



Longitudinal Loading and Nutrient Compositional Gradients in an Agriculturally Managed Watershed in West-Central Wisconsin

by William F. James, Carlos E. Ruiz, John W. Barko, and Harry L. Eakin

PURPOSE: The purpose of this research was to describe and quantify biologically labile and refractory nitrogen and phosphorus species, transformations, and loads along the longitudinal axis of a river draining an intensively managed agricultural watershed.

BACKGROUND: Excessive nutrient runoff (primarily as phosphorus) in agriculturally managed watersheds is a primary cause for eutrophication of Corps of Engineers and other receiving waters. Because agricultural soils are often managed for crop uptake of nitrogen (N), rather than phosphorus (P), additions of fertilizers and manures have resulted in the buildup of soil P in excess of crop needs that can be transported to receiving waters during runoff (Lemunyon and Gilbert 1993, Sharpley et al. 1994, Sharpley 1995). In addition, watersheds managed for livestock (such as dairy operations) rely on frequent soil applications as a means of manure management that also results in the buildup of excessive nutrient levels in the soil. Simulation of N and P runoff via modeling is critical for the development of management scenarios to control excessive nutrient loading in agriculturally managed watersheds. However, algorithms need to be improved to more accurately predict transformations, transport, and fate of biologically labile nutrient forms that are either directly available for biological uptake or that can be recycled in receiving waters. Input data are also needed to verify these model improvements and predictions. The objectives of this study were to examine biologically labile and refractory N and P loadings, composition, and transformations in the agriculturally managed Upper Eau Galle River Watershed, located in west-central Wisconsin.

METHODS: The Upper Eau Galle River basin drains a 123.3-km² watershed above the Eau Galle Reservoir, a Corps of Engineers impoundment located in west-central Wisconsin (Figure 1). Carr Creek is the largest third-order tributary draining into the Upper Eau Galle River with a watershed size of 35 km² (i.e., 28 percent of the entire Upper Eau Galle River watershed). Agricultural land uses are dominated by annual and perennial crop production (i.e., corn, oats, alfalfa, grass hay, soybeans), pasture, and livestock dairy production. Other land uses include CRP (Conservation Reserve Program) and wooded areas. Other than one small town (Woodville; population = 1100) located near the approximate center of the watershed, the residential distribution is sparse and rural.

The watershed is located within the glaciated region of Wisconsin and the dominant soil associations are the Vlasaty-Skyberg, located in the eastern portion of the watershed, and Saltre-Pillot Antigo, located in the Carr Creek watershed (Ashby 1985). Groundwater movement is in a western direction and numerous springs occur throughout the watershed (Ashby 1985).

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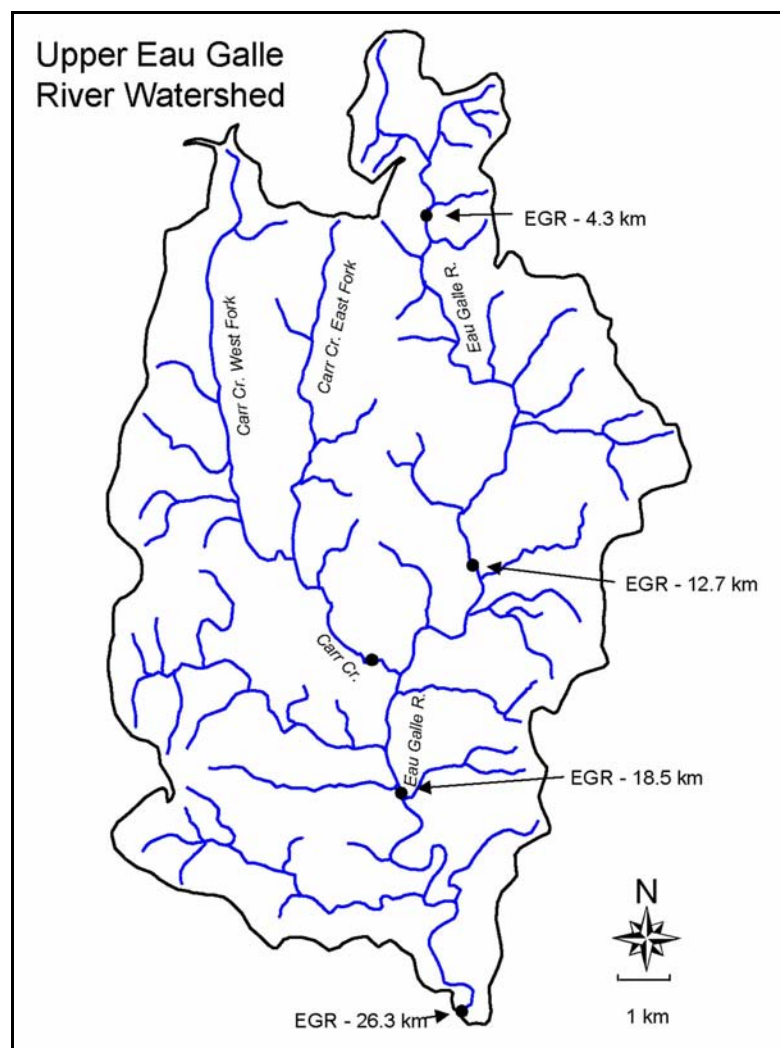


Figure 1. Map of the Upper Eau Galle River watershed above 26.6 river kilometers showing major tributaries. Solid circles indicate sampling and flow gauging stations

Water sampling and flow gauging stations were established on the Upper Eau Galle River at bridges near the headwaters at County Road E (EGR-4.3 km), 60th Avenue (EGR-12.7 km), County Road N (EGR-18.5 km), and near the entrance to the Eau Galle Reservoir (EGR-26.3 km). At each station, stage height was recorded at 15-min intervals (ISCO Model 730 bubbler module or Model 4120 pressure transducer; ISCO Inc., Lincoln, Nebraska). A stage-discharge relationship was determined over a variety of flow regimes to convert stage height to volumetric flow. Precipitation gauges (Dataloggers; Model S-162), placed near the gauging stations, monitored rainfall over 15-min intervals. Flows and precipitation were monitored between May and September 2002.

