Comparison of Ammonium in USA Wet Deposition to Ammonia Emission Estimates

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ABSTRACT

The Acid Deposition Control Title (IV) of the 1990 Clean Air Act Amendments calls for reductions in annual sulfur dioxide and nitrogen oxide emissions in order to "reduce the adverse effects of acid deposition," without addressing emissions of ammonia. Ammonia is present in precipitation and aerosols as the ammonium cation, NH_4^+. Ammonium is rich in nitrogen and together with nitrate comprises virtually all of the inorganic nitrogen deposited by precipitation. A substantial database exists for ammonium in precipitation while the air quality record for ammonium is limited. This paper presents spatial and temporal patterns in the precipitation ammonium record and compares these patterns to those for ammonia emission estimates.

Data from the National Trends Network (NTN) of the National Atmospheric Deposition Program (NADP) are used to examine 5-year average ammonium concentrations in precipitation for two time periods: 1985-89 and 1995-99. The spatial distributions of ammonium concentrations in precipitation in the contiguous United States are shown as maps. These maps were based on objectively-analyzed data from 150 NTN stations that met pre-selected data completeness criteria in both periods. To examine the ammonium changes between these two periods, a difference map was developed in which the objectively-analyzed 1985-89 concentrations were subtracted from the objectively-analyzed 1995-99 concentrations. Ammonium concentrations generally increased over this 10-year interval (mean difference: .054 [s.d. .052] mg/L or +25.6% [s.d. 23.5%], median difference: +.045 mg/L or +22.5%, range: -.051 mg/L to +.317 mg/L or -24.9% to +121%). For each of the time periods the area of highest ammonium concentration extends from northwestern Texas to North Dakota and eastward to southern Michigan.

Emissions of airborne ammonia in the two 5-year periods were estimated in an effort to identify a potential explanation for the ammonium increases in precipitation. Sources considered were livestock manure (beef cattle, dairy cows, pigs, laying hens, broiler chickens, and turkeys), synthetic fertilizer, and automobile exhaust. Emissions from all of these source categories increased, except for dairy cattle (decreased) and beef cattle (about the same). Ammonia emissions from these categories increased by 7.8%, considerably less than the increase in precipitation ammonium concentrations. Possible reasons for this apparent inconsistency are discussed. Mass balance considerations suggest that the estimated ammonia emissions are biased substantially low.

INTRODUCTION

There is considerable interest in developing accurate inventories of atmospheric ammonia emissions. Since ammonia readily reacts with sulfuric acid aerosols, the patterns and trends in ammonia emissions may affect atmospheric visibility, and the composition of $PM_{2.5}$ aerosols. The nitrogen (N) cycling in ecosystems affected by atmospheric N deposition may be affected by the patterns and trends of ammonia emissions. In the last 10-20 years there has been a continual of the shift from many farmers having a few animals to a few farmers having many animals concentrated in compact feeding facilities (CAFOs). CAFOs can lead to locally severe odor and stream water quality problems, which have, therefore heightened interest in atmospheric ammonia emissions and other waste handling and disposal issues associated with these facilities.

In the last 15 years, many publications have addressed the issue of the magnitude of ammonia emissions from various sources. Researchers from northwestern Europe (Netherlands, England, Scotland, Denmark, and Germany) have been particularly active in investigating ammonia emissions.[1,2,3,4,5,6,7,8,9,10,11] There is general agreement that livestock waste is the largest source of ammonia emissions. Livestock densities in parts of Europe (especially the Netherlands) are particularly high. It would be useful to compare ammonia emissions with ambient air concentrations; however, ammonia is not measured by ambient air monitoring networks in the USA. The rural eastern monitoring sites in the U.S. Environmental Protection Agency Clean Air Sampling and Trends Network (CASTNet), in operation since 1987, measure ammonium in aerosols but not ammonia in air. Furthermore, there are few CASTNet sites in states of the Midwest and Great Plains where precipitation chemistry data suggest that ammonium (and thus probably ammonia) concentrations peak. Without data for both gaseous ammonia and ammonium aerosols, one can only roughly estimate the dry deposition of atmospheric N from these sources.

Ammonia vapor and ammonium aerosols are scavenged by precipitation. Atmospheric ammonium is predominately in the form of submicron ammonium sulfate or ammonium bisulfate particles that serve as condensation nuclei, forming cloud droplets. Ammonia vapor dissolves in cloud droplets and undergoes chemical conversion to ammonium. In precipitation samples, ammonium is one of the major ions necessary to understand/calculate the pH of precipitation (Stensland[12] Encyclopedia Article) and as a result is an ion that is always measured by precipitation chemistry networks. As a result, extensive datasets are available to estimate wet deposition of ammonium.

In this paper, we compare the upward (or emission) fluxes of ammonia, using emissions factors from the literature, with the downward (or deposition) fluxes of ammonium in precipitation, using NADP/NTN data. All fluxes are presented in mass units of the element nitrogen, using the notation NH_3-N and NH_4-N. We do this to avoid the confusion, which sometimes appears in the literature, between expressing fluxes in mass units of the molecular ammonia (NH_3 as NH_3) or ammonium (NH_4 as NH_4) and mass units of elemental nitrogen (NH_3 and NH_4 as N).

DATA SOURCES AND METHODS

Two types of data sets are used for this study, precipitation chemistry data and emissions data. Characteristics and data-selection procedures for these two classes of data are discussed in this section.

