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Atmospheric nitrogen in the Mississippi River Basin — emissions, deposition and transport

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Abstract

Atmospheric deposition of nitrogen has been cited as a major factor in the nitrogen saturation of forests in the north-eastern United States and as a contributor to the eutrophication of coastal waters, including the Gulf of Mexico near the mouth of the Mississippi River. Sources of nitrogen emissions and the resulting spatial patterns of nitrogen deposition within the Mississippi River Basin, however, have not been fully documented. An assessment of atmospheric nitrogen in the Mississippi River Basin was therefore conducted in 1998–1999 to: (1) evaluate the forms in which nitrogen is deposited from the atmosphere; (2) quantify the spatial distribution of atmospheric nitrogen deposition throughout the basin; and (3) relate locations of emission sources to spatial deposition patterns to evaluate atmospheric transport. Deposition data collected through the NADP/NTN (National Atmospheric Deposition Program/National Trends Network) and CASTNet (Clean Air Status and Trends Network) were used for this analysis. NO_x Tier 1 emission data by county was obtained for 1992 from the US Environmental Protection Agency (Emissions Trends Viewer CD, 1985–1995, version 1.0, September 1996) and NH_3 emissions data was derived from the 1992 Census of Agriculture (US Department of Commerce. Census of Agriculture, US Summary and County Level Data, US Department of Commerce, Bureau of the Census. Geographic Area series, 1995:1b) or the National Agricultural Statistics Service (US Department of Agriculture. National Agricultural Statistics Service Historical Data. Accessed 7/98 at URL, 1998. http://www.usda.gov/nass/pubs/hisdata.htm). The highest rates of wet deposition of NO_3^- were in the north-eastern part of the basin, downwind of electric utility plants and urban areas, whereas the highest rates of wet deposition of NH_4^+ were in Iowa, near the center of intensive agricultural activities in the Midwest. The lowest rates of atmospheric nitrogen deposition were on the western (windward) side of the basin, which suggests that most of the nitrogen deposited within the basin is derived from internal sources. Atmospheric transport eastward across the basin boundary is greater for NO_3^- than NH_4^+, but a significant amount of NH_4^+ is likely to be transported out of the basin through the formation of $(NH_4)_2SO_4$ and NH_4NO_3 particles — a process that greatly increases the atmospheric residence time of NH_4^+. This process is also a likely factor in the

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atmospheric transport of nitrogen from the Midwest to upland forest regions in the North-East, such as the western Adirondack region of New York, where NH_4^+ constitutes 38% of the total wet deposition of N. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Nitrogen; Atmospheric deposition; Nitrate; Ammonia; Wet deposition; Mississippi river basin

1. Introduction

Through human activities, the deposition of nitrogen from the atmosphere has increased to rates that are of the same magnitude as rates of natural fixation of N_2 (Vitousek et al., 1997). Atmospheric deposition of nitrogen has been recognized as a major factor in the nitrogen saturation of forest ecosystems, in the acidification of freshwater lakes and streams (Stoddard, 1994; Aber et al., 1995; Fenn et al., 1998), and in the eutrophication of coastal waters (Muller and Helsel, 1996). Atmospheric deposition in the Mississippi River Basin also has been identified as a contributor to nitrogen loads in the Mississippi River that are discharged into the Gulf of Mexico (Dinnel, 1998). Eutrophication and hypoxia of an extensive area of the Gulf of Mexico has been linked to nitrogen inputs from the Mississippi River (Turner and Rabalais, 1991).

As part of an effort to determine the primary cause of hypoxia in the Gulf of Mexico, a working group under the direction of the National Science and Technology Council's Committee on the Environment and Natural Resources (CENR) was established in 1997 to quantify the nitrogen budget of the Mississippi River Basin. This task required that all inputs of N, including those from atmospheric deposition, be quantified as accurately as possible. A comprehensive assessment of atmospheric deposition of nitrogen within the Mississippi River Basin was, therefore, conducted. The objectives of this assessment were to: (1) evaluate the forms in which nitrogen is deposited from the atmosphere; (2) quantify the spatial distribution of atmospheric nitrogen deposition throughout the basin; and (3) relate locations of emission sources to spatial deposition patterns to evaluate atmospheric transport. This paper presents the methods and results of this assessment.

2. Methods

2.1. Data acquisition

In general, measurements of atmospheric deposition of nitrogen can be categorized as wet deposition (which falls as rain or snow) or dry deposition (particles or vapor deposited from the atmosphere primarily during periods without precipitation).

Wet deposition is monitored year-round at over 200 sites in the United States through the interagency-supported National Atmospheric Deposition Program/National Trends Network (NADP/NTN). The distribution of these sites is approximately uniform, nationwide, with additional sites located in regions of high-deposition gradients. At each site precipitation is collected for chemical analysis by an automated wet-only deposition collector that remains covered except when precipitation is falling. Through this method, wet deposition of NO_3^-, NH_4^+ and other constituents are determined at weekly intervals. Wet-deposition data used in this report were collected from 1988 through 1996. These data and further information on the NADP/NTN program are available on the World Wide Web (http://nadp.sws.uiuc.edu; accessed for this paper in 1998–1999).

Dry deposition is monitored at approximately 60 sites nationwide through several programs that operate under the US Environmental Protection Agency Clean Air Status and Trends Network (CASTNet; Clarke et al., 1997). Two-thirds of these sites are located east of the Mississippi River; all but three of the remainder are located from the Rocky Mountains to the West Coast. Dry deposition is determined at these sites by measurements of air concentrations taken 10 m above the ground and an inferential model of deposition velocities, as described in Hicks et al.

(1985). Air concentrations are determined by a three-stage filter pack that contains a Teflon filter, a nylon filter, and a cellulose filter, in sequence. Air is continuously pulled through these filters at 1.50 l min^{-1} at eastern sites and 3.00 l min^{-1} at western sites. Particulate NO_3^- and NH_4^+ are collected by the teflon filter, HNO_3 vapor is collected by the nylon filter, and SO_2 is collected by the cellulose filter. Air concentrations of NH_3 are not determined by this sampler. Meteorological and vegetation conditions are also monitored at each site to provide data necessary for modeling deposition velocities. Dry deposition data used in this paper were collected from 1988 (the first complete year of operation at most sites) through 1994. Data from 1995 and 1996 were incomplete at most sites and, therefore, were excluded from the analysis.

