



# Loading of Biologically Available Constituents from an Agricultural Subwatershed in the Redwood River Basin, Minnesota

*by William F. James, John W. Barko,  
Harry L. Eakin, and Gregory W. Eggers*

---

**PURPOSE:** The purpose of this demonstration effort was to quantify flow and loading of sediment and nutrients from the small, agriculturally dominated Judicial Ditch 31, which drains into the Redwood River of the Minnesota River Basin. This information will be important in the refinement and calibration of watershed models.

**BACKGROUND:** Increasingly intensive agricultural practices have led to enhanced watershed runoff of sediment and nutrients such as nitrogen (N) and phosphorus (P) over the last half century. There is a need to improve predictive capabilities for estimating hydrologic and associated material runoff on a watershed-wide basis in order to better evaluate alternatives for reducing the loss of soils and associated nutrients from intensively managed agricultural regions. In addition, information is needed regarding the potential significance of material runoff to downstream biota and water quality. In particular, knowledge is needed regarding the biological availability of material such as labile (i.e., exchangeable with the water column) nitrogen (N) and phosphorus (P) fractions to downstream locations. For instance, although soluble P is usually measured because it constitutes a directly available source to the biota, other labile P fractions bound on suspended sediment eroded from the watershed may also play an important role in biological productivity. Yet, loading of these P fractions is rarely quantified in watershed research. As part of the Land Management System (LMS) initiative of the Corps of Engineers, loadings of suspended sediment and labile N and P fractions were examined from a small subwatershed in the Redwood River Basin, Minnesota. This information will be used to calibrate and refine the Watershed Modeling System (WMS) for forecasting material runoff from intensively managed agricultural watersheds.

**METHODS:** Judicial Ditch (JD) 31, located in Lyon and Lincoln Counties (near Taylor, MN) of the Redwood River Basin, drains an area of approximately 24 km<sup>2</sup> (Figure 1). Created in 1916, it currently encompasses over 11 km of open ditch and 31 km of subsurface drainage tile (Paulson and Philippi 1998). Land use consists primarily of production corn and soybean agriculture. About 0.2 km<sup>2</sup> are currently natural wetland areas, while over 3 km<sup>2</sup> are formerly drained wetlands (Paulson and Philippi 1998).

In May 2000, flow gauging and water quality sampling stations were established in a culvert under State Highway 23, located near the mouth of the ditch before it enters the Redwood River (Figure 1). Instantaneous velocity and stage height were measured at 15-min intervals (between May and November) using an ISCO 4150 area-velocity sensor (ISCO, Inc.). During high flow events, water samples were collected at 3-hr intervals and composited over a 24-hr period using

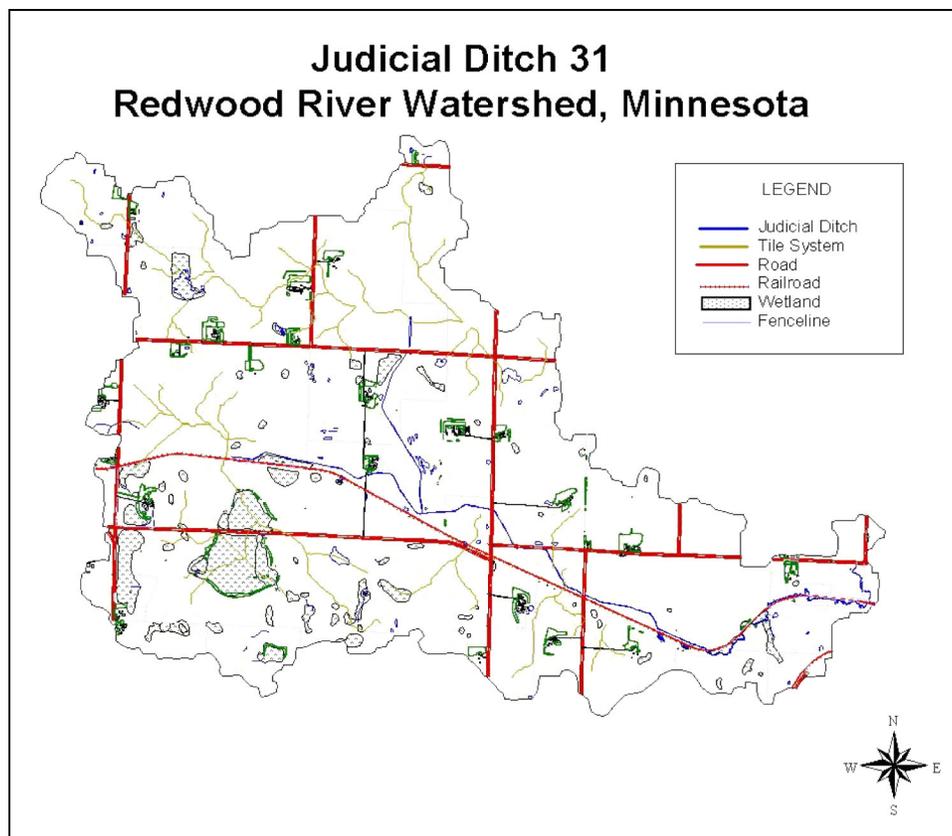


Figure 1. Map of the Judicial Ditch 31 watershed

an ISCO 3700 automated water sampler. Samples were retrieved from the field for processing within 3 days (8-hr round trip between sampling site and the laboratory).

