



Technical Memorandum

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Subject: Detailed Assessment of Phosphorus Sources to Minnesota Watersheds - Atmospheric Deposition

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The purpose of this memorandum is to provide a discussion about Atmospheric Deposition as a source of phosphorus to Minnesota watersheds. This discussion is based on a review of the available literature, consideration of monitoring data and other available support data, and the results of phosphorus loading computations done for each of Minnesota's ten major watershed basins as part of this study. This memorandum is intended to:

- Provide an overview and introduction to this 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
- Discuss the results of the phosphorus loading computations and assessments
- 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

Overview and Introduction to Atmospheric Source(s) of Phosphorus

The importance of nutrient contributions to Minnesota's ecosystems have 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. Agricultural activities (pre-planting field preparations, harvesting) can increase the amount of soil-derived phosphorus in the atmosphere. 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).

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 ($\text{kg ha}^{-1} \text{ yr}^{-1}$) in northern Wisconsin (Rose, 1993; Robertson, 1996) to 0.48 $\text{kg ha}^{-1} \text{ yr}^{-1}$ for north central Minnesota (Verry and Timmons, 1977).

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 for Florida were also reviewed (Dixon 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.

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

Specific estimates of dry deposited phosphorus in Minnesota were not found in the literature review.

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). As noted above, no data on dry deposition of phosphorus in Minnesota was identified.

The MPCA's goal for this project is to provide an updated estimate of wet phosphorus deposition using more recent data and an initial estimate of dry deposited phosphorus for surface waters and wetland areas in Minnesota. The following section discusses the data considered to be the best available at this time for providing estimates of atmospheric phosphorus inputs to Minnesota's river basins and watersheds.

B. Available Data

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

MPCA:

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. PM10 air concentrations determined from particulate filters and elemental speciation of the PM10 mass by X-ray Fluorescence (XRF) analysis for the 30 sites included in the Statewide Air Toxics Monitoring Study (1996-2001).

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, 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	Michigan	Minnesota	North Dakota	Wisconsin
Big Springs Fish Hatchery	Isle Royale Nat. Pk.	Camp Ripley	Icelandic St. Pk	Lac Courte Oreilles Res.
		Cedar Creek		Spooner
		Fond du Lac Res.		Wildcat Mountain St. Pk.
		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.

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 State Climatology Office provides a full QA/QC program for precipitation data; therefore no additional QA/QC was conducted on the precipitation data for the atmospheric component of this project. 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.

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 collocated 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.

It is noted here that 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. The NADP provides a full QA/QC program for sample collection and sample analysis and data reporting. No additional QA/QC on the NADP data was conducted for this project.
- b. Monthly volume-weighted calcium concentrations from four sites (Fernberg, Marcell, Camp Ripley, 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, then merged with the data from the special phosphorus in precipitation study. The NADP provides a full QA/QC program for sample collection, sample analysis and data reporting; therefore no additional QA/QC on the NADP data was conducted for this project.

Particulate (PM10) and elemental concentrations

Data files for PM10 air concentrations and elemental speciation of the PM10 mass by XRF analysis were obtained from the MPCA for the 30 sites included in the Statewide Air Toxics Monitoring Study (1996-2001) (Table 3). In any one year of the study, six sites were in operation. A specific site was in operation for only one year. 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 analysis by XRF. The MPCA staff provided QA/QC for sample collection, sample analysis and data reporting. No additional QA/QC on the MPCA's PM10 filter data was conducted for this project.

A data file was received for each monitoring site. The 30 data files were then merged into a master data file containing all sites for ease of manipulation and calculations.

Table 3. List of randomly selected Minor Civil Divisions to be sampled in the Minnesota Pollution Control Agency's Statewide Air Toxics Monitoring Study

MPCA REGION	SAMPLE YEAR				
	1. 1996-1997	2. 1997-1998	3. 1998-1999	4. 1999-2000	5. 2000-2001
REGION 1 DULUTH	Wagner Township; Aitkin County Tier 5	Hibbing; St. Louis County Tier 3	Duluth; St. Louis County Tier 1	Virginia; St. Louis County Tier 4	Duluth; St. Louis County Tier 1
REGION 2 BRAINERD	Little Falls; Morrison County Tier 3	Elk River; Sherburne County Tier 2	St. Cloud; Stearns County Tier 1	St. Michael; Wright County Tier 4	Fort Ripley; Crow Wing County Tier 5
REGION 3 DETROIT LAKES	Alexandria; Douglas County Tier 3	Fergus Falls; Otter Tail County Tier 2	Brandon Township; Douglas County Tier 5	Perham; Otter Tail County Tier 4	Moorhead; Clay County Tier 1
REGION 4 MARSHALL	Pipestone; Pipestone County Tier 3	Granite Falls; Yellow Medicine County Tier 4	Holloway; Swift County Tier 5	Hutchinson; McLeod County Tier 2	Willmar; Kandiyohi County Tier 1
REGION 5 ROCHESTER	Leon Township; Goodhue County Tier 5	Rochester; Olmsted County Tier 1	Winona; Winona County Tier 2	Albert Lea; Freeborn County Tier 3	North Mankato; Nicollet County Tier 4
REGION 6 TWIN CITIES	Plymouth; Hennepin County Tier 3	Minneapolis; Hennepin County Tier 1	West Lakeland Township; Washington County Tier 5	St. Paul; Ramsey County Tier 2	Apple Valley; Dakota County Tier 4
ADDITIONAL SITES	International Falls; Koochiching County	Warroad; Roseau County	Bemidji; Beltrami County	Silver Bay; Lake County	Grand Rapids; Itasca County

Note: Minor Civil Divisions within a region were segregated into 5 tiers based on population densities. Sites were then selected randomly from within a tier.

The two key parameters to be obtained from the particulate filters were calcium and phosphorus concentrations. Calcium concentrations were typically available for each sampling period. However, upon review of the individual site data files, phosphorus concentrations were not available. Prior to this data review it was assumed phosphorus concentrations would be available from the

particulate filters. Phosphorus concentration data is normally obtained from XRF analysis of particulate filters (Brook et al., 1997). Some of the particulate filters are being re-analyzed by MPCA using a different method that may provide phosphorus concentration data from the particle filters. Data from the re-analysis of the filters should be available in 2004. In the meantime, an alternative method for deriving phosphorus concentrations for the particle filters was employed for this project. This alternative method assumes that the relationship between phosphorus and calcium in precipitation is transferable to the particulate filter data (i.e., the same material being washed out in the precipitation is the same material being dry deposited and collected on the particulate filters). The critical assumptions and the details of calculating phosphorus air concentrations from the particulate filter data is described later in this memorandum.

