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Particulate phosphorus bioavailability as a function of stream flow and land cover

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ABSTRACT

Using total phosphorus concentrations to estimate eutrophication risk is problematic for management purposes, as only some forms of phosphorus are biologically available for phytoplankton growth. This study estimated the bioavailability of particulate phosphorus, in forested, urban, agricultural (i.e. dairy farm) and mixed land cover streams. Sixteen stream sites were sampled during base and storm flow conditions and the following parameters were determined: total suspended solids, total phosphorus, total dissolved phosphorus, particulate phosphorus, percent bioavailable particulate phosphorus (%BAPP), total bioavailable phosphorus and sediment particle size distribution. Algal assays with *Pseudokirchneriella subcapitata* were used to measure %BAPP. Percent BAPP averaged 17%, 26% and 24% for streams draining catchments with forested, mixed use and agricultural land cover, respectively, and %BAPP did not vary significantly between base and storm flow conditions in these stream types. In contrast, %BAPP averaged 73% in the urban streams during baseflows but declined to an average of only 19% during storms. Particle size distributions did not correlate with %BAPP in these samples. During storm events, particulate phosphorus concentrations increased in all streams by an average of 614% and total phosphorus increased by 200%, whereas total BAP (i.e. total dissolved phosphorus+%BAPP × particulate phosphorus) only increased by 72% because on average only 20% of the particulate phosphorus transported during these events was biologically available.

1. Introduction

Eutrophication management in lakes and streams generally focuses on controlling phosphorus (P) inputs to surface waters (Welch, 1992; Carpenter et al., 1998). Increased nutrient concentrations are associated with nuisance cyanobacteria blooms and excessive periphyton accumulation, which can cause taste and odor problems that contribute to the degradation of drinking water supplies and inhibit recreational uses of surface waters (Welch, 1992). Nuisance phytoplankton also compromise the ecological integrity of lakes and streams by interfering with food web dynamics and reducing suitable fish habitat due to bloom-caused anoxia. In addition, some assemblages of cyanobacteria produce toxins that are harmful to humans and animals (Welch, 1992; Carmichael, 1994; Downing et al., 2001).

Stream water P can be separated into particulate and total dissolved phosphorus, PP and TDP, respectively. TDP can be further separated into inorganic (soluble reactive phosphorus or SRP) and organic (dissolved organic phosphorus or DOP) components. Both SRP, and to a somewhat lesser extent DOP, are readily usable by bacteria and phytoplankton (Hatch et al., 1999). However, the bioavailability of DOP may be reduced if it is associated with humic acids (Reynolds and Davies, 2001). Phosphorus attached to particles (i.e. PP) is not immediately available for growth and a variety of physical, chemical and

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biological processes influence the bioavailability of this P fraction. Certain components of PP are readily usable by organisms while others are more or less completely unavailable. Phosphorus that can be utilized by plants and bacteria is called bioavailable phosphorus (BAP). BAP includes nearly all TDP and the fraction of PP that is readily usable; therefore, none of the commonly measured P fractions are accurate measures of total BAP.

The use of TP to estimate eutrophication risk is problematic for management purposes as it overestimates the amount of P that is biologically available to phytoplankton and bacteria. Previous studies have shown that BAP rather than TP provides the most accurate assessment of water quality conditions in lakes and streams (Butkus et al., 1988; Gerdes and Kunst, 1998). Even though none of the P fractions consistently correlate to BAP (Bradford and Peters, 1987; Ekholm and Krogerus, 2003), chemical extraction methods have been used to estimate phosphorus bioavailability (Boström et al., 1982; Sharpley et al., 1992), and SRP is generally considered to be an acceptable measure of the minimum BAP (Reynolds and Davies, 2001).

Dissolved P concentrations are relatively easy to predict compared to TP or especially PP. TDP and SRP concentrations increase due to urbanization or agricultural land cover/land use, vary seasonally and are relatively stable during storm events (Pacini and Gächter, 1999; Brett et al., 2005a, b; Brattebo and Brett, 2006). However, in agricultural catchments, over-application of P-containing fertilizers can greatly increase the mobility of SRP (Heckrath et al., 1995). In general, PP is much more variable than dissolved P (Brattebo and Brett, 2006). Storm events are extremely important for PP dynamics because large portions of annual stream PP loads can be transported attached to sediment and organic matter during only a few major events (Long and Cooke, 1978; Meyer and Likens, 1979; Brett et al., 2005a). Since PP dynamics are coupled to short-term flow fluctuations and sediment transport, and vary depending on catchment land cover, PP transport is considerably more difficult to predict than dissolved P transport (Brett et al., 2005a; Brattebo and Brett, 2006).

The bioavailability of PP is affected by chemical processes like adsorption–desorption, precipitation–dissolution and reduction–oxidation reactions, which regulate the amount of dissolved inorganic P that is released into the water body and/or sorbed to particles. The release of inorganic P from particles is strongly dependent on the concentration gradient between surface-adsorbed P and the inorganic P in the surrounding water (Cowen and Lee, 1976) and may be quite low in SRP-rich environments such as many lake sediments. The bioavailability of PP may be relatively high if P is bound to clays, easily degradable organic matter or if it is only weakly sorbed to particles (Pacini and Gächter, 1999; Reynolds and Davies, 2001). Phosphorus is potentially available when bound to redox-sensitive iron and manganese or pH-sensitive aluminum oxides but is almost completely unavailable when co-precipitated with calcium carbonate or bound with more resistant forms of organic matter like humic acids (Reynolds and Davies, 2001). Pacini and Gächter (1999) observed the relative P concentration of size-fractionated suspended sediments decreased with increasing particle size. However, Brattebo and Brett (2006) did not find a relationship between median particle size and the PP to suspended sediment ratio. Dorich et al. (1984) also found that particle size did not affect the PP content of suspended sediments or PP bioavailability because large aggregates were primarily composed of small P-rich particles like clay and silt.

