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The effects of dissolved organic carbon, acidity and seasonality on metal geochemistry within a forested catchment on the Precambrian Shield, central Ontario, Canada

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Abstract Metal pollution, in combination with other environmental stressors such as acid deposition and climate change, may disturb metal biogeochemical cycles. To investigate the influence of dissolved organic carbon, acidity and seasonality on metal geochemistry, this study has described concentrations of 19 metals as they pass through an acidified forested catchment on the Precambrian Shield in south-central Ontario, Canada. Metal, dissolved organic carbon (DOC) and sulphate (SO_4^{2-}) concentrations fluctuate throughout the catchment compartments as the water passes through and interacts with vegetation, soils and bedrock. Relationships among metals, DOC and SO_4^{2-} are most pronounced in compartments where DOC and SO_4^{2-} exhibit high variability, namely in the throughfall, organic horizon soil water, and wetland-draining stream. Metal, DOC and SO_4^{2-} concentrations varied seasonally in the streams, and temporal coherence occurred among metal, DOC and SO_4^{2-} concentrations in the organic horizon soil water and the wetland-draining stream (PC1). In the wetland-draining stream, the highest DOC, Cr, Cu, Fe, Pb, and V concentrations occur in the summer, whereas concentrations of SO_4^{2-} and most other metals peak in the fall after a period of drought. Despite the rural location, provincial water quality objectives for surface water were exceeded for many metals when the peak fall values occurred.

Keywords Acidity · Dissolved organic carbon · Forest catchment · Metal · Seasonality · Wetland

Introduction

Metals are naturally present in terrestrial, aquatic, and atmospheric environments. However, anthropogenic activities, such as fossil fuel-based power generation, transportation, metal production including both mining and smelting, and waste incineration have increased metal concentrations and fluxes in developed and remote environments in comparison to background levels (Nriagu 1989). Recent estimates show that anthropogenic metal emissions currently equal or surpass natural or background emissions of

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many metals, including Cd, Cu, Hg, Ni, Pb, V, and Zn, on a global basis (Nriagu and Pacyna 1988; Pacyna and Pacyna 2001). Atmospheric emissions are of particular concern due to their potential dispersal and deposition over large areas. Additionally, other stressors such as acidification and climate change may affect the ecosystem processes that control metal cycling (Magnuson et al. 1997; Schindler 2001). Because many metals at sufficient concentrations are toxic to biota, are not readily lost from ecosystems and are continually being released into the environment, there is a strong impetus to understand the factors and processes affecting metal dynamics in the environment.

Many factors affect metal behaviour, including the chemical properties of the metals and of their surroundings, biological processes, hydrology, and climate. Each metal has unique chemical properties, including solubility and binding affinities, which affect speciation and mobility (Stumm and Morgan 1996). Acidity is a "master variable" due to its control over metal solubility and speciation (Drever 1988). Low pH increases the solubility of many metal cations and reduces the capacity of metals to remain adsorbed to solids due to competition for negatively charged binding sites (Van Dijk 1971). Dissolved organic matter, which is usually measured as dissolved organic carbon (DOC), is comprised of organic molecules of different size and composition. It possesses numerous functional groups with negatively charged sites that form strong bonds and complexes with metal ions (Ephraim 1992; Tipping 1998). High DOC concentrations enhance metal complexation and increase metal solubility (Davis and Leckie 1978). Changing climatic conditions could cause more frequent extreme precipitation events, higher temperatures, periods of drought, reduced snow cover and a range of other events (Schindler 2001). These changes may directly alter metal dynamics, while changes to biological processes such as organic matter mineralization and chemical processes such as sulphate export may indirectly affect metals (Devito 1995).

Relationships between metals and other chemical parameters such as pH and DOC have been assessed in field-based studies of forested catchments, but have generally been limited to a small number of metals. Certain metals tend to show strong positive relationships with DOC concentrations (Cu, Pb), whereas others tend to show strong positive relationships with acidity (Cd, Zn; Adkinson et al. 2008; Bergkvist 1987; Lazerte et al. 1989; Watmough and Dillon 2007). Few studies have investigated metal mobility and behaviour in uplands, wetlands, and streams of a forested catchment. This study presents concentrations of 19 metals, DOC, SO_4^{2-}, and pH in bulk deposition, throughfall, the organic and mineral soil water and streams of a small catchment on the southern edge of the Precambrian Shield in central Ontario, Canada over a 2 year period. Relationships among metal concentrations, DOC and acidity are assessed and seasonal patterns in metal concentrations are used to provide additional context for the metal behaviour. The objectives of this paper are to: (1) determine how metal concentrations change as water passes through and interacts with compartments of an acidified forested catchment, (2) evaluate the relative importance of DOC and acidity in controlling concentrations of each metal in hydrological flows throughout the catchment, and (3) assess whether metal concentrations demonstrate seasonal trends in bulk deposition, soil water, and streams.

Materials and methods

Site description

The Plastic Lake catchment is located in Haliburton County, Ontario (45°11′N, 78°50′W), about 20 km south of Dorset, Ontario, Canada. Hydrological and chemical monitoring has been ongoing for almost three decades at this site. The mean annual temperature for the Dorset area is 4.8°C; mean monthly temperatures range from a high of 18.7°C in July to a low of −11.1°C in January (Environment Canada 2002; 30-year average 1971–2000). The mean annual precipitation is 1,100 mm, of which approximately 75% falls as rain. Plastic Lake subcatchment 1 (PC1) covers 23.3 ha, ~25% of the terrestrial area in the catchment (Fig. 1). The long-term monitoring occurs in this subcatchment. Approximately 80% of the area in PC1 drains through the *Sphagnum*-conifer swamp wetland before discharging to the 32.1 ha headwater lake. The main stream draining PC1 frequently dries up in the summer, but flows year round in wetter years (Eimers et al. 2007). Stream water pH is very

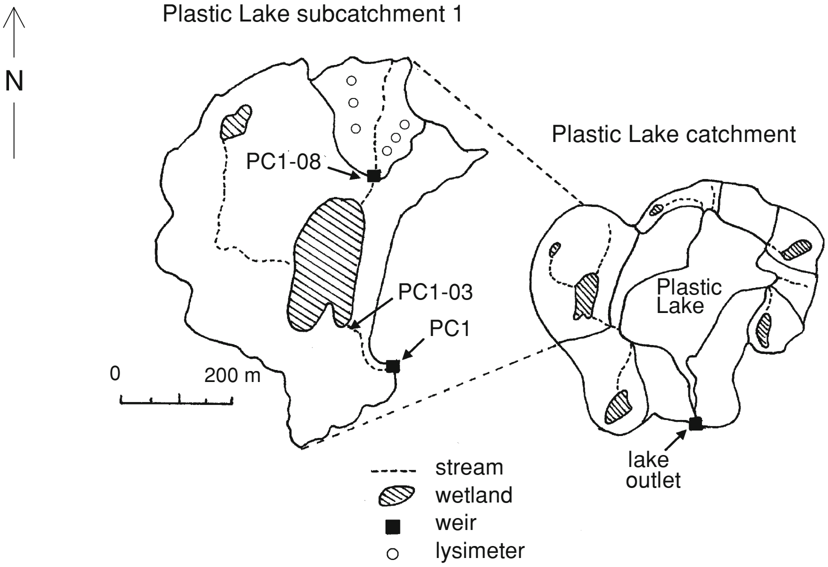

Fig. 1 Map of the Plastic Lake catchment and the PC1 subcatchment showing the locations of streams, swamp wetlands, lysimeter nests and weirs

low due to effects of chronic acid deposition and the low buffering capacity of the thin soils (Watmough et al. 2007).

