Evaluation of an 18-year CMAQ simulation: Seasonal variations and long-term temporal changes in sulfate and nitrate

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This paper compares spatial and seasonal variations and temporal trends in modeled and measured concentrations of sulfur and nitrogen compounds in wet and dry deposition over an 18-year period (1988-2005) over a portion of the northeastern United States. Substantial emissions reduction programs occurred over this time period, including Title IV of the Clean Air Act Amendments of 1990 which primarily resulted in large decreases in sulfur dioxide (SO2) emissions by 1995, and nitrogen oxide (NOx) trading programs which resulted in large decreases in warm season NOx emissions by 2004. Additionally, NOx emissions from mobile sources declined more gradually over this period. The results presented here illustrate the use of both operational and dynamic model evaluation and suggest that the modeling system largely captures the seasonal and long-term changes in sulfur compounds. The modeling system generally captures the long-term trends in nitrogen compounds, but does not reproduce the average seasonal variation or spatial patterns in nitrate.

1. Introduction

In regulatory applications, meteorological and photochemical modeling systems have traditionally been used to simulate air quality and deposition over relatively short time periods, sometimes over multiple-day episodes (e.g. Zhang et al., 2004; Hanna et al., 2001) and rarely for longer than a year (e.g. Godowitch et al., 2010; Tesche et al., 2006). Generally, these model simulations are performed to test the effects of large-scale changes in emissions, often keeping the meteorological fields unchanged. Such simulations are useful for understanding how the modeling system responds to emissions reductions but do not account for the influence of seasonal and year-to-year meteorological variations that occur in the real world which can have effects that are comparable to, if not larger than, changes in emissions.

Here we describe estimates of wet and dry deposition from an 18-year (1988-2005) model simulation over a portion of the northeastern US. Hogrefe et al. (2009a) previously used these long-term model predictions in combination with available observations to estimate historical fine particulate (PM2.5) mass and species composition. Over this 18-year period several large emission reductions programs were enacted to reduce acidic deposition and improve air quality with respect to ozone (O3), regional haze, and PM2.5. Several of these control programs are briefly summarized here. The goal of Title IV of the 1990 Clean Air Act Amendments (CAA) was to reduce sulfur dioxide (SO2) emissions by 10 million tons below 1980 levels in two phases, targeting large electric utility plants primarily in the eastern US (please see http://www.epa.gov/airmarkt/progsregs/arp/basic.html). Phase I began in January 1995, and resulted in substantial (nearly 40%) reductions in SO2 emissions from these facilities. Phase II called for additional reductions in SO2 emissions and also required a 2 million ton reduction in NOx emissions from power plants by 2000. Larger reductions in nitrogen oxide (NOx) emissions were achieved through the Ozone Transport Commission (OTC) NOx Budget Program implemented in 1999, and the NOx SIP Call Budget Trading program implemented in 2004 which targeted major point sources during the O3 season (please see http://www.epa.gov/airmarkt/progsregs/nox/index.html). Super-imposed on these changes in utility NOx emissions were more gradual decreases in mobile source emissions due to improved...
emissions standards and fleet turnover. While there have been documented net declines in emissions of SO2 and NOx over the past 15–20 years, emissions of NH3 by contrast are highly uncertain (e.g. Gilliland et al., 2006). The NH3 emissions sources are dominated by fertilizer use and animal feeding operations, are much smaller than SO2 or NOx by mass, and have likely been increasing in parts of the country where agriculture has become more intensive.

This paper illustrates the value of both operational and dynamical model evaluation, concepts discussed by Dennis et al. (2010) and Hogrefe et al. (2009b) to describe regional-scale O3 concentrations. We compare model predictions and observations of S and N compounds in wet and dry deposition on an average basis using standard statistical and graphical analysis (operational evaluation), as well as examine large-scale and long-term changes in these parameters in the presence of emissions and meteorological variability (dynamic evaluation). Comparison of these seasonal and long-term modeling results with observed changes in deposition can help provide confidence in the use of photochemical grid models for regulatory and research purposes.

