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Barr Engineering Company
4700 West 77th Street • Minneapolis, MN 55435-4803
Phone: 952-832-2600 • Fax: 952-832-2601 • www.barr.com *An EEO Employer*

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Technical Memorandum

To: Marvin Hora, Greg Gross, and Dennis Wasley, Minnesota Pollution Control Agency.
From: Cliff Twaroski, Nadine Czoschke, Tim Anderson
Subject: Detailed Assessment of Phosphorus Sources to Minnesota Watersheds - Atmospheric Deposition: 2007 Update
Date: June 29, 2007
Project: 23/62-853 PHS3 001
c: Greg Wilson, Henry Runke

Introduction

The purpose of this memorandum is to provide an updated discussion about Atmospheric Deposition as a source of phosphorus to Minnesota watersheds. This discussion builds upon an analysis conducted in 2003 for the Minnesota Pollution Control Agency (MPCA) and is based on a review of the available literature, consideration of monitoring data and other available support data, and includes the results of phosphorus loading computations for each of Minnesota's ten major watershed basins. This memorandum is intended to:

- Provide an overview and introduction to the atmosphere as a source of phosphorus
- Describe the results of the literature search and review of available monitoring data
- Discuss the characteristics of each watershed basin as it pertains to this source of phosphorus
- Describe the methodology used to complete the phosphorus loading computations and assessments for this study
- Provide updated estimates of wet and dry phosphorous deposition for each major water basin and compare the updated deposition estimates to the 2003 estimates.
- Discuss the results of the phosphorus loading computations and assessments
- Discuss any new findings from the 2007 analysis regarding background phosphorus deposition and the potential significance of agricultural land use on deposition estimates
- Discuss the uncertainty of the phosphorus loading computations and assessment
- Provide recommendations for future refinements to phosphorus loading estimates and methods for reducing error terms

- Provide recommendations for lowering phosphorus export from this source

Follow-up work to the February 2004 report on the Statewide Phosphorus Study was conducted in April through June 2006. The work in 2006 evaluated the following aspects of atmospheric P deposition:

- A literature review on atmospheric phosphorus deposition to identify new literature since 2002.
- Refine the estimates of atmospheric P deposition:
  - Evaluate the potential geographic variation in the relationship between phosphorus and calcium concentrations in wet deposition.
  - Update the relationship between calcium and phosphorus in dry deposition.
  - Identify the seasonal variations in dry deposition in Minnesota.
  - Potential sources of atmospheric phosphorus as identified through emission estimates.
  - Size distribution of PM in different land use areas in Minnesota.
- Estimate the proportion of phosphorus deposition from agricultural wind erosion
  - determine the utility of calcium as a marker for soil in both wet and dry deposition.
  - Examine the gradients in phosphorus deposition as seen in soil markers across Minnesota.

The analyses were summarized for MPCA in a June 14, 2006 memorandum. An assessment of the available data identified that the relationship of [P] and [Ca] in precipitation could not be refined, seasonality in particle concentrations was not readily apparent, other elements do not improve the prediction of precipitation [P] or particle [P], and partitioning out the contribution of atmospheric P to agricultural runoff could not be accomplished using the available data. However, the work in 2006 identified the following items to be useful in updating estimates of atmospheric P deposition:

- Use of area-weighting or other techniques to interpolate/extrapolate wet and/or dry deposition in the areas between monitoring stations to improve deposition estimates, specifically along basin boundaries.
- Use of particle size distributions from the IMPROVE monitoring network sites located in Minnesota to enhance dry deposition estimates.
- Actual monitored particle P concentrations for use in the dry deposition estimates.

These items have been incorporated into the updated 2007 deposition estimates and are discussed in more detail in the following sections of the report.

Overview of Atmospheric Sources of Phosphorus

The importance of nutrient contributions to Minnesota's ecosystems has been recognized for some time (Verry and Timmons, 1977; Axler et al., 1994). Phosphorus in the atmosphere can be derived from a number of sources, including natural sources such as pollen, soil (from wind erosion) and forest fires, as well as anthropogenic sources such as fertilizer application and oil and coal combustion (Pierrou 1976). Agricultural activities (pre-planting field preparations, harvesting) can increase the amount of soil-derived phosphorus in the atmosphere (Carpenter et al, 1998). Phosphorus can also be released into the atmosphere in vapor form from various materials (sewage sludge, landfills) by microbial reduction processes (Brunner and Bachofen, 2000). However, the predominant form of phosphorus in the atmosphere is as particle-bound phosphorus (Pierrou 1976).

The atmosphere contributes phosphorus and phosphorus-containing material to terrestrial and aquatic ecosystems by wet (precipitation in various forms such as rain, sleet or snow) and dry (very small particles) deposition. Previous work by Pratt et al. (1996) indicates that dry deposition of particles is important to Minnesota ecosystems. Federal agencies have also recognized the importance of dry deposition to ecosystem health (NOAA-ARL, 2003). Subsequently, considerable effort has gone into deriving estimates of dry deposited phosphorus for this project.

Results of Literature Search and Review of Available Monitoring Data

A. Literature Review

Some previous estimates of phosphorus deposition for Minnesota and Wisconsin are provided in Table 1 below, ranging from a low of 0.05 kilograms per hectare per year (kg ha^{-1} yr^{-1}) in northern Wisconsin (Rose, 1993; Robertson, 1996) to 0.48 kg ha^{-1} yr^{-1} for north central Minnesota (Verry and Timmons, 1977).

Table 1. Estimates of phosphorus deposition in Minnesota and Wisconsin.

Deposition Estimate (kg ha^{-1} yr^{-1})	Description	Reference
0.48	Annual precipitation input of total phosphorus for a precipitation year representative of the western Great Lakes region (data collected in north central Minnesota).	Verry and Timmons, 1977 (Table 5)
0.15	Estimated total atmospheric phosphorus in the northern Minnesota; input data for the Minnesota Pollution Control Agency's (MPCA) watershed modeling.	Wilson, 2003
0.3 – 0.4	Estimated total atmospheric phosphorus in the southern and western part of Minnesota; input data for the MPCA's watershed modeling.	Wilson, 2003
0.05	Total atmospheric phosphorus deposition in northern Wisconsin's forest region.	Rose, 1993 (northwest WI) Robertson, 1996 (northeast WI)
0.05	Precipitation total phosphorus loading to Lake Michigan.	Miller et al., 2000
0.2	Estimated total atmospheric phosphorus deposition in southeast Wisconsin's agricultural areas.	Robertson, 1996

A cursory check on the availability of phosphorus deposition information and data was made for other states. Information on phosphorus Total Maximum Daily Load (TMDL) was reviewed for Lake Champlain (Vermont Agency of Natural Resources and New York State Department of Environmental Conservation, 2002) and for four watersheds in Kansas (Mau and Christensen, 2001). Deposition data were also reviewed for Florida (Dixon et al., 1998; Grimshaw and Dolske, 2002; Pollman *et al.*, 2002; Sigua and Tweedale, 2003), Colorado (Mast *et al.*, 2003), New Jersey (Koelliker *et al.*, 2004) and New York (Hu *et al.*, 1998). However, due to these states being distant from Minnesota, it was uncertain as to the applicability of the data to Minnesota's watersheds. Therefore, for the purpose of estimating phosphorus deposition to Minnesota River basins and watersheds within basins, data from other states was not considered applicable.

Biomass burning is indicated as a possible source of atmospheric phosphorus in the Lake Tahoe area (Zhang *et al.*, 2002), Tanzania (Tamatamah *et al.*, 2005), and in the Amazon River basin (Mahowold et al. 2005). Such studies suggest that periods of intense prescribed burns or forest fires may increase the ambient phosphorus content of PM and thus result in temporarily, or seasonally, higher phosphorus deposition. Emission inventory data and ambient air monitoring data are not available from Minnesota to assess the potential contributions from biomass burning or fuel combustion.

The gaseous form of phosphorus, phosphine, has been linked to soil as a potential source. However there is no indication that agricultural soils would be a larger source of phosphine than other soils, nor is it clear if phosphine is a participant in the wet or dry deposition of phosphorus (Glindemann, *et al.*, 2005). Pierrou (1976) identifies there are no stable gaseous phosphorus compounds and that phosphorus only exists adsorbed on particulate matter in the atmosphere.

The literature review indicates that limited data are available from Minnesota sources to estimate phosphorus deposition to the state's river basins. The previous best source of information for precipitation input (wet deposition) of phosphorus to Minnesota watersheds is Verry and Timmons (1977). Specific estimates of dry deposited phosphorus in Minnesota were not found in the literature review.

The goal for this work in 2007 is to provide an updated estimate of total (wet + dry) phosphorus deposition to surface waters and wetland areas in Minnesota. The updated wet deposition estimates follow the same approach used in the 2003 analysis (relying on 1) the established relationship of measured calcium [Ca] and phosphorus [P] concentrations in precipitation at reference sites, and 2) a developed regression equation of [Ca]:[P] to estimate the [P] at other locations in the state based on known [Ca]). The major change to methodology used to estimate wet deposition is the use of an area-weighting calculation for rainfall and [P] for each major river basin. The updated estimates of dry phosphorous deposition now use measured phosphorus concentrations obtained from the analysis of ambient particulate filters available from selected MPCA monitoring stations (MPCA 2005). The following section discusses the data considered to be the best available at this time for providing updated estimates of atmospheric phosphorus inputs to Minnesota's river basins.

B. Available Data

The specific data used to provide an updated estimate of wet, dry and total phosphorus deposition for Minnesota's major river basins are described below.

Minnesota Pollution Control Agency

1. Nutrient (including phosphorus) and metal concentrations in precipitation from a special study conducted from August 1999 to September 2001 at four monitoring sites in Minnesota

2. Ambient phosphorous concentrations in particulate matter for samples collected at five monitoring stations; four of the sites were included in the Statewide Air Toxics Monitoring Study. This statewide study was active from 1996-2001. All samples analyzed from the 5 sites for phosphorous were collected in 2000. These samples were analyzed by ICP-MS in 2006 and 2007 at the Minnesota Department of Health (MDH) laboratory. Monitor air flow data was provided by the MPCA for these samples and calculations were then made to estimate ambient phosphorous concentrations.
3. Concurrent measurements of PM_{10} and $PM_{2.5}$ at five MPCA urban monitoring stations (1999-2003).

National Atmospheric Deposition Program (NADP)

1. Annual volume weighted calcium concentrations in precipitation for the period of record from NADP sites located in, and adjacent to, Minnesota (Table 2).
2. Monthly volume weighted calcium concentrations for four sites (Fernberg, Marcell, Camp Ripley, and Lamberton) for use in establishing the relationship between phosphorus and calcium in precipitation for NADP sites.

Table 2. Annual volume-weighted calcium data obtained from National Atmospheric Deposition Program (NADP) sites for Minnesota's phosphorus assessment project.

Iowa	Wisconsin	Minnesota	North Dakota	South Dakota
Big Springs Fish Hatchery	Wildcat Mountain St. Pk.	Camp Ripley	Icelandic St. Pk	Huron Well Field
		Cedar Creek	Woodworth	
		Fond du Lac Res.		
		Fernberg (Ely)		
		Grindstone Lake		
		Hovland		
		Lamberton		
		Marcell Exp. Forest		
		Wolf Ridge (Finland)		
		Voyageurs Nat. Park		

Additional details on the MPCA and NADP datasets are described in more detail in the next subsection.

Interagency Monitoring of Protected Visual Environments (IMPROVE)

Concentrations of fine and coarse particulate matter for the period of record at four monitoring sites located in the north, southeast, and southwest parts of Minnesota. The two northern sites (the Boundary Waters Canoe Area Wilderness site and the Voyageurs National Park site) are used to estimate the fine and coarse particulate fractions in forested areas. The sites in Blue Mounds State Park in the southwest corner of the state and Great River Bluffs State Park in the southeast corner of the state are used to estimate the fine and coarse particulate fractions in agricultural areas.

Minnesota Department of Natural Resources, State Climatology Office

Annual normal precipitation amount for each river basin basis was obtained from the State Climatology Office. The derivation of the annual normal precipitation amount for each basin, and the dataset used by the State Climatology Office, is discussed in the Basin Hydrology Technical Memorandum for this project. Determinations of 10, 50 and 90% precipitation levels are described in the calculation methodology below.

C. Additional Discussion of the MPCA and NADP Data

Nutrient and metal concentrations in precipitation

1. Phosphorus in Precipitation Study.

   A special two-year study (August 1999 – September 2001) was conducted by the St. Croix Watershed Research Station of the Science Museum of Minnesota to determine nutrient and metal concentrations in precipitation in Minnesota. Precipitation sampling equipment was co-located at four National Atmospheric Deposition Program (NADP) monitoring sites in Minnesota: Fernberg Road (Ely), Marcell, Camp Ripley, and Lamberton (Engstrom et al., 2003). Samples were collected on a 4-week basis, acidified with a small amount of acid, and analyzed for various chemical components, including total calcium and total phosphorus. Appendix A provides additional details regarding sample collection, sample analysis, and quality assurance/quality control (QA/QC) for the phosphorus in precipitation project. The St. Croix Watershed Research Station provided a full QA/QC program for sample collection and sample analysis and data reporting, therefore no additional QA/QC was conducted on the data.

   A limited amount of editing occurred in the special phosphorus in precipitation study dataset to remove specific samples from the statistical analysis because the precipitation volume for that sampling event did not match with the precipitation volume collected at the collocated NADP sampler or NADP rain gauge. Following this data editing, the phosphorus concentrations from the special study, along with NADP calcium data, were used to derive the relationship between phosphorus and calcium in precipitation for the four NADP monitoring sites. The relationship between phosphorus and calcium in precipitation at these four NADP sites was then applied to the entire state. Additional details on deriving the relationship between phosphorus and calcium in precipitation and applying this relationship to the entire state are discussed in a later section of this technical memorandum.

2. NADP calcium concentrations in precipitation.
    a. Annual volume-weighted calcium concentrations were downloaded electronically from the NADP website for the monitoring locations listed in Table 2. A separate data file was downloaded for each monitoring site. These data files were then merged together for ease of data manipulation and calculations.
    b. Monthly volume-weighted calcium concentrations from four sites (Fernberg, Marcell, Camp Ripley, and Lamberton) were downloaded electronically from the NADP website for the 1999 – 2001 time period. The four NADP monitoring sites correspond to the same sites where the special phosphorus in precipitation study was conducted by the St. Croix Watershed Research Station. Separate data files were downloaded for each monitoring site, and then merged with the data from the special phosphors in precipitation study.

Particulate (PM_{10}) and elemental concentrations

Data files for PM_{10} and phosphorous air concentrations were obtained from the MPCA for five sites included in the Statewide Air Toxics Monitoring Study (1996-2001). These sites are Albert Lea, Hutchinson, Mille Lacs, Perham and Silver Bay. Although the study spanned multiple years and sites, only filters from these 5 sites sampled from October 1999 through September 2000 were available for phosphorous analysis. For each site in operation during a given year, particulate filter samples were collected for a 24-hour period every sixth day and submitted to the MPCA's Air Quality Laboratory for determining PM10 mass and longer term storage. Filter samples from the 5 sites were archived in the MPCA's Air Quality Laboratory until 2006-2007 when portions of the filters were submitted to the Minnesota Department of Health (MDH) for analysis by ICP-MS for phosphorous content. Only about 10 samples from each site (spanning the time period Jan 2000 to Sept 2000) were analyzed for phosphorous content. Two batches of filters were submitted for analysis to the MDH laboratory. The laboratory data was subjected to quality assurance/quality control procedures as discussed below.

