# D3. Atmospheric Deposition of Nitrogen in Minnesota Watersheds

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## Background

### Emission sources

Atmospheric nitrogen from natural and human sources can fall on to land and waters through both wet weather deposition in rainfall and snow, or through dry weather deposition when particles and vapor are deposited without precipitation. Sources of nitrogen (N) to the atmosphere include, but are not limited to, automobiles, power plants, livestock manure, fertilizers, and lightning.

Providing a national perspective on sources of reactive N to the environment, the U. S. Environmental Protection Agency's (EPA) Science Advisory Board developed N flux estimates from various sources (Table 1). Each area of the country will have different percentages coming from these sources. Cities will have more combustion sources (mostly NOx) and rural areas will often have more livestock and fertilizer sources (mostly NHx).

**Table 1. United States N inputs to the atmospheric environmental system in 2002. (EPA, 2011)**

| Emission inputs | billion lbs N/yr | % |
|---|---|---|
| NOX-N emissions* | 13.7 | 61 |
| Fossil fuel combustion – transportation | 7.7 | |
| Fossil fuel combustion – utility & industry | 4.2 | |
| Other combustion | 0.9 | |
| Biogenic from soils | 0.7 | |
| Miscellaneous | 0.4 | |
| NHx-N emissions* | 6.8 | 31 |
| Agriculture: livestock NH3-N | 3.5 | |
| Agriculture: fertilizer NH3-N | 2.0 | |
| Agriculture: other NH3-N | 0.2 | |
| Fossil fuel combustion – transportation | 0.4 | |
| Fossil fuel combustion – utility & industry | 0.06 | |
| Other combustion | 0.6 | |
| Miscellaneous | 0.2 | |
| N2O-N emissions | 1.8 | 8 |
| Agriculture: soil management N2O-N (nitrification and denitrification processes) | 1.1 | |
| Agriculture: livestock (manure) N2O-N | 0.06 | |
| Agriculture: field burning agricultural residues | 0.002 | |
| Fossil fuel combustion – transportation | 0.2 | |
| Miscellaneous | 0.2 | |

*NOX-N emissions include nitrate (NO3) and nitrite (NO2), but also include NO, N2O5, HONO, HNO3, PAN and other organo-nitrates. NHx emissions mostly include ammonia (NH3) and ammonium (NH4) (EPA, 2011).

### Objective

Our objective was to estimate typical wet and dry atmospheric inorganic N deposition for each of the 8-digit Hydrologic Unit Code (HUC8) watersheds in Minnesota. Our goal was to develop atmospheric deposition estimates for nitrogen falling directly onto a) land, and b) waters. Our objective was not to determine relative amounts of atmospheric N from specific sources, but rather to estimate the combined N deposition from all sources.

It was beyond the scope of this study to estimate how much of the N deposited in Minnesota originates from Minnesota vs. other states/provinces, nor was it within the scope to estimate how much atmospheric N from Minnesota sources is deposited in other states/provinces. We also did not intend to evaluate all of the environmental effects associated with atmospheric N deposition. A brief summary of environmental concerns related to atmospheric N is included in Chapter A2.

### Approach

The primary approach was to use results from atmospheric deposition modeling conducted by the EPA, and cross-check these results using wet weather monitoring results from the National Atmospheric Deposition Program.

Modeling results for wet and dry N deposition were provided by EPA (Dennis, 2010). The model used by EPA was the Community Multiscale Air Quality (CMAQ) modeling system, which is described in Byun and Schere (2006). The model includes components for meteorological atmospheric states and motions, emissions from natural and man-made sources, and chemical transformation and fate after being injected into the atmosphere. The CMAQ model uses precipitation monitoring results from the National Atmospheric Deposition Program (NADP), and then adds N source information to improve spatial estimates of wet deposition and to model dry deposition amounts.

The modeled results provided by EPA for this study included wet and dry deposition of both oxidized (mostly nitrate and nitrite, but also include NO, $N_2O_5$, HONO, $HNO_3$, PAN and other organo-nitrates) and unoxidized (mostly ammonia and ammonium) forms of N. The N source estimates are from a 2002 base year inventory. The dry deposition is not expected to vary appreciably from year to year, unless major new sources are added or removed, and wet weather deposition can be expected to vary linearly with increases or decreases in precipitation (Dennis, 2011).

