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Riparian zone controls on base cation concentrations in boreal streams

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Received: 13 December 2012 – Accepted: 1 January 2013 – Published: 11 January 2013

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

Forest riparian zones are a major in control of surface water quality. Base cation (BC) concentrations, fluxes, and cycling in the riparian zone merit attention because of increasing concern of negative consequences for re-acidification of surface waters from future climate and forest harvesting scenarios. We present a two-year study of BC and silica (Si) flow-weighted concentrations from 13 riparian zones and 14 streams in a boreal catchment in northern Sweden. The Riparian Flow-Concentration Integration Model (RIM) was used to estimate riparian zone flow-weighted concentrations and tested to predict the stream flow-weighted concentrations. Spatial variation in BC and Si concentrations as well as in flow-weighted concentrations was related to differences in Quaternary deposits, with the largest contribution from lower lying silty sediments and the lowest contribution from wetland areas higher up in the catchment. Temporal stability in the concentrations of most elements, a remarkably stable Mg/Ca ratio in the soil water and a homogeneous mineralogy suggest that the stable patterns found in the riparian zones are a result of distinct mineralogical upslope groundwater signals integrating the chemical signals of biological and chemical weathering. Stream water Mg/Ca ratio indicates that the signal is subsequently maintained in the streams. RIM gave good predictions of Ca, Mg, and Na flow-weighted concentrations in headwater streams. The difficulty in modelling K and Si suggests a stronger biogeochemical influence on these elements. The observed chemical dilution effect with flow in the streams was related to variation in groundwater levels and element concentration profiles in the riparian zones. This study provides a first step toward specific investigations of the vulnerability of riparian zones to changes induced by forest management or climate change, with focus on BC or other compounds.

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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 in maintaining good habitat functioning 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 recharge 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). The RZ can act as a buffer (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). The RZ is a source of these and other organic matter related compounds when organic carbon is mobilized during peak runoff events (Bishop et al., 1995; Hinton et al., 1998). The RZ sink-source function was presented as the third paradox in catchment hydrology and biogeochemistry by Burt (2005) following those postulated by Kirchner (2003) and Bishop et al. (2004).

Base cations (BC) include calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na). All except Na are essential plant nutrients. BC are important for maintaining 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 pool associated with soil organic matter and clay minerals creates an important mechanism of interchange between the soil particles and the solution affecting BC biogeochemical cycles.

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. Increased harvesting might, however, have negative consequences on forest productivity

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and surface water quality (Laudon et al., 2011b; Wall, 2012). Several studies have predicted declines in soil BC pools with more intensive biomass removal associated with whole-tree harvesting (Olsson et al., 1993; Akselsson et al., 2007; Klaminder et al., 2011b). BC losses are also connected to climatic variability (McLaughlin, 2009). This BC depletion might become a serious problem in Scandinavian 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 (Bishop et al., 2004).

The “transmissivity feedback mechanism”, which is mainly applicable to glacial till soils (Rodhe, 1989; Bishop, 1991; McDonnell et al., 1998; Bishop et al., 2011), explains how lateral flow movement to the stream increases dramatically as the groundwater table rises and enters via highly conductive superficial soil layers in the RZ. The result is a large mobilization of “old” or “pre-event” water which eventually reaches the stream (Laudon et al., 2004). The integration of lateral flows and RZ solute concentrations to predict in-stream solute concentrations is the base of the Riparian Flow-Concentration Integration Model (RIM, Seibert et al., 2009). The RIM can be applied in principle to any soil, sediment or weathered parent material including forest till soils. The model 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). Given the strong interest in BC forest cycling, studies focussing on BC are important because of the negative consequences of future climate and harvesting scenarios. BC concentrations, fluxes, and cycling in the RZ have not been extensively examined (McLaughlin, 2009) and merit further study.

Here we present a two-year study of flow-weighted concentrations of BC and silica (Si) from RZ and streams in a boreal landscape in northern Sweden. This is the first application of the RIM approach 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 specific objectives

of this study were to: (1) quantify temporal and spatial trends in BC concentrations in different RZ, (2) identify spatial differences in the contribution of BC to streams from different riparian soil types; (3) identify spatial differences in BC flow-weighted concentrations from streams dominated by different Quaternary deposits, and (4) link riparian and stream chemistry.

2 Study area

2.1 Site characterization

The study was conducted in the 69 km² 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 AMSL resulting in a gentle topography within the catchment. Annual daily mean 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 the precipitation falls as snow. The duration of snow cover is 168 days per year on average (commonly from the end of October until the beginning of May) (Laudon et al., 2011a). Average runoff is 321 mm per year (1981–2009), which results in an average evapotranspiration of 319 mm per year. Land use is 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%). Although Krycklan has remained rather pristine, human activities have influenced the catchment to a limited degree similar to other regions in northern Sweden. Many headwater streams in Northern Sweden were straightened and deepened or they are a consequence of ditching occurring during the early 20th century (Dahlström, 2005). These practices were common to improve drainage and

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thereby forest productivity. For example, 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 (Grabs et al., 2012).

Scots pine (*Pinus sylvestris*) makes up 63% of the tree volume and dominate 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 coast line 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 postglacial 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), the characteristics of which are presented in Table 1. Stream water chemistry is monitored at the outlet 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, or riparian observatory

(ROK) was established in Krycklan in 2007 to obtain a better understanding of the RZ influence on stream water. Thirteen instrumented RZ sites were distributed in RZ across Krycklan (Fig. 1). Locations were selected to cover a wide range of wetness conditions and soil types by using terrain analysis of 1 m-resolution airborne light detection and ranging (LiDAR) in conjunction with detailed field reconnaissance (Grabs et al., 2012). Corresponding subcatchments where these instrumented sites are located are presented in Table 1. 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 (15 cm, 30 cm, 45 cm, 60 cm, and 75 cm) and a perforated PVC tube equipped with an automatic water logging device (Grabs et al., 2012). The arrays are about 2 m from the corresponding stream. In August 2008, pits representative of the existing sites were excavated for soil and mineral characterization of the arrays installed the previous year.

