

Atmospheric Deposition of Nitrogen in the Mississippi River Basin

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ABSTRACT

Atmospheric deposition of nitrogen has been cited as a major factor in the overfertilization of forests (often termed nitrogen saturation) in the northeastern 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 spatial patterns of nitrogen deposition within the Mississippi River Basin, however, have not been fully assessed. The objectives of this study were to (1) quantify the spatial distribution of atmospheric nitrogen deposition throughout the Mississippi River Basin, and (2) relate the locations of emission sources to the spatial deposition patterns to infer patterns of atmospheric transport. 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.

The highest rates of wet deposition of NO_3 were in the northeastern part of the basin where electric utility plants are concentrated, 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 are on the (windward) side of the basin, which suggests that most of the nitrogen deposited within the western 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 $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 particles, which greatly increases the atmospheric residence time of NH_4 . This process may be a factor in the transport of nitrogen from the midwest to upland forest regions in the Northeast, such as the western Adirondack region of New York, where NH_4 constitutes 40 percent of total wet nitrogen deposition.

INTRODUCTION

Through human activities, the deposition of biologically available nitrogen from the atmosphere has increased to rates that are of similar magnitude to rates of natural fixation of N_2 (Vitousek and others, 1997). Atmospheric deposition of nitrogen has been recognized as a major factor in the overfertilization of forest ecosystems in the northeastern United States (often termed nitrogen saturation) and the acidification of freshwater lakes and streams (Stoddard, 1994; Aber and others, 1998; Fenn and others, 1998). Atmospheric deposition of nitrogen also has been identified as an important contributor to the eutrophication and hypoxia of Chesapeake Bay (Magnien and others, 1995) and the Gulf of Mexico (Dinnel, 1997). As part of an

effort to evaluate possible causes of hypoxia in the Gulf of Mexico, a working group under the direction of the Committee on the Environment and Natural Resources (CENR) of the White House Office of Science and Technology was established in 1997 to quantify nitrogen cycling within the Mississippi River Basin; a task that included an assessment of nitrogen deposition from the atmosphere. The objectives of the atmospheric deposition component of this study were to (1) quantify the spatial distribution of atmospheric nitrogen deposition throughout the Mississippi River Basin and (2) relate locations of emission sources to the spatial deposition patterns to infer patterns of atmospheric transport.

APPROACH

The general approach used in this analysis entailed (1) the application of available data, (2) the development of empirical relations for regions for which data were not available, and (3) the use of information from peer-reviewed research publications.

Deposition of nitrogen from the atmosphere can be categorized as either wet deposition (rain or snow) or as dry deposition (particles or vapor deposited from the atmosphere during periods when precipitation is not falling). Wet deposition is monitored year round at about 200 sites across the United States through the NADP/NTN (National Acid Deposition Program/National Trends Network). Data from NADP/NTN sites within the Mississippi Basin were converted with a GIS (geographic information system) from point coverages to polygons that represent the 133 hydrologic accounting units (areas delineated by drainage divides) of the basin. This process entailed (1) creating a grid of 6.25-km² cells, (2) assigning nitrogen deposition values to each cell through inverse distance weighting of the point coverages, and (3) converting the grid coverages to polygons that each represent one of the 133 hydrologic accounting units.

Dry deposition is monitored at about 60 sites through CASTNet (the U. S. Environmental Protection Agency Clean Air Status and Trends Network) through an inferential approach in which dry deposition-rates are obtained from air concentrations (measured with three-stage air samplers) and deposition velocities (the velocity with which gases and particles are deposited onto vegetation surfaces) determined by a mathematical model (Clarke and others, 1997). This approach enables deposition rates to be quantified for NO₃ and NH₄ particles and HNO₃ vapors. Because most of the CASTNet sites are east of the Mississippi River, the spatial distribution of dry deposition data was inadequate for the development of deposition polygons through interpolation. Thus, empirical relations between wet deposition and dry deposition were developed for each of the 14 sites within the Mississippi River Basin at which NADP and CASTNet stations were collocated.

