Modeling and Analysis of the Atmospheric Nitrogen Deposition, North Carolina

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January 2005

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Abstract

The regional-scale Eulerian model, the United States Environmental Protection Agency's Community Multiscale Air Quality (CMAQ) model is used to study concentrations and dry deposition of nitrogen species for North Carolina during the summer season. Model predictions were generally less than observations (except [NO_Y]). Each modeled and measured species featured a similar diurnal trend. A process budget analysis (production and removal evaluation) of NO, NO_2, and NO_Y depicted the model's capability to evaluate various process contributions. Dry deposition rates of NO, NO_2, HNO_3 and NH_3 were calculated using CMAQ, in conjunction with measured wet deposition rates of NO_3^- and NH_4^+ facilitating an assessment of sources, characteristics and impacts of atmospheric nitrogen deposition in North Carolina (NC). Dry deposition of NH_3 contributed 34.2 ± 57.9 μg N m^{-2} hr^{-1}; whereas HNO_3 contributed slightly larger dry deposition of nitrogen, 35.2 ± 16.0 μg N m^{-2} hr^{-1}, in NC. NH_4^+ and NO_3^- hourly-averaged wet deposition fluxes were calculated as 37.3 ± 19.7 μg N m^{-2} hr^{-1} and 40.6 ± 11.8 μg N m^{-2} hr^{-1}, respectively. Within the total nitrogen deposition during the summer season in NC, NH_3 contributes approximately 50% of dry deposition and NO_3^- contributes approximately 50% wet deposition. In addition, model assessments of atmospheric inputs (nitrogen loading) into the Neuse River Estuary in North Carolina revealed that NH_3 is the largest contributor to dry deposition fluxes in the Neuse River basin, making up approximately 47% of the total.

1. Introduction

Nitrogen oxides (NO_X), which play an important role in atmospheric chemistry, have been the focal point of research associated with atmospheric nitrogen compounds in relation to their small-scale processes (spatial and temporal) of turbulent mixing and dispersion e.g. emission and deposition. NO_X are attributed to photochemical smog, acid rain, contamination of drinking water (nitrate), and ozone causing impacts to human health and environmental ecosystems (Erisman et al., 1998). Tropospheric NO_X acts as one key precursor to tropospheric ozone (Albritton et al., 1994; Liu et al., 1980; Liu et al., 1987; Logan, 1983) which is known to reduce plant production in sensitive ecosystems. An increase in NO_X emissions in the southeast United States (which is NO_X limited) is predicted to result in an increase in tropospheric ozone concentrations (Southern Oxidant Study, 1993). The United States has recognized these environmental issues since the promulgation of the Clean Air Act and its Amendments (CAAA, last amended in 1990), which addresses and regulates outlined criteria pollutants (Carbon Monoxide (CO), Nitrogen dioxide (NO_2), Sulfur Dioxide (SO_2), Ozone (O_3), Lead (Pb), and Particulate Matter (PM 10 and 2.5)).

The global tropospheric source strength of NO_X is estimated to be approximately 45 Tg yr^{-1} with associated sinks (wet and dry deposition) of approximately 43 Tg yr^{-1} (Lee et al., 1997; Logan, 1983; Warneck, 2000). Total nitrogen emissions have been estimated approximately at 0.3 Tg yr^{-1} in North Carolina (NCDA, 1996). In North Carolina, the percent of nitrogen emissions from NO_X is estimated at 55%, while the percent of nitrogen from NH_3 is estimated at 45%. Likewise, in NC, estimates reveal that intensive animal agriculture (namely, swine production facilities) contributes approximately 46% of the NH_3-N emissions (NCDENR, 1999). Currently, NC is ranked second in the nation, behind Iowa, for swine production with approximately 2500 hog farms located in eastern NC (NCDA, 1998). These areas of scattered local sources contribute a wide range of NH_3 emission and dry deposition.

Areas of scattered local sources (NO_X and its reduced forms (NH_3)) contribute a wide range of emission and dry deposition. Models need to consider and be able to model dry deposition of certain species (e.g. nitrogen species) close to the source as well as gradients of deposition from emission areas into sensitive ecosystems (Asman, 2001). Some of the models have acquired the capability to evaluate and produce deposition features on timescales of days, months, and years. These capabilities extend to assessing differences between short and long term deposition and their affects on sensitive ecosystems as well as differences among seasonal deposition (Phillips et al., 2004). In order to obtain these assessments, models need to incorporate our knowledge and understanding of the small-scale physical and chemical mechanisms that govern the presence of these species in the atmosphere (Krupa, 2003). Likewise, models are used as a deterministic tool in order to reduce the degree of ambiguity in deposition fluxes regionally, nationally, and globally.

In this study we utilize the United States Environmental Protection Agency's Models-3/Community Multiscale Air Quality (CMAQ) modeling system on a regional scale for North Carolina based on their demonstrated skill of simulating the relevant photochemistry processes, and meteorology processes, to yield grid-averaged concentrations, and deposition of nitrogen species. A process budget analysis (production and removal evaluation) of NO, NO_2, and NO_Y is conducted. We will consider in our model simulations the model's capability to evaluate various physical and chemical process contributions.

Furthermore, this nitrogen species production and removal evaluation can be extended to a quantification of the total nitrogen budget for North Carolina. We wish to quantify the fate of atmospherically deposited nitrogen during summer season in North Carolina terrestrial ecosystems (land and water). The portions of atmospherically deposited nitrogen, which reaches vegetation, soil, and water bodies are expected to be variable depending upon conditions and circumstances (time of year, precipitation, wind direction, wind speed, temperature, etc.). In order to gain insight into the factors controlling the total nitrogen budget we will consider modeled dry deposition rates of NO (nitric oxide), $NO_{2,}$ HNO_3 and NH_3, in conjunction with measured wet deposition rates of nitrate (NO_3^-) and ammonium (NH_4^+). This study will address the relative magnitude associated with each component of the nitrogen budget specifically in North Carolina. In addition, we will make model assessments of atmospheric inputs (loading) into the Neuse River Estuary in North Carolina. An accurate nitrogen budget for affected ecosystems in North Carolina (e.g. Neuse River) will allow abatement strategies the means to address the reduction of nitrogen loading. This study aims to improve the understanding of the spatial variability of these deposition fluxes with respect to the spatial distribution of the sources of nitrogen in North Carolina. This overall evaluation of nitrogen deposition for North Carolina is vital for regional atmospheric transport, transformation, and deposition modeling.

2. Overview of Model Systems

CMAQ is a comprehensive Eulerian air quality modeling and assessment tool constructed to function as part of a flexible and comprehensive chemistry/transport modeling framework which is modular (Jang et al., 1995; Dennis et al., 1996; Byun and Ching, 1999). CMAQ serves as a diverse integration of air quality and deposition framework to assess a broad range of environmental applications while facilitating regulatory and policy decisions. The modeling system is designed as an “open system” where new scientific algorithms and mechanisms can be utilized and evaluated in conjunction with CMAQ processes. Model parameterizations may also be modified to test performance characteristics of dynamical-chemical processes within model simulations, such as tropospheric ozone, visibility, acid deposition, and particulate matter. CMAQ contains a detailed simulation of turbulent diffusion (horizontal and vertical) based on K-theory, horizontal and vertical advection, natural and anthropogenic emissions, dry deposition, and photochemistry (mixing and attenuation of photolysis rates) (Gery et al., 1989; Kasibhatla et al., 1997; and 1998). The modeling system also employs a modified version of the CBM-IV chemical mechanism, which considers gas-phase chemical transformations. The U.S. EPA Biogenic Emission Inventory System 3 (BEIS3), a submodel compatible with the emissions inputs modeling system Sparse Matrix Operator Kernel Emissions (SMOKE), estimates biogenic emissions used within CMAQ (Geron et al., 1994). Among other submodels compiled for SMOKE are mobile, area, and point source emissions. The Ozone Transport Assessment (OTAG) inventory for 1995 provides anthropogenic emissions (Houyoux et al., 1996).

