Boreal forest riparian zones regulate stream sulfate and dissolved organic carbon

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HIGHLIGHTS

- Sulfate is still an important driver of DOC in boreal catchments.
- Riparian zone processes control stream sulfate and DOC independently of up-slope.
- Usefulness of riparian data as a means to predict stream chemistry is time-scale dependent.

GRAPHICAL ABSTRACT
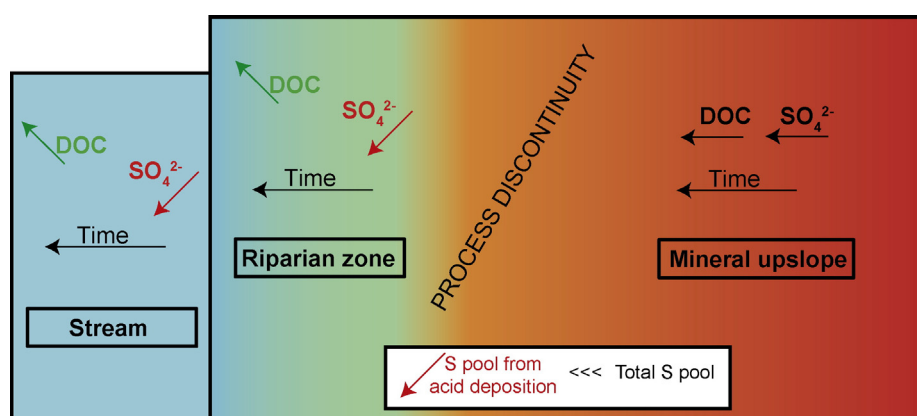
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ABSTRACT

In boreal forest catchments, solute transfer to streams is controlled by hydrological and biogeochemical processes occurring in the riparian zone (RZ). However, RZs are spatially heterogeneous and information about solute chemistry is typically limited. This is problematic when making inferences about stream chemistry. Hypothetically, the strength of links between riparian and stream chemistry is time-scale dependent. Using a ten-year (2003−2012) dataset from a northern Swedish catchment, we evaluated the suitability of RZ data to infer stream dynamics at different time scales. We focus on the role of the RZ versus upslope soils in controlling sulfate (SO_4^{2-}) and dissolved organic carbon (DOC). A priori, declines in acid deposition and redox-mediated SO_4^{2-} pulses control sulfur (S) fluxes and pool dynamics, which in turn affect dissolved organic carbon (DOC). We found that the catchment is currently a net source of S, presumably due to release of the S pool accumulated during the acidification period. In both, RZ and stream, SO_4^{2-} concentrations are declining over time, whereas DOC is increasing. No temporal trends in SO_4^{2-} and DOC were observed in upslope mineral soils. SO_4^{2-} explained the variation of DOC in stream and RZ, but not in upslope mineral soil. Moreover, as SO_4^{2-} decreased with time, temporal variability of DOC increased. These observations indicate that: (1) SO_4^{2-} is still an important driver of DOC trends in boreal catchments and (2) RZ processes control stream SO_4^{2-} and subsequently DOC independently of upslope soils. These phenomena are likely

Abbreviations: RZ, riparian zone.
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occurring in many regions recovering from acidification. Because water flows through a heterogeneous mosaic of RZs before entering the stream, upscaling information from limited RZ data to the catchment level is problematic at short-time scales. However, for long-term trends and annual dynamics, the same data can provide reasonable representations of riparian processes and support meaningful inferences about stream chemistry.

1. Introduction

In boreal forest catchments, the transfer of solutes to streams is predominantly controlled by hydrological and biogeochemical processes occurring in the near-stream riparian zone (RZ) (Gregory et al., 1991; McClain et al., 2003; Bishop et al., 2004), linking terrestrial and aquatic systems. RZs influence catchment dynamics of multiple compounds including organic carbon (Fiebig et al., 1990; Dosskey and Bertsch, 1994; Köhler et al., 2009), nitrogen (Fölster, 2000; Petrone et al., 2007), metals (Bishop et al., 1995; Pellerin et al., 2002), and persistent organic pollutants (Bergknut et al., 2011). However, information on RZ chemistry is generally limited and inferences about stream water chemistry are potentially ambiguous at different time scales because RZs are spatially heterogeneous (Ledesma et al., 2015). Hypothetically, any change in hydrological conditions, notably drought-rewetting cycles, will alter riparian groundwater table levels and transient redox conditions, influencing riparian and, subsequently, stream concentration and fluxes of redox-sensitive compounds (Lidman et al., 2011), including sulfate (SO_4^{2-}) (Devito and Hill, 1997).

Anthropogenic sulfur dioxide (SO_2) emissions and consequent SO_4^{2-} deposition triggered the acidification of terrestrial and aquatic ecosystems in much of Europe and North America (Mylona, 1996; Driscoll et al., 2001; Schöpp et al., 2003). Measures undertaken to reduce emissions in the 1980s effectively decreased SO_4^{2-} deposition and led to acidification recovery in many forest catchments (Fölster and Wilander, 2002; Watmough et al., 2005). Recovery has been slow in some areas (Driscoll et al., 2003; Evans et al., 2014; Futter et al., 2014) in part because the sulfur (S) legacy in the soil, predominantly accumulated in organic S pools (Wieder and Lang, 1988; Houle and Carignan, 1992; Giesler et al., 2005), can be oxidized to SO_4^{2-} and mobilized into surface waters after drought events (Aherne et al., 2008). Redox-mediated SO_4^{2-} pulses have been observed in many forest catchments (Laudon et al., 2004a; Eimers et al., 2008; Laudon, 2008; Vestin et al., 2008; Landre et al., 2009; Kerr et al., 2012) as well as in other ecosystems such as blanket bogs (Clark et al., 2005). However, it is not clear how long such pulses will continue as S pools are depleted in those areas and climate changes. Increased drought frequency is projected for the boreal region (Schlyter et al., 2006; Walker and Johnstone, 2014), potentially leading to an increased severity of redox-driven S acid pulses in the short-term, but also to a more rapid depletion of S pools and thus faster recovery in the medium-term.

In addition to its dominant role as a control on stream acidity in areas affected by anthropogenic acid deposition, S cycling is coupled to dissolved organic carbon (DOC) solubility (Clark et al., 2006; Evans et al., 2012). The decline in SO_4^{2-} deposition is one of the most important drivers of recent increasing DOC trends in European and North American surface waters (Evans et al., 2006; De Wit et al., 2007; Monteith et al., 2007; Erlandsson et al., 2008). Thus, SO_4^{2-} has a fundamental influence on a range of key surface water quality variables, especially in regions historically affected by anthropogenic acidification.

Here, we used ten-year climate, stream flow and chemistry, soil solution chemistry including riparian and upslope profiles in a hillslope transect, groundwater levels, and deposition data from a northern Swedish forest catchment. We aimed to test the suitability of hydrochemical data from a single riparian soil profile to infer stream dynamics at different time scales. We hypothesized that the strength of links between riparian data and stream chemistry is time-scale dependent. For this, we focus on SO_4^{2-} and its connection to DOC. The

specific objectives of the study were: (1) to quantify a long-term boreal forest catchment S mass balance, (2) to investigate the role of the RZ vs. upslope soils in controlling catchment S biogeochemistry, (3) to examine the role of riparian groundwater fluctuations in the mobilization of SO_4^{2-}, and (4) to explore the connection between SO_4^{2-} and DOC over both short-term (episodic, seasonal) and long-term (ten-year) time scales.

2. Material and methods

2.1. Catchment characterization

Västrabäcken, known as C2 (64° 15′ N 19° 46′ E), is a 12 ha, 100% old forest catchment located in Northern Sweden, within the Krycklan Catchment Study (Fig. 1) (Laudon et al., 2013). Mean annual air temperature is 1.9 °C and mean annual precipitation 632 mm year^{-1} (1981–2013). Annual water outputs are divided approximately evenly between runoff and evapotranspiration (Köhler et al., 2008; Oni et al., 2013). The 4–6 week period of spring flood contributes between 40% and 60% of the total annual runoff. Nearly 100% of the tree volume is comprised of two species: Scots pine (*Pinus sylvestris*), found primarily on dry upslope podzols, and Norway spruce (*Picea abies*), common in wet low-lying areas near the stream channel. RZs are largely Histosols covered by *Sphagnum* spp. mosses, though *Vaccinium* spp. are present throughout the catchment. The gneiss bedrock is overlain by several meters of locally-derived Quaternary deposits of glacial till. The stream was straightened and deepened in the 1930s following common practices in Fennoscandia to improve drainage for forest production.

During autumn 1995, a hillslope transect monitoring site was installed near the catchment outlet to provide data across an upslope-riparian continuum (Köhler et al., 2009). This is the so-called S-transect (note that S in this case does not stand for sulfur). It consists of three soil profiles located at 4 (S4), 12 (S12), and 22 (S22) meters from the stream following the local topographic slope and thereby the likely dominant hydrological flowpaths (Fig. 1). The profiles were selected to represent, respectively, riparian peats, transitional soils, and upslope podzols within the catchment. Each profile includes six to seven ceramic suction lysimeters placed at soil depths varying between 5-10 cm and 65–90 cm (Fig. 1). Approximately 15% of the catchment, partially including the S-transect, is located below the highest postglacial coastline, which is around 250–260 m above sea level. Hence, pyrite (FeS_2) is likely present in the mineralogy of the soil C-horizon. However, inorganic S colloids have never been detected in the catchment (Skyllberg et al., 2003) possibly because the influence of deep groundwater at the study catchment is low (Peralta-Tapia et al., 2015). Most of the S stored in the RZ is found in the form of reduced organic S, with lower proportions of sulfonate and SO_4^{2-} (Skyllberg et al., 2003). The isotopic signature of S is denoted by deviations from the standard ratio of ^{32}S to ^{34}S measured in a meteorite collected in California and expressed as $\delta^{34}S$ (in ‰ units). In stream samples in the catchment (including high and low flow conditions), $\delta^{34}S$ is $+6‰$ to $+8‰$ (Björkvald et al., 2009), indicating negligible S contributions from weathering as the typical $\delta^{34}S$ values of S-rich bedrock in the region range from $+0.3$ to $+0.6‰$ (Klaminder et al., 2011). Since 2005, the catchment has likely been a net source of S (Björkvald et al., 2009).