SPATIAL PATTERNS OF DEPOSITION

No trend in the rates of wet deposition of NO₃ or NH₄ during 1984-96 was discerned from values representing the overall basin. The lowest deposition rates for both constituents occurred during the drought years of 1988-89. The highest rates of wet deposition of NO₃ within the basin were in an area that extends from central Ohio eastward to the basin boundary (fig. 1). These rates generally decreased southward and westward from Ohio. The highest rates of wet deposition of NH₄ were centered in Iowa and generally decreased in all directions; the lowest rates were in Montana (fig. 2).

Relations between wet deposition and dry deposition varied considerably among sites, but a positive correlation ($R = 0.42$, $p < 0.01$) was obtained when data from all sites were grouped. For all sites, the average value of total dry deposition (particulate NO₃ and NH₄ plus HNO₃ vapor) divided by the average value of total wet deposition (NO₃ plus NH₄) was 0.47. Because the variability among sites is high, application of this value throughout basin yields an imprecise estimate of dry deposition.

The values for components of wet and dry deposition of nitrogen for sites along a west-to-east transect in the basin for the period December 1, 1992 through November 30, 1993 are shown in figure 3. The deposition of all five components was lowest at the Wyoming site, and total nitrogen deposition at this site was less than half that at the Ohio site. The highest rate of wet deposition of NO₃ was measured at the West Virginia site, whereas the highest rate of wet NH₄ deposition was measured at the Illinois site, and the highest rate of HNO₃ deposition was observed at the Ohio site. The rate of total nitrogen deposition at the Illinois site was more similar to the rate at the West Virginia site than to the rate at the nearby Ohio site. Total dry deposition of nitrogen averaged for all sites, and all seasons, was composed of 81 percent HNO₃ vapor, 16 percent particulate NH₄, and 3 percent particulate NO₃.

