

Linking major and trace element concentrations in a headwater stream to DOC release and hydrologic conditions in a bog and peaty riparian zone



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ABSTRACT

In the organic-rich environments of peatlands and peaty riparian zones, dissolved organic matter (DOM) can act as a carrier for major and trace elements. However, the mobilization and export patterns of elements from these systems are largely unknown. This study elucidates the annual and short-term event-based dynamics of major and trace element concentrations in a headwater stream draining an ombrotrophic peatland and a peaty riparian zone. Elements are expected to exhibit specific export patterns depending on their biogeochemical reactivity and source area. We hypothesize that most elements are released during organic matter decomposition and are co-transported with DOM in the bog catchment, whereas in the riparian zone, other element pools, such as shallow groundwater, also play a major role.

Most of the variance in the data, as revealed by Principal Component Analysis, integrated the DOM concentration pattern (element loadings > 0.8: Al, Ca, Fe, Mg, Mn, Zn, Li, Co, As, Sr, Cd, Pb, and DOC). Ca, Mg and Sr were also found to load on this principal component, suggesting that the main control on element mobilization is not DOM, but rather similar source areas and mobilization processes. The DOM-related export was driven by plant uptake, plant decomposition and the bog water level in terms of hydrologic connectivity. The differences between the bog and the riparian zone were mainly driven by different hydrologic conditions and additional elemental sources, such as mineral weathering. The export patterns of Rb, Cs, K, NO₃⁻ and SO₄²⁻ were predominantly controlled by the season and plant uptake, and they were particularly exported by a surficial fast flow path. In addition to other elements, Ga, Y and Ba were enriched in the upper peat and organic soil layer, likely due to anthropogenic pollution. The specific export pattern of these latter elements indicates their predominant mobilization by the dissolution of dust particles and their subsequent mobilization by coupling to DOM.

1. Introduction

Peatlands and peaty riparian zones store large amounts of organic carbon as peat. Peatlands are a large carbon sink and export large amounts of dissolved organic matter (DOM) to surface water (Aitkenhead et al., 1999; Laudon et al., 2004; Seibert et al., 2009; Strohmeier et al., 2013; Worrall et al., 2002). Both landscapes are known to play a major role in headwater stream chemistry, and riparian zones (RZ) have recently been recognized as biogeochemical “hotspots” (Kuglerová et al., 2014; Tiwari et al., 2017). Peaty riparian zones mainly develop when hill slope groundwater flow converges along streams, creating a waterlogged environment. Even though riparian zones cover only a small area of the catchment, they can have a strong impact on water chemistry (e.g., Tiwari et al., 2017). The characteristic direct interface of the riparian zone with the stream channel leads to a

high impact on stream element concentrations such as nutrients, base cations, metals and trace elements (Ledesma et al., 2013; Seibert et al., 2009; Tiwari et al., 2017). Peatlands, as well as peaty RZ, have the potential to store large amounts of major and trace elements, which are retained by organic matter. Industrialization, fuel combustion and regional mining activities have caused the anthropogenic deposition rates of many elements to far exceed their natural, preindustrial fluxes. For bogs that receive elemental input exclusively from atmospheric deposition, concentrations of up to 2300 mg kg⁻¹ for Pb, 100 mg kg⁻¹ for As and 525 µg kg⁻¹ for Hg in the upper peat layer were reported (Biester et al., 2012). In this environment, DOM might act as a major carrier for metal transport to streams, especially for those elements that otherwise have low solubility, such as U or La (Ingri et al., 2000; Köhler et al., 2014; Lidman et al., 2014; Neubauer et al., 2013a, 2013b). However, iron (oxy)hydroxides have also been found to be important

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carriers for trace elements (Pokrovsky et al., 2006; Pokrovsky and Schott, 2002; Tipping, 1981). Due to their high DOM concentrations and low mineral contributions, headwater streams draining peatlands are naturally acidic, which enhances the solubility of many elements such as iron or aluminum (Tipping et al., 2003). Studies focusing on the influence of peaty riparian zones on stream water quality are mainly limited to DOC and the boreal region. Lidman et al. (2017) presented a comprehensive study of the enrichments of major and trace elements in the riparian zone and the transfer from soil water to receiving surface waters in the boreal region of Sweden. In the same area, Ledesma et al. (2013) described the different export patterns of base cations to surface waters, highlighting the role of the riparian zone. Neubauer et al. (2013b) showed that Cu, Ni, Al and rare earth elements were mainly exported in association with DOM in an Austrian bog runoff, while As and Pb were associated with iron organo-mineral complexes. The role of short-term high-discharge events on stream element concentrations in peatland catchments has been demonstrated for As, Pb, Ti and V exports from peatlands (Broder and Biester, 2015; Graham et al., 2006; Rothwell et al., 2007). A recent increase in DOM concentrations, especially in northern European streams, is attributed to decreases in acid rain deposition or temperature rise (Evans et al., 2005; Freeman et al., 2001; Monteith et al., 2007). Due to the importance of high-discharge events for DOM export from bogs and peaty riparian zones, the predicted changes in precipitation patterns, with more dry periods and frequent heavy rain events (IPCC, 2013), might export even more DOM (e.g., Broder and Biester, 2015; Clark et al., 2007; Grabs et al., 2012; Worrall et al., 2002). Such changes in DOM export will also affect the export of elements from these systems, which might serve as nutrients or act as toxic pollutants in receiving streams. However, until now, the mechanisms controlling major and trace metal mobility and their export in peatland soils have not been well understood.

Although bogs and peaty RZ share an organic-rich and generally wet nature, they differ in terms of their hydrology, mineral soil layer and nutrient status (see Table 1). This results in different biogeochemical conditions, element cycling and finally element export to headwater streams. In contrast to riparian zones or fens, bogs are exclusively rain-fed and only occur when annual precipitation rates are high. The uppermost peat layer of bogs, the acrotelm, is the most active part of the peat body, due to vegetation, water level fluctuations and the resulting aeration of this peat layer. However, the mean water level is generally high in bogs. Within the acrotelm most of the discharge is also generated, as the hydrologic conductivity strongly decreases in the catotelm, which is the deeper peat layer (Evans et al., 1999; Holden and Burt, 2003). Therefore, the influence of the underlying mineral bedrock on element concentrations in the upper peat layer or the draining headwater stream is negligible (Broder and Biester, 2015).

At the peaty RZ, the hydrologic connectivity is different than that of a bog system and is rather similar to that of minerotrophic fens. The high connectivity to the adjacent stream, as well as the water inflow from the uphill catchment, causes frequent and faster water table fluctuations. This results in the higher aeration of the organic-rich upper soil layer and consequently in higher decomposition rates. During base flow conditions, discharge is dominated by shallow

groundwater flow through the mineral soil layer, whereas increasing discharge steadily connects the upper organic-rich soil layer (Broder and Biester, 2015). The connection to uphill mineral soils can be a source of additional dissolved or particulate mineral element input to the RZ.

Thus, major and trace elements might have different sources in bogs and peaty RZ and different biogeochemical and hydrological conditions, which affect the processes of decomposition, complexation, diffusion, adsorption and percolation that control the different element mobilization and export patterns at the bog and RZ. To evaluate the export patterns of major and trace elements, they can be grouped according to their occurrences in bogs and peaty riparian zones and their biogeochemical behavior. Those pooled elements are expected to have similar export patterns, which should enable us to understand the sources and controls of stream element concentrations. The distinguishing features of these groups include whether elements are subjected to plant uptake, have a high or low affinity to organic matter or behave conservatively, and whether they are released during decomposition processes or the weathering of dust particles.

Elements that are subjected to rapid plant uptake mainly cycle in the uppermost soil layer of the bog and the RZ and include nutrients such as potassium or nitrate. The conservative elements include base cations with no biological interactions and low affinity to organic matter. These elements probably originate from the mineral soil layer or shallow groundwater at the RZ, as they are mainly sourced from weathering.

In bogs, however, these elements originate exclusively from atmospheric deposition and probably exhibit a contrasting export pattern. In areas influenced by mining, great amounts of dust particles can be buried and retained in the acrotelm peat layer at the bog, as well as in the organic layer of the peaty RZ. Depending on their biogeochemical reactivity, those elements might have a specific export pattern. Especially, as those elements are normally located in groundwater sources but are enriched in the organic soil layer at these contaminated sites, their affinity to organic, humic substances or mineral phases such as iron oxides is important. Elements that are mobilized by decomposition and have a high affinity for organic matter should show the same export pattern as DOM. However, elements incorporated in organic matter can also be released as dissolved elements to the soil solution by decomposition processes, such as the mineralization of organic matter (Bragazza et al., 1998; Grybos et al., 2007). At the peaty RZ, more frequent water table fluctuations and consequently higher decomposition processes in the peaty riparian zone might enhance this element mobilization process. Additionally, redox-sensitive elements such as Fe, Mn, U or Cr might be strongly influenced by the redox gradient with peat depth when anoxic conditions prevail. Therefore, redox-induced processes such as Fe-oxide precipitation (Riedel et al., 2013) can play a pivotal role, as elements are adsorbed and co-precipitated. The reductive dissolution of these oxides would also release co-precipitated elements (Grybos et al., 2007).