## Atmospheric nitrogen deposition (per acre)

### Statewide and major basin average nitrogen deposition

Basin and statewide averages of modeled dry and wet weather deposition are shown in Table 2. On average across the state, wet weather deposition accounted for 52% of the total atmospheric N deposition, and dry deposition accounted for 48% of the total. The unoxidized fraction represented 62% of the wet plus dry N, with 38% in the oxidized form. The statewide average inorganic N deposition (wet plus dry) is 8.4 pounds/acre/year.

**Table 2. Minnesota basin and statewide spatially weighted averages of wet and dry atmospheric N deposition in pounds/acre based on CMAQ model results for the 2002 base year. Low and high precipitation represent 10th and 90th percentile annual precipitation amounts.**

| Basin | Oxidized wet | Unoxidized wet | Oxidized dry | Unoxidized dry | Avg. precip. yr total N wet + dry | Low precip. yr Total N wet + dry | High precip. yr total N wet + dry |
|---|---|---|---|---|---|---|---|
| Lake Superior | 1.30 | 1.97 | 1.80 | 0.48 | 5.55 | 5.03 | 6.21 |
| Upper Mississippi River | 1.72 | 2.97 | 1.71 | 2.28 | 8.67 | 7.92 | 9.61 |
| Minnesota River | 1.86 | 3.31 | 1.59 | 4.38 | 11.14 | 10.31 | 12.17 |
| St. Croix River | 2.15 | 3.45 | 2.02 | 1.37 | 9.00 | 8.10 | 10.12 |
| Lower Mississippi River | 2.68 | 4.12 | 2.15 | 4.25 | 13.20 | 12.12 | 14.57 |
| Cedar River | 2.23 | 3.51 | 2.02 | 4.67 | 12.44 | 11.52 | 13.58 |
| Des Moines River | 1.77 | 3.17 | 1.57 | 4.81 | 11.32 | 10.53 | 12.31 |
| Red River of the North | 1.09 | 2.10 | 1.19 | 2.06 | 6.44 | 5.93 | 7.08 |
| Rainy River | 1.04 | 1.70 | 1.43 | 0.57 | 4.75 | 4.31 | 5.29 |
| Missouri River | 1.63 | 3.04 | 1.55 | 5.25 | 11.47 | 10.72 | 12.40 |
| MN - Statewide | 1.59 | 2.72 | 1.59 | 2.49 | 8.40 | 7.71 | 9.26 |

## Watershed deposition amounts

Because there is substantial spatial variability across the state in atmospheric N deposition, modeled results for each HUC8 watershed were individually calculated based on a spatial average across each watershed (Appendix D3-1 - Table 1). The pattern of deposition shows higher deposition rates in the southern part of the state, where agriculture, urban, and other human sources are more common (Figures 1, 2, and 3). Inorganic N amounts varied from over 14 pounds/acre in the southern part of the state to just over 4 pounds/acre in the northeastern region, during years of average precipitation.

