



Technical Memorandum

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Subject: Assessment of Bioavailable Fractions of Phosphorus and Annual Phosphorus Discharge for Each Major Basin

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The purpose of this memorandum is to provide a discussion about the bioavailable phosphorus fraction of individual point and nonpoint sources of phosphorus. This discussion is based on a review of the available literature, results of POTW-specific and basin-specific sampling and analysis, and the results of basin-specific total and bioavailable phosphorus annual discharge calculations. This memorandum is intended to:

- Provide an introduction to the forms of phosphorus in the aquatic environment.
- Describe the results of the literature review for each category of point and nonpoint sources.
- Present the results of POTW-specific and basin-specific sampling and analysis for bioavailable phosphorus.
- Compare and summarize estimates of bioavailable phosphorus fraction for each source type.
- Describe methods used for developing estimates of annual phosphorus discharge for each of Minnesota's major watershed basins.
- Present the results of the basin-specific annual discharge calculations.
- Discuss the uncertainty of the bioavailable phosphorus fraction estimates and basin-specific discharge calculations.
- Provide recommendations for future refinements of bioavailable phosphorus fraction estimates and basin-specific discharge calculations.

Introduction to Forms of Phosphorus in the Aquatic Environment

Under natural conditions, phosphorus is typically scarce in the aquatic environment. Human activities, however, have resulted in excessive loading of phosphorus into many freshwater systems. A portion of the total phosphorus concentration in surface waters is available to plants to support their growth. The available portion is commonly called bioavailable phosphorus. Excess bioavailable phosphorus in freshwater systems can result in accelerated plant growth. Phosphorus is the principal nutrient causing excessive growth of algae and other aquatic plants in Minnesota's surface waters.

Phosphorus exists in water in either a dissolved phase or a particulate phase. Dissolved phosphorus is operationally-defined as passing a 0.45 μm filter. Dissolved phosphorus in natural waters is usually found in the form of phosphates (PO_4^{-3}). Dissolved phosphates exist in three forms: inorganic (commonly referred to as orthophosphate or soluble reactive phosphorus- SRP), inorganic polyphosphate (or metaphosphate) and organically bound phosphate. Particulate phosphorus contains phosphorus sorbed to inorganic (mineral) and organic particles, including phosphorus contained within algae. Dissolved inorganic phosphate (orthophosphate) is the form required by plants for growth. Animals can utilize either organic or inorganic phosphate. The analytical procedure for measuring total phosphorus, which includes a sulfuric acid extraction, accounts for all forms of phosphorus, both dissolved and particulate, including phosphorus contained in algae.

Orthophosphates are immediately available in the aquatic environment for algal uptake. Natural processes produce orthophosphates, but major man-influenced sources include: partially treated and untreated sewage; runoff from agricultural sites; and application of some lawn fertilizers.

Orthophosphate concentrations in a water body vary widely over short periods of time as plants take it up and release it.

Polyphosphates are used for treating boiler waters and in detergents. Also, polyphosphates are used in drinking water treatment in many municipalities. In water, polyphosphates are unstable and will eventually convert to orthophosphate and become available for plant uptake.

Organic phosphates (particulate and dissolved) are bound or tied up in plant or animal tissue, waste solids, or associated with other organic matter. Organic phosphates are formed primarily by biological processes. They are contributed to sewage by body waste and food residues, and also may be formed from orthophosphates in biological treatment processes or by receiving water biota. After

decomposition, the organic form can be converted to orthophosphate as a result of microbially-induced mineralization of phosphorus-containing organic matter.

Not all forms of phosphorus are utilized to the same degree or at the same rate by plants and microbial communities. Association of phosphorus with particulate or organic matter reduces bioavailability; such forms of phosphorus are immediately unavailable for uptake by algae. While a significant amount of phosphorus can enter water bodies in an immediately unavailable form, there is the potential for this unavailable phosphorus to undergo physical or chemical cycling process that may convert it (all or partially) to the readily bioavailable form of phosphorus, orthophosphate. For example, the decomposition of organic matter by microbial activities can result in mineralization of phosphorus to orthophosphate. Desorption or dissolution of particle-associated phosphate represents another mechanism of conversion from unavailable to bioavailable forms.

In an assessment of the biological effects of phosphorus, it is important to consider the rate at which unavailable forms of phosphorus become bioavailable within the receiving waters. This is true, since the rate of conversion of unavailable but potentially-bioavailable phosphorus to readily bioavailable phosphorus competes in time with the rate of other processes, for example: adsorption; precipitation; sedimentation; and dilution. Though readily bioavailable phosphorus, orthophosphate, is directly responsible for plant growth, total phosphorus is an equally important indicator of a water body's nutrient status because of these internal cycling processes.

DePinto *et al.* (1986) characterized phosphorus into three forms: orthophosphate – immediately bioavailable for algal uptake; external ultimately-available phosphorus – not immediately available but ultimately converted to orthophosphate at a specific rate; and external refractory phosphorus – not available while in the water column. Total bioavailable phosphorus is then comprised of orthophosphate and the external ultimately-available phosphorus. It is indeed the bioavailable phosphorus that affects the algal production in the aquatic environment in combination with other nutrients (e.g. nitrogen and silicon), light, and temperature. Methodologies for the analysis of the bioavailable phosphorus content of water samples are presented in Attachment A.

Within the aquatic environment, plants, algae, and animals take in orthophosphate and convert it to organic phosphorus as it becomes part of their tissues. After algal death, the phosphorus associated with the minimum cell quota becomes unavailable and the phosphorus that is in excess of internal

level becomes readily bioavailable (Bierman *et al.*, 1980). The unavailable form can remain in water or can settle to the bottom, where bacterial decomposition converts it back to inorganic phosphorus. This inorganic phosphorus re-enters the water column when the bottom gets stirred up by animals, chemical interactions, and water currents. Then it is taken up by plants and the cycle begins again.

Bioavailable Phosphorus Fractions in Individual Point and Nonpoint Sources of Phosphorus

Different sources provide water bodies with a variety of the forms of phosphorus described above, in variable proportions. Phosphorus in lakes and streams comes from both point and nonpoint sources. Point sources are typically publicly-owned wastewater treatment plants (POTWs) and permitted industrial discharges. Point sources usually have distinct pipe discharges to surface water and are regulated under state and federal water pollution permit programs. Phosphorus discharged from wastewater treatment plants may come into the plant from a variety of sources. Nonpoint sources are typically polluted runoff from cities and farmland, erosion and sedimentation, atmospheric deposition, direct input by animals and wildlife, and natural decomposition of rocks and minerals. Nonpoint sources do not have distinct discharge points and are not typically regulated under State water pollution permit programs.

A comprehensive literature search and review was conducted to compile available information on the bioavailable phosphorus fractions of individual point and nonpoint sources of phosphorus to surface waters. The results of this literature review are presented in the following discussion.

Bioavailable Phosphorus in POTW Effluent

The bioavailable phosphorus fraction in POTW effluent is generally assumed to be high compared to that of other sources to surface waters (Lee *et al.*, 1980). Young *et al.* (1982) sampled the effluent from four municipal treatment plants in the vicinity of the Great Lakes during the summer of 1979 for bioavailable phosphorus. They conducted bioassays where measurement of phosphorus taken up by *Scenedesmus* sp. provided the measure of bioavailable phosphorus fraction. They developed a series of relationships among different forms of phosphorus. The following is a summary of those relationships.

On average, 82% of the dissolved phosphorus was bioavailable in the short term (less than 30 days from sample collection). The relationship was:

$$BADP = 0.82 TDP - 0.03$$

where: *BADP* is the bioavailable dissolved phosphorus and *TDP* is the total dissolved phosphorus.

Orthophosphate was a major component of the dissolved phosphorus (69% on average). Moreover, the regression coefficient relating bioavailable dissolved phosphorus to orthophosphate was unity, indicating that the orthophosphate fraction was totally available.

For particulate phosphorus, they found that the bioavailable particulate phosphorus correlated closely with the total particulate phosphorus fractions. On average (with the samples taken from the effluent of the four wastewater treatment plants), 55% of the total particulate phosphorus was bioavailable in the short term (again, less than 30 days). The relationship was:

$$BAPP = 0.55 TPP + 0.02$$

where: *BAPP* is the bioavailable particulate phosphorus and *TPP* is the total particulate phosphorus.

The relationship between the ultimately bioavailable dissolved phosphorus (became bioavailable after 30 days) and total dissolved phosphorus was:

$$UADP = 0.99 TDP - 0.04$$

where: *UADP* is the ultimately bioavailable dissolved phosphorus and *TDP* is the total dissolved phosphorus.

The relationship between the ultimately bioavailable particulate phosphorus and total particulate phosphorus was:

$$UAPP = 0.63 TPP + 0.013$$

where: *UAPP* is the ultimately bioavailable particulate phosphorus and *TPP* is the total particulate phosphorus. This relationship was obtained when bioavailable phosphorus

was regressed on total particulate phosphorus for raw influent, biological effluent, and final effluent of the wastewater treatment plants.

The relationship between the ultimately available phosphorus and total phosphorus was:

$$UAP = 0.83 TP + 0.035$$

where: *UAP* is the ultimately available phosphorus and *TP* is the total phosphorus.

Data from the wastewater treatment plants indicated that 83% of the total wastewater phosphorus in those effluent samples was ultimately available.

Results of Bioavailable Phosphorus Sampling of Minnesota POTWs

In addition to the information gathered from the literature review, effluent from eight Minnesota POTWs was sampled between October 13 and October 17, 2003. Grab samples were collected by Barr Engineering with facilitation from the MPCA. The samples were analyzed for total phosphorus and orthophosphate. The ultimately bioavailable particulate phosphorus was estimated using the relationship developed by Young *et al.* (1982) described above.

The results of this analysis are presented in Table 1. The bioavailable phosphorus fraction in these samples ranged from 75-96%, with an average of 85.5%, which is typical for POTW effluents based on the results of the literature review. Measured particulate phosphorus concentrations also are consistent with expected range based on the literature. Chemical and biological phosphorus removal is implemented at all of these POTWs with the exception of Albert Lea and Wilmar. Albert Lea and Wilmar also have industrial discharges to the POTW that contain high phosphorus levels.

Table 1: Estimated bioavailable phosphorus (BAP) fractions of samples collected from the final effluent of eight Minnesota POTWs.

City	TSS (mg/L)	Total P (mg/L)	Orthophosphate (mg/L)	Particulate P (mg/L)	Ultimately Bioavailable Particulate P (mg/L) [0.63TPP+0.013]	Particulate BAP fraction	Total BAP fraction
Albert Lea	<5.0	5.32	4.31	1.01	0.65	0.64	0.93
Alexandria	<5.0	0.187	0.102	0.085	0.07	0.78	0.90
St. Cloud	<5.0	0.250	0.068	0.182	0.13	0.70	0.78
Fergus Falls	<5.0	0.166	0.019	0.147	0.11	0.72	0.75
Mankato	11	2.04	1.57	0.47	0.31	0.66	0.92
MCES-Metro	<5.0	0.293	0.130	0.163	0.12	0.71	0.84
Rochester	13	0.948	0.286	0.662	0.43	0.65	0.76
Wilmar	10	7.24	6.41	0.83	0.54	0.65	0.96

Bioavailable Phosphorus in Runoff

The contribution of phosphorus from nonpoint sources of runoff has rarely been clearly defined, largely because point sources are often the major and more controllable source of phosphorus loads (Sharpley *et al.*, 2000). In addition, phosphorus losses in land runoff are difficult to quantify due to their diffuse nature. The transfer of phosphorus from terrestrial to aquatic systems in runoff can occur in dissolved and particulate forms. Phosphorus loading from nonpoint sources depends on a large number of factors, such as geology and hydrology of the region, land use, and population density. For example, sandy soils have less retention of phosphorus than clays and high slope and high runoff lead to lower retention.

Caraco (1995) found that population density was related to orthophosphate export from watersheds and predicted 47% of the variation in orthophosphate export in the dataset from 32 large rivers. Other variations could be related to the geochemical factors that alter orthophosphate in rivers or could be due to variability in human behaviors that lead to variable phosphorus export. For example, human agricultural practices, soil composition, diets, detergent use, and extent of sewer services and sewage treatment can vary greatly between different areas. Phosphorus loss from land not only affects the surface runoff, but also gets transferred in subsurface flow (Gaynor and Findley, 1995; Lennox *et al.*, 1997; Haygarth *et al.*, 1998; and Withers *et al.*, 1999).

It has been shown that the orthophosphate concentration in surface runoff is related to the soil phosphorus concentration in the topsoil (McDowell and Sharpley, 2001). For example, Pote *et al.* (1996) found that the orthophosphate concentration in surface runoff was linearly related to phosphorus extracted by Mehlich-3 (r^2 of 0.72), Bray-I (r^2 of 0.75), Olsen (r^2 of 0.72), distilled water (r^2 of 0.82), iron oxide paper (r^2 of 0.82), acidified ammonium oxalate (r^2 of 0.85), and phosphorus sorption saturation (r^2 of 0.77).

Surface runoff from grassland, forest land or nonerosive soils carries little sediment and is generally dominated by dissolved phosphorus, although phosphorus transport attached to colloidal material also may be important where land is overstocked (Haygarth and Jarvis, 1997; Simrad *et al.*, 2000). Sharpley *et al.* (1995) also reported that runoff from grass and forestland carries little sediments, and is therefore, generally dominated by orthophosphate.

As reported by Sharpley *et al.* (1995), the discharge of organic and inorganic phosphorus in runoff from several Atlantic Coastal Plain watersheds was related to soil phosphorus composition. The high organic phosphorus content of forest soils (331 mg/kg; 70% of total phosphorus) contributed 51% of total phosphorus loss in runoff (0.31 kg/ha/y) as particulate organic phosphorus and 10% as dissolved organic phosphorus. For agricultural soils of lower organic phosphorus content (161 mg/kg, 25% of total phosphorus), only 32% of total phosphorus loss in runoff (2.41 kg/ha/y) was particulate organic phosphorus and 1% was dissolved organic phosphorus (Vaithyanathan and Correll, 1992). Similarly, from 16 to 38% of phosphorus in runoff from Polish meadows and cultivated fields and as much as 70% of lake water phosphorus was bound to organic compounds (Szpakowska and Zyczynska-Baloniak, 1989). These losses varied seasonally, with both inorganic and organic phosphorus concentrations in canal and lake water decreasing during summer months (Ryszkowski *et al.*, 1989).

Estimates for urban runoff particulates, tributary particulates and lake sediments in the lower Great Lakes basins by bioassay methods have reported an average of 30% bioavailable phosphorus (Cowen and Lee, 1976; Williams *et al.*, 1980).

Bioavailable Phosphorus in Agricultural Runoff

The sources of phosphorus from agricultural land can include soil phosphorus, manure or fertilizer applications. Those sources of phosphorus emanate from a number of source areas within the landscape and their amount, form, and timing are very variable as a result of short-term and often

unpredictable changes in hydrological conditions and farming practices, including crop rotation, the application of fertilizers and manures, or the movement of animals from one field to another (Lennox *et al.*, 1997).

Phosphorus may be transported to a water body from agricultural lands by leaching, runoff or erosion. The loss of phosphorus in surface runoff from agricultural lands occurs as particulate and dissolved forms (Haygarth and Sharpley, 2000). Particulate phosphorus includes phosphorus associated with soil particles and large molecular-weight or organic matter eroded during flow events and constitute the major proportion of phosphorus transported from most cultivated lands (60-90%, Pietilainen and Rekolainen, 1991).

Several studies have reported that the loss of dissolved phosphorus in surface runoff from agricultural land depends on the phosphorus content of surface soil (STP- soil test P concentration), but that the relationship varies with soil type, tillage, and crop management (Pote *et al.*, 1996; Sharpley *et al.*, 1996). Moreover, it will depend on the topography and soil hydrology.

James *et al.* (2002) used fractionation procedures and phosphorus adsorption-desorption assays to delineate bioavailable forms and refractory or unavailable forms of phosphorus in the runoff of the Redwood River basin, an agriculturally-dominated tributary of the Minnesota River. Over several storm periods monitored in 1999, 75% of the phosphorus load originating from the watershed was in bioavailable forms while only 25% was in refractory forms. Bioavailable particulate forms included phosphorus loosely bound to suspended sediments (19%), phosphorus bound to iron (11%), and bioavailable particulate organic phosphorus (14%). After runoff discharges to receiving waters, the former two forms of bioavailable particulate phosphorus can be transformed to dissolved forms that are available to biota for uptake via eH and pH reactions and kinetic processes, while the latter form can be mineralized via decomposition processes. Bioavailable dissolved forms included orthophosphate and dissolved organic phosphorus.

Several studies have suggested that agricultural management may influence the bioavailability of phosphorus transported in runoff (McDowell and McGregor, 1980; Wendt and Corey, 1980). Concentration and amounts of bioavailable phosphorus in runoff from corn (*Zeamays* L.) were lower from no till compared to conventionally tilled plots under simulated rainfall (Andraski *et al.*, 1985; Mueller *et al.*, 1984). Bioavailable phosphorus in these studies was measured by resin extraction of

unfiltered runoff, and thus includes dissolved phosphorus plus phosphorus desorbed from sediment (Huettl *et al.*, 1979). However, Andraski *et al.* (1985) calculated that bioavailable phosphorus averaged 20% of total phosphorus and was not affected by tillage treatment.

Sharpley *et al.* (1992) assessed the impact of agricultural practices on phosphorus bioavailability in runoff by determining dissolved phosphorus, bioavailable particulate phosphorus, and particulate phosphorus in runoff from 20 watersheds (in the Southern Plains region of Oklahoma and Texas) unfertilized and fertilized, grassed and cropped watersheds over a 5-yr period. Although bioavailable phosphorus and bioavailable particulate phosphorus losses in runoff were reduced by agricultural practices minimizing runoff and erosion, the proportion of phosphorus transported in bioavailable forms increased. Both total phosphorus (14-88% as bioavailable phosphorus) and particulate phosphorus (9-69% as bioavailable particulate phosphorus) bioavailability varied appreciably with agricultural practices. Thus, bioavailable phosphorus is a dynamic function of physical and chemical processes controlling both dissolved phosphorus and bioavailable particulate phosphorus transport. Dissolved phosphorus transport depends on desorption-dissolution reactions controlling phosphorus release from soil, fertilizer reaction products, vegetative cover, and decaying plant residues. Bioavailable particulate phosphorus is a function of physical processes controlling soil loss and particle-size enrichment and chemical properties of the eroded soil material governing phosphorus sorption availability. The authors also found that the percent bioavailability of particulate phosphorus transported in runoff from each of these watersheds decreased with an increase in sediment concentration of runoff averaged for each watershed. They found a linear regression relationship between particulate phosphorus availability and logarithm of sediment concentration (with $r^2 = 0.84$):

$$\text{Particulate Phosphorus Bioavailabilty (\%)} = 82 - 15 \log \text{ sediment conc. (g / L)}$$

This relationship may be attributed to an increased transport of silt- and sand-sized ($>2 \mu\text{m}$) particles, of lower phosphorus content than finer clay-sized ($<2 \mu\text{m}$) particles, as sediment concentration of runoff increases. Further, particulate phosphorus bioavailability may decrease with an increase in size of eroded soil particles, which contain less sorbed phosphorus and more primary mineral phosphorus (i.e., apatite) of lower availability compared with finer clay-sized particles (Dorich *et al.*, 1984; Sharpley *et al.*, 1981; Syers *et al.*, 1973).

O'Connor *et al.*, (2002) compared phosphorus bioavailability of biosolids, manures and fertilizer. They found that phosphorus bioavailability was greater for phosphorus-fertilizer than manures and biosolids. However, if biological phosphorus removal is implemented in the treatment process, phosphorus in biosolids tends to be as bioavailable (74% to 132%) as fertilizer phosphorus. Note that values greater 100% are a result of the uncertainty in the analytical methods used to measure phosphorus forms.

A study conducted by Ekholm and Krogerus (2003), with samples from different sources, concluded that phosphorus in agricultural runoff appeared to be more bioavailable to algae (31%) than phosphorus in forest runoff (16%).

Bioavailable Phosphorus in Atmospheric Deposition

The contribution of phosphorus in rainfall can play an important part in the phosphorus cycle of oligotrophic sites (Carlisle *et al.* 1966; Miller 1961). For Lake Michigan, Murphy and Doskey (1975) reported a 30-fold greater total phosphorus concentration in rainfall than in lake water. Since 25-50% of the total phosphorus in rainfall is soluble, it is directly available to organisms in the lake (Murphy and Doskey 1975; Peters 1977). As a result, most of the enrichment of Clear Lake, Ontario (Schindler and Nighswander 1970) and of several Wisconsin Lakes (Lee 1973) has been attributed to rainfall (Sharpley *et al.* 1995).

The bioavailability of dry deposition or the particulate fraction of wet deposition can be characterized by the bioavailability of phosphorus in the soils in the region.

Increases in the atmospheric deposition of phosphorus may result from annual climatic changes (Sharpley *et al.* 1995). For example, the input of phosphorus in rainfall to an Oklahoma watershed in 1981 (208 g/ha/yr) was much greater than that in either 1982 (49 g/ha/yr) or 1983 (41 g/ha/yr) (Sharpley *et al.* 1985). This increase was attributed to the low annual rainfall in 1980 (642 mm, 105 mm below average). The drier soil was more susceptible to wind erosion and the airborne material increased the phosphorus content of subsequent rainfall and dry deposition.

Comparison of Phosphorus Bioavailability from Different Sources

Many forms of particulate matter in the waters of the State of Minnesota contain a certain amount of bioavailable phosphorus, the actual rate and extent of release of the bioavailable component depends on the physical and chemical characteristics of the material. It also depends on the biological characteristics as well, as the population of the micro-organisms in the suspended material mineralizes the organic detritus material. Young *et al.* (1995) have compared the relative bioavailability of particulate phosphorus from various sources to the Great Lakes by comparing the bioavailable phosphorus in particulate matter from point sources (wastewater suspended solids), and nonpoint sources (suspended solids and bottom sediments from tributaries, lake bottom sediments, and eroding bluff solids from the region). A wastewater treatment plant at Ely, Minnesota was also sampled and it showed the highest rate of release of bioavailable particulate phosphorus (0.27 grams released/gram particulate phosphorus/day, or 0.27/day) among the point and nonpoint sources sampled in that study (Young and DePinto, 1982). The release rate did appear to decline in magnitude as treatment of wastewater progressed from the raw influent → biologically treated effluent → final effluent (i.e., 0.30 /day → 0.27 /day → 0.20 /day). Young and DePinto (1982) summarized the results on relative bioavailability of particulate phosphorus for the point and nonpoint sources (Table 2).

Table 2: Relative bioavailability of particulate phosphorus from various sources to the lower Great Lakes (Young and DePinto 1982)

<p>With respect to total particulate phosphorus:</p> <p>Wastewater (≤ 80%)</p> <p>Bottom sediments (≤ 50%)</p> <p>Tributary suspended sediment (≤ 40%)</p> <p>Eroding bluff (~0)</p>
<p>With respect to rate of release:</p> <p>Wastewater (≤ 0.4 /day)</p> <p>Tributary suspended sediment (≤ 0.2 /day)</p> <p>Bottom sediment (≤ 0.1 /day)</p> <p>Eroding bluffs (~ 0)</p>

Ekholm and Krogerus (2003) analyzed 172 samples (during 1990-2000) representing phosphorus in point and nonpoint sources and in lacustrine matter. The bioavailability of phosphorus expressed as the proportion of potentially bioavailable phosphorus ranged from 3.3 to 89% (Table 3).

Table 3: Proportion of bioavailable phosphorus in total phosphorus by different sources (Ekholm and Krogerus 2003).

Source	Bioavailable P (% of Tot-P)	
	Mean	Min.-Max.
Wastewater effluent from rural population	89	74-98
Biologically treated urban wastewater effluent	83	61-103
Dairy house wastewater	69	27-93
Biologically and chemically treated wastewater effluent	36	0-67
Field runoff	31	15-50
Industrial wastewater effluent	30	4-89
Fish fodder and feces	29	9-72
Large Rivers water	20	3-45
Agricultural rivers	20	12-30
Field surface soils	19	6.8-24
Forest runoff	16	0-55
Lake settling matter	7.9	1.6-21
Lake bottom sediments	3.3	0.1-11

Summary of Literature Review

The above review covers as much research and data from phosphorus bioavailability studies as could be found in the available time and resources. There is a desire to estimate the fraction of phosphorus in each potential source category identified by the MPCA as contributing phosphorus to Minnesota waters. However, the bioavailability of some of these individual source categories has not been studied; therefore, we were not able to find directly applicable estimates for bioavailable fractions in the literature. The general categories for which data are available include: municipal wastewater treatment plants, agricultural, forest and urban runoff, and atmospheric deposition.

