Nutrient Loading Characteristics for Two Sub-watersheds Exhibiting Differing Agricultural Land-Use Practices

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

PURPOSE: The purpose of this research was to describe and quantify biologically labile and refractory nitrogen and phosphorus constituents, transformations, and loads in the runoff of two sub-watersheds exhibiting differing agricultural land-use practices. Runoff was impacted by intensive row-cropping for corn production in one of the watersheds while the other one was impacted by dairy livestock management.

BACKGROUND: Increasing agricultural development in watersheds has resulted in substantial water, sediment, and nutrient loadings, leading to reduced water quality in receiving waters over the past several decades. Accelerated soil and nutrient import from watersheds is exacerbated by agricultural land-use practices that promote intensive row cropping and rapid drainage of soils for crop production. High runoff of nutrient-rich constituents can also occur via dairy and livestock production, coupled with containment of large numbers of animals in barnyard and pasture settings, resulting in reduction of perennial cover, disturbance of soils, and localized soil nutrient enrichment via animal waste. There is a need to manage watersheds for reduction of soil and nutrient losses by implementing best management practices (BMP's) (e.g., conservation tillage, perennial vegetation cover and buffering, terracing, contour strip cropping, animal waste management) and hydrologic and floodplain/wetland restoration measures. To forecast the impacts of watershed rehabilitation and BMP's on hydraulic and sediment/nutrient loadings, models need to be refined to address impacts of various land-use practices on concentrations and loads of sediment and important nutrients like nitrogen and phosphorus in rivers and streams draining watersheds.

The objectives of this research were to examine the impacts of land-use practices on sediment, nitrogen, and phosphorus transformations and loading for two sub-watersheds exhibiting intensive agricultural practices. Fractionation procedures were used to identify biologically labile (i.e., recyclable via chemical transformations or directly available for biological uptake) and refractory (i.e., unavailable for biological uptake and subject to permanent burial) species of phosphorus running off of each watershed. With sediment, nitrogen, and phosphorus loadings entering receiving waters from various agricultural sources including dairies, feedlots (swine, cattle, and poultry), and farm lands (pastures and row crops) watershed models need to be modified to more accurately describe these agricultural practices, address the intensive loadings, and simulate nitrogen and phosphorus transformations and cycling within the watershed and basin.

METHODS: Watershed features for Eight-Mile and French's Run are shown in Table 1. Both sub-watersheds are located within the Upper Eau Galle River basin, a 123-km^2 watershed in

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Table 1
Watershed Characteristics and Land Use in Eight-Mile and French's Run

Description	Eight-Mile Run	French's Run
Area, m^2	2639680	52255
Agriculture, %	33	74
Wooded, %	28	0
CRP, %	35	26
Livestock, %	4	0

west-central Wisconsin that exhibits multiple land uses (Ashby 1985). In general, Eight-Mile Run was about 50 times larger than French's Run and exhibited more diversity in land uses. Land uses were co-dominated by woodlots, agricultural row crops (predominantly corn), and CRP (Conservation Reserve Program) in the Eight-Mile Run watershed. Although livestock containment areas in this watershed represented only ~ 4 percent of the area, this land use was concentrated in one location near the base of the watershed (Figure 1). For managed agricultural regions in the Eight-Mile Run watershed, cornfields were plowed and planted in late April 2002. Managed livestock containment areas (barnyard and fenced pastures) contained about 100 head of Jersey cows. In the French's Run Watershed, corn production accounted for 74 percent of the land coverage (Table 1). The cornfield in the French's Run watershed was plowed in October 2001 and disked and planted in late April 2002. For all cornfields in both watersheds, weeds were controlled via herbicide rather than cultivation.

In the Eight-Mile Run watershed, an automated water sampling and flow gauging station was established upstream of the run's confluence with the Upper Eau Galle River (Figure 1). Stage height was recorded at 15-min intervals using an ISCO 6700 sampler with a 730 bubbler module (ISCO Incorporated, Lincoln, Nebraska). A stage-discharge relationship was determined over a variety of flow regimes to convert stage height to volumetric flow. In the French's Run watershed, sampling and flow gauging equipment were located adjacent to a culvert (30 in. diam) located under 10th Ave. West, in Eau Galle Township. Instantaneous velocity and stage height were measured at 15-min intervals using an ISCO 4150 area-velocity sensor. Precipitation gauges (Dataloggers; Model S-162) placed near each watershed monitored rainfall over 15-min intervals. Flows and precipitation were monitored in both watersheds between May and October 2002.