The PC1 subcatchment is underlain by biotite gneiss with pegmatitic veins (Kirkwood and Nesbitt 1991). Weakly developed orthic humo-ferric and orthic ferro-humic podzols occur on the well drained upland slopes, while humisols and gleysols are present in the swamp wetlands, depressions and stream channels (Dillon and Lazerte 1992). The average soil depth is only 0.5 m, and bedrock outcrops cover ~10% of the area (Dillon and Lazerte 1992). Soils in the Plastic Lake catchment are acidic and the pH of the organic and mineral soils has decreased by approximately 0.2–0.5 pH units over the past 20 years due to acid deposition (Watmough and Dillon 2004). The vegetation is a mixed forest comprised mainly of white pine (*Pinus strobus*), eastern hemlock (*Tsuga canadensis*) and red maple (*Acer rubrum*) on the upland slopes. Striped maple (*Acer pensylvanicum*), white cedar (*Thuja occidentalis*) and black spruce (*Picea mariana*) are present in the stream valleys and lower areas, and the dominant tree species in the wetland is white cedar.

Monitoring and sample collection

A meteorological station is located in a small clearing located adjacent to the PC1 subcatchment. Bulk deposition was collected in an open container fitted with a Teflon-lined funnel (diameter 25 cm) covered with 80 μm Nitex mesh to prevent contamination from debris. Samples were collected for chemical analysis approximately every 2 weeks. The Teflon lining of the bulk deposition collector cracked during the course of the study and leached Cr and Zn into the samples in unknown amounts, so concentrations of these elements in bulk deposition are not reported. This paper reports chemical concentrations for the period from January 2002 to December 2004.

Stream discharge in PC1 was measured continuously in two locations (PC1-08 and PC1) using V-notch weirs and stilling wells with float devices connected to chart recorders. Discharge was calculated based on established stage–discharge relationships for each of the weirs (Scheider et al. 1983). Discharge at an additional location (PC1-03) was calculated using downstream PC1 discharge prorated by differences in source area size. Samples were collected at all three stream sampling locations approximately every 2 weeks, year round (flow permitting). Samples for metal analysis were collected in acid-washed Teflon bottles using clean techniques.

Canopy throughfall was collected every 2–4 weeks, year round, using 20 collectors situated in the upland forest of the PC1 subcatchment. The collectors consisted of 8 cm diameter funnels with 80 μm mesh lined with plastic sample bags. During the winter months, throughfall samples were collected using open buckets. Soil water was collected from five zero-tension lysimeter nests in the upland slopes of the PC1 subcatchment, which were installed in the mid 1980s. In each lysimeter nest in PC1, soil water was collected under the LFH, Ae and B horizons, where these horizons exist (the majority of profiles have no C horizon; Soil Classification Working Group 1998). Soil water samples were collected every 2–4 weeks, year round, when sufficient soil water flows occurred.

Chemical analysis

Sample preparation and analysis was the same for all water samples (bulk precipitation, throughfall, soil water and stream water). During sample collection, samples were filtered using a coarse filter (80 µm). Since colloidal and small particulate matter is not removed, the DOC concentrations represent both dissolved and colloidal organic carbon. A portion of the samples was also passed through a 0.45 µm filter to determine particulate versus "dissolved" concentrations of metals. Dissolved organic carbon concentrations were determined using a Shimadzu Total Carbon Analyser. Sulphate concentrations were determined using a Dionex ion chromatograph. All metal samples were acidified to $<$pH 2 with ultra pure HNO_3 (Optima, Fisher Scientific) prior to analysis. Samples were analysed for 19 metals using a Thermo-Finnigan Element II high resolution single collector Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS). An internal standard (5 ppb Rh) was used to correct for instrument drift. Recoveries were determined using the standard reference material Trace Metals in Natural Water (NIST-1640), and each of the reported certified metals typically had a recovery within ±15% of the stated concentration. Method detection limits (MDLs) were calculated using the mean plus three times the standard deviation of the blank concentrations for each metal, for each analysis. All reported metals were above their respective MDLs in a majority of samples ($>$50% of samples up to 100% of samples, depending on the metal). Beryllium, Li, Tl, and U were below the MDL in greater than 50% of the samples in certain compartments and were not reported in those cases. Where metal concentrations were below the MDL, a value of 0.5 times the MDL was substituted.

Statistical analysis

Multiple regression techniques are frequently used in metal studies due to their ability to determine which predictor variables have the strongest influences on the behaviour of each metal (Sauvé et al. 2000; Tyler and Olsson 2001). Principle components analysis (PCA) was also explored but did not provide a clearer understanding of relationships between metals and DOC and/or acidity. In this study, forward stepwise multiple regressions were used to identify the relative importance of DOC and acidity in controlling concentrations of each metal at different hydrological points throughout the catchment. Metal concentrations were the dependent variables and DOC and SO_4^{2-} concentrations were the independent variables in the regression. A proxy for acidity measured as H^+ was necessary because acidic waters with high DOC concentrations are highly oversaturated with CO_2, which interferes with pH measurements (H^+ was only weakly correlated with metal concentrations). In this study, SO_4^{2-} was used as a measure of acidity: it is well documented that anthropogenic acidification from SO_4^{2-} is the predominant source of acidity in the Plastic Lake catchment (LaZerte and Dillon 1984; Dillon and LaZerte 1992; Watmough et al. 2007). Nitrate concentrations were not included in the analysis, as their concentrations are very low in soil water and streams due to high levels of retention within the Plastic Lake catchment (Dillon and Molot 1990; Watmough and Dillon 2004). Regression coefficients were calculated for each metal in each catchment compartment and the values were adjusted for multiple comparisons using the Bonferroni correction (Cabin and Mitchell 2000). Only relationships described by positive regression coefficients are discussed in this paper; the few negative regression coefficients are assumed to represent indirect associations and are not easily interpreted.

Single-factor ANOVAs were used to test seasonal differences in chemical concentrations in bulk deposition, throughfall, soil water and streams using monthly volume weighted concentrations. The groups of fall (September to November), winter (December to February), spring (March to May) and summer (June to August) were compared. Pearson correlation analysis was used to determine whether monthly volume-weighted concentrations of metals, DOC and SO_4^{2-} concentrations exhibited similar temporal trends in both soil water and streams. The data were log-transformed for the multiple regression analyses due to the prevalence of positively skewed distributions. Standard scores were calculated by subtracting overall mean concentrations from monthly concentrations and dividing by the standard deviation; standardization results in each variable having a range of approximately +3 to −3 with a mean centred on zero.

Results

Concentrations

Concentrations of all metals were generally lowest in bulk deposition (Table 1), and concentrations of several metals (Cu, Fe, Pb, Rb, Tl, and V) were also low in the upland stream (PC1-08). Metal concentrations were highest in soil water (LFH, Ae and B horizons), although the highest concentrations occurred at different horizons for different metals. Concentrations of many metals (As, Cd, Cu, Mn, Pb, Rb, Tl, and V) were elevated in the LFH horizon soil water, and several of these elements (As, Cd, Rb, Tl, and V) were also elevated in the Ae horizon. A few elements had the highest concentrations in the Ae horizon, including Al, Ba, Cr, and Fe. The highest Co concentration was in the B horizon, while the remaining metals (Li, Ni, Sr, U, and Zn) exhibited no pronounced pattern with depth. Stream concentrations of metals were similar to or lower than soil water concentrations for most metals. Concentrations of As, Co, Cr, Cu, Fe, Pb, Rb, and V were highest in the wetland-draining stream (PC1-03, PC1) and low in the upland stream (PC1-08). Concentrations of the remaining metals (Al, Ba, Cd, Li, Mn, Ni, Tl, U, and Zn) did not differ much between streams.

