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From soil water to surface water – how the riparian zone controls element transport from a boreal forest to a stream

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Abstract. Boreal headwaters are often lined by strips of highly organic soils, which are the last terrestrial environment to leave an imprint on discharging groundwater before it enters a stream. Because these riparian soils are so different from the Podzol soils that dominate much of the boreal landscape, they are known to have a major impact on the biogeochemistry of important elements such as C, N, P and Fe and the transfer of these elements from terrestrial to aquatic ecosystems. For most elements, however, the role of the riparian zone has remained unclear, although it should be expected that the mobility of many elements is affected by changes in, for example, pH, redox potential and concentration of organic carbon as they are transported through the riparian zone. Therefore, soil water and groundwater was sampled at different depths along a 22 m hillslope transect in the Krycklan catchment in northern Sweden using soil lysimeters and analysed for a large number of major and trace elements (Al, As, B, Ba, Ca, Cd, Cl, Co, Cr, Cs, Cu, Fe, K, La, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Si, Sr, Th, Ti, U, V, Zn, Zr) and other parameters such as sulfate and total organic carbon (TOC). The results showed that the concentrations of most investigated elements increased substantially (up to 60 times) as the water flowed from the uphill mineral soils and into the riparian zone, largely as a result of higher TOC concentrations. The stream water concentrations of these elements were typically somewhat lower than in the riparian zone, but still considerably higher than in the uphill mineral soils, which suggests that riparian soils have a decisive impact on the water quality of boreal streams. The degree of enrichment in the riparian zone for different elements could be linked to the affinity for organic matter, indicating that the pattern with strongly elevated concentrations in riparian soils is typical for organophilic substances. One likely explanation is that the solubility of many organophilic elements increases as a result of the higher concentrations of TOC in the riparian zone. Elements with low or modest affinity for organic matter (e.g. Na, Cl, K, Mg and Ca) occurred in similar or lower concentrations in the riparian zone. Despite the elevated concentrations of many elements in riparian soil water and groundwater, no increase in the concentrations in biota could be observed (bilberry leaves and spruce shoots).

1 Introduction

The riparian zone is the interface between the terrestrial landscape and the streams and rivers draining it. Hence, the riparian soils are often the last material that the groundwater is in contact with before it becomes surface water. Although it normally occupies only a minor fraction of the total catchment area, it can therefore have a disproportionately high impact on the water quality of streams, rivers and lakes over wide spatial scales (1–1000 km^2; Billett and Cresser, 1992; Smart et al., 2001; Seibert et al., 2009). Likewise, because of its strategic location in the landscape, the riparian soils may also exert the ultimate control over the fate and transit times of nutrients, pollutants and other substances in the terrestrial ecosystems. The importance of the concept of the riparian zone hinges on the fact that riparian soils can be profoundly different from the uphill soils that dominate the landscape (Sauer et al., 2007). In the boreal region, shallower groundwater levels and generally wetter conditions tend to prevail in the vicinity of stream channels (Grabs et al., 2012). As a result, there is often an accumulation of organic matter, which creates more wetland-like conditions in the riparian zone. This is particularly common along smaller streams, which despite their size contribute significantly to the runoff generation even in large rivers in force of their number (Bishop et al., 2008; Lassaletta et al., 2010). In the case of carbon the significance of the riparian zone is well established when it comes to both dissolved organic carbon (DOC) and CO_2 (e.g. Fiebig et al., 1990; Hinton et al., 1998; Oquist et al., 2009; Lyon et al., 2011; Winterdahl et al., 2011; Grabs et al., 2012; Knorr, 2013; Leith, 2015; Ledesma et al., 2015). However, the special biogeochemical conditions of the riparian zone also have consequences for the transport of widely different substances such as nitrogen (Hill, 1996; Cirmo and McDonnell, 1997; Sabater et al., 2003), phosphorus (Mulholland, 1992), base cations (Ledesma et al., 2013), aluminium (Cory et al., 2007), mercury (Bishop et al., 2009), persistent organic pollutants (Bergknut et al., 2011) and pesticides (Vidon et al., 2010). Furthermore, the riparian zone is gaining increasing recognition as an ecological hotspot (Jansson et al., 2007; Kuglerová et al., 2013; Nilsson et al., 2013). As a consequence, precautions are often taken in modern forestry in order to reduce the deleterious impact of logging on riparian soils (Moore and Richardson, 2012; Kuglerová et al., 2014; Tiwari et al., 2016).

For the vast majority of elements, however, the role of the riparian zone remains unexplored. Yet, there are good reasons to hypothesise that the riparian soils influence the transport of many more substances than the examples given above. In the boreal region the mobility of many metals and miscellaneous hydrophobic substances is strongly connected to the presence of organic matter, by accumulation in both peat and other forms of solid organic matter (e.g. González et al., 2006; Cloy et al., 2009; Lidman et al., 2013) as well as by transport by organic colloids and particles (e.g. Gustafsson et al., 2000; Dahlqvist et al., 2007; Pokrovsky et al., 2010). The accumulation of organic matter in the riparian zone is also associated with fundamental chemical parameters such as pH and redox potential, which are well known to influence the speciation and mobility of many elements. The purpose of this study was therefore to broaden the perspective on riparian soils by investigating the behaviour of a wider range of elements as they are transported across the chemical gradients of the riparian zone in a boreal hillslope transect, starting in an uphill Podzol profile and following the chemical evolution of the groundwater all the way to the stream. One reason is that each of the 32 elements (plus TOC and sulfate) included in this study are important per se, for instance as micronutrients (e.g. Se, Ni, Cu, Zn, Mn), as pollutants (e.g. Cd, V, Cs, U, As) and as tracers for important processes (e.g. Cl, Zr). More importantly, however, a multi-element approach to the riparian chemistry, which allows a comparison of different elements with contrasting or corresponding biogeochemical properties, can first and foremost help identify the most important processes taking place in the riparian soils and contribute to a more over-arching understanding of the functioning of riparian soils. In the best case, it can also help us predict how various substances will be affected based on their biogeochemical properties (Lidman et al., 2014). In order to capture the temporal variability in the soil water and groundwater chemistry along the transect, samples were collect at 10 sampling occasions between January and October, covering the hydrologically most active period at the studied site. This approach resulted in a large number of data, so the intention here is not to discuss any of the investigated elements in particular detail but rather to provide a general description of how the water chemistry changes with respect to various types of elements as the water passes through the riparian zone. We believe that a better appreciation of the riparian zone is important for assessing both the water quality and the long-term mass balance of the boreal landscape with respect to weathering products, pollutants, nutrients and other substances.