While the dissolved phosphorus from any of these sources can generally be assumed to be 100% bioavailable, the particulate phosphorus associated with these various source categories in general exhibit a wide range of bioavailability.

For point sources, the fraction of total phosphorus in the discharge that is bioavailable is not only governed by the sources of phosphorus to the treatment plant influent (e.g., human wastes, household cleaners, groundwater infiltration, etc.) but it will be dependent on the treatment train being employed within the plant. Data are generally available for wastewater treatment plant influent and effluent, however not for all individual phosphorus source categories. Knowing, however, that household cleaners and detergents are amended with polyphosphates, it is reasonable to assume that virtually 100% of these categories will ultimately become available by hydrolysis to orthophosphates.

For nonpoint sources, the input of total phosphorus and bioavailable phosphorus will be strongly dependent on the land use from which the phosphorus load is derived (e.g., agricultural runoff will be different from forestland runoff). Furthermore, agricultural practices can affect bioavailable phosphorus appreciably. Another determinant is the surficial geology within the watershed. We have seen, for example, that phosphorus associated with calcareous minerals like apatite is much less bioavailable than phosphorus adsorbed to iron-oxide minerals. At any rate the particulate phosphorus in non-point sources derived from land runoff tends to be less bioavailable than point source particulate phosphorus.

Bioavailable phosphorus fractions for each of the specific source categories of interest were estimated by combining the results of the literature review with best professional judgment to specify a most likely value for a number of the phosphorus source categories listed by the MPCA as being of interest. A range was also estimated in an attempt to cover the potential range site-specific determinations might show. These estimates are presented in Table 4. These estimates of bioavailable fraction should be used with care, understanding the uncertainty inherent in each estimate. Nevertheless, they can be used to assess relative contributions of bioavailable phosphorus from the source categories to assist in planning additional data collection or targeting specific sources for control.

As evident from the literature review, wide ranges of bioavailable fractions were noted for runoff sources, while estimation techniques for the bioavailable fraction from POTW effluent were better quantified. Future refinements to the estimation of bioavailable fractions of various phosphorous sources would be benefited by additional sample collection and analysis to best represent the source of interest.

Table 4. Estimates of Bioavailable Phosphorus Fractions for Specific Source Categories.

Phosphorus Sources		Fraction of PP that is Bioavailable (Range)	Fraction of PP that is Bioavailable (Most Likely)	Fraction of DP that is Bioavailable (Most Likely)	Fraction of TP that is Particulate (Most Likely)	Estimate of TP that is Bioavailable (Most Likely)
Point Sources	Automatic Dishwasher Detergent	NA	NA	1.0	0.0	1.0
	Dentifrices (toothpastes)	0 – 0.1	0.05	NA	1.0	0.05
	Other Household Cleaners or Non-ingested Sources	NA	NA	1.0	0.0	1.0
	Food Soils/Garbage Disposal Wastes	0.7 – 0.9	0.8	1.0	0.9	0.8
	Human Waste Products	0.7 - 0.9	0.8	1.0	0.3	0.94
	Raw/Finished Water Supply	0.4 - 0.6	0.5	1.0	0.1	0.95
	Groundwater Intrusion (I&I)	0.2 - 0.5	0.3	1.0	0.5	0.65
	Process Water	0.2 - 1.0	0.7	1.0	0.1	0.97
	Noncontact Cooling Water	0.4 - 0.8	0.6	1.0	0.3	0.88
	Car Washes	0.2 - 0.8	0.5	1.0	0.3	0.85
	POTW Effluent	0.6 – 0.8	0.7	1.0	0.5	0.855
	Privately Owned Wastewater Treatment Systems for Domestic Use (effluent)	0.6 - 0.9	0.8	1.0	0.3	0.94
	Commercial/Industrial Wastewater Treatment Systems (effluent)	0.2 - 0.8	0.6	1.0	0.3	0.88

Phosphorus Sources		Fraction of PP that is Bioavailable (Range)	Fraction of PP that is Bioavailable (Most Likely)	Fraction of DP that is Bioavailable (Most Likely)	Fraction of TP that is Particulate (Most Likely)	Estimate of TP that is Bioavailable (Most Likely)	
Non-Point Sources	Individual Sewage Treatment Systems		0.6 - 0.9	0.8	1.0	0.2	0.96
	Agricultural Runoff	Improperly Managed Manure	0.5 - 0.7	0.6	1.0	0.5	0.80
		Crop Land Runoff	0.2 - 0.7	0.4	1.0	0.7	0.58
	Urban Runoff	Turfed Surfaces	0.2 - 0.7	0.4	1.0	0.7	0.58
		Impervious Surfaces	0.10 - 0.5	0.2	1.0	0.5	0.60
	Forested Land		0.2 - 0.5	0.3	1.0	0.8	0.44
	Roadway and Sidewalk Deicing Chemicals	salt	0.2 - 0.8	0.6	1.0	0.2	0.92
		sand	0.1 - 0.3	0.2	1.0	0.8	0.36
	Stream Bank Erosion		0.1 - 0.5	0.3	1.0	0.8	0.44
	Atmospheric Deposition	Dry	0.05 - 0.4	0.2	NA	1.0	0.2
		Wet	0.05 - 0.4	0.2	1.0	0.6	0.5

Basin-wide Annual Phosphorus Discharge Calculations

Basin-specific analyses of existing hydrologic and water quality data were conducted to develop estimates of the annual total and bioavailable phosphorus discharge for each of the major Minnesota surface water basins. All annual calculations were based on the water year (October-September). While these calculations do not provide direct information on the specific point and nonpoint sources contributing to each basin, they can be used in a number of ways: 1) provide a check on the sum of point and nonpoint phosphorus loads for each basin; 2) provide a relative comparison between basins of annual phosphorus loads, yields, and ambient surface water concentrations and compare to land uses in the basins; and 3) provide some initial understanding of the relative water quality benefits to be gained by phosphorus source controls.

Methodology

For each major basin, basin-specific characteristics and data were compiled and analyzed. This information included drainage area and approximate land cover percentages as presented in separate technical memorandums for this project. Land uses were taken from USGS National Land Cover Database (1992). Soil phosphorus content for each major basin was estimated from soil phosphorus data compiled by Dr. Mulla at the University of Minnesota, Department of Soil, Water and Climate. Bray phosphorus values for all counties except Anoka (no data available there) were available in GIS format. Bray-P values were converted to soil total phosphorus content using the following two-step conversion provided by Dr. Mulla:

To convert Bray-P to soil total phosphorus content:

$$\text{Olsen-P} = 0.7117 * (\text{Bray-P})$$

$$\text{Soil Total Phosphorus Content [mg/kg]} = 3.3173 * (\text{Olsen-P}) + 453.79$$

The conversion of Bray-P to total phosphorus is applicable on a state-wide basis. Soil total phosphorus content values were then area-weighted and used to calculate area-weighted average soil total phosphorus content for each major basin. The results of this analysis are presented in Table 5.

Table 5: Average soil phosphorus content for each Basin in Minnesota.

Major Basin	Area (sq. mi.)	Area-weighted Bray-P	Area-weighted Average Soil Total Phosphorus Content (mg/kg)
Cedar River	1,028	32.21	529.84
Des Moines River	1,535	23.04	508.18
Lake Superior	6,149	28.91	522.04
Lower Mississippi (Below St. Croix)	6,317	39.35	546.69
Minnesota River	14,933	24.37	511.33
Missouri	1,782	13.69	486.10
Rainy River	11,236	25.65	514.36
Red River	17,741	18.02	496.34
St. Croix River	3,528	41.19	551.03
Upper Mississippi (Above St. Croix)	20,100	29.70	523.90
Statewide	84,349	26.48	516.30

Representative USGS flow gauges were selected for each basin. These gauges are a subset of the gauges selected for analyses of hydrologic conditions, as presented in the Basin Hydrology Technical Memorandum. Flow rate and water quality data were compiled for these gauges. Water quality data available from the Minnesota Pollution Control Agency (MPCA) was also compiled for water quality sampling locations at or near the representative USGS gauging stations. This data included results of queries of the Environmental Data Access (EDA) database, available on-line and containing data for calendar years 1985-1992. MPCA queries of recent STORET data provided a third source of water quality data. Finally, data from the USGS Long Term Resource Monitoring Program (LTRMP) were compiled for stations in the Lower Mississippi basin. Parameters of interest included suspended sediment (analyzed as either suspended sediment concentrations (SSC)), total nonfilterable residue or total suspended solids (TSS)), total phosphorus (TP), and total dissolved phosphorus or orthophosphate (both assumed to represent total dissolved phosphorus (TDP) for this analysis). Water quality data collected from 1979 to the present were considered for use in these analyses.

When available data permitted, concurrent flow suspended sediment, total phosphorus, and total dissolved phosphorus data were plotted and a simple power function was fit to the data ($y=aQ^b$). While more complex methods are available for developing rating curves, the power function has proven to be an efficient means of relating suspended sediment and phosphorus concentrations to flow (Dolan *et al.*, 1981; Asselman, 2000; and Horowitz, 2002). Best professional judgment was used to determine whether the relationship was better represented by a simple average of the water quality parameter when the correlation coefficient for the fitted power function was very small (typically less than 0.1).

Following the development of rating curves for solids, total phosphorus, and total dissolved phosphorus, the fitted power equations, and in some cases simple averages, were applied to calculate concentrations for daily flow values for the water years identified as representing low, average and high flow conditions in each watershed. Particulate phosphorus was calculated as the difference between the total phosphorus and total dissolved phosphorus predictions. If sufficient total dissolved phosphorus or orthophosphate measurements had not been available to develop a rating curve, particulate phosphorus concentrations could have been estimated by multiplying the predicted suspended sediment concentration by the soil total phosphorus content for that basin, and then adjusting the resulting value with a potency factor. The potency factor is a site-specific calibration parameter accounting for such things as land use and agricultural practices.

When sufficient data was available for TP and TDP rating curves:

$$\text{Total Particulate Phosphorus (TPP)} = \text{TP} - \text{TDP}$$

When insufficient data for TDP rating curves:

$$\text{TPP} = \text{Suspended Sediment (SS)} * \text{Soil Phosphorus Content} * \text{Potency Factor (PF)}$$

Bioavailable fraction of particulate phosphorus was estimated based on the results of the literature review and the recent water quality data collected as part of this project. The literature review produced values ranging from 5% to 40% of suspended sediment particulate phosphorus being bioavailable (see Attachment B for more details). Between September 24, 2003 and October 21, 2003, MPCA, with facilitation from Barr, collected one 10-liter stream sample from each of the ten major watersheds and analyzed the samples using a base-extractable inorganic P testing procedure adapted from Young *et al.* (1988). The results of these analyses are presented in Table 6.

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These watershed-specific samples resulted in a range of 3%-31% of particulate phosphorus as bioavailable, consistent with the literature review results. Because a single sample from each watershed does not provide much certainty, a statewide average value of 18% was applied in the calculations.

Subsequent to calculating the solids and phosphorus concentrations and fractions bioavailable, the daily mass loading rates were calculated using flow and concentration and then summed over the water years of interest.

Table 6: Estimated BAP fractions of samples collected from ten Minnesota rivers.

Basin/Date/ Location/ID	Solids, total suspend ed (mg/L)	Phosphorus, total (mg/l)	Particulate Phosphorus (mg total P/g dry weight solids)	Orthophospha te (mg/L)	Particulate Phosphorus, NaOH Extractable (mg/l)	Particulate NaOH Extractable Phosphorus (mg of NaOH extractable P/g dry weight solids)	Bioavailable Particulate P (mg P/g) [[Ultimately avail PP = 1.08 NaOH -P-0.008]]	Bioavailable Particulate Phosphorus Fraction
Lake Superior Basin								
Date: 10/13/2003								
BRULE R UPSTRM OF US-61 AT JUDGE CR MAGNEY PARK								
BRU-0.4	<5.0	0.014		<0.006	--			
BRU-0.4	<100	0.185	2.8	--	0.012	0.106	0.11	0.038
Solids								
BRU-0.4	<100	0.149	2.25	--	0.007	0.063	0.06	0.027
Solids								
BRU-0.4	<100	0.169	2.55	--	0.007	0.063	0.06	0.024
Solids								
							Average =	3%
Cedar River Basin								
Date: 10/08/2003								
CEDAR RIVER AT CSAH-4, 3 MILES SOUTH OF AUSTIN								
CD-10	48	0.694		0.570	--			
CD-10 Solids	740	7.69	10.4	--	0.171	1.4	1.49	0.143
CD-10 Solids	830	7.71	9.3	--	0.217	1.6	1.69	0.182
CD-10 Solids	1300	7.47	5.7	--	0.435	2.0	2.16	0.376
							Average =	23%
Minnesota River Basin								
Date: 10/14/2003								
MINNESOTA R UNDER LANDING LIGHTS FT. SNELLING PK								
MI-3.5	18	0.124	--	0.037	--			
MI-3.5 Solids	1200	5.43	4.5	--	0.089	0.4	0.47	0.104
MI-3.5 Solids	1100	5.29	4.8	--	0.079	0.4	0.46	0.095
MI-3.5 Solids	1100	5.40	4.9	--	0.080	0.4	0.46	0.094
							Average =	10%

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Basin/Date/ Location/ID	Solids, total suspend ed (mg/L)	Phosphorus, total (mg/l)	Particulate Phosphorus (mg total P/g dry weight solids)	Orthophospha te (mg/L)	Particulate Phosphorus, NaOH Extractable (mg/l)	Particulate NaOH Extractable Phosphorus (mg of NaOH extractable P/g dry weight solids)	Bioavailable Particulate P (mg P/g) [[Ultimately avail PP = 1.08 NaOH -P-0.008]]	Bioavailable Particulate Phosphorus Fraction
Red River Basin								
Date: 10/12/2003								
OTTER TAIL R BRIDGE ON 4TH ST N AT BRECKENRIDGE								
OT-RIV	12	0.036	--	<0.006	--			
OT-RIV Solids	1400	1.61	1.2	--	0.073	0.3	0.33	0.287
OT-RIV Solids	1300	1.60	1.2	--	0.037	0.2	0.18	0.143
OT-RIV Solids	1300	1.62	1.2	--	0.037	0.2	0.18	0.142
							Average =	14%
Lower Mississippi River Basin								
Date: 09/24/2003								
ROOT RIVER AT BRIDGE ON MN-26 3 MI EAST OF HOKAH								
RT-3	15	0.054	--	0.037 h	--			
RT-3 Solids	1500	2.12	1.4	--	0.044	0.2	0.18	0.129
RT-3 Solids	1600	2.12	1.3	--	0.048	0.2	0.19	0.141
RT-3 Solids	1600	2.00	1.3	--	0.042	0.2	0.16	0.130
							Average =	13%
Lake Superior Basin								
Date: 10/13/2003								
ST LOUIS RIVER AT BRIDGE ON MN-23 AT FOND DU LAC								
SL-9	<5.0	0.029	--	0.006	--			
SL-9 Solids	190	0.508	2.7	--	0.024	0.8	0.81	0.303
SL-9 Solids	140	0.479	3.4	--	0.023	1.0	1.06	0.309
SL-9 Solids	140	0.515	3.7	--	0.025	1.1	1.15	0.312
							Average =	31%
St. Croix River Basin								
Date: 10/06/2003								
SN-10: SNAKE R BRIDGE AT CSAH-9, 2 MI NE OF PINE CITY								
SN-10	9	0.051	--	<0.006	--			
SN-10 Solids	980	4.99	5.1	--	0.228	1.4	1.50	0.295
SN-10 Solids	1000	4.87	4.9	--	0.241	1.4	1.55	0.319
SN-10 Solids	1100	5.01	4.6	--	0.232	1.3	1.36	0.298

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Basin/Date/ Location/ID	Solids, total suspend ed (mg/L)	Phosphorus, total (mg/l)	Particulate Phosphorus (mg total P/g dry weight solids)	Orthophospha te (mg/L)	Particulate Phosphorus, NaOH Extractable (mg/l)	Particulate NaOH Extractable Phosphorus (mg of NaOH extractable P/g dry weight solids)	Bioavailable Particulate P (mg P/g) [[Ultimately avail PP = 1.08 NaOH -P-0.008]]	Bioavailable Particulate Phosphorus Fraction
							Average =	30%
Upper Mississippi River Basin								
Date: 10/14/2003								
MISSISSIPPI R MPLS WATERWORKS INTAKE AT FRIDLEY								
UM-859	8	0.041	--	0.006	--			
UM-859 Solids	410	1.81	4.4	--	0.086	1.3	1.35	0.306
UM-859 Solids	390	1.81	4.6	--	0.087	1.3	1.44	0.310
UM-859 Solids	420	1.85	4.4	--	0.088	1.3	1.35	0.306
							Average =	31%
Missouri River Basin								
Date: 10/21/2003								
ROCK RIVER BR ON STATELINE RD 10 MI S OF LUVERNE								
RO-0	5	0.055	--	0.012	--			
RO-0 Solids	560	3.49	6.2	--	0.121	1.3	1.39	0.223
RO-0 Solids	520	3.44	6.6	--	0.119	1.4	1.47	0.223
RO-0 Solids	540	3.34	6.2	--	0.119	1.3	1.42	0.230
							Average =	23%
Des Moines River Basin								
Date: 10/21/2003								
W FK DES MOINES R CSAH-23 BRIDGE S OF PETERSBURG								
WDM-3	34	0.331	--	<0.006	--			
WDM-3 Solids	2300	16.3	7.1	--	0.164	0.4	0.45	0.064
WDM-3 Solids	2400	16.8	7.0	--	0.136	0.3	0.36	0.051
WDM-3 Solids	2400	16	6.7	--	0.142	0.4	0.38	0.056
							Average =	6%

-- Not analyzed.

h EPA sample extraction or analysis holding time was exceeded.

Results of Basin Discharge and Bioavailable Fraction Calculations

The results of the basin discharge calculations and resulting bioavailable fractions are presented in Tables 7, 8 and 9 and Figures 1-17. Attachment C contains summary sheets for each major basin and additional sheets when multiple locations were included in developing an estimate for an individual basin. Only one location was used in the Minnesota River, Upper Mississippi River and Des Moines River basins. In these cases, the discharge calculations were adjusted using a drainage area ratio multiplier (basin area:drainage area at monitoring location). No monitoring locations with sufficient water quality data were identified in either the Cedar River or Missouri River basins. For these cases, water quality relationships to flow from the Des Moines River basin were applied. The Des Moines, Cedar and Missouri River basins in Minnesota share similar land use characteristics and are located relatively close to each other. Multiple stations were used in the following basins: Lower Mississippi River; St. Croix River; Lake Superior; Rainy River; and Red River. In these cases, discharge calculations were conducted at monitoring locations in subwatersheds. The discharge calculations at each location were adjusted using a drainage area multiplier and then added within a basin such that the entire basin area was represented. In the case of the St. Croix River basin, the discharge calculations at the Snake and Kettle Rivers were used equally to represent the entire basin. In the case of the Lake Superior basin, a monitoring location on the St. Louis River represented the St. Louis River drainage area while a monitoring location on the Baptism River represented the remainder of the basin. In the case of the Rainy River basin, monitoring locations on the Rainy River and Little Fork Rivers were assumed to equally represent the entire basin. In the case of the Red River basin, monitoring locations in the Red Lake River and Otter Tail River watersheds represented their respective drainage areas, while a monitoring location on the Wild Rice River represented the remainder of the basin. All drainage area multipliers are presented in the summary sheets in Attachment C.

Annual suspended sediment yields ranged from 6.2 lbs/acre/yr for low flow years in the St. Croix River basin, to 73.9 lbs/acre/yr in the Minnesota River basin, and a statewide average of 31.4 lbs/acre/yr. During high flow years, suspended sediment yields were considerably higher, ranging from 21 lbs/acre/yr in the Lake Superior basin to 528 lbs/acre/yr in the Lower Mississippi River basin, and a statewide average of 215 lbs/acre/yr. Average flow conditions produced a statewide-suspended sediment area-weighted average of 104 lbs/acre/yr.

Annual total phosphorus yields ranged from 0.023 lb/acre/yr during low flow years in the Lake Superior basin, to 1.056 lbs/acre/yr during high flow years in the Lower Mississippi River basin. The unusually high phosphorus yield in the Lower Mississippi River was based on two USGS gauging stations, one on the Cannon River at Welch, MN. Water quality data were somewhat limited at this site (28 total phosphorus samples) and showed no correlation with flow. An average total phosphorus concentration of 0.21 mg/l was applied in the discharge calculations. This site is influenced by an upstream discharge and may not be representative of other areas of the Lower Mississippi River basin. The other site was on the Root River near Beaver, MN. This site was selected to represent the remainder of the Lower Mississippi River basin outside of the Cannon River. USGS Long Term Monitoring Program (LTRMP) water quality data were available and showed a very strong response to increasing flows, with rapidly increasing solids and phosphorus concentrations with increases in flow. Water quality data were not available for significantly high flows and, therefore, extrapolation of the rating curves to higher flows than what were monitored is questionable. LTRMP data at a site on the Whitewater River were also evaluated and here too a very strong response to increasing flows was observed. Data at locations on the Zumbro River in the Lower Mississippi River basin were also evaluated but insufficient data were available to develop rating curves. Average flow conditions produced a statewide total phosphorus yield of 0.202 lb/acre/yr.

Total dissolved phosphorus yields were estimated as low as 0.005 lb/acre/yr in the Des Moines River, Cedar River, Missouri River, and Lake Superior basins during low flow years. The Cedar and Missouri River basins did not contain sufficient data to produce basin-specific estimates, but because of their proximity to the Des Moines River basin and similar land covers, the same rates were applied to these basins. High flow years produced total dissolved phosphorus yields as high as 0.312 lb/acre/yr in the Lower Mississippi River basin. Average flow conditions produced a statewide total dissolved phosphorus yield of 0.066 lb/acre/yr.

Particulate phosphorus yields during low flow conditions were lowest in the Red River basin at 0.024 lb/acre/yr. Particulate phosphorus yields were highest in the Lower Mississippi River basin at 0.744 lb/acre/yr during high flow years. Average flow conditions produced a statewide total particulate phosphorus yield of 0.136 lb/acre/yr.

All dissolved phosphorus was considered bioavailable, and 18% of the particulate phosphorus was considered bioavailable as discussed previously. Total bioavailable phosphorus yields were estimated

as low as 0.008 lb/acre/yr in the Lake Superior basin during low flow years. High flow years produced total bioavailable phosphorus yields as high as 0.446 lb/acre/yr in the Lower Mississippi River basin. Average flow conditions produced a statewide total bioavailable phosphorus yield of 0.090 lb/acre/yr.

The resulting bioavailable fraction of total phosphorus ranged from 27% to 53% at low flow, with the lowest fraction in the Des Moines, Cedar and Missouri River basins, and the highest fraction in the Lower Mississippi River basin. During high flow conditions the range for total bioavailable phosphorus was 34% (Des Moines River, Cedar River, Missouri River, and Lake Superior basins) to 54% (Minnesota River basin). At average flow conditions the statewide bioavailable fraction was estimated at 45%.

Table 7: Summary of estimated annual basin discharge for low, average and high flow conditions.