2. Databases

2.1. Model description

The reader is referred to Hogrefe et al. (2009a) for details of the modeling setup, and a brief overview is presented here. The modeling system used in this study consists of the non-hydrostatic fifth-generation mesoscale model (MM5; e.g. Dudhia, 1993) regional meteorological model; the Sparse Matrix Operator Kernel Emissions (SMOKE; e.g. Houyoux et al., 2000) processing system for anthropogenic emissions; the Biogenic Emissions Inventory System (BEIS3.12; e.g. Schwede et al., 2005) for natural emissions; and the Community Multiscale Air Quality (CMAQ v4.6; e.g. Byun and Schere, 2006) model to predict hourly concentrations and wet and dry deposition of about 80 gas-phase and aerosol species. The model utilized 15 vertical layers up to ~15 km, with the top of the lowest layer set to 38 m. Gas-phase chemistry in CMAQ was simulated using the CB-IV mechanism (Gery et al., 1989), while aerosol chemistry was simulated with the “aero4” module (Byun and Schere, 2006). The simulations also included aqueous phase chemistry. The model simulation covered January 1, 1988—December 31, 2005. The simulation was performed on two nested grids with 36 km and 12 km horizontal grid spacing, and only the results from the 12 km domain, depicted in Fig. 1, are included in this analysis.

Because the modeling results are crucially dependent on the variation in emissions, a more in-depth description of the anthropogenic emissions development is presented here. The different components of anthropogenic emissions — point, area, and mobile sources — were available for different discrete years over the 18-year time period, and interpolation had to be performed for years when they weren’t available (Hogrefe et al., 2009a). We are not aware of a single source of anthropogenic emissions suitable for air quality modeling for the entire period. For the purposes of this study, nonroad emissions have been included as area sources. Area and nonroad sources were obtained from the US Environmental Protection Agency (EPA) National Emission Trends (NET) database for 1990 and 1996–2000 (US EPA 2005). The 1990 area sources were applied for 1988 and 1989, while the emissions for 1991–1995 were linearly interpolated between 1990 and 1996. Onroad sources from 1988 to 2000 were estimated from county-level vehicle miles travelled (VMT) data using the MOBILE6 model (http://www.epa.gov/oms/m6.htm). Stack-level point source emissions for 1990, 1996, 1999, and 2001 were available from the NET database. The 1990 point sources were applied for 1988—1994, the 1996 point sources were applied to 1995, 1996, 1999, and 2000 point sources were applied for 2001. Area and mobile sources for 2001 were developed by the US EPA in support of the Clean Air Interstate Rule (http://www.epa.gov/CAIR/technical.html). For the 2002–2005 period, we incorporated the 2002 “base year” and 2009 “future year” emissions developed by the OTC in support of regional haze, O3 and PM2.5 planning (OTC, 2007). The 2009 emissions, which included numerous federal and state emissions reduction programs, were used to linearly interpolate area emissions and VMT estimates for 2003–2005. Finally, the 2000–2005 point source emissions were adjusted when data from continuous emission monitors (CEM) data were available.

Fig. 2a–c displays the annual emissions of SO2, NOx, and NH3 across the modeling domain from 1990 to 2005 in five-year increments. Not surprisingly, SO2 emissions are dominated by point sources, and the modeled SO2 emissions are more than 40% lower in the 2005 portion of the simulation than in the early 1990s. Modeled emissions of NOx have been declining since the late 1980s, with the largest declines (more than 40%) in the mobile and point source sectors. Modeled emissions of NH3 are almost exclusively from area and nonroad sources, with the modeled 2005 emissions about 20% higher than in the early years of the simulation.

2.2. Observational database

Several networks have been monitoring ambient concentrations and wet and dry deposition across North America for several decades, and most of these sites are in rural areas, away from large urban centers and point sources. These networks were established to characterize spatial patterns and seasonal and long-term trends in deposition, as well as assess the effectiveness of regulatory programs such as those in the CAAA. They also provide valuable data for the development and evaluation of photochemical models such as CMAQ.

Weekly average gas-phase and aerosol concentrations and dry deposition have been measured by the Clean Air Status and Trends Network (CASTNet; http://www.epa.gov/castnet) since the 1980s. Gas-phase species include SO2 and nitric acid (HNO3), while aerosol...
sources are shown in gray, and area sources (including nonroad) are shown in black. Obtained for the 28 CASTNet sites within the modeling domain that species include particulate sulfate (SO₄), nitrate (NO₃), ammonium (NH₄), chloride, and base cations. Weekly average air concentrations of SO₂, NO₃ total NO₃ (HNO₃ + particulate NO₃), and NH₄ were obtained for the 28 CASTNet sites within the modeling domain that had at least six months of data during the 18-year period. The CASTNet sites are shown as squares in Fig. 1. It is worth noting that dry deposition is not directly measured, rather it is inferred using local landscape and micrometeorological data. Because dry deposition based on observed data is highly parameterized it is difficult to evaluate model predictions of dry deposition. Also, since air concentrations more easily related to precursor emissions it was decided to examine air concentrations rather than inferred dry deposition in this paper.

