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Hydrogeochemistry of Fe and Mn in small boreal streams: The role of seasonality, landscape type and scale

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Abstract

Stream water from a stream network of 15 small boreal catchments (0.03-67 km²) in northern Sweden was analyzed for unfiltered (total) and filtered ($<0.4 \mu m$) concentrations of iron (Fe_{tot} and Fe_{<0.4}) and manganese (Mn_{tot} and Mn_{<0.4}). The purpose was to investigate the temporal and spatial dynamics of Fe, Mn and dissolved organic carbon (DOC) as influenced by snow melt driven spring floods and landscape properties, in particular the proportion of wetland area. During spring flood, concentrations of Fetot, Fe_{<0.4}, Mn_{tot}, Mn_{<0.4} and DOC increased in streams with forested catchments (<2% wetland area). In catchments with high coverage of wetlands (>30% wetland area) the opposite behavior was observed. The hydrogeochemistry of Fe was highly dependent on wetlands as shown by the strong positive correlation of the Fe_{tot}/Al_{tot} ratio with wetland coverage ($r^2 = 0.89, p < 0.001$). Furthermore, PCA analysis showed that at base flow Fe_{tot} and $Fe_{<0.4}$ were positively associated with wetlands and DOC, whereas they were not associated during peak flow at spring flood. The temporal variation of Fe was likely related to varying hydrological pathways. At peak discharge Fetot was associated with variables like silt coverage, which highlights the importance of particulates during high discharge events. For Mn there was no significant correlation with wetlands, instead, PCA analysis showed that during spring flood Mn was apparently more dependent on the supply of minerogenic particulates from silt deposits on the stream banks of some of the streams. The influence of minerogenic particulates on the concentration of, in particular, Mn was greatest in the larger, lower gradient streams, characterized by silt deposits in the near-stream zone. In the small forested streams underlain by till, DOC was of greater importance for the observed concentrations, as indicated by the positive correlation of both Fetot and $Fe_{<0.4}$ with DOC ($r^2 = 0.77$ and $r^2 = 0.76$, p < 0.001) at the smallest headwater forest site. In conclusion, wetland area and DOC were important for Fe concentrations in this boreal stream network, whereas silt deposits strongly influenced Mn concentrations. This study highlights the importance of studying stream water chemistry from a landscape perspective in order to address future environmental issues concerning mobility of Fe, Mn and associated trace metals. © 2008 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

In the boreal region of Sweden, where wetlands constitute 25% of the land area, coniferous forests are interspersed with lakes and peat wetlands. This heterogeneity of landscape elements contributes to a spatial and temporal

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Both iron (Fe) and manganese (Mn) are present in low concentrations in the pH and redox range of most natural

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variability in stream water chemistry (Humborg et al., 2004; Temnerud and Bishop, 2005; Buffam, 2007). Moreover, the geochemistry of streams is to a large extent influenced by processes taking place in headwater areas (Johnson et al., 2000; Ingri et al., 2005) and the chemical signature of streams is substantially influenced by soil processes, soil depth, surficial sediment type, and water flow path length (Hope et al., 1997; Wolock et al., 1997; Aitkenhead et al., 1999; Johnson et al., 2000; Ågren et al., 2007).

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aquatic systems (Berner, 1978; Wedepohl, 1978) which is due to the low solubility of their thermodynamically stable oxidation states, Fe(III) and Mn(IV) (Berner, 1978; Wedepohl, 1978; Stumm and Morgan, 1996). The major differences in the redox chemistry of Fe and Mn are that (1) the oxidation of Mn(II) to Mn(III, IV) usually proceeds slower (even if catalyzed) than the oxidation of Fe(II) to Fe(III) and (2) the reduction of Mn, occurs at a higher redox potential than that required for reduction of Fe (Stumm, 1992). Furthermore, the oxidation of both Fe and Mn is pH dependent and proceeds more slowly in acidic waters (Stumm and Morgan, 1996). DOC strongly interacts with both dissolved and particulate Fe species (Tipping et al., 1981; Davis, 1982; Warren and Haack, 2001) and a recent study has shown that organic matter increases the solubility of iron oxides (Weber et al., 2006). On the contrary, Mn has been shown to be only weakly bound to DOC (Carpenter, 1983; Laxen et al., 1984; de Vitre et al., 1988) although a more recent study has shown that about 50% of Mn in fresh water was humic-complexed (Graham et al., 2002). The Fe and Mn oxyhydroxides are, along with suspended primary minerals and organic matter, important carriers for trace metals in stream water (Tipping, 1981; Davis, 1984; Benoit, 1995; Pokrovsky and Schott, 2002; Pekka et al., 2004; Pokrovsky et al., 2006). Since Fe and Mn are insoluble in their oxidized forms but soluble in their reduced forms (Laxen and Chandler, 1983), environments where redox processes are predominant (e.g. wetlands, stagnant streams) are of great importance for the supply of Fe, Mn and other metals to streams (Shiller, 1997).

A number of recent studies have been carried out in both streams and rivers at high latitudes to study the temporal behavior of major elements (Pekka et al., 2004; Ingri et al., 2005; Cory et al., 2006), trace elements (Pontér et al., 1990; Shiller, 1997; Pokrovsky and Schott, 2002; Rember and Trefry, 2004) and DOC (Laudon et al., 2004; Finlay et al., 2006; Buffam et al., 2007). In these regions the spring flood is the major annual hydrological event, resulting in increased concentrations of trace metals, suspended particulate matter (SPM) (Pontér et al., 1992; Rember and Trefry, 2004; Holemann et al., 2005) and DOC (Shafer et al., 1997; Laudon and Bishop, 1999; Rember and Trefry, 2004) whereas major elements are diluted (Ingri et al., 2005; Buffam et al., 2007). An increase of dissolved concentrations of Fe and Mn by a factor of 10-20 during spring flood has been reported (Borg, 1986; Pontér et al., 1990; Borg et al., 1995; Rember and Trefry, 2004; Holemann et al., 2005). Moreover, several studies (Pontér et al., 1990; Shafer et al., 1997; Sherrell and Ross, 1999) have shown the importance of suspended particulate matter (SPM) as a carrier for Fe, Mn and other trace metals. However, previous studies of temporal variations of Fe and Mn in running waters have not given any special attention to the spatial and temporal patterns of an entire stream network. More importantly, previous studies have not focused on the influence of catchment properties and catchment hydrological processes on stream chemistry from a landscape perspective. In order to inform water management authorities which usually make decisions at the landscape scale or larger scale it is important to increase the knowledge of the behavior of metals in streams deriving from different landscape elements.