At both stream sampling locations, 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-µm filter for soluble constituent determination. Soluble reactive P (SRP), ammonium-N (NH_4-N), and nitrate-nitrite-N (NO_3NO_2-N) was analyzed using automated analytical techniques (Lachat Quikchem Autoanalyzer, Hach Company, Lachat Div., Loveland, Colorado). Total and total soluble N and P were analyzed colorimetrically using Lachet QuikChem procedures following digestion with alkaline potassium persulfate according to Ameel et al. (1993). For particulate components, sample aliquots were retained on glass fiber

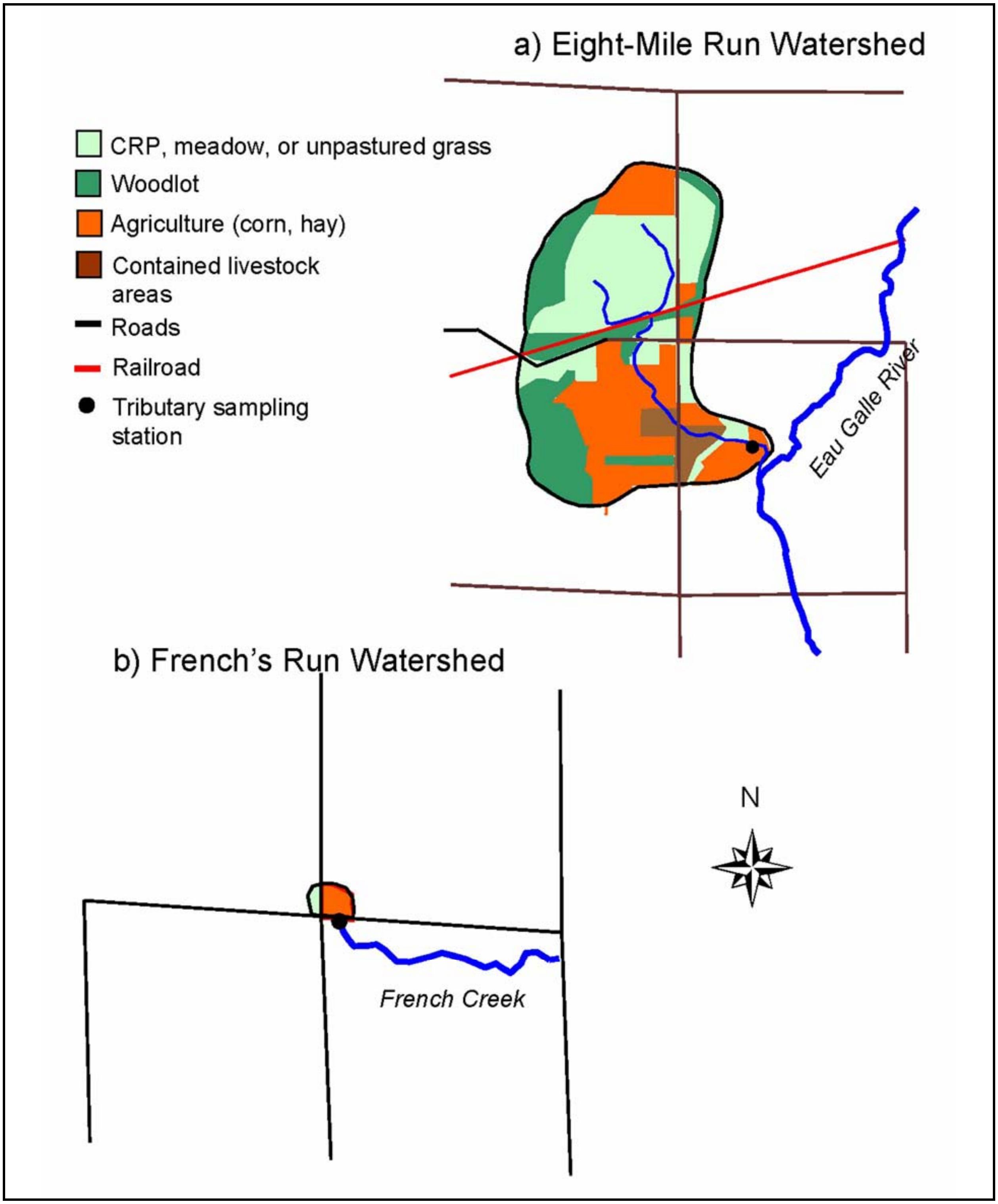

Figure 1. Features and land-use characteristics of the Eight-Mile and French's Run watersheds

filters (Gelman Metricel; 2-µ nominal pore size). For total suspended solids (TSS) and particulate organic matter (POM), suspended material was dried at 105 ^oC to a constant weight, then ignited at 500 ^oC in a muffle furnace (American Public Health Association (APHA) 1998). Sequential fractionation of inorganic P in the sediments was conducted according to Hieltjes 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 P (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 PP was calculated as the difference between reactive and nonreactive sodium hydroxide-extractable P. 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). Table 2 describes operationally defined PP fractions measured in this study and biological availability. 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 NH_4-N and NO_3NO_2-N.

