Recognizing the intrinsic bias in using a small sample of precipitation events to approximate average rainfall (since no single storm event can replicate long-term average rainfall patterns), the modeled wet deposition amounts were scaled by climatologically observed precipitation within each model grid cell following the approach of *Dennis et al.* [1990b]; these were then compared against the measured wet deposition amounts. For the comparisons reported here, measurements from 44 CASTNet sites and 124 NADP sites located within the model domain were used. A 75% completeness criterion was used for averaging the ambient measurements from CASTNet. To minimize possible bias arising from missing data, a more stringent 90% completeness criterion was used in accumulating the NADP deposition measurements. Both networks have excellent spatial coverage across the eastern U.S. (refer to Figure 1) and thus the comparisons provide an opportunity to assess the performance of the model in not only capturing the spatial variability but also seasonal variations in both ambient levels and wet deposition amounts.

[23] The degree of correspondence between the modeled and measured ambient concentrations and wet deposition amounts was examined for various species both on a climatological annual and seasonal basis. In the subsequent discussion, we use the term correlation to denote this degree of correspondence between the model and measurements. Figure 2 presents scatter- plots of the relationship between model predicted climatological annual averages and corresponding measurements of ambient concentrations and wet deposition amounts for selected ions that are important in determining aerosol composition and wet deposition amounts in the eastern U.S. In general, with the exception of NH_4^+ wet deposition, good agreement for model predicted annual estimates are noted with R^2 in the range of 0.6–0.7 for both ambient concentrations (Figures 2a–2c) and wet deposition amounts (Figures 2d–2f). These correlations are reasonable given that they are based on comparing grid-averaged values with point measurements [*Schere*, 1988; *McKeen et al.*, 1991]. The poor R^2 for wet NH_4^+ deposition (Figure 2e) results from discrepancies between model and measurements at a few sites characterized by relatively large model over and under predictions, though the overall correlation is quite good; without the four outliers the $R^2 = 0.36$. Since similar outliers are not noted for SO_4^{2-} and NO_3^- wet deposition, these discrepancies in NH_4^+ wet deposition can be attributed to arise primarily from large uncertainties associated with spatial variability of NH_3 emissions in the inventory. As discussed earlier, the NH_3 emissions correction factors are intended to be regionally representative and do not account for local spatial variability in the emissions.

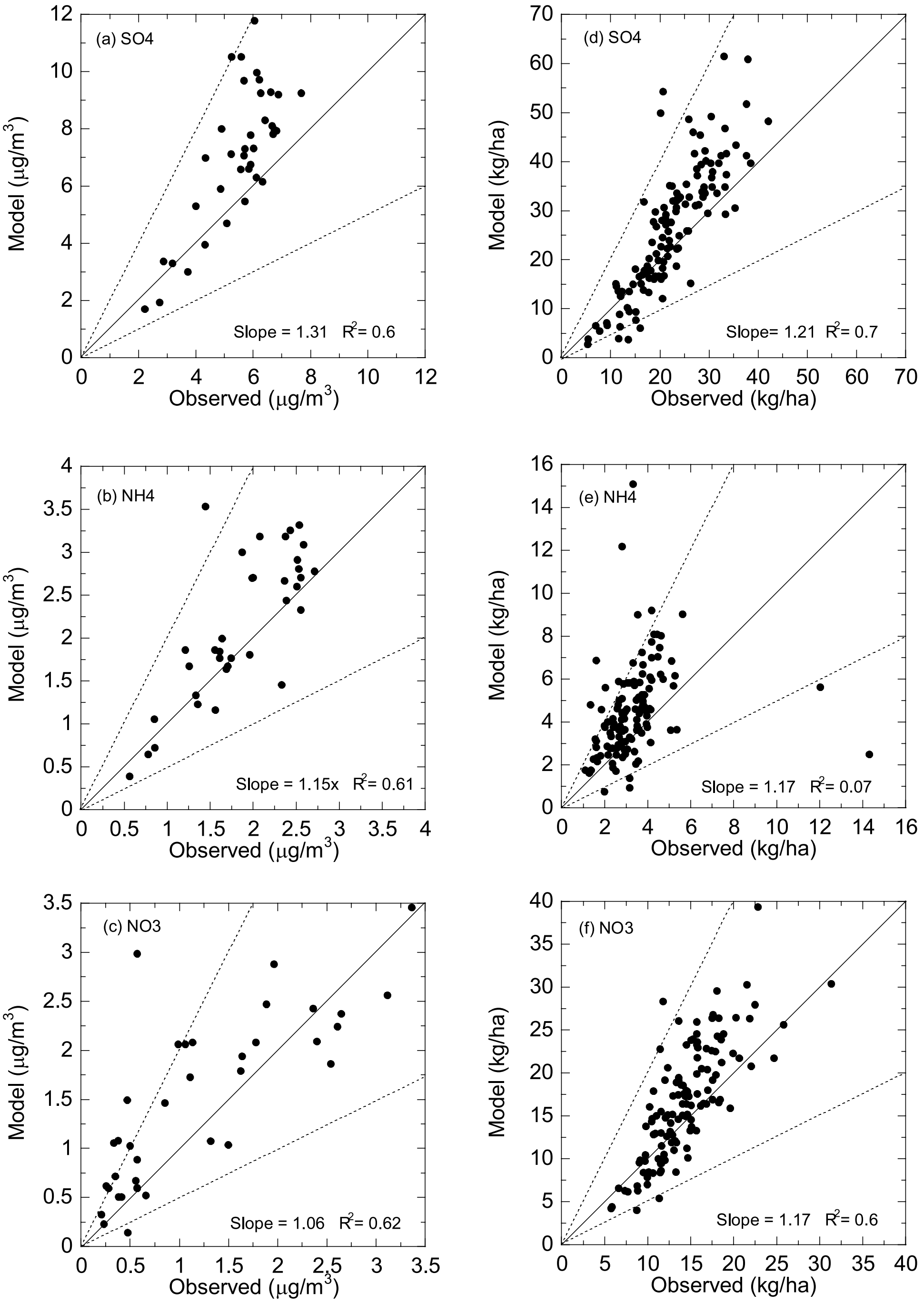


Figure 2. Comparison of model simulated annual climatological averages with measurements: (a)–(c) comparison of ambient levels with CASTNet data; (d)–(f) comparison of wet deposition amounts with NADP data. Solid line indicates 1:1 line, dotted lines indicate 1:2 and 2:1 ratios. Slope and coefficient of determination (R^2) of the model-observed correlation are also indicated.

Thus, in a given region if a particular source category is missing in the base inventory, the corrected emissions would still be significantly under estimated. Consequently, over (under) estimation of local NH_3 emissions can contribute to local over (under) prediction of wet NH_4^+ deposition.

[24] Seasonal variations in temperature, precipitation, NH_3 emissions, atmospheric chemistry and consequently production of sulfate and nitric acid can lead to seasonal variations in the cycling and budgets of both reduced and oxidized nitrogen compounds. To assess the ability of the model to capture such seasonal variability in the cycling of these compounds, Figures 3–6 present comparisons of climatological average seasonal model predictions with measurements for the same set of species as in Figure 2. Moderate to good correlation (R^2 ~ 0.3–0.7) between model and measurements are noted for ambient concentrations of SO_4^{2-}, NO_3^-, and NH_4^+ across the four seasons; similar correlations were also found for model predicted