Here, we studied the ten-year period 2003–2012, that is from the time when regular monitoring started in the study area until the latest
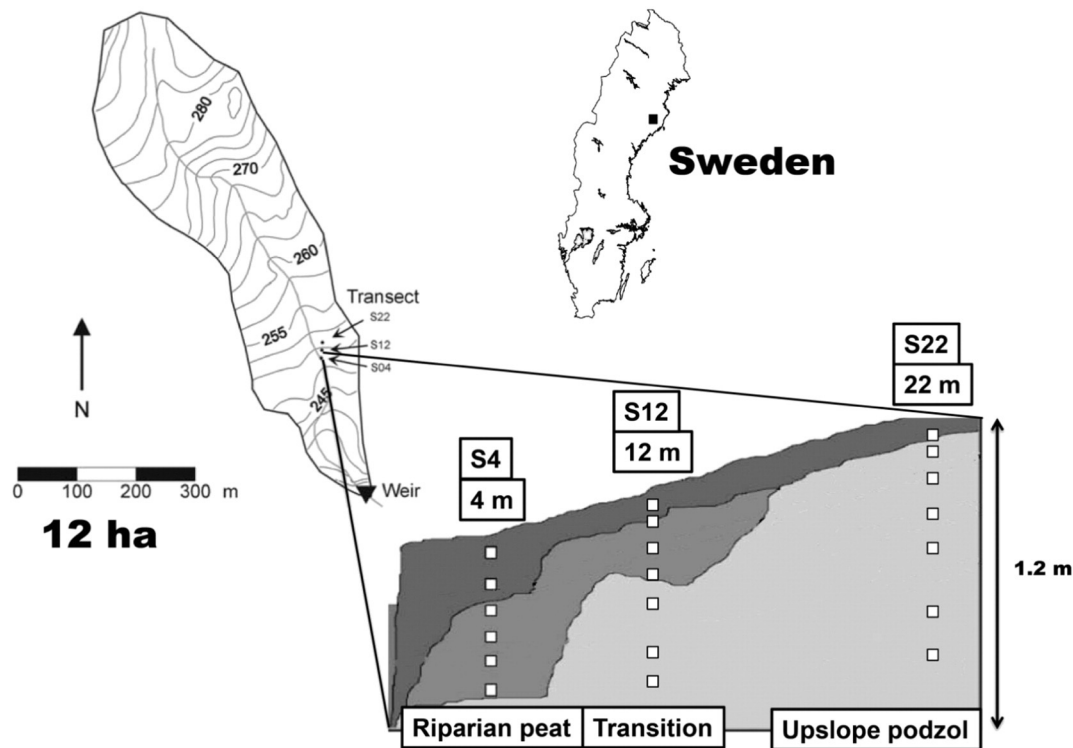
Fig. 1. Map of the study site including location within Sweden (black square), shape of the catchment with location of the soil transect and weir for discharge measurement (inverse black triangle), and profile representation of the studied hillslope. White squares represent position of the suction lysimeters within the soil profiles (10, 25, 35, 45, 55, and 65 cm in S4; 5, 10, 20, 30, 40, 60, and 70 cm in S12; 6, 12, 20, 35, 50, 75, and 90 cm in S22). Dark grey, grey, and light grey areas represent organic, semi-organic, and mineral soils respectively. The Fig. is an adaptation of those used by Laudon et al. (2004b) and Köhler et al. (2009).

available data (Laudon et al., 2013). SO_4^{2-} concentrations and fluxes will be expressed as the mass of S per unit volume (concentrations) or per unit of area and time (fluxes) and referred to as sulfate sulfur (S-SO_4^{2-}).

2.2. Data sources

Long-term (1981 to present) climate data, including daily air temperature and precipitation, were available as part of a reference monitoring program at the Vindeln Experimental Forest (Laudon et al., 2013). The meteorological station is located, approximately at the same elevation, 1 km southwest from the S-transect. Stream water discharge at the outlet of C2 was measured using a pressure transducer connected to a Campbell Scientific data logger that records hourly water heights in a 90° V-notch in the stream. An established stage-discharge rating curve was used to calculate daily stream flow values from the daily average water levels monitored by the logger. Due to missing discharge records, data from a 50 m downstream location, known as C7 (Laudon et al., 2013), with a similar specific discharge ($R^2 = 0.93$, $p < 0.0001$) was used to hindcast stream flow back to 2003 in C2. This calculated flow was used in the whole study period (2003–2012) in order to have an internally consistent time series.

Sampling of stream water began in 1986 and was then integrated into the regular monitoring program of the Krycklan Catchment Study in 2003 (Laudon et al., 2013). A total of 262 stream S-SO_4^{2-} measurements were available for the period 2003–2012. Soil water sampling from the lysimeters in the S-transect began in 1996. Measurements of S-SO4²⁻ were made on a regular basis, approximately monthly with higher frequency during spring flood, from 2003 in S4 and from 2004 in S12 and S22. Corresponding total S and DOC measurements were available for almost all stream and soil solution samples. Soil water was manually collected from the lysimeters using acid-washed Milli-Q rinsed Duran glass bottles. Total S was measured using inductively

coupled atomic emission spectroscopy (ICP-AES) and SO_4^{2-} was measured by liquid chromatography of ions. DOC was measured as total organic carbon (TOC) by a Shimadzu TOC-5000 using catalytic combustion. In both stream (Ågren et al., 2007) and soil water (Ledesma et al., 2015) samples from the catchment, DOC and TOC are effectively equivalent so the term DOC is used here. Detailed information about sampling procedures and chemical analyses can be found elsewhere (Cory et al., 2007; Björkvald et al., 2009; Köhler et al., 2009; Winterdahl et al. 2011; Laudon et al., 2013).

During the installation of the S-transect, solid soil samples were collected from each depth where a suction lysimeter was placed for future chemical characterization of these soil layers. Carbon content in the samples was measured by combustion and presented by Nyberg et al. (2001). Recently, part of the remaining store of these samples was analyzed for total S content using an ECS 4010 Elemental Combustion System (Costech International S.p.A). Soil S pools were estimated for each profile in the S-transect as to represent riparian, transitional, and upslope pools. Carbon content was used to calculate bulk density using the logarithmic relationship presented by Ledesma et al. (2015) for these two variables from samples throughout Krycklan. The product of bulk density and S content was integrated over a one meter profile in order to roughly estimate area-specific S pools at the three profiles. Considering stoniness can be important when estimating element pools in soils (Stendahl et al., 2009). Nevertheless, stoniness in the three soil profiles is small and was discarded following previous studies in the S-transect (Nyberg et al., 2001).

Groundwater levels from wells close to the lysimeters at S4, S12, and S22 were recorded hourly using data loggers (WT-HR 64 K) during June 2013 to October 2014. Hourly records were averaged to daily values for the period of observation. The total number of daily records was 348, 345, and 360 (S4, S12, and S22, respectively) because device failure precluded a full time series for the observation period (Fig. 2).
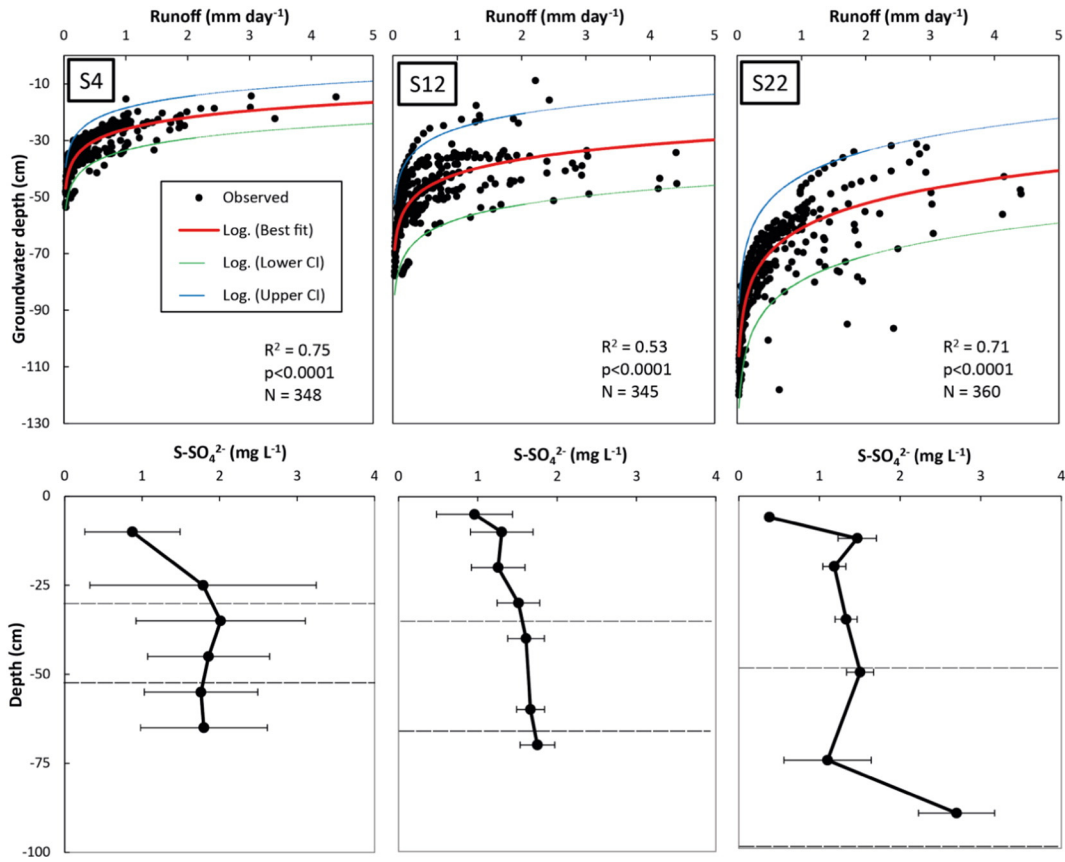
Fig. 2. Relationship between stream specific discharge and groundwater levels (three upper panels) at each of the three soil profiles studied (S4, S12, and S22). Best and lower and upper confidence interval fits (from a logarithmic function) are also displayed. Sulfate sulfur ($S\text{-}SO_4^{2-}$) concentration profiles in the corresponding soil profiles are shown in the three lower panels. Circles represent average concentrations at each layer and horizontal lines are standard deviations for the period 2003–2012. Dotted horizontal lines are 2.5th and 97.5th percentiles of groundwater table positions using lower confidence interval fit (S4) and best fits (S12 and S22), and represent the soil section with highest contribute to solute and water fluxes (or dominant source layer).

Modelled S deposition data for 1880–2020 were available from the European Monitoring and Evaluation Programme (EMEP). We used forest annual S deposition estimates from the 50 × 50 km grid cell where the catchment is located (Zetterberg et al., 2014). Open field measured S deposition from the catchment was available for the period 1985–2007. The linear relationship between EMEP and measured S deposition ($R^2 = 0.88$ for the overlapping period, Fig. A1) was used to generate a full time series of data for 1880–2020 (Fig. 3), i.e. the EMEP values used here were offset with measured data.

2.3. Calculations and statistics

Due to the characteristic exponential decrease in hydraulic conductivity with depth in boreal forest soils (Nyberg, 1995), flowpaths hydrologically connected to the streams are predominantly restricted to a 'dominant source layer' (DSL) (Ledesma et al., 2015). Here, we use the riparian flow-concentration integration model (RIM) approach (Bishop et al., 2004; Seibert et al., 2009; Grabs et al., 2012; Ledesma et al., 2013) to estimate lateral $S\text{-}SO_4^{2-}$ fluxes at the three S-transect soil profiles. The approach is analogous to the way in which riverine fluxes are estimated (Ledesma et al., 2013) and it has been widely implemented in previous studies for similar purposes including estimation of lateral fluxes in upslope soils (e.g. Cory et al., 2007; Köhler et al., 2009; Öquist et al., 2009). A detailed description of the method with equations can be found in the above-mentioned references. Here we present a brief description.