The presented study aims to elucidate spatiotemporal major and trace element concentration dynamics from a bog and a peaty riparian zone catchment to gain a further understanding of the generation and

Table 1
Summary of the main characteristics of bogs and peaty riparian zones.

Character	Bog	Peaty riparian zone
Hydrology	- Hydrologic conductivity high in uppermost peat layer, exponential decrease with depth - Low water level fluctuations (~0–30 cm) - No groundwater influence	- Hydrologic conductivity comparably high through whole soil profile. - Large water level fluctuations - Groundwater influence
Element input	Atmospheric deposition	Shallow groundwater, mineral weathering, atmospheric deposition
Nutrient status	Poor	Generally richer than bogs
Mineral soil layer	None	Existent
Organic soil layer	Exclusively present (> 30 cm)	Present (> 15 cm)

controls of element export. Both systems are critical for headwater stream chemistry, but respond differently to changing hydrological conditions. We hypothesize that in these organic-rich systems, DOM concentrations are a major predictor of element concentrations that have a high affinity for organic matter and are released to pore waters by the same mobilization processes, i.e., decomposition. Based on previous studies of DOC (Broder et al., 2017), we expect that hydrologic (pre)conditions and seasonality have great impacts on element stream concentrations, causing either concentration peaks or a dilution effect during high-discharge events. We assume that concentrations in the riparian zone are more affected by changes in hydrologic conditions than those at the bog site due to changing hydrologic flow paths. Furthermore, we expect that elements, depending on their biogeochemical reactivity and origin within each system, exhibit specific export patterns. Therefore, patterns in element concentrations reflect element sources, e.g., shallow groundwater, the organic-rich upper soil layer in the riparian zone or the near-surface peat layer in the bog catchment. Additionally, export patterns might reflect whether elements occur bound to organic matter or as a mineral phase in dust particles. It might also allow us to derive hypotheses on element mobilization in the peat body or riparian zone.

To test our hypotheses, we chose a headwater stream catchment in the Harz Mountains (Germany). The Odersprung stream originates within a bog and further discharges through a peaty riparian zone. The site was exposed to high anthropogenic deposition in the past, which led to an enrichment of metals in the organic layer or upper peat layer. High-discharge events were specifically considered in our sampling design. We reduced the complexity by means of principal component analysis, with the aim to group elements with similar export dynamics.

2. Materials and methods

2.1. Study area

The Odersprung catchment (51°46.3830 N, 10°33.8160 E, elevation approximately 800 m a.s.l.) is located in the Harz Mountains in northern central Germany. The headwater stream originates as an erosion rill in the Odersprung bog. Thus, the subcatchment is limited to parts of the bog area (sampling site 1, Fig. 1) until the stream enters the adjacent spruce forest, which has mineral soils and a peaty riparian zone (sampling site 2, Fig. 1). The stream hydrology is characterized by

a quick response to rainfall events. A detailed description of the hydrologic regime is given in (Broder and Biester, 2015). The bog vegetation mainly consists of *Sphagnum magellanicum* and *S. rubellum*, associated with *Eriophorum angustifolium* and *Molina caerulea* (Baumann, 2009). The riparian zone is covered by *Picea abies* and *Vaccinium myrtillus*. The mean peat depth is approximately 3 m at the bog site, while the riparian zone has accumulated up to 1 m of organic deposits. Historic mining activities in the Harz Mountains dating back to the Roman time period contributed to the high anthropogenic deposition of many trace elements such as As, Pb, Zn, or Cu (Dalitz, 1994; Kempter and Frenzel, 2000), which led to their enrichment in the upper layer of the regional bogs and the organic soil layer in the Harz Mountains (Biester et al., 2012).

2.2. Water sample collection and on-site monitoring

Discharge water sampling was conducted from snowmelt until the beginning of snowfall in 2013 and 2014. Water samples were taken by an automated water sampler (ISCO 3700, Teledyne, USA) in a six-day interval. The Teflon hose was automatically rinsed with sample water before each sampling. To ensure sample quality, blank samples were run and grab samples were taken occasionally in 50 mL PE tubes, which were previously rinsed twice with sample. High-resolution storm event sampling in a 3-h interval was conducted at several occasions in spring and fall. During snowmelt periods, a diurnal sampling resolution was applied. For discharge quantification, a V-notch weir was installed at the bog outlet. The water stage at the discharge weir and water level within the bog were monitored in 15-min. intervals by means of a water level logger (Odyssey Dataflow Systems, New Zealand). Temperature, humidity and precipitation (using a tipping-bucket rain-gauge and tinytag tgp 4500 and 4810, Gemini, Belgium) were monitored on site during the whole sampling period.

2.3. Element analyses

All water samples were vacuum filtered with a 0.45 µm nylon filter and stored at 4 °C. Samples were analyzed for total dissolved organic carbon by thermo-catalytic oxidation using the NPOC method (non-purgeable organic carbon; Analytik Jena multi N/C 2100S, Germany). Major and trace element concentrations (Al, As, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, K, La, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, S, Sb, Se, Sr, U,

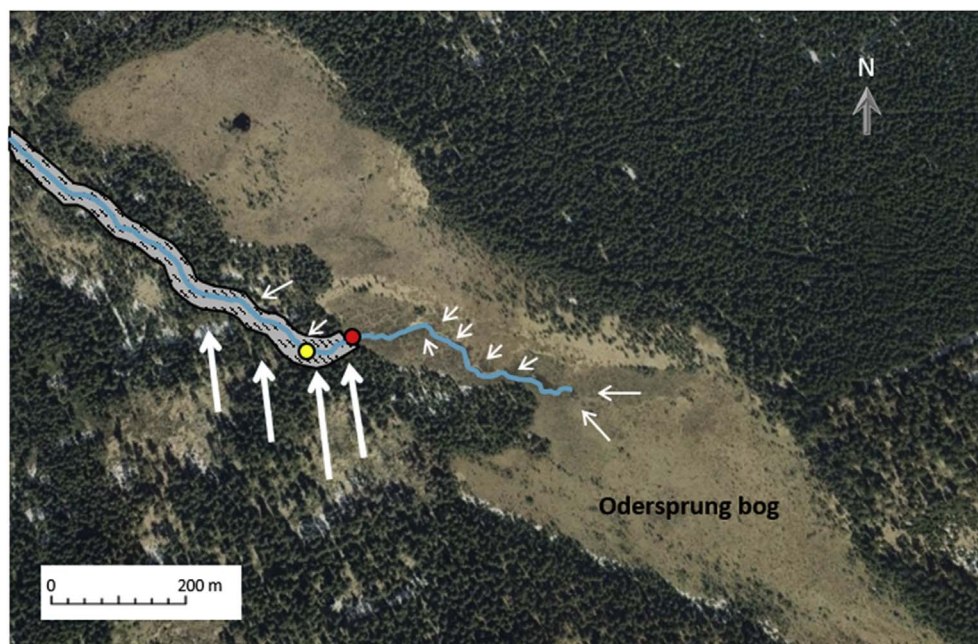


Fig. 1. Study area in the Harz Mountains. The sampling locations are marked as red (bog site) and yellow (RZ) circles. The dashed area indicates the wet, organic-rich riparian zone; the white arrows indicate water flow directions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

V, Y, Zn, Zr) were determined by means of an ICP-OES (Varian 715-ES, USA) and an ICP-MS (Agilent 7700; USA). The measurement quality was checked by certified reference materials (SPS-SW 1 and SLRS-4, riverine water, National Research Council, Canada). Concentrations of chloride, nitrate and sulfate were analyzed by ion chromatography with chemical suppression and conductivity detection (Metrohm, 761 Compact IC, Swiss).

2.4. Statistical methods and flux calculations

The datasets of all stream water samples were grouped for each site (bog and riparian zone) and split into a low-resolution annual record and a high-resolution event sampling record for separate principal component analysis (PCA). PCA was performed on z-transformed stream water concentration data using a varimax rotation solution and providing that the Kaiser-Meyer-Olkin Measure of Sampling Adequacy was > 0.7. The discussed results include all PCs explaining 10% or more of the total variability. Overall, the included PCs explained 69% (bog annual data set)–78% (forest event data set) of the total variability of the analyzed data set. All PCs with element loadings can be found in the Supplement. A Pearson correlation analyses (2-tailed, 0.01 level of significance) was also conducted on the z-transformed datasets. Significant differences between sites (bog and riparian zone) and data sets (annual and event) were tested by the Mann-Whitney test (0.05 level of significance). All statistics were performed using IBM SPSS Statistics 24.

Annual element fluxes, as well as fluxes of the highest discharge during 10% of the time record were calculated using Equation (1) according to method 5 of Walling and Webb (1985) and Littlewood (1992):

$$Load = K \times Q_r \left(\frac{\sum_{i=1}^n C_i Q_i}{\sum_{i=1}^n Q_i} \right) \quad (1)$$

where the conversion factor K comprises the number of seconds per year or 10% of the annual time record. Q_r is the mean discharge calculated from the continuous discharge measurements for the respective time interval, and C_i and Q_i are the measured instantaneous concentrations and corresponding discharge measurements, respectively. The numbers (n) of samples were 170 and 29, respectively. Fluxes were obtained by dividing the calculated loads by the catchment size. The standard error and 95% confidence limits were calculated after Hope et al. (1997).