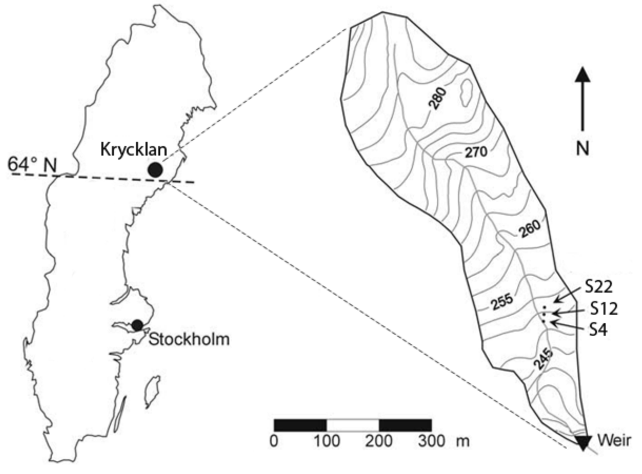

Figure 1. Map of Sweden showing the location of the Krycklan catchment (left) and the Västrabäcken (C2) catchment (right). The location of the sampling sites (S4, S12 and S22) in the investigated transect are shown along with the elevation above sea level (m). Note that the lysimeters are located along the flow direction of the groundwater and not perpendicularly to the stream.

2 Material and methods

2.1 Site description

The study was conducted in the Krycklan catchment in northern Sweden (Laudon et al., 2013). The investigated transect is located by a first-order stream ($0.12\,km^2$), referred to as Västrabäcken or C2 in previous publications, which is one of the main sites included in the Krycklan Catchment Study (Fig. 1). The local climate is cold temperate with an mean annual temperature of 1.8 °C (1981–2010), ranging from −9.5 °C in January to 14.7 °C in July (Laudon et al., 2013). The mean annual precipitation is 614 mm, of which roughly half is lost by evapotranspiration and half by runoff. The snow cover remains for 168 days per year on average (1980–2007), varying in maximum depth between 43 and 113 cm. The maximum soil frost depth varies between 2.5 and 79 cm (1993–2007) depending on factors such as temperature and the timing and depth of the snow (Haei et al., 2010). The entire catchment is covered by century-old coniferous forest, mainly Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*), with elements of deciduous trees and shrubs.

The soils in the Västrabäcken catchment are made up of locally derived till, mostly several metres deep (such as by the investigated transect). The mineralogy is dominated by quartz (40 %), K-feldspar (25 %), plagioclase (23 %), amphibolites (7 %), muscovite (4 %) and chlorite (1 %; Ledesma et al., 2013). At ca. 1 m, however, there is a compact layer of basal till with substantially lower hydraulic conductivity than shallower soil horizons (Table S2 in the Supplement; Bishop, 1991). Previous investigations of the hydrology in the transect have indicated that most of the water transport takes place in above this compact till layer (Rodhe, 1989; Laudon et al., 2004; Peralta-Tapia et al., 2014). The stream channel was deepened, partially straightened and probably also extended further up in the catchment by manual ditching in the 1920s. Ditching of forests was a common practise in Fennoscandia at this time, and a large portion of the Swedish headwaters have therefore been affected in a similar way (Dahlstrom et al., 2005). The purpose was to improve the drainage, thereby counteracting the paludification and increasing the forest productivity. Exposed roots of some older trees in the riparian zone reveal that there may have been a lowering of the ground level as a result of the ditching. Presumably peat, which had been building up under the previously wetter conditions, has begun to decay, causing the ground surface to sink by ca. 20–30 cm in some places.

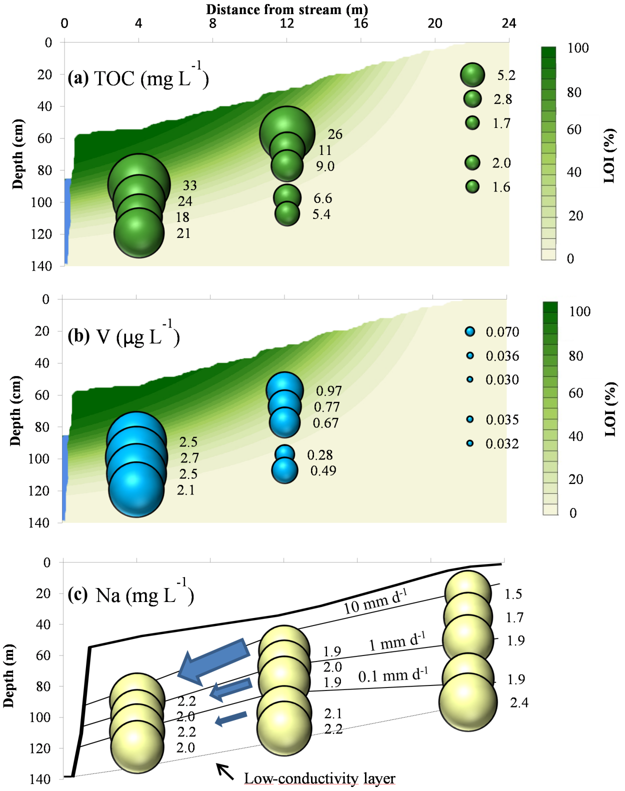

Figure 2. Average soil water and groundwater concentrations of TOC **(a)**, vanadium **(b)** and sodium **(c)** in the investigated transect. The area of the bubbles is proportional to the concentration, which in turn is given next to each bubble. The background illustrates the loss on ignition (LOI, %) in the two upper examples. The bottom subplot illustrates the approximate groundwater levels at different stream discharge based on Laudon et al. (2004). The distance from the stream is measured along the flow pathway of the groundwater.

The investigated transect is located ca. 300 m upstream of the catchment outlet and consists of three sampling sites (S4, S12 and S22) located 4, 12 and 22 m, respectively, from the stream as measured along the flow pathway of the groundwater, which was identified using hydrological tracers (Fig. 1). At each sampling site ceramic suction lysimeters were installed in 1995, allowing regular sampling of soil water and groundwater at different depths in the three soil horizons. In this study four depths at S4 and five depths each at S12 and S22 were sampled. Each lysimeter is referred to by the name of sampling site followed by the depth in centimetres, e.g. S4–45. S22 represents an iron Podzol with clearly developed soil horizons. As such it is typical for most of the investigated catchment and in a broader sense also for boreal forests in general. At the surface there is a ca. 8 cm thick organic layer (so-called mor), but apart from that the content of organic matter is low (< 0.8 % below 10 cm; Table S1). The uppermost lysimeter (S22–20) is located at the lower end of the E horizon, which reaches from 8 to 20 cm. Then there are three lysimeters (S22–35, S22–50 and S22–75) in the B horizon, which has a hardpan around 75 cm. Finally, there is one lysimeter in the C horizon (S22–90), which starts at ca. 80 cm. This lysimeter is also located in the compact basal till with notably lower conductivity (Table S2). As the groundwater approaches the stream the Podzol gradually gives way to more organic Histosols as a result of the increasingly wet conditions closer to the stream. S4 and S12 can both be considered to represent the riparian zone and lack any distinct soil horizons. The thickness of the organic layer increases from 20 to 30 cm at S12 to ca. 80 cm at S4 (Fig. S1 in the Supplement). This accumulation of organic matter in the riparian zone is typical for this and other headwaters in the Krycklan catchment (Fig. S2; Grabs et al., 2012). The slope is not particularly steep with an inclination of ca. 3 %, which can be compared to the average inclination of the Västrabäcken catchment, 8.7 %. Uphill from S22 the slope continues ca. 100–120 m to the water divide (Fig. 1). Previous research has demonstrated that in all three soil profiles (S4, S12 and S22) there is a clear relationship between the groundwater level and stream discharge (Laudon et al., 2004; Seibert et al., 2009). The discharge increases exponentially with rising groundwater levels following the so-called transmissivity feedback mechanism, which suggests that much of the water transport takes place the uppermost saturated soil layers (Fig. 2; Bishop et al., 2011). This is also related to the porosity of the soils, which varies from 36 to 83 % with higher values in more organic soils and, consequently, a decline with depth in all profiles (Table 2). Further details on the transect can be found previous publications (Nyberg et al., 2001; Stähli et al., 2001).