Samples were passed through a 0.45 μm filter to determine “dissolved” concentrations of metals. For the majority of metals, 0.45 μm filtered versus coarse filtered metal concentrations were very similar (data not shown), indicating that metals are nearly entirely dissolved in bulk deposition, throughfall, soil water and streams. One exception is the upland stream (PC1-08) where 0.45 μm filtered concentrations of several metals (Ba, Cr, Cu, Ni, Pb, Sr and Zn) were 20–30% less than the coarse filtered concentrations, suggesting that these metals are not entirely dissolved in this stream. Overall it appears that using the coarse filtered sample data offers a safe approximation of dissolved concentrations of metals.

Because Plastic Lake is well studied, many papers have reported on the major nutrient chemistry of the catchment (for example, see Dillon and Molot 1990; Watmough and Dillon 2004; Watmough et al. 2007) as well as DOC and SO_4^{2-} chemistry; however, since the latter two most directly affect metal behaviour they will be discussed here. Mean volume weighted concentrations of DOC and SO_4^{2-} were lowest in bulk deposition, but increased as water passed through the forest canopy (Table 2). Sulphate concentrations were approximately double in throughfall compared with bulk deposition, whereas DOC was more than 10 times greater. Dissolved organic carbon and SO_4^{2-} concentrations in the LFH soil solution were approximately twice as great as throughfall. Dissolved organic carbon concentrations decreased with depth in the soil profile whereas SO_4^{2-} concentrations were slightly higher in the B horizon compared with the Ae horizon. Dissolved organic carbon and SO_4^{2-} concentrations were much lower in the upland stream than in the wetland-draining stream (PC1-03 and PC1). The pH of bulk deposition was only 4.59. The pH increased slightly in throughfall, decreased in the organic horizon soil water, increased through the mineral soil water up to 4.84 in the upland stream (PC1-08). The pH was substantially lower in the wetland-draining stream (PC1-03; 4.24).

Multiple regressions

Greater numbers of significant relationships were found in catchment compartments with elevated and highly variable DOC and SO_4^{2-} concentrations (Table 3; Appendix). Only seven metals had significant relationships in bulk deposition, R^2 values were fairly low ($R^2 = 0.08$–0.50), and most metals were related to SO_4^{2-} concentrations (Ba, Cd, Co, Sr, and V), although relationships with DOC were also observed (Mn, Rb). In contrast to bulk deposition, throughfall concentrations of 15 metals were significantly related to either DOC or SO_4^{2-}, and these models explained a greater amount of variation ($R^2 = 0.20$–0.77). Again, most metals were related

Table 1 Annual volume weighted concentrations (upper values) and standard deviations (italicized lower values) in μg L^{-1} of metals measured in each compartment in the Plastic Lake catchment from September 2002 to August 2003

Location	Al	As	Ba	Be	Cd	Co	Cr	Cu	Fe	Li	Mn	Ni	Pb	Rb	Sr	Tl	U	V	Zn
BD	15.1	0.12	1.3	NQ	0.09	0.03	NA	1.02	17.6	NQ	5.3	0.53	0.41	0.19	0.8	NQ	NQ	0.15	NA
	11.4	*0.07*	*0.7*		*0.05*	*0.02*		*0.75*	*12.7*		*4.5*	*0.42*	*0.26*	*0.21*	*0.6*			*0.08*	
TF	30.5	0.13	2.7	NQ	0.12	0.06	0.10	1.22	20.9	NQ	123	0.52	0.52	5.35	2.2	0.028	NQ	0.19	18.6
	20	*0.08*	*1.3*		*0.06*	*0.03*	*0.06*	*0.88*	*14.3*		*84*	*0.31*	*0.25*	*5.42*	*1.2*	*0.021*		*0.11*	*11.9*
LFH	366	0.47	28.8	0.04	0.30	0.46	0.29	1.64	148	0.32	205	2.07	6.27	13.1	12.9	0.060	0.007	0.58	43.9
	281	*0.41*	*15.3*	*0.04*	*0.23*	*0.42*	*0.13*	*0.94*	*102*	*0.19*	*154*	*1.12*	*4.20*	*9.3*	*6.9*	*0.054*	*0.005*	*0.35*	*34.2*
Ae	945	0.39	41.9	0.06	0.24	0.56	0.51	1.94	240	0.52	110	2.48	2.05	10.3	14.0	0.052	0.007	0.44	41.8
	496	*0.23*	*21.8*	*0.03*	*0.14*	*0.51*	*0.29*	*1.38*	*181*	*0.22*	*90*	*1.19*	*1.76*	*7.9*	*6.2*	*0.033*	*0.006*	*0.26*	*20.4*
B	699	0.13	38.6	0.10	0.16	1.09	0.24	0.62	42.8	0.72	49	1.68	0.09	0.47	11.7	0.013	0.014	0.12	40.5
	230	*0.10*	*10.4*	*0.06*	*0.08*	*0.50*	*0.11*	*0.65*	*60.5*	*0.37*	*37*	*0.55*	*0.11*	*0.55*	*3.0*	*0.009*	*0.010*	*0.12*	*15.7*
PC1-08	461	0.19	31.6	0.10	0.16	0.35	0.16	0.22	6.5	0.77	88.3	1.41	0.05	0.51	11.9	0.009	0.010	0.05	33.7
	102	*0.06*	*5.2*	*0.02*	*0.03*	*0.18*	*0.12*	*0.43*	*4.3*	*0.25*	*23.6*	*0.29*	*0.05*	*0.12*	*1.4*	*0.007*	*0.007*	*0.04*	*6.1*
PC1-03	375	0.31	36.3	0.09	0.17	1.04	0.30	0.29	163	0.63	91.9	1.12	0.51	0.32	17.8	0.007	0.008	0.41	35.8
	149	*0.21*	*5.3*	*0.04*	*0.06*	*0.18*	*0.10*	*0.20*	*211*	*0.22*	*16.1*	*0.38*	*0.33*	*0.21*	*9.1*	*0.004*	*0.006*	*0.08*	*13.8*
PC1	501	0.32	37.2	0.10	0.19	1.13	0.34	0.75	212	0.71	105	1.34	0.88	1.04	19.1	0.013	0.016	0.39	38.0
	191	*0.19*	*19.8*	*0.05*	*0.13*	*0.60*	*0.16*	*0.46*	*276*	*0.28*	*56*	*0.54*	*0.30*	*0.32*	*12.1*	*0.007*	*0.031*	*0.23*	*19.2*

NA, not applicable; NQ, not quantifiable (>50% of values were below the method detection limit); BD, bulk deposition; TF, throughfall, LFH, LFH soil solution; Ae, Ae soil solution; PC1-08, upland stream; PC1-03, wetland-draining stream; PC1, wetland-draining stream to SO_4^{2-} concentrations (Al, As, Ba, Cd, Co, Cr, Mn, Ni, Sr, V, and Zn), while a few metals exhibited positive relationships with DOC (Cu, Fe, Mn and Rb).

In the LFH soil water, significant relationships were found for 16 metals, although slightly less variation was explained ($R^2 = 0.14$–0.58) than in throughfall. In contrast to throughfall, DOC has increased importance, being related to all significantly predicted metals (Al, As, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Sr, Tl, V, and Zn). Several metals were also significantly related to SO_4^{2-}, including Ba, Cd, Mn, Ni, Sr, and Zn. Progressively fewer significant relationships with DOC were found as water passed down from the organic soil to the mineral soil. In the Ae horizon soil water, R^2 values ranged from 0.17 to 0.53, and out of 14 significant relationships, concentrations of 12 metals were related to DOC (Al, As, Ba, Cr, Fe, Mn, Ni, Pb, Rb, Sr, Tl, and V) and five metals were related to SO_4 (Ba, Co, Mn, Sr and Zn). In the B horizon soil water, R^2 values ranged from 0.24 to 0.95, and out of 14 significant relationships, only five metals were related to DOC (Al, Cr, Fe, Rb and V) while ten metals were related to SO_4^{2-} (Al, Ba, Be, Cd, Co, Li, Mn, Ni, Sr and Zn).