Watershed Basin Characteristics

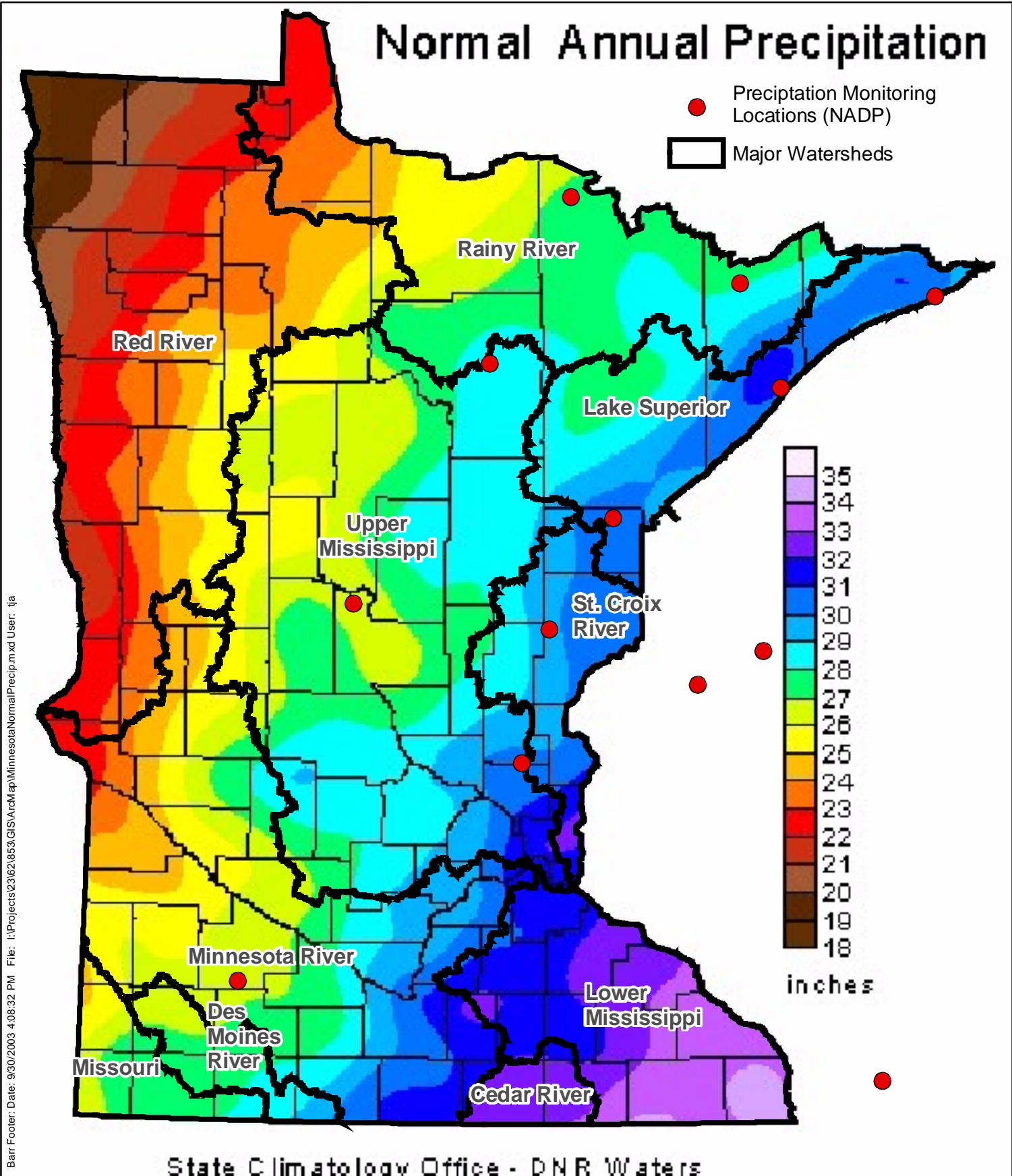
Atmospheric inputs of nutrients to watersheds is highly dependent upon precipitation amounts. Typically for sulfur and nitrogen, precipitation accounts for a majority (50-80%) of total inputs, while dry deposition typically accounts for the balance of total inputs (Pratt et al., 1996). It is currently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

Figure 1 provides a precipitation map of Minnesota, with normal annual precipitation isopleths overlain on the river basins and with NADP monitoring sites identified. 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 precipitation amount can range from 33 to 34 inches in the southeast corner to less than 20 inches in the northwest corner of the state, respectively. Given the assumption that precipitation is the predominant source of atmospheric phosphorus for a river basin or specific watershed, the difference in precipitation amount can 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).

Normal Annual Precipitation



Annual Precipitation Average

1971 - 2000

Data sources include National Weather Service, DNR Forestry, Soil and Water Conservation Districts, and others

300 to 1400 precipitation observers gathered data over 30 year period (seasonally varying)
10 KM grids of monthly precipitation totals created for month-year using "Surfer"

State Climatology Office, DNR-Waters

FIGURE 1
Normal Annual Precipitation
Amounts for Minnesota

- Mississippi River – upper: precipitation amount ranges from ~ 25 inches in the northwest portion (Hubbard-Wadena-Cass 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 (Kitson 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. This project uses an annual average precipitation amount for a basin. Given the gradient in precipitation amount across the state (Figure 1), a different estimate of wet phosphorus deposition can be obtained for various part of a basin that will be different from the deposition estimate using this annual average precipitation for the basin. It is expected that the use of a dry year (90th percentile) and a wet year (10th percentile) in estimating wet deposition will encompass the range of potential deposition amounts and address the within basin and site-to-site variability that is known to exist.

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 dominated by agriculture will have more phosphorus being dry deposited (e.g., Red River, Cedar River, Minnesota River) while those river basins with little agriculture would be expected to have less phosphorus being dry deposited (e.g., Rainy River, Lake Superior). However, as noted by Verry and Timmons (1977), river basins with little agriculture may still receive a notable input of particulate phosphorus due to large regional precipitation or dust storm events. Therefore, it may be possible that regional events may limit the importance of local site influence for dry deposition inputs for a river basin.

