

Hydrologic and biogeochemical controls on trace element export from northern Wisconsin wetlands

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Received: 5 August 2007 / Accepted: 17 June 2008 / Published online: 17 July 2008
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Abstract Wetlands play an important role in determining the water quality of streams and are generally considered to act as a sink for many reactive species. However, retention of chemical constituents varies seasonally and is affected by hydrologic and biogeochemical processes including water source, mineral weathering, DOC and SPM cycling, redox status, precipitation/dissolution/adsorption, and seasonal events. Relatively little is known about the influence of these factors on trace element cycling in wetland-influenced streams. To explore the role of wetlands with respect to the retention/release of trace elements to streams, we examined temporal and spatial patterns of concentrations of a large suite of trace elements (via ICP-MS) and geochemical drivers in five streams and wetland rivulets draining natural wetlands in a northern

Wisconsin watershed as well as in their groundwater sources (terrestrial recharge, lake recharge, and older lake recharge). We performed principal components analyses of the concentrations of elements and their geochemical drivers in both the streams and rivulets to assist in the identification of factors regulating trace element concentrations. Variation in trace and major element concentrations among the streams was strongly related to the proportion of terrestrial recharge contributing to the stream. A dominant influence of water source on rivulet chemistry was supported by association of groundwater-sourced elements (Ba, Ca, Cs, Mg, Na, Si, Sr) with the primary statistical factor. DOC appeared in the first principal component factor for the streams and in the second factor for the rivulets. Strong correlations of Al, Cd, Ce, Cu, La, Pb, Ti, and Zn with DOC supported the important influence of DOC on trace metal cycling. A number of elements in the rivulets (Al, La, Pb, Ti) and streams (Al, Ce, Cr, Cu, La, Pb, Ti, Zn) had a significant particulate cycle. Redox cycling and precipitation/dissolution reactions involving Fe and Mn likely impacted Cu and Mo as evidenced by the low levels in the rivulets. Variance in Fe, Mn and the metal oxy-anions was associated with factors related to redox cycling and adsorption reactions in the wetland sediments. In streams, DOC and metals with a high affinity for DOC were associated with a factor which also included negative loadings for groundwater-sourced elements, reflecting the importance of seasonal hydrologic events

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which flush DOC and metals from wetland sediments and dilute groundwater sourced metals. Redox processes were of secondary importance in the streams but of primary significance in the rivulets, documenting the importance of anoxic conditions in wetland sediments on groundwater en route to the stream.

Keywords Trace elements · Metals · Wetlands · Streams · Biogeochemistry

Introduction

The influence of wetlands in regulating the water quality of streams has received considerable attention (Gilliam 1994; Johnson 1986; Rember and Trefry 2004; Sinclair et al. 1989). For many systems and species, wetlands act as a chemical sink. For example, Emmett et al. found that a riparian wetland effected a reduction of dissolved nitrogen (38%), phosphate (94%), aluminum (21%), iron (54%), dissolved organic carbon (DOC) (34%), and silica (21%) loadings to a stream at the outflow of a forested catchment. Dubinski et al. (1986) observed retention of approximately 50% of the cadmium, chromium, copper, and zinc, as well as 30% of the lead, in sewage sludge applied to the surface soils of a freshwater tidal wetland. Similarly, Khan and Brush (1994) found that nutrients and metals were retained in the sediments of a freshwater tidal marsh. However, wetlands may also serve as a seasonally-variable source of trace elements to streams. For example, export can result from the microbially-mediated anaerobic decomposition of organic matter and the subsequent reduction of Fe and Mn oxy-hydroxides which releases trace elements adsorbed to the Fe/Mn oxy-hydroxides (Abdelfattah and Wada 1981; Carroll et al. 1998; Fox and Doner 2003; La Force et al. 2002; Trolard et al. 1995).

Though it is clear that biogeochemical processes occurring in wetlands have the potential to influence stream chemistry, few investigations have examined the geochemical controls influencing trace metals in natural wetland-dominated streams (Bendell-Young et al. 2002; Olivie-Lauquet et al. 2001) and even fewer have looked beyond a narrow suite of trace elements. Thus, considerable uncertainty remains over the mechanisms regulating trace metal chemistry in wetland-influenced streams.

The overall goal of this research was to move towards an improved understanding of the role of hydrologic and biogeochemical processes in influencing the export of trace elements from wetlands through analysis of element concentrations as well as hydrologic and biogeochemical drivers in streams, wetlands, and their groundwater sources. By examining a very large suite of 39 elements, we sought to provide critical new information on poorly-researched elements and a more robust picture of factors regulating contrasting groups of trace elements in wetland-stream systems. Many of the trace elements are toxic, and anthropogenic source contributions to even remote watersheds are large. Thus a more complete understanding of the factors regulating their behavior is important in assessing their impact on aquatic systems. In this paper, we provide a comparison of trace element levels in three northern Wisconsin streams and two wetland rivulets associated with catchments of varying wetland area and contrasting hydrologic regimes and water sources. In addition, we present a statistical analysis of trace elements and indicators of biogeochemical processes in the streams and rivulets. Our work addresses the following general questions:

- (1) How do stream water provenance and biogeochemical processes influence trace element levels in wetland-influenced streams?
- (2) What is the impact of seasonal hydrologic events on trace element levels in streams?
- (3) Which hydrologic and/or biogeochemical processes appear to be most important in influencing trace element cycling in wetland-influenced streams?

The influence of water source and seasonal events on major element stream geochemistry and biogeochemical processes linked to trace element cycling in these systems is described by Kerr (2007). We expect water source and flowpath to be a primary factor driving differences between the streams and rivulets and seasonal hydrologic events to have a large influence on trace metals. With respect to identifying dominant biogeochemical and hydrologic processes, we used factor analysis to support our interpretations of the main processes controlling the observed trace element behavior in the three study systems.

Methods

Site description

The research was carried out within the Trout Lake watershed located in the Northern Highlands Lake District of north-central Wisconsin (Fig. 1). This area is also a research site of the U.S. Geological Survey's Water, Energy, and Biogeochemical Budgets (WEBB) Program (Elder et al. 1992) and the National Science Foundation's Long-Term Ecological Research (LTER) Program (Magnuson et al. 1984).

Three tributary streams feeding Trout Lake, namely Allequash Creek, Stevenson Creek, and North Creek, were the primary research sites (Table 1). Allequash Creek exhibits weak to moderate ground-water discharging conditions, where ground-water

flows from the aquifer to the stream, along the reach of stream above our sampling site. The reach of Stevenson Creek under consideration in this study provides a hydrologic contrast in that it is a groundwater recharge system where surface water from the stream flows to the aquifer. A nearby culvert and a steep embankment contribute to the downwelling conditions present at the Stevenson Creek site. North Creek exhibits weak groundwater discharge conditions and thus falls in-between Allequash Creek and Stevenson Creek hydrologically. The hydrologic sub-systems in the region are ground-water dominated, in most cases, with ground-water accounting for >90% of annual stream flow in Allequash Creek. Wetlands make up 22, 7, and 14% of the Allequash, Stevenson, and North Creek sub-basins watersheds above the primary sampling site in each system (Elder et al. 2000).

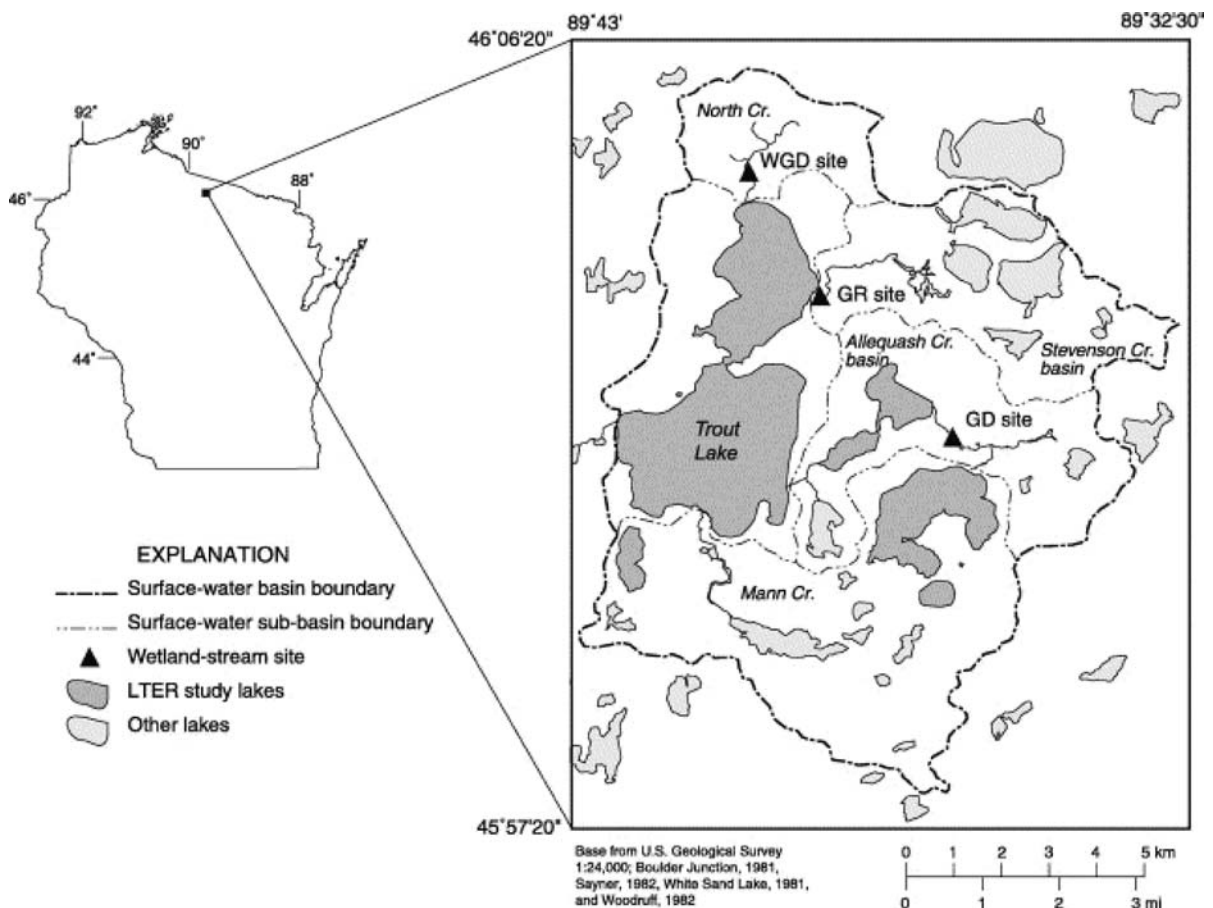


Fig. 1 Map of the study area in Wisconsin (USA). Wetland-stream sites GD, WGD, and GR refer to groundwater discharge, weak groundwater discharge, and groundwater recharge conditions, respectively. Modified from Hunt et al. (2006)