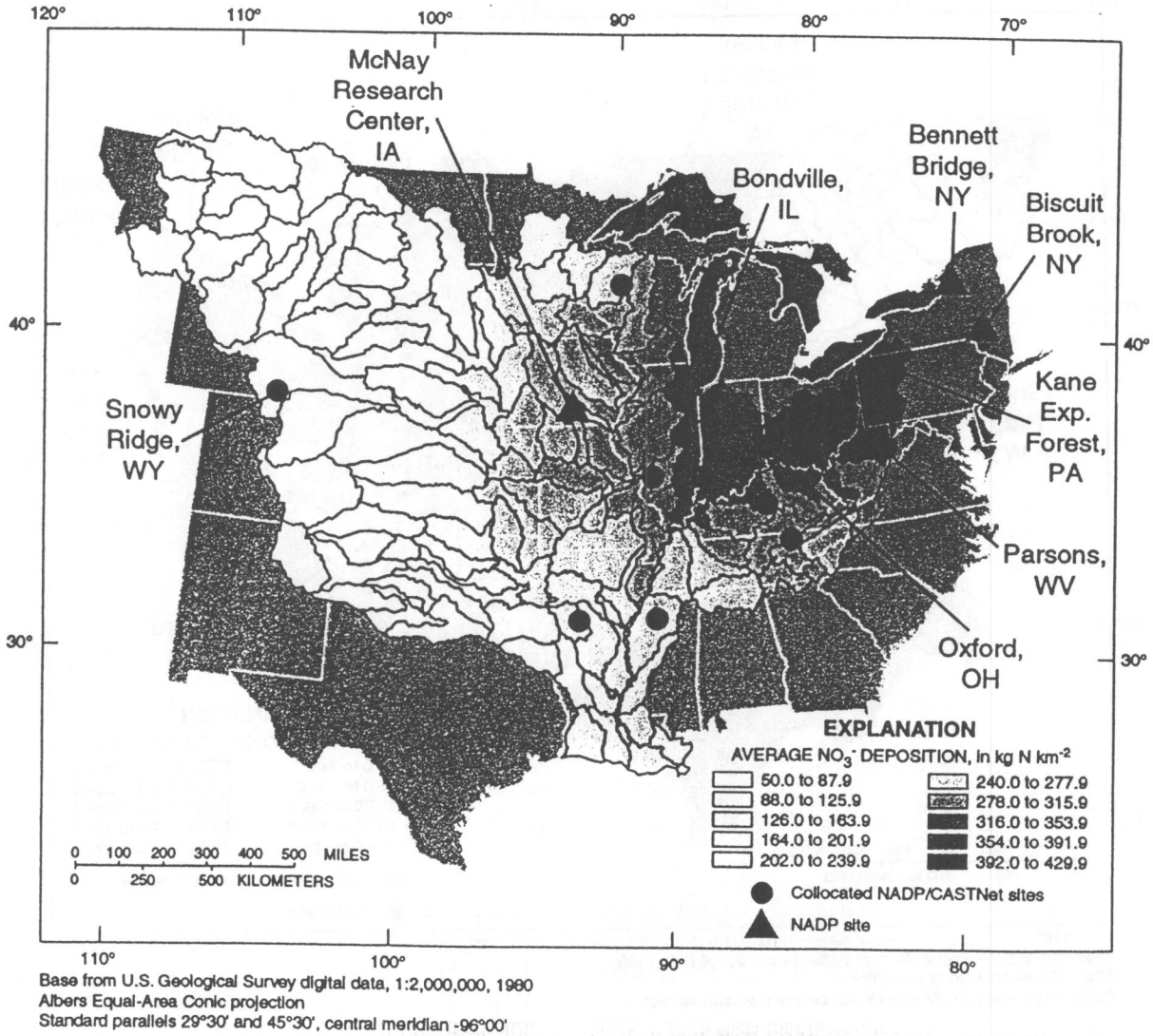

Fig. 1. Wet deposition of NO_3^-, averaged for 1990–1996, in the 133 hydrologic accounting units that make up the Mississippi River Basin. Blue circles indicate where NADP (National Atmospheric Deposition Program) and CASTNet (Clean Air Status and Trends Network) sites are collocated; blue triangles indicate specific NADP sites discussed in the text.

To evaluate nitrogen emissions from combustion, NO_x Tier 1 emission data by county were obtained for 1992 from the US EPA (Emissions Trends Viewer CD, 1985–1995, version 1.0, September 1996). Nitrogen emission data from agricultural activities were developed, by county, from several sources. Volatilization of nitrogen from fertilizer application was estimated from the 1992 Census of Agriculture (US Department of Commerce, 1995) and information on volatilization rates given in Meisinger and Randal (1991). Nitrogen emissions from animal manure were estimated from loss coefficients listed in Meisinger and Randal (1991) and the Midwest Planning Service-Lifestock Waste Subcommittee (1985), and manure production data from the 1992 Census of Agriculture (US Department of Commerce, 1995) or the National Agricultural Statistics Ser-