In standing water bodies, particle settling velocity, which is primarily a function of particle size, has a strong influence on PP bioavailability. In addition, small particles may combine to form larger aggregates that settle more quickly than predicted based on size alone. Hatch et al. (1999) suggested that microbial colonization may also increase the sedimentation rate of suspended particles. Furthermore, microbial mineralization of lake sediments releases BAP back into the water column, but Cowen and Lee (1976) observed that biological influences are less important than chemical processes in regulating BAP concentrations in lakes.

Total BAP is the combined bioavailability of the different P forms, of which TDP has usually been found to be highly bioavailable (Cowen and Lee, 1976; Sharpley et al., 1992; Auer et al., 1998; Reynolds and Davies, 2001; Ekholm and Krogerus, 2003). However, the percentage of PP that is bioavailable (%BAPP) is highly variable. Previous studies found %BAPP values were frequently less than 20% for forested streams (Ellis and Stanford, 1988; Ekholm and Krogerus, 2003). Several studies have measured %BAPP in stream catchments with multiple land use types and found values ranging from 5% to 48% (DePinto et al., 1981; Young et al., 1985; Auer et al., 1998). Cowen and Lee (1976) found %BAPP ranged from 8% to 55% in urban streams. Agricultural streams have %BAPP ranges from less than 5% to 69%, depending on the type of agriculture considered (Dorich et al., 1984; Sharpley et al., 1992; Ekholm and Krogerus, 2003). Gerdes and Kunst (1998) measured %BAPP for a number of P sources including rainwater, which ranged from 19% to 33%, to groundwater, which ranged from 41% to 77%.

The wide variability in PP bioavailability suggests that both flow characteristics and land cover/land use impacts may be important. Streams are characterized by higher TDP/PP ratios during baseflow conditions when the sediment transport capacity is low and fine bed sediments are the primary source of PP (Pacini and Gächter, 1999). Since PP is transported to streams attached to suspended sediment, the quantity and type of sediment in stormwater runoff will influence the concentration of BAP by varying the relative amounts of TDP and PP entering the stream. The amount of total suspended solids (TSS) in runoff is affected by land cover characteristics, and especially erosion, stream channel down-cutting, stream flows and soil saturation (Pacini and Gächter, 1999). Disturbed catchments like those in urban and agricultural areas are likely to exhibit greater stream bank erosion (May et al., 1997).

Stream flow and land cover are also expected to directly influence the bioavailability of PP. During baseflow, suspended sediments are characterized by small particles with a high organic P content as well as leaf litter and periphyton (Pacini and Gächter, 1999). Since urban catchments are characterized by increased impervious surface area, runoff rates are higher for a given rainfall rate than in non-urbanized catchments (Booth, 1991). Therefore, stormwater runoff may entrain larger-sized sand particles which tend to have lower P contents (Sharpley et al., 1992). In addition, forested catchments generally have wider and more continuous riparian buffer strips (Booth, 1991; May et al., 1997), which trap both suspended sediments and nutrients, and prevent some sediment particles from reaching the stream (Peterjohn and Correll, 1984; Osborne and Kovacic, 1993). Urban and agricultural catchments often lack riparian vegetation along stream banks (May et al., 1997).

The literature on PP bioavailability presents highly variable results. Moreover, many studies do not explicitly compare land cover types or measure %BAPP during baseflow conditions. The objective of this study was to compare %BAPP in Puget Sound lowland streams draining catchments with different land cover/land uses during base and storm flow conditions. The following hypotheses were tested: (1) the percentage of PP that is bioavailable varies between catchments dominated by forested, urban, mixed and agricultural land cover streams, (2) this percentage is higher during baseflow than storm conditions, and similarly (3) the particle size distribution of suspended sediments is correlated with PP bioavailability.

2. Methods

2.1. *Study sites*

Streams were chosen based on their land cover/land use characteristics and most of the streams sampled were located within the Lake Washington/Sammamish basin. Two agricultural and one forested stream were located in the Green/Duwamish River basin, and one agricultural stream was in the Snohomish River basin. None of the study streams received major point source nutrient inputs. The majority of streams were chosen from sites concurrently monitored for water quality and flow by the USGS, or King and Snohomish Counties, to ensure baseline water quality and discharge data were available. Sample sites were classified as forested, urban, mixed or agricultural streams according to the types of land cover and land uses within their catchments (Table 1) as determined from a 1998 Landsat satellite image (Brett et al., 2005b) and a Washington State Department of Ecology (WA DOE) dairy farm location database. Forested sites were characterized by at least 50% forest cover and included Issaquah, Tibbets, May and Covington Creeks. Urban sites had 75% or greater urban land cover and included Thornton, Juanita, McAleer, Lyon and Forbes Creeks. Mixed streams were defined as sites where at least 25% forest and 40% urban land covers were present and included Swamp, North, Little Bear and Big Bear Creeks. In this study, only catchments with dairy farms were considered as agricultural sites because row crop agriculture is not prevalent in the immediate Seattle area. The agricultural streams sampled had animal unit (AU) densities averaged over their entire catchments of at least 40 AU/km^2, where one animal unit corresponds to one adult cow (WA DOE, 2003). The agricultural sites sampled were Mill, Newaukum and French Creeks.