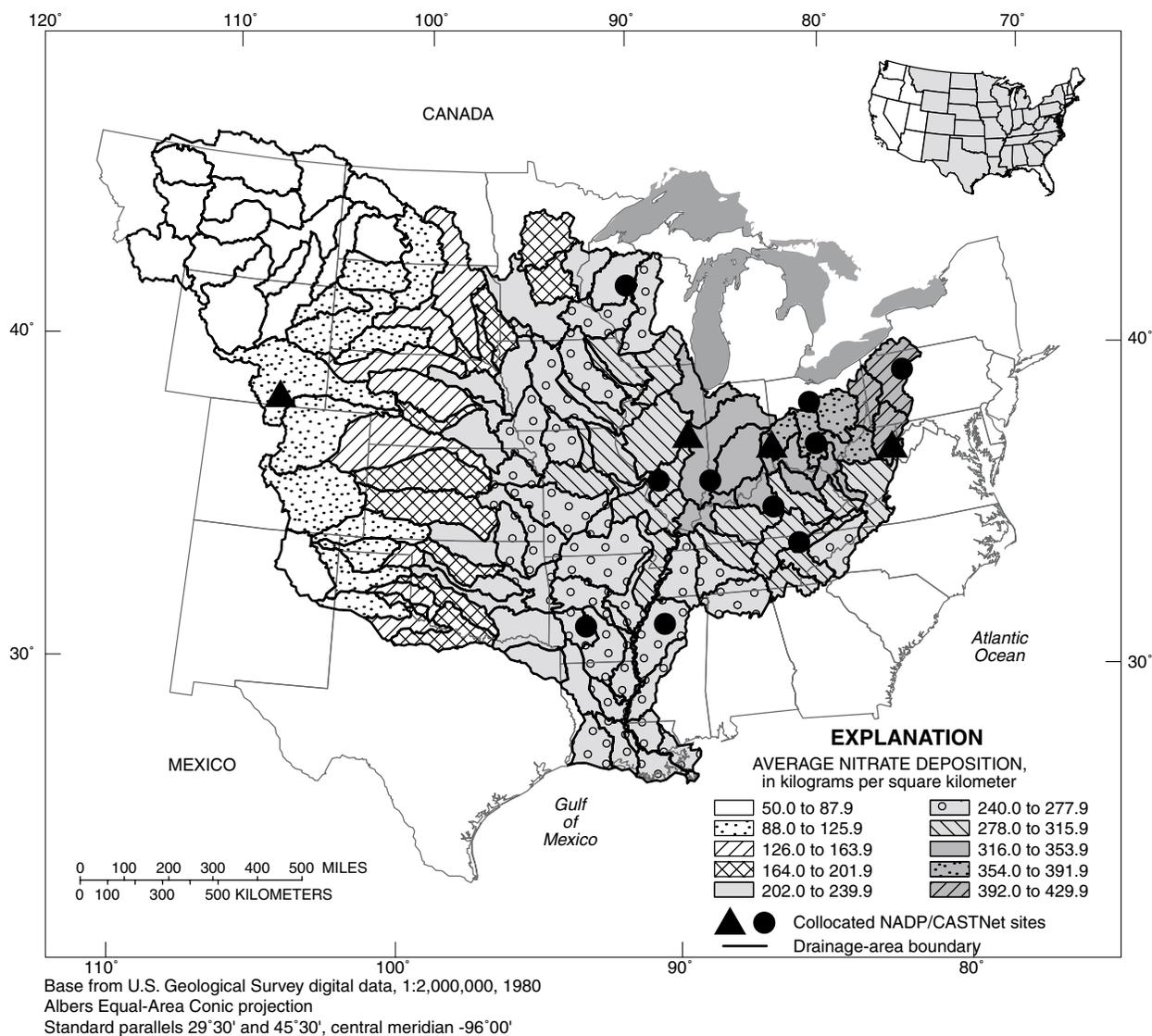


Figure 1. Wet deposition of NO_3 , averaged for 1990-96, in the 133 accounting units that make up the Mississippi River Basin. Dry deposition rates for sites indicated by triangles are given in figure 3.

EMISSIONS SOURCES AND ATMOSPHERIC TRANSPORT

The regional patterns of wet deposition of NO_3 and NH_4 within the Mississippi River Basin reflect emissions sources and atmospheric-transport processes. The highest rates of NO_3 deposition were measured in Ohio and Pennsylvania (fig. 1), northeast of the concentration of electric utility plants in southern Indiana and western Kentucky (NAPAP, 1993). Fossil-fuel combustion is a known source of NO and NO_2 , which are oxidized in the atmosphere to form HNO_3 vapor and particulate NO_3 (U. S. Environmental

Protection Agency, 1997). Although HNO_3 vapor has a high deposition velocity and a relatively short residence time, it can react with other pollutants such as NH_3 to form particles with low deposition velocities that can be transported hundreds of miles. Particulate NO_3 also tends to have a low deposition velocity that facilitates long-range transport. Significant atmospheric transport of nitrogen from midwestern powerplants to the northeastern States has been well established (NAPAP, 1993).