Blank filters were analyzed at the same time as the sample filters. The first set of blank filters analyzed in February 2007 were the same brand and from the same batch as those filters used in the particulate sampling conducted for the Statewide Air Toxics Monitoring Study and these blank filters had been stored in the same general area as the used filters. The second set of blank filters were also of the same brand and batch as were used in the Statewide Air Toxics Monitoring Study, however, these blanks were not stored in the same manner or location as the sample filters and the first batch of blank filters.

In this second batch of blank filters, some blanks had a very high phosphorous concentration. In particular three of the blanks had a phosphorous concentration higher than any of the sample filters. These three blanks from the second batch of blank filters were not included in the analysis and it was assumed that the different storage conditions may have resulted in the non-representative blanks.

After determining the level of phosphorous in the blanks, there were two samples in the Mille Lacs dataset that had phosphorous levels below the concentrations found on the blanks. These two samples were subsequently eliminated from the Mille Lacs dataset to prevent a negative phosphorus concentration from being used in calculating a site average. The removal of these two data points, however, may have biased the Mille Lacs dataset toward the higher value samples. Also, one outlier was determined in the Silver Bay dataset using a T-test (p-value = 0.00095). Other high value outliers have been previously identified by the MPCA (2005) at the Silver Bay site for other parameters using other analysis techniques and those data were removed from MPCA's dataset. Subsequently, this data point in question was eliminated from the Silver Bay dataset for this analysis.

Watershed Basin Characteristics

Atmospheric inputs of nutrients to watersheds are highly dependent upon precipitation amounts. For sulfur and nitrogen, precipitation typically accounts for a majority (50-80%) of total inputs, while dry deposition typically accounts for the balance of total inputs (Pratt *et al.*, 1996). It is currently assumed that precipitation inputs of phosphorus are important, but the limited data for phosphorus does not yet provide a clear picture of the actual relationship between precipitation inputs versus dry deposition inputs.

Figure 1 provides a precipitation map of Minnesota, with normal annual precipitation isopleths shown in conjunction with the river basin boundaries. In general, the eastern one quarter of the state receives 30+

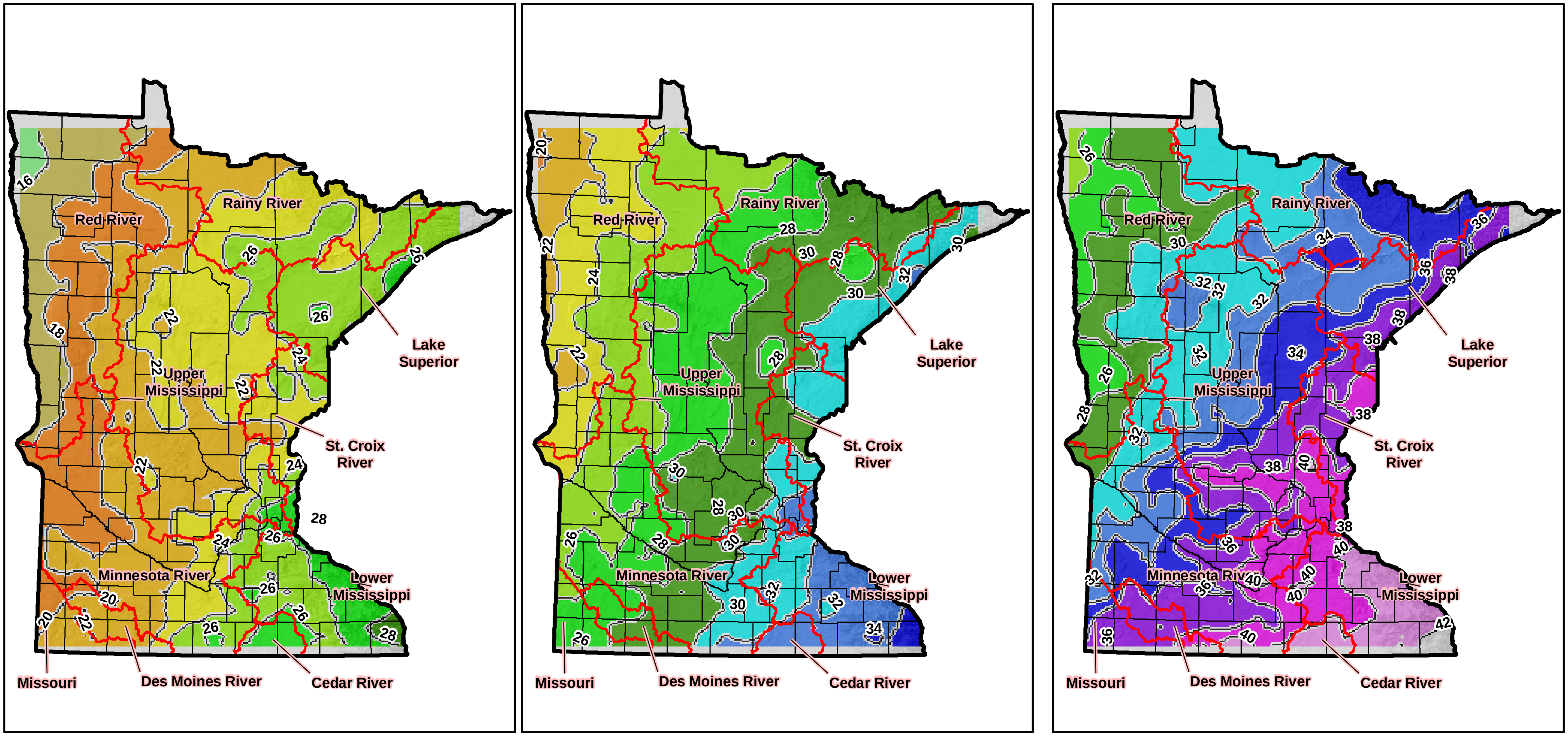
inches of precipitation while the western half of the state receives less than 25 inches of precipitation. The most dramatic change in precipitation is from southeast to northwest, where in an average year, precipitation amount can range from 33 to 34 inches in the southeast corner of the state to less than 20 inches in the northwest corner of the state. Given the assumption that precipitation is the predominant source of atmospheric phosphorus for a river basin or specific watershed, the difference in precipitation amounts within a river basin is expected to have a significant effect on phosphorus wet deposition estimates.

Figure 1 shows that significant gradients in precipitation amount exist for the following basins:

- Minnesota River: precipitation amount ranges from ~ 21 inches in the western tip (Big Stone County) to ~ 31 in the southeast part of the basin (Faribault and Waseca Counties).
- Mississippi River – Upper: precipitation amount ranges from ~ 25 inches in the west portion (Pope to Beltrami Counties) to ~ 33 inches in the southeast corner in the Twin Cities metropolitan area.
- Red River: precipitation amount ranges from ~ 18 inches in the northwest corner of the basin (Kittson County) to ~ 25 inches in the eastern protrusion in Koochiching and Beltrami Counties.
- Rainy River: precipitation amount ranges from ~ 22 inches in the northwest corner (Lake of the Woods County) to ~ 30 inches in the eastern edge along the Lake Superior Highlands (Lake County).

The other river basins do not exhibit the notable difference in precipitation amount that is exhibited by the basins listed above. Due to the notable difference in precipitation amount in the basins listed above, estimates of wet phosphorus deposition can be significantly different depending upon the precipitation data used for the estimate. For precipitation monitoring, an individual monitoring site can provide representative data for the surrounding region if the site is adequately selected (NOAA-ARL, 2003). However, precipitation amount within a basin, as well as from year-to-year, will influence the estimate of wet phosphorus deposition. Thus, a grid-based calculation methodology is employed in the estimates presented here (2007). This method considers the precipitation amount associated with the areas of waters and wetlands in Minnesota. In addition, wet deposition is calculated for a dry year (10th percentile), wet year (90th percentile) and average year (50th percentile) to provide a total range for wet deposition estimates.

Dry deposition is more dependent upon local site conditions; therefore, an individual monitoring site may not be representative of the surrounding region because the controlling factors for dry deposition are typically surface driven and may not be regionally representative (NOAA-ARL, 2003). For total nitrogen, Pratt *et al.* (1996) estimated dry deposition to range from 9-17% of total N deposition, depending upon location in the state and sampling year. Other researchers (Likens *et al.*, 1990; Lindberg *et al.*, 1986) have identified dry deposition of nitrogen to account for as much as 40-60% of total deposition. In addition, Lindberg *et al*. (1986) identified coarse particles contributing 83 times more nitrogen than fine particles on an absolute basis. This earlier data on the importance of coarse particles for dry deposition of nutrients is confirmed by Meyers (2003) based on work in Florida where large particles greater than 10 microns in size accounted for only 15% of the particle mass but a more significant amount of the phosphorus deposition. Based on the above discussion, it could reasonably be expected that river basins with less precipitation will have more phosphorus being dry deposited (e.g., Red River, Cedar River, Minnesota River) while those river basins with higher precipitation would be expected to have less phosphorus being dry deposited (e.g., Lake Superior). However, as noted by Verry and Timmons (1977), river basins may still receive a notable input of particulate phosphorus due to large regional precipitation or dust storm events. For example, signs of Saharan dust storms have been observed in the particulate matter in rural Illinois (Kim *et al.*, 2005). Therefore, it may be possible that regional events may limit the importance of local site influence for dry deposition inputs for some areas.



DRY (10 PERCENTILE) YEAR **AVERAGE (50 PERCENTILE) YEAR** **WET (90 PERCENTILE) YEAR**

40 20 0 40 80 120

Miles

☐ Major Watersheds

Annual Rainfall (inches)

🟩	14.9 - 16	🟨	22.1 - 24	🟦	34.1 - 36
🟨	16.1 - 18	🟩	24.1 - 26	🟪	36.1 - 38
🟧	18.1 - 20	🟩	26.1 - 28	🟪	38.1 - 40
🟧	20.1 - 22	🟩	28.1 - 30	🟪	40.1 - 42
		🟦	30.1 - 32	⬜	42.1 - 44
		🟦	32.1 - 34		

NOTE: Based on 1979-2002 precipitation data provided by the Minnesota State Climatology Department. Pearson Type III Distribution was used to estimate rainfall distribution using gridded annual values of rainfall. No effort was made to determine if Pearson Type III provides best fit for the data.

Figure 1
RAINFALL DISTRIBUTION FOR
DRY, AVERAGE AND WET YEARS

Barr Footer: Date: 6/26/2007 4:44:17 PM File: I:\Projects\23\62\853\GIS\PDeposition\Maps\Report\Figure 1 Rainfall for Dry Average Wet Years.mxd User: TJA

Approach and Methodology for Phosphorus Loading Computations

The MPCA's intent for this project is to provide an updated estimate of phosphorus deposition for each river basin using the best available information from Minnesota.

A. Critical assumptions

Prior to initiating deposition calculations, a number of assumptions were made to assist in developing the approach and methodology for wet and dry phosphorus deposition calculations. These critical assumptions are listed below.

1. Deposition estimates are for surface waters only. Deposition estimates to terrestrial areas are not estimated since the phosphorus loading will already be accounted for in the landform and soils (runoff) estimates.

2. Deposition estimates are to be provided for three moisture regimes: low precipitation year, average precipitation year, high precipitation year.

3. Wet deposition:
    a. Phosphorus (P) is to be normalized to Ca for estimating [P] in precipitation. The relationship of [Ca] to [P] in precipitation at the study sites is sufficiently strong to extrapolate the relationship to other locations in the state.
    b. For estimating wet deposition, the areas between monitoring stations may be represented using area-weighted averages for precipitation.

4. Dry deposition:
    a. PM_{10} filter samples analyzed for phosphorous content are from a nine month period during the one year of monitoring conducted at a site and is considered to be representative of an annual average. Because only 9 months of data are available, seasonality in dry phosphorus deposition could not be adequately addressed.
    b. The phosphorous content of particulate matter is consistent with land use/land cover across the state; areas with similar land use/land cover having similar ambient phosphorous concentrations.

    c. Only urban/industrial areas in the GIS database with area equal or greater than 2500 contiguous acres (comparable to a medium sized city) are considered urban areas in the calculation of dry deposition within a major river basin.
    d. Coarse particulate matter (2.5 microns to 10 microns) is likely from local sources (Redfield; Meyers 2003).

5. Data from a monitoring site (precipitation or particulate) is representative of surrounding areas.

6. Precipitation and PM_{10} filter samples were collected under “normal or typical” conditions with regard to meteorology (average or typical year with regard to precipitation, no frequent large or severe storm events, etc.).

B. Wet Deposition

The original methodology used to estimate wet phosphorus deposition in 2003 is detailed in the February 2004 report on the Statewide Phosphorus Study and in a technical memorandum (Barr Engineering Co., 2003). The methodology used in this 2007 update is outlined below.

1. Establishing the relationship between phosphorus and calcium in precipitation.
    a. NADP routinely analyzes rain samples for pH, alkalinity, major cations (including calcium and potassium) and major anions (including sulfate, nitrate). Since calcium concentrations are available for all samples that were analyzed, and calcium is a signature for soil contributions, the relationship between phosphorus and calcium would need to be established. The use of NADP data also provides some consistency in the data used for estimating wet phosphorus deposition.
    b. The best source of phosphorus in precipitation data is the special study conducted by the St. Croix Watershed Research Station. The total phosphorus concentrations (hereafter denoted as total [P]) in precipitation data was determined from August 1991 – September 2001 at 4 sites: Fernberg (Ely), Marcell, Camp Ripley, Lamberton; referred to as “reference sites”. The special study also provided measurements of total [Ca] in precipitation.
    c. An initial analysis identified that the total [Ca] from the special study was approximately two times greater than the [Ca] reported by NADP for the same time period. The NADP does not acidify samples; therefore the NADP reports dissolved [Ca]. To compensate for NADP

reporting dissolved [Ca], and to provide the best estimate of [P] in precipitation from the auxiliary (NADP) sites, it was determined that the relationship between [P] and [Ca] in precipitation should be determined by using the total [P] concentrations from the special study conducted by the St. Croix Watershed Research Station and the dissolved [Ca] reported by NADP for these same "reference" sites.

   d. The volume-weighted relationship on a sample-by-sample basis between total [P] in precipitation and dissolved [Ca] in precipitation from NADP at these same reference sites (collocated sampling occurred) was established by MPCA staff (Dr. Ed Swain, 2003) through regression analysis:

$y = 0.0671x - 0.4586$ ($R^2 = 0.47$)

Where: y = Total phosphorus in micrograms per liter (µg/L)
x = NADP calcium (dissolved) in µg/L.