2.1 Model domain selection

The modeling domain was selected to adequately portray the conditions within North Carolina so as to estimate the NC nitrogen budget and thus the total deposition affecting the Neuse River. The horizontal domain of CMAQ includes 34×42 cells using a 36-km horizontal grid resolution. The vertical domain from the surface to 100 mb is discretized utilizing 22 layers of variable resolutions. The time period considered in model simulations and validation of concentrations is from July 14 to July 29, 1995, in order to investigate summer environmental and meteorological factors (e.g. high temperatures, strong solar radiation and increased biogenic emissions) with respect to nitrogen volatilization (concentrations of NO, NO_2, NO_X ($NO+NO_2$)

and NO_Y). The year 1995 was chosen due to the availability of nitrogen species measurements. For the same reason, the time period considered in model dry deposition simulations is from June 30 to July 14, 1999 (12:00p.m. – 12:00a.m. EST). Nitrogen deposition rates for NC summer conditions were investigated using a 32-km horizontal grid resolution. The year 1999 (different from concentration predictions) was selected due to the accessibility of wet nitrogen deposition data. Earlier model simulations conducted over the eastern U.S. provided time-varying lateral boundary conditions for various model species for both model validation and study case periods (Kang et al., 2003).

2.2 Chemistry Mechanism

The chemical mechanism, compilation of chemical reactions where by atmospheric chemical species are used in CMAQ is the modified version of the Carbon Bond Mechanism IV (CB4) (Gery et al., 1989). These modifications to the base mechanisms enhance the connections and representations between atmospheric aerosol and aqueous chemistry processes. The CB4 mechanism utilized by CMAQ consists of 36 species and 93 chemical reactions where nine primary organic species (directly emitted into the atmosphere) are specified in the mechanism representing carbon-carbon bond structures. Those species represented directly are ethene, isoprene, and formaldehyde (see Gery et al., 1989).

2.3 Dry Deposition Scheme (Algorithm)

Dry deposition represents the removal of pollutants (airborne gaseous and particulate matter) from the atmosphere to the earth’s surface (Arya, 1999; Byun and Ching, 1999). The complexity of factors affecting the rate of transfer, deposition velocity (v_d), (such as physical, chemical, and biological), make it difficult to generalize the process. CMAQ adopts estimation methods of dry deposition from Wesley (1989) and Walcek (1987). The following expression of deposition velocity is derived to compute the related flux of a particular pollutant to a specific surface:

$$v_d = -F_c / \bar{c} \tag{1}$$

Estimation of deposition velocities considers elements of meteorology and land-use/surface models (Walcek, 1987). CMAQ characterizes turbulence and stability using the aerodynamic resistance approach,

$$v_d = \left(r_a + r_b + r_c\right)^{-1} \tag{2}$$

where the aerodynamic resistance (r_a) and the quasi-laminar boundary layer resistance (r_b) are parameterized based on surface roughness and friction velocity (Pleim et al., 2001; Xiu and Pleim, 2001; Wesley, 1989; Walcek, 1987; Wesley and Hicks, 1977). Likewise, canopy (surface) resistance (r_c) is a function of insolation and season, land-use type, and surface wetness (Walcek et al., 1986).

3. Description of Data

3.1 Observed Data

Measured hourly concentrations of NO, NO_X ($NO+NO_2$) and NO_Y ($NO_Y = NO + NO_2 + HNO_3 + HONO + HO_2NO_2 + NO_3 + 2N_2O_5 + PAN$) were obtained from the Environmental Protection Agency’s Air Quality System (AQS) (formerly the Aerometric Information Retrieval System (AIRS)) database for the time period and domain of model simulations in question. AQS includes both compliance data and emissions on air pollution point sources regulated by the U.S. EPA and/or state and local air regulatory agencies. Averaged

AQS data over 16 stations located within NC grid cells were extracted out of 323 monitoring stations nationwide in 1995.

3.2 Wet Deposition Data

Wet deposition of NH_4^+ and NO_3^- was compiled from 8 monitoring networks in North Carolina during 1999 from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN, 2002), in order to evaluate against relative dry deposition estimates and thus estimate the total nitrogen budget for NC (Figure 1; Table 1). Although the number of monitoring stations was limited, the spatial resolution between the monitoring stations seems to be reasonable while considering urban (including industry and major highways) and rural (including intensive agriculture farms) areas, and mountain and coastal areas. The NADP network is a cooperative research support program encompassing the State Agricultural Experiment Stations (NRSP-3) Federal and State Agencies and Non-Governmental Research Organizations. The nationwide network is a monitoring data collection effort of geographical and temporal long-term trends on the chemistry of precipitation, which has grown since 1978 (first year of data collection) with 22 stations, to over 200 sites across the continental United States, Alaska, and Puerto Rico, and the Virgin Islands. The network attempts to collect data based on the chemistry of precipitation for examination of geographical and temporal long-term trends (NADP/NTN, 2002).

NADP calculates deposition based on precipitation samples collected on a weekly basis at each station. For a particular time period in question (season, annual, etc.), a precipitation weighted mean concentration (PWM) is calculated for the time period using valid weekly samples. These weighted-mean concentration values are multiplied by the total precipitation for the period to calculate the total deposition for the period.

The wet deposition means were based on the individual stations obtained from NADP/NTN for summer 1999 in NC. The wet deposition data were averaged for each available measurement site within the NC domain. The calculation of wet deposition utilizes:

$$C_w = \frac{\sum_{i=1,n}(C_i P_i)}{\sum_{i=1,n}(P_i)} \tag{3}$$

where C_w is the precipitation-weighted mean (mg L^{-1}), calculated from the number of valid samples for the summer 1999 season. C_i, individual valid sample is then weighted by P_i, individual precipitation amount for each sample. The wet deposition flux, F_{wet} (mmoles liter^{-1})

$$F_{wet} = C_w P_t \tag{4}$$

where P_t (mm H_20) is the total precipitation over the averaging time period (final units: (μg m^{-2} hr^{-1}).

4. Results and discussions

4.1 Limitations associated with Observations and Model Predictions

Currently, model simulations have been conducted to evaluate the performance of CMAQ relative to observations of NO, NO_X and NO_Y concentrations during July 14 to July 29, 1995 in North Carolina. Several limiting factors influence a direct comparison between observations and model predictions. Models need to consider concentration of species close to the source (local influences) as well as those transported downwind into sensitive ecosystems, where measurements are taken. However, CMAQ depends on the model resolution to produce grid-average concentrations. CMAQ is also limited by parameterization of boundary layer fields, meteorology (growth of clouds), biogenic emissions, physical/chemical and deposition schemes, etc. Due to these limiting factors we will consider in our evaluations the model's capability to describe mean concentration profiles and vertical physical/chemical exchange processes effectively. Model and observed concentration calculations are made on a daily basis every hour for 15 days during the summer 1995.

4.2 Model versus Observed Concentrations

Figure 2 presents the comparison of hourly-averaged CMAQ simulations with observations from July 14 to July 29, 1995 for nitrogen species: NO, NO_2, NO_X ($NO+NO_2$) and NO_Y observations with model simulations. Modeled concentrations are determined from grid cells that correspond to monitoring stations. Even though the model under predicted NO and NO_2 (especially NO), and over predicted NO_Y, the diurnal trends for all three species are consistent. Modeled and measured values show fair agreement when considering that nitrogen species concentrations has a high spatial variability (position of the point of measurement or simulation compared to local sources). Moreover, a linear regression analysis and corresponding R^2 values displayed a strong correlation between predictions and observations (Figure 3). The weakest correlation ($R^2 = 0.31$) was within NO observed and predicted concentrations where there was a noticeable lag in diurnal peaks and concentrations were considerably less during early morning hours (12:00 a.m. to 5:00 a.m.) and late evening hours (8:00 p.m. to 12:00 a.m.). Under-predicted NO concentrations maybe attributed to incorrect emissions used in the model. However, when combining $NO + NO_2 = NO_X$ a greater correlation emerged ($R^2 = 0.73$), reflecting the relatively close predicted diurnal pattern (two peaks during morning and evening). The strongest correlation ($R^2 = 0.87$) observed was between measured and predicted concentrations of total reactive nitrogen. Modeled simulations over-predicted NO_Y concentrations, but represented the diurnal trend with consistent peaks in concentrations throughout the hourly-averaged 15-day summer season.

4.3 Process Budgets

A process budget analysis of each nitrogen species (NO, NO_2, NO_Y) was performed by CMAQ in North Carolina during the summer season, 1995 (Figure 4). A true modularity of physical/chemical processes is one key feature of CMAQ's model platforms. The model budgets were analyzed in terms of a variety of physical/chemical processes (contribution) such as chemistry, emission, dry deposition, horizontal and vertical advection, and horizontal and vertical diffusion (Kang et al., 2003). The vertical budget of each process is evaluated based on the weighted contribution from each layer (*Bi*):

$$Bi = \frac{\sum_{j=1}^{N} (\sigma_{j-1} - \sigma_j) C_j}{\sum_{j=1}^{N} (\sigma_{j-1} - \sigma_j)} \tag{5}$$

where σ_j is the boundary σ value of the j^{th} layer, Cj is the contribution of the process (ppbV/hr) at the j^{th} layer, and N is the number of vertical layers ($N = 12$ in this calculation) (Kang et al., 2003).

