Article

Spatial distribution and temporal variability in the forms of phosphorus in the Beaver River subwatershed of Lake Simcoe, Ontario, Canada

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Abstract

Agricultural runoff is an important source of phosphorus (P) to surface waters. This paper investigated the relationship between agricultural land use and the forms of P (i.e., total phosphorus [TP], total dissolved phosphorus [TDP], and soluble reactive phosphorus [SRP]) in streams draining 8 headwater subcatchments in the Beaver River subwatershed, a major inflow to Lake Simcoe, which is a large hard-water lake in south-central Canada. The time period of analysis had a strong influence on the results. There was no relationship between percent total agriculture and average TP when concentrations were averaged over the entire 12-month (Jun 2010–May 2011) monitoring period, whereas there were significant positive correlations between agricultural land use and average TP during the summer season (Jun–Aug). Significant correlations between average stream TDP and SRP and percent pastureland were observed, although relationships were again dependent on the time period of analysis. Concentrations of TP, TDP, and SRP were highly variable over time, with maximum concentrations occurring during the winter months. This was illustrated by a single rain-on-snow event (11 mm) on 5 March 2011, when samples taken 3–4 h apart varied by as much as 100%. These results indicate that winter storm-targeted sampling is likely necessary to capture the full range of annual variability in P forms and concentrations.

Key words: headwater streams, Lake Simcoe, land use, phosphorus, rain events, runoff, soluble reactive phosphorus

Introduction

Runoff from agricultural land is an important nonpoint source of nutrients to surface waters (Carpenter et al. 1998, Boesch et al. 2001, Hart et al. 2002). While subsurface pathways are important routes of phosphorus (P) loss in some agricultural systems (e.g., soils with tile drainage, or those dominated by macropore drainage; Vidon and Cuadra 2011), surface runoff is the primary route of P loss in most watersheds (Hart et al. 2002). This means that surface properties (e.g., slope, vegetation cover, soil erodibility), surface disturbance (e.g., livestock grazing, tillage), P applications to the surface (e.g., in manure or chemical fertilizers), and storm events (e.g., mobilization of surface-deposited P and particulates) may all influence P losses from agricultural land (Carpenter et al. 1998, Reynolds and Davies 2001, Hart et al. 2002, Beaulieu 2004, Macrae et al. 2007a).

Although most nutrient–trophic status relationships are based on total phosphorus (TP), considering the various forms of P can be useful when evaluating both sources and potential impacts. TP may be divided into particulate P (>0.45 µm) and total dissolved P (TDP; ≤0.45 µm), although the filter pore size is arbitrary (Holtan et al. 1988, Livingstone 2002). TDP can be further divided into organic and inorganic fractions (Holtan et al. 1988).

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Within the dissolved form of P, orthophosphate is the form that autotrophs and algae utilize preferentially (Holtan et al. 1988, Reynolds and Davies 2001). Soluble reactive phosphorus (SRP), which is an operationally defined parameter, is sometimes used as an estimate of orthophosphate, although the method undoubtedly includes other chemical species that are easily hydrolyzed under the reaction conditions. Nevertheless, SRP may be a reasonable estimate of the biologically available forms of P (BAP; Holtan et al. 1988), particularly when concentrations are high. High SRP concentrations have been linked to agricultural activities (Hart et al. 1999, Macrae et al. 2007b) because orthophosphate is a major component of most commercial fertilizers and livestock manure.

Agricultural land, including both cultivated crop and pasture areas, represents approximately half of the Lake Simcoe watershed (Palmer et al. 2011). Lake Simcoe has experienced symptoms of eutrophication since the 1970s, including excessive algal growth and low hypolimnetic oxygen levels; as a consequence, substantial management effort has been directed toward reducing P inputs to the lake (Winter et al. 2007, LSRCA 2013). Although the TP load to the lake in the past decade (average of 72 tonnes yr^{-1} between 2002 and 2007) was substantially lower than the load measured in the 1980s and 1990s (~100 tonnes yr^{-1}) as a result of concerted efforts to reduce inputs, current P inputs to the lake are still higher than the estimated natural presettlement load of 32 tonnes yr^{-1}. Currently, the largest source of P to the lake is via tributary export, which contributed approximately 44 tonnes yr^{-1} during 2004–2007 (LSRCA 2009, Palmer et al. 2011). Agricultural runoff, particularly from livestock operations, has been identified as an important source of P to the lake (Winter et al. 2002).