2. Extrapolating the relationship of [P] and [Ca] in precipitation to other locations.
   a. The regression analysis based on total [P] and dissolved [Ca] concentrations for the reference sites was then used to estimate [P] in precipitation at other NADP monitoring sites (referred to as "auxiliary sites"). Annual volume-weighted [Ca] in precipitation data (annual volume weighted average) were obtained for the auxiliary sites from NADP and the regression equation from above was then used to estimate total [P] in precipitation for each auxiliary site.
   b. The auxiliary monitoring sites will supplement the information from the reference sites in calculating wet phosphorus deposition to specific basins. Figure 2 shows the reference and auxiliary sites where the point value of phosphorous concentrations in precipitation was measured or estimated.

3. Calculating wet phosphorus deposition

   Four data sets were necessary to estimate the annual wet deposition of phosphorous across the State of Minnesota for dry, average and wet conditions. These data sets are: 1) distribution of the average concentration of phosphorous in precipitation across the state, 2) water and wetlands surfaces, 3) major river basins and 4) precipitation distribution (in inches) across the state for dry, average and wet years.

a. The kriging algorithm in Surfer software was used to develop a statewide distribution of phosphorous concentration in precipitation based on the point value estimates of the [P] in precipitation from the NADP reference and auxiliary sites. A one-kilometer grid for [P] in µg/liter was interpolated and then imported into the ArcMap GIS program for further analysis. Figure 3 shows the results of this process as well as the data locations.

b. Water and wetlands surfaces were extracted from the 1992 USGS National Landcover Database (NLCD). The 1992 data were used for the 2007 estimates to be consistent with the areas of waters and wetlands assessed in the 2003 estimate. The resulting data consisted of a 30 meter grid of surface waters across the state. All water/wetland areas were reclassified with a value of 1; all upland areas were assigned a value of 0.

c. Major river basins were derived from data developed by the Minnesota DNR. The dataset consists of 10 polygons representing the major river basins within the State of Minnesota.

d. Instead of a state-wide precipitation analysis, only basin average precipitation was used. For this analysis, monthly precipitation data were used to develop 10, 50 and 90 percentile grids for nearly the entire state. Monthly data for 1979 – 2002 from the State Climatology Group was used to develop annual precipitation grids at 10 kilometer spacing across most of Minnesota. A Pearson Type III distribution was then applied to each 10 kilometer grid point and a 10, 50, and 90th percentile was extracted. These data were then used to develop a grid of rainfall across the state for the three climatic conditions used**.** This grid was then divided into the 10 polygons representing the major river basins in Minnesota. Figure 1 shows maps of the three rainfall distributions.

e. A map calculation was performed in GIS by multiplying the [P], the rainfall amount and water surface grids (including conversion factors). The result was a grid of wet phosphorous deposition in units of mass. ArcMap Spatial Analyst was used to summarize the total mass of phosphorus for each major river basin. An adjustment factor was used for each basin to account for areas within a basin where no phosphorus concentration or rainfall data were available. These areas are shown in gray in the rainfall distributions in Figure 1. To account for these areas, an area weighting was done based on the ratio of total basin size and the area of each basin for which data were available. The total P load calculated for each watershed was multiplied by this ratio to derive the final wet deposition estimates.

★ NADP Monitoring Sites

▭ Major Basins

0 12.5 25 50 75 100 125

Miles

FIGURE 2
Location of NADP Monitoring Sites
Used to Estimate Wet Phosphorus
Depostition

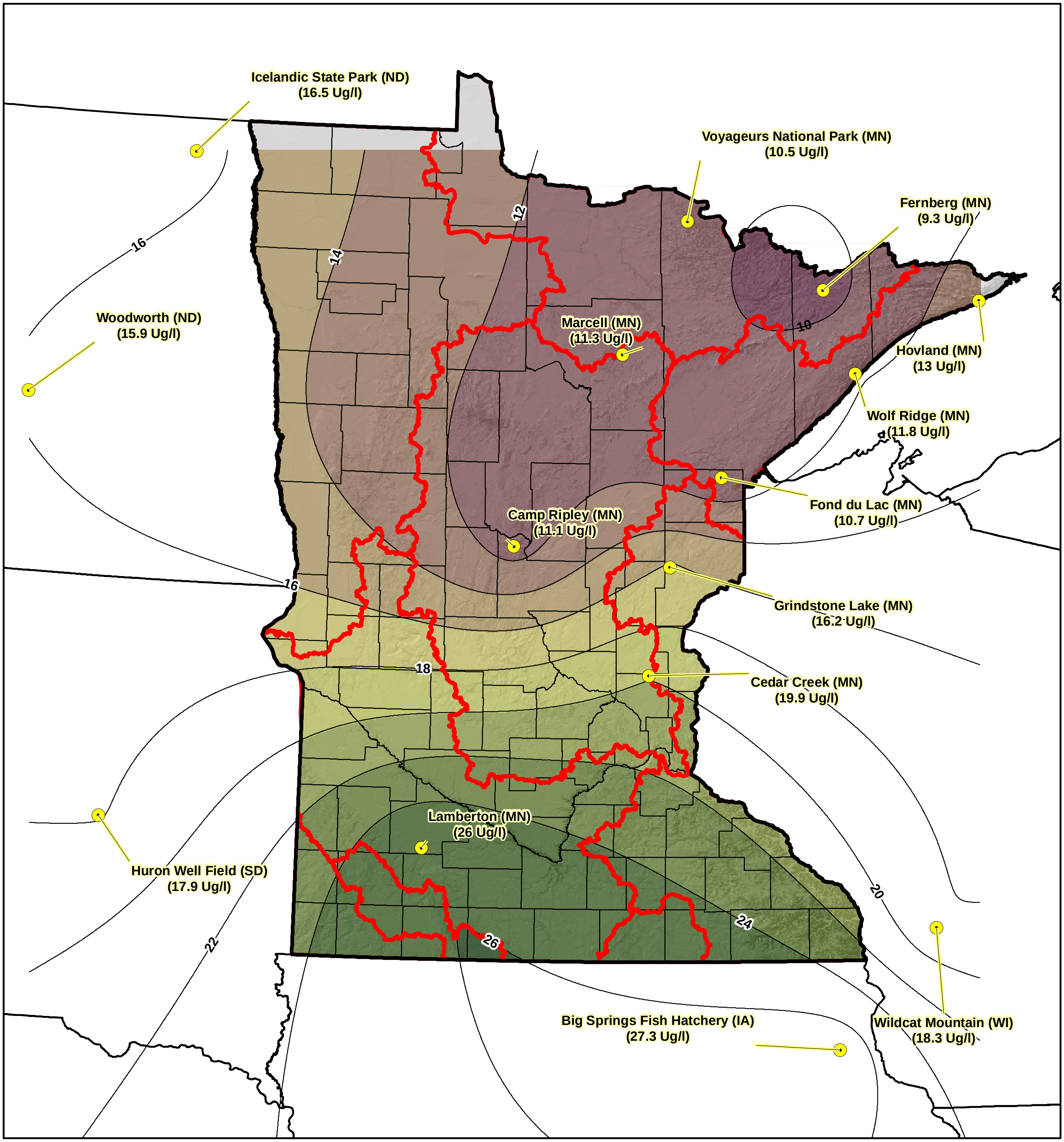


Figure 3
Interpolated Concentrations
of Phosphorous in Precipitation

C. Dry Deposition

The methodology used in 2003 to estimate dry phosphorus deposition relied on the phosphorus and calcium relationship in wet precipitation. The relationship of phosphorus and calcium in precipitation was assumed to be similar for particles and the relationship was transferred to dry deposition through the use of a regression equation of particle [Ca] to estimate particle [P]. The methodology is detailed in the Barr Engineering (2003) technical memorandum on phosphorous deposition. The methodology used in this estimate (2007) relies on actual measurements of particle [P] and is outlined below.

1. The use of measured phosphorous concentrations from particle filters.
    a. Currently the best source of data regarding phosphorous concentrations associated with ambient particulate matter is the 2006-2007 ICP-MS measurements on MPCA's archived filters. The particle filter samples are from 5 sites: Albert Lea, Hutchinson, Perham, Mille Lacs and Silver Bay (Figure 4). All filter samples were collected in 2000 and stored at the MPCA Air Quality Laboratory until analysis in 2006 and 2007 at the MDH laboratory. The average phosphorous concentrations determined from these filters are summarized in Table 3.
    b. The primary land use within a one-mile and five-mile radius of each of these 5 monitoring stations was determined using a GIS database (Table 3). Based on land use in a five-mile radius, Silver Bay and Mille Lacs are considered "forested" sites, while Albert Lea, Hutchinson, and Perham are considered "agriculture" sites. The phosphorous concentrations at Silver Bay and Mille Lacs are statistically different from Albert Lea, Hutchinson and Perham (95% confidence interval, 2-tailed T-test). However Perham (agriculture site) is similar to (i.e., not statistically different from) Albert Lea and Hutchinson (both urban sites using the 1 km distance land use information in Table 3). These comparisons indicate that the 3 urban and agricultural sites have similar phosphorous concentrations but as a group the 3 sites have different phosphorus concentrations than the forested sites (Mille Lacs and Silver Bay).
    c. The land use designations and the average ambient phosphorus concentrations from the 5 sites (Albert Lea, Hutchinson, Perham, Silver Bay, Mille Lacs) were extrapolated to other areas of the state. Specifically, the average [P] in Perham, Albert Lea, and Hutchinson was used to represent agricultural areas; the average [P] in Silver Bay and Mille Lacs was

used to represent forested areas; the average [P] in Albert Lea and Hutchinson was used to represent urban areas. These average phosphorous concentrations were applied to all areas of the state that had similar land use within each major river basin.

2. Statewide application of the particle [P] concentrations from the 5 sites required identifying similar land uses. The entire state was classified into three categories of land use: urban, forest and agriculture. The USGS 2001 NLCD landcover was used as a basis for defining these three land classes. This USGS landcover layer corresponds closely with the dates phosphorous data was collected
    a. Urban areas were defined as areas which had a minimum of 2,500 acres of contiguous urban land cover. These land covers are defined as: developed open space, developed low intensity, developed medium intensity and developed high intensity. The NLCD landcover was resampled from 30 meters to 200 meters to remove the transportation links that exists between cities (typically the widths of the roads are less than 200 meters). The resulting areas were then converted to shapefile format and all non-urban landcover surrounded by the urban areas were reclassified as urban. Finally, all urban areas with less than 2,500 acres were deleted from the shapefile.
    b. The separation of non-urban areas between agriculture and forest was accomplished by summarizing the percent cultivated crops landcover (from the NLCD) that exists in each township. The areas that had less than 10 percent cultivated crops were assumed to be forested; the remaining was assumed to be agriculture. The distribution of landcover is shown in Figure 5.
    c. Once the landcover was developed, the areas of water and wetlands within each of the three land covers and within each of the 10 major river basins were determined using GIS.

3. Estimated size distribution of particulate matter.
    a. IMPROVE monitoring stations measure both fine and coarse particulate concentrations concurrently. Figure 6 shows the location of IMPROVE sites from which data were used to estimate particle size distributions for specific land use/land cover types. Data from the IMPROVE sites in Voyageurs National Park and the BWCAW were used to estimate the fine and coarse particulate fractions in forested areas. Data from the Blue Mounds

State Park and Great River Bluffs State Park sites were used to estimate the fine and coarse fractions in agricultural areas. The location of Great River Bluffs State Park in southeast Minnesota indicates that it is actually sited in a forested area that is surrounded by agricultural lands. Because of the predominance of agriculture in the surrounding region, data from both of this IMPROVE sites is used estimate particle size distributions for agricultural areas. Supporting the extrapolation of particle size distribution data from Great River Bluffs State Park to agriculture areas is the fact that that the size distribution at Great River Bluffs State Park is statistically similar to that at Blue Mounds State Park and Lake Sugema State Park (IA), which are both in agricultural dominated areas. In addition, these three sites (Blue Mounds, Great River Bluffs, Lake Sugema) are statistically different from the particle size distributions monitored at the forested Boundary Waters and Voyageurs sites.

b. The use of the particle size distributions from the IMPROVE sites provides for a refinement in the dry deposition estimates. A second change in the dry deposition calculations is the refinement in the coarse and fine particle fractions used in the calculations based on data from the four IMPROVE sites in Minnesota. The 2003 estimates used values for fine and coarse particulate fractions that are associated with urban areas, whereas specific fractions for agricultural and forested areas are used in the 2007 estimates. Both agricultural and forest particulate size distributions have a higher percentage of fine particulate compared to urban areas. Because the deposition rate for fine particulate matter is lower than for coarse particulate matter and most of the state is either forested of agricultural, the application of land-use based fine and coarse particulate fractions partially offsets the increase due to higher phosphorous concentrations in the 2007 estimates.

c. The MPCA's air monitoring program provided concurrent data on PM_{10} and $PM_{2.5}$ in four metro area sites and one site in Virginia, MN. The locations of these sites are shown in Figure 6. The data from these sites was used to determine the fine and coarse particulate fractions in urban areas.

4. Calculating dry phosphorus deposition

a. Phosphorous concentrations associated with ambient particulate matter were calculated based on land use. The percent of all surface waters in each land use category for each basin were determined in GIS as described above (see Figure 5).

b. Calculation components for phosphorus deposition in a basin:
    - Estimated phosphorus air concentration by land use as shown in Table 3.
    - The area associated with each land use category in the basin.
    - The estimated phosphorus air concentration was split into two size fractions based on IMPROVE or MPCA data according to the land use as shown in Table 4.
    - A deposition velocity for each particle size fraction was estimated based on the information from Meyers (2003):
      Fine fraction deposition velocity = 0.5 centimeters per second (cm/s);
      Coarse fraction deposition velocity = 3 cm/s.
    - The coarse and fine particle deposition was summed together to provide a “total” particle deposition estimate for each land use category.
    - The sum of the deposition for each land use category is the total for the basin.
    - Conversion factors: convert seconds to years, cm to meters, acres to hectares, and $\mu g/m^3$ to kg/ha.

The following is noted for the dry deposition estimates:

- No adjustments were made in the estimation of dry deposition in a dry or a wet year because data are not available at this time to derive estimates of dry deposition during different precipitation regimes.
- Seasonality in dry deposition is not addressed in the deposition estimates primarily because particle [P] data are not available for all seasons from the 5 particle monitoring sites (Silver Bay, Mille Lacs, Perham, Hutchinson, and Albert Lea).