In this study, we investigate the temporal and spatial variation of Fe and Mn as total (unfiltered) and dissolved (i.e. filterpassing, $<0.4 \,\mu$ m) concentrations in a boreal stream network. We compare the hydrogeochemistry of Fe and Mn between forested catchments and wetland influenced catchments, in order to establish relationships between observed concentrations of Fe and Mn with landscape characteristics (e.g. wetland area) and other stream chemistry parameters. The main objective of this study was to evaluate the importance of seasonality and landscape characteristics determining the temporal and spatial hydrogeochemistry of Fe and Mn in stream water. The hypotheses of this work were that (1) Fe and Mn correlate positively with increasing coverage of wetlands within the catchment (spatial hypothesis), (2) high discharge, especially during spring flood, will result in increased concentrations of Fe and Mn (flow hypothesis) and (3) an increased influence of particles (mineral and/or organic) will increase the concentration of Fe and Mn (particulate hypothesis).

2. SITE DESCRIPTION

This study was undertaken as a part of the multidisciplinary Krycklan Catchment Study. The study area comprises a boreal stream network of 15 streams in the upper 67 km² of the Krycklan catchment (Fig. 1, Table 1) in northern Sweden. The 15 sub-catchments, hereafter referred to as C1-C16 (note that C11 does not exist) are all located in the vicinity of Vindeln Experimental Forests (64°14'N, 19°46'E), approximately 30 km from the Baltic Sea. Soil hydrological parameters, stream flow and climate have been monitored since 1980 (Bishop et al., 1990; Fölster et al., 2003) in the 0.5 km² sub-catchment of C7 (also called Svartberget in many publications, composed of C7 and the head waters C2 and C4). The streams are first order headwater streams to fourth order streams with catchment areas ranging from 0.03 km² to 67 km² (Table 1). The majority of the streams (9 of 15) are independent of one another although many of the larger streams receive flow from upstream regions.

2.1. Geology, quaternary deposits and topography

The Svecofennian bedrock consists predominately of metasediments/metagreywacke (\sim 93%) with some acid and intermediate metavolcanic rocks (\sim 4%) and basic metavolcanic rocks (\sim 3%). The topography of the Kryck-lan catchment ranges from 369 m above sea level in the northwest to 130 m above sea level at the catchment outlet in the southeast.

Dominating quaternary deposits are glacial till and peat (SGU, 1995) (Table 1), the thickness of the till varies up to tens of meters (Ivarsson and Johnsson, 1988). In the forest soils well-developed podzols are common (Bishop et al., 1994) but in the riparian zone organic soils (histosols) are common (Bishop et al., 1995). The northwestern parts of the Krycklan catchment (44%) are situated above the highest coastline (HC) (~255 m above sea level) (Ågren et al.,



Fig. 1. Location of the study area, the Krycklan catchment, in northern Sweden. Numbers refer to sampling locations. Further details on sampling sites in Table 1. A more detailed map of the study area is found in Laudon et al. (2007).

2007). The upstream regions of the catchment are characterized by glacial till interspersed with small wetland areas. In the southern, lower reaches of the catchment, located below HC (56%), the stream channels meander through deposits of silt/fine sand. These postglacial surficial sediments are dominated by silt, deposited in the distal part of a post glacial delta, and cover up to 59% of the lower lying sub-catchments (Ivarsson and Johnsson, 1988; Ågren et al., 2007).

2.2. Climate and hydrology

Mean annual temperature is +1.3 °C (1980–1998) and mean annual period with snow cover is 171 days (Ottosson Löfvenius et al., 2003). Mean annual precipitation is approximately 600 mm (1981–1998), of which 35% falls as snow. The mean annual runoff is approximately 325 mm and one third of the runoff occurs during spring flood in April–May (Lindström et al., 2002).

2.3. Vegetation and land use

The study area is situated in the mid-boreal vegetation zone (Gustafsson and Ahlén, 1996) and Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*) forest and wetlands are the main land cover types in the region. The main part of the Krycklan catchment is forested (88%) and wetlands, dominated by *Sphagnum* spp., constitute about 8% of the catchment area. Many of the small sub-catchments are influenced by a large percentage of wetlands. All but one sub-catchment are dominated by boreal coniferous forest and the coverage of wetlands ranges from 0% to 76%. One of the sampling sites (C5) drains a small humic-rich lake and sub-catchment C15 comprises a number of upstream lakes.

3. METHODS

3.1. Water discharge

Water level was recorded hourly using a 90° V-notch weir in a heated dam house at C7 in order to calculate hourly stream discharge, using measurements of stream height and established height-discharge rating curves (Buffam et al., 2007). Water level was also recorded semi-continuously at the other 14 sites, but due to gaps in measurement (mostly during freezing winter conditions), for this study daily discharge was estimated at all sites by assuming the same areally weighted (specific) discharge as that at site C7. The validity of this assumption was evaluated with direct discharge measurements using salt dilution or bucket flow (N = 259) at the 15 different sites covering a wide range of flow conditions. According to these unpublished measurements the differences in daily discharge values between other sites and C7 were greatest during low flow but the overall mean differences were small (<20%) and also the mean bias for all measurements was small (<5%) at all flow levels. Furthermore, discharge measurements have shown that maximum spring discharge at all sites occurred within a single 72-h period (Buffam et al.,