3 Study design

3.1 General overview

The study is based on both soil water chemistry from 13 RZ sites and stream chemistry from 14 streams in Krycklan (note that stream C8 was not included as sampling has been terminated). Data from these sites were used for calculation of annual BC and Si flow-weighted concentrations during 2008 and 2009. Mean temperature was 2.9°C in 2008 and 2.1°C in 2009, slightly higher than the long-term mean 1.8°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). Thus, subsequent flow-weighted concentrations calculations were based on annual averages of the two years. Flow-weighted concentrations in the streams were calculated by integration of daily flow and daily interpolated concentrations. The RIM approach (Seibert et al., 2009; Winterdahl et al., 2011a) was used to calculate flow-weighted average

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concentrations from the riparian sites. Daily flow was recorded at site C7 (Fig. 1c) and flow-weighted concentrations were estimated assuming homogeneous specific discharge in the catchment. It should be noticed that actual fluxes would be proportional to the flow-weighted concentrations (or flow-weighted average concentrations) calculated here and thereby the relative differences between sites would be equal.

3.2 Flow measurements

Flow 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% (Laudon et al., 2007). The observed flow at C7 was used to calculate flow-weighted concentrations in both the riparian and the stream sites based on the assumption that 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).

3.3 Soil water measurements and calculation of flow-weighted concentrations

3.3.1 Measurements

Soil water samples were manually collected from suction lysimeters at 13 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 are presented in Table 2. The samples were kept dark and cool prior to being sub-sampled within 24 h and frozen for future chemical analysis. Individual BC concentrations (Ca^{2+} , Mg^{2+} , K^+ , and Na^+) and

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Si were measured using inductively coupled atomic emission spectroscopy (ICP-AES). A campaign concentration value for each element, site, and depth was assumed 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, for example, 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 described by Grabs et al. (2012). That gave a total of 448 campaign concentration values, i.e. 86 % of the total 520 possible concentrations.

3.3.2 Calculation of flow-weighted concentrations

Flow-weighted concentrations were calculated by integration of lateral water fluxes and continuous profiles of solute concentrations using the RIM approach (Seibert et al., 2009). 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 (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 in Scandinavia (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.

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

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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 every mm were calculated 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_{flow} , mg L^{-1}) for each element and site was then calculated by integrating the product of flow-weights and average soil water concentrations (C_{avg} , mg L^{-1}) over the saturated part of the soil profile, i.e. the conductive layers below the groundwater level (Eq. 3). Modelled groundwater tables ($z_{\text{GW}}^{\text{mod}}$) (Fig. 3) were back-calculated with Eq. (1) using daily measurements of flow and used to calculate daily loads 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 average 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. 3), i.e. overland flow was discarded in accordance with Grabs et al. (2012). Annual flow-weighted average concentrations were subsequently calculated by dividing total annual flow-concentrations by the total annual flow-weights. Overall flow-weighted concentrations in the period 2008–2009 were then calculated as the mean value of

annual flow-weighted average concentrations.

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

3.3.3 Sensitivity and uncertainty analyses

Given the temporal stability in BC and Si concentrations in the ROK sites (detailed results are presented further below), average campaign concentration profiles were used to calculate annual flow-weighted average concentrations. Nevertheless, 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 ± 1.96 standard deviations of the modelled estimates with respect to the observations at each site.

3.4 Stream water measurements and calculation of flow-weighted concentrations

In total, 52 water samples were collected from each of the 14 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. Bottles were kept dark and cool prior to chemical analysis. 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

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volume of water discharged and expressed in mg L^{-1} , i.e. the result only depended on the concentration and the relative differences in daily flow. The observed flow at site C7 in L s^{-1} was used to perform the calculations for all the sites. Overall flow-weighted concentrations for 2008–2009 were then calculated as the mean value for the 2 yr.

3.5 Statistical analyses

Analysis of variance (ANOVA) and *t*-test were used to evaluate differences in BC concentrations between campaigns in the riparian sites. The significance level was set to $p < 0.01$. 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 Quaternary deposit proportions in the corresponding subcatchments (Table 1) as predictors. In a PLS model $R^2 Y$ 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 BC concentration profiles in the ROK

4.1.1 Spatial variation

Riparian sites were classified 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) (Figs. 4 and 5). This will be referred to as site class in the following. Accounting for all riparian sites and depths, means and standard

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5 deviations of campaign concentrations showed that Ca was the dominant BC in the soil solution ($4.0 \pm 3.1 \text{ mgL}^{-1}$), followed by Na ($2.2 \pm 0.8 \text{ mgL}^{-1}$), Mg ($1.3 \pm 1.0 \text{ mgL}^{-1}$) and K ($0.9 \pm 0.8 \text{ mgL}^{-1}$). Si had the highest concentrations of all of the elements analysed ($8.3 \pm 2.9 \text{ mgL}^{-1}$). For Ca, wet till sites had spatially stable concentrations although the absolute mean values differed from $0.8 \pm 0.2 \text{ mgL}^{-1}$ in R8 to $4.0 \pm 0.5 \text{ mgL}^{-1}$ in R2 (Fig. 4). Both 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 wetland classified as a mire (C4) (Fig. 1c). Dry and humid till sites had higher concentrations deeper in the profile (Fig. 4). Combined Ca concentrations for all sites belonging to these two classes varied from $1.9 \pm 0.7 \text{ mgL}^{-1}$ at 15 cm depth to $3.9 \pm 1.1 \text{ mgL}^{-1}$ at 75 cm depth. Sites located in the sedimentary area showed no clear pattern. While site R15 presented a vertical profile with intermediate concentrations ($2.3 \pm 0.4 \text{ mgL}^{-1}$), sites R11 and R14 were BC hotspots with average Ca concentrations of $11.8 \pm 1.7 \text{ mgL}^{-1}$ ($14.2 \pm 1.7 \text{ mgL}^{-1}$ at 30 cm) and $7.8 \pm 0.9 \text{ mgL}^{-1}$ respectively. The BC concentrations in these silty-sediment sites were significantly higher than in the rest of the sites (Fig. 4). This general picture presented for Ca was observed for the other elements, which was indicated by high correlations with Ca: Na ($R^2 = 0.73$; $p < 0.0001$), K ($R^2 = 0.72$; $p < 0.0001$), Si ($R^2 = 0.67$; $p < 0.0001$), and especially Mg ($R^2 = 0.96$; $p < 0.0001$; Fig. 6). However, near-surface (15 cm depth) K concentrations were relatively high at several sites (R6, R7, R10 and R12 in Fig. 5). Campaign concentrations for all elements and sites can be found in the Supplement.