Estimated Annual Basin Discharge (metric tons/year)							
Basin	Area (sq. mi.)	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus	Fraction Bioavailable
Low Flow Year							
<i>Minnesota River</i>	14,939	321,201	475	151	324	210	44%
<i>Upper Mississippi River</i>	20,100	85,110	508	179	329	238	47%
<i>Lower Mississippi River</i>	6,317	48,612	238	102	135	127	53%
<i>Des Moines River</i>	1,535	4,566	20	2.2	18	5	27%
<i>Cedar River*</i>	1,028	3,058	14	1.4	12	4	27%
<i>Missouri River*</i>	1,782	5,300	24	2.5	21	6	27%
<i>St. Croix River</i>	3,528	6,355	85	29	56	39	46%
<i>Lake Superior</i>	6,149	13,537	42	8	33	14	35%
<i>Rainy River</i>	11,236	132,422	223	85	137	110	49%
<i>Red River</i>	17,741	151,146	188	66	122	88	47%
<i>Statewide</i>	84,355	771,306	1,816	627	1,188	841	46%
Average Flow Year							
<i>Minnesota River</i>	14,939	958,291	1,254	458	796	601	48%
<i>Upper Mississippi River</i>	20,100	212,614	997	365	632	478	48%
<i>Lower Mississippi River</i>	6,317	342,383	789	237	552	336	43%
<i>Des Moines River</i>	1,535	36,052	161	26	135	50	31%
<i>Cedar River*</i>	1,028	24,144	108	17	90	34	31%
<i>Missouri River*</i>	1,782	41,853	187	30	157	58	31%
<i>St. Croix River</i>	3,528	12,426	155	52	103	70	45%
<i>Lake Superior</i>	6,149	27,768	78	15	62	26	34%
<i>Rainy River</i>	11,236	217,316	346	129	217	168	49%
<i>Red River</i>	17,741	683,510	884	287	597	395	45%
<i>Statewide</i>	84,355	2,556,355	4,957	1,616	3,341	2,217	45%
High Flow Year							
<i>Minnesota River</i>	14,939	2,110,290	2,330	1,030	1,299	1,264	54%
<i>Upper Mississippi River</i>	20,100	409,504	1,545	584	961	757	49%
<i>Lower Mississippi River</i>	6,317	971,031	1,940	573	1,368	819	42%
<i>Des Moines River</i>	1,535	77,843	347	66	281	116	34%
<i>Cedar River*</i>	1,028	52,132	233	44	188	78	34%
<i>Missouri River*</i>	1,782	90,369	403	76	327	135	34%
<i>St. Croix River</i>	3,528	28,605	254	78	176	110	43%
<i>Lake Superior</i>	6,149	37,152	100	19	81	34	34%
<i>Rainy River</i>	11,236	467,087	528	176	352	239	45%
<i>Red River</i>	17,741	1,038,447	1,359	420	938	589	43%
<i>Statewide</i>	84,355	5,282,460	9,038	3,067	5,971	4,142	46%

*Based on water quality data for the Des Moines River basin.

Table 8: Summary of estimated annual basin yields for low, average and high flow conditions.

Estimated Annual Basin Yield (lbs/acre/yr)					
Basin	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year					
<i>Minnesota River</i>	73.9	0.109	0.035	0.074	0.048
<i>Upper Mississippi River</i>	14.6	0.087	0.031	0.056	0.041
<i>Lower Mississippi River</i>	26.5	0.129	0.056	0.074	0.069
<i>Des Moines River</i>	10.2	0.046	0.005	0.041	0.012
<i>Cedar River*</i>	10.2	0.046	0.005	0.041	0.012
<i>Missouri River*</i>	10.2	0.046	0.005	0.041	0.012
<i>St. Croix River</i>	6.2	0.083	0.029	0.054	0.038
<i>Lake Superior</i>	7.6	0.023	0.005	0.019	0.008
<i>Rainy River</i>	40.5	0.068	0.026	0.042	0.034
<i>Red River</i>	29.3	0.036	0.013	0.024	0.017
<i>Statewide</i>	31.4	0.074	0.026	0.048	0.034
Average Flow Year					
<i>Minnesota River</i>	221	0.288	0.105	0.183	0.138
<i>Upper Mississippi River</i>	36	0.170	0.062	0.108	0.082
<i>Lower Mississippi River</i>	186	0.430	0.129	0.301	0.183
<i>Des Moines River</i>	81	0.360	0.058	0.302	0.112
<i>Cedar River*</i>	81	0.360	0.058	0.302	0.112
<i>Missouri River*</i>	81	0.360	0.058	0.302	0.112
<i>St. Croix River</i>	12	0.151	0.050	0.100	0.068
<i>Lake Superior</i>	16	0.043	0.008	0.035	0.015
<i>Rainy River</i>	66	0.106	0.040	0.066	0.051
<i>Red River</i>	132	0.171	0.056	0.116	0.076
<i>Statewide</i>	104	0.202	0.066	0.136	0.090
High Flow Year					
<i>Minnesota River</i>	486	0.536	0.237	0.299	0.291
<i>Upper Mississippi River</i>	70	0.264	0.100	0.164	0.130
<i>Lower Mississippi River</i>	528	1.056	0.312	0.744	0.446
<i>Des Moines River</i>	174	0.778	0.147	0.630	0.261
<i>Cedar River*</i>	174	0.778	0.147	0.630	0.261
<i>Missouri River*</i>	174	0.778	0.147	0.630	0.261
<i>St. Croix River</i>	28	0.247	0.076	0.171	0.107
<i>Lake Superior</i>	21	0.056	0.011	0.045	0.019
<i>Rainy River</i>	143	0.162	0.054	0.108	0.073
<i>Red River</i>	201	0.263	0.081	0.182	0.114
<i>Statewide</i>	215	0.368	0.125	0.243	0.169

*Based on water quality data for the Des Moines River basin.

Table 9. Summary of estimated annual flow weighted mean concentrations for low, average and high flow conditions.

Estimated Annual Flow Weighted Mean Concentration (mg/l)					
Basin	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year					
<i>Minnesota River</i>	152.7	0.226	0.072	0.154	0.100
<i>Upper Mississippi River</i>	14.3	0.085	0.030	0.055	0.040
<i>Lower Mississippi River</i>	24.9	0.100	0.038	0.063	0.049
<i>Des Moines River</i>	66.7	0.298	0.031	0.266	0.079
<i>Cedar River*</i>	66.7	0.298	0.031	0.266	0.079
<i>Missouri River*</i>	66.7	0.298	0.031	0.266	0.079
<i>St. Croix River</i>	4.4	0.068	0.024	0.045	0.032
<i>Lake Superior</i>	10.6	0.030	0.011	0.019	0.014
<i>Rainy River</i>	28.3	0.047	0.018	0.029	0.023
<i>Red River</i>	77.0	0.095	0.036	0.058	0.047
Average Flow Year					
<i>Minnesota River</i>	187	0.245	0.089	0.155	0.117
<i>Upper Mississippi River</i>	21	0.100	0.037	0.064	0.048
<i>Lower Mississippi River</i>	81	0.186	0.055	0.131	0.079
<i>Des Moines River</i>	67	0.298	0.048	0.249	0.093
<i>Cedar River*</i>	67	0.298	0.048	0.249	0.093
<i>Missouri River*</i>	67	0.298	0.048	0.249	0.093
<i>St. Croix River</i>	5	0.071	0.024	0.047	0.032
<i>Lake Superior</i>	14	0.033	0.011	0.022	0.015
<i>Rainy River</i>	30	0.048	0.018	0.030	0.023
<i>Red River</i>	104	0.133	0.044	0.089	0.060
High Flow Year					
<i>Minnesota River</i>	244	0.270	0.119	0.150	0.146
<i>Upper Mississippi River</i>	30	0.114	0.043	0.071	0.056
<i>Lower Mississippi River</i>	150	0.286	0.079	0.207	0.116
<i>Des Moines River</i>	67	0.298	0.056	0.242	0.099
<i>Cedar River*</i>	67	0.298	0.056	0.242	0.099
<i>Missouri River*</i>	67	0.298	0.056	0.242	0.099
<i>St. Croix River</i>	8	0.075	0.024	0.052	0.033
<i>Lake Superior</i>	15	0.035	0.011	0.023	0.015
<i>Rainy River</i>	47	0.054	0.018	0.036	0.024
<i>Red River</i>	124	0.164	0.051	0.113	0.071

*Based on water quality data for the Des Moines River basin.

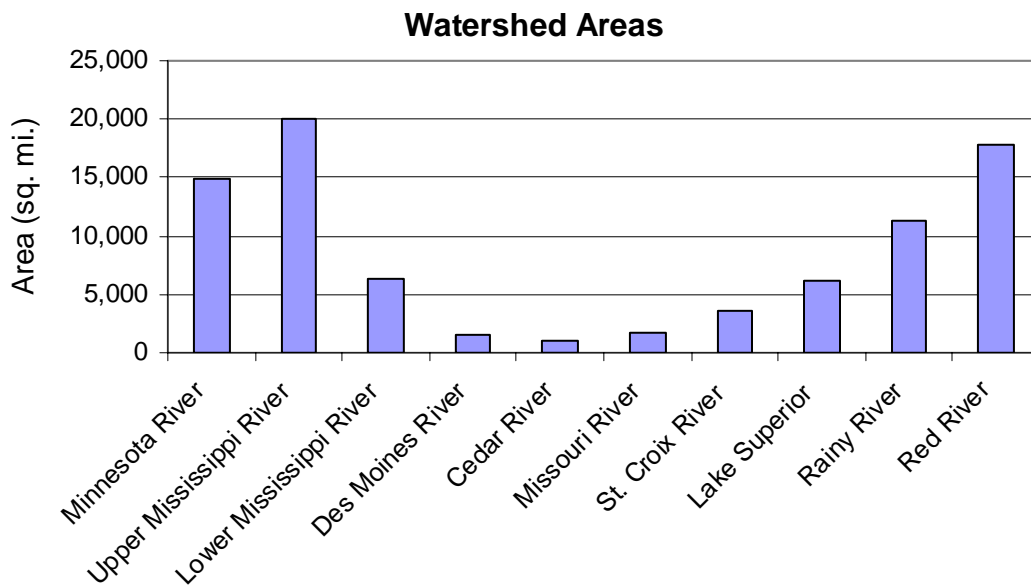


Figure 1: Watershed areas for each of the ten major watersheds.

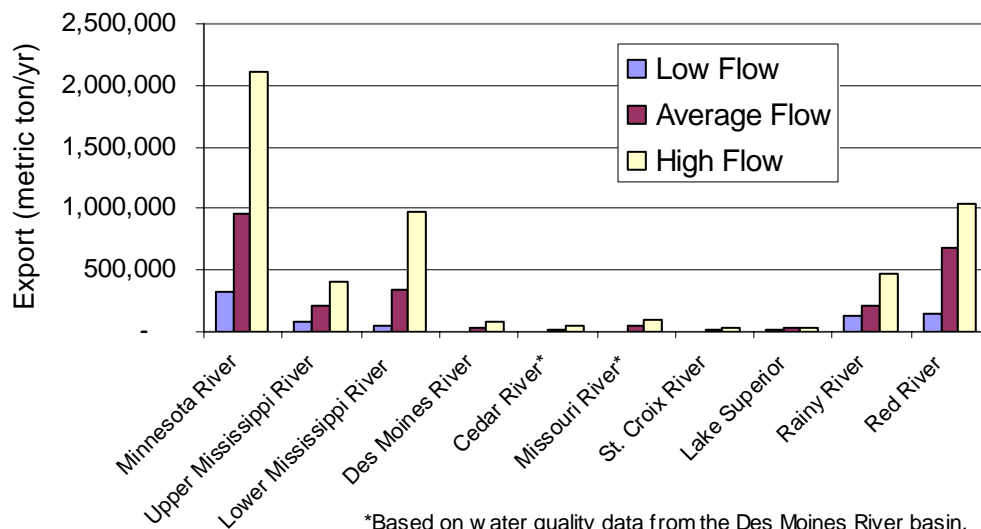


Figure 2: Estimated annual suspended sediment discharge for each of the ten major basins.

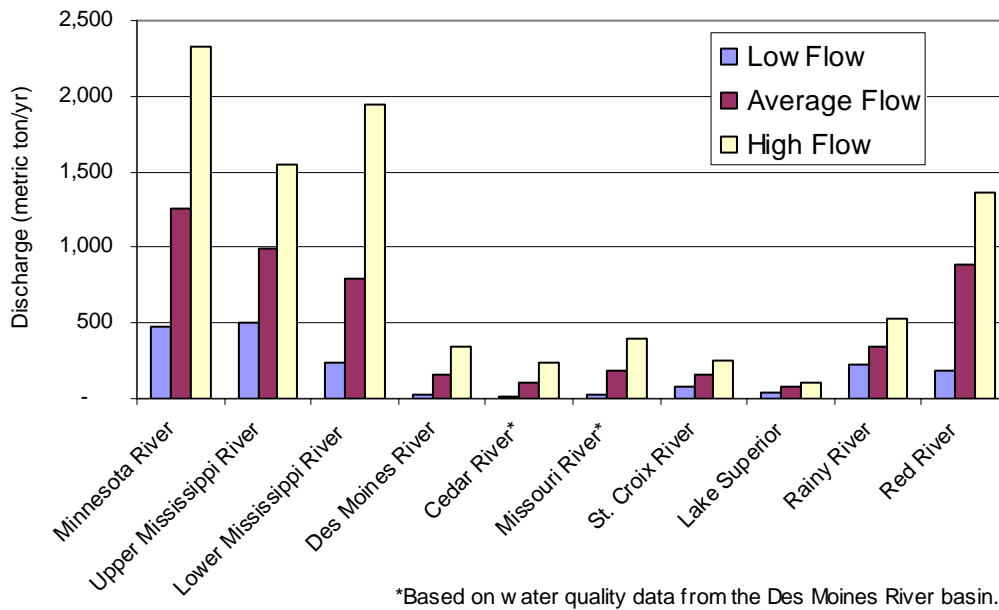


Figure 3: Estimated annual total phosphorus discharge for each of the ten major basins.

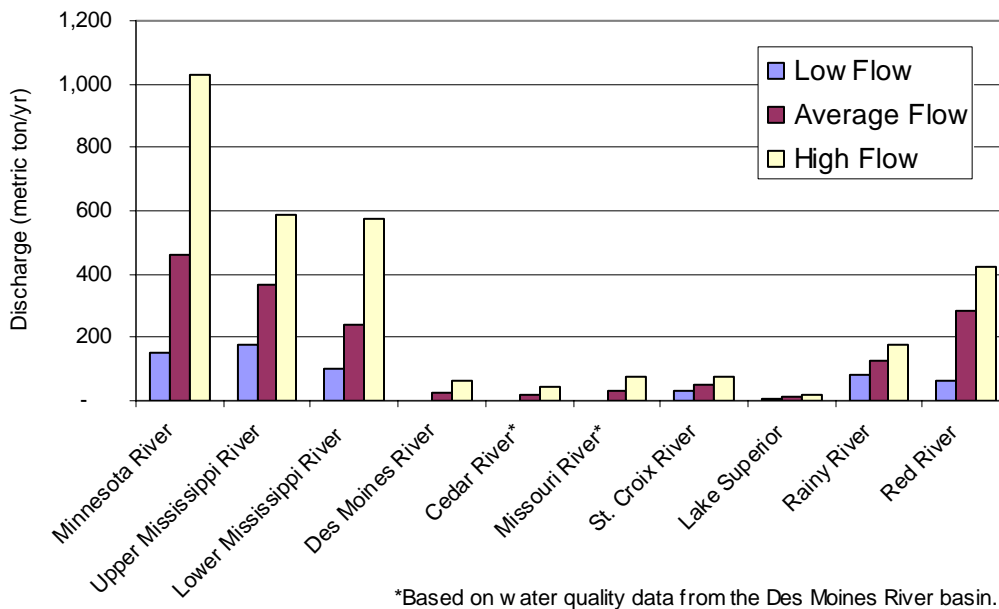


Figure 4: Estimated annual total dissolved phosphorus discharge for each of the ten major basins.

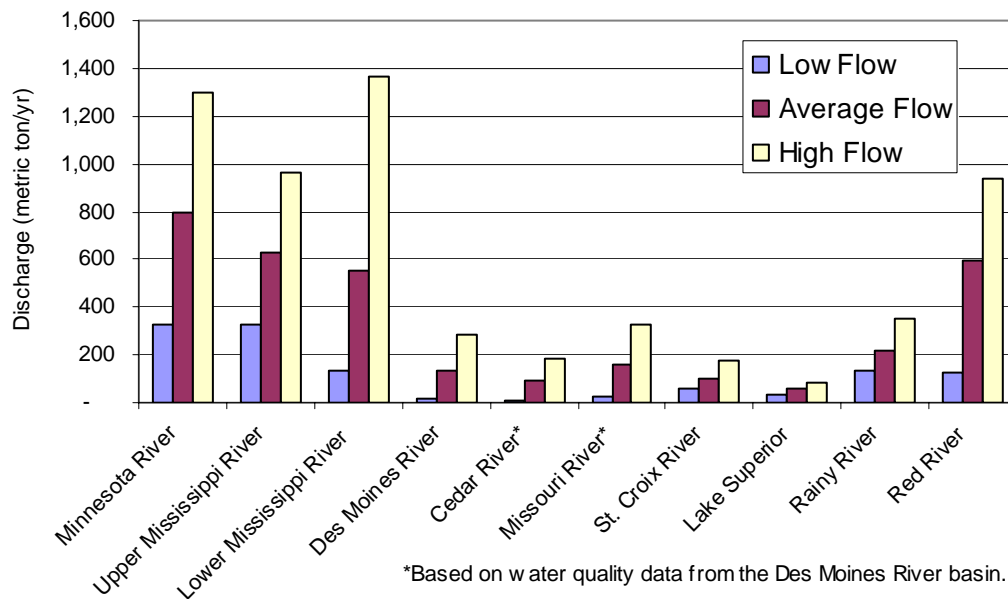


Figure 5: Estimated annual total particulate phosphorus discharge for each of the ten major basins.

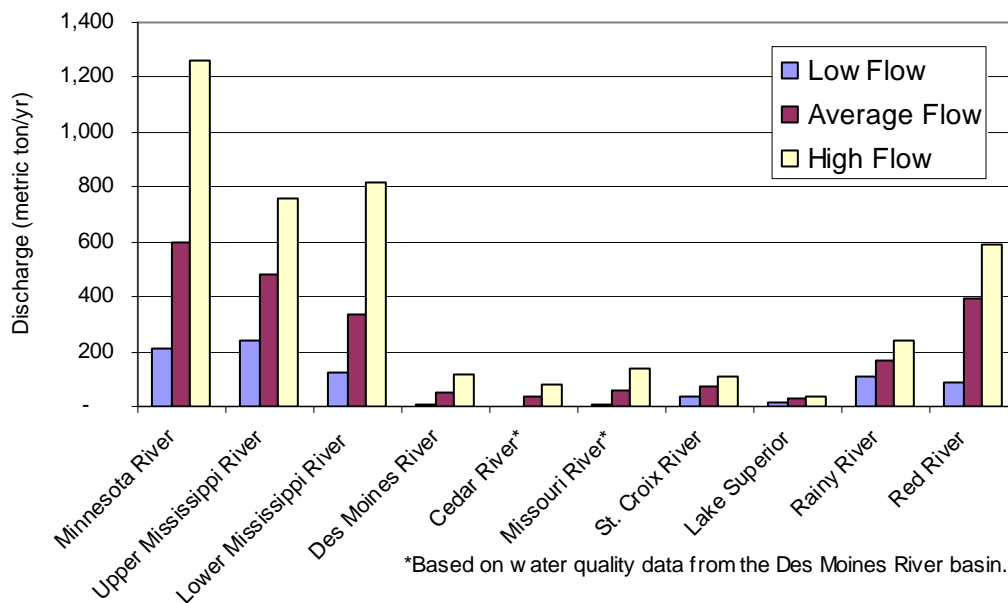


Figure 6: Estimated annual bioavailable phosphorus discharge for each of the ten major basins.

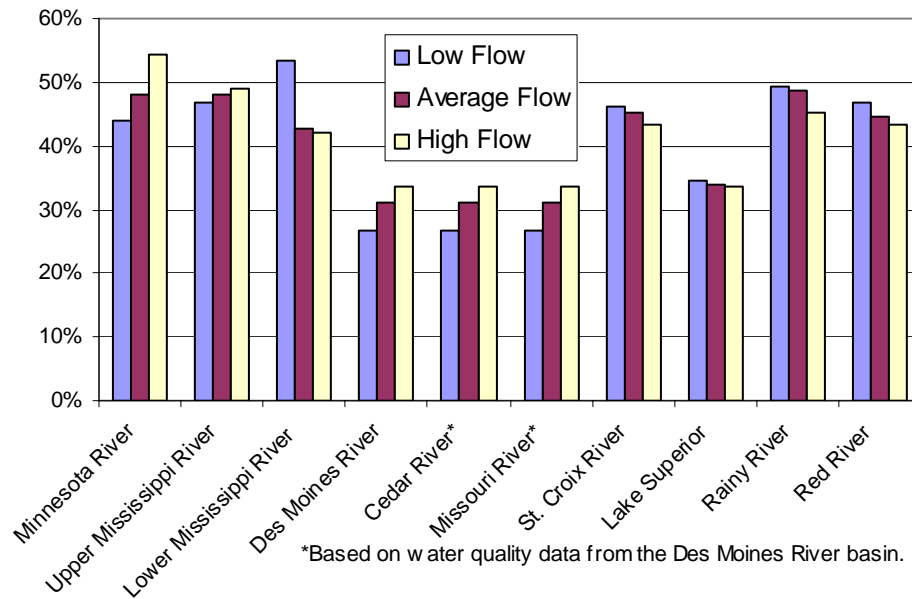


Figure 7: Estimated annual bioavailable phosphorus fractions for each of the ten major basins.

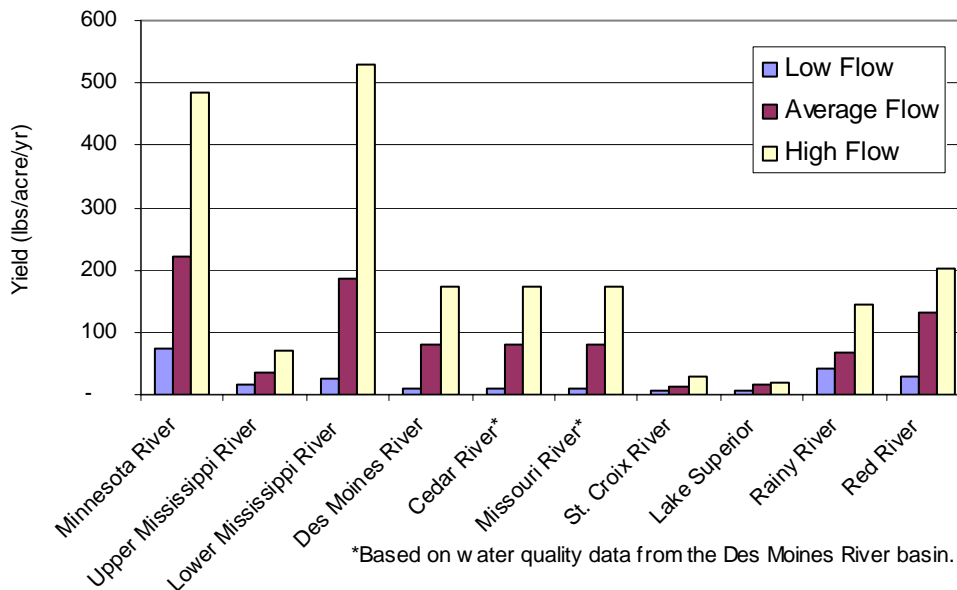


Figure 8: Estimated annual suspended sediment yields for each of the ten major basins.

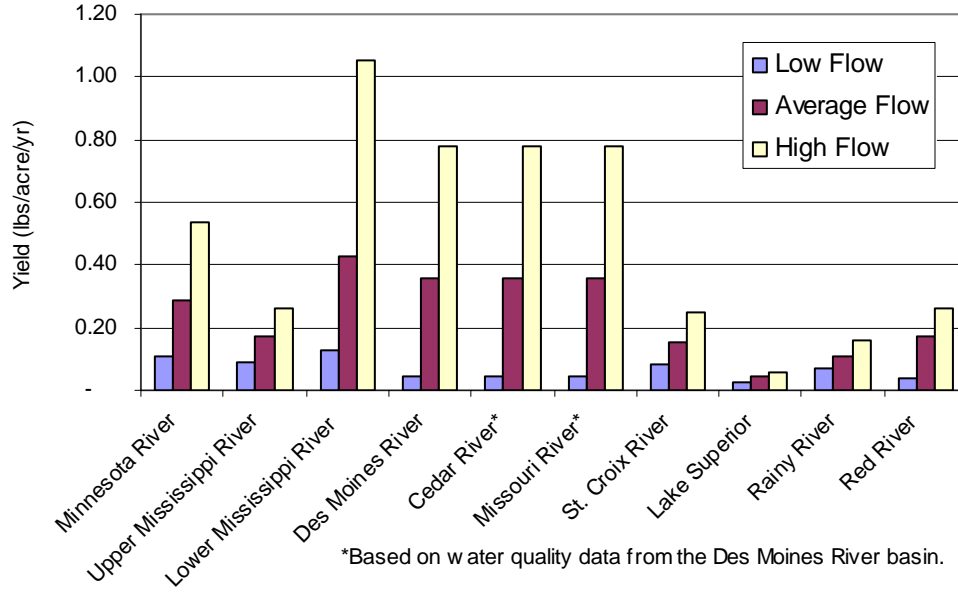


Figure 9: Estimated annual total phosphorus yields for each of the ten major basins.