During storm inflows, water samples were collected at short time intervals (15-30 min) with automated sampling equipment (ISCO 3700 or 6700 samplers), and composited into daily, flow-weighted samples for chemical analysis. In the laboratory, a portion was filtered through a 0.45- μ m filter for soluble constituent determination. Soluble reactive P (SRP), ammonium-N ($\text{NH}_4\text{-N}$), and nitrate-nitrite-N ($\text{NO}_3\text{NO}_2\text{-N}$) were analyzed using automated analytical techniques (Lachat Quikchem Autoanalyzer, Hach Company, Lachat Div., Loveland, Colorado). Total soluble N and P were analyzed colorimetrically using Lachat QuikChem procedures following digestion with alkaline potassium persulfate according to Ameer et al. (1993). For particulate components, sample aliquots were retained on glass fiber filters (Gelman Metricel; 2 μ nominal pore size). For total suspended solids (TSS) and particulate organic matter (POM), suspended material was dried at 105 °C to a constant weight, then ignited at 500 °C in a muffle furnace (American Public Health Association (APHA) 1998). Sequential fractionation of inorganic P in the TSS was conducted according to Hietjies and Lijklema (1980) and Nürnberg (1988) for the determination of ammonium-chloride-extractable particulate P (PP; loosely bound P), bicarbonate-dithionite-extractable PP (i.e., iron-bound PP), sodium hydroxide-extractable P (i.e., aluminum-bound PP), and hydrochloric acid-

extractable PP (i.e., calcium-bound PP). A subsample of the sodium hydroxide extract was digested with potassium persulfate to determine nonreactive sodium hydroxide-extractable PP (Psenner and Puckso 1988). Labile particulate organic/polyphosphate P was calculated as the difference between reactive and nonreactive sodium hydroxide-extractable PP. PP remaining on the filter after the hydrochloric acid extraction was digested with potassium persulfate and 5 N sulfuric acid for determination of refractory organic PP. Each extraction was filtered through a 0.45- μm filter, adjusted to pH 7, and analyzed for SRP using the ascorbic acid method (APHA 1998). Samples for total N and P were predigested with alkaline potassium persulfate (Ameel et al. 1993) before analysis using automated analytical procedures. Particulate organic nitrogen was calculated as the difference between total and total soluble nitrogen. Soluble organic nitrogen was calculated as total soluble nitrogen minus the sum of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{NO}_2\text{-N}$. Table 1 describes operationally defined P fractions measured in this study and biological availability.

Table 1 Operationally Defined Phosphorus Fractions		
Variable	Extractant	Biological Availability and Susceptibility to Recycling Pathways
Loosely bound P	1 M ammonium chloride	Biologically labile; available for uptake and can be recycled via eH and pH reactions and equilibrium processes.
Iron-bound P	0.11 M sodium bicarbonate-dithionate	Biologically labile; available for uptake and can be recycled via eH and pH reactions and equilibrium processes.
Aluminum-bound P	0.1 N sodium hydroxide	Biologically refractory; generally unavailable for biological use and subject to burial.
Calcium-bound P	0.5 N hydrochloric acid	Biologically refractory; generally unavailable for biological use and subject to burial.
Labile organic/ polyphosphate P	Persulfate digestion of the NaOH extraction	Biologically labile; Polyphosphates are available for biological uptake. Also recycled via bacterial mineralization and surplus storage in cells.
Refractory organic P	Persulfate digestion of remaining particulate P	Biologically refractory; generally unavailable for biological use and subject to burial.
¹ Labile = Subject to recycling pathways or direct availability to the biota. Refractory = Low biological availability and subject to burial.		

To measure P sorption characteristics of TSS loads, the remaining composited sample was centrifuged at 500 g and decanted to separate particulate from soluble phases. Sediment aliquots ($\sim 500 \text{ mg L}^{-1}$ dry weight equivalent) were subjected to a series of SRP (KH_2PO_4 as SRP) standards ranging from 0 to 1.0 mg L^{-1} (i.e., 0, 0.125, 0.250, 0.500, and 1.00 mg L^{-1}) for examination of P adsorption and desorption over a 24-hr period. The dry weight equivalent dry mass used in the sorption assays fell within the range of TSS concentrations measured during

storm runoff in the watershed. Untreated tap water from the laboratory was used as the water medium because it was phosphate-free and exhibited very similar cationic strength, conductivity, and pH to that of surface water from the Eau Galle River. 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 and then sampled and analyzed for SRP (APHA 1998). The sediment systems were maintained under oxic conditions at a pH of ~ 8.0 to 8.3 and a temperature of ~ 20 °C during shaking.

The change in SRP mass (i.e., initial SRP - final SRP; mg) over the 24-hr period was divided by the dry mass equivalent of wet sediment used in the experiment to determine the quantity of P desorbed or adsorbed (mg P kg^{-1} sediment). These data were plotted as a function of the equilibrium SRP concentration after 24 hr of incubation to determine the linear adsorption coefficient (K_d ; L kg^{-1}), the equilibrium P concentration (EPC; mg P L^{-1} ; the point where net sorption is zero), and the native adsorbed P (S_o ; mg P kg^{-1} sediment; initial P adsorbed to the sediment). The K_d and S_o were calculated via regression analysis as the slope and the y-intercept, respectively, from linear relationships between final SRP concentrations and the quantity of P sorbed at low equilibrium concentrations (Pant and Reddy 2001). The EPC was calculated as S_o divided by K_d .

Summer constituent loading rates and flow-weighted concentrations were determined using the software program FLUX (Walker 1996). Constituent loading was calculated either as the product of a flow-weighted average concentration and mean flow over different flow strata or by linear regression analysis of concentration versus flow. Constituent loading at individual stations were also normalized with respect to the watershed area above each station (Table 2).

Table 2
Watershed Areas Above Loading Stations Located in the Upper Eau Galle River Watershed

Loading Station	Watershed Area (km^2)
EGR-4.3	6.9
EGR-12.7	32.8
EGR-18.5	101.1
EGR-26.3	123.3
Carr Creek	35.0

RESULTS AND DISCUSSION:

TSS and Phosphorus. The Upper Eau Galle River responded to several storm events during summer 2002, with peaks in flow along its longitudinal axis (Figure 2). Peaks in flow occurred in early May, early and late June, mid-August, and late August through early September. Flows were near nominal during a dry period between July and early August.