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 agreed upon 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 needed 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. Calcium (Ca) is a marker for soil contributions. All of the Ca found in precipitation or on the PM10 filters is due to soil.
4. Phosphorus (P) is to be normalized to Ca; the P:Ca ratio found in precipitation is the same ratio for particles; since all of the Ca is assumed to be due to soil, all of the P is due to soil.

5. Particles washed out in precipitation are the same size and type of particles being dry deposited.
6. PM10 monitoring at a site was conducted for one year, therefore the average annual concentration of Ca and P are to be used; therefore, seasonality in dry deposition is addressed through the use of annual average concentrations.
7. Data from a monitoring site (precipitation or particulate) is representative of other areas within a river basin.
8. Precipitation and PM10 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

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) 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 on 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

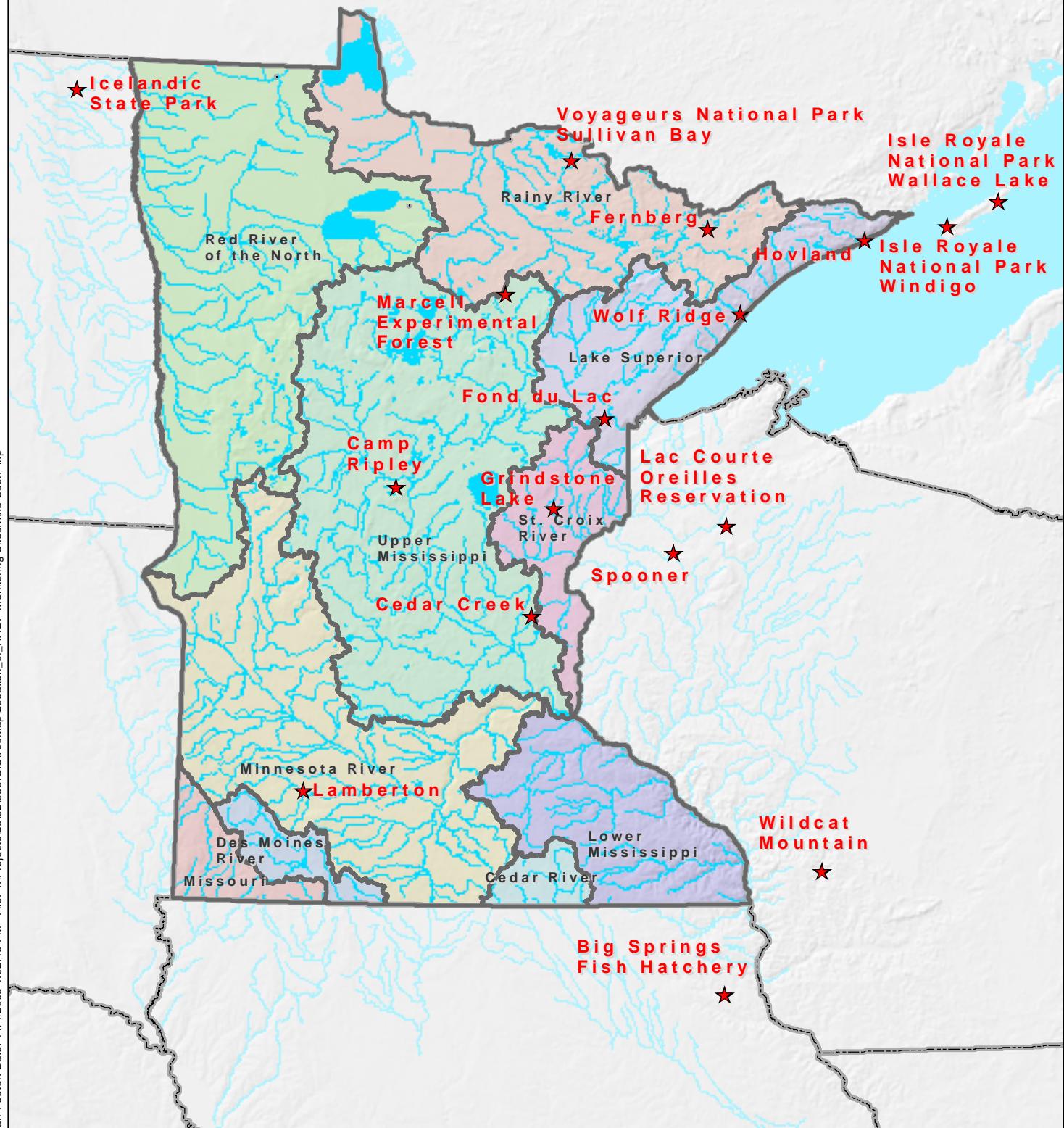
special study conducted by the St. Croix Watershed Research Station and the dissolved [Ca] reported by NADP for these same “reference” sites.

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:

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

Where: y = Total phosphorus in micrograms per liter ($\mu\text{g}/\text{L}$)
 x = NADP calcium (dissolved) in $\mu\text{g}/\text{L}$.

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.
3. Calculating wet phosphorus deposition
 - a. Monitoring sites locations were mapped with respect to basin boundaries and assignments to watershed made based on site locations (spatial distribution of sites provided in Figure 2):
 - Cedar River: Lamberton
 - Des Moines River: Lamberton
 - Lake Superior: Hovland, Wolf Ridge, Fond du Lac
 - Minnesota River: Lamberton
 - Mississippi (Upper): Marcell, Camp Ripley, Cedar Creek
 - Mississippi (Lower): Wildcat Mountain
 - Missouri River: Lamberton



 Major Basins

 NADP Monitoring Sites

 NORTH

0 12.5 25 50 75 100 Miles

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

Rainy River: Voyageurs Nat. Park, Marcell, Fernberg

Red River: Icelandic State Park

St. Croix River: Grindstone Lake, Cedar Creek

- b. Calculation components for phosphorus deposition in a basin:
 - o Annual average precipitation for the basin (obtained from State Climatology Office)
 - o [P] in precipitation (annual, volume weighted average; measured at one of the reference sites or estimated for one of the auxiliary sites; if more than one site assigned to a basin then the average [P] in precipitation used in the deposition calculation)
 - o Area estimate (hectares or acres) of open surface water (surface water + wetland as designated in GIS) in a basin.

