



# Riparian zone control on base cation concentration in boreal streams

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**Abstract.** Riparian zones (RZ) are a major factor controlling water chemistry in forest streams. Base cations' (BC) concentrations, fluxes, and cycling in the RZ merit attention because a changing climate and increased forest harvesting could have negative consequences, including re-acidification, for boreal surface waters. We present a two-year study of BC and silica (Si) flow-weighted concentrations from 13 RZ and 14 streams in different landscape elements of a boreal catchment in northern Sweden. The spatial variation in BC and Si dynamics in both RZ and streams was explained by differences in landscape element type, with highest concentrations in silty sediments and lowest concentrations in peat-dominated wetland areas. Temporal stability in BC and Si concentrations in riparian soil water, remarkably stable Mg/Ca ratios, and homogeneous mineralogy suggest that patterns found in the RZ are a result of a distinct mineralogical upslope signal in groundwater. Stream water Mg/Ca ratios indicate that the signal is subsequently maintained in the streams. Flow-weighted concentrations of Ca, Mg, and Na in headwater streams were represented by the corresponding concentrations in the RZ, which were estimated using the Riparian Flow-Concentration Integration Model (RIM) approach. Stream and RZ flow-weighted concentrations differed for K and Si, suggesting a stronger biogeochemical influence on these elements, including K recirculation by vegetation and retention of Si within the RZ. Potential increases in groundwater levels linked to forest harvesting or changes in precipitation regimes would tend to reduce BC concentrations from RZ to streams, potentially leading to episodic acidification.

## 1 Introduction

The riparian zone (RZ) is located immediately adjacent to streams and comprises the last soil environment through which soil water flows before becoming surface water. The RZ is important for habitat function (Gundersen et al., 2010) as well as in controlling water quality (Cirimo and McDonnell, 1997; Luke et al., 2007; Vidon et al., 2010). In forest catchments, saturated discharge areas in RZ till soils contribute more effectively to stream runoff peaks than the considerably larger upslope areas (Dunne and Black, 1970; Rodhe, 1989; McGlynn and McDonnell, 2003). The RZ also influences stream organic carbon dynamics much more than upland soils (Dosskey and Bertsch, 1994; Köhler et al., 2009) and provides important ecosystem services in acid-sensitive headwaters (Ågren and Löfgren, 2012). It can act as a buffer of acidity (Löfgren et al., 2011), or sink for inorganic nitrogen (Fölster, 2000; Petrone et al., 2007; Futter et al., 2010) and retain organic pollutants (Bergknut et al., 2011) or metals such as aluminium (Pellerin et al., 2002; Ross et al., 2008). Base cations (BC) are transported from upslope soils through RZ to streams, although their concentrations, fluxes, and cycling in the transition terrestrial-aquatic compartment have not been extensively examined (McLaughlin, 2009).

BC include calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na), all of which except Na are essential plant nutrients. They help to maintain soil fertility and play an important role in the acidification status of soils and surface waters. Mineral weathering is the ultimate BC source, but atmospheric deposition can be important in some regions.

Plant uptake and litter fall recirculates BC. The exchangeable BC pool associated with soil organic matter and clay minerals creates an important mechanism of interchange between soil particles and the solution affecting BC biogeochemical cycles. Several studies have predicted declines in soil BC pools caused by more intensive biomass removal associated with more intensive forest harvesting (Olsson et al., 1993; Akselsson et al., 2007; Klaminder et al., 2011b). The demand for forest biomass has increased in recent years in many countries due to changes in energy policy to substitute fossil fuels by renewable sources and might have negative consequences on forest productivity and surface water quality (Laudon et al., 2011b; Wall, 2012). BC losses are also connected to climatic variability (McLaughlin, 2009). These factors may cause serious problems in Scandinavian forest till soils where BC-enriched waters contribute relatively little to total BC fluxes into the streams because their location in the lower part of the soil profile is often associated with low hydraulic conductivity (Nyberg, 1995). The behaviour of Silica (Si) in boreal forest soils and streams is similar to that of BC (Oni et al., 2013). However, unlike BC, Si in boreal forest soils and streams is derived almost exclusively from mineral weathering.

In boreal forest till soils, strong increases in saturated hydraulic conductivities towards the soil surface can cause dramatic increases in the lateral flow movement to the stream as precipitation or snowmelt events cause the groundwater table to rise and soil water to enter the stream via highly conductive superficial soil layers in the RZ. This phenomenon is known as the “transmissivity feedback mechanism” (Rodhe, 1989; Bishop, 1991; McDonnell et al., 1998; Bishop et al., 2011). The transmissivity feedback mechanism results in a large mobilization to the stream of “old” or “pre-event” water during rainfall or snowmelt events (Laudon et al., 2004). The integration of lateral flows and RZ solute concentrations to predict in-stream solute concentrations is the basis of the Riparian Flow-Concentration Integration Model (RIM, Seibert et al., 2009). RIM can be applied in principle to any soil, sediment or weathered parent material including forest till soils. The approach was first conceptualized by Bishop et al. (2004) and has since been used to quantify fluxes of organic carbon (Köhler et al., 2009; Ågren et al., 2010; Winterdahl et al., 2011a, b; Grabs et al., 2012), inorganic carbon (Öquist et al., 2009), nitrogen (Petroni et al., 2007), and lead (Klaminder et al., 2006). RIM takes point measurements of chemical concentration at a series of depths and then performs an interpolation to provide a continuous estimate of chemical concentration at all depths in the RZ. This chemical concentration profile is then multiplied by an estimated lateral discharge profile to derive volume weighted concentration or flux estimates for an entire RZ profile. Conceptually, RIM is very similar to the process of estimating riverine fluxes in which point measurements of chemical concentration are interpolated through time to provide a continuous chemical time series which is then multiplied by a continu-

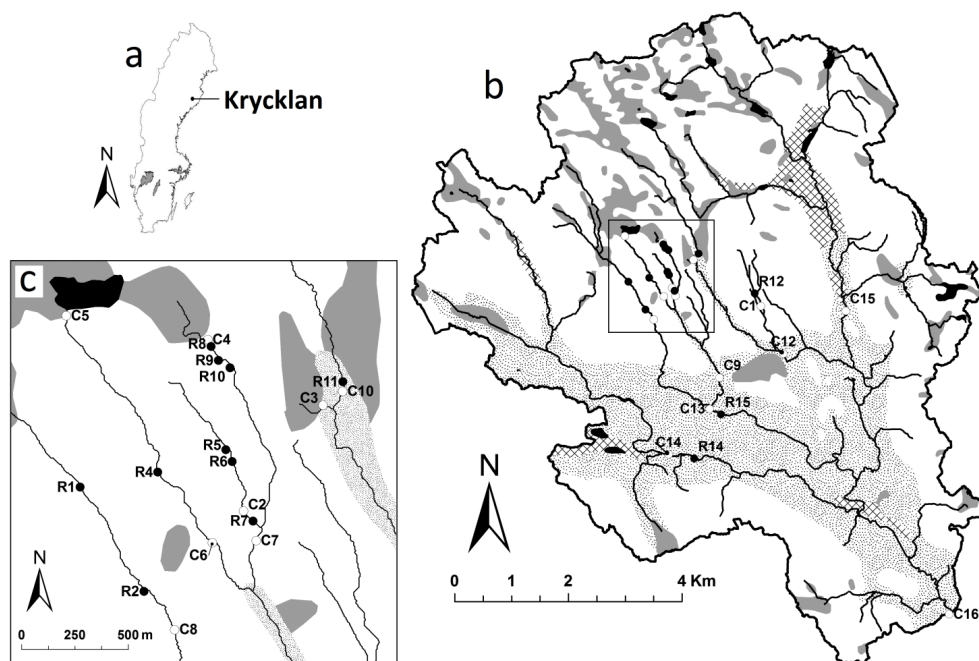
ous flow record to estimate fluxes. While RIM integrates over depth, riverine flux estimation integrates over time.

Here we present a two-year study of flow-weighted concentrations of BC and Si from RZ and streams in a boreal landscape in northern Sweden. This is the first application of RIM to study BC dynamics in forest soils and streams. The studied systems range from first-order headwater streams in till soils to catchments of third and fourth order streams underlain by silty sediments. The main objective of the study was to better understand relationships between BC and Si in RZ soils and adjacent surface waters. Specific objectives were to: (1) identify temporal and spatial trends in BC concentrations in RZ draining different landscape element types, (2) identify spatial differences in BC flow-weighted concentrations from streams dominated by different landscape element types, (3) investigate whether RZ element concentrations represent flow-weighted concentrations in headwater streams, and (4) test the sensitivity of riparian flow-weighted concentrations to changes in groundwater levels as potential effects of forest management and climate change.

## 2 Study area

### 2.1 Catchment characterization

The study was conducted in the 68 km<sup>2</sup> boreal Krycklan catchment (Fig. 1). The catchment has been intensively monitored for multidisciplinary research projects within the Krycklan Catchment Study (KCS) since 2002, but also includes the Svartberget catchment where monitoring began in 1981. Krycklan is located approximately 50 km northwest from the city of Umeå and 60 km west from the Baltic Sea with the outlet located at 64°12' N 19°52' E. Elevation ranges from 126 to 372 m a.m.s.l. resulting in a gentle topography within the catchment. Annual mean daily temperature is 1.8 °C and annual mean precipitation is 640 mm (1981–2010) with an average temperature in January and June of −9.5 °C and 11.9 °C, respectively. Approximately half of the precipitation falls as snow. The duration of snow cover is on average 168 days per year (commonly from the end of October until the beginning of May) (Laudon et al., 2011a). Average runoff is 321 mm yr<sup>−1</sup> (1981–2009), which results in an average evapotranspiration of 319 mm per year. Land cover types are dominated by forest (87%), with lower proportions of peat-dominated wetlands (9%), lakes (1%), and arable land in the lower lying parts of the catchment (3%). The catchment, and the boreal region as a whole, can be conceptualized as a series of different landscape element types (Oni et al., 2013). In the Krycklan region, relevant landscape elements include open water, bedrock, upland forest till soils, upland peat, and lowland sediments which are primarily forest-covered but also support the small amount of arable land found in the Fennoscandic boreal.