Table 1 Wetland area of the Trout Lake tributary catchments

Stream	Surface water drainage area (km ²)	Groundwater drainage area (km ²)	Wetland area	
			(km ²)	%
Allequash (study reach)	21.8 (4.6)	35.0	1.0	9 (22)
Stevenson at Trout Lake	20.6	15.0	1.5	7
North at Trout Lake	9.3	9.0	1.3	14

Field sampling preparation

All water sampling was conducted using trace metal clean techniques developed during past studies of trace metal cycling in lakes and watersheds (Babiarz et al. 1998, 2001; Hurley et al. 1996, 1998; Shafer and Armstrong 1991; Shafer et al. 1997, 1999). Briefly: low-density polyethylene bottles used for trace metal sample collection were soaked in 20% v/v HNO₃ (reagent grade) for 2 days, rinsed, soaked in 1% v/v HNO₃ (trace metal grade) for 2 days, rinsed, dried, and double-bagged in HDPE zip-lock bags. Teflon tubing and filter adapters used in sample collection were rinsed with MilliQ water, placed in a heated (170°C) concentrated nitric acid bath overnight, rinsed four times with MilliQ water, dried, and double-bagged. C-Flex peri-pump head tubing used during sample collection was rinsed with MilliQ, placed in a room temperature 10% HCl bath for 2–3 days, dried, and double-bagged. The 0.45 µm high-capacity polypropylene capsule filters (Meissner) were prepared by soaking the filter in 20% HCl for 2 days, draining and filling the capsule with 1% HCl to soak for two more days, then draining and rinsing the capsule with MilliQ before double-bagging in HDPE zip-lock bags. Low-density polyethylene (LDPE) bottles used for nitrogen species sample collection were soaked in 10% HCl for 1 day, dried, and single-bagged. Glass vials and bottles used for dissolved organic carbon (DOC), sulfide, and specific UV absorption (SUVA) sample collection were soaked in 10% HCl for 2–3 days, rinsed and dried, then ashed at 475°C for 8 hours and single-bagged after cooling. Glass vials (headspace free) used for ¹⁸O/²H were soaked in 10% HCl for 2–3 days, rinsed, dried, and single-bagged.

Field sampling

Extensive field sampling campaigns at Allequash and Stevenson Creeks' watersheds were conducted between March 2004 and October 2005. In addition,

Allequash Creek, Stevenson Creek and North Creek were sampled year round on a monthly basis with higher intensity during melt periods. Two rivulets originating in the riparian wetland and feeding into Allequash Creek were also sampled monthly during this period. Groundwater samples from hillslopes and sediments/aquifers underlying the wetland were collected from wells and piezometers installed by the U.S. Geological Survey (Elder et al. 1992; USGS 2006). Stream discharge was monitored continuously at the Allequash Creek and Stevenson Creek sampling sites with streamflow gages operated and maintained by the U.S. Geological Survey (Elder et al. 1992). Stream waters and groundwaters were sampled using a system consisting of all-Teflon sampling lines, trace-metal clean C-flex pump-head tubing, and a peristaltic pump with in-line filtration (Babiarz et al. 1998, 2001; Hurley et al. 1996, 1998; Shafer and Armstrong 1991; Shafer et al. 1997, 1999). Unfiltered stream samples were collected for determination of suspended particulate matter (SPM) concentration and total trace metal concentrations. Discrete stream and groundwater samples were collected for filtered metals, nitrogen species, dissolved organic carbon (DOC), specific UV absorption (SUVA), water isotopes, sulfide, and Fe(II). Analytes were stabilized immediately after collection using appropriate preservatives. Measurements of temperature, pH, dissolved oxygen, and specific conductance were made in-situ using a Hydrolab Scout2 Sonde.

Laboratory analysis

Trace/major elements

Samples were acidified with 50% v/v Ultrex grade HNO₃ to yield 1.6% (~0.25 N) HNO₃ and a pH < 2. A large suite (38 total) of elements (Na, K, Ca, Mg, Al, Si, S, P, As, Mn, Fe, Co, Ni, Cu, Zn, Cd, Ag, Pb, V, Cr, Mo, Sb, Tl, U, Sr, Ba, Li, Ti, Rb, Cs, La, Y, Sn, Ce, Eu, Ho, Yb, Pt) were quantified on a Thermo-

Finnigan Element 2. This is a magnetic-sector inductively coupled plasma mass spectrometer capable of multi-element analysis at concentrations ranging from low pg/l to tens of mg/l (at higher resolutions). Mass resolution (low (300), medium (5,000) and high (10,000)) was optimized for each element to maximize sensitivity but ensure resolution of spectral interferences. Multi-element standards were prepared to match the concentration range found in the samples (e.g. Ca: 0.01–20 ppm, Na, Mg, S: 0.01–5 ppm, Si: 1–10 ppm, Fe: 0.004–6 ppm, trace metals: 0.02–10 ppb). Aqueous samples were introduced into the plasma with a peristaltic pump at a rate of 0.5 ml/min. The internal standard addition (net 2 µg/l gallium, indium, and bismuth in 2% HNO₃) was done on-line with the aid of a mixing coil prior to the FEP low-flow nebulizer and quartz cyclonic spray chamber sample introduction system. Routine quality assurance measures include the acquisition of multiple isotopes, extensive blank measurements, duplicate sample analysis, matrix spike recoveries, and frequent analysis of the standard reference material SLRS-4. Quality assurance data including median sample to blank concentration ratios and percent recoveries of certified reference materials are shown in Tables 2, 3 respectively.

DOC

DOC measurements were made using a Shimadzu TOC-V CSH/CSN Total Organic Carbon Analyzer. A calibration curve (potassium hydrogen phthalate) followed by two Milli-Q blanks was run every 10 samples. A second source carbon standard prepared from NH₂C(CH₂OH)₃ was used for quality assurance. Reported DOC concentrations were obtained by averaging the results from duplicate samples (minimum three replicates each) analyzed during separate instrument runs. Analytical precision was typically in the range of 1–4%.

SUVA

UV–VIS scans (250–820 nm) were performed on a Shimadzu UV-2401PC UV–VIS Recording Spectrophotometer. Samples were allowed to warm to room temperature prior to analysis. Quartz cells of both 1.0 and 10.0 cm path lengths were used to provide accurate absorbances at higher wavelengths. SUVA₂₅₄ values

Table 2 Median element blank concentrations and sample: blank ratios from ICP-MS analysis

Element	Median blank concentration (<i>n</i> = 168)	Median sample concentration (<i>n</i> = 660)	Median sample: blank ratio
Ag (nM)	0.0081	0.020	23
Al (µM)	0.0016	0.26	1,567
As (nM)	0.017	4.6	270
Ba (µM)	0.00003	0.052	18,934
Ca (µM)	0.050	260	5,195
Cd (nM)	0.0011	0.018	17
Ce (nM)	0.0003	0.22	774
Co (nM)	0.0024	0.59	250
Cr (nM)	0.017	6.0	352
Cs (nM)	0.0005	0.012	267
Cu (nM)	0.031	1.0	33
Eu (nM)	0.0006	0.048	84
Fe (µM)	0.0045	25	5,530
Ho (nM)	0.0001	0.0088	94
K (µM)	0.011	15	1,431
La (nM)	0.0002	0.13	772
Li (µM)	0.0003	0.044	145
Mg (µM)	0.012	114	9,888
Mn (µM)	0.0001	0.91	9,592
Mo (nM)	0.018	0.85	47
Na (µM)	0.018	71	4,262
Ni (nM)	0.051	1.3	26
P (µM)	0.0013	0.20	153
Pb (nM)	0.0023	0.13	56
Pt (nM)	0.0006	0.0026	4
Rb (nM)	0.0090	3.8	421
S (µM)	0.19	18	95
Sb (nM)	0.0009	0.058	68
Si (µM)	0.13	238	1,831
Sn (nM)	0.14	0.18	1
Sr (µM)	0.0001	0.22	4,402
Ti (nM)	0.031	5.1	162
Tl (nM)	0.0001	0.0033	32
U (nM)	0.0001	0.070	495
V (µM)	0.00001	0.014	1,866
Y (nM)	0.0011	0.39	359
Yb (nM)	0.0001	0.016	291
Zn (nM)	0.21	4.1	20

were determined by dividing the UV absorbance at 254 nm by the DOC concentration and are given in units of liter per mole carbon per meter (l*⁻¹*mol OC⁻¹*cm⁻¹).

Table 3 Median measured concentrations of certified reference material (SLRS-4) and percent recoveries

Element	Certified value (µg/l)	Median measured value (µg/l) (n = 46)	Median percent recovery
Al	54	55	102.1
As	0.68	0.79	116.2
Ba	12.2	12.9	105.7
Ca	6,200	6,003	96.8
Cd	0.012	0.015	127.9
Co	0.033	0.036	110.4
Cr	0.33	0.31	94.2
Cu	1.81	1.87	103.1
Fe	103	103	99.5
K	590	628	106.4
Mg	1,600	1,568	98.0
Mn	3.37	3.40	101.0
Mo	0.21	0.20	94.4
Na	2,300	2,214	96.3
Ni	0.67	0.72	107.4
Pb	0.086	0.079	91.8
Sb	0.23	0.27	117.3
Sr	26.3	27.8	105.8
U	0.05	0.05	102.1
V	0.32	0.35	109.5
Zn	0.93	1.29	138.8

Values were corrected for Fe interference, according to the relationship found by Weishaar et al. (2003), by subtracting $0.085 \cdot [\text{Fe}^{3+} \text{ (mg/l)}]$ from the UV absorbance value.

Nitrogen speciation

Ammonia and Nitrate + Nitrite were determined on sulfuric acid stabilized samples on Lachat QuickChem 8000 flow injection analyzers. The phenolate/nitroprusside chemistry was used for the ammonia measurement, and the cadmium reduction/sulfanilamide—*N*-1-naphthylethylenediamine · 2HCl method was used for nitrate + nitrite determination. Limits of detection (LOD's) were 4 and 3 ppb, respectively. Precision at >20 ppb was better than 10%.

SPM

SPM determination was performed using 0.4 µm 47-mm polycarbonate filters in a plastic filtration

apparatus. Filters were immediately frozen, then oven dried for 24 h at 38°C. Tared filters were re-weighed on a microbalance to a significance level of 1 µg.

Oxygen-18 isotopes

Isotopic analysis was performed by the USGS—Reston Stable Isotope Laboratory in Reston, Virginia. Samples were measured for ^{18}O using an automated version (Revesz and Coplen 2003) of the CO_2 equilibration technique of Epstein and Mayeda (1953). Results are reported in per mill relative to VSMOW (Vienna Standard Mean Ocean Water) and normalized (Coplen 1994) on scales such that the oxygen isotopic value of SLAP (Standard Light Antarctic Precipitation) is −55.5 per mill. The analytic error (2σ) of the oxygen isotopic results is 0.2 per mill.