Daily groundwater tables at each profile were related to stream specific discharge using logarithmic functions (Fig. 2). Using the regression equation of these relations and applying Darcy's law (Seibert et al., 2009), it is possible to estimate lateral flows within soil layers for any given stream discharge. This means that for any given stream discharge, lateral flows at any given soil layer are proportional to the stream discharge-groundwater table curve. Subsequently, $S\text{-}SO_4^{2-}$ concentrations at the S-transect profiles were linearly interpolated in space, vertically from 0 to 2 m depth, and in time, from 2003 to 2012, in order to
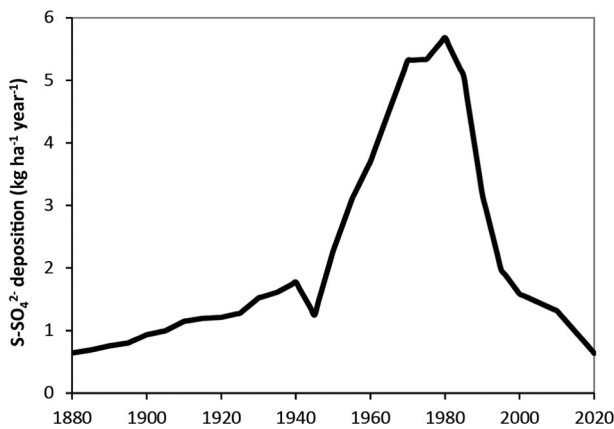

Fig. 3. Atmospheric sulfate sulfur ($S\text{-}SO_4^{2-}$) deposition time series (1880–2020) in the study area from the European Monitoring and Evaluation Program (EMEP) corrected with open field measured data.

generate daily concentration profile time series. For S12 and S22, which measurements started in 2004, concentrations were assumed constant from the first available measurement back to 2003. This is a sensible assumption because concentrations in these two profiles were temporally stable in the dominant source layer, especially if compared with concentrations at S4 (Fig. 2). The concentration profiles were then multiplied by the lateral flow profiles to estimate lateral S-SO$_4^{2-}$ fluxes at S4, S12, and S22. This integration is made below the estimated groundwater table because it is assumed that horizontal water flux occurs in the direction of the hydraulic gradient from higher to lower altitudes following Darcy's law only in saturated layers (Seibert et al., 2009). From the equations describing the groundwater table-discharge relation it was possible to calculate daily groundwater tables at each profile for the study period, as stream discharge data were complete. Thus, fluxes and flow-weighted concentrations can be trivially estimated at different time resolutions using the constructed daily lateral discharge and daily chemical concentration profiles. The upper and lower 95% confidence intervals of the groundwater table-discharge regressions (Fig. 2) were also used to calculate potential upper and lower lateral flows and to provide an estimate of uncertainty in lateral S-SO$_4^{2-}$ flow-weighted concentrations and fluxes. At the riparian site S4, the lower confidence interval is presented as the best estimate of the groundwater table-discharge relationship because old measurements from a contiguous well are systematically ca. 15 cm lower (Winterdahl et al. 2011) suggesting that the actual groundwater table position at the lysimeters is likely deeper. Moreover, the relationship between riparian and stream chemistry was more consistent using deeper estimates of groundwater levels.

We evaluated the significance of annual trends in S-SO$_4^{2-}$ and DOC concentrations and Theil's slopes for the period 2003–2012 (or 2004–2012 for S12 and S22) using seasonal Mann–Kendall tests (Mann, 1945). This non-parametric test has been proven robust in evaluating temporal trends in water quality-related parameters (Prechtel et al.,

2001; Evans et al., 2005; Lepistö et al., 2008; Oni et al., 2013). Monthly averages of S-SO$_4^{2-}$ and DOC concentrations from stream and all soil water lysimeters as well as annual deposition were used in the analyses. Simple linear regression models were used to investigate the importance of hydroclimatic variables including precipitation and groundwater tables in controlling stream and riparian S-SO$_4^{2-}$ concentrations. Multiple linear regressions were used to predict monthly S-SO$_4^{2-}$ flow-weighted concentrations in the stream. Power functions were used to fit regression curves between DOC (dependent variable) and S-SO$_4^{2-}$ (independent variable) concentrations for stream samples and for the individual lysimeter samples (Table 1).

3. Results and discussion

3.1. Long-term S mass balance

Comparison between total S and S-SO$_4^{2-}$ concentrations for all stream and soil water samples in the study period showed that about 95% of all S mobilized and transported in the catchment was in the form of SO$_4^{2-}$ (Fig. A2). Hence, all fluxes presented here based on S-SO$_4^{2-}$ measurements can be approximated to total S. The total S mass in soil samples varied between 0.01% and 0.36%, with higher values in organic horizons and lower values in mineral layers, consistent with the expectation that S in forest catchments tend to accumulate in organic pools (Wieder and Lang, 1988; Houle and Carignan, 1992; Giesler et al., 2005). As a consequence, the area-specific S pool within the first meter of soil in the RZ was 25% higher than in the transitional soil and nearly double than in the upslope podzol (Fig. 4). The greater bulk density of mineral soils did not compensate for the significantly lower elemental S content. Roughly, RZs cover 10% of the total catchment area, transitional soils 20%, and podzols 70% (Bishop et al., 1995; Laudon et al., 2004b), so there is a total area-specific S pool of ca. 3000 kg ha^{-1} in the first meter of soil across the entire catchment.

Table 1

Summary of sulfate sulfur (S-SO$_4^{2-}$) and dissolved organic carbon (DOC) concentration trends (2003–2012), including Theil's slope and significance level from seasonal Mann–Kendall analyses, in deposition, stream, riparian (S4), transitional (S12), and upslope (S22) waters (columns 6 to 9). Note that the number of samples indicated in those refers to monthly averages. The coefficient of determination (R^2) of the relationship (as a power function) between DOC (dependent variable) and S-SO$_4^{2-}$ (independent variable) for the stream water and soil water at every lysimeter (column 5) together with the number of samples with both compounds measured (column 4) are also indicated. The percentage of time that a lysimeter depth was below the groundwater table is indicated in column 3 as a saturation percentile.

Location	Depth (cm)	Saturation percentile (%)	DOC-S-SO$_4^{2-}$ samples (n)	DOC-S-SO$_4^{2-}$ R^2	S-SO$_4^{2-}$ Samples (n monthly)	S-SO$_4^{2-}$ Theil's slope (mg L^{-1} yr^{-1})	DOC Samples (n monthly)	DOC Theil's slope (mg L^{-1} yr^{-1})
Deposition	–	–	–	–	10	−0.01[***]	–	–
Stream	–	–	253	0.40[***]	103	−0.13[**]	107	0.70[**]
S4	10	0.0	29	N·S.	38	N·S.	41	N·S.
S4	25	2.3	63	N.S.	69	−0.28[**]	56	−3.96[**]
S4	35	23	54	0.73[***]	59	−0.27[**]	57	2.78[**]
S4	45	72	66	0.77[***]	70	−0.22[***]	58	2.22[**]
S4	55	99	70	0.74[***]	76	−0.22[**]	60	1.96[**]
S4	65	100	67	0.80[***]	72	−0.23[**]	59	2.21[**]
S12	5	0.0	20	0.37[**]	32	N.S.	20	N.S.
S12	10	0.0	25	0.23[*]	35	N.S.	26	N.S.
S12	20	0.0	12	0.45[*]	16	N.S.	17	N.S.
S12	30	1.7	48	0.37[***]	55	−0.08[**]	43	0.38
S12	40	13	46	0.31[***]	55	−0.08[**]	42	0.30[*]
S12	60	84	44	0.34[***]	52	−0.07[**]	39	0.31[*]
S12	70	99	47	0.44[***]	55	−0.08[**]	42	0.25[**]
S22	6	0.0	1	N.S.	1	N.S.	1	N.S.
S22	12	0.0	43	0.66[***]	47	N.S.	42	N.S.
S22	20	0.0	30	0.19[*]	38	N.S.	36	N.S.
S22	35	0.4	21	N.S	24	N.S.	28	N.S.
S22	50	5.6	45	N.S	54	N.S.	40	N.S.
S22	75	46	27	0.78[***]	34	N.S.	32	N.S.
S22	90	80	44	N.S	47	N.S.	41	0.20[***]

– not applicable

N.S. non-significant

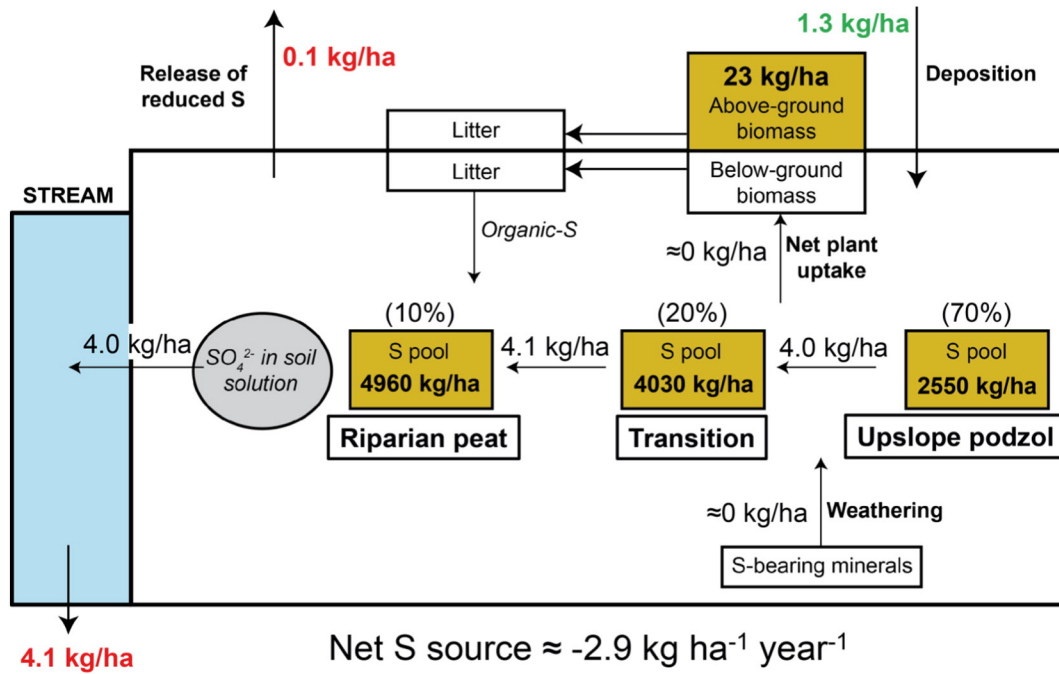[*] $p < 0.05$

[**] $p < 0.01$

[***] $p < 0.001$

Fig. 4. Mass balance of sulfur (S) for the study catchment for the ten-year period 2003–2012. All flux values (expressed as kg/ha) are based on annual averages and therefore no interannual variability or trends are considered. The release of reduced S gases is an upper limit estimation based on data presented by Åkerblom et al. (2013). The S pool estimate in the above ground biomass is based on data from Albrektson and Lundmark (1991). The net plant S uptake in an old forest such as the one in the study catchment is negligible, however the immobilization need in a growing forest could be as much as 0.4 kg ha^{-1} year^{-1} (Albrektson and Lundmark, 1991). Inputs from weathering from S-bearing minerals are neglected. The approximate fraction that each represented soil (riparian peat, transition, and upslope podzol) occupies in the catchment is presented within brackets.

There are two potential original sources of this S: atmospheric deposition and weathering. There is no evidence of weathering inputs from S-bearing minerals because inorganic S colloids have never been detected (Skyllberg et al., 2003) and the range in isotopic stream S measurements are far from typical values for pyrite and other S-bearing minerals (Björkvald et al., 2009; Klaminder et al., 2011). During the period of peak S-deposition (1950–2000), an estimated 200 kg S ha^{-1} were deposited from the atmosphere (Fig. 3), a small amount compared to the total accumulated since the last glaciation. Assuming a constant deposition equal to the 1880 value (Fig. 3) from the end of the glacial period (around 6000 years ago) to the year 1880, the total S-input from the atmosphere has been ca. 4000 kg S ha^{-1}. Thus, taking into account today's pools, if no other sources are considered and the initial pool was exiguous, roughly 75% of the atmospheric S-inputs have been retained since the last glaciation.