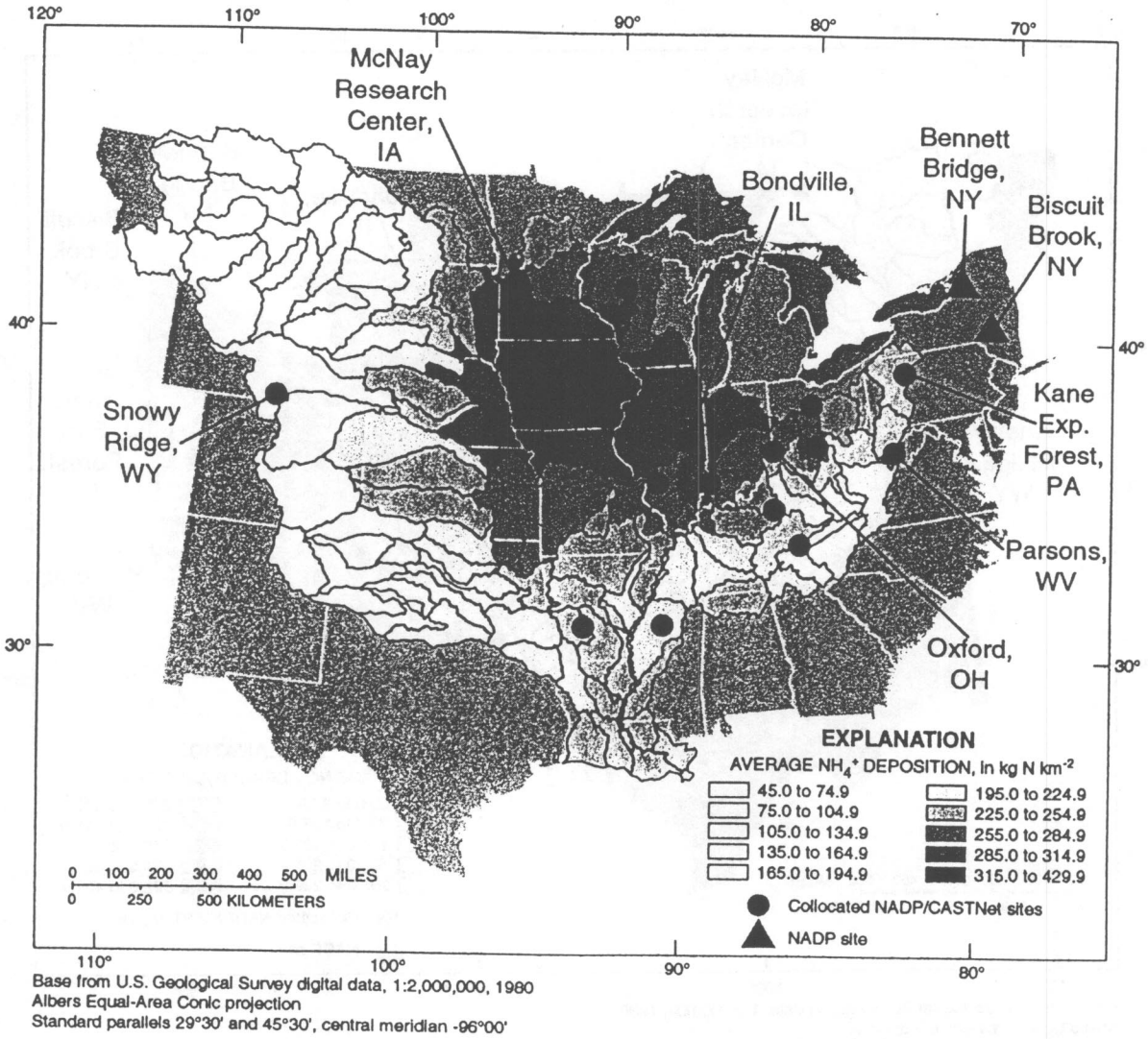

Fig. 2. Wet deposition of NH_4^+, averaged for 1990–1996, in the 133 hydrologic accounting units that make up the Mississippi River Basin. Blue circles indicate where NADP (National Atmospheric Deposition Program) and CASTNet (Clean Air Status and Trends Network) sites are collocated; blue triangles indicate specific NADP sites discussed in the text.

vice (1998). Nitrogen volatilization from senescing plants was estimated from: (1) data provided by the National Agricultural Statistics Service (1998); (2) the 1992 Census of Agriculture (US Department of Commerce, 1995); and (3) volatilization rates from the literature. Details of the methods used to estimate nitrogen emissions from fertilizer application, animal manure handling and crop senescence are available in Goolsby et al. (1999).

2.2. Development of spatial data coverages

Wet deposition data from the NADP/NTN data base were converted to ARC/INFO point coverages of annual wet deposition of NO_3^- and NH_4^+. ARC/INFOs IDW (Inverse Distance-weighted Interpolation) was performed on the point coverages to create a grid of 6.25-km^2 cells over the coterminous United States. Annual deposition values for each cell were calculated by IDW from a distance-weighted combination of sample points. The resulting ARC/INFO GRIDs were converted to: (1) a polygon that represented the entire Mississippi Basin; and (2) polygons that represented the 133 hydrologic accounting units (determined by drainage divides) that comprise the basin, by summing the cell values within each polygon. Mean annual deposition for 12 states within the basin was similarly determined from the 6.25-km^2 grid cells and also with the model of Grimm and Lynch (1997), which incorporates National Weather Service precipitation data, elevation, and aspect to determine the spatial distribution of atmospheric deposition.

County data on emissions from agricultural activities and combustion were generalized to the 133 hydrologic accounting units by area-weighted averaging of the county values.

2.3. Relation between wet and dry deposition

CASTNet monitoring data were not suitable for spatial interpolation of dry deposition measurements in the Mississippi River Basin because sites were too sparse west of the Mississippi River. Thirteen sites were, therefore, selected within the Mississippi Basin where both dry- and wet-deposition data were available to determine whether wet-deposition data collected at NADP/NTN sites could be used to estimate dry deposition within the basin. Wet-deposition data collected at Snowy Ridge, Wyoming (site code WY00) and CASTNet data collected at Centennial, Wyoming