Mean daily flow was lowest at EGR-4.3 and increased with increasing distance from the headwaters (Figure 3). Flow increased considerably between stations EGR-12.7 and EGR-18.5 due to inflows from Carr Creek, which drains a large portion of the western region of the Upper Eau Galle watershed. Abrupt increases in TSS and total P and N loadings also occurred at EGR-18.5 (Figure 3), indicating loading influences from Carr Creek. In contrast, loading changes for these constituents were much smaller between EGR-4.3 and EGR-12.7 and between EGR-18.5 and EGR-26.3. Although not statistically significant (t-test; SAS 1994), the sum of the loads

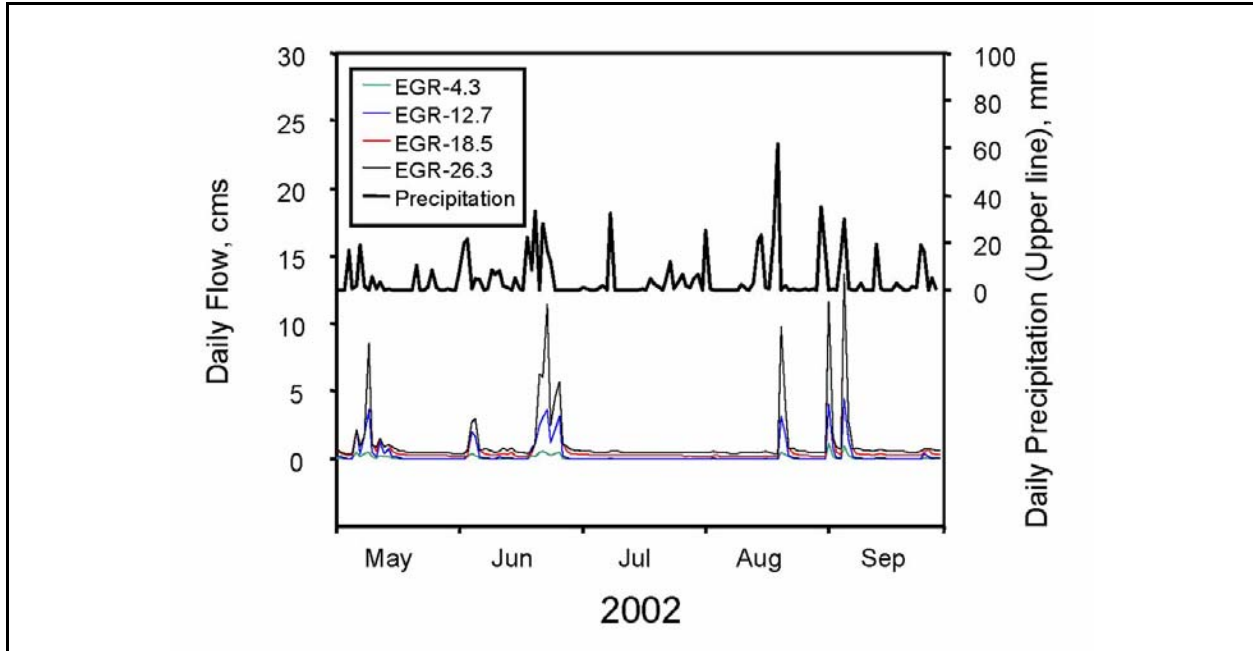


Figure 2. Variations in mean daily flow (cms; cubic meters per second) at Upper Eau Galle River (EGR) kilometers 4.3, 12.7, 18.5, and 26.3 and daily precipitation between May and September 2002

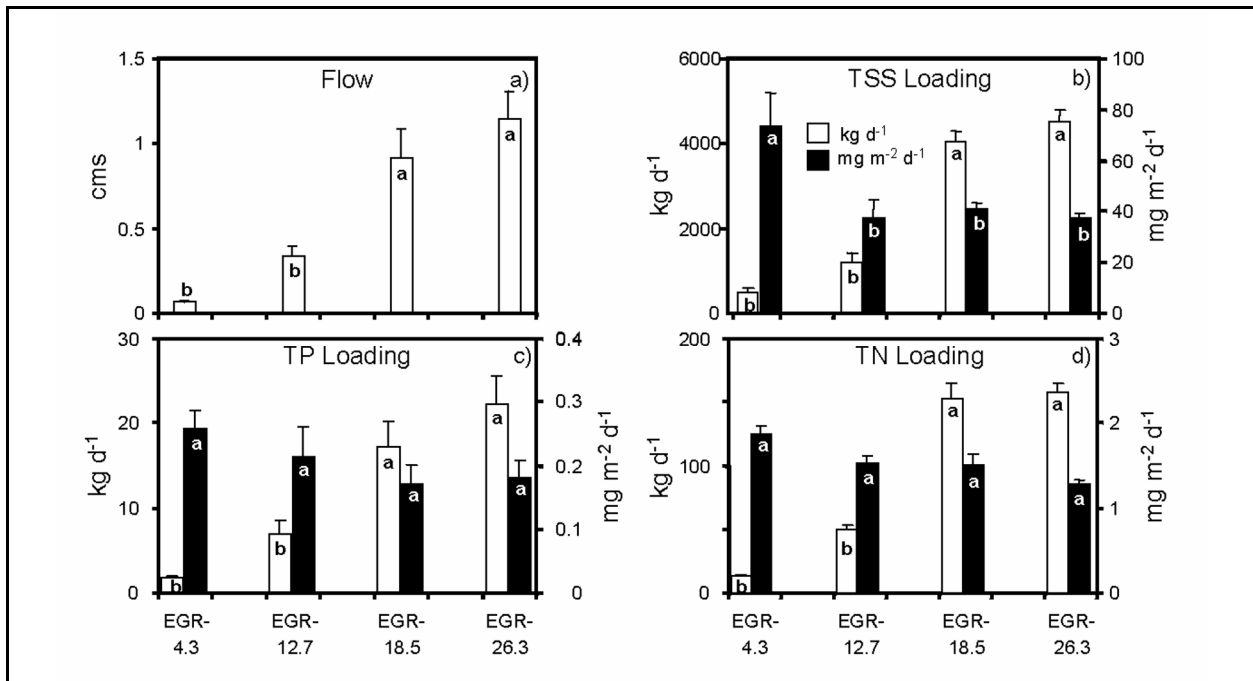


Figure 3. Mean flow (a), total suspended solids (TSS, b), total phosphorus (TP, c), and total nitrogen (TN, d) loading (kg d^{-1}) between May and September 2002, at Upper Eau Galle River (EGR) kilometers 4.3, 12.7, 18.5, and 26.3. Areal export rate estimates ($\text{mg m}^{-2} \text{d}^{-1}$) are weighted with respect to watershed area above each sampling station. Vertical lines above bars represent 1 standard deviation. Letters between stations represent significant differences ($p < 0.05$) in means based on ANOVA (SAS Institute 1994)

originating from EGR-12.7 and Carr Creek were slightly greater than the load estimated at EGR-18.5 for TSS (5013 kg d⁻¹ versus 4065 kg d⁻¹, respectively) and total P (20.4 kg d⁻¹ versus 17.2 kg d⁻¹, respectively). This pattern suggested possible retention of a small portion of these loads in the floodplain upstream of EGR-18.5.