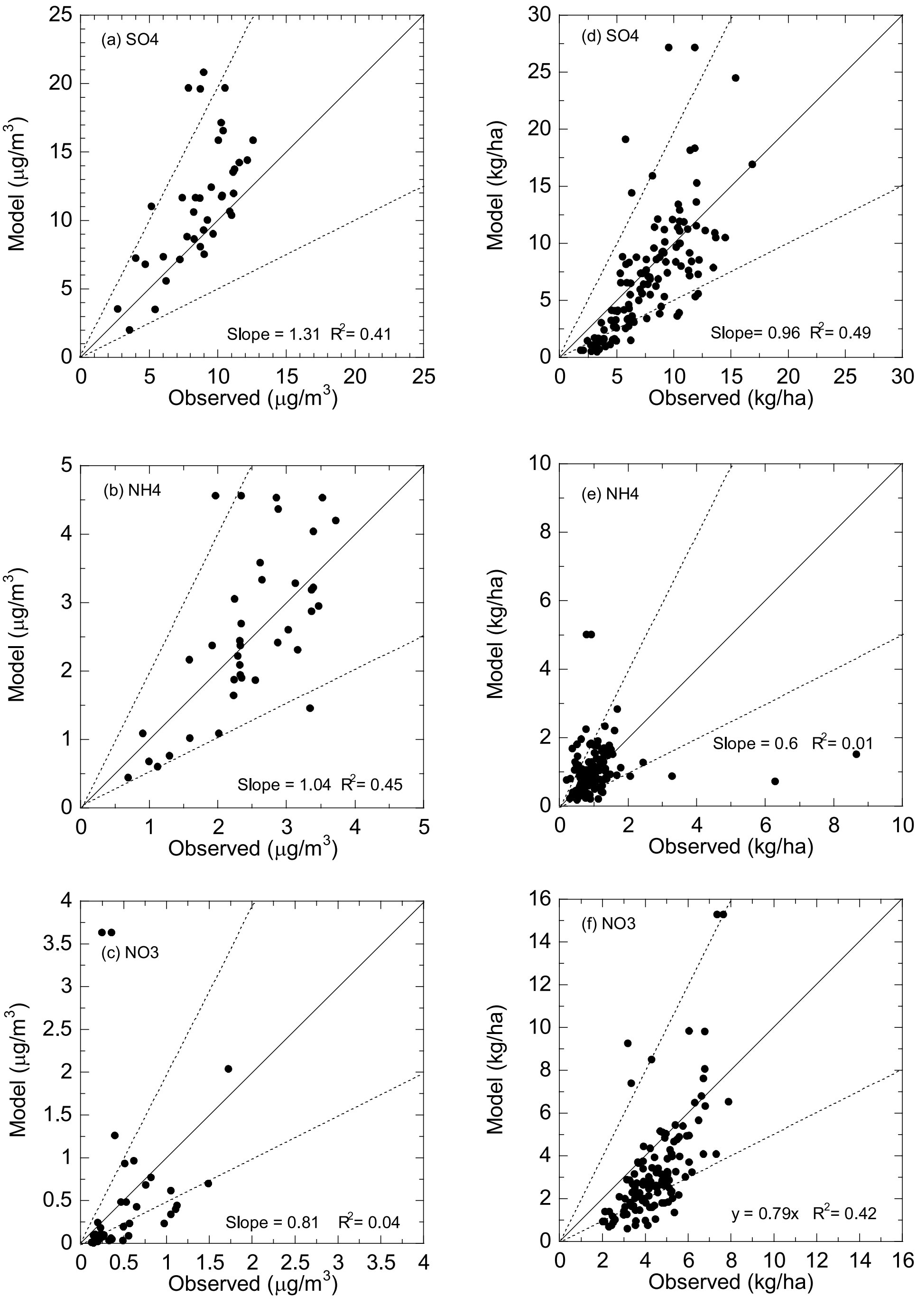


Figure 3. Comparison of model simulated climatological averages for summer with measurements: (a)–(c) comparison of ambient levels with CASTNet data; (d)–(f) comparison of wet deposition amounts with NADP data. Solid line indicates 1:1 line, dotted lines indicate 1:2 and 2:1 ratios. Slope and coefficient of determination (R^2) of the model-observed correlation are also indicated.

SO_2 and HNO_3 (not shown). These comparisons indicate that the model captures both the spatial variability and seasonal trends in the gas-phase concentrations and major aerosol constituents over the eastern U.S. and suggests a sufficient degree of confidence in the model's representation of the chemical pathways associated with the production and partitioning of the inorganic aerosol, which is the major constituent of the total aerosol mass in the region. To further examine the ability of the model to capture the seasonal cycles, Figure 7 presents comparisons of predicted and observed mean ambient concentrations over the study region for various gas and aerosol species. In constructing these mean values, we have considered model predictions only at grid nodes corresponding to locations of measurement sites; also shown are the modeled and observed ±1 standard deviations. Higher ambient levels of SO_2 and NO_3^- are observed during the cool seasons (winter and fall) compared to the warm seasons (summer and spring). In

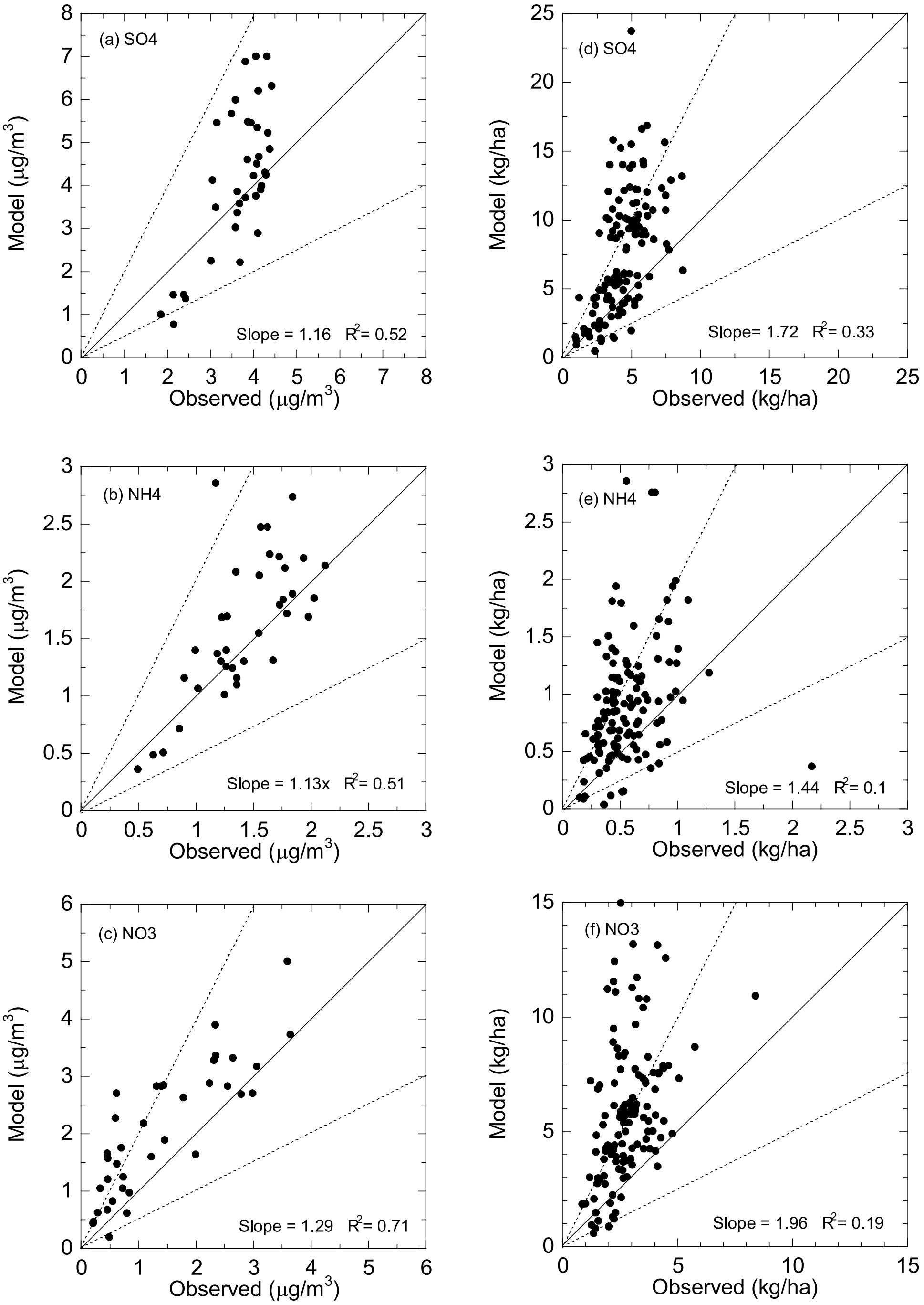


Figure 4. Comparison of model simulated climatological averages for fall with measurements: (a)–(c) comparison of ambient levels with CASTNet data; (d)–(f) comparison of wet deposition amounts with NADP data. Solid line indicates 1:1 line, dotted lines indicate 1:2 and 2:1 ratios. Slope and coefficient of determination (R^2) of the model-observed correlation are also indicated.

contrast, HNO_3, SO_4^{2-}, and NH_4^+ follow an inverse seasonal trend with higher warm season and lower cool season concentrations. Higher HNO_3 and SO_4^{2-} during the warm seasons result from more active photochemistry and temperature dependent oxidation pathways. Higher NH_3 emissions coupled with the availability of SO_4^{2-} and HNO_3 result in higher NH_4^+ levels during the warm period. Lower SO_4^{2-} levels during the cool periods result in higher availability of NH_3 to react with HNO_3 to form particulate NO_3^-. This is consistent with measurements presented by *Sickles* [1999], which indicate complete neutralization of airborne sulfuric acid ($NH_4^+/SO_4^{2-} \sim 2$) during winter, while incomplete neutralization ($NH_4^+/SO_4^{2-} < 2$) during warmer periods. This is also reflected in the modeled-observed correlations for ambient NO_3^-, which show higher R^2 ($\sim$0.7) during the cooler periods (winter and fall) when the airborne NO_3^- spatial signal is stronger. It should also be noted that the CASTNet ambient nitrogen species and SO_2