C. Dry Deposition

1. Establishing the relationship between phosphorus and calcium on particle filters.
 - a. The relationship of phosphorus and calcium on the particle filters is assumed to be the same as the relationship of phosphorus and calcium in precipitation; the soil dust being washed out in precipitation is the same dust being dry deposited and collected on the PM10 filters.
 - b. The best source of phosphorus and calcium in precipitation data is the special study conducted by the St. Croix Watershed Research Station. The total phosphorus and calcium concentrations (hereafter denoted as total [P]) and total [Ca] in precipitation data) determined from August 1991 – September 2001 at 4 sites: Fernberg (Ely), Marcell, Camp Ripley, Lamberton; referred to as “reference sites”.
 - c. The relationship on a sample-by-sample basis (milligrams per square meter; mg/m²) between total [P] and total [Ca] in precipitation at the 4 reference sites was established through regression analysis:

$$y = 0.0289x \quad (\text{through zero}) \quad (R^2 = 0.42)$$

Where: y = Total phosphorus in micrograms per square meter ($\mu\text{g}/\text{m}^2$)

x = Total calcium in $\mu\text{g}/\text{m}^2$.

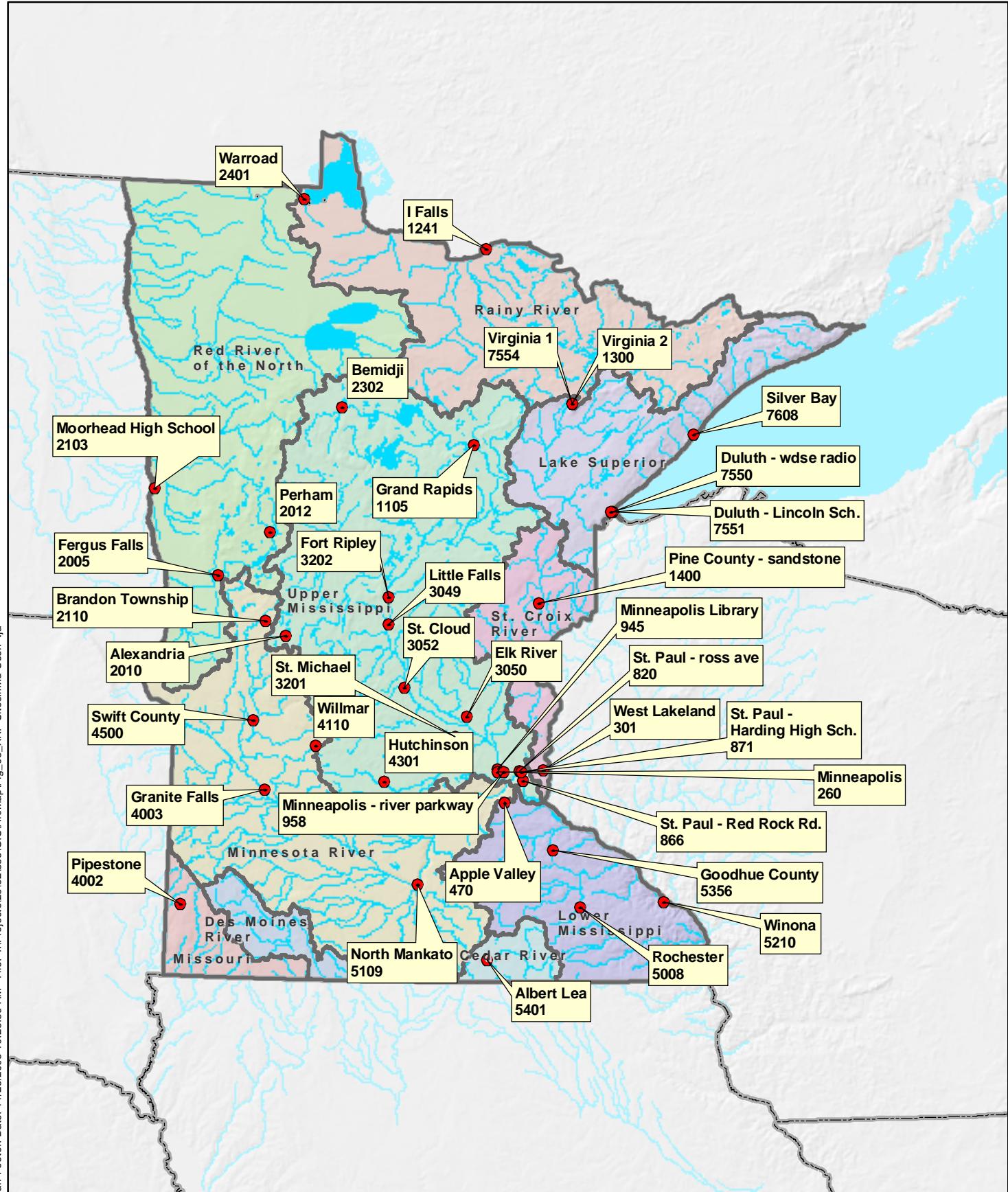
2. Extrapolating the relationship of [P] and [Ca] from precipitation to the particulate filters.
 - a. Since the regression equation for [P] and [Ca] in precipitation goes through zero, this regression equation can be applied to data from other media under the assumption that the ratio is the same (i.e., particulate filter data) without having to convert units. Essentially forcing the regression equation through zero creates a ratio of [P] to [Ca] that can be applied to other data.
 - b. In this regard, the regression equation from above can be modified as follows for application to the particle filter data:

$$y = 0.0289x \quad (\text{through zero}) \quad (R^2 = 0.42)$$

Where: y = Total phosphorus in micrograms per square meter cubic meter ($\mu\text{g}/\text{m}^3$)
 x = Total calcium in $\mu\text{g}/\text{m}^3$.

3. Estimating [P] in air at the MPCA's air monitoring locations.
 - a. The regression equation from 2.b. was then used to estimate [P] in ambient air at the MPCA air monitoring sites. Annual [Ca] concentrations in micrograms per cubic meter were calculated for each monitoring site (Table 3) based on the individual sample [Ca] concentrations. The annual average [Ca] in air is then used in the regression equation to derive an estimate of annual average [P] in air.