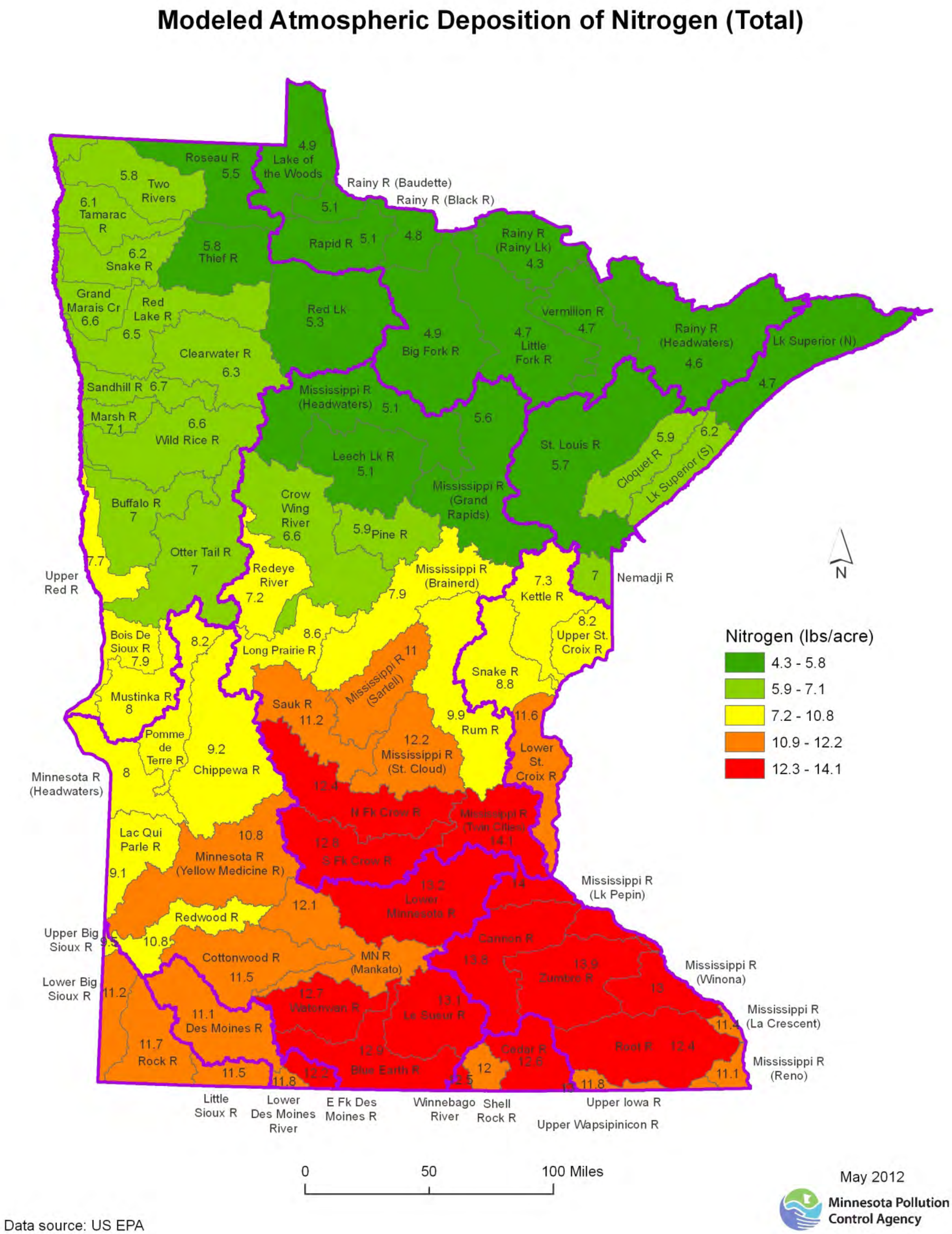


**Figure 1. Total annual inorganic N deposition estimated by the CMAQ model, including both wet and dry deposition.