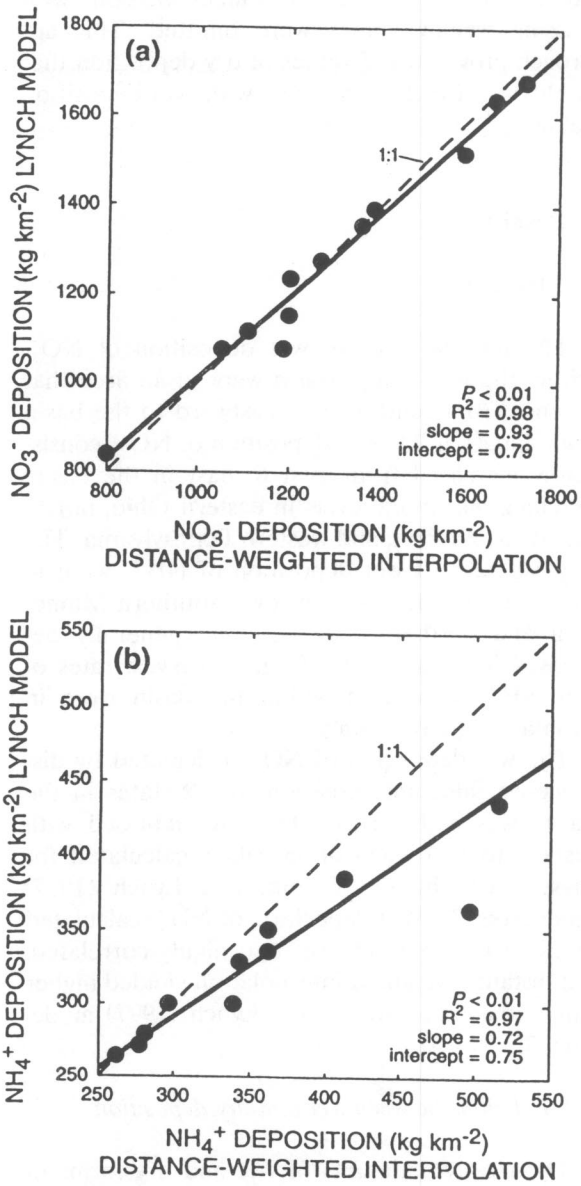

Fig. 3. Atmospheric deposition of (a) NO_3^- and (b) NH_4^+ for 12 states in the Mississippi River Basin calculated by the model of Grimm and Lynch (1997), plotted as a function of values obtained by distance-weighted interpolation.

(site code CNT169) were also paired because these sites are less than 100 km apart and represented the only data from the western part of the basin that could be used to relate dry- and wet-deposition measurements. Seasonal values were compiled from the weekly data of these 14 sites for December–February, March–May, June–August and September–November. Seasons with missing weekly values were omitted. This approach provided 147 values of dry deposition that could be directly compared with wet-deposition values.

3. Results

3.1. Wet deposition

The highest rates of wet deposition of NO_3^- within the Mississippi Basin were in an area that extends from central Ohio eastward to the basin boundary (Fig. 1). Wet deposition of NO_3^- consistently increased from west to east in the basin, reaching maximum levels in eastern Ohio, northern West Virginia, and western Pennsylvania. The highest rates of wet deposition of NH_4^+ were in the center of the basin, in Iowa, southern Minnesota and northern Missouri, and generally decreased in all directions (Fig. 2). Lowest rates of wet NH_4^+ deposition within the basin were in Montana and Wyoming.

The wet deposition of NO_3^-, calculated by distance-weighted interpolation for 12 states in the basin, was highly correlated and unbiased with respect to NO_3^--deposition values calculated for these states by the Grimm and Lynch (1997) model (Fig. 3). Wet deposition of NH_4^+ calculated by these two methods was also highly correlated, but distance-weighted interpolation yielded higher values than the Grimm and Lynch (1997) model (Fig. 3).

3.2. Relations between wet and dry deposition

The relative amounts of wet and dry forms of nitrogen deposition were generally similar among four sites that were selected to span the longitude of the basin (Fig. 4). At all sites, the largest

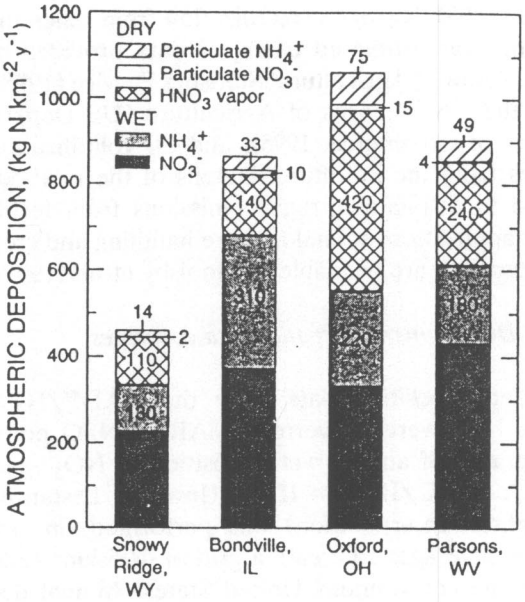

Fig. 4. Chemical species of wet and dry nitrogen deposition measured from December 1992 through November 1993 at four sites within the Mississippi River Basin.

component of dry deposition was HNO_3 vapor, followed by particulate NH_4^+ and particulate NO_3^-. The largest component of wet deposition was NO_3^-, although NH_4^+ values approached NO_3^- values at the Illinois site. Deposition of all five forms of nitrogen measured by NADP/NTN and CASTNet monitoring was lowest at the westernmost site in Wyoming. Wet deposition of NO_3^- was highest at the West Virginia site, whereas the highest wet deposition of NH_4^+ was at the Illinois site, and the highest HNO_3 deposition was at the Ohio site.

A statistically significant positive correlation was observed between total dry deposition and total wet deposition for the seasonal data at the 14 sites, although much of the variability in dry deposition measurements was not explained by wet deposition measurements (Fig. 5). Considerable variability in total dry deposition measurements was observed among sites, and no geographical pattern was evident. This variation is illustrated by data from Parsons, WV, USA and Kane Experimental Forest, PA, USA (Fig. 6). The slope of the relation between wet and dry deposi-

