Impacts: Fate and Deposition

Trends of Nitrogen and Sulfur in U.S. Precipitation — the Roles of Combustion-Related and Agricultural Emissions

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Abstract

For more than a quarter century, the National Atmospheric Deposition Program - National Trends Network (NADP-NTN) has measured the acids, nutrients, and base cations in U.S. precipitation. NADP-NTN data are used to evaluate regional and seasonal variations and long-term trends in precipitation chemistry. Trends result from the combined effects of changes in natural and human-induced pollutant emissions, physical and chemical transformations, and weather.

Results of a Seasonal Kendall Trend test of 1985 - 2004 NADP/NTN data demonstrate that statistically significant trends have occurred in the chemistry of U.S. precipitation. Over this 20-year period, dissolved inorganic nitrogen concentrations (nitrate-N + ammonium-N) decreased in the northeastern U.S. and increased in mid-continental states from eastern Washington, Oregon, and California to the Mississippi River Valley. In these mid-continental states, both ammonium, largely from agricultural sources, and nitrate, largely from combustion sources, increased at most sites. In contrast, sulfate concentrations decreased throughout much of the continental U.S.

This paper will examine the roles of combustion-related and agricultural emissions, as well as the changing relationships between airborne nitrogen and sulfur species in affecting these trends.

Introduction

Widespread, statistically-significant increases in ammonium concentrations in precipitation have occurred throughout much of the continental United States (Lehmann et al., 2005). The figure, below, displays the direction and magnitude of Sen's median estimators of the 20-year (1985-2004) ammonium concentration trends at 159 NADP/NTN sites (Lehmann et al., 2006). Upward trends are largest in mid-continental states, where there is a large area with increases exceeding 50 percent (>2.5 percent per year). Throughout much of this area, sulfate concentrations decreased (Lehmann et al., 2005; Lehmann et al., 2006).

Ammonium and sulfate react to form stable submicron aerosols that can be transported long distances (> 500 km) in the atmosphere. The relative amounts of these species affect the chemical makeup of the aerosols, but under atmospheric conditions the various combinations of ammonium and sulfate are stable. Once the ammonium concentration exceeds the amount that will combine with sulfate, the excess can form ammonium nitrate, a labile aerosol at equilibrium with gas-phase ammonia and nitric acid (Seinfeld and Pandis, 1998). These gases are highly soluble, increasing the likelihood of being deposited short (< 500 km) rather than long distances from the source before deposition. Modeling results have indicated that when sulfur and nitrogen oxide emissions are reduced in relation to ammonia emissions, ammonia remains in the reactive gas phase, significantly reducing the transport distance and leading to local deposition (Hov and Hjollo, 1994).

Sulfate decreases, accompanying recent sulfur oxide emissions reductions (Lynch et al., 2000), have resulted in an increase in the number of precipitation samples in which the chemical equivalents of ammonium exceed sulfate (Lehmann et al., 2006). This shift from an atmosphere with a sulfate excess to one with an ammonium excess can affect ammonium deposition patterns, possibly resulting in increased deposition close to sources.