4. Calculating dry phosphorus deposition
 - a. Monitoring sites locations were mapped with respect to basin boundaries (spatial distribution of sites provided in Figure 3):
Cedar River: Albert Lea
Des Moines River: Pipestone
Lake Superior: Virginia (2 sites), Duluth (2), Silver Bay, Hibbing
Minnesota River: North Mankato, Brandon Township, Granite Falls, Willmar, Swift County
Mississippi (Upper): St. Paul (3), Minneapolis (3), Bemidji, Elk River, Fort Ripley, Alexandria, Hutchinson, St. Cloud, St. Michael, Grand Rapids, Little Falls



Major Basins
Monitoring Sites

NORTH
0 12.5 25 50 75 100 Miles

FIGURE 3
Approximate Locations of the
MPCA's Statewide Air Toxics
Monitoring Sites Used to Estimate Dry
Phosphorus Deposition

Mississippi (Lower): Rochester, Goodhue County, Apple Valley, Winona

Missouri River: Pipestone

Rainy River: Warroad, International Falls

Red River: Fergus Falls, Moorhead, Perham

St. Croix River: West Lakeland, Pine County (Sandstone)

b. Calculation components for phosphorus deposition in a basin:

- Estimated phosphorus air concentration; if more than one site assigned to a basin then the average phosphorus in air concentration used in the deposition calculation.
- The estimated phosphorus air concentration (or the average phosphorus air concentration if more than one site is in a basin) is to be split into two size fractions based on MPCA collocated PM10 and PM2.5 samplers (average from 5 sites):

42% fine fraction (< 2.5 microns)

58% coarse fraction

[Note: The fine:coarse ratios found in the MPCA PM10/PM2.5 data are similar to those found by Brook et al. (1997) across all Canadian sites, rural and urban. A critical assumption for this data is that the PM2.5/PM10 ratios for urban sites is the same as for rural sites.]

- 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 is summed together to provide a “total” particle deposition estimate.
- Conversion factors: convert seconds to years, cm to meters, and $\mu\text{g}/\text{m}^3$ to kg/ha.

The reader should note that for the dry deposition estimate, 1) 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. 2) Seasonality is incorporated into the deposition estimates

through the use of approximately one year of data from each monitoring site; however, seasonal deposition is not specifically calculated for this project due to the emphasis on providing annual average deposition values for each river basin.

Results of Phosphorus Loading Computations and Assessments

Wet Deposition

Estimates of average wet phosphorus deposition (average precipitation) range from $\sim 0.069 \text{ kg ha}^{-1} \text{ yr}^{-1}$ in the Red River basin to $0.212 \text{ kg ha}^{-1} \text{ yr}^{-1}$ in the Cedar River basin (Table 4). When factoring in dry/wet years, the range in potential wet phosphorus deposition is from approximately $0.059 \text{ kg ha}^{-1} \text{ yr}^{-1}$ in the Red River basin (dry year) to $0.273 \text{ kg ha}^{-1} \text{ yr}^{-1}$ in the Cedar River basin (wet year) (Table 4).

Table 4 also provides estimates of average phosphorus deposition (average precipitation) for the respective basins, which ranges from $\sim 2,100 \text{ kg/yr}$ for the Cedar River to $\sim 155,850 \text{ kg/yr}$ for the Upper Mississippi.

As identified in Table 4, the estimate of phosphorus deposition for each basin is based on the area identified as “water” or “wetland” in the GIS database.

Dry Deposition

Estimates of average dry phosphorus deposition (assuming average precipitation year) range from $\sim 0.028 \text{ kg ha}^{-1} \text{ yr}^{-1}$ in the St. Croix River basin to $\sim 0.241 \text{ kg ha}^{-1} \text{ yr}^{-1}$ in the Cedar River basin (Table 5).

The reader should note that 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.

Table 4
Estimated Wet Phosphorus Deposition to Minnesota Basins

Basin	NADP Station [1]	Total		Low Precipitation		Average Precipitation		High Precipitation		Basin Waters and Wetland Area [5a]	Basin Waters and Wetland Area [5b]	% of Total Basin Land	Low Precipitation Phosphorus (kg ha ⁻¹ yr ⁻¹)	Average Precipitation Phosphorus (kg ha ⁻¹ yr ⁻¹)	High Precipitation Phosphorus (kg ha ⁻¹ yr ⁻¹)	Average Phosphorus Deposition to Waters and Wetlands (kg/yr)	Average Phosphorus Deposition to Waters and Wetlands (lb/yr)
		Ca conc. [2]	P conc. [3]	Volume [4]	Volume [4]	Volume [4]	Area [5a]	Area [5b]	Area								
		(ug/L)	(ug/L)	(inches/yr)	(inches/yr)	(inches/yr)	(acres)	(hectares)									
Cedar River	Lamberton (MN)	348.75	25.98	27.50	32.10	41.30	24,523	9,924	3.7				0.181	0.212	0.273	2,102	4,635
Des Moines River	Lamberton (MN)	348.75	25.98	22.00	28.00	36.80	53,771	21,761	5.5				0.145	0.185	0.243	4,020	8,865
Lake Superior	Hovland (MN)	200.00	12.95														
	Wolf Ridge (MN)	183.33	11.83														
	Fond du Lac (MN)	165.71	10.65														
	Average	183.02	11.81	25.50	29.10	35.10	1,312,101	531,000	33.3				0.077	0.087	0.105	46,364	102,233
Minnesota River	Lamberton (MN)	348.75	25.98	22.10	28.10	34.80	742,441	300,462	7.8				0.146	0.185	0.230	55,709	122,838
Mississippi, Lower [7]	Wildcat Mountain (WI)	279.29	18.27	27.00	33.30	39.80	204,450	82,740	5.1				0.125	0.155	0.185	12,785	28,190
Mississippi, Upper [8]	Marcell (MN)	199.20	11.34														
	Camp Ripley (MN)	212.00	11.07														
	Cedar Creek (MN)	303.33	19.88														
	Average	238.18	14.10	22.60	28.10	34.30	3,826,925	1,548,735	29.7				0.081	0.101	0.123	155,847	343,642
Missouri River	Lamberton (MN)	348.75	25.98	21.10	27.20	35.60	29,691	12,016	2.6				0.139	0.179	0.235	2,156	4,755
Rainy River	Voyageurs National Park (MN)	163.33	10.49														
	Fernberg (MN)	182.17	9.28														
	Marcell (MN)	199.20	11.34														
	Average	181.57	10.37	22.40	26.20	32.10	3,770,048	1,525,718	52.4				0.059	0.069	0.085	105,303	232,194
Red River	Icelandic State Park (ND)	252.50	16.47	18.60	23.30	28.90	2,698,658	1,092,132	23.8				0.078	0.097	0.121	106,467	234,760
St. Croix River	Fond du Lac (MN)	165.71	10.65														
	Grindstone Lake (MN)	248.33	16.19														
	Cedar Creek (MN)	303.33	19.88														
	Average	239.13	15.58	23.70	30.60	37.60	680,145	275,251	30.1				0.094	0.121	0.149	33,322	73,474
TOTAL	All Sites Average	276.87	19.05				13,342,753	5,399,738					1.125	1.391	1.747	524,075	1,155,586

Note:

[1] National Atmospheric Deposition Program (NADP) monitoring sites that were used to derive estimates of phosphorus deposition for the basin.

