Bioavailable Phosphorus in Fine-Sized Sediments Transported from Agricultural Fields

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Sediments transported from agricultural fields in surface and subsurface waters contain particulate P (PP) that could be partitioned into two pools—one available for aquatic organisms including cyanobacteria, namely bioavailable particulate P (BAPP, determined by 0.1 mol L^{-1} NaOH extraction), and the remainder not bioavailable (non-BAPP). This study aimed to quantify the PP and BAPP concentrations in surface runoff and tile drainage water from eight agricultural fields with clay and sandy soils in the Missisquoi Bay region of Quebec, Canada. Particulate P in surface and drainage water varied spatially (among fields) and temporally, with concentrations as high as 3181 μg P L^{-1} in surface runoff and 1346 μg P L^{-1} in tile drainage. About 30% of PP was BAPP regardless of the drainage pathway. The PP and BAPP concentrations were related linearly ($R^2 = 0.86$) to total suspended solids (TSS) in fine (0.05–1-μm) and coarse (1–100-μm) fractions. About 68% of the PP in clay soils and 50% of the PP in sandy soils were associated with the 0.05- to 1-μm size particles, which had more BAPP, on average 0.46 g P kg^{-1}, than the coarser 1- to 100-μm fraction (0.22 g P kg^{-1}). Soil parameters such as Mehlich-3 extractable (M3) P, M3Fe, and the degree of soil P saturation were related to the PP and BAPP concentrations in TSS and particle size fractions. We concluded that sediments with particle size <1 μm contained more BAPP and their loss from agricultural fields could contribute to the eutrophication downstream.

Abbreviations: ANCOVA, analysis of covariance; BAPP, bioavailable particulate phosphorus; DSPS, degree of soil phosphorus saturation; M3, Mehlich-3 extractable; MRP, molybdate-reactive phosphorus; non-BAPP, nonbioavailable particulate phosphorus; PP, particulate phosphorus; PSD, particle size distribution; soil organic matter; TSS, total suspended sediments.

Lake Champlain is a large freshwater lake (3211 km^2) that spans the international boundary between Quebec, Canada, and Vermont and New York in the United States. This lake experiences episodic blooms of cyanobacteria, which increases the cost of water treatment for the surrounding municipalities that obtain their drinking water from the lake and limits recreational activities (swimming, fishing, and boating). Eutrophication of Lake Champlain is attributed to anthropogenic activities that have increased the P concentration in watersheds that drain into the lake (Seltzer and Wang, 2004). For example, nonpoint sources account for >90% of the annual P load (167 Mg P yr^{-1}) entering Missisquoi Bay in Quebec at the northern end of the lake (Hegman et al., 1999). Agricultural activities are an important source of diffuse pollution in Missisquoi Bay, contributing an estimated 39% of the annual P load (Troy et al., 2007).

Transport of P from agricultural land to surface water occurs predominantly through overland flow in many watersheds (Haygarth and Jarvis, 1999; Nash et al., 2002) and during snowmelt and soil thawing periods in Quebec (Michaud et al., 2004); however, subsurface flow through artificial tile drains was reported to account for 40% of the total P exported from agricultural fields located along the Pike River, a tributary of Missisquoi Bay (Enright and Madramootoo, 2004).

In the St. Lawrence Lowlands of Quebec, most of the total P transported through surface runoff and tile drains was bound to sediments (Enright and Madramootoo, 2004; Macrae et al., 2007). In tile drains of corn (*Zea mays* L.) production fields, the PP accounted for >50% of the total P in water samples during peak flow events, with concentrations ranging between 0.8 and 2.1 g P kg^{-1} TSS (Beauchemin et al., 1998, 2003b).

The BAPP is the fraction of PP that is readily available to cyanobacteria and other aquatic organisms and represents about 30% of the PP lost from agricultural fields (Sharpley et al., 1992); however, considerable variation in BAPP concentration was reported in agricultural runoff (Dorich et al., 1984), which may be due to land use (Ellison and Brett, 2006), cropping systems, and tillage methods (Sharpley et al., 1992). Michaud and Laverdière (2004) reported that soil type accounted for 70% of the variability in the percentage of BAPP found in the PP (i.e., the BAPP/PP ratio) of surface runoff water. In an alpine stream, Pacini and Gachter (1999) reported that BAPP was concentrated in fine-sized suspended sediments with a median diameter of 6 μm due to the erosion and transport in runoff of P-rich clay minerals that originated from the topsoil.

While the results of Pacini and Gachter (1999) suggest that BAPP is associated with clays or clay-sized materials, the colloidal fraction (1 nm–1 μm) is another type of suspended sediment found in runoff water from agricultural fields (Heathwaite et al., 2005). Turner et al. (2004) observed colloidal P associated with particles from 3 nm to 1 μm in diameter, which accounted for up to 50% of the molybdate-reactive P (MRP), defined as soluble free phosphate, in surface runoff water from an alkaline agricultural soil. These colloidal P complexes were not stable in acidic solution and, consequently, the MRP measured by the Murphy and Riley (1962) method overestimated the proportion of soluble P in the colloidal fraction. Cumbie and McKay (1999) concluded that colloidal P was less strongly sorbed to the soil matrix than other fine-sized PP, meaning that colloidal P could make a greater contribution to P transfer from soils to surface waters and might be susceptible to transport across long distances in watercourses. Characterizing the particle size distribution (PSD) of the TSS, including the colloidal fraction, in runoff and tile drain waters is necessary to determine the sedimentation time, the depth distribution of the TSS within the water column, and the sorption capacity of the TSS in aquatic systems (Bilotta and Brazier, 2008). Evaluating the PP, BAPP, and non-BAPP concentrations in TSS fractions can provide insight into P transport in surface runoff and tile drain waters, which can then be used to improve strategies for reducing particle-associated P movement from agricultural fields to surface water systems.

This study investigated the seasonal variation in PP, BAPP, and non-BAPP concentrations and TSS in surface runoff and tile drain waters from eight agricultural fields with contrasting soil textures (clayey or sandy) along the Ewing subwatershed in the Missisquoi Bay region of Quebec, Canada. The objectives of this study were: (i) to determine the PP concentration (BAPP and non-BAPP) of the TSS in surface runoff and tile drainage waters from the agricultural fields to test the hypothesis that the PP content of the TSS will be affected by the drainage pathway, (ii) to determine the PP and BAPP concentrations in TSS fractions and test the hypothesis that fine-sized fractions will have greater P concentration and more bioavailable P than coarse fractions, and (iii) to relate the concentration and bioavailability of particle-associated P to soil physicochemical properties such as texture, pH, and extractable nutrient concentrations.