3. Results and discussion

3.1. Stream water chemistry of the bog and riparian zone site

Almost all elements showed significantly different mean stream water concentrations at the two monitored sites (Mann-Whitney test, 0.05 level of significance). This only excludes Mg, Cu and chloride in the annual data set and Cr in the event data set (Table 2). Fig. 2 displays increasing or decreasing element concentrations from the bog to the riparian zone expressed as the ratio of the average element concentrations in the riparian zone to the average values of the bog site (enrichment factor). The majority of element concentrations were higher at the site influenced by the riparian zone than at the bog site (enrichment factors > 1), where stream water exclusively originated from the ombrotrophic peatland (Fig. 2). The enrichment factors were even higher when comparing concentrations during the high-resolution measurements, which mainly comprised high-discharge events. The highest increase in concentration was measured for NO_3^- (enrichment factors of 7.3 and 10.4, respectively) followed by Al, Rb, K, Zr, La and Pb, which had concentrations more than twice as high as those at the bog site for both data sets. The relative concentration increase of DOC at the riparian zone was moderate, with factors of 1.2 for the annual

data set and 1.3 for the event data set. The significantly lower concentrations of most elements at the bog site reflect the nutrient-poor nature of the bog system and the absence of significant minerogenic water input within the bog and the sampled stream. The stronger increase of most elements at the riparian zone reflects the additional mineral source from uphill soils or the shallow groundwater. Higher nitrate levels are probably caused by the aeration of the organic layer, thus enhancing decomposition processes and thereby fueling nitrification but inhibiting anaerobic denitrification. Additionally, the difference in vegetation and higher deposition rates under spruce forest stands compared to a treeless *sphagnum*-dominated bog results in a higher nitrogen supply (Böhlmann et al., 2005). Higher stream concentration levels of Al, U and La at a boreal forested site compared to a bog site have previously been reported (Köhler et al., 2014). Compared to the concentration levels given by Lidman et al. (2014) for an uncontaminated boreal catchment, the concentrations for Cu and Ba were high, while those of Cr, U and Y were similar and those of Al, Ca, La, Mg, Na, Ni and Sr were lower. Rothwell et al. (2007, 2011) reported As, Cu, Ni, Pb, V and Zn stream concentrations from a bog catchment (Upper North Grain), which is similarly polluted by mining and industrial activities. Compared to the concentrations there, the concentration levels at our contaminated bog catchment were generally lower, except for Pb.

Elements were enriched at the riparian zone compared to the bog site, and significant concentration differences were also monitored between the annual and the event data sets at each site. At the bog site, most element concentrations, including DOC, were significantly lower in the event data set, indicating decreasing concentrations when discharge was high. Only Y, Ba and Ga significantly increased (Fig. 2, Table 2). At the riparian zone stream, concentrations decreased only moderately during event sampling, and a greater fraction even increased. However, concentrations of DOC show a similar shift to moderately lower concentrations during high-discharge events similar to the bog site. The contrasting concentration trends between the sites have been described previously by Björkvald et al. (2008) and Köhler et al. (2014) for Fe, Mn, Al, U and La in a boreal catchment. These concentration changes reflect the different hydrologic responses to rainfall events in both systems. At the bog site, the water level is generally high and fluctuates in the upper 30 cm peat depth. Under dry preconditions, additional water input thus connects surficial element pools. However, wet preconditions or longer rainfall events quickly cause a dilution effect when discharge increases and fast surface and overland flow paths start to develop (Broder and Biester, 2015). In contrast to the bog, the riparian zone is subjected to lower water levels under base flow conditions and a rise of water level during rainfall events connects the organic-rich upper soil layer and concomitant additional element pools (Broder et al., 2017; Grabs et al., 2012; Hood et al., 2006). The lower element concentrations, especially during events at the bog site compared to the riparian zone, note that bogs do not primarily contribute to peak stream concentrations during events. In contrast, the concentration increases during high-discharge events at the riparian zone emphasize its major role for stream water element concentration variability induced by hydrologic conditions, even though it covers a smaller catchment area than the bog. It may be assumed that the dynamic at the peaty riparian zone is also valid for percolating minerotrophic fens. Degraded bogs also generate larger water level fluctuations with concomitant increased decomposition and a strong decline in hydrologic conductivity (Fraser et al., 2001). These degraded systems might exhibit greater concentration increases than bogs during high-discharge events, due to the hydrological connection of larger additional pools after dry conditions, whereas they also lack additional groundwater sources.

The Principal Component Analysis of each data set successfully reduced the complexity by grouping elements with similar export patterns on one Principal Component (PC). All four PCA produced similar element groups, strengthening the causal coherence behind this statistic

Table 2

Pearson correlation coefficients (R^2) for DOC to element concentrations (after z transformation) for the bog and riparian zone, annual and event data sets. Only significant correlations at a level of 0.01 are included. Concentrations are given as the means with standard deviations (SD). Asterisks indicate a significant difference in mean concentrations between the two sites.

element	Bog				RZ			
	Annual		Event		Annual		Event	
	R^2	Mean c. \pm SD [$\mu\text{g L}^{-1}$]	R^2	Mean c. \pm SD [$\mu\text{g L}^{-1}$]	R^2	Mean c. \pm SD [$\mu\text{g L}^{-1}$]	R^2	Mean c. \pm SD [$\mu\text{g L}^{-1}$]
Al	0.701	76 \pm 39*	0.976	53 \pm 29*	0.552	229 \pm 99*	0.448	262 \pm 90*
As	0.901	1.1 \pm 0.3*	0.981	0.90 \pm 0.43*	0.776	1.7 \pm 0.4*	0.909	1.60 \pm 0.5*
Ba		3.3 \pm 1.9*		4.8 \pm 2.7*		4.7 \pm 1.8*		6.7 \pm 2.8*
Be		0.05 \pm 0.03*	0.330	0.05 \pm 0.02*	0.350	0.06 \pm 0.02*	0.670	0.06 \pm 0.02*
Ca	0.888	310 \pm 120*	0.949	220 \pm 190*	0.805	400 \pm 130*	0.923	340 \pm 180*
Cd	0.779	0.14 \pm 0.05*	0.811	0.11 \pm 0.07*	0.696	0.20 \pm 0.07*	0.862	0.19 \pm 0.08*
Cl ⁻	0.575	1.1 * 10 ³ \pm 0.4 * 10 ³	0.856	0.7 * 10 ³ \pm 0.6 * 10 ³ *	0.431	1.2* 10 ³ \pm 0.4 * 10 ³	0.777	0.8 * 10 ³ \pm 0.5 * 10 ³ *
Co	0.629	0.09 \pm 0.03*	0.899	0.07 \pm 0.03*	0.783	0.12 \pm 0.03*	0.892	0.11 \pm 0.04*
Cr	0.383	0.48 \pm 0.19*	0.605	0.43 \pm 0.20	0.556	0.57 \pm 0.18*	0.937	0.46 \pm 0.17
Cs		0.02 \pm 0.02*	0.494	1.1 0.01*		0.04 \pm 0.02*		0.03 \pm 0.01*
Cu		4.0 \pm 4.4		1.9 \pm 1.2*		3.4 \pm 2.6	0.392	1.9 \pm 0.5*
DOC		24 * 10 ³ \pm 7* 10 ³ *		19 * 10 ³ \pm 9 * 10 ³ *		30 * 10 ³ \pm 6 * 10 ³ *		25 * 10 ³ \pm 8 * 10 ³ *
Fe	0.922	217 \pm 67*	0.910	184.5 \pm 94.7*	0.890	300 \pm 87*	0.937	270 \pm 102*
Ga		1.1 \pm 0.5*		1.4 \pm 0.7*		1.4 \pm 0.5*		1.8 \pm 0.6*
In	-0.342	0.09 \pm 0.11*	-0.296	0.07 \pm 0.11*	-0.387	0.11 \pm 0.10*	-0.482	0.15 \pm 0.11*
K		70 \pm 80*		30 \pm 40*	-0.363	170 \pm 170*	-0.302	240 \pm 160*
La	0.465	0.09 \pm 0.04*	0.313	0.07 \pm 0.04*	0.566	0.20 \pm 0.09*	0.679	0.20 \pm 0.08*
Li	0.728	0.21 \pm 0.08*	0.958	0.15 \pm 0.09*	0.449	0.39 \pm 0.17*	0.843	0.32 \pm 0.12*
Mg	0.883	150 \pm 60	0.945	100 \pm 90*	0.718	170 \pm 60	0.905	130 \pm 80*
Mn	0.742	3.6 \pm 1.7*	0.934	3.0 \pm 2.1*	0.407	6.1 \pm 2.4*	0.712	6.7 \pm 2.8*
Mo	0.316	0.10 \pm 0.05*	0.811	0.07 \pm 0.05*	0.385	0.12 \pm 0.06*	0.767	0.10 \pm 0.05*
Na	0.450	630 \pm 190*	0.831	460 \pm 190*	0.489	710 \pm 120*	0.679	630 \pm 170*
Ni	0.570	0.49 \pm 0.17*	0.718	0.34 \pm 0.20*	0.718	0.54 \pm 0.15*	0.926	0.44 \pm 0.16*
NO ₃ ⁻		60 \pm 90*		80 \pm 120*		404 \pm 720*		870 \pm 790*
Pb	0.821	6.1 \pm 2.4*	0.944	4.4 \pm 2.7*	0.684	12 \pm 5*	0.821	12 \pm 5*
Rb		0.37 \pm 0.29*	0.344	0.19 \pm 0.14*		0.95 \pm 0.73*	-0.305	1.3 \pm 0.6*
S		460 \pm 610*	0.600	240 \pm 200*	0.303	480 \pm 310*	0.541	410 \pm 230*
Se	0.579	0.22 \pm 0.07*	0.619	0.19 \pm 0.09*	0.641	0.28 \pm 0.07*	0.737	0.25 \pm 0.08*
SO ₄ ²⁻	-0.425	430 \pm 250*		450 \pm 190*		570 \pm 370*	-0.254	650 \pm 270*
Sr	0.818	2.0 \pm 0.8*	0.951	1.4 \pm 1.0*	0.841	2.5 \pm 0.8*	0.936	2.0 \pm 1.0*
U		0.03 \pm 0.02*	-0.399	0.03 \pm 0.01*	0.315	0.05 \pm 0.02*		0.05 \pm 0.01*
V	0.422	0.60 \pm 0.13*	0.576	0.60 \pm 0.15*	0.588	0.82 \pm 0.22*	0.557	0.86 \pm 0.18*
Y		0.16 \pm 0.14*	-0.490	0.25 \pm 0.16*		0.32 \pm 0.21*		0.48 \pm 0.22*
Zn	0.834	23 \pm 10*	0.944	17 \pm 15*	0.701	28 \pm 10*	0.826	23 \pm 17*
Zr	0.351	1.4 \pm 1.1*	0.704	0.72 \pm 0.56*		3.0 \pm 2.9*		2.2 \pm 0.9*