**

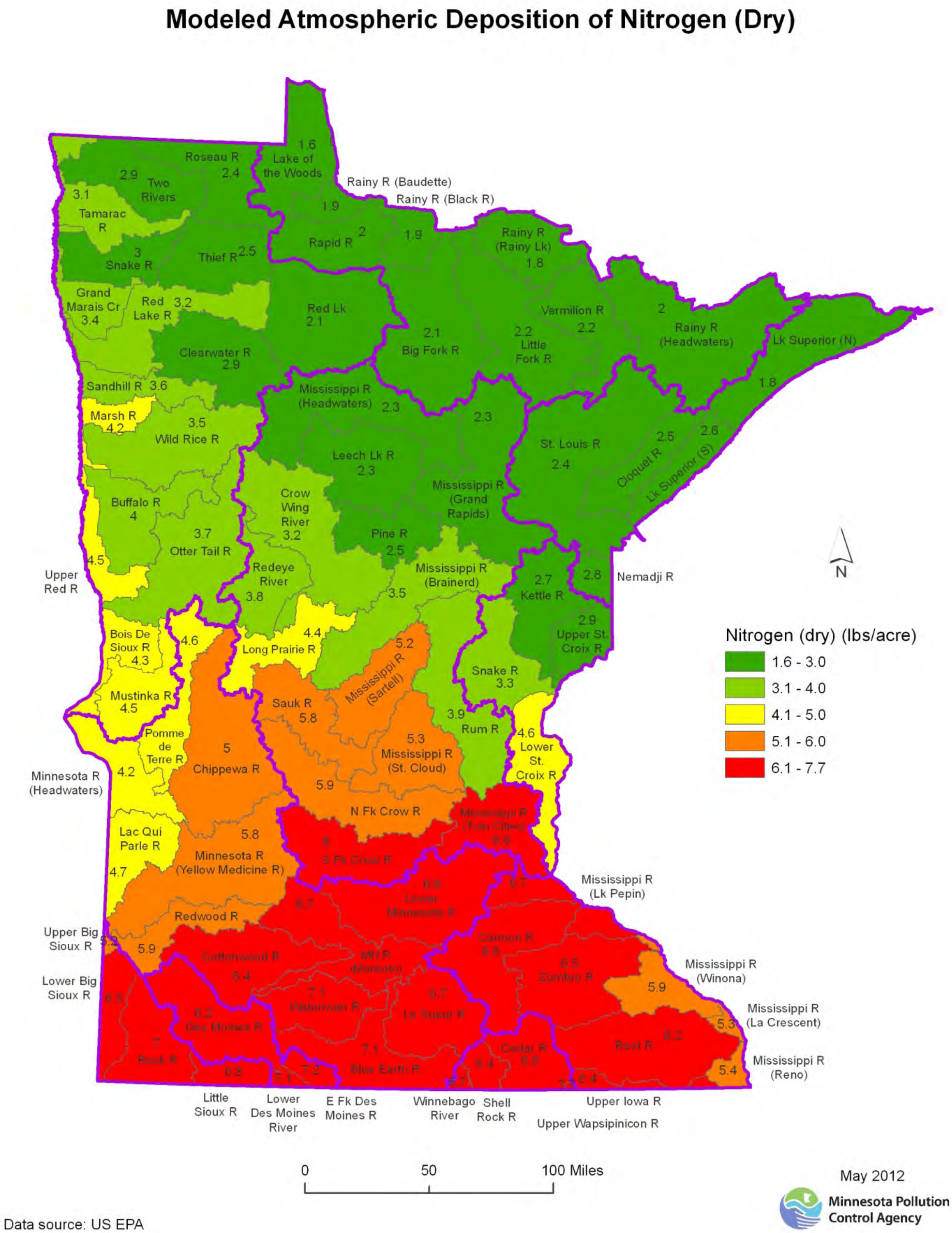


**Figure 2. Total annual inorganic N *DRY* deposition estimated by the CMAQ model, and spatially averaged across the HUC8 watersheds.**