**Fig. 1.** Location of the Krycklan catchment within Sweden (a). In (b): shape of the Krycklan catchment with streams (black lines), lakes (black areas), peat (grey areas), till, thin soils and bedrock (white areas), silt-sandy sediments and gravel (dotted areas), glacio-fluvial alluvium (cross-hatched areas), stream site locations (white circles), and riparian site locations (black circles). In (c): zoom to the highlighted square in (b) with the rest of the stream site locations and the rest of the riparian site locations.

Although Krycklan has remained rather pristine, human activities have influenced the catchment similarly to other forests in the region. Many headwater streams in Northern Sweden were straightened and deepened to improve drainage and forest productivity during the early 20th century (Dahlström, 2005). Both Västrabäcken (C2) and Kalkällsbäcken (C7) (Fig. 1c) were deepened in the 1920s. The impact of forest management in the area is low. The catchment has never been clear-cut but some of the larger trees were removed in the early 1920s (Cory et al., 2007). When the area became a research forest in 1923, low-intensity forestry continued to be practiced. Currently, less than 1 % of the total area is harvested per year with no management at all in the 25 % of the catchment occupying the central part.

Scots pine (*Pinus sylvestris*) makes up 63 % of the tree volume and dominates in dry upslope areas. Norway spruce (*Picea abies*) makes up 27 % and is more common in wet low-lying areas, whereas deciduous forests stands, mainly birch (*Betula spp.*), contribute 10 % of the total tree volume and are mainly located in the RZ. Acidic peat-dominated wetlands (i.e. mires or bogs) are characterized by *Sphagnum spp.* mosses.

The gneissic bedrock consists of Svecofennian rocks with 93 % metasediments and metagraywacke, 4 % acid and intermediate metavolcanic rocks, and 3 % basic metavolcanic rocks (Ågren et al., 2007). The highest postglacial coastline

in the region is 255–260 m (Buffam et al., 2008), which results in 44 % of the catchment lying above this level (Ågren et al., 2007). The bedrock in the upper part of the catchment is overlain by Quaternary deposits of glacial till, consisting mainly of unsorted sediments of sand and silt varying in thickness up to tens of meters. Below the highest postglacial coastline, glacio-fluvial sediments are more commonly found with a large proportion of silt deposits formed by a post-glacial river delta (Fig. 1b). The sediment deposits form a thick layer through which the larger traversing streams have deeply incised channels, forming ravines and bluffs of up to 30 m height. Throughout the catchment and especially in the upper parts, well-developed iron podzols are common in upslope areas and organic-rich soils are common in the RZ.

## 2.2 Monitored streams and Riparian Observatory in Krycklan (ROK)

KCS comprises 15 partially nested subcatchments (Fig. 1, Table 1). Stream water chemistry is monitored at the outlets of the 15 subcatchments with a frequency that varies from monthly during low winter flow to 2 days-weekly during spring flood. A network of lysimeter arrays (hereafter referred to as Riparian Observatory in Krycklan; ROK) was established in 2007 to obtain a better understanding of the RZ influence on stream water. Thirteen instrumented sites were distributed in RZ across the catchment (Fig. 1). Locations were selected to cover a representative range of landscape

element types. Wetness conditions and soil types were identified by terrain analysis of 1 m-resolution airborne light detection and ranging (LiDAR) in conjunction with detailed field reconnaissance (Grabs et al. 2012). Ten of the instrumented sites were located in till soils, two in the sediment part of the catchment and one in the transition between sediment and till (Fig. 1). RZ in the till soils were further classified into wet, humid, and dry sites. Most of the riparian sampling sites located in till soils and the transition site had a thick peat layer ( $\geq 30$  cm), whereas the sites located in the sediment area had very shallow organic horizons over mineral soils. The lysimeter array at each site consists of a pair of ceramic cup suction lysimeters (pore size  $1 \pm 0.1 \mu\text{m}$ ) at 5 different soil depths including O-layers (15 cm, 30 cm, 45 cm, 60 cm, and 75 cm) and a perforated PVC tube equipped with an automatic water level logging device. The arrays are about 2 m from the corresponding stream. More information about the ROK sites may be found in Grabs et al. (2012). Both the stream and RZ sample collection locations will be referred to as sites hereafter.

### 3 Methodology

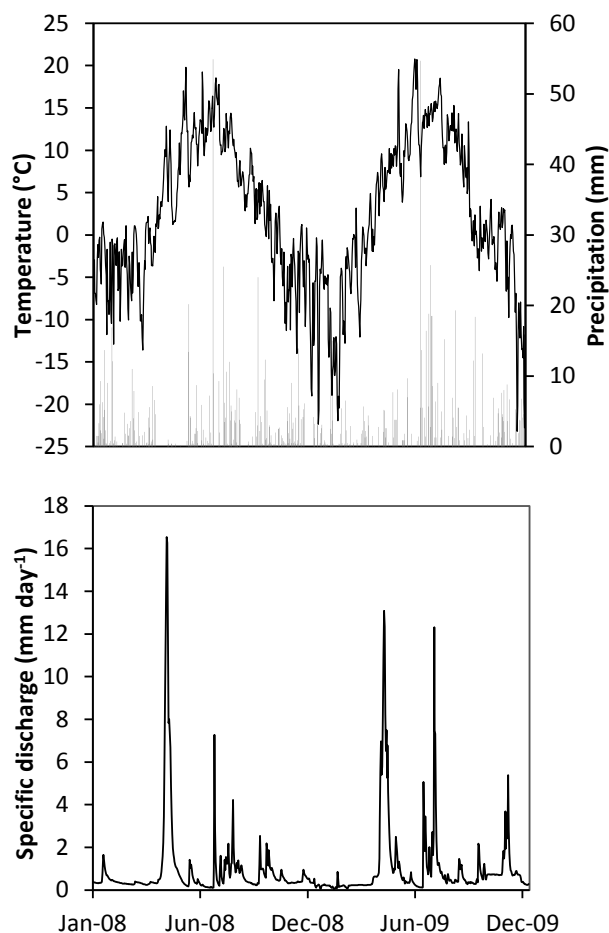
#### 3.1 General overview

This study was based on both soil water chemistry from the 13 ROK RZ sites and water chemistry from 14 monitored streams in Krycklan (note that stream C8 was not included as sampling has been terminated) during 2008 and 2009 (Fig. 1). First, spatial and temporal variations in BC and Si concentrations were investigated separately for riparian and stream sites (Sects. 4.1 and 4.2). The Mg/Ca ratio in riparian soil water samples was related to the mineralogy of the ROK sites and compared to Mg/Ca ratios in stream water samples (Sect. 4.3). Finally, flow-weighted concentrations in riparian and stream sites were estimated and comparisons made across headwater subcatchments (Sect. 4.4).

Annual BC and Si flow-weighted concentrations were based on samples collected during 2008–2009. Mean temperature was  $2.9^\circ\text{C}$  in 2008 and  $2.1^\circ\text{C}$  in 2009, slightly higher than the long-term mean  $1.8^\circ\text{C}$ . Water balances were similar in both years (Fig. 2) and close to the long-term mean. In 2008 the spring-flood runoff was larger than in 2009. However, larger summer-autumn runoff events in 2009 resulted in similar annual runoff (Fig. 2).

#### 3.2 Summary of the sampling procedure

Soil water samples were manually collected from suction lysimeters at the 13 ROK sites on 8 occasions in summer and autumn of 2008 and 2009 using acid-washed Milli-Q-rinsed Duran glass bottles (Grabs et al., 2012). Specific discharge and weather conditions during and 10 days prior to the 8 sampling campaigns were recorded (Table 2). In total, 52 water samples were collected from each of the 14



**Fig. 2.** Daily temperature and precipitation measured at the Krycklan catchment (above) and areal-specific discharge measured at site C7 (below) during 2008 and 2009.

stream sites (Fig. 1) during 2008 and 2009 as part of the regular KCS monitoring program. Acid-washed high-density polyethylene bottles (250 mL) were used for sample collection. RZ and stream samples were kept dark and cool prior to being sub-sampled within 24 hours and frozen for future chemical analysis. Individual BC concentrations (Ca, Mg, K, and Na) and Si were measured using inductively coupled atomic emission spectroscopy (ICP-AES).

In August 2008, soil pits representative of the existing ROK sites were excavated for characterizing mineralogy of the different landscape element types. X-ray diffraction (PANalytical X'Pert Pro PW3050/60) and Fourier Transformation infrared spectroscopy (FTIR, Perkin Elmer spectrum 100) were used for mineralogical identification and quantification following the procedure described in Niedermayr et al. (2013).

**Table 1.** Stream subcatchment characteristics including stream sampling site designations (column 1), corresponding RZ sampling sites (column 4), and land cover type proportions (columns 6 to 9, the sum of which adds up to 100 %). For the PLS analysis, land cover was divided up in the landscape element types shown in columns 9 to 17 (the sum of which also adds up to 100 %) that include open water, bedrock, peat and Quaternary deposits.

Site	Name	Stream order	Riparian sites	Area (km <sup>2</sup> )	Forest (%)	Wetland (%)	Arable (%)	Lake (%)	Bedrock (%)	Peat (%)	Till (%)	Silt (%)	Sand (%)	Alluvial (%)	Gravel (%)	Thin soils (%)
C1	Risbäcken	2	R12	0.48	98	2	0	0	0	0	92.1	0	0	0	0	7.9
C2	Västrabäcken	1	R5, 6, 7	0.12	100	0	0	0	0	0	84.2	0	0	0	0	15.7
C3	Lillmyrbäcken	1		0.04	59.1	40.4	0.4	0	0	53.2	43.2	0	3.7	0	0	0
C4	Kalkällsmyren	1	R8	0.18	55.9	44.1	0	0	0	51.1	22	0	0	0	0	27
C5	Stortjärnen Outlet	1		0.65	54	39.6	0	6.4	0	47.8	40.4	0	0	0	0	5.5
C6	Stortjärnbäcken	1	R4	1.10	71.4	24.8	0	3.8	2.5	28.7	53.7	0	0	0	0	11.3
C7	Kalkällsbäcken	2	R9, 10	0.47	82	18	0	0	0	19.4	65.2	0	0	0	0	15.4
C8	Fulbäcken	2	R1, 2	2.30	88.1	11.9	0	0	1.7	17	62.8	0	0	0	0	18.6
C9	Nyängesbäcken	3		2.88	84.4	14.1	0	1.5	1.7	15.2	69.1	4.1	0	0	1.6	6.8
C10	Stormyrbäcken	2	R11	3.36	73.9	26.1	0	0	0	28.8	59.9	0	0.5	0	0	10.8
C12	Nymyrbäcken	3		5.44	82.6	17.4	0	0	0	19.2	66.6	1.5	4.3	0	0	8.4
C13	Långbäcken	3	R15	7.00	88.2	10.3	0.8	0.7	1.3	11.8	60.9	15.9	0	0	0.7	8.9
C14	Åhedbäcken	3	R14	14.10	90.2	5.4	3.7	0.7	1.6	6.6	44.9	34.7	0	3.4	0	8.1
C15	Övre Krycklan	4		20.13	81.6	14.5	1.5	2.4	0.7	14.5	64.8	1.8	0	7.6	0	8.1
C16	Krycklan	4		68.91	87.3	8.7	3.1	0.9	1.2	9.4	50.8	26.6	0.3	3.3	0.1	7.4

**Table 2.** Sampling campaign dates for collection of lysimeter soil water from the riparian sites including discharge and weather conditions.