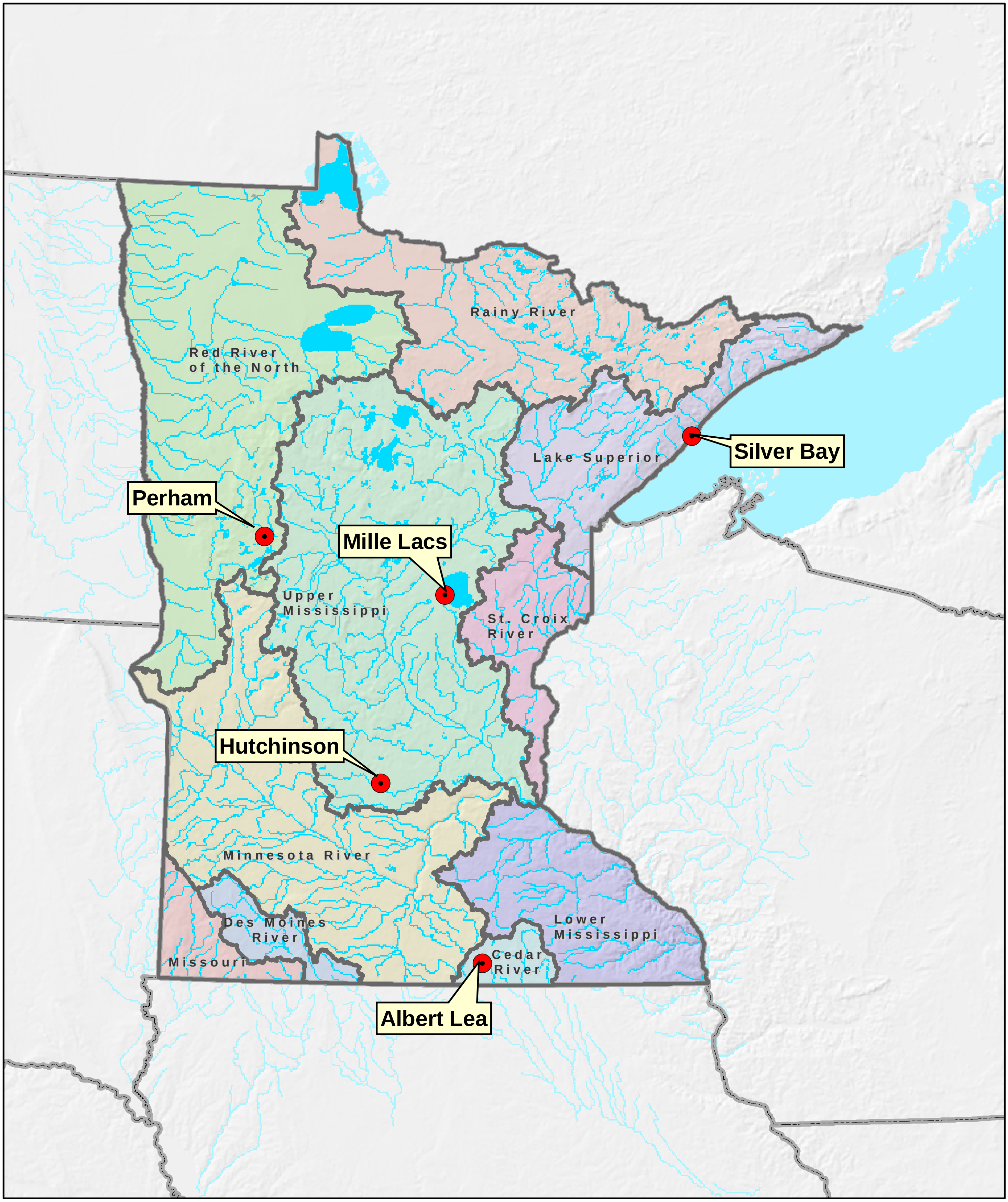


FIGURE 4
Approximate Locations of the
MPCA's Monitoring Sites
Used to Estimate Dry
Phosphorus Deposition

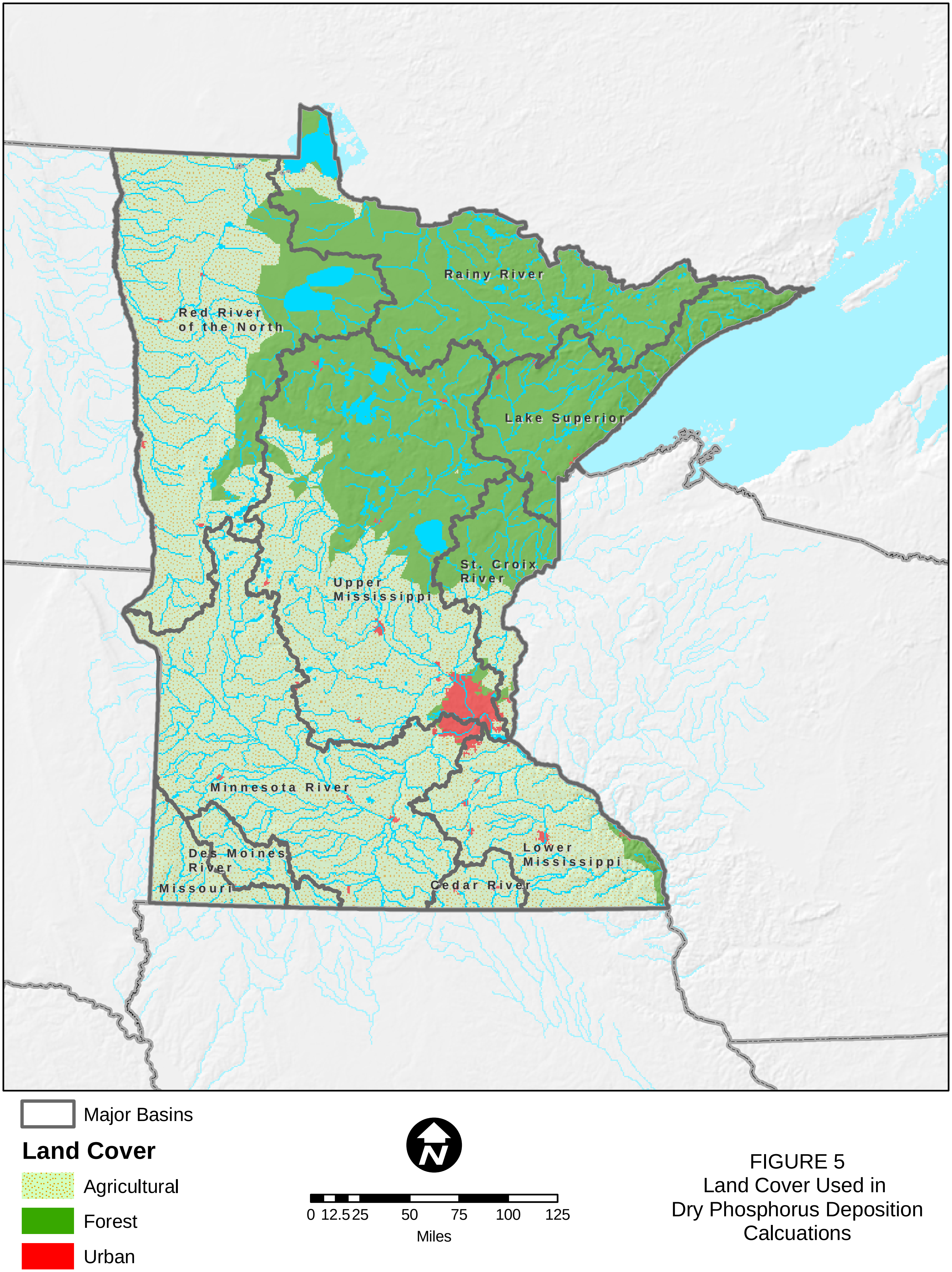


FIGURE 5
Land Cover Used in
Dry Phosphorus Deposition
Calcuations

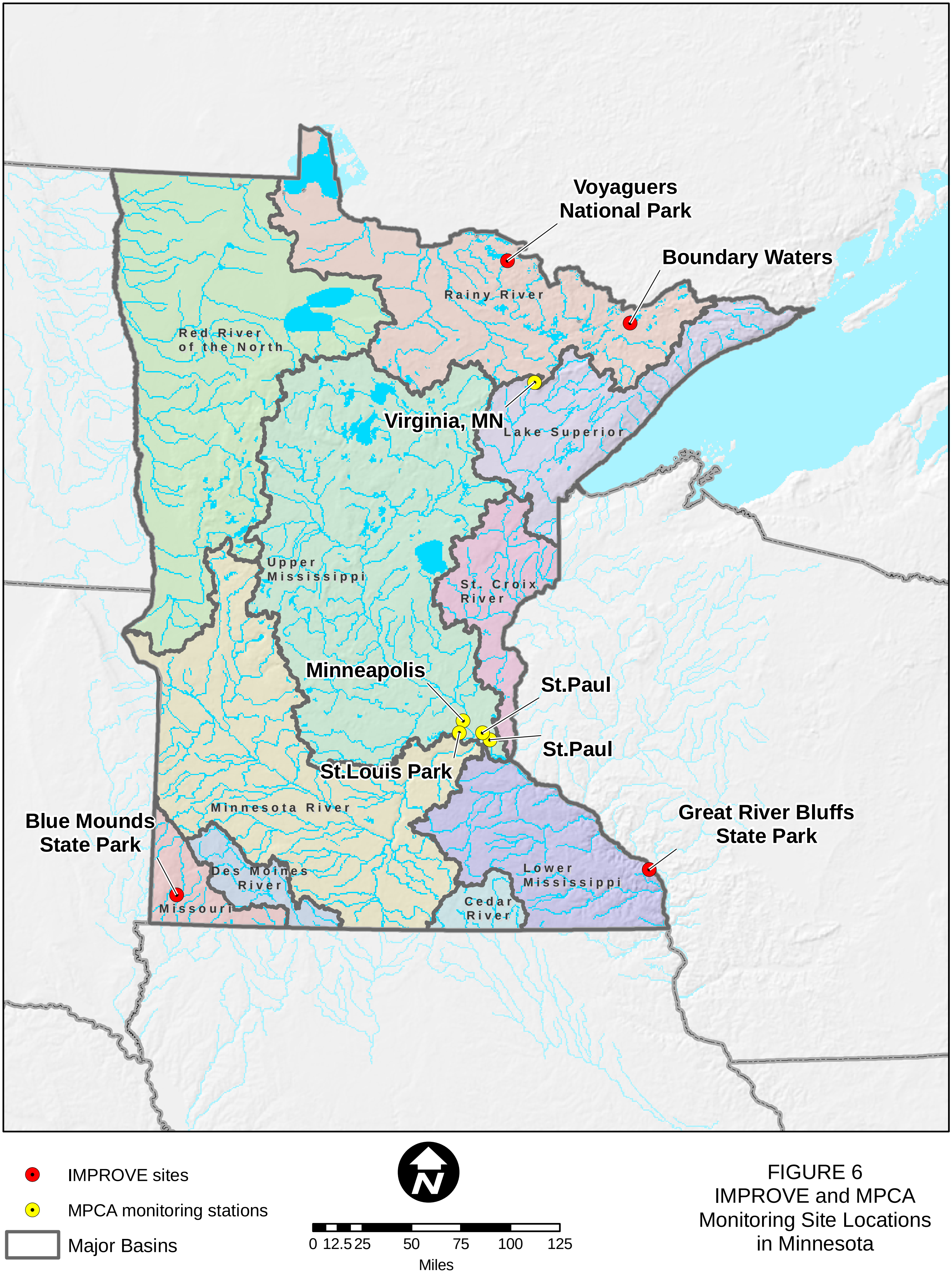


FIGURE 6
IMPROVE and MPCA
Monitoring Site Locations
in Minnesota

Table 3. Particulate based ambient phosphorous concentrations in Minnesota calculated from ICP -MS measurements of MPCA's archived PM_{10} filter samples for selected monitoring sites and the primary land use around each monitoring site.

Monitoring site	Average Phosphorous concentration, µg/m^3	Primary land use 1-mile radius of monitor	Primary land use 5-mile radius of monitor
Albert Lea	0.0472	Urban	Agriculture
Hutchinson	0.0541	Urban	Agriculture
Mille Lacs	0.0228	Forest	Forest
Perham	0.0499	Agriculture	Agriculture
Silver Bay	0.0286	Forest	Forest
Average Agriculture	*0.0504*		
Average Forest	*0.0257*		
Average Urban	*0.0506*		

Table 4. Size distributions of particulate matter for specific land use categories.

Land Use	Fine Fraction (%)	Coarse Fraction (%)
Forest [1]	63.4	36.6
Agriculture [2]	52.1	47.9
Urban [3]	42.3	57.7

[1] Particle size distributions for forest areas determined from IMPROVE monitoring data collected in northern Minnesota: Voyageurs National Park (VOYA2) and Boundary Waters Canoe Area Wilderness.(BOWA1)

[2] Particle size distributions for agriculture areas determined from IMPROVE monitoring data: collected in southern Minnesota: Blue Mounds State Park in southwestern Minnesota and Great River Bluffs State Park in southeast Minnesota.

[3] Particle size distributions for urban areas determined from MPCA monitoring sites in Virginia and from the Twin Cities.

Results of Phosphorus Loading Computations and Assessments

The deposition estimates calculated and discussed in this report are for deposition directly to waters and wetlands. Any atmospheric deposition to land is already accounted for in previous determinations of phosphorous loading from runoff (see critical assumptions).

A. Wet Deposition

Estimates of average wet phosphorus deposition (average precipitation) range from 0.073 kg ha^{-1} yr^{-1} in the Rainy River basin to 0.198 kg ha^{-1} yr^{-1} in the Cedar River basin (Table 5). When factoring in dry/wet years, the range in potential wet phosphorus deposition is from approximately 0.060 kg ha^{-1} yr^{-1} in the Rainy River basin (dry year) to 0.250 kg ha^{-1} yr^{-1} in the Cedar River basin (wet year) (Table 5).

Table 5 also provides estimates of average phosphorus loading (average precipitation) for the respective basins, which ranges from 1,533 kg/yr for the Missouri River to 151,488 kg/yr for the Upper Mississippi River basin. As identified in Table 5, the estimate of phosphorus deposition for each basin is based on the area identified as “water” or “wetland” in the GIS database.

B. Dry Deposition

Estimates of average dry phosphorus deposition (assuming average precipitation year) range from 0.115 kg ha^{-1} yr^{-1} in the Lake Superior basin to 0.271 kg ha^{-1} yr^{-1} in the Cedar River basin (Table 6). The total mass of phosphorous dry deposited ranges from 2,684 kg/yr in the Cedar River basin to 263,309 kg/yr in the Upper Mississippi River basin. The rate of dry deposition is highly dependent on the major land use in the basin. Basins that are predominantly agricultural such as the Minnesota, Des Moines, Missouri and Cedar River have the higher deposition rates. The basins with almost no agriculture such as the Rainy River and Lake Superior have lower rates of dry deposition.

As previously discussed, no adjustments were made in estimating dry deposition for a dry or a wet year. Data are not available at this time to derive estimates of dry deposition during different precipitation regimes.