4.1.2 Temporal variation

25 The temporal variations in Ca and K concentrations are represented as the differences between minimum and maximum campaign concentrations at each depth (Figs. 4 and 5). Including all depths and sites, the mean of the standard deviations for Ca (11 %), Mg (8 %), Na (8 %), and Si (7 %) were within or close to the analytical measurement error (SLU, 2012). No statistical differences between campaigns were observed for any of these elements. In contrast, the temporal variation of K was higher in all sites,

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except in R11 and R14, and the mean standard deviation for all depths and sites was 33%. The campaign concentrations of K in August 2008 were significantly higher than the concentrations in June of the same year ($p < 0.01$).

4.2 The Mg/Ca ratio in relation to mineralogy

5 The Mg/Ca ratios for all samples from the RZ soil solution were similar to Mg/Ca ratios from the stream water samples, all of which were remarkably stable (Fig. 6). However, statistical differences were detected between the Mg/Ca ratio in the RZ and the ratio in the streams (Table 3). Riparian site R9 deviated strongly from the general relationship. The overall mean Mg/Ca ratio for all riparian soil water samples was 0.35 ± 0.10 ,
10 whereas the Mg/Ca ratio for site R9 was significantly higher ($Mg/Ca = 0.63 \pm 0.34$). The mineralogy was rather homogeneous among sites with the exception of site R9 (Table 4), as showed by the analyses of the samples taken during August 2008 to characterize the ROK (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
15 in comparison to the other sites (Table 4).

4.3 Stream BC concentrations

BC and Si concentrations in the stream sites were negatively correlated to specific discharge ($p < 0.01$), except for K (Fig. 7a–c; Supplement). In general, correlations to flow were stronger for Na and Si than for Mg and Ca. The Krycklan outlet had high
20 correlations for all elements including K ($p < 0.0001$) (Fig. 7d). The dilution was small in forest subcatchments (Fig. 7a) whereas a stronger dilution effect was noticeable in wetland dominated sites (Fig. 7b).

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4.4 Riparian and stream BC flow-weighted concentrations

4.4.1 Flow-weighted concentrations in riparian sites 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, i.e. scenario SU1, are presented in the Supplement. Not surprisingly, sites R11 and R14 had the highest 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. 8; Supplement). In general, rising groundwater tables would decrease the 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_{Gw}^{mod} varies. For example, site R9, the most sensitive, had significantly lower concentrations

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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. 4 and 5). 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 relied on 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. 4 and 5). For most of the cases, the variation in $z_{\text{GW}}^{\text{mod}}$ did not change the flow-weighted concentrations more than 15 %.

4.4.2 Flow-weighted concentrations in stream sites and PLS analysis

All BC flow-weighted concentrations increased downstream in the catchment, especially in the sites located in the sedimentary area 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 Quaternary deposit proportions in the corresponding subcatchments (Table 1) as predictors in a PLS analysis. Quaternary deposits 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 ($\text{VIP} > 1$) 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 mass balances are maintained; test the applicability of RIM; and gain insights into RZ behaviour. In our case, that is C4 and R8; C2 and R5, R6, and R7; and C6 and R4 (Fig. 9). Headwater streams receive by definition 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. 9). Ca, Mg and Na matched well, however, some discrepancies were observed for K. For example, the estimates of K were too high in site R5 compared to site C2 and too low in site R8 compared to site C4 (Fig. 9b). For Si, flow-weighted concentrations were noticeably lower in the streams (Fig. 9c). Site R7 showed higher flow-weighted concentrations for all elements than the corresponding stream C2 and the other riparian sites in the subcatchment. In general, higher flow-weighted concentrations throughout the sedimentary area towards the outlet corresponded with higher RZ flow-weighted concentrations downstream in the catchment (Supplement). For example, sites R11 and R14 which are representative of the sedimentary area had significantly higher flow-weighted concentrations than the other riparian sites. 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 (see for example site R7 and R12). An average value of the flow-weighted concentrations from all the riparian sites fitted to the outlet of the catchment (site C16) similarly to the RZ and stream in the headwaters (Fig. 9).

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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 sites, especially those belonging to the same site class (Figs. 4 and 5). 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 indicates a source limitation, i.e. lower mineral content at this site. Higher concentrations of K, Na, and SiO₂ were observed in a forest RZ compared with a wetland RZ by McLaughlin (2009), although there Ca and Mg were similar between the two types. Site R11 and site R14, which are located in the sedimentary part of the catchment, showed the highest concentrations. 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 larger mineral contact (Warfvinge and Sverdrup, 1992; Ågren et al., 2007). The PLS analysis confirmed the importance of soil characteristics as controls of BC and Si abundance. In contrast, site R15, also located in the sediment area of the catchment, had concentrations which were similar to those found in 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.

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5.1.2 Temporal variation

The general temporal stability of BC and Si concentrations at each depth and site is remarkable. K presented more variation in concentration which led to larger variation in flow-weighted concentrations. No statistically significant differences were detected between campaigns for any element except in one case for K. High K concentrations in the beginning of August 2008, especially at 15 and 30 cm depth, could have been caused by release of K from decaying plant matter at the end of the growing season. 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. Potential reasons for the temporal stability of BC concentrations are: (1) the buffering of cation concentrations within the riparian soils or (2) a characteristic but comparable constant upslope signal that integrates deposition, plant uptake, and weathering at each site. This is discussed below.