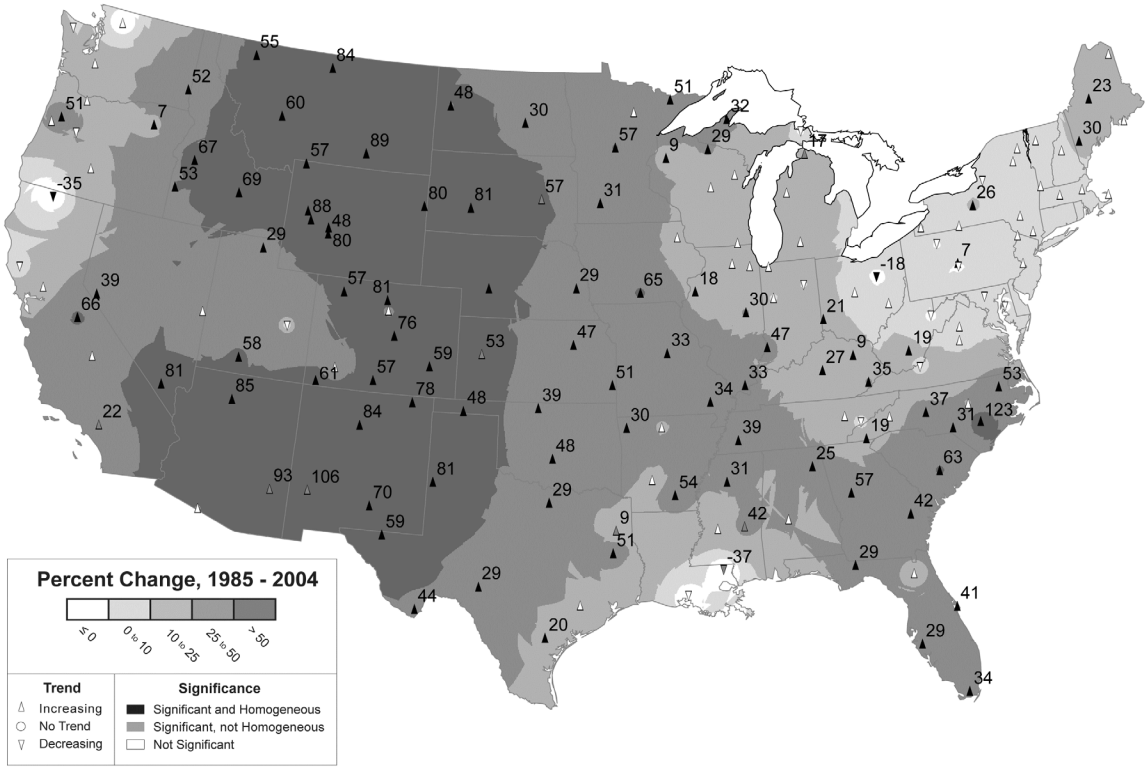

Figure 1. Ammonium concentration trends in precipitation at 159 NADP/NTN sites (Winter 1985 – Fall 2004). Symbols display trend significance ($p \leq 0.10$) and seasonal homogeneity ($p > 0.10$). Numbers display percent changes (Sen's estimators), where trends are significant.

Methods

This paper will report the 20-year concentration and deposition trends of sulfate, ammonium, nitrate, and dissolved inorganic nitrogen (ammonium-N + nitrate-N) in precipitation. Sulfate and nitrate are related to emissions of sulfur and nitrogen oxides, which originate mostly from fuel combustion. Trends of sulfur and nitrogen oxide emissions will be compared with trends of sulfate and nitrate in precipitation. Ammonium in precipitation is related to ammonia emissions, which originate mostly from agricultural activities, and to the relative amounts of gaseous ammonia or particulate ammonium sulfate or ammonium nitrate that are captured in and below clouds. Trends of ammonium in precipitation will be compared with trends of ammonia emissions, as well as changes in the physical and chemical forms of ammonia/ammonium scavenged by precipitation.

Neither of the large regional or U.S. national air quality networks (Clean Air Status and Trends Network, Interagency Monitoring of Protected Visual Environment network) measure gaseous ammonia, nor do they discriminate between particulate ammonium sulfate or ammonium nitrate measurements. As a consequence, it is not possible to examine changes in airborne ammonia and ammonium on a regional or national scale. Instead, changes in the ratio of ammonium to sulfate in precipitation will be used to infer changes in the relative amounts of gaseous and aerosol ammonium. In addition, it is not possible to track changes in ammonia emissions over the 20-year trend period (1985-2004) examined in this paper. The U.S.

Environmental Protection Agency (EPA) only started reporting ammonia emissions estimates in 1990. To complement the EPA estimates, ammonia emissions will be calculated using the Carnegie Mellon Ammonia Model (Carnegie Mellon University, 2004), which combines emission factors and agricultural activity (e.g., numbers of cattle, swine, poultry, and dairy and amount of fertilizer applications) to compute emission fluxes.

Together, the emissions and air chemistry changes will be used to evaluate the cause of reported ammonium wet deposition trends.

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Reactive Nitrogen Species and Nitrogen Deposition in the North China Plain

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Abstract

The North China Plain (NCP) is called the granary of China since it provides more than 30% of China's total wheat and corn production. Winter wheat – summer maize crop rotation systems with nitrogen applications of up to 600 kg N ha^{-1} yr^{-1} are most common. The nitrogen efficiency of these crop rotations is often below 30% and considerable amounts of nitrogen are lost both by leaching and by emission of gaseous nitrogen species. These emissions from crop rotations, together with emissions from animal husbandry and with growing emissions of oxidised nitrogen species from traffic exhaust, are expected to generate high atmospheric concentrations of reactive nitrogen species and high amounts of nitrogen deposition. A monitoring network for wet and dry deposition of nitrogen was established at several locations in 2003. Here we present recent data on atmospheric concentrations and deposition of reactive nitrogen species in the NCP and report on approaches involving plants for the biomonitoring of N deposition.