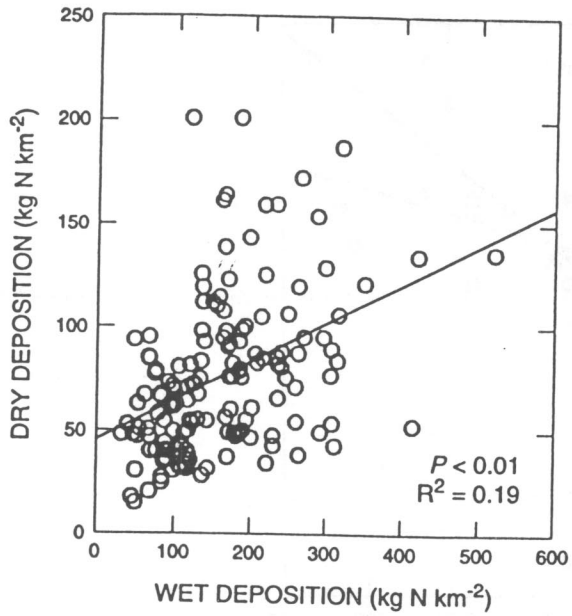

Fig. 5. Total dry deposition as a function of total wet deposition at 14 sites in the Mississippi River Basin where dry- and wet-deposition measurement stations are collocated. Values represent seasonal totals (winter, December–February; spring, March–May; summer, June–August; fall, September–November) from January 1989–November 1994.

tion differed considerably between these two sites, although this difference was not statistically significant as a result of a large amount of unexplained variability.

The average total dry deposition (particulate NO_3^- and NH_4^+ plus HNO_3 vapor) divided by the average value of total wet deposition (NO_3^- plus NH_4^+) for the 14 sites was 0.47. Individual values of total dry deposition divided by total wet deposition ranged from 0.13 to 1.9, but 76% of these values were from 0.13 to 0.69 (Fig. 7), and the median value was 0.45. If averaged for all sites, and all seasons, total dry nitrogen deposition was comprised of 81% HNO_3 vapor, 16% particulate NH_4^+, and 3% particulate NO_3^-.

3.3. Nitrogen emissions, deposition and transport

Emissions of NO_x were positively related to wet deposition of NO_3^- when compared by hydrologic accounting unit, but a considerable amount of unexplained variation is evident (Fig. 8a), which is consistent with the tendency of NO_x compounds to be transported over distances that exceed the dimensions of most hydrologic accounting units. The estimate of total NO_x emissions for the entire basin exceeded the estimate of total NO_3^- deposition by more than a factor of 2 (Table 1). The counties within the basin in which the highest levels of NO_x are emitted tend to be concentrated in Illinois, Indiana, Ohio and Pennsylvania (Fig. 9).

Emissions of NH_3 were also positively related to wet deposition of NH_4^+, but this relation was somewhat stronger than that observed for emissions of NO_x and wet deposition of NH_4^+ (Fig. 8b). Estimates of total NH_3 emissions within the basin exceeded total NH_4^+ deposition estimates by a factor of 6 (Table 1). Release from senescing crops was estimated to be the largest source of NH_4^+ in the basin, followed by animal manure and crop fertilization. At McNay Research Center, IA, USA, located in the region of highest NH_4^+ deposition within the basin, NH_4^+ comprised 55.4% of total wet nitrogen deposition, whereas at Delaware, OH, USA, in the eastern portion of the basin, NH_4^+ comprised 41.8% of total wet nitrogen deposition (Table 2). At sites in New York, outside of the basin, NH_4^+ comprised a lower percentage of total wet nitrogen deposition than at the Iowa or Ohio sites, but deposition of NH_4^+ at Bennett Bridge, NY, USA, was higher than at either of these sites (Table 2).

4. Discussion

4.1. Emissions and atmospheric transport

The regional patterns of wet deposition of NO_3^- and NH_4^+ reflect the regional patterns of emissions and atmospheric transport processes. The highest rates of NO_3^- deposition occur in Ohio and Pennsylvania, downwind of high-emitting power plants and large urban areas with high transportation emissions (NAPAP, 1993). Fossil fuel combustion for electricity generation has been established as a major source of NO and NO_2, which are oxidized in the atmosphere to form HNO_3 vapor and dissolved and particulate

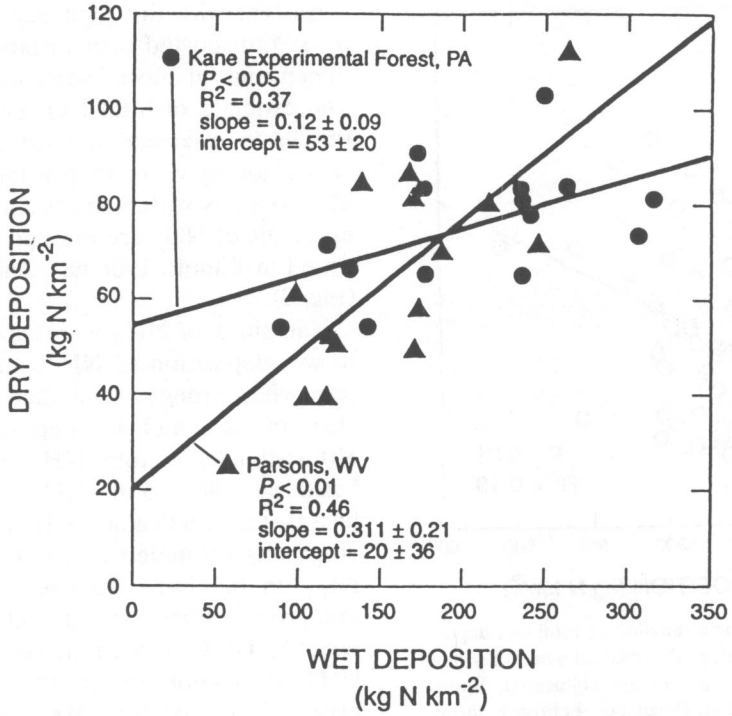

Fig. 6. Dry deposition as a function of wet deposition at Kane Experimental Forest, PA, USA, and Parsons, WV, USA. Values represent seasonal totals (winter, December–February; spring, March–May; summer, June–August; fall, September–November) from January 1989–November 1994. Slopes and intercepts of best-fit lines are given ±95% confidence intervals.