Sulfur species

Sulfate was measured by ion chromatography while sulfide was measured using an ion-selective electrode. Sulfide samples were collected directly into sulfide anti-oxidant buffer (SAOB) (1:1) in the field and analyzed immediately upon returning to the lab (typically within 24 h). A calibration curve was prepared using $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and a continuing verification standard was run every 10 samples. Sulfide levels in streams were negligible (typically < 0.3 µM) in comparison to sulfate values. The LOD for sulfide was 0.05 µM.

Iron speciation

Ferrous iron (Fe(II)) concentration was determined using the ferrozine method (Stookey 1970). Ferrozine was added immediately upon sample collection in the field with minimal exposure to air. Absorbance of the colored complex was determined at 562 nm on a Shimadzu UV-2401PC UV-VIS Recording Spectrophotometer.

Statistical analysis

Principal component analyses were performed using Systat® Version 11.00.01 software. Pairwise deletion and varimax rotation were specified. The following environmental and geochemical drivers were included in the analysis: Julian day, stream discharge,

temperature, pH, DO, specific conductance, SPM, DOC, SUVA₂₅₄, NH_4^+ , $\text{NO}_2^- + \text{NO}_3^-$, and SO_4^{2-} . The filterable elements analyzed include: Ag, Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cs, Cu, Eu, Fe, Hg, Ho, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pt, Rb, S, Sb, Si, Sn, Sr, Ti, Tl, U, V, Y, Yb, and Zn. The particulate metals included were: Al, Cd, Ce, Cr, Cs, Cu, Eu, Fe, Hg, La, Mn, Pb, Ti, Yb, and Zn. A separate principal components analysis containing the aforementioned variables was first performed for each individual stream and rivulet, but the results were very similar among the three streams and among the two rivulets. Thus, we pooled the data for the streams (Allequash Creek, Stevenson Creek, and North Creek) and rivulets (Rivulet1 and Rivulet2). The results from principal components analysis performed on the pooled data sets are presented here. Elements deemed to be representative of important geochemical processes in the system (Mineral weathering: Ca; Metal transport by DOC and SPM: Al, Ce, La, Pb, Zn; Redox status and precipitation/dissolution/adsorption: Cu, Fe, Mo, SO_4^{2-}) are discussed in detail. Elements with behavior similar to the representative elements or which showed little variation among waters are not discussed here.

Results

Trace and major element concentrations are influenced by hydrologic sourcing/events and a variety of geochemical processes including: mineral weathering, transport by DOC, transport by SPM, redox cycling, and by precipitation/dissolution and adsorption/desorption reactions. To assess the importance of many of these factors on individual elements, we examined patterns among elemental concentrations in the streams, rivulets, and groundwater sources (terrestrial recharge, lake recharge, older lake recharge) as related to water source, seasonality, and particle partitioning. Statistical correlation and principal components analysis were used to support our interpretations of the relative importance of geochemical factors driving trace element chemistry in the study systems. Median elemental concentrations are given in Table 4. Concentrations varied widely among the source waters, but were more similar among the three streams (see Cu, Ca, and SO_4^{2-} as examples). The coefficients of variation from the

pooled data set (all five streams and rivulets) for each of the elements are shown in Fig. 2. Values ranged from 0.2 to 2 but fell between 0.5 and 1 for the majority of elements. Major elements tended to have lower coefficients of variation (20–40%). Variability in DOC was also relatively low (50%) and several elements (examples including Cd, Cr, Cu, Pb, Sb) fell within the 50–70% range. Higher variability (80–100%) was seen for Mo, Mn, Sn, V, and Zn. Iron was among a number of elements with variability greater than 100%.

The principal components analysis provided insight into the factors influencing trace element cycling by grouping intercorrelated variables together, thereby helping to identify the nature of the relationship among the variables. Factor loadings plots (see example in Fig. 3) show the clustering of variables resulting from the analysis. Clusters of variables at the extremes of the factors load highly on the respective factors. We focused on the top three factors determined for each stream or rivulet. The nature of the influences underlying additional factors was less clear and not used in our interpretations.

We attempted to provide geochemically-based explanations for the observed groupings of the variables loading on each factor. Variables loading on the three factors for both the streams and rivulets are listed in Table 5. ‘Factor 1’ in the streams included several elements with a high affinity for DOC (Al, Cd, Cu, Hg, La, Pb, Ti, Yb, Zn) which load positively on the factor and groundwater-sourced elements (Ba, Ca, Mg, Na, Si, Sr) which load negatively on the factor. ‘Factor 2’ was comprised of redox sensitive elements (Fe, Mn, SO_4^{2-}) and oxy-anions (Cr, Mo, U, V), while ‘Factor 3’ contained SPM and particulate forms of metals (Al, Ce, Cr, Cu, Pb, Ti, Yb, Zn). In the rivulets, groundwater-sourced elements (Ba, Ca, Mg, Na, Si, Sr) and redox sensitive metals (Fe, Mn, SO_4^{2-}), all loaded on ‘Factor 1’. ‘Factor 2’ contained DOC-influenced elements (Cd, Ce, Cu, La, Pb, Tl, Zn) and oxy-anions (As, Cr, Mo, U, V) while ‘Factor 3’ contained particulate metals (Al, Ce, La, Pb, Ti, Yb). Several of the variables included in the analysis did not load on the three principal factors identified and thus are not included in the lists. These variables include: Ag, As, Cd(P), Co, discharge, Eu, Eu(P), Hg(P), Ho, K, Li, methyl-Hg, Mn(P), NH_4^+ , Ni, NO_3^- , pH, P, specific conductance, Sn, temp., Tl, (streams); Ag, Cd(P), Cr(P), Cu(P), Co,

Table 4 Median concentration (standard deviation) of elements (nM), pH, and DO (mg/l) in groundwater and surface water

	GW (lake)	GW (older)	GW (terr)	Allequash	Stevenson	North	Rivulet1	Rivulet2
pH	6.3 (0.2)	8.2 (0.1)	6.4 (0.1)	7.0 (0.5)	7.0 (0.7)	7.1 (1.0)	6.6 (0.8)	6.4 (0.9)
DO	0.4 (0.4)	0.5 (0.7)	7.6 (1.3)	8.6 (1.8)	7.4 (2.7)	9.7 (3.0)	4.2 (1.9)	4.6 (1.6)
Ag	0.03 (0.08)	0.01 (0.03)	0.01 (0.07)	0.02 (0.14)	0.01 (0.09)	0.01 (0.08)	0.03 (0.19)	0.04 (0.18)
Al*	0.03 (0.05)	0.04 (0.01)	0.03 (0.05)	0.23 (0.19)	0.14 (0.22)	0.48 (0.4)	0.26 (0.12)	0.33 (0.13)
As	1.2 (0.5)	9.2 (3.7)	0.7 (0.1)	4.8 (0.8)	4.4 (1.7)	5.8 (0.9)	2.5 (1.2)	2.1 (0.7)
Ba*	0.01 (0)	0.05 (0)	0.02 (0)	0.04 (0.01)	0.05 (0.01)	0.03 (0.01)	0.04 (0.01)	0.03 (0.01)
DOC*	76.1 (3.3)	88.1 (3.7)	69.2 (11)	278.3 (98)	283.5 (103.4)	375.4 (267.9)	334.3 (139.4)	409.3 (102.9)
Ca*	153.9 (16.6)	405.5 (33.3)	206.4 (26.2)	284.2 (47.9)	312 (56.8)	264.1 (53.9)	175 (45.3)	153.6 (30.3)
Cd	0.05 (0.02)	0.01 (0.01)	0.01 (0.01)	0.02 (0.02)	0.02 (0.01)	0.03 (0.02)	0.01 (0.01)	0.01 (0.01)
Ce	0.91 (0.63)	0.01 (0.01)	0.02 (0.05)	0.18 (0.09)	0.22 (0.14)	0.15 (0.13)	0.13 (0.05)	0.09 (0.07)
Co	0.46 (0.06)	0.09 (0.02)	0.35 (0.04)	0.37 (0.19)	0.65 (0.21)	0.36 (0.12)	0.24 (0.14)	0.44 (0.16)
Cr	0.3 (1.4)	0.1 (2.8)	11.1 (1)	6.7 (1.2)	4.4 (1.3)	8.7 (1.6)	1.8 (0.7)	1.2 (0.4)
Cs	0 (0)	0.01 (0.01)	0 (0)	0.01 (0)	0.01 (0.01)	0.03 (0.04)	0.01 (0)	0.01 (0)
Cu	7 (1)	0.1 (0)	3.6 (1.1)	1.2 (0.6)	1.3 (0.7)	1.2 (0.9)	0.2 (0.6)	0.4 (0.5)
Eu	0.03 (0.01)	0.04 (0.04)	0.04 (0.01)	0.02 (0.02)	0.03 (0.02)	0.02 (0.01)	0.02 (0.02)	0.02 (0.02)
Fe*	0.09 (0.06)	0.34 (0.11)	0.01 (0.02)	4.03 (1.17)	8.54 (3.12)	1.33 (0.91)	27.01 (32.95)	20.34 (5.42)
Hg	NA	NA	NA	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
MeHg	NA	NA	NA	0.001 (0)	0.001 (0)	0.001 (0.001)	0.001 (0)	0.001 (0)
Ho	0.01 (0)	0.001 (0)	0.015 (0.005)	0.004 (5.436)	0.005 (4.96)	0.003 (5.303)	0.004 (4.263)	0.002 (1.865)
K*	11.6 (1)	22.9 (2.3)	13.6 (1.5)	14.8 (2.5)	17.4 (5)	21.7 (5.7)	10.1 (2.7)	10.5 (3.7)
La	0.54 (0.16)	0.01 (0.01)	0.71 (0.25)	0.07 (0.04)	0.1 (0.05)	0.06 (0.05)	0.06 (0.02)	0.04 (0.02)
Li*	0 (0)	0.04 (0)	0.03 (0.05)	0.08 (0.02)	0.1 (0.02)	0.17 (0.04)	0.04 (0.01)	0.03 (0.03)
Mg*	73.7 (7)	136.4 (8.6)	102 (15.4)	122.2 (24.3)	135.1 (28.7)	95 (20.2)	87.7 (22.8)	74.7 (16.6)
Mn*	0.38 (0.03)	1.26 (0.19)	0 (0)	0.31 (0.12)	0.83 (0.48)	0.14 (0.08)	0.85 (0.7)	0.52 (0.15)
Mo	0.5 (0.3)	1.1 (1)	1 (0.2)	1.6 (0.3)	1.2 (0.2)	3.6 (1.1)	0.2 (0.1)	0.2 (0.1)
NH ₄ ⁺ *	0.3 (0.1)	12 (0.2)	0.1 (0.1)	1.8 (1.4)	1.5 (2.2)	1.5 (1.2)	3.7 (4.6)	6.2 (1.8)
NO ₃ [*]	0 (0.2)	0 (0)	2.6 (0.3)	1.7 (3)	1.4 (5.9)	3.3 (8.4)	0.7 (2.7)	0.9 (3.2)
Na*	48.8 (3.1)	76.7 (5)	62.4 (6.6)	69.8 (11.5)	68.5 (14.5)	58.6 (16.2)	70.2 (13.4)	65.1 (12.2)
Ni	0.62 (0.78)	0.35 (0.48)	0.69 (1.08)	0.92 (2.77)	1.08 (0.91)	0.95 (0.81)	0.77 (0.45)	0.97 (1.16)
P*	0.04 (0.01)	0.94 (0.29)	0.04 (0.03)	0.17 (0.06)	0.1 (0.06)	0.2 (0.11)	0.15 (0.11)	0.08 (0.06)
Pb	0.01 (0.01)	0 (0.01)	0 (0)	0.2 (0.12)	0.19 (0.11)	0.24 (0.2)	0.19 (0.1)	0.15 (0.11)
Pt	0.002 (0.001)	0.002 (0.001)	0.004 (0.052)	0.001 (0.027)	0.001 (0.038)	0.002 (0.042)	0.001 (0.001)	0.001 (0.055)
Rb	6 (0.5)	4.4 (0.1)	0.6 (0.1)	1.8 (0.8)	3.4 (1.4)	3.7 (2.4)	3.8 (1.1)	3.7 (1.2)
S ²⁻ *	0.01 (0.01)	0.25 (0.30)	0.00 (0.10)	0.00 (0.10)	0.03 (0.11)	0.04 (0.12)	0.23 (0.24)	0.77 (0.47)
SO ₄ ^{2*}	35.3 (1.8)	1.9 (0.5)	62.2 (7.8)	47.2 (6.3)	29 (6.6)	56.1 (9.2)	5.5 (5.7)	10.1 (4.9)
Sb	0.15 (0.14)	0.03 (0.05)	0.04 (0.01)	0.12 (0.09)	0.1 (0.05)	0.11 (0.05)	0.05 (0.04)	0.07 (0.06)
Si*	75.3 (7.7)	215 (36.8)	208.9 (25.8)	190.2 (41.3)	210 (58.4)	159.9 (44.5)	246.1 (46.5)	206.7 (27.4)
Sn	0.1 (0.24)	0.23 (1.03)	0.14 (0.96)	0.14 (0.19)	0.18 (0.2)	0.17 (0.12)	0.11 (0.08)	0.2 (0.31)
Sr*	0.15 (0.01)	0.32 (0.01)	0.21 (0.01)	0.21 (0.03)	0.24 (0.04)	0.2 (0.03)	0.18 (0.05)	0.15 (0.03)
Ti	0.27 (0.18)	0.13 (0.04)	0.46 (0.2)	3.1 (2.46)	3.98 (2.74)	4.59 (4.43)	3 (1.33)	2.85 (1.48)
Tl	0.008 (0.001)	0.002 (0.003)	0.005 (0.001)	0.005 (0.001)	0.004 (0.003)	0.008 (0.005)	0.003 (0.002)	0.004 (0.002)
U	0.01 (0.01)	0 (0)	0.05 (0.11)	0.21 (0.06)	0.34 (0.1)	2.55 (1.06)	0.01 (0)	0.01 (0)
V*	0.06 (0)	0.01 (0)	0.02 (0.02)	0.03 (0.01)	0.01 (0)	0.03 (0.01)	0 (0)	0 (0)
Y	0.68 (0.16)	0.1 (0.04)	1.47 (0.34)	0.13 (0.09)	0.3 (0.13)	0.13 (0.11)	0.22 (0.09)	0.11 (0.07)
Yb	0.03 (0)	0 (0.01)	0.04 (0.01)	0.01 (0)	0.01 (0)	0.01 (0.01)	0.01 (0)	0 (0)
Zn	2.2 (6)	0.3 (0.2)	2.4 (8.5)	3.7 (3.5)	4.7 (6.9)	7.3 (5.9)	2.9 (2.7)	2.4 (1.6)