Data from the NADP/NTN database[13] were used to produce 5-year precipitation-weighted average ammonium concentrations in precipitation for two time periods: 1985-89 and 1995-99. The precipitation amount data were from measurements made at each site using a dual-traverse weighing-type raingage. For those infrequent cases where the raingage was inoperative or the raingage measurements were invalid the precipitation amount was determined from the volume of the sample collected in the precipitation chemistry sampler. Contour maps were made to show the spatial distributions of ammonium concentrations in precipitation in the contiguous USA. ArcView® Spatial Analyst was used to calculate regular grid-point values every 2.5 km, using the irregularly spaced site data within a 500 km radius of each grid-point. In calculating grid-point values, site data points were weighted using a factor proportional to the inverse distance cubed between the site locations and the grid-point locations. Difference fields were calculated by subtracting the grid-point values of the two time periods. Software contoured the field of grid-point values. The final result is a set of contour maps of objectively analyzed precipitation chemistry data.

Wet deposition was calculated for various areas of the USA. The ion deposition at a site for any summary period was obtained by multiplying the average ion concentration by the total precipitation for the site (as determined by the raingage). Raingage values are available for weeks when precipitation chemistry data may be missing due to equipment failure or due to failure to meet data screening standards. Thus the wet deposition at a site determined by this method will sometimes exceed that determined by summing the weekly deposition values for valid chemical samples. The ion deposition to any area was determined by using the objective analysis procedure described above to get deposition values for the summary period for grid-points separated by 2.5 km. The total deposition to any area was calculated by summing the deposition values for the grid-points located inside the boundary of the area being considered.

A screening procedure was applied to the data for each NADP/NTN site as a means to ensure that the data were representative. Only samples from the NADP database[13] without a flag in the "Invalcode" column and of "Lab Type W" were used. The former means that the NADP has identified the sample as being valid. "Lab Type W" means that at least 35 mL of sample reached the central laboratory, which indicates that at least two hundredths of an inch of precipitation was collected during the sampling period. Only sites meeting the following criteria for both five-year periods were used in the analysis: 1) Valid chemistry samples were obtained from at least 70 percent of the time and 70 percent of the total measured precipitation, 2) precipitation measurements were obtained for at least 85 percent of the time, and 3) The ratio of the accumulated precipitation depth, estimated by the sample volume, was at least 75 percent of the accumulated precipitation depth, measured by a precipitation gauge. These criteria are slightly relaxed from those applied by NADP/NTN to select representative sites for annual summaries.[13]

The NADP/NTN has several noteworthy characteristics:

1) The sampling site locations were selected to provide precipitation chemistry data that would be representative of a region as opposed to a local area that might be dominated by a few pollution sources or by an urban area.
2) Sites are long-term; 168 sites have operated for 15 or more years.
3) Each site collects samples with the same model automatic wet-dry collector. All sites are also equipped with a recording raingage, a wet-dry open/close event recorder, a high-quality pH meter, a high-quality conductivity meter, and a balance to determine the weight of the samples before they are sent to the Central Analytical Laboratory (CAL).
4) Each site is serviced every Tuesday morning at approximately 9 AM local time. The precipitation is transferred to a shipping bottle and sent to the CAL each week. The collection bucket is sent to CAL for cleaning whether or not precipitation has occurred..
5) There is only one CAL for the NADP/NTN. Since the project began in 1978, the CAL has been located at the Illinois State Water Survey in Champaign, IL. This laboratory measures the chemical parameters for each rain and snow sample and returns clean sampling containers to the field sites. All samples are filtered within one working day after receipt at the laboratory, which provides an operational definition of the soluble constituents measured.
6) A very thorough data screening/flagging system is in place so that the NADP/NTN data tend to be free of glitches. Data users need not invest time to clean up the data.
7) A very extensive QA/QC program is in place. The U.S. Geological Survey operates an external QA program for the NADP/NTN, which includes submitting double blind QA samples to the CAL several times per month. The U.S. EPA funds a site audit program for the NADP/NTN with sites being visited every 2-3 years.
8) The data are available to everyone, free of charge, 6-8 months after the samples are collected.

The spatial pattern of emissions of ammonia to the atmosphere can be compared to NADP ammonium concentration or to ammonium deposition. We believe that the comparison to concentration is most appropriate. Therefore for two five-year periods we will compare the estimated change in ammonia emissions to the change in precipitation ammonium concentrations. We have examined the correlation of annual ammonium concentration in precipitation to annual precipitation amount, for each of the NADP sites. In general no statistically significant linear correlation was found. This means, for example, that if emissions over the USA were the same for two five-year periods we would expect the average ammonium concentration in precipitation to also be the same but if the precipitation amount had increased by 20% then the ion deposition would increase by 20%. To remove the confounding effect of an increase in precipitation amount we will use the same precipitation amount field for both of our five-year periods.

The emissions of ammonia to the atmosphere will be calculated by multiplying emission factors by source strength. Table 1 shows the eleven source categories considered for the global ammonia emissions inventory for 1992 constructed by Bouwman et al., 1997.[2] On a global basis the oceans are an important source, contributing 15.2%, but are a small source for continental areas. Sutton et al.[14] estimated 81% of the 1996 ammonia emissions for the United Kingdom to be from agricultural activities (livestock and fertilizer). A recent emissions trends report from USEPA[15] estimates 71% of the ammonia emissions to be from livestock, 15% from fertilizer, 3% from light-duty gas vehicles & motorcycles (on-road vehicles) and 11% from all other sources.

Table 2 lists the five sets of ammonia (NH_3-N) emission factors used in this study. Available resources limited the source categories that we could include. We chose to use emission factors that were used in three recently published papers on ammonia emissions.[2,10,16] For agricultural source categories, we used the values from the three papers, although not all categories were specified in each paper. Sutton et al.[10] did an extensive literature review literature to arrive at best estimates of the ammonia emission factors for Great Britain and these are shown in the column labeled GB1995-B (where GB indicates Great Britain, 1995 is the year of the publication, and B indicates that it was a best estimate). Low (L) and high (H) emission factors from Sutton et al.[10] are listed in the columns labeled GB1995-L and GB1995-H, respectively. They gave single values for broilers and hens, and for dairy cows and beef cattle, (see Table 2) instead of separating these categories. For each source category they critically reviewed the literature to come up with uncertainty values that represent their range of possible values for the emission factors. By grouping their largest possible values for emission factors for each catergory into a "high" set, and the same for the "low" set, we have formed two extreme sets of emission factors that are useful in sensitivity tests in the comparison to wet deposition fluxes.