Most wet deposition networks analyze precipitation for pH, conductance, and major cations and anions. For this study, precipitation amount and concentrations of SO₄, NO₃, and NH₄ in wet deposition were obtained from several networks with sites in the model domain: (1) weekly data from the National Atmospheric Deposition Program National Trends Network (NADP/NTN; http://nadp.sws.uiuc.edu/ntn; 43 sites), (2) single-storm data from the Atmospheric Integrated Research Monitoring Network (AIRMoN; http://nadp.sws.uiuc.edu/airmon; 6 sites), and (3) daily data from Environment Canada’s National Atmospheric Chemistry (NAtChem) Precipitation Chemistry database (http://www.msc-smc.ec.gc.ca/natchem/precip/index_e.html; 10 sites). Three of the AIRMoN sites — Oxford, OH, Penn State, PA, and Underhill, VT — are collocated with NADP/NTN sites. A total of 59 wet deposition sites were used in this analysis, shown as circles in Fig. 1.

The observed daily and weekly data were examined in several different ways. First, all concentrations were aggregated into seasons defined as winter (January–March, ”JFM”), spring (April–June, “AMJ”), summer (July–September, “JAS”), and fall (October–December, “OND”) over the 1988–2005 period, and average values for each season were computed at each site. The same calculation was also performed for the model data, considering only those time periods when valid observed data were collected. The average seasonal concentrations of each S and N species were compared using the data from all sites. The differences in the concentrations before and after the large emission reductions from Title IV of the CAAA were then computed at those sites having three years of data prior to (1992–1994) and after (1995–1997) this reduction program was instituted. We also examined the spatial patterns in each parameter by examining the average annual concentrations for a given year, namely 2005. Finally, the long-term trends in the daily/weekly data were examined using the non-parametric Seasonal Kendall Tau test (Hirsch and Slack, 1984) to detect changes in concentrations in wet and dry deposition at those sites having at least 10 years of data. Twenty of the 28 dry deposition sites (shaded squares in Fig. 1) and 32 of the 59 wet deposition sites (shaded circles in Fig. 1) were used to examine temporal trends in this manner.

3. Results

3.1. Seasonal variations

Fig. 3 displays the average observed and predicted seasonal variations in precipitation and concentrations of each of the N and S species (left axis), as well as the coefficient of determination ($r^2$) between the two (right axis). The observed concentrations are displayed with asterisks, the modeled concentrations are shown with filled circles, and the coefficients of determination are shown as shaded bars. In terms of seasonal variation, there is good agreement between spatially and temporally averaged observed and predicted precipitation, dry SO₂ (Fig. 3a), dry SO₄ (Fig. 3b), and wet SO₂ (Fig. 3c). In any given season, however, the model overpredicted SO₂ by 3–7 µg m$^{$-2$}$. Hence, while the modeling system may be overestimating SO₂ emissions, allocating too many SO₂ emissions to the lowest model layer, or underestimating the dry deposition of SO₂, CMAQ is largely able to reproduce the chemical and physical processes that control SO₂ formation, transport, and removal from the atmosphere. The average seasonal variation in dry and wet NO₃ (Fig. 3e–f) is not as well defined, and is driven in part by variation in the partitioning of total NO₃ into gas-phase HNO₃ and particulate NO₃. Since there are so few reliable measurements of gas-phase HNO₃ and NH₃, this partitioning is difficult to investigate in a systematic manner. In general, the model overpredicts dry NO₃ (Fig. 3e) by roughly 20–40% in most seasons, and underpredicts wet NO₃ (Fig. 3f) by a similar amount. These differences in NO₂ species are likely due to large uncertainties in both the measured data and the estimates of NOₓ emissions, as well as limitations in the parameterizations of chemical and physical processes that govern NOₓ formation and deposition in the model.
CMAQ reproduces the seasonal variation in dry NH$_4$ (Fig. 3g) qualitatively, but slightly underestimates the amplitude of the seasonal variation. In terms of wet NH$_4$ (Fig. 3h), CMAQ overpredicts during all seasons except the fall.

The highest degree of correlation occurs for the dry S and N species compared to the corresponding wet species, due in part to the fact that precipitation processes are not a limiting factor in dry deposition. Note that the $r^2$ for precipitation (Fig. 3d) only ranges from about 0.2 to 0.5, highlighting the difficulty in predicting precipitation timing and location even on a seasonal average basis, and suggesting that some of the seemingly good agreement between the observed and predicted seasonal average precipitation amounts may be due to compensating errors. The $r^2$ for wet SO$_4$ (Fig. 3c) is a little higher than for wet NO$_3$ (Fig. 3f) and NH$_4$ (Fig. 3h), perhaps due to the fact that even though all three species are affected by precipitation amount, emissions of precursors and atmospheric processes are better characterized in the model for SO$_4$.