MATERIALS AND METHODS
Description of the Subwatershed and Sampling Sites

The Ewing Brook (45°9′21″ N, 73°4′36″ W, shown in Fig. 1) is a 32.2-km^2 subwatershed of the Pike River watershed, a tributary to the Missisquoi Bay of Lake Champlain, which spans the Canada–United States border between Quebec and Vermont and New York. Along the Ewing subwatershed, eight agricultural fields having artificial tile drainage and contrasting soil texture (five fields had sandy loam soil, three fields had clay loam soil) were chosen for this study (Fig. 1). The soil characteristics of the Ap horizon (0–20 cm) in each field are given in Table 1. Soil samples were collected using a hand probe, yielding one to three composite (10–15 cores) samples per field based on surface morphology. Pits were dug at one representative location per composite area in each field to evaluate the subsurface soil characteristics and to allow the removal of one sample per field for soil physicochemical analysis. The sandy loam soils in Fields 1 to 3 were classified as Typic Endoaquods and Fields 4 and 5 as Humic Haplorthods. Clay loam soils were classified as Aquic Dystrocryepts for Fields 6 and 7 and Typic Humaquepts for Field 8. The fields were relatively flat, with a maximum slope of 2% in Fields 4 and 5. The surface drainage area ranged from 2.8 to 8.1 ha based on an elevation model. The tile-drained area was slightly larger, based on an estimate from the field drainage map, due to the fact that the surface morphology created multiple drainage outlets in the field surface.

When this study began in fall 2008, all fields were in the corn phase of a corn–soybean [*Glycine max* (L.) Merr.] rotation on conventionally tilled soils (plowed in the fall and harrowed in the spring). No fertilizer was applied during the sampling period. For Fields 1, 6, and 8, producers typically applied hog manure (15–25 kg P ha^{-1}, 35–40 kg N ha^{-1}) in the spring before the corn phase of the rotation. In Fields 4, 5, and 7, liquid dairy manure was typically applied t the same rate (15–25 kg P ha^{-1}, 35–40 kg N ha^{-1}) before seedbed preparation. Only inorganic fertilizer was spread in Fields 2 and 3 at rates of 15 to 20 kg P ha^{-1} and 75 to 90 kg N ha^{-1}. In all fields, inorganic P fertilizer was band applied at seeding at a rate of 10 to 20 kg P ha^{-1}, along with 20 to 50 kg N ha^{-1} applied in the crop row at seeding and sidedressed following corn emergence in spring. The fields that received dairy manure were hay fields in 2003 to 2007 after a previous corn–soybean rotation. The other fields (1, 2, 3, 6, and 8) had been in the corn–soybean rotation for the last 8 yr. The soil M3P content of the Ap horizon was considered very high for Fields 1 and 5, high for Fields 2 and 4, and medium for the other fields (Table 1). The degree of soil P saturation [DSPS from M3-extractable nutrients, P/(Al + Fe)] was considered normal for fields with a corn–soybean rotation, with values ranging from 3.4 to 13.8% for the sandy soils and 3.6 to
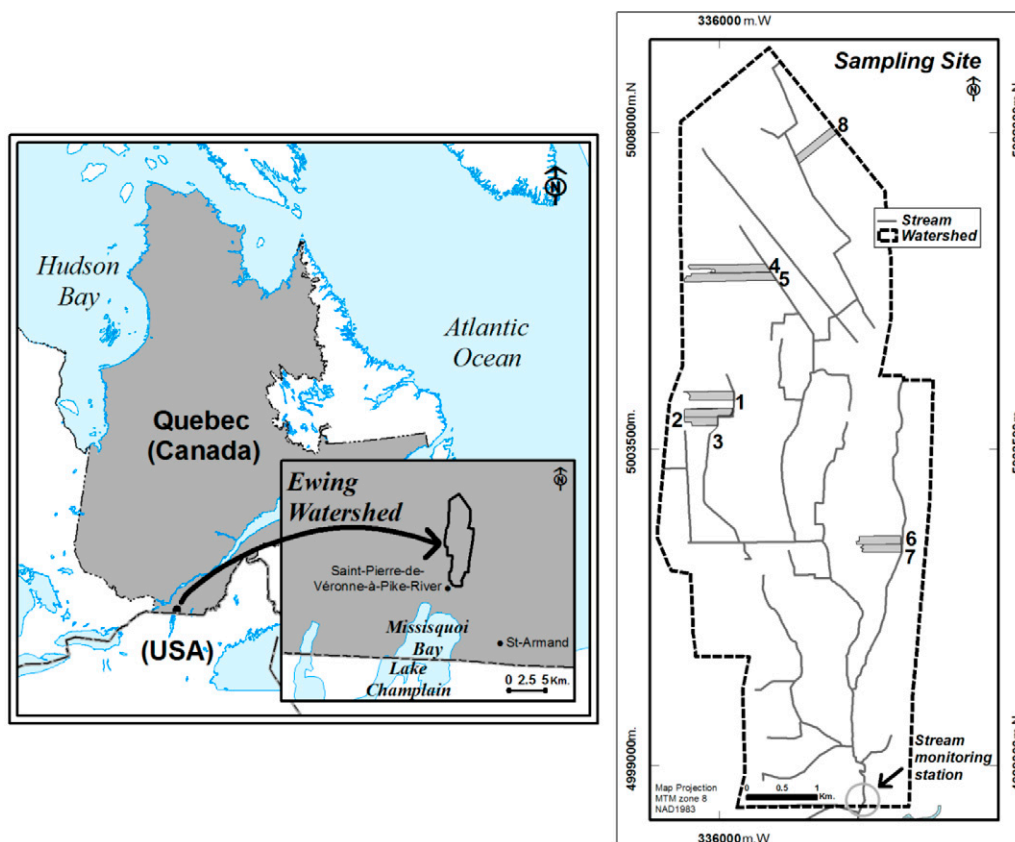
Fig. 1. Location of the Ewing subwatershed (Quebec, Canada) and experimental fields.

6.0% for the clay soils. Soil organic matter (SOM) was typical for agricultural fields in this area—between 22 and 35 g SOM kg^{-1} of soil.

Tile drains had been installed at least 30 yr before this study at a depth of 1.1 to 1.3 m in the C horizon of these fields. Except for Fields 2 and 3, the soil lies over lacustrine or marine low-drained clay layers starting at 90 cm below the soil surface. The soil texture at the depth of the tile drains was sandy loam in Field 2 and silt loam in Field 3. Soil P levels in the C horizon were 10-fold lower than in the A horizon (on average, 6.1 mg M3P kg^{-1} with <1% DSPS, data not shown).