2.2. *Sample collection and processing*

Grab samples were collected in acid washed, polyethylene bottles during baseflow conditions and storm events between October 2003 and May 2004. Sampling sites were located

Table 1 – Percent land cover and animal unit (AU) density for each of the 16 study streams

Stream	Land type classification	Forest (%)	Urban total (%)	Urban forest (%)	Urban grassy (%)	Urban paved (%)	Other (%)	AU density (#AU/km^2)
Covington	Forest	**75**	19	12	4	3	6	0
Issaquah	Forest	**73**	22	15	5	2	5	0
Tibbets	Forest	**73**	22	9	8	5	5	0
May	Forest	**56**	36	19	15	2	8	0
Big Bear	Mixed	**46**	**46**	33	11	2	8	0
Little Bear	Mixed	**39**	**51**	31	13	7	9	0
North	Mixed	**27**	**62**	30	24	7	11	0
Swamp	Mixed	**28**	**62**	28	24	10	10	0
Forbes	Urban	18	**75**	40	26	9	7	0
Lyon	Urban	19	**76**	46	27	3	5	0
McAleer	Urban	14	**76**	37	28	11	10	0
Juanita	Urban	13	**82**	41	33	8	6	0
Thornton	Urban	6	**87**	38	37	12	7	0
Mill	Agricultural	16	65	22	37	7	19	**179**
Newaukum	Agricultural	38	30	13	15	2	33	**73**
French	Agricultural	33	9				58	**43**

Urban total is the sum of urban forest, urban grassy and urban paved. Other includes grass, shrub, crop, bare soil and water. Since French Creek was classified according to vegetation type, urban and other categories are approximate. Land cover data supplied by Brett et al. (2005b) and Beyerlein and Brascher (1998). AU densities were averaged over entire catchment areas and were determined from a dairy farm dataset specifying location and number of animal units per farm compiled by the Washington State Department of Ecology (WA DOE, 2003).

immediately upstream of each stream's confluence with major lakes or rivers. All streams were sampled once during baseflow conditions, and again during storm events. Some stream sites were sampled multiple times until the TSS concentration of the storm sample was clearly elevated above the baseflow sample. The storm samples had to meet one of the following two criteria: TSS was twice that of the baseflow sample or TSS increased by at least 15 mg/L over the baseflow sample. Storm samples were always collected during the rising limb of the hydrograph. Samples were stored on ice until returning to the lab, where 100 mL of each sample was filtered within 24 h through 0.45-μm surfactant-free Nalgene syringe filters for TDP/SRP analyses and another 100 mL sample of raw water was processed for TP analyses. Samples were refrigerated and those not analyzed within 3 days were frozen.

TSS was determined using 1.5-μm, Whatman 934-AH filters according to Standard Methods (APHA, SM 2540 D, 1998), with three replicates for each sample. TP and TDP were determined using acid persulfate digestion and the ascorbic acid colorimetric method, following the procedures outlined in Standard Methods (SM 4500-P) using six standards (0, 25, 50, 100, 200 and 400 μg P/L) and a Shimadzu UV-1601 spectrophotometer. The method detection limit was 2 μg/L for TP and 1 μg/L for TDP. In eight cases, SRP was determined instead of TDP, so in these cases, SRP was multiplied by 1.43 to obtain an estimate of TDP. This correction factor was based on the average SRP/TDP ratio of the eight samples in which both forms were measured ($0.70 \pm 0.12; \pm 1$ SD). PP was calculated as the difference between TP and TDP. Sediment particle size distributions up to 250 μm in diameter for the raw water samples were measured using a Sequoia Scientific, Inc., LISST Portable laser particle size analyzer. These distributions were represented as the volume of particles per size increment.

2.3. *Algal bioassays*

Fourteen-day algal bioassays with P-starved *Pseudokirchneriella subcapitata* (formerly *Selenastrum capricornutum*) were used to determine %BAPP. The cultures were maintained in nutrient medium as described by Miller et al. (1978). To starve the algae, cultures were centrifuged, rinsed in P-free nutrient medium, and then resuspended in P-free medium for 9–12 days. For the P-free medium, KCl was used in place of K_2HPO_4. Stream water samples were also centrifuged to concentrate suspended sediments for use in the assays (Ellis and Stanford, 1988). Only wet sediments were used because it has been shown that drying sediments can decrease BAP by up to 65% due to changes in the composition of the P fractions (Twinch, 1987). The concentrated sediments were rinsed and resuspended in P-free medium. Standards with known KH_2PO_4 concentrations were incubated for each set of observations. Seven standards (0, 10, 20, 35, 50, 75 and 100 μg P/L) were run and four replicates for each sample and two replicates for each standard were used. These bioassays were carried out in 125 mL Erlenmeyer flasks filled to a sample volume of 50 mL. All of the flasks were autoclaved with acid-wash (0.1 M HCl) between each experiment to minimize contamination. The prepared flasks were inoculated with algae to an initial concentration of 10^3 cells/mL. The cultures were incubated at $24 \pm 2\,^{\circ}$C under continuous fluorescent lighting of $4300\,\text{lm} \pm 10\%$ as outlined in Standard Methods (SM 8111) and Miller et al. (1978). In addition, the flasks were agitated constantly at a speed of 60 rpm and hand swirled every few days if algal cell sedimentation was apparent.

After the 14-day incubation period, algal cell density was measured by counting the number of cells in a known sample volume using a Coulter Multisizer II particle size analyzer. A 100-μm aperture was used in the Coulter counter; the cell size for *Pseudokirchneriella* is approximately 6–7 μm. Each sample was read three times and averaged. Prior to these readings, the machine was blanked using parallel sediment suspensions from the samples which had not been inoculated with algae. The BAP concentration for each treatment flask was determined by fitting a linear curve to the 0–50 μg/L standards and back-calculating the BAPP concentration using the observed cell counts. Percent BAPP was calculated by dividing the BAPP concentration by the PP concentration in the sample. The bioassay results represent maximum potential bioavailability for the model phytoplankter *Pseudokirchneriella*, given that near optimal temperature, light and nutrients (except P) for this algae were utilized in the laboratory experiments.