[2] Average volume weighted calcium concentration for the monitoring station's period of record; volume-weighted averages calculated by NADP.

[3] For reference sites (special study conducted at the Fernberg, Marcell, Camp Ripley, and Lamberton sites): phosphorus concentration used directly from the special study.

For auxiliary sites: the phosphorus concentration in rainfall is calculated per the following regression equation derived from the reference sites: $y = 0.0677x - 0.4586$ (y is Total Phosphorus in ug/L and x is NADP calcium in ug/L)

If more than one monitoring site is applied to a basin, then the average [P] in rainfall is used to derive the estimate of P deposition.

[4] 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).

[5a] Basin area is that part of the basin within the state's borders designated as "Water" or "Wetland" in the GIS database.

[5b] Hectares = acres / 2.471 [1 ha = 2.471 acres]

[6] Deposition calculation

[P] in rainfall x rainfall amount x basin area x unit conversion factors = P deposition (kg/yr) over basin

[P] deposition (kg/yr) over basin x (1/basin area) = P deposition kg/ha/yr

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

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

Table 5
Estimated Dry Phosphorus Deposition to Minnesota Basins

Basin	XRF Station [1]	Total		Course Deposition Velocity [4]	Fine Deposition Velocity [4]	Course Deposition Rate [5]	Fine Deposition Rate [5]	Total Deposition [6]	Basin Waters and Wetland Area [7a]	Basin Waters and Wetland Area [7b]	% of Total Basin Land Area	Phosphorus Deposition to Waters and Wetlands (kg/yr)	Phosphorus Deposition to Waters and Wetlands (lb/yr)	
		Ca conc. [2] (ug/m3)	P conc. [3] (ug/m3)											
Cedar River	Albert Lea	1.355	0.039	3.0	0.5	0.215	0.026	0.241	24,523	9,924	3.7	2,390	5,270	
Des Moines River	Pipestone	0.386	0.011	3.0	0.5	0.061	0.007	0.069	53,771	21,761	5.5	1,493	3,293	
Lake Superior	Virginia (Site 7554)	0.603	0.017	3.0	0.5	0.096	0.012							
	Duluth - Lincoln Sch.	0.249	0.007	3.0	0.5	0.040	0.005							
	Silver Bay	0.241	0.007	3.0	0.5	0.038	0.005							
	Virginia (Site 1300)	0.216	0.006	3.0	0.5	0.034	0.004							
	Duluth - wdse radio	0.115	0.003	3.0	0.5	0.018	0.002							
	Hibbing	0.086	0.002	3.0	0.5	0.014	0.002							
	Average	0.252	0.007			0.040	0.005	0.045	1,312,101	531,000	33.3	23,753	52,376	
Minnesota River	North Mankato	0.740	0.021	3.0	0.5	0.117	0.014							
	Brandon Township	0.430	0.012	3.0	0.5	0.068	0.008							
	Granite Falls	0.395	0.011	3.0	0.5	0.063	0.008							
	Willmar	0.291	0.008	3.0	0.5	0.046	0.006							
	Swift County	0.284	0.008	3.0	0.5	0.045	0.005							
	Average	0.428	0.012			0.068	0.008	0.076	742,441	300,462	7.8	22,858	50,402	
Mississippi, Lower [8]	Rochester	0.659	0.019	3.0	0.5	0.105	0.013							
	Goodhue County	0.633	0.018	3.0	0.5	0.100	0.012							
	Apple Valley	0.445	0.013	3.0	0.5	0.071	0.009							
	Winona	0.344	0.010	3.0	0.5	0.055	0.007							
	Average	0.520	0.015			0.083	0.010	0.092	204,450	82,740	29.7	7,650	16,868	
Mississippi, Upper [9]	St. Paul - Red Rock Rd.	1.324	0.038	3.0	0.5	0.210	0.025							
	Minneapolis Library	0.729	0.021	3.0	0.5	0.116	0.014							
	St. Paul - ross ave	0.577	0.017	3.0	0.5	0.092	0.011							
	Bemidji	0.394	0.011	3.0	0.5	0.062	0.008							
	Minneapolis - river parkway	0.350	0.010	3.0	0.5	0.056	0.007							
	St. Paul - Harding High Sch.	0.346	0.010	3.0	0.5	0.055	0.007							
	Minneapolis	0.308	0.009	3.0	0.5	0.049	0.006							
	Elk River	0.298	0.009	3.0	0.5	0.047	0.006							
	Fort Ripley	0.272	0.008	3.0	0.5	0.043	0.005							
	Alexandria	0.254	0.007	3.0	0.5	0.040	0.005							
	Hutchinson	0.243	0.007	3.0	0.5	0.039	0.005							
	St. Cloud	0.239	0.007	3.0	0.5	0.038	0.005							
	St. Michael	0.236	0.007	3.0	0.5	0.037	0.005							
	Grand Rapids	0.201	0.006	3.0	0.5	0.032	0.004							
	Little Falls	0.160	0.005	3.0	0.5	0.025	0.003							
	Average	0.395	0.011			0.063	0.008	0.070	3,826,925	1,548,735	5.1	108,811	239,928	
Missouri	Pipestone	0.386	0.011	3.0	0.5	0.061	0.007	0.069	29,691	12,016	2.6	825	1,818	
Rainy River	Warroad	0.382	0.011	3.0	0.5	0.061	0.007							
	I Falls	0.103	0.003	3.0	0.5	0.016	0.002							
	Average	0.243	0.007			0.038	0.005	0.043	3,770,048	1,525,718	52.4	65,761	145,003	
Red River	Fergus Falls	0.683	0.020	3.0	0.5	0.108	0.013							
	Moorhead High School	0.678	0.020	3.0	0.5	0.107	0.013							
	Perham	0.499	0.014	3.0	0.5	0.079	0.010							
	Average	0.620	0.018			0.098	0.012	0.110	2,698,658	1,092,132	23.8	120,376	265,430	
St. Croix River	West Lakeland	0.204	0.006	3.0	0.5	0.032	0.004							
	Pine County - sandstone	0.111	0.003	3.0	0.5	0.018	0.002							
	Average	0.158	0.005			0.025	0.003	0.028	680,145	275,251	30.1	7,711	17,002	
TOTAL								0.843	13,342,753	5,399,738		361,629	797,391	
Note:														
[1]	MPCA's Statewide Air Toxics Monitoring Study (XRF) monitoring sites that were used to derive estimates of phosphorus deposition for the basin.													
[2]	Average calcium concentration for the monitoring station's period of study (1996 to 2001).													
[3]	Phosphorus concentrations were calculated using the calcium to phosphorus correlation in wet deposition from the special study conducted at the Fernberg, Marcell, Camp Ripley, and Lamberton sites.													
[4]	Dry deposition was assumed to contain the same chemical composition as wet deposition. The phosphorus concentrations were calculated per the following regression equation $y = (0.0289x)$													
[4]	If more than one monitoring site is applied to a basin, then the average [P]concentration for all of the sites in the basin is used to derive the estimated P concentration.													
[5]	The deposition velocities are based on recent estimates for phosphorus deposition in Florida and personal communications with Tilden Meyers, NOAA, Oak Ridge National Laboratory.													
[5]	Course deposition calculation													
	[P] concentration x PM10 course size fraction in percent x course deposition velocity x unit conversion factors = Course P deposition (kg/ha/yr) over basin.													
	The PM10 course size fraction (>2.5) was calculated to be 58% of the total PM10. PM10 size fraction was calculated from the five monitoring site in Minnesota that have co-located PM2.5 and PM10 monitors.													
[5]	Fine deposition calculation													
	[P] concentration x PM10 fine size fraction in percent x fine deposition velocity x unit conversion factors = Fine P deposition (kg ha ⁻¹ yr ⁻¹) over basin.													
	The PM10 fine size fraction (<2.5) was calculated to be 42% of the total PM10. PM10 size fraction was calculated from the five monitoring site in Minnesota that have co-located PM2.5 and PM10 monitors.													
[6]	Total deposition = sum of course deposition rate and fine deposition rate.													
[7a]	Basin area is that part of the basin within the state's borders designated as "Water" or "Wetland" in the GIS database.													
[7b]	Hectares = acres / 2.471 (1 ha = 2.471 acres)													
[8]	Lower Mississippi is that part of the Mississippi downstream of where the St.Croix River merges with the Mississippi.													
[9]	Upper Mississippi is that part of the Mississippi upstream of where the St.Croix River merges with the Mississippi.													