Water Sampling from Surface Runoff and Tile Drains

Water was collected from tile drains on 19 sampling dates from 1 Oct. 2008 to 31 May 2009 during periods of peak flow. There was no snow in the fields at any sampling date. Surface runoff water was collected when available, on nine of these sampling dates. Water from tile drains was collected using a probe that allowed discrete sampling when the tile drain outlets were immersed (i.e., below the stream water level). This probe consisted of a 5-mm-i.d. tube inserted in the tile drain 5 m before the outlet. A manual vacuum pump was attached to the tube and coupled with a 2-L Erlenmeyer flask to collect 500 mL of water from the tile drain. The water sample was transferred to a high-density polyethylene plastic bottle and kept at 4°C until chemical analysis was performed within a 3-wk period. The chemical composition (P and N forms, TSS, pH, and electrical conductivity) of the water extracted from the tile drains using the probe was similar to that of the water collected from the drain outlet

Table 1. Soil characteristics (Ap horizon, 0–20 cm) of eight agricultural fields with tile drainage and surface runoff water collection in the Ewing subwatershed, Quebec, Canada.

Field	Soil series	Clay	Silt	Sand	Total P†	M3P‡	DSPS§	M3Ca‡	SOM¶	pH#	Field surface area	Tile drainage area
		—— g kg^{-1} ——			mg kg^{-1}	mg kg^{-1}	%	mg kg^{-1}	g kg^{-1}		—— ha ——	
1	Saint-Jude	200	140	660	627	114	9.5	1090	26	6.78	8.1	9.5
2	Saint-Jude	230	420	350	776	78	6.1	885	32	5.13	2.8	4.5
3	Saint-Jude	180	220	600	544	44	3.4	1013	35	5.66	4.3	7.3
4	Grande Ligne	150	180	670	724	91	10.1	1460	29	7.15	2.8	5.5
5	Grande Ligne	160	150	700	819	118	13.8	1430	29	6.96	3.4	4.6
6	Saint-Sebastien	390	360	260	1100	60	6.0	2737	34	6.94	3.2	5.0
7	Saint-Sebastien	390	360	260	1100	60	6.0	2737	34	6.83	3.4	6.4
8	Sabrevois	340	330	330	1023	32	3.6	2236	22	6.72	4.5	6.8

† Total P extraction by soil acid digestion as described by USEPA (1996).

‡ Mehlich-3 extraction as described by Tran et al. (1990).

§ Degree of soil P saturation index based on Mehlich-3 extraction, M3P/M3(Al + Fe).

¶ Soil organic matter based on Walkley and Black (1934).
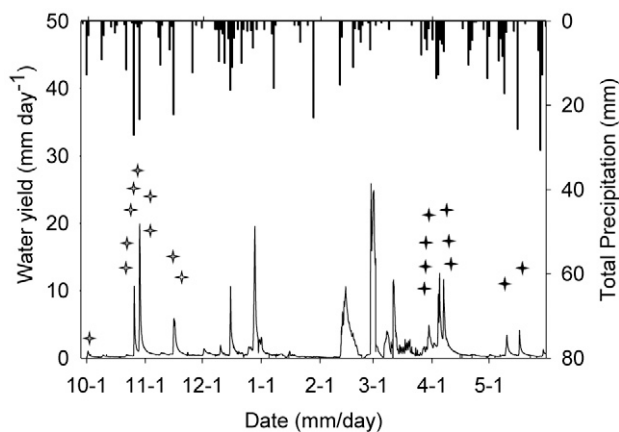
1:2 soil/water ratio.

Fig. 2. Hydrograph of the Ewing subwatershed (y_1 axis) and total daily precipitation (y_2 axis) between 1 Oct. 2008 and 31 May 2009. Crosses indicate discrete water sampling events during this period.

when not immersed (data not shown). Surface water samples were collected by hand in the surface drainage gutter (in fields), upstream of surface catch inlets systematically installed following the design of Brochu and Desjardins (1993). The dates of each discrete water sampling event, as well as the water yield at the Ewing outlet and the total daily precipitation during the study period, are shown in Fig. 2.

Water Sample Analysis

The TSS was determined following water filtration through a 0.45-μm filter (Greenberg et al., 1992a). Recovery of TSS was about 95%, verified by testing the recovery of 1 g L^{-1} of Kaojet (Thiele Kaolin Co., Sandersville, GA) with a median distribution (D_{50}) of 1.0 μm dispersed in deionized water. The MRP was determined on filtered samples (<0.45 μm) using the molybdenum blue method of Murphy and Riley (1962). Bioavailable P (BAP, in μg L^{-1}) was determined using the 0.1 mol L^{-1} NaOH extraction method (Sharpley et al., 1991), while the total P (TP, μg L^{-1}) concentration was measured using the persulfate digestion technique (Greenberg et al., 1992b). The PP (in μg L^{-1}) was calculated as the difference between TP and MRP and considered the soluble P:

$$PP = TP - MRP \qquad [1]$$

Bioavailable particulate P (μg L^{-1}) was calculated as:

$$BAPP = BAP - MRP \qquad [2]$$

Nonbioavailable P (μg L^{-1}) was the difference between PP and BAPP:

$$non\text{-}BAPP = PP - BAPP \qquad [3]$$

Particle Size Analysis

Particle size analysis of the TSS (<0.45 μm) in the water samples from surface runoff and tile drainage was done with a Mastersizer 2000 (Malvern Instruments, Malvern, UK) equipped with a Hydro2000G sampler. This technique uses the capacity of a particle in suspension to diffract light as a function of its volume. The diffracted light intensity is measured at different angles and the equivalent sphere volume is calculated based on the Mie theory. The instrument has the capa-

bility to measure particle diameters between 0.02 and 2000 μm. The samples were not subject to chemical treatment but were diluted in deionized water to produce an absorbance intensity between 5 and 8%. The suspension was sonicated for 5 min before data acquisition at 630 nm. Data were acquired for 30 s and the mean of three repeated acquisitions was recorded for six samples per field by pooling the surface and subsurface water samples. A refractive index of 1.59 for illite was selected, based on Weidler and Friedrich (2007). Two standards, 1.0 g L^{-1} of Kaofine (D_{50} = 0.46 μm) and 1.0 g L^{-1} of Kaojet (D_{50} = 1.0 μm) (Thiele Kaolin Co.) were used to validate the device signal. After sonication, the PSD in the water samples was reproducible for 3 mo when samples were stored at 4°C and samples were analyzed within a 2-mo period. Therefore, the sonication process was effective in disrupting aggregates and agglomerates formed through flocculation during the storage period.

The PSD (on a mass basis) in the water samples was estimated by the following equation:

$$\%PD(TSS) = M_d \qquad [4]$$

where %Pd is the percentage of particles less than a specific size (v/v), TSS is total suspended sediments (mg L^{-1}), and M_d is the particle mass in a given size class (mg L^{-1}). Two common assumptions in the particle size sedimentation procedures are: (i) the suspended particles are spherical and (ii) suspended particles in the same size interval have the same density. Consequently, the mass distribution of suspended particles was equal to their volume distribution due to a constant mass density for particles of all sizes found in the water samples.