Based on measured output fluxes for 2003–2012, the catchment is currently a net S source of 2.9 kg S ha^{-1} year^{-1} (Fig. 4). This is consistent with a large number of studies from North American and European forest catchments affected by anthropogenic acidification (Prechtel et al., 2001; Mörth et al., 2005; Mitchell and Likens, 2011). Mitchell et al. (2001) suggested that the current imbalance between atmospheric deposition and S-SO$_4^{2-}$ fluxes could be explained by net mineralization of organic S in combination with weathering. The majority of studies suggest that S mineralization is the dominant contributor to the current imbalance, likely caused by remnant S from the period of peak acid deposition (Mörth et al., 2005). Given the absence of known S weathering sources at Krycklan, we therefore attribute all of the observed losses to net mineralization, i.e. oxidation of organic S pools. According to an experiment using coniferous forest soils (Houle et al., 2001), however, only 1% of the total organic S pool is active, i.e. participates in the redox S cycle. Therefore, even if small compared with the total pools, the anthropogenic inputs during the acid deposition period could have been high enough to disrupt this 'active S pool'. The approximate decline in S pools during the studied period was 0.1% year^{-1}

(Fig. 4). Thus, whilst depletion of the total S may have been marginal, the active S pool might have been significantly affected.

3.2. Riparian versus upslope controls on stream SO$_4^{2-}$: long-term trends and inter- and intra-annual dynamics

The seasonal Mann–Kendall test showed significant negative trends for S-SO$_4^{2-}$ concentrations (2003–2012) in atmospheric deposition, stream water, and most soil layers in the RZ and transitional soil (Table 1). All depths in S4 and S12 that intermittently experienced saturated conditions and therefore belong to the dominant source layer, i.e. the soil section that contributes the most to the lateral fluxes, had significant downward trends (Table 1). Those are the most hydrologically connected layers and therefore the most important ones for regulating stream water chemistry. The magnitude of the annual decrease in S-SO$_4^{2-}$ was higher in the RZ (>0.20 mg L^{-1} year^{-1}, equating to a >80% decrease) than in the transitional soil (around 0.08 mg L^{-1} year^{-1} or about 40% decrease), and intermediate in the stream (0.13 mg L^{-1} year^{-1}, a 65% decrease). Annual S-SO$_4^{2-}$ concentrations in atmospheric deposition were approximately one order of magnitude smaller than in the RZ and decreased 0.01 mg L^{-1} year^{-1}, from 0.25 mg L^{-1} to 0.14 mg L^{-1} (i.e. a 45% decrease). No significant S-SO$_4^{2-}$ trends were found in the upslope profile.

Uncertainties in annual flow-weighted concentrations and fluxes derived from the groundwater table-discharge regression were low, with coefficients of variation of 10% in S4, 8% in S12, and 18% in S22 (Table A1). Mean annual S-SO$_4^{2-}$ fluxes (2003–2012) were roughly equal in stream, RZ, transition, and upslope, i.e. around 4.0 kg S ha^{-1} year^{-1} (Fig. 4). If only the long-term mass balance was taken into account, the RZ would appear to be a passive conduit of SO$_4^{2-}$. However, comparisons between annual flow-weighted concentrations and fluxes in the three soil profiles and in the stream revealed strong correlations between the stream and the riparian site, whereas this correlation became weaker in the transitional
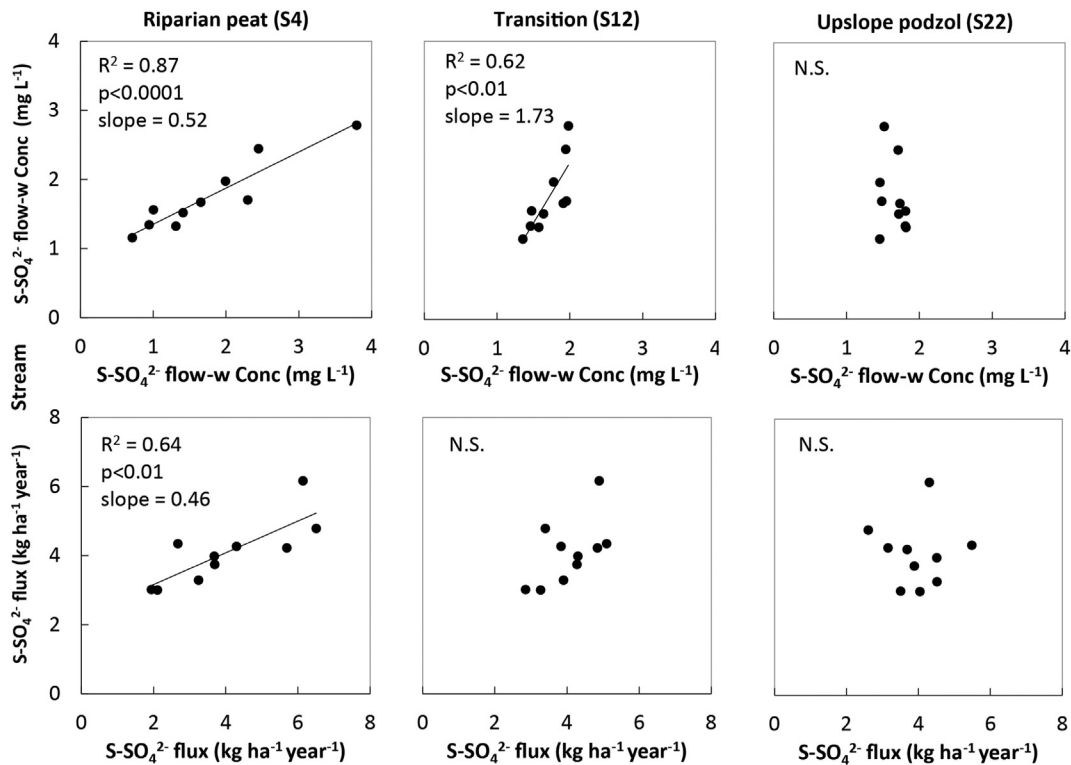
Fig. 5. Relationships between sulfate sulfur (S-SO$_4^{2-}$) annual flow-weighted concentrations (denoted as flow-w Conc) and fluxes in the stream and S-SO$_4^{2-}$ annual flow-weighted concentrations and fluxes in the three soil profiles (S4, S12, and S22).

site, and non- significant in the upslope site (Fig. 5). The strong correlation between stream and riparian S-SO$_4^{2-}$ flow-weighted concentrations and fluxes is an indication of similar annual dynamics. This demonstrates the utility of RZ data to infer stream dynamics at this time scale. The combination of long-term negative trends in both riparian and stream S-SO$_4^{2-}$, and the correlation in annual flow-weighted concentration and flux dynamics, together with the lack of trend and correlation with the upslope soil, provides evidence of RZ regulation of stream long-term and annual SO$_4^{2-}$ dynamics. The mineralization of S-bearing organic material by specialized bacteria is likely the main mechanism of SO$_4^{2-}$ mobilization in the RZ (Strickland and Fitzgerald, 1987; Houle et al., 2001), as suggested by the stream isotope signature in this and other catchments (Mörth et al., 2005; Björkvald et al., 2009). Therefore we argue that the RZ is not a mere passive conduit of SO$_4^{2-}$. Instead, upslope inputs of SO$_4^{2-}$ are processed and regulated in the RZ before entering the stream.

There was an apparent lag between absolute values in S deposition and in lateral S-SO$_4^{2-}$ fluxes. The decreasing values of lateral S-SO$_4^{2-}$ flux in the RZ during the study period corresponded with those of the atmospheric deposition during the late 1980s and 1990s (Fig. 3, Fig. 5). This suggests a delay of about 15 years in the response in the RZ, which is in line with both previous field studies (Dillon and LaZerte, 1992; Prechtel et al., 2001; Mörth et al., 2005) and modeling exercises with organic soils (Tipping and Hurley, 1988). Because of the refractory nature of the reservoir, organic S pools were and still are being slowly decomposed and lost as SO$_4^{2-}$ by lateral export in the RZ (Houle et al., 2001). In contrast, the invariant upslope S-SO$_4^{2-}$ fluxes indicated that other mechanisms operate in the upslope podzols. There are two main mechanisms that could give rise to the lack of upslope response: mineral soils had already responded to decreasing SO$_4^{2-}$ deposition before 2003, or alternatively are responding even more slowly than organic RZs. The magnitude of the estimated S-SO$_4^{2-}$ flux from the upslope site (Fig. 5) is comparable to the high atmospheric inputs during the high S deposition period (Fig. 3), which suggests that the process is slower than in RZ. Specifically, a slow desorption of

previously adsorbed SO$_4^{2-}$ on mineral surfaces (Houle et al., 2001; Borken et al., 2011; Löfgren et al., 2011), which can last for several decades (Manderscheid et al., 2000; Alewell, 2001) could be operating here.

Intra-annually, stream and RZ S-SO$_4^{2-}$ dynamics did not entirely coincide (Fig. 6). Specifically, stream S-SO$_4^{2-}$ concentrations were more dynamic and showed higher peaks than RZ S-SO$_4^{2-}$ concentrations. We plotted the residuals of the regression relating monthly S-S-SO$_4^{2-}$ flow-weighted concentrations in the stream and in the RZ (Fig. 7a) against accumulated monthly runoff and found a significant logarithmic relationship (Fig. 7b). Higher positive residuals, i.e. where RZ concentrations under-predicted stream concentrations, were observed in periods with lower accumulated runoff. We interpret this as evidence that, during base flow, other riparian areas within the catchment contribute more SO$_4^{2-}$ to stream water than the S4 measurement site. For example, more organic-rich RZs may hold larger S pools that are subject to greater oxidization and mobilization during low flow conditions. To test this hypothesis, we performed a multiple linear regression model to predict monthly S-SO$_4^{2-}$ flow-weighted concentrations in the stream from monthly S-SO$_4^{2-}$ flow-weighted concentrations in the RZ and logarithmic monthly accumulated runoff (Fig. 7c). This indeed improved the prediction of stream SO$_4^{2-}$. To further support this idea, we investigated S-SO$_4^{2-}$ concentrations in three other riparian profiles located in the same catchment. The three profiles were sampled in 8 occasions between 2008 and 2009 at different soil depths (Fig. 8). The comparison revealed that the concentration profiles for these four sites within the catchment differed, and include RZs with both higher and lower S-SO$_4^{2-}$ concentrations than those observed at the S4 site. Thus, vertical changes in flowpaths in the entire RZ area that are driven by amount of precipitation and hydrology are important to infer stream chemistry at the time scale of days to months. This heterogeneity within the RZ clearly limits the extent to which it is possible to infer stream chemistry from a single riparian profile over short time scales. The heterogeneity is caused by local hydromorphological variations that create different rates of organic
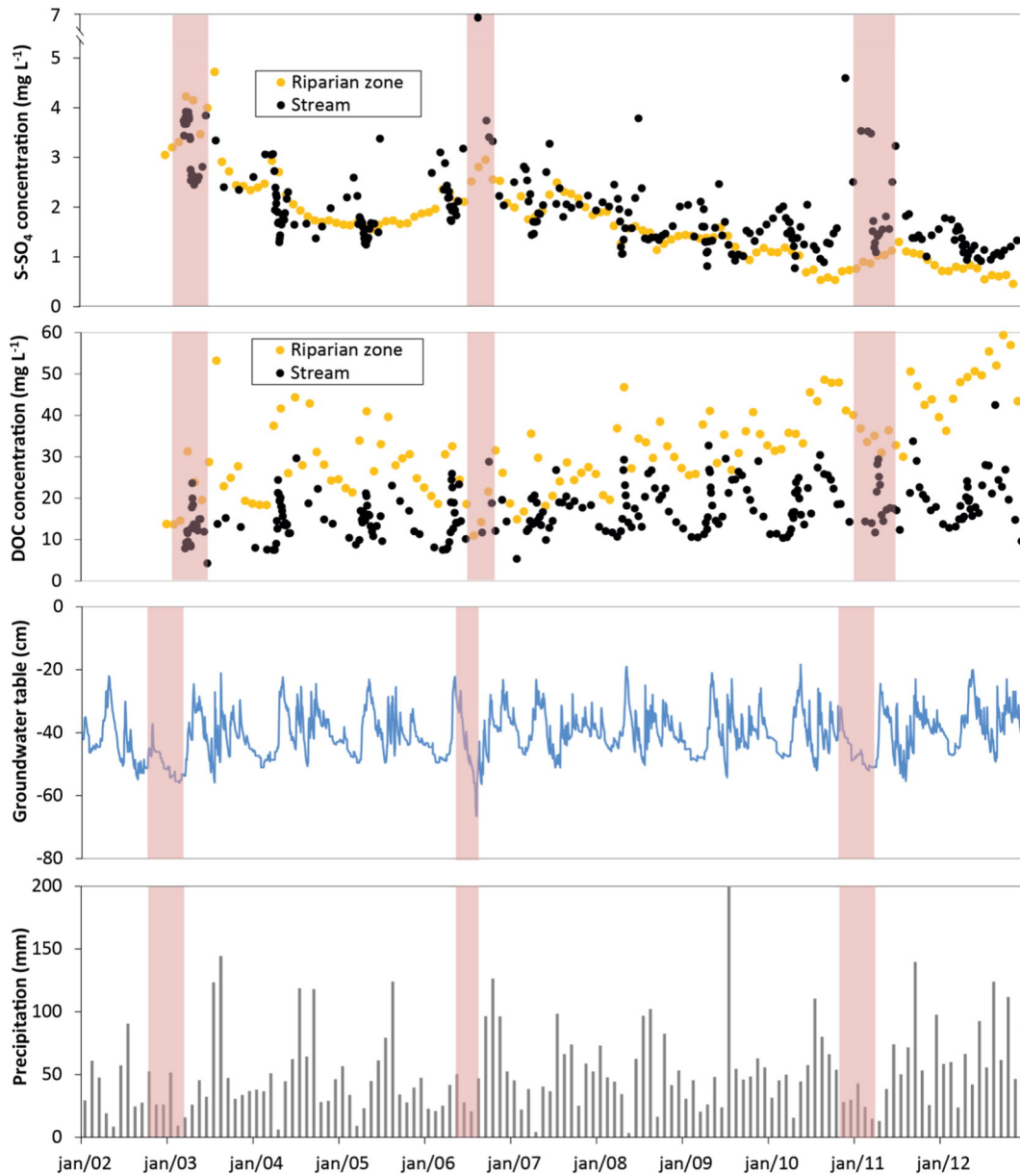
Fig. 6. Stream and riparian sulfate sulfur ($S-SO_4^{2-}$) concentration time series (upper panel), stream and riparian dissolved organic carbon (DOC) concentration time series (middle upper panel), riparian groundwater table time series (middle lower panel), and monthly precipitation time series (lower panel) for the study period (2003–2012). Note that monthly $S-SO_4^{2-}$ and DOC flow-weighted concentrations based on the full riparian profile from RIM calculations are plotted in the case of the riparian zone. Three examples of periods with observable episodic increases in $S-SO_4^{2-}$ concentrations and the antecedent (note therefore shifted to the left) groundwater table and precipitation are highlighted.