In the laboratory, a portion was filtered through a 0.45- $\mu\text{m}$  filter for soluble constituent determination. Soluble reactive P (SRP), ammonium-N ( $\text{NH}_4\text{-N}$ ), and nitrate-nitrite-N ( $\text{NO}_2\text{NO}_3\text{-N}$ ) were analyzed using automated analytical techniques (Lachat Quikchem Autoanalyzer, Zellweger Analytics, Lachat Div., Milwaukee, WI). For particulate components, another sample portion was retained on glass fiber filters (Whatman). For total suspended sediment (TSS) and particulate organic matter (POM), suspended material was dried at 105 °C to a constant weight, then combusted at 500 °C for 1 hr (American Public Health Association (APHA) 1992). A modified sequential fractionation of inorganic phosphorus in the sediments was conducted according to Hieltjes and Lijklema (1980) and Nürnberg (1988) for the determination of labile P constituents. Loosely bound and iron-bound P were extracted using ammonium-chloride and bicarbonate-dithionite, respectively. Labile organic P was determined after extraction with sodium hydroxide followed by digestion with potassium persulfate (Psenner and Puckso 1988). Labile organic P was calculated as the difference between reactive and nonreactive NaOH-extractable P. Each extraction was filtered through a 0.45- $\mu\text{m}$  filter, adjusted to pH 7, and analyzed for SRP. Samples for total N and P were predigested with alkaline potassium persulfate according to Ameal, Axler, and Owen (1993) before analysis using automated analytical procedures (see above). Daily flux of materials was estimated using the software program FLUX (Walker 1996).

P adsorption-desorption characteristics of the TSS load were determined by combining several daily composited samples collected in early July into one sample representing a storm hydrograph. This sample was centrifuged at 2500 rpm for 30 min and decanted to separate particulate from soluble phases. Sediment aliquots (~500 mg/L dry weight equivalent) were subjected to a series of SRP ( $\text{KH}_2\text{PO}_4$  as SRP) standards ranging from 0 to 1.0 mg/L (i.e., 0, 0.125, 0.250, 0.500, and 1.00 mg/L) for examination of P adsorption and desorption over a 24-hr period. Untreated tap water from the laboratory was used as the water medium because it was phosphate-free. Chloroform (0.1 percent) was added to inhibit biological activity. The sediment systems, containing sediment, tap water, and known concentrations of SRP, were shaken uniformly for 24 hr, then sampled and analyzed for SRP (APHA 1992). The sediment systems were maintained under oxic conditions at a pH of approximately 8.0 to 8.3 and a temperature of approximately 20 °C .

Adsorption and desorption were calculated as the change in SRP (i.e., SRP at 0 hr minus SRP at 24 hr) normalized with respect to sediment dry mass (i.e., mg SRP/g dry mass) and plotted as a function of final SRP concentration (Froelich 1988). The equilibrium phosphate concentration (EPC, mg/L) was calculated as the concentration where net sorption was zero (i.e., often called the crossover point (Mayer and Gloss 1980)). The linear adsorption coefficient (k, L/g) was calculated as the linear slope near the EPC. The native adsorbed phosphate (NAP, mg/g sediment) was calculated as  $\text{NAP} = (k) \times (\text{EPC})$ .

**RESULTS AND DISCUSSION:** Peaks in mean daily flow occurred in mid-May, early June, July, and early August in conjunction with periods of precipitation over the watershed (Figure 2).

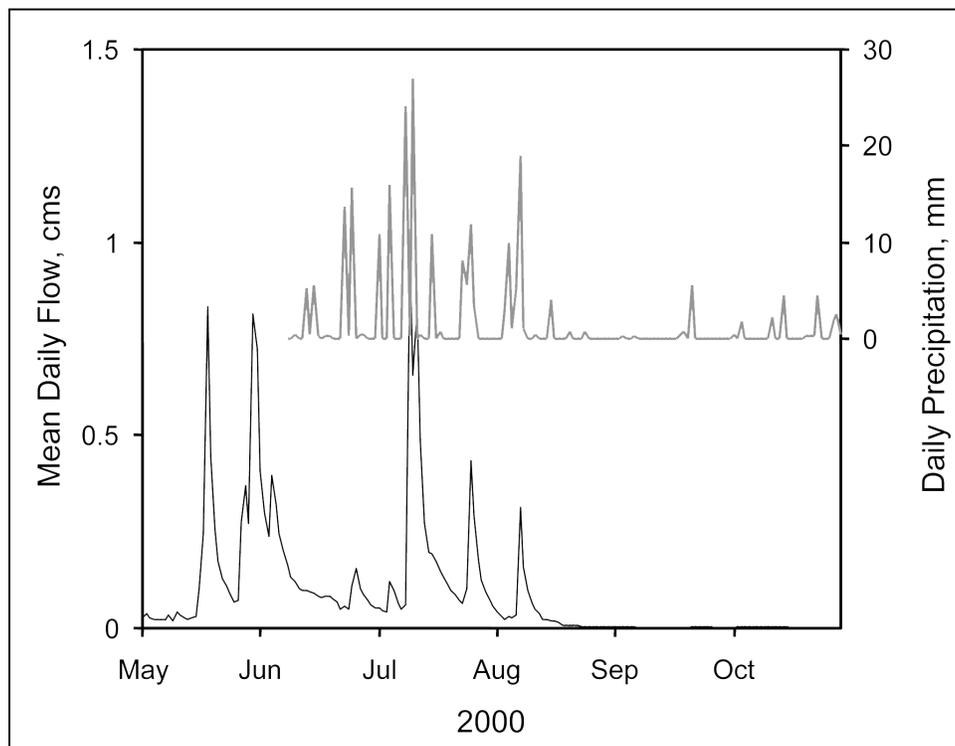


Figure 2. Seasonal variations in mean daily flow (black line) and daily precipitation (grey line) in 2000