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, which is further demonstrated by the high correlation between all the elements studied here. The Mg/Ca ratio was temporally and spatially stable in all riparian sites and depths, with the exception of site R9. The fact that this site also had a different mineralogy indicates that the riparian soil solution is strongly imprinted by an upslope mineralogical signal. Specifically, the higher content of Mg-rich chlorite can explain the higher Mg concentration at site R9 (Table 4). Weathering rate estimates in the area vary widely (Klaminder et al., 2011b). The Mg/Ca ratio in the soil solution presented here is similar to the Mg/Ca ratio from the weathering rates presented by Olsson and Melkerud (2000) (Mg/Ca = 0.39) but it

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is different from the estimates presented by Van der Salm et al. (1999) ($Mg/Ca = 0.78$). The rates are dependent on the depth considered (Klaminder et al., 2011b) and within-site differences may reach up to several hundred per cent depending on the method used (Futter et al., 2012), so an attempt to characterize soil solution chemistry from weathering estimates is difficult. 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 ratio and stability in the stream sites indicate that the signal is subsequently maintained in the surface waters of the catchment (Fig. 6). The statistically significant difference that was detected between the RZ and stream Mg/Ca ratios (Table 3) can be attributed to the high statistical power ($n < 1424$) but there is probably no environmental significance because the difference between the slopes is lower than the analytical error. The same test was performed using Mg and Ca flow-weighted concentrations in both riparian and stream sites ($n < 27$, data not shown). In this case Ca was the only parameter that significantly predicted Mg ($R^2 = 0.98$; $p < 0.0001$) with no differences between stream and riparian sites. All above findings support that the stable RZ patterns are a result of distinct mineralogical upslope signals integrating the chemical erosion signals of biological and chemical weathering.

5.3 Uncertainties in the riparian flow-weighted concentration estimations

Sources of uncertainty in catchment studies and in the use of models include measurement errors, representation of processes, and model simplifications. The uncertainties in flow measurements and the use of specific discharges in the area have been reported in previous studies (Ågren et al., 2007; Laudon et al., 2007). Recently, Lyon et al. (2012) presented a larger variability in specific discharge between subcatchments in Krycklan than previously documented. With no better estimates available, we consider measured flows from the C7 site are the best available data to estimate specific

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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). A number of assumptions made in this study are worth commenting on:

- (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 depends on the element but it is generally quite low (Supplement). It should be noted that this is 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. 3). However, the sensitivity analysis SU2 revealed little influence of the uncertainty in $z_{\text{GW}}^{\text{mod}}$ on the 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 presented at another riparian site in the same study area (Laudon et al., 2004). Nevertheless, for some cases, the 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. 9). This can be attributed to $z_{\text{GW}}^{\text{mod}}$ varying in lower parts of the

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profile where concentrations were higher. Site R7 was one of the most sensitive to changes in $z_{\text{GW}}^{\text{mod}}$ (Fig. 8) 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. 3c).

(3) Assumption of no overland flow. Overland flow was not considered because it violates the assumption of matrix flow when fitting 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 it has been suggested in the area surrounding site R8 (Laudon et al., 2007). This hypothesis is also consistent with the stronger dilution effect seen at site C4 (Fig. 7b).

(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. Therefore it is important to have good estimates of the chemistry in these upper conductive layers when calculating flow-weighted concentrations with RIM. 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

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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. 4 and 5) 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 mass balances comparisons demonstrate a general over-estimation of RZ flow-weighted concentrations (Fig. 9), 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 Mg/Ca relationship (Fig. 6) clearly demonstrates the connection between RZ soil water chemistry and stream water chemistry. Also, the observed BC and Si dilution in the streams during high discharge conditions (Fig. 7) is consistent with the general shape of the concentration profiles (Fig. 4) and the sensitivity analysis of SU2 (Fig. 8): groundwater levels rose during these events and entered the upper layers of the RZ soil profiles which usually have lower element concentrations (Fig. 4). Thus, the flow-weighted concentrations in water leaving the RZ decreased, reducing the concentrations in the stream. SU2 (Fig. 8) 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 discharge at the same time in the streams are small because concentration profiles only vary slightly in RZ and because the slope of the concentration-discharge relationship in the streams indicates near-chemostatic behaviour (Godsey et al., 2009) (Fig. 7; 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. Löfgren et al. (2010) also presented concentrations of Ca and Mg in RZ close to the stream levels in another catchment in 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 SiO₂ between a stream and two riparian sites in a boreal catchment in Canada. Importantly however, we compare flow-weighted concentrations for mass balance calculations rather than the previous studies that compared concentrations.

Estimates of Ca, Mg, and Na flow-weighted concentrations were similar between the riparian sites and the corresponding headwater streams, even in the mire wetland site C4 (Fig. 9a). This supports the first conceptualization of the RIM, by which lateral RZ fluxes are the sources of water that control the chemistry in the stream on an annual time scale 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. This approach may not be valid for those elements which are strongly influenced by temporal variable biological cycles, i.e. K or Si. Riparian wetlands are potential sinks of amorphous Si (Struyf and Conley, 2009) and retention of amorphous silica has been described to control the exports of dissolved silica 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 done with caution because of the mixture of waters from different subcatchments. Downstream increases in BC concentrations in the Krycklan catchment has been reported by others (Buffam et al., 2008; Klaminder et al., 2011a), which is in agreement with the larger flow-weighted concentrations in the downstream sites presented here. This is also supported by the larger flow-weighted concentrations estimated in the riparian sites located in the sedimentary area. RZ in those areas contribute with more BC, but the signal of these soils is attenuated by large order streams that contain water from the upper part of the catchment. Longer water residence time, i.e. larger proportion of deep