Bouwman et al.[2] also did an extensive literature review to develop a set of global emission factors for developed countries and another set for developing countries, with the former being used in Table 2 and labeled as G1997 (with the "G" referring to global). These authors also did not separate the emissions factors for broilers and hens, so the same value is assigned to both categories in Table 2. For cattle Bouwman et al.[2] gave two emission factors, one (20.4) that clearly seems to apply to dairy cows only (not including beef cows) and the other (7.8) to all cattle except dairy cows.

The last set of emission factors for animals, labeled NC1998, were calculated from data given in Aneja et al.[16] where they calculated emissions for North Carolina sources. Aneja et al. cite a Batteye et al.,1994 report[17] as the basis of their emission factors. Our review of the Batteye et al.[17] report discovered some misinterpretation problems that cause their composite hog emission factor to be elevated by 80% compared to the 1992 Asman report that they intended to follow. This problem also has also influenced animal ammonia emissions for hogs reported by USEPA.[13,18]

Bouwman et al.[2] gave ammonia emission factors for several different types of synthetic fertilizer, ranging from a 15% loss rate (to the atmosphere) for urea applied in temperate latitudes, 8% for ammonium sulfate, 4% for anhydrous ammonia, to 2% for nitrate solutions. These values vary considerably for different application methods and soil conditions. With proper incorporation of the fertilizer into the soil, the emissions factors are lower than those just listed. A composite fertilizer loss rate of 3% was chosen since Bouwman et al.[2] did not provide one. The same value was selected for the NC1998 set of emission factors.

Automobile emissions contribute only a small amount to the global ammonia emissions but were included because of their potential importance in **urban** areas (Kean et al.[19] and Ralof[20]). We used an emission factor of 60 mg/km[19] and an estimated mileage of 12,000 km/yr per person to arrive at an emission factor of .6 kg/yr/person as NH_3-N. This same value was used with each of the 5 sets of emission factors.

Goolsby et al.[21] considered ammonia emissions from crops to be important. Sutton et al.[10] indicated that they considered this source to be included in their emission factors for fertilizer. Aneja et al.[16], and a related paper, by Walker et al.[22] do not mention ammonia emissions from crops nor does the Batteye et al.[17] report that they cite as the basis for their emission factors. Bouwman et al.[2] discuss ammonia emission from crops and assign a NH_3-N emission factor of 2.5 kg/ha/yr for this source, recognizing that it is very uncertain. If this were included in their fertilizer EF then their global emission of fertilizer would have increased by 40%. For this paper we have not explicitly included emissions from crops.

Animal emission factors in Table 2 are reported in units of kg/yr/animal place used. Consider the emission factor for turkeys, which is 0.7kg/yr/animal place. This assumes that a turkey is present in an "animal place" for 365 days a year. If a Minnesota farmer has 100,000 turkeys in his buildings for only the six warm months and the buildings are empty the rest of the year, then the number of "animal places used" is 50,000. If an ammonia source is a building that has places for twenty dairy cows, but in fact is occupied for all 365 days by only ten dairy cows, then an inventory of the dairy cows would indicate that ten animal places are used for the year. The USDA cattle and hog inventories give the number of "animal places used" for the year that can be multiplied by the emission factors in Table 2 to get annual emissions shown in Table 3. In Europe, the same type of inventory is conducted for broilers and turkeys but this information is not available in the USA. Rather, the total annual production of broilers and turkeys is available from the USDA. To use production rather than census data with emission factors in Table 1, one must convert the production numbers to number of animal places used, by dividing by the number of flocks per year that pass through the turkey and broiler buildings. For North Carolina, Walker et al.[22] assumed 5.75 flocks per year for broilers and 3.5 flocks per year for turkeys. Averaged over the USA, with a considerable number of turkeys raised in northern states where heating costs are substantial, we assume that 2.0 turkey flocks would be raised each year and 6.0 broiler flocks.

Animal emission factors are available for subclasses of animals (e.g. sows, piglets < 60 pounds, pigs from 60 to 119 pounds, etc). Using the annual inventory results for the number of animals in each subclass, one can calculate the weighted average emission factors appropriate for the entire class of animals, and these are sometimes called composite emission factors. The composite emission factors for animals, generally having been developed in European studies, are generally assumed to be appropriate for use in the USA. Complications develop because different countries use different subclasses. For example, the youngest pigs in the USA are grouped into the <60 pound category while in Europe they are grouped in the <20 kg category. Thus, emission factors developed for subclasses of animals in Europe will not translate directly to the subclasses in the USA. Similarly the composite cattle emission factor developed for Denmark will be different than the one calculated for the USA, where there is a different ratio of dairy cows to beef cattle. It can also be difficult to know exactly what is meant by a term like "beef cattle" or "poultry" unless one reads the original report where the emission factors were developed. For example, Sutton et al. 1995[10] use the term poultry to include broilers and laying hens, while others use the term to refer to broilers, laying hens, turkeys, and ducks. The message is that nomenclature and definitions are important complications to consider as one tries to compare emission factors in different papers and reports.

RESULTS and DISCUSSION

For this study the main objective is to compare reduced nitrogen (NH_3-N) emission estimates (NH_3-N upward fluxes) to precipitation ammonium fluxes (NH_4-N downward fluxes). This will be done for the 48 contiguous states and for 3 subgroups of these states. The comparison will be done in the context of a mass balance, emission = wet deposition + dry deposition - net horizontal transport, with simple assumptions being made concerning the latter two unmeasured terms.