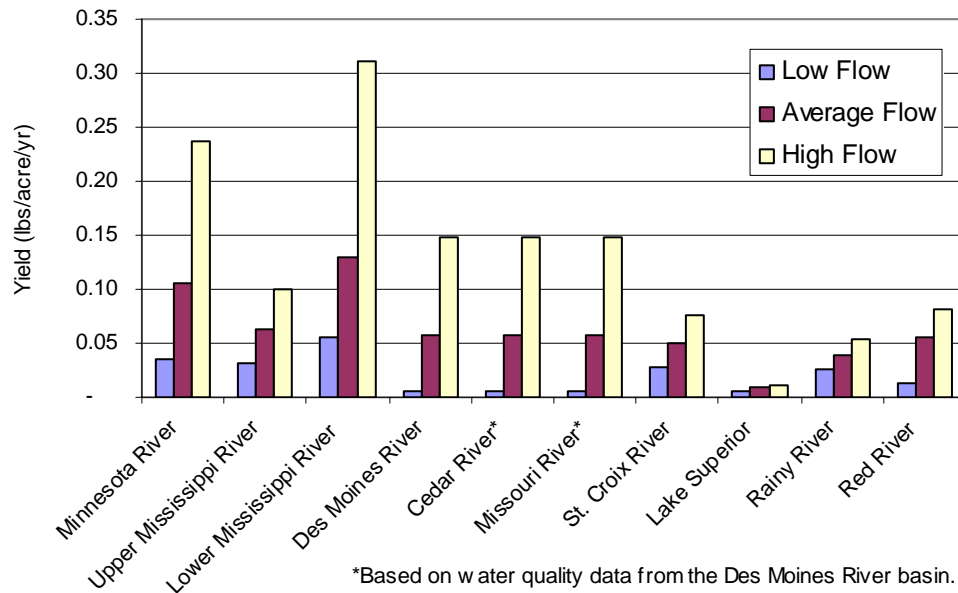


Figure 10: Estimated annual total dissolved phosphorus yields for each of the ten major basins.

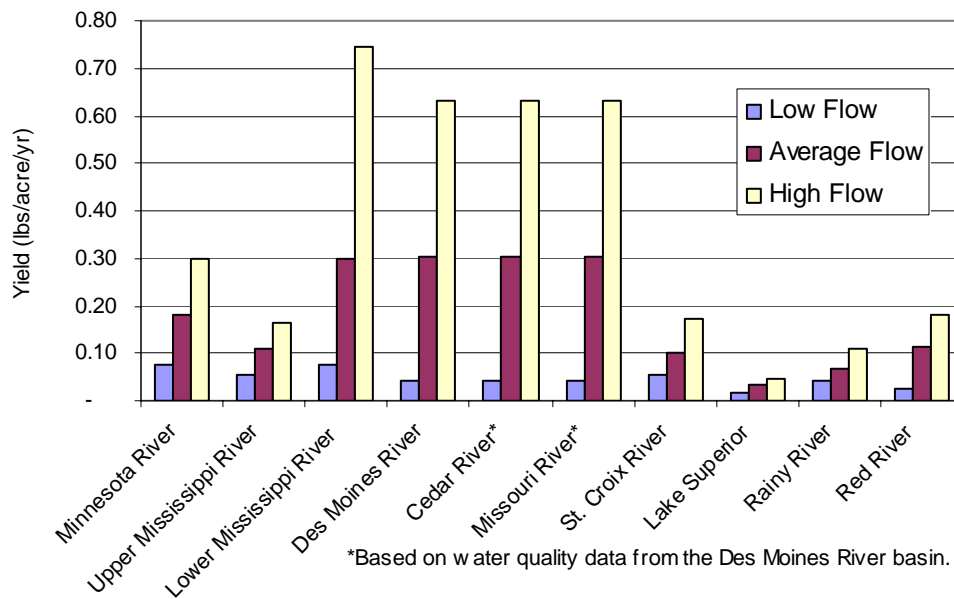


Figure 11: Estimated annual total particulate phosphorus yields for each of the ten major basins.

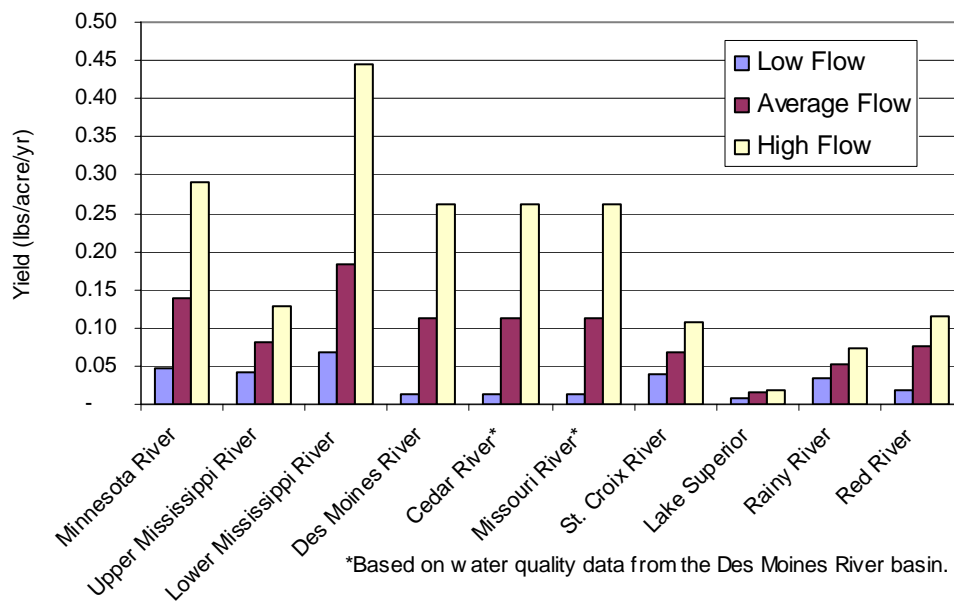


Figure 12: Estimated annual bioavailable phosphorus yields for each of the ten major basins.

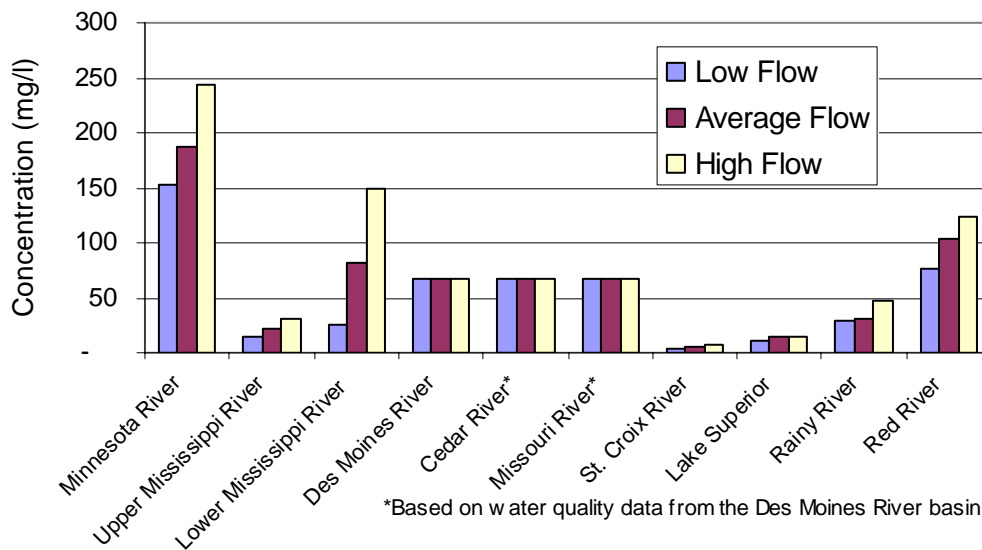


Figure 13: Estimated annual flow weighted mean concentration for suspended sediment for each of the ten major basins.

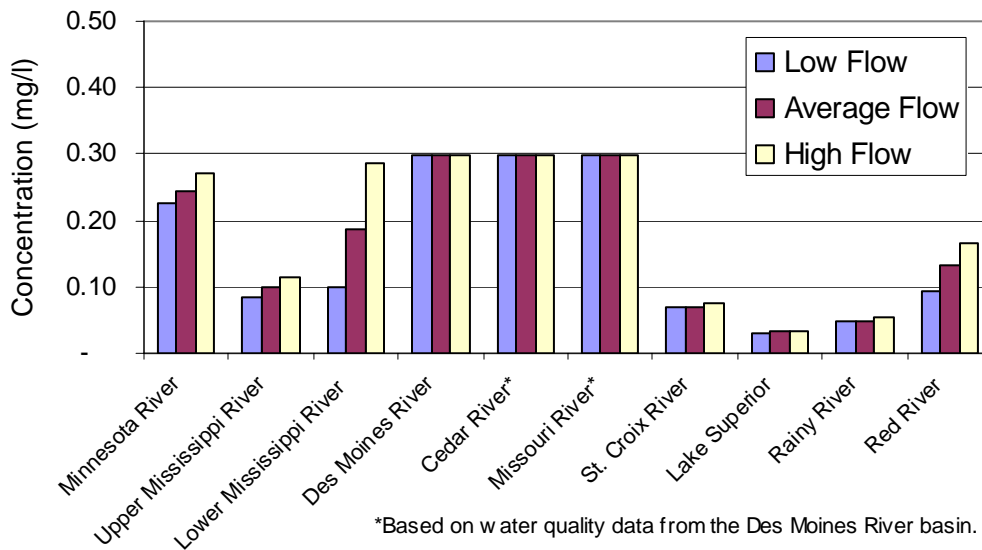


Figure 14: Estimated annual flow weighted mean concentration for total phosphorus for each of the ten major basins.

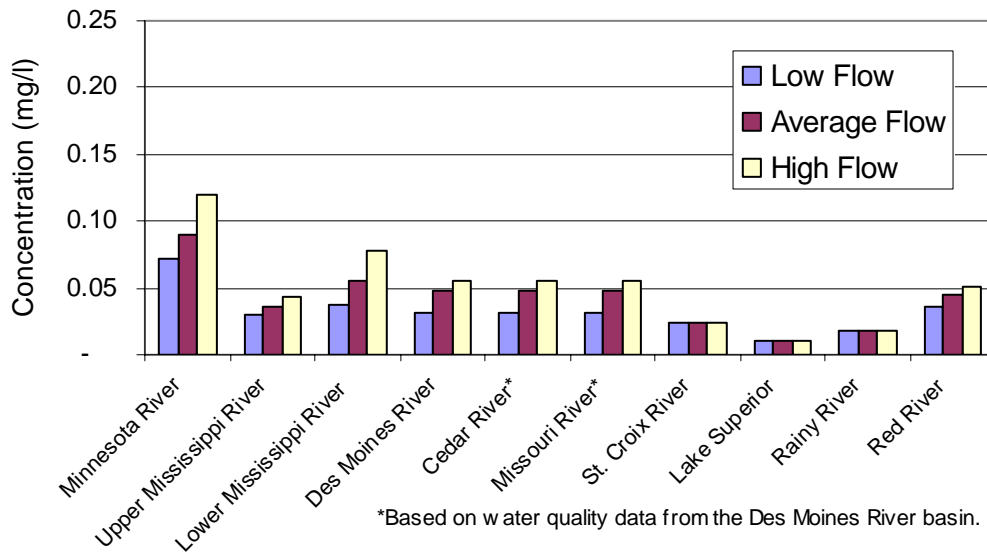


Figure 15: Estimated annual flow weighted mean concentration for total dissolved phosphorus for each of the ten major basins.

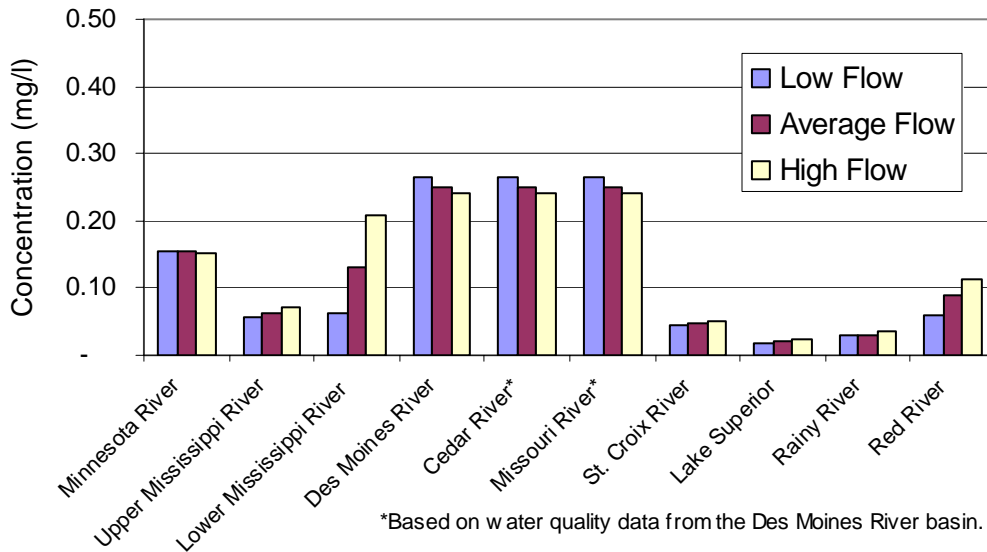


Figure 16: Estimated annual flow weighted mean concentration for total particulate phosphorus for each of the ten major basins.

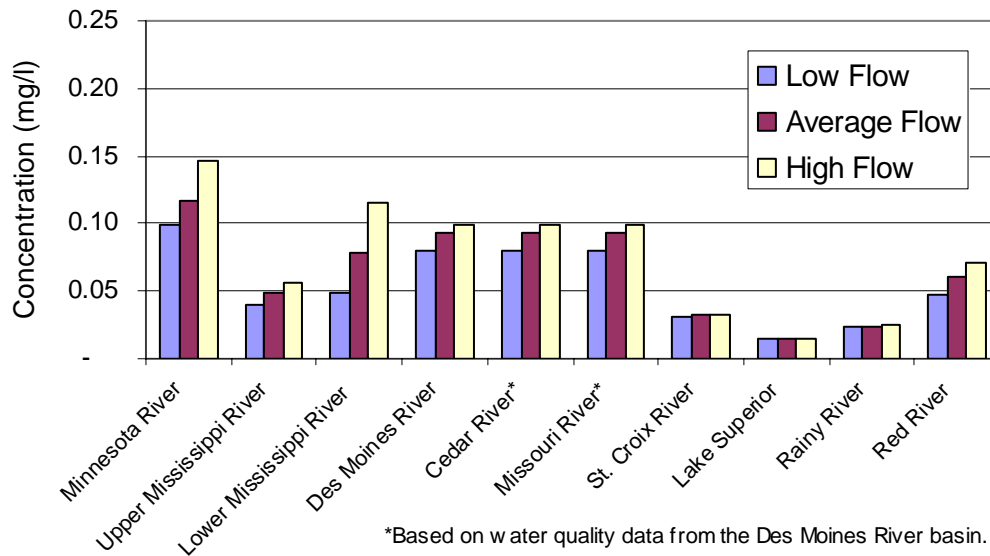


Figure 17: Estimated annual flow weighted mean concentration for total bioavailable phosphorus for each of the ten major basins.

Bioavailable Phosphorus Variability and Uncertainty

The uncertainty associated with the basin scale export estimates was not quantified, but is expected to be significant. Results from USGS studies of the St. Croix River Basin (Lenz *et al.*, 2001 and Lenz and Robertson, 2002) were compared to the results of this study as a check on the accuracy of the methods applied. In the USGS studies, more complex methods were applied in the development of suspended sediment and total phosphorus loads at the Snake and Kettle River gauging stations for the 1999 water year. Comparisons of the results are presented in Table 10. The results of this study generally fall within the 95th percent confidence interval as calculated and reported in the USGS study. Also, as is typical with the simple approach to the development of rating curves used in this study, the results are generally lower. Note that even with the more complex methods applied in the USGS study, the range associated with the 95th percent confidence interval is approximately $\pm 40\%$ for the sediment load estimates and $\pm 20\%$ on the total phosphorus estimates for this single year.

Table 10. Comparison of annual loads from USGS St. Croix River study and this study.

Gauging Station	Annual load, water year 1999 (metric tons/yr)			
	Sediment		Total Phosphorus	
	<i>USGS</i>	<i>Results of this Study</i>	<i>USGS</i>	<i>Results of this Study</i>
<i>Snake River</i>	3,050 (95 th -percent confidence interval = 1,780 to 4,320)	2,017	37.4 (95 th -percent confidence interval = 29.5 to 45.4)	38
<i>Kettle River</i>	5,970 (95 th -percent confidence interval = 3,660 to 8,290)	3,732	43.4 (95 th -percent confidence interval = 34.94 to 51.8)	34

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As part of the USGS Long Term Resource Monitoring Program (LTRMP), the USGS has also calculated annual loads for suspended sediment, total phosphorus, and dissolved phosphorus at locations on the Minnesota River and the Mississippi River. Results of loading estimates are presented on the USGS Upper Midwest Environmental Sciences Center (http://www.umesc.usgs.gov/data_library/sediment_nutrients/streams/streams.html). These estimates are compared to the results of this study in Table 11. The comparison shows the results of this study again being generally less than the USGS results.

While there is significant uncertainty associated with the basin discharge calculations, the estimates presented are useful in assessing the relative discharge of the different forms of phosphorus from the basins and at different flow conditions, but care should be taken in using these estimates as predictors of absolute magnitudes of phosphorus loads.

Table 11. Comparison of annual loads from USGS LTRMP study and this study.

Monitoring Location	Water year	Annual load (metric tons/yr)					
		Sediment		Total Phosphorus		Dissolved Phosphorus	
		USGS	Results of this Study	USGS	Results of this Study	USGS	Results of this Study
<i>Minnesota River near Jordan</i>	Low Flow (1981)	472,868-500,863	300,858	584-589	465	194-211	141
	Average Flow (1985)	1,185,567-1,215,541	1,014,532	1,232-1,290	1,334	588-730	485
	High Flow (1986)	2,486,545-2,592,112	2,077,906	2,223-2,353	2,478	1,211-1,613	1,004
<i>Mississippi River near Anoka</i>	Low Flow (1989)	102,286-105,213	77,347	651-673	448	322-330	158
	Average Flow (1995)	195,394-204,458	188,759	1,253-1,273	935	757-794	339
	High Flow (1986)	517,356-549,192	486,458	2,521-2,586	1,850	1,255-1,373	701

Point Sources Not Accounted for in Basin Discharge Calculations

The method used for calculating basin discharge depended on an assumption that the gauge(s) chosen represented the discharge for the entire basin, including both point and non-point source contributions. This assumption is likely adequate for representation of the non-point sources as they are spread out over large areas. But because of the specific placement of point source discharges and the potential for relatively large phosphorus contributions, this assumption may not hold true. To evaluate this concern, point sources were located when latitude and longitude data were readily available. A determination was then made whether or not the point source discharged within the drainage area of the representative gauge(s). Unfortunately, of the 820 point sources identified in this study, only 480 had readily available latitude and longitude information. Of these 480, 252 were within the drainage areas of the representative gauges and 228 discharged outside. The estimated annual phosphorus loads for the point sources in each basin were tabulated to assess the magnitude of the loads represented by the gauges, those not represented by the gauges, and those of unknown location. This information is presented in Table 12. The results show the significance of both the point sources outside of the discharge calculation and those with unknown location.

The calculated basin discharges include upstream point sources, and to some extent account for point source loads below the representative gauge as the discharge at the gauge is multiplied by a drainage ratio factor. But the point sources below the gauge are adequately represented only to the degree that the point sources below a gauge discharge a similar load per area as those above the gauge. Where they are different, care needs to be taken in how the basin discharge estimates are used.

Table 12. Point source phosphorus loads inside and outside of gauged drainage areas.

Basin	Annual total phosphorus load (metric ton/year)			
	Total point source load	Located within discharge calculation	Located outside of discharge calculation	Unknown
Minnesota River	372	117.9	45.4	208.4
Upper Mississippi River	1,180 ¹	194.9	897.1 ¹	88.1
Lower Mississippi River	267	83.3	129.8	54.2
Des Moines River	56	42.4	-	13.1
Cedar River	57	19.3	-	37.5
Missouri River	13	6.7	-	6.4
St. Croix River	22	4.6	16.0	1.5
Lake Superior	35	9.1	23.4	2.5
Rainy River	44	2.7	0.7	40.8
Red River	63	17.5	35.6	9.6
Statewide	2,109	499	1,148	462

¹ Includes 868 metric tons/yr from the MCES Metro WWTF. This load is expected to be reduced by approximately 581 metric tons/yr associated with a 1 mg P/l effluent discharge limit effective 12/31/05.

Recommendations for Future Refinements of Basin Discharge Calculations

Phosphorus discharge estimates on a basin scale may be improved by application of more complex rating curve estimation techniques, for example including flow and seasonal stratification. Also, additional assessment of the portion of discharge at each gauge that can be attributed to POTW discharges would help understanding the observed differences. The assessment conducted focused on gauges and data at the downstream reaches of the watershed, therefore quantifying the cumulative impacts of all sources within the watershed, both point and non-point and from the various land cover types. Assessment of gauges and data representing small drainage areas with a homogeneous land cover might prove useful in isolating the phosphorus loadings from a particular land cover.

Literature Cited

- Andraski, B.J., Mueller, D.H., and Daniel, T.C. 1985. Phosphorus losses in runoff as affected by tillage. *Soil Sci. Soc. Am. J.* 49:1523-1527.
- Asselman, N.E.W. 2000. Fitting and interpretation of sediment rating curves. *Journal of Hydrology*, 234: 228-248.
- Bannerman, R.T., Armstrong, D.E., Harris, R.F., and Holdren, C.C. 1975. Phosphorus release and uptake by Lake Ontario sediments. Ecol. Res. Ser. USEPA Rep. 660/3-750-066. U.S. Gov. Print. Office, Washington, DC.
- Breuwisma A. and Silva, S. 1992. Phosphorus fertilization and environmental effects in the Netherlands and the Po region (Italy). Rep. 57. Agric. Res. Dep. The Winand Staring Center for Integrated Land, soil and Water Res., Wageningen, the Netherlands.
- Bierman, V.J. Jr., Dolan, D.M., Stoermer, E.F., Gannon, J.E., and Smith, V.E. 1980. The development and calibration of a spatially simplified multi-class phytoplankton model for Saginaw Bay, Lake Huron. Great Lakes Environmental Planning Study, Contribution No. 33.
- Caraco, N.F. 1995. Chapter 14: Influence Of Human Populations On Phosphorus Transfers To Aquatic Systems: A Regional Scale Study Using Large Rivers. In SCOPE 54: Phosphorus in the Global Environment - Transfers, Cycles and Management. H. Tiessen (ed.), 1995, 480 pp, Wiley, U.K.
- Carignan, R. and Kalff, J. 1980. Phosphorus sources for aquatic weeds: Water or sediments? *Science*. 207:987-989.
- Carlisle, A., Brown, A.H.F. and White, E.J. 1966. The organic matter and nutrient elements in precipitation beneath sessile oak (*Quercus petraea*) canopy. *J. Ecol.* 54:87-98.
- Cowen, W.F. and Lee, G.F. 1976. Phosphorus available in particulate materials transported by urban runoff. *J. Wat. Pollu. Control. Fed.* 48:580-591.
- DePinto, J.V., Young, T.C., Martin, S.C. 1981. Algal-Availability of Phosphorus in Suspended Sediments from Lower Great Lakes Tributaries. *J. Great Lakes Res.* 7(3):311-325.
- DePinto, J.V., Young, T.C. and Salisbury, D.K. 1986. Impact of phosphorus availability on modeling phytoplankton dynamics. *Dutch Hydrobiological Bulletin* 20(1/2):225-243.
- DePinto, J.V., Young, T.C., Bonner, J.S., Rodgers, P.W. 1986. Microbial recycle of phytoplankton phosphorus. *Can. J. Fish. Aquat. Sci.* 43(2):336-342.
- Dolan, D.M., Yui, A.K., and Geist, R.D. 1981. Evaluation of River Load Estimation Methods for Total Phosphorus. *J. Great Lakes Res.* 7(3):207-214.
- Dorich, R.A., Nelson, D.W., and Sommers, L.E. 1980. Algal bioavailability of sediment phosphorus in drainage water of the Black creek watershed. *J. Environ. Qual.* 9:557-563.
- Dorich, R.A., Nelson, D.W., and Sommers, L.E. 1984. Algal availability of phosphorus in suspended stream sediments of varying particle size. *J. Environ. Qual.* 13:82-86.
- Dorich, R.A., Nelson, D.W., and Sommers, L.E. 1985. Estimating algal available phosphorus in suspended sediments by chemical extraction. *J. Environ. Qual.* 14:400-405.
- Engle, D.L. and Sarnelle, O. 1990. Algal use of sedimentary phosphorus from an Amazon floodplain lake: Implications for total phosphorus analysis in turbid waters. *Limnol. Oceanogr.* 35:483-490.