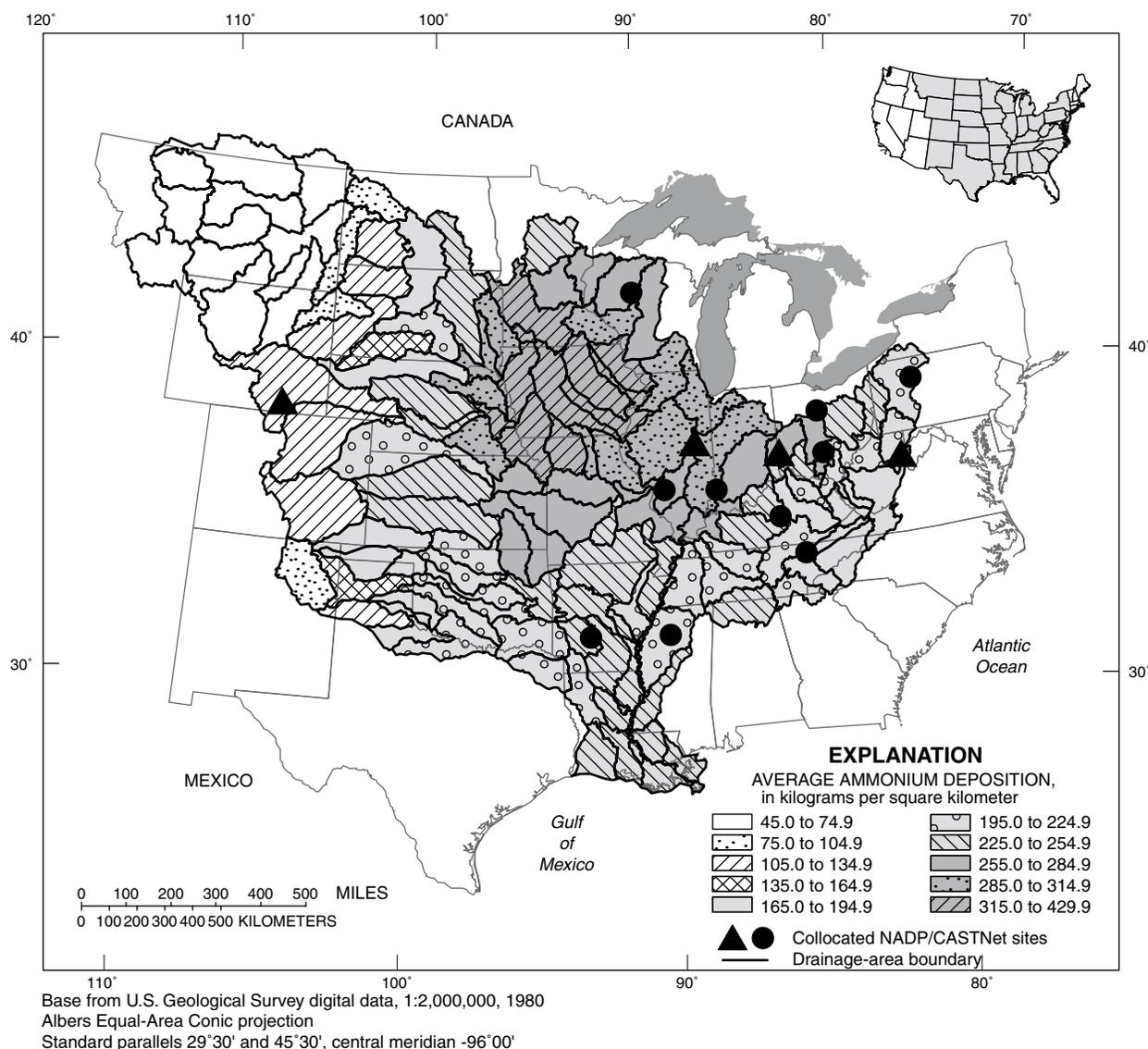


Figure 2. Wet deposition of NH_4 , averaged for 1990-96, in the 133 accounting units that make up the Mississippi River Basin. Dry deposition rates for sites indicated by triangles are given in figure 3.

Wet and dry deposition of NH_4 have generally been attributed to NH_3 emissions from high concentrations of livestock and nitrogen fertilization of croplands (Vitousek and others, 1997). Emissions from automobiles can also contribute atmospheric NH_3 , but estimates of NH_3 emissions from automobiles did not exceed agricultural sources in the South Coast Air Basin of California, which includes Los Angeles and surrounding developed areas (Fraser and Cass, 1998). The highest rates of wet NH_4 deposition in the Mississippi Basin are centered in Iowa, a predominantly agricultural state.

Unlike the NO and NO_2 released from fossil-fuel combustion, NH_3 is emitted to the atmosphere in a highly water-soluble form that is readily removed from the atmosphere by precipitation. As a result, NH_3 tends to be deposited closer to its sources than are other forms of nitrogen. An NH_3 transport model by Asman and van Jaarsvelt (1992) indicated that 46 percent of emitted NH_3 was deposited within 50 km of the source; 40 percent as dry deposition and 6 percent as wet deposition. Results from a separate modeling study (Ferm, 1998) indicated that 49 percent of NH_3 emitted in a 22,000- km^2 region in Sweden was deposited

within this region; 21 percent as dry deposition and 28 percent as wet deposition.