*Indicates units are in μM

Fig. 2 Coefficient of variation for 38 elements. Data for all streams and rivulets were pooled

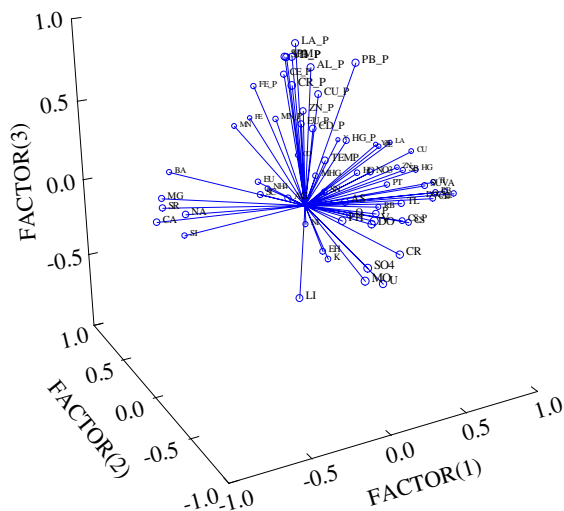
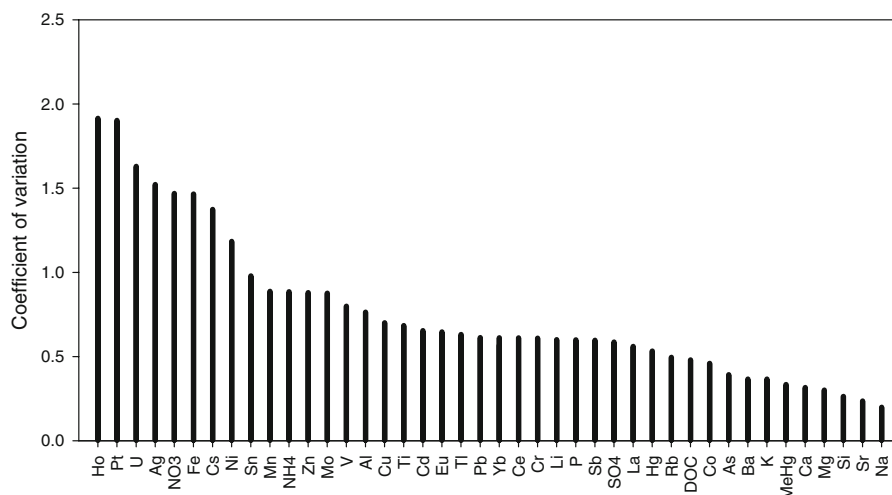


Fig. 3 Factor loadings for combined streams (Allequash Creek, Stevenson Creek, North Creek). The points in the plot are variables, and the coordinates are the rotated loadings

Eu, Eu(P), Li, methyl-Hg, Mn(P), Ni, Pt, Rb, Sn, SPM, Zn(P) (rivulets). It is clear from the full suite of measured redox-sensitive tracers that the rivulets are the site of more active redox cycling than the streams. This active cycling results in the continuous production of “fresh” iron-oxide particles. Certain elements (e.g. potentially redox sensitive As) loaded on a particular factor (Factor 2) in the rivulets but not in the streams, indicating the influence of the associated factor is better reflected in the rivulet data than the stream data. Factor 2 in the rivulets incorporates both the oxyanion and DOC-reactive elements, and the loading of As here suggests that sorption to oxide

surfaces or binding to oxides associated with DOC may be influencing As levels more so than direct redox cycling ($\text{III} \leftrightarrow \text{V}$). Suspended particle concentrations in both the stream and rivulet systems are very low and exhibit high organic matter and relatively low clay content. These conditions/characteristics are unfavorable for particle-partitioning of marginally reactive solutes, e.g. K, Li, and Tl. (e.g. sorption of K to clay minerals). The alkali metals (K, Rb, Cs) and alkaline earths (Mg, Ca, Sr, Ba), however, do exhibit moderate to strong loadings on Factor 1 in the streams and rivulets which we interpret as reflecting water source contributions. For the alkali metals, the loadings are greater for Rb and Cs, which likely reflects their greater preference (over K) for clay mineral partitioning. pH was relatively invariant, thus explaining its lack of inclusion in the three principal factors. Concentrations of Ag and Pt were near analytical detection levels while levels of Ni and Sn were variable but not driven by ‘Factors 1–3’.

To address the robustness of the factor outputs, we assessed the sensitivity of the three-factor principal components analyses with respect to the following: (1) Five-factor versus three-factor extraction, (2) exclusion of variables which did not load on any of the three factors, (3) inclusion of only the top 10 variables loading on each of the three factors, (4) exclusion of spring melt data, and (5) separation of data by year. When the PCA was run with five factors rather than three factors, the magnitudes of the loadings varied minimally (1–2%) and a few variables switched factors (more so in the rivulet PCA than the stream PCA), but the overall trends were

Table 5 Variables comprising the factors influencing trace element cycling in streams and rivulets of the Trout Lake watershed

Streams			Rivulets		
Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
Al	Fe	La(P)	Sr	Ce	Ti(P)
Ti	Mo(–)	SPM	Ca	La	Al(P)
DOC	SO ₄ ^{2–} (–)	Yb(P)	Ba	Pb	La(P)
Pb	Mn	Ti(P)	Cs	Ti	Ho
Cu	V(–)	Pb(P)	Mn	Zn	Sp. Cond(–)
La	Co	Al(P)	Mg	Cr	Pb(P)
Ca(–)	Cr(–)	Cr(P)	Si	Cd	Yb(P)
Hg	U(–)	Ce(P)	Fe	Cu	NH ₄ ⁺ (–)
Zn	Fe(P)	Cu(P)	Na	Mo	Ce(P)
Yb	DO(–)	Zn(P)	SO ₄ ^{2–} (–)	U	DO
Sr(–)			Sb(–)	Al	
Ce			Temp	Yb	
Cd			SUVA(–)	DOC	
Mg(–)			K	V	
Sb			NO ₃ [–] (–)	Cs(P)	
Na(–)			Fe(P)	As	
SUVA			pH	Y	
Y			Hg(P)(–)	P	
Pt				Tl	
Cs				Hg	
Rb					
Si(–)					
Ba(–)					
Cs(P)					

(P) indicates particle phase.
(–) indicates a negative factor loading. Variables are included when $r > 0.5$ and are listed from highest to lowest r value

preserved. The additional factors (4 and 5) each accounted for a small amount (<7%) of variance. In the streams, discharge and several monovalent ions (As, K, Li, U) loaded on 'Factor 4', possibly indicating groundwater influence, while Ho, NH₄⁺, specific conductance, and temperature loaded on 'Factor 5'. In the rivulets, Al(P), Ce(P), Cr(P), Eu(P), Fe(P), Pb(P), and Yb(P), loaded on 'Factor 4' (clearly particulate-driven), while Co, methyl-Hg, specific conductance and Rb loaded on 'Factor 5'. Exclusion of variables which did not load on the original three factors also resulted in some variation in the magnitudes of loadings and the switching of some (<7) variables to different factors (again more so in the rivulet PCA than the stream PCA) but the overall results and interpretation were unchanged. Inclusion of only the top 10 variables loading on each of the three factors resulted in a different order for the factors, meaning a different percentage of variance

explained by each factor. However, the factors were comprised of the same variables. Removal of the spring melt data resulted in only minor changes in the magnitudes of variable loadings and the composition of the factors. Separation of the data by year (March 2004–January 2005: 44 data points for the streams, 15 data points for the rivulets; and February 2005–September 2005: 32 data points for the streams, 22 data points for the rivulets) yielded more pronounced changes in loading magnitudes and factor composition and also altered the percentage of variance explained by factors in the streams. Overall, these results suggest that the PCA was most sensitive to removal of some of the variables loading on the three factors and separation of the data by year. Still, the overarching factors were reasonably robust and the variables generally showed the same trends.