2.2 Sampling and analyses

Soil water and groundwater (i.e. both from the saturated and the unsaturated zone) were collected on 10 occasions during 2008 by attaching vacuum bottles to the tubes that are connected to each of the ceramic cups in the soils. The investigation period started during winter baseflow conditions in January and ended in October, when the system again had returned to winter baseflow conditions. Samples were collected every month with the exception of June, when two samples were collected, and September, which was omitted. This sampling strategy was assumed to capture the most active period both in hydrological and biogeochemical terms. This means that there are in most cases 10 observations from each depth in each profile, but in certain cases there are values missing either because sufficient amounts of water could not be collected due to soil frost or drought or because the concentrations of some elements in some cases were below detection limit.

In S4 four lysimeters were sampled, reaching from 35 to 65 cm in depth. This covers the most hydrologically dynamic part of the profile, since S4–35 was never saturated, except possibly briefly in connection with the peak flow of the spring flood, and S4–65 was constantly saturated, except for a few weeks in the middle of the summer. In S12 five lysimeters covering a depth from 20 to 70 cm were sampled. S12–20 is believed never to have been saturated, while the groundwater level occasionally may have fallen below S12–70 during the driest parts of the summer. In S22 five lysimeters reaching from 20 to 90 cm were sampled. Except in connection with the peak flow of the spring flood S22–20 is expected to have been above the groundwater table, whereas S22–75 and S22–90 are expected to have been in the saturated zone throughout the entire sampling period. Approximate groundwater levels at different discharge are shown in the bottom subplot of Fig. 2. As the groundwater loggers were out of order during the sampling period, the groundwater levels were reconstructed using continuous discharge measurements form a nearby station, where a pressure transducer continuously measures the water height at a V-notch weir (Fig. 1; Seibert et al., 2009). Previous research has shown that the groundwater levels in all three soil profiles are correlated with the discharge (Laudon et al., 2004). Hence, the discharge data were used to estimate the groundwater levels using slightly revised regression from Laudon et al. (2004) with R^2 values of 0.96 (S4), 0.94 (S12) and 0.87 (S22), respectively ($p < 0.001$).

The chemical analyses included Cl, sulfate, total organic carbon (TOC), Al, As, B, Ba, Be, Ca, Cd, rare earth elements (REEs), Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Si, Sr, Th, Ti, Tl, U, V, Zn and Zr. Because of the large similarities between the REEs, only La is presented in this study in order to save space and make graphs and tables clearer and more manageable. The fractionation within the lanthanide series will for this reason have to be addressed elsewhere. pH was not directly measured in the water samples from 2008, but based on previous measurements in this transect (1996–1998) there is a strong relationship between pH on the one hand and TOC and Ca on the other (Fig. S3), which was used to estimate the pH of the analysed water samples in this study. The average prediction error was 0.24 pH units. Additional analyses of water from the adjacent stream (referred to as C2 or Västrabäcken in previous studies) were taken from the material presented by Lidman et al. (2014).

The soil water and groundwater was sampled by attaching vacuum bottles to the lysimeters for 2–3 days. The lysimeters were carefully installed in 1995, so any effects of disturbance on the soils were expected to have evanesced. The samples were filtered (0.45 µm) and acidified to pH < 2 with ultrapure double-distilled HNO_3. TOC was then analysed by a Shimadzu TOC-VCPH instrument. Previous research in Krycklan has demonstrated that the amount of particulate organic carbon rarely exceeds a few percent in these systems, so TOC is essentially equal to the dissolved organic carbon (DOC; Laudon et al., 2011). Anions were measured by ion chromatography (Dionex ICS-90, Sunnyvale, Ca, USA; 4 mm i.d. AG14 and AS14 columns) using a suppressor and conductivity detector. All other elements were analysed by ICP-MS (Perkin-Elmer ELAN 6000).

The speciation of elements in the riparian soil water was calculated using thermodynamic modelling in Visual MINTEQ 3.1 (Gustafsson, 2017). The binding to DOC was modelled using the Stockholm Humic Model as described by Sjostedt et al. (2010). The modelled association with DOC (in %) was then used as an index for the affinity for organic matter (Ω) based on the definition suggested by Lidman et al. (2014). An element with Ω close to 100 % is considered to have strong affinity for organic matter, whereas an element with Ω close to 0 % is considered to have low affinity for organic matter. In one regression analysis Ω was transformed using the logit function:

$$\mathrm{logit}(\Omega) = \log\left(\frac{\Omega}{1-\Omega}\right). \tag{1}$$

All statistical analyses, including the principal component analysis (PCA), were made in R (R Core Team, 2014). In order to remove all missing values Cr and Th were excluded

Table 1. Average element concentrations at different depths in the three investigated soil profiles. All concentrations are given in $\mu g\,L^{-1}$ except for TOC, which is given in $mg\,L^{-1}$. The number of samples included in the averages varies from 1 to 10, depending on availability of soil water, detection limits etc. See Table S3 for corresponding relative standard deviations. The last column illustrates the enrichment in the riparian zone (the ratio between the average concentration in S4 and S22, respectively).