Table 1Quaternary deposits and landcover of the 15 studied sub-catchments

Site	Site name	Stream order	Area (km ²)	Land cover				Surfici	al sedir	Landcover		
No.				Forest (%)	Wetland (%)	Lake (%)	Arable (%)	Peat (%)	Silt (%)	Till (%)	Thin soils ^b (%)	type ^c
C1	Risbäcken	1	0.66	98.7	1.3	0	0	0	0	94	6	Forested
C2	Västrabäcken	1	0.14	100	0	0	0	0	0	86	14	Forested
C3	Lillmyrsbäcken	1	0.03	24.0	76.0	0	0	85	0	0	0	Wetland
C4	Kallkälsmyren	1	0.19	59.6	40.4	0	0	60	0	9	32	Wetland
C5	Stortjärnen	1	0.85	59.0	36.3	4.7	0	41	0	48	6	Wetland
	Outlet											
C6	Stortjärnsbäcken	1	1.3	72.8	24.1	3.1	0	28	0	57	10	Mixed
C7	Kallkälsbäcken	2	0.50	85.1	14.9	0	0	18	0	68	15	Mixed
C8	Fulbäcken	2	2.5	88.7	11.3	0	0	16	0	63	20	Mixed
C9	Nyängesbäcken	2	3.1	84.9	13.8	1.3	0	15	6	69	6	Mixed
C10	Stormyrbäcken	2	2.9	74.2	25.8	0	0	29	0	58	11	Mixed
C12	Nymyrbäcken	3	5.4	84.1	15.5	0	0.3	18	3	66	8	Mixed
C13	Långbäcken	3	7.2	89.1	9.9	0.6	0.4	12	16	60	10	Mixed
C14	Åhedbäcken	3	14	90.4	5.1	0.6	3.9	8	31	50	8	Mixed
C15	Övre Krycklan	4	20	83.2	14.0	1.7	1.0	13	2	66	8	Mixed
C16	Krycklan	4	67	88.0	8.3	0.7	3.0	9	27	52	7	Mixed

^a Source: Swedish Geological Survey (SGU, 1995). Rare surficial sediment types (sand, gravel and glaciofluvial sediments) were excluded from this table and from statistical analyses.

^b Thin or discontinuous soil cover (<50 cm) which generally is till. Bedrock is found within 50 cm of the surface (SGU, 1995).

^c Landcover type defined by percent wetland coverage, where forested <2% wetland, mixed 2–30% wetland, and wetland >30% wetland (Buffam et al., 2007).

2007). The results from these measurements confirm that the flow in the different streams was generally synchronous and that on an annual basis the effect of different daily flows evens out, affirming our use of the same specific discharge for all sites in calculating annual flow-weighted mean concentrations as in the current study. In general the longer the time period considered, the lower the error in total discharge.

3.2. Sample collection

The collection of water samples from the 15 streams (Fig. 1 and Table 1) was focused on the spring flood. Monthly sampling from January 2004 to December 2005 was intensified during the spring flood events (April–May), when samples were collected approximately every second day. During 2004 and 2005 approximately 825 samples were collected for analysis during 54 sampling occasions.

Thoroughly acid-washed high density polyethylene (HDPE) bottles were individually packed in polyethylene bags and were not opened until sampling. All bottles were rinsed with stream water prior to grab sample collection of approximately 1000 ml of stream water from the middle of the stream. The sampling bottles were filled to the brim in order to reduce the chemical effects of air in the head space. After collection the sampling bottle was kept in the dark at 4 °C in the polyethylene bag until further treatment.

3.3. Sample treatment and chemical analyses

Shortly after returning to the laboratory, the pH was measured immediately upon opening the sealed containers with little/no headspace. The measurements were taken at room temperature with gentle stirring (at ambient pCO₂, not air-equilibrated), using a Ross 8102 low-conductivity combination electrode (ThermoOrion). Sub-samples for DOC analysis were kept frozen until analysis and DOC concentrations were determined using a Shimadzu TOC- V_{CPH} analyzer after acidification and sparging to eliminate inorganic carbon (detailed methods described in Buffam, 2007). The analytical precision of the DOC analysis based on replicate injections averaged less than 2%. A previous study in the area (Laudon et al., 2004) also found that the particulate organic carbon is low (<5% of total) at both low and high flow, therefore DOC in this study is considered equivalent to total organic carbon (TOC).

Prior to analysis of Fe, Mn and major cations, the water samples were filtered whereby the suspended fraction $(>0.4 \,\mu\text{m})$ was separated from the filtered fraction ($<0.4 \mu m$). The filtration was performed as soon as possible, usually within 12-48 h after collection. All filtration equipment was thoroughly acid-washed and rinsed in ultra clean water prior to filtration in a Class 100 clean air laminar flow hood in a clean room laboratory. Millipore isopore[™] polycarbonate membrane filters, pore size 0.4 µm and diameter of 47 mm, were loaded in filter holders (Millipore SWIN-EX-47), rinsed with 50 ml ultra clean water and finally conditioned with 30 ml of sample water. Samples were shaken thoroughly in order to suspend all particulate matter and then the samples were filtered using a syringe. A sub-sample of unfiltered sample was collected for total analysis of Fe, Mn and major cations. The unfiltered and filtered samples were acidified with 1 ml suprapure HNO₃ (Merck) per 100 ml sample and were stored in the dark at 4 °C until analysis.

Unfiltered and filtered (i.e. filterpassing, $<0.4 \mu$ m) concentrations, here referred to as "total" and " $<0.4 \mu$ m" concentration, respectively, of major cations (Al, Ca, K, Mg, Na, Si), Fe and Mn were analyzed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES Varian Vista Pro Ax). A sea spray nebulizer and a micro-concentric spray chamber were used which permits particles up to 75 µm to pass through and into the plasma. To ensure the accuracy of the analysis an external certified standard (Spectrapure Standards SPS-SW1) was analyzed on a regular basis. The uncertainty was always less than 2%. Note that the filter passing fraction most likely contains some colloidal material.

Blanks were performed for each sampling occasion to check the contamination induced by sampling and filtration. For Fe and Mn and all major elements the concentrations in the blanks were below detection limits. Reproducibility was checked several times by performing the filtration twice for the same sample. For Fe the difference between two succeeding filtrations was 3%, while for Mn the difference was 2%.

3.4. Suspended material

At one sampling occasion during spring flood in 2004 and at one occasion during summer low flow 2004, the total amount of suspended solids (TSS), particulate organic matter (POM) and minerogenic suspended solids (SSmin) were determined for each stream. The sampled water was filtered using a pre-weighed 47 mm Whatman GF/F 0.7 μ m nominal pore size glass fiber filter, dried for 18 h at 55 °C and weighed for TSS. The filter was ashed for 2 h at 525 °C and the remaining material constituted the SSmin. POM was calculated as the difference between TSS and SSmin.