Figure 1 shows the precipitation-weighted average ammonium concentrations at 150 NADP/NTN sites for two 5-year periods, P1=1985-1989 and P2=1995-1999. Each site is shown as a dot. The concentration values are as milligrams per liter (mg/L) of the ion, not of the element (i.e. NH_4-NH_4), following the typical presentation of ammonium data by NADP/NTN. Later in this section, when comparisons are made to emissions, the precipitation concentrations will be converted to deposition, expressed as the element (NH_4-N). A region of high concentrations extends from northwestern Texas to southwestern Minnesota with a lobe extending eastward to Michigan and Indiana. Lower concentrations occur along the coastal margins of the country.

Some sites, such as the site in northern Utah, near Logan, have high values compared to nearby sites. A recent site visit showed that the Logan site is in a basin surrounded by mountains, so air stagnation episodes are likely to contribute to high ammonium values. The site may only reflect conditions in this basin although the objective analysis produces an area of very high values larger than the basin (see Figure 1). Photographs of the area (see http://nadp.sws.uiuc.edu/nadpdata/) show high mountains to the east and west of the site. Farms with livestock occupy the countryside for many miles around the site. A fairly large cattle feedlot about two kilometers southeast of the site surely contributes to the unusually high ammonium concentrations. The second site in Utah with elevated ammonium values is located on the grounds of a high school on the northwestern edge of the small town of Green River. During a visit to Green River a strong odor was noted near the municipal waste treatment lagoons a few kilometers south-southeast of the sampling site. A local resident suggested that this odor has been a concern for the town for some time. It seems likely that this lagoon contributes to elevated ammonium values at this site. The California site with elevated ammonium is on agricultural experiment farms of the University of California at Davis. Although livestock were not noticed in the immediate area during a site visit, most certainly synthetic fertilizers, another ammonium source, were applied to the crops in this intensely farmed area. The Pawnee Grasslands site in northeastern Colorado has elevated ammonium, especially noticeable on the map for the 1985-1989 period. One of the authors visited this site, noticing it to be surrounded for many kilometers by pastures with some grazing cattle. Many large cattle feedlots were noticed about 20-30 kilometers to the south-southeast, with a particularly large one about 20 kilometers from the site. Finally, note the somewhat elevated ammonium concentration for the 1995-1999 period at the most southeasterly site in North Carolina. A visit to the site a few years ago showed many big hog or poultry confinement operations in the county but not in the immediate vicinity of the site. A recent paper discusses the North Carolina ammonium data in detail Walker 2000.[22]

To more easily examine changes between the two time periods, a concentration difference map is shown in Figure 2. The objectively-analyzed 1985-89 concentrations were subtracted from the objectively-analyzed 1995-99 concentrations at each of the 2.5 km by 2.5 km grid-points. Ammonium concentrations increased over a very large area with the largest increases in the center of the country. Although this conclusion is not backed by any statistical test, the spatial coherence shown in Figure 2 makes the conclusion very firm. Summary statistics for the gridpoint concentration differences are as follows: mean difference: +.054 [s.d. .052] mg/L or +25.6% [s.d. 23.5%], median difference: +.045 mg/L or +22.5%, range: -.051 mg/L to +.317 mg/L or -24.9% to +121%.

In Table 3, the source strength columns list the number of people or animals and the kilograms of fertilizer used in the 48 contiguous states. Comparing these columns for the period 1985-1989 (P1) and the period 1995-1999 (P2) one should note that the values are all larger in P2, except for the number of dairy cows and the number of beef cattle (referring to all cattle except dairy cows). Looking at the emissions column for P1 or P2, one notes that beef cattle is the dominant emissions source, with fertilizer less than half as large, followed by hogs, then dairy cows or broilers, depending on the point. However, the total emissions increase from P1 to P2 is determined most strongly by the broiler category (increasing by about 80,000,000 kg of NH_3-N). If Table 3 were based on NC2000 emission factors instead of G1997 emissions factors, the situation would change since NC2000 has a hog emission factor that is 94% larger and a broiler emission factor that is 45% smaller. Finally, note the “% emission increase” values in the last column in Table 3, and recognize that these values remain the same when one of the other emission factor sets in Table 2 is used in Table 3.

In Table 5, we compare NH_3-N emissions with NH_4-N wet deposition, using the three subgroups of states shown in Table 4. The east-14 states all touch the Atlantic Ocean, except for Vermont. The west-11 states are the Rocky Mountain States and West Coast States. The middle-23 states include the Plains states and the states in the Ohio River Valley. The middle-23 states have the highest concentrations of ammonium in precipitation (cf Figure 1) and the largest increase in ammonium from P1 to P2 (cf Figure 2). On average, the mid-latitude westerlies advect ammonia toward north-northeast, so ammonia emitted in TX and OK tends to be deposited in Midwestern States, while emissions in North Carolina tend to be deposited over the Atlantic. For the 48 states (bottom row of Table 5) 2,851 units of NH_3-N are emitted based on GB1995-B emission factors and 1,150 units are wet deposited. Wet deposition is 57% of emissions, which seems unreasonably high. From Figure 1, it is evident that ammonium concentrations are high in and downwind (i.e. north and east) of the ammonia source areas. From the higher concentrations along the Canadian border than the Gulf Coast, we can surmise that there is a net transport of ammonia/ammonium out of the USA. We also expect dry deposition to be substantial. If we assume the net transport out of the USA is 20% and wet and dry deposition are equal, then the wet deposition fraction should be 40% instead of 56% (west 11) or 61% (middle 23) shown in Table 5 for GB1995-B emissions. It is reassuring to see a wet fraction of 39% for the east 14 states, where a large fraction of North Carolina emissions, which dominate the region, would be transported off shore.