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groundwater, is another mechanism that would allow greater mineral contact and thus larger BC concentrations (Walker et al., 2003; Klaminder et al., 2011a). 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 was a new view in comparison to 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 flow-paths and the problem of linking stream water that represents the integration of multiple terrestrial sources to one or few single points. All those circumstances are important for BC and Si also. However, we have shown how long-term flow-weighted concentration estimates in headwater RZ represent 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 and might explain each other. The observed mismatches at some sites could be explained by the aforementioned uncertainties in the calculations. This might be true for catchments with a homogeneous mineralogy, which we believe was the driver at our site. This is different from compounds like organic carbon which shows larger variation and is influenced by more

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heterogeneous factors such as temperature, water content or topography (Winterdahl et al., 2011a; Grabs et al., 2012). 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 mass balance calculations based on a single RZ and streams are problematic for nutrients such as nitrogen because of the potentially large spatial variability and the difference between the measured groundwater chemistry and the water that actually enters the stream. This could explain why the comparisons are less accurate in the case of K and Si in our work.

5.6 Implications for surface water quality and further investigations

Potential implications for BC fluxes after increased harvesting can be related to transient changes in hydrology and to longer lasting effects of BC removal. Increasing runoff following harvesting has been observed in many distant parts of the world including Sweden (Sørensen et al., 2009; Futter et al., 2010) and China (Zhang et al., 2012). The effects include higher concentrations of DOC in surface waters from elevation of groundwater tables that reach organic matter rich layers before entering a stream (Schelker et al., 2012). Higher groundwater levels after harvesting (Bosch and Hewlett, 1982) would imply lower BC concentrations in RZ water entering the stream according to our results (Fig. 8), potentially leading to episodic acidification. The change that we have shown here is small but stream sites with steeper dilution profiles (Fig. 7b) and RZ that display large concentration changes across the median groundwater level (type site R9 in Figs. 4 and 5) would be more vulnerable.

The expected depletion in BC pools from forest harvesting (Olsson et al., 1993; Sverdrup et al., 2005; Belyazid et al., 2006; Akselsson et al., 2007; Klaminder et al., 2011b) and the effects of climate change are potentially more long-lasting. The fact that some of the streams in the area were created artificially by ditching adds more unknown effects on the water quality (Åström et al., 2001). 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

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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-discuss.net/10/739/2013/>

[bgd-10-739-2013-supplement.pdf](#)

Acknowledgement. This study is part of the Krycklan catchment study which is funded by VR, Formas (ForWater), Mistra (Future Forest), SKB and the Kempe Foundation. MNF was funded by the Mistra Future Forests programme.

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Table 1. Stream subcatchment characteristics including land use (columns 6 to 9) and Quaternary deposit (columns 10 to 17 and 8) proportions and corresponding riparian zone sites.

Site	Name	Stream order	Riparian sites	Area (km ²)	Forest (%)	Wetland (%)	Lake (%)	Arable (%)	Peat (%)	Till (%)	Silt (%)	Sand (%)	Alluvial (%)	Gravel (%)	Bedrock (%)	Thin soils (%)
C1	Risbäcken	2	R12	0.48	98	2	0	0	0	92.1	0	0	0	0	0	7.9
C2	Västrabäcken	1	R5,6,7	0.12	100	0	0	0	0	84.2	0	0	0	0	0	15.7
C3	Lillmyrbäcken	1		0.04	59.1	40.4	0	0.4	53.2	43.2	0	3.7	0	0	0	0
C4	Kalkällsmyren	1	R8	0.18	55.9	44.1	0	0	51.1	22	0	0	0	0	0	27
C5	Storjärnen Outlet	1		0.65	54	39.6	6.4	0	47.8	40.4	0	0	0	0	0	5.5
C6	Storjärnbäcken	1	R4	1.10	71.4	24.8	3.8	0	28.7	53.7	0	0	0	0	2.5	11.3
C7	Kalkällsbäcken	2	R9,10	0.47	82	18	0	0	19.4	65.2	0	0	0	0	0	15.4
C8	Fulbäcken	2	R1 R2	2.30	88.1	11.9	0	0	17	62.8	0	0	0	0	1.7	18.6
C9	Nyängesbäcken	3		2.88	84.4	14.1	1.5	0	15.2	69.1	4.1	0	0	1.6	1.7	6.8
C10	Stormyrbäcken	2	R11	3.36	73.9	26.1	0	0	28.8	59.9	0	0.5	0	0	0	10.8
C12	Nymyrbäcken	3		5.44	82.6	17.4	0	0	19.2	66.6	1.5	4.3	0	0	0	8.4
C13	Långbäcken	3	R15	7.00	88.2	10.3	0.7	0.8	11.8	60.9	15.9	0	0	0.7	1.3	8.9
C14	Åhedbäcken	3	R14	14.10	90.2	5.4	0.7	3.7	6.6	44.9	34.7	0	3.4	0	1.6	8.1
C15	Övre Krycklan	4		20.13	81.6	14.5	2.4	1.5	14.5	64.8	1.8	0	7.6	0	0.7	8.1
C16	Krycklan	4		68.91	87.3	8.7	0.9	3.1	9.4	50.8	26.6	0.3	3.3	0.1	1.2	7.4

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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 ⁻¹)	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

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Table 3. 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

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Table 4. 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