Loads weighted with respect to unit watershed area were either greatest in the headwaters of the Upper Eau Galle River at EGR-4.3 (i.e., for TSS) or generally uniform between the four stations (i.e., for total N and P; Figure 3). The occurrence of homogeneous areal nutrient loading rates along the longitudinal axis of the Upper Eau Galle River suggested that the land-use mosaic was uniform in the watershed. In contrast, longitudinal differences in areal constituent loading and concentration along the longitudinal axis of a river basin can reflect influences of sub-watershed geomorphology, land-use practices, and point-source inputs, as found in the upper Mississippi River basin (James et al. 1999).

Mean concentrations of TSS were greatest in the headwaters of the Upper Eau Galle River (Figure 4). TSS concentrations declined downstream and were uniform between EG-12.7 and EGR-26.3, similar to patterns observed for areal constituent loading rates. Station EGR-4.3 also exhibited greater concentrations of particulate P in the runoff compared to downstream stations (Figure 5). However, there were no statistically significant differences in concentrations of total P as a function of distance from headwaters.

Soluble forms of phosphorus (primarily as SRP) comprised between 48 and 57 percent of the flow-weighted concentration of total P over all stations (Figure 5). Labile particulate forms of phosphorus were dominated by the loosely bound and iron-bound PP fraction while the refractory particulate component was primarily in the form of calcium-bound PP. Station EGR-4.3 exhibited the greatest concentrations of refractory organic particulate PP compared to the other stations.

For Upper Galle River inflows entering Eau Galle Reservoir at EGR-26.3, 79 percent of the flow-weighted total P concentration was composed of labile P forms (i.e., soluble P plus labile PP; Figure 6). SRP is directly available for algal growth, while phosphomonoesters (as a part of SUP) can be converted to ortho-P via enzymatic activity under P-limiting conditions (Franko and Heath 1979). Loosely bound and iron-bound PP fractions, which comprised a large portion of the labile particulate PP fraction, can be recycled in receiving waters via equilibrium reactions, and eH and pH reactions (Mortimer 1971; James et al. 1996). Labile organic PP can be recycled via bacterially mediated reactions (mineralization and enzymatic hydrolysis of polyphosphate forms; Gächter et al. 1988, Gächter and Meyer 1993, Hupfer et al. 1995).

Mean P equilibrium characteristics of TSS loads are shown in Figure 7. Overall, considerable P desorption occurred from TSS at SRP concentrations less than ~ 0.15 mg L⁻¹ for all stations. At high ambient SRP concentrations, adsorption of soluble P onto TSS occurred. The EPC was very high and similar to flow-weighted mean SRP concentrations determined over the summer period at each station (Figure 8), suggesting regulation of ambient SRP via equilibrium processes with TSS in the runoff. The linear adsorption coefficient was near 1 L kg⁻¹ for all stations (Table 3),

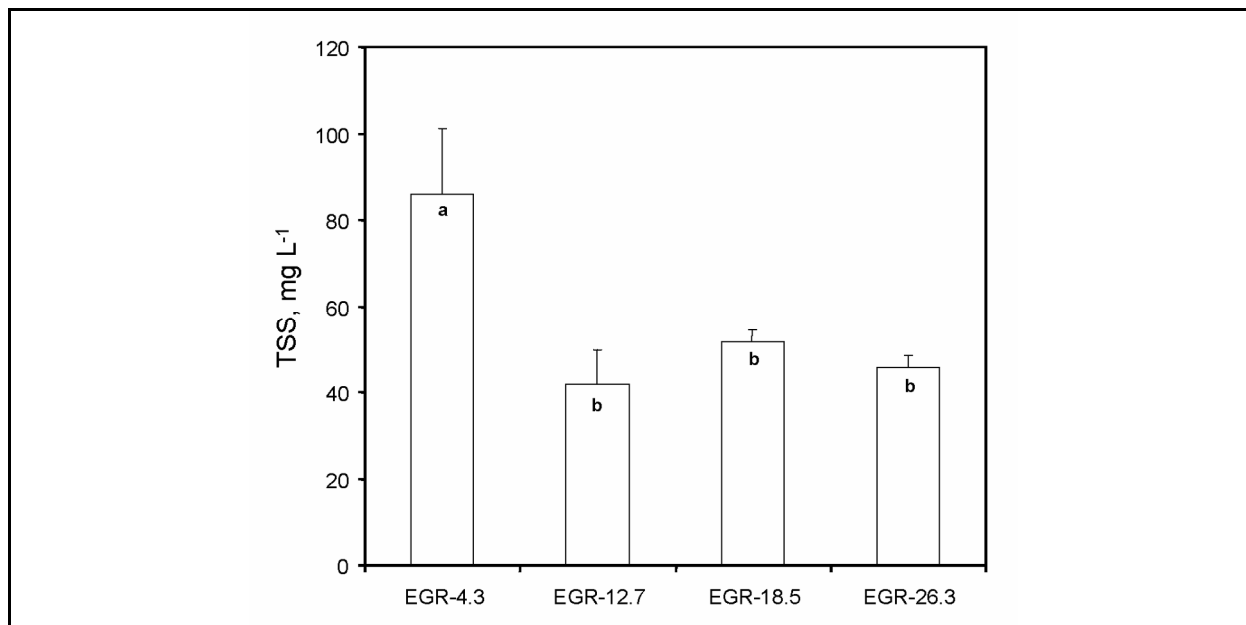


Figure 4. The mean, flow-weighted concentration of total suspended solids (TSS) between May and September 2002, at Upper Eau Galle River (EGR) kilometers 4.3, 12.7, 18.5, and 26.3. Vertical lines above bars represent 1 standard deviation. Letters between stations represent significant differences ($p < 0.05$) in means based on ANOVA (SAS Institute 1994)