### 3.2. Spatial patterns in average concentration

**Fig. 4a–h** displays the 2005 average observed and modeled concentrations of SO$_2$, SO$_4$, NO$_3$, and NH$_4$ from the 22 CASTNet sites that had at least 75% valid data during the year. Fig. 4a–h displays the precipitation amount and precipitation-weighted SO$_4$, NO$_3$, and NH$_4$ concentrations from the 52 wet deposition sites that had at least 75% valid data during 2005. In general, the model reproduced the overall spatial patterns in S compounds at CASTNet sites rather well, with the highest SO$_2$ and SO$_4$ concentrations in the Ohio River Valley region. High SO$_4$ concentrations also occurred in urban/suburban sites in Maryland and New Jersey. In an absolute sense, CMAQ overpredicted SO$_2$ concentrations at 20 of the 22 sites, on average by $2\mu g m^{-3}$ but as much as 8 $\mu g m^{-3}$ (compare Fig. 4a–b). On the other hand, Fig. 4c–d show that the CMAQ predictions of SO$_4$ were slightly underestimated at most CASTNet sites. In contrast to SO$_4$, concentrations of NO$_3$ were overestimated at all 22 sites, by an average of about 25% (compare Fig. 4e–f). In the case of NH$_4$ (Fig. 4g–h), CMAQ overpredicted SO$_4$ concentrations at 12 sites and underestimated concentrations at the other 10 sites. Since NH$_4$ in the ambient atmosphere is generally present as ammonium sulfate (or bisulfate) and ammonium nitrate, compensating model biases—namely underpredictions of SO$_4$ and overpredictions of NO$_3$—affect concentrations of NH$_4$.

**Fig. 5a–b** shows that the modeling system reproduces the pattern in precipitation at wet deposition sites in the central part of the domain well, but tended to underpredict annual precipitation at several southern sites (especially those near the Atlantic coast) and a number of sites through New York and the New England states. The model tended to overpredict precipitation at sites in Michigan and Ontario. Overall, the model underpredicted annual precipitation at 29 of the 52 sites shown in the panels of Fig. 5. Like ambient dry SO$_4$, concentrations of wet SO$_4$ were generally well predicted in terms of spatial patterns and magnitude (compare
Overall, wet SO$_4$ was underpredicted at 33 sites, but on average by less than 10%. Fig. 5e–f displays NO$_3$, which was underpredicted at all 46 sites by an average of 30%. Much larger underpredictions occurred at sites in Michigan and Ontario where the precipitation was overpredicted, suggesting that the model tended to dilute wet NO$_3$ concentrations more than was observed. The same may be true for wet NH$_4$, which also exhibits large relative underpredictions at sites in Michigan and Ontario, and overall was underpredicted at 35 of the 52 sites (compare Fig. 5g–h).

3.3. Changes attributed to emission reductions

Fig. 6a–c shows scatter plots of predicted and observed percentage changes in the concentrations of each species averaged over the three-years prior to (1992–1994) and after (1995–1997) implementation of Phase I of Title IV of the CAAA. Sixteen of the 28 dry deposition sites and 33 of the 59 wet deposition sites had data from at least 9 of the 12 seasons in each three-year period prior to and after implementation of Phase I, and only those sites are included in Fig. 6. Not surprisingly, the largest percent changes occurred for the S species (Fig. 6a), since Phase I primarily targeted SO$_2$ emissions. The observed and predicted changes in S species are generally consistent with the approximately 40% decreases in SO$_2$ emissions from Phase I of Title IV of the CAAA, and range from decreases of nearly 50% to slight increases, with most of the sites exhibiting decreases of about 10–30%. This suggests that the photochemical processes affecting SO$_2$ and SO$_4$ are generally well characterized in the model. The changes in N species (NO$_3$ in Fig. 6b, NH$_4$ in Fig. 6c) were generally smaller than the changes in S species, ranging from decreases of about 0–30% to small (<10%) increases. This is not surprising since the changes in NO$_x$ emissions from the utility sector were small during this time period. Mobile source emissions of NO$_x$ changed more gradually over the 18-year period, so that the changes over these two consecutive three-year periods are not as evident as they would be over the entire period. The predicted changes in NO$_3$ were generally similar to those observed, and regional changes in NH$_4$ are affected by changes in SO$_4$ and NO$_x$ precursors as well as by changes in agricultural emissions of NH$_3$. The results presented in this section illustrate the

Fig. 4. The 2005 average concentrations at CASTNet sites: (a) observed SO$_2$, (b) predicted SO$_2$, (c) observed SO$_4$, (d) predicted SO$_4$, (e) observed NO$_3$, (f) predicted NO$_3$, (g) observed NH$_4$, and (h) predicted NH$_4$. All units are $\text{ng m}^{-3}$. 