Nearly dry conditions between mid-August and October resulted in no measurable daily flow from the watershed. During precipitation events, the hydrograph typically exhibited a rapid rise in flow followed by a long tail of slowly declining flow (Figure 3). In addition, there was also only a short time lag between peaks in precipitation and peaks in flow. These patterns suggested the occurrence of an initial rapid period of surface runoff from the watershed in conjunction with the precipitation event, followed by a longer period of subsurface drainage through soils and into the tile systems associated with the ditch.

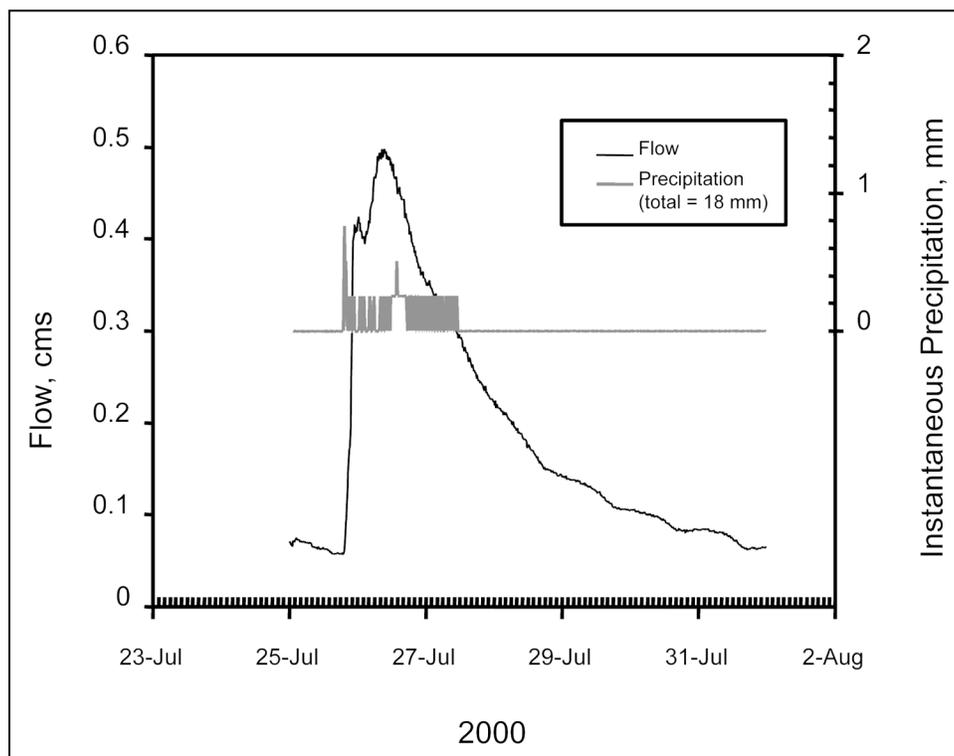


Figure 3. Variation in instantaneous flow and precipitation during a storm period in July

For most variables, a positive linear relationship existed between concentration and flow (Figure 4), suggesting relationships between surface runoff and scouring of soils and associated nutrients. An exception to this pattern occurred for nitrogen species. Total nitrogen and  $\text{NO}_2\text{NO}_3\text{-N}$  appeared to vary in a stepwise manner from a low constant concentration at flows less than 0.06 cms to a high constant concentration at flows above 0.06 cms (Figure 4). Concentrations of  $\text{NH}_4\text{-N}$  were low and appeared to be nearly constant throughout the range of flows.

Overall, peaks in flow were an important factor resulting in elevated material loadings from the watershed, as positive relationships existed between flow and loading (Figure 2 versus Figures 5 through 7). For all variables, greatest peaks in loading occurred in May, early June, and Mid-July (Figures 5-7). For P constituents over the period May through October, SRP loading accounted for approximately 14 percent of the total P load from the watershed (Table 1). Labile sediment P fractions collectively accounted for approximately 70 percent of the total P loading, with organic