Campaign	Date of sampling	Specific discharge (mm day <sup>-1</sup> )	10-day antecedent discharge (mm)	Average temperature (°C)	Average 10-day antecedent temperature (°C)	Precipitation (mm)	10-day antecedent precipitation (mm)
0802	22 Jun 2008	0.34	7.4	13	11	2.6	14
0803	27–28 Jul 2008	0.43	14	16	15	0.0	68
0804	25–26 Aug 2008	1.2	17	11	12	4.7	27
0805	23–24 Sep 2008	0.31	3.7	9.7	5.5	0.0	1.0
0806	23 Oct 2008	1.5	12	−0.4	2.6	0.2	30
0901	7 Jun 2009	0.30	7.3	4.7	10	0.9	9.0
0902	2 Aug 2009	1.2	43	16	15	1.3	82
0903	20 Sep 2009	0.27	5.5	9.2	9	0.0	3.7

### 3.3 Discharge measurements

Discharge was continuously measured at site C7 (Fig. 1c) using a 90° V-notch weir located in a heated hut. Established stage-discharge rating curves were used to calculate daily flow values from water levels monitored at the weir. Uncertainties in flows were estimated to be below 5 % at this site (Laudon et al., 2007). We assumed that the areal-specific discharge was the same all over the catchment. Ågren et al. (2007) estimated two uncertainties from this assumption: (1) ±12 % due to differences in subcatchment evapotranspiration and (2) ±12 % due to differences in flow regime (maximum in spring flood). Specific discharge has been used to calculate fluxes in Krycklan in many other studies (see for example Björkvald et al., 2008; Köhler et al., 2008; Wallin et al., 2010). It should be noted that because of the assumption of homogeneous specific discharge, actual fluxes would be proportional to the flow-weighted concentrations calculated here and hence the relative differences between sites would be equal.

### 3.4 Calculation of flow-weighted concentrations

#### 3.4.1 Riparian zones

In order to calculate BC and Si flow-weighted concentrations in the ROK sites we adapted the assumptions and routines presented in Grabs et al. (2012), which used RIM (Bishop et al., 2004). Figure 3 shows a conceptual representation of the calculations.

A campaign concentration value for each element, site, and depth was estimated by averaging the measurements from the two lysimeters. The potential number of samples was 1040 (8 campaigns, 13 sites, 5 depths, 2 lysimeters), i.e. 520 campaign concentrations, but not all samples were available due to e.g., failure of some lysimeters or too little water collected from relatively dry soil layers. The total number of samples available was 702. Missing values for lysimeters when a single replicate was available were estimated using a scaling factor as described by Grabs et al. (2012). That

gave a total of 448 campaign concentration values, i.e. 86 % of the total 520 possible concentrations.

The loggers placed at the 13 ROK sites measured hourly groundwater levels from May 2008 to September 2009. For each site, binned observed groundwater tables ( $z_{\text{Gw}}^{\text{obs}}$ , mm) were fit to areal-specific discharge measured at site C7 ( $Q$ , mm) using an offset parameter ( $h_0$ , mm) (Grabs et al., 2012). Thus, for each site it was possible to fit a curve described by Eq. (1), where  $a$  (mm) is a flow parameter and  $b$  ( $\text{mm}^{-1}$ ) is an exponential parameter describing the water flux curve (Grabs et al., 2012). This method was based on the assumption that groundwater and runoff dynamics are similar in near-stream areas, as has been shown in glacial till soils (Rodhe, 1987; Bishop, 1991; Moldan and Wright, 1998; Seibert et al., 2003). It was not possible to fit a curve for site R14 due to the low variation of  $z_{\text{Gw}}^{\text{obs}}$ . Instead, for site R14 the parameter  $b$  was assumed to be the same as for site R15 based on their similar soil properties.

$$Q = e^{b \cdot ((z_{\text{Gw}}^{\text{obs}} - h_0) + a)} \quad (1)$$

Continuous solute concentration profiles for each element and site were estimated by linear interpolation between average values of the 8 campaigns (or the number of campaigns available) at each depth. Values were estimated for a 1 m-deep profile, starting from soil surface  $z = 0$  mm and at 1 mm intervals. The concentration between 15 cm and the top of the profile was assumed to be constant and equal to the average campaign concentration at 15 cm. Concentrations between 75 cm and 1 m were assumed to be equal to the average campaign concentration at 75 cm. Flow-weights ( $w$ , dimensionless) describe the incremental lateral discharge at each site (Grabs et al., 2012), i.e., a proxy for the hydraulic conductivity of each soil layer. Flow-weights were calculated every mm using Eq. (2), where  $z$  (mm) is the depth in the profile and  $b$  is the exponential parameter used to describe the variation of flow with depth in Eq. (1).

$$w = e^{(z \cdot b)} \quad (2)$$

A daily flow-concentration, ( $C_{\text{flow}}$ ,  $\text{mg L}^{-1}$ ) for each element and site was then calculated by integrating the product of flow-weights and average soil water concentrations ( $C_{\text{avg}}$ ,  $\text{mg L}^{-1}$ ) over the saturated part of the soil profile, i.e. the conductive layers below the groundwater level (Eq. 3, Fig. 3). Modelled groundwater tables ( $z_{\text{Gw}}^{\text{mod}}$ ) (Fig. 4) were back-calculated with Eq. (1) using daily measurements of flow and used to calculate daily  $C_{\text{flow}}$  because of gaps in the record of  $z_{\text{Gw}}^{\text{obs}}$ . For site R14,  $z_{\text{Gw}}^{\text{mod}}$  was assumed to be constant and equal to the mean of the observed values. The upper boundary when calculating  $z_{\text{Gw}}^{\text{mod}}$  was set to 0 mm and thus  $z_{\text{Gw}}^{\text{mod}}$  higher than 0 mm were assumed to be 0 mm (Fig. 4), i.e. overland flow was discarded in accordance with Grabs et al. (2012). Annual flow-weighted average concentrations ( $C_{\text{flow-w}}$ ,  $\text{mg L}^{-1}$ ) were subsequently calculated by dividing the annual sum of daily flow-concentrations by the annual sum of daily flow-weights (Eq. 4, Fig. 3) as described in

Eq. (5). Overall flow-weighted concentrations in the period 2008–2009 were then calculated as the mean value of annual flow-weighted average concentrations.

$$\text{Daily } C_{\text{flow}} = \int_{-1000 \text{ mm}}^{z_{\text{Gw}}^{\text{mod}}} w(z) \cdot C_{\text{avg}} dz \quad (3)$$

$$\text{Daily } w = \int_{-1000 \text{ mm}}^{z_{\text{Gw}}^{\text{mod}}} w(z) dz \quad (4)$$

$$\text{Annual } C_{\text{flow-w}} = \frac{\sum_{1 \text{ January}}^{31 \text{ December}} \text{Daily } C_{\text{flow}}}{\sum_{1 \text{ January}}^{31 \text{ December}} \text{Daily } w} \quad (5)$$

### 3.4.2 Streams

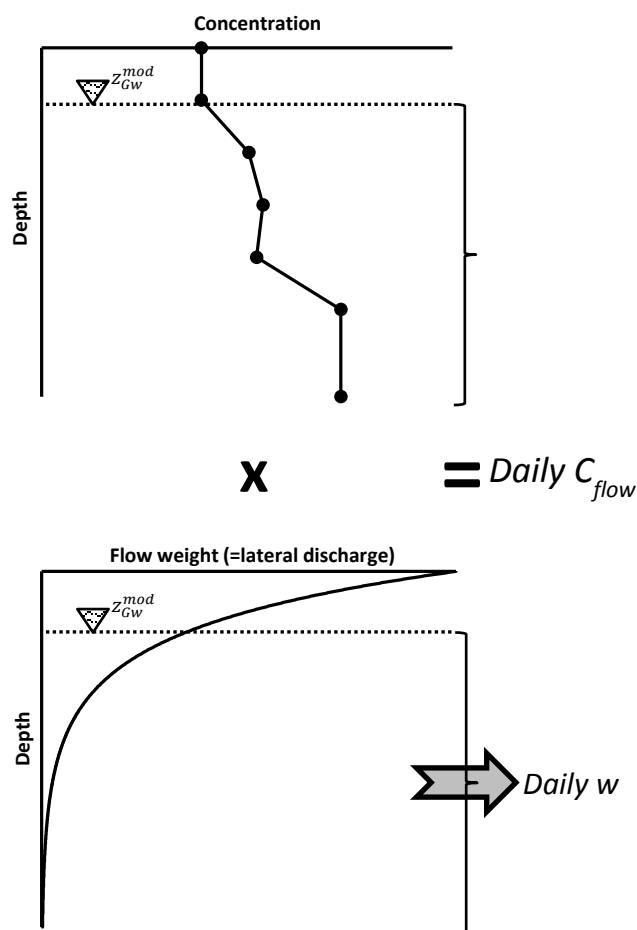
Annual chemical loads were calculated by linear interpolations between observed concentrations to complete daily series and then summing daily products of concentrations and flows (Ledesma et al., 2012). Flow-weighted concentrations were obtained by dividing the annual load by the annual total volume of water discharged and expressed in  $\text{mg L}^{-1}$ , i.e. the result only depended on the concentration and the relative differences in daily flow. The observed discharge at site C7 was used as the best estimate of discharge for all stream sites. Flows for each stream were estimated by multiplying the areal-specific discharge from C7 by the catchment area drained by the stream. Overall flow-weighted concentrations for 2008–2009 were then calculated as the mean value for the two years.