TOTAL P Deposition

Estimates of average “total” (wet + dry) phosphorus deposition range from $\sim 0.102 \text{ kg ha}^{-1} \text{ yr}^{-1}$ in the Rainy River basin (dry year) to $0.513 \text{ kg ha}^{-1} \text{ yr}^{-1}$ in the Cedar River basin (wet year) (Table 6). The largest phosphorus loading of $\sim 299,044 \text{ kg/yr}$ is found in the Upper Mississippi basin.

As noted in Table 6, 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 6 use the same dry deposition value, which adds uncertainty to the deposition estimates and therefore the results from Table 6 should be used cautiously.

Table 6
Estimated Total Phosphorus Deposition to Minnesota Basins

													Waters and Wetland Basin Loading Estimate					
			Dry Year			Average Year		Wet Year					Dry Year	Average Year	Wet Year			
Low		Average		High		Total	Total	Total	Total				Total	Total	Total			
Basin	Precipitation	Precipitation	Precipitation	Dry	(wet+dry)	(wet+dry)	(wet+dry)	Basin Waters	Basin Waters	Basin	(wet+dry)	(wet+dry)	Phosphorus	Phosphorus	Phosphorus	Phosphorus	Phosphorus	
Deposition	Deposition	Deposition	Deposition	Deposition	Deposition	Deposition	Deposition	and Wetland Area	and Wetland Area	Land Area	Deposition	Deposition	Deposition	Deposition	Deposition	Deposition	Deposition	
	[1]	[1]	[1]	[2]	[3a]	[3b]	[3c]	[4a]	[4b]	[5]	[6a]	[7]	[6b]	[7]	[6c]	[7]		
	(kg ha ⁻¹ yr ⁻¹)	(acres)	(hectares)		(kg/yr)	(lb/yr)	(kg/yr)	(lb/yr)	(kg/yr)	(lb/yr)								
Cedar River	0.1815	0.2118	0.2725	0.2408	0.4223	0.4526	0.5133	24,523	9,924	3.7	4,191	9,241	4,492	9,905	5,095	11,233		
Des Moines River	0.1452	0.1848	0.2428	0.0686	0.2138	0.2534	0.3114	53,771	21,761	5.5	4,652	10,258	5,514	12,158	6,777	14,944		
Lake Superior	0.0765	0.0873	0.1053	0.0447	0.1212	0.1320	0.1501	1,312,101	531,000	33.3	64,382	141,962	70,118	154,610	79,677	175,689		
Minnesota River	0.1458	0.1854	0.2296	0.0761	0.2219	0.2615	0.3057	742,441	300,462	7.8	66,672	147,011	78,567	173,240	91,850	202,529		
Mississippi, Lower [8]	0.1253	0.1545	0.1847	0.0925	0.2177	0.2470	0.2771	204,450	82,740	5.1	18,016	39,725	20,435	45,058	22,930	50,561		
Mississippi, Upper [9]	0.0809	0.1006	0.1228	0.0703	0.1512	0.1709	0.1931	3,826,925	1,548,735	29.7	234,154	516,309	264,658	583,570	299,044	659,391		
Missouri River	0.1392	0.1795	0.2349	0.0686	0.2079	0.2481	0.3035	29,691	12,016	2.6	2,497	5,507	2,981	6,573	3,647	8,042		
Rainy River	0.0590	0.0690	0.0846	0.0431	0.1021	0.1121	0.1277	3,770,048	1,525,718	52.4	155,792	343,520	171,065	377,197	194,778	429,485		
Red River	0.0778	0.0975	0.1209	0.1102	0.1880	0.2077	0.2311	2,698,658	1,092,132	23.8	205,367	452,835	226,843	500,190	252,432	556,613		
St. Croix River	0.0938	0.1211	0.1488	0.0280	0.1218	0.1491	0.1768	680,145	275,251	30.1	33,518	73,908	41,032	90,476	48,655	107,284		
State Wide Totals								13,342,753	5,399,738		789,241	1,740,277	885,704	1,952,977	1,004,885	2,215,770		
Note:																		
[1] The phosphorus deposition rates from dry, average and wet precipitation volumes. 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). See Table 4 for calculation methods.																		
[2] Includes coarse and fine dry deposition, See Table 5 for calculation methods. Calculations assumed to be for an "average" precipitation year. There is insufficient information to estimate deposition for a dry or wet year; therefore, dry deposition is only estimated for what is assumed to be an "average" year.																		
[3a] Total deposition = low precipitation phosphorus deposition + dry deposition																		
[3b] Total deposition = average precipitation deposition + dry deposition																		
[3c] Total deposition = high precipitation phosphorus deposition + dry deposition																		
[4a] Basin area is that part of the basin within the state's borders designated as "Water" or "Wetland" in the GIS database. Surface water included open water, woody wetlands and emergent herbaceous wetlands as defined by the USGS National Landcover database (~1992). This is a landsat based raster data set developed by the USGS with a minimum mapping unit of 30 meters.																		
[4b] Hectares = acres / 2.471 [1 ha = 2.471 acres]																		
[5] The percentage of the total land area within a river basin that is designated as water or wetland surface water.																		
[6a] The total phosphorus deposition rate to the basin water or wetland surface waters. The low precipitation deposition rate + dry deposition rate was used to calculate this total.																		
[6b] The total phosphorus deposition rate to the basin water or wetland surface waters. The average precipitation deposition rate + dry deposition rate was used to calculate this total.																		
[6c] The total phosphorus deposition rate to the basin water or wetland surface waters. The high precipitation deposition rate + dry deposition rate was used to calculate this total.																		
[7] Pounds = kilograms x 2.205 [1 kg = 2.205 lb]																		
[8] Lower Mississippi is that part of the Mississippi downstream of where the St.Croix River merges with the Mississippi.																		
[9] Upper Mississippi is that part of the Mississippi upstream of where the St.Croix River merges with the Mississippi.																		