- Ekholm P. and Krogerus, K. 2003. Determining algal-available phosphorus of differing origin: routine phosphorus analyses versus algal assays. *Hydrobiologia* 492: 29-42.
- Gaynor, J.D. and W.I. and Findlay. 1995. Soil and phosphorus loss from conservation and conventional tillage in corn production. *J. Environ. Qual.* 24:734-741.
- Golterman, H.L. 1977. Sediments as a source of phosphate for algal growth. In: Golterman, H.L. (Ed.) *Interactions Between Sediments and Fresh Water*. Symposium at Amsterdam, The Netherlands, 1976, pp. 286-293.
- Hanna, M. 1989. Biologically available phosphorus: Estimation and prediction using an anion-exchange resin. *Can. J. Fish. Aquat. Sci.* 46:638-643.
- Haygarth, P.M. and Jarvis, S.C. 1997. Soil derived phosphorus in surface runoff from grazed grassland lysimeters. *Water Res.* 11:140-148.
- Haygarth, P.M., Hepworth, L. and Jarvis, S.C. 1998. Forms of phosphorus transfer in hydrological pathways from soil under grazed pasture. *European J. Soil Sci.* 49:65-72.
- Haygarth, P.M. and Sharpley, A.N. 2000. Terminology for phosphorus transfer. *J. Environ. Qual.* 29:10-15.
- Hedley, M.J., Mortvedt, J.J., Bolan, N.S., and Syer, J.K. 1995. Chapter 5: Phosphorus Fertility Management in Agroecosystems. In SCOPE 54: Phosphorus in the Global Environment - Transfers, Cycles and Management. H. Tiessen ed., 1995, 480 pp, Wiley, U.K.
- Horowitz, A.J. 2002. The use of rating (transport) curves to predict suspended sediment concentration: A matter of temporal resolution. Turbidity and Other Sediment Surrogates Workshop, April 30-May 2, 2002, Reno, Nevada.
- Huettl, P.J., Wendt, R.C. and Corey, R.B. 1979. Prediction of algal-available phosphorus in runoff suspensions. *J. Environ. Qual.* 8:130-132.
- Jacoby, J.M., Lynch, D.D., Welch, E.B., and Perkins, M.S. 1982. Internal phosphorus loading in a shallow eutrophic lake. *Water Res.* 16:911-919.
- James, W.F., Barko, J.W., and Eakin, H.L. 2002. Labile and refractory forms of phosphorus in runoff of the Redwood River basin, Minnesota. *J. Freshwater Ecology.* 17(2):297-304.
- Kamprath, E.J. 1991. Appropriate measurements of phosphorus availability in soils of the semi-arid tropics. In: Johansen, C., Lee, K.K. and Saharwat, KL (Eds.) Phosphorus nutrition of grain legumines in the semi arid tropics. ICRISAT, India. pp. 23-31.
- Klapwijk, S.P., Kroon, J.M.W. and Meijer, M.L. 1982. Available phosphorus in lake sediments in the Netherlands. *Hydrobiologia.* 92:491-500.
- Larsen. D.P., Shults, D.W. and Malueg, K.W. 1981. Summer internal phosphorus supplies in Shagawa Lake, Minnesota. *Limnol. Oceanogr.* 26:740-753.
- Lee, G.F. 1973. Role of phosphorus in eutrophication and diffuse source control. *Water Res.* 7: 111-128.
- Lee, G.F., Jones, R.A., and Rast, W. 1980. Availability of phosphorus to phytoplankton and its implications for phosphorus management strategies, pp. 259-308. In Phosphorus Management Strategies for Lakes, R. C. Loehr, C. S. Martin, W. Rast (eds.), Ann Arbor Science Publ., Inc.

- Lennox, S.D., Foy, R.H., Smith, R.V. and Jordan, C. 1997. Estimating the contribution from agriculture to the phosphorus load in surface water. P. 55-75. In H. Tunney, O.T. Carton, P.C. Brookes, and A.E. Johnston (ed.) Phosphorus loss from soil to water. CAB Int. Press, Cambridge, UK.
- Lenz, B.N. 2001. Nutrient and Suspended-Sediment Concentrations and Loads, and Benthic-Invertebrate Data for Tributaries to the St. Croix River, Wisconsin and Minnesota, 1997-99. USGS Water-Resources Investigations Report 01-4162.
- Lenz, B.N. and Robertson, D.M. 2002. Response of the St. Croix River Pools, Wisconsin and Minnesota, to Various Phosphorus-Loading Scenarios. USGS Water-Resources Investigations Report 02-4181.
- Li, W.C., Armstrong, D.E., Williams, J.D., Harris, R.F. and Syers, J.K. (1972). Rate and extent of phosphate exchange in lake sediments. *Soil Sci. Soc. Am. Proc.* 36:279-285.
- Logan, T.J. 1977. Levels of plant available phosphorus in agricultural soils in the Lake Erie Drainage Basin. Lake Erie Wastewater Management Study Report. U.S. Army Engineer District, Buffalo.
- Logan, T.J. 1978. Chemical extraction as an index of bioavailability of phosphorus in Lake Erie basin suspended sediments. Lake Erie Wastewater Management Study Report. U.S. Army Engineer District, Buffalo.
- Logan, T.J., Oloya, T.O., and Yaksich, S.M. 1979. Phosphate characteristics and bioavailability of suspended sediments from streams draining into Lake Erie. *J. Great Lakes Res.* 5:112-123.
- Logan, T.J., Verhoff, F.H., and DePinto, J.V. 1979a. Biological availability of total phosphorus. Lake Erie Wastewater Management Study, U. S. Army Engineer District, Buffalo.
- Martin, Scott C., 1983. Bioavailability of Sediment Phosphorus Inputs to the Lower Great Lakes, Ph.D., Department of Civil and Environmental Engineering, Clarkson College of Technology (December, 1983).
- McDowell, R.W., Sharpley, A.N., Kleinman, P.J.A., and Gburek, W.J. 2001. Hydrological and source management of pollutants at the soil profile scale. In P.M. Haygarth and S.C. Jarvis (ed.) Agriculture, hydrology and water quality. CAB Int. Press, Oxon, England.
- McDowell, L.L., and McGregor, K.C. 1980. Nitrogen and phosphorus losses in runoff from no-till soybeans. *Trans. ASAE* 23:643-648.
- Miller, R.B. 1961. Chemical composition of rainwater at Taita, New Zealand, 1956-1958. *N.Z. J. Sci.* 4:844-853.
- Mueller, D.H., Wendt, R.C., and Daniel, T.C. 1984. Phosphorus losses as affected by tillage and manure application. *Soil Sci. Am. J.* 48:901-905.
- Murphy, T.J. and Doskey, P.V. 1975. Inputs of phosphorus from precipitation to Lake Michigan. U.S. EPA Report No. 600/3-75-005. Duluth, Minnesota.
- Murphy, J. and Riley, J.P. 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta.* 27:31-36.
- Nurnberg, G.K., Dillon, P.J. and McQueen, D.J. 1986. Internal phosphorus load in an oligotrophic precambrian shield lake with an anoxic hypolimnion. *Can. J. Fish. Aquat. Sci.*, 43:574-580.
- Nurnberg, G. and Peters, R.H. 1984. Biological availability of soluble reactive phosphorus in anoxic and oxic freshwaters. *Can. J. Fish. Aquat. Sci.* 41:757-765.

- O'Connor, G.A., Sarkar, D., Graetz, D.A., and Elliott, H.A. 2002. Characterizing forms, solubility, bioavailabilities, and mineralization rates of phosphorus in biosolids, commercial fertilizers, and manures (Phase I). Water Environment Research Federation.
- Omerink, J.M. 1976. The influence of land use on stream nutrient levels. USEPA Ecological Research Series, EPA-600/3-76-014.
- Peters, R.H. 1977. Availability of atmospheric orthophosphate. *J. Fish. Res. Bd. Can.* 34:918-924.
- Pietilainen, O.P. and Rekolainen, S. 1991. Dissolved reactive and total phosphorus load from agricultural and forested basins to surface waters in Finland. *Aqua Fennica* 21, 127-136.
- Porcella, D.B., Kumazar, J.S. and Middlebrooks, E.J. 1970. Biological effects on sediment-water nutrient interchange. *J. Sanit. Eng. Div., Proc. Am. Soc. Civil Eng.* 96:911-926.
- Pote, D.H., Danile, T.C., Sharpley, A.N., Moore, P.A., Edwards, D.R., and Nichols, D.J. 1996. Relating extractable phosphorus to phosphorus losses in runoff. *Soil Sci. Soc. Am. J.* 60:855-859.
- Rigler, F.H. 1966. Radiobiological analysis of inorganic phosphorus in lake water. *Tech. Internat. Verein. Limnol.* 16:456-470.
- Rigler, F.H. 1968. Further observations inconsistent with the hypothesis that the molybdenum blue method measures orthophosphate in lake waters. *Limnol. Oceanogr.* 13:7-13.
- Ryszkowski, L. and Bartoszewicz, A. 1989. Impact of agricultural landscape structure on cycling of inorganic nutrients. In: Clarholm, M. and Bergstrom, L. (Eds.) Ecology of arable land. Kluwer Academic Publ., Dordrecht. pp. 241-246.
- Sagher, A., Harris, R.F., and Armstrong, D.E. 1975. Availability of sediment phosphorus to microorganisms. Water Res. Cent. Tech. Rep. WIS WRC 74-01. Univ. of Wisconsin, Madison.
- Sagher, A. 1976. Availability of soil runoff phosphorus to algae. Ph.D. dissertation, University of Wisconsin, Madison.
- Schindler, D.W. and Nighswander, J.E. 1970. Nutrient supply and primary production in Clear Lake, eastern Ontario. *J. Fish. Res. Board Can.* 27:260-262.
- Sharpley, A.N., Menzel, R.G., Smith, S.J., Rhoades, E.D., and Olness, A.E. 1981. The sorption of soluble phosphorus by soil material during transport in runoff from cropped and grassed watersheds. *J. Environ. Qual.* 10:211-215.
- Sharpley, A.N., Jones, C.A., Grey, C. and Cole, C.V. 1984. A simplified soil and plant phosphorus model II: Prediction of labile, organic and sorbed phosphorus. *Soil Sci. Soc. Am. J.* 48:805-809.
- Sharpley, A.N., Smith, S.J., Menzel, R.G. and Westerman, R.L. 1985. The chemical composition of rain in the Southern Plains and its impact on soil and water quality. Oklahoma State Univ. Agric. Expt. Station Tech. Bull. T162.
- Sharpley, A.N., Smith, S.J., Jones, O.R., Berg, W.A., and Coleman, G.A. 1992. The transport of bioavailable phosphorus in agricultural runoff. *J. Environ. Qual.* 21:30-35.
- Sharpley, A.N., Hedley, M.J., Sibbesen, E., Hillbricht-Ilkowska, A., House, W.A., and Ryszkowski, L. 1995. Chapter 11: Phosphorus Transfers From Terrestrial To Aquatic Ecosystems. In SCOPE 54: Phosphorus in the Global Environment - Transfers, Cycles and Management. H. Tiessen ed., 1995, 480 pp, Wiley, U.K.

- Sharpley, A.N., T.C. Daniel, J.T. Sims, and D.H. Pote. 1996. Determining environmentally sound soil phosphorus levels. *J. Soil Wat. Conserv.* 51:160-165.
- Sharpley, A.N., Beegle, D.G., Gburek., W.J., Weld, J. and Folmar, G. 1998. Modification and application of the phosphorus index screening tool to identify critical sources of phosphorus in the Upper Chesapeake Bay Watershed. Final Rep. To the Scientific and Technical Advisory Committee to the Chesapeake Bay Program. Chesapeake Bay Program. Annapolis, MD.
- Sharpley, A.N. and Tunney, H. 2000. Phosphorus research strategies to meet agricultural and environmental challenges of the 21st century. *J. Environ Qual.* 29:176-181.
- Simrad, R.R., Beauchemin, S. and Haygarth, P.M. 2000. Potential for preferential pathways for phosphorus transport. *J. Environ. Qual.* 29:97-105.
- Sonzogni, W.C., Chesters, G., Coote, D.R., Jeffs, D.N., Konard, J.C., Ostry, R.C., and Robinson, J.B. 1980. Pollution from land runoff. *Environ. Sci. Technol.* 14:148-153.
- Syers, J.K., Harris, R.F., and Armstrong, D.E. 1973. Phosphate chemistry in lake sediments. *J. Environ. Qual.* 2:1-14.
- Szpakowska, B. and Zyczynska-Baloniak, I. 1989. The effect of environmental pollution on the migration of chemical compounds in water in a agricultural landscape. *Ecology International Bulletin.* 17:41-52.
- Tarapchak, S.J. and Rubitschum, C. 1981. Comparisons of soluble reactive phosphorus and orthophosphorus concentrations at an offshore station in southern Lake Michigan. *J. Great Lakes Res.* 7:290-298.
- Theis, T.L. and McCabe, P.J. 1978. Phosphorus dynamics in hypereutrophic lake sediments. *Water Res.*, 12:677-685.
- Vaithyanathan, P. and Correll, D.L. 1992. The Rhode River watershed: Phosphorus distribution and export in forest and agricultural soils. *J. Environ. Qual.* 21:280-288.
- Walton, C.P. and Lee, G.F. 1972. A biological evaluation of the molybdenum blue method for orthophosphate analysis. *Tech. Int. Ver. Limnol.* 18:676-684.
- Wendt, R.C. and Corey, R.B. 1980. Phosphorus variations in surface runoff from agricultural lands as a function of land use. *J. Environ. Qual.* 9:130-136.
- Williams, J.D.H., Syers, J.K., Harris, R.F., and Armstrong, D.E. 1971. Fractionation of inorganic phosphate in calcareous lake sediments. *Soil Sci. Soc. Amer. Proc.* 35:250-255.
- Williams, J.D.H., Shear, H., and Thomas, R.L. 1980. Availability to *Scenedesmus quadricauda* of different forms of phosphorus in sedimentary materials in the Great Lakes. *Limnol. Oceanogr.* 25:1-11.
- Withers, P.J.A., R.M. Dils, and R.A. Hodgkinson. 1999. Transfer of phosphorus from small agricultural basins with variable soil types and land use. P. 20-29. In Impact of land-use change on nutrient loads from diffuse sources. International Association of Hydrological Sciences Symp., Birmingham, England. 19-20 July 1999. IAHS, Wallingford, UK.
- Young, T.C., J.V. DePinto, Flint, S.E., Switzenbaum, M.S., and Edzwald, J.K. 1982. Algal Availability of Phosphorus in Municipal Wastewaters. *Jour. Water Pollut. Control Fed.* 54, 1505-1516.

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- Young, T.C. and DePinto., J.V. 1981. Algal-Availability of Particulate Phosphorus from Diffuse and Point Sources in the Lower Great Lakes Basin," in Sediment/Freshwater Interaction, Proceedings of 2nd International Symposium on the Interactions Between Sediments and Freshwater, Kingston, Ontario. Developments in Hydrobiology, V. 9, P.G. Sly (ed.), 111-119 (1982).
- Young, T.C., DePinto, J.V., and Hughes, B.J. 1988. Comparative study of methods for estimating bioavailable particulate phosphorus. Chemical and Biological characterization of sludges, sediments, dredge spoils, and drilling muds. ASTM STP 976. J.J. Lichtenberg, J.A. Winter, C.I. Weber, and L. Fradkin (ed.). American Society for Testing and Materials, Philadelphia, 1988, pp. 69-80.
- Young, T.C., DePinto, J.V., Martin, S.C., Bonner, J.S. 1995. Algal-available Particulate Phosphorus in the Great Lakes Basin. *J. Great Lakes Res.* 111(5):434-446.

Attachment A

Methods for Bioavailable Phosphorus Analysis

Two approaches are generally used to estimate bioavailable phosphorus fractions in the aquatic environment, bioassay and chemical extraction. These two methodologies are briefly discussed. Methods for measuring the bioavailability of phosphorus in soils are also presented.

Bioassay

A bioassay can be used to measure the bioavailable phosphorus content of water samples. A bioassay quantifies either growth (assuming constant phosphorus stoichiometry) or uptake of phosphorus by the test organism, usually a phosphorus-starved planktonic alga, to estimate bioavailability. The bioassay technique provides a direct measurement of phosphorus taken up by the test algal species (DePinto *et al.*, 1981). This method has been used for estimating the bioavailability of phosphorus in Lake Ontario tributary and urban runoff samples (Cowan and Lee, 1976), soil runoff suspensions (Sagher, 1976), Lake Ontario sediment samples (Williams *et al.*, 1980), and sediment samples from other lakes (Golterman *et al.*, 1977).

Young *et al.* (1982) conducted bioassays on the particulate phosphorus in wastewater samples collected from four municipal treatment plants. They used a two-chamber device, with one side lighted (assay side) for the test algae and one darkened (decay side) for the wastewater particulates and 1-1 glass bottles for the dissolved phosphorus bioassays.

To separate the dissolved and the particulate phases of phosphorus, the sample is filtered generally using a 0.45 μm pore diameter membrane filter. The filtering process separates the filtrate from the residual remaining on the filter. The filtrate contains the dissolved phosphorus, most of which is immediately or ultimately bioavailable. The residual contains the particulate phosphorus, none of which is immediately bioavailable, but a portion of it may ultimately become bioavailable. For samples collected from streams and lakes this would include phosphorus contained in the algae collected in the original sample. The residual is placed in the dark chamber. Following decay and/or desorption, phosphorus may be released and pass through the filter separating the two chambers. Once in the lighted chamber it is available for uptake by the phosphorus-starved test algae.

However, some fine colloidal materials less than 0.45 μm may pass through the filter and be hydrolyzed or dissolved by the strong acid medium of the colorimetric procedure of Murphy and Riley (1962). Thus, bioavailable phosphorus in the filtrate may be overestimated, particularly at low orthophosphate concentrations (Rigler, 1966; Tarapchak and Rubitschun, 1981). Although Walton and Lee (1972) found that orthophosphate was essentially entirely bioavailable using standard bioassay procedures, several investigators have reported that only 50 to 95% of orthophosphate was actually bioavailable (Nurnberg and Peters, 1984; Rigler 1968) in surface runoff.

Chemical Extraction

Chemical extraction is a methodology used to estimate the bioavailability of particulate phosphorus in a water sample. This methodology was developed originally for agricultural crops and soils. Chemically defined bioavailability is a sequence of extractions of phosphorus from particulate matter in an increasing order of extractions rigor that yields phosphorus fractions in a sequence of decreasing bioavailability. This method has been applied to suspended sediments in Great lakes tributaries (Logan, 1978; Logan *et al.*, 1979; Martin, 1983), urban runoff (Cowan and Lee, 1976), and a variety of lake sediments (Williams *et al.*, 1971).

Chemical extractions that have been used to measure the bioavailable particulate phosphorus content of eroded soil material are NaOH (Logan *et al.*, 1979; Sagher *et al.* 1975), NH_4F (Dorich *et al.*, 1980; Porcella *et al.*, 1970), ion exchange resins (Hanna, 1989; Huettl *et al.*, 1979), and citrate-dithionite-bicarbonate (CDB) (Logan *et al.*, 1979). The weaker extractants and short-term resin extractions may represent phosphorus available to algae in the photic zone of lakes under aerobic conditions. Once sediment settles to the bottom of the lake, sediment phosphorus bioavailability will be increased by development of reducing conditions at the sediment-water interface (Li *et al.*, 1972; Nurnberg *et al.*, 1986). Under these conditions, NaOH-extractable phosphorus may underestimate phosphorus bioavailability and CDB (Logan *et al.*, 1979) may be more appropriate as it removes a greater proportion of Fe- and Al-bound P. Thus, CDB should more accurately reflect long-term bioavailability (>30 d) of sediment phosphorus under reducing conditions found in the anoxic hypolimnion of stratified lakes (Sharpley *et al.*, 1995). For example, in a study of the phosphorus dynamics of two shallow hypereutrophic lakes in Indiana, Theis and McCabe (1978) found that the dissolved phosphorus concentration of lake water was reduced by sorption during oxic periods and increased by release of sediment phosphorus during anoxic periods. This release of phosphorus from

sediment can supply bioavailable phosphorus for several years after deposition (Jacoby *et al.*, 1982; Larsen *et al.*, 1981). Consequently, bioavailable phosphorus estimates should be used in conjunction with information on the physicochemical properties of source sediment (e.g., degree of aggregation, texture, settling velocity, clay mineralogy) and receiving lake (e.g., depth of photic zone, degree of surface mixing, development of reducing conditions, water residence time).

Often, the chemical extraction methods have been applied in parallel with bioassay methods to chemically characterize bioavailable phosphorus. As a result, some chemically-determined fractions of particulate phosphorus have been shown to be directly related with bioassay results on bioavailable phosphorus (Golterman, 1977; Dorich *et al.*, 1980; Williams *et al.*, 1980; Martin, 1983).

Chemical extraction methods for measurement of particulate phosphorus bioavailability are relatively rapid and inexpensive; however, a bioassay can represent a more realistic measure of the amount of particulate phosphorus that is available for algal uptake (Young *et al.*, 1995). Bioassays, on the other hand, are time-consuming, tedious, relatively expensive, and imprecise.

Soil Test Methods

Soil test methods that estimate plant availability of soil phosphorus are generally used for relating phosphorus in runoff to soil phosphorus content. Alternative approaches that reflect soil phosphorus release to surface and subsurface runoff include water extractable phosphorus, Fe-oxide phosphorus, and phosphorus sorption saturation of the surface 5 cm of soil (Breeuwsma and Silva, 1992; Sharpley *et al.*, 1998). Hedley *et al.* (1995) presented various tests that have been developed in different countries to suit the forms of phosphorus present in their agricultural soils. Those include Mehlich, Olsen, Bray 1, and Bray 2 tests. The form of soil phosphorus extracted by each test is determined by its solution pH and the reaction of the ions present in the extractant with sorbed or mineral phosphorus. For instance, the HCO₃⁻ and OH⁻ in the bicarbonate extract promote desorption of phosphorus from CaCO₃ and Fe and Al hydrous oxide surfaces. Bray 1 extractable phosphorus are highly correlated to Al- and Fe-P in such soils (Hedley *et al.*, 1995). Where data on soil phosphorus depletion by plants are not available, Sharpley *et al.* (1984) have used resin extraction results from calcareous, weakly weathered and strongly weathered soils to rank the suitability of different soil phosphorus tests. Kamprath (1991) summarizes their results as: The Olsen extraction is suitable for calcareous and weakly weathered acid soils and less suitable on strongly weathered soils where Bray 1 and Mehlich tests are more appropriate.