### 3.5 Sensitivity and uncertainty analyses

Given the temporal stability in BC and Si concentrations in the ROK sites (detailed results are presented below), average campaign concentration profiles were used to calculate annual flow-weighted average concentrations. Flow-weighted concentrations were also calculated using minimum and maximum campaign concentration profiles. The three concentration profiles (average, maximum, and minimum) were used in two different scenarios:

(SU1): to estimate the potential magnitude of variations of flow-weighted concentrations for each element and ROK site based on  $z_{\text{Gw}}^{\text{mod}}$ .

(SU2): to assess the sensitivity of BC flow-weighted concentrations to uncertainties in groundwater table levels by allowing  $z_{\text{Gw}}^{\text{mod}}$  to vary between  $\pm 1.96$  standard deviations of the modelled estimates with respect to the observations at each site.



**Fig. 3.** Schematic representation of how the RIM approach was applied to calculate annual flow-weighted concentrations ( $C_{\text{flow-w}}$ ) from riparian soil profiles. The product of concentrations and flow-weights is integrated below the modelled groundwater table ( $z_{\text{GW}}^{\text{mod}}$ ) in a daily basis to obtain daily flow-concentrations ( $C_{\text{flow}}$ ). Daily flow-weights ( $w$ ) are obtained by integrating flow-weights below ( $z_{\text{GW}}^{\text{mod}}$ ) in a daily basis. Annual  $C_{\text{flow-w}}$  is the result of dividing the summation of daily  $C_{\text{flow}}$  by the summation of daily  $w$  over a year.

### 3.6 Statistical analyses

Riparian sites were classified according to landscape element type following Grabs et al. (2012). First the sites were classified according to the underlying parent material (glacial till or glacio-fluvial sediments dominated by silt). The sites located on till were further classified according to their median  $z_{\text{GW}}^{\text{mod}}$  (dry, humid, and wet). This will be referred to as site class in the following. Spatial and temporal trends in BC and Si concentrations were investigated following the approach presented by Futter et al. (2011) to partition variation between different sources. A series of analyses of variance (ANOVAs) were performed so as to estimate the relative contribution of riparian site class, riparian site, depth in the profile, and sampling campaign to the total variation in BC and Si campaign concentrations. The fraction of total variation

**Table 3.** Relative contribution (%) of riparian site class, depth in the profile, and sampling campaign to the total variation in BC and Si campaign concentrations in the ROK sites.

Element	Site class	Depth	Campaign	Site + Residual
Ca	43.9	1.2	0.5	54.5
Mg	42.5	1.0	0.4	56.1
K	49.1	2.0	1.0	47.9
Na	38.6	1.9	1.0	58.5
Si	20.2	4.4	0.5	75.0

ascribed to each component was equal to the sum of squares for that component divided by the total sum of squares from the ANOVA.

A partial least squares (PLS) analysis (Chin et al., 2003) was performed to explore catchment geologic controls on BC dynamics. BC and Si flow-weighted concentrations from the stream sites were set as response variables and landscape element-type proportions, including open water, peat, bedrock, and Quaternary deposits in the corresponding sub-catchments were set as predictors. (Table 1). In a PLS model  $R^2Y$  indicates how much variation in the response variables is explained by the predictors,  $Q^2$  indicates how well the model predicts ( $Q^2 > 0.5$  are considered good models), and Variable Important for the Projection (VIP) indicates the relative importance of the predictors ( $\text{VIP} > 1$  indicate important variables) (Eriksson et al., 1999).

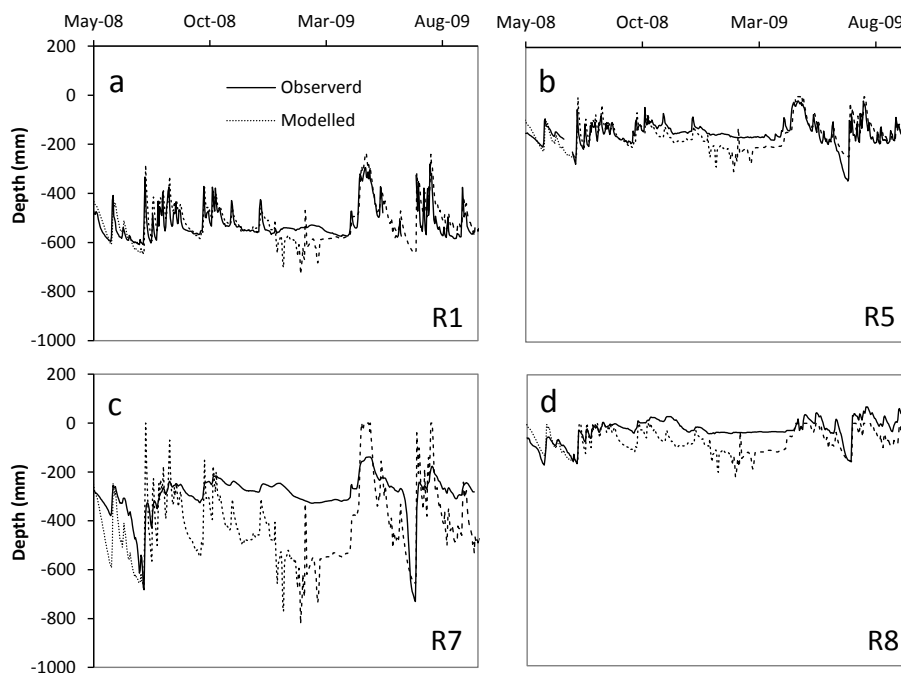
## 4 Results

### 4.1 Riparian BC concentration profiles

#### 4.1.1 Spatial variation

Accounting for all riparian sites and depths, means of campaign concentrations showed that Ca was the dominant BC in the soil solution ( $4.0 \pm 3.1 \text{ mg L}^{-1}$ ) ( $\pm\text{SD}$ ), followed by Na ( $2.2 \pm 0.8 \text{ mg L}^{-1}$ ), Mg ( $1.3 \pm 1.0 \text{ mg L}^{-1}$ ) and K ( $0.9 \pm 0.8 \text{ mg L}^{-1}$ ) (Figs. 5 and 6). Si had the highest concentrations of all of the elements analysed ( $8.3 \pm 2.9 \text{ mg L}^{-1}$ ).

The partition of variance (Table 3) revealed that site class, and hence landscape element type, was the factor explaining most of variability in BC and Si campaign concentrations. Sites R11 and R14 were hotspots with average Ca concentrations of  $11.8 \pm 1.7 \text{ mg L}^{-1}$  ( $14.2 \pm 1.7 \text{ mg L}^{-1}$  at 30 cm) and  $7.8 \pm 0.9 \text{ mg L}^{-1}$ , respectively (Fig. 5). The Ca concentrations in these two silty-sediment sites were notably higher than in the till sites (Fig. 5). Site R15, also belonging to the sediment class, presented a vertical profile with intermediate concentrations ( $2.3 \pm 0.4 \text{ mg L}^{-1}$ ). Wet till sites had spatially stable concentrations, although the absolute mean values differed from  $0.8 \pm 0.2 \text{ mg L}^{-1}$  in R8 to  $4.0 \pm 0.5 \text{ mg L}^{-1}$  in



**Fig. 4.** Comparison of observed and modelled groundwater tables for the period with overlapping data (May 2008 to September 2009) at some selected riparian sites including R1 (a), R5 (b), R7 (c), and R8 (d).

R2 (Fig. 5). Both of these sites have soils where deep peat development is favoured by wet conditions, but R2 is located in a forest catchment (C8) and R8 in a mire wetland (C4) (Fig. 1c). The depth of sampling had little influence on the variability in BC and Si campaign concentrations taking into account all the riparian sites (Table 3), but it was observed that dry and humid till classes had higher concentrations deeper in the profile (Fig. 5). Combined Ca concentrations for all sites belonging to these two classes varied from  $1.9 \pm 0.7 \text{ mg L}^{-1}$  at 15 cm depth to  $3.9 \pm 1.1 \text{ mg L}^{-1}$  at 75 cm depth.

This general picture presented for Ca was observed for the other elements, which was indicated by high correlations with Ca: Na ( $R^2 = 0.73$ ), K ( $R^2 = 0.72$ ), Si ( $R^2 = 0.67$ ), and especially Mg ( $R^2 = 0.96$ ; Fig. 7). However, near-surface (15 cm depth) K concentrations were relatively high at several sites (R6, R7, R10 and R12 in Fig. 6). Campaign concentrations for all elements and sites can be found in the Supplement.

#### 4.1.2 Temporal variation

The temporal variations in Ca and K concentrations are represented as the difference between minimum and maximum campaign concentrations at each depth (Figs. 5 and 6). Including all depths and sites, the mean of the relative standard deviations for Ca (11 %), Mg (8 %), Na (8 %), and Si (7 %) were within or close to the analytical measurement error (SLU, 2012). The temporal variation of K was higher than

for the other elements in all sites, except in R11 and R14, and the mean relative standard deviation for all depths and sites was 33 %. The partition of variance (Table 3) showed a negligible influence ( $\leq 1.0$  %) of the time when the samples were collected in the variation of BC and Si campaign concentrations.