evaluation. In the following section, PCs with an explanatory power of > 10% will be discussed in terms of the represented element fraction, element sources and specific export pattern.

3.2. Elements related to DOM

The majority of element stream concentrations show a significant correlation to DOC concentrations at both sites (Table 2). However, as discussed in the next section, even elements with a significant correlation exhibit quite different export patterns. This questions the causal explanatory power of simple correlations. However, only Ca, Fe and Sr are strongly correlated with DOC in all four data sets with $R^2 > 0.8$. In general, more elements are strongly correlated with DOC at the bog site (additionally Mg, Zn, As, Sr, and Pb) than at the riparian zone, indicating an additional source such as shallow groundwater besides the upper organic-rich soil layer where DOM builds up. At both sites, more elements correlate when only samples from the event data set are considered.

Congruently with the results from the Pearson correlations, the first principal component (PC), which explains most of the variance, represents the DOC fraction at the bog site (Fig. 3). The PC 1 explains 35% of the total variance in the annual data set and as much as 50% in the event dataset. The majority of the analyzed elements load mainly on this component. A strong PCA correlation (> 0.8) was found for Ca, Fe, Mg, Mn, Zn, As, Sr and Cd at the annual record and additionally for Al, Li, Co, chloride and Pb for the event record. This implies that these

elements exhibit the same export pattern as DOC. A strong dependence of As and Pb export to DOC at this bog site was previously described (Broder and Biester, 2015). The stream concentrations of the elements that load on this PC are characterized by a strong dependence on season and hydrologic (pre)conditions in this system (Fig. 5). The general concentration pattern is characterized by the lowest concentrations during snowmelt and spring, whereas concentrations were highest in late summer and fall (Fig. 5). Lower concentrations during rain events under wet preconditions were attributed to an exhaustion effect as well as a dilution effect, when overland flow prevails. However, short-time high-discharge events have over-proportional contributions to element export, as they connect all available element pools, when the whole acrotelm contributes to the bog discharge (Broder and Biester, 2015). This is even the case when concentrations decrease, as this is compensated by discharging water quantities. The exports during 10% of the time record with the highest discharge were calculated to contribute 47% to Mg and Zn, 48% to Ca, 50% to Al, Fe and Sr, 52% to Mn, 59% to Cd, 60% to Co and 61% to annual chloride bog export (Table 3). This clearly highlights the importance of high-discharge events not only for DOC but also for other elements, which must be accounted for in export studies.

Although the results confirm that most elements exhibit the same export pattern as DOC, such correlations are not a verification of true co-transport with DOM (Neubauer et al., 2013b). As described previously, most discharge is generated in the acrotelm down to a depth of approx. 30 cm in this bog (Broder and Biester, 2015). Elements of

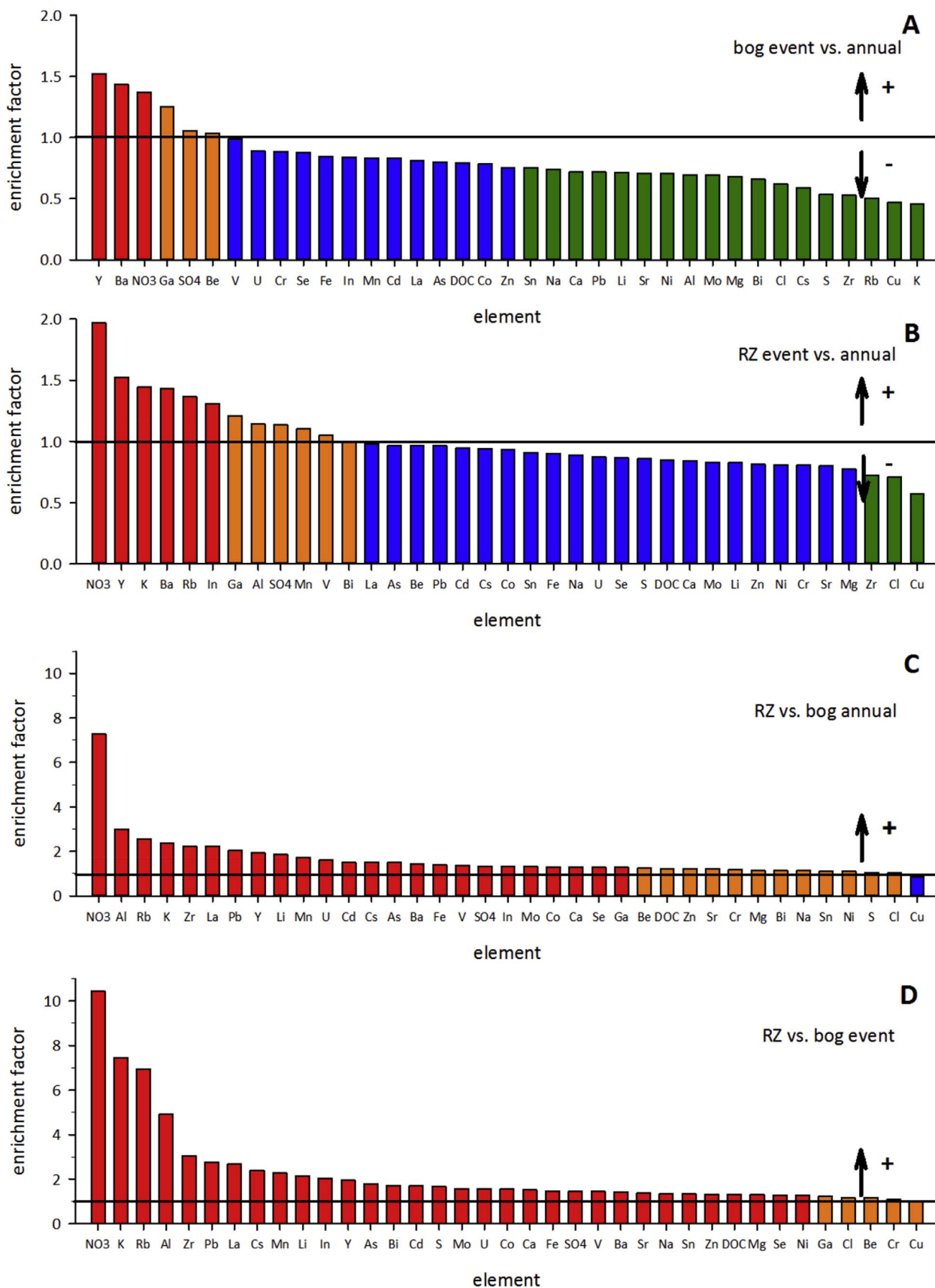


Fig. 2. Enrichment factors for all elements sorted from highest to lowest. Panels A and B display enrichments during events against the annual data set for the bog and the riparian zone (RZ) stream concentrations. Panel C and D depict enrichment factors of the RZ against the bog site for the event and annual data sets. Red-colored bars indicate an enrichment factor of > 1.25, and orange bars indicate factors between 1.25 and 1. Depletion factors between 1 and 0.75 are indicated by blue bars, and green bars represent depletions of < 0.75. The black line highlights the boundary between enrichment and depletion (enrichment factor of 1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