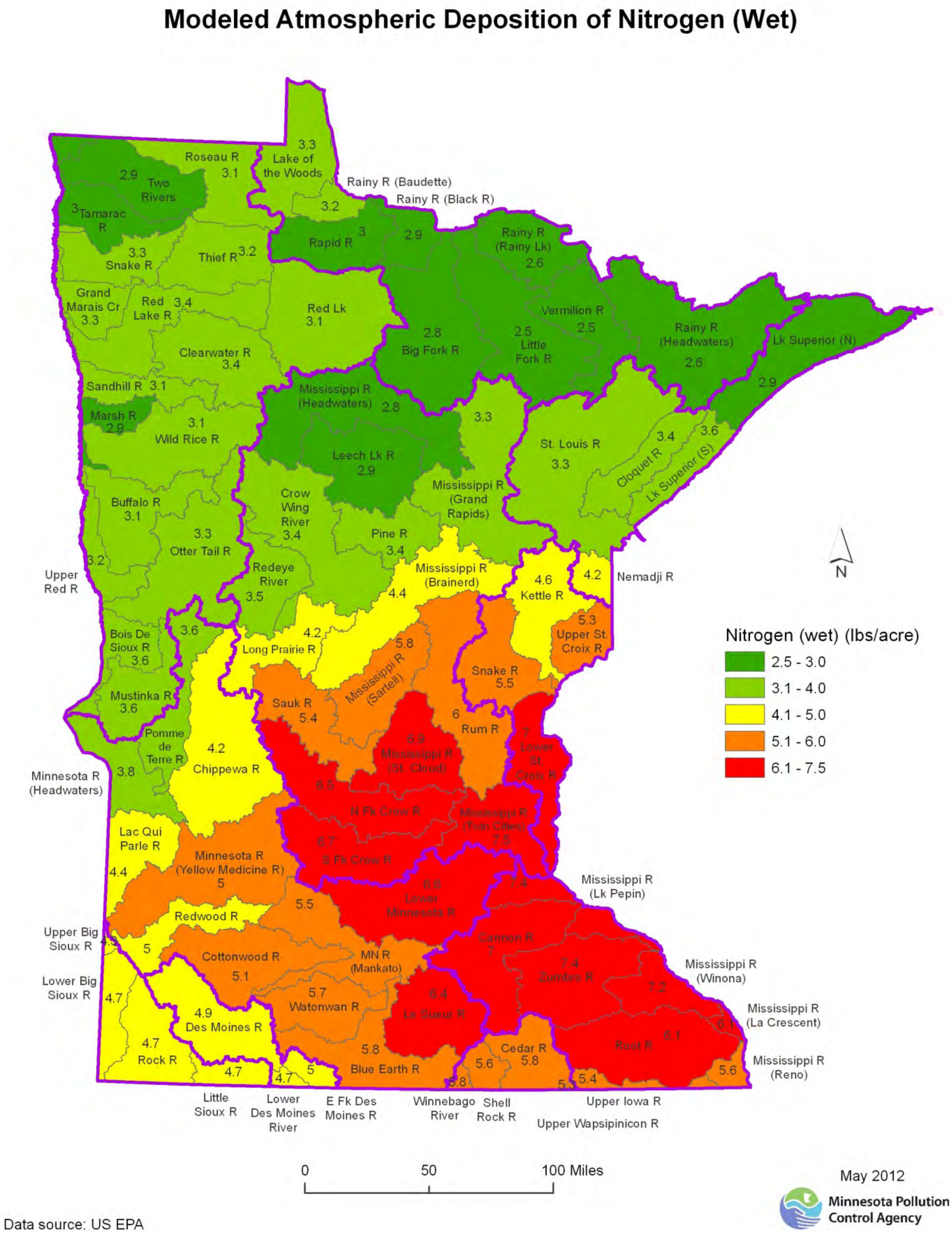


**Figure 3. Total annual inorganic N *WET* deposition estimated by the CMAQ model, and spatially averaged across the HUC8 watersheds.**

## Direct deposition into waters

Most of the atmospheric deposition of N falls on land, where it mixes with the soil to be a source of N for vegetation, or in some situations becomes part of the surface runoff nutrient losses. Yet some falls directly into waters. We used spatial data layers and GIS software, along with CMAQ modeled results, to estimate the amount of N which falls during average precipitation years onto a) dry land, b) wetlands and marshes, c) lakes, and d) rivers and streams.

### Calculation of surface water area

To calculate the surface area for rivers, we used three classes of streams within the high resolution 1:24,000 scale National Hydrography Dataset (NHD) including stream/river, canal/ditch, and connector. We then ran the intersect command in ArcGIS 10 (ESRI, 2010) using the NHD and the Minnesota Department of Natural Resources (DNR) HUC8 watershed data layer. We used the summarize command in ArcGIS to sum the total stream length for each watershed. We then multiplied the total stream length values by the average estimated width value of seven meters to obtain a final estimate of stream surface area.

For lake surface area calculations, we considered using the high resolution NHD but found numerous errors in the dataset, and we felt that the medium resolution 1:100,000 scale NHD would provide a more accurate assessment. We calculated surface area for lakes using two classes of water bodies within the medium resolution NHD including lake/pond and reservoir. We ran the intersect command in ArcGIS using the NHD and the DNR HUC8 watershed data layer. We then used the summarize command in ArcGIS to sum the total lake area for each watershed.

To calculate surface area for wetlands, we considered using the high-resolution NHD, but the primary wetland class, swamp/marsh was not populated for this data layer. We also considered using the National Wetlands Inventory (NWI), however this dataset for Minnesota is dated, it was developed circa 1980, and it is our understanding that the accuracy of wetlands in the medium resolution NHD is better than the NWI. Therefore, we calculated surface area for wetlands using the swamp/marsh class in the medium resolution NHD. We ran the intersect command in ArcGIS using the NHD and the DNR HUC8 watershed data layer. We then used the summarize command in ArcGIS to sum the total wetland area for each watershed.

### Results – into waters

Based on this assessment, 374 million pounds (82.5%) of inorganic N falls onto land in Minnesota and 79 million pounds (17.5%) falls directly into lakes, marshes, wetlands and rivers. For wet and dry years, these amounts would be expected to average about 10% lower and higher, respectively, across the state. Of the N falling directly into waters, over 97% falls into lakes and marshes, which have a high capacity for assimilating and reducing N levels (see Appendix B5-2). About 2.1 million pounds, or 2.5% of the total falling into waters, falls directly into rivers, streams, and creeks. Specific annual estimated amounts falling directly into waters in different basins and HUC8 watersheds are included in Table 4 and Table 2 in Appendix D3-1.