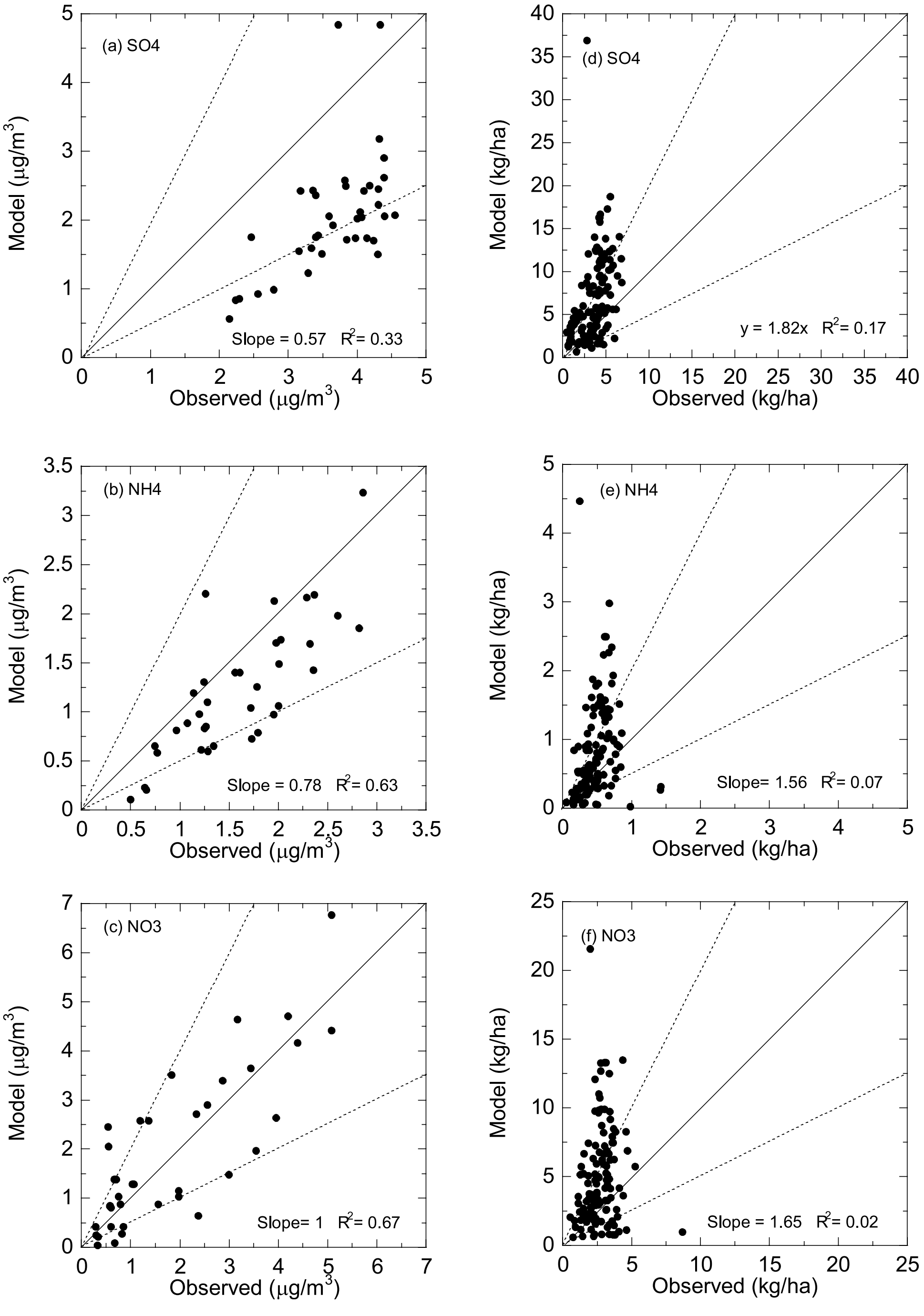


Figure 5. Comparison of model simulated climatological averages for winter with measurements: (a)–(c) comparison of ambient levels with CASTNet data; (d)–(f) comparison of wet deposition amounts with NADP data. Solid line indicates 1:1 line, dotted lines indicate 1:2 and 2:1 ratios. Slope and coefficient of determination (R^2) of the model-observed correlation are also indicated.

data are subject to intrinsic measurement bias associated with instrument precision and also temperature dependent volatilization of particulate NH_4NO_3 [e.g., *Sickles*, 1999). In context of such variability in the measurements, the model-observed correlations and comparison of predicted and observed seasonal trends are in reasonable agreement and further illustrate the ability of the model to represent seasonal variation in the chemical pathways for SO_x and NO_x and its linkage with those for NH_x.

[25] Model wet deposition amounts also show moderate agreement with measured values across the four seasons (Figures 3d–3f, 4d–4f, 5d–5f, and 6d–6f); the comparatively weaker agreement for NH_4^+ wet deposition results from a few outliers as noted previously. A noticable feature from these figures is that the agreement is better during the warmer periods (summer and spring) compared to the cool seasons (winter and fall). In particular, during the cool seasons the model tends to consistently over predict the