matter accumulation, transport, and processing of chemical elements (Grabs et al., 2012; Herndon et al., 2015; Ledesma et al., 2015). Nevertheless, by understanding the nature of this heterogeneity and associated biogeochemical processes, it is possible to relate RZ and stream $S-SO4^{2-}$ concentrations at longer time scales.

3.3. Precipitation and groundwater table influence on stream and riparian SO_4^{2-}

Intra-annual variations in stream $S-SO_4^{2-}$ concentrations were, in general, characterized by higher values in winter and lower values after spring flood (Fig. 6). This is opposite to the temporal patterns observed for DOC in boreal catchments (Erlandsson et al., 2008; Köhler et al., 2008). However, episodic increases in $S-SO_4^{2-}$ were common and independent of season. These episodic increases were preceded by periods with low accumulated precipitation and low

groundwater levels in the RZ, as illustrated on a number of occasions in Fig. 6 (especially during summer 2006).

We tested simple linear regression models to predict $S-SO_4^{2-}$ concentrations in the stream from antecedent annual accumulated precipitation and $S-SO_4^{2-}$ concentrations in the 45 cm riparian layer from antecedent annual average groundwater table in the RZ. The 45 cm riparian layer was chosen to represent the RZ because of its location within the dominant source layer (Fig. 2). Moreover, the lysimeter here was below the groundwater surface during 72% of the study period (Table 1), thus although anoxic conditions are likely to have prevailed, this layer experienced episodic aeration and resulting S oxidation and thus is a good representative of the processes of interest. We found significant correlations for both precipitation versus stream and groundwater levels versus RZ $S-SO_4^{2-}$ (Fig. A3). These correlations were observed despite both stream and riparian $S-SO_4^{2-}$ concentrations having negative trends during the study period, whereas precipitation and groundwater
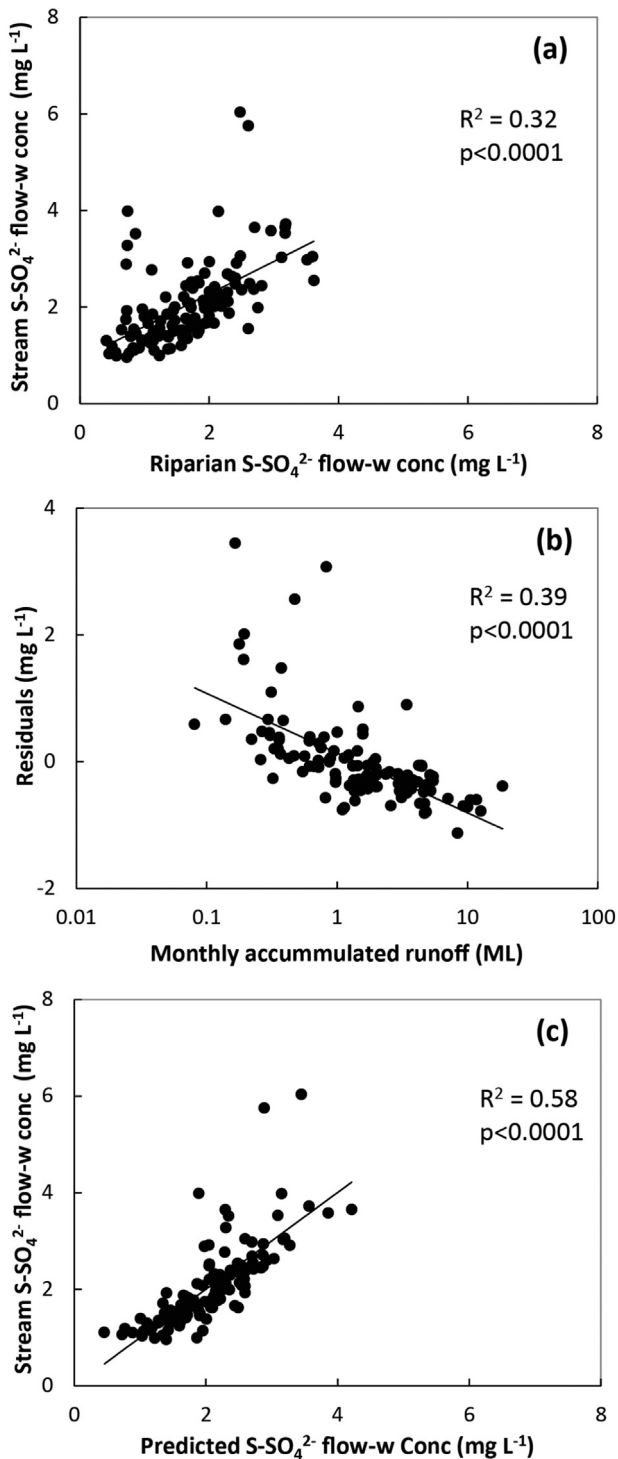
Fig. 7. Linear relationship between monthly sulfate sulfur (S-SO$_4^{2-}$) flow-weighted concentrations (denoted as flow-w conc) in the stream and monthly S-SO$_4^{2-}$ flow-weighted concentrations in the riparian peat profile S4 (a). Relationship between residuals of the regression in (a) and monthly accumulated runoff (b). In (c), multiple linear regression model predicting monthly S-SO$_4^{2-}$ flow-weighted concentrations in the stream from monthly S-SO$_4^{2-}$ flow-weighted concentrations in the riparian peat profile S4 and logarithmic monthly accumulated runoff (y = 6.8 + 0.65*riparian sulfate − 0.94*(log)accumulated runoff).

tables showed no trends. Based on visual inspection of the data, we observed an apparent shift in the relationship between groundwater table and riparian S-SO$_4^{2-}$ concentrations in around 2008–09 (Fig. A3). Considering these two periods separately (2003–2008 and 2009–2012), the antecedent annual average groundwater table explained 82% of the

variation in riparian S-SO$_4^{2-}$ concentrations between 2003 and 2008, and 54% between 2009 and 2012. The offset between the two periods implies that, for a similar degree of groundwater table drawdown today (and in the future), peak S-SO$_4^{2-}$ concentrations will be lower than in the past, suggesting that the surplus S pool from the acidification period is being depleted. Indeed, distribution plots of stream S-SO$_4^{2-}$ concentrations as a function of discharge conditions reflected a decrease in the period 2009–2012 in comparison to the period 2003–2008, especially at higher flows (Fig. 9). This was also clear for the 45 cm riparian layer. Due to the stability in upslope S-SO$_4^{2-}$ concentrations no relation between SO$_4^{2-}$ in mineral soils and precipitation or groundwater table was found (data not shown), which is consistent with previous studies (Eimers et al., 2003).

These results support the interpretation that moisture status and transient redox conditions exert a strong control on S transformations and SO$_4^{2-}$ mobilization in catchments (Dillon and LaZerte, 1992; Devito and Hill, 1997; Eimers et al., 2003; Clark et al., 2005; Kang et al., 2014). This has also been observed in lab experiments with peat soils (Rezanezhad et al., 2014). Commonly, dry periods are associated with a three-step process, which we assume here is controlled by the RZ: (1) a drop in RZ groundwater levels, (2) a subsequent increase in riparian soil water S-SO$_4^{2-}$ concentrations following the microbial oxidation of reduced organic S compounds, and (3) an increase in SO$_4^{2-}$ concentrations in the stream when the groundwater table rises again and mobilize the riparian SO$_4^{2-}$. We conclude that these processes, which have previously been mainly associated with extensive peatland and wetland systems, also operate at the smaller scale of RZs.

3.4. Connection with DOC and implications for DOC drivers and catchment biogeochemistry

Surface water DOC concentrations are increasing in much of Scandinavia, Europe, and North America (Vuorenmaa et al., 2006; Monteith et al., 2007; Ledesma et al., 2012; Futter et al., 2014). Declines in SO$_4^{2-}$ deposition (Evans et al., 2006; De Wit et al., 2007; Monteith et al., 2007; Borken et al., 2011) and climatic factors (Hongve et al., 2004; Köhler et al., 2008) are generally considered the main drivers of the observed trends, although their relative importance continues to be debated (Clark et al., 2010), and other hypotheses have been proposed (Freeman et al., 2004; Findlay, 2005; Wilson and Xenopoulos, 2008). Atmospheric deposition and climate are not necessarily exclusive drivers, as they may operate on varying temporal scales (episodic to seasonal to long-term) and vary in importance depending on geographic location (e.g. whether close to or remote from acidifying emission sources) (Clark et al., 2010; Winterdahl et al., 2014).