One possible explanation for the unreasonably large wet deposition fractions (57%, 56%, and 61% in Table 5) is that ammonia emissions are underestimated by the GB1995-B emission factors. The last column in Table 5 lists wet fractions using GB1995-H emission factors. These factors give a much larger NH_3-N emissions and much lower wet deposition fractions, which are more reasonable.

Another explanation for wet fractions being too large is that wet deposition values for NH_4-N are biased high. We do not think this is the case. Indeed, there is evidence in the literature of some loss of NH_4 from the weekly NTN samples due to biodegradation (Butler, et al.).[24, 25, 26, 27] NH_4-N loss means the NTN values are low, maybe by 10-20%, and in the wrong direction to decrease the wet deposition fraction. Further, recall from the methods section that we used the P1 precipitation amount to calculate wet deposition for both P1 and P2. The P2 precipitation is about 20% larger than the P1 precipitation. If P2 precipitation values had been used, then the wet deposition fraction would be even larger, not smaller. We feel the wet deposition value for ammonium is less biased and more precise than the ammonia emissions and emission factors.

Another way to examine this issue is by considering a different chemical constituent. Table 6 lists the results for sulfur dioxide emissions and sulfate wet deposition. The SO_2-S emissions are from USEPA; note that 1999 emissions data were not available on the USEPA web site so the average annual emissions by state for P2 were determined with data for a four-year period, 1995-1998. Compared to ammonia emissions, the sulfur dioxide emissions have much greater certainty. Compared to wet deposition of NH_4-N, the SO_4-S wet deposition values should be more accurate since there is no known bias related to the sampling procedure. Also we feel that NTN sites are less likely to be influenced by local SO_2-S sources, as compared to total NH_3-N sources, which give somewhat more accurate SO_4S deposition values. The sulfur wet deposition fractions in Table 6 are substantially lower than the analogous values in Table 5. Sulfur dioxide is emitted from elevated sources, while ammonia is emitted from ground-level sources, so it is likely that a larger fraction of ammonia is dry deposited than sulfur dioxide. This argues for the wet deposition fraction being **smaller** for ammonia than for sulfur dioxide, contrary to the results in Table 5 and 6. Counteracting this tendency is that elevated emissions might lead to greater sulfur dioxide export from the USA. Similarly, the location of large sulfur dioxide sources in the Ohio River Valley and the large ammonia sources much further south would lead one to expect greater transport to Canada and the Atlantic for sulfur compared to N from ammonia. If net sulfur transport out of the USA for sulfur is assumed to be 40% and if wet and dry deposition are equal, then the wet deposition fraction is 30%. This is similar to the west-11 states value in Table 6 but higher than the east-14 and middle-23 states values. If net transport out of the USA for N from ammonia is assumed to be 20% and if wet and dry deposition are equal, then the wet deposition fraction is 40%, which is midway between the two values for the middle-23 states in Table 6. If instead net transport is 20% and dry deposition is twice as large as wet deposition, then the wet deposition fraction is 27%. The weight of evidence suggests that the ammonia wet deposition fractions should be well below .6, and the values of about .25 using GB1995-H “high” emissions factors are not unreasonable.

Another way to evaluate the estimated USA ammonia emissions is to compare P2 –P1 emission changes with P2 – P1 deposition changes. In this approach we assume that the fraction of emissions being wet deposited and the sum of the dry deposition and net transport fractions are the same in P1 and P2.

Differences in average annual NH_3-N emitted between the two periods are given in Table 7 for the five sets of emission factors. For the 48 states the emission increase ranges from 119,000 to 230,000 metric tons of N while the increase in wet deposition is 213,000 metric tons of N. This is an impossible result, regardless of the emission factor set chosen, because increases in dry deposition and net transport out-of-the-48-states must also come from the emission increase. If the wet deposition fraction for NH_3-N is 33.33%, then the emissions would have needed to increase by 639,000. This is 178% to 437% larger than the estimated emission increases in Table 7. However, compared to the total annual emissions in P1 of 1,871,900 metric tons/yr, shown in Table 3 for G1997 emission factors, the discrepancy of 639,000-146,000= 493,000 is 26%.

Using the source strength data in Table 3 here are some ways to have the emissions increase value to be 639,000 instead of 146,000:

1) Increase the magnitude of the emission factors by a factor of 4.37 to account for the entire 493,000. Although the emission factors are uncertain, a bias of a factor of 4.37 seems unlikely. It should be noted that larger values for the emission factors do help correct the mass balance issue discussed in relation to Tables 5 and 6.
2) Add in a missing emission category, which increased from P1 to P2. If emissions from crops were a large missing term, but the number of hectares emitting (i.e. source strength) remained constant and the emission factor remained constant, then the missing category would not contribute to the missing 493,000 but would help correct the mass balance issue discussed in relation to Tables 5 and 6.
3) Have EF's that vary with time. For example, if cattle feedlots became larger from P1 to P2, perhaps the effective EF increased. Or, if feedlots shifted south to areas of warmer temperatures, then maybe the effective EF would have increased (due to greater volatilization of animal waste products). Or if P2 were simply warmer than P1, then many of the EF's might have increased. In fact we calculated the average temperature for the two periods and found the average temperature during P1to be 52.084°F and the average temperature during P2 to be 52.550°F (http://www.cdc.noaa.gov/Timeseries/). The warmer condition in P2 would in general increase ammonia emissions.
4) Finally, if the fractions of wet, dry, and net transport changed from P1 to P2, then the increase in wet emission of 213,000 metric tons of N can be accounted for. For example, if the P1 fractions for wet, dry, and net transport were 30%, 40%, and 50%, respectively, while the P2 fractions were 38%, 34%, and 28%, then the 213,000 increase in wet deposition is accounted for without needing any of the changes in the No. 3 item listed above. We doubt that data sets exist that would allow even a detailed regional chemistry model to definitely resolve which of the two sets of flux fractions are closer to the true values.