Emission accounts for almost all NO production, while chemistry (56%) and vertical diffusion (44%) are responsible for the removal of NO. NO_2 is contributed by local chemistry (80%) and emission (20%). NO_2 removal processes involved vertical diffusion (74%), dry deposition (20%), horizontal advection (4%), and vertical advection (2%). Emission of NO_Y is shown to contribute solely to the production of NO_Y (100%) during the study period within the evaluated grid cells. This result raises some questions, since by definition NO_Y should include all the oxidized nitrogen species that are formed through chemical and photochemical processes in the atmosphere. In the model, NO_Y is limited by a few species (see definition of NO_Y in Section 3.1) and the oxidized species are originated from NO and NO_2. This suggests that during the study period, in the grid cells evaluated, NO_Y production is solely from NO and NO_2 contributions. The dominating processes of NO_Y removal are dry deposition (54%) and vertical diffusion (35%) with the remaining contribution accounted by chemistry (7%), horizontal advection (3%) and vertical advection (1%). Horizontal and vertical advections were insignificant in the removal process of each budget analysis. This may be explained by the dominant transport of vertical diffusion in the domain.

4.4 Modeled Dry Deposition

In order to gain insight into the factors controlling the total nitrogen budget we will consider modeled dry deposition rates of NO, NO_2, HNO_3 and NH_3 employing CMAQ, in conjunction with NADP measured wet deposition rates of NO_3^- and NH_4^+. This study will address the relative magnitude associated with each source of the nitrogen budget. An assessment of nitrogen deposition fluxes for affected ecosystems in North Carolina (e.g. Neuse River Estuary is considered here) will allow abatement strategies the means to address the reduction of nitrogen loading.

Significant factors that influence the fate of exchange of a gas species between the air and earth's surface are gas concentration gradient between the air and surface, and the level of atmospheric turbulence and stability (Asman et al., 1994). If the concentration at the surface is relatively high ($r_c > 0$) emission occurs, whereas, if the concentration at the surface of the earth is relatively low ($r_c \rightarrow 0$), dry deposition occurs. This study utilizes the definition of the hourly-averaged downward flux of a depositing material as the product of the estimated deposition velocity and the hourly averaged concentration at a reference height near the surface (Arya, 1999) based on hourly-averaged fluxes.

Figures 5 and 6 show mean modeled NO, NO_2, NH_3, and HNO_3 dry deposition in North Carolina during summer 1999, respectively. NO dry deposition is relatively low (4.67 ± 4.2 μg N m^{-2} hr^{-1}) compared to the other simulated nitrogen species deposition fluxes. These minimal depositions are a direct result of the rapid conversion of NO to NO_2 (NO+O) during the diurnal photochemistry process. Figure 5a points out that the largest NO deposition rates were found in regions of major metropolitan areas, which follow main interstate highways, 85, 95 and 40 in NC. These particular sources of increased NO deposition are the result of fuel combustion and resulting motor vehicle exhausts in areas (1) Raleigh/Durham (Wake/Durham counties), (2) Greensboro/Winston Salem/High Point (Gilford/Forsyth counties), and (3) Charlotte (Mecklenburg County) shown in Figure 5a. Nitrogen dioxide displays a similar deposition pattern, where the largest deposition fluxes are located in urban areas with the greatest rush-hour traffic patterns (Figure 5b). Within NC, the average NO_2 deposition flux is 15.15 ± 9.98 μg N m^{-2} hr^{-1}.

NH_3 dry deposition (34.17 ± 57.89 μg N m^{-2} hr^{-1}) clearly shows the influence of intensive agriculture and animal farms located in eastern NC where NH_3 dry deposition rates are greatest (Figure 6a). The largest deposition fluxes are found in the six county region of Sampson, Duplin, Bladen, Lenoir, Wayne, and Greene counties in NC. These counties are directly located in the heart of eastern NC where there are approximately 2500 hog farms and 10 million swine. These areas of concentrated animal farms contribute to large NH_3 emissions and subsequent dry deposition over a large region. Aneja et al. (1998, 2000) estimated that the total NH_3 emissions in NC from swine facilities is approximately 68,540 tons of nitrogen emitted annually whereas cattle, broilers, turkeys, and chickens combined emit 61,583 t N yr^{-1}. Seasonally, NH_3 concentrations are observed to be greater in spring and summer, when high temperatures, are responsible for increased microbial activity and volatilization rates of soils, fertilizers, and animal wastes from intensively managed agriculture (Aneja et al., 2000, 2001a,b).

Figure 6b shows that HNO_3 deposition fluxes are lowest in the eastern portion of the state possibly due to the gas to particle conversion (HNO_3 + NH_3) to ammonium nitrate (NH_4NO_3). HNO_3 deposition trends show the influence of a major highway with maximum deposition rates found along Interstate 85 and 95. North Carolina average HNO_3 dry deposition rate for summer 1999 is 35.24 ± 15.96 μg N m^{-2} hr^{-1}. The rate of conversion between the oxidation of reactive nitrogen to HNO_3 is highly variable, with a lifetime of hours to days depending upon source, season, meteorology, relative humidity, and photochemical activity (Logan, 1983).

Figure 7 presents the modeled diurnal variations of dry deposition rates of (a) NO, (b) NO_2, (c) NH_3, and (d) HNO_3. Time series plots represent averages of hourly deposition over the 15 days of model simulations (June 30 to July 14, 1999) in NC. The diurnal patterns of NO and NO_2 feature two peaks that are related to work rush-hour traffic patterns in the morning and evening (Figure 7a,b). The dramatic increase in both NO and NO_2 during early morning hours and the subsequent drop in both deposition rates at night is the consequence of photolysis and thus photolytic reactions involving emissions of NO_X (motor vehicle exhaust). Nonetheless, the nominal deposition fluxes of NO as compared to NO_2 are due to the rapid conversion of NO to NO_2 (NO+O) during the diurnal photochemistry process. The time series plot of hourly-averaged diurnal deposition of HNO_3 (Figure 7d) shows the effect of diurnal increase in temperature from sunrise (cresting at noon), which then begins to decline until collapsing in the late evening. This diurnal pattern follows the photochemical reactions within (NO_2 + OH) radical to form HNO_3 (increasing the oxidizing capacity), where OH reactivity is at its maximum during midday. The fate of HNO_3 is determined by its susceptibility to coalesce with either aerosols or water in the atmosphere and thus return to the earth's surface as acidic deposition.

The diurnal variation of NH_3 dry deposition shows two peaks, one in the morning, which can be explained in terms of increase in deposition velocity, while the reason for the second peak in deposition during the evening is unclear (Figure 7c). The first diurnal peak is related to the parameterization of dry deposition velocity ($v_d = (r_a + r_b + r_c)^{-1}$) used in CMAQ (see Section 2.3). This equation can be explained by the typical meteorological/environmental conditions occurring: as the sun rises in the morning, stomata in vegetation open and hence canopy (surface) resistance (r_c), which is a function of insolation and season, land-use type, and surface wetness (Walcek et al., 1986), goes to zero (Finkelstein et al., 2001). Noting that $r_a \gg r_c$, it is apparent that turbulence primarily influences the maximum possible deposition velocity or emission rate (Andersen et al., 1999). Assuming that the gas is readily absorbed at the surface, $r_c = 0$. Therefore, during early morning hours after sunrise deposition tends to increase. After sunrise, throughout the day atmospheric mixing increases as temperature increases, promoting greater instability and boundary layer growth. CMAQ considers the effects of atmospheric stability and turbulence on deposition velocity of NH_3 through its parameterization in terms of friction velocity. Friction velocity, a measure of mean wind shear and shear-generated turbulence near the surface in both the canopy layer and above the canopy homogeneous surface layer, is found to be well correlated with dry deposition velocity, and is one of the most important variables (Arya, 1999). During the second evening peak there may be a possible influence of dew forming with higher relative humidities, which has been shown to promote deposition under certain conditions (Andersen et al., 1999). Therefore, this peak also shows the effect of other meteorological parameters (Sutton et al., 1994; Andersen et al., 1999).