Statistical Analysis

Descriptive statistics (mean, standard deviation, and maximum and minimum values) were used to characterize the TSS and concentrations of PP, BAPP, and non-BAPP in water from tile drains and surface runoff from each agricultural field. All P concentration and TSS data were logarithmically transformed to normalize their distribution before statistical analysis. The effects of drainage pathway (tile drainage or surface runoff) and agricultural field (eight fields) on PP, BAPP, and non-BAPP concentrations were tested with analysis of covariance (ANCOVA). The ANCOVA was run with JMP 8.0 software (SAS Institute, 2008), considering each P form as a dependent variable, TSS as the covariate, and using the separate slope procedure to evaluate the fixed effects (drainage, field, and the drainage × field interaction).

To estimate the particulate-associated P in the TSS, linear relationships between PP, BAPP, and non-BAPP from water samples (pooled data from tile drains and surface runoff in Fields 2–8) and the TSS were calculated with an orthogonal fitting curve using an equal variance between TSS and PP forms (0.5/0.5) and an α value of 0.05. This technique minimizes the error of the slope induced by extreme TSS concentrations, and the slope of the line was the mean P content in the TSS (PPc) from all sampling events (g kg^{-1} TSS). The PPc in the submicron and micrometric fraction classes (n = 1, 2; g kg^{-1} TSS) was determined for each field. Data (n = 6) were fit to the following equation with the standard least square procedures (effect of leverage) using JMP 8.0 software (SAS Institute, 2008):

Table 2. Mean concentration of total suspended sediments (TSS), particulate P (PP), bioavailable particulate P (BAPP), and nonbio-available particulate P (non-BAPP) in tile drain water and surface runoff water.

Field	Tile drain water				Surface runoff water			
	TSS	PP	BAPP	non-BAPP	TSS	PP	BAPP	non-BAPP
	mg L^{-1}	——————μg L^{-1}——————			mg L^{-1}	——————μg L^{-1}——————		
1	9 (8)	33 (17)	18 (9)	16 (13)	105 (90)	207 (200)	99 (103)	108 (108)
	0–19†	8–77	6–41	0–36	26–352	50–769	9–364	15–405†
2	96 (106)	153(143)	44 (48)	113 (139)	547 (680)	825 (882)	267 (405)	558 (540)
	0–748	5–1346	0–457	0–889	78–1936	156–2627	17–1348	139–1279
3	62 (100)	114 (84)	14 (19)	99 (71)	707 (730)	917 (886)	294 (231)	624 (664)
	1–118	20–217	0–50	20–167	107–2571	177–3181	68–802	109–2379
4	71 (106)	138 (159)	47 (60)	91 (105)	345 (383)	682 (649)	183 (158)	498 (514)
	0–445	7–647	0–268	7–379	22–1192	71–2010	0–485	71–1525
5	34 (56)	77 (126)	66 (103)	331 (507)	220 (328)	596 (583)	237 (201)	358 (405)
	0–204	0–435	0–115	0–320	17–1160	114–2152	13–642	68–1510
6	73 (80)	123 (150)	23 (46)	100 (108)	355 (505)	337 (253)	96 (97)	241 (160)
	0–308	7–622	0–196	0–426	31–1867	97–925	0–300	97–625
7	51 (61)	81 (83)	19 (130)	62 (41)	206 (107)	302 (163)	97 (68)	235 (97)
	0–360	1–569	0–170	0–399	71–368	158–681	27–246	131–435
8	212 (242)	265 (261)	100 (110)	165 (177)	844 (535)	1077 (767)	418 (275)	658 (542)
	0–807	13–1127	0–382	13–745	198–1906	259–2928	62–984	197–1944

† Means with standard deviations in parentheses and the concentration range.

$$\text{PPc, BAPPc, non-BAPP} = M_{d1}(PPc_1) + M_{d2}(PPc_2) + \varepsilon \qquad [5]$$

where M_d is the mass of each size class (1 or 2) from Eq. [4] (mg L^{-1}), and ε is an error term. No difference at the 0.05 level of significance was calculated between modeled PPc (Eq. [5]) and surface and sub-surface water. The concentration of each PP form (PP, BAPP, and non-BAPP) in the submicron and micrometric fraction sediments was compared with a t-test at $\alpha \leq 0.05$.

The Pearson correlation coefficients between PPc and soil physi-cochemical properties were generated by JMP 8.0. A stepwise regression procedure was then used to determine predictive expressions for the PPc in relation to soil properties of the agricultural fields ($n = 8$). The inclusion of explanatory variables in the linear equation was based on the lowest value of Akaike's information criterion given by JMP 8.0, then by an adjusted R^2 value >0.70, and finally by a significance level of $\alpha \leq 0.05$.

RESULTS AND DISCUSSION
Temporal and Spatial Variation in Concentrations of Particulate Phosphorus Forms in Drainage Water

As expected, there was considerable temporal variation in the TSS and concentrations of PP forms (PP, BAPP. and non-BAPP) in water emitted from the agricultural fields. The TSS values were between 0 and 807 mg L^{-1} in tile drainage and from 0 to 2571 mg L^{-1} in surface runoff water (Table 2). The PP concentration was between 0 and 1346 μg L^{-1} in tile drainage and up to 3181 μg L^{-1} in surface runoff water (Table 2). The BAPP was about 30 ± 27% of the PP and the remainder was non-BAPP (Table 2). The high standard error was due to measurement error at low PP concentrations (<50 μg L^{-1}). These values are similar to other reports from humid temperate regions. The PP concentration in tile drain water was 9 to 329 μg P L^{-1} in a study by Beauchemin et al. (1998), whereas Uusitalo et al. (2001) reported higher values (up to 1240 ± 1390 μg PP L^{-1}) in drainage water from clay soils. In surface runoff, the mean PP concentration was 1270 ± 1390 μg L^{-1} in the study of Uusitalo et al. (2001). The high PP values reported at some sampling dates in this study were probably due to the fact that most water samples were collected during peak events when surface runoff and subsurface drain flow occurred simultaneously.

We expected PP to be associated with sediments transported in tile drains and surface runoff, particularly the fine-size materials in eroded sediments. This was confirmed by the ANCOVA, which indicated that TSS was an important covariable in the analysis, except in Field 1 where TSS was not significant at the $\alpha = 0.05$ level for tile drain water, so these data were excluded from the statistical analysis of fixed effects in Table 3. The covariance analysis showed a significant ($P \leq 0.05$) difference between fields for PP and non-BAPP concentrations in water (Table 3). Drainage pathway was significant ($P \leq 0.05$), with greater PP/TSS and BAPP/TSS concentrations in tile drains than surface runoff, but the field × drainage interaction was not significant for any particulate-associated P, meaning that the drainage pathway (tile drain or surface) was not systematically generating TSS with different PP concentrations in each field.