Phosphorus Loading Variability and Uncertainty

Variability in the Data

Wet Deposition

- Annual average precipitation was used to estimate wet phosphorus deposition. 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.

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 four “reference” NADP sites used for the phosphorus-in-precipitation study, and the auxiliary NADP sites, are assumed to be representative for the various basins where they have been assigned. However, there is some uncertainty as to the representativeness of some monitoring sites to specific basins. For example, the Lamberton monitoring site is assumed to be representative for all of southwest Minnesota, including the Minnesota River basin which encompasses a large area from the

western border to where it joins the Mississippi River near the Twin Cities. We believe the application of the Lamberton monitoring site data to most of southwestern Minnesota is appropriate, but it does introduce some uncertainty into the calculations due to the large area of the state that is represented by this one monitoring site.

- Wet phosphorus deposition may be underestimated for the Red River basin due to the use of [Ca] in precipitation data from Icelandic State Park, North Dakota, which is on the west side of the Red River Valley. A station on the east side of the Red River Valley may have higher [Ca] in precipitation concentrations than Icelandic State Park due to prevailing winds carrying more dust from the valley to a monitoring site on the east side of the valley. We are not sure this is the case, but the location of Icelandic State Park on the west edge of the Red River valley introduces some uncertainty into the estimate for this basin.

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). However, in this application, it was assumed that the MPCA's air toxics monitoring sites were representative of large areas (i.e., the basins in which they were located or to where they were assigned) because they provide an estimate of ambient air PM10 concentrations as opposed to actually measuring dry deposition. There is some uncertainty associated with this assumption because it is possible that the PM10 and Ca concentrations measured on the filters are due to unique local factors that may not occur on a wide scale or in other parts of a river basin. In this case dry deposition could be under-or -overestimated for a specific river basin. The estimates of dry phosphorus deposition may also be under-or-overestimated by applying data collected from population centers to rural areas. The working assumption is that the factors resulting in PM10 and Ca concentrations at the monitoring sites occur on a wide scale or in other parts of the river basin. Again, there is uncertainty in this assumption.
- The relationship of [P] and [Ca] found in precipitation was assumed to be applicable to the particle (PM10) data and the [P] and [Ca] on the filters would be in a similar ratio as found in the precipitation. Currently there are no data supporting this assumption and therefore this assumption adds to the uncertainty in the estimate of dry deposited phosphorus.

Recommendations for Future Refinements

The following recommendations are made to 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 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 identify significant differences in the [P] and [Ca] relationship due to regional differences, and further improve the ability to extrapolate the findings to other locations 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. Analysis of the collected PM10 filters using an appropriate analytical method to determine phosphorus concentrations and use this data to determine if the [P] and [Ca] relationship on the filters is similar to, or different from, the [P] and [Ca] relationship in precipitation.
5. 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.
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.

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.

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From: Cliff Twaroski and Ron Reding
Subject: Detailed Assessment of Phosphorus Sources to Minnesota Watersheds – Atmospheric Deposition
Date: November 25, 2003
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Northern one-half to one-third of MN:	15 kg/km ² ·yr ⁻¹
Central:	30+ kg/km ² ·yr ⁻¹
Southern part of MN with wind erosion:	30 – 40 kg/km ² ·yr ⁻¹

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 included 4 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

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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°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 °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 °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 (KH₂PO₄) that has been dried for one hour at 105 °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 (KNO₃) 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 μ g P/L. Allowable recoveries for check standards were +/- 10% with some exceptions of the low TP check standard of 5.0 μ g P/L. Since the detection limit of the Total Phosphorus method is close to 5.0 μ g 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 μ g 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 μ g 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 μ g 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 autoanalyzer (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:

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

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 (PO₄³⁻) 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:

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

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 H₂SO₄ 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 blown 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 ($Y = 84.5 + 16.2 * X$, $R^2 = .56$) 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 °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 H₂SO₄ to each bottle, cap tightly, and shake to mix. Place loosely capped bottles back into autoclave for an additional 30 min at 121 °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 (K₂S₂O₈) in approximately 900 mL of DI reagent grade water. When dissolved, bring to volume.

11 N Sulfuric Acid (H₂SO₄)

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 (KH₂PO₄) 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 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 NO₃⁻

To a 1-L volumetric, dissolve 1.444 g potassium nitrate (KNO₃) 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 °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 1 st Valve		
Load Period		

LACHAT REAGENTS

PHOSPHORUS MANIFOLD

Stock Ammonium Molybdate Solution

To a 1-L volumetric, dissolve 40.0 g ammonium molybdate tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ 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 $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot 1/2\text{H}_2\text{O}$) 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 $(\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na})$. 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 ($\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$) 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