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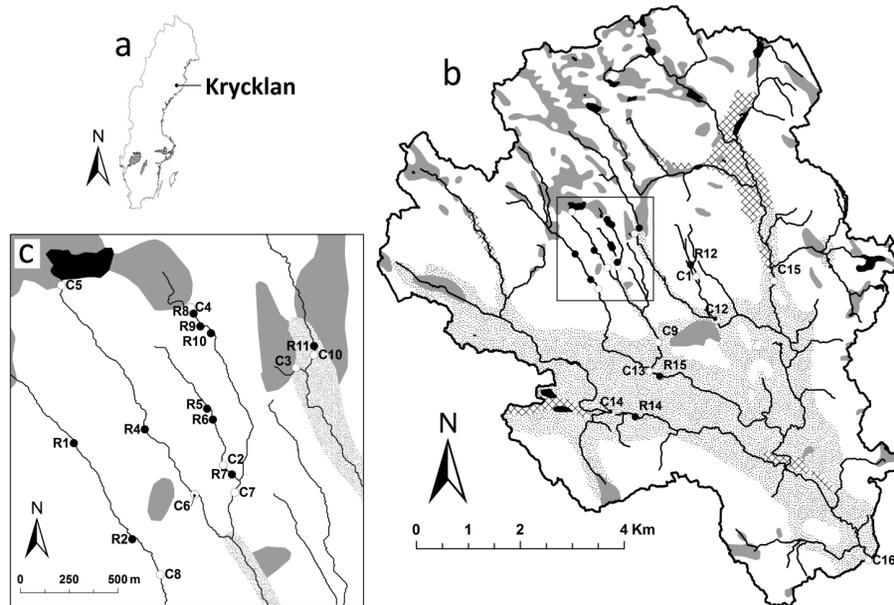


Fig. 1. Location of the Krycklan catchment within Sweden (a). In (b): shape of the Krycklan catchment with streams (black lines), lakes (black areas), peat (grey areas), till, thin soils and bedrock (white areas), silt- sandy sediments and gravel (dotted areas), glacio-fluvial alluvium (cross-hatched 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.

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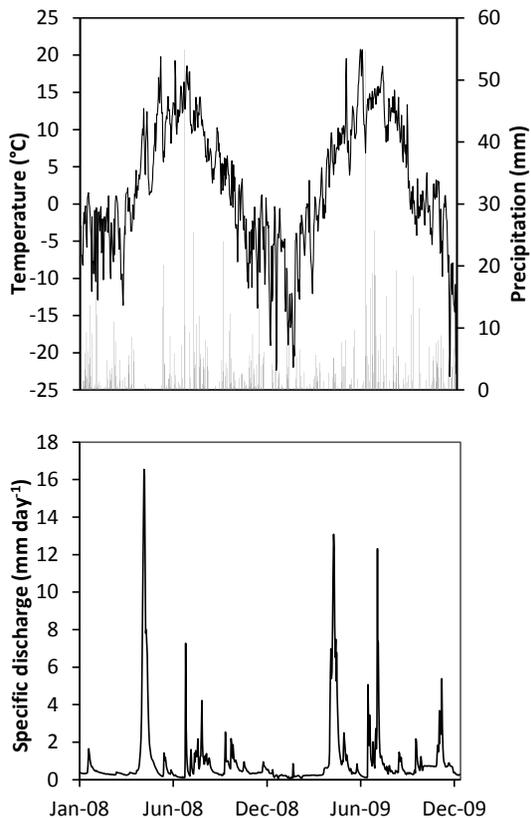


Fig. 2. Daily temperature and precipitation measured at the Krycklan catchment (above) and areal-specific discharge measured at site C7 (below) during 2008 and 2009.

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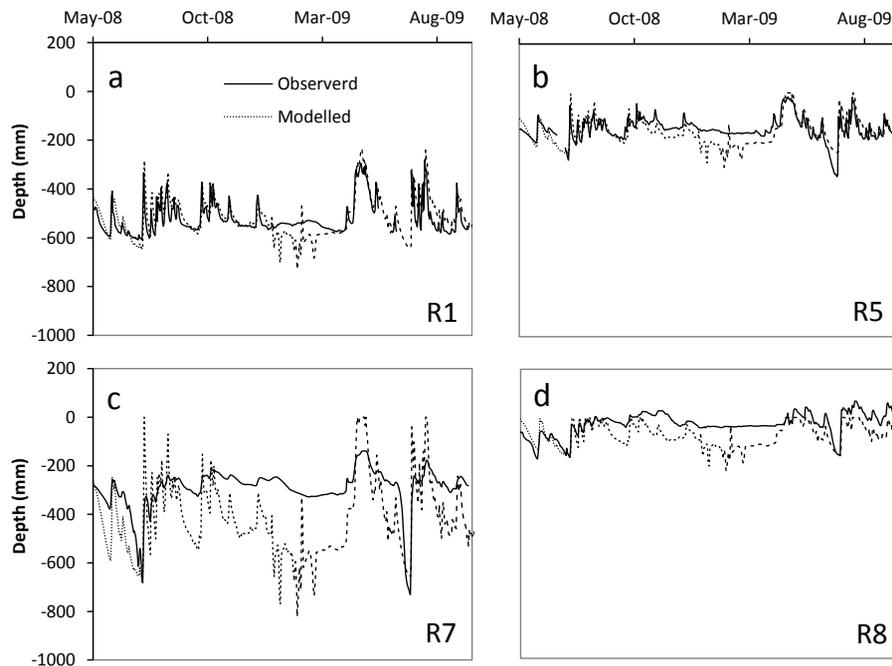


Fig. 3. Comparison of observed and modelled groundwater tables for the period with overlapping data (May 2008 to September 2009) at some selected riparian sites including R1 (a), R5 (b), R7 (c), and R8 (d).