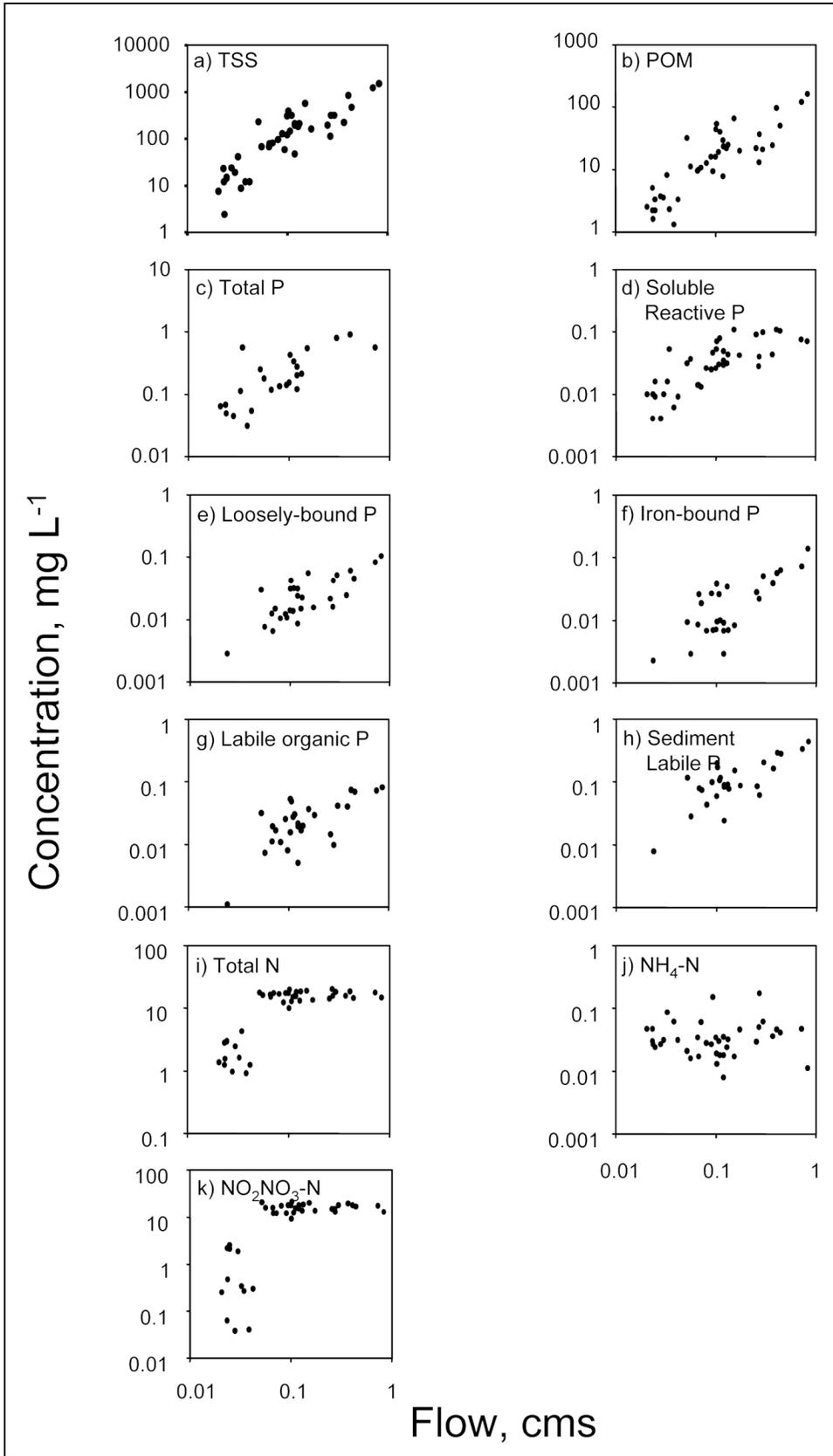


Figure 4. Relationships between flow and concentration for various constituents

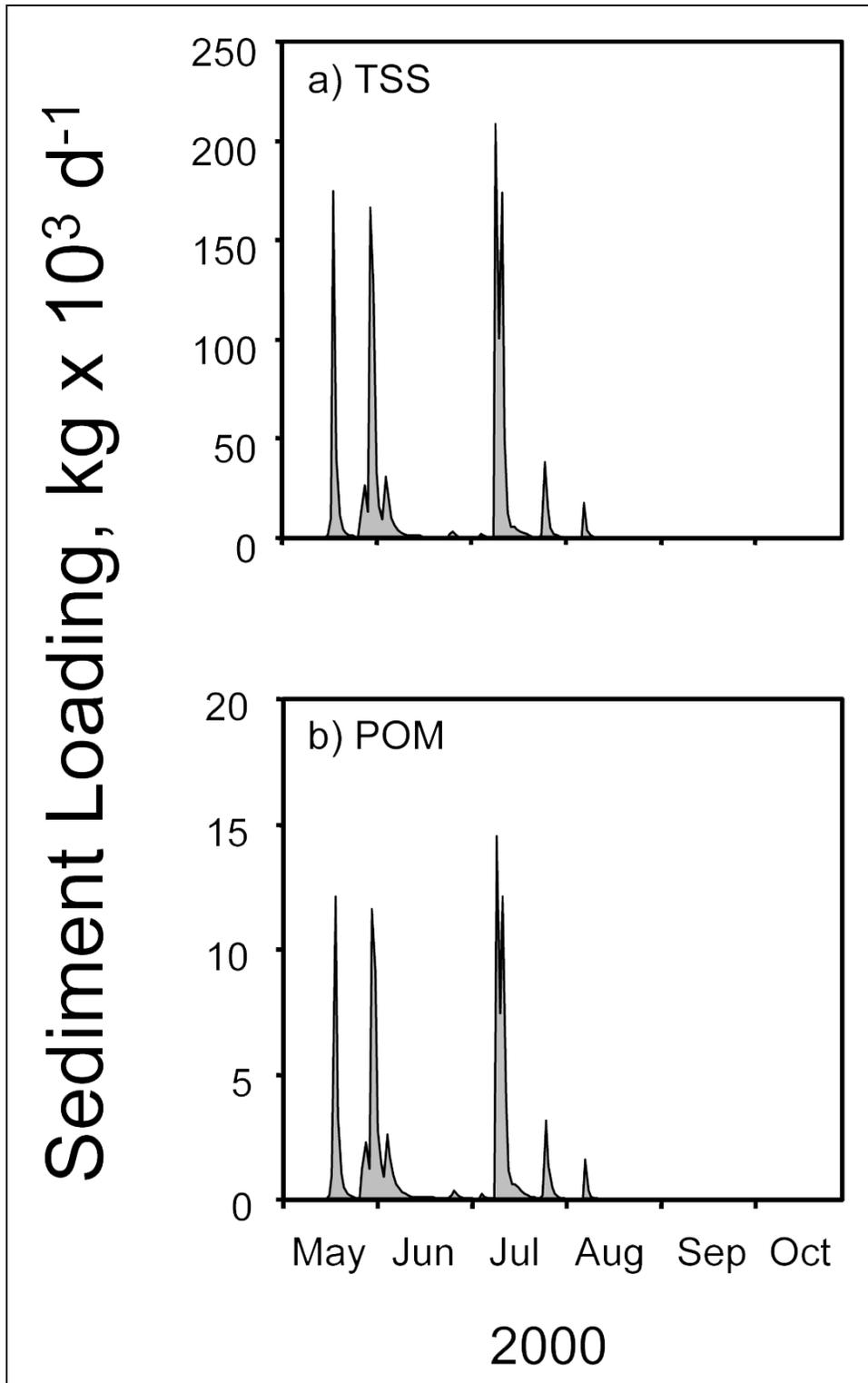


Figure 5. Mean daily loading of total suspended sediment (TSS) and particulate organic matter (POM) in 