NO_3^- aerosols. Particulate NO_3^- can have a long residence time in the atmosphere, which facilitates long-range transport. HNO_3 vapor has a relatively short residence time, although it can react with other pollutants such as NH_3 to form particles with low deposition velocities. Atmospheric transport of nitrogen from mid-western power plants to the north-eastern states has been well documented (NAPAP, 1993). Comparison of emissions with deposition of oxidized nitrogen compounds demonstrates the significance of the Mississippi River Basin as an exporter of atmospheric NO_3^- (Table 1). Total deposition within the basin was likely to have been underestimated by NADP and CASTNet data, however, because the monitoring sites of these programs are located away from urban areas and other emissions sources. Emission data presented in Table 1 did include urban areas, therefore, export of NO_x compounds probably was somewhat overestimated.

Eastward transport of emitted NH_3 has received considerably less attention than NO_x transport, but the atmospheric budget listed in Table 1 indicates that the Mississippi River Basin is also a significant exporter of NH_4^+. The highest levels of wet NH_4^+ deposition in the Mississippi Basin are centered in Iowa, a predominantly agricultural state. Wet and dry deposition of NH_4^+ have generally been attributed to NH_3 emissions from high concentrations of livestock, nitrogen fertilization of croplands (Vitousek et al., 1997), and crop senescence (Goolsby et al., 1999). Of these three agricultural sources, crop senescence might be the largest. Estimates of emissions from crop senescence have the greatest uncertainty, however, as a result of seasonal and climatic effects on the complex physiological and micrometeorological processes involved.

Emissions from automobiles also can contribute atmospheric NH_3, but this emission source did not exceed agricultural sources in the South

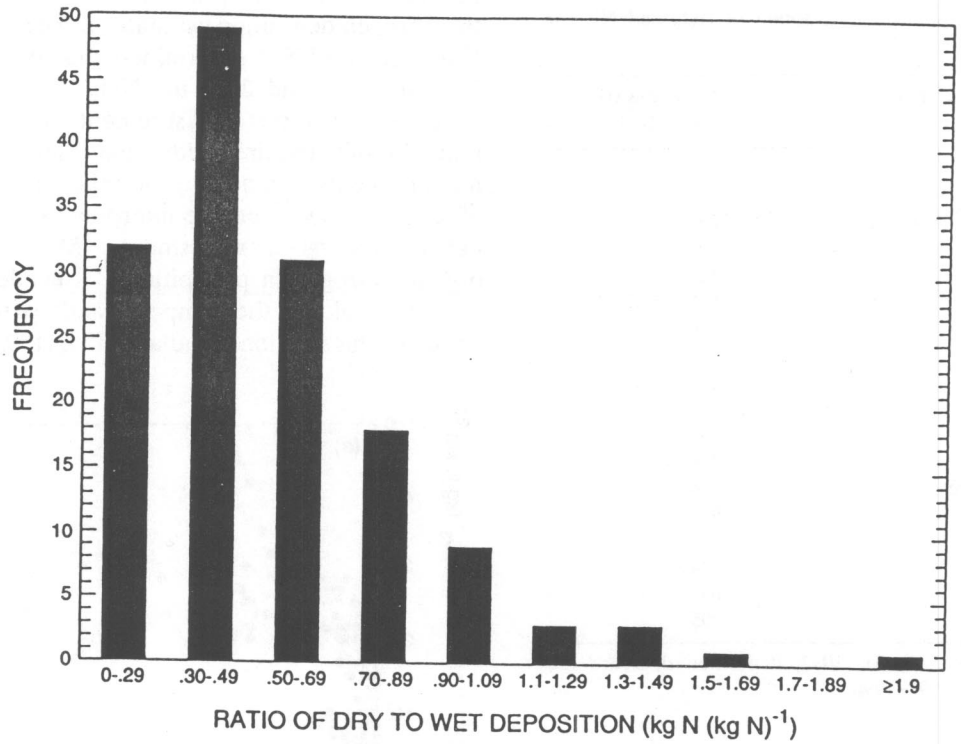

Fig. 7. Distribution of the ratio of dry deposition to wet deposition at 14 sites in the Mississippi River Basin where dry- and wet-deposition measurement stations are colocated. Values represent seasonal totals (winter, December–February; spring, March–May; summer, June–August; fall, September–November) from January 1989–November 1994.

Coast Air Basin of California, which includes Los Angeles and surrounding developed areas (Fraser and Cass, 1998). Automobile emissions of NH_3 within the Mississippi Basin are, therefore, probably small relative to agricultural emissions.

Unlike NO and NO_2 emitted through fossil fuel combustion, NH_3 that is released to the atmosphere is already in a highly water-soluble form that is effectively scavenged by precipitation (Ferm, 1998). As a result, NH_3 is deposited closer to its source than other forms of atmospheric nitrogen. Transport distance, however, depends on wind speed and reactions with other pollutants. Modeled estimates of NH_3 transport by Asman and van Jaarsveld (1992) indicated that 46% of emitted NH_3 was deposited within 50 km of the source; 40% as dry deposition, and 6% as wet deposition. Results from a separate modeling effort described in Ferm (1998) indicated that 49% of NH_3 emitted in a 22000 km^2 region in Sweden was deposited within this same region; 21% as dry deposition and 28% as wet deposition.

Although a large fraction of emitted NH_3 tends to be deposited near its source, high atmospheric concentrations of SO_2 and NO_x in the atmosphere greatly increases transport by converting NH_3 to particulate NH_4, which has a low deposition velocity. Deposition research in The Netherlands found that NH_x deposition beyond 300 km of the source was halved approximately every 450 km, a pattern similar to that of SO_2 (Ferm, 1998). High emissions of SO_2 and NO_x in Illinois, Kentucky, Indiana, and Ohio are likely to enhance the transport of NH_3 emitted from the agricultural regions of these same states eastward across the basin boundary.

4.2. Uncertainty of deposition measurements

Based on NADP/NTN and CASTNet data,

Table 1
Atmospheric emission and deposition of NO_x and NH_x in Mississippi River Basin[a]

Type of emission or deposition	Metric tons (t) of N ($\times 10^3$)
NO_x	
Emission	
All point and area sources	2715
Deposition	
Dry	427
Wet	611
Total	1038
NH_x	
Emission	
Crop fertilizer	133
Manure	1488
Crop senescence	3326
Total	4947
Deposition	
Dry	144
Wet	651
Total	795

[a]Emission data are for 1992; deposition data are the annual means for 1990–1996.