At this time we cite no specific evidence to evaluate the importance of any of these four items, and other items should maybe be added to the list. We simply note that this is a list of items that might be worthy of exploration and evaluation in future research to explain the discrepancies in mass balance and time trends that are reported in this paper. Perhaps each of the four items above make a partial contribution to the resolving the data issues.

In summary, we feel that the P1 to P2 differences have less power than the mass balance discussion related to Tables 5 and 6 in suggesting that there is a missing ammonia source, but suggest several possible explanations that merit further research.

CONCLUSIONS

Spatial and temporal patterns of the ammonium concentrations in NADP/NTN precipitation samples, grouped into two 5-year periods are presented. Ammonium concentrations were highest for sites from northwestern Texas to the Dakotas and eastward to southern Michigan. The concentrations were generally higher in the1995-99 time period as compared to the 1985-89 period. Summary statistics for the grid-point concentration differences between these two periods are as follows: mean difference: +.054 [s.d. .052] mg/L or +25.6% [s.d. 23.5%], median difference: +.045 mg/L or +22.5%, range: -.051 mg/L to +.317 mg/L or -24.9% to +121%.

A mass balance approach, wherein the wet deposition fraction (wet deposition /emissions) of ammonia emissions is examined, suggests that ammonia emissions are substantially underestimated for the major sources considered, or that one or more other major sources are missing. An emission factor set, G1997, based on Bouwman et al. 1997,[2] gives annual NH_3-N emissions of 2,018,000 metric tons in the late 1980's for the 48 contiguous states of the USA. An emission estimate of 4,391,000 metric tons is obtained by using the highest emission factors from Sutton et al. 1995.[14] The high Sutton et al. emission factors give wet deposition fractions that seem reasonable while the G1997 emission factors give values that seem unreasonable.

The estimated increase in ammonia emissions for the 1995-99 period compared to the 1985-89 period is consistent with the direction of the change in wet deposition. However, the magnitude of the emissions change is much too small, for all of the five sets of emission factors unless the fractions of wet deposition, dry deposition, and net transport are different for the two time periods. Having emission factors that are not constant, but are larger for the second time period, can also achieve consistency between the emissions change and the wet deposition change.

It would be useful to run atmospheric chemistry models to examine issues raised in this study. Ammonia emission sources that have not been well characterized, such as crops, should be studied more to see if they provide the missing ammonia emissions suggested by this study.

ACKNOWLEDGEMENT

This work was supported in part by the National Atmospheric Deposition Program (NADP), a National Research Support Project (NRSP-3) of the State Agricultural Experiment Stations (SAES). Support for NADP is provided by federal and state agencies, universities, and other non-governmental organizations, as well as the SAES. The NADP Program Office is housed at the Illinois State Water Survey, which is an affiliated agency of the University of Illinois and a division of the Illinois Department of Natural Resources. This work was also supported in part by the Illinois Council on Food and Agricultural Research Project IDACF00S1-041-5A WS.

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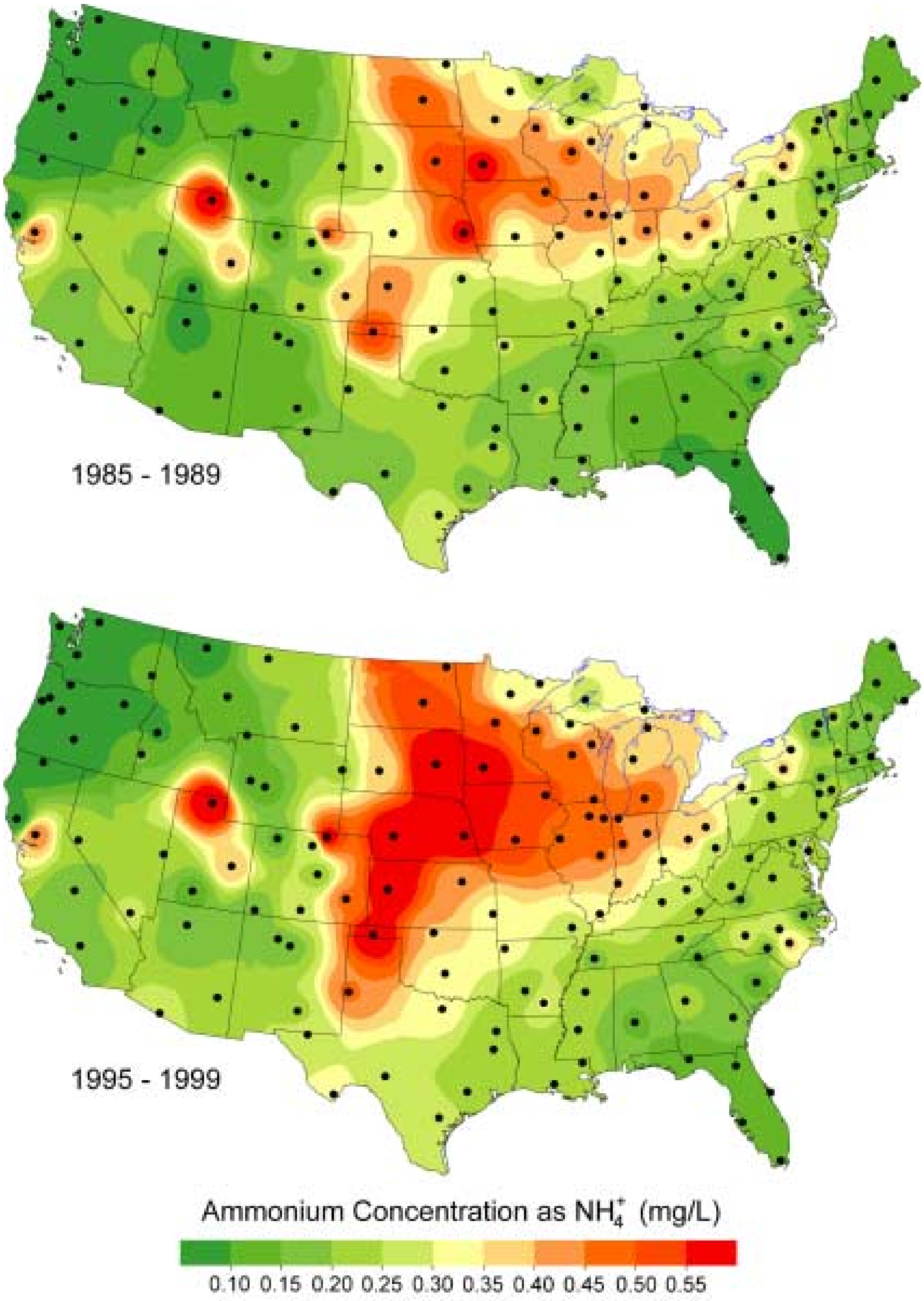