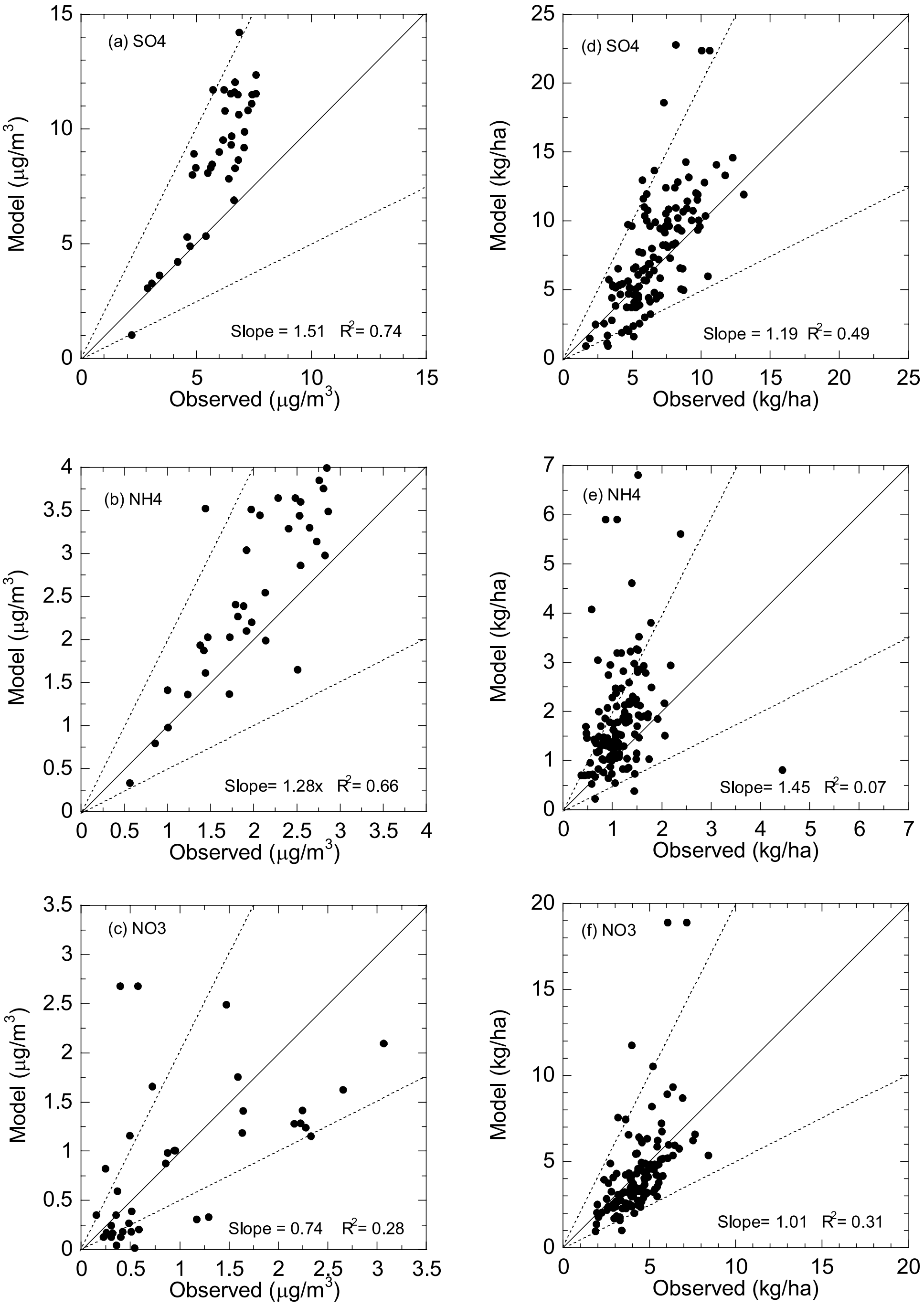
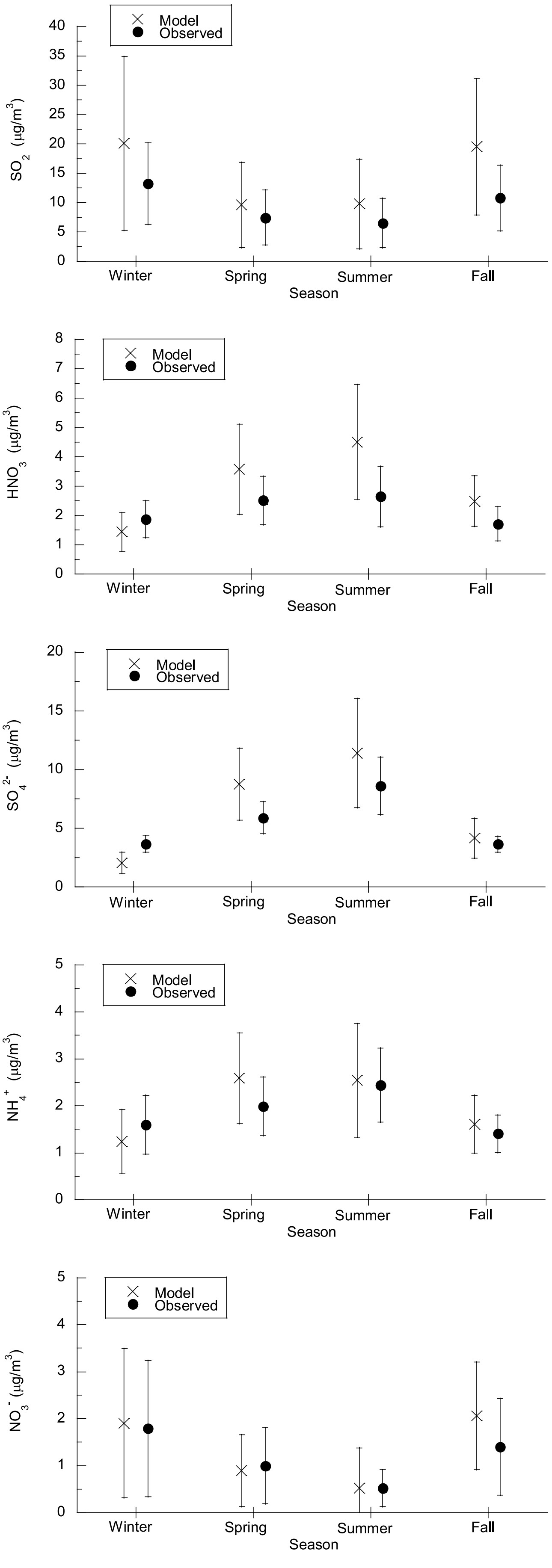


Figure 6. Comparison of model simulated climatological averages for spring with measurements: (a)–(c) comparison of ambient levels with CASTNet data; (d)–(f) comparison of wet deposition amounts with NADP data. Solid line indicates 1:1 line, dotted lines indicate 1:2 and 2:1 ratios. Slope and coefficient of determination (R^2) of the model-observed correlation are also indicated.

wet deposition amounts of all constituents. This consistent over prediction can be attributed to the treatment of clouds and modeled precipitation. In the Extended-RADM, we retained the original RADM cloud module physics. Since the approach primarily treats convective clouds and does not include detailed snow and ice phase microphysics, it systematically overestimates the cloud water and consequently the deposition amounts during the cooler months even when convective activity is not as prominent as during summer. The quantification of the model nitrogen wet deposition bias however is not straightforward. Cross comparison of wet deposition measurements from a co-located NADP and Canadian Air and Precipitation Monitoring Network (CAPMoN) site by *Vet et al.* [1989] and *Sirois et al.* [2000] suggests significant differences between annual depositions measured by the two networks; the NADP measurements were about 16% lower for nitrate and about 32% lower for ammonium. Other comparative studies [e.g.,



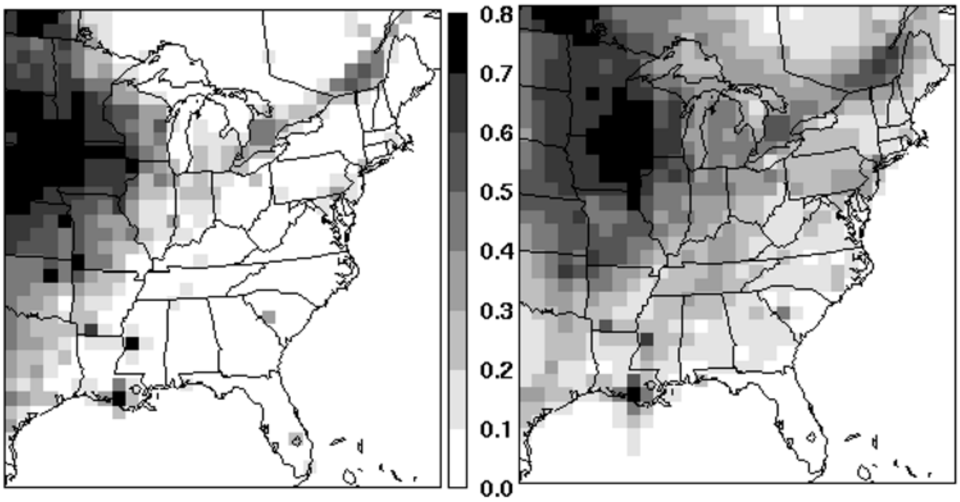
Ramundo and Seastedt, 1990; *Lamb and Comrie*, 1993; *Butler and Likens*, 1998] also report a bias in NH_4^+ wet deposition amounts, with the NADP measurements consistently showing lower amounts, presumably resulting from biological degradation during the relatively long time the samples remain in the field or in transit to the laboratory. The potential variability in the magnitude of the measurement bias, both by site and season is however not well characterized. In view of this intrinsic low bias in measurements, the over-predictions in modeled wet depositions of reduced nitrogen are probably less severe than illustrated in Figures 3–6. Nevertheless, the consistent over prediction in wet deposition across all species indicates a shortcoming of the model parameterization during the cool season.

3.3. Gas-Particle Partitioning of Airborne Nitrogen

[26] Since the atmospheric removal processes for gas and aerosol phase nitrogen species are quite different, the ability to model the relative gas and aerosol amounts of airborne nitrogen species is critical for accurately describing their spatial distributions and quantifying their atmospheric budgets. Figure 8 presents model predicted annual average partitioning ratios for reduced and oxidized nitrogen. The ratio, NH_3/NH_x (shown in Figure 8a), is an indicator of the gas-aerosol partitioning of the emitted NH_3 and consequently has bearing on the model's ability to describe both the atmospheric transport of NH_3 near a source and the transport of NH_4^+ over long distances. Figure 8b presents a similar ratio of the predicted particulate phase nitrate to the total nitrate (TNO3 = NO_3^- + HNO_3). In general, higher values of the NH_3/NH_x ratio are observed in regions with high NH_3 emissions such as Iowa. Additionally, a west to east spatial gradient is also quite prominent in the eastern U.S. This gradient is related to the availability of sulfate, HNO_3, and NH_3. Since the eastern part of the domain is typically characterized by higher sulfate and HNO_3 concentrations, a greater fraction of the emitted NH_3 is converted to NH_4^+, resulting in the observed spatial gradient. The spatial distribution of the NO_3^-/TNO_3 ratio (Figure 8b) is qualitatively similar to that of NH_3/NH_x and is dictated by the relative availability of free NH_3, since HNO_3 is relatively abundant. It may be noted that the depicted ratios along the model domain boundary cells could be influenced by the lateral boundary conditions which were set to clean background conditions; however, the effects of these boundary conditions does not propagate far as the system equilibrates rapidly.