	S4				S12					S22					Enrichment
Depth (cm)	35	45	55	65	20	30	40	60	70	20	35	50	75	90	S4 / S22
Al	1700	1400	1200	1400	1200	640	520	410	330	68	1.6	13	8.4	50	51
As	0.95	0.99	0.83	0.60	0.88	0.37	0.22	0.22	0.37	0.057	0.0026	0.19	0.17	0.027	9.4
B	6.3	5.2	4.5	5.1	8.6	5.0	4.3	4.9	4.5	4.2	3.9	3.9	4.4	3.6	1.3
Ba	35	25	25	26	16	16	15	11	10	13	6.0	5.9	6.5	7.8	3.5
Be	0.20	0.16	0.15	0.21	0.17	0.11	0.091	0.099	0.11	0.0098	0.0047	0.0087	0.0080	0.0078	23
Ca	900	1100	1300	1100	810	1600	1800	2000	2100	1100	920	1000	1000	3500	0.73
Cd	0.12	0.16	0.12	0.13	0.061	0.044	0.046	0.070	0.096	0.016	0.012	0.010	0.017	0.0092	10
Cl	1.0	1.1	1.0	1.1	0.99	0.97	0.96	0.97	0.96	0.51	0.72	0.94	0.87	0.79	1.4
Co	1.4	1.5	1.3	1.5	0.70	0.94	1.1	1.1	1.4	0.23	0.11	0.17	0.14	0.027	11
Cr	2.2	1.7	1.4	1.6	1.7	0.75	0.54	0.44	0.40	0.25	n/a	0.15	n/a	n/a	8.6
Cs	0.017	0.022	0.039	0.015	0.075	0.019	0.013	0.011	0.013	0.012	0.0054	0.0074	0.0078	0.010	2.7
Cu	2.3	4.0	2.6	4.5	2.6	2.7	1.8	3.9	3.1	0.84	0.77	0.65	0.51	0.82	4.7
Fe	1400	1500	1300	740	370	110	57	55	160	5.3	74	24	42	43	33
K	110	120	170	100	480	190	150	250	370	360	120	210	210	1000	0.33
Li	3.6	3.2	3.2	3.5	2.6	2.5	2.7	2.7	2.6	0.52	0.48	0.58	1.4	0.67	4.6
La	2.2	1.7	1.6	1.5	1.3	0.87	0.73	1.4	1.6	0.24	0.013	0.088	0.043	0.17	16
Mg	300	380	500	350	420	500	500	590	590	320	310	360	340	1100	0.79
Mn	6.4	9.5	13	8.7	7.4	8.0	79	15	21	0.38	0.39	0.22	0.25	3.9	9.1
Na	2200	2000	2100	2000	1900	2000	1900	2100	2200	1500	1700	1900	1900	2400	1.1
Ni	3.0	3.9	3.5	3.7	1.2	1.5	1.7	1.9	2.5	0.83	0.23	0.29	0.30	0.80	7.2
Pb	0.67	0.28	0.29	1.0	0.48	0.18	0.19	0.15	0.11	0.055	0.0018	0.10	0.087	0.15	7.1
pH	4.3	4.5	4.7	4.6	4.4	4.9	4.9	5.1	5.2	4.8	4.8	4.8	4.8	5.9	0.90
Rb	0.79	1.3	1.9	0.71	2.8	1.2	1.0	1.7	2.5	1.9	0.68	0.83	0.82	1.8	0.97
Se	0.15	0.16	0.13	0.15	0.10	0.17	0.19	0.14	0.23	0.032	0.070	0.15	0.86	0.085	0.62
Si	8400	7900	8100	8000	6300	6800	6300	7400	7900	5100	4500	4400	4200	7900	1.6
SO4	4900	5200	5200	5400	4400	4800	5200	5400	5700	3700	3700	4500	4200	8300	1.1
Sr	14	14	14	15	10	17	20	20	20	12	12	9.8	9.7	17	1.2
Th	0.27	0.20	0.18	0.17	0.13	0.067	0.055	0.068	0.084	0.0046	n/a	n/a	n/a	n/a	45
Ti	1.4	1.1	0.83	0.96	0.87	0.38	0.25	0.18	0.20	0.065	0.045	0.076	0.060	0.083	16
Tl	0.028	0.030	0.032	0.021	0.028	0.026	0.017	0.017	0.041	0.0091	0.0038	0.0091	0.0070	0.00094	4.6
TOC	33	24	19	21	26	11	8.5	6.6	5.4	5.2	2.8	1.7	2.0	1.6	9.1
U	0.13	0.093	0.11	0.079	0.084	0.062	0.043	0.092	0.19	0.014	n/a	0.00081	0.00050	0.0095	17
V	2.5	2.7	2.7	2.1	0.97	0.86	0.62	0.28	0.49	0.070	0.036	0.030	0.035	0.032	62
Zn	9.2	12	16	13	15	6.6	6.8	5.6	7.4	6.3	3.1	3.5	4.3	3.4	3.1
Zr	450	300	300	280	220	120	92	120	140	11	0.69	1.8	n/a	16	45

from the PCA of the soil water and groundwater and one value each for U and Zr were interpolated from the two surrounding lysimeters (Table 1). Because pH was modelled it was not included in the PCA. The variables were scaled and centred, but no rotation was used. All statistical analyses were done using average concentrations except in Fig. S4.

The concentrations in biota in the riparian zone and in the upslope soil, respectively, were analysed by collecting fresh bilberry leaves (*Vaccinium myrtillus*) and spruce shoots (*Picea abies*) early in the growing season (11 June 2013). Two grouped samples of each species were collected in the vicinity of the lysimeters at S4 and S22, respectively. A screening of the element concentrations were made using ICP-MS at a commercial laboratory (ALS Global, Luleå, Sweden) following certified standard procedures. We report the results for the 19 elements, which were measured with an accuracy of two of more significant digits.

3 Results and discussion

3.1 Soil water and groundwater chemistry

For most elements there was a substantial increase in the concentrations along the transect, from the upslope profile (S22) to the riparian profile (S4; Tables 1, S3). These patterns, which were persistent throughout the year, are exemplified by TOC and V in Fig. 2. In the case of TOC the increase in riparian soil water and groundwater (up to $33\,mg\,L^{-1}$ on average) was not surprising given that the content of organic matter in the riparian soils is substantially higher than in upslope soils, which typically contained only a few milligrams per litre (Fig. S1). This trend is typical for the riparian soils of many small boreal streams (Grabs et al., 2012). V followed that same trend as TOC with substantially higher (nearly 2 orders of magnitude) concentrations in the riparian zone. However, there were also elements, whose concentrations did not increase markedly in the riparian zone. One such exam-

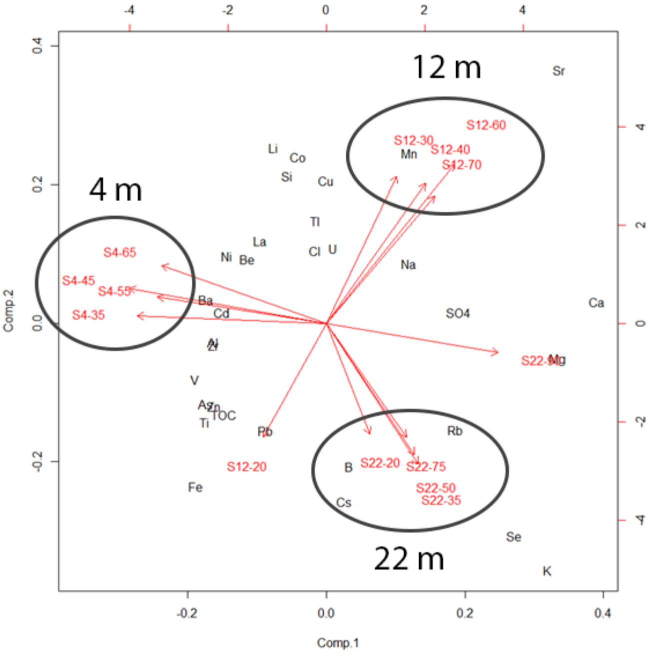

Figure 3. PCA biplot for the average concentrations in each of the lysimeters. Most lysimeters located at the same distance from the stream ended up close to one another.