The similarity in the PP concentrations of water from both transport pathways implies that preferential flow was important in transferring sediments containing P from the top of the soil profile (e.g., 0–20 cm below the soil surface) to tile drains (McDowell and Wilcock, 2004; Uusitalo et al., 2001, 2003). We posit that topsoil is the source of most PP detected in tile drains. This is supported by Foster et al. (2003); using radionuclide tracers (^{137}Cs and ^{210}Pb), they estimated that suspended sediments originating from the top-soil could account for 73% of the TSS exported through drains.

As there was no difference in the PP composition (BAPP and non-BAPP) of the TSS in tile drainage and surface runoff waters within each field, we pooled the PP data for all drainage water samples in each field to describe the association of PP and TSS. There was a positive linear relationship between PP and TSS in water samples (pooled data from tile drains and surface runoff) collected during the sampling period (1 Oct. 2008– 31 May 2009) from each field. Figure 3 shows a typical relationship between PP and TSS, which was observed consistently in all fields. Pearson correlation coefficients describing these relationships were significant ($P \leq 0.05$), with r values greater than 0.78 for PP, 0.62 for BAPP, and 0.66 for non-BAPP (Table 4). The PP

Table 3. The *F* ratios and statistical probabilities associated with the fixed effects on particulate P (PP), bioavailable particulate P (BAPP), and nonbioavailable particulate P (non-BAPP) concentrations in tile drain water and surface runoff water collected from agricultural fields in the Ewing subwatershed, Quebec, Canada. Data were evaluated by ANCOVA using total suspended sediments as the covariable.

Fixed effects	Parameter	PP	BAPP	non-BAPP
Field	*F*	3.85	0.65	11.5
	P > *F*	0.05	NS†	<0.01
Drainage pathway	*F*	4.76	8.07	0.01
	P > *F*	0.03	<0.01	NS
Field × drainage	*F*	0.54	1.27	0.07
	P > *F*	NS	NS	NS

† NS, not significant at the 0.05 probability level.

Table 4. Slope of the regression line describing the relationship between particulate P (PP), bioavailable particulate P (BAPP) and non-bioavailable particulate P (non-BAPP). Water samples were collected from tile drains and surface runoff in eight agricultural fields in the Ewing subwatershed, Quebec, Canada. Data were pooled among drainage pathways and sampling events (up to 19 sampling events between October 1, 2008 and May 31, 2009). Slopes were calculated using a linear orthogonal fit (variance ratio 0.5/0.5) and Pearson correlation coefficients (*r*) describe the strength of the relationship between PP forms and TSS; all *r* values are significant at the 0.05 probability level.

Field	PP		BAPP		non-BAPP	
	g kg^{-1}	*r*	g kg^{-1}	*r**	g kg^{-1}	*r*
1	2.00 (0.20)†	0.78	0.80 (0.10)	0.62	1.19 (0.10)	0.66
2	1.90 (0.05)	0.99	0.71 (0.04)	0.93	1.24 (0.05)	0.95
3	1.25 (0.03)	0.97	0.45 (0.04)	0.94	0.90 (0.05)	0.95
4	1.80 (0.05)	0.98	0.50 (0.03)	0.93	1.40 (0.04)	0.95
5	2.37 (0.02)	0.99	0.60 (0.02)	0.91	1.51 (0.01)	0.99
6	1.89 (0.11)	0.97	0.61 (0.06)	0.80	1.20 (0.06)	0.87
7	1.54 (0.11)	0.90	0.73 (0.06)	0.91	0.80 (0.08)	0.85
8	1.37 (0.05)	0.97	0.51 (0.02)	0.88	0.88 (0.05)	0.86

† Standard error in parentheses.

concentration was from 1.25 to 2.37 g P kg^{-1} TSS, with BAPP accounting for about 33% (±7%, values ranged from 23 to 47%) of the PP, which is similar to the 26 ± 5% BAPP in agricultural stream waters reported by Ellison and Brett (2006).

Fluctuations in the concentration of particulate-associated P within one rainfall event were not investigated, although this could provide insight into the relationship between PP and hydrologic conditions during a single event. In tile drains, the colloidal-P contribution to TSS can be expected to be different during base flow than during peak flow. For example, colloid concentrations and their chemical composition in leaching water can be influenced by the flow rate. Comparing low to high flow rates of water leached from sandy soil columns, Kaplan et al. (1993) observed a decrease in the size and concentration of colloids that tended to have a higher Fe content. Particulate P export from agricultural fields in tile drainage water, however, has been reported to occur predominantly during the short periods of peak flows, which transport PP originating from the topsoil to drains by macropore flow (Vidon and Cuadra, 2011). Further work is needed to measure the fluctuation in PP concentration, in relation to suspended sediments, at varying moments of a rainfall event.

Particle Size Distribution of Total Suspended Sediments as Affected by Drainage Pathways

The TSS in tile drainage and surface runoff waters had similar PSDs, exhibiting a bimodal distribution between 0.05 and
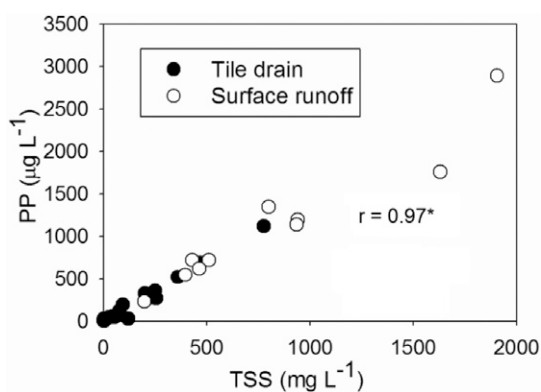

Fig. 3. Typical relationship between particulate P (PP) and total suspended sediment (TSS) in water sampled from tile drains and surface runoff. Data were collected from Field 8 in the Ewing subwatershed (Quebec, Canada). *Significant at the 0.05 probability level.

100 μm in most fields (Fig. 4), except for Field 1 at some sampling events (data not shown). We distinguished two fractions: a submicron fraction (<1 μm) and a micrometric fraction (1–100 μm). Fine sand size material (>100 μm) was found occasionally as a third distinct peak on the PSD curve of surface runoff samples from the sandy fields, but the quantities were negligible (<3% of the total particle volume), probably due to the flat landscape in the subwatershed. The observed PSDs agree with the results of McDowell and Wilcock (2004), who reported PSDs between 0.2 and ~100 μm for TSS in a dairy catchment area. A logarithmic bimodal distribution was also observed in their study but was dominated by 1- to 100-μm size particles.