Table 5. Estimates of wet phosphorous deposition by major river basin in Minnesota - 2007 update

Average Year

Major Watershed	Average Precipitation (inches) [1]	Mean P Concentration (ug/l) [2]	Watershed Area (acres)	Water & Wetland Area (acres) [3]	Watershed Area (hectares)	Water & Wetland Area (hectares)	Total Wet Deposition From GIS (lbs) [4]	Area Adjustment [5]	Adjusted Watershed Total (lb/yr) [6]	Adjusted Watershed Total (kg/yr) [6]	Wet Deposition (lbs/acre/yr) [7]	Wet Deposition (kg/ha/yr) [7]
Cedar River	32.38	25.1	657,731	24,497	266,180	9,914	2,910	1.488	4,330	1,964	0.177	0.198
Des Moines River	27.84	25.4	982,696	53,756	397,691	21,755	7,616	1.119	8,525	3,867	0.159	0.178
Lake Superior	29.83	11.1	3,935,149	1,311,913	1,592,533	530,924	92,290	1.072	98,918	44,869	0.075	0.085
Lower Mississippi	32.72	23.1	4,042,995	202,902	1,636,178	82,113	31,952	1.083	34,612	15,700	0.171	0.191
Minnesota River	27.63	22.3	9,567,116	743,405	3,871,759	300,852	95,360	1.022	97,418	44,189	0.131	0.147
Missouri	26.74	24.3	1,140,476	29,748	461,544	12,039	2,751	1.228	3,379	1,533	0.114	0.127
Rainy River	27.38	10.9	7,191,069	3,768,677	2,910,186	1,525,163	229,002	1.065	243,897	110,632	0.065	0.073
Red River	23.32	13.8	11,354,481	2,697,358	4,595,095	1,091,606	176,708	1.077	190,271	86,307	0.071	0.079
St. Croix River	30.21	16.3	2,258,192	680,161	913,878	275,257	72,620	1.000	72,620	32,940	0.107	0.120
Upper Mississippi	27.87	14.7	12,863,982	3,826,678	5,205,982	1,548,635	333,969	1.000	333,969	151,488	0.087	0.098
TOTAL			53,993,887	13,339,094	21,851,027	5,398,257	1,045,178		1,087,938	493,489		

Dry Year

Major Watershed	Average Precipitation (inches) [1]	Mean P Concentration (ug/l) [2]	Watershed Area (acres)	Water & Wetland Area (acres) [3]	Watershed Area (hectares)	Water & Wetland Area (hectares)	Total Wet Deposition From GIS (lbs) [4]	Area Adjustment [5]	Adjusted Watershed Total (lb/yr) [6]	Adjusted Watershed Total (kg/yr) [6]	Wet Deposition (lbs/acre/yr) [7]	Wet Deposition (kg/ha/yr) [7]
Cedar River	26.65	25.1	657,731	24,497	266,180	9,914	2,387	1.488	3,551	1,611	0.145	0.162
Des Moines River	20.94	25.4	982,696	53,756	397,691	21,755	5,668	1.119	6,344	2,878	0.118	0.132
Lake Superior	25.09	11.1	3,935,149	1,311,913	1,592,533	530,924	77,962	1.072	83,560	37,903	0.064	0.071
Lower Mississippi	26.20	23.1	4,042,995	202,902	1,636,178	82,113	25,650	1.083	27,785	12,603	0.137	0.153
Minnesota River	21.23	22.3	9,567,116	743,405	3,871,759	300,852	74,025	1.022	75,622	34,302	0.102	0.114
Missouri	20.43	24.3	1,140,476	29,748	461,544	12,039	2,103	1.228	2,583	1,172	0.087	0.097
Rainy River	22.72	10.9	7,191,069	3,768,677	2,910,186	1,525,163	189,277	1.065	201,588	91,440	0.053	0.060
Red River	18.50	13.8	11,354,481	2,697,358	4,595,095	1,091,606	142,370	1.077	153,297	69,536	0.057	0.064
St. Croix River	23.57	16.3	2,258,192	680,161	913,878	275,257	56,576	1.000	56,576	25,663	0.083	0.093
Upper Mississippi	22.36	14.7	12,863,982	3,826,678	5,205,982	1,548,635	268,047	1.000	268,047	121,586	0.070	0.079
TOTAL	21.91	16.4	53,993,887	13,339,094	21,851,027	5,398,257	844,065		878,955	398,694	0.066	0.074

Wet Year

Major Watershed	Average Precipitation (inches) [1]	Mean P Concentration (ug/l) [2]	Watershed Area (acres)	Water & Wetland Area (acres) [3]	Watershed Area (hectares)	Water & Wetland Area (hectares)	Total Wet Deposition From GIS (lbs) [4]	Area Adjustment [5]	Adjusted Watershed Total (lb/yr) [6]	Adjusted Watershed Total (kg/yr) [6]	Wet Deposition (lbs/acre/yr) [7]	Wet Deposition (kg/ha/yr) [7]
Cedar River	40.58	25.1	657,731	24,497	266,180	9,914	3,667	1.488	5,456	2,475	0.223	0.250
Des Moines River	37.23	25.4	982,696	53,756	397,691	21,755	10,196	1.119	11,412	5,177	0.212	0.238
Lake Superior	35.49	11.1	3,935,149	1,311,913	1,592,533	530,924	109,465	1.072	117,326	53,219	0.089	0.100
Lower Mississippi	40.34	23.1	4,042,995	202,902	1,636,178	82,113	39,452	1.083	42,737	19,385	0.211	0.236
Minnesota River	35.24	22.3	9,567,116	743,405	3,871,759	300,852	121,228	1.022	123,844	56,176	0.167	0.187
Missouri	35.81	24.3	1,140,476	29,748	461,544	12,039	3,668	1.228	4,504	2,043	0.151	0.170
Rainy River	32.76	10.9	7,191,069	3,768,677	2,910,186	1,525,163	274,563	1.065	292,422	132,642	0.078	0.087
Red River	28.90	13.8	11,354,481	2,697,358	4,595,095	1,091,606	216,501	1.077	233,118	105,742	0.086	0.097
St. Croix River	37.74	16.3	2,258,192	680,161	913,878	275,257	90,790	1.000	90,790	41,182	0.133	0.150
Upper Mississippi	34.37	14.7	12,863,982	3,826,678	5,205,982	1,548,635	411,039	1.000	411,039	186,447	0.107	0.120
TOTAL	33.98	16.4	53,993,887	13,339,094	21,851,027	5,398,257	1,280,569		1,332,648	604,489	0.100	0.112

Table 5. Estimates of wet phosphorous deposition by major river basin in Minnesota - 2007 update

[1] Dry, average and wet year precipitation volume data based on the 1979-2002 period (using water years october-september). The dry period is defined as the 10th percentile frequency value, the average is the 50th percentile and the wet is the 90th percentile. Derived by the State of Minnesota, State Climatology Office, Dept. of Natural Resources-Waters (2003).

[2] Basin area is that part of the basin within the state's borders designated as "Water" or "Wetland" in the GIS database.

[3] Phosphorous concentration is the area weighted average of the the NADP sites shown in Figure XX. The phosphorous concentration at each site wasdetermined using the the phosphorus concentration in rainfall calculated per the following regression equation derived from the St. Croix Special Study reference sites: $y = 0.0671x - 0.4586$ (y is Total Phosphorus in ug/L and x is NADP calcium in ug/L).

[4] Area weighted layers of phosphorous concentration, precipitation and location of waters & wetlands were used along with appropriate unit conversions to calculate deposition by pixel. These GIS results were summed by basin for a basin total. Deposition by pixel = precipitation * phosphorous concentration * waters & wetland area. This estimate only includes areas that have complete GIS data for all parameters (see note [2]).

[5] GIS data for precipitation does not cover the entire state (see the grey areas on Figure XX). For areas with no data an area weighted average was used to determine the adjustment factor for the waters and wetlands that are in the areas with no GIS data.

[6] The total deposition including areas that lacked GIS data for precipitation. This estimate includes the entire basin area.

[7] Average wet deposition rate based on total deposition and the area of waters and wetlands in the basin.

Table 6. Estimates of dry phosphorous deposition by major river basin in Minnesota - 2007 update

Basin	**Land Use Type**	**Percent of total surface waters [3]**	**Total P conc. [1]** (ug/m3)	**Fraction Coarse [2]**	**Fraction Fine [2]**	**Dry Deposition Rate [3]** (kg ha^{-1} yr^{-1})	**Basin Average Rate** (kg ha^{-1} yr^{-1})	**Basin Waters & Wetland Area [4]** (acres)	**Percent of Total Basin Land Area**	**Phosphorous Deposition to Waters & Wetlands** (kg/yr)
Cedar River	Agriculture	97.6%	0.0504	0.479	0.521	0.270		23,902		2609.5
	Forest	0.0%	0.0257	0.366	0.634	0.114		0		0.0
	Urban	2.4%	0.0506	0.577	0.423	0.310		595		74.6
	Total						**0.271**	24,497	3.7%	**2684.1**
Des Moines River	Agriculture	100.0%	0.0504	0.479	0.521	0.270		53,739		5866.8
	Forest	0.0%	0.0257	0.366	0.634	0.114		0		0.0
	Urban	0.0%	0.0506	0.577	0.423	0.310		17		2.1
	Total						**0.270**	53,756	5.5%	**5869.0**
Lake Superior	Agriculture	0.0%	0.0504	0.479	0.521	0.270		0		0.0
	Forest	99.7%	0.0257	0.366	0.634	0.114		1,308,499		60630.3
	Urban	0.3%	0.0506	0.577	0.423	0.310		3,414		428.3
	Total						**0.115**	1,311,913	33.3%	**61058.6**
Minnesota River	Agriculture	96.6%	0.0504	0.479	0.521	0.270		717,369		78316.9
	Forest	0.3%	0.0257	0.366	0.634	0.114		2,395		111.0
	Urban	3.1%	0.0506	0.577	0.423	0.310		22,963		2881.4
	Total						**0.271**	742,727	7.8%	**81309.2**
Mississippi, Lower [5]	Agriculture	79.4%	0.0504	0.479	0.521	0.270		161,172		17595.5
	Forest	19.3%	0.0257	0.366	0.634	0.114		39,068		1810.2
	Urban	1.3%	0.0506	0.577	0.423	0.310		2,661		334.0
	Total						**0.240**	202,902	29.7%	**19739.7**
Mississippi, Upper [6]	Agriculture	34.4%	0.0504	0.479	0.521	0.270		1,315,253		143589.2
	Forest	64.5%	0.0257	0.366	0.634	0.114		2,469,082		114406.7
	Urban	1.1%	0.0506	0.577	0.423	0.310		42,338		5312.6
	Total						**0.170**	3,826,674	5.1%	**263308.6**
Missouri	Agriculture	99.9%	0.0504	0.479	0.521	0.270		29,713		3243.8
	Forest	0.0%	0.0257	0.366	0.634	0.114		0		0.0
	Urban	0.1%	0.0506	0.577	0.423	0.310		35		4.4
	Total						**0.270**	29,748	2.6%	**3248.3**
Rainy River	Agriculture	3.7%	0.0504	0.479	0.521	0.270		139,226		15199.6
	Forest	96.3%	0.0257	0.366	0.634	0.114		3,629,456		168173.5
	Urban	0.0%	0.0506	0.577	0.423	0.310		0		0.0
	Total						**0.120**	3,768,682	52.4%	**183373.1**
St. Croix River	Agriculture	23.2%	0.0504	0.479	0.521	0.270		157,663		17212.4
	Forest	76.7%	0.0257	0.366	0.634	0.114		521,634		24170.3
	Urban	0.1%	0.0506	0.577	0.423	0.310		863		108.3
	Total						**0.151**	680,160	30.1%	**41491.1**
Red River	Agriculture	43.4%	0.0504	0.479	0.521	0.270		1,170,654		127803.0
	Forest	56.6%	0.0257	0.366	0.634	0.114		1,525,842		70701.0
	Urban	0.0%	0.0506	0.577	0.423	0.310		867		108.7
	Total						**0.182**	2,697,363	23.8%	**198612.8**
Minnesota Total										860694.4

[1] Phosphorous concentrations at Albert Lea, Hutchinson, Perham, Mille Lacs and Silver Bay were determined from ICP-MS analysis of archived PM10 filters collected from the Air Toxics Network in 2000. Phosphorous concentrations in Agricultural areas is the average of the measured phosphorous concentrations at Albert Lea, Hutchinson and Perham. Phosphorous concentrations in Forested areas is the average of the measured phosphorous concentrations at Mille Lacs and Silver Bay. Phosphorous concentrations in Urban areas is the averag of the measured phosphorous concentrations at Albert Lea and Hutchinson.

[2] The PM10 course size fraction (>2.5) was calculated to be 47.9% of total PM10 in agricultural areas and 36.6% of total PM10 in forested areas and 58% of total PM10 in urban areas. The fine size fraction (PM2.5) was calculated as 52.1% of total PM10 in agricultural areas and 63.4% of total PM10 in forested areas and 42% of total PM10 in urban areas. PM10 size fraction was calculated from the IMPROVE or Air Toxics monitoring sites in Minesota that have co-located PM2.5 and PM10 monitors. BOWA1 and VOYA2 are monitoring stations located in forested areas and BLMO1 and GRRI1 are monitoring stations in agricultural areas. Air Toxics monitoring sites in Virginia and 4 metro areas are used to determine the urban size distribution.

[3] Deposition rate = [P] * (coarse fracion * coarse deposition velocity + fine fraction * fine deposition velocity) * unit conversions. Coarse and fine deposition velocities are based on recent estimates for phosphorus deposition in Florida and personal communications with Tilden Meyers, NOAA, Oak Ridge National Laboratory. Coarse = 3.0 cm/sec, Fine = 0.5 cm/sec.

[4] Basin area is that part of the basin within the state's borders designated as "Water" or "Wetland" in the GIS database. Urban areas are cities larger than 2500 sq acres as determined in the GIS database. Agricultural areas are regions where greater than XX% of the land use is defined as agriculture in the GIS database. All remaining areas are defined as forested regions. 1 hectare = 2.471 acres

[5] Lower Mississippi is that part of the Mississippi downstream of where the St.Croix River merges with the Mississippi.

[6] Upper Mississippi is that part of the Mississippi upstream of where the St.Croix River merges with the Mississippi.

C. TOTAL P Deposition

Estimates of average “total” (wet + dry) phosphorus deposition range from ~ 0.180 kg ha^{-1} yr^{-1} in the Rainy River basin (dry year) to 0.520 kg ha^{-1} yr^{-1} in the Cedar River basin (wet year) (Table 7). Overall, for the average year, the estimated total P deposition rates are similar to those presented in Table 1.

During an average precipitation year, the largest phosphorus loading of ~ 414,797 kg/yr is estimated for the Upper Mississippi River basin.

As noted in Table 7, dry deposition could only be estimated for an “average” year due to the lack of available data for estimating deposition during a wet or dry year. Therefore, total (wet + dry) estimates for the dry, average, and wet years for each basin in Table 7 use the same dry deposition value, which adds uncertainty to the deposition estimates.