Introduction

During the last decade China´s economic growth has been much faster than in most other countries, which lead to alarming levels of environmental pollution in some regions (He et al., 2002). Also agriculture experienced major changes in the past years, with the North China Plain (NCP) being the largest and most intensively used agricultural region.

The current situation of China's agriculture is rather intricate. On the one hand a growing population demands an increasing food production, which can only be met by reaching a higher productivity of the sector. On the other hand the availability and sustainability of arable land is limited and in some regions it is decreasing with the ongoing urbanisation.

At present China is the country with the highest consumption of N-fertilisers in the world and the excessive and unbalanced use of mineral fertilisers is a major environmental concern (Pacholski, 2003). At the same time the increasing car fleet causes traffic related problems and increasing emissions of oxidised nitrogen. In Beijing alone, the number of vehicles increased by a factor of 4 from 0.66 million in 1994 to 2.6 million in 2005 and vehicle emissions of NO_x and particulate matter (PM) are expected to further increase. Besides the traffic, industrial facilities and co-generation power plants may be regarded as the most important sources of urban air pollution. Energy use and air pollution have been synonymous in China for decades, especially in urban areas. In rural areas, air pollution is also severe because a significant amount of industry that is highly dependent on coal as an energy source is located in the countryside (Tang, 2004).

The study region (NCP) is indicative of all the ecological and health related problems listed above. It is called "China's granary" because it has the highest agricultural productivity nationwide with a dominance of double cropping systems involving winter wheat and summer maize. It provides approximately 41 % of wheat and 25 % of maize yield of China's total grain yield (Böning-Zilkens, 2004).

Extensive and non-sustainable nitrogen fertilizer applications of up to 600 kg N ha^{-1} yr^{-1} are most common. However, the nitrogen efficiency of the crop rotations is often below 30% and considerable amounts of nitrogen are lost both by leaching into the groundwater and by emission of gaseous nitrogen species into the atmosphere.

The NCP is located at the east of Taihang and Funiu mountains, covering parts of the provinces of Beijing, Hebei, Tianjin, Shandong, Henan, Anhui and Jiangsu. This means not only emissions from fertilised and

manured fields but also emissions from animal husbandry in NCP particularly in the surroundings of Beijing contribute to the high loads of reduced nitrogen. Being mixed with the NO_x-emissions from industry and traffic, these emissions are expected to generate high concentrations of reactive nitrogen species and high deposition loads (Galloway, 2003).

Up to now reliable estimates of NO_x and NH_y in the NCP are largely lacking, and a monitoring network comparable to European (e.g. Schmitt et al., 2005) or US standards does not yet exist. The present study thus aims to monitor air pollution and nitrogen deposition and its effects in the NCP.

Material and Methods

The total nitrogen deposition in the NCP is being investigated in the framework of an international DFG-funded research training group performed by China's Agricultural University (CAU) and the University of Hohenheim, Germany (http://rtgchina.uni-hohenheim.de). The project is divided into three parts addressing wet deposition, dry deposition and effects related bioindication.

A monitoring network for bulk nitrogen deposition was established in the NCP in 2003 with 15 stations. Bulk deposition is routinely monitored similar to Europe using standard rain gauges (SDM6, Tianjin Weather Equipment Inc., China). In addition, in 2004 three monitoring stations have been equipped to monitor wet-only deposition using an Auto Precipitation and Dust Sampler (APS-III, Wuhan Tianhong Inc., China).

Measurements of both the gaseous and particulate nitrogen species have been commenced in 2005 in order to investigate dry deposition. In different locations at three experimental farms of the CAU we operate passive samplers (Radiello) to measure ammonia on a fortnightly basis. Furthermore, a High Volume Sampler (Digitel DHA-80) has been installed to collect total suspended particulate matter (TSP), PM10 and PM2.5 at a site near Beijing. In spring 2006 a nitrogen oxide analyzer will be installed as well.