Aluminum (Al) is an element often used as an indicator of rock derived particles (Sholkovitz and Copland, 1982). Since the uptake of Al in biota is limited and Al is a common rock forming element it is a useful indicator of the concentration of rock derived particles. By calculating the ratio of Fe_{tot}/Al_{tot} and Mn_{tot}/Al_{tot} the influence of particles (mainly silt fraction) on the concentration of Fe and Mn is normalized.

3.5. Data analyses

3.5.1. Principal component analysis (PCA)

PCA was used to find a set of uncorrelated linear combinations, which is able to explain most of the variance of the original multivariate data (Hotelling, 1933; Shaw, 2003). Stream water chemistry data of samples collected from January through May, encompassing the spring floods of 2004 and 2005, were grouped into two hydrological periods: winter base flow (N = 110) and peak flow (N = 122). The periods were determined from the hydrograph of C7. The PCA was performed by STATISTICA 7.1[©] for each hydrological period using stream chemistry data (Fe, Mn, Al, Ca, Si, pH, and DOC) from the 15 sites together with information on catchment area and the coverage of different landscape variables (wetland, forest, lake, arable land) and information from the Swedish Geological Survey on surficial sediment type (till, peat, silt, glaciofluvial deposits, thin soils, and rock, where rock refers to exposed bedrock and thin soils to <50 cm of surficial sediments). Unfiltered and filtered concentrations of Fe and Mn (Fe_{tot}, Fe_{<0.4}, Mn_{tot} and Mn_{<0.4}, respectively) were used as active ordination variables and all other variables were used as supplementary variables.

3.5.2. Weighted discharge

Average element concentrations (C_{avg}) for 2004–2005 were calculated from weighted concentrations for each sampling occasion using the following formula, modified from Paces (1983):

$$C_{\text{avg}} = \frac{\sum \frac{C_n + C_{n+1}}{2} \times (V_{n+1} - V_n)}{V_{\text{tot}}}$$

where n = sampling occasion number; C = element concentration in μ g L⁻¹; V = discharge in mm day⁻¹; $V_{tot} =$ accumulated water discharge (mm).

4. RESULTS

4.1. Discharge and water chemistry

Based on the hydrograph for C7, 2004 was a wetter year than 2005, especially during the summer months. However, the spring flood events of 2004 and 2005 were similar and lasted from mid-April to late-May. Peak flow occurred on May 4th in 2004 and on May 5th in 2005. At spring flood 2004 the discharge increased approximately by a factor of 35 from 0.2 mm day⁻¹ to 6.8 mm day⁻¹. The discharge at peak flow during spring flood 2005 was about 9.7 mm day⁻¹, which corresponds to a 50-fold increase. Further information on the hydrology of 2004 is found in Buffam et al. (2007).

Average pH for all streams in 2004–2005 ranged from 4.1 to 6.5 (Table 2). Lowest pH, was observed in a small headwater wetland site (C3) and highest pH was observed in Krycklan (C16) the largest stream in the study. This sampling site is downstream of all other sites and the water chemistry is to a large extent influenced by processes in the upstream regions. The highest concentrations of DOC were observed at the wetland headwater sites (C3 and C4). The average (discharge weighted) concentration of total Fe (Fe_{tot}) ranged from 363 µg L⁻¹ in a small wetland headwater (C3) to 2542 µg L⁻¹ at C16, the catchment outlet. The average concentration of total Mn (Mn_{tot}) ranged from 3.1 µg L⁻¹ to 61 µg L⁻¹. The wetland headwater streams (C3 and C4) showed the lowest average concentrations of Mn_{tot} and C16 the highest.

4.2. Temporal variation of Fe, Mn, DOC and pH in contrasting catchments

4.2.1. Forested catchment

The temporal patterns of DOC and pH in the forested headwater streams C1 and C2 (here represented by stream C2) were characterized by increasing concentrations of DOC and decreasing pH during events of high discharge (Fig. 2). In 2004 DOC increased by a factor of 3 at spring flood and pH dropped from 5.8 to 4.6.

Tal	ole	2

Average (discharge-weighted) total concentrations (unfiltered) of various stream chemistry parameters for water samples collected from 15 streams during 2004–2005

Site No.	Wetland (%)	$\begin{array}{c} Al \\ (\mu g \; L^{-1}) \end{array}$	$\begin{array}{c} Ca \\ (\mu g \ L^{-1}) \end{array}$	$\begin{array}{c} Fe \\ (\mu g \; L^{-1}) \end{array}$	$\begin{array}{c} K \\ (\mu g \; L^{-1}) \end{array}$	$\frac{Mg}{(\mu g \ L^{-1})}$	$\begin{array}{c} Mn \\ (\mu g \; L^{-1}) \end{array}$	$Na \ (\mu g \ L^{-1})$	$\begin{array}{c} Si \\ (\mu g \; L^{-1}) \end{array}$	pН	Cond. $(\mu s \ cm^{-1})$	$\begin{array}{c} \text{DOC} \\ (\text{mg } L^{-1}) \end{array}$	Ν	Spring (mg L	(flood		Sumn (mg L	ther base (1^{-1})	flow
														TSS ^a	POM ^a	SSmin ^a	TSS ^b	POM ^b	SSmin ^b
C1	1.3	514	1989	997	519	888	22.8	1964	5937	5.4	33.0	19.1	55	4.6	2.4	2.1	1.0	1.0	0.0
C2	0	501	1668	724	234	713	11.0	1791	5395	5.1	32.7	17.9	54	1.4	1.4	0.0	0.6	0.5	0.1
C3	76	228	630	364	78	225	3.1	538	1643	4.1	46.2	33.1	41	0.9	0.9	0.0	0.3	0.4	
C4	40	79	952	1027	221	352	7.4	796	2214	4.4	31.6	29.3	55	1.5	1.8	_	0.4	0.6	_
C5	36	120	1182	1830	257	400	12.4	865	2685	4.8	22.7	20.7	54	1.6	1.4	0.2	1.2	1.1	0.1
C6	24	177	1606	1732	373	571	16.3	1224	3751	5.5	23.5	17.3	54	7.9	5.2	2.7	4.5	3.2	1.3
C7	15	263	1621	1162	325	621	12.1	1384	4195	5.0	29.1	22.5	55	5.6	3.1	2.5	0.1	0.1	0.0
C8	11	349	1942	1274	424	687	18.4	1565	4761	5.3	28.6	22.5	54	3.0	1.7	1.3	2.4	1.9	0.5
C9	14	318	2111	1492	474	762	32.2	1581	4990	5.8	28.9	15.6	52	32	6.7	25	4.1	3.1	1.0
C10	26	174	1632	1366	432	549	14.2	1283	4021	5.3	25.8	19.1	55	1.7	1.3	0.3	3.0	2.1	0.9
C12	16	574	1925	1766	563	774	29.7	1547	5323	5.6	27.4	17.7	55	58	5.8	52	6.4	3.0	3.3
C13	10	492	2086	1638	567	827	38.5	1650	5215	5.8	27.8	17.5	55	129	8.3	121	2.9	2.3	0.5
C14	5.1	325	2675	1183	911	952	41.5	1785	4899	6.3	33.0	12.1	54	12.1	2.3	9.8	4.2	1.8	2.4
C15	14	200	2437	879	693	789	23.6	1607	4253	6.4	29.0	12.3	55	12.6	3.4	9.2	1.8	1.1	0.7
C16	8.3	1078	3165	2542	1247	1401	61.1	1947	6658	6.5	36.7	11.5	55	282	16	266	3.1	1.5	1.7