Only two significant relationships were found in the dilute upland PC1-08 stream, where V concentrations were related to DOC and Be concentrations were related to SO_4^{2-} ($R^2 = 0.32$–0.35). After passing through the wetland, many strong relationships appeared in the wetland stream at PC1-03 ($R^2 = 0.27$–0.91). Dissolved organic carbon concentrations were related to all 13 significantly predicted metals (Al, Ba, Be, Cd, Co, Fe, Mn, Ni, Pb, Sr, V and Zn) except U. Many metals were also positively related to SO_4 concentrations (Ba, Be, Cd, Co, Mn, Sr, and Zn) while Fe and U exhibited negative relationships with SO_4^{2-}. The regression equations for the wetland-draining stream at the PC1 sampling location are similar to those found upstream at PC1-03 (see Appendix). Weak but significant regressions were found for four additional metals (As, Cu, Li and Rb) and slightly less variation in metal concentrations is explained ($R^2 = 0.10$–0.78).

Table 2 Annual volume weighted concentrations (upper values) and standard deviations (italicized lower values) in mg L^{-1} (except pH) of DOC, SO_4^{2-} and pH values measured in each compartment in the Plastic Lake catchment from September 2002 to August 2003

Location	DOC	SO_4^{2-}	pH
BD	0.9	1.78	4.59
	0.8	*1.00*	*0.30*
TF	12.1	3.90	4.81
	6.8	*1.63*	*0.59*
LFH	47.2	5.60	4.40
	22.0	*3.61*	*0.40*
Ae	36.2	5.14	4.67
	17.8	*2.50*	*0.36*
B	5.4	6.92	4.72
	4.8	*2.63*	*0.25*
PC1-08	3.4	2.67	4.84
	1.0	*0.51*	*0.16*
PC1-03	14.5	9.64	4.24
	7.9	*6.34*	*0.15*
PC1	13.1	9.60	4.41
	7.0	*5.51*	*0.19*

Seasonal variability

Few significant seasonal differences were found in bulk deposition or throughfall concentrations of metals, DOC or SO_4^{2-} (data not shown), whereas many were found in the LFH soil water and wetland-draining stream (PC1-03 and PC1; Table 4). In the LFH soil water, the lowest concentrations of most metals and DOC were observed in the springtime and higher concentrations were observed during the remainder of the year, particularly during the summer and fall. In the wetland-draining stream (PC1), concentrations of most metals, SO_4^{2-} and DOC were lowest in the spring. Concentrations of metals and DOC were highest in the summer and fall, and SO_4^{2-} concentrations were especially high in the fall months. Stream discharge was ten times greater in the spring (total spring discharge 284 mm m^{-2}) than in the summer (total summer discharge 26 mm m^{-2}).

In the LFH soil water, metal and DOC volume-weighted concentrations were temporally coherent (Fig. 2). Concentrations were low in the late winter and spring months, increased in the summer, increased even further in the fall months and remained high in early winter. In the wetland-draining stream (PC1-03), separate temporal trends existed for DOC and DOC-related metals compared

Table 3 Positive significant regressions between metals, DOC and SO_4^{2-} concentrations in all eight compartments in the Plastic Lake catchment

	DOC				DOC + SO_4^{2-}				SO_4^{2-}				Not significant
BD	Rb 0.26**				Mn 0.50**				Ba 0.33***	Cd 0.08*	Co 0.23***	Sr 0.33***	Al, As, Be, Cr, Cu, Fe, Li, Ni, Pb, Tl, U, Zn
									V 0.10*				
TF	Cu 0.22**	Fe 0.47***	Rb 0.59***	Tl 0.29***					Al 0.41***	As 0.20***	Ba 0.77***	Cd 0.31***	Be, Li, U
									Co 0.42***	Cr 0.45***	Mn 0.59***	Ni 0.38***	
									Sr 0.76***	V 0.54***	Zn 0.24***		
LFH	Al 0.32***	As 0.31***	Co 0.26***	Cr 0.28***	Ba 0.55*	Cd 0.51***	Mn 0.31*	Ni 0.48*					Be, Rb, U
	Cu 0.29***	Fe 0.30***	Li 0.17**	Pb 0.27***	Sr 0.58***	Zn 0.38***							
	Tl 0.14*	V 0.33***											
Ae	Al 0.22**	As 0.31**	Cr 0.17*	Fe 0.44***	Ba 0.46**	Ni 0.47**	Sr 0.40*		Co 0.31***	Zn 0.53***			Be, Cd, Cu, Li, U
	Mn 0.22*	Pb 0.35***	Rb 0.47***	Tl 0.42***									
	V 0.44***												
B	Cr 0.42***	Fe 0.63**	Rb 0.50*	V 0.49**	Al 0.66*				Ba 0.61***	Be 0.64***	Cd 0.24*	Co 0.95***	As, Cu, Pb, Tl, U
									Li 0.30***	Mn 0.35**	Ni 0.44***	Sr 0.63***	
									Zn 0.60***				
PC1-08	V 0.30**								Be 0.35**				Al, As, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Rb, Sr, Tl, U, Zn
PC1-03	Al 0.47***	Fe 0.74***	Pb 0.45**	V 0.27**	Ba 0.91***	Be 0.45***	Cd 0.63***	Co 0.77***					As, Cr, Cu, Li, Rb, Tl, U
					Mn 0.73**	Ni 0.47*	Sr 0.90***	Zn 0.74***					
PC1	Al 0.55***	As 0.36**	Cu 0.14*	Fe 0.51***	Ba 0.76***	Cd 0.23***	Co 0.78***	Mn 0.58*	Be 0.45***	Li 0.33***			Cr, Tl
	Pb 0.48***	Rb 0.10*	U 0.43*	V 0.51***	Ni 0.55***	Sr 0.75***	Zn 0.59***						

DOC denotes positive a DOC relationship only, DOC + SO_4^{2-} denotes a positive relationship with both DOC and SO_4^{2-}, and SO_4^{2-} denotes a positive SO_4^{2-} relationship only. R^2 values and statistical significance are also shown

Statistical significance is for $\alpha = 0.05$; * $p < 0.025$; ** $p < 0.01$; *** $p < 0.001$

Table 4 Mean seasonal concentrations of metals, DOC, SO_4^{2-} and pH in the forest floor soil water and the main stream