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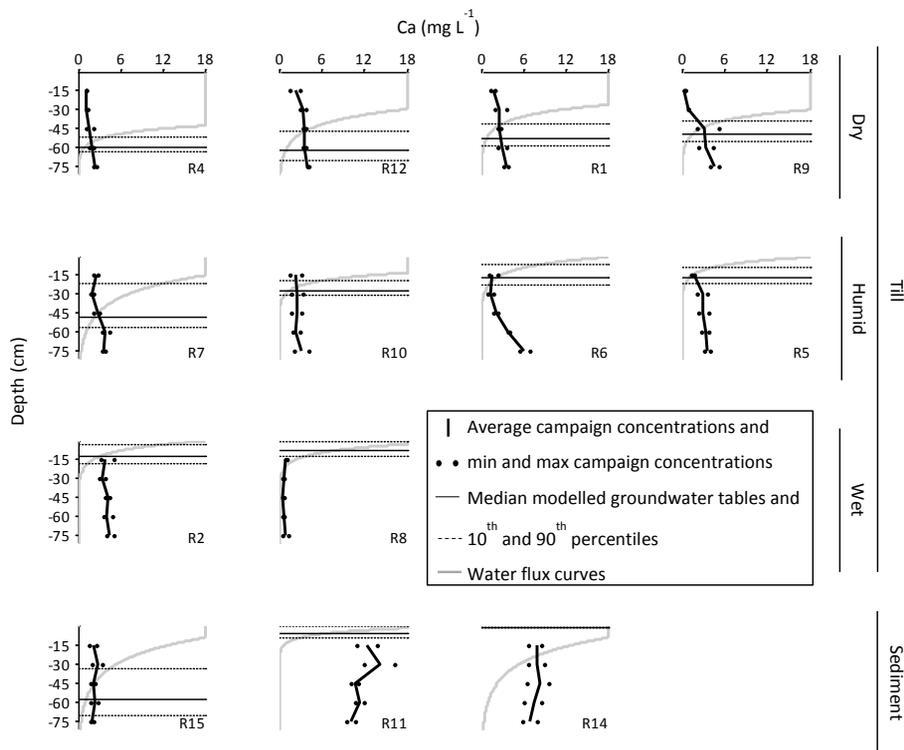


Fig. 4. Interpolated average campaign concentration profiles of Ca for the 13 riparian sites in Krycklan (vertical black lines). Concentrations measured at 8 occasions during 2008 and 2009. Plots also include minimum and maximum campaign concentrations (black circles), median modelled groundwater tables (horizontal black lines), 10th and 90th percentiles of groundwater table positions (horizontal dotted lines), and water flux curves (light grey lines).

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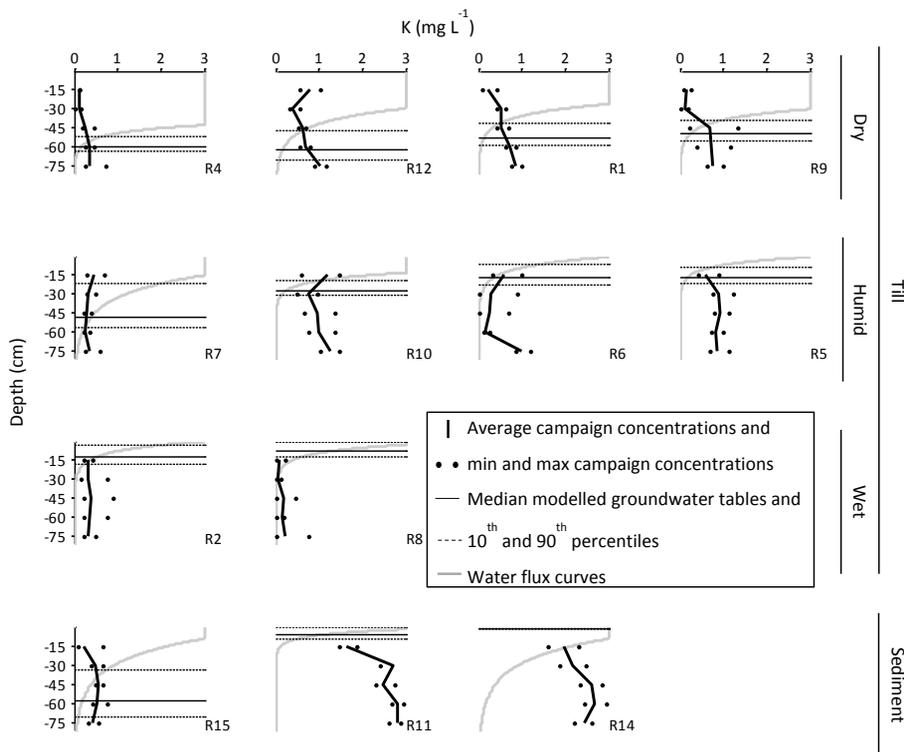


Fig. 5. Interpolated average campaign concentration profiles of K for the 13 riparian sites in Krycklan (vertical black lines). Concentrations measured at 8 occasions during 2008 and 2009. Plots also include minimum and maximum campaign concentrations (black circles), median modelled groundwater tables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

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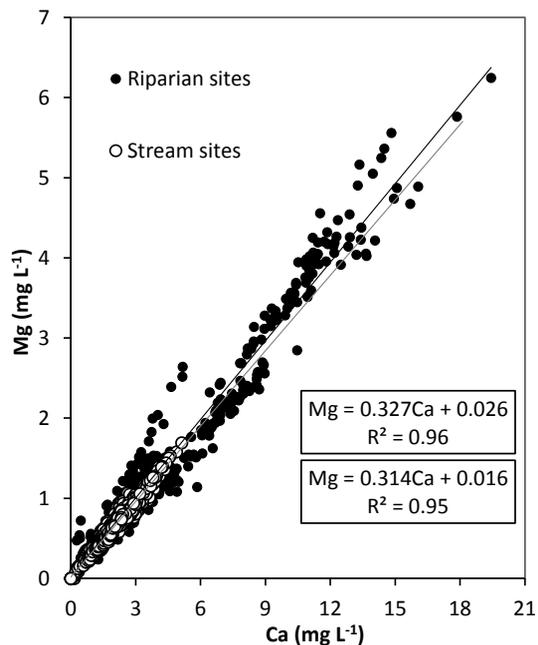


Fig. 6. Relationship between Mg and Ca in all riparian soil water samples ($N = 702$) and all stream water samples ($N = 722$) and equations describing them (above equation: riparian samples; below equation: stream samples).