The drivers of the patterns in the trace element chemistry of these systems include: (1) seasonal

Table 6 Geochemical or hydrologic nature of the factors explaining the relationship between trace elements and geochemical drivers in Allequash Creek, Stevenson Creek, North Creek, Rivulet1, and Rivulet2

Factor	Nature of factor	
	Streams	Rivulets
1	Seasonal hydrologic events	Water source/redox
2	Redox/oxy-anions	DOC/oxy-anions
3	Particle-partitioning	Particle-partitioning

hydrologic events, (2) redox/oxy-anions, (3) water source/redox, (4) DOC, and (5) particle-partitioning, and our interpretation of the nature of these factors is summarized in Table 6. Some overlap between these categories was observed, resulting from differences between the streams and rivulets. For instance, Ca loads (negatively) on the ‘seasonal hydrologic events’ factor in the streams and (positively) on the ‘water source/redox’ factor in the rivulets. The ‘seasonal hydrologic events’ driver includes two groups of elements: those which are flushed from wetland sediments as a result of seasonal hydrologic events, and those which are groundwater sourced and experience a dilution effect as a result of seasonal hydrologic events. The ‘redox/oxy-anions’ driver includes both metal oxy-anions, most of which are redox sensitive, and cationic redox-sensitive elements. ‘Water source/redox’ is a driver encompassing elements influenced by weathering reactions along hydrologic flowpaths and is thus influenced by water-mineral contact time. This driver also includes redox sensitive metals (Fe, Mn). The ‘DOC’ driver incorporates DOC and numerous metals with a high affinity for DOC. The ‘particle-partitioning’ driver includes SPM and metals which tend to have a significant particulate fraction and/or a high particle-partition coefficient. In the case of the rivulets, SPM is not included in the ‘particle-partitioning’ factor.

The three primary factors identified accounted for nearly half of the variance in the trace element concentration data (Table 7). The ‘seasonal hydrologic events’ driver explained the largest percentage of the variance (22%) for the streams while ‘water source/redox’ accounted for the largest percentage of the variance (24%) in the rivulets. ‘Redox/oxy-anions’ accounted for 14% of the variance in the streams. ‘DOC’ explained 19% of the variance in the

Table 7 Percent variance explained by the factors influencing trace metal cycling in Allequash Creek, Stevenson Creek, North Creek, Rivulet1, and Rivulet2

Factor	% Variance explained by factor	
	Streams	Rivulets
1	22	24
2	14	18
3	13	11
Total	49	53

rivulets. The ‘particle-partitioning’ driver explained 11 and 13% of the variance in the streams and rivulets, respectively.

Discussion

Water source

Water source factors interact with biogeochemical processing in the wetland to determine the retention and fate of elements in the larger system. A detailed discussion of the water sources contributing to the streams and rivulets, as determined mainly by $\delta^{18}\text{O}$ measurements, is presented by Kerr (2007). Briefly, the streams in the Trout Lake watershed are primarily comprised of two end members: lake-derived groundwater and terrestrially-derived groundwater. Lake-derived groundwater flows along long (old) and short (young) flowpaths, while the terrestrial-sourced groundwater represents meteoric water that has infiltrated through the surface soils. All of the groundwaters may be modified by interactions in the wetland and hyporheic zone before reaching the streams. In Allequash Creek, lake-derived groundwater contributes between 61 and 73% of the baseflow while terrestrially-derived groundwater contributes 27–39%. North Creek contains a higher percentage of terrestrial recharge while Stevenson Creek contains a lower percentage of terrestrial recharge. The rivulets appear to represent lake-derived shallow groundwater that flows through wetland soils before emerging.

The effect of water source on trace elements in the watershed was evident when stream geochemistries were compared (Table 4). Trace element concentrations in Allequash Creek and Stevenson Creek were generally similar, however, levels in North Creek

differed significantly in many cases from that presented in Allequash and Stevenson Creeks. Given that North Creek receives a higher proportion of water that has traveled along shorter, shallower terrestrial flowpaths than either Allequash Creek or Stevenson Creek, we expect North Creek to have higher levels of elements sourced from surface soils and lower levels of groundwater sourced elements. The soils in the Trout Lake area are spodosols enriched in Al (Peters et al. 2006). These soils are also rich in K and Fe (Aide and Pavich 2002; Bockheim and Crowley 2002). Indeed, soil-sourced elements such as Al and Mo were higher by >200%; K and Cr were higher by 30%; Cs was 300% higher, Li was 50% greater; Tl was 60% higher; Zn was 70% higher; and U was 800% greater in North Creek than in the other streams. Furthermore, groundwater sourced elements Ca, Mg, Na, and Si were 20–30% lower while Fe and Mn were 60–80% lower in North Creek.

The principal components analysis suggests that water source is the primary factor accounting for the differences in chemical composition of the streams and rivulets (Table 5). ‘Factor 1’ for the rivulets was deemed the ‘water source’ driver because several groundwater-sourced major elements (Ba, Ca, Cs, Fe, Mg, Mn, Na, Si, Sr) which positively load on this factor. Given that ‘Factor 1’ explains the greatest percentage of variance, we reason that water source is the most important driver influencing the major composition of the rivulets. Thus, the principal components analysis supports our interpretation of the rivulets as being representative of wetland-influenced, lake-derived groundwater while the streams are under greater influence of terrestrially-derived (meteoric) groundwater.

Mineral weathering and groundwater flowpath

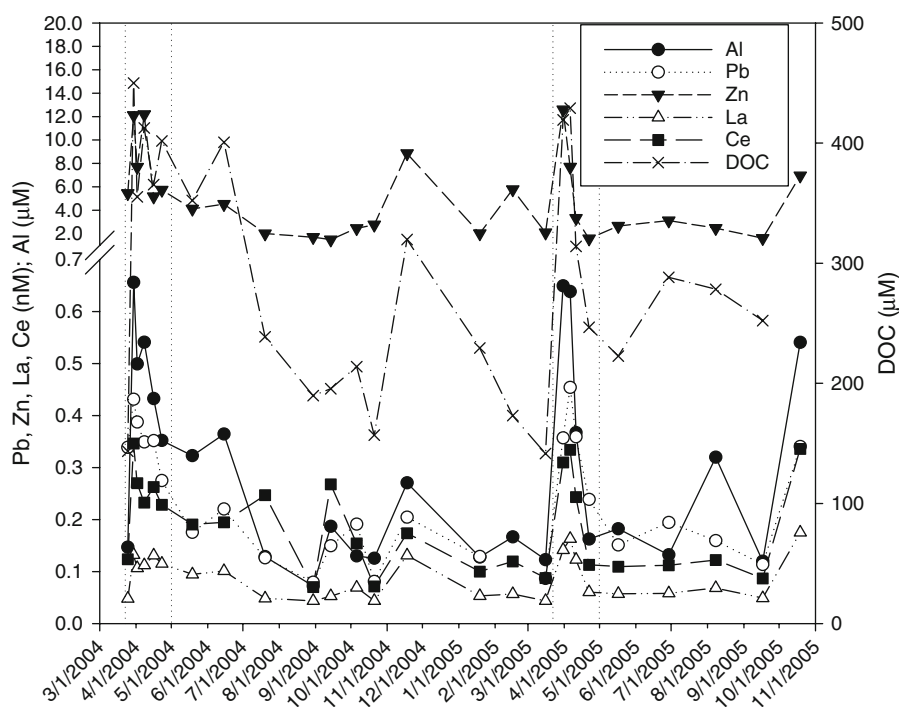
The influence of mineral weathering can be seen in comparing concentrations of major and trace elements in ‘younger’ and ‘older’ groundwater derived from lake water recharge. The chemical composition of the lake-derived groundwater varies as a function of water-mineral contact time. As groundwater moves along flowpaths from Big Muskellunge Lake toward Allequash Creek (Kerr 2007), weathering reactions produce an increase in the major elements (Ca, K, Mg, Na, and Si) derived from minerals present in the area, primarily quartz, plagioclase, and

K-feldspar but also epidote, amphibole, pyroxene, chlorite, and biotite (Bowser and Jones 2002). The influence of weathering was reflected in the 2 to 3-fold increase in concentrations of these five elements in older as compared to younger lake recharge groundwater (Masbruch 2005) (Table 4). The other alkali and alkaline earth metals measured (Cs, Li, Ba, and Sr), except for Rb, were also higher in the older lake recharge than the lake recharge groundwater. Arsenic and Eu exhibited similar trends. Given that groundwater dominates baseflow in the streams, mineral weathering is expected to have a dominant influence on stream chemistry for these elements. Indeed, concentrations of Ca, K, Mg, and Na in Allequash Creek fell between the older lake recharge and terrestrial recharge concentrations (Table 4).

We found Ca to be a reasonably conservative tracer in the low-carbonate, weathering dominated Trout Lake system based on comparison to $\delta^{18}\text{O}$ values and its strong correlation to other alkaline earth metals (Table 8). While the measured tracers ^{18}O -water and Na were invaluable in identifying flowpaths and age (Kerr 2007), Ca can provide an indication of water-mineral contact time and relative flowpath length, making it a more descriptive tracer in this system than, for instance, Cl. The use of Ca as an indicator of water-mineral contact time in the Allequash Basin has been established by the work of Pint et al. 2003, and Walker et al. 2003. These studies also document that in the carbonate poor (calcium concentrations in the primary end-member recharge sources is <200 μM) circum-neutral groundwaters of this system that Ca behaves nearly conservatively. Through the use of multiple isotope systematics (strontium and oxygen isotope ratios) to isolate groundwater velocity influence from groundwater age, Walker et al. 2003 demonstrate that calcium concentrations are strongly correlated with flowpath length. Ca is representative of many of the groundwater-sourced elements. Correlations with other alkaline earth elements are strong (Mg: $r = 0.89$; Sr: $r = 0.89$) and with alkali metals somewhat less (Li: $r = 0.67$; Na: $r = 0.48$; K: $r = 0.59$). In the case of Na and K, the poorer correlation may reflect a less pronounced change in concentration with age for Na and K as compared Ca, Mg and Si (Bowser and Jones 2002). In addition, the higher concentrations of K, Li, and Cs in North Creek than in the other streams indicate alternate sources of these elements to North

Table 8 Percentage of terrestrial recharge and lake recharge in Allequash Creek determined using a two-member mixing model based on $\delta^{18}\text{O}$ and Ca data

	[GW (terr)]	[GW (older)]	Baseflow (cfs)	Terrestrial recharge flow (cfs)	Lake recharge flow (cfs)	% Terrestrial recharge	% Lake recharge
$\delta^{18}\text{O}$	-11.7‰	-6.6‰	3.4	2.5	0.9	73	27
Ca	206 μM	406 μM	3.4	2.1	1.3	61	39

Fig. 4 Time series of DOC, Al, Pb, Zn, La, and Ce in Allequash Creek. Vertical lines indicate melt periods

Creek (and likely to Allequash and Stevenson Creeks, perhaps explaining some of the variability). Given that North Creek receives more terrestrially-derived groundwater, these elements are likely released from soil under favorable hydrologic conditions.