Previous studies in the Lake Simcoe watershed attempted to evaluate the effect of land use on TP loads using measurements made at the outlet of major tributaries (Winter et al. 2002, 2007, Wilson 2009, Palmer et al. 2011, Whitehead et al. 2011); however, the drainage areas of these monitored tributaries are large (up to 380 km^2) and include multiple land uses, making it difficult to ascertain the effect of any specific land use on the TP flux. No studies on individual small headwater streams (i.e., ≤10 km^2) have occurred within these major subcatchments where the number of different land uses is greatly reduced, and few data are available on the forms of P other than TP, and particularly on the spatial and temporal variability of the forms of P, within subcatchments.

The objectives of this study were to (1) examine the spatial relationships between the forms of phosphorus (TP, TDP, and SRP) and land use in 8 headwater subcatchments that vary in land cover (6 predominantly agricultural, 2 predominantly wetland–woodland), and (2) examine temporal variability (among seasons and during a single storm) in the concentrations of TP, TDP, and SRP over the course of a hydrologic year.

Study site

The Beaver River (44°25’55”N; 79°9’54”W at the mouth) drains one of the largest subwatersheds (327 km^2) in the Lake Simcoe watershed (LSRCA 2010; Fig. 1) and is the second largest tributary source of TP to the lake. Land use in the Beaver River subwatersheds is predominantly agricultural (63%), consisting of both cropland (28%; includes row crops, market gardening, orchards, sod farms) and pastureland (35%). Natural landscapes including wetlands and deciduous and coniferous forest cover approximately 31% of the catchment, while only 4% is classified as urban (Winter et al. 2007). Bedrock geology is primarily limestone and shale, covered by thick deposits of gravel, sand, silt, and clay resulting from glacial deposition (Johnson 1997, LSRCA 2010). The Oak Ridges Moraine aquifer system supplies water to the upper portion of the Beaver River subwatershed (BRSW).

Climate in the BRSW is classified as Dfb, or midlatitude humid with severe winters, no dry season, and hot summers, according to the Köppen-Geiger climate classification system (Kottek et al. 2006). The average annual (1990–2011) precipitation in the BRSW (estimated at an Environment Canada station, Udora, ON) is 886 ± 34 mm (based on the 1 Jun–31 May hydrologic year) and the average annual air temperature is 6.8 ± 0.2 °C. During the winter months (Dec–Feb) the monthly average air temperature ranges from −15.2 °C (minimum) to −0.1 °C (maximum), while the monthly average summer (Jun–Aug) air temperature ranges from 15.4 to 22.1 °C. Total precipitation (834 mm) and average temperature (5.4 °C) during the year of intensive study (2010–2011) were similar to the long-term averages.

Methods

Field design

Eight, small (≤10 km^2) headwater (1st to 3rd order) streams were selected in the BRSW (BVR 04, 09, 11, 13, 14, 26, 27, and 28) for intensive study to encompass a wide range in land use from 97% agriculture (BVR11) to <5% agriculture (BVR26). The type of agriculture was further classified into “pastureland” (livestock grazing) and “cropland” (primarily row crops). Two of the 8 sites (BVR26 and BVR27) were dominated by “natural heritage” land cover, including wetland plus woodland (Table 1). In addition, one sampling station was established on the main channel of the Beaver River (BVR03), approximately 50 m above the outlet to the lake, and in close proximity to the Lake Simcoe Region

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Conservation Authority's long-term monitoring station (Fig. 1). The channel outlet site was sampled to allow comparison of water quality with the headwater streams. While there were no Water Pollution Control Plants (WPCPs) above any of the headwater stream sampling stations, 2 WPCPs were located on the main channel of the Beaver River, approximately 12 and 25 km upstream of the BVR03 station.

Watershed boundaries and the stream network dataset were supplied by the Ontario Ministry of Natural Resources, and the classification of land use in the BRSW was based on the ecological land classification provided by the Lake Simcoe Region Conservation Authority as determined by analysis of orthophotography from 2000 to 2004.