2000. Loading was estimated with the software program FLUX (Walker 1996)

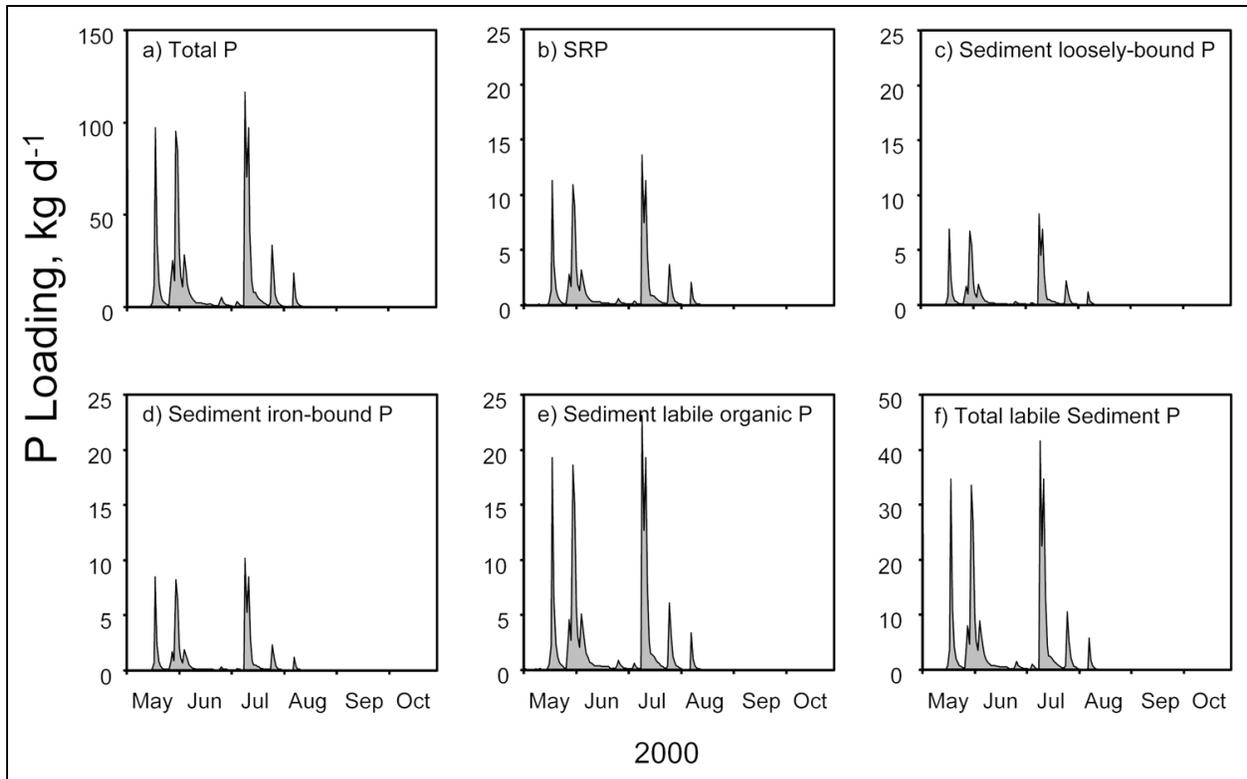


Figure 6. Mean daily loading of various soluble and particulate phosphorus constituents in 2000. Loading was estimated with the software program FLUX (Walker 1996)