For the statewide source assessment comparison of N into lakes and streams from major sources (Chapter D1), we used the atmospheric deposition into rivers and lakes and did not include deposition into wetlands and marshes. Wetlands can remove large quantities of nitrogen (see Appendix B5-2), and most atmospheric deposition falling into wetlands is not expected to leave the wetlands and move into streams, rivers or lakes.

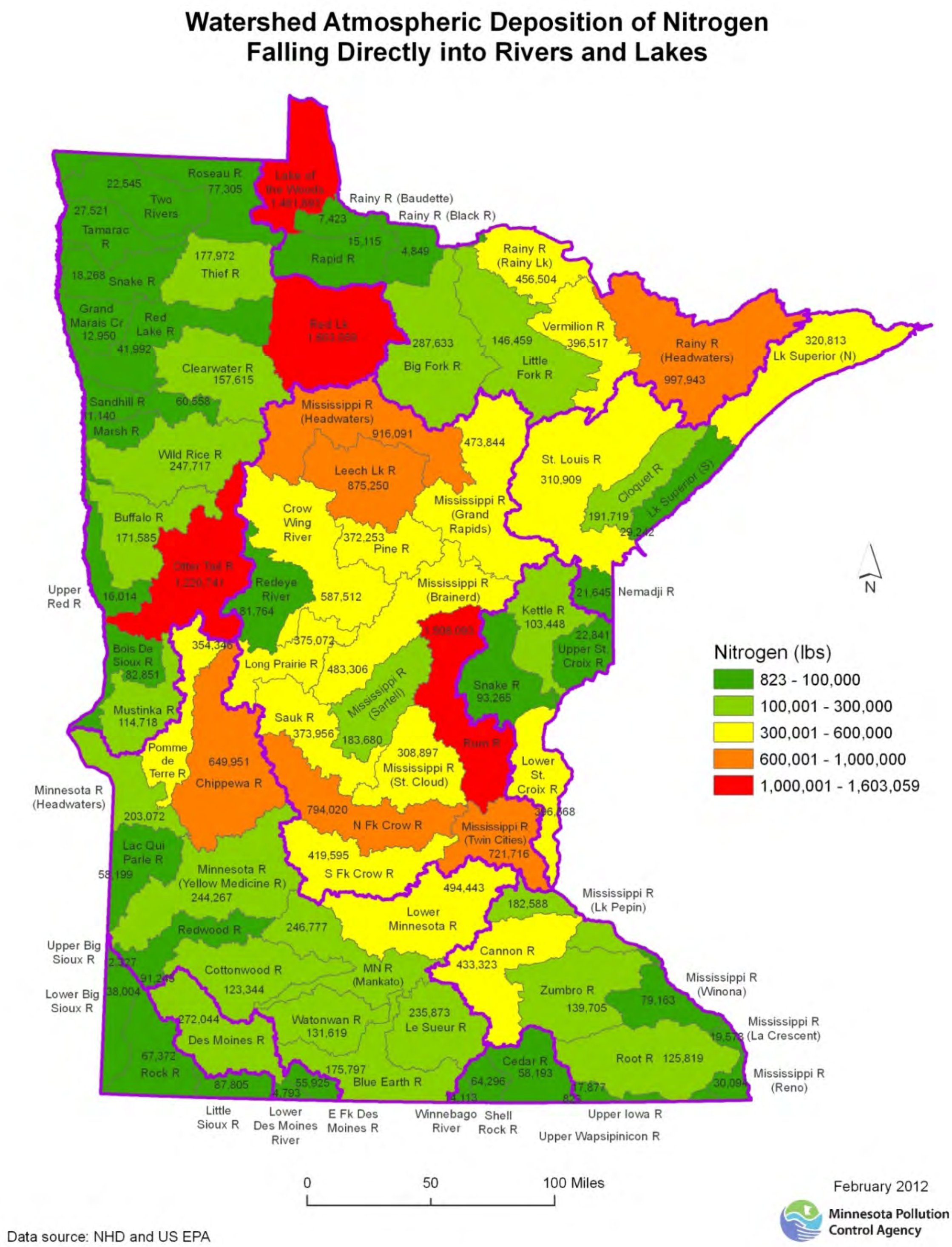


**Figure 4. Estimated annual amount of wet plus dry oxidized and unoxidized inorganic N falling directly into rivers and lakes in each HUC8 watershed (note that this does not include wetland deposition).**