Table 2
Operationally Defined Phosphorus Fractions[1]

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 (~500 mg/L dry weight equivalent) were subjected to a series of SRP (potassium dihydrogen phosphate; KH_2PO_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. The concentration of suspended sediment used in the study fell within the range of concentrations occurring naturally in the two watersheds during periods of elevated inflow. 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 (Detenbeck and Brezonik 1991). 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 ^{o}C .

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 Kd 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.

Daily constituent loading rates 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 was also normalized with respect to the watershed area above each station.

RESULTS: Several storms occurred between May and September (Figures 2 and 3). Daily precipitation patterns over the two watersheds were very similar, ranging between a summer average of 4.5 mm d^{-1} for Eight-Mile Run and 4.9 mm d^{-1} for French's Run. Maximum daily precipitation of 64.5 mm d^{-1} occurred in late August. Peaks in daily flow from each watershed in May and June coincided with periods of peak daily precipitation. The hydrograph typically rose rapidly within a few hours of storm passage, as shown for flows for French's Run in June (Figure 4). Flows from the two watersheds diminished to zero in July through early August in conjunction with infrequent and minor precipitation events, warmer air temperatures, generally dry conditions, and the development of crop cover. Tributaries draining these watersheds were completely dry during this period. High runoff from each watershed in late August was associated with a large storm which produced a maximum in daily precipitation for the summer period. A series of precipitation events exceeding 20 mm d^{-1} resulted in peaks in flow from the two watersheds in September. The average runoff coefficient over the summer period was three times higher for French's Run (0.003 m d^{-1}) than for Eight-Mile Run (0.001 m d^{-1}).

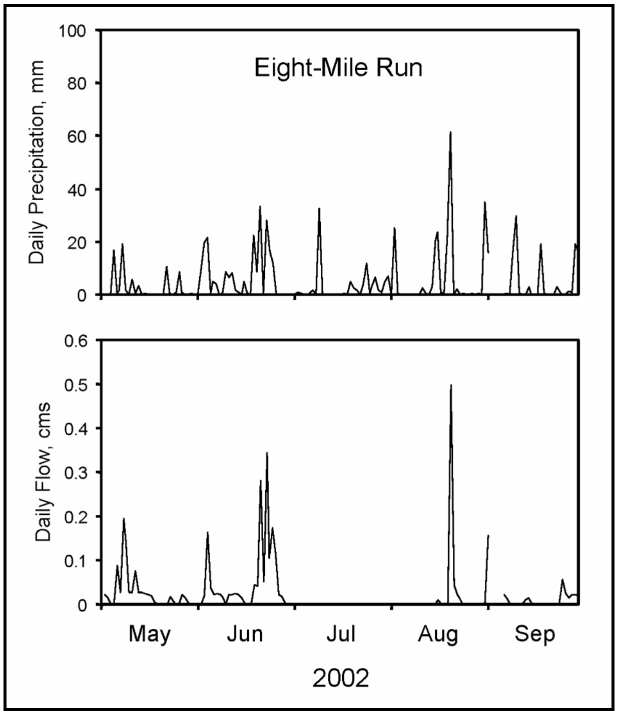

Figure 2. Variations in daily precipitation (upper panel) and flow (lower panel) between May and September 2002 in the Eight-Mile Run watershed

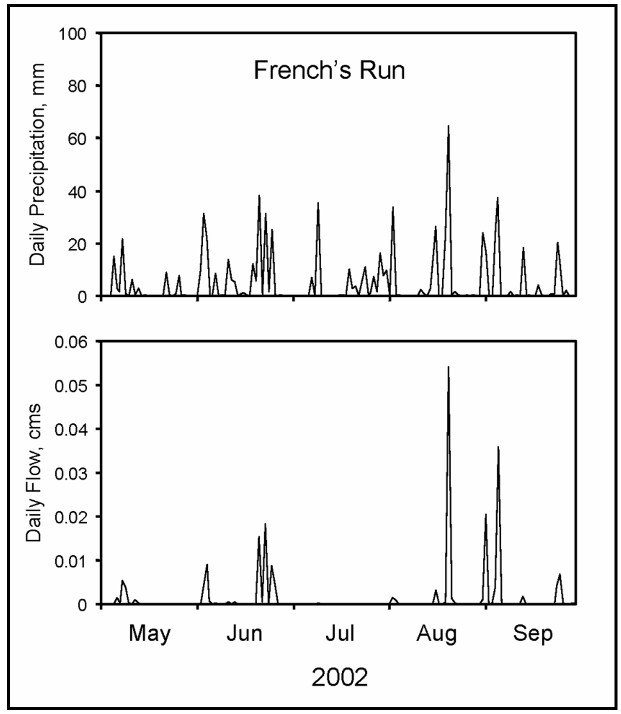

Figure 3. Variations in daily precipitation (upper panel) and flow (lower panel) between May and September in the French's Run watershed