Attachment B

Bioavailable Phosphorus in Suspended and Deposited Sediments

Previous studies have indicated three major factors determining a stream's total and bioavailable phosphorus loads: basin geochemistry (Logan, 1978); land use activities (Omerink, 1976) and agricultural practices (Logan, 1977). DePinto, *et al.* (1981) chemically analyzed suspended sediments collected from five tributaries (Maumee, Sandusky, and Cuyahoga in Ohio and Cattaraugus and Genesee Rivers in New York) for several forms of phosphorus and bioassayed these sediments under aerobic conditions to measure the release of algal-available phosphorus. The bioassay data for all samples, interpreted through a first order model of available phosphorus release, showed an average of 21.8 percent of the total particulate phosphorus available to *Selenastrum capricornutum* and available phosphorus was released at an average rate of 0.154 grams per gram of total phosphorus in the sample per day (0.154/day). Amounts of available phosphorus varied considerably between tributaries of Ohio and New York. Table 1 presents the extractable phosphorus fractions in tributary suspended sediment samples (NaOH-P = sodium hydroxide extractable P, CDB-P= citrate-dithionite-biocarbonate extractable P, HCL-P = hydrochloric acid extractable P, Residual-P = total Particulate P not extracted with above sequence).

Acid-extractable (apatite) fractions are suggested to be low availability (Logan *et al.*, 1979a). Apatite is a family of phosphates containing calcium, iron, chlorine, and several other elements in varying quantities. The only common mineral of phosphorus is apatite, $\text{Ca}_5\text{F}(\text{PO}_4)_3$. Non-apatite fractions of inorganic phosphorus (base- and reductant-extractable) correlated well with levels of bioassayed algal-available phosphorus in the suspended sediment samples; however, the first-order release coefficients showed little dependency on the particulate phosphorus characteristics. Among the tributaries in Ohio, the non-apatite fractions of inorganic phosphorus (reactive NaOH- and CDB-extractable) are considered to be of high biological availability (Logan *et al.*, 1979a).

In summary, the tributaries may be classified into two distinct groups with respect to the distribution of phosphorus fractions: the Ohio rivers, which had suspended sediments which were relatively rich in non-apatite forms of phosphorus; and the New York rivers, wherein the sediments were impoverished of non-apatite forms, especially those which were base-extractable, but were enriched in apatite forms of phosphorus. The Ohio tributary sediments originated from generally low relief,

cropland-pasture watersheds, on the other hand the NY tributary sediments arose from steep slope, forest pasture watersheds and so had relatively low levels of available phosphorus.

Table 1: The extractable phosphorus fractions in tributary suspended sediment samples (NaOH-P = sodium hydroxide extractable P, CDB-P= citrate-dithionite-bicarbonate extractable P, HCL-P = hydrochloric acid extractable P, Residual-P = total Particulate P not extracted with above sequence).

River	Total Sediment P ($\mu\text{gP}/\text{mg dry wt}$)	Extractable Fractions (as % of total Sediment P)				
		NaOH-P		CDB-P	HCl-P	Residual P
		Total	Reactive			
Maumee River, Ohio	1.16	30.1	20.3	20.6	8.8	10.6
Sandusky River, Ohio	1.06	34.2	22.4	22.6	5.4	10.2
Cuyahoga River, Ohio	1.25	43.4	32.1	23.6	15.3	5.1
Cattaraugus River (South Branch), NY	0.60	12.7	7.7	13.7	50.8	8.0
Genesee River, NY	0.99	24.2	17.2	18.9	27.6	7.8

Other studies describe the bioavailable phosphorus fractions from different systems. Fluvial sediments from two streams in Ontario were estimated to contain bioavailable phosphorus in amounts equal to 24 and 37% of the total particulate phosphorus (Williams *et al.*, 1980). Urban runoff, mainly from residential areas of Madison, Wisconsin, contained bioavailable particulate phosphorus that averaged 30% of the total particulate phosphorus for 13 samples (Cowan and Lee, 1976). The authors also determined that up to 23% of the particulate phosphorus in snow samples, from the Madison area, was bioavailable. These results and the studies conducted by Sonzogni *et al.* 1980 suggest that generally less than 40% of the particulate phosphorus in diffuse tributary sources to the Great Lakes is biologically available.

The bioavailability of particulate phosphorus in deposited sediments is generally greater than that of suspended sediments, possibly due to the incorporation of phosphorus rich detrital material in the deposits. Release of bioavailable phosphorus from suspended sediment occurs mostly by chemical desorption, whereas bioavailable phosphorus associated with deposited sediments is released more slowly because the dominant process is microbial mineralization. A summary of bioavailable phosphorus study results for suspended and bedded sediments is presented in Table 2.

Table 2: Percent bioavailability of Particulate Phosphorus transported in several lake tributaries draining agricultural watersheds and in deposited lake sediments (Sharpley *et al.* 1995).

Location	Procedure	Bioavailable %	Total P g kg ⁻¹	Reference
Suspended Sediment in Tributaries				
Indiana	Bioassay	21	0.2-0.7	Dorich <i>et al.</i> (1985)
	NaOH	8		
Great Lakes	Bioassay	0-47	0.5-1.4	DePinto <i>et al.</i> (1981)
	NaOH	4-38		
Lake Erie	NaOH	14-42	0.6-1.5	Logan <i>et al.</i> (1979)
Amazon R.	NaOH	21-38	0.4-1.1	Engle & Sarnelle (1990)
Deposited Sediments				
Quebec	Resin	8-25	0.8-1.2	Carignan & Kalff (1980)
Netherlands	Bioassay	0-41	0.4-4.8	Klapwijk <i>et al.</i> (1982)
Wisconsin	NaOH	60-95	0.6-3.9	Sagher <i>et al.</i> (1975)
Lake Ontario	NaOH	2-60		Bannerman <i>et al.</i> 1975
Great Lakes	NaOH	27	0.4-1.4	Williams <i>et al.</i> (1980)

Young and DePinto (1982) developed a relationship between the reactive NaOH-extractable phosphorus and ultimate bioavailable phosphorus for tributary suspended solids as:

$$UAAP = 1.08 \text{ NaOH extractableP} - 0.008$$

where: *UAAP* is the ultimate bioavailable phosphorus.

Solids in natural waters have two primary origins. The solids produced by the photosynthesis process are termed as autochthonous and the solids originating in the drainage basin are termed as allochthonous. DePinto *et al.* (1986) have explored the difference between the bioavailability of allochthonous and autochthonous particulate phosphorus to estimate the form and reactivity of phosphorus loadings to the Lower Laurentian Great Lakes. The comparison and analysis of parallel bioassay and chemical fraction results on suspended sediments collected from 6 different lower Great Lakes tributaries revealed that the most reasonable surrogate measure of biologically available particulate phosphorus is the reactive NaOH-extractable phosphorus (R-NaOH-P) fraction (DePinto *et al.*, 1986). They found a very good correlation ($r = 0.7790$, $p < 0.001$) between R-NaOH-P and the bioassay-determined values of bioavailable phosphorus. The CDB-P and the sum of R-NaOH-P and

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CDB-P (considered to be measure of non-apatite inorganic phosphorus in sediments) also correlated well with the ultimately bioavailable phosphorus. However, the decision to rely on the R-NaOH-P alone for estimation of bioavailable phosphorus was based on data from 17 of the 40 samples for which the distribution of phosphorus among the chemically defined fractions was determined before and after the bioassays. The authors also found an excellent correlation between the decrease in R-NaOH-P and algal uptake of phosphorus during bioassays on individual samples. This provided very strong evidence in favor of using the R-NaOH-P/ultimately-bioavailable phosphorus correlation to extrapolate their results to basin-wide data sets.

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Attachment C

Basin Discharge Summary Sheets

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Minnesota River

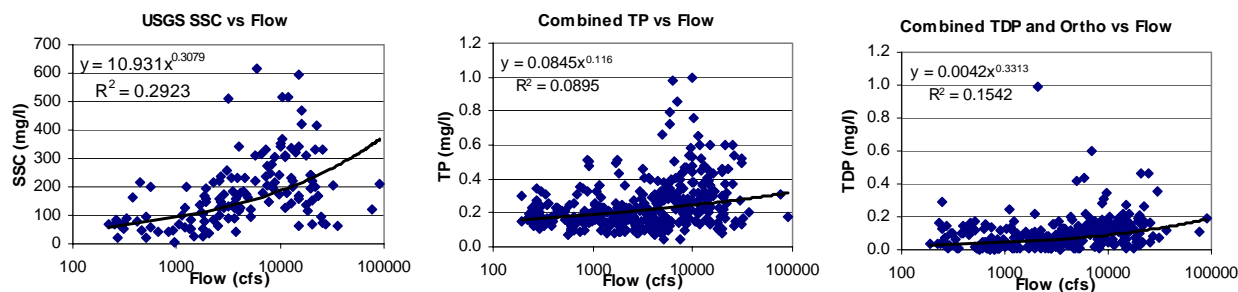
Basin Specific Total Phosphorus and Bioavailable Phosphorus Summary

Approximate basin area (sq. mi.): 14,939 (in Minnesota)
Representative USGS Gauge: #05330000 Minnesota River near Jordan, MN
Representative MPCA EDA Site: MWCC040 Minn River near Jordan at Co 9 bridge
 Approximate drainage area at gauge (sq. mi.): 16,200
 Total basin to gauged area multiplier: 0.922 (<1 because only interested in area within Minnesota)

Compiled Water Quality Data

USGS (Water Years 1979-1998)	Count (n)
Suspended sediment concentration (SSC) mg/l:	134
Phosphorus, water, unfiltered (TP) (mg/l):	171
Phosphorus, water, filtered (TDP) (mg/l):	166
MPCA EDA Data Extraction (1985-1992)	
Phosphorus, total (TP) (mg/l as P):	214
Phosphorus, dissolved orthophosphate (mg/l P):	135

Rating Curves



Estimated Annual Basin Load (metric tons/year)

Representative Years		Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus	Fraction Bioavailable
Low Flow Year	1981	277,391	429	130	299	184	43%
	1990	329,196	472	156	316	213	45%
	2000	357,016	525	168	356	232	44%
	Average	321,201	475	151	324	210	44%
Average Flow Year	1985	935,399	1,230	447	783	588	48%
	1998	890,220	1,161	426	735	558	48%
	1999	1,049,252	1,370	501	869	658	48%
	Average	958,291	1,254	458	796	601	48%
High Flow Year	1986	1,915,830	2,280	926	1,354	1,170	51%
	1997	2,016,096	2,275	982	1,294	1,215	53%
	2001	2,398,943	2,433	1,183	1,250	1,408	58%
	Average	2,110,290	2,330	1,030	1,299	1,264	54%

Estimated Annual Basin Yield (lbs/acre/yr)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	74	0.11	0.03	0.07	0.05
Average Flow Year	221	0.29	0.11	0.18	0.14
High Flow Year	486	0.54	0.24	0.30	0.29

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	152.7	0.226	0.072	0.154	0.100
Average Flow Year	186.9	0.245	0.089	0.155	0.117
High Flow Year	244.4	0.270	0.119	0.150	0.146

Upper Mississippi River Basin Specific Total Phosphorus and Bioavailable Phosphorus Summary

Approximate basin area (sq. mi.): 20,100

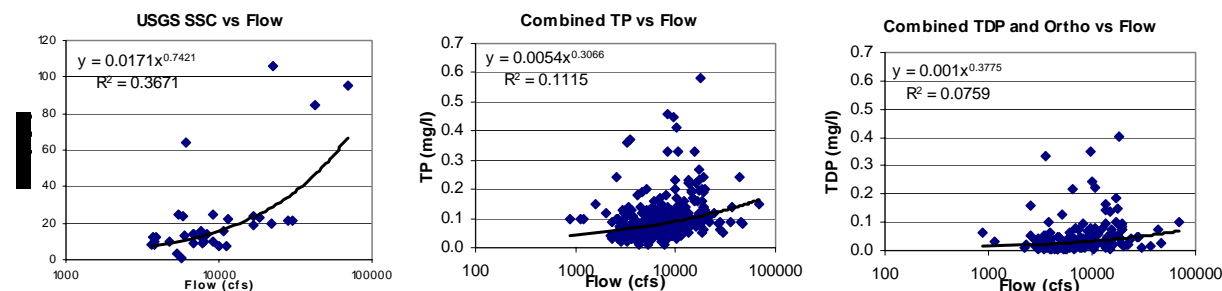
Representative USGS Gauge: #05288500 Mississippi River Near Anoka, MN
Representative MPCA EDA Site: MWCC006 MISSISSIPPI R UPST L&D 1, 0.2MI DS FORD PKWY
Representative MPCA STORET Site: S000-024 MISSISSIPPI R MPLS WATERWORKS INTAKE AT FRIDLEY

Approximate drainage area at gauge (sq. mi.): 19,100
 Total watershed to gauged area multiplier: 1.052

Compiled Water Quality Data

USGS (Water Years 1984-1998)	Count (n)
Suspended sediment concentration (SSC) mg/l:	35
Phosphorus, water, unfiltered (TP) (mg/l):	25
Phosphorus, water, filtered (TDP) (mg/l):	25
<i>MPCA EDA Data Extraction (1985-1992)</i>	
Phosphorus, total (TP) (mg/l as P):	220
Phosphorus, orthophosphate as P (mg/l P):	133
<i>MPCA New STORET Data (1999-2002)</i>	
Phosphorus as P (mg/l):	15

Rating Curves



Estimated Annual Basin Load (metric tons/year)

Representative Years		Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus	Fraction Bioavailable
Low Flow Year	1989	81,369	471	166	305	221	47%
	1990	90,080	520	184	336	244	47%
	2000	83,881	534	186	347	249	47%
	<i>Average</i>	<i>85,110</i>	<i>508</i>	<i>179</i>	<i>329</i>	<i>238</i>	<i>47%</i>
Average Flow Year	1982	241,673	1,045	387	658	505	48%
	1995	198,574	984	357	627	470	48%
	2002	197,596	961	350	611	460	48%
	<i>Average</i>	<i>212,614</i>	<i>997</i>	<i>365</i>	<i>632</i>	<i>478</i>	<i>48%</i>
High Flow Year	1986	511,754	1,946	737	1,209	954	49%
	1997	319,259	1,273	476	797	620	49%
	2001	397,499	1,418	540	877	698	49%
	<i>Average</i>	<i>409,504</i>	<i>1,545</i>	<i>584</i>	<i>961</i>	<i>757</i>	<i>49%</i>

Estimated Annual Basin Yield (lbs/acre/yr)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	15	0.087	0.031	0.056	0.041
Average Flow Year	36	0.170	0.062	0.108	0.082
High Flow Year	70	0.264	0.100	0.164	0.130

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	14.3	0.085	0.030	0.055	0.040
Average Flow Year	21.4	0.100	0.037	0.064	0.048
High Flow Year	30.3	0.114	0.043	0.071	0.056

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**Lower Mississippi River
 Basin Specific Total Phosphorus and Bioavailable Phosphorus Summary**

Approximate basin area (sq. mi.): 6,317 (in Minnesota)

Representative USGS Gauge: #05355200 Cannon River at Welch, MN
Representative MPCA STORET Site: S001-784 CANNON R, BRG AT 9TH ST N IN CITY OF CANNON FALLS

Approximate drainage area at gauge (sq. mi.): 1,340

Representative USGS Gauge: #05385000 Root River Near Houston, MN
Representative LTRMP Site: RO00.1M Root River near confluence with Mississippi River

Approximate drainage area at LTRMP site (sq.mi.) 1,660
 Total basin to gauged area multiplier: 2.998 (assume Root River represents the remainder of the Lower Mississippi Basin in Minnesota)

Compiled Water Quality Data

See Summary information on separate sheets for the Cannon and Root Rivers

Rating Curves

See Summary information on separate sheets for the Cannon and Root Rivers

Estimated Annual Basin Load (metric tons/year)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus	Fraction Bioavailable
Low Flow Year	48,612	238	102	135	127	53%
Average Flow Year	342,383	789	237	552	336	43%
High Flow Year	971,031	1,940	573	1,368	819	42%

Estimated Annual Basin Yield (lbs/acre/yr)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	26.5	0.129	0.056	0.074	0.069
Average Flow Year	186	0.430	0.129	0.301	0.183
High Flow Year	528	1.056	0.312	0.744	0.446

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	25	0.100	0.038	0.063	0.049
Average Flow Year	81	0.186	0.055	0.131	0.079
High Flow Year	150	0.286	0.079	0.207	0.116

Lower Mississippi River - Cannon River
Watershed Specific Total Phosphorus and Bioavailable Phosphorus Summary

Approximate watershed area (sq. mi.): **1,340**

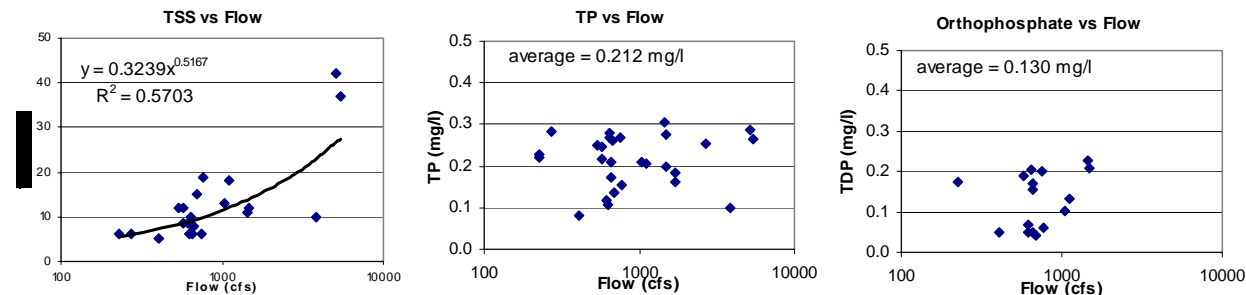
Representative USGS Gauge: #05355200 Cannon River at Welch, MN
Representative MPCA STORET Site: S001-784 CANNON R, BRG AT 9TH ST N IN CITY OF CANNON FALLS

Approximate drainage area at gauge (sq. mi.): **1,340**
 Total watershed to gauged area multiplier: **1.000**

Compiled Water Quality Data

	Count (n)
<i>No useful USGS water quality data available</i>	
<i>No useful MPCA EDA Data available</i>	
<i>MPCA New STORET Data (2001-2002)</i>	
Total Suspended Sediment (TSS) (mg/l):	22
Phosphorus as P (mg/l):	28
Phosphorus, orthophosphate as P (mg/l):	16

Rating Curves



Estimated Annual Watershed Load (metric tons/year)

Representative Years		Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus	Fraction Bioavailable
Low Flow Year	1996	8,092	145	89	56	99	68%
	2002	6,775	127	78	49	86	68%
	<i>Average</i>	7,433	136	83	53	93	68%
Average Flow Year	1994	9,711	171	105	66	117	68%
	1998	19,624	229	140	89	156	68%
	<i>Average</i>	14,668	200	123	77	137	68%
High Flow Year	1973	<i>No flow data</i>	<i>No flow data</i>	<i>No flow data</i>	<i>No flow data</i>	<i>No flow data</i>	<i>No flow data</i>
	1974	<i>No flow data</i>	<i>No flow data</i>	<i>No flow data</i>	<i>No flow data</i>	<i>No flow data</i>	<i>No flow data</i>
	1993	41,890	404	247	156	276	68%
	<i>Average</i>	41,890	404	247	156	276	68%

Estimated Annual Watershed Yield (lbs/acre/yr)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	19	0.35	0.21	0.13	0.24
Average Flow Year	38	0.51	0.31	0.20	0.35
High Flow Year	107	1.04	0.63	0.40	0.71

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	11.6	0.212	0.130	0.082	0.145
Average Flow Year	15.1	0.212	0.130	0.082	0.145
High Flow Year	22.0	0.212	0.130	0.082	0.145

To: Hal Runke and Greg Wilson, Barr Engineering
 From: Hans Holmberg, Joe DePinto and Jagjit Kaur, LTI
 Subject: Assessment of Bioavailable Fractions of Phosphorus
 Date: January 16, 2004
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**Lower Mississippi River - Root River
 Watershed Specific Total Phosphorus and Bioavailable Phosphorus Summary**

Approximate watershed area (sq. mi.): **1,660**

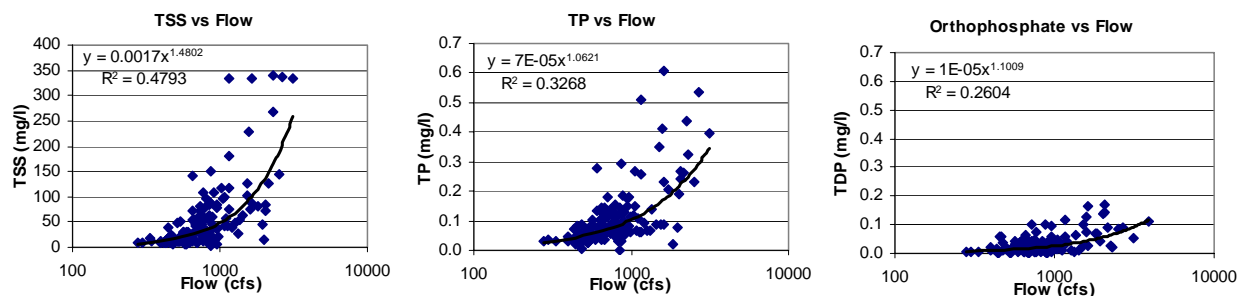
Representative USGS Gauge: #05385000 Root River Near Houston, MN
 Representative LTRMP Site: RO00.1M Root River near confluence with Mississippi River

Approximate drainage area at gauge (sq. mi.): **1,270**
 Approximate drainage area at LTRMP site (sq.mi.): **1,660**
 Total watershed to gauged area multiplier: **1.307**

Compiled Water Quality Data

	Count (n)
<i>LTRMP Data (1991-1998)</i>	
Total Suspended Sediment (TSS) (mg/l):	149
Phosphorus as P (mg/l):	140
Phosphorus, orthophosphate as P (mg/l):	151

Rating Curves



Estimated Annual Watershed Load (metric tons/year)

Representative Years		Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus	Fraction Bioavailable
Low Flow Year	1977	13,734	34	6	28	11	33%
	2002	<i>No flow data</i>	<i>No flow data</i>	<i>No flow data</i>	<i>No flow data</i>	<i>No flow data</i>	<i>No flow data</i>
	<i>Average</i>	13,734	34	6	28	11	33%
Average Flow Year	1994	89,145	170	33	137	57	34%
	1998	129,464	224	44	180	76	34%
	<i>Average</i>	109,304	197	38	158	67	34%
High Flow Year	1973	282,818	476	101	375	168	35%
	1974	251,219	425	90	336	150	35%
	1993	395,664	636	135	501	225	35%
	<i>Average</i>	309,900	513	108	404	181	35%

Estimated Annual Watershed Yield (lbs/acre/yr)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	28	0.07	0.01	0.06	0.02
Average Flow Year	226	0.41	0.08	0.33	0.14
High Flow Year	642	1.06	0.22	0.84	0.38

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	28.5	0.070	0.013	0.057	0.023
Average Flow Year	99.4	0.179	0.035	0.144	0.061
High Flow Year	184.4	0.306	0.065	0.241	0.108

To: Hal Runke and Greg Wilson, Barr Engineering
 From: Hans Holmberg, Joe DePinto and Jagjit Kaur, LTI
 Subject: Assessment of Bioavailable Fractions of Phosphorus
 Date: January 16, 2004
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Des Moines River

Basin Specific Total Phosphorus and Bioavailable Phosphorus Summary

Approximate basin area (sq. mi.): **1,535** (in Minnesota)

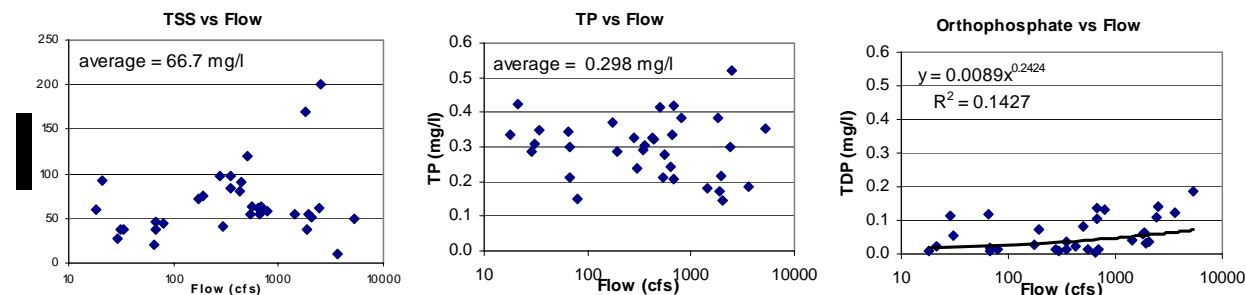
Representative USGS Gauge: #05476000 Des Moines River at Jackson, MN
 Representative MPCA STORET Site: S000-027 DES MOINES R.-W FORK AT JACKSON