	Winter	Spring	Summer	Fall	*p*
LFH					
pH	4.48	4.25	4.29	4.31	NS
DOC (mg L^{-1})	51.9	26.4	46.3	67.0	0.005
SO_4^{2-} (mg L^{-1})	9.92	8.63	6.18	6.88	NS
Al (μg L^{-1})	319	321	277	361	NS
As (μg L^{-1})	0.42	0.33	0.42	0.47	NS
Ba (μg L^{-1})	31.4	23.5	32.1	35.6	0.021
Be (μg L^{-1})	0.023	0.025	0.039	0.014	NS
Cd (μg L^{-1})	0.40	0.22	1.15	2.09	0.029
Co (μg L^{-1})	0.52	0.50	0.43	0.49	NS
Cr (μg L^{-1})	0.36	0.25	0.28	0.40	NS
Cu (μg L^{-1})	1.48	1.05	1.82	2.03	0.036
Fe (μg L^{-1})	196	105	127	204	NS
Li (μg L^{-1})	0.34	0.47	0.32	0.43	0.012
Mn (μg L^{-1})	242	101	196	325	NS
Ni (μg L^{-1})	2.36	1.35	2.00	3.09	0.021
Pb (μg L^{-1})	10.7	4.6	5.9	10.5	0.035
Rb (μg L^{-1})	15.6	9.4	21.6	16.1	0.021
Sr (μg L^{-1})	15.2	10.0	14.3	17.1	0.020
Tl (μg L^{-1})	0.051	0.034	0.076	0.090	NS
U (μg L^{-1})	0.014	0.011	0.008	0.014	0.007
V (μg L^{-1})	0.61	0.35	0.50	0.88	NS
Zn (μg L^{-1})	50.3	30.3	46.0	57.7	NS
PC1					
pH	4.30	4.35	4.63	4.35	0.001
DOC (mg L^{-1})	11.5	10.3	23.6	18.6	<0.001
SO_4^{2-} (mg L^{-1})	10.7	6.0	1.8	23.8	<0.001
Al (μg L^{-1})	404	360	517	741	NS
As (μg L^{-1})	0.23	0.30	0.40	0.22	NS
Ba (μg L^{-1})	37.2	22.0	22.9	91.1	<0.001
Be (μg L^{-1})	0.10	0.07	0.06	0.17	0.022
Cd (μg L^{-1})	0.16	0.10	0.12	0.42	<0.001
Co (μg L^{-1})	1.03	0.67	0.70	2.65	<0.001
Cr (μg L^{-1})	0.25	0.30	0.78	0.28	<0.001
Cu (μg L^{-1})	0.49	0.59	1.15	0.48	0.020
Fe (μg L^{-1})	209	160	577	243	0.007
Li (μg L^{-1})	0.64	0.64	0.67	1.00	NS
Mn (μg L^{-1})	100	62	48	267	<0.001
Ni (μg L^{-1})	1.27	0.91	1.26	2.63	<0.001
Pb (μg L^{-1})	0.26	0.31	0.74	0.41	0.001
Rb (μg L^{-1})	0.49	0.37	0.34	1.25	<0.001
Sr (μg L^{-1})	22.9	10.8	11.3	54.4	<0.001
Tl (μg L^{-1})	0.021	0.018	0.011	0.019	NS
U (μg L^{-1})	0.021	0.011	0.020	0.017	NS
V (μg L^{-1})	0.31	0.30	0.55	0.50	0.025
Zn (μg L^{-1})	39.9	22.6	24.1	84.4	<0.001

The statistical significance of seasonal differences is shown by the *p*-value ($\alpha = 0.05$)

NS, not significant for $\alpha = 0.05$

with SO_4^{2-} and SO_4^{2-}-related metals. Dissolved organic carbon and DOC-related metal concentrations (As, Cr, Cu, Fe, Pb, and V) increased in the summer months before drought conditions occur. Sulphate and SO_4^{2-}-related metal concentrations (Al, Ba, Cd, Co, Mn, Ni, Sr, Rb, and Zn) increased in the

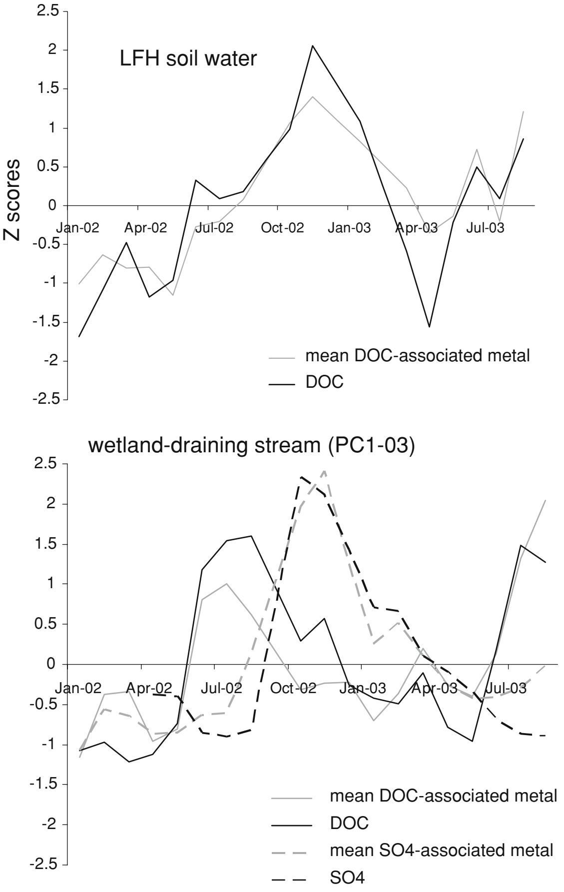

Fig. 2 Standardized monthly volume weighted concentrations of **a** metals and DOC in the LFH soil water and **b** DOC-related metals, DOC, SO_4^{2-}-related metals and SO_4^{2-} in the main stream for the period January 2002 to August 2003

fall months after the summer drought and declined through to the following summer.

Discussion

Bulk deposition

Concentrations of metals in bulk deposition at Plastic Lake were considerably lower than in deposition to developed areas, and similar to or less than deposition to other remote sites in this geographical area (Gelinas and Schmit 1998; Pirrone and Keeler 1996; Sweet et al. 1998). Additionally, metal deposition to Plastic Lake was generally substantially lower than it was 25 years prior due to reductions in metal emissions (Jeffries and Snyder 1981; Pacyna and Pacyna 2001). Although metal concentrations were low, certain metals may still be enriched over background levels. Enrichment factors are determined by comparing concentration ratios of a given metal to a lithogenic metal (such as Al) in bulk deposition and in average crustal material (Duce et al. 1975; Steinnes and Friedland 2006). (Average crustal metal concentrations were used because bedrock concentrations for Plastic Lake were not available). In bulk deposition at Plastic Lake, low to medium enrichment (1–100 times) was found Ba, Co, Cr, Fe, Mn, Ni, Rb, Sr and V, and high to very high enrichment (100–1,000 times or greater) was found for As, Cd, Cu, Pb and Zn. Metal enrichment in deposition to Plastic Lake is characteristically similar to long range atmospheric metal pollution across the globe (Nriagu and Pacyna 1988; Berg et al. 1995; Steinnes and Friedland 2006).

Despite the fact that certain metals are highly enriched in bulk deposition at this site, few significant relationships among metals, SO_4^{2-} and DOC concentrations were found. Other studies have found correlations among Cu, Pb, Zn and SO_4^{2-} (an indicator of anthropogenic emissions) in bulk deposition (Ross 1987; Lawlor and Tipping 2003); however, the metals associated with SO_4^{2-} in this study are not primarily from anthropogenic sources. Relationships with DOC in bulk deposition appear to indicate a biogenic source of Rb and Mn, potentially emitted as aerosols from vegetation (Artaxo et al. 1988). The lack of strong relationships likely results from the small range of metal, DOC and SO_4^{2-} concentrations in bulk deposition. The bimonthly sampling regime obscures variability occurring among and within precipitation events. Additionally, it is easier to detect relationships in multiple sites along a pollution gradient where a greater range of concentrations exists.

