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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, NO_3^- and SO_4^{2-} 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 rainfed 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)