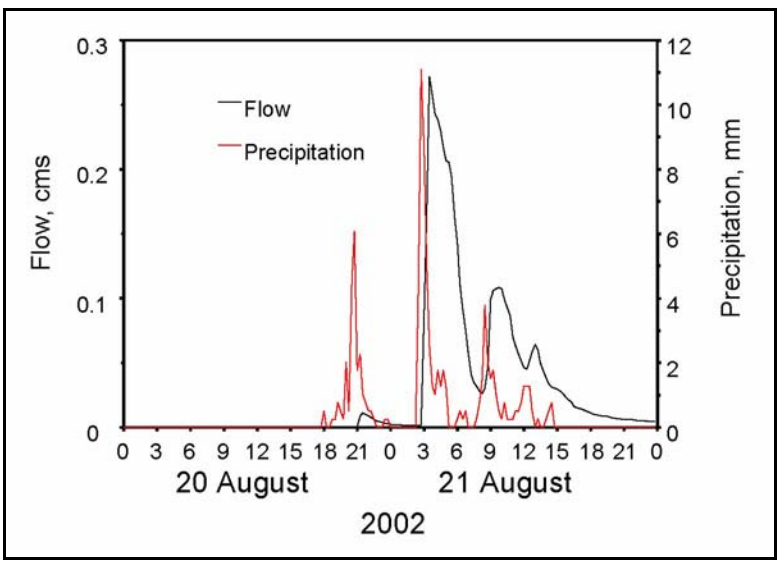

Figure 4. Variations in precipitation and flow in the French's Run watershed during a storm event on 20-21 August 2002

There were marked differences in phosphorus loading and constituent composition as an apparent result of differing land-use impact on runoff within each watershed. In the Eight-Mile Run watershed, total phosphorus loads over the summer period were composed of predominantly soluble P (Figure 5 and Table 3). Although particulate P accounted for only ~37 percent of the total P load from this watershed, 65 percent of this material was biologically labile (i.e., loosely bound, iron-bound, and organic/poly-P particulate P). Thus, soluble P and labile particulate P loading from the Eight-mile Run watershed, considered to be available for biological uptake either directly or indirectly via recycling pathways, accounted for 87 percent of the total P load.