4.5 Estimated nitrogen deposition

Table 2 presents dry and wet nitrogen deposition totals in North Carolina during Summer 1999 based on dry deposition estimates from CMAQ model simulations for June 30 – July 14, 1999 and wet deposition estimates from NADP/NTN (2002) for Summer (June-August) 1999. Dry deposition estimates include NO, NO_2, HNO_3, and NH_3, where the combination of NO and NO_2 are predicted to contribute approximately 20.0 μg N m^{-2} hr^{-1}, and HNO_3 contributes 35.2 ± 16.0 μg N m^{-2} hr^{-1}. Likewise, NH_3 contributes 34.2 ± 57.9 μg N m^{-2} hr^{-1} to dry deposition of nitrogen in NC.

The role of N wet deposition in North Carolina was evaluated against the contribution of NH_4^+ and NO_3^-, which shows that the range of hourly-averaged NH_4^+ deposition fluxes were between 14.0 and 82.0 μg N m^{-2} hr^{-1} (average of 37.3 ±19.7 μg N m^{-2} hr^{-1}). Hourly-averaged NO_3^- deposition rates were estimated at 40.6 (±11.8) μg N m^{-2} hr^{-1} with hourly-averaged deposition fluxes ranging from 24.0 to 55.0 μg N m^{-2} hr^{-1}. NH_3 contributes 38% of the total dry deposition component and NH_4^+ contributes 48% of the total wet deposition component. The distribution of deposition between wet and dry were generally equal; with 46% wet deposition and 53% dry deposition. Based on these results we note that approximately 50% of NH_X or NO_3^- is due to dry and wet processes occurring during the summer season in NC. Likewise, nitric acid (HNO_3) and nitrate (NO_3^-) which are secondary products resulting from NO and NO_2, are considered to be principal compounds of nitrogen deposition (Huebert et al., 1988; Meyers et al., 1989).

4.6 Estimated nitrogen deposition to the Neuse River Estuary

The Neuse River Estuary is approximately 16,000 km^2 and part of the second largest estuary system in the United States, namely the Albemarle-Pamlico Estuary System (Whitall and Pearl, 2001). Biodiversity changes in this watershed are resulting in eutrophication in sensitive ecosystems promoting fish kills, microbial and algal decomposition (Pearl et al., 1998). The American Rivers Foundation has listed the Neuse River as one of the twenty most threatened riverine-estuarine systems in the U.S (Whitall and Pearl, 2001). Pearl and Whitall, 1999 have established an increase in wet atmospheric deposition of nitrogen in eastern NC, in conjunction with relative increases in NH_4^+ and NO_3^- deposition. Statewide nitrogen emissions total 0.3 Tg yr^{-1}, thus the contribution of N emissions to the coastal plain of NC total 0.15 Tg yr^{-1} (NCDAQ, 1997). Whitall and Pearl (2001) have estimated the contribution of wet deposition to the Neuse River watershed based on atmospheric deposition of nitrogen inputs within the range of 15 to 51%. Their model outputs (N retention model and in-stream riverine degradation model) predicted a “best fit” value of 1412.5 Mg yr^{-1} of atmospherically deposited nitrogen to the estuary, i.e. 24% of the total flux (atmospherically deposited N) to the watershed. Total wet N deposition (deposited to land) and direct deposition to the estuary was measured approximately 15,026 (±5266) Mg yr^{-1} and 384.9 Mg yr^{-1}, respectively. Moreover, Whitall and Pearl (2001) only considered the contribution of wet deposition fluxes of nitrogen to the Neuse watershed, where seasonal wet deposition totals were greatest in spring (March-May) and summer (June-August). Nitrate was the dominant nitrogen species found within measured wet deposition, similar to wet deposition estimated from NADP measurements for NC in the summer of 1999. Therefore, in this study we utilize CMAQ model system to estimate the contribution of dry deposition to the Neuse River Basin.

Table 3 lists the estimated nitrogen budget for dry deposition contributed to the Neuse River watershed in North Carolina during summer, 1999. NH_3 is predicted to be the largest contributor to dry deposition fluxes in and around the Neuse River, making up 47% of the total. This large NH_3 deposition contribution is consistent with increasing intensively managed agriculture (swine and poultry facilities) in eastern NC. These areas are NH_3 enriched due to the volatilization from animal waste. Acknowledgment of these environmental issues are emerging, e.g. since 1997, a moratorium has been implemented on new or existing corporate hog farms. The second largest dominant chemical species is HNO_3, contributing an average of 36.0 (±16.1) $\mu g\ N\ m^{-2}\ hr^{-1}$. Whereas, NO and NO_2 provided the smallest contribution of 5.6 (±3.75) $\mu g\ N\ m^{-2}\ hr^{-1}$ and 17.1 (±7.32) $\mu g\ N\ m^{-2}\ hr^{-1}$, respectively. These predicted values of dry deposition offer a significant addition to deposition fluxes in the nitrogen budget for the Neuse River.

5. Conclusions

In this study U.S. EPA's CMAQ model was used to predict concentrations and deposition of nitrogen species. The model tends to under predict NO and NO_2, while over predict NO_Y, but the diurnal variations are in good agreement with observations. Process budget analysis shows that emission accounts for almost all NO production, while chemistry and vertical diffusion are responsible for the removal of NO. NO_2 production and removal processes are dominated by local chemistry and vertical diffusion, respectfully. Likewise, NO_Y production is only from NO and NO_2 during the study period and in the grid cells evaluated; dry deposition and vertical diffusion are the dominating processes of NO_Y removal.

The nitrogen species production and removal mechanisms are evaluated to quantify the total nitrogen budget (dry and wet deposition processes) for North Carolina. CMAQ predicted NO and NO_2 (cumulatively) to contribute approximately 20.0 μg N m^{-2} hr^{-1}, and NH_3 to contribute 34.2 ± 57.9 μg N m^{-2} hr^{-1}. HNO_3 contributed the largest dry deposition of nitrogen in NC, 35.2 ± 16.0 μg N m^{-2} hr^{-1}. The average wet deposition fluxes were 37.3 ± 19.7 μg N m^{-2} hr^{-1} and average NO_3^- deposition rates were estimated at 40.6 ± 11.8 μg N m^{-2} hr^{-1}. NH_3 contributed 38% of the total dry deposition component and NH_4^+ contributed 48% of the total wet deposition component. The distributions of deposition among wet and dry were generally equal with 46% wet deposition and 53% dry deposition. Approximately 50% of NH_X or NO_3^- is due to dry and wet processes occurring during the summer season in NC.

In addition, model assessments of atmospheric inputs (nitrogen loading) into the Neuse River Estuary in North Carolina revealed NH_3 was the largest contributor to dry deposition fluxes in the Neuse River basin, making up approximately 47% of the total. This large NH_3 deposition contribution is consistent with increasing intensively managed agriculture (swine and poultry facilities) in eastern NC. Future research should consider regional air quality models, with suitable modifications incorporating ammonia chemistry, for simulating some interesting episodes of transport, transformation and deposition of ammonia in eastern North Carolina. Such simulations will be useful for assessing the possible impacts of ammonia sources on the spatial variation of ammonia concentration and deposition flux, and their role in overenrichment of North Carolina water bodies (rivers and estuaries). Likewise, a credible extrapolation of dry deposition velocities of ammonia could be developed for forest areas which cover a substantial portion of eastern North Carolina.

The second largest dominant chemical species is HNO_3, contributing an average of 36.0 ± 16.1 μg N m^{-2} hr^{-1}, followed by NO_2 (17.1 ± 7.32 μg N m^{-2} hr^{-1}) and NO (5.6 ± 3.75 μg N m^{-2} hr^{-1}). The mean total dry deposition was calculated to be 111.2 μg N m^{-2} hr^{-1} (1750 kg N hr^{-1}; 15,340 Mg N yr^{-1}). This dry deposition estimation shows a relative contribution of 50% to the total (wet + dry) nitrogen deposition when compared to Whitall and Pearl's (2001) estimation of wet deposition annual mean total (956 mg N m^{-2} yr^{-1}; 15,026 Mg N yr^{-1}).

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Table 1. Measured summer (June-August) 1999 wet deposition of NH_4^+ and NO_3^- at 8 NADP sites in North Carolina (kg/ha). [Source: National Atmospheric Deposition Program (NRSP-3)/National Trends Network (2002)].