Total suspended solids (TSS), particulate organic matter (POM) and minerogenic suspended solids (SSmin) from two sampling occasions in 2004. Electrical conductivity was measured at room temperature. N is the number of samples for all analyses except conductivity, for which there were 23-28 samples. Analytical precision is 2% for element concentrations and DOC, except for Ca (4%). For TSS, POM and SSmin the analytical precision is $\pm 0.5 \text{ mg L}^{-1}$.

^a Results from one sampling occasion during spring flood 2004 (2004-04-28).
^b Results from one sampling occasion during summer base flow 2004 (2004-08-27).



Fig. 2. Temporal variations in water discharge, pH, DOC, Fe and Mn (total and $<0.4 \mu m$ filtered) in a forested headwater stream (C2) during 2004–2005. Stream water discharge was estimated from the discharge at the index site C7, by assuming the same specific discharge.

There was no significant correlation between Fe and Mn. The temporal patterns of Fe and Mn showed that there were only slight differences between total and filtered (<0.4) concentrations, both increased and peaked on the rising limb of the spring flood. During spring flood 2004 Fe_{tot} and Fe_{<0.4} increased by a factor of about 4 and in 2005 by a factor of about 2. Maximum COC, two weeks prior to spring flood peak discharge. At C2 Fe_{tot} and Fe_{<0.4} correlated well with DOC ($r^2 = 0.77$ and $r^2 = 0.76$, respectively, p < 0.001). At C1 the correlation was not as strong but still significant ($r^2 = 0.44$ and $r^2 = 0.36$, respectively, p < 0.001).

 Mn_{tot} and $Mn_{<0.4}$ ranged by a factor of about 3, from 8 µg L⁻¹ prior to spring flood to 28 µg L⁻¹ at spring peak

flow in 2005. The concentration peak of Mn, which also coincided with maximum DOC immediately prior to peak discharge at spring flood, was more pronounced in 2005 than in 2004. Similar temporal patterns of Fe_{tot} , $Fe_{<0.4}$, Mn_{tot} and $Mn_{<0.4}$ were also observed at the other forested headwater stream C1.

4.2.2. Wetland catchment

The wetland influenced streams (C3, C4 and C5) (here represented by headwater stream C4) were characterized by high winter base flow DOC and decreasing DOC concentrations at spring flood, followed by increased DOC during summer (Fig. 3). In stream C4, pH ranged from 4.1 to 5.6 with the lowest pH observed at spring flood.



Fig. 3. Temporal variations in water discharge, pH, DOC, Fe and Mn (total and $\leq 0.4 \mu m$ filtered) in a wetland headwater stream (C4) during 2004–2005. Stream water discharge was estimated from the discharge at the index site C7, by assuming the same specific discharge.

In all wetland influenced streams differences between total and dissolved fractions of Fe and Mn were small. Highest concentrations of both Fe and Mn were observed at winter base flow in January 2004. At C4 during spring flood Fe_{tot}, Fe_{<0.4}, Mn_{tot} and Mn_{<0.4} decreased rapidly, by a factor of about 10. Highest concentrations of Mn were observed at the same time as the highest concentrations of Fe. The correlations (r^2 , p < 0.05) between DOC and Fe_{tot}, Fe_{<0.4}, Mn_{tot} and Mn_{<0.4} were 0.32, 0.40, 0.15 and 0.17, respectively.

4.2.3. Mixed catchment: catchment outlet (C16)

At the catchment outlet, C16, the temporal pattern of DOC and pH was similar to that observed at C2. DOC ranged by a factor of about 7, from lowest concentrations at winter base flow to highest during the summer's first rain in 2004 (Fig. 4). The pH at this site was highest of the 15 sampled streams. There was a significant difference between total and filtered ($<0.4 \mu$ m) concentrations (Fe and Mn: p < 0.0001), especially marked at spring peak flow, when

Fe_{tot} increased by a factor of 15, and Mn_{tot} increased by a factor of 8. Fe_{<0,4} and Mn_{<0,4} only increased by a factor of about 2. At peak flow in 2004 only 13% of the Fe and 14% of the Mn was transported in the fraction <0.4 µm and in 2005 Fe_{<0,4} constituted 20% and Mn_{<0,4} 18%. No correlation was found between DOC and either of Fe_{<0,4} or Mn_{<0,4}. The correlation (r^2 , p < 0.05) between DOC and Fe_{tot} and Mn_{tot} was 0.18 and 0.20, respectively.

4.3. Principal component analysis

4.3.1. Winter base flow

During winter base flow the variables used in PC1 and PC2 explained 94% of the total variation in the Fe and Mn concentrations (Table 3 and Fig. 5A). Fe_{tot} and Fe_{<0.4} were near one another on the PC ordination, as were Mn_{tot} and Mn_{<0.4}, implying that total and filtered (<0.4 μ m) fractions behaved similarly. This result reflects that, during winter base flow, Fe_{tot} was dominated by Fe_{<0.4} and that there was not much particulate Fe and



Fig. 4. Temporal variations in water discharge, pH, DOC, Fe and Mn (total and $<0.4 \,\mu$ m filtered) in Krycklan River, the catchment outlet (C16) during 2004–2005. Stream water discharge was estimated from the discharge at the index site C7, by assuming the same specific discharge.