Our results showed that the submicron-fraction was the dominant particle size class in the tile drains regardless of soil texture. At some sampling events, submicron fraction materials were more abundant in tile drainage than surface runoff water in Fields 3 and 4 (Fig. 4), indicating that colloids and clays tended to be transported through soil macropores while larger micrometric fraction materials were probably filtered out as the water moved through the soil profile. Considering all sampling events, no difference was observed between the PSD of the TSS in surface and subsurface drainage water for all fields. Therefore, our results do not support the hypothesis that the PSD of the TSS was affected by the drainage pathway.

Phosphorus Contribution of Submicron and Micrometric Fraction Particles in Total Suspended Sediments

The concentration of submicron- and micrometric-fraction particles within the TSS plotted against the PP concentrations in water samples (subsurface and surface runoff) gave significant linear relationships ($P \le 0.05$), indicating that the PP concentration increased with an increasing TSS in the water samples (Fig. 5); however, the slopes of the lines describing these relationships were distinct for the two classes of suspended particles. The
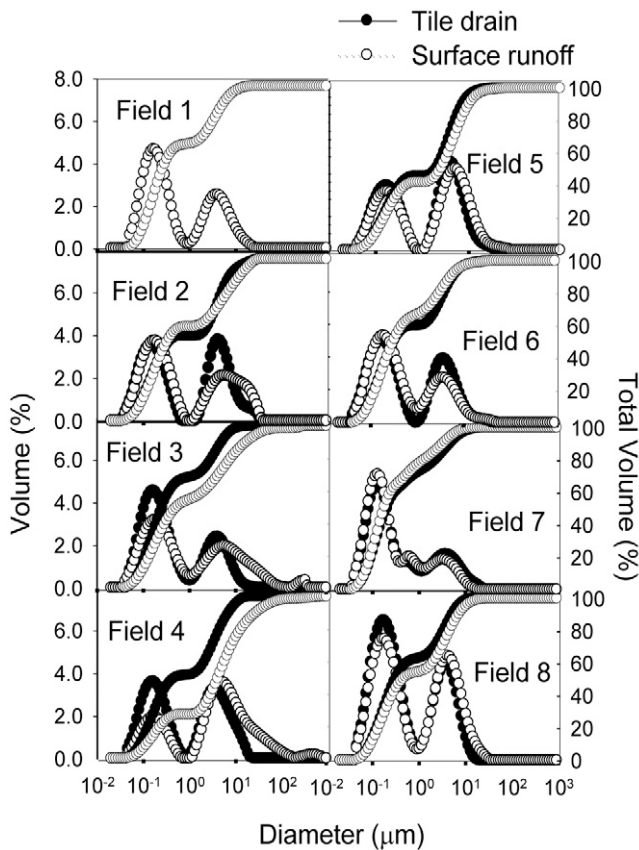
Fig. 4. Particle size distribution by volume and total volume in the tile drain discharge and runoff from each field on 28 Oct. 2008.

Fig. 5. Typical relationship between particulate P (PP) forms and total suspended sediments (TSS) size classes of <1 and 1 to 100 µm particles. Pooled data (subsurface and surface runoff) was from Field 8 in the Ewing subwatershed (Quebec, Canada). **Significant at the 0.01 probability level. ***Significant at the 0.001 probability level.

in submicron-fraction than micrometric-fraction particles (0.66 vs. 0.36 g P kg^{-1}, respectively; Fig. 6c). These observations partially support the hypothesis that there is more PP and BAPP associated with fine-textured particles (i.e., submicron-fraction particles) than coarse-textured particles in the TSS transported from agricultural fields because it was only valid for clay soils. No significant relationship ($P > 0.05$) was calculated between PP content and the percentage in the submicron fraction, suggesting that other sediment properties influenced the PP content of the TSS.

Relationship between Phosphorus Concentration in Total Suspended Sediment Fractions and Soil Physicochemical Properties

Soil P bioavailability is controlled by two processes: adsorption and precipitation. Adsorption reactions involve charged sesquioxides (i.e., Fe and Al oxides) on soil mineral surfaces, whereas precipitation refers to the interaction of phosphates with Ca^{2+} in the soil solution. Therefore, the PP associated with sediments in water emitted from agricultural fields should be related to soil physicochemical properties. Correlation analysis revealed that there was generally no correlation among PP forms in drainage sediments, except for PP and non-BAPP of the 1- to 100-µm class ($r = 0.82$, Table 5). Correlation analysis of PP with selected soil properties was significant ($P < 0.05$) for the Ap horizon (0–20 cm) but not for the B horizon (30–90 cm) or the C horizon (>90 cm); significant correlations with Ap horizon soil physicochemical properties are shown in Table 5. The PP concentration in the 1- to 100-µm class was positively correlated with the M3P concentration and the DSPS and negatively correlated with clay content (Table 5). The BAPP <1-µm concentration was positively related to the M3Fe concentration, while non-BAPP <1 µm was significantly ($P \leq 0.05$) correlated with the M3Ca concentration (Table 5). Multivariate analysis relating PP, BAPP, and non-BAPP with soil physicochemical properties was consistent with simple correlation analysis and permitted us to assess the additive effects among soil physicochemical properties and PP content. In the TSS (1–100 µm), 80% of the variation in the PP concentration was predicted by the M3P concentration. The M3P concentration and clay content were important predictors of the PP concentration in the submicron-fraction material, but the PP concentration in the micrometric-fraction material was

slope of the line in Fig. 5, indicative of the PP/TSS concentration, showed that submicron-fraction particles had greater P concentrations than micrometric-fraction particles ($P \leq 0.05$). These linear relations were specific to each field. The constant relation between the particles size and the PP composition contrasts with the results of Pacini and Gachter (1999), who observed a decrease in the PP concentration with increasing particle size in sediments from an alpine river, which led them to propose that the active surface area was the dominant mechanism controlling PP enrichment and speciation in particle size classes.