Measured SO$_4^{2-}$ and DOC from the stream and soil transect showed remarkably consistent opposite long- and short-term patterns (Fig. 6; Fig. 9). In the long-term, positive trends in DOC and negative trends in S-SO$_4^{2-}$ were observed in the stream and the dominant source layer of the RZ, whereas no trends were observed in the upslope mineral soil (Table 1). In the short-term, power functions of DOC versus S-SO$_4^{2-}$ concentrations (Fig. A4) explained >70% of the variability in DOC in the soil water samples from all riparian layers hydrologically connected to the stream (35 to 65 cm depth, Table 1). In stream samples, the explained variation was 40%, still highly statistically significant ($p < 0.001$). In soil water samples from the mineral upslope podzol, there was no significant relationships between S-SO$_4^{2-}$ and DOC concentrations in most layers. However, at some depths a number of outliers generated a significant correlation that should be interpreted with caution because statistical significance in this case does not necessarily imply causality (Fig. A4).

We hypothesize that an increase in organic matter solubility following an increase in humic charge (Kalbitz et al., 2000) and reduced ionic strength (Stumm and Morgan, 1996; Hruška et al., 2009) is the mechanism by which a reduction in SO$_4^{2-}$ increases DOC mobilization. Thus,
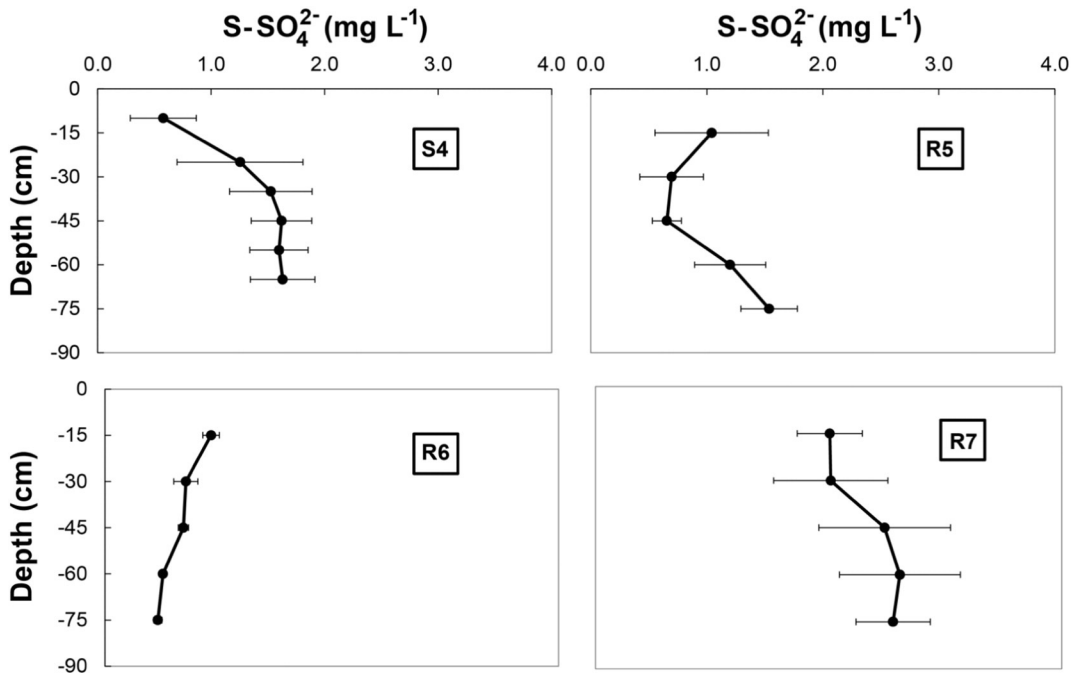
Fig. 8. Sulfate sulfur (S-SO$_4^{2-}$) concentration profiles in the riparian zone site presented in the study (S4) and in three other riparian soils within the same catchment (R5, R6, and R7). Circles represent average concentrations at each layer and horizontal lines are standard deviations. Displayed data belong to the period 2008–2009. Concentrations in R5, R6, and R7 are from total sulfur (S) measurements and thus a proxy for S-SO$_4^{2-}$.
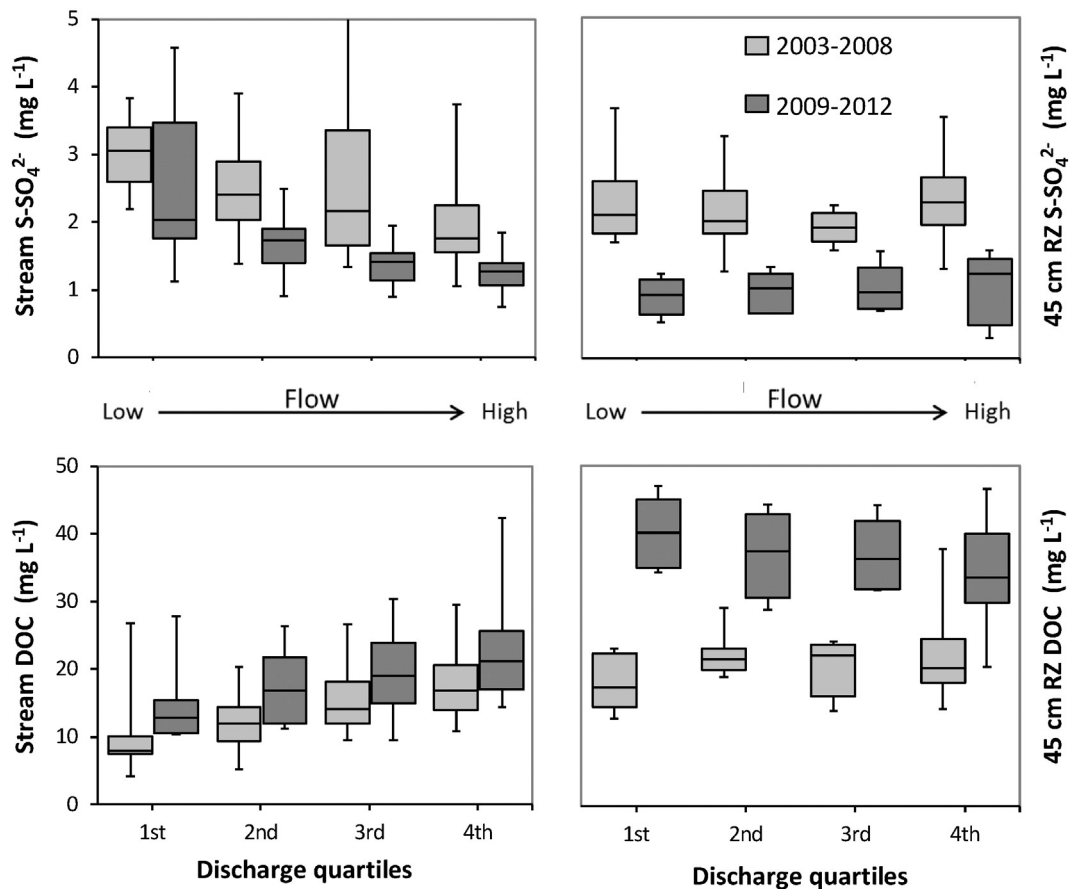

Fig. 9. Box plots including median, 25th percentile, 75th percentile, minimum and maximum sulfate sulfur (S-SO$_4^{2-}$) and dissolved organic carbon (DOC) concentrations in the stream and at 45 cm depth in the riparian zone (RZ) in relation to discharge quartiles. Box plots are divided into two periods: 2003–2008 and 2009–2012.

there are two ways in which SO_4^{2-} drives DOC dynamics in the stream and RZ: (i) the long-term decrease in SO_4^{2-} deposition drives a long-term increase in DOC via acidity/ionic strength effects, and (ii) short-term fluctuations in hydrology (drought-rewetting) driving S redox processes in the RZ which in turn drive variations in DOC via solubility effects. In the upslope mineral soils with low organic matter content and low DOC concentrations, adsorption-desorption mechanisms are likely more important (Manderscheid et al., 2000; Houle et al., 2001). Moreover, the decrease in riparian and stream SO_4^{2-} has coincided not only with an increase in mean DOC concentrations, but also with an increasing range and variability of DOC in both surface and soil waters, (compare earlier and later periods in Fig. 9). This is consistent with observations from other regions where stream DOC concentrations have increased (e.g. Evans et al., 2006; Hytteborn et al., 2015).

These observations imply that: (1) SO_4^{2-} is still an important driver of DOC trends in northern headwater catchments and (2) RZ processes control SO_4^{2-} and subsequently DOC concentrations in the stream independently of upslope soils. Löfgren and Zetterberg (2011) already pointed out that DOC leaching from the RZ appears to be primarily responsible for observed DOC trends in catchments with a combination of upslope mineral soils and near-stream organic soils because of apparent discrepancies between stream and mineral soil trends. This is further supported by other studies highlighting the importance of organic as opposed to mineral soils for current DOC trends (Borken et al., 2011; Hruška et al., 2014), although other studies have shown more mixed responses (Stutter et al., 2011). It is hence relevant to ask whether climate relationships with DOC can be accounted for without considering SO_4^{2-}. For example, Köhler et al. (2008) showed a relationship between wet years and increased DOC in this catchment. We did not quantify this effect, but may speculate that this relationship might, at least partly, be indirectly causal according to the mechanism described here: weather variations could also be driving SO_4^{2-} variations, which in turn affect DOC, both in the short and the long-term. Independently of the chemical effects, climate will always have an effect on DOC through enhancement or suppression of biological processes (Clark et al., 2010). However, modeling DOC and evaluating drivers of DOC trends without considering the potential intermediary role of SO_4^{2-} could be misleading.

The ongoing depletion of the residual S pool from the peak acidification period, in combination with the sustained potential of RZs to export DOC (Ledesma et al., 2015) is likely to bring DOC concentrations to higher levels. This is in line with studies that infer from lake sediments that DOC concentrations in surface waters were suppressed during peak acidification (Bragée et al., 2015; Valinia et al., 2015), and with process-based models describing the effects of S deposition on DOC leaching (Futter et al., 2009; Rowe et al., 2014).

4. Conclusions

The relative importance of the RZ versus the upslope area as the source of DOC to streams and regulator of acidification effects continue to be debated (Sawicka et al., 2016). We have shown that present-day decreasing SO_4^{2-} trends in stream and riparian waters are responding to decreasing trends in anthropogenic SO_4^{2-} deposition with a decadal delay. The absence of clear trends in upslope SO_4^{2-} suggests that the recovery in mineral soils could be slower and demonstrates a process discontinuity between RZs and the rest of the catchment. RZs thus appear to act as biogeochemical reactors for S derived from current or previous direct deposition or from upslope inputs and the main regulator of SO_4^{2-} transfer to the stream.

Long-term trends and annual dynamics in SO_4^{2-} and DOC were similar in the stream and in the riparian profile that formed the focus of this study. At these time scales, one riparian profile might be a good representative of the near-stream organic soils of a catchment, which in turn determine the variation in stream chemistry. However, as water flows through a heterogeneous spatial mosaic of RZs before

entering the stream, upscaling information from a single riparian profile to the catchment level is problematic in short-time scales. A distributed representation is needed to accurately infer stream chemistry variation from an integrated riparian signal at short-time scales.

The results presented here from a boreal forest catchment, which experienced relatively low rates of anthropogenic acid deposition, suggest that larger areas of boreal forest may have been more impacted by acidification than has often been assumed (Futter et al. 2011; Oni et al., 2013; Futter et al., 2014; Winterdahl et al., 2014). This in turn suggests that SO_4^{2-} may have been an important driver of DOC trends, even in relatively remote regions. Greater awareness of the importance of acid deposition should improve our ability to correctly attribute past changes (largely based on observational data obtained during a period of rapidly declining S-deposition) and therefore our ability to correctly predict the future trajectory of water quality response to changes in this and other drivers, such as changing climate or land-use. As long-term responses to acid deposition appear to have been strongly regulated by riparian soil processes, these findings also suggest that effective RZ management is the key to effective mitigation of the adverse effects of other environmental change drivers, as these become increasingly important on water quality in the boreal forest.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.03.230.