[27] A comparison of the annual modeled NO_3^-/TNO_3 ratio with observations from the CASTNet sites is presented as a scatterplot in Figure 9a; a reasonably good correlation between the modeled and observed values is noted. Figure 9b illustrates the predicted seasonal variation in domain mean of the ratio and its comparison with observed trends. The depicted seasonal cycle in the ratio is also evident from the individual seasonal cycle of NO_3^- and

Figure 7. (opposte) Simulated seasonal variation in ambient concentrations of various species and comparison with observations from the CASTNet network. Filled circles and X's indicate observed and modeled mean values, respectively, while vertical lines represent 1 standard deviation.



(a) NH3/NHx

(b) NO3 / TNO3

Figure 8. Simulated surface level spatial distribution of gas/particle portioning of (a) reduced nitrogen (represented by the ratio NH_3/NH_x) and (b) oxidized nitrogen (represented by the ratio $NO_3^-/(HNO_3 + NO_3^-)$). See color version of this figure at back of this issue.

HNO_3 (Figure 7) with high winter and low summer values. For the eastern U.S., particulate nitrate constitutes approximately half of the total airborne oxidized nitrogen during winter, while it constitutes only 10–15% during summer. Taken together, Figures 8 and 9 suggest that the model is able to capture the linkages between the oxidized and reduced nitrogen forms in the atmosphere and also their relative partitioning between the gas and the particulate phase.

[28] Table 2 presents comparisons of the modeled NH_3/NH_x ratio with limited available observations. Among these, the Bondville, IL and Research Triangle Park, NC measurements can be considered to be regionally representative as they are sufficiently far from major NH_3 emission source regions. Clinton, NC is in the middle of a region surrounded by high density of NH_3 emission sources in eastern North Carolina. Also shown in the table are results from two additional sensitivity simulations wherein NH_3 emissions in a single grid cell in eastern North Carolina were perturbed to examine the modeled reduced nitrogen partitioning and compare with more recent measurements in this region. These perturbations were performed to allow the NH_3 emissions in the grid cell to grow to estimated 1990 (in

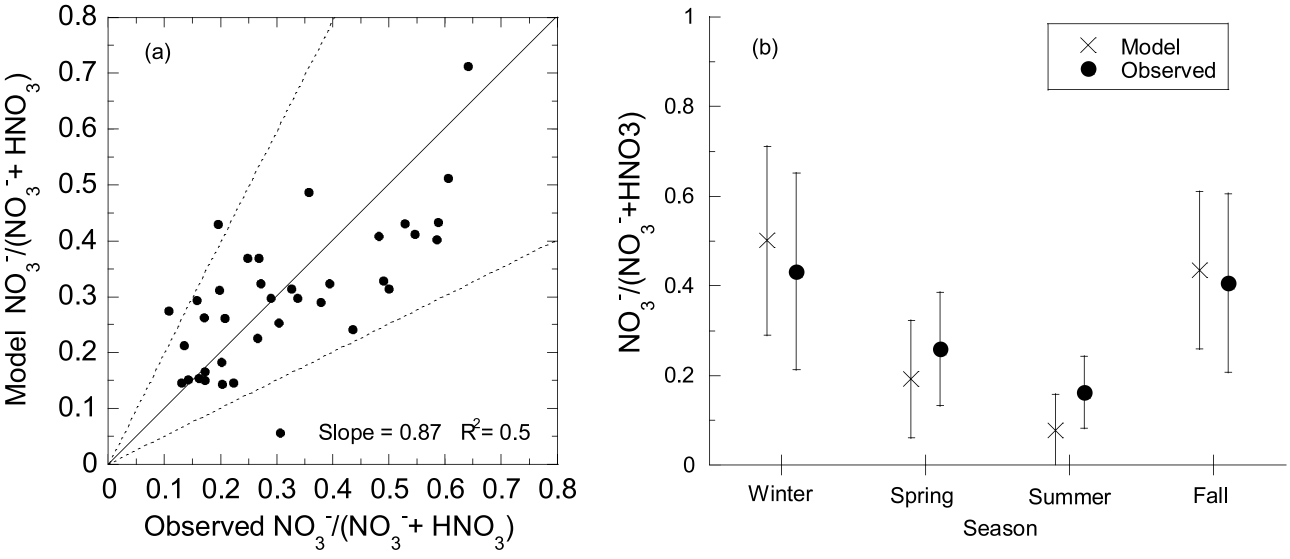


Figure 9. Comparison of modeled and observed $NO_3^-/(HNO_3 + NO_3^-)$ ratio. (a) Scatterplot of annual climatological model and observed ratio; solid line indicates 1:1 line, dotted lines indicate 1:2 and 2:1 ratios; slope and coefficient of determination (R^2) of the model-observed correlation are also indicated. (b) Seasonal variation of model (X's) and observed (filled circles) domain mean ratio; vertical lines indicate 1 standard deviation.

Table 2. Comparison of Predicted NH_3/NH_x With Measurements at Selected Locations

Site Name	Observed	Model (Base)	Model (2×)[a]	Model (4×)[a]
Bondville, IL[b]	0.29	0.31	0.31	0.31
RTP, NC[c]	0.24	0.17	0.18	0.22
Clinton, NC[d]	0.71	0.30	0.38	0.55

[a] 2× and 4× represent sensitivity runs where emissions in a single grid cell in North Carolina were doubled and quadrupled, respectively.

[b] Bondville measurements for years 1989–1990.

[c] RTP measurements for the year 1989.

[d] Clinton measurements for the year 1997.

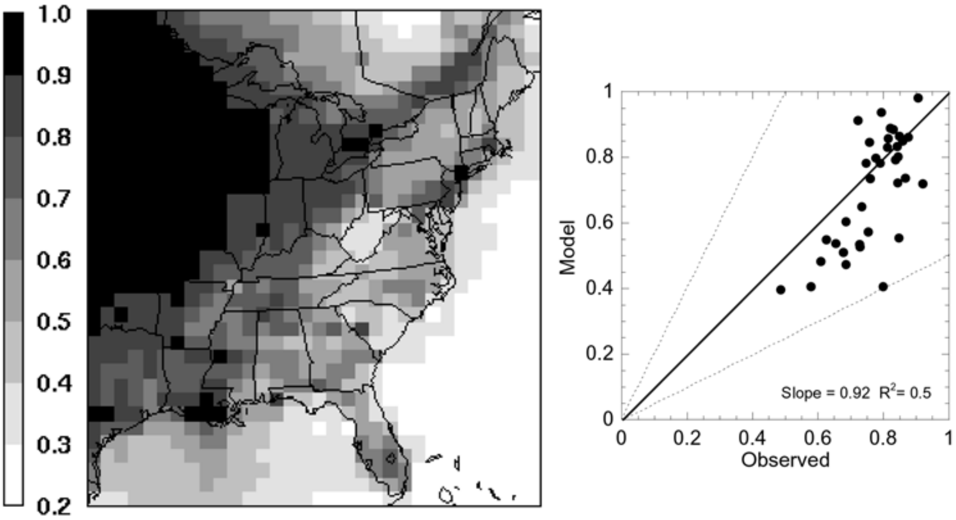
the 2× case) and 1996 (in the 4× case) values inferred from the U.S. EPA National Emissions Inventory (T. Pierce, personal communication, 2000) and to be more consistent with the growth in NH_3 emissions in the region resulting from intense growth in the commercial hog industry since the early 1990s [*Aneja et al.*, 2000]. For most sites, reasonably good agreement between the model and observed values occur. Also, comparison between the model predicted values for the base and perturbation cases at the Clinton site indicate that the model is showing the right sensitivity; it may be noted that an 80 km grid resolution is unlikely to resolve the observations in the vicinity of a major NH_3 source. Additionally, since NH_3 exerts a direct influence on atmospheric budgets of oxidized nitrogen by providing a pathway for formation of particulate nitrate, the ability of the model to capture the gas/particle partitioning of oxidized nitrogen species (depicted in Figure 9) also provides an indirect measure of the ability of the model to represent similar partitioning of the reduced species.