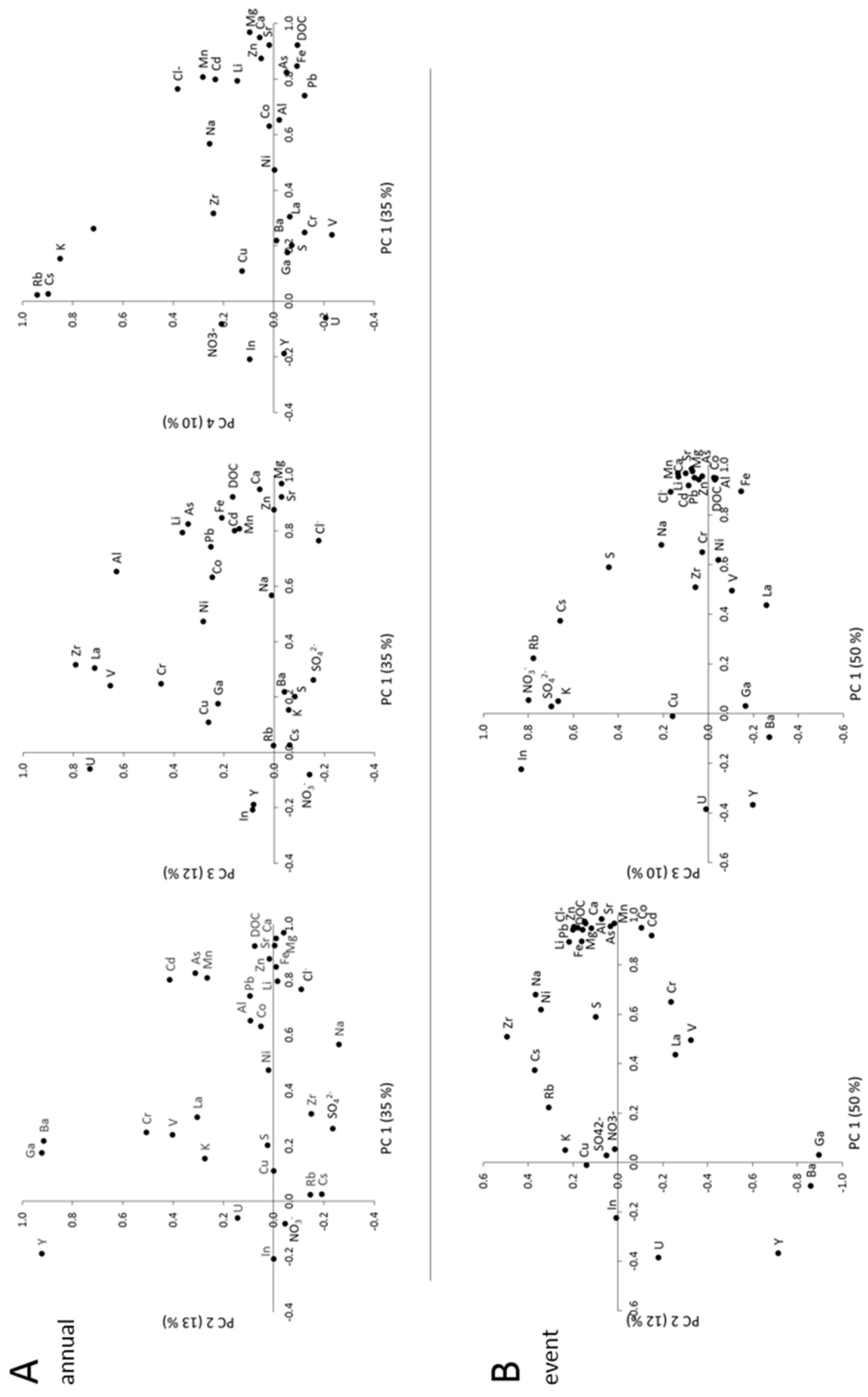


Fig. 3. Element loadings of the PCA at the bog site for the annual (A) and event (B) data sets. Only Principal Components (PC) explaining > 10% of total variance are depicted.

Table 3
Annual element exports from the bog, additionally differentiated by season (snowmelt, spring, summer, fall) and contribution of the highest 10% of discharge.

Element	Annual flux (g ha ⁻¹ a ⁻¹)	Seasonal distributions (%)				Contribution upper 10% discharge (%)
		Snowmelt	Spring	Summer	Fall	
Discharge		20	26	11	48	
Al	460 ± 95	5	15	17	63	50
As	7.8 ± 1.2	6	17	16	60	56
Ba	41 ± 8.0	5	46	12	38	64
Be	0.55 ± 0.06	11	24	16	49	70
Ca	1.95*10 ⁻³ ± 491	7	10	17	66	48
Cd	1.1 ± 0.2	7	18	15	60	59
Cl ⁻	8.0*10 ⁻³ ± 2.8*10 ⁻³	10	7	13	70	61
Co	0.76 ± 0.11	6	16	14	63	60
Cr	4.6 ± 0.7	5	23	11	61	70
Cs	0.2 ± 0.06	35	12	6	47	49
Cu	19 ± 4.7	11	23	11	55	50
DOC	166*10 ⁻³ ± 25*10 ⁻³	6	17	15	61	52
Fe	1.60*10 ⁻³ ± 294	5	16	14	65	50
Ga	14 ± 2.3	6	39	10	44	71
In	1.3 ± 0.5	67	8	5	20	89
K	636 ± 263	28	12	15	45	55
La	0.81 ± 0.11	1	27	10	62	64
Li	1.41 ± 0.23	10	13	17	61	55
Mg	909 ± 219	6	10	19	65	47
Mn	26 ± 5.0	9	14	19	58	52
Mo	0.7 ± 0.2	1	11	10	78	55
Na	4.26*10 ⁻³ ± 621	18	15	16	52	51
Ni	3.2 ± 0.6	4	16	16	65	52
NO ₃ ⁻	1.47*10 ⁻³ ± 659	42	9	3	47	87
Pb	41 ± 13	8	14	13	64	51
Rb	3.4 ± 1.3	38	11	8	43	48
SO ₄ ²⁻	6.75*10 ⁻³ ± 919	29	21	4	46	68
Sr	13 ± 2.8	7	13	18	63	50
U	0.36 ± 0.04	16	28	8	48	71
V	5.8 ± 0.5	10	26	13	51	63
Y	2.37 ± 0.4	15	41	7	37	69
Zn	148 ± 37	6	11	17	67	47
Zr	6.9 ± 1.8	4	10	19	67	50

mineral origin can only be derived from the deposition and accumulation of dust within the peat. Since the mineral soil phase is absent and organic matter is dominant, it is likely that elements occur as metal-organic complexes. Of the correlating elements, Fe, Al, As and Pb have a high affinity for organic matter and thus co-transport with DOM is likely, as has been shown in similar organic-rich systems (e.g., Helmer et al., 1990; Lidman et al., 2014; Neubauer et al., 2013a). Also, chloride, which is often assumed to be inert, is known to form organohalogen complexes in peat (Biester et al., 2004). However, elements such as Ca, Mg and Sr are known to have a low affinity for DOM (Lidman et al., 2014; Pokrovsky et al., 2006) and are thus suspected to be truly dissolved in these systems and to exhibit a different export pattern. However, the concentrations of these elements are low in a bog system, and Ca, Fe, Mg, Mn, and Sr are influenced by plant uptake (Bragazza et al., 1998; Griffiths and Sebestyen, 2016). Therefore, the main source of these elements in bogs is probably decomposition and the upper peat layer. Thus, elements that are normally attributed to groundwater influence and do not preferentially bind to organic matter can be clearly related to upper peat layer sources in these organic-rich systems. Moreover, other elements (e.g., Cr, Cu, La, U, Y) that have a high affinity for DOM and have been found to highly correlate with DOC concentrations in other catchments (Ingri et al., 2000), exhibit different export dynamics. These findings suggest that the main control on correlating export patterns is not affinity to DOM, but rather the same source area and the same mobilization process within the peat. In this case, the dominating mobilization processes of these elements are decomposition and concurrent transport when sources get connected depending on hydrology. Therefore, seasonality and hydrologic pre-conditions mainly determine element export patterns as microbial decomposition processes strongly depend on temperature. In addition,

hydrologic conditions within the bog determine the readily mobile element concentrations as the pool builds up until it gets hydrologically connected and depleted due to transport to the discharging stream.

At the riparian zone, the first component explains a great part of the data variability, with 29% of the annual data set and 46% of the event data set. However, the annual PCA displays no clear DOC component, as DOC seems to load on both PC 1 (0.76) and PC 2 (0.50) (Fig. 4). High loadings on PC 1 and low susceptibility to PC 2 show Mg, Zn, Sr, Ca, and Na and Cl moderately. Those elements are truly dissolved and mobile (Jarvie et al., 2012; Pokrovsky et al., 2006). Contrarily, PC 2 mainly represents La, U, Al, V, and Pb. Those elements are normally less mobile but are known to bind to DOM. A groundwater contribution to the stream water concentrations of these elements is thus likely. This is supported by the higher enrichment factors between the bog and the riparian zone for these elements compared to DOC, especially for Al, La and Pb (> 2 EF; Fig. 2). However, those elements are also known to be enriched in the upper soil profile (Pokrovsky et al., 2005; Tyler, 2004, 2005), except for Al, which is also due to the anthropogenic pollution by mining activities in the Harz Mountains (Biester et al., 2012 and unpublished data).