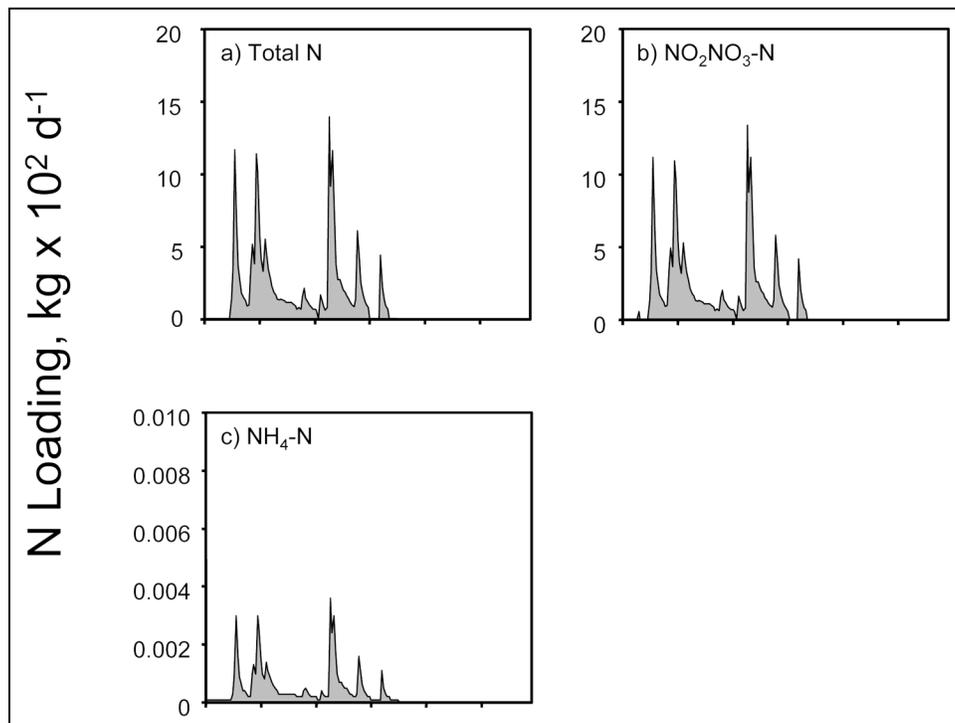


Figure 7. Mean daily loading of nitrogen constituents in 2000. Loading was estimated with the software program FLUX (Walker 1996)

**Table 1**  
**Loading, Flow-Weighted Concentration, Coefficient of Variation (CV), and Percentage of Total Phosphorus (P) Load for Various P Constituents from JD 31 for the Period May through October 2000**

Variable	kg	mg/L	CV	Percent of Total P
Total P	862	0.579	0.17	
Soluble Reactive P	124	0.083	0.17	14.3
Sediment Loosely Bound P	73	0.049	0.014	8.5
Sediment Iron-Bound P	76	0.054	0.13	8.9
Sediment Labile Organic P	435	0.292	0.13	50.4

P constituting the greatest labile sediment P load from the watershed. Thus, measured labile P from the watershed represented more than 80 percent of the total P loading during that period. Similarly, James, Barko, and Eakin (2001) found that these constituents (i.e., SRP, loosely bound P, iron-bound P, labile organic P) constituted 68 percent of the total P load from the entire Redwood River Basin. The total N load was dominated by inorganic N fractions, with NO<sub>2</sub>NO<sub>3</sub>-N dominating the overall N load (Table 2). High concentrations of NO<sub>2</sub>NO<sub>3</sub>-N are likely attributable to breakdown and oxidation via nitrification of organic N-based and ammonia-based fertilizers.

**Table 2**  
**Loading, Flow-Weighted Concentration, Coefficient of Variation (CV), and Percentage of Total Nitrogen (N) Load for Various N Constituents from JD 31 for the Period May through October**

Variable	kg	mg/L	CV	Percent of total N
Total N	22960	15.4	0.03	
Ammonium-N	63	0.4	0.19	0.3
Nitrate-nitrite-N	21994	14.8	0.04	95.8

One important implication of export of predominantly labile P fractions from the JD 31 watershed is that these constituents can be used by planktonic and benthic biota at downstream locations as a nutrient source for growth. While SRP is immediately available for uptake by algae, P that is loosely bound to sediment or associated with iron can also be recycled to the water column via diffusive and kinetic processes. Diffusive flux of P can occur via ligand exchange at high pH and via oxidation-reduction reactions (James, Barko, and Eakin 1996). The adsorption-desorption characteristics of suspended sediment collected during periods of high flow indicated that desorption of P occurred at low ambient SRP concentrations, while adsorption occurred as SRP increased above 0.050 mg/L (Figure 8). The EPC and k for suspended sediments originating from the watershed were high compared to other studies (Meyer (1979); Mayer and Gloss (1980); studies cited in Froelich (1988); Olila and Reddy (1993)), indicating the occurrence of a high buffering capacity for P that could potentially exert an influence on ambient SRP concentration. However, the EPC for suspended sediments was lower than the flow-weighted SRP concentration (EPC = 0.051 mg/L 0.004 S.D. versus 0.083 mg/L