3.4. Coupling Between Inorganic Particulate Species

[29] As indicated earlier the inorganic aerosol composition over the continental eastern U.S. is regulated by the SO_4^{2-}-NO_3^--NH_4^+-H_2O equilibrium, which in turn arises from the chemical and thermodynamic coupling between reduced nitrogen species with oxides of sulfur and nitrogen. The relative amounts of these primary constituents, also determines atmospheric acidity. From a chemical compositional perspective it is desirable to assess the degree to which acidic species (SO_4^{2-} and NO_3^-) are neutralized by airborne NH_4^+. Following *Adams et al.* [1999], we define the degree of neutralization as the ratio of the equivalent of basic species to the equivalents of acidic species,

$$\text{Degree of Neutralization} = \left[NH_4^+\right] / \left(2\left[SO_4^{2-}\right] + \left[NO_3^-\right]\right).$$

A value of one for degree of neutralization indicates that all the sulfate and nitrate is fully neutralized and exists as ammonium sulfate and ammonium nitrate, respectively; lower values indicate more acidic aerosols. This definition provides a convenient measure of the models ability to represent the chemical coupling between the various species and also its ability to represent the inorganic aerosol compositional characteristics. The regional distribution of the degree of neutralization on an annual basis over the continental eastern U.S. is shown in Figure 10a; correlation of modeled values with measurements are illustrated in Figure 10b. The degree of neutralization varies significantly between 40–95% on the regional basis. This spatial variability is captured well by the model (R^2 = 0.5; Figure 10b). The spatial distribution of the degree of neutralization is a strong function of the spatial distribution of the NH_3 emissions and strength as is evident from the west to east gradient, with more neutralized aerosols in regions of higher NH_3 emissions. Seasonal variations in the modeled degree of neutralization and its comparisons with observed values are illustrated in Figure 11. In general the model is able to capture both the spatial and seasonal variation in the degree of neutralization. Both the model and



(a)

(b)

Figure 10. Degree of neutralization (defined in text). (a) Simulated annual average distribution at the surface. (b) Comparison with observed value based on CASTNet data; solid line indicates 1:1 line, dotted lines indicate 1:2 and 2:1 ratios; slope and coefficient of determination (R^2) of the model-observed correlation are also indicated. See color version of this figure at back of this issue.

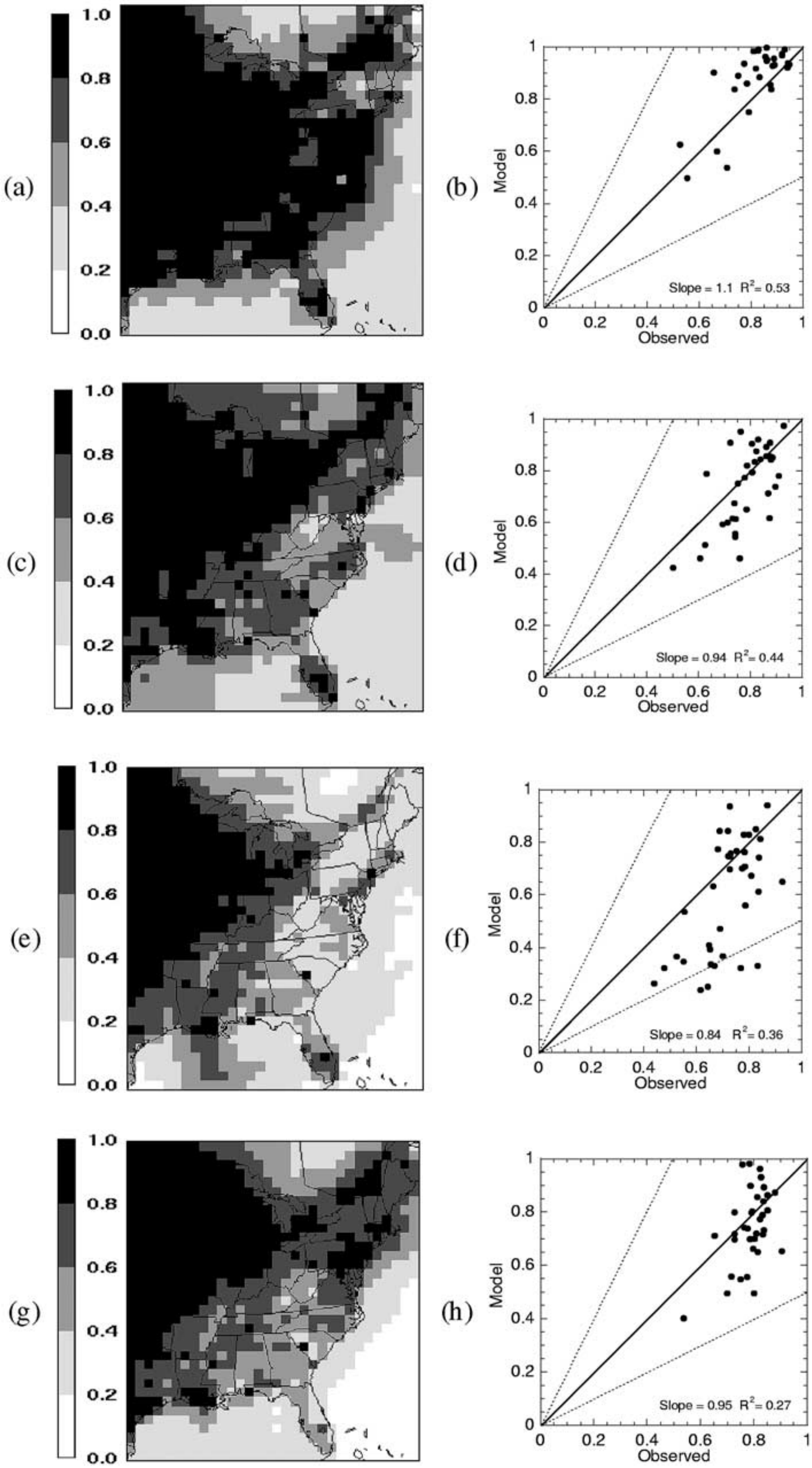


Figure 11. Seasonal variation in degree of neutralization for winter (a, b), spring (c, d), summer (e, f), and fall (g, h). Tiles plot on the left show simulated distributions at the surface. Scatterplots on the right show correlations between these modeled and observed degree of neutralization. See color version of this figure at back of this issue.

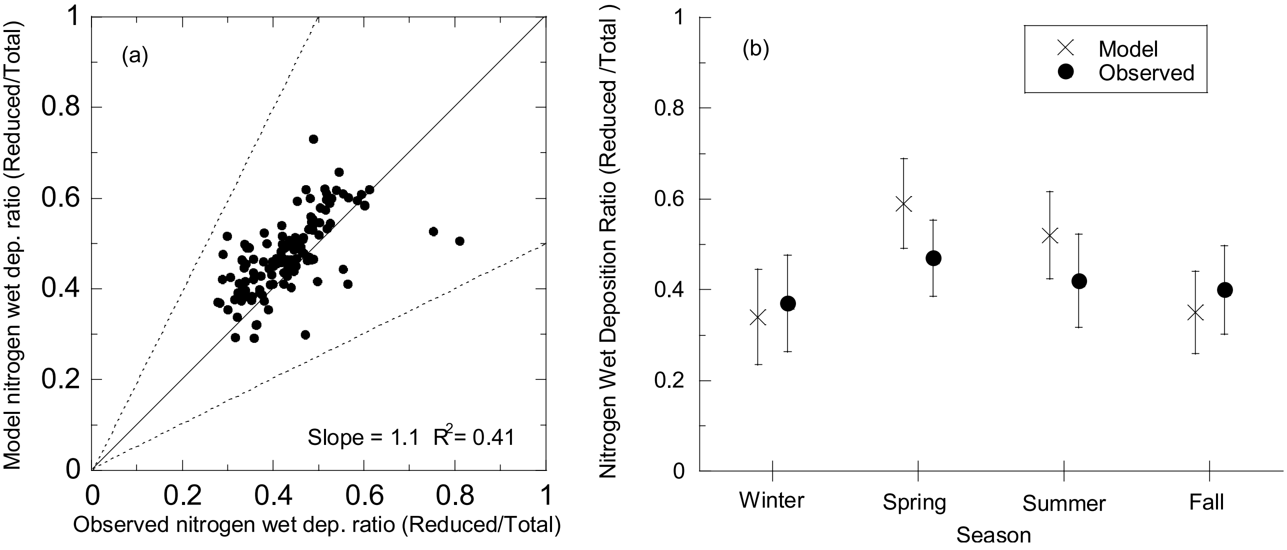


Figure 12. Relative contribution of reduced nitrogen to total nitrogen wet deposition in the eastern U.S. (a) Scatterplot of annual average model and observed values. (b) Seasonal variation of model (X's) and observed (filled circles) domain mean ratio; vertical lines indicate 1 standard deviation.

the measurements show highest degree of neutralization during winter, with large portions of the domain being characterized by aerosols that are nearly fully neutralized (>90%). In contrast, during summer, the degree of neutralization exhibits greater spatial variability resulting from greater spatial variability in airborne SO_4^{2-} levels.