Sample collection

Stream water was sampled approximately biweekly over the hydrologic year (Jun 2010–May 2011), although weather conditions in January and February limited sample collection to single occasions during these months. Samples were collected upstream of roadways to avoid contamination from road washoff. Samples for both TP and TDP were first filtered in the field using 80 µm Nitex mesh to remove large particulate debris that would

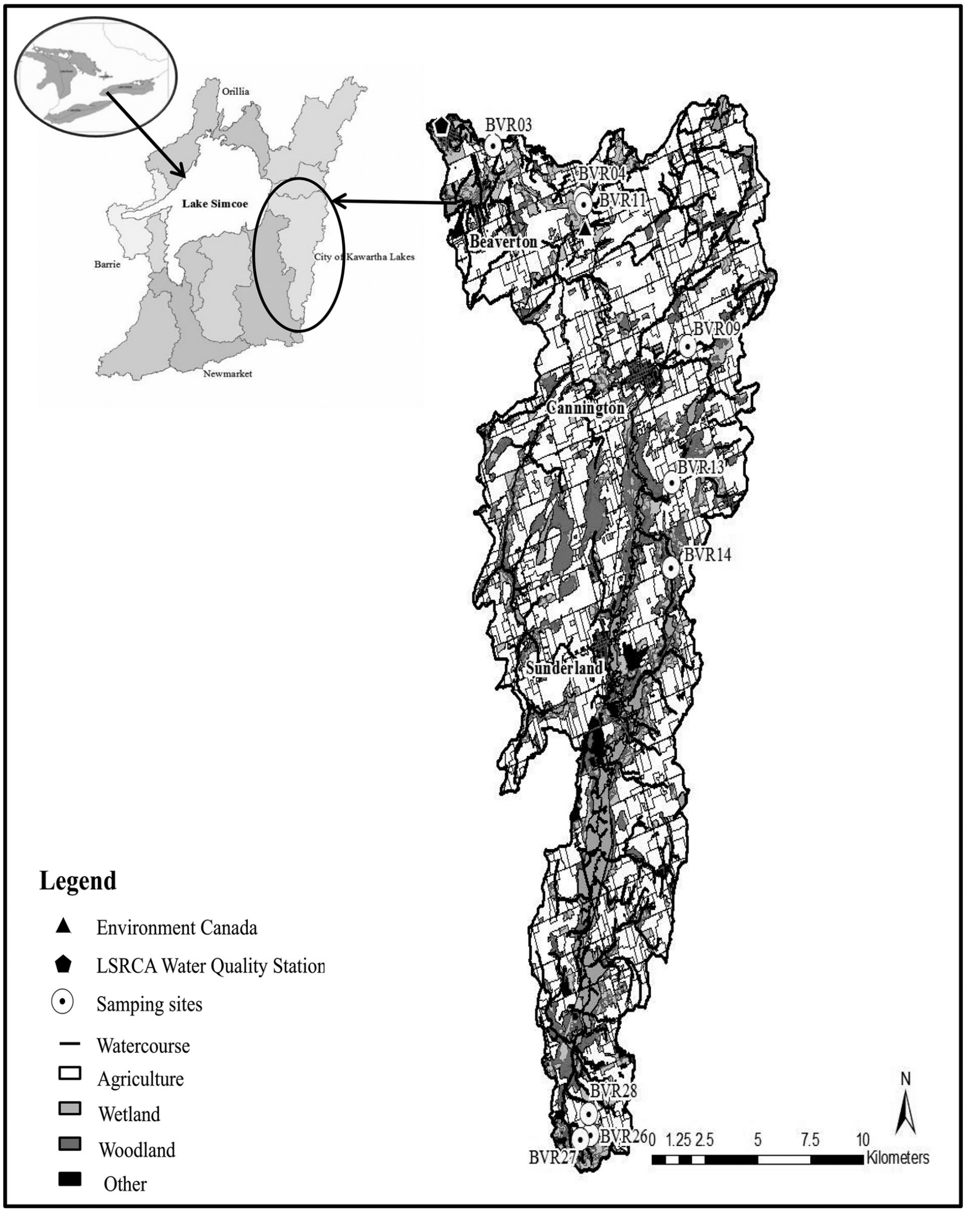

Fig. 1. Beaver River subwatershed within the greater Lake Simcoe watershed. Stream sampling stations are indicated relative to land use within the subwatershed.

Table 1. Summary of land use at each subcatchment in the Beaver River subwatershed.