2.4. *Statistical analyses*

Each of the measured parameters were analyzed using a two-factor ANOVA for land cover type and flow state using a critical α-level of 0.05 using log transformed data (except for %BAPP and the particle diameter percentiles). The data were log transformed whenever this transformation caused their distribution to more closely approximate a normal distribution, and were left untransformed when they were initially quasi-normally distributed. We also compared TSS versus TP and PP concentrations using regressions of log–log transformed data. Finally, we compared the %BAPP data against the particle size distribution data using untransformed data.

3. Results

Based on the criterion that storm TSS concentrations must be higher than baseflow TSS concentrations, suitable storm samples were not obtained for Big Bear (mixed land cover) and French (agricultural) Creeks. Although the majority of stream sites easily met the criteria for TSS, Big Bear and French Creeks were both sampled multiple times but the sediment pulse commonly associated with storms probably passed through the system before samples could be collected. Therefore, the mixed land category includes four baseflow samples and three storm samples. The agricultural category contains three baseflow samples and two storm samples. The forest and urban land categories are complete with four and five samples, respectively, for both baseflow and storm conditions. Geometric mean or arithmetic mean values for TSS, TP, TDP, PP, %BAPP and total BAP are presented in Table 2. Particle size distributions were not determined for four baseflow samples: Thornton, McAleer, Lyon (all urban) and Swamp (mixed land cover) Creeks. Average values for the

Table 2 – Average TSS, TP, TDP, PP and %BAPP grouped by stream land cover type and flow state

Land cover type	Flow state	TSS (mg/L)	TP (μg/L)	TDP (μg/L)	PP (μg/L)	%BAPP	Total BAP (μg/L)
Forested	Baseflow	4	30	18	10	20	20
Forested	Storm	83	155	30	114	13	44
Forested[a]	Storm	31	78	25	52	12	31
Mixed	Baseflow	12	55	35	19	29	40
Mixed	Storm	37	100	34	65	22	49
Urban	Baseflow	16	69	50	16	73	61
Urban	Storm	110	255	57	187	19	92
Agricultural	Baseflow	24	133	66	31	22	73
Agricultural	Storm	53	313	111	145	26	149

Geometric means were calculated for TSS, TP, TDP and PP while arithmetic means are given for %BAPP.

[a] Without Tibbets Creek storm sample.

Table 3 – Average 10th, 25th, 50th, 75th and 90th particle size percentiles grouped by stream land cover type and flow state

Land cover type	Flow state	Particle size diameter percentiles (μm)				
		10th	25th	50th	75th	90th
Forested	Baseflow	12±8	26±14	54±21	108±43	155±36
Forested	Storm	16±7	34±15	63±19	106±19	160±4
Mixed	Baseflow	13±3	24±5	48±2	74±3	114±14
Mixed	Storm	8±2	18±7	45±11	93±16	171±5
Urban	Baseflow	11±2	24±6	50±3	84±6	136±34
Urban	Storm	18±10	36±13	70±11	122±15	168±23
Agricultural	Baseflow	13±3	25±3	52±6	92±27	132±43
Agricultural	Storm	13±11	33±27	67±33	126±32	180±1

These values represent the volume of particles per size increment, e.g. the 90th percentile means 10% of the total sediment volume was found in particles with larger diameters. The values reported are the mean±1 SD.

10th, 25th, 50th, 75th and 90th particle diameter percentiles are given in Table 3.

3.1. *Statistical results*

In general, flow state (base or storm flow) had the greatest impact on TSS, TP and PP concentrations and explained 42%, 36% and 51% of the variation in their concentrations, respectively (Table 4). Catchment land cover type also significantly influenced TP concentrations and explained 21% of the variation for this constituent, but the TSS and PP concentrations observed in the samples collected for this study were not statistically associated with our land cover categories. Conversely, TDP concentrations were significantly related to catchment land cover (which explained 44% of the variation) but not to flow state. Percent BAPP was significantly associated with both land cover type and flow state as well as the interaction between these factors (Table 4). However, %BAPP during baseflow in the urban streams (which averaged 73%) was the only specific case that was significantly different from the others (which ranged between 13% and 29%). Total BAP was primarily associated with land cover (38% of variance explained) and to a lesser but still significant extent with flow state (11% of variance explained). The 75th and 90th particle size percentiles were significantly associated with the flow state and explained 17% and 33%, respectively, of the variation in these data (Table 5). However, the 10th, 25th and 50th particle size percentiles were not significantly related to flow state. None of the particle size percentiles assessed were significantly related to land cover type.

The storm sample collected from Tibbets Creek, a forested stream, had extremely high TSS, TP and PP concentrations, which only affected the ANOVA results for TSS and the 50th particle diameter percentile. If the Tibbets Creek storm sample was not included in these analyses, land cover type was significant for TSS concentrations and explained 25% of the variation. Flow state was also significant for the 50th size percentile, explaining 16% of the variation. The ANOVA results for TP, PP, TDP, %BAPP and all of the other particle size percentiles are unaffected by the exclusion of the Tibbets Creek storm sample.

Although log TSS was strongly correlated with both log TP ($r^2 = 0.80$) and log PP ($r^2 = 0.79$; Fig. 1), none of the particle size percentiles were strongly correlated with log TSS, log PP or %BAPP. TSS was weakly correlated with the 90th ($r^2 = 0.11$) size percentile. PP was also weakly correlated with the 75th percentile ($r^2 = 0.11$) and more strongly correlated with the 90th ($r^2 = 0.26$) percentile. The P content of the suspended

Table 4 – Two-factor ANOVA for log TSS, log TP, log TDP, log PP, %BAPP and log total BAP using all of the stream samples ($n = 30$)