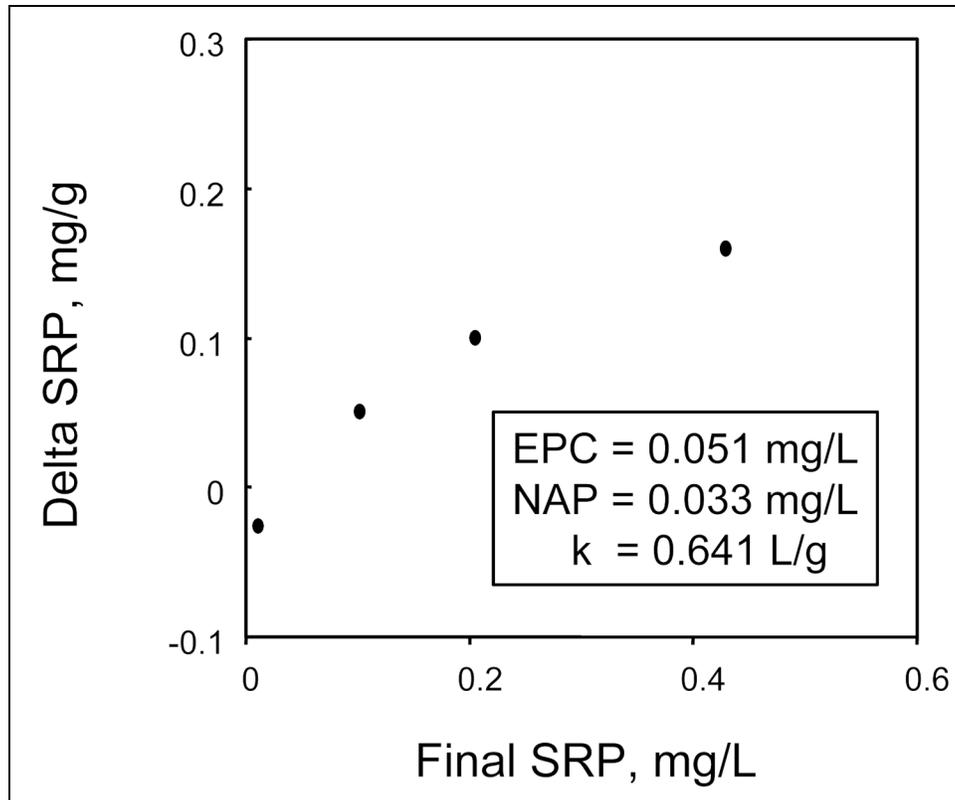


Figure 8. Sorption characteristics for suspended sediment collected during a high inflow event in July. EPC = Equilibrium phosphate concentration, NAP = Native adsorbed phosphorus, k = linear sorption coefficient. Final SRP represents the aqueous P concentration, Delta SRP represents sorption (positive value) or desorption (negative value)

0.014 S.D.), suggesting that other factors, in addition to kinetic control, were playing a role in the regulation of ambient SRP in the runoff.

The dominance of SRP and the labile organic P fraction in the runoff water may be a consequence of agricultural activity in the watershed. Others (Beauchemin, Simard, and Cluis 1998; Stamm et al. 1998; Leinweber, Eckhardt, and Meissner 1999) have found high concentrations of soluble P in tile drainage flows and leachate from intensively managed agricultural soils. Stamm et al. (1998) suggested that labile phosphorus concentrations were greater in arable soils treated with inorganic fertilizers and that agricultural management, which promoted organic matter conservation in the soil, led to higher proportions of labile P and greater susceptibility to P leaching from soils. Direct mineralization of labile organic P fractions via bacteria activity represents another P recycling pathway that could result in P leaching from soils.

High  $\text{NO}_2\text{-NO}_3\text{-N}$  concentrations from JD 31 may be related to continuous corn and corn-soybean rotations in the watershed that require higher fertilization rates than other farming practices such as corn-alfalfa rotations. Gast, Nelson, and Randall (1978); Randall and Iragavarapu (1995); and Randall et al. (1997) demonstrated positive relationships between nitrate

concentrations in the subsurface runoff from tile drainage systems and N fertilization rates. They also found that nitrate concentrations were greater in the subsurface runoff from tile systems draining continuous corn, corn-soybean, and soybean crops versus corn rotations with alfalfa and other crops, which require minimal tillage for a year or more.

In conclusion, runoff from the agriculturally dominated JD 31 watershed appears to be enriched in labile P fractions and  $\text{NO}_2\text{NO}_3\text{-N}$  and represents an important input to downstream locations. This information will be important in watershed model calibration and evaluation of BMP's to improve water quality.

**ACKNOWLEDGMENTS:** This research was funded by the Water Operations Technical Support (WOTS) Program. The authors gratefully acknowledge Mses. Laura Blegen, Alyssa Boock, Susan Fox (ASCI Corp.), and Messrs. Dale Dressel (ASCI Corp.), Alan Lamphere, Matthew Pommier, and Eric Secrist of the Eau Galle Aquatic Ecology Laboratory, ERDC, Spring Valley, WI, for sampling, fractionation, and chemical analyses.