Mn. On the main axis, PC1, which explained 59% of the variance of Fe and Mn, quaternary deposits were important for Mn; i.e. high concentrations of Mn_{tot} and $Mn_{<0.4}$ were associated with silty catchments and low concentrations were associated with till catchments (Table 3). On the second axis, PC2, which explained 34% of the variance, there was a forest-wetland gradient. High concentrations of both Fe_{tot} and Fe_{<0.4} were associated with DOC and catchments with a large proportion of peat wetlands whereas low concentrations were associated with forested catchments. High concentrations of both Mn_{tot} and $Mn_{<0.4}$ were associated with forested catchments. High concentrations were associated with forested catchments and low concentrations were associated with peat wetland catchments and DOC.

4.3.2. Spring peak flow

During peak spring flood 88% of the total variance in the Fe and Mn concentrations was explained by PC1 and PC2 (Table 3 and Fig. 5B). PC1, explaining 67% of the variance, showed high concentrations of Fe and Mn (both total and $\leq 0.4 \mu$ m) associated with large, silty catchments

whereas low concentrations were associated with catchments with a large proportion of wetlands. On PC2, $Fe_{<0,4}$ showed high loading, and was associated with catchments including lakes. DOC was also associated with high $Fe_{<0,4}$. During spring flood both Mn_{tot} and $Mn_{<0,4}$ were associated with large, silty catchments.

4.4. Influence of particulates and landscape properties

4.4.1. Particulates

The catchments containing silt deposits (C9, C12, C13, C14, C15 and C16) all showed large differences in concentrations of Fe and Mn between unfiltered and filtered samples (Table 4). During 2004 and 2005, at Krycklan (C16) only 25% and 39% of the Fe and Mn, respectively, was transported in the size fraction $<0.4 \,\mu$ m, calculated from discharge-weighted averages. At the headwater sites where there are no silt deposits the difference in average concentration between unfiltered and filtered samples was small (at C2: Fe 5.9%, Mn 2.9% and at C4: 7.5% and 7.3%,

Table 3

Loadings from PCA on stream water chemistry and landscape variables calculated from samples from 15 streams during base flow and peak spring flood in 2004–2005

	Base fl	ow	Peak flow		
	PC1	PC2	PC1	PC2	
Fe _{tot}	-0.80	-0.53	-0.92		
Fe _{diss}	-0.67	-0.69	-0.61	0.76	
Mn _{tot}	-0.81	0.54	-0.88	-0.42	
Mn _{diss}	-0.79	0.57	-0.84		
Al			-0.86	-0.36	
Ca		0.65	-0.78		
Si		0.62	-0.88		
pH		0.68	-0.55	-0.34	
DOC		-0.72		0.49	
Forest		0.73	-0.42		
Wetland		-0.76	0.45		
Lake		-0.33		0.56	
Arable	-0.33	0.50	-0.40	-0.47	
Glaciofluval		0.35		-0.35	
Thin Soils		-0.48			
Peat		-0.75	0.45		
Silt	-0.50	0.58			
Till	0.48	0.43			
Area		0.51	-0.59	-0.44	
Explained variance (%)	59.4	34.2	67.3	20.4	
Total explained variance (%) (PC1–PC5)	93	8.6	87	7.7	

Explained variance and loadings are reported for the first two principal components (PC1 and PC2). Loadings primarily controlling the component (>0.5) are marked in bold, loadings <0.3 are omitted.

respectively), however, still statistically different (paired *t*-test: C2: Fe p < 0.01, Mn p < 0.01; C4: Fe p < 0.001, Mn p < 0.0001).

Total suspended sediment (TSS) at C16 during spring flood 2004 was 282 mg L^{-1} of which 94% was of minerogenic origin (Table 2). At summer base flow in August 2004 the TSS at C16 was 3.1 mg L^{-1} of which 55% was of minerogenic origin. The lowest concentration of SSmin at spring flood was observed at one of the forested headwater sites (C2) and at the wetland headwater sites (C3, C4 and C5).

We analyzed the "particulate concentration" of Fe and Mn, by subtracting the concentrations in filtered samples from the total concentrations and compared the concentrations to the minerogenic suspended solids (SSmin) at spring flood 2004. Strong correlations were obtained between the "particulate concentrations" and SSmin for Fe ($r^2 = 0.99$, p < 0.001) and Mn ($r^2 = 0.74$, p = 0.001) (Fig. 6). The strong positive correlations further support the importance of suspended sediments for the observed concentrations of Fe and Mn during spring flood. If the sites with >3% of surficial silt deposits (C9, C12, C13, C14, and C16) were excluded the correlation was slightly reduced for both Fe $(r^2 = 0.87, p < 0.001)$ and Mn $(r^2 = 0.46, p = 0.03)$. Moreover, multiple linear regressions of average concentrations of Mntot and Fetot, using silt and catchment area as predictor variables, showed that silt and catchment area were equally important for the observed concentration of Mn_{tot} in the 15 catchments, explaining 88% of the variability of Mn_{tot}. However, silt and catchment area were of less significance for Fetot, explaining only 46% of the variability which was dominated by catchment area.



Fig. 5. Ordination plots for PCA (January through May for 2004 and 2005) based on individual samples for all 15 streams during (A) winter base flow, (B) spring peak flow. Similar direction of the variables indicates high positive association, divergent variables indicate high negative association. Perpendicular variables indicate no association between variables. The percentage of data variation for each axis is shown on the x- and y-axes.

Table 4

Discharge-weighted average concentrations (2004–2005) for Fe and Mn in each stream, showing the difference between unfiltered (total concentrations) and filtered (concentrations in the fraction $<0.4 \ \mu m$) samples

Site	Fe _{tot}	Fe<0.4	Mn _{tot}	Mn _{<0.4}
No.	$(\mu g L^{-1})$	$(\mu g L^{-1})$	$(\mu g L^{-1})$	$(\mu g L^{-1})$
C1	997	829	22.8	20.7
C2	724	681	11.0	10.5
C3	364	364	3.1	3.1
C4	1027	950	7.4	6.8
C5	1830	1681	12.4	11.8
C6	1732	1286	16.3	14.0
C7	1162	1041	12.1	11.1
C8	1274	1113	18.4	16.9
C9	1492	925	32.2	26.3
C10	1366	1150	14.2	13.2
C12	1766	1006	29.7	22.6
C13	1638	995	38.5	34.8
C14	1183	645	41.5	16.5
C15	879	555	23.6	12.5
C16	2542	644	61.1	24.3

N = 41 for C3 and N = 51-55 for all other streams.