References

Ågren, A., Buffam, I., Jansson, M., Laudon, H., 2007. Importance of seasonality and small streams for the landscape regulation of dissolved organic carbon export. J. Geophys. Res. Biogeosci. 112, G03003.

Aherne, J., Futter, M.N., Dillon, P.J., 2008. The impacts of future climate change and sulphur emission reductions on acidification recovery at Plastic Lake, Ontario. Hydrol. Earth Syst. Sci. 12, 383–392.

Åkerblom, S., Bishop, K., Björn, E., Lambertsson, L., Eriksson, T., Nilsson, M.B., 2013. Significant interaction effects from sulfate deposition and climate on sulfur concentrations constitute major controls on methylmercury production in peatlands. Geochim. Cosmochim. Acta 102, 1–11.

Albrektson, A., Lundmark, T., 1991. Vegetationens storlek och omsättning inom en barrskog i norra Sverige, samt näring i vegetation och mark och dess omsättning i samband med växandet (in Swedish). Sveriges Lantbruksuniversitet IfS.

Alewell, C., 2001. Predicting reversibility of acidification: the European sulfur story. Water Air Soil Pollut. 130, 1271–1276.

Bergknut, M., Wiberg, K., Klaminder, J., 2011. Vertical and lateral redistribution of POPs in soils developed along a hydrological gradient. Environ. Sci. Technol. 45, 10378–10384.

Bishop, K., Lee, Y.H., Pettersson, C., Allard, B., 1995. Terrestrial sources of methylmercury in surface waters: the importance of the riparian zone on the Svartberget catchment. Water Air Soil Pollut. 80, 435–444.

Bishop, K., Seibert, J., Köhler, S., Laudon, H., 2004. Resolving the double paradox of rapidly mobilized old water with highly variable responses in runoff chemistry. Hydrol. Process. 18, 185–189.

Björkvald, L., Giesler, R., Laudon, H., Humborg, C., Mörth, C.M., 2009. Landscape variations in stream water SO_4^{2-} and $\delta^{34}S_{SO4}$ in a boreal stream network. Geochim. Cosmochim. Acta 73, 4648–4660.

Borken, W., Ahrens, B., Schulz, C., Zimmermann, L., 2011. Site-to-site variability and temporal trends of DOC concentrations and fluxes in temperate forest soils. Glob. Chang. Biol. 17, 2428–2443.

Bragée, P., Mazier, F., Nielsen, A.B., Rosén, P., Fredh, D., Broström, A., et al., 2015. Historical TOC concentration minima during peak sulfur deposition in two Swedish lakes. Biogeosciences 12, 307–322.

Clark, J.M., Chapman, P.J., Adamson, J.K., Lane, S.N., 2005. Influence of drought-induced acidification on the mobility of dissolved organic carbon in peat soils. Glob. Chang. Biol. 11, 791–809.

Clark, J.M., Chapman, P.J., Heathwaite, A.L., Adamson, J.K., 2006. Suppression of dissolved organic carbon by sulfate induced acidification during simulated droughts. Environ. Sci. Technol. 40, 1776–1783.

Clark, J.M., Bottrell, S.H., Evans, C.D., Monteith, D.T., Bartlett, R., Rose, R., et al., 2010. The importance of the relationship between scale and process in understanding long-term DOC dynamics. Sci. Total Environ. 408, 2768–2775.

Cory, N., Laudon, H., Köhler, S., Seibert, J., Bishop, K., 2007. Evolution of soil solution aluminum during transport along a forested boreal hillslope. J. Geophys. Res. Biogeosci. 112, G03014.

De Wit, H.A., Mulder, J., Hindar, A., Hole, L., 2007. Long-term increase in dissolved organic carbon in streamwaters in Norway is response to reduced acid deposition. Environ. Sci. Technol. 41, 7706–7713.

Devito, K.J., Hill, A.R., 1997. Sulphate dynamics in relation to groundwater — surface water interactions in headwater wetlands of the southern Canadian Shield. Hydrol. Process. 11, 485–500.

Dillon, P.J., LaZerte, B.D., 1992. Response of the Plastic Lake catchment, Ontario, to reduced sulfur deposition. Environ. Pollut. 77, 211–217.

Dosskey, M.G., Bertsch, P.M., 1994. Forest sources and pathways of organic-matter transport to a blackwater stream: a hydrological approach. Biogeochemistry 24, 1–19.

Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Butler, T.J., Cronan, C.S., Eagar, C., et al., 2001. Acidic deposition in the Northeastern United States: sources and inputs, ecosystem effects, and management strategies. Bioscience 51, 180–198.

Driscoll, C.T., Driscoll, K.M., Roy, K.M., Mitchell, M.J., 2003. Chemical response of lakes in the Adirondack region of New York to declines in acidic deposition. Environ. Sci. Technol. 37, 2036–2042.

Eimers, M.C., Dillon, P.J., Schiff, S.L., Jeffries, D.S., 2003. The effects of drying and re-wetting and increased temperature on sulphate release from upland and wetland material. Soil Biol. Biochem. 35, 1663–1673.

Eimers, M.C., Watmough, S.A., Buttle, J.M., Dillon, P.J., 2008. Examination of the potential relationship between droughts, sulphate and dissolved organic carbon at a wetland-draining stream. Glob. Chang. Biol. 14, 938–948.

Erlandsson, M., Buffam, I., Fölster, J., Laudon, H., Temnerud, J., Weyhenmeyer, G.A., et al., 2008. Thirty-five years of synchrony in the organic matter concentrations of Swedish rivers explained by variation in flow and sulphate. Glob. Chang. Biol. 14, 1191–1198.

Evans, C.D., Monteith, D.T., Cooper, D.M., 2005. Long-term increases in surface water dissolved organic carbon: observations, possible causes and environmental impacts. Environ. Pollut. 137, 55–71.

Evans, C.D., Chapman, P.J., Clark, J.M., Monteith, D.T., Cresser, M.S., 2006. Alternative explanations for rising dissolved organic carbon export from organic soils. Glob. Chang. Biol. 12, 2044–2053.

Evans, C.D., Jones, T.G., Burden, A., Ostle, N., Zielinski, P., Cooper, M.D.A., et al., 2012. Acidity controls on dissolved organic carbon mobility in organic soils. Glob. Chang. Biol. 18, 3317–3331.

Evans, C.D., Chadwick, T., Norris, D., Rowe, E.C., Heaton, T.H.E., Brown, P., et al., 2014. Persistent surface water acidification in an organic soil-dominated upland region subject to high atmospheric deposition: the North York Moors, UK. Ecol. Indic. 37, 304–316.

Fiebig, D.M., Lock, M.A., Neal, C., 1990. Soil-water in the riparian zone as a source of carbon for a headwater stream. J. Hydrol. 116, 217–237.

Findlay, S.E.G., 2005. Increased carbon transport in the Hudson River: unexpected consequence of nitrogen deposition? Front. Ecol. Environ. 3, 133–137.

Fölster, J., 2000. The near-stream zone is a source of nitrogen in a Swedish forested catchment. J. Environ. Qual. 29, 883–893.

Fölster, J., Wilander, A., 2002. Recovery from acidification in Swedish forest streams. Environ. Pollut. 117, 379–389.

Freeman, C., Fenner, N., Ostle, N.J., Kang, H., Dowrick, D.J., Reynolds, B., et al., 2004. Export of dissolved organic carbon from peatlands under elevated carbon dioxide levels. Nature 430, 195–198.

Futter, M.N., Forsius, M., Holmberg, M., Starr, M., 2009. A long-term simulation of the effects of acidic deposition and climate change on surface water dissolved organic carbon concentrations in a boreal catchment. Hydrol. Res. 40, 291–305.

Futter, M.N., Löfgren, S., Köhler, S.J., Lundin, L., Moldan, F., Bringmark, L., 2011a. Simulating dissolved organic carbon dynamics at the Swedish integrated catchments model for carbon, INCA-C. Ambio 40, 906–919.

Futter, M.N., Valinia, S., Löfgren, S., Kohler, S.J., Fölster, J., 2014. Long-term trends in water chemistry of acid-sensitive Swedish lakes show slow recovery from historic acidification. Ambio 43, 77–90.

Giesler, R., Mörth, C.M., Mellqvist, E., Torssander, P., 2005. The humus layer determines SO_4^{2-} isotope values in the mineral soil. Biogeochemistry 74, 3–20.

Grabs, T., Bishop, K., Laudon, H., Lyon, S.W., Seibert, J., 2012. Riparian zone hydrology and soil water total organic carbon (TOC): implications for spatial variability and upscaling of lateral riparian TOC exports. Biogeosciences 9, 3901–3916.

Gregory, S.V., Swanson, F.J., McKee, W.A., Cummins, K.W., 1991. An ecosystem perspective of riparian zones. Bioscience 41, 540–551.

Herndon, E.M., Dere, A.L., Sullivan, P.L., Norris, D., Reynolds, B., Brantley, S.L., 2015. Landscape heterogeneity drives contrasting concentration-discharge relationships in shale headwater catchments. Hydrol. Earth Syst. Sci. 19, 3333–3347.

Hongve, D., Riise, G., Kristiansen, J.F., 2004. Increased colour and organic acid concentrations in Norwegian forest lakes and drinking water — a result of increased precipitation? Aquat. Sci. 66, 231–238.

Houle, D., Carignan, R., 1992. Sulfur speciation and distribution in soils and aboveground biomass of a boreal coniferous forest. Biogeochemistry 16, 63–82.

Houle, D., Carignan, R., Ouimet, R., 2001. Soil organic sulfur dynamics in a coniferous forest. Biogeochemistry 53, 105–124.

Hruška, J., Krám, P., McDowell, W.H., Oulehle, F., 2009. Increased dissolved organic carbon (DOC) in central European streams is driven by reductions in ionic strength rather than climate change or decreasing acidity. Environ. Sci. Technol. 43, 4320–4326.

Hruška, J., Krám, P., Moldan, F., Oulehle, F., Evans, C.D., Wright, R.F., et al., 2014. Changes in soil dissolved organic carbon affect reconstructed history and projected future trends in surface water acidification. Water Air Soil Pollut. 225, 1–13.

Hytteborn, J.K., Temnerud, J., Alexander, R.B., Boyer, E.W., Futter, M.N., Fröberg, M., et al., 2015. Patterns and predictability in the intra-annual organic carbon variability across the boreal and hemiboreal landscape. Sci. Total Environ. 520, 260–269.

Kalbitz, K., Solinger, S., Park, J.H., Michalzik, B., Matzner, E., 2000. Controls on the dynamics of dissolved organic matter in soils: a review. Soil Sci. 165, 277–304.

Kang, P.G., Mitchell, M.J., Mayer, B., Campbell, J.L., 2014. Isotopic evidence for determining the sources of dissolved organic sulfur in a forested catchment. Environ. Sci. Technol. 48, 11259–11267.

Kerr, J.G., Eimers, M.C., Creed, I.F., Adams, M.B., Beall, F., Burns, D., et al., 2012. The effect of seasonal drying on sulphate dynamics in streams across Southeastern Canada and the Northeastern USA. Biogeochemistry 111, 393–409.

Klaminder, J., Grip, H., Mörth, C.M., Laudon, H., 2011. Carbon mineralization and pyrite oxidation in groundwater: importance for silicate weathering in boreal forest soils and stream base-flow chemistry. Appl. Geochem. 26, 319–324.