ple is Na, which occurred in relatively stable concentrations around 2 mg L^{-1} (Fig. 2).

pH was estimated to decrease from S22 (on average 5.1) to S4 (on average 4.5) with generally increasing pH with depth in all profiles and a maximum of 5.9 in S22–90. Hence, the pH gradient experienced by the substances transported from the uphill Podzol to the riparian zone is approximately in the order of 0.5–1 pH unit. This shift in pH may, however, have palpable consequences for the speciation of many metals and the solubility of solid phases such as $Al(OH)_3$ and various Fe precipitates (Gustafsson et al., 2001; Sauer et al., 2007; Sjostedt et al., 2010), especially when combined with the increase in TOC (Fig. 2). In the case of Al, the average concentrations in the investigated lysimeters ranged from 1.6 µg L^{-1} in S22–35 to 1700 µg L^{-1} in S4–35 – a difference of more than 3 orders of magnitude. Similar trends for Al have previously been observed in this transect (Cory et al., 2007). Fe was also strongly enriched in riparian soil water with average concentrations ranging from 5.3 µg L^{-1} at the bottom of the E horizon (S22–20) to 1500 µg L^{-1} in S4–45. Previous studies using X-ray absorption spectroscopy (XAS) have demonstrated that both Fe^{2+} and Fe^{3+} are present throughout the transect, but in the riparian zone the Fe speciation was completely dominated by organic Fe complexes (Sundman et al., 2014). The dominance of organically bound Fe in the riparian zone is consistent with the absence of Fe colloids in the adjacent stream (Neubauer et al., 2013). This observation is important because Fe colloids are an important vector for many major and trace elements in boreal rivers (Gustafsson et al., 2000; Dahlqvist et al., 2007). If no Fe colloids are present, however, organic colloids are likely to play the lead role in transporting more insoluble elements through the riparian zone. Only as the streams become larger will Fe colloids gradually appear in the stream water (Neubauer et al., 2013). A prerequisite for this is that pH increases with increasing catchment area, while the TOC concentration decreases, which causes both Fe and Al to precipitate (Köhler et al., 2014; Lidman et al., 2014). This is in turn related to less organic matter in the riparian soils of larger streams and an increasing influence from deeper groundwater, which entirely may bypass the riparian soils (Peralta-Tapia et al., 2015; Lidman et al., 2016).

3.2 Principal component analysis (PCA)

In order to further explore the trends in the soil water and groundwater chemistry a PCA was conducted (Fig. 3). There was a considerable variance in the dataset, and the first two principal components could only explain in total 57 % of the variance with PC1 contributing with 33 % and PC2 with 24 %. A noteworthy pattern in Fig. 3 is that most lysimeters from the same profile fall close to one another. This suggests that the variance in the transect mainly is horizontal rather than vertical. This underlines the relevance of the concept of the riparian zone, since it demonstrates that the riparian profile (S4) is decisively different from the upslope mineral soil (S22). The only deviations from the division into S4, S12 and S22, respectively, were the deepest lysimeter in S22 (S22–90) and the shallowest lysimeter in S12 (S12–20). In the case of the former, there was a notable decrease in the hydraulic conductivity below ca. 80 cm in S22 (Table S2), suggesting that the exchange between S22–90 and shallower soil layers is limited. This lysimeter was for instance characterised by high concentrations of base cations, particularly K, Ca and Mg, and higher pH (Table 1). It has been demonstrated that the concentration of base cations in the area tends to increase with the age of the groundwater (Klaminder et al., 2011), which supports the idea that S22–90 represents a less hydrologically active layer. As concerns S12–20, it represents a more organic soil with higher TOC concentrations than the deeper horizons of S12 (Figs. S1; 2).

Most of the elements are found on the same side of the biplot as the S4 lysimeters (e.g. Ba, Cd, Al, Zr and Ni), indicating that they occurred in higher concentrations in the riparian zone. However, some of them (e.g. Li, Co, Si, Cu and Tl) are shifted towards the S12 lysimeters, while others (e.g. Pb, Fe, As, Zn, TOC, Ti and V) are shifted slightly towards the S22 lysimeters. A strong association with the S12 lysimeters is mainly displayed by Mn and Sr, signifying that they occurred in higher concentrations in S12. The S22 lysimeters are surrounded by the alkali metals K, Rb and Cs, as well as B and Se. In the case of Se the higher concentrations in S22 may be related to the more oxidising conditions, since the solubility of Se easily decreases in more reducing environments

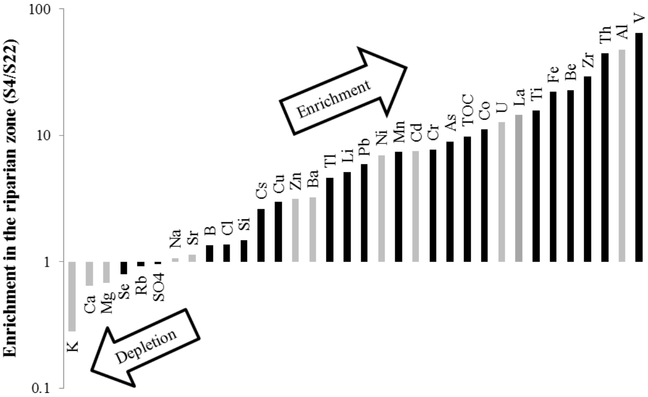

Figure 4. Relative enrichment in the riparian soil water and groundwater expressed as the ratio between the average concentration in the riparian profile (S4) and the average concentration of the upslope Podzol profile (S22). Elements marked in grey are included in the regression in Fig. 5.

(Gustafsson and Johnsson, 1992). The special patterns of Se in the soil water and groundwater are also consistent with the dynamic behaviour of Se concentrations in the adjacent stream (Lidman et al., 2011). Finally, some major ions like Ca, Mg, Na and sulfate are found in between the S12 and the S22 lysimeters in the biplot.

3.3 Enrichment in the riparian zone

The grouping of the lysimeters at the same distance from the stream suggests that it is possible to reduce some of the complexity of the dataset by investigating the average concentrations at each of the sites. Since the principal change in the soil water and groundwater chemistry occurred laterally along the transect, a comparison of the average concentrations in the riparian zone (S4) to the average concentrations in the upslope mineral soil (S22) can give a fair overview of the major trend in the transect (Table 1). Figure 4 shows the ratio between the average concentrations in S4 the average concentrations in S22 for all investigated elements. It is clear that, for the vast majority, higher concentrations were observed in the riparian zone. Only a few elements – most notably K, but also Ca, Mg and Se – showed a contrasting pattern with higher concentrations in the uphill soils, while yet a few others, e.g. Rb, Na and sulfate, occurred in similar concentrations throughout the transect. However, a closer look at the observations (Table 1) shows that the higher average concentrations of K, Ca and Mg in the mineral soil (S22) can be attributed to the deepest lysimeter in S22, which also stood out in the PCA (Fig. 3). Thus, excluding this sample from the averages will remove most of the differences between S4 and S22 for K, Ca and Mg.