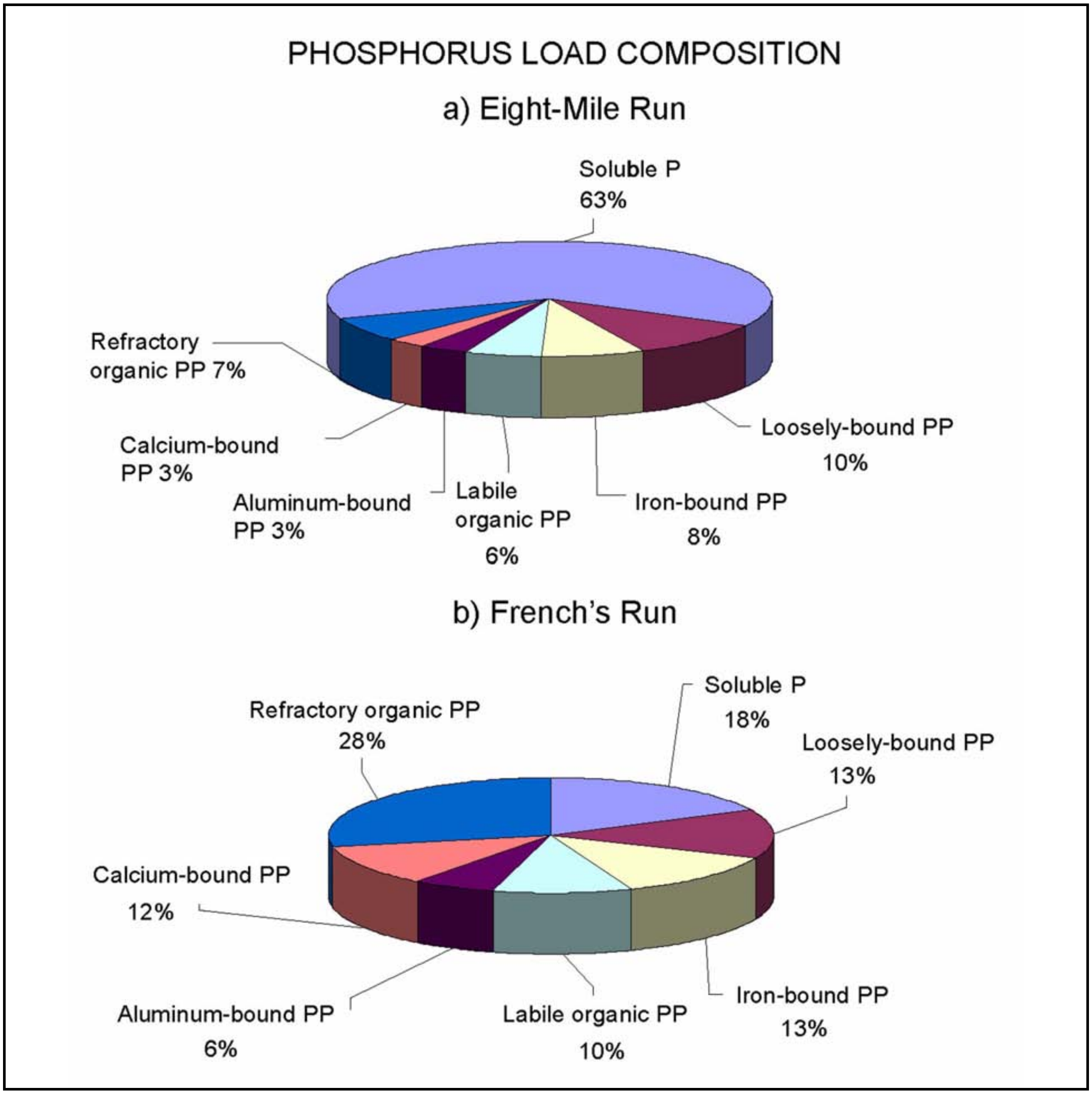

Figure 5. Composition of phosphorus loads in the a) Eight-Mile Run and b) French's Run watersheds

Table 3
Daily Loading, Areal Daily Loading, Mean Concentration, and the Coefficient of Variation (C.V.) of Various Constituents for Eight-Mile and French's Run Between May and October 2002

Variable	Eight-Mile Run				French's Run			
	Load (kg/d)	Areal Load (mg m^{-2} d^{-1})	Concen-tration (mg/L)	C.V.	Load (kg/d)	Areal Load (mg m^{-2} d^{-1})	Concen-tration (mg/L)	C.V.
Total Suspended Solids	435	165	163.2	0.25	104	1990	609.3	0.31
Particulate Organic Matter	62.1	23.4	23.3	0.29	7.7	147	45.0	0.27
Total Nitrogen	7.12	2.70	2.670	0.12	1.43	27.44	8.401	0.26
Total Soluble Nitrogen	4.67	1.77	1.752	0.06	0.84	16.04	4.905	0.39
Nitrate-Nitrite-Nitrogen	1.51	0.57	0.565	0.18	0.67	12.76	3.904	0.48
Ammonium-Nitrogen	0.34	0.13	0.126	0.24	0.01	0.25	0.078	0.13
Total Phosphorus	1.56	0.59	0.613	0.16	0.25	4.99	1.531	0.30
Total Soluble Phosphorus	0.93	0.35	0.400	0.13	0.05	0.88	0.271	0.12
Soluble Reactive Phosphorus	0.92	0.34	0.392	0.11	0.04	0.75	0.228	0.06
Total Particulate Phosphorus	0.64	0.24	0.209	0.23	0.17	3.31	1.016	0.44
Loosely Bound Particulate P	0.17	0.07	0.037	0.28	0.03	0.56	0.170	0.49
Iron-Bound Particulate P	0.13	0.05	0.049	0.24	0.03	0.54	0.162	0.54
Aluminum-Bound Particulate P	0.06	0.02	0.022	0.29	0.01	0.25	0.078	0.45
Calcium-Bound Particulate P	0.05	0.02	0.019	0.51	0.03	0.48	0.149	0.45
Labile Organic/Poly-P Particulate P	0.10	0.04	0.037	0.22	0.02	0.42	0.127	0.56
Refractory Organic Particulate P	0.12	0.05	0.045	0.32	0.06	1.17	0.354	0.44

In contrast to Eight-Mile Run, total P loads from the French's Run watershed were composed of predominantly particulate components (82 percent of the total P load; Figure 5 and Table 3). Forty-six percent of the total P load was composed of refractory particulate P components (i.e., aluminum-bound, calcium-bound, and refractory organic particulate P). Labile particulate and soluble phosphorus loading from French's Run represented only 44 percent of the total P load. In general, areal phosphorus loading characteristics were much higher for French's Run versus Eight-Mile Run (Table 2).

The compositional quality (i.e., mg g^{-1} basis) of the PP loads also varied between the two watersheds (Figure 6). PP from Eight-mile Run exhibited significantly greater concentrations of loosely bound PP, iron-bound PP, and organic/poly-P PP than French's Run. Conversely, French's Run exhibited significantly greater concentrations of the more refractory aluminum-bound, calcium-bound, and refractory organic PP than Eight-Mile Run.