In the eight agricultural fields of this study, the PP apportioned to the submicron-fraction and micrometric-fraction particles was similar, although the submicron-fraction material contributed, on average, 0.99 g P kg^{-1} TSS compared with 0.79 g P kg^{-1} TSS for the micrometric-fraction material (Fig. 6a). Water from the fields with clay soils (Fields 6, 7, and 8), however, had 68% PP associated with submicron particles, indicating the dominant ($P < 0.01$) contribution of this size fraction to the PP leaving the agricultural fields (Fig. 6a). In drainage water from the sandy soils (Fields 1–5), the average values were 50% of PP in the submicron-fraction particles and 50% of PP in the micrometric-fraction particles (Fig. 6a). Across eight fields, the BAPP concentration was significantly greater ($P = 0.003$) in the submicron-fraction than micrometric-fraction particles (0.46 vs. 0.22 g P kg^{-1} respectively; Fig. 6b). No enrichment of size classes was observed for non-BAPP when all fields were considered, but the clay soils (Fields 6, 7, and 8) had a significantly ($P < 0.001$) greater non-BAPP contribution
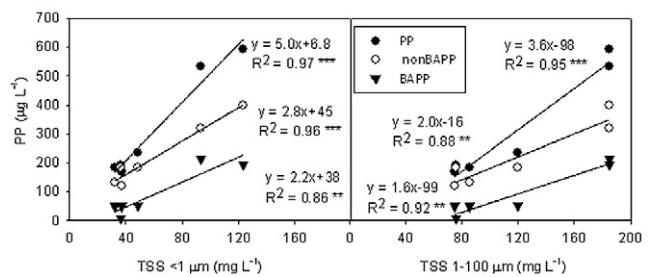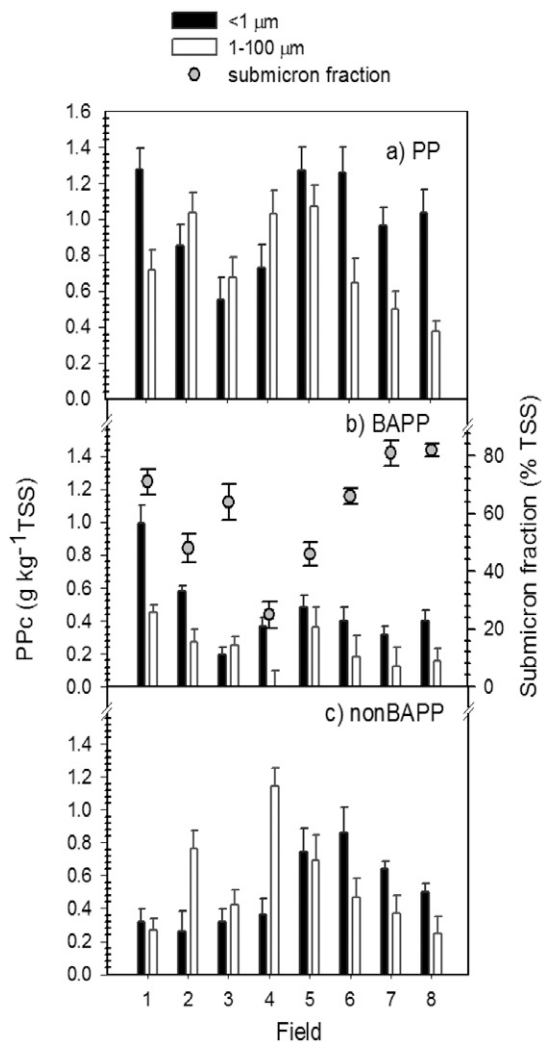
Fig. 6. Mean (a) particulate P (PP), b) bioavailable particulate P (BAPP), and (c) nonbioavailable particulate P (non-BAPP) concentrations in submicron material (<1 μm) and micrometric material (1–100 μm) of total suspended sediments (TSS) from eight agricultural fields (Ewing subwatershed, Quebec Canada). Data points on (b) are the mean submicron contribution to TSS for each field. The bars on each column and data points are the standard errors of the mean.

positively related to DSPS and negatively related to soil pH (Table 6). The BAPP concentration in the TSS and the clay fraction were positively related to the M3Fe concentration, but BAPP in the micrometric-fraction material was mostly explained by the M3P concentration and DSPS. Soil properties related to the non-BAPP concentration included DSPS (in the TSS), M3P and M3Ca concentrations (submicron-fraction particles), and clay, silt, and pH (micrometric-fraction particles) (Table 6). The PP concentrations in the TSS and sediment fractions were positively related to the M3P concentration and DSPS, suggesting greater P concentration in sediments with an increase in soil test P levels, consistent with the P budget and P index approaches to managing P losses from agricultural soils (Lemunyon and Gilbert, 1993).

A P index approach may be suitable for managing the BAPP associated with the micrometric fraction in sediments lost from agricultural soils; however, the BAPP in the TSS and submicron-fraction particles was associated strongly with M3Fe. This may suggest that BAPP in submicron-fraction materials consists of

phosphates that are adsorbed specifically to amorphous Fe sesquioxides. Sesquioxide sorption appears to be a major controller of P bioavailability in sediment. Following mechanical soil separation, Scalenghe et al. (2007) measured a greater Fe oxide concentration in the submicron-fraction material, accompanied by a greater P adsorption capacity and greater resin-extractable P concentration than in larger materials. In contrast, non-BAPP in the submicron-fraction materials was associated with M3Ca, which could mean that part of the non-BAPP is precipitated with Ca^{2+} ions. These results need to be interpreted with caution, however, due to the relatively small data set used for the analysis. We cannot overlook the influence of soil texture and pH on the concentration of particulate-associated P in the TSS because these were retained as explanatory variables in three of the nine predictive equations (Table 6).

The correlation between M3Ca and the non-BAPP pool in submicron-fraction particles could indicate that Ca precipitation has the potential to reduce the amount of bioavailable P in tile drainage and surface runoff water, effectively limiting eutrophication in water bodies that receive sediments from agricultural fields. In Quebec soils, Ca–P precipitation was reported to be an important P sink in arable calcareous soils and even acid soils that received Ca inputs from long-term manure and lime applications (Simard et al., 1995). The Ca–P precipitates were associated with size fractions 5 to 50 and >50 μm in most podzolic and gleysolic Canadian soils, except for one podzol soil (pH = 5.6) where Fe–P complexes dominated (Halstead, 1967). Using x-ray absorption near edge structure spectroscopy, Beauchemin et al. (2003a) reported that hydroxyapatite was the dominant form of Ca–P in slightly alkaline to acidic soils but this form tends be solubilized as soil conditions become more acidic (Laverdière and Karam, 1984). Octocalcium phosphate and brushite were also detected but less important. Calcium can also play a role in the formation of colloidal P. Turner et al. (2004) reported that colloidal P (0.003–1 μm) was correlated with the Ca concentration due to the formation of inorganic colloidal Ca–P complexes. In an alpine watershed with bicarbonated-calcic waters, Poulenard et al. (2008) reported that well-crystallized Ca-bound P accounted for an important part of the suspended sediment with >5% P content, although the majority of PP was associated with sediments dominated by amorphous Al- and Fe-rich materials. Further investigation into P precipitation reactions in suspended sediments from agricultural fields is needed.