NADP Site ID	Station	Latitude	Longitude	Deposition (kg/ha)	
				NH_4^+	NO_3^-
NC03	Lewiston Bertie Co.	36.1325	-77.1714	0.83	3.42
NC06	Beaufort Carteret Co.	34.8845	-76.6214	0.40	2.80
NC25	Coweeta Macon Co.	35.0605	-83.4305	0.97	3.20
NC34	Piedmont Rowan Co.	35.697	-80.6225	1.06	5.22
NC35	Clinton Sampson Co.	35.0258	-78.2783	2.32	5.33
NC36	Jordan Creek Scotland Co.	34.9708	-79.5283	1.09	4.75
NC41	Finley Farm Wake Co.	35.7283	-78.6803	0.76	2.37
NC45	Mt. Mitchell Yancey Co.	35.7353	-82.2861	1.01	4.65

Table 2. (a) Total Nitrogen deposition (dry and wet) in North Carolina during Summer, 1999; (b) Total Nitrogen dry deposition contributed to the Neuse River watershed in North Carolina during Summer, 1999.

(a) **Summer 1999**	**North Carolina Estimated Nitrogen Budget (μg N m^{-2} hr^{-1})**		
Dry Deposition[a]	***Average***	***Minimum***	***Maximum***
NO	4.67 (±4.2)	0.0	29.12
NO_2	15.15 (±9.98)	0.0	66.47
NH_3	34.17 (±57.89)	0.0	440.92
HNO_3	35.24 (±15.96)	5.4	76.8
Wet Deposition[b]	***Average***	***Minimum***	***Maximum***
NH_4^+	37.34 (±19.65)	14.09	81.72
NO_3^-	40.6 (±11.79)	24.24	54.51

(b) **Summer 1999**	**Neuse River Estimated Nitrogen Budget (μg N m^{-2} hr^{-1})**		
Dry Deposition[a]	***Average***	***Minimum***	***Maximum***
NO	5.6 (±3.75)	1.5	17.1
NO_2	17.1 (±7.32)	6.1	34.6
NH_3	52.5 (±55.85)	4.7	195.4
HNO_3	36.0 (±16.1)	17.2	65.3

[a] Estimates based on Community Multi-Scale Air Quality (CMAQ) model simulations for June 30 – July 14, 1999.

[b] Estimates based on National Atmospheric Deposition Program (NRSP-3)/National Trends Network (2002) for Summer (June-August) 1999.

Figure Captions

Figure 1. North Carolina NADP network measurement sites considered for wet deposition of NH_4^+ and NO_3^-; Stations: NC03, Bertie County; NC06, Carteret County; NC25, Macon County; NC34, Rowan County; NC35, Sampson County; NC36, Scotland County; NC41, Wake County; and NC45, Yancey County (Source: NADP/NTN, 2002).

Figure 2. Comparison of hourly-averaged Models-3/CMAQ simulations with observations from July 14 to July 29, 1995 for nitrogen species: (a) NO; (b) NO_2; and (c) NO_Y. (Note: Hourly-averages were based on station location.)

Figure 3. Linear regression of hourly-averaged CMAQ simulations versus hourly-averaged observations from July 14 to July 29, 1995 for nitrogen species: (a) NO; (b) NO_2; and (c) NO_Y. (Note: Hourly-averaged observations are averaged over 16 stations (Section 3.3.1) and model hourly-averages are produced from corresponding grid-cells (station locations).)

Figure 4. Process budget analysis of NO, NO_2, and NO_Y.during summer time (July 14 to July 29, 1995) for North Carolina. VDIF: Vertical Diffusion; VADV: Vertical Advection; HADV: Horizontal Advection; EMIS: Emission; DDEP: Dry Deposition; CHEM: Chemistry.

Figure 5. CMAQ model estimated dry deposition for Summer 1999: (a) Mean NO Dry Deposition ($\mu g\ m^{-2}\ hr^{-1}$); (b) Mean NO_2 Dry Deposition ($\mu g\ m^{-2}\ hr^{-1}$).

Figure 6. CMAQ model estimated dry deposition for Summer 1999: (a) Mean NH_3 Dry Deposition ($\mu g\ m^{-2}\ hr^{-1}$); (b) Mean HNO_3 Dry Deposition ($\mu g\ m^{-2}\ hr^{-1}$).

Figure 7. Hourly-averaged diurnal deposition trends of (a) NO, (b) NO_2, (c) NH_3, and (d) HNO_3. Time series plot represents the hourly-averaged deposition throughout the 15 days of CMAQ model simulations (June 30-July 14, 1999).

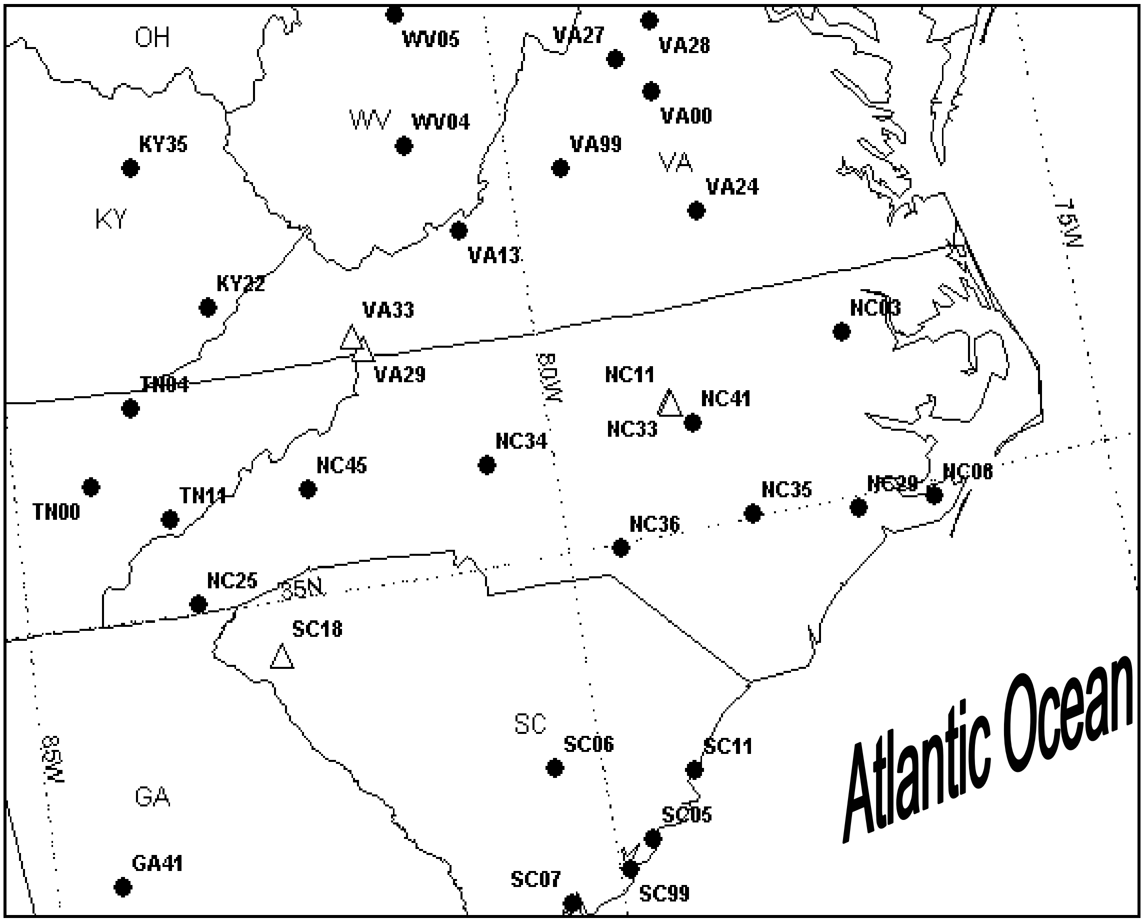

OH
WV05
VA27
VA28
WV
WV04
VA00
KY35
VA99
VA
VA24
KY
VA13
75W
KY22
NC03
VA33
VA29
80W
NC11
NC41
TN04
NC33
NC34
NC45
NC35
NC29
NC08
TN00
TN11
NC36
NC25
35N
SC18
SC
SC06
SC11
85W
GA
Atlantic Ocean
SC05
GA41
SC07
SC99

Figure 1.