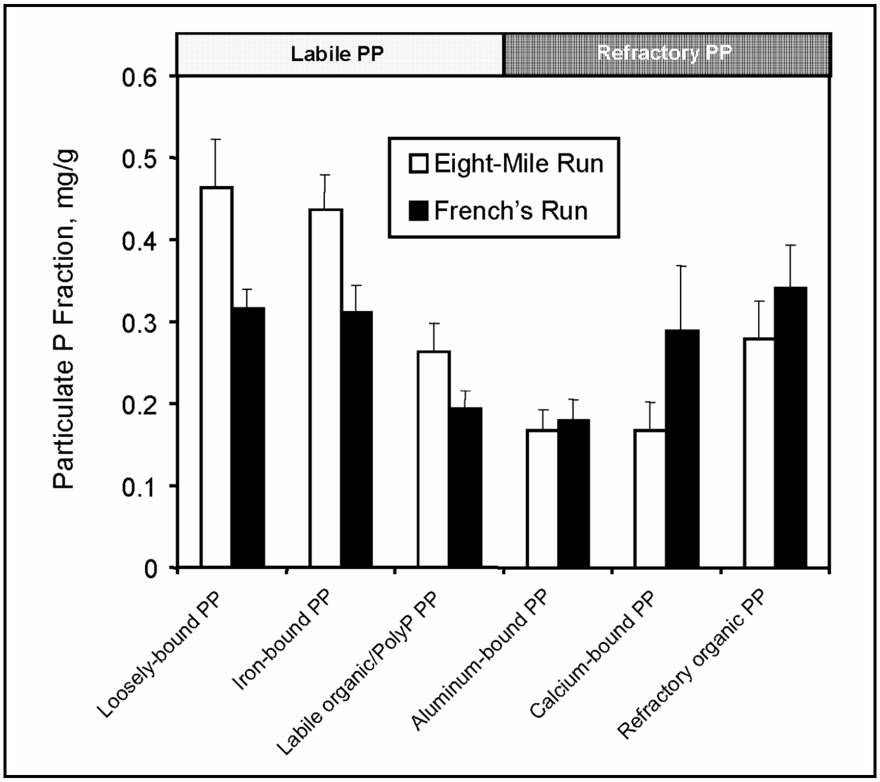

Figure 6. Composition of labile (i.e., subject to recycling pathways) and refractory (i.e., subject to burial) particulate phosphorus (PP) in the runoff of Eight-Mile and French's Run

Sorption characteristics of the PP loads originating from each watershed are shown in Figure 7. Overall, K_d was similar and moderate for each watershed, compared to K_d for other TSS and aquatic sediments (Olila and Reddy 1993, Reddy et al. 1996, Pant and Reddy 2001), suggesting moderate to high buffering capabilities for phosphate under conditions of P disequilibrium (Table 4). The EPC and S_o were very high for TSS loads from each watershed. However, both the EPC and S_o were significantly greater for TSS loads originating from Eight-Mile Run versus those from French's Run.

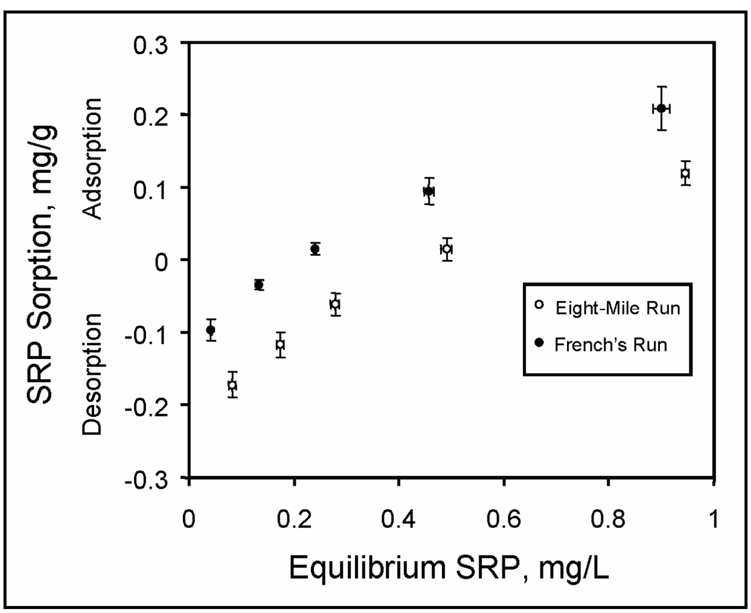

Figure 7. Phosphorus sorption characteristics for total suspended solids in the runoff of Eight-Mile and French's Run. SRP = soluble reactive phosphorus 2

Table 4
Mean Linear Absorption Coefficient (K_d), Native Adsorbed Phosphorus (NAP), and the Equilibrium Phosphorus Concentration (EPC) of Total Suspended Solids Loads from the Eight-Mile and French's Run Watersheds[1]

Variable	Eight-Mile Run (n=11)	French's Run (n=15)
K_d (L kg^{-1})	593 (61)[a]	567 (62)[a]
NAP (mg kg^{-1})	228 (24)[a]	160 (16)[b]
EPC (mg L^{-1})	0.414 (0.049)[a]	0.210 (0.017)[b]

[1] Numbers in parentheses represent 1 standard error; letters indicate significant differences at the 5-percent level or less based on ANOVA (SAS Institute 1994).