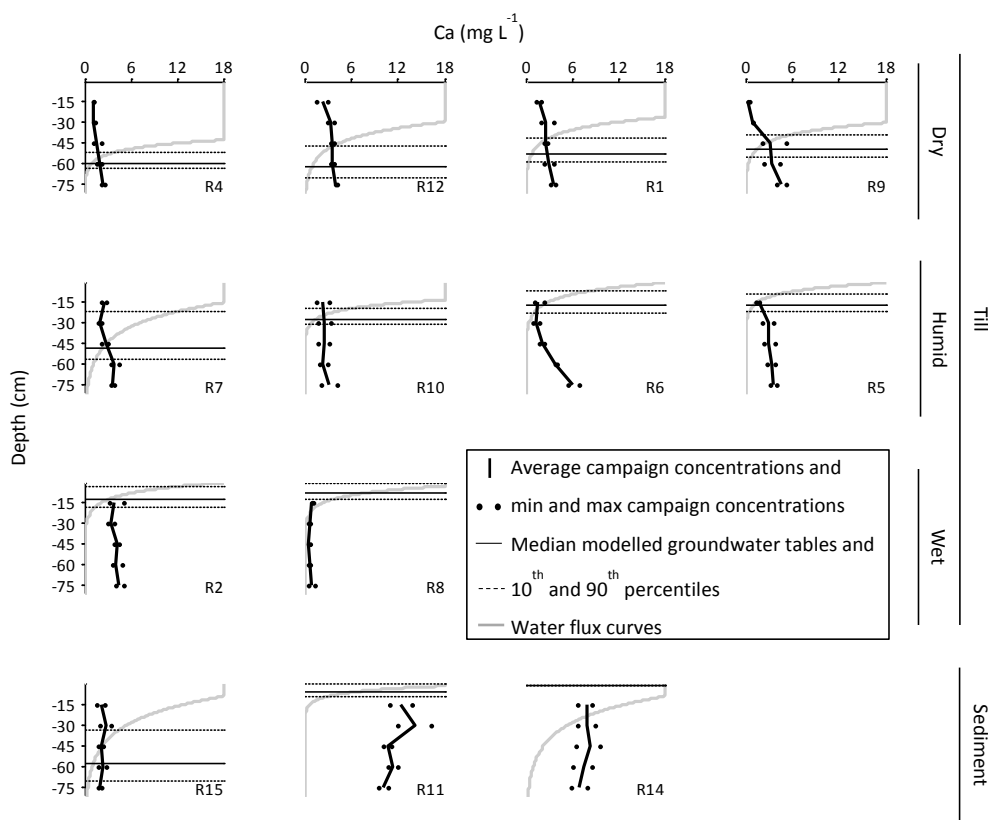
#### 4.2 Stream BC concentrations

Except for K, BC and Si concentrations in the stream sites tended to dilute at higher flows (Fig. 8a, b, and c; Supplement). In general, this pattern was stronger for Na and Si than for Mg and Ca. The Krycklan outlet had strong concentration-discharge relationships for all elements including K (Fig. 8d). The dilution of element concentrations with increasing flow (indicated by the steepness of the slopes in the Fig. 8 plots) was small in forest subcatchments (Fig. 8a), whereas a stronger dilution effect was noted in wetland-dominated sites (Fig. 8b).

#### 4.3 The Mg/Ca ratio in relation to mineralogy

The Mg/Ca ratios for all samples from the RZ soil solution were close to Mg/Ca ratios from the stream water samples, all of which were remarkably stable (Fig. 7). However, nominal differences were detected between the Mg/Ca ratio in the RZ and the ratio in the streams (Table 4). Riparian site R9 deviated strongly from the general relationship. The overall mean Mg/Ca ratio for all riparian soil water samples was  $0.35 \pm 0.10$ , whereas the Mg/Ca ratio for site R9 was





**Fig. 5.** Interpolated average campaign concentration profiles of Ca for the 13 riparian sites in Krycklan (vertical black lines). Concentrations measured at 8 occasions during 2008 and 2009. Plots also include minimum and maximum campaign concentrations (black circles), median modelled groundwater tables (horizontal black lines), 10th and 90th percentiles of groundwater table positions (horizontal dotted lines), and water flux curves (light grey lines).

**Table 4.** Parameter estimates from the differences between the Mg-Ca relationship in the riparian soil water samples and the Mg-Ca relationship in the stream water samples.

Term	Estimate	Std error	<i>t</i> Ratio	Prob >   <i>t</i>
Intercept	0.02	< 0.01	2.50	0.013
Ca	0.32	< 0.01	94.9	< 0.0001
Stream or Riparian	0.02	< 0.01	4.58	< 0.0001
Interaction	0.01	< 0.01	1.99	0.047

significantly higher ( $Mg/Ca = 0.63 \pm 0.34$ ). The mineralogy was rather homogeneous among sites with the exception of site R9 (Table 5, Supplement). Six groups of minerals were identified in all sites analysed and site R9 showed different ranges in the content of three of those groups in comparison to the other sites (Table 5).

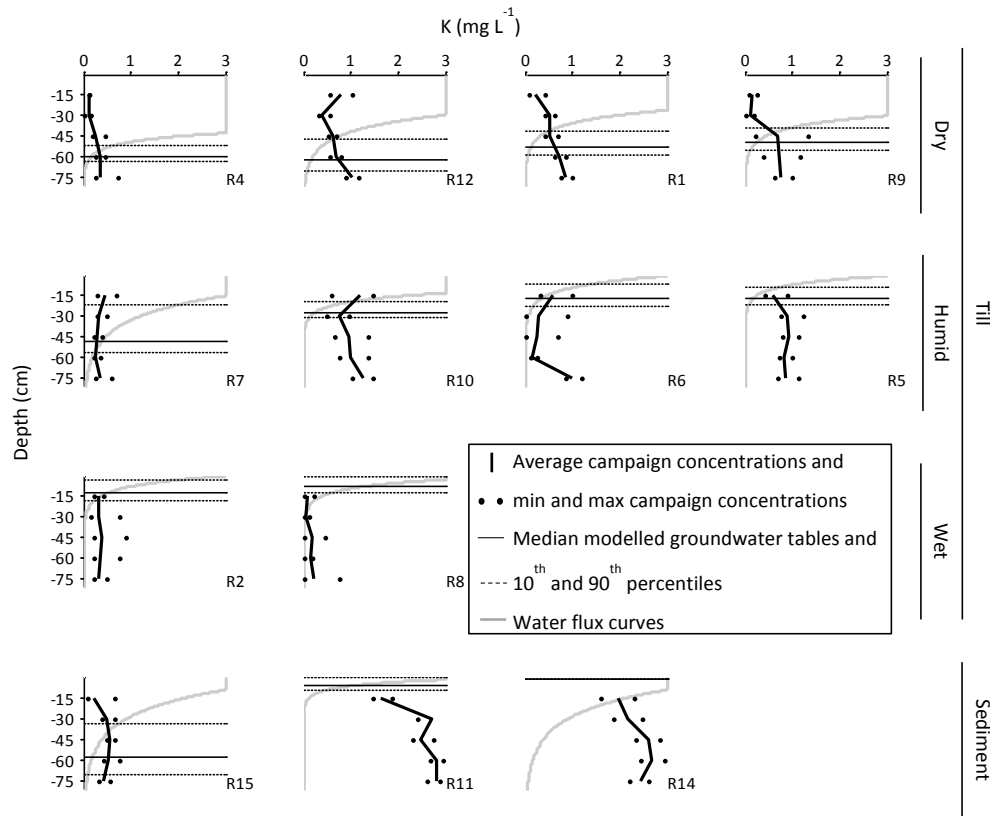
**Table 5.** Mineralogical content in riparian soil samples excluding site R9 ( $N = 17$ ) and in site R9 ( $N = 3$ ).

Mineral type	Content (%)	Content in R9 (%)
Quartz	31–43	9–15
Plagioclase	20–25	14–16
K-Feldspar	16–33	14–43
Amphibolites	7–21	0–32
Muscovite	2–16	3–10
Chlorite	1–4	5–21

#### 4.4 Riparian and stream BC flow-weighted concentrations

##### 4.4.1 Riparian flow-weighted concentrations and sensitivity/uncertainty analyses

The estimated BC and Si flow-weighted concentrations for both riparian and stream sites including flow-weighted minimum and maximum concentrations in the riparian sites and sensitivity analyses (SU1 and SU2) are presented in the Supplement. Not surprisingly, sites R11 and R14 had the highest



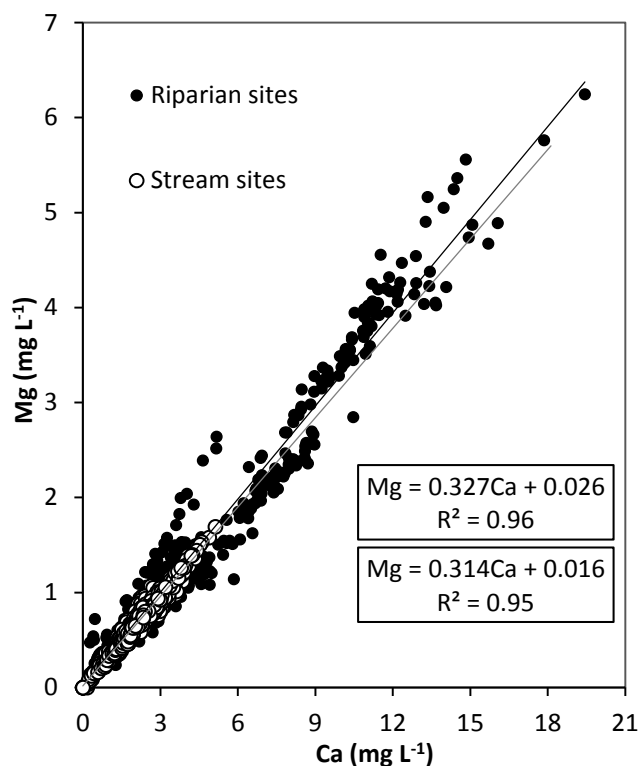
**Fig. 6.** Interpolated average campaign concentration profiles of K for the 13 riparian sites in Krycklan (vertical black lines). Concentrations measured at 8 occasions during 2008 and 2009. Plots also include minimum and maximum campaign concentrations (black circles), median modelled groundwater tables (horizontal black lines), 10th and 90th percentiles of groundwater table positions (horizontal dotted lines), and water flux curves (light grey lines).

flow-weighted average concentrations in all cases as a consequence of the high concentrations in these sites. An exception to this was the high Na and Si flow-weighted concentrations observed at some forest sites (see for example sites R7 and R12). The lowest flow-weighted concentrations were estimated from site R8, located in the vicinity of a mire wetland.

In scenario SU1 we compared the potential range of flow-weighted concentrations for the different elements by using minimum and maximum campaign concentrations at each depth and site. Accounting for all riparian sites, Ca and Mg varied similarly between  $-18\%$  to  $+19\%$  of the flow-weighted average and Na and Si between  $-9\%$  and  $+11\%$  of the flow-weighted average. In contrast, the range of K flow-weighted concentrations was higher, between  $-31\%$  and  $+53\%$  of the flow-weighted average (Supplement).