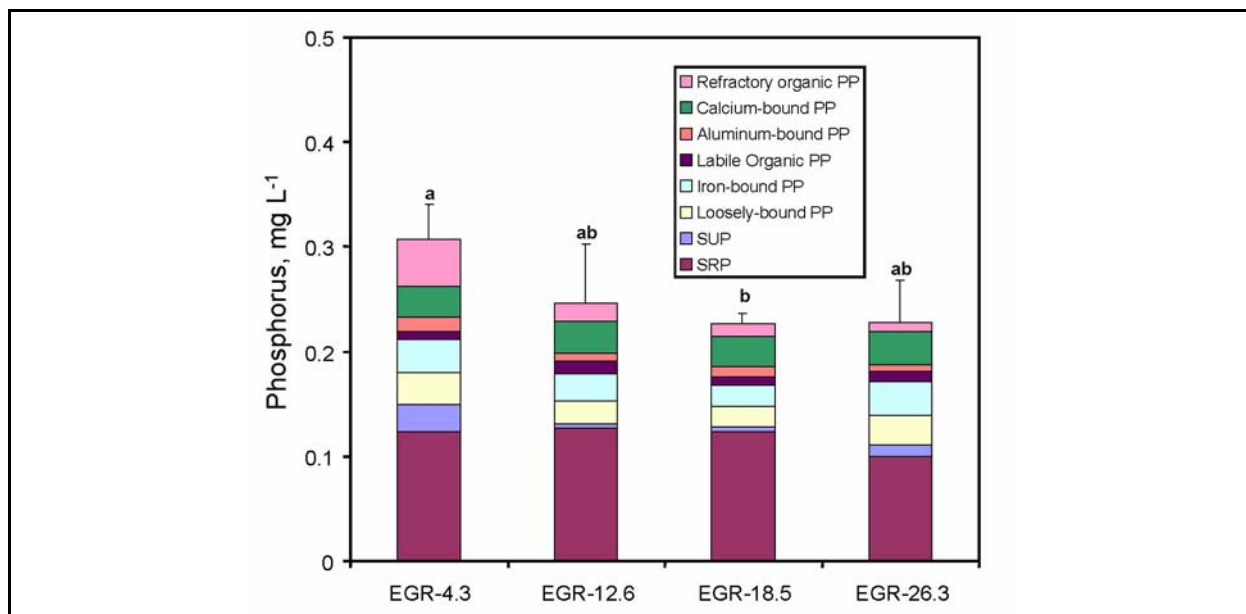


Figure 5. The mean, flow-weighted concentration of total phosphorus and phosphorus species between May and September 2002, at Upper Eau Galle River (EGR) kilometers 4.3, 12.7, 18.5, and 26.3. PP = particulate phosphorus; SUP = soluble unreactive phosphorus; SRP = soluble reactive phosphorus. Vertical lines above bars represent 1 standard deviation for the mean total phosphorus concentration. Letters between stations represent significant differences ($p < 0.05$) in means based on ANOVA (SAS Institute 1994).

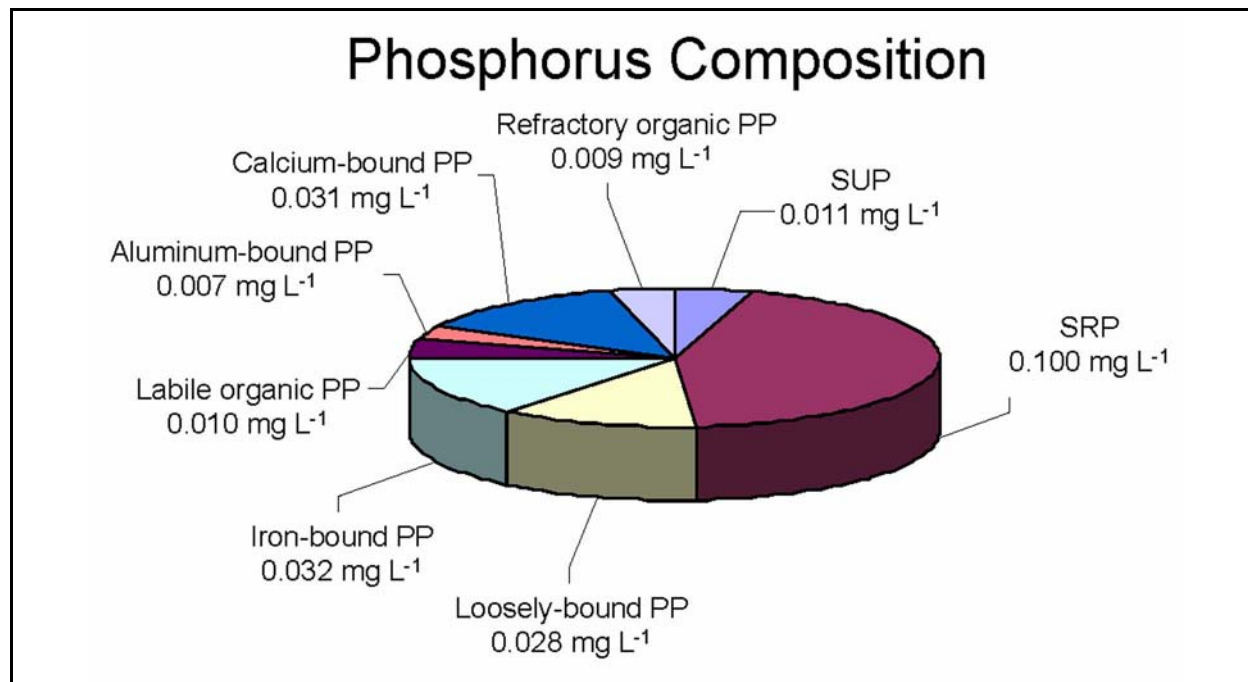


Figure 6. Pie chart showing the percent composition and mean, flow-weighted concentrations of various phosphorus species for phosphorus loads at river kilometer 26.6 of the Upper Eau Galle River