Figure 1. Precipitation weighted ammonium concentrations (NH_4^+ as NH_4^+) for two five-year time periods for 150 NADP/NTN sites.

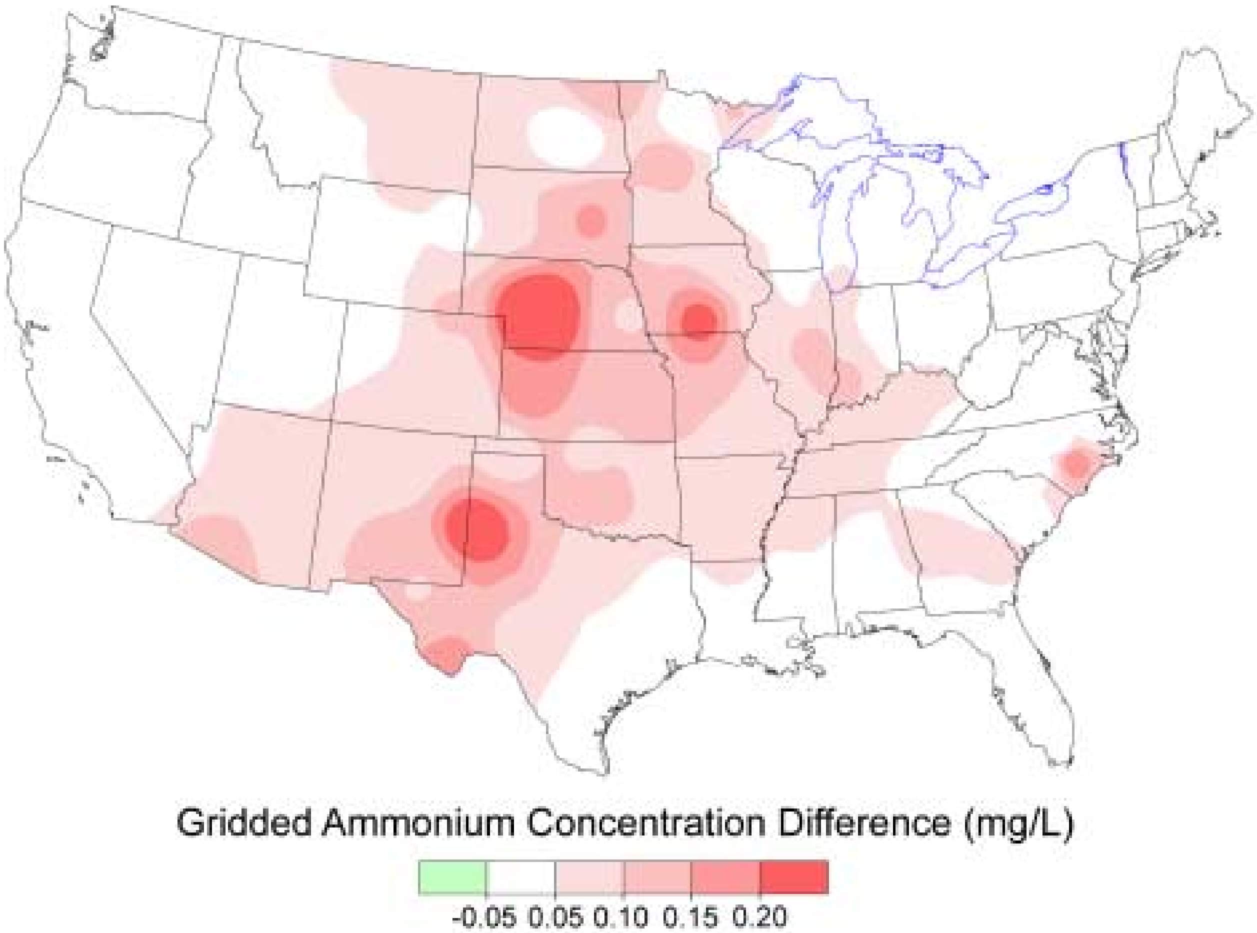

Figure 2. Ammonium ion (NH_4^+ as NH_4^+) concentration differences for precipitation where the objectively gridded values for the 1985-89 period were subtracted from the 1995-99 values.