Metal transport by DOC

Complexation with DOC is an important biogeochemical process affecting trace element cycling. Sequestration by DOC reduces adsorptive losses to solid surfaces and enhances metal transport from wetland sediment porewaters to streams. Al and Pb are representative of metals with a high affinity for DOC (Christensen et al. 1999; Helmer et al. 1990; Schnitze and Skinner 1967; Sposito 1986) and their association with DOC is supported by metal-DOC Pearson correlation coefficients for the stream and

rivulet dataset ($r = 0.86$ and $r = 0.74$, respectively) while La ($r = 0.55$), Ce ($r = 0.52$) and Zn ($r = 0.55$) are also correlated with DOC. Concentrations of all five metals were 2–3 times higher in the streams in the spring, when DOM and associated inorganic colloids are flushed from the wetland (Fig. 4). In the rivulets, the increase in concentrations of these metals during the spring was lower (1–2 times), likely because of a reduced influence of terrestrially-derived groundwater which flushes DOC from the wetlands during the spring. Levels of Al and Pb were very low (Al: 0.02–0.04 μM ; Pb: 0.003–0.008 nM) in the groundwater (terrestrial-recharge, lake-recharge, and older lake-recharge) indicating that wetland sediments are the source of these metals to the streams along very shallow near-surface flowpaths (Table 4).

La was lower in the streams and rivulets (0.04–0.1 nM) than in the lake recharge (0.54 nM) or

terrestrial recharge (0.71 nM) but higher than in the older lake recharge (0.01 nM) (Table 4). La in the lake recharge is likely derived from deep lake sediments. As the lake recharge groundwater flows toward the stream, La likely partitions to aquifer sediments along the flowpath. The lower levels in the rivulets as compared to the lake recharge also suggest concentrations of La in the groundwater decrease as flowpath length increases. Levels in Allequash Creek fell between the terrestrial recharge, which contains sediment-derived La, and the older lake recharge groundwater, apparently reflecting a mixing of the groundwater sources.

Zn concentrations were also lower in the older lake recharge (0.3 nM) than in the lake recharge (2.2 nM) or terrestrial recharge (2.4 nM) but otherwise levels in the streams and rivulets were comparable (2.4–7.3 nM) to those in the terrestrial and lake recharge groundwater (Table 4). As was observed with La, relative levels in the groundwater sources suggest that long water-mineral contact times lead to a loss of Zn from the groundwater, likely as a result of partitioning to sediments. Seasonal hydrologic events appear to release Zn from wetland sediments to the streams suggesting a strong terrestrial surface source.

Ce tended to track La with the important exception of lower levels of Ce in the terrestrial recharge (Table 4). The relatively low levels of Ce (0.03 nM) as compared to La (0.71 nM) in terrestrial recharge may be indicative of the ‘Ce anomaly’ (a decrease in Ce relative to La and Pr) which occurs under oxic conditions when Ce(III) is oxidized to Ce(IV) and removed by precipitation of $\text{CeO}_2(\text{s})$ or adsorption to Fe/Mn oxyhydroxides (Gruau et al. 2004; Haley et al. 2004). As observed with La, Ce in the lake recharge is apparently removed as the groundwater moves through the subsurface. High levels of dissolved Fe (20–27 μM) in the rivulets (Table 4) suggest an influence of reductive dissolution of Fe oxyhydroxides. Ce concentrations were higher in the groundwater dominated rivulets (0.09–0.13 nM) than in older lake recharge (0.01 nM), suggesting that release of Ce by reductive dissolution of Fe/Mn oxyhydroxides, which strongly adsorb rare earth elements (Gruau et al. 2004), may influence Ce at this location. Complexation of Ce by DOC ($r = 0.52$) is also an important factor in this system, given that Ce levels in the streams were higher (0.15–0.22 nM) than in the groundwater dominated rivulets (0.09–

0.13 nM) and higher in the streams during spring melt (0.35–0.59 nM). Indeed, the rare earth elements are strongly complexed by organic matter as indicated by their high stability constants (Tang and Johannesson 2003). Thus, the wetland soils likely contain Ce complexed with DOC whose release to the streams is enhanced during hydrologic events. Since terrestrial recharge makes up a larger percentage of stream input than lake recharge and Ce levels are higher in Allequash Creek (0.22 nM) than in the terrestrial recharge (0.03 nM), the wetland clearly is a source of Ce to the stream.

Dissolved organic carbon emerged as the most influential variable explaining trace element variance in the streams of the Trout Lake watershed along with a suite of other metals with a documented tendency to complex with DOC and associated inorganic colloids (Al, Ti, Cu, Zn, Cd, La, Ce, and Pb) (Table 5). DOC also contributed to the second most important factor explaining trace element variance in the rivulets along with the same set of metals. Though the factor analysis implies that complexation with DOC is an important influence on concentrations and transport of a number of trace elements in the Trout Lake watershed, we cannot characterize the nature of the association between DOC and the trace elements from patterns in their concentrations.

Metal transport by SPM

Data on partitioning of metals to suspended particulate matter (SPM) provides insight into the mode of export. Thus, partition coefficients are a valuable metric for describing the biogeochemistry of trace metals. Metals in the particulate fraction are subject to removal by filtration and settling, while those in the dissolved phase are preferentially influenced by sorption and complexation reactions. Geochemical variables such as DOC, properties of SPM, and specific conductance influence partitioning of metals to SPM (Shafer et al. 1999).

Median particulate fractions (%) for Al, Cd, Ce, Cs, Cu, Fe, La, Pb, Ti, Yb, and Zn are presented in (Table 9). Values ranged from 7 to 51%. The amount (%) of metal in the particulate fraction is a function of both the particle abundance (SPM) and the partition coefficient. Thus, the relatively low amounts of metals in the particulate fraction reflect the low concentrations of SPM in streams and rivulets.

Table 9 Median particulate fraction (%) of Al, Cd, Ce, Cs, Cu, Fe, La, Pb, Ti, Yb, and Zn in Allequash Creek, Stevenson Creek, North Creek, Rivulet1 and Rivulet2

	Allequash Creek	Stevenson Creek	North Creek	Rivulet1	Rivulet2
Al	37 ± 23	35 ± 19	18 ± 15	29 ± 13	18 ± 13
Cd	27 ± 21	26 ± 17	14 ± 16	15 ± 22	24 ± 19
Ce	42 ± 23	35 ± 18	17 ± 21	38 ± 18	35 ± 15
Cs	33 ± 25	21 ± 26	20 ± 22	18 ± 27	17 ± 27
Cu	24 ± 20	28 ± 17	35 ± 14	38 ± 29	41 ± 24
Fe	21 ± 16	40 ± 15	17 ± 16	29 ± 12	17 ± 11
La	43 ± 21	38 ± 18	26 ± 18	44 ± 17	37 ± 14
Pb	29 ± 23	36 ± 20	27 ± 20	51 ± 23	42 ± 15
Ti	47 ± 26	42 ± 18	12 ± 22	31 ± 18	20 ± 19
Yb	23 ± 22	23 ± 14	13 ± 17	17 ± 13	21 ± 18
Zn	28 ± 24	20 ± 19	16 ± 18	23 ± 14	7 ± 13

Rankings of the metals according to particulate fraction vary among the streams and rivulets, but Zn tended to have a lower (7–28%) particulate fraction than the other metals. Partition coefficients (K_D), defined as the ratio of particle-bound metal ($\mu\text{g/kg}$) to filterable metal concentrations ($\mu\text{g/l}$), are reflective of the properties of the individual metal as well as the characteristics of the particle involved in the adsorption–desorption reaction (Pankow and McKenzie 1991). The K_D values for representative metals with a tendency to form surface complexes (Ce, Cu, La, Pb, and Zn) varied with both season and water type (Fig. 5). Values were noticeably greater in the fall, except for Zn. This may reflect the low DOC concentrations during the fall, leading to reduced sequestration of metals by DOC and higher K_D values. Lower K_D values during the spring melt, coincident with DOC flushing, observed in Allequash Creek and Rivulet2, provided further evidence of the sensitivity of K_D to changes in DOC concentrations. Zn showed less seasonal variation in K_D values, despite a DOC-correlation similar to those for La, Ce, and Cu. Zn also tended to have lower K_D values ($1.5\text{E} + 04$ to $2.7\text{E} + 05$ l/kg) than the other metals, possibly because Zn has an intermediate affinity for both DOC and mineral surfaces, making K_D values sensitive to changes in both DOC and SPM concentrations (Shafer et al. 1997, 2004).

Partitioning to particles was the third most influential factor influencing trace element variance in both the streams and rivulets (Table 6). SPM concentration, in the case of the streams, as well as metals with a strong affinity for organic ligands are included in this factor. This indicates that, for several

trace elements, stream concentrations are in part supported by transport of trace metals via partitioning to particles which is strongly dependent on metal type and SPM concentration in the Trout Lake watershed.

Redox status and precipitation/dissolution/adsorption processes

Wetland sediments are typically anoxic and thus sites of reductive biogeochemical processes, specifically Fe(III) and sulfate reduction, mediated by microbes present in the sediments (Billon et al. 2001; Kerr 2007; Olivie-Lauquet et al. 2001). Adsorption, dissolution, and precipitation processes are intimately connected to redox cycling in that the reductive dissolution of iron(III) oxyhydroxides can release metals adsorbed to these particles or colloids, and metals can precipitate as metal sulfide complexes under reducing conditions.