**POINTS OF CONTACT:** This technical note was written by Messrs. William F. James and Harry L. Eakin of the Eau Galle Aquatic Ecology Laboratory, Environmental Laboratory (EL), Engineer Research and Development Center (ERDC); Dr. John W. Barko, EL, ERDC; and Mr. Gregory W. Eggers of the U.S. Army Engineer District, St. Paul, Army Corps of Engineers Centre. For additional information, contact the managers of the Water Operations Technical Support (WOTS) Program, Dr. Barko (601-634-3654, [John.W.Barko@erdc.usace.army.mil](mailto:John.W.Barko@erdc.usace.army.mil)) or Mr. Robert C. Gunkel (601-634-3722, [Robert.C.Gunkel@erdc.usace.army.mil](mailto:Robert.C.Gunkel@erdc.usace.army.mil)). This technical note should be cited as follows:

James, W. F., Barko, J. W., Eakin, H. L., and Eggers, G. W. (2001). "Loading of biologically available constituents from an agricultural subwatershed in the Redwood River Basin, Minnesota," *Water Quality Technical Notes Collection* (ERDC WQTN-PD-10), U.S. Army Engineer Research and Development Center, Vicksburg, MS.

## REFERENCES

- Ameel, J. J., Axler, R. P., and Owen, C. J. (1993). "Persulfate digestion for determination of total nitrogen and phosphorus in low nutrient waters," *Am. Environ. Lab.* (October 1993), 8-10.
- American Public Health Association. (1992). "Standard methods for the examination of water and wastewater," 18th ed.
- Beauchemin, S., Simard, R., and Cluis, D. (1998). "Forms and concentration of phosphorus in drainage water of twenty-seven tile-drained soils," *J. Environ. Qual.* 27:721-728.
- Froelich, P. N. (1988). "Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism," *Limnol. Oceanogr.* 33:49-668.
- Gast, R. G., Nelson, W. W., and Randall, G. W. (1978). "Nitrogen accumulation in soils and loss in tile drainage following nitrogen applications to continuous corn," *J. Environ. Qual.* 7:258-261.

- Hieltjes, A. H., and Lijklema, L. (1980). "Fractionation of inorganic phosphorus in calcareous sediments," *J. Environ. Qual.* 8:130-132.
- James, W. F., Barko, J. W., and Field, S. J. (1996). "Phosphorus mobilization from littoral sediments of an inlet region in Lake Delavan, Wisconsin," *Arch. Hydrobiol.* 138:245-257.
- James, W. F., Barko, J. W., and Eakin, H. L. (2001). "Phosphorus loading from the Redwood River Basin: Fractionation of labile and refractory components," Water Quality Technical Notes Collection (ERDC WQTN-PD-08), U.S. Army Engineer Research and Development Center, Vicksburg, MS. [www.wes.army.mil/pubs/wqtncont.html](http://www.wes.army.mil/pubs/wqtncont.html)
- Leinweber, P., Eckhardt, K-U, and Meissner, R. (1999). "Management effects on forms of phosphorus in soil and leaching losses," *Europe. J. Soil Sci.* 50:413-424.
- Mayer, L. M., and Gloss, S. P. (1980). "Buffering of silica and phosphate in a turbid river," *Limnol. Oceanogr.* 25:12-25.
- Meyer, J. L. (1979). "The role of sediments and bryophytes in phosphorus dynamics in a headwater stream ecosystem," *Limnol. Oceanogr.* 24:365-375.
- Nürnberg, G. K. (1988). "Prediction of phosphorus release rates from total and reductant soluble phosphorus in anoxic lake sediments," *Can. J. Fish. Aquat. Sci.* 44:960-966.
- Olila, O. G., and Reddy, K. R. (1993). "Phosphorus sorption characteristics of sediments in shallow eutrophic lakes of Florida," *Arch. Hydrobiol.* 129:45-65.
- Paulson, J., and Philippi, N. (1998). "Wetlands initiative," [www.wetlands-initiative.org/pub/redwood.html](http://www.wetlands-initiative.org/pub/redwood.html)
- Psenner, R., and Puckso, R. (1988). "Phosphorus fractionation: Advantages and limits of the method for the study of sediment P origins and interactions," *Arch. Hydrobiol. Biel. Erg. Limnol.* 30:43-59.
- Randall, G. W., and Iragavarapu, T. K. (1995). "Impact of long-term tillage systems for continuous corn on nitrate leaching to tile drainage," *J. Environ. Qual.* 24:360-366.
- Randall, G. W., Huggins, D. R., Russell, M. P., Fuchs, D. J., Nelson, W. W., and Anderson, J. L. (1997). "Nitrate losses through subsurface tile drainage in conservation reserve program, alfalfa, and row crop systems," *J. Environ. Qual.* 26:1240-1247.
- Stamm, C., Flüßler, H., Gächter, R., Leuenberger, J., Wenderli, H. (1998). "Preferential transport of phosphorus in drained grasslands," *J. Environ. Qual.* 27:515-522.
- Walker, W. W. (1996). "Simplified procedures for eutrophication assessment and prediction: User Manual," Instruction Report W-96-2, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

**NOTE:** The contents of this technical note are not to be used for advertising, publication, or promotional purposes. Citation of trade names does not constitute an official endorsement or approval of the use of such products.