Throughfall

Concentrations of metals, DOC and SO_4^{2-} are greater in throughfall than in bulk deposition due to enhanced capture of dry deposition, foliar leaching and evaporation of precipitation from the canopy (Neary and Gizyn 1994), although the canopy can also adsorb deposited metals (Petty and Lindberg 1990). Throughfall concentrations of metals are mostly related to SO_4 due to concurrent dry deposition of metals and SO_4^{2-} to the canopy surface. Despite its relationship with SO_4^{2-}, H^+ is adsorbed by foliage and exchanged for other cations, making the pH of throughfall higher than bulk deposition (Houle et al. 1999). The strong relationships with SO_4^{2-} emphasize the importance of dry deposition of metals to the forest canopy. DOC also influences metal concentrations in throughfall. Positive relationships with DOC (shown by Cu, Fe, Rb, and Tl) could indicate leaching losses of metals, and foliar leaching of Rb is well known (Rea et al. 2001). DOC released from foliage could bind metals, enhancing the release of metals in throughfall. Hou et al. (2005) also observed correlations among Al, Fe, Mn, and DOC concentrations in throughfall.

Forest floor

Tree roots, microbes and other soil biota that alter the chemistry of the organic soil horizon, affecting metal dynamics. Organic matter mineralization produces high soil water DOC concentrations, enabling metal leaching from soil binding sites. Natural and anthropogenic acidity of this layer enhances metal release by increasing metal solubility and competition for soil binding sites. Evaporative concentration of solutes increases metal concentrations in soil water ($\sim$50% of precipitation is lost as evapotranspiration at PC1; Devito et al. 1989). Metals exhibiting the highest concentrations in the LFH soil water are those with strong DOC associations (As, Cu, Pb, Rb, Tl and V) or those especially available for plant uptake (Mn and Cd; Navratil et al. 2007; Tyler 2004). In the forest floor soil water, all metals are associated with DOC, indicating that DOC production is a primary factor enhancing metal mobility in this horizon. Metal-organic matter binding strengths have been determined by many researchers, but comparison of these values is difficult because the actual binding strength depends on the type of organic matter and competing ligands in the soil solution (Bodek 1988). Nevertheless, it is generally agreed that Al, Cr, Cu, Fe, Pb are strongly binding, Cd, Co, Ni, Zn are weakly binding and Ba, Mn and Sr are very weakly binding (Schnitzer 1969; Van Dijk 1971; Bergkvist 1987; Bergkvist et al. 1989; Tipping 1998; Lawlor and Tipping 2003). Metals significantly related to SO_4^{2-} in the DOC-rich forest floor were those with lower binding capacities for DOC (Ba, Mn and Sr), which are more susceptible to competition by protons or other positively charged ions for organic matter binding sites (Dillon et al. 1988).

Mineral soil and upland stream

The predominant hydrological pathway through the shallow soils at Plastic Lake is vertically through the soil profile to the bedrock and then laterally across the bedrock down to the stream; macropore flow channelling water through the soil and along the bedrock surface is common at this site (Buttle and McDonald 2002; Buttle et al. 2004; Peters et al. 1995). Concentrations of Al, Ba, Cr and Fe are highest in the mineral Ae horizon soil water, indicating that this horizon is a mineral weathering source of these elements. In the B horizon, concentrations of many metals (Al, As, Ba, Cd, Cr, Cu, Pb, Rb, Tl, and V) and DOC decline due to adsorption and cation exchange processes in the relatively deep mineral soil layer. The mineral B horizon retains most DOC (Dalva and Moore 1991; Froberg et al. 2006; Bergkvist 1987) observed similar decreases in Cr, Cu, Fe, and Pb concentrations in the B horizon of acidic podzols in Sweden.

While DOC is still a significant predictor of metal concentrations in the mineral soil water, progressively fewer relationships with DOC are observed with depth while the relative importance of SO_4^{2-} in predicting metal concentrations increases. Certain metals (including Ba, Be, Cd, Co, Mn, Ni, Sr, and Zn) consistently demonstrate positive relationships with SO_4^{2-} in soil water. Macropore flow, which reduces the amount of contact between soil solution and soil, may contribute to the consistency of these relationships (Beven and Germann 1982). In addition to the strong acid anion SO_4^{2-} being a proxy for acidity, it is also a charged species whose presence in solution must be balanced by counter-ions. All metal ions (except for As and oxidized Cr) form positively charged species in solution, and consequently may be driven into solution by the elevated SO_4^{2-} concentrations in the mineral soil water (this process would be more important for the less-strongly binding metals). Weathering is an important source of metals abundant in soils and bedrock, such as Al, Ba, Fe, Mn, and Sr, although metal weathering rates are difficult to quantify (Lawlor and Tipping 2003; LaZerte 1986). At Plastic Lake, soil water concentrations of Al, Ba, Be, Co, and Li increase with depth, indicating a weathering source of these metals. Weathering sources are likely also important for other metals that had low enrichment in deposition but had low concentrations in the B horizon soil water due to strong binding affinities (Cr, Fe) or cycling by vegetation (Mn, Sr, Rb). Significant relationships were found for most metals in soil water but for only two metals in the upland stream (PC1-08). The smallest range of DOC and SO_4^{2-} concentrations occurred in the upland stream, which likely precluded the detection of relationships among metals, DOC and SO_4^{2-}.

Swamp wetland and main stream

The thin tills in the Plastic Lake catchment produce seasonally variable flows into the swamp wetland, causing water table fluctuations (Devito et al. 1996). The changing redox conditions enhance chemical transformations in the upper layer of the wetland (Bayley et al. 1986; Devito and Dillon 1993). Mean concentrations of most metals are similar in the upland and wetland streams; however, a few metals (Fe, Pb and V) have substantially higher concentrations in the wetland stream likely due to DOC binding and export. Redox conditions may also contribute to the elevated concentrations of Fe, which is soluble under reducing conditions. Dissolved organic carbon concentrations exhibit a large range in the wetland-discharging stream due to the seasonal nature of DOC production (Dalva and Moore 1991; Hinton et al. 1997) although the range is somewhat lower than in the LFH soil water. The greatest range of SO_4^{2-} concentrations is found in this stream due to the drought conditions occurring in the summer of 2002. Under drought conditions, the water table drops, causing oxidation of sulphur stored in wetlands that is released as a pulse of sulphuric acid upon rewetting; this pattern has been well studied in the PC1 swamp wetland (Devito 1995; Dillon and LaZerte 1992; Eimers et al. 2007).

The large range of concentrations in the wetland-draining stream enables the characterization of relationships among metals, DOC and SO_4^{2-}. Similar to the forest floor soil water, DOC is an important parameter affecting metal concentrations in the wetland discharge (PC1-03). All metals with significant regressions are positively associated with DOC. The metals that are related to DOC concentrations alone (Al, Fe, Pb, and V) are those with high binding affinities for organic matter, while metals with lower binding affinities (Ba, Be, Cd, Co, Mn, Sr, and Zn) are also related to SO_4^{2-}. Similar relationships between metals, DOC and SO_4^{2-} in wetland discharges have previously been found at this and other sites (Adkinson et al. 2008; Tipping et al. 2003). Wet and stagnant conditions in the wetland create a reducing environment that affects metal speciation and solubility. Reduced Fe^{2+} and Mn^{2+} are soluble and other metals may be affected by redox conditions as well. Copper binds organic matter strongly (Sauvé et al. 1997) yet is not significantly related to DOC in the wetland-draining stream even though other strong binders (Al, Fe and Pb) are significantly related to DOC in this stream, and Cu is significantly related to DOC in the LFH soil water. The chemical nature of DOC in the wetland may differ from the soil solution due to different sources (*Sphagnum* moss instead of leaves and bark) and decomposition processes (anoxic versus oxic biodegradation), although it is uncertain whether Cu has lower affinities for wetland DOC. An alternative possibility is that Cu^{2+} is converted to CuS or Cu_2S, which occurs under reducing conditions even at low pH when sulphide is present. Similar behaviour was observed by Grybos et al. (2007) where Cu concentrations were not directly related to DOC or pH in a wetland, and an earlier study at Plastic Lake also found no significant relationships between Cu and DOC or acidity in the wetland (Schut et al.1986). The water table drawdown could also oxidize metals, affecting their solubility and export in the post drought period; this may have occurred to a slight extent for Fe but not Mn, which had high concentrations at that time. Based on topographical surveys, ~80% of the upland forest area in the PC1 catchment drains through the *Sphagnum*-conifer swamp and the remainder drains directly to the lower portion of the wetland-draining stream (PC1). A similar range of metal, DOC and SO_4^{2-} concentrations are found in the upper and lower reaches of the wetland-draining stream, and the relationships amongst metals, DOC and SO_4^{2-} observed directly upstream at PC1-03 generally remain.