Source	df	MS	F-test	P-value	% variance
Total suspended solids					
Land cover type	3	0.23	1.38	0.2757	8
Flow state	1	3.77	22.86	0.0001	42
Interaction	3	0.30	1.82	0.1739	10
Error	22	0.17			40
Total phosphorus					
Land cover type	3	0.32	4.12	0.0185	21
Flow state	1	1.61	20.94	0.0001	36
Interaction	3	0.08	0.98	0.4207	5
Error	22	0.08			38
Total dissolved phosphorus					
Land cover type	3	0.38	6.53	0.0025	44
Flow state	1	0.10	1.69	0.2077	4
Interaction	3	0.02	0.40	0.7560	3
Error	22	0.06			50
Particulate phosphorus					
Land cover type	3	0.13	0.74	0.5413	4
Flow state	1	4.81	27.27	0.0001	51
Interaction	3	0.14	0.77	0.5246	4
Error	22	0.18			41
% Bioavailable particulate phosphorus					
Land cover type	3	0.14	7.97	0.0009	30
Flow state	1	0.18	10.11	0.0043	13
Interaction	3	0.14	7.96	0.0009	30
Error	22	0.02			28
Total bioavailable phosphorus					
Land cover type	3	0.39	5.88	0.0042	38
Flow state	1	0.34	5.03	0.0353	11
Interaction	3	0.03	0.47	0.7044	3
Error	22	0.07			48

The percent variation explained by a given factor was calculated by dividing the sum of squares for that factor by the total sum of squares.

sediments (PP/TSS) was only weakly correlated with the 90th ($r^2 = 0.15$) size percentile. All of the other size percentiles had coefficients of determination less than 0.1 for TSS, PP and PP/TSS. None of the particle size percentiles were significantly correlated with %BAPP.

3.2. *Forested streams*

In the forested streams, TSS concentrations averaged 4.3 mg/L during baseflow and increased by a factor of 19 to an average of 83 mg/L during storms (Fig. 2). In addition, all three P fractions were higher in the storm than the baseflow samples (Figs. 3–5). The smallest increase was observed for the TDP concentrations, which increased 60% from an average of 18 during baseflow to an average of 30 μg/L during storms. In contrast, the average TP concentration showed a five-fold increase from 30 to 155 μg/L and PP concentrations had a more than ten-fold increase from 10 to 114 μg/L. Algal assays revealed that a mean of 20±5% and 13±3% of PP is bioavailable during baseflow and storm flow, respectively (Fig. 6). Without the Tibbets Creek storm sample, the average TSS concentrations only increased by a factor of 7 to 31 mg/L. TP nearly tripled to 78 μg/L and PP increased by a factor of 5 to an average of 52 μg/L. However, neither average TDP nor %BAPP changed significantly when the Tibbets Creek sample was excluded.

3.3. *Mixed land cover streams*

TSS concentrations in the mixed land cover streams were three times higher on average in the storm samples (37 compared to 12 mg/L for baseflow samples) (Fig. 2). Both TP and PP concentrations were higher in the storm samples (Figs. 3 and 5), while average TDP concentrations were nearly identical and approximately 35 μg/L (Fig. 4). The average storm TP concentration of 100 μg/L was nearly double the baseflow concentration of 55 μg/L. The difference between the storm and baseflow samples was even greater for PP. The average storm PP concentration was 65 μg/L which was three times higher than the baseflow concentration of 19 μg/L. The %BAPP means for the mixed streams were 29±6% during baseflow and 22±6% during storms (Fig. 6).

Table 5 – Two-factor ANOVA for the 10th, 25th, 50th, 75th and 90th particle size percentiles using all of the available stream samples ($n = 26$)

Source	df	MS	F-test	P-value	% variance
10th percentile particle diameter					
Land cover type	3	20	0.41	0.7490	5.7
Flow state	1	11	0.23	0.6407	1.1
Interaction	3	30	0.62	0.6100	8.8
Error	18	49			84.4
25th percentile particle diameter					
Land cover type	3	119	0.74	0.5398	9.6
Flow state	1	184	1.15	0.2968	5.0
Interaction	3	94	0.59	0.6286	7.7
Error	18	160			77.7
50th percentile particle diameter					
Land cover type	3	231	0.95	0.4371	11.3
Flow state	1	633	2.60	0.1241	10.3
Interaction	3	139	0.57	0.6408	6.8
Error	18	243			71.5
75th percentile particle diameter					
Land cover type	3	820	1.40	0.2746	14.0
Flow state	1	2919	5.00	0.0383	16.6
Interaction	3	561	0.96	0.4333	9.6
Error	18	584			59.8
90th percentile particle diameter					
Land cover type	3	284	0.45	0.7233	3.8
Flow state	1	7404	11.63	0.0031	33.0
Interaction	3	907	1.43	0.2683	12.1
Error	18	636			51.1

The percent variation explained by a given factor was calculated by dividing the sum of squares for that factor by the total sum of squares.

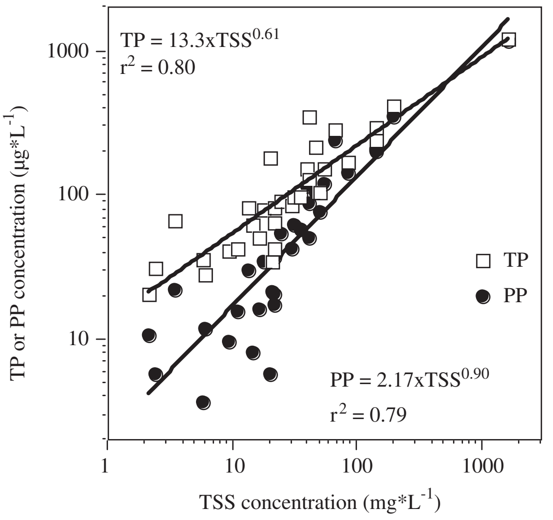

Fig. 1 – Power function fits for log–log plots of TSS and TP (open squares) and TSS and PP (closed circles) for all of the stream sites ($n = 30$).