Land use cover (%)	BVR04	BVR09	BVR11	BVR13	BVR14	BVR28	BVR26	BVR27
Total Agriculture	58	73	97	59	60	50	3.3	5
Cropland	32	14	65	32	38	29	2.9	0.9
Pastureland	25	58	32	27	23	21	0.4	4
Wetland + Woodland	38	24	3	35	35	44	84	90
Wetland	9	19	0.8	17	20	7	12	18
Woodland	29	5	2	18	15	37	73	70
Other[1]	4	3	0.4	6	4	6	13	6
Area (km^2)	3	8	3	10	5	1	0.4	0.6

[1]Other represents aggregate, commercial, golf course, rail, road, rural, and urban development.

potentially bias the results (OMOE 2007). A portion of this water was poured into 35 mL borosilicate glass autoanalyzer tubes for TP analysis, while an additional portion was filtered in the field using a 0.45 µm syringe filter into 35 mL autoanalyzer tubes for TDP analysis. SRP samples were similarly filtered in the field, in sequence, through 200 µm Nitex mesh followed by 0.2 µm nylon membrane syringe filter into 35 mL borosilicate glass tubes.

Chemical analysis

All samples were stored at 4 °C in glass digestion tubes until analysis, which occurred within 2 weeks of sample collection. TP and TDP were analyzed at the Dorset Environmental Science Centre using a Technicon Instruments Autoanalyer II, Single Channel Colorimeter employing ascorbic acid-molybdate colorimetry following autoclave digestion with sulphuric acid (OMOE 2007). SRP was measured manually at Trent University. SRP samples were determined using the standard molybdenum blue colorimetric method using a UV/VIS spectrophotometer with a 10 cm path length cuvette (Lambda 25, Perkin Elmer, Waltham, Massachusetts, USA), which followed the method outlined by Stainton et al. (1977; detection limit = 0.20 µg L^{-1}).

Data analysis

Phosphorus concentration data were averaged seasonally (i.e., summer: Jun, Jul, and Aug) and over the hydrologic year (i.e., 1 Jun 2010 to 31 May 2011), inclusive. Concentrations were not volume-weighted because stream flow data were not available at all sites. Instead, to account for slight changes in sampling frequency among months, concentrations were first averaged for each month, and then individual months were averaged to compute seasonal (i.e., summer, n = 3), or annual (n = 12) means. Because SRP data were not available for May 2011, annual averages for SRP are for the period June 2010 to April 2011.

To examine associations between land use and P fractions including TP, TDP, and SRP, data were first tested for normality using the Shapiro-Wilk normality test. A Pearson correlation analysis was then used to test for the statistical significance of correlations between land use and P forms (significant at $p < 0.05$). SigmaPlot 11.0 (Systat Software Inc., Chicago, Illinois, USA) was used for all statistical analyses.

Results

Associations between land use and water quality

Average TP concentrations across the 8 headwater sites ranged from 17 to 67 µg L^{-1}, and exceeded the Provincial Water Quality Objective of 30 µg L^{-1} at 5 of the 8 sites, including BVR 26, which is dominated by wetland+ woodland (Fig. 2; Table 1). Concentrations of dissolved P, including TDP and SRP also often exceeded 30 µg L^{-1} at BVR09, which has the greatest proportion of pastureland (Fig. 2; Table 1). Concentrations of TP, TDP, and SRP were generally similar to, or higher, at the headwater sites compared with BVR03, at the channel outlet (Fig. 2).

Correlations between land use and P varied depending on both the form of P and the time period considered. For example, there was no association between TP and the proportion of agriculture (total, pastureland, or cropland) when concentrations were averaged for the entire hydrologic year, whereas SRP was positively correlated with percent total agriculture and pastureland, and TDP was positively associated with percent pastureland only (Table 2). In addition, there were significant negative correlations between average TP and the proportion of wetland and SRP and the percentage of wetland+woodland and woodland, respectively (Table 2).

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Table 2. Correlation coefficients between proportion of land use and forms of P across the 8 subcatchments; concentrations averaged over the 12 month hydrologic year. * indicates significance at $p < 0.05$.