Table 7. Estimated total phosphorous deposition to Minnesota river basins - 2007 update

Major Watershed	Wet Deposition Rate, average year (kg/ha/yr)	Wet Deposition Rate, dry year (kg/ha/yr)	Wet Deposition Rate, wet year (kg/ha/yr)	Dry Deposition Rate, (kg/ha/yr)	Total Deposition Rate, average year (kg/ha/yr)	Total Deposition Rate, dry year (kg/ha/yr)	Total Deposition Rate, wet year (kg/ha/yr)	Water & Wetland Area (acres)	Wet Deposition, average year (kg/yr)	Wet Deposition, dry year (kg/yr)	Wet Deposition, wet year (kg/yr)	Dry Deposition (kg/yr)	Total Deposition, average year (kg/yr)	Total Deposition, dry year (kg/yr)	Total Deposition, wet year (kg/yr)
Cedar River	0.20	0.16	0.25	0.27	0.469	0.433	0.520	24,497	1,964	1,611	2,475	2,684	4,648	4,295	5,159
Des Moines River	0.18	0.13	0.24	0.27	0.448	0.402	0.508	53,756	3,867	2,878	5,177	5,869	9,736	8,747	11,046
Lake Superior	0.08	0.07	0.10	0.12	0.200	0.186	0.215	1,311,913	44,869	37,903	53,219	61,059	105,928	98,962	114,277
Lower Mississippi	0.19	0.15	0.24	0.24	0.432	0.394	0.476	202,902	15,700	12,603	19,385	19,740	35,440	32,343	39,125
Minnesota River	0.15	0.11	0.19	0.27	0.417	0.385	0.457	743,405	44,189	34,302	56,176	81,309	125,498	115,611	137,485
Missouri	0.13	0.10	0.17	0.27	0.397	0.367	0.440	29,748	1,533	1,172	2,043	3,248	4,781	4,420	5,291
Rainy River	0.07	0.06	0.09	0.12	0.193	0.180	0.207	3,768,677	110,632	91,440	132,642	183,373	294,005	274,814	316,016
Red River	0.08	0.06	0.10	0.18	0.261	0.246	0.279	2,697,358	86,307	69,536	105,742	198,613	284,920	268,148	304,355
St. Croix River	0.12	0.09	0.15	0.15	0.270	0.244	0.300	680,161	32,940	25,663	41,182	41,491	74,431	67,154	82,673
Upper Mississippi	0.10	0.08	0.12	0.17	0.268	0.249	0.290	3,826,678	151,488	121,586	186,447	263,309	414,797	384,895	449,756
TOTAL								13,339,094	493,489	398,694	604,489	860,694	1,354,183	1,259,389	1,465,184

Comparison of 2003 and 2007 Estimates of Phosphorous Deposition

A comparison of the estimates for wet, dry and total phosphorous deposition made in 2003 and 2007 is shown in Table 8.

A. Wet Deposition

The 2003 and 2007 estimates for wet deposition are similar for most river basins. A few exceptions are as follows. The 2007 estimate show a 21% decrease in the Minnesota River basin, a 23% increase in the Lower Mississippi basin, a 29% decrease in the Missouri River basin and a 19% decrease in the Red River basin compared to the 2003 estimates. The changes in the wet deposition estimates are likely due to the use of grid-based precipitation amounts in the 2007 calculations that better account for the gradient in precipitation across the state in contrast to the approach in 2003 that used an average precipitation value applied to an entire basin.

B. Dry Deposition

The 2007 dry phosphorus deposition estimates are higher in all basins compared to the estimates in 2003. This increase is due to the fact that the [P] measured on PM_{10} filters and used in the 2007 calculations is higher than the particle [P] concentrations estimated in 2003 by a regression equation using [Ca] concentrations on PM_{10} filters and the Ca:P relationship from precipitation. The difference in measured versus estimated particle [P] implies that relationship between calcium and phosphorous in precipitation is different than the relationship between calcium and phosphorus associated with PM_{10}.

It is noted that the Cedar River basin shows the least change between the 2003 and 2007 estimates. A likely reason is that in the 2003 estimates, the Cedar River basin estimates relied on PM_{10} and [Ca] data from Albert Lea and the estimated [P] in particulate matter for the Albert Lea site was considered anomalously high compared to all other monitoring stations. However, the particle [P] data now available for Albert Lea indicates that the estimated particle [P] used in the 2003 analysis may be more representative than had previously been thought. In other basins, the 2007 estimates show increases ranging from 65% to almost 300% (3 times) more dry phosphorous deposition than had been calculated in 2003.

C. Total Deposition

The 2007 estimates of total phosphorous deposition increased for all basins with the exception of the Cedar River basin. In the Cedar River basin the 2003 and 2007 estimates only differ by 3%. The increase in estimated total deposition in all other basins is driven by the increases in estimated dry deposition. The notable decrease in wet deposition in some basins is more than offset by the increase in dry deposition in the 2007 estimates.

The percent of total deposition that is attributed to dry deposition also increased in every basin. The percentage of total deposition that is attributed to dry deposition ranges from 55.7% in the Lower Mississippi to 69.7% in the Red River and the average for the state as a whole is 63.6%. In the 2003 estimate, the average percent of total deposition as dry deposition was, on average 40.8% for the state.

The 2003 estimate for the state that dry deposition is approximately 41% of total statewide deposition is at the low end of the range according to the estimates for nitrogen deposition calculated by Likens *et al.* (1990) and Lindberg *et al.* (1986). In contrast, the 2007 estimate that dry deposition is approximately 64% of total deposition and is near the high end of the range.

Table 8. Comparison of the 2003 and 2007 estimates of phosphorous deposition to Minnesota major river basins

Basin	**Wet Deposition (kg/yr)**		**Percent**	**Dry Deposition (kg/yr)**		**Percent**	**% of Total as Dry**		**Total Deposition (kg/yr)**		**Percent**
	2003	**2007**	**Change**	**2003**	**2007**	**Change**	**2003**	**2007**	**2003**	**2007**	**Change**
Cedar River	2,102	1,964	-7%	2,390	2,684	12%	53.2%	57.7%	4,492	4,648	3%
Des Moines River	4,020	3,867	-4%	1,493	5,869	293%	27.1%	60.3%	5,514	9,736	77%
Lake Superior	46,364	44,869	-3%	23,753	61,059	157%	33.9%	57.6%	70,118	105,928	51%
Minnesota River	55,709	44,189	-21%	22,858	81,309	256%	29.1%	64.8%	78,567	125,498	60%
Mississippi, Lower	12,785	15,700	23%	7,650	19,740	158%	37.4%	55.7%	20,435	35,440	73%
Mississippi, Upper	155,847	151,488	-3%	108,811	263,309	142%	41.1%	63.5%	264,658	414,797	57%
Missouri	2,156	1,533	-29%	825	3,248	294%	27.7%	67.9%	2,981	4,781	60%
Rainy River	105,303	110,632	5%	65,761	183,373	179%	38.4%	62.4%	171,065	294,005	72%
St. Croix River	33,322	32,940	-1%	7,711	41,491	438%	18.8%	55.7%	41,032	74,431	81%
Red River	106,467	86,307	-19%	120,376	198,613	65%	53.1%	69.7%	226,843	284,920	26%
Statewide Total									885,704	1,354,183	53%

Comparison of 2003 and 2007 Atmospheric Phosphorus Loads to Total Phosphorous Loading

A comparison of the 2003 and 2007 atmospheric P loading estimates to total phosphorous loading for each major river basin is provided in Table 9. Statewide, the phosphorous loading from atmospheric deposition (total; wet+dry) is approximately 13% of total phosphorus loading using the 2003 estimate of atmospheric P deposition, and 19% using the 2007 estimate of atmospheric P deposition. The increase in the contribution of atmospheric P deposition to total P loading is most likely due to the higher 2007 dry deposition estimates.

A comparison by major river basin shows that most of the increase in percentage of total loading is in the more forested river basins (Table 9). The percent of total loading as atmospheric deposition in the Rainy River basin is 40.6% based on the 2003 estimates and 54.0% based on the 2007 estimates. In the Lake Superior basin atmospheric deposition is 26.5% of total loading based on the 2003 estimates and 35.3% based on the 2007 estimates.

Much smaller changes in the percentage of atmospheric deposition contributing to total loading between the 2003 and 2007 estimates are shown in Table 9 in the predominantly agricultural river basins. In the Cedar River basin the percent of total loading as atmospheric deposition is 3.7% based on the 2003 estimates and 3.9% based on the 2007 estimates. In the Missouri River and Des Moines River basins the percents are 2.8% and 4.7% respectively based on the 2003 estimates and 4.4% and 8.0% based on the 2007 estimates. In the Minnesota River basin the percent atmospheric deposition based on the 2003 estimates is 5.4% of total loading in comparison to 8.3% based on the 2007 estimates.

Table 9. Comparison of total phosphorous deposition load in relation to estimated total loading to a basin for the 2003 and 2007 estimates. Comparisons are for an average precipitation year.

	2003 [1]					2007 [2]				
Basin	Point [1]	Non-Point (includes Total Atmospheric P Load)	Estimated Total Load (Point + Non-Point)	Atmospheric Total P Load (wet + dry)	Atmospheric Load as a % of Estimated Total Load	Point	Non-Point (adjusted) [3] (includes Total Atmospheric P Load)	Estimated Total Load (adjusted) [3] (Point + Non-Point)	Atmospheric Total P Load (wet + dry)	Atmospheric Load as a % of Estimated Total Load
	kg/yr	kg/yr	kg/yr	kg/yr		kg/yr	kg/yr	kg/yr	kg/yr	
Cedar River	56,813	62,989	119,802	4,492	3.7%	56,813	63,145	119,958	4,648	3.9%
Des Moines River	55,580	61,417	116,997	5,514	4.7%	55,580	65,639	121,219	9,736	8.0%
Lake Superior	34,782	229,660	264,442	70,118	26.5%	34,782	265,470	300,252	105,928	35.3%
Lower Mississippi	267,259	684,196	951,455	20,435	2.1%	267,259	699,201	966,460	35,440	3.7%
Minnesota River	371,745	1,095,489	1,467,234	78,567	5.4%	371,745	1,142,420	1,514,165	125,498	8.3%
Missouri River	13,122	93,099	106,221	2,981	2.8%	13,122	94,899	108,021	4,781	4.4%
Rainy River	44,238	377,109	421,347	171,065	40.6%	44,238	500,049	544,287	294,005	54.0%
Red River	78,154	714,730	792,884	226,843	28.6%	78,154	772,807	850,961	284,920	33.5%
St. Croix River	22,069	184,786	206,855	41,032	19.8%	22,069	218,185	240,254	74,431	31.0%
Upper Mississippi	1,180,141	1,156,229	2,336,370	264,658	11.3%	1,180,141	1,306,368	2,486,509	414,797	16.7%
Statewide	2,123,930	4,659,704	6,783,634	885,705	13.1%	2,123,930	5,128,183	7,252,113	1,354,184	18.7%

[1] Estimates of P loading for point and non-point sources obtained from "Detailed Assessment of Phosphorus Sources to Minnesota Watersheds", .
Prepared for the Minnesota Pollution Control Agency by Barr Engineering Company. February 2004

[2] The only change to P loading estimate in 2007 is due to the updated estimates of atmsopheric deposition.

[3] Estimate of non-point P loading is adjused to include the 2007 estimate of total (wet+dry) atmospheric P depositon.

Estimates of Background Phosphorus Dry Deposition

As previously presented in Table 3, the Silver Bay and Mille Lacs particle monitoring sites are identified as predominantly forested sites based on land use within 5 km of the monitoring site, while the Perham, Hutchinson, and Albert Lea sites are considered agricultural sites. The measured particle [P] for the Mille Lacs and Silver Bay sites is lower by a factor of 2 (statistically significant at the 0.1 level) compared to the measured particle [P] at Perham, Hutchinson, and Albert Lea. The similarity of the particle [P] concentrations at the forested Silver Bay and Mille Lacs sites, and their significantly lower particle [P] concentration than at the 3 agricultural monitoring sites, suggests that the particle [P] measured at the Silver Bay and Mille Lacs sites may represent a background concentration. Using data from both sites, the estimated background particle [P] concentration is approximately 0.0026 µg/m^3.

The specific source of the particle [P] in the forested areas is unknown. The available information for particle size distributions in northern Minnesota from the IMPROVE monitoring sites in Voyageurs National Park and the Boundary Waters suggests that the particle [P] may be associated with fine particles (2.5 microns in size or smaller). Data from Table 4 indicates that in forested areas the fine fraction accounts for 63% of the measured particles while the coarse fraction (particle size of 2.5 to 10 microns) accounts for 37% of the measured particles. If the particle [P] is associated with the fine fraction, it suggests that the particle [P] may be associated with distant sources as opposed to more local sources.

Potential Influence of Agricultural and Urban Land Use on Phosphorus Deposition

If the average particle [P] concentration of 0.026 µg/m^3 for the Silver Bay and Mille Lacs sites (Table 3) is used as a background concentration, then the estimated [P] in ambient air for the agricultural sites (Table 3) suggests that phosphorus enrichment is occurring at the agricultural sites; that is, the agricultural sites have a factor of 2 more particle [P] than at forested sites. The specific source of the increased particle [P] at the agricultural sites is unknown. It is known that wind erosion of soils is more prevalent in agricultural areas than in forested areas. The statistically higher particle [P] at agricultural sites and the prevalence of wind erosion of soils occurring in agricultural areas suggests that the potential source of the increased particle [P] may be related to agricultural land use. However, under the time constraints of the project did not allow for this topic to be more fully explored.

Phosphorus Loading Variability and Uncertainty

Variability in the Data

Wet Deposition

- Annual average precipitation amounts from 2000-2001 were used to establish the [P] and [Ca] relationship at the 4 NADP reference sites in order to estimate wet phosphorus deposition for other locations in the state. Precipitation can vary significantly from year to year. The estimate of phosphorus deposition in any given year could be significantly different from the annual average wet phosphorus deposition calculated in this project for each river basin. Therefore, the results of this project should be used cautiously in other applications.

Dry Deposition

- No adjustments were made in the estimation of dry deposition in a dry or a wet year. Data are not available at this time to derive estimates of dry deposition during different precipitation regimes. Variability in the amount of dry deposited phosphorus due to different moisture regimes was assumed to remain constant for this project.
- Phosphorus concentration data from particulate filters were available for 9 months. It is recognized that the data likely vary from season-to-season and from year-to-year. However. the limited amount of data precluded an assessment of seasonality or year-to-year variations.

Uncertainty in the Data

Wet Deposition

- Establishing the relationship of [P] and [Ca] in precipitation from a limited number of sites (4 reference sites) for a limited time period (2 years) introduces some uncertainty into the wet deposition calculations. It is assumed the two years during which the data were collected are representative precipitation years and were not unduly influenced by unique large storm events. The inclusion of more monitoring sites, for a longer period of time, would likely improve the data to provide a better relationship of [P] and [Ca] in precipitation.
- An individual monitoring site can provide representative data for the surrounding region if the site is adequately selected (NOAA-ARL, 2003). The grid-based area weighting assumes a predictable rate of change in the phosphorous concentrations between monitoring sites and that local source influences are not significant in regard to the precipitation [P]. In addition, the area

weighting technique requires a distribution of sites/data over a wide geographic area. Data were particularly sparse in the border areas, particularly in the northern part of the Red River basin, and this introduces additional uncertainty into the deposition estimates.