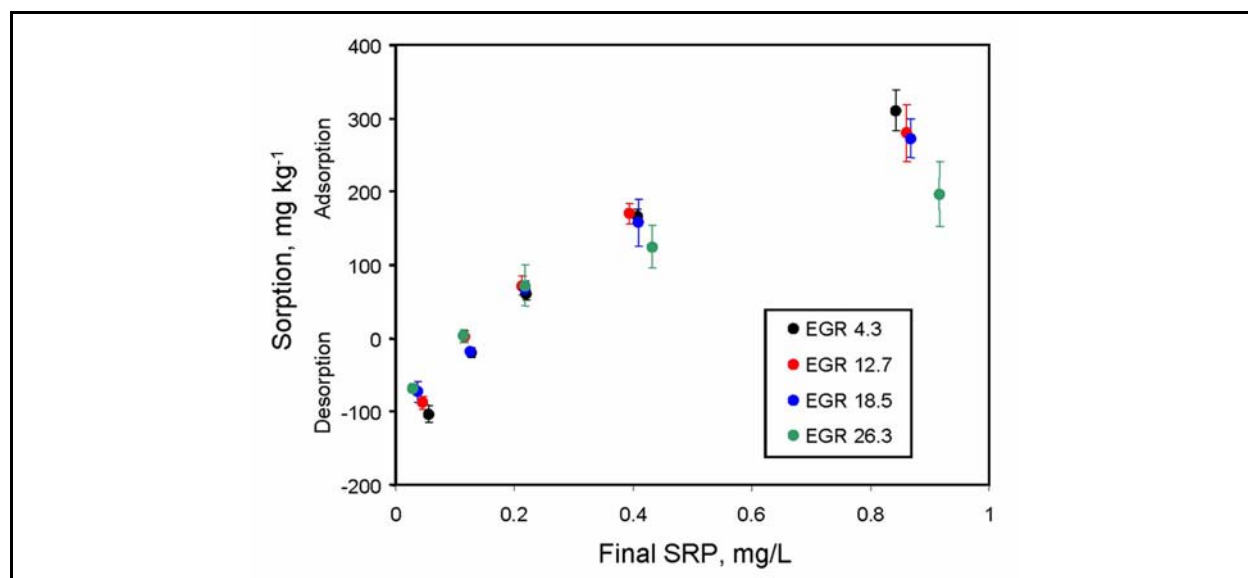


Figure 7. Adsorption and desorption characteristics as a function of ambient soluble reactive phosphorus (SRP) concentration for total suspended solids collected during storm events at Upper Eau Galle River (EGR) kilometers 4.3, 12.7, 18.5, and 26.3. Vertical lines indicate 1 standard deviation

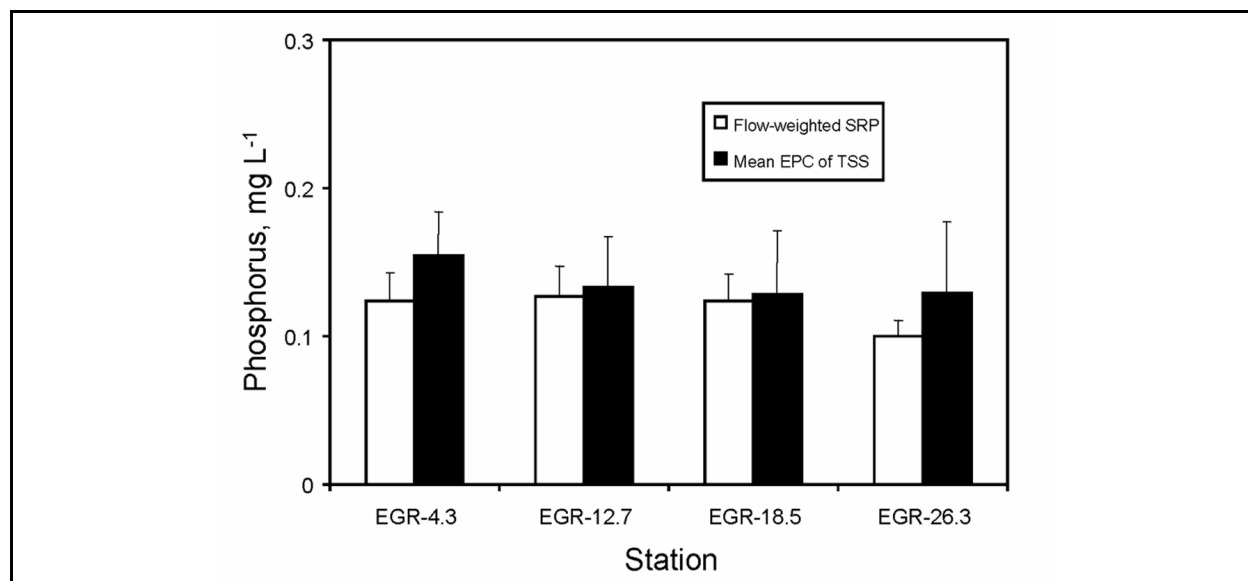


Figure 8. A comparison of mean, flow-weighted, soluble reactive phosphorus (SRP) concentrations and the mean equilibrium phosphorus concentration (EPC) for total suspended solids (TSS) loads at Upper Eau Galle River (EGR) kilometers 4.3, 12.7, 18.5, and 26.3. Vertical lines indicate 1 standard deviation. No significant differences were found between flow-weighted SRP concentration and the EPC of TSS (t-test; SAS Institute 1994)

Table 3 Mean ($\pm$ 1 S.E.) Equilibrium Phosphate Concentration (EPC), Linear Adsorption Coefficient (K_d), and Native Adsorbed Phosphorus (S_o) for Suspended Solids Runoff at Various Stations in the Upper Eau Galle River Watershed			
Station	EPC (mg/L)	K_d (L/kg)	S_o (kg/L)
EGR 4.3	0.154 (0.010)	1017 (106)	159 (22)
EGR 12.7	0.133 (0.013)	981 (136)	126 (17)
EGR 18.5	0.128 (0.022)	777 (70)	101 (21)
EGR 26.3	0.129 (0.024)	791 (202)	88 (2)

indicating a strong buffering capacity for ambient P under conditions of P disequilibrium. The EPC for TSS loads in the Upper Eau Galle River was high relative to other studies (Meyer 1979; Mayer and Gloss 1980; Froelich 1988; Olila and Reddy 1993) and may reflect soil management practices (i.e., fertilizer and manure subsidies).