The annual sample score record shows that samples during higher discharge mainly have high scores on PC 2, whereas summer drought samples, where the shallow groundwater contribution to discharge is highest, have low scores on PC 2 (Fig. 6). In general, the variability of PC 2 over the annual record is high, with lower values during base flow and peaks during small events. The component was only diluted under extraordinarily high discharge conditions such as one fall event in 2014 where overland flow probably prevailed (Fig. 6). This pattern indicates that the elements La, U, Al, V, and Pb (PC 2) probably do not originate from shallow groundwater but that the source is located in the peaty

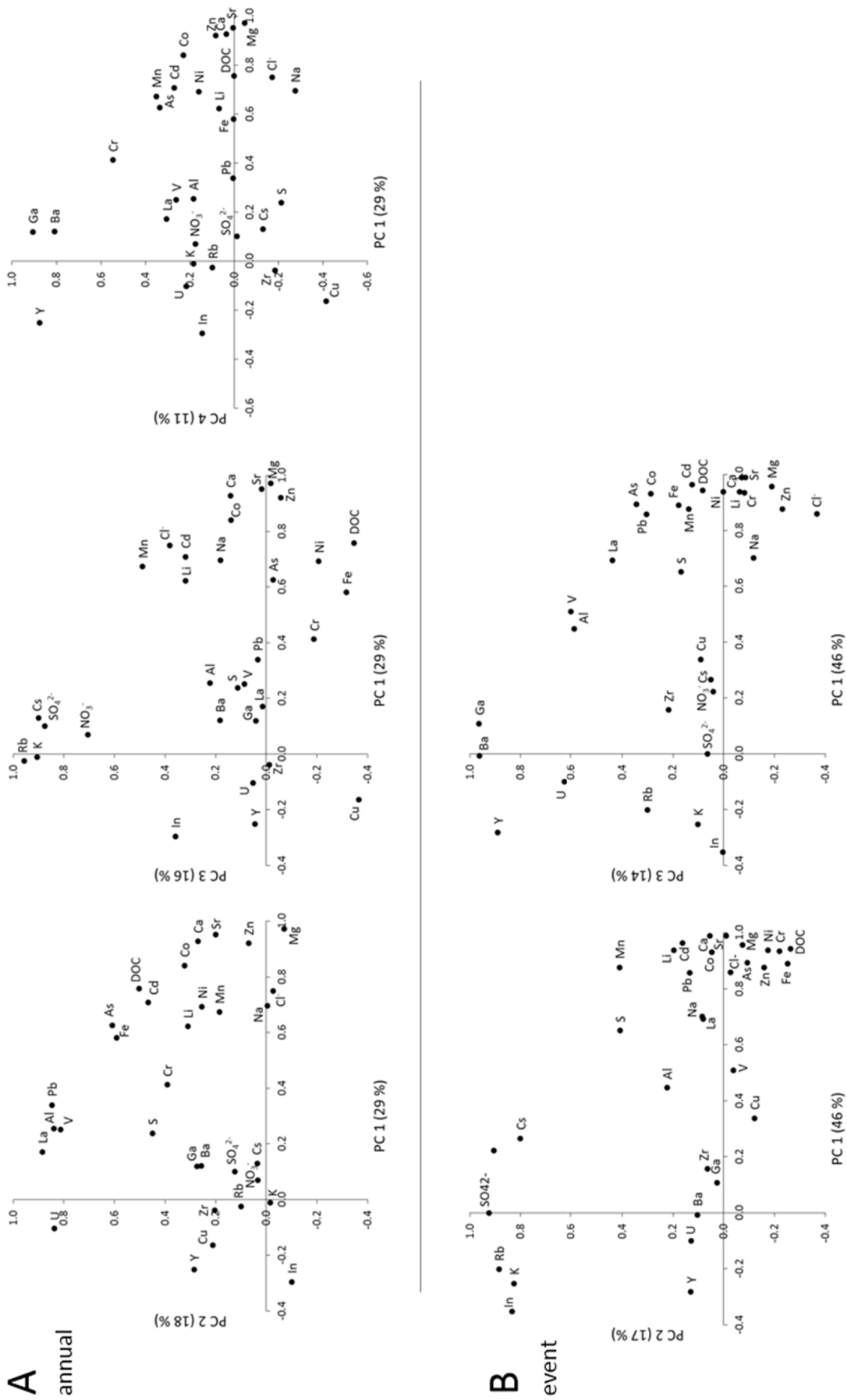


Fig. 4. Element loadings of the PCA at the riparian zone site for the annual (A) and event (B) data sets. Only Principal Components (PC) explaining > 10% of the total variance are depicted.

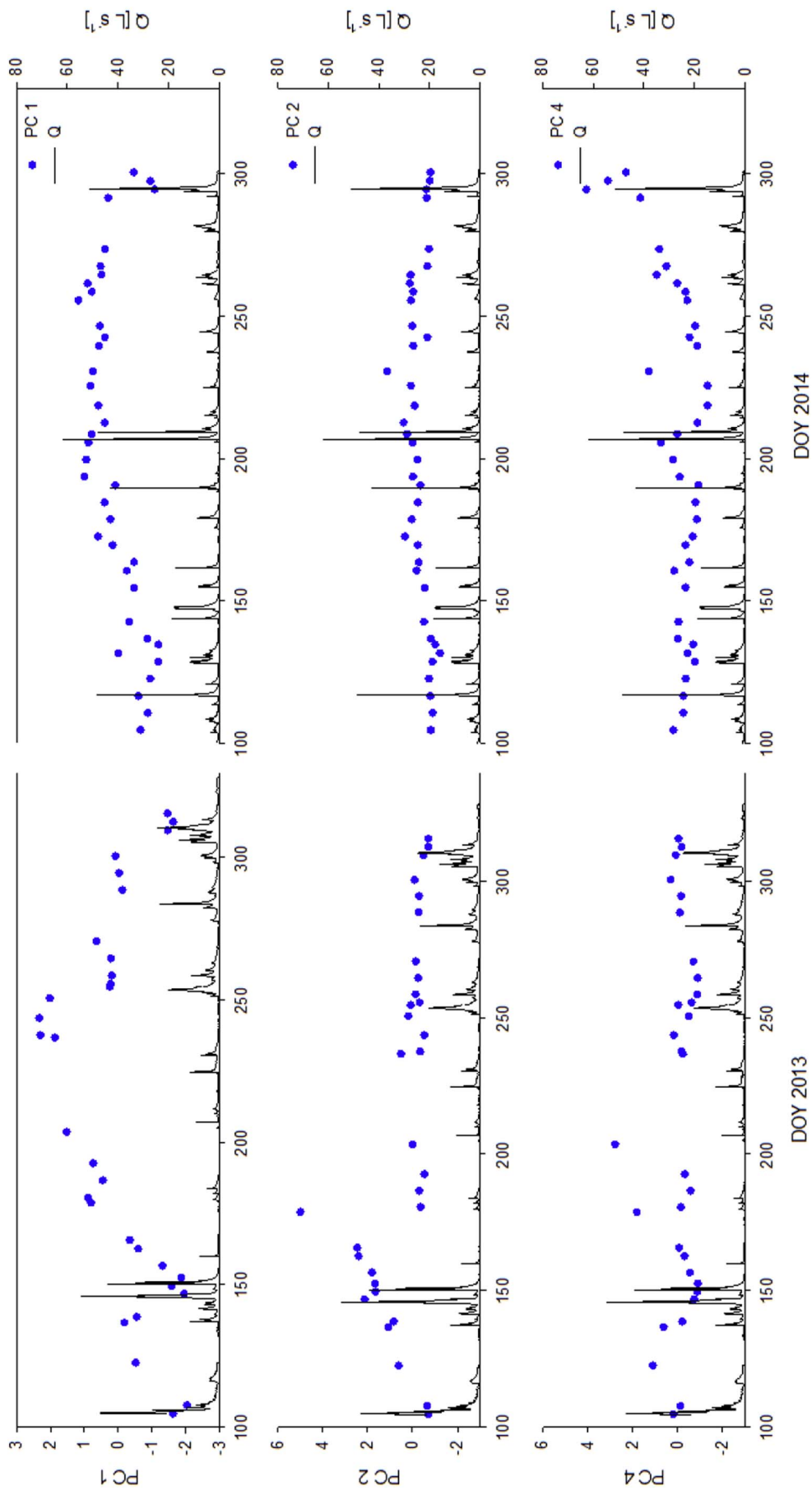


Fig. 5. Annual record of the principal components (PC) at the bog site. Blue points indicate sample scores, and the black line represents the discharge record. PC 1: DOC and related elements; PC 2: Y, Ga, Ba; PC 4: Rb, Cs, K, SO_4^{2-} . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