Marked differences in nitrogen constituent loadings were also observed between the two watersheds (Figure 8 and Table 3). Concentrations and areal loadings of total and total soluble nitrogen (and particulate organic nitrogen by difference) were much higher in French's Run than in Eight-Mile Run. Soluble nitrogen loads from Eight-Mile Run were dominated by soluble organic N components versus French's Run soluble N loads, which were dominated by NO_3NO_2-N. As with phosphorus constituents, areal nitrogen loads were greatest from French's Run in contrast to Eight-Mile Run.

DISCUSSION: For P runoff and transformations, the most pronounced difference between the two watersheds was the dominance of PP species loading from French's Run versus soluble P species loading from Eight-Mile Run. This difference in runoff characteristics was likely attributable to differences in land-use patterns between the two watersheds. Intensive corn production, lack of vegetative cover between rows, and poor contouring for agricultural fields in the French's Run watershed apparently resulted in substantial particle erosion. A substantial portion of the PP from this watershed was also in the refractory organic P form, which may have been associated with decomposed corn stubble incorporated into the soil.

In the Eight-Mile Run watershed, relatively high concentrations of soluble P in the runoff were probably linked to P solubilization from soils with a high manure content (Sharpley et al. 1994) located in the dairy livestock containment areas adjacent to the tributary. Even though dairy livestock land-use areas occupied only 4 percent of the watershed, it appeared this land-use feature had a marked impact on runoff and loading to Eight-Mile Run relative to the other land-use features. Soils in dairy livestock containment areas of Eight-Mile Run and the Eau Galle watershed exhibited significantly greater organic matter, total P, Mehlich-3 P, and water-extractable P than soils from other land-use areas (James, in press), suggesting enrichment of readily solubilized phosphorus in the soils by manure incorporation. Equilibrium processes between TSS and aqueous phases may have also played an important role in causing very high SRP concentrations in the runoff of this watershed. Although particulate P concentrations were lower relative to soluble P, ~60 percent of this component was comprised of biologically