The far right side of Fig. 4, i.e. the elements which are most strongly enriched in the riparian zone, is occupied by metals, which are well known for their low solubility, e.g. Zr, Th and Al. The most extreme example is V, with more than 60 times higher concentrations in the riparian zone than in the mineral soils further up in the transect. Unlike Zr, Th and Al the speciation of V is directly affected by the redox conditions, which may contribute to the differences in its concentrations (Agnieszka and Barbara, 2012). However, it should be noted that the Th concentrations in S22 fell below the detection limit in all but one of the lysimeters (Table 1). This was the shallowest lysimeter (at 20 cm) with the highest TOC concentration. Therefore, there are good reasons to believe that the enrichment factors (S4 / S22) for Th and also Cr were underestimated. If it is assumed that the Th concentration in S22 is correlated with the TOC concentration or that it follows the same pattern as Zr and V, this would be enough to push the S4 / S22 ratio well above 100.

The general impression from both the PCA (Fig. 3) and, more specifically, the S4 / S22 ratio (Fig. 4) is that more insoluble or immobile elements tend to occur in higher relative concentrations in the riparian zone, while generally more mobile elements such as the base cations and anions like Cl and sulfate occur in more uniform concentrations throughout the transect. In boreal waters more immobile elements are often to a large extent transported by colloids, typically Fe colloids or organic colloids, which tend to represent two different colloidal populations (Lyven et al., 2003). As discussed above, the Fe colloids appear to be missing in the riparian zone, leaving only the organic colloids as possible carriers (Neubauer et al., 2013). There is also strong evidence that organic matter is responsible for carrying a wide range of elements in boreal waters (e.g Gustafsson et al., 2000; Pokrovsky et al., 2005; Andersson et al., 2006; Dahlqvist et al., 2007; Pokrovsky et al., 2010; Vasyukova et al., 2010; Aiken et al., 2011). Furthermore, it has been demonstrated that the affinity for organic matter of various metals is essential for understanding their transport and spatial variability in the boreal landscape (Lidman et al., 2014). Using the same definition of the affinity for organic matter as was proposed by Lidman et al. (2014) makes it possible to quantitatively test the hypothesis that the enrichment in the riparian soil water and groundwater was related to the affinity for organic matter. Figure 5 shows the S4 / S22 ratio, i.e. the enrichment in the riparian zone (S4) as compared to the upslope mineral soil (S22), as a function of the affinity for organic matter. The affinity for organic matter is expressed in percent and represents the proportion of each element that is expected to be bound to DOC in the soil water and groundwater of S4, but in this application it was used mainly as an index for the strength of the affinity for organic matter.

The selection of elements in Fig. 5 was based on the analysed elements and the available thermodynamic constants in Visual MINTEQ 3.1 (Gustafsson, 2017). Some elements like Fe and Mn were excluded because uncertainties regarding their oxidation state make the affinity for organic matter ill-defined. U was, however, included as U^{6+} despite its redox chemistry, since any presence of U^{4+} just would increase

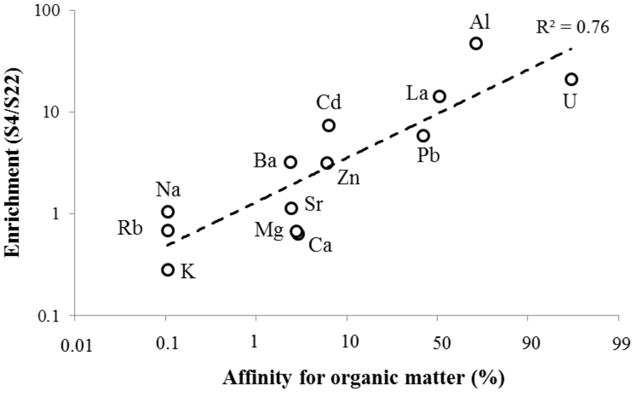

Figure 5. Enrichment in average groundwater/soil water concentration when comparing the riparian zone (S4) and the upslope Podzol (S22) as a function of the affinity for organic matter. The affinity for organic matter is plotted on a logit scale (Eq. 1).

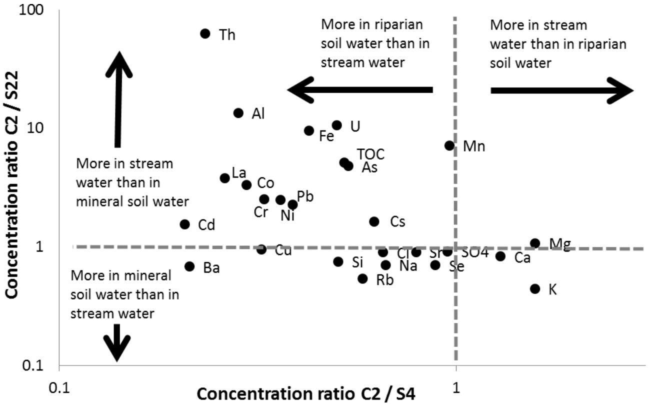

Figure 6. Ratios between the average concentrations in stream water (C2) and riparian soil water (S; horizontal axis) and between the average concentrations in stream water (C2) and mineral soil water (S22; vertical axis). Elements above the dashed horizontal line occur in higher concentrations in the stream water than in the mineral soil water. Elements to the left of the vertical lines occur in higher concentrations in the riparian soil water than in the stream water. The selection of elements is based on the available measurements in this study and the stream water data presented by Lidman et al. (2014).

the already high affinity for organic matter of U^{6+} ($>96\,\%$) slightly. As can be seen in Fig. 5, where the affinity for organic matter has been transformed using the logit function (Eq. 1), there was a strong positive correlation between the affinity for organic matter and the enrichment in the riparian soil water and groundwater ($r = 0.88$, $p < 0.01$). The modelling also indicated that many of the elements, which are enriched in the riparian zone, would not be soluble in such high concentrations had it not been for the high TOC concentrations. Yet, Fig. 5 cannot be taken as direct evidence that each of the enriched elements in the riparian zone is governed primarily by TOC as there also may be other controlling factors, especially in the uphill Podzol profile (S22), where the TOC concentration was low, but it strongly suggests that TOC is a crucial parameter for understanding the role of the riparian soils.

Although it is beyond the scope of this work to analyse the time series for all the investigated elements in the lysimeters, it is illustrative to look at a few examples that can shed further light on the role of organic matter in riparian soils. Ti is one example of a relatively insoluble metal, which should have a low mobility unless there is some carrier phase such as TOC present. Figure S4 shows all of the observations of Ti plotted against TOC, revealing a strong positive correlation ($r = 0.97$, $p < 0.001$) between Ti and TOC for all soil water samples. Clearly, high Ti concentrations were encountered solely in samples with high TOC concentrations. The significance of TOC was also supported by the temporal variability of organophilic elements in the soil water and groundwater, at least in the more organic soils. One example is Al, which in each of the lysimeters in S4 had a significant ($p > 0.05$) positive correlation ($r > 0.84$) to TOC when looking throughout the entire sampling period (see details in Fig. S5). At times when TOC increased, so did Al, supporting the hypothesis that the mobilisation and transport of organophilic elements in the riparian zone largely could be controlled by TOC. Similar patterns were, however, absent in S22, so the mobility of Al in these inorganic soils was evidently controlled by other processes. For instance, it has been shown that the mobility of Al in the Bs horizon of Podzol soils can be limited by the precipitation of $Al(OH)_3$ and in some cases imogolite (Gustafsson et al., 2001). Hence, while the large differences in TOC concentrations between the uphill mineral soils and the riparian zone were responsible for the elevated levels of many elements in the riparian soil water, this does not necessarily imply that it also controls their mobility in each of the investigated soil layers.