Practical Implications

In the flat landscape of the Ewing subwatershed in the Missisquoi Bay region, tile drains are an important pathway transporting BAPP from agricultural soils to surface waters. Because BAPP represents about 30% of the PP associated with the TSS entering drainage waters and eventually being transported downstream, abatement strategies are needed to reduce P loading through tile drains. These measures would complement surface runoff controls. Catchment beds could trap part of the TSS exiting tile drains and thereby reduce the PP load entering surface waters. These catchment beds should consider soil tex-

Table 5. Pearson correlation coefficients between particulate P (PP), bioavailable particulate P (BAPP), nonbioavailable particulate P (non-BAPP), Mehlich-3 extractable P, Ca, Fe, and Al concentrations (M3P, M3Ca, M3Fe, and M3Al, respectively), Mehlich-3 degree of soil P saturation (DSPS), soil pH, and soil clay and silt contents (Ap horizon, 0–20 cm), and the submicron fraction (<1 μm) and the micrometric fraction (1–100 μm) of the total suspended sediments.

	PP <1 μm	BAPP <1 μm	non-BAPP <1 μm	PP 1–100 μm	BAPP 1–100 μm	non-BAPP 1–100 μm	M3P	DSPS	M3Ca	M3Fe	M3Al	Clay	Silt
BAPP <1 μm	0.59												
non-BAPP <1 μm	0.61	−0.26											
PP 1–100 μm	−0.07	0.19	−0.20										
BAPP 1–100 μm	0.49	0.68	−0.09	0.15									
non-BAPP 1–100 μm	−0.35	−0.19	−0.17	0.82*	−0.43								
M3P	0.46	0.66	−0.02	0.72*	0.51	0.38							
DSPS	0.29	0.27	0.13	0.73*	0.07	0.65	0.85**						
M3Ca	0.35	−0.36	0.76*	−0.63	−0.47	−0.33	−0.44	−0.25					
M3Fe	0.52	0.81*	−0.12	0.32	0.55	−0.03	0.58	0.18	−0.22				
M3Al	−0.55	−0.02	−0.60	0.04	0.35	−0.18	−0.20	−0.49	−0.60	−0.01			
Clay	0.29	−0.19	0.50	−0.77*	−0.28	−0.57	−0.62	−0.63	0.86**	0.01	−0.29		
Silt	−0.11	−0.28	0.13	−0.33	−0.34	−0.16	−0.62	−0.66	0.44	0.17	0.04	0.74*	
pH	0.51	0.07	0.55	−0.16	−0.23	0.02	0.28	0.53	0.54	−0.19	−0.82*	0.12	−0.45

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.

ture in agricultural fields because texture influences the proportion of fine vs. large particles (i.e., submicron-fraction vs. micrometric-fraction materials) in drainage and runoff waters. Clay soils emit a greater proportion of BAPP in submicron-fraction particles than sandy soils, thus the catchment bed would have to be larger in regions with clay soils than in those with sandy soils to effectively reduce the PP concentration associated with TSS. We also noted that the fine particles (i.e., submicron material) are enriched in BAPP and that this BAPP is correlated with soil M3Fe, thus driven by sorption–desorption kinetics linked to oxic–anoxic cycles. These conditions would have to be monitored in the catchment bed to avoid generating more BAPP. Adding Ca amendments could be one way to transform BAPP into non-BAPP, although further study is needed to determine the stability of Ca–P complexes associated with various particle size classes (e.g., colloidal Ca–P and Ca–P in submicron-fraction and micrometric-fraction materials).

CONCLUSIONS

The PP, BAPP, and non-BAPP concentrations were strongly and positively related to TSS during the peak flow events monitored at eight agricultural fields. The similarity of PP concentrations in water-eroded sediment measured from both outflow pathways (tile drains and surface runoff) suggests that PP, BAPP, and non-BAPP originate in the topsoil and are either transported through subsurface preferential flow or in runoff water. The particle distribution in water-eroded sediments showed a bimodal distribution, with submicron-fraction (<1-μm) and micrometric-fraction (1–100-μm) particles as the dominant size classes in the experimental fields. The size distribution was similar for both drainage pathways. The submicron material accounted for the majority of PP and BAPP in the TSS of drainage water coming from the clay soils. For the sandy soils, the proportion of PP associated with TSS size classes was variable and not solely dependent on soil texture. Other soil physicochemical properties in the Ap horizon that were predictors of the PP concentration in

the TSS were: pH; soil M3P, M3Ca, and M3Fe concentrations; and the DSPS. The BAPP concentration in the TSS and in the submicron-fraction of the sediments was strongly explained by the M3Fe concentration and linked to adsorption–desorption processes, whereas non-BAPP in the submicron fraction was related to the DSPS and the M3P and M3Ca concentrations. Understanding the size and concentration of particles within the TSS and their associated PP compounds should be considered when designing P abatement strategies for agriculture that promote TSS settling before water is discharged to aquatic systems. Understanding the impact of TSS on downstream water quality will require knowledge of the sorption–desorption and flocculation processes occurring as P-rich sediments and colloids are transported in the stream. The BAPP represented 23 to 47% of the PP concentration in drainage waters from agricultural fields

Table 6. Prediction expressions for the concentrations of particulate P (PPc), bioavailable particulate P (BAPPc), and nonbioavailable particulate P (non-BAPPc) in the total suspended sediments (TSS) and the submicron (<1 μm) and micrometric (1–100 μm) fractions of the TSS in tile drain water and surface runoff water in relation to soil physicochemical properties ($n = 8$). Soil properties were: Mehlich-3 extractable P, Fe, and Ca concentrations (M3P, M3Fe, and M3Ca, respectively), the degree of soil P saturation [DSPS, P/(Al + Fe)], pH, and soil clay and silt contents (Ap horizon, 0–20 cm). Explanatory variables were included if significant at $P \leq 0.05$.

Equation	R^2	P
TSS		
$PP = 0.93 + 1.1 \times 10^{-2}\ M3P$	0.80	0.0029
$BAPP = 0.14 + 1.9 \times 10^{-3}\ M3Fe$	0.80	0.0026
$non\text{-}BAPP = 0.75 + 4.9\ DSPS$	0.73	0.0072
Submicron particles		
$PPc = 9.1 \times 10^{-3}\ M3P + 2.8 \times 10^{-2}\ clay - 0.36$	0.74	0.035
$BAPPc = 3.96 \times 10^{-3}\ M3Fe - 9.55 \times 10^{-3}\ silt - 0.24$	0.84	0.010
$Non\text{-}BAPPc = 2.80 \times 10^{-3}\ M3P + 2.74 \times 10^{-4}\ M3Ca + 0.17$	0.71	0.046
Micrometric particles		
$PPc = 2.05 + 6.7\ DSPS - 0.28\ pH$	0.96	0.0005
$BAPPc = 7.0 \times 10^{-3} + 7.4 \times 10^{-3}\ M3P - 4.2\ DSPS$	0.97	0.0139
$Non\text{-}BAPPc = -2.4 - 7.12 \times 10^{-2}\ clay + 5.5 \times 10^{-2}\ silt + 0.50\ pH$	0.87	0.0191

and merits further investigation due to its potential bioavailability to aquatic organisms.

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