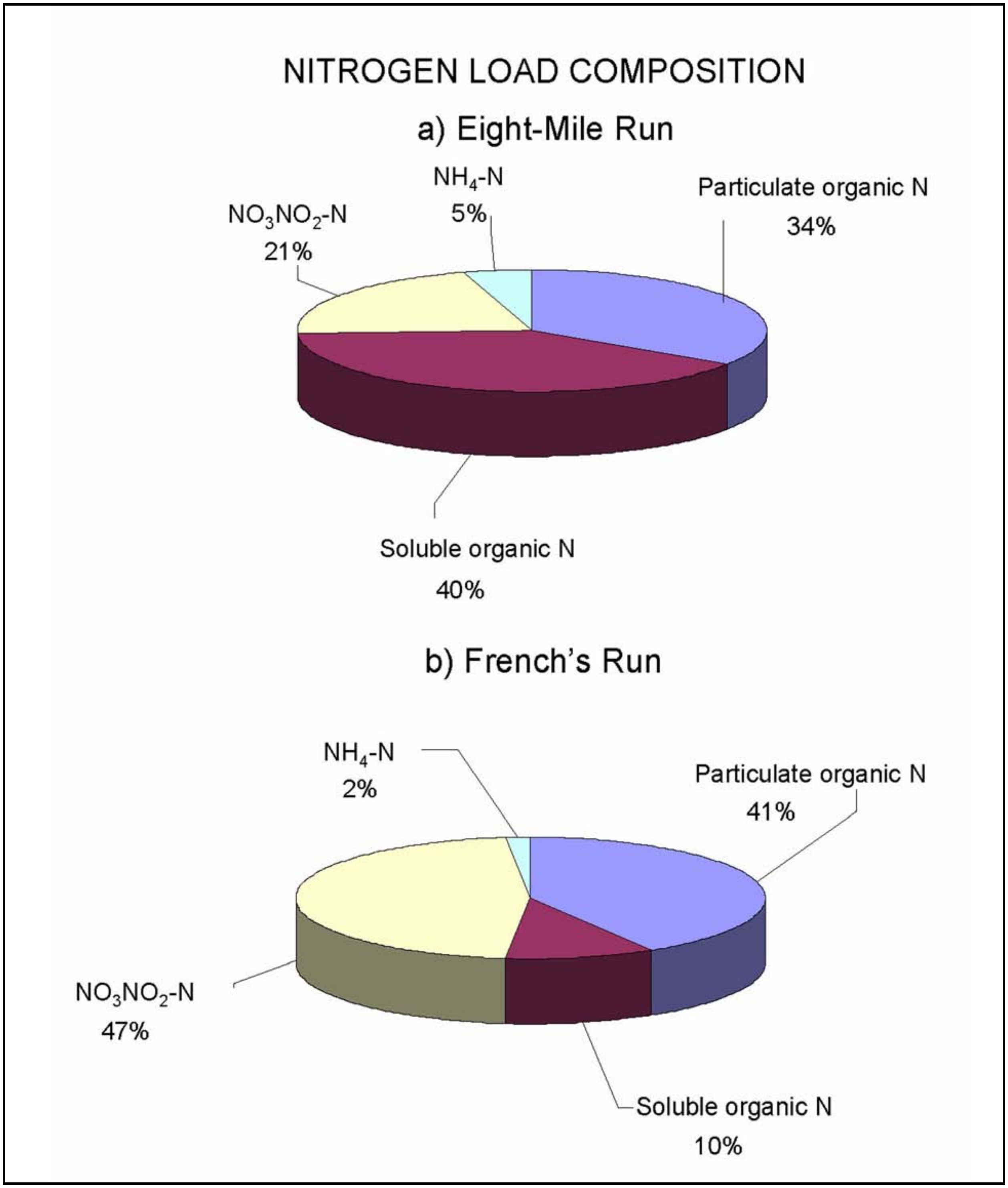

Figure 8. Composition of nitrogen loads in the a) Eight-Mile Run and b) French's Run watersheds

labile P and forms that were reactive to equilibrium processes. In particular, the EPC of TSS in runoff from the Eight-mile watershed was very high (Table 4), reflecting the mean flow-weighted SRP concentration of the runoff (Table 3), and TSS exhibited very high desorption fluxes at low concentrations of aqueous SRP, suggesting enrichment of P binding sites on soils (i.e., loosely bound and iron-bound PP, Figure 6) from readily solubilized P in manure. Reddy et al. (1978) also found that manure amendments increased the EPC of soils tremendously.

Equilibrium processes between particles and aqueous phases appeared to be largely responsible for control of soluble P concentrations in the runoff of French's Run. The EPC of particulate loads (0.210 mg/L) coincided closely with flow-weighted concentrations of SRP observed for French's Run during the summer period (Tables 3 and 4). This pattern, coupled with a high PP:SP ratio for the runoff, suggested equilibrium control of soluble P in the runoff of French's Run. Results strongly suggested that eroded soils in the runoff can regulate soluble P concentrations in receiving waters through equilibrium processes and this fact needs to be considered in watershed management and eutrophication assessment (Sharpley et al. 1981; Klotz 1988).

Overall, 87 and 54 percent of the P runoff from Eight-Mile and French's Runs, respectively, was in a biologically labile form and potentially available for biological uptake either directly or via recycling pathways. Soluble N species accounted for 26 and 49 percent of the N runoff from Eight-mile and French's Runs, respectively. Soluble P forms are generally directly available for uptake or can be converted to available forms via enzymatic reactions (Franko and Heath 1979). Loosely bound and iron-bound particulate P can be recycled through diffusive and kinetic processes at downstream locations. Diffusive P flux from deposited P loads can occur via eH and pH reactions (James and Barko 2004). Kinetic P flux can occur via equilibrium processes between TSS and aqueous phases.

Differing land-use patterns also appeared to be responsible, in large part, for differences in the composition of nitrogen species in the runoff from each watershed. The N composition of French's Run was dominated by nitrate-nitrite-N, suggesting nitrification of fertilizers added to the fields in the spring. Like P, soluble organic N species in the runoff of Eight-Mile Run were probably also associated with solubilization from manure-laden soils from dairy livestock land-use areas.

SUMMARY: Both watersheds contained areas of intensive agricultural land management, which appeared to play an important role in the composition and quality of runoff during storms. Dairy livestock management in the Eight-mile Run watershed appeared to promote relatively high loadings of soluble P species. Land managed for intensive row-crop production in the French's Run watershed was associated with high loadings of particulate P species. In both watersheds, TSS exhibited a high EPC and high desorption potential under conditions of P disequilibrium, suggesting enrichment of soils with P as a result of management practices. P enrichment of TSS was greatest for runoff from the Eight-mile Run watershed in conjunction with manure-laden soils, resulting in a significantly greater mean EPC and S_o compared to TSS from French's Run. The common practice of spring fertilization with anhydrous NH_4-N to increase corn yield, as in the French's Run watershed, appeared to be linked to high nitrate-nitrite-N runoff, suggesting N transformations via nitrification. Higher concentrations and loads of soluble organic N and NH_4-N from the Eight-mile Run watershed appeared to be linked to manure-laden soils and mineralization of particulate organic N. Runoff of biologically labile particulate and soluble material was also associated with these land-use practices. This material can be utilized by biota either directly via uptake or indirectly via recycling pathways at downstream locations and receiving waters.

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