Dry Deposition

- An individual monitoring site is not considered to be necessarily representative of the surrounding region because the controlling factors for dry deposition are surface driven and are not regionally representative (NOAA-ARL, 2003). In this application, it was assumed that the 5 MPCA air toxics monitoring sites analyzed for particle phosphorous were representative of areas with similar land use. There is some uncertainty associated with this assumption because it is possible that the phosphorous concentrations measured on the filters are due to unique local factors that may not occur on a wide scale. In this case, dry deposition could be under-or-overestimated for a specific area.
- The estimates of dry phosphorus deposition may also be under-or-overestimated by applying data collected from population centers to more rural areas. The working assumption is that the factors resulting in phosphorous concentrations at the monitoring sites occur on a wide scale or in other areas of similar land use. Again, there is uncertainty in this assumption.
- There is uncertainty associated with the analysis performed to determine the phosphorous concentrations in PM_{10}. These filters had been archived for 6-7 years before analysis and actual field blanks that had been stored under similar conditions were not available. The phosphorous concentrations determined from these measurements may result in an under-or-overestimate of dry phosphorous deposition.
- There is uncertainty associated with the determination of fine and coarse particulate fraction. In particular, the two monitoring site used to represent forested areas are in northern Minnesota, which has predominantly coniferous forests. Applying these values to areas of other types of forests may under-or-over-estimate dry deposition in those areas.
- There is uncertainty associated with the deposition velocities assigned to the particle size categories used in the dry deposition estimates. The deposition velocities are affected by terrain and vegetation features. The deposition velocities may under- or over-estimate dry phosphorus deposition.

Potential Future Refinements to Atmospheric Deposition Estimates and Supplemental Analyses

The following list of items are suggested as ways to potentially improve the estimates of atmospheric (wet and dry) phosphorus deposition.

1. Additional one to two years of monitoring for [P] and [Ca] in precipitation to determine the representativeness and robustness of the original relationship between [Ca] and [P] in precipitation and improve the ability to extrapolate the findings from the research sites to other locations in the state.
2. Additional sites should be included in the wet deposition monitoring network, particularly in southwest and western Minnesota, to measure the [P] and [Ca] relationship in these areas and compare to the [P] and [Ca} relationship in forested areas. This additional information will likely improve the ability to extrapolate the findings to other agricultural land use/land cover areas in the state.
3. Assess the variability in annual dry deposition in relation to changes in annual precipitation to determine the significance of this project assuming dry deposition is constant for low, average, and high precipitation years.
4. Additional particulate monitoring (TSP, PM10) in other areas of the state should be conducted, with a particular emphasis on rural areas and determine whether extrapolation of the particulate filter data to larger regions or river basins is appropriate. Such monitoring should take large enough samples that the filters can be analyzed directly for phosphorous.
5. Collection of coarse (2.5 to 10 microns) and fine fraction (2.5 microns or less) particulate matter in forested and agricultural areas and analysis of the coarse and fine fractions for phosphorus and calcium (and other elements if possible) to determine the partitioning of phosphorus to each fraction.
6. A source apportionment study, using chemical mass balance or similar approach, for phosphorus should be conducted to determine if sources other than soil are significant, or could be significant, for phosphorus deposition.
7. Additional monitoring data from agricultural areas could then be used to further assess the importance of atmospheric deposition to agricultural runoff and determine the relative contribution of atmospheric deposition to agricultural runoff.

Recommendations for Lowering Phosphorus Export

Soil dust is assumed to be the largest source of atmospheric phosphorus. Therefore, reducing soil dust, particularly from agricultural fields, through the application of best management practices (shelterbelts, no till planting, use of cover crops, etc.) would seem to be a high priority. Another potential activity on a much smaller and local scale to reduce soil dust might include the periodic wetting of exposed soil at large construction sites during dry periods to minimize soil dust being entrained into the air due to wind erosion and to emphasize re-vegetating developments as quickly as possible after construction is completed.

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Northern one-half to one-third of MN:	15 $kg/km^2 \cdot yr^{-1}$
Central:	30+ $kg/km^2 \cdot yr^{-1}$
Southern part of MN with wind erosion:	30 – 40 $kg/km^2 \cdot yr^{-1}$

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Appendix A

Phosphorus in Precipitation Study

(Conducted by the St. Croix Watershed Research Station)

(Write-ups as received from the MPCA, September 2003)

INTRODUCTION

Four sites included4 sites (sample times, every 4 weeks), data logger to record precipitation data. MDN website. MDN program

SAMPLE HANDLING

One-liter Teflon sample bottle weights were etched onto bottle. Frontier Geosciences Inc. (Seattle, WA) were responsible for all acid washing of the Teflon sample bottles and sample trains (including inserts) using a perchloric-nitric acid cleaning procedure (claiming proprietary information on procedure). Sample bottles and trains were bagged and shipped by Frontier to each of the four sites. The 1-liter Teflon sample bottles were precharged with 20 (± 0.1) mL 10% v/v HCl preservative (final concentration of preservative = 1.13 N HCl) by Frontier Geosciences (high purity HCl was purchased from Seastar Chemicals cat. # BA-04-0500-certificate of analysis attached).

Sample operators at each of the four sites were responsible for changing the sample bottles at four-week intervals during the two-year study. However, at times, sample bottles were changed sooner due to sample overflow. Also, at times, sample bottles were changed later due to inclement weather, or replacement sample bottles were not available. In some instances, sample bottles were removed and a new sample bottle was not replaced until a later time resulting in missed precipitation collection. At each change out or sampling period, the site operator filled out a data sheet indicating start and stop times of each sample and any other notes that were appropriate.

When changed by the site operators, the one-liter Teflon sample bottles were shipped from each of the four sites to the St. Croix Watershed Research Station (SCWRS) via FedEx (next day). Upon arrival at SCWRS, data sheets were verified and filed, while samples were weighed and recorded. Sample bottle weights (etched into each bottle) were noted and used to calculate the normality of each sample (sample weight including preservative minus sample bottle weight). Samples were refrigerated at 4^{o}C until analyzed. Usually received sample bottles were held until a batch of 40 samples could be run for nutrients and/or trace metals.

LABORATORY ANALYSIS

Samples received at the St. Croix Watershed Research Station were digested and analyzed for Total Phosphorus and Total Nitrogen (TP/TN). Samples were also digested for trace metals and sent to the University of Minnesota Geochemistry Lab (Department of Geology and Geophysics) for trace metal analysis.

Nutrient Dual Digestion

A sample dual digestion (modified from Ameel et. al. and Jones, ND Dept. of Health. unpublished) for both total phosphorus and total nitrogen (TP/TN, unfiltered) was performed in 60-mL high density polyethylene (HDPE) acid washed bottles. 20 g (± 0.5 g) were weighed into a preweighed HDPE digestion bottle on an analytical balance; weights were recorded. Five mL of digestion solution (sodium hydroxide and potassium persulfate) was added. Bottles were loosely capped and autoclaved at 121 ^{o}C and 16 psi for 15 min. Samples were removed from the autoclave and cooled in a freezer for 20-30 minutes. When cooled, 0.5 mL of 11 N H2SO4 was added to each bottle. Bottles were again placed back into the autoclave for an additional 30 minutes at 121 ^{o}C and 16 psi. Samples were again cooled in a freezer and weighed back. Dilutions were calculated based on sample weight, reagent added, and weight loss during digestion.

Phosphorus calibration standards were diluted from a 250 µg P/L working stock standard. The working stock standard was diluted from a 25 mg P/L stock standard made by dissolving 0.1099 g primary standard grade anhydrous potassium phosphate monobasic (KH_2PO_4) that has been dried for one hour at 105 ^{o}C in 1000 mL DIW. Nitrate calibration standards were diluted from a 200.0 mg N/L stock standard made by dissolving 1.444 g potassium nitrate (KNO_2) in 1000 mL DIW.

Mixed quality control check standards (QCSPEX-Nut, SPEX CertiPrep, Inc., Metuchen, NJ) were purchased for both total phosphorus and total nitrogen and diluted to manufacture's specifications. A midrange and low check standard for total nitrogen was diluted to 10.0 and 0.30 mg N/L. Separate dilutions were made for total phosphorus check standards at 100, 25, and 5.0 µg P/L. Allowable recoveries for check standards were +/- 10% with some exceptions of the low TP check standard of 5.0 µg P/L. Since the detection limit of the Total Phosphorus method is close to 5.0 µg P/L, percent relative difference of this low check standard was allowed to be above 10 percent. Instrument blanks as well as procedural blanks were included during analysis and were required to be below 5.0 µg P/L. Over ten percent of the samples were run in duplicate (a duplicate sample is one which has a separate digestion from the original), and aside from a couple of samples, had a percent relative difference less than 10 (some duplicates were less than 5.0 µg P/L). Digestion efficiency standards for both nitrogen (glutamic acid, 1.00 and 8.00 mg N/L) and phosphorus (adenosine 5”-triphosphate disodium salt hydrate, 25 and 100 µg P/L) were included to verify complete conversion of organic species during digestion. Typically the Total Nitrogen efficiency standards were 20-30 percent more than expected (indicating a greater amount of conversion) and Total Phosphorus efficiency standards were usually at least 95% complete. Laboratory fortified samples and spikes were also included to verify no matrix interference and typically had a percent relative difference from the expected value of less than 10. All calibration and check standards as well as blanks, samples, and duplicates were digested in the same manner before analysis.

Total nitrogen analyses were determined on a QuickChem 8000 dual-channel nutrient autoanlayzer (Lachat Instruments, Milwaukee, WI). During the digestion, Organic-N and Ammonium-N are converted to nitrate+nitrite-N. This reduced nitrate plus the original nitrate+nitrite was determined using the cadmium reduction method (Lachat Instruments method 10-107-04-1-A). Nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) forms a magenta color which is read at 520 nm. Seven nitrate calibration standards (0.0, 0.20, 0.40, 1.00, 4.0, 8.0, 20.0 mg N/L) were used to generate a first-order polynomial which uses linear regression to calculate a best fit straight line for all the calibration points. The resulting first-order polynomial is then used for calculating concentration:

$$\text{Concentration} = C(1)\,Y + C(0) \qquad (5)$$

Where:
C(1) = calibration curve first-order coefficient (slope),
C(0) = calibration curve constant term (concentration axis intercept), and

Y = analyte response (peak area)

Direct chemistry was applied to all peaks formed from this method. Direct chemistry calculates only peaks that go positive from the baseline (peak area > 0). Peak base width and threshold values are assumed and then calculated to activate this chemistry. Calibration failure criteria were set for each calibration curve generated. The minimum correlation coefficient allowed (r value) was 0.9900, however, an r value of 1.0000 was usually observed. The detection limit for this method is 0.2 - 20.0 mg N/L as NO3- or NO2-.

Total Phosphorus

Total phosphorus was determined using a QuickChem 8000 dual-channel nutrient autoanalyzer (Lachat Instruments, Milwaukee WI). During the digestion, Organic-P is converted to orthophosphate. The orthophosphate ion (PO_4^{3-}) reacts to form a complex, which absorbs light at 880 nm. The absorbance is proportional to the concentration of orthophosphate in the sample. A modified Lachat manifold for orthophosphate (based on EPA method 365.1) was used to measure total phosphorus simultaneously with total nitrogen. The calibration range used for total phosphorus was 200, 100, 50, 25, 10, 5, 0 µg P/L. A second-order polynomial produced a more suitable calibration fit for the total phosphorus calibration curve. The resulting equation for a second-order polynomial is as follows:

$$\text{Concentration} = C(2)\ Y2 + C(1)\ Y + C(0) \qquad (6)$$

where:
C(2) = calibration curve second-order coefficient,
C(1) = calibration curve first-order coefficient,
C(0) = calibration curve constant term (concentration axis intercept), and

Y = analyte response (peak area)

A 0.231 *N* H_2SO_4 carrier was used on the phosphorus manifold to avoid sample/carrier mismatch. A Bipolar chemistry was used when integrating the peaks. An r-value of 0.9900 was the minimum correlation coefficient, but typically r-values generated around 0.9995 or higher.

Trace Metals

A trace metal extraction was performed at the St. Croix Watershed Research Station on the received samples. Over ten percent of the samples were run in duplicate. Procedural blanks were included with each batch extracted. Twenty-five ml of sample were poured into a 60-mL Teflon bottle, sample weight was recorded. Depending on the normality of the sample (determined by sample weight and 20 ml preservative), either 2.5 N high purity HCl (Seastar, Baseline) or Type 1 reagent grade DI water was added to adjust each sample to 0.5 N. Samples were loosely capped and digested in an oven at 85oC for 30 min. When samples had cooled, weights were recorded and dilutions calculated. The digested samples were then sent to the University of Minnesota Geochemistry Lab (Department of Geology and Geophysics) to be analyzed on a Perkin Elmer Sciex Elan 5000 inductively coupled plasma mass spectrometer (ICP-MS) for Ni, Cu, Cd, Pb(206, 207, 208), Zn, Cr, Co, Se, Fe, Mn, Ca (and Ba in year 1).

Nickel, Chromium, Cobalt, Selenium, and to some extent Copper and Cadmium showed sample matrix interferences on the ICP-MS. Copper and Cadmium values are reported but should be viewed with caution. Nickel, Chromium, Cobalt, and Selenium values were not used. Barium was analyzed during the first year of the study, but was not analyzed during the second year. Lead isotopes were analyzed and a 206/207 ratio is reported for each year. See QA/QC output.

DATA REDUCTION/CALCULATION

Precipitation data was collected using a rain gauge at each of the four sites and recorded using a datalogger. This information was downloaded from the MDN website. Funnel cross sectional area was also determined and precipitation was calculated using this along with sample weight. This was then compared with the rain gauge data. It appears that the funnel area/sample weight calculation method seemed to underestimate the amount of precipitation that fell when compared to the rain gauge data. This may most likely be due to the inefficiency of the sample collectors (especially in winter when snow can blow in or out of the funnels). Because of this, the precipitation data used is from the rain gauges and is also the data reported on the web site. At certain sites during certain times throughout this two-year study, the data loggers would malfunction and not collect data during precipitation events. In these cases, the MDN web site precipitation manager was contacted and his estimates were given for this missing data (viewed as grayed area in spreadsheet).

During year one of the study, there were two samples that were analyzed for total nitrogen but not total phosphorus. A regression using total nitrogen as an indicator of total phosphorus was generated ($Y = 84.5 + 16.2 * X$, $R2 = .56$) and total phosphorus was predicted (highlighted in blue on the spreadsheet). This regression only used samples from year one of the study.

During sample intervals where no sample exists or where an analysis was not measured and a regression could not be used or where results seemed suspect, the averaged results of adjacent sample time periods (during that year or during the other year of the study) were used and then multiplied by the *actual* precipitation that fell during the interval in question. See Table 1 for samples that had averaged values reported and why (also see spread sheet for samples intervals used to average missing sample periods). Because sample intervals many times contained varying amount of days, an attempt was made to use intervals with close to the same number of days (i.e. this is why some missing sample intervals used a different amount of intervals for an average). Results highlighted in green on the spreadsheet are averages from other intervals (and can be found on bottom of spreadsheet). The averaged mass results were used and then back-calculated to determine (ug/L, mg/L, ng/g).