Scenario SU2 was performed to estimate how sensitive the flow-weighted concentrations were to uncertainties in groundwater levels (Fig. 9; Supplement). In general, rising groundwater tables would decrease flow-weighted BC concentrations, whereas falling groundwater levels would imply higher concentrations. This is related to the fact that,

in general, BC concentrations were higher deeper in the RZ soil profile. Thus, lower groundwater levels would result in a lower volume of water per concentration unit, i.e. higher flow-weighted concentrations (and vice versa). The opposite occurred for the sites with higher concentrations of K in the upper horizon. Therefore, the sensitivity is site-specific and dependent on the shape of the concentration profile where  $z_{\text{Gw}}^{\text{mod}}$  varies. For example, site R9, the most sensitive, had notably lower concentrations of all the elements at 30 cm depth than at 45 cm depth, and  $z_{\text{Gw}}^{\text{mod}}$  varied in this area of the profile (Figs. 5 and 6). In contrast, site R11, which had variation within concentration profiles, showed very low sensitivity to variation in groundwater levels. This is explained by the fact that  $z_{\text{Gw}}^{\text{mod}}$  here varied on the top layer of the soil (above 15 cm), where concentrations were assumed to be constant. Site R15, with the most dynamic  $z_{\text{Gw}}^{\text{mod}}$  and the largest uncertainty, had low sensitivity (below 10% variation in flow-weighted concentrations) as a result of the practically vertical concentration profiles. The differences between elements followed the same principle. Site R6 was sensitive for K but not for Ca due to the different shape in concentration profiles between K and Ca (Figs. 5 and 6). For most of the cases, the



**Fig. 7.** Relationship between Mg and Ca in all riparian soil water samples ( $N = 702$ ) and all stream water samples ( $N = 722$ ) and equations describing them (above equation: riparian samples; below equation: stream samples).

variation in  $z_{\text{Gw}}^{\text{mod}}$  did not change the flow-weighted concentrations more than 15 % (Fig. 9).

#### 4.4.2 Stream flow-weighted concentrations and PLS analysis

All BC flow-weighted concentrations increased downstream in the catchment, especially in the sites located in the sedimentary landscape element and at the catchment outlet where the highest BC concentrations were observed (Supplement). As an exception to this, the highest flow-weighted concentrations for Na and Si were estimated for the two most forest-dominated sites C1 and C2 (Table 1). Low BC flow-weighted concentrations were generally associated with sites characterized by a high proportion of wetlands (C3, C4, and C5).

BC and Si flow-weighted concentrations in all stream sites were used as response variables and landscape element type proportions in the corresponding subcatchments (Table 1) as predictors in a PLS analysis. Landscape element type predicted most of the variation in flow-weighted concentrations ( $R^2Y = 0.88$ ) with a high prediction ability ( $Q^2 = 0.75$ ). Individually, Si and Na were predicted better ( $R^2Y = 0.93$ ;  $Q^2 = 0.82$ ) than K ( $R^2Y = 0.79$ ;  $Q^2 = 0.63$ ), and Ca and Mg were in the range of the overall model. The important

predictors ( $VIP > 1$ ) were in decreasing order: percentage of peat, percentage of silt, and percentage of till.

#### 4.4.3 Linking riparian and stream flow-weighted concentrations

Flow-weighted concentrations from riparian and stream sites can be compared in headwaters to test whether net fluxes are maintained and to gain insights into RZ behaviour. In our case, that is C4 and R8; C2 and R5, R6, and R7; and C6 and R4 (Fig. 10). By definition, headwater streams receive no water from other upstream catchments and their chemistry should be represented by their RZ. In general, flow-weighted concentrations in headwater streams were within or slightly below the range of flow-weighted concentration estimates in the corresponding RZ (Fig. 10). Ca, Mg and Na matched well; however, some discrepancies were observed for K. For example, concentrations of K were higher in site R5 compared to site C2 and lower in site R8 compared to site C4 (Fig. 10b). For Si, flow-weighted concentrations were noticeably lower in the streams (Fig. 10c). Site R7 showed higher flow-weighted concentrations for all elements than the corresponding stream C2 and the other riparian sites in the sub-catchment.

Higher flow-weighted concentrations throughout the sedimentary area towards the outlet corresponded with higher RZ flow-weighted concentrations downstream in the catchment (Supplement). Sites R11 and R14 in the sedimentary landscape element type had notably higher flow-weighted concentrations than those observed in other landscape element types. Moreover, the highest Na and Si flow-weighted concentrations found in C1 and C2 were in agreement with high flow-weighted concentrations estimated in corresponding riparian sites for these elements (sites R7 and R12).

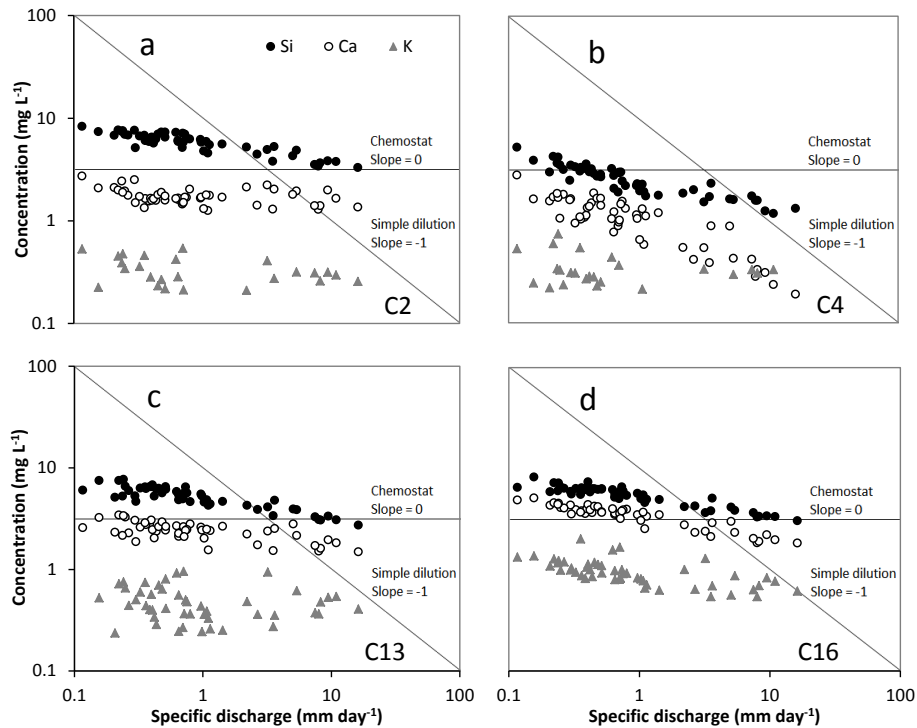
## 5 Discussion

### 5.1 Spatial and temporal variation in the ROK BC concentrations

#### 5.1.1 Spatial variation

The shape of the concentration profiles was similar between RZ sites, especially those belonging to the same site class (Figs. 5 and 6). Dry and humid till sites had, in general, higher concentrations deeper in the profile, probably representing water with longer soil/mineral contact time (Löfgren et al., 2010). This is in agreement with other studies in Sweden (Vestin et al., 2006, 2008).

The variability in absolute concentrations between sites was large. Site R8, which receives water from a contiguous mire wetland showed the lowest BC and Si concentrations. This suggests a source limitation, i.e. lower mineral content at this site. Higher concentrations of K, Na, and Si were observed in a forest RZ compared with a wetland RZ



**Fig. 8.** Measured concentration and specific discharge relationships for Ca, K, and Si at some selected stream sites during 2008 and 2009, including C2 (typical forest catchment) (a), C4 (typical peat-dominated wetland catchment) (b), C13 (outlet of the upper part of the catchment) (c), and C16 (outlet of the catchment) (d). Mg resembled Ca and Na resembled Si.

by McLaughlin (2009), although there Ca and Mg were similar between the two landscape element types.

Site R11 and site R14, located in the sedimentary landscape element type, showed the highest concentrations of BC and Si. The differences in the Quaternary deposits between sites in the upper unsorted till soils and the sites downstream underlain by sorted fine sediments may explain this and support the hypothesis that the higher specific surface area of the silt enhances weathering reactions by allowing more effective mineral contact (Warfvinge and Sverdrup, 1992; Ågren et al., 2007). The PLS analysis confirmed the importance of landscape element type as controls of BC and Si. In contrast, site R15, also located in the sediment area of the catchment, had concentrations which were similar to those found in the till sites. The lower part of the profile in site R15 is influenced by soil water enriched in organic carbon which could originate from buried organic matter, drainage water from an adjacent agricultural land or hyporheic fluxes from the stream (Grabs et al., 2012), all of which would tend to dilute BC concentrations.

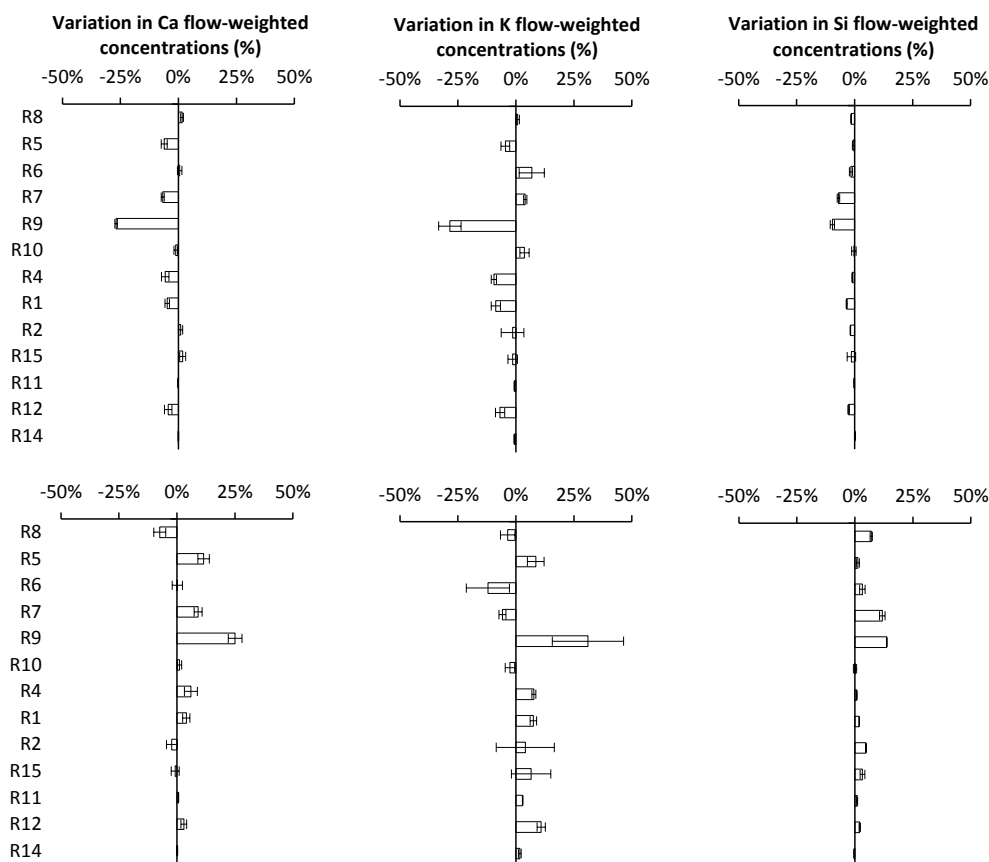
### 5.1.2 Temporal variation

The general temporal stability of BC and Si concentrations at each depth and site is worth commenting on. We found a negligible influence of time of sampling on variation in BC and Si campaign concentrations (Table 3). K presented more

temporal variation than the other elements, mostly related to a peak in concentrations in the end of August 2008, especially at 15 and 30 cm depth (data not explicitly shown). This could have been caused by the release of K from decaying plant matter at the end of the growing season (Tukey, 1970). In contrast to the results presented here, Vestin et al. (2008) found temporal trends for Ca, K, and Si in a forest catchment in Sweden. However, they used more superficial soil water measurements than those presented here. Our results are in agreement with those presented by Burns et al. (1998), who found little temporal variation in BC concentrations in subsurface flow from upslope sites in a forest catchment in North America. Therefore, the temporal stability in the BC and Si concentrations in the ROK could be indicating a strong and stable upslope influence in the riparian chemistry.