3.4. *Urban streams*

Large differences between the baseflow and storm samples for the urban streams were present for all of the measured variables except TDP, which was 50 µg/L during baseflow and on average only increased 13% to 57 µg/L during storms (Fig. 4). TSS concentrations increased by a factor of 7 from 16 mg/L during baseflow to 110 mg/L during storms (Fig. 2). Both TP and PP increased considerably during storms over baseflow conditions: by a factor of 4 from 69 to 255 µg/L for TP (Fig. 3) and by a factor of 12 from 16 to 187 µg/L for PP (Fig. 5). The mean %BAPP was 73±13% during baseflow and only 19±3% during storms (Fig. 6).

3.5. *Agricultural streams*

The average TSS concentrations in the agricultural streams doubled from 24 mg/L during baseflow to 53 mg/L during storms (Fig. 2). TP more than doubled from an average of 133 in the baseflow samples to 313 µg/L in the storm samples (Fig. 3), while the average storm PP concentration of 145 µg/L was nearly five times the average baseflow concentration of 31 µg/L (Fig. 5). TDP was also higher during storms, increasing 68% from an average of 66 to 111 µg/L (Fig. 4). The %BAPP averages for the agricultural streams were 22±5% for the baseflow samples and 26±5% for the storm samples (Fig. 6). If the French Creek baseflow sample is excluded because the corresponding storm sample is missing, the baseflow %BAPP mean is 28±6%, which is essentially identical to that for the storm samples.

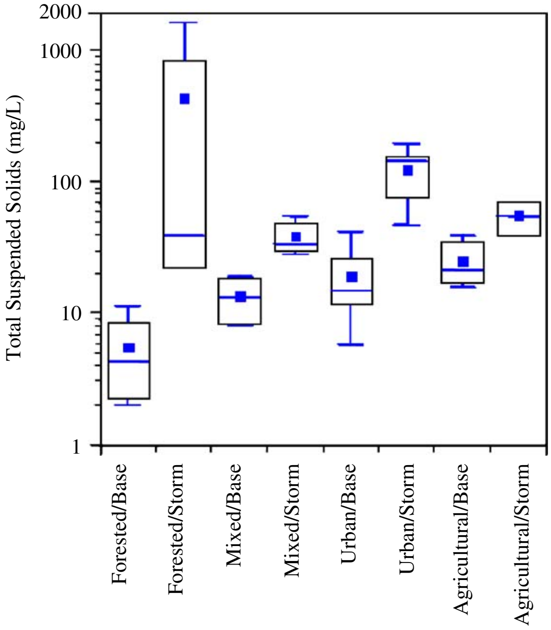

Fig. 2 – Box and whisker plot for total suspended solids grouped by catchment land cover type and flow state for all of the stream sites ($n = 30$). In all the box and whisker plots, the whiskers represent the 10th and 90th percentiles, the outer edges of the boxes represent the 25th and 75th percentiles, and the horizontal lines within the boxes represent the median and the small black boxes represent the sample mean.

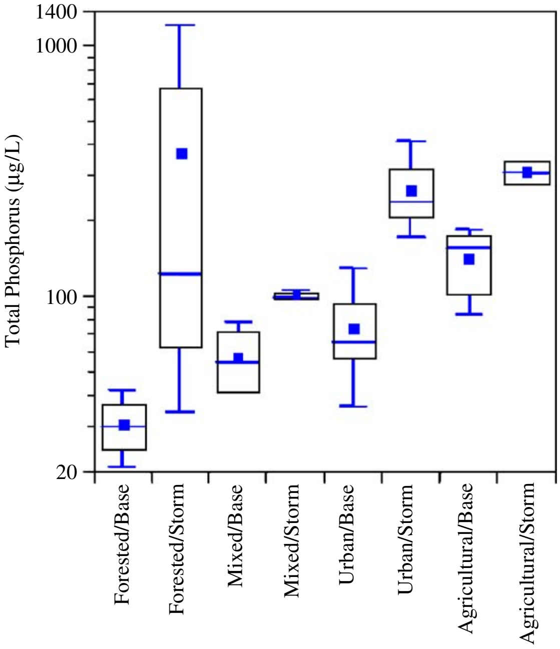

Fig. 3 – Box and whisker plot for total phosphorus grouped by catchment land cover type and flow state for all of the stream sites ($n = 30$).

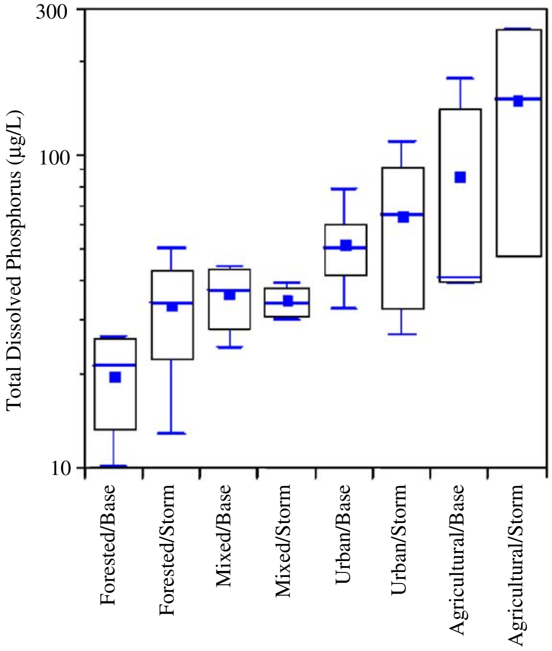

Fig. 4 – Box and whisker plot for total dissolved phosphorus grouped by catchment land cover type and flow state for all of the stream sites ($n = 30$).