3.4 Influence on the stream water chemistry

The analyses of the soil water and groundwater along the investigated transect demonstrated that the riparian zone can induce considerable changes in the water chemistry. It is therefore pertinent to ask what influence the riparian zone has on the stream water quality. Had there been no differences between the riparian zone and the uphill mineral soils, one should expect the stream water to resemble the groundwater in S22. However, since the groundwater changes character as it enters the organic riparian soil, one might expect that stream water chemistry instead would resemble the riparian groundwater. When comparing the uphill mineral soil (S22) to the stream (C2), many elements (e.g. Th, Al, U, Fe and La) occurred in considerably higher concentrations (up to 60 times) in the stream water than in the soil water (Fig. 6). Yet, stream water concentrations were missing for some of the metals, e.g. V and Zr, which showed the largest enrichment in the riparian soil water. The difference between the stream water and the uphill soil water is remarkable given that this Podzol profile should be reasonably representative for the vast majority of soils throughout the catchment. For example, rapid degradation of TOC and subsequent precipitation of Fe, Al and associated elements are typical processes in the development of Podzols (Gustafsson et al., 2001; Sauer et al., 2007; Sundman et al., 2014). This illustrates that the riparian zone has a profound impact also on the stream water chemistry for a wide range of elements, particularly those with a strong affinity for organic matter (Fig. 5).

When comparing the riparian soil water (S4) to the stream water (C2), the concentrations were in many cases higher in the riparian soil than in the stream (up to 4–5 times). In other words there was no perfect match between the riparian soil water and the stream water (Fig. 6). However, the riparian soil water in this study represents only a single transect, whereas the stream water displays an integrated signal for the entire catchment. Although the overall appearance and functioning of the investigated transect should be representative for the catchment at large, there is also a longitudinal variation in the composition of the riparian zone along the stream. For example, the riparian zone of the investigated transect represented an area with higher content of organic carbon (around the 3rd quartile) than most reaches of the stream (Figs. S1 and S2). If the interpretation that the organic matter is controlling the transport of these elements is correct, that could explain why the studied riparian zone exhibited higher concentrations than the stream. Differences in the content of organic matter in the riparian zone along the stream are known to derive from variations in the topography and the groundwater flow pathways (Tiwari et al., 2016). This hypothesis is also supported by the fact that the TOC concentrations in the riparian zone were higher than in the stream (Fig. 6).

There were only three elements, Ca, Mg and K, which displayed the opposite pattern: higher concentrations in the stream water (C2) than in the riparian soil water (S4; Fig. 6). These three elements also stood out in the measurements in the transect because they occurred in higher concentrations in the mineral soil (S22) than in the riparian soil (S4), mainly due to the high concentrations in the deepest lysimeter in S22 (Fig. 4). In the case of Ca and Mg, the agreement between the mineral soil water (S22) and the stream water (C2) was good, whereas the K concentration in the stream water was more than twice as high as in the mineral soil water. K and to some extent Rb were the only examples of elements with notably higher concentrations in the stream water than in the three soil profiles. The higher concentrations of base cations like K, Ca and Mg in the stream water could indicate a contribution of deeper groundwater to the stream, but at the same time related weathering products such as Sr, Na, Rb, Cs and Si all showed relatively uniform concentrations throughout the transect and the stream. It is possible that the differences again are caused by longitudinal heterogeneities along the stream.

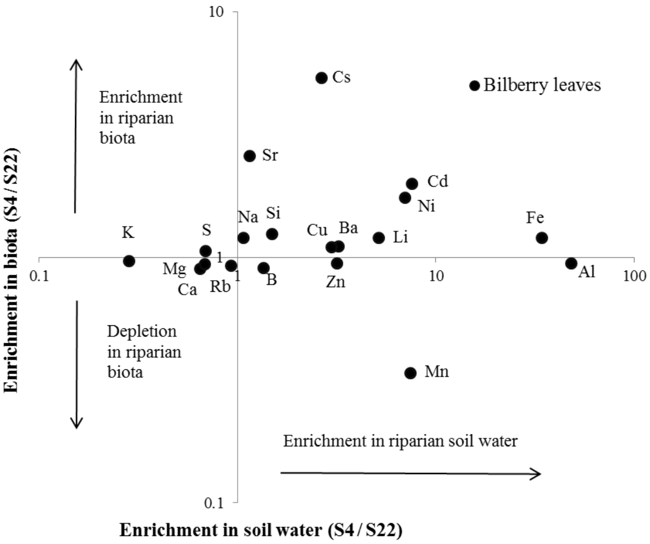

Figure 7. Enrichment of elements in bilberry leaves vs. enrichment in soil water when comparing the uphill site (S22) and the riparian site (S4).

3.5 A hotspot for transfer of pollutants to biota?

Higher species richness in the riparian zone of stream reaches with high groundwater discharge is a clear sign that the ecological community can benefit from the flow of nutrients into the riparian zone (Kuglerová et al., 2013). However, not only nutrients but also a large range of potentially toxic substances tend to accumulate in the riparian zone. It is therefore pertinent to ask whether there also is an elevated accumulation in riparian biota, which could constitute an important exposure pathway for hazardous substances. The screening of bilberry leaves and spruce shoots from the riparian forest (near S4) and the uphill forest (near S22), respectively, showed no clear relationship between the concentrations in soil water and the concentrations in biota (Table S4; Figs. 7 and S6). Also, when considering the more unreliable results for elements, which were only reported with one significant digit (e.g. Sb, Pb, Cr, La, Ti, V and Zr), there were no clear signs of elevated concentrations in riparian biota. (Possible exceptions were, however, As, Co and Mo.) One important explanation is probably that elements with high riparian concentrations largely are bound to TOC (Fig. 5). For a wide range of elements it has been shown that the bioavailability tends to decrease when they are bound to organic matter, e.g. Pb (Van Sprang et al., 2015), U (Trenfield et al., 2011a, b), Ni (Weng et al., 2004; Deleebeeck et al., 2009), Cu (Deruytter et al., 2014) and Zn (De Schamphelaere et al., 2005). In addition, it is possible that the plants are able to regulate the uptake and/or disposal of certain elements.