### 5.2 The role of mineralogy

Si was found in the soil solution in relatively high concentrations, suggesting the presence of weathering products in RZ soil water. This is further demonstrated by the high correlation between all elements studied here. We used the Mg/Ca ratio to investigate homogeneity within the catchment. Changes in Mg/Ca ratio could potentially indicate ion-exchange reactions but our results showed temporally and spatially stable ratios in all riparian sites and depths (Fig. 7), with the exception of site R9. The fact that this site also had



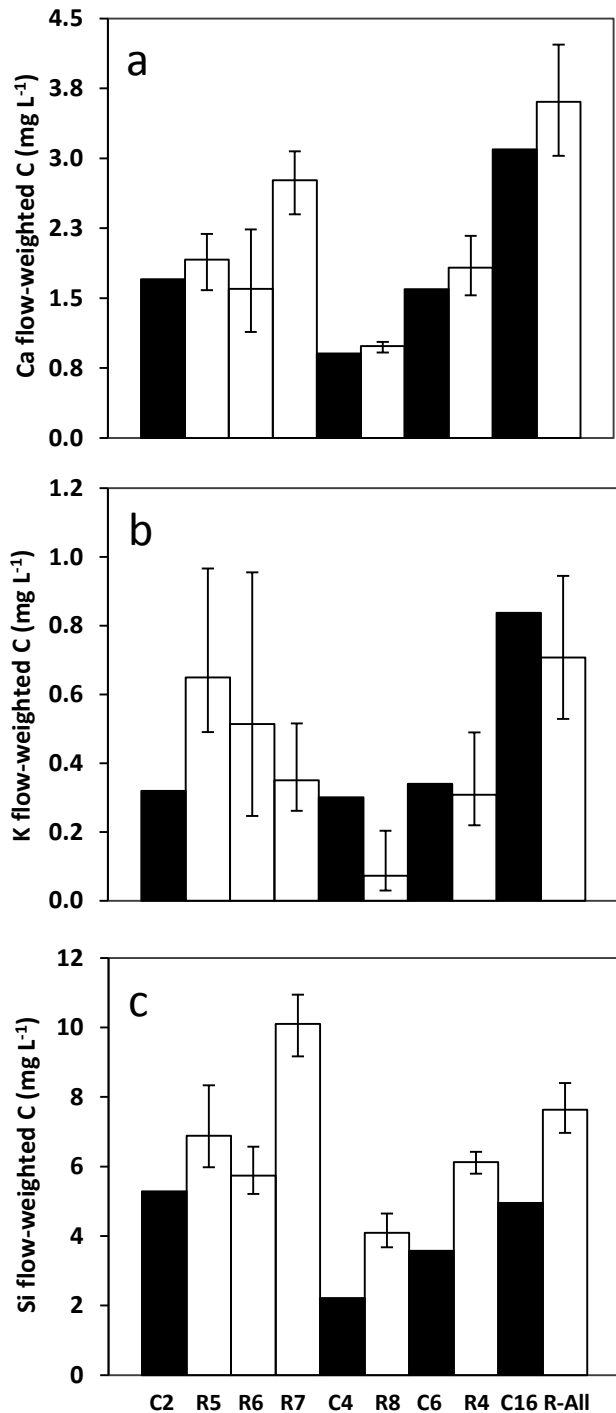
**Fig. 9.** Scenario SU2. Mean variation in maximum, average and minimum flow-weighted concentration for Ca, K, and Si for each riparian site after varying modelled groundwater tables  $+1.96$  standard deviations of the modelled estimates with respect to the observations at each site (above) and  $-1.96$  standard deviations (below). Error bars represent standard deviations. Mg resembled Ca and Na resembled Si. The sites are sorted from those located in small headwaters to those located in larger subcatchments downstream.

a different mineralogy indicates that the riparian soil solution is strongly imprinted by a mineralogical signal. Specifically, the higher content of Mg-rich chlorite can explain the higher Mg concentration at site R9 (Table 5). Water of mineral soil origin supports the transmissivity feedback concept (Rodhe, 1989; McDonnell et al., 1998; Laudon et al., 2004; Bishop et al., 2011) in which upslope “old” or “pre-event” water (i.e. groundwater) is the main source of RZ water and refutes other suggested sources such as water infiltrated from seeps (Vidon and Smith, 2007) or precipitation inputs. The near-constant Mg/Ca ratio and stability in the stream sites indicate that the mineralogical signal is subsequently maintained in the surface waters of the catchment during all flow conditions (Fig. 7). We interpret these stable patterns as a result of distinct mineralogical upslope signals integrating the chemical signals of biological and chemical weathering that are not changed through the RZ by ion-exchange reactions. The nominally significant difference that was detected between the RZ and stream Mg/Ca ratios (Table 4) can be attributed to the high statistical power ( $n = 1424$ ) but we suggest that there is no environmental significance because the difference

between the slopes is lower than the analytical error and the true statistical significance is almost certainly less due to lack of independence of measurements.

### 5.3 Uncertainties in the riparian flow-weighted concentration estimations

Sources of uncertainty in catchment studies include measurement errors, representation of processes, and simplifications. The uncertainties in flow measurements and the use of specific discharges in the Krycklan catchment have been reported in previous studies (Ågren et al., 2007; Laudon et al., 2007). With no better estimates available, we consider measured flows from the C7 site to be the best available data to estimate areal-specific discharge and calculate flow-weighted concentrations in our study. This approach has been used previously at the KCS (Ågren et al., 2007; Björkvald et al., 2008; Köhler et al., 2008; Wallin et al., 2010) and elsewhere (Bayley et al., 1992; Landre et al., 2009). A number of assumptions made in this study are worth commenting on:



**Fig. 10.** Comparison of RIM estimated flow-weighted concentrations from riparian sites and corresponding first-order streams and from all riparian sites as average (R-All) and the outlet of the Krycklan catchment (C16) including Ca (a), K (b), and Si (c). R5, R6, and R7 should be compared with C2; R8 with C4; R4 with C6; and R-All with C16. Error bars indicate potential maximum and minimum flow-weighted concentrations in riparian zones using maximum and minimum campaign concentrations. Mg and Na resembled Ca.

1. Use of average campaign concentrations. The temporal stability influenced the decision to calculate flow-weighted concentrations using average campaign concentrations and maximum and minimum as upper and lower potential limits. Scenario SU1 showed that the potential range in flow-weighted concentrations is element-dependent but generally low (Supplement). It should be noted that SU1 presents an extreme scenario and that the real uncertainty is probably lower.
2. Use of  $z_{\text{Gw}}^{\text{mod}}$ . Accurate data on groundwater spatiotemporal dynamics are essential to accurately estimate the transport of solutes from RZ to streams (Lyon et al., 2011). As there were gaps in the available RZ groundwater level measurements, we used modelled values to estimate riparian flow-weighted concentrations. Binned  $z_{\text{Gw}}^{\text{obs}}$  corresponded well with binned specific discharge (Grabs et al., 2012). We thus believe that the model results are a good representation of groundwater levels. Further comparisons of observed and modelled values showed that modelled values generally under-estimated observed groundwater levels, especially in the winter (Fig. 4). However, the sensitivity analysis SU2 revealed little influence of uncertainty in  $z_{\text{Gw}}^{\text{mod}}$  on overall flow-weighted concentrations. It should be noted that different relationships between runoff and groundwater levels from periods with and without soil frost have been reported at another riparian site in the same study area (Laudon et al., 2004). Nevertheless, in some cases, under-estimation of winter groundwater levels could have led to erroneous estimates. For example, site R7 had unusually high flow-weighted concentrations compared to the corresponding stream and the other two nearby riparian sites (Fig. 10). This can be attributed to  $z_{\text{Gw}}^{\text{mod}}$  varying in lower parts of the profile where concentrations were higher. Site R7 was one of the most sensitive to changes in  $z_{\text{Gw}}^{\text{mod}}$  (Fig. 9) and thereby groundwater model under-estimations could have caused over-estimations in flow-weighted concentrations. Moreover, the model fit in this site was worse than in other sites (Fig. 4c).
3. Assumption of no overland flow. Overland flow was not considered because it violates the assumption of matrix flow when fitting lateral flow profiles (Grabs et al., 2012) and because surface runoff has been rarely observed in the area (Bishop et al., 1995). However, the model equation that fitted  $z_{\text{Gw}}^{\text{mod}}$  and specific discharge predicted overland flow in some sites at times of high discharge such as spring flood (Supplement). The proportion of the total lateral flow of those sites as overland flow was estimated from modelled values by assuming constant velocity over the ground equal to the velocity at  $z = 0$  mm (Supplement). The proportion is close to 20 % for the wettest sites R2, R8 and R11. These results could be an artefact of the fitting curve,

but assuming that surface runoff might have indeed occurred and that the chemistry of this water would be different, i.e. “event water” with lower BC concentrations, the flow-weighted concentrations for those sites could have been over-estimated. This could be important when overland flow is “return flow”, but especially when overland flow is generated over frozen soil, as has been suggested for the area surrounding site R8 (Laudon et al., 2007). This hypothesis is also consistent with the stronger dilution effect seen at site C4 (Fig. 8b).