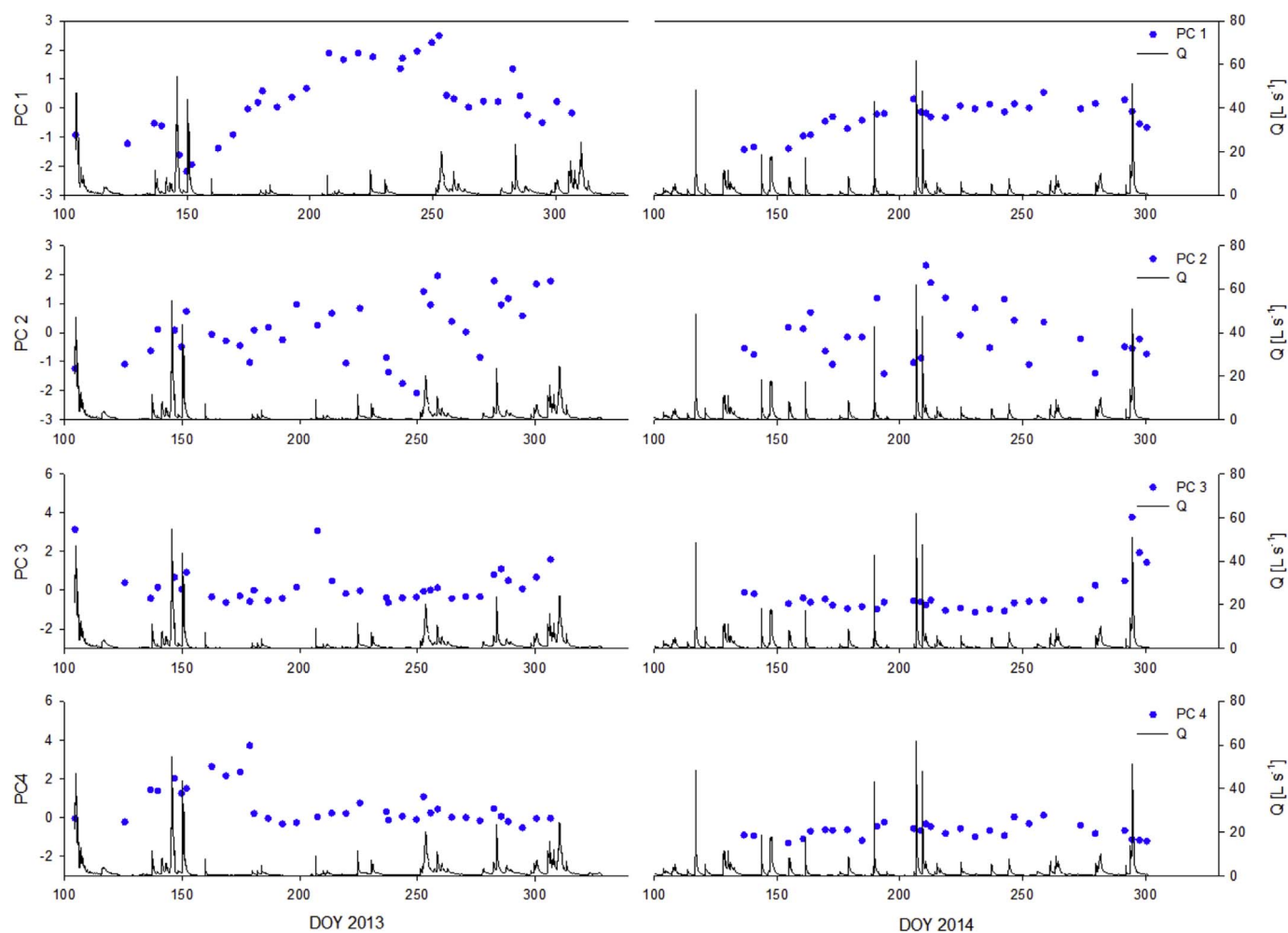


Fig. 6. Annual record of the principal components (PC) at the riparian zone site. Blue points indicate sample scores, and the black line represents the discharge record. PC 1: Mg, Zn, Sr, Ca, Na, Cl, Cd, DOC; PC 2: La, U, Pb, Al, V; PC 3: Rb, K, Cs, SO_4^{2-} , NO_3^- ; PC 4: Ga, Y, Ba. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

soil layer of the riparian zone itself, which is hydrologically connected when the water level increases during rainfall events (Broder et al., 2017). This is also in line with the results of the riparian zone event data set, where most of these elements, which represent PC 2 in the annual data set, score on a clear DOC component. This data set mainly represents high-discharge events where the peaty soil layer becomes hydrologically connected and DOC concentrations mainly originate from these layers.

In contrast, the concentrations of Mg, Zn, Sr, Ca, Na and Cl indicated by scores of PC 1 show a steady increase during summer drought in 2013 and scores during the wetter year 2014 that were lower than those in 2013 (Fig. 6). This suggests that the elements of PC 1 (Mg, Zn, Sr, Ca, Na, Cl) are exported by shallow groundwater at the riparian zone. It also seems that PC 1 is influenced by seasonality, with higher values in summer and early fall coinciding with higher biological activity (Fig. 6). This suggests that the source of these elements is not the weathering of the granitic bedrock but rather, the upper organic layer where the elements recirculate due to plant uptake and litter decay (Lidman et al., 2017; Tyler, 2004). Those elements scoring on PC 1 are expected to be predominantly dissolved and do not bind to organic matter. Therefore, they are not retained by sorption to organic matter and probably percolate through the organic soil profile and are transported by shallow groundwater flow to the surface water. These elements load on the DOC component only for the event data set. This indicates export via the upper peaty soil layer only when these layers get hydrologically connected during rain events, which further supports

this hypothesis.

Summarizing the pattern of PC 1 at both sites, the main control on element export at the bog site is decomposition of organic matter. Elements such as Ca, Mg or Sr, which have no affinity for organic matter, exhibit similar export patterns, as there is no groundwater component similar to that in the riparian zone. At the riparian zone, the DOM-related export splits into two components. On the one hand, truly dissolved elements that are released in the upper soil layer percolate downward and get exported by shallow groundwater. On the other hand, elements that are also released in the upper organic layer are retained there due to their binding to organic matter. They only get exported when high water level hydrologically connects this upper soil layer. However, the applied methods cannot distinguish if elements are truly bound to DOM, which is the next step to unravel element export from this system.

3.3. Element pool controlled by season and plant uptake

The elements and anions of Rb, Cs, K, sulfate, nitrate and In in the event data sets load strongly on separate PCs at both sites (Figs. 3 and 4). These element concentration patterns are characterized by high concentrations during snowmelt and an initial peak during rain events, as well as strong changes in element to DOC ratios. This change was especially pronounced at the riparian zone. The concentrations of snowmelt clearly differed for these elements compared to any other (Figs. 5 and 6). During snowmelt, overland flow mainly prevails at both

subcatchments (Broder and Biester, 2015). Therefore, the dilution effect of DOC during snowmelt is attributed to the dilution caused by melting snow packs, as well as low biological activity (Dyson et al., 2011). The enrichment of the mentioned elements at both sites might be partly explained by deposition over the winter period and partly explained by an enrichment in the uppermost peat layer due to low biological activity and low nutrient uptake. Even though Rb and Cs are not nutrients, they are also affected by plant uptake (Dahlqvist et al., 2007; Lidman et al., 2017). Nitrate and sulfate indicate that waters are oxygenated. Deeper water sources at the bog site are thought to be anoxic (Knorr, 2013) and can thus be excluded here. A decrease of sample scores during summer drought in the riparian zone also hints at a source in the upper layer here and not in the shallow groundwater. During rain events, nitrate and sulfate especially show an initial flushing peak before the DOC peak, indicating a source in a very fast hydrologic pathway, which is overland flow. Knorr (2013) also described an initial flushing peak of nitrate at rain events under dry preconditions in a fen catchment and attributed this to a fast shallow surface flow path. The high leaching of K from decomposing litter has been reported previously for peatlands; high K concentrations were found before the start of the vegetation period, where K was not consumed by plant growth (e.g., Bragazza et al., 1998; Sundstrom et al., 2000). This also explains the high concentrations during snowmelt, whereas summer concentrations were rather low (Fig. 6). Higher concentrations at the end of fall coincide with the release of K by plant decay at the end of the growing season (Ledesma et al., 2013; Tukey, 1970). During the rather mild winter between 2013/2014, it can be reckoned that the export of these elements successively occurred during the winter period, which was not covered by our measurements. As no snowmelt event was taking place, this might also explain the low concentrations of Rb, Cs, K, sulfate and nitrate in the beginning of 2014. In contrast, during colder winters with a continuous snow cover, as in 2012/2013, the hydrological connection of the upper peat layer to the stream ceases, resulting in a pulse-like element export during snowmelt. Casson et al. (2012) reported high nitrate concentrations during snowmelt independent of landscape type in the catchment. Furthermore, they perceived lower nitrate concentrations in early spring when the winter was warmer. In a boreal river, the alkali metals K, Rb and Cs were also elevated during spring flooding, which was connected to the enrichment of these elements in the topsoil (Dahlqvist et al., 2007; Tyler, 2004).