Hydrologic year (1 June 2010–31 May 2011)	TP	TDP	SRP
Total Agriculture	0.406	0.686	0.883*
Cropland	0.471	0.628	0.282
Pastureland	0.177	0.904*	0.851*
Wetland + Woodland	–0.418	–0.686	–0.889*
Wetland	–0.888*	–0.076	–0.309
Woodland	–0.204	–0.700	–0.852*

Table 3. Correlation coefficients between proportion of land use and forms of P across the 8 subcatchments; concentrations averaged over the 3 month summer period. * indicates significance at $p < 0.05$.

Summer months (June to August 2010)	TP	TDP	SRP
Total Agriculture	0.732*	0.455	0.271
Cropland	0.916*	0.556	0.361
Pastureland	0.241	0.199	0.069
Wetland + Woodland	–0.734*	–0.470	–0.290
Wetland	–0.804*	0.004	0.202
Woodland	–0.558	-0.494	–0.358

In contrast, when data were averaged over the summer months only, TP was positively correlated with both total agriculture and percent cropland, and negatively correlated with wetland+woodland and wetland, respectively, whereas there were no significant associations between either summer-averaged SRP or TDP and any category of land use (Table 3).

Temporal variability

Unexpectedly, maximum concentrations of TP, TDP, and SRP were measured at most sites during the winter months, in association with rain-on-snow events on 18 February and 5 March 2011 (Fig. 3). Maximum TP concentrations were also observed during these events (up to 202 µg L^{-1}) at the 2 wetland+woodland dominated sites (BVR26 and BVR27). To further evaluate temporal variability in water quality, 4 primarily agricultural (≥50% total agriculture) streams were sampled twice during the 5 March event. Concentrations of TP, TDP, and SRP varied dramatically between the 2 sampling visits, such that samples taken 3–4 h apart differed by as much as 100% (Table 4). The direction of change in TP, however, was not consistent among sites, with TP decreasing between sampling visits at 3 of the 4 sites (BVR09, 11, and 28) and increasing at BVR13 (Table 4).

Discussion

Land use and forms of phosphorus

Ongoing, long-term monitoring efforts in the Lake Simcoe watershed are focussed on sampling the catchment outlets because a central objective has been to quantify tributary inputs to the lake (e.g., Winter et al. 2002, OMOE 2010). Management efforts to limit P inputs to the lake require more detailed spatial information on P release from subcatchments, however, because water quality information from smaller subcatchments may be more readily interpreted with respect to land use. In this study, consistent associations between agricultural land use and P concentrations in streams were not observed.

Although TP, TDP, and SRP concentrations were generally higher at the headwater streams than at the outlet, average TP and SRP at BVR26, a wetland+ woodland dominated stream, also exceeded outlet concentrations as well as TP levels at some of the most agricultural streams (e.g., BVR13 and 14), indicating that relationships between water quality and land use are not straightforward even at the smaller spatial scale.

Instead, correlations between P forms and the proportion of agriculture within subwatersheds were dependent on both the form of P considered and the time period of analysis, such that there was no relationship between land use and TP when values were averaged over the hydrologic year, whereas TP means for the summer months were significantly correlated with land use. The summer is a common time to investigate the effects of land use on water quality because this is when base flow conditions dominate and agricultural activity is greatest (e.g., fertilizer application, tillage, livestock access to streams), which together maximize the potential to observe these effects (e.g., Gelbrecht et al. 2005, Bowes et al. 2007, Castillo et al. 2012). For example, Wilson (2009) found a strong relationship between the concentration of TP (and TDP) and the percentage of cropland (which ranged between 1 and 75%) in watersheds in south-central Ontario during midsummer base flow conditions, although these correlations were based on a single month of sampling.

Similarly, the time period of analysis influenced the relationship between land use and the so-called bioavailable fractions of P; however, the opposite pattern was observed, such that the proportion of pastureland within subcatchments was positively correlated with annual