Table 1. Magnitudes of global ammonia emissions for eleven source categories as estimated by Bouwman *et al.* 1997.[2]

1	Domestic Animals		40.3%
	Dairy Cows	Sheep	
	Other Cattle	Goats	
	Pigs	Buffalo	
	Chickens	Camels	
	Turkeys	Horses	
2	Synthetic Nitrogen Fertilizers		16.9%
	Urea	Ammonium nitrate	
	Anhydrous ammonia	Calcium ammonium nitrate	
	Ammonium sulfate	Nitrogen solutions	
	Ammonium carbonate (China)	Monoammonium phosphate	
	Diammonium phosphate	Other NP-N, NK-N, NPK-N, and other compound N	
3	Crops (annual and permanent crops)		6.7%
4	Biomass Burning		4.0%
	Agriculture waste burning		
	Savanna burning		
	Deforestation		
5	Other Biofuel Burning		4.9%
6	Natural Ecosystems		4.5%
	Soils under natural vegetation		
	Natural vegetation		
7	Oceans		15.2%
8	Humans (breath, sweat, excretion-sewage plants, cats and dogs)		4.9%
9	Fossil Fuel Combustion		.2%
10	Industrial Processes		.4%
11	Wild Animals		.2%

Table 2. Emission factors for annual NH_3-N emissions.

Sources	GB1995-L	GB1995-H	GB1995-B	NC2000	G1997	Units
Automobiles	.600	.60	.600	.600	.60	kg/yr/person
Fertilizer	.015	.05	.024	.030	.03	percent loss
Dairy Cows	8.300	27.00	17.000	20.70	20.40	kg/yr/animal place used
Beef Cattle	8.300	27.00	17.000	20.70	7.80	kg/yr/animal place used
Hog	3.100	5.70	4.300	8.360	4.00	kg/yr/animal place used
Turkeys	.480	.95	.700	.270	.70	kg/yr/animal place used
Broilers	.150	.30	.220	.120	.18	kg/yr/animal place used
Hens	.150	.30	.220	.140	.18	kg/yr/animal place used

Table 3. Average annual emissions of NH_3-N for period one (P1) (1985-89) and for period two (P2) (1995-99) for the 48 contiguous states using G1997 emission factors.

Source	P1 Source Strength	P1 Emissions (Kg)	P2 Source Strength	P2 Emissions (Kg)	% Emission Increase
Population (Autos)	246,400,000	147,900,000	264,900,000	158,900,000	7.49
Fertilizer Used	9,697,400,000	290,900,000	10,699,600,000	321,000,000	10.34
Dairy Cows	10,500,000	213,400,000	9,300,000	189,200,000	-11.35
Beef Cattle	92,000,000	717,700,000	91,900,000	716,900,000	-0.11
Hog	53,300,000	213,400,000	59,400,000	237,500,000	11.31
Turkeys	110,700,000	77,500,000	140,200,000	98,100,000	26.67
Broilers	808,500,000	145,500,000	1,244,200,000	224,000,000	53.89
Hens	364,400,000	65,600,000	400,500,000	72,100,000	9.89
Total		1,871,900,000		2,017,700,000	7.79

Table 4. State Groupings.

Groups	Abbreviation	List of States in a Group
14 Eastern States + DC	East-14	ME, NH, VT, MA, RI, CT, NJ, DE, MD, DC, VA, NC, SC, GA and FL
23 Middle States	Middle-23	NY, PA, WV, KY, TN, AL, MS, OH, MI, IN, WI, IL, MN, IA, MO, AR, LA, ND, SD, NE, KS, OK, and TX
11 Western States	West-11	MT, WY, CO, NM, ID, UT, AZ, NV, WA, OR, and CA
All 48 States and DC		

Table 5. Estimated annual NH_3-N emissions (using various emission factors) and NH_4-N wet deposition, grouped as in Table 4, for the 1995-99 period (thousands of metric tons/yr). Precipitation amounts are for the 1985-89 period.

	GB1995-L Emission	GB1995-H Emission	GB1995-B Emission	NC2000 Emissions	G1997 Emission	Wet Dep.	Wet/ GB1995-B	Wet/ GB1995-H
Easr-14	260	573	399	401	320	126	0.39	0.22
Middle-23	1,141	3,094	1,990	2,372	1,389	851	0.61	0.28
West-11	256	724	463	541	309	173	0.56	0.24
All 48 & DC	1,657	4,391	2,851	3,314	2,018	1,150	0.57	0.26

Table 6. Estimated annual SO_2-S emission (using USEPA database) and SO_2-S wet deposition to various groups of states for the 1995-98 period (thousands of metric tons/yr). Precipitation amounts are for the 1985-89 period.

	USEPA Emission	NADP Wet Dep.	Wet Dep./ Emission
14 Eastern States + DC	1,811	380	0.21
23 Middle States	6,311	1,494	0.24
11 Western States	626	206	0.33
All 48 States & DC	8,748	2,080	0.24

Table 7. Difference of estimated annual NH_3-N emission (using various emission factors) and NH_4-N wet deposition to various groups of states for the 1995-99 period minus the1985-89 period (thousands of metric tons/yr). For both time periods the wet concentrations are multiplied by the precipitation for the 1985-89 period.

	GB1995-L Emission	GB1995H Emission	GB1995-B Emission	NC2000 Emission	G1997 Emission	Wet Dep Emission	Wet/ GB1995-B	Wet/ GB1995-H
East-14	45	81	61	63	57	20	0.35	0.25
Middle-23	56	103	74	29	59	160	2.71	1.55
West-11	17	46	29	38	29	33	1.14	0.72
All 48 States	119	230	164	130	146	213	1.46	0.93

Table 8. Difference of estimated annual SO_2-S emission (using USEPA database) and SO_2-S wet deposition to various groups of states for the 1995-98 period minus the1985-89 period (thousands of metric tons/yr). For both time periods the wet concentrations are multiplied by the precipitation for the 1985-89 period.

	USEPA Emission	NADP Wet Dep.	Wet Dep. Emission
14 Eastern States + DC	-128	-128	1.00
23 Middle States	-1,416	-364	0.26
11 Western States	-151	-60	0.40
All 48 States	-1,696	-552	0.33