Fig. 5c–d).
effects of a large reduction in emissions over a short period of time, and long-term trends in each of these parameters will be discussed in the following section.

3.4. Long-term trends

Fig. 7a–b displays the range in trends (boxes) and average trends (asterisks) in dry and wet S and N species and precipitation at those sites having at least 10 years of data. Only statistically significant ($p < 0.1$) trends are displayed, with the range in observed trends shown as shaded boxes, and the range in modeled trends shown as unshaded boxes. The number of sites with significant trends is shown in parentheses. A large majority of the dry SO$_2$, and wet and dry SO$_4$ and NO$_3$ trends were statistically significant declines. While trends in SO$_4$ and NO$_3$ were generally consistent between CMAQ and observations, CMAQ predicted much larger decreases in SO$_2$ concentrations, on average about twice as large as the observed trend. This suggests that the modeled trends in SO$_2$ emissions were considerably larger than what actually occurred. While this seems to contradict the percentage changes depicted in Fig. 6a, recall from Fig. 3a that the modeling system on average overpredicted absolute SO$_2$ concentrations by about 3–7 $\mu$g m$^{-3}$. It is worth noting that prior to 1995 CMAQ overpredicted SO$_2$ by about 5.9 $\mu$g m$^{-3}$, while from 1995 onward CMAQ overpredicted SO$_2$ by about 3.6 $\mu$g m$^{-3}$. On a percentage basis, in contrast, there was very little change in the degree of CMAQ overprediction — 55% prior to 1995 versus 52% after 1995 — so it is not surprising that the absolute changes in SO$_2$ were larger from the model.

Over this period, there were only a few sites that exhibited significant increases in precipitation, but observed and predicted trends were not statistically different from zero at most of the wet deposition sites. Trends in wet and dry NH$_4$ were generally much smaller than trends in the other species, and were only significant at a few sites. Interestingly, predicted decreases in dry NH$_4$ were significant at 16 of the 20 long-term sites, whereas observed trends were slightly positive but significant at only 4 of the 20 long-term sites. While this current study can only examine NH$_4$ trends in a limited manner, future multi-year modeling simulations should continue to examine changes in NH$_4$ as precursor emissions change, agricultural practices continue to evolve, and emissions inventories of NH$_3$ improve.
Fig. 6. Observed and predicted percent changes in S and N species after implementation of Phase I of Title IV of the CAAA (1995–97 versus 1992–94). (a) SO$_2$ and SO$_4$, (b) NO$_3$, and (c) NH$_4$.

Fig. 7. Seasonal Kendall Tau trend estimates in (a) dry S and N species (20 sites), and (b) precipitation and wet S and N species (32 sites) at sites having 10 or more years of data. The boxes denote the range in trend estimates (observed trends as shaded boxes, predicted trends as unshaded boxes), the asterisks denote the average trends, and the numbers in parentheses denote the numbers of sites having significant ($p < 0.1$) trends.
4. Discussion

This paper compares various observed and modeled compounds in wet and dry deposition in the northeastern US over an 18-year period, much longer than typical model applications. The results suggest that the CMAQ system generally reproduces seasonal and spatial patterns and temporal trends in S compounds well. The model seems to capture long-term trends in NO3 well, but the model performance for NO3 varies widely over different seasons. Trends in NH4 are generally much smaller than those of SO4 and NO3, and trying to estimate NH4 trends is difficult given the uncertainties in emissions of precursors and physical and chemical processes that control atmospheric NH4. It should be noted that the model domain in this study only includes a portion of the northeastern United States, and future work could examine the results of similar studies for other regions of the country.

A multi-year simulation such as the one analyzed in this paper can not only shed light on spatial patterns and seasonal variations, but also on long-term trends in the presence of emissions changes and meteorological and climatological variability. The dynamic model evaluation approaches applied in this paper provide complementary insight into model performance over multiple years compared to those gained by operational evaluation through standard graphical and statistical means, as well as diagnostic evaluation and sensitivity tests.

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