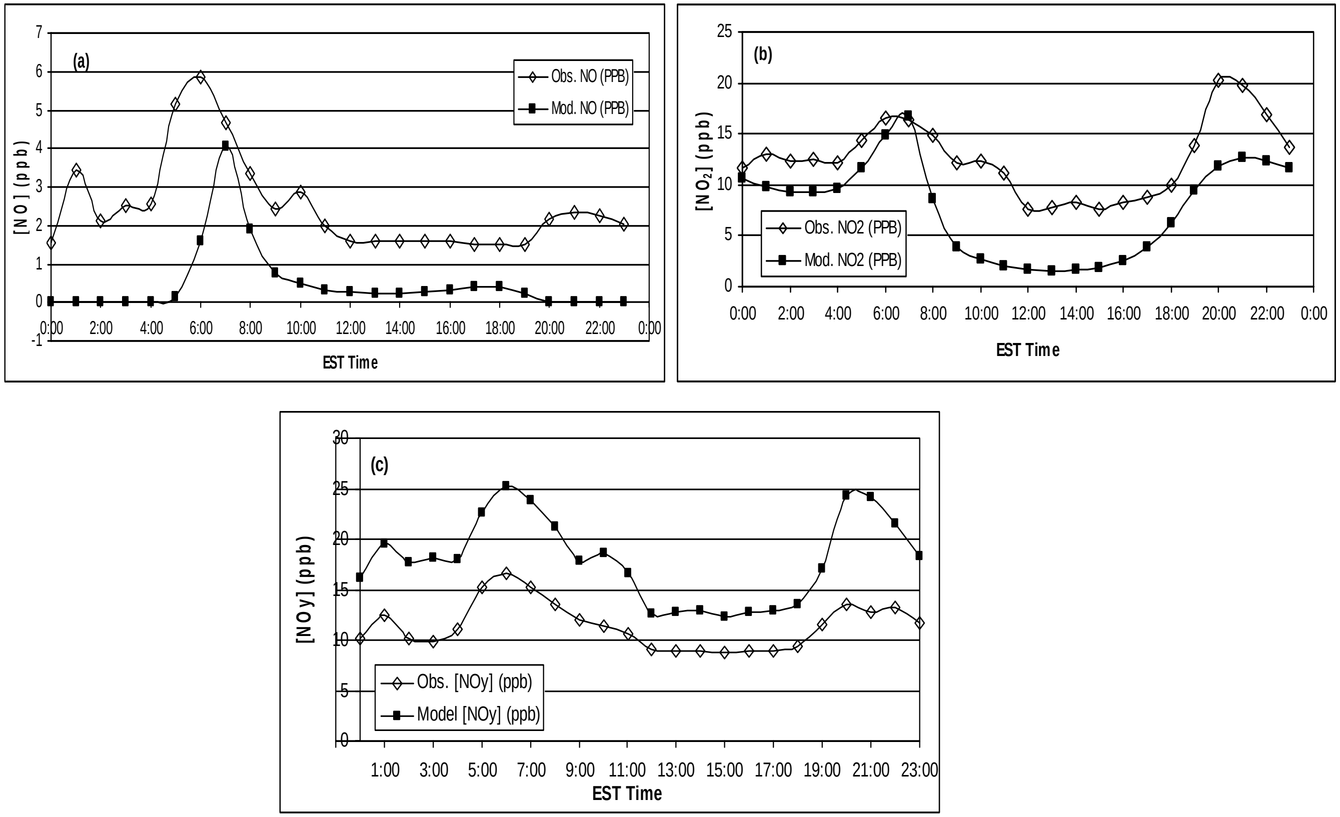

(a)
[N O] (p p b)
7
6
5
4
3
2
1
0
-1
0:00
2:00
4:00
6:00
8:00
10:00
12:00
14:00
16:00
18:00
20:00
22:00
0:00
EST Time
Obs. NO (PPB)
Mod. NO (PPB)
(b)
[N O₂] (p p b)
25
20
15
10
5
0
0:00
2:00
4:00
6:00
8:00
10:00
12:00
14:00
16:00
18:00
20:00
22:00
0:00
EST Time
Obs. NO2 (PPB)
Mod. NO2 (PPB)
(c)
[N O y] (p p b)
30
25
20
15
10
5
0
1:00
3:00
5:00
7:00
9:00
11:00
13:00
15:00
17:00
19:00
21:00
23:00
EST Time
Obs. [NOy] (ppb)
Model [NOy] (ppb)

Figure 2.

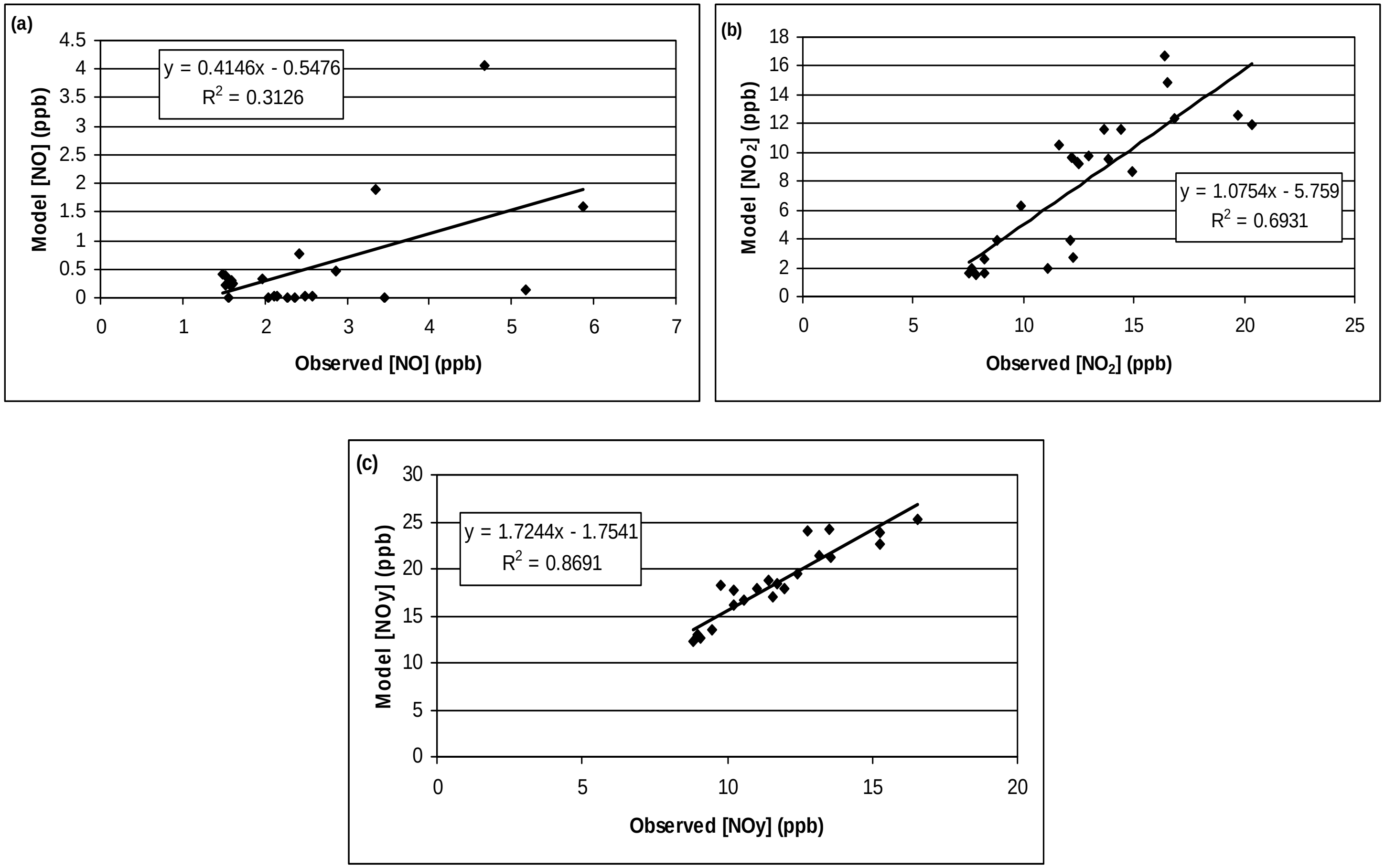

(a)
y = 0.4146x - 0.5476
$R^2 = 0.3126$
Model [NO] (ppb)
Observed [NO] (ppb)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
0
1
2
3
4
5
6
7
(b)
y = 1.0754x - 5.759
$R^2 = 0.6931$
Model [NO_2] (ppb)
Observed [NO_2] (ppb)
0
2
4
6
8
10
12
14
16
18
0
5
10
15
20
25
(c)
y = 1.7244x - 1.7541
$R^2 = 0.8691$
Model [NOy] (ppb)
Observed [NOy] (ppb)
0
5
10
15
20
25
30
0
5
10
15
20

Figure 3.