4.4.2. Landscape properties

Wetland influenced catchments showed high concentrations of $Fe_{<0.4}$ in comparison to more forest dominated catchments of similar size and larger, mixed catchments (Fig. 7). In particular, the wetland headwater streams C4 and C5 showed high concentrations of $Fe_{<0.4}$. On the contrary, highest concentrations of $Mn_{<0.4}$ were observed in the larger streams in mixed catchments (Fig. 7). In particular, high concentration and high variability of $Mn_{<0.4}$ was observed at C13.

No significant correlation was found between average Fe_{tot} or Fe_{<0.4} (discharge-weighted) and wetland coverage.

5. DISCUSSION

5.1. Flow-related variations of Fe and Mn in forested vs. wetland catchments

In this study, the seasonal patterns of pH and DOC in forested catchments were characterized by a decrease in pH and an increase in DOC at spring flood. This is a typical pattern for this region (Laudon et al., 2000; Andersson and Nilsson, 2002; Cory et al., 2006; Buffam et al., 2007) and other studies have also reported increased concentrations of DOC at high discharge (Shafer et al., 1997; Rember and Trefry, 2004). In forested catchments we also observed increased concentrations of total and filtered (<0.4 µm) Fe and Mn during spring flood. Similar flow-related variations of Fettot, pH and TOC as observed in this study have been reported from the Kalix River (Andersson et al., 2006). The seasonal pattern of Fe closely resembles that of DOC, in particular during spring flood when the concentration increases and is synchronized with DOC prior to maximum discharge. The high correlation of Fe_{tot} and $Fe_{<0.4}$ with DOC at C2 ($r^2 = 0.77$ and $r^2 = 0.76$, p < 0.001) is most probably attributed to colloidal organic matter; Fe is mainly transported as colloidal Fe associated with DOC (Andersson et al., 2006; Ingri et al., 2006). The increased concentrations of DOC also contributed to increased concentrations of Fe since high concentrations of soluble



Fig. 6. Linear regression plot of "particulate" Fe (Fe_{tot} minus Fe_{diss}) and minerogenic suspended sediments (SSmin). Numbers refer to sampling sites. Inserted panel shows linear regression of low concentration data. Results from one sampling event during spring flood 2004.



Fig. 7. Box and whisker plots of $Fe_{<0.4}$ (top panel) and $Mn_{<0.4}$ (lower panel) from 15 streams during 2004 and 2005, showing the differences between catchments of different size and land cover (forested, wetland and mixed catchments). Numbers refer to sampling sites. Upper/lower whiskers extend to the maximum/minimum data point within 1.5 box heights from the top/bottom of the box.



Fig. 8. Linear regression of Fe_{tot}/Al_{tot} and percentage wetland coverage, based on calculated averages (discharge weighted) for each sampling site. Numbers refer to sampling sites. Site C3 was excluded from the linear regression.

organically complexed Fe are related to high concentrations of organic compounds in the upper soil layers (Lydersen et al., 2002; Abesser et al., 2006) which then are flushed into the stream by rising water tables during spring flood (Hornberger et al., 1994; Bishop et al., 2004). Manganese did not show significant correlation with DOC at the forested sites, which may be due to the fact that Mn does not form complexes with organic matter to the same extent as Fe does (Carpenter, 1983; Laxen et al., 1984; Young and Harvey, 1992).

At the catchment outlet (C16), DOC was of less importance for the observed concentration of Fe_{tot} and $Fe_{<0.4}$. Instead, the minerogenic contributions from erosion of silt deposits on the stream banks, in combination with the pH decline, contributed to an increase in Fe_{tot} and $Fe_{<0.4}$. during spring flood.

In the headwater wetland sites, a pH decrease was observed during spring flood when DOC also decreased. This pH decrease is most likely attributed to dilution of base cations and acid neutralizing capacity which previously has been investigated in detail in the studied streams (Laudon et al., 1999; Bishop et al., 2000; Hruška et al., 2001; Buffam et al., 2007). In headwater wetland sites, the seasonal pattern of DOC (Buffam et al., 2007), total and filtered (<0.4 µm) Fe and Mn was opposite that of the forested sites. In the wetland streams the highest concentrations of Fe and Mn were observed during winter, prior to spring flood. The high concentrations prior to spring flood probably result from the anoxic conditions during winter, when the frozen peat further limits the supply of oxygen to underlying peat layers and Fe and Mn are released into the water as dissolved species (Goulet and Pick, 2001). Moreover, the wetland influenced headwater stream (C4) is surrounded by forest and during low flow there is some groundwater contribution. An isotopic study of O¹⁸ (Laudon et al., 2007) at the wetland headwater site (C4) has shown that there are flow pathways along layers of higher hydrological conductivity at a depth of 200-250 cm. At spring flood melt water infiltrated in the surrounding forest soils flows along these deep flow pathways. During winter base flow, these flow pathways may intersect deeper anoxic layers in the peat and contribute with anoxic groundwater, releasing dissolved Fe and Mn to the wetland influenced stream. However, during spring flood, the continuous layer of frozen peat limits infiltration whereby overland and rapid surficial flow of melt water dilutes the stream water (Laudon et al., 2007). Hence, the reduced concentrations of DOC, Fe and Mn in wetland headwaters are most likely caused by dilution by melt water.

5.2. Fe and Mn hydrogeochemistry: influence of landscape properties

Our results are consistent with the spatial hypothesis that the hydrogeochemistry of Fe in small boreal streams is influenced by landscape properties and in particular wetlands. It has previously been reported that formation of strongly bound Fe–organic complexes is enhanced by low pH of mineral-poor wetlands (Young and Harvey, 1992). However, for Mn we did not observe the same dependence on wetlands. The PCA showed positive association of Fe_{tot} and $Fe_{<0.4}$ with wetlands and DOC at winter base flow, indicating that DOC was an important carrier for Fe during this period. At peak flow, Fe_{tot} and $Fe_{<0.4}$ were not associated with wetlands, suggesting that the sources and/or hydrological pathways for Fe were altered during peak flow. Furthermore, the importance of particulates in the transport was enhanced during high discharge, indicated by the shift of Fe_{tot} in the PCA from association with wetlands and DOC at base flow.