Approximate drainage area at gauge (sq. mi.): **1,250**
 Total basin to gauged area multiplier: **1.228**

Compiled Water Quality Data

	Count (n)
<i>No useful USGS water quality data available</i>	
<i>No useful MPCA EDA Data available</i>	
<i>MPCA New STORET Data (2001-2002)</i>	
Total Suspended Sediment (TSS) (mg/l):	34
Phosphorus as P (mg/l):	34
Phosphorus, orthophosphate as P (mg/l):	31

Rating Curves



Estimated Annual Basin Load (metric tons/year)

Representative Years		Suspended	Total	Total Dissolved	Total	Total	Fraction
		Sediment	Phosphorus	Phosphorus	Particulate	Bioavailable	Bioavailable
Low Flow Year	1989	3,609	16	1.6	14	4.2	26%
	1990	4,192	19	1.9	17	4.9	26%
	2000	5,896	26	2.9	23	7.1	27%
	<i>Average</i>	<i>4,566</i>	<i>20</i>	<i>2.2</i>	<i>18</i>	<i>5.4</i>	<i>27%</i>
Average Flow Year	1987	36,628	163	26	138	50	31%
	1991	31,848	142	25	117	46	32%
	1999	39,678	177	27	150	54	31%
	<i>Average</i>	<i>36,052</i>	<i>161</i>	<i>26</i>	<i>135</i>	<i>50</i>	<i>31%</i>
High Flow Year	1983	87,662	391	74	317	131	33%
	1984	81,950	366	76	290	128	35%
	1994	63,917	285	48	237	91	32%
	<i>Average</i>	<i>77,843</i>	<i>347</i>	<i>66</i>	<i>281</i>	<i>116</i>	<i>34%</i>

Estimated Annual Basin Yield (lbs/acre/yr)

Flow Condition	Suspended	Total	Total Dissolved	Total	Total
	Sediment	Phosphorus	Phosphorus	Particulate	Bioavailable
Low Flow Year	10	0.046	0.005	0.041	0.012
Average Flow Year	81	0.360	0.058	0.302	0.112
High Flow Year	174	0.778	0.147	0.630	0.261

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Flow Condition	Suspended	Total	Total Dissolved	Total	Total
	Sediment	Phosphorus	Phosphorus	Particulate	Bioavailable
Low Flow Year	66.7	0.298	0.031	0.266	0.079
Average Flow Year	66.7	0.298	0.048	0.249	0.093
High Flow Year	66.7	0.298	0.056	0.242	0.099

Cedar River

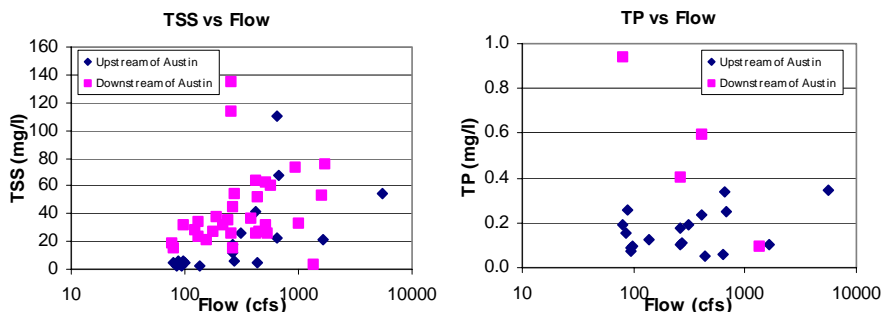
Basin Specific Total Phosphorus and Bioavailable Phosphorus Summary

Approximate basin area (sq. mi.):	1,028	<i>(in Minnesota)</i>
Representative USGS Gauge:	#05457000	Cedar River near Austin, MN
Representative MPCA STORET Site:	S000-136	CEDAR RIVER AT CSAH-4, 3 MILES SOUTH OF AUSTIN
Representative MPCA STORET Site:	S000-137	CEDAR RIVER AT CSAH-2, 0.5 MILES EAST OF LANSING
Approximate drainage area at gauge (sq. mi.):	399	
Total basin to gauged area multiplier:	2.576	

Compiled Water Quality Data

	Count (n)
No useful USGS water quality data available	
No MPCA EDA Data Available	
MPCA New STORET Data (1999-2002)	
Total suspended solids (TSS) (mg/l):	50
Phosphorus as P (mg/l):	22

Rating Curves



The apparent impact of the Austin WWTP at the USGS gauge and insufficient data restrict the use of rating curves for developing annual load estimations and bioavailable fractions for the Cedar River basin.

Estimated Annual Basin Load (metric tons/year)

Using annual loads for the Des Moines River Basin based on similar land use characteristics, adjusted for drainage area

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Phosphorus		Fraction Bioavailable
				Particulate Phosphorus	Bioavailable Phosphorus	
Low Flow Year	3,058	14	1.4	12	3.6	27%
Average Flow Year	24,144	108	17	90	34	31%
High Flow Year	52,132	233	44	188	78	34%

Estimated Annual Basin Yield (lb/acre/yr)

Using annual yields for the Des Moines River Basin based on similar land use characteristics

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Phosphorus	
				Particulate Phosphorus	Bioavailable Phosphorus
Low Flow Year	10	0.046	0.005	0.041	0.012
Average Flow Year	81	0.360	0.058	0.302	0.112
High Flow Year	174	0.778	0.147	0.630	0.261

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Using flow weighted mean concentrations for the Des Moines River Basin based on similar land use characteristics

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Phosphorus	
				Particulate Phosphorus	Bioavailable Phosphorus
Low Flow Year	66.7	0.298	0.031	0.266	0.079
Average Flow Year	66.7	0.298	0.048	0.249	0.093
High Flow Year	66.7	0.298	0.056	0.242	0.099

To: Hal Runke and Greg Wilson, Barr Engineering
 From: Hans Holmberg, Joe DePinto and Jagjit Kaur, LTI
 Subject: Assessment of Bioavailable Fractions of Phosphorus
 Date: January 16, 2004
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Missouri River

Basin Specific Total Phosphorus and Bioavailable Phosphorus Summary

Approximate basin area (sq. mi.): **1,782** (in Minnesota)

Representative USGS Gauge: #06483270 Rock River at Rock Rapids, IA

Approximate drainage area at gauge (sq. mi.): **788**

Total basin to gauged area multiplier: **2.261**

Compiled Water Quality Data

Count (n)

No useful USGS water quality data available

No MPCA EDA Data available

No MPCA New STORET Data available

Rating Curves

Insufficient data restrict the use of rating curves for developing annual load estimations and bioavailable fractions for the Rock River watershed, and therefore, the Missouri Basin in Minnesota.

Estimated Annual Basin Load (metric tons/year)

Using annual loads for the Des Moines River Basin based on similar land use characteristics, adjusted for drainage area

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus	Fraction Bioavailable
Low Flow Year	5,300	24	2.5	21	6.3	27%
Average Flow Year	41,853	187	30	157	58	31%
High Flow Year	90,369	403	76	327	135	34%

Estimated Annual Basin Yield (lbs/acre/yr)

Using annual yields for the Des Moines River Basin based on similar land use characteristics

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	10	0.046	0.005	0.041	0.012
Average Flow Year	81	0.360	0.058	0.302	0.112
High Flow Year	174	0.778	0.147	0.630	0.261

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Using flow weighted mean concentrations for the Des Moines River Basin based on similar land use characteristics

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	66.7	0.298	0.031	0.266	0.079
Average Flow Year	66.7	0.298	0.048	0.249	0.093
High Flow Year	66.7	0.298	0.056	0.242	0.099

To: Hal Runke and Greg Wilson, Barr Engineering
 From: Hans Holmberg, Joe DePinto and Jagjit Kaur, LTI
 Subject: Assessment of Bioavailable Fractions of Phosphorus
 Date: January 16, 2004
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St. Croix River

Basin Specific Total Phosphorus and Bioavailable Phosphorus Summary

Approximate basin area (sq. mi.):	3,528	<i>(in Minnesota)</i>
Representative USGS Gauge:	#05338500	Snake River near Pine City, MN
Representative MPCA STORET Site:	S000-198	SNAKE R BRIDGE AT CSAH-9, 2 MI NE OF PINE CITY
Approximate drainage area at gauge (sq. mi.): 958		
Representative USGS Gauge:	#05336700	Kettle River below Sandstone, MN
Representative MPCA STORET Site:	S000-121	KETTLE R BRIDGE ON MN-48, 4.5 MI E OF HINCKLEY
Approximate drainage area at gauge (sq. mi.): 868		
Total basin to gauged area multiplier:	1.932	<i>(assume Snake and Kettle Rivers equally represent the remainder of the St. Croix Basin in Minnesota)</i>

Compiled Water Quality Data

See Summary information on separate sheets for the Snake and Kettle Rivers

Rating Curves

See Summary information on separate sheets for the Snake and Kettle Rivers

Estimated Annual Basin Load (metric tons/year)

Representative Years		Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus	Fraction Bioavailable
Low Flow Year	1987	No flow data	No flow data	No flow data	No flow data	No flow data	No flow data
	1988	No flow data	No flow data	No flow data	No flow data	No flow data	No flow data
	1998	6,355	85	29	56	39	46%
	Average	6,355	85	29	56	39	46%
Average Flow Year	1994	12,068	145	48	97	66	45%
	1995	14,100	181	60	120	82	45%
	1999	11,108	139	46	92	63	46%
	Average	12,426	155	52	103	70	45%
High Flow Year	1986	No flow data	No flow data	No flow data	No flow data	No flow data	No flow data
	2001	28,605	254	78	176	110	43%
	Average	28,605	254	78	176	110	43%

Estimated Annual Basin Yield (lbs/acre/yr)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Average Flow Year	12	0.151	0.050	0.100	0.068
High Flow Year	28	0.247	0.076	0.171	0.107

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Average Flow Year	5	0.071	0.024	0.047	0.032
High Flow Year	8	0.075	0.024	0.052	0.033

St. Croix River - Snake River
Watershed Specific Total Phosphorus and Bioavailable Phosphorus Summary

Approximate watershed area (sq. mi.): **958**

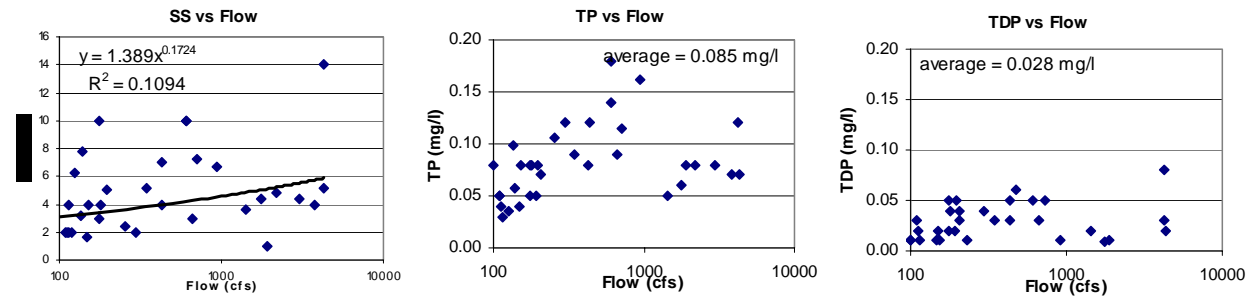
Representative USGS Gauge: #05338500 Snake River near Pine City, MN
 Representative MPCA STORET Site: S000-198 SNAKE R BRIDGE AT CSAH-9, 2 MI NE OF PINE CITY

Approximate drainage area at gauge (sq. mi.): **958**
 Total watershed to gauged area multiplier: **1.000**

Compiled Water Quality Data

USGS (Water Years 1979-1998)	Count (n)
Suspended sediment concentration (SSC) mg/l:	13
Phosphorus, water, unfiltered (TP) (mg/l):	15
Phosphorus, water, filtered (TDP) (mg/l):	12 (excluded one outlier)
Orthophosphate, water, filtered, as P (mg/l):	10
No MPCA EDA data available	
MPCA New STORET Data (1999-2002)	
Total suspended solids (TSS) (mg/l):	20 (excluded one outlier)
Phosphorus as P (mg/l):	21
Phosphorus, orthophosphate as P (mg/l):	10

Rating Curves



Estimated Annual Watershed Load (metric tons/year)

Representative Years		Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus	Fraction Bioavailable
Low Flow Year	1987	No flow data	No flow data	No flow data	No flow data	No flow data	No flow data
	1988	No flow data	No flow data	No flow data	No flow data	No flow data	No flow data
	1998	1,117	23	8	15	11	45%
	Average	1,117	23	8	15	11	45%
Average Flow Year	1994	2,325	43	14	28	19	45%
	1995	3,335	59	20	39	27	45%
	1999	2,017	38	13	25	17	45%
	Average	2,559	47	16	31	21	45%
High Flow Year	1986	No flow data	No flow data	No flow data	No flow data	No flow data	No flow data
	2001	4,968	74	25	50	34	45%
	Average	4,968	74	25	50	34	45%

Estimated Annual Watershed Yield (lbs/acre/yr)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	4.0	0.083	0.028	0.055	0.038
Average Flow Year	9	0.168	0.056	0.112	0.076
High Flow Year	18	0.267	0.089	0.178	0.121

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	4.1	0.085	0.028	0.057	0.039
Average Flow Year	4.6	0.085	0.028	0.057	0.039
High Flow Year	5.7	0.085	0.028	0.057	0.039

St. Croix River - Kettle River
Watershed Specific Total Phosphorus and Bioavailable Phosphorus Summary

Approximate watershed area (sq. mi.): **868**

Representative USGS Gauge: #05336700 Kettle River below Sandstone, MN
 Representative MPCA STORET Site: S000-121 KETTLE R BRIDGE ON MN-48, 4.5 MI E OF HINCKLEY
 Approximate drainage area at gauge (sq. mi.): **868**
 Total watershed to gauged area multiplier: **1.000**

Compiled Water Quality Data

Count (n)

No useful USGS water quality data available

No MPCA EDA data available

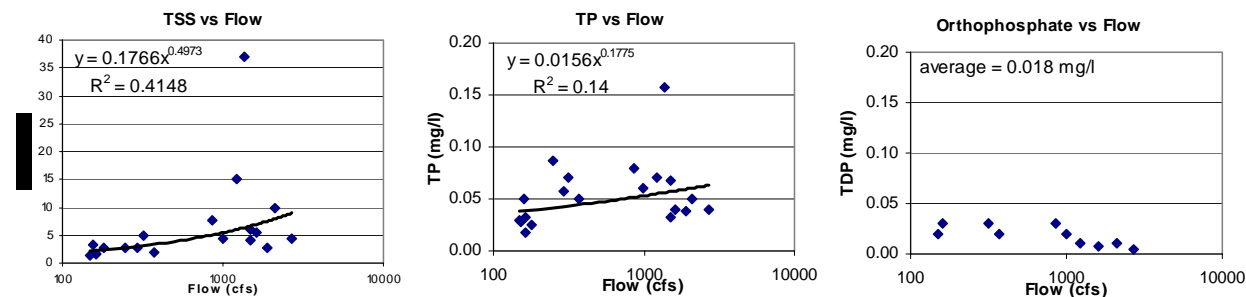
MPCA New STORET Data (1999-2002)

Total suspended solids (TSS) (mg/l): **19**

Phosphorus as P (mg/l): **20**

Phosphorus, orthophosphate as P (mg/l): **10**

Rating Curves



Estimated Annual Watershed Load (metric tons/year)

Representative Years		Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus	Fraction Bioavailable
Low Flow Year	1987	1,443	17	6.4	10.2	8.2	50%
	1988	1,408	14	5.2	8.9	6.8	48%
	1998	2,172	21	7.4	13.5	9.8	47%
	Average	1,674	17	6.3	10.9	8.3	48%
Average Flow Year	1994	3,921	33	11	22	15	45%
	1995	3,963	34	11	23	15	45%
	1999	3,732	34	11	22	15	46%
	Average	3,872	33	11	22	15	45%
High Flow Year	1986	11,476	76	22	54	32	42%
	2001	9,837	57	16	41	23	40%
	Average	10,657	67	19	48	27	41%

Estimated Annual Watershed Yield (lbs/acre/yr)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	6.6	0.068	0.025	0.043	0.033
Average Flow Year	15	0.132	0.044	0.088	0.060
High Flow Year	42	0.264	0.074	0.189	0.108

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	4.8	0.049	0.018	0.031	0.024
Average Flow Year	6.3	0.055	0.018	0.036	0.025
High Flow Year	10.5	0.065	0.018	0.047	0.027

To: Hal Runke and Greg Wilson, Barr Engineering
 From: Hans Holmberg, Joe DePinto and Jagjit Kaur, LTI
 Subject: Assessment of Bioavailable Fractions of Phosphorus
 Date: January 16, 2004
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Lake Superior
Basin Specific Total Phosphorus and Bioavailable Phosphorus Summary

Approximate basin area (sq. mi.): **6,149** (in Minnesota)

Representative USGS Gauge: #04024000 St. Louis River at Scanlon, MN
Representative MPCA EDA Site: SL 297 ST. LOUIS RIVER AT USH-61 BRIDGE
Representative MPCA STORET Site: S000-046 ST LOUIS R. OLD USH-61 AT SCANLON

Approximate drainage area at gauge (sq. mi.): **3,430**

Total St. Louis River watershed area (sq. mi.): **3,634** (includes a small portion in Wisconsin)

Total watershed to gauged area multiplier: **1.059**

Representative USGS Gauge: #04014500 Baptism River near Beaver Bay, MN

Representative MPCA EDA Site: 110 BAPTISM RIVER

Approximate drainage area at gauge (sq. mi.): **140**

Lake Superior drainage area outside of St. Louis River (sq. mi.): **2,515**

Assume Baptism represents this area, gauged area multiplier: **17.964**

Compiled Water Quality Data

See Summary information on separate sheets for the St. Louis and Baptism Rivers

Rating Curves

See Summary information on separate sheets for the St. Louis and Baptism Rivers

Estimated Annual Basin Load (metric tons/year)

Representative Years		Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus	Fraction Bioavailable
Low Flow Year	1980	12,231	40	8	33	13	33%
	1988	12,461	40	7	32	13	33%
	1990	15,918	45	10	35	17	37%
	Average	13,537	42	8	33	14	35%
Average Flow Year	1981	24,474	70	13	58	23	33%
	1992	27,885	80	16	63	28	35%
	1993	30,945	83	17	66	29	35%
	Average	27,768	78	15	62	26	34%
High Flow Year	1983	39,490	104	20	84	35	34%
	1984	34,813	95	18	77	32	34%
	Average	37,152	100	19	81	34	34%

Estimated Annual Basin Yield (lbs/acre/year)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	7.6	0.023	0.005	0.019	0.008
Average Flow Year	15.5	0.043	0.008	0.035	0.015
High Flow Year	20.8	0.056	0.011	0.045	0.019

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	11	0.030	0.011	0.019	0.014
Average Flow Year	14	0.033	0.011	0.022	0.015
High Flow Year	15	0.035	0.011	0.023	0.015

Lake Superior - St. Louis River
Watershed Specific Total Phosphorus and Bioavailable Phosphorus Summary

Approximate watershed area (sq. mi.): 3,430

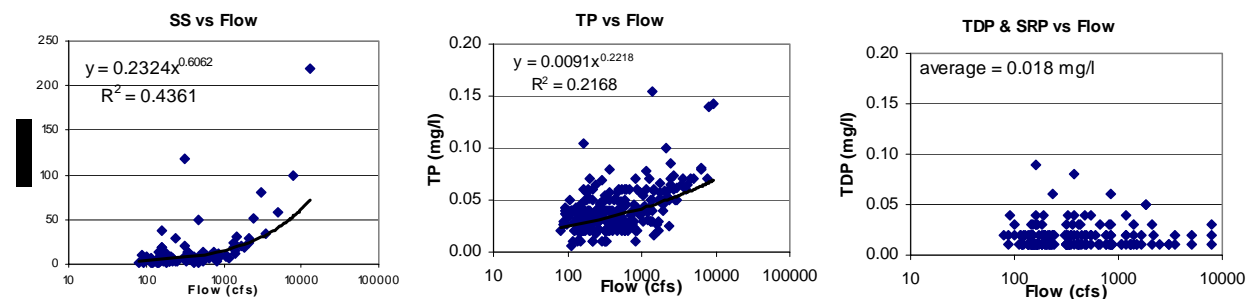
Representative USGS Gauge: #04024000 St. Louis River at Scanlon, MN
Representative MPCA EDA Site: SL 297 ST. LOUIS RIVER AT USH-61 BRIDGE
Representative MPCA STORET Site: S000-046 ST LOUIS R. OLD USH-61 AT SCANLON

Approximate drainage area at gauge (sq. mi.): 3,430
 Total watershed to gauged area multiplier: 1.000

Compiled Water Quality Data

USGS (Water Years 1979-1994)	Count (n)
Suspended sediment concentration (SSC) mg/l:	98
Phosphorus, water, unfiltered (TP) (mg/l):	99 (excluded one outlier)
Phosphorus, water, filtered (TDP) (mg/l):	99 (excluded one outlier)
Orthophosphate, water, filtered, as P (SRP) (mg/l):	80
MPCA EDA (Water Year 1979-1996)	
Phosphorus, Total (mg/l as P):	158
MPCA New STORET Data (2001)	
Phosphorus as P (mg/l):	8

Rating Curves



Estimated Annual Watershed Load (metric tons/year)

Representative Years		Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus	Fraction Bioavailable
Low Flow Year	1980	3,796	11.3	5.4	5.9	6.5	57%
	1988	3,993	11.0	5.1	5.9	6.2	56%
	1990	8,203	19.9	8.4	11.4	10.5	53%
	Average	5,331	14.7	6.3	7.7	7.7	55%
Average Flow Year	1981	9,847	22.4	9.2	13.3	11.6	52%
	1992	13,091	30.9	12.6	18.3	15.9	52%
	1993	15,885	33.7	13.1	20.6	16.8	50%
	Average	12,941	29.0	11.6	17.4	14.8	51%
High Flow Year	1983	19,877	41.6	15.9	25.7	20.5	49%
	1984	16,025	35.1	13.9	21.3	17.7	50%
	Average	17,951	38.3	14.9	23.5	19.1	50%

Estimated Annual Watershed Yield (lbs/acre/year)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	5.3	0.014	0.006	0.008	0.008
Average Flow Year	13.0	0.029	0.012	0.017	0.015
High Flow Year	18.0	0.038	0.015	0.024	0.019

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	14.7	0.040	0.018	0.022	0.022
Average Flow Year	19.9	0.045	0.018	0.027	0.023
High Flow Year	21.7	0.046	0.018	0.028	0.023

To: Hal Runke and Greg Wilson, Barr Engineering
 From: Hans Holmberg, Joe DePinto and Jagjit Kaur, LTI
 Subject: Assessment of Bioavailable Fractions of Phosphorus
 Date: January 16, 2004
 Page: C-15

Lake Superior - Baptis River
Watershed Specific Total Phosphorus and Bioavailable Phosphorus Summary

Approximate watershed area (sq. mi.): **140**

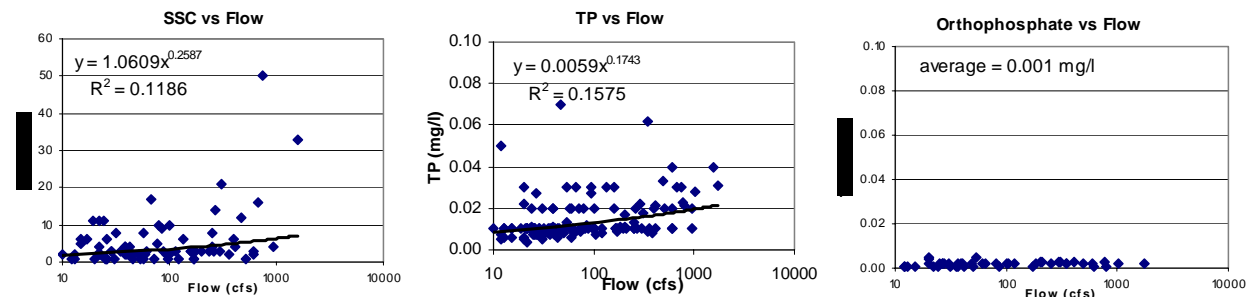
Representative USGS Gauge: #04014500 Baptis River near Beaver Bay, MN
 Representative MPCA EDA Site: 110 BAPTISM RIVER