In order to study the effects of nitrogen deposition an active biomonitoring system was tested in 2005 at the three sites in NCP and at various locations in SW-Germany. Clones of a European grass species, which is known to have spread in past decennia in regions with high nitrogen deposition loads, were used for these experiments (using the system of VDI, 2003). We wanted to test the hypothesis if unfertilised test plants exposed in the field could use the local nitrogen deposition in order to increase biomass and nitrogen levels (Franzaring & Fangmeier, 2004). Another plant related method applied in the project, is the ITNI ^{15}N-dilution technique similar to the method developed by Mehlert et al. (1995) and Russow et al. (2001), which was used to estimate plant (winter wheat and maize) availability and total amount of N deposition at the same three sites as the active biomonitoring system.

Results and Discussion

First results from the monitoring campaigns suggest nitrogen deposition in the NCP to be as high as 70 kg ha^{-1} yr^{-1}. In Beijing, bulk deposition of inorganic N averaged about 30 kg N ha^{-1} yr^{-1} with ratios of NH_4-N to NO_3-N up to 2.2. Inputs of organic N from precipitation were measurable but were much smaller than those of inorganic N. Bulk deposition of N, in particular NH_4-N, was significantly higher than wet-only deposition, indicating substantial contribution of large-size particulate matter (e.g., dust from agricultural activities) to bulk N deposition in NCP. The difference between bulk and wet-only deposition of inorganic N was around 8.4 kg N ha^{-1} during the main rainy season in 2003 and 2004, which was equal to 45% of wet-only N deposition in the same period (Liu et al., 2006, in press). Obviously, as part of dry deposition, the additional N in bulk deposition relative to wet-only deposition mainly derived from large-size PM or dust, whose fall-down is driven by gravity. The initial results suggest that dry deposition of N was substantial in NCP in particular Beijing.

The levels of particulate matter (PM10) exceed European (50 µg m^{-3}) and even Chinese (150 µg m^{-3}) thresholds by far. Also the EU standard for the number of tolerated daily exceedances is not met in the Beijing area. Results of our PM10 measurements showed 125 exceedances of the daily mean European threshold during only five months. In comparison the quantity of exceedances of the European daily mean threshold in rural European regions is less than 20 times per year (BUWAL, 2005). The maximum daily mean of 429 µg m^{-3} also reflects the high PM peak concentrations in Beijing area. Although the PM monitoring site is located in an agricultural setting we note that the air quality at this site is much affected

by air masses from the nearby Beijing mega city. Primary pollutants (NO_x, VOCs, SO_2 and TSP) from the city and their secondary products (ozone and secondary particulates) will thus also be present here. This is indicated by the high concentrations of PM2.5, which is normally made up from secondary particulates. Analyses of the chemical composition of the PM10 samples are on the way to characterize the major sources of the dry particulate deposition. First results indicate that there is not much nitrogen present in the PM10 fraction. However, other particle associated pollutants (heavy metals and organic compounds) may pose ecological and health risks in this area.

In order to also address the gaseous dry N-deposition we determined ammonia concentrations at various sites in the NCP. The levels showed strong seasonal and spatial variability and a correlation to the dust loads at the Beijing site. Latter finding indicates that air pollution may be strongly affected by agricultural activities at that site.

Ammonia monitoring and biomonitoring were synchronised in order to study the potential effects of nitrogen deposition to plants. Although not native to China, clones of the bioindicator species survived the exposure in the three NCP locations. However, plants of the temperate grass species were taller in the German locations and plant weight generally declined from north to south due to higher average temperatures and shorter day length at lower latitudes. Average ammonia concentrations at the German reference sites varied from 2.3 to 7.3 $\mu g\ m^{-3}$, which are rather low concentrations just above the background levels. In China seasonal ammonia levels were in the range from 10 to 43 $\mu g\ m^{-3}$, which indicates intensive agricultural activity. While in Germany plant growth parameters (height, dry weight) were not related to the (low) ammonia concentrations, senescence proved to be somewhat retarded in plants exposed to higher ammonia levels. It therefore seems that the availability of airborne reduced nitrogen may increase the vitality or reduce senescence in this plant species. At the Chinese sites, however, where higher ammonia concentrations were recorded, no correlations between ammonia, growth parameters and senescence were identified.

To quantify atmospheric N deposition a ^{15}N dilution technique is being used, which also relies on using plants. Quantification of the total N deposition in NCP with model plants is going on with winter wheat and the analysis of maize is on the way. Final results including both maize and winter wheat will indicate the total airborne N input into a soil-plant system in NCP.