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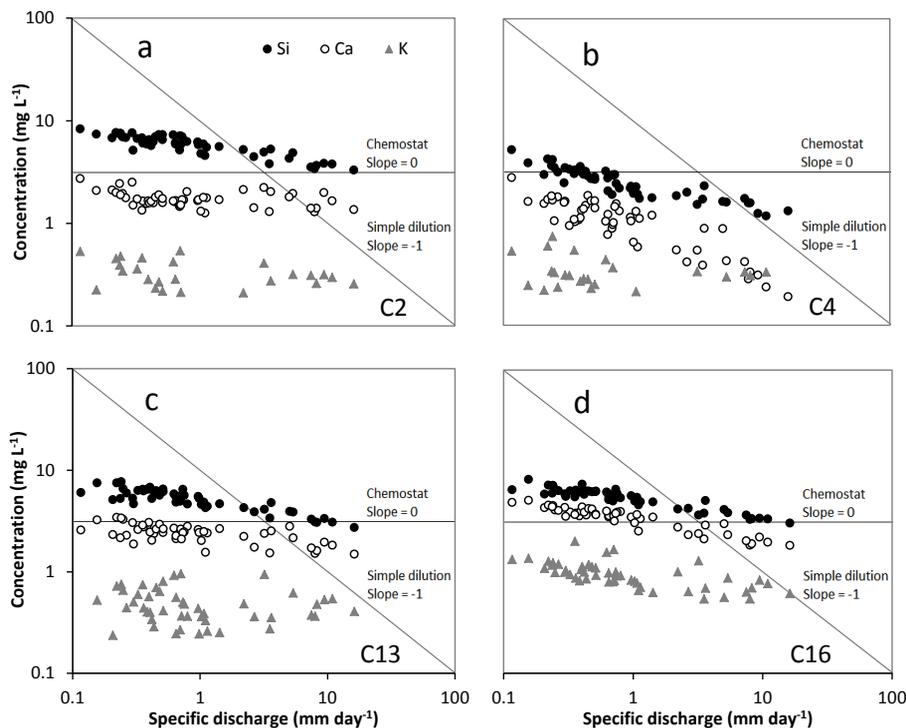


Fig. 7. Concentration-discharge relationships for Ca, K, and Si at some selected stream sites during 2008 and 2009 including C2 (typical forest catchment) (a), C4 (typical wetland catchment) (b), C13 (outlet of the upper part of the catchment) (c), and C16 (outlet of the catchment) (d). Mg resembled Ca and Na resembled Si.

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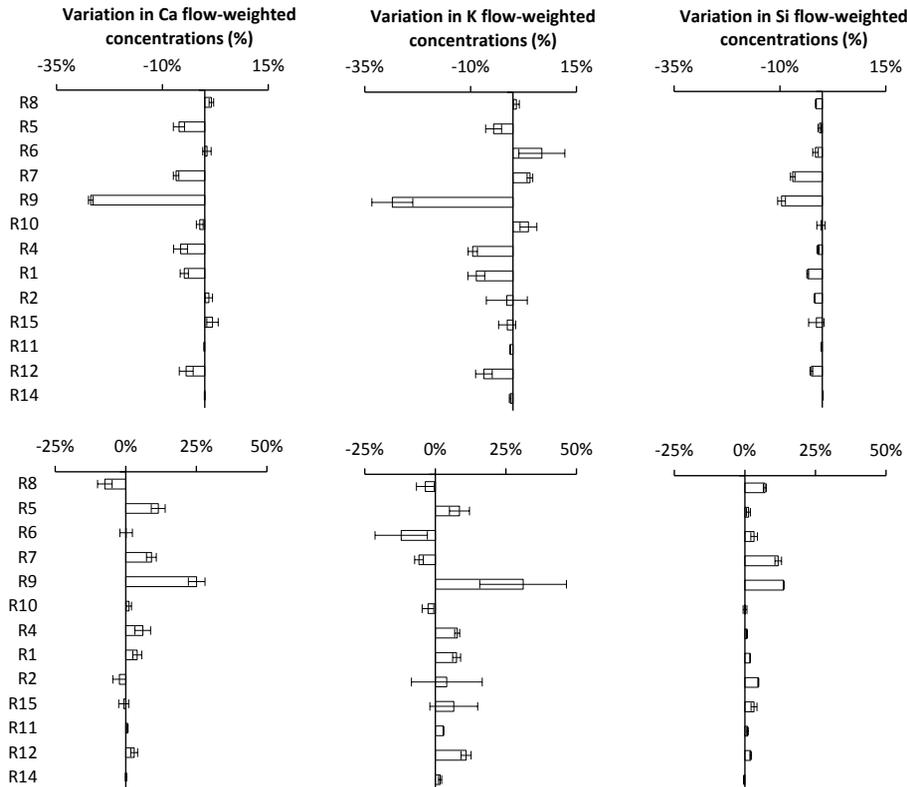


Fig. 8. Scenario SU2. Mean variation in maximum, average and minimum flow-weighted concentration for Ca, K, and Si for each riparian site after varying modelled groundwater tables $+1.96$ standard deviations of the modelled estimates with respect to the observations at each site (above) and -1.96 standard deviations (below). Error bars represent standard deviations. Mg resembled Ca and Na resembled Si.

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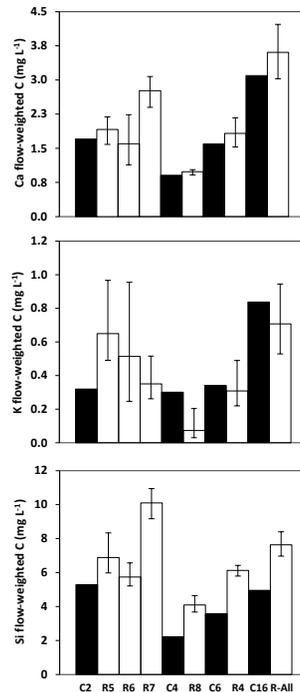


Fig. 9. Comparison of RIM estimated flow-weighted concentrations from riparian sites and corresponding first order streams and from all riparian sites (R-All) as average and the outlet of the Krycklan catchment including Ca (a), K (b), and Si (c). R5, R6, and R7 should be compared with C2; R8 with C4; 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.

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