Köhler, S.J., Buffam, I., Laudon, H., Bishop, K.H., 2008. Climate's control of intra-annual and interannual variability of total organic carbon concentration and flux in two contrasting boreal landscape elements. J. Geophys. Res. Biogeosci. 113, G03012.

Köhler, S.J., Buffam, I., Seibert, J., Bishop, K.H., Laudon, H., 2009. Dynamics of stream water TOC concentrations in a boreal headwater catchment: controlling factors and implications for climate scenarios. J. Hydrol. 373, 44–56.

Landre, A.L., Watmough, S.A., Dillon, P.J., 2009. The effects of dissolved organic carbon, acidity and seasonality on metal geochemistry within a forested catchment on the Precambrian Shield, Central Ontario, Canada. Biogeochemistry 93, 271–289.

Laudon, H., 2008. Recovery from episodic acidification delayed by drought and high sea salt deposition. Hydrol. Earth Syst. Sci. 12, 363–370.

Laudon, H., Dillon, P.J., Eimers, M.C., Semkin, R.G., Jeffries, D.S., 2004a. Climate-induced episodic acidification of streams in Central Ontario. Environ. Sci. Technol. 38, 6009–6015.

Laudon, H., Seibert, J., Köhler, S., Bishop, K., 2004b. Hydrological flow paths during snowmelt: congruence between hydrometric measurements and oxygen 18 in meltwater, soil water, and runoff. Water Resour. Res. 40, W03102.

Laudon, H., Taberman, I., Ågren, A., Futter, M., Ottosson-Löfvenius, M., Bishop, K., 2013. The Krycklan catchment study—a flagship infrastructure for hydrology, biogeochemistry, and climate research in the boreal landscape. Water Resour. Res. 49, 7154–7158.

Ledesma, J.L.J., Köhler, S.J., Futter, M.N., 2012. Long-term dynamics of dissolved organic carbon: implications for drinking water supply. Sci. Total Environ. 432, 1–11.

Ledesma, J.L.J., Grabs, T., Futter, M.N., Bishop, K.H., Laudon, H., Köhler, S.J., 2013. Riparian zone control on base cation concentration in boreal streams. Biogeosciences 10, 3849–3868.

Ledesma, J.L.J., Grabs, T., Bishop, K.H., Schiff, S.L., Köhler, S.J., 2015. Potential for long-term transfer of dissolved organic carbon from riparian zones to streams in boreal catchments. Glob. Chang. Biol. 21, 2963–2979.

Lepistö, A., Kortelainen, P., Mattsson, T., 2008. Increased organic C and N leaching in a northern boreal river basin in Finland. Glob. Biogeochem. Cycles 22, GB3029.

Lidman, F., Mörth, C.M., Björkvald, L., Laudon, H., 2011. Selenium dynamics in boreal streams: the role of wetlands and changing groundwater tables. Environ. Sci. Technol. 45, 2677–2683.

Löfgren, S., Zetterberg, T., 2011. Decreased DOC concentrations in soil water in forested areas in Southern Sweden during 1987–2008. Sci. Total Environ. 409, 1916–1926.

Löfgren, S., Aastrup, M., Bringmark, L., Hultberg, H., Lewin-Pihlblad, L., Lundin, L., et al., 2011. Recovery of soil water, groundwater, and streamwater from acidification at the Swedish integrated monitoring catchments. Ambio 40, 836–856.

Manderscheid, B., Schweisser, T., Lischeid, G., Alewell, C., Matzner, E., 2000. Sulfate pools in the weathered substrata of a forested catchment. Soil Sci. Soc. Am. J. 64, 1078–1082.

Mann, H.B., 1945. Nonparametric tests against trend. Econometrica 13, 245–259.

McClain, M.E., Boyer, E.W., Dent, C.L., Gergel, S.E., Grimm, N.B., Groffman, P.M., et al., 2003. Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. Ecosystems 6, 301–312.

Mitchell, M.J., Likens, G.E., 2011. Watershed sulfur biogeochemistry: shift from atmospheric deposition dominance to climatic regulation. Environ. Sci. Technol. 45, 5267–5271.

Mitchell, M.J., Mayer, B., Bailey, S.W., Hornbeck, J.W., Alewell, C., Driscoll, C.T., et al., 2001. Use of stable isotope ratios for evaluating sulfur sources and losses at the Hubbard Brook experimental Forest. Water Air Soil Pollut. 130, 75–86.

Monteith, D.T., Stoddard, J.L., Evans, C.D., de Wit, H.A., Forsius, M., Høgåsen, T., et al., 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Nature 450, 537–540.

Mörth, C.M., Torssander, P., Kjønaas, O.J., Stuanes, A.O., Moldan, F., Giesler, R., 2005. Mineralization of organic sulfur delays recovery from anthropogenic acidification. Environ. Sci. Technol. 39, 5234–5240.

Mylona, S., 1996. Sulphur dioxide emissions in Europe 1880–1991 and their effect on sulphur concentrations and depositions. Tellus Ser. B Chem. Phys. Meteorol. 48, 662–689.

Nyberg, L., 1995. Water flow path interactions with soil hydraulic properties in till soil at Gårdsjön, Sweden. J. Hydrol. 170, 255–275.

Nyberg, L., Stähli, M., Mellander, P.-E., Bishop, K.H., 2001. Soil frost effects on soil water and runoff dynamics along a boreal forest transect: 1. Field investigations. Hydrol. Process. 15, 909–926.

Oni, S.K., Futter, M.N., Bishop, K., Köhler, S.J., Ottosson-Löfvenius, M., Laudon, H., 2013. Long-term patterns in dissolved organic carbon, major elements and trace metals in boreal headwater catchments: trends, mechanisms and heterogeneity. Biogeosciences 10, 2315–2330.

Öquist, M.G., Wallin, M., Seibert, J., Bishop, K., Laudon, H., 2009. Dissolved inorganic carbon export across the soil/stream interface and its fate in a boreal headwater stream. Environ. Sci. Technol. 43, 7364–7369.

Pellerin, B.A., Fernández, I.J., Norton, S.A., Kahl, J.S., 2002. Soil aluminum distribution in the near-stream zone at the Bear Brook watershed in Maine. Water Air Soil Pollut. 134, 189–204.

Peralta-Tapia, A., Sponseller, R.A., Ågren, A., Tetzlaff, D., Soulsby, C., Laudon, H., 2015. Scale-dependent groundwater contributions influence patterns of winter baseflow stream chemistry in boreal catchments. J. Geophys. Res. Biogeosci. 120, 847–858.

Petrone, K., Buffam, I., Laudon, H., 2007. Hydrologic and biotic control of nitrogen export during snowmelt: a combined conservative and reactive tracer approach. Water Resour. Res. 43, W06420.

Prechtel, A., Alewell, C., Armbruster, M., Bittersohl, J., Cullen, J.M., Evans, C.D., et al., 2001. Response of sulphur dynamics in European catchments to decreasing sulphate deposition. Hydrol. Earth Syst. Sci. 5, 311–325.

Rezanezhad, F., Couture, R.M., Kovac, R., O'Connell, D., Van Cappellen, P., 2014. Water table fluctuations and soil biogeochemistry: an experimental approach using an automated soil column system. J. Hydrol. 509, 245–256.

Rowe, E.C., Tipping, E., Posch, M., Oulehle, F., Cooper, D.M., Jones, T.G., et al., 2014. Predicting nitrogen and acidity effects on long-term dynamics of dissolved organic matter. Environ. Pollut. 184, 271–282.

Sawicka, K., Monteith, D.T., Vanguelova, E.I., Wade, A.J., Clark, J.M., 2016. Fine-scale temporal characterization of trends in soil water dissolved organic carbon and potential drivers Ecological Indicators. in press.

Schlyter, P., Stjernquist, I., Bärring, L., Jönsson, A.M., Nilsson, C., 2006. Assessment of the impacts of climate change and weather extremes on boreal forests in Northern Europe, focusing on Norway spruce. Clim. Res. 31, 75–84.

Schöpp, W., Posch, M., Mylona, S., Johansson, M., 2003. Long-term development of acid deposition (1880–2030) in sensitive freshwater regions in Europe. Hydrol. Earth Syst. Sci. 7, 436–446.

Seibert, J., Grabs, T., Köhler, S., Laudon, H., Winterdahl, M., Bishop, K., 2009. Linking soil- and stream-water chemistry based on a riparian flow-concentration integration model. Hydrol. Earth Syst. Sci. 13, 2287–2297.

Skyllberg, U., Qian, J., Frech, W., Xia, K., Bleam, W.F., 2003. Distribution of mercury, methyl mercury and organic sulphur species in soil, soil solution and stream of a boreal forest catchment. Biogeochemistry 64, 53–76.

Stendahl, J., Lundin, L., Nilsson, T., 2009. The stone and Boulder content of Swedish forest soils. Catena 77, 285–291.

Strickland, T.C., Fitzgerald, J.W., 1987. Bacterial production of organic sulfur in a forest litter extract. Soil Biol. Biochem. 19, 771–774.

Stumm, W., Morgan, J.J., 1996. Aquatic chemistry: Chemical equilibria and rates in natural waters. Wiley.

Stutter, M.I., Lumsdon, D.G., Rowland, A.P., 2011. Three representative UK moorland soils show differences in decadal release of dissolved organic carbon in response to environmental change. Biogeosciences 8, 3661–3675.

Tipping, E., Hurley, M.A., 1988. A model of solid-solution interactions in acid organic soils, based on the complexation properties of humic substances. J. Soil Sci. 39, 505–519.

Valinia, S., Futter, M.N., Cosby, B.J., Rosén, P., Fölster, J., 2015. Simple models to estimate historical and recent changes of total organic carbon concentrations in lakes. Environ. Sci. Technol. 49, 386–394.

Vestin, J.L.K., Norström, S.H., Bylund, D., Mellander, P.-E., Lundström, U.S., 2008. Soil solution and stream water chemistry in a forested catchment I: dynamics. Geoderma 144, 256–270.

Vuorenmaa, J., Forsius, M., Mannio, J., 2006. Increasing trends of total organic carbon concentrations in small forest lakes in Finland from 1987 to 2003. Sci. Total Environ. 365, 47–65.

Walker, X., Johnstone, J.F., 2014. Widespread negative correlations between black spruce growth and temperature across topographic moisture gradients in the boreal forest. Environ. Res. Lett. 9, 1–9.

Watmough, S.A., Aherne, J., Alewell, C., Arp, P., Bailey, S., Clair, T., et al., 2005. Sulphate, nitrogen and base cation budgets at 21 forested catchments in Canada, the United States and Europe. Environ. Monit. Assess. 109, 1–36.

Wieder, R.K., Lang, G.E., 1988. Cycling of inorganic and organic sulfur in peat from big run bog, West Virginia. Biogeochemistry 5, 221–242.

Wilson, H.F., Xenopoulos, M.A., 2008. Ecosystem and seasonal control of stream dissolved organic carbon along a gradient of land use. Ecosystems 11, 555–568.

Winterdahl, M., Futter, M., Köhler, S., Laudon, H., Seibert, J., Bishop, K., 2011b. Riparian soil temperature modification of the relationship between flow and dissolved organic carbon concentration in a boreal stream. Water Resour. Res. 47, W08532.

Winterdahl, M., Erlandsson, M., Futter, M.N., Weyhenmeyer, G.A., Bishop, K., 2014. Intra-annual variability of organic carbon concentrations in running waters: drivers along a climatic gradient. Glob. Biogeochem. Cycles 28, 451–464.

Zetterberg, T., Köhler, S.J., Löfgren, S., 2014. Sensitivity analyses of MAGIC modelled predictions of future impacts of whole-tree harvest on soil calcium supply and stream acid neutralizing capacity. Sci. Total Environ. 494, 187–201.