The calculated element fluxes at the bog site highlight the importance of snowmelt and high-discharge events for the export of elements that are mainly controlled by plant uptake. Snowmelt contributed over-proportionally to the annual export rates with 28% of K, 29% of SO_4^{2-} , 35% of Cs, 38% of Rb and 42% of NO_3^- , compared to 6% of DOC export (Table 3). However, the highest export rates ranging from 43 to 47% are attributed to the fall season with frequent storm events. As much as 87% of NO_3^- gets flushed during the 10% of highest discharge.

Overall, it can be assumed that the alkali metals of K, Rb, Cs and the nutrients of NO_3^- and SO_4^{2-} are mainly exported by a fast flow path during high-discharge events and are quickly exhausted after an initial flush. The source area can be assumed to be the uppermost litter or peat layer. As these elements are rapidly utilized by vegetation, exports are higher when plant uptake decreases in fall or is low in winter and early spring.

3.4. Element pool controlled by the dissolution of mineral dust particles in the bog

In all four data sets, Ga, Y and Ba strongly load on one separate PC together. The stream concentrations of these PC elements were high in spring 2013 and low during snowmelt (Fig. 7). No seasonal trend like that of DOC is perceived at both sites (Figs. 5 and 6). Pore water and solid phase concentrations at the bog site show an enrichment of those elements between depths of 10 and 40 cm in peat with decreasing

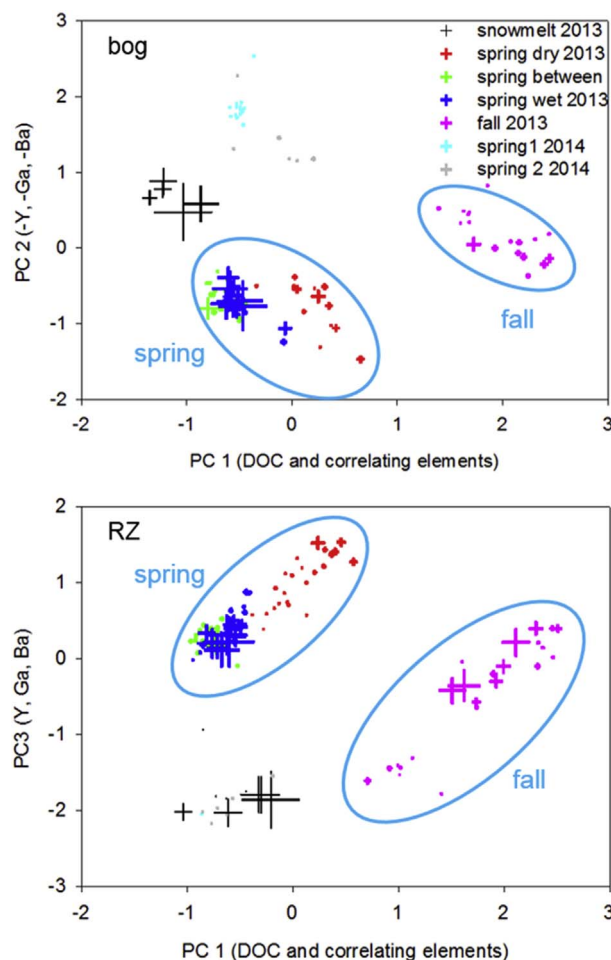


Fig. 7. Sample scores on PCs for DOC and Y, Ba and Ga for the event data set of the bog site (top) and the riparian zone (bottom). The size of the crosses indicates relevant discharge quantity. Note that Y, Ga and Ba are negatively correlated to PC 2 in the top panel.

concentrations toward the surface layer (see Supporting Information). These peaks can be attributed to anthropogenic deposition by mining activities (Biester et al., 2012; Kempter and Frenzel, 2000) and are also probably the main source of these elements at the riparian zone, as the anthropogenic pollution is far higher than the mineral background. Ga, Y and Ba have low solubility, but Ga and Y are known to have an affinity for organic matter. While Ba generally exhibits low affinity to DOM, it has been shown that almost all pore-water Ba was bound to DOM under conditions specific to ombrotrophic peatlands (Sader et al., 2011). The absence of a seasonal trend indicates that these elements are neither influenced by plant uptake nor mobilized by decomposition processes. The low concentrations during snowmelt are probably generated by the dilution effect of overland flow and surface-near flow paths at that time. A possible mobilization process for Ga, Y and Ba is that chemically and physically weathered mineral dust particles during winter and associated elements might be subsequently mobilized by DOM in spring. The increasing availability of DOM with the beginning of spring, as well as the newly established hydrologic conductivity after snowmelt, leads to increasing export. The low spring 2014 concentrations can be explained by a continuous hydrologic conductivity to discharge during winter, limiting the pool accumulation. A mobilization by DOC seems to be likely as the PCs of Ga, Y and Ba correlate with the PCs of DOC when separated for each single event, indicating that the concentrations of Ga, Y and Ba increase when DOC increases (Fig. 7). This implies that the correlation over the whole annual data set is biased by season-dependent DOC production. This is also imprinted in the export rates separated by season. Whereas Ga, Y and Ba export

Table 4
Summary of element sources, main mobilization processes and export conditions.

Main mobilization process	Site	Source	Exemplary elements	Main export, season and hydrologic conditions
decomposition	Bog	Upper peat layer	DOM, Fe, Al, As, Pb Ca, Mg, Sr...	summer, early fall, especially high-discharge events with dry preconditions
	RZ	Organic layer, shallow groundwater	DOM, Fe, Al, As, Pb ... Ca, Mg, Sr...	summer, early fall, high-discharge events summer, early fall, shallow groundwater and discharge events
Fresh litter decomposition, leaching	Bog RZ	plants, upper peat or litter layer	K, NO ₃ , SO ₄ ...	snowmelt, fall, fast surface or overland flow
weathering/dissolution of dust and subsequent binding to DOM	Bog RZ	mineral dust particles	Ga, Y, Ba	spring, high-discharge events

39%, 41% and 46% during spring, respectively, the spring season only contributes 17% to the DOC annual fluxes. Although export in fall is still high (between 37 and 44%), Ga, Y and Ba contribute less than DOC (61%). As the PC trends are similar at the bog and the riparian zone, it can be assumed that Ga, Y and Ba also mainly originate from the organic-rich layer, as the anthropogenic pollution is much higher than the mineral background. Since these elements have a low solubility, they remain in the upper layer and are also exported along with DOC here.

Overall, this specific export pattern is probably characteristic for elements that prevail as mineral dust particles in peat or the organic layer. The dominating mobilization process is apparently the dissolution of mineral particles by physical or chemical reactions and consecutive binding to organic matter, leading to their export along with DOM. As they are only minorly influenced by plant uptake and incorporation into plant material, they are not primarily released by decomposition processes.

4. Conclusions

The main element mobilization processes and exporting flow paths are summarized in Table 4. This study demonstrated that most elements (Ca, Fe, Mg, Mn, Zn, As, Sr, Cd, Al, Li, Co, Cl and Pb) exhibited the same export pattern as DOM at the bog site. Additionally, elements with low affinity to DOM, such as Ca, Mg, or Sr, exhibited this pattern; thus, it can be concluded that the main control was the same source area and similar mobilization processes and not elemental affinity to DOM. All of the elements that were strongly related to DOM export circulate in the upper peat layer due to decomposition and plant uptake. As decomposition is the main mobilization process, seasonality plays an important role, as does water level in terms of hydrologic connectivity because transport to the discharging stream depletes the readily mobile element pool. The previously described export patterns for DOC also apply to these elements. This includes over-proportional export during high-discharge events, as well as an exhaustion or dilution effect by overland flow during high discharge under wet preconditions at the bog site. This leads to lower mean concentrations during events, which demonstrates the importance of bogs for stream water quality. An over-proportional contribution of high discharge to annual element export was expressed in approximately 50% of the annual element export taking place under 10% of the highest discharge.

At the riparian zone, larger element concentration variability occurred, as higher discharge successively connected greater parts of the organic-rich peat layer and additional element pools with rising water levels. Furthermore, element concentration levels here were generally higher due to the additional source of mineral weathering. Due to the additional shallow groundwater flow path and the higher hydraulic conductivity in all soil layers, different export patterns prevail at the peaty riparian zone compared to the bog site. Elements released in the upper soil layer but with low affinity to DOM percolate downward and are exported by shallow groundwater, whereas elements bound to organic matter mainly get exported by high-discharge events, when the

upper soil layer becomes connected.

The nutrients K, NO₃⁻ and SO₄²⁻ were mainly controlled by plant uptake and almost exclusively exported by a fast flow path during high discharge at both sites. The main export occurred during snowmelt and in the fall, when plant uptake is low. The elements Ga, Y, and Ba appear to predominantly originate from the dissolution of mineral dust particles and are not influenced by plant uptake and decomposition processes. This leads to an export pattern with higher concentrations in spring, when the upper organic soil layer becomes hydrologically connected. The characterization of element sources in the peat layer is a challenge for future research, as their existence as mineral dust phases or bound to organic matter is crucial for element export in these systems.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apgeochem.2017.11.003>.

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