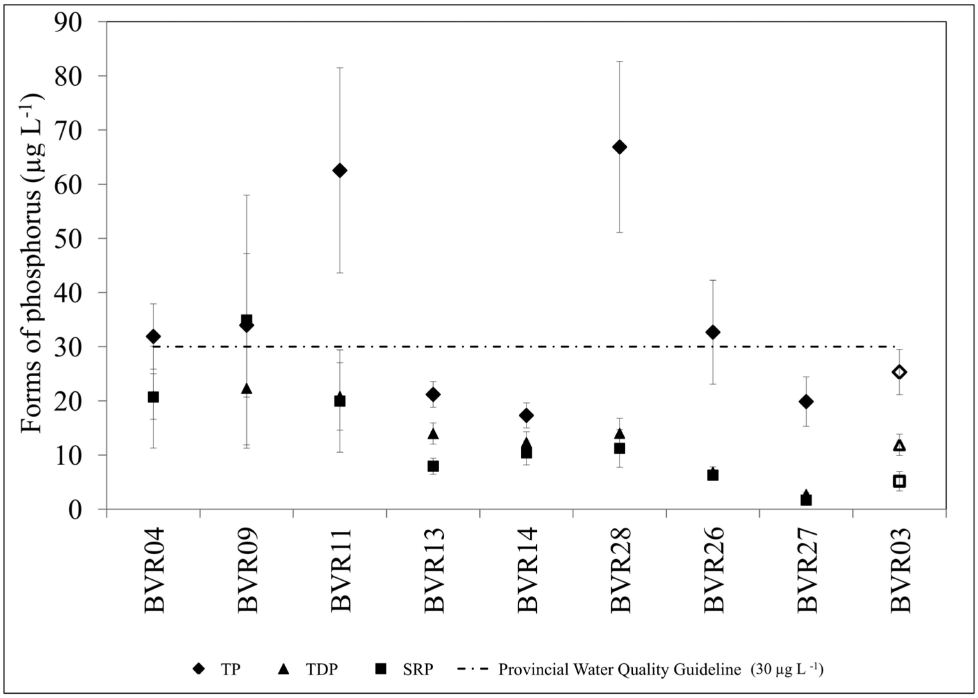

Fig. 2. Mean (± standard deviation) TP, TDP, and SRP concentrations at the 8 headwater sites (closed symbols) and single main channel sampling station (open symbols), located near the outlet to Lake Simcoe. The Provincial Water Quality Objective for TP (30 µg L^{-1}) is indicated by the dotted line.