4. Assumption of constant concentration from  $z = -150$  mm to  $z = 0$  mm. Upper layers in the soil profile are believed to be more hydrologically conductive and quantitatively more important for lateral flow generation. Although we presented data from some relatively dry sites, RZ usually are wet areas close to saturation. Here we assumed a constant concentration in the shallowest part of the soil profile equal to the concentration at  $z = -150$  mm. However, the shape of the profile concentrations in some sites suggests a decreasing concentration from 15 cm depth to the surface. For example, site R11 showed a strong decline in concentrations from 30 cm depth to 15 cm depth (Figs. 5 and 6) and this decline may continue to occur from 15 cm depth to the top. Our assumption of constant concentrations could partially explain the high estimates at that or other sites.

The assumptions that we have discussed highlight potential sources of uncertainty in our calculations. As the net fluxes comparisons demonstrate a general over-estimation of RZ flow-weighted concentrations (Fig. 10), we conclude that all above assumptions might have contributed to the overall uncertainty. Fluxes from riparian sites to the streams would be proportional to the flow-weighted concentrations calculated here because of the assumption of specific discharge. Therefore, discussions regarding flow-weighted concentrations can be related to fluxes.

#### 5.4 Linking riparian and stream chemistry

The near-constant Mg/Ca relationship (Fig. 7) clearly demonstrates the connection between RZ and stream water chemistry. Also, the observed BC and Si dilution in the streams during high discharge conditions (Fig. 8) is consistent with the general shape of the concentration profiles (Fig. 5) and the sensitivity analysis of SU2 (Fig. 9): groundwater levels rose during these events and entered the upper layers of RZ soil profiles, which usually have lower element concentrations (Fig. 5). Thus, the flow-weighted concentrations in water leaving the RZ decreased, reducing the concentrations in the stream. SU2 (Fig. 9) indicated that most of the RZ sites would contribute runoff with lower BC concentrations if water levels were higher. Both the dilution from higher RZ groundwater tables and from increasing dis-

charge at the same time in the streams are small. Concentration profiles only vary slightly in RZ and the slope of the concentration-discharge relationship in the streams indicates near-chemostatic behaviour (Godsey et al., 2009) (Fig. 8; Supplement). Vestin et al. (2008) highlighted how stream chemistry (Ca and Si but not K) mirrored upper riparian soil water chemistry during high flow and deeper riparian horizons during baseflow in their catchment in central Sweden. Our results are also in agreement with McLaughlin (2009) who found similar concentrations of Ca and Mg and lower concentrations of K, Na and Si between a stream and two riparian sites in a boreal catchment in Canada.

Estimates of Ca, Mg, and Na flow-weighted concentrations were similar between riparian sites and corresponding headwater streams, even in the mire wetland site C4 (Fig. 10a). This supports RIM conceptual model in which lateral RZ fluxes are the sources of water that control stream chemistry on an annual timescale in catchments where matrix flow predominates (Seibert et al., 2009). This further demonstrates the small direct influence of deposition, i.e. precipitation water, in the catchment and the larger importance of older deeper soil water. Strong influence of biogeochemical cycling could explain why stream and RZ flow-weighted concentrations differed for K and Si. It has been shown that a larger K temporal variation could be linked to temporal vegetation recirculation. Riparian wetlands are potential sinks of amorphous Si (Struyf and Conley, 2009) and retention of amorphous Si has been shown to control the exports of dissolved Si from the RZ to the stream (Struyf et al., 2009) in accordance with our findings at the wetland site R8.

Direct comparisons between higher order stream and RZ sites should be made with caution because of the mixture of waters from different subcatchments. Downstream increases in BC concentrations in the Krycklan catchment have been reported by others (Buffam et al., 2008; Klaminder et al., 2011a). This is in agreement with the higher flow-weighted concentrations in the downstream sites presented here and further supported by higher flow-weighted concentrations estimated for riparian sites located in sedimentary areas. RZ in those areas contribute more BC, but the signal of these soils is attenuated by higher order streams that contain water from the upper parts of the catchment. Longer water residence time, i.e. a larger proportion of deep groundwater, is another mechanism that would allow greater mineral contact and thus higher BC concentrations (Warfvinge and Sverdrup, 1992; Walker et al., 2003).

Si and Na flow-weighted concentrations were both high in the forest streams and the corresponding RZ, notwithstanding the over-estimation in Si flow-weighted concentrations. These higher Na and Si flow-weighted concentrations may reflect higher biological weathering in the fully forest-dominated sites. Flow-weighted concentrations of BC and Si are low in streams draining subcatchments with a higher proportion of wetlands and in the riparian site with more wetland influence (R8).

### 5.5 Representativeness of riparian zones in BC flow-weighted concentrations

Grabs et al. (2012) and Lyon et al. (2011) discussed how distributed representations of RZ are needed in catchment-landscape scale studies to accurately reproduce surface water chemistry, and especially organic carbon, because of the heterogeneity in concentration profiles and groundwater table positions. This differs from previous lumped conceptualizations which were based on a single RZ as representative of an entire catchment (Bishop et al., 2004; Vestin et al., 2008; Seibert et al., 2009). Single transects have been described as non-fully representative for other compounds such as aluminium (Cory et al., 2007). Löfgren et al. (2011) also pointed out the simplicity of lumped representations. They attributed this to uncertainties in water flowpaths and the problem of linking stream water that represents the integration of multiple terrestrial sources to one or few soil water sampling points. All those circumstances are also relevant for BC and Si. However, here we have shown how annual flow-weighted concentrations in headwater RZ represent annual flow-weighted concentrations in corresponding streams and how the flow-weighted concentrations in both large-order streams and corresponding riparian sites follow a similar pattern. The observed mismatches at some sites could be explained by the aforementioned uncertainties in calculations. On the other hand, compounds like organic carbon are affected to a larger extent than BC by heterogeneous factors such as temperature, water content or topography (Köhler et al., 2008; Winterdahl et al., 2011a; Grabs et al., 2012) and might show more variation within RZ. Some other processes such as vegetation recirculation (K) and retention within the RZ (Si) need also to be taken into account. Regarding this, von Schiller et al. (2011) argue that net fluxes comparisons based on a single RZ are problematic for nutrients such as nitrogen because of the potentially large spatial variability and differences between measured groundwater chemistry and the water that actually enters the stream. This could partially explain why the comparisons are less accurate in the case of K and Si in our work.

### 5.6 Potential implications for surface water quality

Increasing runoff following harvesting has been observed in many parts of the world, including Sweden (Sørensen et al., 2009; Futter et al., 2010), Canada (Kreutzweiser et al., 2008), and China (Zhang et al., 2012). The effects include elevation in groundwater levels (Bosch and Hewlett, 1982), which has also been linked to changes in precipitation regimes related to climate change (Hongve et al., 2004). Our results show low sensitivity in BC concentrations in RZ water entering the stream to changes in groundwater levels (Fig. 9), although in general concentrations would be lower, potentially leading to episodic acidification because acid neutralizing capacity (ANC) would decrease. Stream sites with steeper dilu-

tion profiles (Fig. 8b) and RZ that display large concentration changes across the median groundwater level (type site R9 in Figs. 5 and 6) would be more vulnerable.

## 6 Concluding remarks and further investigations

RZ located in soils underlain by sorted fine sediments dominated by silt had higher BC and Si concentrations than RZ located in areas dominated by unsorted till. This difference explained most of the variation in concentrations between RZ. A clear increase in concentrations down the soil profile in most of the riparian sites located in till areas, probably representing water with longer soil/mineral contact time, was observed. Spatial variation in BC and Si flow-weighted concentrations in the streams was explained by differences in landscape element type, with the largest contribution from lower lying silty sediments and the lowest contribution from peat areas higher up in the catchment. The combined results from both RZ and streams indicate that soils dominated by sorted silt are hotspots for BC and Si, whereas wetland areas are limited sources. Landscape element type is a useful predictor of RZ chemistry. This finding supports a conceptual model of the boreal landscape as a mosaic of distinct landscape elements with biogeochemically distinct signatures contributing to surface water chemistry (Köhler et al., 2008; Oni et al., 2013).

We conclude that a characteristic but comparable constant upslope signal that integrates deposition, plant uptake, and weathering is maintained through all RZ and subsequently imported to the stream waters. This is supported by: (1) the temporal stability in the concentrations of BC and Si, (2) the remarkably stable Mg/Ca ratio in riparian soil and stream waters, and (3) the homogeneous mineralogy in the catchment. Future work should investigate upslope conditions to confirm these findings.

The observed chemical dilution effect with flow in the streams was related to variation in groundwater levels and element concentration profiles in the RZ. In headwater streams, RZ flow-weighted concentrations of Ca, Mg and Na resembled those in corresponding streams. Net fluxes were not maintained for K and Si, suggesting a stronger biogeochemical influence on these elements. The suggested mechanisms are vegetation recirculation (K) and retention within the RZ (Si). The high flow-weighted concentrations in RZs located in sedimentary soils were attenuated in higher order streams that contain water from the upper part of the catchment. This indicates that headwaters may be more vulnerable to upslope changes. The importance of headwaters for management strategies has been already reported (Bishop et al., 2008), especially in relation to pH (Ågren and Löfgren, 2012).

BC flow-weighted concentrations from RZ to streams showed low sensitivity to changes in groundwater levels, although rising groundwater levels would tend to reduce the BC flow-weighted concentrations from RZ to streams. This



could lead to potential episodic acidification if groundwater levels are altered by forest harvesting or climate change. The role of BC pools linked to organic matter-rich RZ in buffering acidification could not be investigated with the data presented here. It could be significant and should be studied in the future. This is especially important in the long-term because many studies have predicted depletion in BC pools associated with forest harvesting (Sverdrup et al., 2005; Belyazid et al., 2006; Akselsson et al., 2007).

The vulnerability of boreal catchments to changes induced by forest management or climate changes that create disturbances in biogeochemical reactions and hydrological variability can be addressed in future researches by estimating the RZ buffer capacity, i.e. a comparison of lateral exports to the stores in different, operationally defined pools.

**Supplementary material related to this article is available online at: <http://www.biogeosciences.net/10/3849/2013/bg-10-3849-2013-supplement.pdf>.**

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