3.5. Fractions of Reduced and Oxidized Nitrogen Wet Deposition

[30] The characterization of relative contributions of reduced and oxidized nitrogen species to total deposition can also provide insights into model performance and its representation of the physical and chemical pathways governing the atmospheric budgets of these species. The relative amounts of reduced and oxidized nitrogen, delivered through atmospheric deposition to sensitive ecosystems is also of interest to ecological studies assessing nutrient loading [*Paerl*, 1997; *Paerl et al.*, 2002]. To help elucidate the ability of the model to characterize the relative amounts deposited, we examined the fractional contribution of reduced nitrogen to the total nitrogen wet deposition, denoted nitrogen wet deposition ratio. Examination of this wet deposition ratio is also useful in understanding the spatial and seasonal behavior in deposition patterns as it effectively reduces the impact of any systematic bias associated with both measurement and model structural attributes. Figure 12 presents comparisons of this predicted wet deposition ratio with that derived similarly from the NADP measurements. Model and observed correlation of the wet deposition ratio based on annual averages is presented in Figure 12a and indicate that the model captures the spatial variability well. On an annual domain wide basis, the model estimates 47 (±8)% of the total nitrogen wet deposition to be in the reduced form, which is in good agreement with the observed value of 43 (±9)% inferred from the NADP data. Comparison of seasonal variation in the predicted domain mean nitrogen wet deposition ratio with measured values in Figure 12b illustrates that the model also captures the seasonal trends with a warm season high and an inter-season variation in the 35–60% range.

4. Conclusions

[31] An enhanced version of the Regional Acid Deposition Model (termed, the Extended RADM) has been developed to aid in the exploration of the cycling of both reduced and oxidized nitrogen in the troposphere. The model has the ability to dynamically represent the various competing physical and chemical processes that govern the fate of emitted NH_3. Model simulations for 30 representative cases were aggregated to construct climatological annual and seasonal averages. Comparison of these model predicted values with measurements from regional networks suggest that the model can capture the spatial and seasonal trends in ambient concentrations and wet deposition amounts of various species. The correlations for these model-observed comparisons were found to be good for most species examined, with R^2 values generally in the range of 0.4–0.7. These correlations are as good as can be expected given that they are based on comparing grid-averaged values with point measurements. Comparatively weaker R^2 were noted between model and observed NH_4^+ wet deposition and arise from uncertainties in the spatial variability in NH_3 emissions.

[32] The 1985 NAPAP NH_3 emissions inventory used in this study, has previously been suggested to be highly uncertain. To account for uncertainties in both the magnitude and seasonal variability of NH_3 emissions in the inventory used, regional seasonal correction factors for NH_3 emissions were developed through successive model applications and detailed comparisons with measurements of ambient levels and deposition amounts. These analyses suggest that on an annual basis, the 1985 NAPAP NH_3 emissions inventory is a factor of 2.75 low. The estimated emissions correction factors show significant seasonal variation and yield maximum NH_3 emissions during sum-

mer, followed by spring, fall and winter, a trend that is in agreement with recent NH_3 flux measurements. These calculations also suggest that the range between summer and winter NH_3 emissions is a factor of 3–4. For European conditions, *Asman* [1992] found a factor of 2.2 difference in NH_3 emissions between the warm and cool months. The larger differences in seasonal variations reported here are due to larger variations in seasonal temperatures in the U.S. and consequently larger variations in NH_3 emissions due to volatilization. It should however be noted that this simple model inversion analysis is dependent on details of the source categories specified in the base inventory and may not accurately account for local variability in emissions associated with missing source categories. This is demonstrated through sensitivity simulations involving perturbations to NH_3 emissions in a single grid cell in eastern North Carolina, a region that has witnessed a significant increase in emissions due to intense growth in the hog industry in the past decade [*Walker et al.*, 2000]. Growing the emissions locally to the estimated values, however, provides model results that are consistent with recent measurements in the region.

[33] The relative amounts of reduced and oxidized nitrogen in the gas and particle phase are also captured well by the model and are in agreement with available measurements. The ratio of particle to total oxidized nitrogen shows a distinct seasonal cycle with a winter high (about 50%) and summer low (10–15%). The NH_3/NH_x ratio exhibits significant spatial variability and is a strong function of the distribution of NH_3 sources and availability of sulfate and HNO_3. The measured magnitude of the ratio in regions of high NH_3 source density is typically >0.9 and decreases rapidly downwind. The gas-particle partitioning of reduced nitrogen compounds represented by this ratio is captured by the model at downwind sites as indicated through comparisons against a limited set of available measurements. The 80 km horizontal grid resolution used in this study however limits the ability of the model to resolve the variability in this ratio in the vicinity of NH_3 sources. We show that the model is able to represent the chemical coupling between reduced nitrogen species and oxides of sulfur and nitrogen in the troposphere and consequently the inorganic aerosol chemical composition over the eastern U.S. by comparing the modeled degree of neutralization of acidic aerosol with that inferred from measurements. The spatial trends in the degree of neutralization show that on an annual basis the eastern U.S. is, by and large, NH_3 limited. Only one geographic region shows full neutralization of the inorganic acidic particles. In that region the model calculations suggest there should be excess NH_3 throughout the year. Both the model calculations and the measurements show highest degree of neutralization during winter, with large portions of the eastern U.S. being characterized by aerosols that are nearly fully neutralized (>90%). However, for the rest of the year much of the eastern U.S. is NH_3 limited.

[34] Our model calculations, which are representative of emissions levels during the late 1980s-early 1990s period, also indicate that on an annual domain wide basis, reduced nitrogen species contribute 47(±8)% of the total nitrogen wet deposition in the eastern U.S. This is in good agreement with the measured value of 43(±9)% that is representative of this period. Our model calculations also suggest that even though the eastern U.S. is NH_3 limited, there is sufficient NH_3 to affect dry deposition of reduced nitrogen. On a domain wide basis, the NH_3 dry deposition is estimated to be 1–2 times greater than the NH_4^+ dry deposition, and highlights the importance of including its contribution in nitrogen budget calculations. Since NH_3 dry deposition is not currently estimated by the monitoring networks, reduced nitrogen deposition budgets estimated solely from NH_4^+ wet deposition measurements are likely being underestimated. If the modeled dry deposition amounts are also taken into account, our calculations suggest that the relative proportions of oxidized and reduced nitrogen to the total nitrogen deposition (wet + dry) in the region are 65% and 35%, respectively.

[35] The impact of the uncertainties in the magnitude of NH_3 dry deposition velocity on model predicted ambient levels and deposition amounts were investigated through simulations involving perturbations to the modeled V_d values. With a doubling of the NH_3 deposition velocity, the dry deposition of NH_3 doubles and NH_x dry deposition increases by 85–90%. Ambient concentrations of reduced nitrogen decreases by approximately 10% and wet deposition of ammonium decreases by 10% as well. The total wet + dry NH_x deposition increases by 12% and the fraction of total NH_x deposition accounted for by dry deposition increases from 22% to 36%. The 10% reduction in wet deposition is expected because process budget analyses for ammonia indicate that less then 10% of NH_3 emissions are deposited locally; the other 90% are mixed up from the surface, converted to NH_4^+ aerosol, and escape to long-range transport. Doubling NH_3 dry deposition reduces the NH_x involved in long-range transport by 10%.

[36] Although the model calculations are in good agreement with measurements, they can be further refined through improvements in various aspects of the model. The 80 km horizontal grid resolution used in this study is too coarse to adequately resolve near source local processes. For instance, dry deposition and bi-directional exchange between the atmosphere and the surface may play an important role in regulating the budgets of NH_3 near the source. Additional measurements on surface (land and water) NH_3 fluxes and improvements in specification of land-use could help improve the model representation of such processes. Finer resolution would also enable better resolution of local NH_3 emissions and provide more meaningful comparisons with measurements from sites located in such regions. Updated NH_3 emissions inventories for the U.S. have also become available recently [e.g., *EPA*, 2002]. While these inventories provide more accurate annual ammonia emissions estimates compared to the 1985 NAPAP inventory, they do not apportion the emissions seasonally. Our results have also provided guidance for the use of more sophisticated model inversion techniques in development of seasonal ammonia emissions from these emerging inventories [*Gilliland et al.*, 2001].