Outlook

As the results on atmospheric N-deposition measured with the presented methods confirm high levels of wet and dry deposition in NCP, we plan to continue the series of measurements in 2006. We will then strongly focus on integrating the different approaches to monitor wet, gaseous and particulate matter deposition and consider the sources and chemistry of nitrogen deposition as well as its relationship to the local meteorology. Furthermore an ecological impact study of nitrogen deposition effects on plants and semi-natural vegetation using suited biomonitoring approaches will be set up.

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Dry Deposition of Ammonia in the Vicinity of a Swine Production Facility

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Abstract

While animal production facilities have been identified as important sources of atmospheric NH3, there are no estimates of local NH3 dry deposition for U.S. sites. Such estimates are necessary to estimate net farm-scale emissions and for assessing the risk of neighboring ecosystems to nitrogen deposition. This project investigates the dry deposition of NH3 around a 5000 head swine production facility located in eastern North Carolina. Passive samplers are used to measure weekly-integrated NH3 concentrations along horizontal gradients from the lagoon/barn complex out to a distance of 500 m. Dry deposition is estimated using a canopy compensation point model. Here we present data for the period April, 2003 to August, 2005 with emphasis on modeling results and uncertainty. Dry deposition rates range from 200 kg NH3-N/ha/yr within 25 m of the lagoon/barn complex to 5 kg NH3-N/ha/yr at a distance of 500 m. Assuming a steady-state emission factor of 6.0 kg NH3/animal/yr, NH3 dry deposition over the nearest 500 m from the barn/lagoon complex accounted for 11.6 (± 3.5)% of emissions between July, 2003 and July, 2004.

Biogeochemical and Ecological Impacts and Ramifications of Atmospheric Nitrogen Deposition to Estuarine and Coastal Waters

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Abstract

Atmospheric deposition of nitrogen (AD-N) is a major contributor of externally-supplied or "new" nitrogen (N) to N-sensitive estuarine and coastal waters. Watershed N export estimates indicate that AD-N can be a significant source of N input to these waters (indirect AD-N). Direct deposition to these waters is an additionally important new N source that can bypass the terrestrial and in-stream filters that process N entering via the watershed. In European and North American coastal waters downwind of anthropogenic emission sources, AD-N contributes from 10 to over 40 percent of new N loading, and can be the single largest source of new N impacting these waters. In developing regions of the world, AD-N is one of the most rapidly expanding sources of new N. In North Carolina, USA, AD-N deposition has at least doubled since the 1970's as a result of urbanization (chiefly NOx) and more recently agricultural growth (NHX and organic N). Recent growth and intensification of animal operations in the Midwest and coastal regions (e.g., Mid-Atlantic coastal plain) have been linked to increasing amounts of NHX deposition, according to a 3 decadal analysis of the National Atmospheric Deposition Program (NADP) wet deposition network. Ammonia emitted from these operations accounts for approximately half the AD-N in nearby estuarine and Atlantic coastal waters. The ecological ramifications of this growing N source in N-sensitive estuarine and coastal waters include eutrophication, manifested as algal blooms, hypoxia and food web alterations. The role of AD-N in eutrophication dynamics depends on sources, chemical forms and amounts of N and interactions with other atmospheric nutrient sources (Fe). Trophic and biogeochemical effects of AD-N are dependent on physical conditions, including stratification, residence time, and optical properties of receiving waters. Quantitative and qualitative aspects of AD-N and other atmospheric nutrient sources may promote major biotic changes now apparent in these waters, including the proliferation of harmful algal blooms, declines in water quality and loss of fisheries habitat. Because of its relatively large contribution to total new N loading and potential biogeochemical and ecological importance in N sensitive waters, AD-N requires attention from local and regional air/watershed nutrient budgeting and management perspectives.

The Fate and Transport of Ammonia at the Local to Regional Level

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Extended Abstract

Atmospheric deposition of nitrogen (N) is a major contributor to eutrophication of estuarine and coastal waters. It is estimated to contribute 20-35% of the N load to east coast and gulf coast estuaries in the United States. Most of the N loading is contributed indirectly by first depositing on the watershed. Currently, oxidized-N from nitrogen oxide (NO_x) emissions from combustion is the major source of N in total (wet + dry) atmospheric deposition. With the anticipated control of NO_x emissions, to reduce ozone, model projections suggest that reduced-N from ammonia (NH_3) emissions will become the major source of atmospheric N deposition in the future. Agriculture is by far the largest contributor to ammonia emissions.