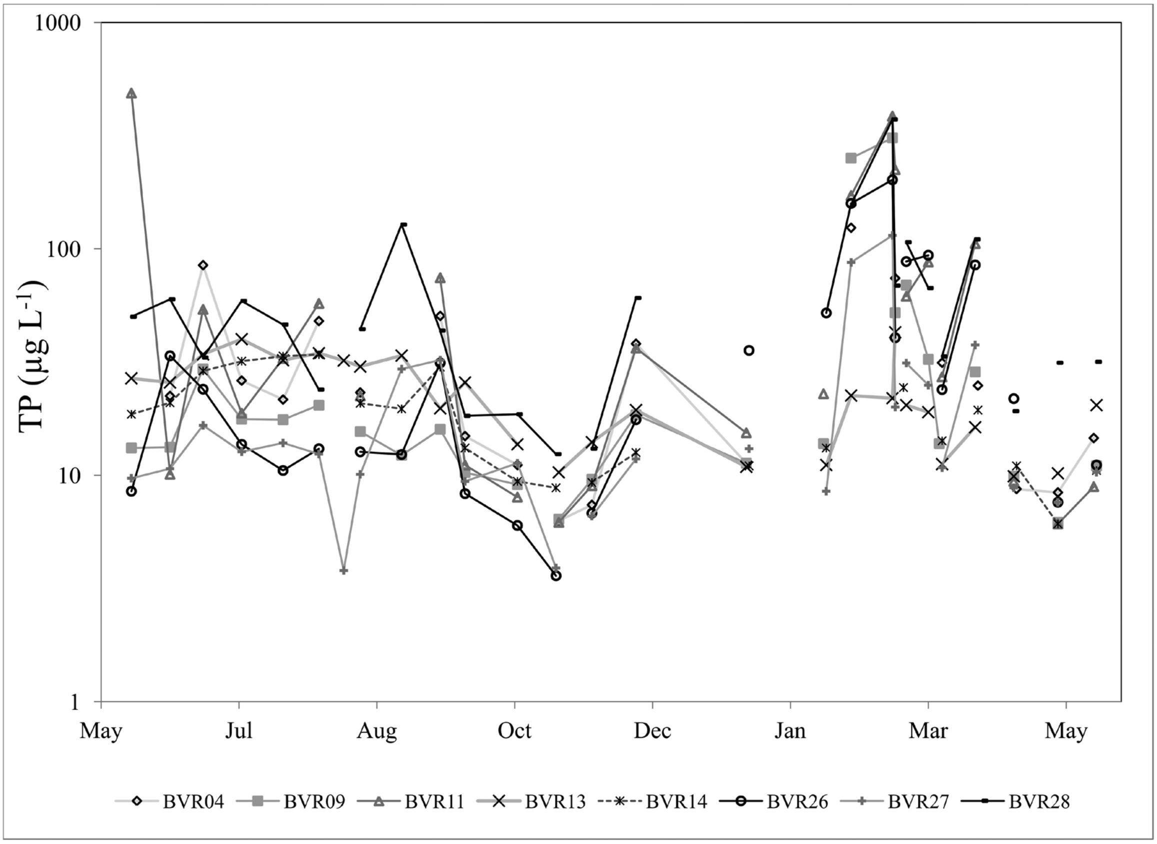

Fig. 3. Total P concentrations measured at the 8 headwater sites through the 2010–2011 hydrologic year. Note the log-scale of the y-axis.

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Table 4. Repeated measurements of P concentrations at 4 streams during a rain-on-snow event on 5 March 2011.

Site	Time	TP (µg L^{-1})	TDP (µg L^{-1})	SRP (µg L^{-1})	Area (km^2)
BVR09	12:19	348	224	253	8.33
	15:45	270	192	197	
BVR11	13:12	422	119	96.8	3.00
	16:15	349	118	122	
BVR13	11:41	16.9	9.70	5.35	10.1
	15:24	26.9	13.5	8.39	
BVR28	10:22	473	60.4	50.2	1.07
	14:44	273	74.7	71.7	

averages of TDP and SRP, whereas there was no correlation during the summer months. These results highlight the temporal variability of stream P and suggest that correlations between land use and stream P must be based on longer-term (i.e., >1 year) sampling efforts that include the full range in variability of stream P.

Temporal variability

High TDP and SRP concentrations measured during 2 rain-on-snow events largely determined the strength and significance of the correlation between SRP and pastureland. Correlations were not significant when February and March values were removed from the annual calculation (data not shown), possibly because P in precipitation was transported relatively conservatively to the streams during these runoff events. TP concentrations in winter rain and snow in this region are very low compared with the growing season (Brown et al. 2011), however, so it is unlikely that snow melt and rain water alone can explain the magnitude of increase in P observed during these events. Similarly, rainwater and snowmelt cannot explain increases in TDP and SRP; although these forms of P are not routinely monitored in deposition, their concentrations would be lower than TP. The authors have observed manure applied to snow in the pasture-dominated catchments, and high TP, TDP, and SRP concentrations during winter rain-on-snow events may be the result of relatively rapid transfer of P associated with manure during a time of the year when there is little potential for biological or abiotic (due to snow cover and limited soil contact) retention. Macrae et al. (2007a, 2007b) similarly observed maximum TP and SRP concentrations during winter melt/rain-on-snow events at Strawberry Creek, south-central Ontario. Moog and Whiting (2002) and Jarvie et al. (2010) also reported high concentrations of TP and SRP during the winter compared with the spring and summer in streams that were influenced by agricultural activities. In each of these cases, high winter TP and SRP levels were attributed to manure application to snow or frozen ground, which was readily mobilized in rain-on-snow runoff. Smaller, but still substantial increases in P observed at the 2 wetland+woodland-dominated sites are difficult to attribute to manure application because pastureland accounts for <5% of total land use in these 2 catchments. Overall, relatively high TP concentrations at these 2 natural heritage sites that are comparable to some of the most agricultural streams (i.e., BVR13 and BVR14) are perplexing and require further investigation.

Conclusions

Consistent associations between land use and P forms in subcatchments of the BRSW were not observed, and instead correlations were dependent on both the form of P and the time period considered. Maximum P concentrations were observed during the winter and in particular during 2 rain-on-snow events. High temporal variability in P concentrations, particularly during winter runoff events, contributed to inconsistencies in relationships between land use and water quality. In addition, these results indicate that tributary export may be greatly underestimated if winter runoff events are not captured in monitoring programs. Although we cannot determine with certainty that manure application to snow is the source of high winter P concentrations, these results suggest that more monitoring and management focus be placed on the winter season.

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