[37] Over the past decade, emissions levels of both SO_2 and NO_x in the eastern U.S. have been reduced due to clean air regulations directed toward the control of acid deposition and tropospheric ozone, and are likely to change further in the future. On the other hand, emission levels of NH_3 are likely to increase due to growth in the animal agriculture industry. These evolving emission scenarios will impact

both the tropospheric chemical composition as well as the amounts of nitrogen deposition and the relative fractions of reduced and oxidized forms therein. The Extended-RADM provides a modeling tool to explore such issues in the future.

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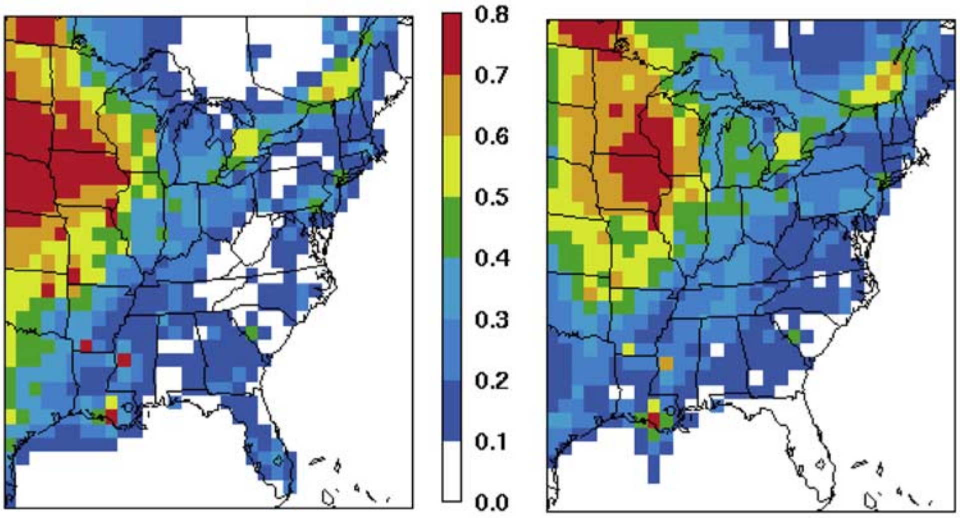
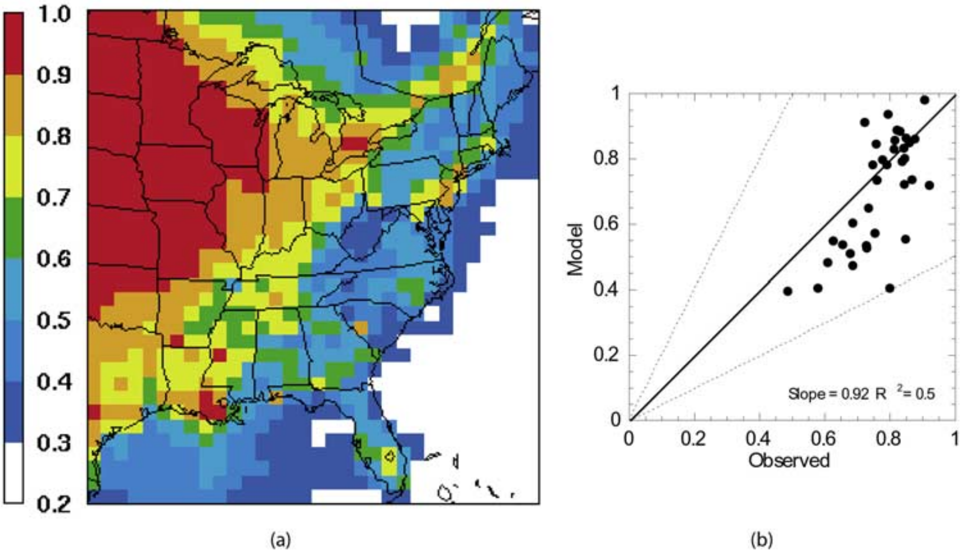


(a) NH_3/NH_x (b) NO_3^-/TNO_3

Figure 8. Simulated surface level spatial distribution of gas/particle portioning of (a) reduced nitrogen (represented by the ratio NH_3/NH_x) and (b) oxidized nitrogen (represented by the ratio $NO_3^-/(HNO_3 + NO_3^-)$).



(a) (b)

Figure 10. Degree of neutralization (defined in text). (a) Simulated annual average distribution at the surface. (b) Comparison with observed value based on CASTNet data; solid line indicates 1:1 line, dotted lines indicate 1:2 and 2:1 ratios; slope and coefficient of determination (R^2) of the model-observed correlation are also indicated.

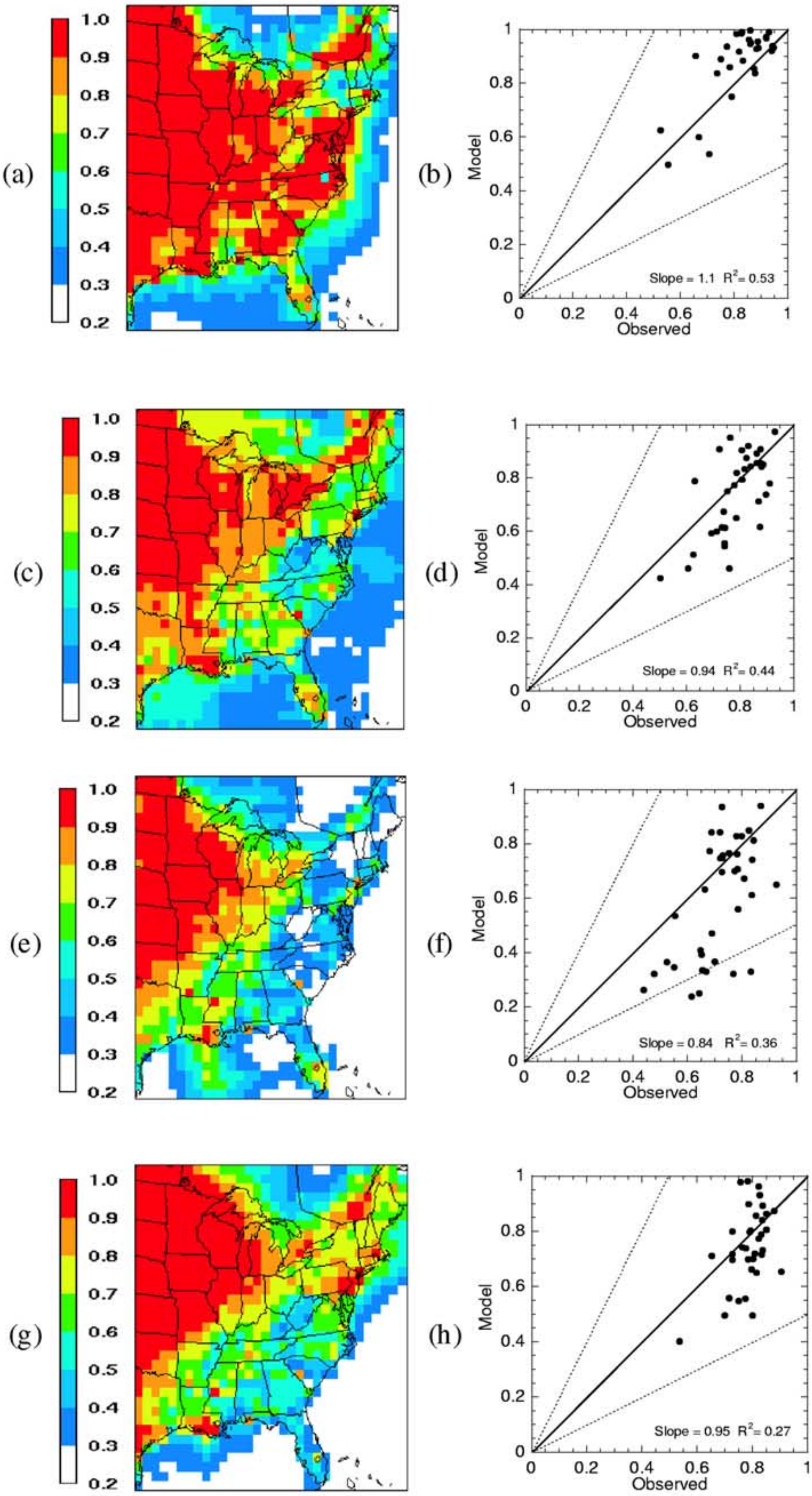


Figure 11. Seasonal variation in degree of neutralization for winter (a, b), spring (c, d), summer (e, f), and fall (g, h). Tiles plot on the left show simulated distributions at the surface. Scatterplots on the right show correlations between these modeled and observed degree of neutralization.