Cu is a redox-sensitive metal which is also influenced by DOC ($r = 0.45$). Cu concentrations were higher (2.5–3.9 nM) in the streams during the spring (Fig. 6), similar to other metals with strong affinities for DOC, when DOC was flushed from the sediments during spring melt. Cu concentrations in the rivulets increased 2-fold during the spring but were generally lower (0.2–0.4 nM) than concentrations in the streams, possibly as a result of redox cycling (Billon et al. 2001; Huerta-Diaz et al. 1998). Cu in the wetland sediment porewaters may precipitate from solution as a sulfide or iron-sulfide complex. Levels of Cu in the rivulets (0.2–0.4 nM) and the older lake recharge (0.07 nM) were similar, but much lower than in the terrestrial recharge

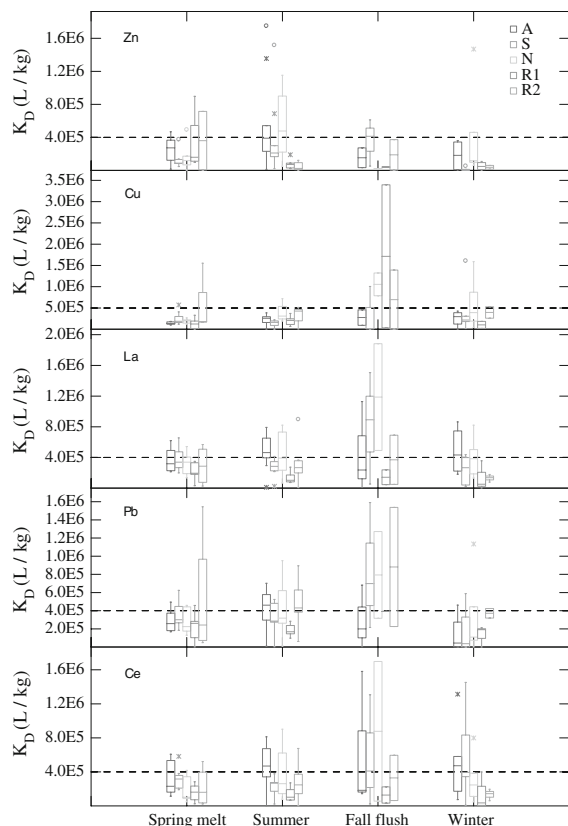


Fig. 5 Partition coefficients for Ce, Pb, La, Cu, and Zn in Allequash Creek (A), Stevenson Creek (S), North Creek (N), Rivulet1 (R1), and Rivulet2 (R2) averaged on a seasonal basis. The center line in the box plot marks the median value, the box edges mark the first and third quartiles, the ‘whiskers’ span 1.5 times the first and third quartiles, while values within three times the first and third quartiles are marked with an asterisk. Values outside of this range are indicated with an open circle

(3.6 nM) or lake recharge (7.0 nM) (Table 4). This loss of Cu as the lake recharge moves towards the stream may be due to adsorption to mineral surfaces or precipitation as Cu sulfide in anoxic zones. Copper speciation modeling using MINEQL+ (Schecher and McAvoy 1998) suggests that Cu sulfides are the dominant aqueous species in the Allequash wetland porewaters, and calculations indicate that the solubility product of covellite ($\log K = -22.27$) (Shea and Helz 1989) is consistently exceeded in these waters. Since levels of Cu in the streams were between those in the older lake recharge and terrestrial recharge, terrestrial recharge is likely the main source of Cu in the streams.

Oxy-anions are also an indicator of redox status. Mo was strongly correlated to other oxy-anions with r

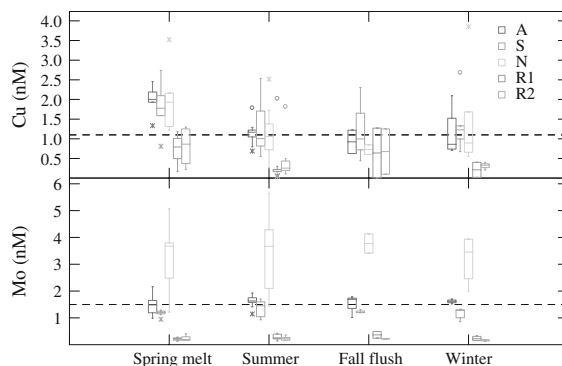
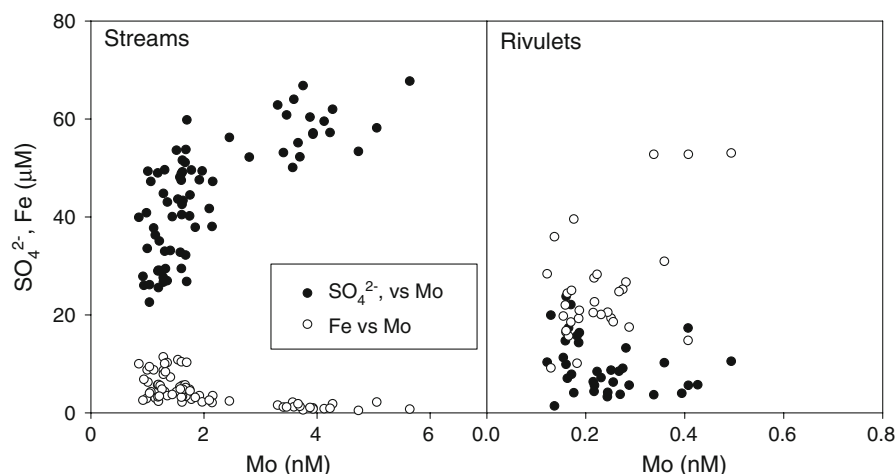


Fig. 6 Concentrations of Cu and Mo in Allequash Creek (A), Stevenson Creek (S), North Creek (N), Rivulet1 (R1), and Rivulet2 (R2) averaged on a seasonal basis. The center line in the box plot marks the median value, the box edges mark the first and third quartiles, the ‘whiskers’ span 1.5 times the first and third quartiles, while values within three times the first and third quartiles are marked with an asterisk. Values outside of this range are indicated with an open circle. Reference line indicates the average value for the streams and rivulets

values of 0.86, 0.82, 0.82, and 0.75 for U (UO_2^{2-}), V (VO_4^{3-}), Cr (CrO_4^{2-}), and As (AsO_4^{3-}), respectively. Given the strong correlation with Mo, Cr is likely present as Cr(VI), though some Cr(III) may be present given the influence of reducing wetland sediments on the streams and rivulets in this area. Arsenic could be present as either As(V) or As(III). Mo is also strongly correlated to sulfate ($r = 0.84$). Indeed, the Mo cycle is intimately tied to the sulfur cycle (Howarth et al. 1992), and the inorganic chemistry of the most oxidized form of Mo, molybdate (MoO_4^{2-}), is very similar to that of sulfate. Given that the trends seen for Mo are similar to those seen for SO_4^{2-} , the two elements are likely influenced by the same processes. The trends in median concentrations of iron among the streams and rivulets (Table 4) were essentially opposite those seen for Mo and SO_4^{2-} . Iron levels were lowest in North Creek (1.3 μM) and highest in the rivulets (20–27 μM). This suggests redox processes control Mo either directly or through coupling with redox cycles of S and Fe. Figure 7 shows the relationships between Mo, SO_4^{2-} , and Fe in the streams and rivulets—note the significantly lower Mo levels in the rivulets. As discussed above, Mo is strongly correlated to SO_4^{2-} . This trend is more evident in the streams where the sulfate and Mo levels are higher (sulfate and Mo are sourced primarily from surface water and these elements are depleted in the groundwater-dominated rivulets). The lack of a

Fig. 7 Scatter plots of Mo versus SO_4^{2-} and Fe in the streams and rivulets



relationship between Mo and SO_4^{2-} in the rivulets along with a moderate correlation between filterable Fe (nearly all Fe(II)) and Mo ($r = 0.52$), reflects, in part, the much lower Mo and SO_4^{2-} levels, but also demonstrates that the surrounding anoxic wetland sediments are influencing Mo levels. Reductive dissolution of Mo–Fe–S species in the sediments could result in the correlation between filterable Fe and Mo in the rivulets, but not with sulfate (sulfate is not a direct player in Mo-complex formation). Molybdenum is considered a proxy for reductive processes in marine environments, and is sequestered in reducing sediments as a result of a complex chain of reactions in which sulfide is involved (Erickson and Helz 2000; Lyons et al. 2003; Poulson et al. 2006; Tribovillard et al. 2004; Zheng et al. 2000). Considerable uncertainty remains in defining the exact mechanism of Mo sequestration, but a direct sulfide precipitation process is unlikely (MoS_2 and MoS_3 are not sufficiently insoluble), and studies indicate that Mo^{6+} is resistant to reduction in most anoxic sediment environments. Current efforts are focused on the hypothesis that sulfide drives a change in Mo speciation that makes it more susceptible to scavenging/coprecipitation by/with Fe-containing phases. Studies by Erickson and Helz (2000) implicate thiomolybdate species, particularly the mono-sulfide form ($\text{MoO}_3\text{S}^{2-}$) as the principle, susceptible, species. If the thiomolybdate mechanism is active, given the relatively short residence time in the Allequash system, and slow kinetics of complex formation, the mono-sulfide form would likely predominate. The mechanism and rate of molybdenum sequestration is

very sensitive to sulfide concentration—dissolved Mo can coprecipitate as a Mo–Fe–S complex when sulfide levels are $\sim 0.1 \mu\text{M}$ and precipitate as Mo–S when sulfide levels are $>100 \mu\text{M}$ (Zheng et al. 2000). The former would likely be the primary mechanism for sequestration in wetland sediments in this system where sulfide levels were $<10 \mu\text{M}$.

Levels of Mo were very low (0.2 nM) in the rivulets and high (3.6 nM) in North Creek (Fig. 6). This order-of-magnitude contrast in Mo concentrations between sulfide-reduced groundwater and oxic surface water environments is clear evidence of the involvement of sulfide in Mo geochemistry. The levels of Mo in the rivulets (0.2 nM) were slightly lower than those found in the lake recharge groundwater (0.5 nM), which appears to be feeding the rivulets (Table 4), again suggesting iron sulfides play a role in controlling Mo levels in the rivulets. Since North Creek has a larger meteoric water component, the higher levels of Mo are likely supported by the surrounding surface soils. Levels in Allequash Creek (1.6 nM) were similar to those found in the terrestrial recharge (1.0 nM) and older lake recharge (1.1 nM). Levels in the streams and rivulets were seasonally constant. The relative Mo concentrations in the streams and rivulets (Fig. 6) exhibited the same trend as observed for median pH: North (7.12) > Allequash (7.04) > Stevenson (6.95) > R1 (6.61) > R2 (6.36). Thus, it seems that, in addition to redox processes, water source plays a role in influencing levels of Mo in the streams in this system.