**Table 4. Atmospheric deposition estimates of wet+dry inorganic N falling directly into rivers and streams, marshes/wetlands, lakes, dry-land, and the total onto all land and waters. Results are shown for each of the major basins in the state.**

| Basin | Rivers | Marsh | Lake | Land | Total |
|---|---|---|---|---|---|
| Lake Superior | 97,525 | 4,761,219 | 812,006 | 16,166,410 | 21,837,160 |
| Upper Mississippi River | 401,053 | 12,780,788 | 8,955,538 | 89,432,276 | 111,569,654 |
| Minnesota River | 553,936 | 757,661 | 2,640,104 | 102,810,198 | 106,761,900 |
| St. Croix River | 80,860 | 2,913,266 | 474,632 | 16,777,994 | 20,246,753 |
| Lower Mississippi River | 435,344 | 345,523 | 576,129 | 51,859,283 | 53,216,278 |
| Cedar River | 44,561 | 47,015 | 94,418 | 8,091,877 | 8,277,871 |
| Des Moines River | 57,190 | 36,554 | 275,639 | 10,770,989 | 11,140,371 |
| Red River of the North | 328,772 | 7,720,136 | 3,974,825 | 60,896,642 | 72,920,375 |
| Rainy River | 108,812 | 10,834,347 | 3,722,212 | 19,651,106 | 34,316,476 |
| Missouri River | 112,501 | 7,413 | 82,828 | 12,881,475 | 13,084,217 |
| **MN - Statewide** | **2,220, 553** | **40,203,921** | **21,608,332** | **389,338,250** | **453,371,055** |

## Comparing modeled results with wet deposition measurements

Wet weather deposition data from the NADP were compared to CMAQ-modeled results. We accessed the NADP on-line data base nadp.sws.uiuc.edu/ to obtain inorganic N (nitrate+nitrite-N plus ammonium-N) deposition information for sites in and near Minnesota. Our search was limited to those sites for which deposition information was available for each year between 1999 and 2009. Eight Minnesota locations met these criteria. We combined the Minnesota results along with information from monitoring locations in Iowa, Wisconsin, South Dakota, and North Dakota.

We used data from 24 monitoring sites in Minnesota and neighboring states together with a kriging method in ArcGIS to create an interpolated spatial data layer of mean annual wet weather inorganic N deposition amounts (1999 to 2009). We then used this interpolated data layer together with a zonal statistics method in ArcGIS to calculate the average annual deposition amount, in pounds per acre, for each HUC8 watershed in Minnesota. Results from this process are shown in Figure 5, which shows the average wet weather inorganic N deposition from Minnesota based on the interpolated NADP data.

The pattern of deposition determined from precipitation monitoring is very similar to modeled results using CMAQ (Figure 5), with higher amounts in the southern part of the state and lowest amounts in the north. The CMAQ results estimate slightly higher wet weather deposition in the southeast and central Minnesota and slightly lower deposition in the northeast, as compared to the NADP-based estimates. However, the results are similar enough to provide assurance in the reasonableness of CMAQ results provided by the EPA.