Nitrogen. Similar to total P, flow-weighted mean total N concentrations were not significantly different at stations located along the Eau Galle River (Figure 9). Over all stations, soluble organic N and $\text{NO}_3\text{NO}_2\text{-N}$ comprised most of the total N concentration. In contrast, $\text{NH}_4\text{-N}$ represented only a small fraction of the total N concentration. Particulate organic N fluctuated along the longitudinal axis of the river, exhibiting the highest concentrations at EGR-4.3 and EGR-26.3. For inflows entering the Eau Galle River at EGR-26.3, the composition of total N was co-dominated by the particulate organic N, soluble organic N, and $\text{NO}_3\text{NO}_2\text{-N}$ fractions (Figure 10). $\text{NH}_4\text{-N}$ concentrations were negligible.

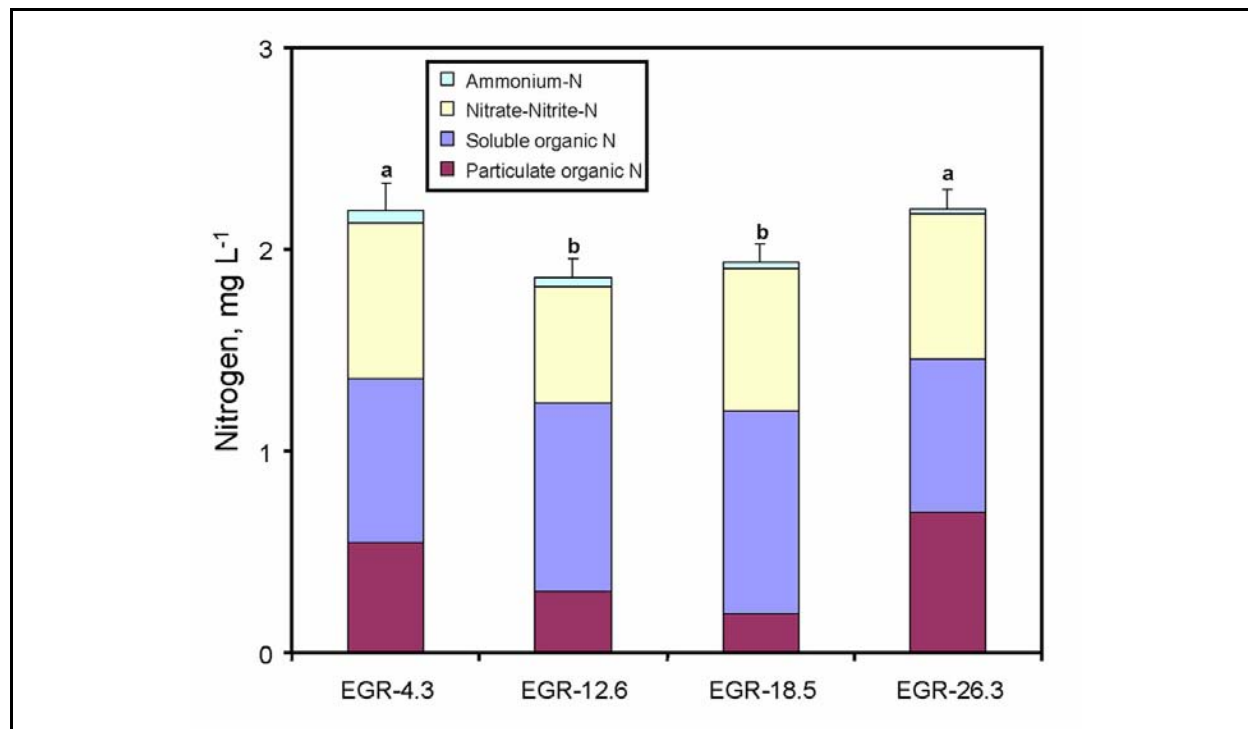


Figure 9. The mean, flow-weighted concentration of total nitrogen (N) and nitrogen species between May and September 2002 at Upper Eau Galle River (EGR) kilometers 4.3, 12.7, 18.5, and 26.3. Vertical lines above bars represent 1 standard deviation for the mean total nitrogen concentration. Letters between stations represent significant differences ($p < 0.05$) in means based on ANOVA (SAS Institute 1994)

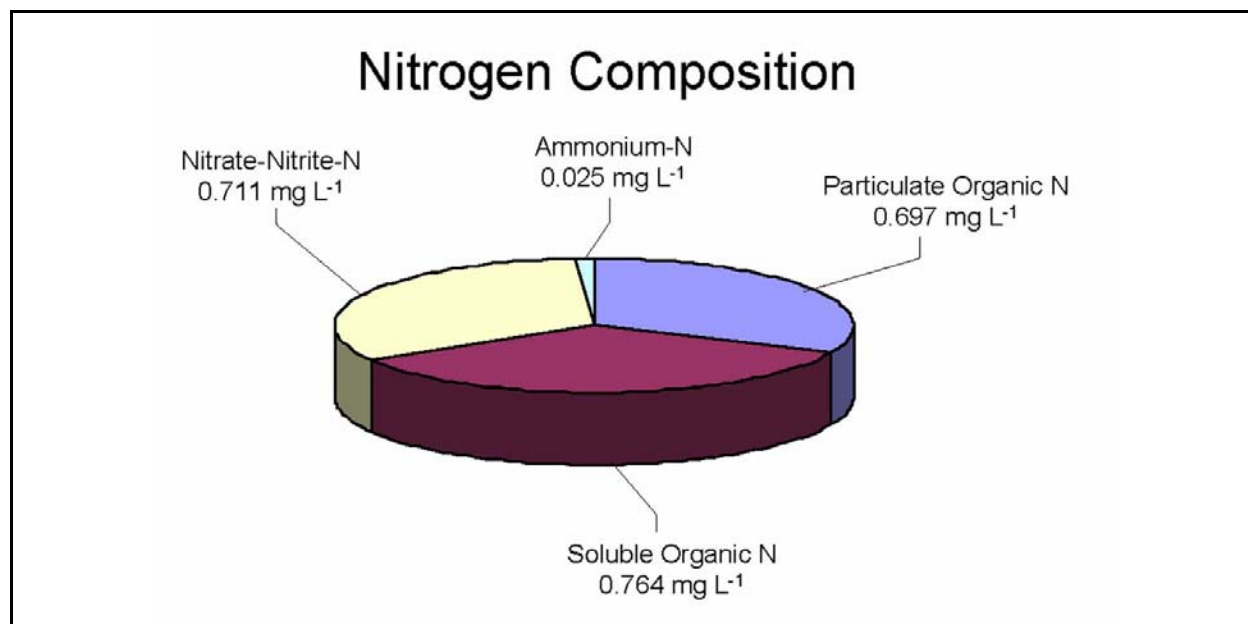


Figure 10. Pie chart showing the percent composition and mean, flow-weighted, concentrations of various nitrogen species for phosphorus loads at river kilometer 26.6 of the Upper Eau Galle River