Seasonal variability of metal concentrations

The climate in central Ontario consists of distinct seasons with changing temperature and precipitation levels throughout the year, and biological processes and hydrological events have a seasonal nature. Dissolved organic carbon, SO_4^{2-} and some metals demonstrate distinct seasonal patterns in some compartments but not in others. Few seasonal differences were observed in bulk deposition, which contrasts with other studies that have found higher concentrations of metals in the summer months (Jeffries and Snyder 1981; Lawson and Mason 2001; Lindberg and Turner 1988). Seasonal changes in the forest floor chemistry were related to DOC concentrations, which are highest in summer and fall when warm, moist conditions promote microbial decomposition, and are lowest in spring due to low decomposition rates and snowmelt dilution (Christ and David 1996; Eimers et al. 2008). Additionally, the chemical nature of DOC changes over time as mineralization progresses (especially under coniferous forests; McDowell and Likens 1988; Schiff et al. 1997; Don and Kalbitz 2005). Concentrations of most metals were temporally coherent with DOC concentrations in the LFH horizon soil water. Variability between years suggests that weather (and in the long term, climate) conditions ultimately control DOC and metal concentrations in the LFH soil water. While seasonal trends of DOC concentrations have been characterized for forest soil water (Froberg et al. 2006; Kaiser et al. 2002; Michalzik and Matzner 1999), few if any studies have investigated seasonal trends and coherence among of a suite of metal concentrations.

The wetland-draining stream demonstrates strong seasonal trends. The lowest concentrations occur in the spring for most metals, DOC and SO_4^{2-} when stream discharge is the highest and dilutes streams the most. However, concentrations are not solely controlled by stream discharge, as relationships between metal concentrations and discharge are weak to non-existent in the wetland-draining stream (data not shown). Additionally, DOC concentrations are generally not related to discharge in wetland-draining streams due to the large volumes of high DOC water stored in wetlands (Eckhardt and Moore 1990). In the wetland-draining stream (PC1-03 and PC1), concentrations of some metals (Cr, Cu, Fe, Pb, and V) are highest in the summer when warm temperatures enhance DOC production and reduce stream flow due to evapotranspiration (Dalva and Moore 1991; Eimers et al. 2008; Schiff et al. 1998). Concentrations of DOC and DOC-related metals increased during early summer, and the concentrations levelled off in the first summer when the streams ceased flowing, but continued to climb in the second year when stream flow was continuous. Most other metals have low concentrations in the summer and exhibit the highest concentrations in the fall (Ba, Cd, Co, Mn, Ni, Rb, Sr, and Zn) coincident with peak SO_4^{2-}

Table 5 Maximum observed concentrations of metals, DOC, SO_4^{2-} and pH in the PC1 stream between January 2002 and August 2004 ($n = 69$)

Chemical (units)	Maximum observed concentration (minimum pH)	Guideline value	Frequency of exceedance (%)	Date
DOC (mg L^{-1})	31.6	–	–	Summer 18/08/2004
pH	**3.96**	**6.5–8.5**[a]	**100**	**Winter 21/01/2004**
SO_4^{2-} (mg L^{-1})	25	–	–	Fall 13/11/2002
Al (μg L^{-1})	**931**	**15**[b]	**NP**	**Fall 13/11/2002**
As (μg L^{-1})	0.98	5	0	Fall 17/10/2003
Ba (μg L^{-1})	107	–	–	Fall 06/11/2002
Be (μg L^{-1})	0.21	–	–	Fall 21/11/2002
Cd (μg L^{-1})	**0.52**	**0.1**	**52**	**Fall 13/11/2002**
Co (μg L^{-1})	**3.21**	**1**	**19**	**Fall 13/11/2002**
Cr (μg L^{-1})	0.74	8.9	0	Summer 30/07/2003
Cu (μg L^{-1})	**1.69**	**1**	**8**	**Summer 04/06/2002**
Fe (μg L^{-1})	**1,240**	**300**	**36**	**Summer 24/08/2004**
Li (μg L^{-1})	1.22	–	–	Fall 26/09/2003
Mn (μg L^{-1})	298	–	–	Fall 06/11/2002
Ni (μg L^{-1})	3.29	25	0	Fall 13/11/2002
Pb (μg L^{-1})	**1.4**	**1**	**14**	**Summer 26/07/2004**
Rb (μg L^{-1})	1.8	–	–	Fall 26/09/2003
Sr (μg L^{-1})	62.5	–	–	Fall 06/11/2002
Tl (μg L^{-1})	0.040	0.3	0	Fall 13/11/2002
U (μg L^{-1})	0.051	5	0	Summer 24/08/2004
V (μg L^{-1})	1.18	6	0	Summer 24/08/2004
Zn (μg L^{-1})	**106**	**20**	**66**	**Fall 13/11/2002**

The Ontario Provincial Water Quality Objectives (PWQO) for the protection of aquatic life in surface water are shown and exceedances are highlighted in bold text. Interim guideline values are used in cases where they exist. Guideline values are for total metal concentrations unless otherwise noted

– No guideline value, *NP* direct comparison not possible

[a] The PWQO states that surface water pH should be maintained between 6.5 and 8.5 to protect aquatic life, although the naturally acidic wetland-draining stream may never have reached that range

[b] The Al guideline value is for inorganic Al, however, a previous study of the wetland-draining stream found that ~50% of Al was inorganic (LaZerte et al. 1988) so it is highly likely that the guideline is exceeded

concentrations, as has previously been described (Tipping et al. 2003; Adkinson et al. 2008). In this instance, SO_4^{2-} appears to have stronger control over metal behaviour, as metals with lower binding affinities for organic matter are easily outcompeted for binding sites by protons and are simultaneously released into solution. This particular pattern was observed in a drought year, and likely would not occur to the same extent in wetter years.

Exceedances of surface water guidelines for metals

This discussion has focused on annual or monthly average volume weighted concentrations. However, actual measured concentrations demonstrate even greater variability over time. Despite the rural location and low levels of metal deposition, several metals in the PC1 stream exceed the Ontario Provincial Water Quality Objectives (PWQO) for the protection of aquatic life in surface water (MOE 1994), including Al, Cd, Co, Cu, Fe, Pb and Zn (Table 5). Notably, Al, Cd, Co and Zn all exhibit their maximum observed concentrations in the same sample, collected under highly acidic conditions after the drought period in November 2002 ($SO_4^{2-} = 25$ mg L^{-1}, pH = 4.11). The maximum values of Cu, Fe and Pb occur in the summer months. Despite exceeding the PWQO guideline, these metals are likely complexed with DOC, which substantially reduces metal toxicity (Di Toro et al. 2001).