The relatively high level of dissolved Mo in North Creek may also reflect the low level of particulate Mn

and Fe. In oxic surface waters, the Mo oxy-anion (and other oxy-anions) may be associated with positively charged Mn and Fe oxyhydroxide particles, thus lowering dissolved Mo levels. In moderately reducing, non-sulfidic environments, the Mo is released back into solution. Though Mo has not been found to associate with Fe oxyhydroxides in marine environments, association with Fe may occur at lower pH levels (<7) when Fe oxyhydroxides have a net positive surface charge (Goldberg et al. 1998). Indeed, a negative correlation between dissolved Mo and both particulate Fe ($r = -0.43$) and dissolved Fe ($r = -0.64$) was found in the streams. A negative correlation was also observed between Mo and both dissolved Mn ($r = -0.46$) and particulate Mn ($r = -0.32$) (Fig. 7). Similar negative correlations were seen for dissolved and particulate Fe/Mn and V, Cr, and U. These inverse relationships support a Mo–Mn/Fe oxyhydroxide association. As levels of Mn/Fe oxyhydroxide particles increase, dissolved Mo levels should decrease as sorption to the particle surface proceeds. The fact that this relationship is observed for both dissolved and particulate Fe fractions may just indicate that dissolved Fe is a proxy for particulate Fe in the streams (plausible given the strong correlation [$r = 0.78$] between Fe-dissolved and Fe-particulate) and there is no colloidal binding of Mo. Other investigations show that most ‘dissolved’ Fe in oxic streams is in fact colloidal (Ross and Sherrell 1999). The opposite trends were seen in the rivulets where correlations between dissolved/particulate Fe and dissolved Mn are positive (Mo–Fe: $r = 0.52$; Mo–Fe(P): $r = 0.48$; Mo–Mn: $r = 0.60$). Similar positive correlations were seen for V and Cr but not U. The positive correlation between dissolved Fe/Mn and Mo may reflect an increase of dissolved Mo in association with reductive dissolution of Fe/Mn oxyhydroxides. In the rivulets, the filterable Fe and Mn concentrations reflect a truly dissolved phase. The positive correlation between particulate Fe and Mo may simply reflect a positive correlation between dissolved and particulate Fe.

The principal components analysis also supports the general importance of redox status in influencing trace elements in the streams and rivulets. ‘Factor 2’ of the streams is comprised almost completely of redox-sensitive metals (Fe, Mn), which load positively on the factor, and oxy-anions, which load

negatively on the factor (Table 5). Indeed, DO also negatively loads on this factor. This pattern makes geochemical sense since as DO levels decrease, levels of dissolved Fe and Mn should increase as a result of the reduction of Fe/Mn oxyhydroxides. The decreasing levels of oxy-anions with increasing levels of dissolved Fe and Mn likely involves adsorption reactions and/or loss due to metal sulfide formations. In the case of the rivulets, Fe and Mn are associated with ‘Factor 1’ (water source/redox). However, the oxy-anions load positively on the Rivulets—Factor 1, likely as a result of the dissolution of Fe/Mn oxyhydroxides to which oxy-anions are adsorbed.

Seasonal events

Filtrable Al, Ce, Cu, La, Pb, and Zn (and other correlated elements Ti, Hg, Yb, Cd and Sb) concentrations were all highest during spring melt (Fig. 4). Average concentrations of each of these elements doubled during the melt period. Given that these metals all have a high affinity for DOC ($r_{Al} = 0.86$, $r_{Ce} = 0.52$, $r_{Cu} = 0.45$, $r_{La} = 0.55$, $r_{Pb} = 0.74$, $r_{Zn} = 0.55$), the metals are likely flushed from wetland sediments during the spring melt as DOC-metal or colloidal DOM-metal complexes. Filtrable K, Ca and Si showed the opposite trend, i.e., lower concentration during the spring as a result of dilution. The major seasonal patterns in metal concentrations can be summarized as follows: (1) Higher in streams and rivulets during spring melt (Al, Cd, Ce, Hg, La, Pb, Sb, Ti, Yb, Zn); (2) Same as ‘1’ but streams consistently higher than rivulets (Cu); (3) Spring melt insensitive, highest in North Creek, and lowest in rivulets (As, Cr, Cs, Li, Mo, SO_4^{2-} , U, V); (4) Spring melt insensitive, highest in rivulets (Fe, Mn); (5) Increase from spring to winter (Ba, Ca, K, Mg, Na, Si, Sr) due to an increasing ratio of groundwater to surface water in the stream. These patterns indicate that hydrologic events (flushing of DOM-complexed metals from the wetland and dilution of “conservative” elements) are the primary drivers of seasonality in trace metal levels.

In the case of the streams, the factor which included DOC and metals with a high affinity for DOC (Factor 1) also included groundwater-sourced elements with negative loadings (Table 5). This implies that the factor is not fundamentally a reflection of metal complexation by DOC but rather

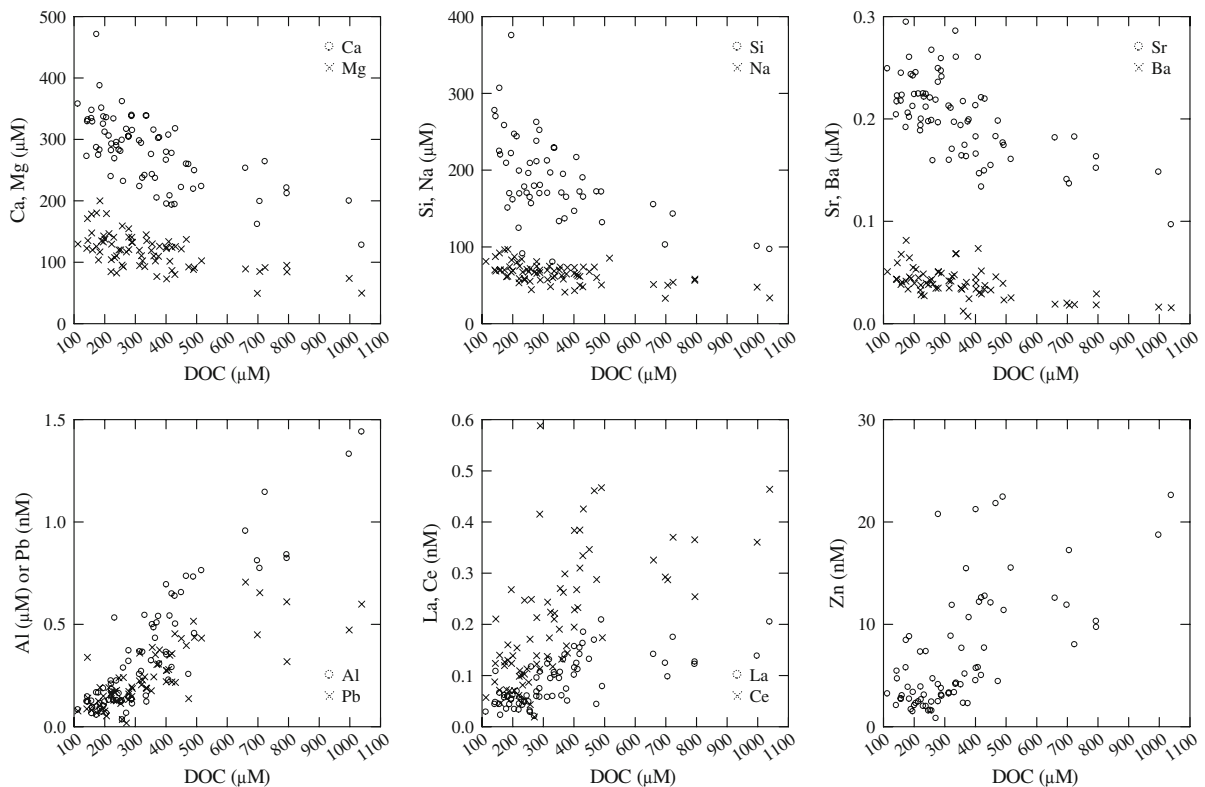


Fig. 8 Scatter plots of DOC versus Al, Pb, La, Ce, Zn, Ca, Mg, Si, Na, Sr, and Ba in the streams

seasonal hydrologic events which impact DOC and correlated metals as well as groundwater sourced elements which are diluted by the influx of snowmelt to the streams in the spring. Thus, the most important influences explaining trace element variance in the streams of the Trout Lake watershed, as suggested by the principal components analysis, are seasonal hydrologic events (Table 6). Such events include spring melt and likely storms, though the latter are not represented in our dataset. If DOC is considered a proxy for seasonal hydrologic events, positive correlations between DOC and metals with a high affinity for DOC (Al, Ce, La, Pb, Zn) and negative correlations between DOC and groundwater sourced elements (Ba, Ca, Mg, Na, Si, Sr) (Fig. 8) support this interpretation of the statistical analysis. It is interesting to note that when we excluded the spring melt data from the principal components analysis, the overall composition and order of the factors remained unchanged. Apparently, spring melt was not the only driver of the observed trends. Hydrologic processes

such as the general increase in the ratio of groundwater to surface water over a season affect trace element variance year-round, thus supporting the principal components analysis results even without spring melt. In addition, export of metals and DOC occurs during non-event times and the relationship between them remains, regardless of spring melt. The ‘seasonal hydrologic events’ factor (Factor 1) explained only 22% of the variance in the stream trace element concentration data while the other factors (Factors 2 and 3) not related to hydrology or spring melt explained 27% of the variance. Thus, non-hydrologic factors explained a greater percentage of the variance than the seasonal hydrologic events factor. However, further temporal restrictions of the dataset might yield changes in the relative roles of the statistical factors. Though seasonal hydrologic events were found to be an important influence on trace element variance, accounting for 22% of the variance in the streams, 51% of the variance seen in our dataset remains unaccounted for.

Conclusions

We conclude that water source is the dominant factor influencing major elements while seasonal hydrological events are the most important processes influencing trace element export from wetland sediments to streams in the Trout Lake watershed. Redox processes are of secondary importance to the streams but primary importance to the rivulets, emphasizing the impact of anoxic conditions in wetland sediments on groundwater en route to the stream. During non-event times, the relative importance of redox processes may increase. The elements influenced by water source and subject to dilution during seasonal hydrologic events include Ba, Ca, K, Mg, Na, Si, and Sr. Elements primarily influenced by DOC and subject to flushing during spring melt include Al, Cd, Ce, Hg, La, Pb, Sb, Ti, Yb, and Zn. Redox-sensitive driver elements Fe, Mn and SO_4^{2-} were shown to have a controlling influence over several of the oxy-anion metals (As, Cr, Mo, U, and V). Given the role of seasonal hydrologic events in influencing trace element cycling, any disturbances to the system which affect these seasonal events will impact the fate and transport of metals in wetland systems.

This study allowed for an assessment of the influence of different water sources on stream chemistry and showed that the influence of water source was especially pronounced in the groundwater-fed rivulets. In studying the groundwater-dominated wetland rivulets, we were also able to better understand the influence of the wetland sediments on trace element cycling and the sourcing of trace elements. Hydrologic regime did not have a major influence on trace element concentrations in the streams we investigated. Concentrations of most trace elements were similar in Allequash Creek (upwelling) and Stevenson Creek (downwelling). The results from this study should be applicable to other groundwater-dominated, wetland-influenced watersheds of similar geology.

Acknowledgements This work was funded by the National Science Foundation (Grant No.: EAR-0229650). Special thanks go to Randall Hunt and John Walker at the U.S. Geological Survey for their assistance and collaboration on this project. This work could not have been completed without the contributions of Jackson Helmer and all those who assisted with field sampling and laboratory analysis.

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