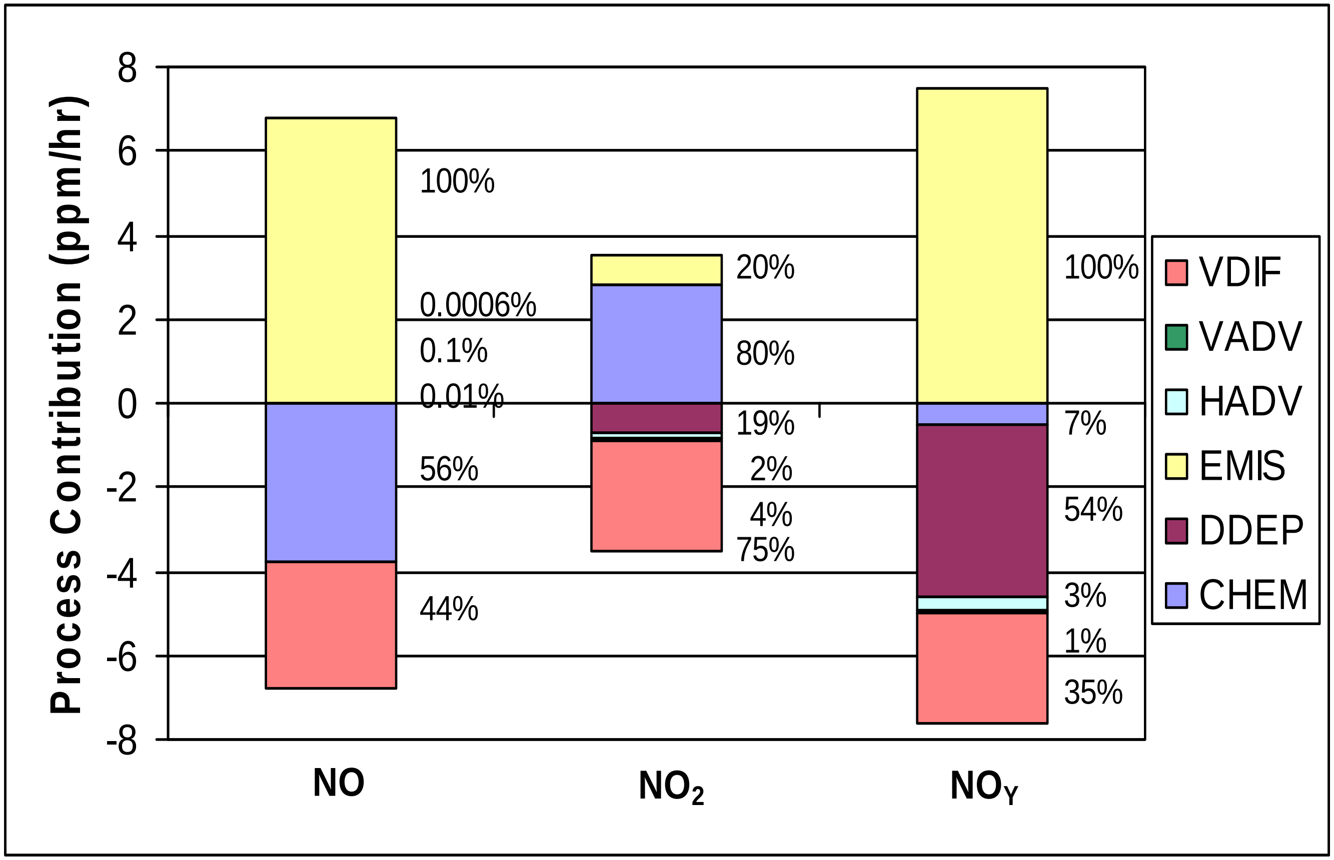
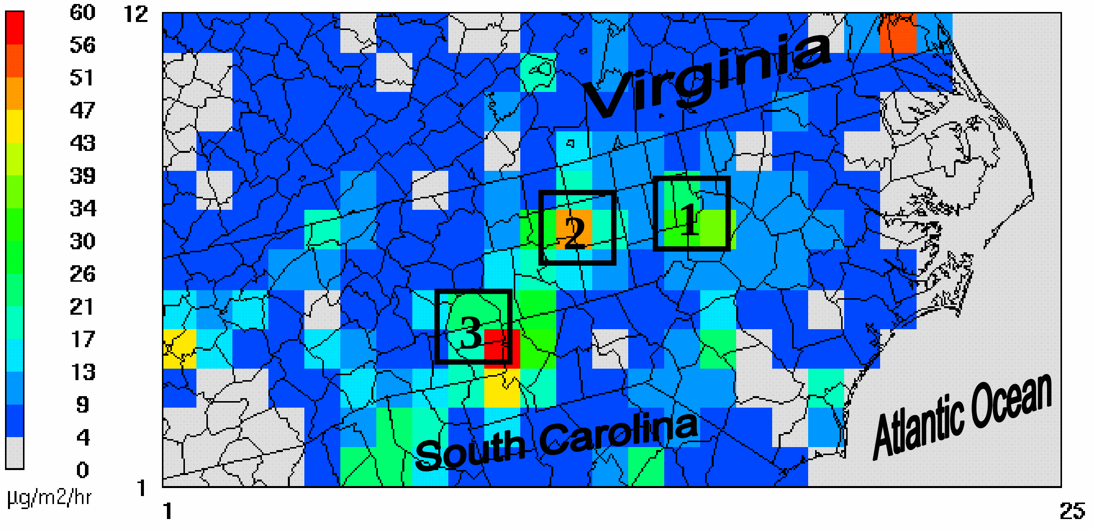

Process Contribution (ppm/hr)
8
6
4
2
0
-2
-4
-6
-8
NO
NO_2
NO_Y
100%
0.0006%
0.1%
0.01%
56%
44%
20%
80%
19%
2%
4%
75%
100%
7%
54%
3%
1%
35%
VDIF
VADV
HADV
EMIS
DDEP
CHEM

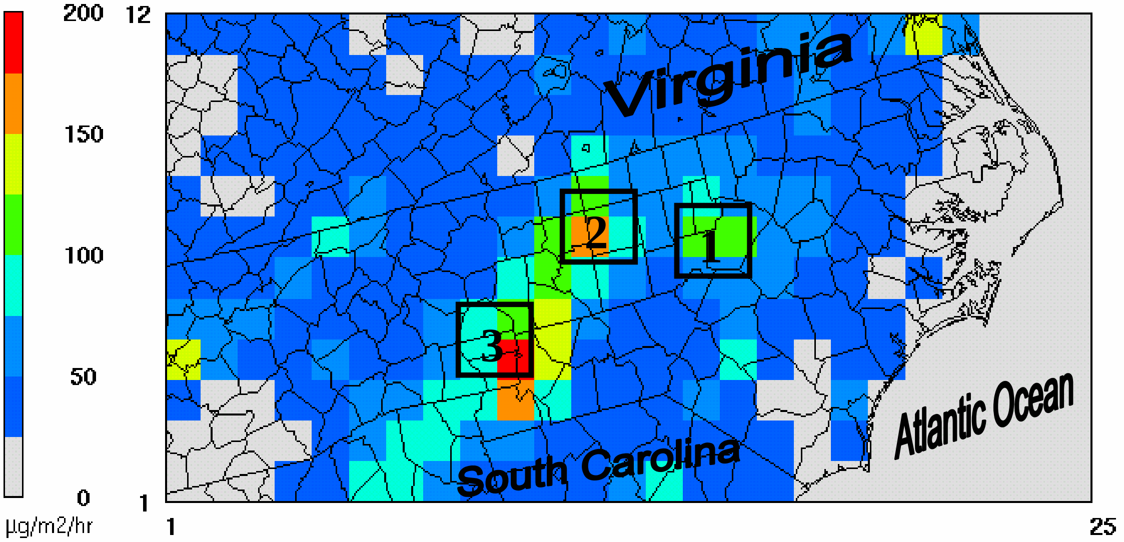
Figure 4.