Approximate drainage area at gauge (sq. mi.): **140**
 Total watershed to gauged area multiplier: **1.000**

Compiled Water Quality Data

USGS (Water Years 1979-1993)	Count (n)	
Suspended sediment concentration (SSC) mg/l:	75	
Phosphorus, water, unfiltered (TP) (mg/l):	71	<i>(excluded three outliers)</i>
MPCA EDA (Water Year 1979-1983)		
Phosphorus as P (mg/l):	59	<i>(excluded one outlier)</i>
Phosphorus, orthophosphate as P (mg/l):	48	<i>(adjusted non-detects to 1/2 the detection limit)</i>
No MPCA New STORET data available		

Rating Curves



Estimated Annual Watershed Load (metric tons/year)

Representative Years		Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus	Fraction Bioavailable
Low Flow Year	1980	457	1.56	0.10	1.46	0.36	23%
	1988	458	1.56	0.10	1.46	0.36	23%
	1990	402	1.34	0.08	1.26	0.31	23%
	Average	439	1.49	0.09	1.39	0.34	23%
Average Flow Year	1981	782	2.60	0.16	2.44	0.60	23%
	1992	780	2.61	0.16	2.45	0.60	23%
	1993	786	2.61	0.16	2.45	0.60	23%
	Average	783	2.61	0.16	2.45	0.60	23%
High Flow Year	1983	1,026	3.35	0.19	3.16	0.76	23%
	1984	993	3.23	0.19	3.05	0.73	23%
	Average	1,009	3.29	0.19	3.10	0.75	23%

Estimated Annual Watershed Yield (lb/acre/year)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	11	0.037	0.002	0.034	0.008
Average Flow Year	19	0.064	0.004	0.060	0.015
High Flow Year	25	0.081	0.005	0.076	0.018

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	4.7	0.016	0.001	0.015	0.004
Average Flow Year	5.0	0.017	0.001	0.016	0.004
High Flow Year	5.3	0.017	0.001	0.016	0.004

Rainy River

Basin Specific Total Phosphorus and Bioavailable Phosphorus Summary

Approximate basin area (sq. mi.):	11,236	<i>(in Minnesota)</i>
Representative USGS Gauge:	#05133500	Rainy River at Manitou Rapids, MN
Approximate drainage area at gauge (sq. mi.):	19,400	<i>(includes drainage from Canada)</i>
Weighting factor	0.290	<i>(assume drainage area at this gauge is representative of half of the Rainy River basin in Minnesota)</i>
Representative USGS Gauge:	#05131500	Little Fork River at Littlefork, MN
Approximate drainage area at gauge (sq. mi.):	1,680	
Weighting factor for Rainy River basin:	3.344	<i>(assume Little Fork is representative of half of the Rainy River basin in Minnesota)</i>

Compiled Water Quality Data

See Summary information on separate sheets for the Rainy and Little Fork Rivers

Rating Curves

See Summary information on separate sheets for the Rainy and Little Fork Rivers

Estimated Annual Basin Load (metric tons/year)

Representative Years		Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus	Fraction Bioavailable
Low Flow Year	1977	134,285	183	64	118	86	47%
	1980	89,597	176	70	106	89	50%
	2002	173,386	309	121	188	155	50%
	<i>Average</i>	<i>132,422</i>	<i>223</i>	<i>85</i>	<i>137</i>	<i>110</i>	<i>49%</i>
Average Flow Year	1992	145,574	286	114	172	145	51%
	1993	204,907	341	128	213	167	49%
	1997	301,469	411	146	266	193	47%
	<i>Average</i>	<i>217,316</i>	<i>346</i>	<i>129</i>	<i>217</i>	<i>168</i>	<i>49%</i>
High Flow Year	1975	437,618	470	154	316	210	45%
	1996	421,768	514	176	338	237	46%
	2001	541,876	600	198	402	270	45%
	<i>Average</i>	<i>467,087</i>	<i>528</i>	<i>176</i>	<i>352</i>	<i>239</i>	<i>45%</i>

Estimated Annual Basin Yield (lbs/acre/yr)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	41	0.068	0.026	0.042	0.034
Average Flow Year	66	0.106	0.040	0.066	0.051
High Flow Year	143	0.162	0.054	0.108	0.073

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	28	0.047	0.018	0.029	0.023
Average Flow Year	30	0.048	0.018	0.030	0.023
High Flow Year	47	0.054	0.018	0.036	0.024

Rainy River - Rainy River Watershed Specific Total Phosphorus and Bioavailable Phosphorus Summary

Approximate watershed area (sq. mi.): 11,236 (in Minnesota)
Representative USGS Gauge: #05133500 Rainy River at Manitou Rapids, MN

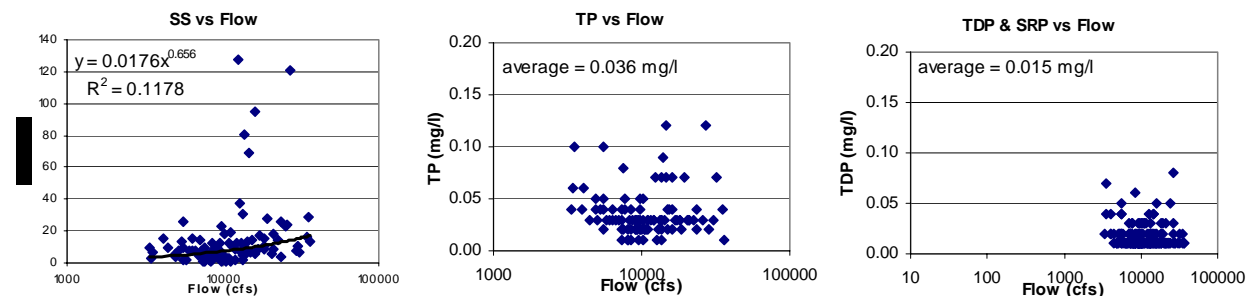
Approximate drainage area at gauge (sq. mi.): 19,400
 Total watershed to gauged area multiplier: 1.000

Compiled Water Quality Data

USGS (Water Years 1979-1994)	Count (n)
Suspended sediment concentration (SSC) mg/l:	104
Phosphorus, water, unfiltered (TP) (mg/l):	102 (excluded 2 outliers)
Phosphorus, water, filtered (TDP) (mg/l):	104 (non-detects set to 1/2 the D.L.)
Orthophosphate, water, filtered, as P (SRP) (mg/l):	79

No MPCA EDA data available
 MPCA New STORET data available

Rating Curves



Estimated Annual Watershed Load (metric tons/year)

Representative Years		Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus	Fraction Bioavailable
Low Flow Year	1977	43,177	186	78	108	98	53%
	1980	43,513	232	98	134	122	53%
	2002	175,498	488	206	283	257	53%
	Average	87,396	302	127	175	159	53%
Average Flow Year	1992	134,443	452	190	262	238	53%
	1993	136,157	462	195	267	243	53%
	1997	149,444	475	200	275	250	53%
	Average	140,015	463	195	268	243	53%
High Flow Year	1975	150,691	476	200	275	250	53%
	1996	237,705	629	265	364	330	53%
	2001	270,482	653	275	378	343	53%
	Average	219,626	586	247	339	308	53%

Estimated Annual Watershed Yield (lbs/acre/yr)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	27	0.092	0.039	0.054	0.049
Average Flow Year	43	0.142	0.060	0.082	0.074
High Flow Year	67	0.179	0.076	0.104	0.094

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	9.2	0.036	0.015	0.021	0.019
Average Flow Year	10.8	0.036	0.015	0.021	0.019
High Flow Year	13.2	0.036	0.015	0.021	0.019

Rainy River - Little Fork River
Watershed Specific Total Phosphorus and Bioavailable Phosphorus Summary

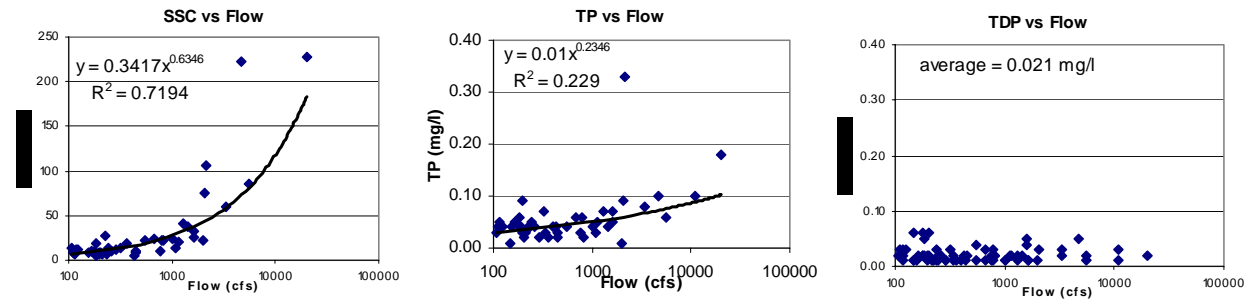
Approximate watershed area (sq. mi.): **1,680**

Representative USGS Gauge: #05131500 Little Fork River at Littlefork, MN
 Approximate drainage area at gauge (sq. mi.): **1,680**
 Total watershed to gauged area multiplier: **1.000**

Compiled Water Quality Data

USGS (Water Years 1979-1986)	Count (n)	
Suspended sediment concentration (SSC) mg/l:	44	
Phosphorus, water, unfiltered (TP) (mg/l):	48	
Phosphorus, water, filtered (TDP) (mg/l):	47	(excluded one outlier)
Orthophosphate, water, filtered, as P (SRP) (mg/l):	22	(excluded one outlier)
No MPCA EDA data available		
No MPCA New STORET data available		

Rating Curves



Estimated Annual Watershed Load (metric tons/year)

Representative Years		Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus	Fraction Bioavailable
Low Flow Year	1977	36,417	39	12	26	17	45%
	1980	23,025	33	12	20	16	49%
	2002	36,651	50	18	32	24	48%
	Average	32,031	40	14	26	19	47%
Average Flow Year	1992	31,890	46	17	29	23	49%
	1993	49,484	62	22	40	29	46%
	1997	77,209	82	26	56	36	44%
	Average	52,861	63	22	42	29	46%
High Flow Year	1975	117,815	99	29	71	41	42%
	1996	105,540	99	30	70	42	43%
	2001	138,619	123	35	87	51	42%
	Average	120,658	107	31	76	45	42%

Estimated Annual Watershed Yield (lbs/acre/yr)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	66	0.083	0.030	0.053	0.039
Average Flow Year	108	0.130	0.044	0.085	0.060
High Flow Year	247	0.219	0.064	0.155	0.092

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	47.4	0.059	0.021	0.038	0.028
Average Flow Year	49.5	0.061	0.021	0.040	0.028
High Flow Year	81.1	0.072	0.021	0.051	0.030

To: Hal Runke and Greg Wilson, Barr Engineering
 From: Hans Holmberg, Joe DePinto and Jagjit Kaur, LTI
 Subject: Assessment of Bioavailable Fractions of Phosphorus
 Date: January 16, 2004
 Page: C-19

**Red River
 Basin Specific Total Phosphorus and Bioavailable Phosphorus Summary**

Approximate basin area (sq. mi.): 17,741 (in Minnesota)

Representative USGS Gauge: #05046000 Otter Tail River Below Orwell Dam near Fergus Falls, MN
Representative MPCA STORET Site: S000-003 OTTERTAIL R BLW ORWELL DAM, CSAH-15, 8 MI SW OF FERGUS FALLS

Approximate drainage area at gauge (sq. mi.): 1,740
 Weighting factor for Red River Basin: 1.00 (assume Otter Tail watershed is not representative of other portions of the Red River Basin)

Representative USGS Gauge: #05064000 Wild Rice River at Hendrum, MN
Representative MPCA STORET Site: S000-216 WILD RICE R. USH-75 N OF HENDRUM

Approximate drainage area at gauge (sq. mi.): 1,560
 Weighting factor for Red River Basin: 6.88 (assume Wild Rice watershed is representative of the Red River Basin outside of the Otter Tail and Red Lake watersheds)

Representative USGS Gauge: #05079000 Red Lake River at Crookston, MN
Representative MPCA STORET Site: S000-031 RED LAKE RIVER AT BRIDGE ON CSAH-15 AT FISHER

Approximate drainage area at gauge (sq. mi.): 5,270
 Weighting factor for Red River Basin: 1.00 (assume Red Lake River watershed is not representative of other portions of the Red River Basin)

Compiled Water Quality Data

See Summary information on separate sheets for the Otter Tail, Wild Rice, and Red Lake Rivers

Rating Curves

See Summary information on separate sheets for the Otter Tail, Wild Rice, and Red Lake Rivers

Estimated Annual Basin Load (metric tons/year)

Representative Years		Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus	Fraction Bioavailable
Low Flow Year	1989	308,644	388	127	261	174	45%
	1990	73,542	87	35	52	45	51%
	1991	71,252	89	36	53	45	51%
	Average	151,146	188	66	122	88	47%
Average Flow Year	1994	365,516	461	164	298	217	47%
	1995	495,399	615	213	401	286	46%
	2002	1,189,614	1,576	485	1,091	681	43%
	Average	683,510	884	287	597	395	45%
High Flow Year	1997	1,122,144	1,499	446	1,053	636	42%
	1998	941,478	1,206	387	819	534	44%
	2001	1,051,717	1,371	428	943	598	44%
	Average	1,038,447	1,359	420	938	589	43%

Estimated Annual Basin Yield (lbs/acre/yr)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	29	0.036	0.013	0.024	0.017
Average Flow Year	132	0.171	0.056	0.116	0.076
High Flow Year	201	0.263	0.081	0.182	0.114

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	77	0.095	0.036	0.058	0.047
Average Flow Year	104	0.133	0.044	0.089	0.060
High Flow Year	124	0.164	0.051	0.113	0.071

To: Hal Runke and Greg Wilson, Barr Engineering
 From: Hans Holmberg, Joe DePinto and Jagjit Kaur, LTI
 Subject: Assessment of Bioavailable Fractions of Phosphorus
 Date: January 16, 2004
 Page: C-20

Red River - Otter Tail River
Watershed Specific Total Phosphorus and Bioavailable Phosphorus Summary

Approximate watershed area (sq. mi.): 1,740

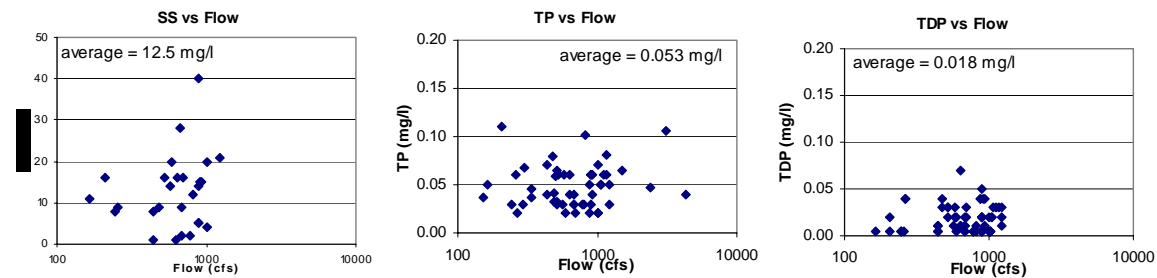
Representative USGS Gauge: #05046000 Otter Tail River Below Orwell Dam near Fergus Falls, MN
Representative MPCA STORET Site: S002-003 OTTERTAIL R BLW ORWELL DAM, CSAH-15, 8 MI SW OF FERGUS FALLS

Approximate drainage area at gauge (sq. mi.): **1,740**
 Total watershed to gauged area multiplier: **1.000**

Compiled Water Quality Data

USGS (Water Years 1985-1995)	Count (n)
Suspended sediment concentration (SSC) mg/l:	27
Phosphorus, water, unfiltered (TP) (mg/l):	38
Phosphorus, water, filtered (TDP) (mg/l):	34
Orthophosphate, water, filtered, as P (mg/l):	29 (non-detects adjusted to 1/2 the D.L.)
No MPCA EDA data available	
MPCA New STORET Data (2001-2002)	
Phosphorus as P (mg/l):	16

Rating Curves



Estimated Annual Watershed Load (metric tons/year)

Representative Years		Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus	Fraction Bioavailable
Low Flow Year	1989	3,019	13	4	8	6	46%
	1990	2,989	13	4	8	6	46%
	1991	3,800	16	5	11	7	46%
	Average	3,269	14	5	9	6	46%
Average Flow Year	1994	7,544	32	11	21	15	46%
	1995	5,549	24	8	16	11	46%
	2002	12,925	55	19	36	25	46%
	Average	8,673	37	12	24	17	46%
High Flow Year	1997	7,747	33	11	22	15	46%
	1998	7,713	33	11	22	15	46%
	2001	8,874	38	13	25	17	46%
	Average	8,111	34	12	23	16	46%

Estimated Annual Watershed Yield (lbs/acre/yr)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	6.5	0.027	0.009	0.018	0.013
Average Flow Year	17	0.073	0.025	0.048	0.033
High Flow Year	16	0.068	0.023	0.045	0.031

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	12.5	0.053	0.018	0.035	0.024
Average Flow Year	12.5	0.053	0.018	0.035	0.024
High Flow Year	12.5	0.053	0.018	0.035	0.024

To: Hal Runke and Greg Wilson, Barr Engineering
 From: Hans Holmberg, Joe DePinto and Jagjit Kaur, LTI
 Subject: Assessment of Bioavailable Fractions of Phosphorus
 Date: January 16, 2004
 Page: C-21

Red River - Wild Rice

Watershed Specific Total Phosphorus and Bioavailable Phosphorus Summary

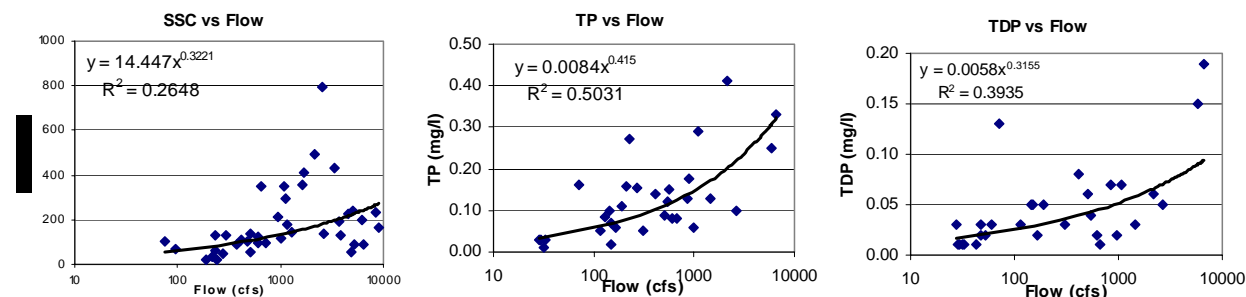
Approximate watershed area (sq. mi.): **1,560**
 Representative USGS Gauge: #05064000 Wild Rice River at Hendrum, MN
 Representative MPCA STORET Site: S000-216 WILD RICE R. USH-75 N OF HENDRUM

Approximate drainage area at gauge (sq. mi.): **1,560**
 Total watershed to gauged area multiplier: **1.000**

Compiled Water Quality Data

USGS (Water Years 1979-2001)	Count (n)
Suspended sediment concentration (SSC) mg/l:	40
Phosphorus, water, unfiltered (TP) (mg/l):	24
Phosphorus, water, filtered (TDP) (mg/l):	30
No MPCA EDA data available	
MPCA New STORET Data (1999-2002)	
Phosphorus as P (mg/l):	7

Rating Curves



Estimated Annual Watershed Load (metric tons/year)

Representative Years		Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus	Fraction Bioavailable
Low Flow Year	1989	41,501	49	16	33	22	44%
	1990	9,831	10	4	6	5	50%
	1991	9,174	9	4	6	5	50%
	Average	20,169	23	8	15	10	46%
Average Flow Year	1994	44,486	49	17	31	23	47%
	1995	61,659	68	24	45	32	46%
	2002	156,355	195	59	135	84	43%
	Average	87,500	104	33	71	46	44%
High Flow Year	1997	137,353	172	52	119	74	43%
	1998	123,828	149	47	102	66	44%
	2001	134,530	164	51	113	72	44%
	Average	131,904	161	50	111	70	44%

Estimated Annual Watershed Yield (lbs/acre/yr)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	44	0.050	0.017	0.033	0.023
Average Flow Year	193	0.229	0.074	0.156	0.102
High Flow Year	291	0.356	0.111	0.245	0.155

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	112.1	0.122	0.043	0.079	0.057
Average Flow Year	146.5	0.170	0.056	0.114	0.077
High Flow Year	176.2	0.216	0.067	0.149	0.094

**Red River - Red Lake River
 Watershed Specific Total Phosphorus and Bioavailable Phosphorus Summary**

Approximate watershed area (sq. mi.): **5,270**

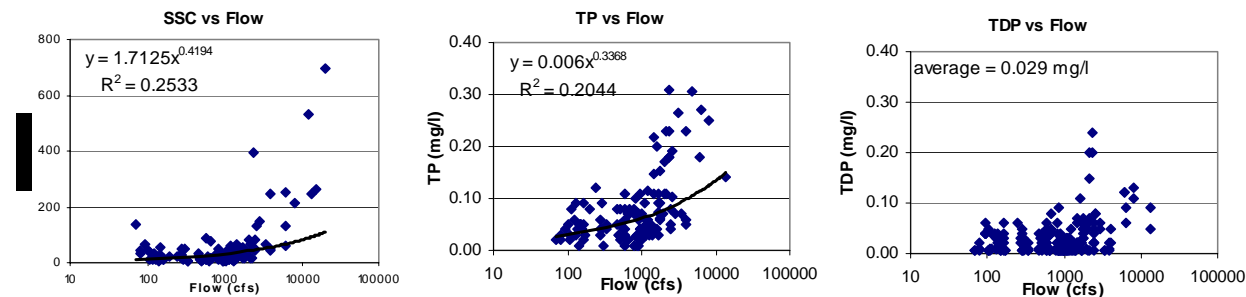
Representative USGS Gauge: #05079000 Red Lake River at Crookston, MN
Representative MPCA STORET Site: S000-031 RED LAKE RIVER AT BRIDGE ON CSAH-15 AT FISHER

Approximate drainage area at gauge (sq. mi.): **5,270**
 Total watershed to gauged area multiplier: **1.000**

Compiled Water Quality Data

USGS (Water Years 1979-2001)	Count (n)
Suspended sediment concentration (SSC) mg/l:	120
Phosphorus, water, unfiltered (TP) (mg/l):	119
Phosphorus, water, filtered (TDP) (mg/l):	118 (excluded 2 outliers) (non-detects set to 1/2 the D.L.)
Orthophosphate, water, filtered, (mg/l):	102 (non-detects set to 1/2 the D.L.)
No MPCA EDA data available	
MPCA New STORET Data (2000-2002)	
Phosphorus as P (mg/l):	16

Rating Curves



Estimated Annual Watershed Load (metric tons/year)

Representative Years		Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus	Fraction Bioavailable
Low Flow Year	1989	20,143	37	14	23	18	49%
	1990	2,924	6	5	2	5	79%
	1991	4,345	9	6	3	7	72%
	Average	9,138	17	8	9	10	57%
Average Flow Year	1994	51,961	96	35	60	46	48%
	1995	65,704	120	43	77	57	47%
	2002	101,143	180	57	123	79	44%
	Average	72,936	132	45	87	61	46%
High Flow Year	1997	169,565	286	76	210	113	40%
	1998	81,973	149	51	98	69	46%
	2001	117,430	206	63	144	89	43%
	Average	122,989	214	63	151	90	42%

Estimated Annual Watershed Yield (lbs/acre/yr)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	6.0	0.011	0.005	0.006	0.006
Average Flow Year	47.6	0.086	0.029	0.057	0.040
High Flow Year	80.2	0.139	0.041	0.098	0.059

Estimated Annual Flow Weighted Mean Concentration (mg/l)

Flow Condition	Suspended Sediment	Total Phosphorus	Total Dissolved Phosphorus	Total Particulate Phosphorus	Total Bioavailable Phosphorus
Low Flow Year	26.7	0.053	0.029	0.024	0.033
Average Flow Year	46.2	0.084	0.029	0.055	0.039
High Flow Year	55.3	0.097	0.029	0.068	0.041