NH_4^+ deposition represents approximately 35% of total nitrogen deposition in the basin, but the collection methods of both programs probably result in an underestimation of this fraction. Some of the NH_4^+ collected by NADP/NTN wet-only collectors may be converted to organic nitrogen through microbial assimilation between the time of deposition and the weekly collection (Vet et al., 1989). Butler and Likens (1998) found that NADP weekly sampling underestimated event sampling by approximately 14%. Also, the three-stage filter pack used in the CASTNet program is designed to collect NH_4^+ particles, but not gaseous NH_3, which has a deposition velocity approximately five times higher than that of the NH_4^+ particles (Ferm, 1998). Deposition of gaseous NH_3 may, therefore, represent a significant fraction of dry deposition, but primarily in the vicinity of sources because of its short atmospheric residence time. Locations of NADP/NTN collectors, however, do not avoid agricultural areas and, therefore, in some cases, may include deposition of locally derived NH_3.

The NADP/NTN measurements of wet deposition of NO_3^- and NH_4^+ are the least uncertain of the nitrogen deposition estimates discussed above. Nilles et al. (1994) determined that precision is 7% for NO_3^- and 20% for NH_4^+. The wet-only collector is a direct measurement of deposition that doesn't require additional meteorological measurements or modeling, and the large number of sites nationwide enable interpolation for regional or watershed assessments. Monitoring of organic nitrogen in precipitation is needed, however, to evaluate the temporal and spatial variability of this fraction. Scudlark et al. (1998) found

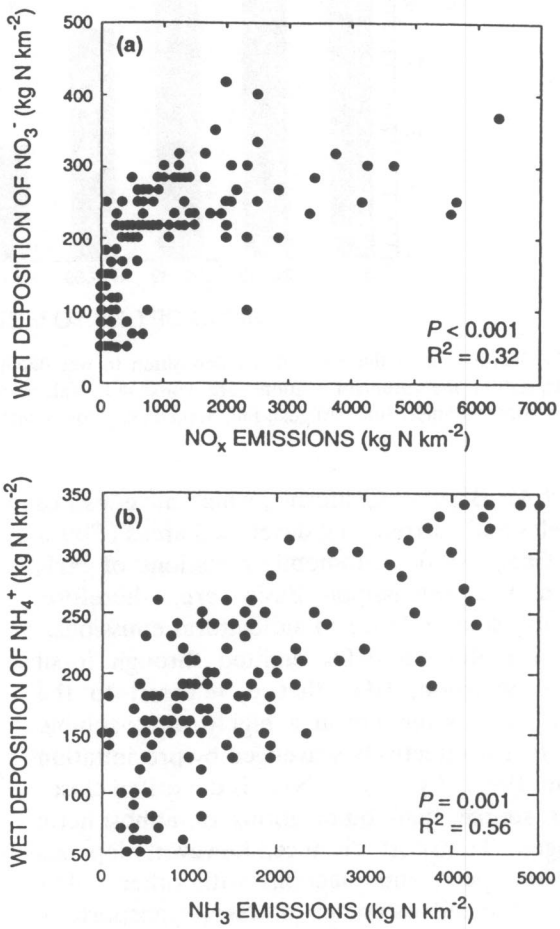

Fig. 8. (a) Wet deposition of NO_3^- as a linear function of NO_x emissions in the 133 hydrologic accounting units that make up the Mississippi River Basin. (b) Wet deposition of NH_4^+ as a linear function of NH_3 emissions from animal manure, crop fertilization and crop senescence, in the 133 hydrologic accounting units that make up the Mississippi River Basin.

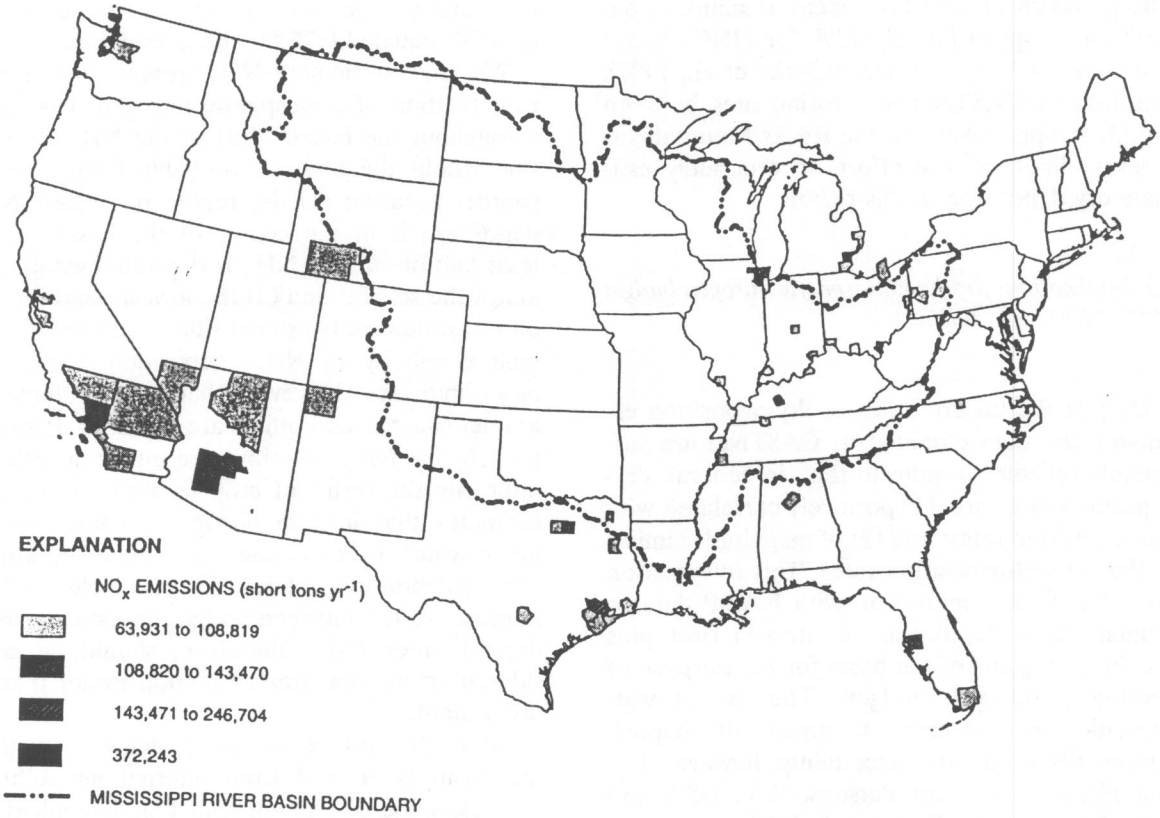

Fig. 9. Mean annual emissions of NO_x for 1985–1995 for the 50 counties with highest emissions in the United States.

that organic nitrogen was approximately 25% of total wet deposition in Chesapeake Bay.