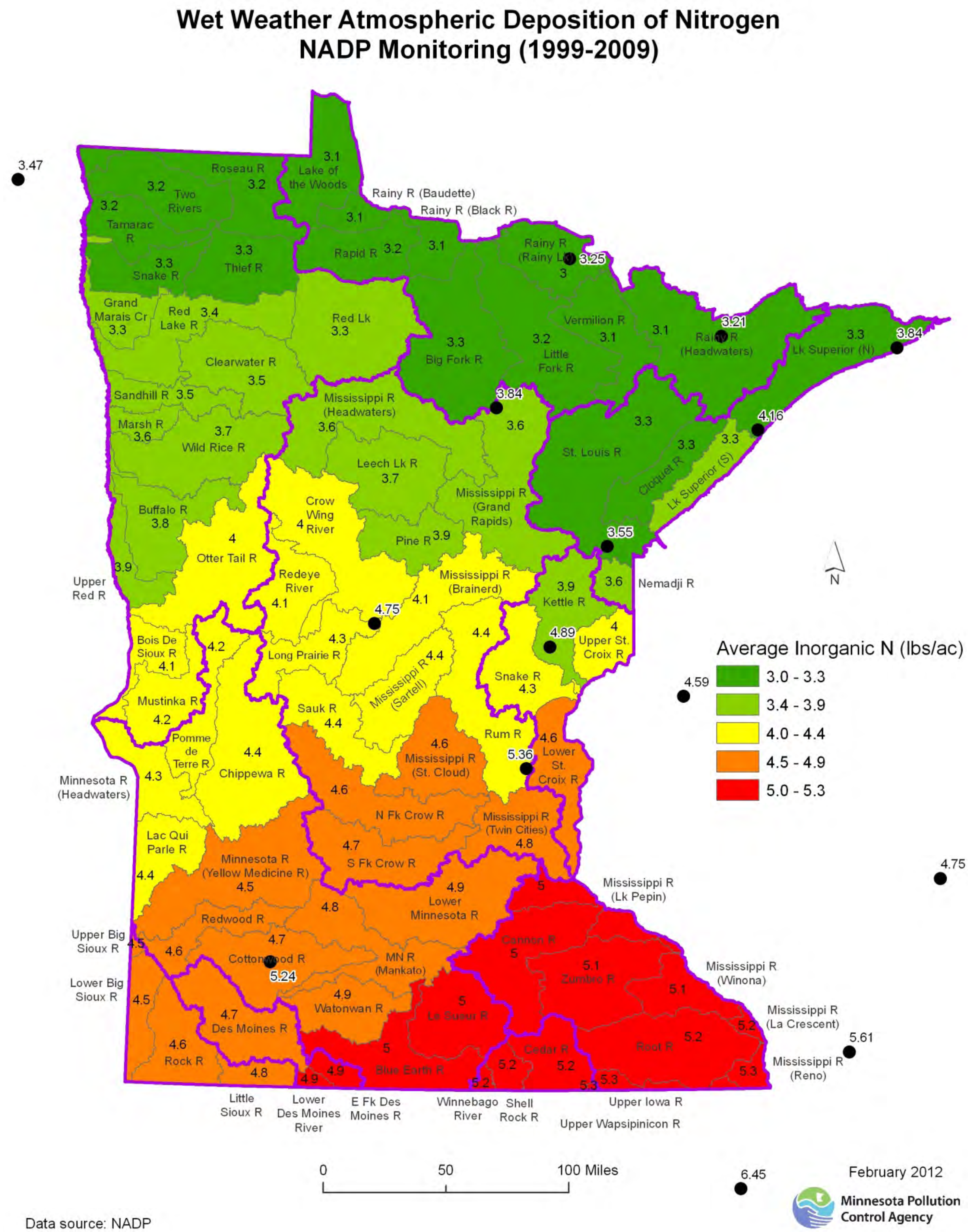


**Figure 5. Inorganic N monitored from wet weather deposition (average between 1999 and 2009). Data source NADP. Amounts between monitoring points (triangles) were interpolated.**

## Organic nitrogen

Organic N deposition is not included in the CMAQ modeled results. Organic N deposition is likely to contribute to atmospheric deposition total nitrogen inputs, although the magnitude of the deposition rate is highly uncertain. Goolsby et al. (1999) noted that if the fraction of organic N/total N in wet deposition measured in a 1998 study by Scudlark is assumed to be similar to the fraction that occurs in the Mississippi Basin, wet deposition of organic N in the Mississippi Basin can be estimated as 25% of the total wet deposition. The EPA concluded from the literature that organic N can be about 10% as much as the NOx from atmospheric deposition, but could be as much as 30% (EPA, 2011). This would mean that the organic N deposition likely represents an additional 4% to 13% of the total wet and dry inorganic atmospheric deposition.

With limited information and no modeled results, along with the relatively small expected contribution from organic N, we did not include an organic N amount in the predicted atmospheric deposition for this study.

## Summary

Based on the Community Multiscale Air Quality-modeled results provided by the EPA, wet plus dry atmospheric inorganic N deposition contributes between 4 and 14 pounds annually per acre to Minnesota soil and water, averaging 8.4 pounds/acre/year across the state. Atmospheric deposition is highest in the south and southeast parts of the state and lowest in the north and northeast where fewer urban and agricultural sources exist. The annual wet and dry deposition amounts are nearly equal, on average, across the state. The inorganic N in wet plus dry deposition is about 62% unoxidized (NHx – mostly ammonia and ammonium) and 38% oxidized (N0x - nitrite, nitrate, other). Approximately 82.5% of total statewide inorganic N deposition falls onto land (374 million pounds), and 17.5% (79 million pounds) falls directly into lakes, marshes, wetlands, and flowing waters. Of the N falling directly into waters, 97.5% falls into lakes and marshes, and about 2.5% (2.1 million pounds) falls directly into rivers, streams, and creeks.

## References

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