Modeling needs in relation to findings. An important need for watershed model improvement is identification and prediction of biologically available forms of nutrients from field runoff in the watershed, transport to receiving waters, recycling, and fate. Determining only total and soluble P loading does not always provide sufficient information regarding the potential for recycling and biological uptake in receiving waters. For instance, partitioning of total P into functional labile and refractory components revealed that the loosely bound and iron-bound PP fractions were important constituents of Upper Eau Galle River loads entering the reservoir. James et al. (1997) found that greater than 50 percent of the P loading originating from the Eau Galle watershed can be retained as bottom sediment in the reservoir. Internal P loading from both profundal and littoral sediments in the reservoir, driven by eH and pH reactions, is high (range = 3.2 to 8.1 mg m⁻² d⁻¹; James et al. (1993)), and believed to be driven primarily by iron-phosphorus associations and ligand exchange mechanisms (James et al. 1990; James and Barko 1991). Thus, knowledge of loading and storage of loosely bound and iron-bound PP to this as well as other aquatic systems, and management to reduce these inputs would be critical in future water quality improvement of the reservoir. Watershed models that identify hydrologically sensitive areas (Gburek and Sharpley 1998; Walter et al. 2000, 2001) and predict source inputs of these (and other) labile PP fractions would be valuable in the development and implementation of BMP's to reduce runoff to receiving waters that are biologically responsive to these constituent inputs.

A significant finding of this study was the occurrence of high concentrations of SRP in the runoff along the watershed's longitudinal axis and an apparent link to equilibrium processes between TSS and aqueous phases. Sharpley et al. (1993) suggested that preferential transport of clays, coupled with P adsorption-desorption processes, could increase (or decrease) the bioavailability of P as loads moved through the watershed, depending on equilibrium relationships between solid and aqueous phases. In the Upper Eau Galle River watershed, surface soil P is heavily subsidized with manure and fertilizer inputs in agricultural areas, resulting in very high mean crop-available P concentrations ranging between 120 and 180 ppm (as Mehlich-3 P; James, unpublished data). James et al. (2004) found that the EPC and S₀ of TSS in field runoff of agricultural land uses increased as a function of increasing P management of the landscape (i.e., livestock containment areas versus cornfields versus woodlots). This pattern suggested that binding sites on soils were becoming more saturated with P in managed areas of the landscape, resulting in higher EPC and greater P desorption potential under conditions of P disequilibrium (Ruiz et al. 1997). Both the mean EPC and flow-weighted SRP concentrations of Eau Galle River flows were high (>0.1 mg L⁻¹), indicating influences from source soils eroded from phosphorus-subsidized agricultural areas of the landscape. The strong correspondence between flow-weighted SRP concentrations along the longitudinal axis of the watershed and the EPC of the TSS indicated that equilibrium processes, derived from agricultural soil erosion, were largely regulating SRP concentrations as constituent loads move downstream into receiving waters.

With the exception of the headwaters, longitudinal concentration gradients for both N and P constituents were minor, suggesting a relatively homogeneous landscape mosaic throughout most of the watershed. In particular, it appeared that concentrations of most constituents were slightly diluted as loads moved downstream, suggesting the possibility that hydrologic runoff was increasing at a faster rate than constituent runoff and/or some temporary retention of

constituent loads (via sedimentation) was occurring along the floodplain. In contrast to these patterns, longitudinally increasing constituent concentrations could signify changes in land use (i.e., increased soil management or urban runoff) and/or erosion of floodplain material. The current results suggest that some temporary retention of a small portion of the loads moving through the landscape occurred in the floodplain of the watershed between EGR-12.7 and EGR-18.5, due to loading influences from Carr Creek, a major tributary inflow of the Upper Eau Galle River system. This retained material may be transported downstream at a later date.

The nitrogen composition of loads in the Upper Eau Galle River was varied, with nearly equal percentages of particulate and soluble organic N and nitrate-nitrite-N. Ammonium-N comprised only a small portion of the total N. On a field scale level, James et al. (2004) found that ammonium-N represented a much higher percentage and concentration (range= 3.6 to 7.0 mg L⁻¹) of the runoff from barnyards, cornfields and hay meadows (alfalfa and grass), land uses which dominate the watershed landscape. Since dairy operations are prevalent in the watershed, manure, a rich source of ammonium-N, is often used as a soil nutrient subsidy on corn and is also spread on hayfields after cutting, partly as a means of reducing manure surplus. Differences in the N composition between field-scale runoff (i.e., ammonium-N dominated) and loads moving down the mainstem (nitrate-nitrite-N dominated) suggest the occurrence of nitrification (conversion of ammonium-N to nitrate-nitrite-N).

SUMMARY: Results from this study suggested that biologically labile PP forms (particularly loosely bound and iron-bound PP) and soluble N and P need to be considered in watershed-receiving water models. Labile PP forms can be recycled and become available for biological productivity. Study results also suggest that equilibrium processes are important in partitioning particulate and soluble P forms in the runoff. For agriculturally managed watersheds, equilibrium processes between TSS and aqueous phases may result in very high SRP concentrations in the runoff due to P desorption from particles. Apparent high EPC between TSS and aqueous phases in runoff was most likely due to management of soils for crop uptake of N (not P) with fertilizers and manure that led to the buildup of excessive P in the soil and saturation of binding sites on soil particles with P. These processes need to be incorporated into transformation and transport algorithms that describe P and N movement through the landscape.

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