(a)



Mean Modeled NO Dry Deposition in North Carolina during Summer 1999

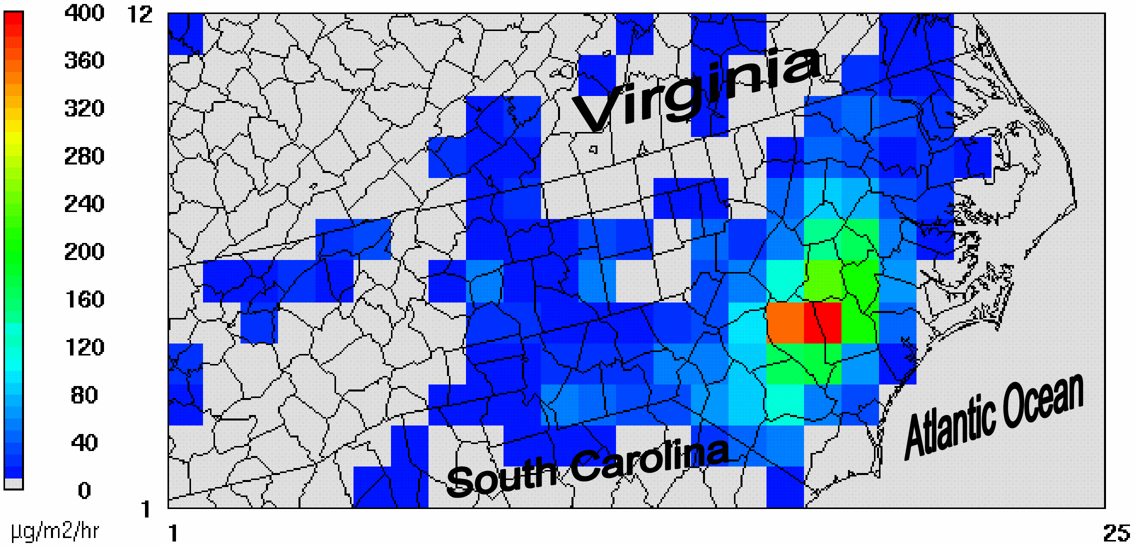
(b)



Mean Modeled NO_2 Dry Deposition in North Carolina during Summer 1999

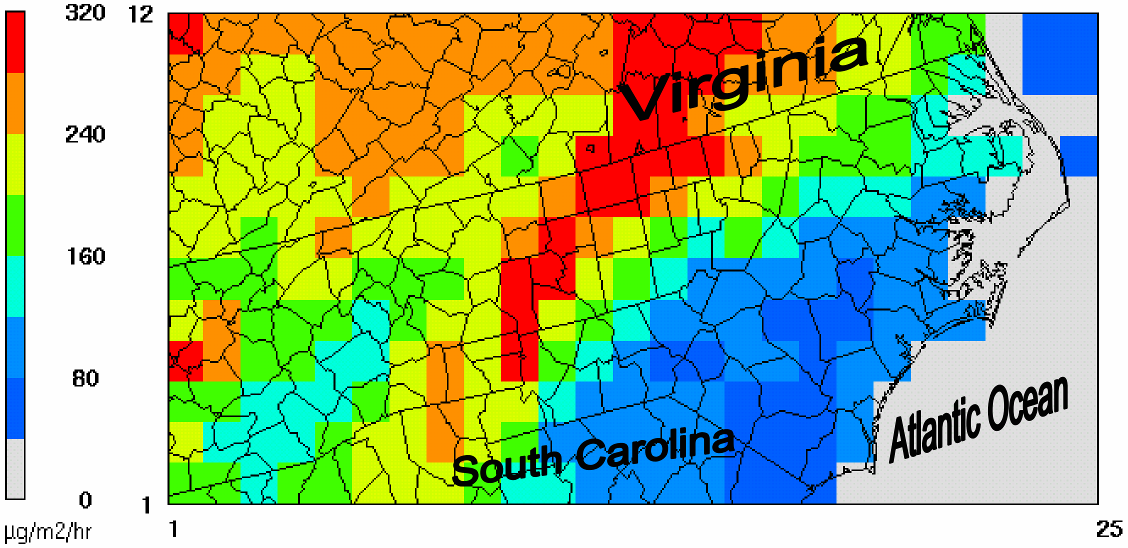
Figure 5a,b

(a)



Mean Modeled NH_3 Dry Deposition in North Carolina during Summer 1999

(b)



Mean Modeled HNO_3 Dry Deposition in North Carolina during Summer 1999

Figure 6.

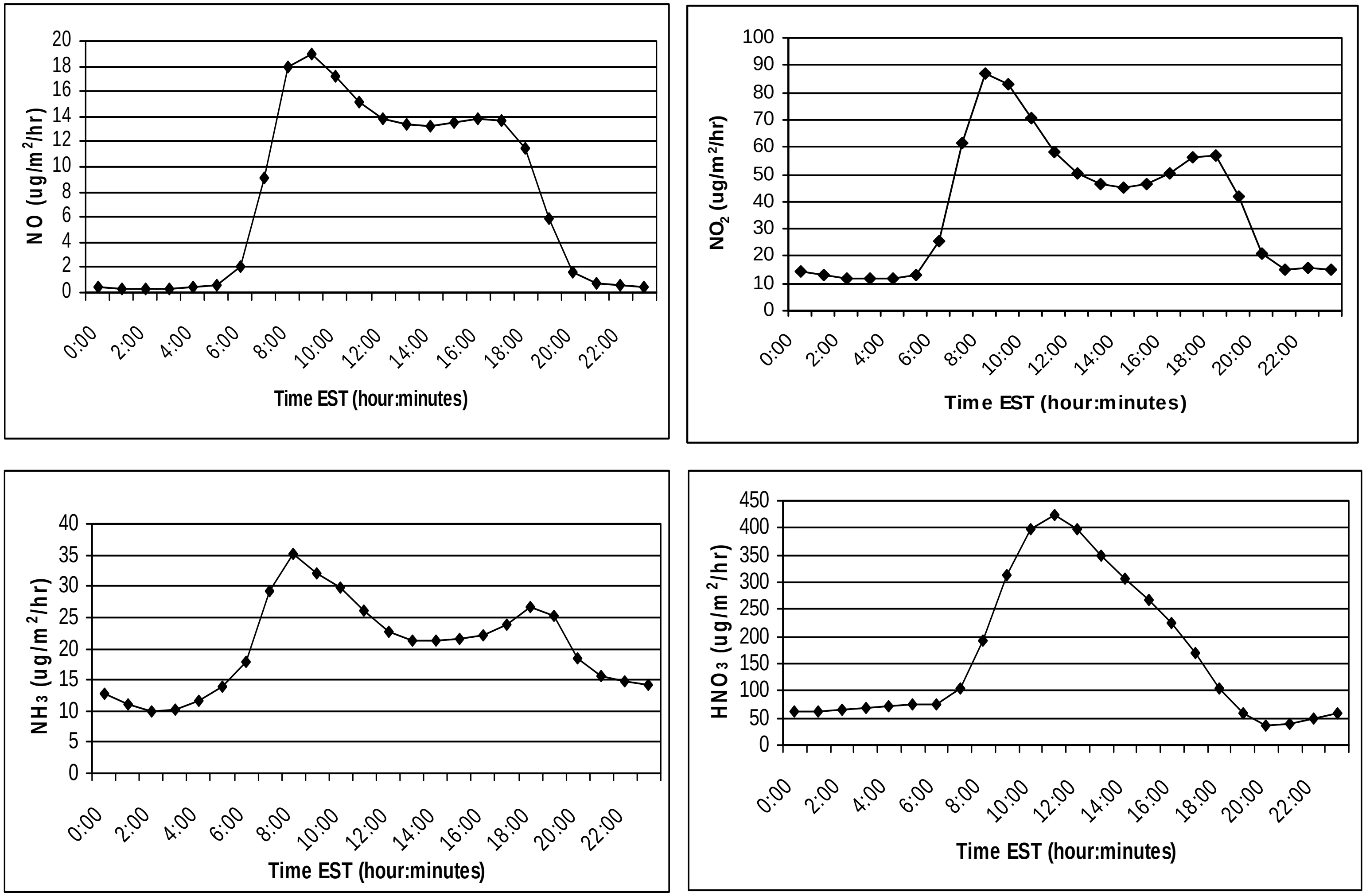

N O (ug/m²/hr)
0
2
4
6
8
10
12
14
16
18
20
NO₂ (ug/m²/hr)
0
10
20
30
40
50
60
70
80
90
100
NH₃ (ug/m²/hr)
0
5
10
15
20
25
30
35
40
HNO₃ (ug/m²/hr)
0
50
100
150
200
250
300
350
400
450
0:00
2:00
4:00
6:00
8:00
10:00
12:00
14:00
16:00
18:00
20:00
22:00
Time EST (hour:minutes)

Figure 7.