In contrast, both Mntot and Mn<0.4 were associated with silt deposits during base flow as well as during spring peak flow. These results are consistent with a previous study, i.e. Shafer et al. (1997), who also observed increased trace metal concentrations in watersheds with silty soils. In addition, at peak flow, wetlands were not associated with DOC indicating that the wetland-derived DOC was diluted by melt waters during snow melt (Laudon et al., 2004; Buffam et al., 2007). Mn correlated poorly with DOC which also has been shown in previous studies (Carpenter, 1983; Laxen et al., 1984; de Vitre et al., 1988), though another study showed that about 50% of Mn in stream waters is humiccomplexed (Graham et al., 2002). In our study, the absence of the hypothesized positive correlation between Mn and wetlands may be attributed to several factors. Previous studies in northern Sweden (Pontér et al., 1990, 1992) have attributed an increase of dissolved Mn during spring flood to a supply of Mn-rich waters from wetlands. However, these studies have encompassed larger catchments where the contribution of deeply derived groundwater probably is larger than in our small catchments. Moreover, these previous studies of larger systems have included ice covered lakes, where anoxic conditions in the winter contribute to enhanced reduction of Mn (and Fe) to dissolved species. However, in the Krycklan catchment there are only a few small lakes. Furthermore, Mn appears to be more dependent on the minerogenic supply via groundwater than Fe. The wetlands in this study are Sphagnum dominated and have low pH and low alkalinity. Hence, they can be considered to be mineral poor, although there may be some mineral groundwater influence at low flow. It has been reported that the peat geochemistry of Mn is highly dependent on the mineral groundwater supply to the wetland where mineral-poor peatlands had less easily reducible Mn in comparison to mineral-rich fens (Bendell-Young, 1999). On the contrary, the variability of reducible Fe between peatlands was not dependent on whether the peatland was mineralrich or mineral poor. It was concluded that mineral-poor peatlands may still receive significant amounts of Fe from groundwater contribution whereas this was not the case for Mn. Most probably the supply of Mn to the wetlands in this study is limited whereby the concentrations in the wetland influenced streams also show low concentrations of Mn.

The correlation of the Fe_{tot}/Al_{tot} ratio (Fig. 8) and the $Fe_{<0.4}/Al_{<0.4}$ ratio with wetland coverage was strong, indicating that there was a significant correlation between Fe and wetland coverage when the variance due to mineral particles was accounted for. This result shows that reducing environments are important for the supply of Fe to stream

waters. However, there was no correlation of the Mn_{tot}/Al_{tot} ratio and the $Mn_{<0.4}/Al_{<0.4}$ ratio with wetland coverage. This result is most probably due to fluctuations of the ground water level, i.e. redox changes, leading to more or less enriched layers of Mn and therefore certain flowpaths are Mn limited in the wetland influenced sites. A previous study of peat geochemistry demonstrated that Mn reduction occurs in the upper 10–50 cm of the peat layer (Koretsky et al., 2007). In the wetlands of this study the dominating flow paths may transect deeper sections and hence the dissolved Mn is not mobilized to the streams.

5.3. Fe and Mn hydrogeochemistry: influence of particulates

Downstream in the Krycklan stream network erosion of silt deposits from stream banks was important for the concentration of suspended particulate matter. Erosion in these streams contributed to Fe and Mn being transported mainly as particulates of minerogenic origin. At the catchment outlet, C16, the minerogenic part of the total suspended solids was 150 times higher at spring flood in comparison to summer base flow. The large differences in concentration of Fe and Mn between unfiltered and filtered samples in the streams of catchment with silt deposits (C9, C12, C13, C14, C15 and C16) further indicate that these elements are mainly transported as particulates. In these streams 37-81% of Fe and 17-72% of Mn was transported as "particulates" (Fetot-Fe<0.4) during 2004-2005. In the wetland headwater streams (C3, C4 and C5) the corresponding range was 3-6% and 0.1-3%, for Fe and Mn, respectively. In the forested headwater streams (C1 and C2) particulates only constituted 3-14% of Fetot and 3-7% of $Mn_{tot}\!.$ The minerogenic contribution from the silt deposits are most probably the reason for the increase in Fetot and Mntot in the larger, silt influenced streams. However, multiple regressions of average Mn_{tot} and Fe_{tot}, showed that silt and catchment area were equally important for the observed concentration of total Mn, explaining 88% of the variability of Mn. However, silt and catchment area were not of significance for average concentrations of Fe_{tot}. In the smaller streams the supply of minerogenic particulate matter is limited and Fe and Mn are mainly transported as dissolved species or as colloids of a size <0.4 µm. Since a substantial part of the colloidal Fe will pass through a filter with a pore size of $0.4 \,\mu\text{m}$, the "dissolved" fraction is not only dissolved Fe but also includes colloidal material (Danielsson, 1982), raising the apparent concentration of "dissolved" Fe (Kennedy et al., 1974). A considerable part of the analyzed filtered fraction ($<0.4 \,\mu m$) in the headwater streams, where the concentrations of minerogenic suspended solids are low, is probably colloidal Fe.

6. CONCLUSIONS

- The hydrogeochemistry of Fe is highly dependent on the coverage of wetlands. However, for Mn no significant correlation to wetland coverage was observed.
- At winter base flow total and filtered (<0.4 μm) concentrations of Fe were associated with wetlands and DOC.

During spring peak flow total concentrations of Fe were associated with large catchments containing silt deposits, showing the importance of particulates for the transportation of Fe during high discharge events. Total and filtered ($<0.4 \mu m$) concentrations of Mn were associated with large, forested catchments with silt deposits during winter base flow as well as during spring peak flow.

- The importance of particulates was most significant for the larger streams, characterized by silt deposits on the stream banks.
- In forested headwater streams DOC is of significance for the observed increased concentrations of Fe during high discharge. Mn did not show any strong correlation with DOC.

According to our results wetlands, organic carbon and particulates are of great importance for Fe and Mn in stream water. More studies on how variations in landscape properties affect surface water chemistry are needed to further evaluate the temporal and spatial variation of Fe and Mn and other trace metals. This study highlights the importance of including a landscape perspective when studying stream water chemistry.

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