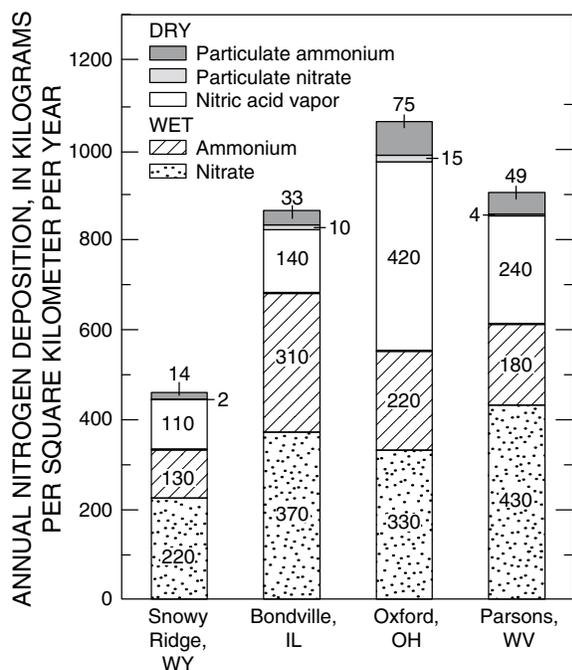


Figure 3. Chemical fractions of wet and dry nitrogen deposition at 4 sites selected along a west-to-east transect across the Mississippi River Basin, December 1992 through November 1993. Sites indicated as triangles on figures 1 and 2.

Transport of NH_3 , depends on wind speed and reactions with other pollutants. Although about half of the emitted NH_3 tends to be deposited near its source, reactions with H_2SO_4 and HNO_3 form particulate NH_4 , which is transported more readily than NH_3 (Ferm, 1998). High atmospheric concentrations of SO_2 and NO_x in areas where emissions of NH_3 are high can therefore lead to long-range transport of NH_3 . Research in the Netherlands has shown that deposition of NH_x beyond 300 km of the source was halved approximately every 450 km; a pattern similar to that of SO_x compounds (Ferm, 1998). Thus, high emissions of SO_2 and NO_x in Illinois, Kentucky, Indiana, and Ohio are likely to enhance the transport of NH_4 from the agricultural regions in the central part of the Mississippi Basin to eastern sections of the basin and beyond. Long-range transport is the most likely explanation for the similarity between wet deposition rates of NH_4 measured in 1996 at NADP stations in Iowa and at Bennett Bridge, N.Y. (Table 1). The New York

site is remote from sources of NH_3 emissions, but is located in an area with high rates of acid deposition.

On the basis of NADP and CASTNet data, NH_4 deposition represents about 35 percent of total nitrogen deposition in the Mississippi Basin, but the collection methods of both programs probably contribute to an underestimation of this fraction. Some of the NH_4 collected by NADP buckets may be converted to organic nitrogen through microbial assimilation between the time of deposition and the weekly collection (Vet and others, 1989). Also, the three-stage filter pack used in the CASTNet program is designed to collect NH_4 particles, but not NH_3 , whose deposition velocity is about 5 times higher than that of the NH_4 particles (Ferm, 1998). The deposition of gaseous NH_3 , therefore, is likely to represent a higher fraction of dry deposition close to sources, than indicated by CASNet measurements.

Table 1. Wet deposition of NH_4 and NO_3 for 1996 in kilograms per square kilometer per year, and the deposition ratio for these two ions.

Site	NH_4	NO_3	NH_4/NO_3
Bennett Bridge, New York	410	690	0.60
McNay Reseach Center, Iowa	280	210	1.3
Big Springs, Iowa	300	360	0.8

CONSIDERATIONS FOR THE NITROGEN BUDGET OF THE MISSISSIPPI RIVER 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 similar magnitude to 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 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). A value of 0.75 was obtained by Dinnel (1998) for this fraction of dry deposition of HNO_3 and NO_3 from CASTNet and NADP data from 1990-92.

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 likely to be from internal sources because (1) the region of highest NH_3 deposition is in the center of the basin, (2) half or more 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 subbasins are net sources, whereas other subbasins are net sinks. Because most of the NH_4 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 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.

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