In some disciplinary areas the conventional wisdom is that all of the NH_3 emissions deposit locally, an idea that is not consistent with what we know in the atmospheric community.

Early budget studies with regional air quality models carried out by the first two authors suggested that at emission hot spots only a very small fraction of the ammonia emissions is dry deposited locally. Most of the emissions are lofted into the atmospheric mixed layer and transported away from the hot spot. However, the ammonia deposition velocities calculated by the regional models were very low compared to those measured in Europe. Subsequently, the deposition velocity algorithms in the Community Multiscale Air Quality model, CMAQ (Byun and Ching, 1999; Byun and Schere, 2005), were updated in 2004 with the result that the ammonia deposition velocities now calculated are much higher.

We have undertaken a new set of budget studies with version 4.5 of CMAQ at a 12-km grid size for a domain covering the eastern United States. Process analysis outputs from CMAQ, quantifying the contribution of advection, deposition and chemical processes contributing to the concentrations within a grid cell, and brute-force sensitivity analyses are used to provide the information for the budget analyses. The budget analysis has also been extended to include wet deposition as well as dry deposition and to examine the total ammonia (particulate ammonium + gaseous ammonia) budget. Total ammonia is termed NH_X. Preliminary results for June 2002 illustrate a number of findings from the fate and transport budget analysis.

At the highest emission rate cells (termed hot spots) the surface NH_X fate or budget is dominated by turbulent transport or vertical mixing. The turbulent mixing transports a majority of the surface NH_3 emissions up and away from the surface and into the atmospheric mixed layer (planetary boundary layer). Typically 2/3rds of the emissions are moved aloft. Once aloft, most of the ammonia (more than 2/3rds) is transported by horizontal advection (winds) away from the hot spot and a small fraction is converted to aerosol ammonium and an even smaller fraction is wet deposited.

Local, dry plus wet (total) deposition is an important, though not dominant, loss pathway for the ammonia emissions. With CMAQ version 4.5, approximately a quarter (15-30%) of the hot spot emissions deposit locally in the same grid cell as the emissions. The largest contributor, by far, to the local total deposition is dry deposition. For the hot spot and close-by surrounding model grid cells, dry deposition is significantly higher than wet deposition. Dry-to-wet deposition ratios for the hot spot grid cells can range from 2-10.

We also cast a wider box around the hot spots to encompass regions the size of states and larger to study the regional behavior of the ammonia budget. All of the emissions from grid cells within the box are counted in addition to the hot spot emissions. The budget is assessed throughout the vertical extent of the model which includes the mixed layer as well as the free troposphere. As the box size is increased, the emitted ammonia is increasingly converted to ammonium. At the same time, as the size of the budget domain increases, the fraction of the NH_X budget that is wet deposited increases, the fraction of the budget transported out of the domain decreases, and the fraction dry deposited rapidly stabilizes. When the box is the order of 500 km on a side then the regional ammonia emission budget tends to be divided almost equally between dry deposition, wet deposition and transport out of the region. As the domain of analysis increases further to 900-1,000 km, wet deposition becomes the major loss pathway for the regional emission budget; transport out of the domain becomes the minor loss pathway with the dry deposition fraction tending to remain about the same.

It is interesting to note that over the hot spot the NH_X dry deposition is basically all from ammonia. As the box size for the budget analysis increases, dry deposition is still dominated by deposition of ammonia gas with particulate ammonium making only a modest contribution. Over the hot spot, ammonia gas is a major contributor to the NH_X wet deposition. But as the box size increases, wet deposition is increasingly dominated by ammonium and gaseous ammonia is only a modest contributor to it.

Investigation of the magnitude of the ammonia dry deposition velocities in CMAQ suggests that they are much too high. Data from ammonia deposition field study experiments in North Carolina formed a basis for this judgment. Thus, the local budget estimates for dry deposition from CMAQ 4.5 are expected to be on the high side. To provide a more balanced assessment of the ammonia fate and transport, a sensitivity run with CMAQ has been developed in which the calculated ammonia deposition velocities are much lower, representing what is believed to be a lower bound. Ammonia emission fate and transport budget estimates will then be described in terms of an upper and lower bound from the regional air quality model analyses.

Disclaimer

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