Summary of metal behaviour

Although metal concentrations and relationships with DOC and SO_4^{2-} are quite variable throughout the catchment, the general characteristics of each metal can be summarized (Table 6). Five of the metals studied (As, Cd, Cu, Pb and Zn) appear to be highly enriched in bulk deposition. The highest concentrations of metals generally occur in the soil solution. Regression equations indicated that both DOC and SO_4^{2-} are important predictors of metal concentrations, with DOC appearing to be more important in

Table 6 Summary of observed metal behaviour (enrichment, concentrations and chemical relationships) in the Plastic Lake catchment

Metal	Enriched in bulk deposition?	Highest concentration observed in	Behaviour most related[a] to	Exceeds PWQO guideline in PC1?
Al	No	Ae soil water	DOC	**Yes**
As	**Yes**	LFH soil water	DOC	No
Ba	No	Ae soil water	SO_4 and DOC	No
Be	No	B soil water/wetland-draining stream	SO_4 and DOC	No
Cd	**Yes**	LFH soil water	SO_4 and DOC	**Yes**
Co	No	B soil water	SO_4 and DOC	**Yes**
Cr	No	Ae soil water	DOC and SO_4	No
Cu	**Yes**	LFH soil water	DOC	**Yes**
Fe	No	Ae soil water	DOC	**Yes**
Li	No	Upland stream	SO_4 and DOC	No
Mn	No	LFH soil water	SO_4 and DOC	No
Ni	No	Soil water	SO_4 and DOC	No
Pb	**Yes**	LFH soil water	DOC	**Yes**
Rb	No	Soil water	DOC	No
Sr	No	Soil water	SO_4 and DOC	No
Tl	No	Soil water	DOC	No
U	No	Wetland-draining stream	DOC	No
V	No	LFH soil water	DOC	No
Zn	**Yes**	Soil water	SO_4 and DOC	**Yes**

[a] Greatest number of significant regressions

Bold type indicates bulk deposition enrichment and/or guideline exceedance of a metal the upper soil horizons and wetland-draining streams and SO_4^{2-} (acidity) being more important in bulk deposition, throughfall and mineral soil water. The highest concentrations in the wetland-draining stream generally occurred in the summer (for DOC, Cu, Fe, Pb, and V) and fall (for SO_4^{2-} and most other metals). Plastic Lake is sensitive to impacts of pollution, and despite the remote location, provincial water quality objectives were exceeded in the main stream for several metals, including Al, Cd, Co, Cu, Fe, Pb, and Zn. Several of the metals that exceed guideline values have anthropogenic sources (Cd, Cu, Pb, and Zn), while the remaining metals are primarily lithogenic in origin (Al, Co, Fe).

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Appendix

See Table 7.

Table 7 Forward stepwise multiple regression equations for metal concentrations using DOC and SO_4 as predictor variables

	DOC	SO_4^{2-}	Intercept	R^2	
BD					$n = 77$
Ba		0.45	0.10	0.33	***
Cd		0.05	0.02	0.08	*
Co		0.03	0.00	0.23	***
Mn	0.69	0.87	0.12	0.50	**
Rb	0.19		−0.03	0.26	**
Sr		0.50	0.01	0.33	***
V		0.06	0.03	0.10	*
TF					$n = 103$
Al		0.82	0.79	0.41	***
As		0.11	0.01	0.20	***
Ba		0.81	0.11	0.77	***
Cd		0.10	0.00	0.31	***
Co	−0.03	0.09	0.00	0.42	***
Cr		0.08	−0.02	0.45	***
Cu	0.23		0.08	0.22	**
Fe	0.49		0.55	0.47	***
Mn		1.26	0.96	0.59	***
Ni		0.27	−0.01	0.38	***
Rb	0.80		−0.20	0.59	***
Sr		0.85	0.01	0.76	***
Tl	0.02		0.00	0.29	***
V		0.19	−0.02	0.54	***
Zn		0.87	0.91	0.24	***
LFH					$n = 68$
Al	0.90		0.88	0.32	***
As	0.22		−0.30	0.31	***
Ba	0.75	0.37	−0.12	0.55	*
Cd	0.19	0.17	−0.34	0.51	***
Co	0.20		−0.31	0.26	***
Cr	0.13		−0.16	0.28	***
Cu	0.38		−0.38	0.29	***
Fe	0.84		0.74	0.30	***
Li	0.12		−0.13	0.17	**
Mn	0.55	0.87	0.61	0.31	*
Ni	0.53	0.30	−0.67	0.48	*
Pb	0.68		−0.63	0.27	***
Sr	0.65	0.44	−0.31	0.58	***
Tl	0.03		−0.06	0.14	*
V	0.28		−0.34	0.33	***
Zn	0.84	0.75	−0.46	0.38	***
Ae					$n = 55$
Al	0.32		2.20	0.22	**
As	0.14		−0.14	0.31	**
Ba	0.37	0.46	0.67	0.46	**
Co		0.37	−0.11	0.31	***
Cr	0.13		−0.03	0.17	*
Fe	0.97		0.76	0.44	***
Mn	0.57		0.59	0.22	*
Ni	0.26	0.31	−0.11	0.47	**
Pb	0.53		−0.39	0.35	***
Rb	1.01		−0.62	0.47	***
Sr	0.27	0.32	0.49	0.40	*
Tl	0.03		−0.04	0.42	***
V	0.20		−0.15	0.44	***
Zn		0.80	0.64	0.53	***
B					$n = 32$
Al	0.73	1.60	0.95	0.66	*
Ba		0.96	0.55	0.61	***
Be	−0.04	0.07	0.02	0.64	***

Table 7 continued

	DOC	SO_4^{2-}	Intercept	R^2	
Cd		0.06	0.02	0.24	*
Co	−0.24	0.44	0.11	0.95	***
Cr	0.11		0.05	0.42	***
Fe	2.14	−1.27	0.67	0.63	**
Li		0.22	0.05	0.30	***
Mn		1.13	0.63	0.35	**
Ni		0.30	0.12	0.44	***
Rb	0.28	−0.18	0.10	0.50	*
Sr		0.67	0.40	0.63	***
V	0.11	−0.09	0.05	0.49	**
Zn		1.01	0.51	0.60	***
PC1-08					$n = 40$
Be		0.03	−0.16	0.35	**
V	0.02		−0.01	0.30	**
PC1-03					$n = 52$
Al	0.66		1.66	0.47	***
Ba	0.65	0.43	0.28	0.91	***
Be	0.05	0.05	−0.06	0.84	***
Cd	0.09	0.07	−0.11	0.89	***
Co	0.32	0.20	−0.30	0.77	***
Fe	0.64	−0.40	1.84	0.74	***
Mn	0.46	0.48	0.88	0.73	**
Ni	0.33	0.10	−0.16	0.47	*
Pb	0.18		0.05	0.45	**
Sr	0.61	0.47	0.05	0.90	***
U		−0.004	0.005	0.58	***
V	0.06		0.04	0.27	**
Zn	0.61	0.41	0.35	0.74	***
PC1					$n = 69$
Al	0.83		1.56	0.55	***
As	0.14		−0.01	0.36	**
Ba	0.62	0.58	0.25	0.76	***
Be		0.05	−0.05	0.45	***
Cd	0.09	0.08	−0.11	0.63	***
Co	0.43	0.32	−0.49	0.78	***
Cu	0.16		0.00	0.14	*
Fe	1.05		1.30	0.51	***
Li		0.15	0.07	0.33	***
Mn	0.41	0.65	0.81	0.58	*
Ni	0.40	0.19	−0.29	0.55	***
Pb	0.24		−0.05	0.48	***
Rb	0.19		−0.11	0.10	*
Sr	0.62	0.61	−0.03	0.75	***
U	0.01	−0.01	0.00	0.43	*
V	0.25		−0.14	0.51	***
Zn	0.62	0.58	0.25	0.59	***

For each compartment, only those metals shown had significant relationships

* $p < 0.025$, ** $p < 0.01$, *** $p < 0.001$

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