The level of uncertainty for dry deposition is difficult to quantify. Eddy correlation techniques provide a direct measurement that can be compared with the filter pack-inferential modeling approach, but this method can only be used for short measurement periods (30–120 min) and cannot be used to measure HNO_3 deposition. The accuracy of dry deposition estimates of HNO_3 vapor and NO_3^- particles has been subjectively determined by Clarke et al. (1997) to be 40%.

Table 2
Average annual atmospheric wet deposition of NH_4^+ and NO_3^- at National Atmospheric Deposition Program (NADP) stations in the mid-western and eastern United States, 1990–1996[a]

Site name	NADP code	Elevation (m)	NH_4^+ (kg Nha^{-1})	NO_3^- (kg Nha^{-1})	NH_4^+ (% of total N)
McNay Research Center, IA, USA	IA23	320	3.37	2.71	55.4
Delaware, OH, USA	OH17	285	3.00	4.18	41.8
Parsons, WV, USA	WV18	505	2.25	4.45	33.6
Biscuit Brook, NY, USA	NY68	629	2.25	4.56	33.1
Bennett Bridge, NY, USA	NY52	245	3.75	6.23	37.8

[a]Total N equals wet deposition of NH_4^+ plus NO_3^-.

The precision of CASTNet measurements of deposition, is approximately 12% for HNO_3 vapor and 17% for NO_3^- particles (Clarke et al., 1997). The lack of CASTNet monitoring sites between the Mississippi River and the Rocky Mountains is a severe limitation on efforts to accurately estimate dry deposition in this region.

4.3. Implications for the atmospheric nitrogen budget of the Mississippi Basin

Despite the uncertainties of dry-deposition estimates, the data obtained by CASTNet are sufficiently reliable to indicate that, in general, dry-deposition rates are: (1) positively correlated with wet-deposition rates; and (2) of magnitude similar to that of wet-deposition rates. This information can be used in conjunction with NADP data to estimate total deposition of nitrogen (wet plus dry) in subregions of the basin for the purpose of developing nitrogen budgets. The use of wet-deposition measurements to predict dry deposition entails substantial uncertainty, however. For example, sites at both Parsons, WV, USA and Kane Experimental Forest, PA, USA, are in upland forested regions on the eastern side of the basin that receive similar amounts of atmospheric deposition, but the linear regression models for these two sites could yield considerably different results.

The wet and dry deposition of NO_3^- compounds should be considered a budget input because these compounds originate largely from the combustion of fossil fuels and otherwise would be unavailable for biological utilization. Dry deposition of HNO_3 and NO_3^- can be approximated throughout the basin by multiplying the wet deposition of NO_3^- by 0.70 (dry deposition of NO_3^- divided by wet deposition of NO_3^-, for the 14 sites at which wet and dry deposition stations were collocated). It must be noted, however, that 12 of the 14 colocated stations were east of the Mississippi River, a factor that ascribes considerable uncertainty to values for the western part of the basin. Dinnel (1998) estimated from CASTNet and NADP/NTN data from 1990 to 1992 that the ratio of dry deposition of NO_3^- to wet deposition of NO_3^- equaled 0.75 for the overall basin.

Wet and particulate NH_4^+ represent a significant fraction of atmospheric nitrogen deposition throughout the basin. Most of the NH_4^+ deposition within the basin is probably from internal sources because: (1) the region of highest NH_3 deposition is in the center of the basin; (2) at least half of emitted NH_3 is deposited within 300 km of the source; and (3) the lowest deposition is on the windward (western) side of the basin. The high variability of NH_4^+ deposition within the basin indicates, however, that some sub-basins are net sources, and others are net sinks. Because most of the NH_3 emissions are either directly or indirectly the result of crop fertilization, budget estimates that include nitrogen fertilizer as an input would overestimate total inputs if atmospheric deposition of NH_4^+ was also included. For purposes of the nitrogen budget, the atmospheric deposition of NH_4^+, therefore, should be considered an internal transformation rather than a basin input.

Although most of the NH_4^+ deposited within the basin is derived from internal agricultural sources, some of the nitrogen that is applied as fertilizer eventually leaves the basin through atmospheric transport. Even if crop senescence is excluded, emissions from manure and fertilizer applications exceed estimated total deposition of NH_4^+ by a factor of two. High rates of deposition downwind of the Midwestern agricultural region supports the probability that the Mississippi River Basin is a net source of atmospheric NH_4^+.

5. Conclusion

Fossil fuel combustion and agricultural activities in the Midwest produce high emissions of both oxidized and reduced forms of nitrogen that lead to high levels of NO_3^- deposition in the north-eastern part of the basin and high levels of NH_4^+ deposition in the central part. Although atmospheric-nitrogen budgets for the Mississippi Basin must be considered approximate, these

budgets indicate that as much as half of the nitrogen emitted within the basin may be transported eastward to be deposited outside of the basin. This process reduces the magnitude of nitrogen deposition within the basin, but contributes significant amounts of nitrogen to sensitive forested watersheds in the east, where atmospheric deposition of nitrogen has increased nitrogen availability to levels that have contributed to high rates of soil nitrification, soil acidification and surface-water degradation (Stoddard, 1994; Aber et al., 1995; Peterjohn et al., 1996).

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