Sample Collection Time Period	Reason Original Sample Was Not Used	Averaged Sample Time Periods Used To Calculate Result
Lamberton		
4	TP result suspect	Regression of TN samples from Year 1 of study
6	Too little sample for analysis of nutrients and trace metals	5, 7, 18, 19, 20
16	Original Cu result suspect	15, 17, 2, 3, 4
24	Too little sample for analysis of nutrients	23, 25, 10, 11, 12
26	Original nutrient results suspect	25, 14, 12, 13, 1
Camp Ripley		
5	TP result suspect	Regression of TN samples from Year 1 of study
18	Too little sample for analysis of nutrients and trace metals	17, 19, 4, 5, 6
20	Too little sample for analysis of nutrients and trace metals	19, 21, 6, 7, 8
28	Original nutrient results suspect	13, 12, 1, 14, 25, 26, 27
Marcell		
4	Original Cu result suspect	3, 2, 16, 17, 18, 19, 20, 6
5	Original Cu result suspect	19, 20, 6, 18, 17
14	No sample received	27, 13, 26, 1, 15
Fernberg		
2	No sample received	1, 17, 3, 18
4	No sample received	3, 18, 1, 17, 5, 6, 19
8	Original nutrient results suspect, Original Cu result suspect	21, 7, 20, 22,
9	Original Cu result suspect	22, 21, 10, 11, 23, 24
16	No sample received	15, 28, 1, 17
29	No sample received	28, 15, 17, 1

Phosphorus in Precipitation Study

SOP #1

Total P and Total N (TPTN) and/or Dissolved P and Dissolved N (DPDN) Digestion

(6/13/00 Kelly Thommes)

DIGESTION:

1. Samples will be analyzed on the Lachat autoanalyzer for both Total Phosphorus and Total Nitrogen (TPTN, unfiltered) and/or Dissolved Phosphorus and Dissolved Nitrogen (DPDN, filtered through a 0.45 µm filter). Forty-eight samples can be processed per batch (this includes QA/QC samples).

2. Print out sample names using the plastic labels and place on acid-washed 60-mL HDPE bottles. Include project initials, site #, type of water sample (SW or GW), TPTN or DPDN, site name, date, and time. Include calibration standards, check standards, blanks, digestion efficiency standards, duplicates, spikes, lab-fortified blanks, and samples. Ten percent blanks and duplicates should be included. If enough sample exists, use the same sample for the duplicate as for the spiked sample. Include one spiked-sample and one lab-fortified blank for phosphorus and one spiked-sample and one lab-fortified blank for nitrogen. Use Deionized (DI) water for the zero calibration standards, blanks, and lab-fortified blanks.

3. Using the spreadsheet generated for labels, record the weight of the labeled bottles (with cap) using the analytical balance connected to the laptop computer.

4. Remove cap, and tare the 60-mL HDPE bottle on the balance. Pour 20 g (+/- 0.5 g) calibration standard, check standard, efficiency standard, duplicate, blank, or sample into the 60-mL HDPE bottle. Remove the bottle and replace cap. Tare the balance and record weight of the bottle+sample with cap.

5. When pouring out the spiked-sample or lab-fortified blank, record the sample weight (20 g +/- 0.5 g). Using a calibrated auto pipette, add 3 mL of the 100 µg P/L calibration standard for the phosphorus spiked-sample and phosphorus lab-fortified blank. Add 3 mL of the 8.00 mg N/L

calibration standard for the nitrogen spiked-sample and nitrogen lab-fortified blank. Record weights of spike added.

6. Using the calibrated 5-mL auto pipette, add 5 mL of digestion solution (made from the ND-SOP) to each bottle. Cap tightly and shake to mix. Place loosely capped sample bottles in autoclave and digest for 15 min at 121 ^{o}C and 16 psi. Remove samples from autoclave and cool in freezer for 20-30 min (keep caps loosened). When cool enough to handle, add 0.5 mL of 11 *N* H_2SO_4 to each bottle, cap tightly, and shake to mix. Place loosely capped bottles back into autoclave for an additional 30 min at 121 ^{o}C and 16 psi. Again, cool samples in freezer. When cool enough to handle, tightly cap and shake bottles. Dry bottles if wet and record bottle+sample weight.

7. Samples can now be run using the Lachat autoanalyzer. Samples should be run preferably the same day or no more than a couple of days after the digestion.

DIGESTION REAGENTS AND STANDARDS:

Digestion Solution

To a 1-L volumetric, dissolve 10.48 g of granular sodium hydroxide (NaOH) and 42 g of potassium persulfate ($K_2S_2O_8$) in approximately 900 mL of DI reagent grade water. When dissolved, bring to volume.

11 *N* Sulfuric Acid (H_2SO_4)

To a 1-L volumetric and in a fumehood, add 305 mL of concentrated sulfuric acid to about 600 mL of DI reagent grade water. The volumetric should be surrounded by an ice bath while at the same time swirled to reduce the heat. When cool, bring to volume.

Phosphorus Stock Standard 25 mg P/L

To a 1-L volumetric, dissolve 0.1099 g primary standard grade anhydrous potassium phosphate monobasic (KH_2PO_4) that has been dried for one hour or overnight at 105 ^{o}C in about 800 mL DI reagent grade water. Bring to volume and invert to mix.

Phosphorus Working Stock Standard 250 µg P/L

To a 1-L volumetric, dilute 10 mL Phosphorus Stock Standard to the mark with DI reagent grade water. Invert to mix.

Nitrogen Stock Standard 200.0 mg N/L as NO_3^-

To a 1-L volumetric, dissolve 1.444 g potassium nitrate (KNO_3) in about 600 mL DI reagent grade water. Dilute to mark and invert to mix.

Phosphorus Working Standards 0, 5, 10, 25, 50, 100, 200 µg P/L

5 µg P/L	5 mL of P Working Stock Standard (250 µg P/L) in a 250-mL volumetric
10 µg P/L	10 mL of P Working Stock Standard (250 µg P/L) in a 250-mL volumetric
25 µg P/L	0.25 mL of P Stock Standard (25 mg P/L) in a 250-mL volumetric
50 µg P/L	0.50 mL of P Stock Standard (25 mg P/L) in a 250-mL volumetric
100 µg P/L	1.00 mL of P Stock Standard (25 mg P/L) in a 250-mL volumetric
200 µg P/L	2.00 mL of P Stock Standard (25 mg P/L) in a 250-mL volumetric

Nitrogen Working Standards 0.00, 0.20, 0.40, 1.00, 4.0, 8.0, 20.0 mg N/L

0.20 mg N/L	0.25 mL of N Stock Standard (200.0 mg N/L) in a 250-mL volumetric
0.40 mg N/L	0.50 mL of N Stock Standard (200.0 mg N/L) in a 250-mL volumetric
1.00 mg N/L	1.25 mL of N Stock Standard (200.0 mg N/L) in a 250-mL volumetric
4.0 mg N/L	5.00 mL of N Stock Standard (200.0 mg N/L) in a 250-mL volumetric
8.0 mg N/L	10.0 mL of N Stock Standard (200.0 mg N/L) in a 250-mL volumetric
20.0 mg N/L	25.0 mL of N Stock Standard (200.0 mg N/L) in a 250-mL volumetric

Check Standards Amp 2 for TN and TP (Record Lot # on volumetric and bench sheet)

5 µg P/L, 25 µg P/L, 100 µg P/L with 0.30 mg N/L, 10 mg N/L

Stock Adenosine 5'-triphosphate disodium salt hydrate (Aldrich A26209) 99% pure, 50 mg P/L

To a 1-L volumetric, dissolve 0.2996 g Adenosine 5'-triphosphate disodium salt hydrate that has been dried for one hour or overnight at 105 °C in about 800 mL DI reagent grade water. Bring to volume and invert to mix.

Phosphorus Efficiency Standard 100 µg P/L

To a 250-mL volumetric, add 0.50 mL Stock Adenosine (50 mg P/L) and bring to volume.

Phosphorus Efficiency Standard 25 µg P/L

To a 250-mL volumetric, add 0.125 mL Stock Adenosine (50 mg P/L) and bring to volume.

Stock Glutamic Acid 100 mg N/L

To a 1-L volumetric, dissolve 1.3366 g glutamic acid that has been dried for one hour or overnight at 105 ^{o}C in about 800 mL DI reagent grade water. Bring to volume and invert to mix.

Nitrogen Efficiency Standard 8.00 mg N/L

To a 250-mL volumetric, add 20.0 mL Stock Glutamic Acid (100 mg N/L) and bring to volume.

Nitrogen Efficiency Standard 1.00 mg N/L

To a 250-mL volumetric, add 2.50 mL Stock Glutamic Acid (100 mg N/L) and bring to volume.

AUTOMATED COLORIMETRIC PROCEDURE ON THE LACHAT QUICHEM 8000 AUTOANALYZER

	Phosphorus	Nitrogen
Method	SCWRS Method	10-107-04-1-A
Sample Loop	133 cm	Microloop
Interference Filter	880 nm	520 nm
Chemistry	Bipolar	Direct
Inject to Peak Start		
Peak Base Width		
% Width Tolerance		
Threshold		
Method Cycle Period		
Probe in Sample		
Sample reaches 1st Valve		
Load Period		

LACHAT REAGENTS

PHOSPHORUS MANIFOLD

Stock Ammonium Molybdate Solution

To a 1-L volumetric, dissolve 40.0 g ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}\bullet 4H_2O$) in approximately 800 mL of DI reagent grade water. Dilute to mark and mix with a magnetic stirrer for at least four hours. Store in plastic and refrigerate.

Stock Antimony Potassium Tartrate Solution

To a 1-L volumetric, dissolve 3.0 g antimony potassium tartrate (potassium antimony tartrate hemihydrate $K(SbO)C_4H_4O_6\bullet 1/2H_2O$) in approximately 800 mL of DI reagent grade water. Dilute to mark and mix with a magnetic stirrer until dissolved. Store in a dark bottle and refrigerate.

Working Molybdate Color Reagent

To a 1-L volumetric, add approximately 500 mL DI reagent grade water and 20 mL concentrated H_2SO_4. Swirl until cool and add 213 mL of Stock Ammonium Molybdate Solution, then add 72 mL of Stock Antimony Potassium Tartrate Solution. Dilute to mark and invert to mix. Degas with helium.

Working Ascorbic Acid

To a 1-L volumetric, dissolve 60.0 g ascorbic acid in approximately 900 mL of DI reagent grade water. When dissolved, dilute to mark. Degas with helium. Add 1.0 g sodium dodecyl sulfate ($CH_3(CH_2)_{11}OSO_3Na$). Invert to mix. Prepare fresh weekly.

Phosphate Carrier 0.231 N H_2SO_4

Dilute 21 mL of 11 N Sulfuric Acid to 1-L volumetric with DI reagent grade water. Degas with helium.

Sodium Hydroxide-EDTA Rinse

To a 500-mL volumetric, dissolve 32.5 g sodium hydroxide (NaOH) and 3 g tetrasodium ethylenediamine tetraacetic acid (Na_4EDTA). Dilute to mark and invert to mix. Store at room temperature. Use this to clean phosphorus manifold lines. Pump reagent through for about five minutes followed by DI water for five minutes.

NITROGEN MANIFOLD

15 *N* Sodium Hydroxide (NaOH)

To a 500-mL volumetric, add 75 g NaOH very slowly to approximately 250 mL of DI reagent grade water. Caution: the solution will get very hot. Swirl until dissolved. Cool and store in a plastic bottle at room temperature.

Ammonium Chloride Buffer, pH 8.5

To a 1-L volumetric, dissolve 85.0 g ammonium chloride (NH_4Cl) and 1.0 g disodium ethylenediamine tetraacetic acid dihydrate ($Na_2EDTA•2H_2O$) in approximately 800 mL DI reagent grade water. Dilute to mark and invert to mix. Adjust pH to 8.5 with 15 N sodium hydroxide.

Sulfanilimide Color Reagent

To a 1-L volumetric, add approximately 800 mL DI reagent grade water. Add 100 mL 85% phosphoric acid (H_3PO_4), 40.0 g sulfanilimide, and 1.0 g N-(1-naphthyl)ethylenediamine dihydrochloride (NED). Shake until wetted and stir to dissolve for 30 min. Dilute to mark and invert to mix. Store in a dark bottle. This solution is stable for one month.

REFERENCES

Standard Operating Procedure For the Analysis of Total Phosphorus and Total Nitrogen in Water From an Alkaline Persulfate Digest, North Dakota Dept. of Health, Chemistry Div.

EPA (March 1983) Method 353.2 (colorimetric automated, cadmium reduction)

Lachat (Aug 1994) QuikChem Method 10-107-04-1-A (Nitrate/Nitrite)

Lachat (Feb 1996) QuickChem Method 10-115-01-1-B (Determination of Orthophosphate by FIA Colorimetry)

Phosphorus in Precipitation Study

SOP #2

Trace Metal Extraction for Precipitation Samples

(5/15/00 Kelly Thommes)

1. Make up 1 L of 2.5 N HCl. Use high purity acid from Seastar. Include lot # of acid on bench sheet. When making up acid, anything coming into contact with the acid must be *extremely* clean. Volumetric should be acid washed, triple rinsed with DI water, and rinsed with a small amount of the high purity acid before using. Use a final rinse of DI water.

2. Teflon sample bottles must be labeled with the special plastic lab labels. MPCA sample #'s should be printed on the labels using the laser printer.

3. We will be running 10% duplicates. After every 10th sample, include a duplicate sample from that batch. Include 1 lab blank per batch and also run field blanks (acid preservative sent to us) as samples if available.

4. Record weight of Teflon bottle (including cap) on bench sheet (use laptop hooked to top-loading balance).

5. While wearing gloves, pour out 25 mL of sample into 60-mL Teflon bottle. Record sample weight on bench sheet.

6. Working from bench sheet , add 2.5 N HCl in calculated amount to adjust samples to 0.5 N. Use lab adjustable pipette that has been calibrated prior to each addition. Record weight (using balance) on bench sheet. Swirl sample to mix.

7. In some instances the sample will need to be diluted with DI-water to adjust the sample to 0.5 N. Use DI-water that has been recently taken from the *"point of use gun"* on the Millipore DI unit. Record weight of DI-water added.

8. Loosely cap bottles and digest in oven at 85 °C for 30 min. Include a PP bottle with DI and thermometer to determine when samples reach 85 °C (usually 1-1.5 hours) and then digest for 30 min. after samples have reached the appropriate temperature.

9. After digestion, cool completely in a refrigerator or freezer, cap tightly, and weigh bottle on balance. Record weight.

10. Calculate dilution and sample matrix.

11. Digested samples should be stored in refrigerator prior to sending to U of MN (Rick Knurr) for ICP-MS analysis. Send Rick approximately 100 ml of sample matrix for standards (i.e. 0.5 N HCl sample matrix-dilute 2.5 N HCl).

Trace metals of interest: Ni, Cu, Cd, Pb, Zn, Cr, Co, Se, Fe, Mn, Ca, Al