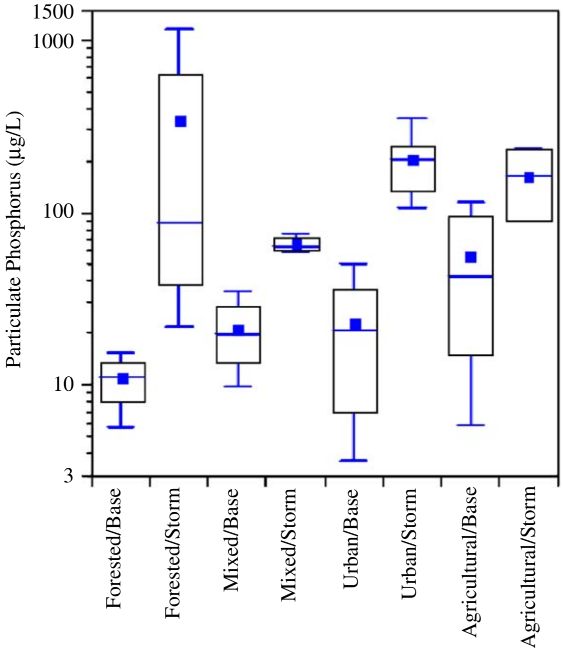

Fig. 5 – Box and whisker plot for particulate phosphorus grouped by catchment land cover type and flow state for all of the stream sites ($n = 30$).

3.6. *QA/QC results*

TSS was measured in triplicate, TP and TDP were run in duplicate and %BAPP was determined using four replicates per sample. The average standard deviation for all of the TSS

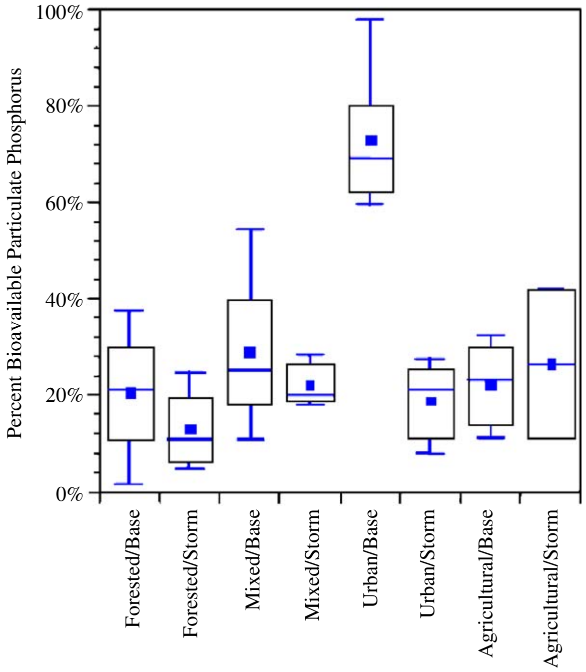

Fig. 6 – Box and whisker plot for percent bioavailable particulate phosphorus grouped by catchment land cover type and flow state for all of the stream sites (*n* = 30).

replicates was 8.8 mg/L with an average coefficient of variation of 27%. All of the samples had TP and TDP concentrations above the method detection limits of 2 and 1 μg/L, respectively. The sample TDP concentrations were all within the 0–400 μg/L range for the standards. Only two of the sample TP concentrations were higher: one urban storm sample was 4% higher than the 400 μg/L standard, and the Tibbets Creek storm sample was 204% higher but the results have been analyzed both with and without this sample included with the other forested streams . The TP and TDP concentrations had average standard deviations of 7 and 1 μg/L and average coefficients of variation of 5% and 3%, respectively. The average standard deviation for %BAPP was 6% with an average coefficient of variation of 26%.

4. Discussion

The first hypothesis that %BAPP varies between the different land cover/land use categories was supported during baseflow when %BAPP was substantially higher in the urban streams, but was not supported during storms when %BAPP ranged between 13% and 29% for all of the land cover/land use categories assessed. The second hypothesis that %BAPP is higher during baseflow was only supported for the urban streams. The third hypothesis that particle size correlates with %BAPP was not supported by the results of this study.

4.1. *Total suspended solids*

TSS concentrations were most influenced by flow state and TSS was higher during storms than baseflow conditions in all of the study sites. This result was in part a direct consequence of the study design which was intended to ensure that representative storm samples were collected (i.e. rising flows equate with increased TSS concentrations; Pacini and Gächter, 1999). If the Tibbets Creek storm sample was excluded from the analyses, TSS was also significantly related to land cover type with higher concentrations in the more urbanized streams. Urbanized catchments are characterized by large impervious surface areas and urbanized stream channels are often incised (Booth, 1991). During storms, high surface runoff rates resulting from decreased water storage capacity in the catchment sustain increased suspended sediment transport to the stream channel. During baseflow, low flows continually erode incised stream banks which suspend new sediments within the water column. In contrast, forested catchments retain an absorbent "duff-layer" of leaf litter that inhibits surface runoff from reaching the stream (May et al., 1997).

TSS concentrations were also higher in the agricultural streams than in the forested and mixed land cover streams. Similar to urban streams, agricultural streams suffer from channel instability and erosion due to tillage, a lack of riparian vegetation and because agricultural catchments have also been stripped of the forest duff-layer that provides water storage. Although TSS concentrations were highest in the agricultural streams during baseflow, TSS was with one exception highest in the urban streams during storms. These results imply that channel erosion due to a high percentage of impervious surface area in the urban catchments strongly affected storm water TSS concentrations.

4.2. *Phosphorus speciation*

TDP was the dominant P fraction during baseflow and PP was the dominant P fraction during storms. Therefore, fluctuations in TP over time were driven by baseflow TDP concentrations and storm flow PP concentrations. This result has been well documented (Meyer and Likens, 1979; Pacini and Gächter, 1999; Brattebo and Brett, 2006) and was expected given that PP is associated with TSS transport as shown by the high correlation between the two parameters. In contrast, TDP concentrations were similar between the two flow conditions, except in agricultural streams, and were not significantly related to flow state which has also been previously observed (Meyer and Likens, 1979; Brattebo and Brett, 2006).