While plants growing in the riparian zone generally did not have higher concentrations of elements that accumulate in riparian soil water, there were two notable exceptions: Cs and Mn. In the case of Cs, 2–3 times higher concentrations in the soil water led to 4–5 times higher concentrations in biota. Since Cs is considered to have low affinity for organic matter, the elevated concentrations are probably not directly linked to TOC (Fan et al., 2014). Instead, factors such as lower amount of mineral surfaces and lower pH could allow higher concentrations of more bioavailable Cs ions in the riparian soil water, leading to elevated concentrations in biota. In the case of Mn the concentrations in riparian biota were lower, which possibly could be related to its redox chemistry (Fig. 7).

3.6 The role of riparian soils in the boreal landscape

The perhaps most important observation in this study was the large differences between the riparian soils and the uphill forest soils. As discussed above, these differences have previously been known for a number of elements, but judging from this study the enrichment in riparian soil water is more the rule than the exception (Fig. 4). Since the enrichment in riparian soil water could be linked to the affinity for organic matter (Fig. 5), similar enrichment should be expected for many other metals and organophilic substances in general, e.g. organic pollutants (Bergknut et al., 2011). A crucial question then is unavoidably how representative the investigated transect would be at larger spatial scales. Even in a small catchment like this one ($0.12\,\text{km}^2$) the chemistry of the draining stream does not agree completely with either the water of the riparian zone or that of the uphill mineral soil (Fig. 6). Given the heterogeneity and complexity of the natural landscape it is doubtful whether it would at all be possible to find something like a representative transect. In all catchments there is likely to be substantial longitudinal and transverse variation in state factors such as topography, grain size distribution and mineralogy, which in turn gives rise to a heterogeneity in hydrology and biogeochemistry (Ledesma et al., 2015). These differences are likely to only increase when trying to compare different catchments to one another. Nevertheless, it was clear that the composition of the stream water had been significantly influenced by the riparian zone, e.g. by gaining substantially higher concentrations of TOC and organophilic elements (Fig. 4). As concerns the stream, in turn, it is known from previous research that it is, in many respects, typical for forested catchments in the area (Cory et al., 2006; Björkvald et al., 2008; Lidman et al., 2012, 2014; Köhler et al., 2014). Despite their size, small streams and headwaters are important for generating runoff in the boreal landscape, even in large rivers (Bishop et al., 2008). Therefore, on a more conceptual level the gradient represented by this transect from relatively dry organic-poor mineral soils in uphill locations to wetter organic soils near the streams is surely not atypical for the boreal landscape (Sauer et al., 2007; Grabs et al., 2012). If the water quality of these streams and the transfer of TOC and associated elements largely are controlled by riparian soils, as suggested by this study, there are also good reasons to believe that the effects of the riparian soils have implications at much larger scales than the investigated transect (Laudon et al., 2011; Ledesma et al., 2015). These effects include affecting the balance between organic colloids and Fe colloids, lowering pH and elevating the concentration of TOC and many organophilic elements (Lyven et al., 2003; Neubauer et al., 2013; Köhler et al., 2014; Ledesma et al., 2015).

What, then, does the long-term mass balance for the riparian zone look like? For an element like C, which ultimately is derived from the atmosphere, it is not hard to see how riparian soils can become a major source of TOC to the streams (Fiebig et al., 1990; Agren et al., 2008; Lyon et al., 2011). More intriguing are the associated elements, which in a similar manner to TOC have a major source in the riparian zone. These elements, however, are largely derived from weathering of local soils, but it is unclear where in the catchment this weathering takes place and what the long-term role riparian soils play in the boreal landscape. One hypothesis is that there is a preferential net weathering in the riparian zone. This could, for instance, be related to the higher TOC concentrations and the lower pH as compared to the uphill soils (Erlandsson et al., 2016). This would imply that much of the weathering of organophilic metals is limited to a small fraction of the landscape. Another hypothesis is that these elements initially were released mainly in the upslope mineral soils, which cover much larger areas than the riparian soils, and then have been transported to the riparian zone. Discussing the sources of Al in this transect, Cory et al. (2007) hypothesised that there could be a flushing from uphill mineral soils to the riparian zone in connection with hydrological episodes such as the spring flood. The results of this study do, however, not support that hypothesis. The Al concentrations in the riparian zone (S4 and S12) were at all sampling occasions throughout the year substantially higher than in the uphill mineral soil (S22), so it seems unavoidable to draw the conclusion that the riparian zone currently is a net source for Al (and other organophilic elements) during all parts of the year. Hence, if one wishes to stick with the hypothesis that the vast part of the weathering of these elements has occurred throughout the catchment, rather than specifically in the riparian zone, one has to assume that most of the organophilic metals, which now are being released from the riparian zone, were brought there and somehow accumulated during some earlier stage, when the riparian zone acted as a sink. For instance, it is possible that organophilic metals historically accumulated in the organic matter of the riparian zone in the same way as they still do in boreal mires (Lidman et al., 2013, 2014). However, as a result of some change in the system, e.g. the ditching of the stream in the early 20th century, these metals are now being released from the solid organic matter as it decomposes. Under this scenario the current stream chemistry of this and presumably many of all the other ditched streams would represent a historical anomaly. Which hypothesis is true – preferential weathering in the riparian zone or historical accumulation in combination with present mobilisation – seems precarious to answer based only on the water chemistry throughout the transect. Instead this will require a more detailed investigation of the solid phase as well. A better understanding of the mass balance of the riparian zone would further elucidate how various substances – nutrients as well as pollutants – are transported from boreal forests to surface waters and help assess the effects of human perturbations such as logging, ditching and climate change on the quality of boreal waters.

4 Conclusions

The results of this study demonstrated that riparian soils have a profound effect on the element transport from a boreal forest hillslope to the draining stream, particularly when it comes to elements with a high affinity for organic matter. For some elements the concentrations in the riparian zone were nearly 100 times higher than in the mineral soils less than 20 m upslope. It could be demonstrated that the degree of enrichment was related to the affinity for organic matter. Whereas elements with low affinity for organic matter occurred in fairly uniform concentrations throughout the transect, elements with a high affinity for organic matter were strongly enriched. This enrichment also had implications for the stream water, which tended to have higher concentrations of TOC and organophilic elements than the soil water and groundwater of uphill soils. As a consequence, it can be expected that the water quality of boreal surface waters, especially in smaller catchments and with respect to TOC and organophilic elements, can be quite different from that of the groundwater and soil water throughout most of the catchment. This emphasises the importance of the riparian zone for understanding the water quality of the boreal landscape and the long-term transfer of solutes from terrestrial to aquatic ecosystems. Despite the strong enrichment of organophilic elements in the riparian soil water no signs of elevated concentrations in riparian biota were observed. At present the riparian zone constitutes a source for a wide range of elements, but further studies are needed to determine the long-term mass balance of the riparian zone and the underlying causes of the enrichment. The results of this study emphasise that riparian zone is crucial for understanding the long-term fluxes of nutrients and pollutants in the boreal landscape as well as the historical and future water quality of boreal surface waters in the wake of a changing climate and modern forestry.

Data availability. The data will be made available through the website of the Krycklan Catchment Study (www.slu.se/Krycklan).

The Supplement related to this article is available online at https://doi.org/10.5194/bg-14-3001-2017-supplement.

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