TDP relates to land cover type and both TP and TDP concentrations increased with increasing urbanization. Important anthropogenic sources of P in urbanized catchments include pet wastes, fertilizers and septic system effluents. During both flow states, TP and TDP concentrations were highest in the agricultural streams. Presumably this is due to the leaching of dissolved P from the catchment's soil which may have a build-up of manure from dairy operations. Particulate P concentrations increased markedly during storms and were not significantly correlated with land cover type. Similar to TSS, PP was highest in the agricultural streams during baseflow and highest in the urban streams during storms. Regardless of the flow condition, PP concentrations were higher in the agricultural streams than the forested or mixed land cover streams. Again, since PP is transported attached to suspended sediment, PP dynamics matched TSS dynamics. Since TP is a combination of TDP and PP concentrations, TP was significantly influenced by both flow state and land cover type.

4.3. *Percent bioavailable particulate phosphorus*

Percent BAPP was substantially elevated in the urban streams during baseflow (mean = 73%) compared to these same streams during storm events (mean = 19%) (Fig. 6). Percent BAPP did not change with increasing urbanization (i.e. forest→mixed use→urban) during storms even though marked increases in TSS and P concentrations were evident. In the forest, mixed use and agricultural catchment streams %BAPP was generally low (range of means = 13–29%) during both baseflow and storm events. Although a study on agricultural streams by Sharpley et al. (1992) concluded that both surface runoff and erosion contributed to higher BAPP concentrations, storm runoff did not seem to play an important role in influencing %BAPP for streams in this study.

It is important to note that although PP bioavailability in urban streams was nearly four times higher during baseflow, much larger amounts of BAPP were transported during storms in these streams due to the combination of higher PP concentrations and much higher stream flows during these events. For example, this study and that of Brattebo and Brett (2006) found that PP concentrations in urban streams may increase by a factor of 12 during storms and (Booth, 1999) showed that urban streams typically have much higher peak flows and somewhat lower baseflows than forest streams in the same climatic region. The agricultural stream category showed the most variable results and was the most incomplete in this study. The relatively high storm %BAPP average, however, suggests that storms may have the most significant impact on agricultural stream water quality given that both TDP and PP concentrations showed considerable increases during storms.

4.4. *Total bioavailable phosphorus*

Total BAP concentrations were estimated as the TDP concentration plus the concentration of PP that is bioavailable, as determined from the algal assays. Storm event total BAP concentrations were larger than baseflow concentrations for all land cover types. Total BAP concentrations also increased with increasing urbanization (i.e. from the forested to the urban catchments) and were highest in the agricultural streams (Fig. 7). These trends mimicked those for TP, but BAP concentrations were 28±14% lower than TP concentrations during baseflow and 62±10% lower during storm events when averaged over all of the land cover categories. These results highlight that TP is not a reliable estimate of BAP. This is particularly true during storm events, which is especially important because in many streams a large proportion of TP transport occurs during only a few storms.

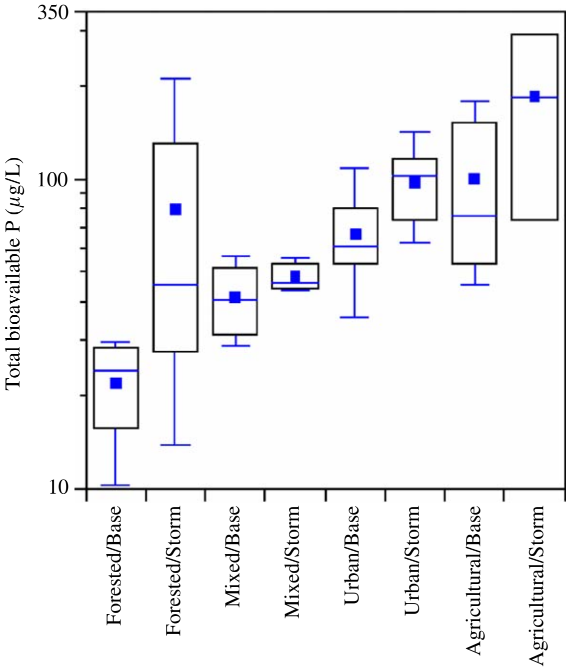

Fig. 7 – Box and whisker plot for total bioavailable phosphorus concentration grouped by catchment land cover type and flow state for all of the stream sites (*n* = 30).

4.5. *Particle size distributions*

Although differences in particle size distributions were significant between flow states, no significant difference was found between particle size distributions for the four land cover categories. Although particle size was expected to have an important influence on PP bioavailability, no significant correlations were found between %BAPP and any of the particle size percentiles. In addition, only weak correlations were observed between TSS, PP or the P content of suspended sediments and the particle size percentiles. This is in contrast to the results of Pacini and Gächter (1999) who when looking at size-fractionated sediments found a strong relationship between the median sediment particle size and the P content of those sediments. However, the size-fractionated sediments Pacini and Gächter examined included a much wider range of particle sizes (2–200 μm median diameter) compared to this study and Brattebo and Brett (2006) where median sediment particle diameters only varied two to three fold within streams. Therefore, the results of this study do not support the hypothesis that median particle size correlates with the P content of suspended sediments or the proportion of PP that is bioavailable. This is probably because we did not size fractionate the sediments considered in our study and thus only examined a narrow range of median sediment sizes.

5. Conclusions

TSS, TP and PP were all higher during storms, while TDP varied little during storms, except in the agricultural streams where TDP increased substantially over baseflow concentrations. TSS, TP and TDP were all higher in the more disturbed urban and agricultural streams and lowest in the forested streams. Percent BAPP was greatly elevated in the urban streams during baseflow, but otherwise similar in the other stream types during both flow states. The particle size distributions accounted for very little of the variation in %BAPP. Total P over-estimated total BAP by 28±12% during baseflow and by 62±10% during storm events.

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