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Baseflow and stormflow metal concentrations in streams draining contaminated peat moorlands in the Peak District National Park (UK)

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Summary Leaching of previously deposited metals from atmospherically contaminated peat moorlands to receiving surface waters is an area of concern. Headwater streams in the Peak District National Park were sampled during baseflow and stormflow conditions to investigate the spatial and temporal variability in dissolved metal concentrations, the source of dissolved metals and the role of dissolved organic carbon (DOC) in the mobilisation and transport of dissolved metals. Under baseflow and stormflow conditions, Cu, Ni, Pb, Ti, V and Zn concentrations are highly variable. The results of this study reveal that Cu, Ni, Pb, V and Zn are leached from the contaminated peat soils into headwater streams. Ni and Zn are mobile within the peatland fluvial system due to poor sorption of these metals to organic matter. Elevated Zn concentrations in the headwater streams can be explained by the severely acidic nature of surface waters in this region. Stepwise multiple linear regression analysis reveals that the most important variable in explaining stormflow Pb, Ti and V concentrations is DOC. Due to the strong complexation of these metals by DOC, the export of dissolved Pb, Ti and V in peatland systems is likely to be controlled by DOC availability. Elevated stormflow dissolved Pb concentrations are due to the large store of Pb within the peat soils and high stream water DOC concentrations in surface waters of this upland area. Contemporary dissolved metal export from peat moorlands in the Peak District National Park may provide an analogue for future dissolved metal export in other contaminated peatland systems.

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Introduction

During the last few hundred years, many upland sites in the UK have been contaminated by the atmospheric deposition of metals derived from emissions associated with industry, transport and power generation (Smith et al., 2005; Tipping et al., 2006). Blanket peat moorlands, which characterise many upland locations in the UK, receive contaminant inputs solely from the atmosphere (Shotyk, 2002). High concentrations of potentially toxic metals, such as Cd, Cu and Pb, are concentrated in the top few centimetres of blanket peats at many sites around the UK (e.g. Livett et al., 1979; Markert and Thornton, 1990; Mighall et al., 2002; Tipping et al., 2003; Farmer et al., 2005; Rothwell et al., 2005; Smith et al., 2005). There has been recent concern about the mobilisation and transport of previously deposited metals from peat soils to receiving surface waters and also on the effects that such contaminants may have on aquatic ecosystems (e.g. Lawlor and Tipping, 2003; Tipping et al., 2003b, 2006; Vinogradoff et al., 2005; Graham et al., 2006). Determination of heavy metal concentrations in upland headwater streams has tended to focus on forested catchments (e.g. Durand et al., 1994; Wang and Benoit, 1996; Neal et al., 1996) and mining-affected sites (e.g. Azcue et al., 1995; Brydie and Polya, 2003). Although leaching of metals from atmospherically contaminated peatland catchments has been highlighted as a potential environmental hazard, there is limited data on metal concentrations in streams draining heavily polluted peatland environments.

The transport of metals in fluvial systems is controlled by physical, chemical and biological conditions (Salomons and Forstner, 1984). High concentrations of complexing agents and H^+ ions in solution can lead to the release of metals from soils and sediments into solution (Franchi and Davis, 1997). Streams that drain catchments dominated by blanket peat are typified by high concentrations of dissolved organic carbon (DOC). This is due to the carbon-rich nature of peat soils (Worrall et al., 2002). DOC in waters offers a useful indication of humic substances since a large proportion of the DOC is usually in humic substances (Tipping, 2002). Humic substances are major complexing agents in natural waters and control the behaviour and mobility of many metals in fluvial systems (Gao et al., 1999). The role of DOC in mobilising and transporting metals in fluvial systems has been reported in a variety of contexts, including snowmelt events in the Alaskan Artic (Rember and Trefry, 2004), contaminated wetlands in Germany (Kalbitz and Wennrich, 1998) and forested and cultivated catchments in mid-western Finland affected by acid sulphate soils (Astrom and Corin, 2000). In blanket peats, the onset of rainfall causes the water table level to rise in the acrotelm (top few centimetres of the peat) (Holden and Burt, 2003). Near-surface acrotelm drainage flushes accumulated stores of DOC into peatland fluvial systems, resulting in elevated DOC concentrations during high flow (Worrall et al., 2002). Under stormflow conditions, the acidity of waters draining blanket peat catchments also increases (Worrall et al., 2003). This is due to the flushing of organic acids from the acrotelm and the export of H^+ ion rich waters, due to cation exchange in the peat (Chapman et al., 1993; Gorham et al., 1984). Therefore, acidic, DOC-rich waters draining the contaminated top few centimetres of the peat layer have the potential to release dissolved metals to receiving surface waters.

Blanket peat fluvial systems exhibit flashy hydrological regimes (Holden and Burt, 2003). Studies on storm event hydrochemistry in upland peat catchments have focused upon major cations and anions (e.g. Chapman et al., 1993; Soulsby, 1995; Cresser et al., 1997; Heal et al., 2002; Worrall et al., 2003). However, a recent study by Graham et al. (2006) revealed that stormflow can play a major role in the release of dissolved Pb from peatland soils. Albeit, there is still a lack of detailed information on the role of stormflow in dissolved metal export from severely contaminated peat catchments.

There is often significant heterogeneity in hydrochemical characteristics of waters in upland headwater catchments (Shand et al., 2005). Therefore, accurate assessments of dissolved metals in fluvial systems should include detailed baseflow and stormflow sampling (Droppo and Jaskot, 1995). Spot sampling regimes used for water quality assessment may not cover the full hydrological conditions of fluvial systems, and this is especially true in systems where there are large departures from the average condition. The relationship between river flow, dissolved metal concentrations and other hydrochemical variables can be complex (Neal et al., 1997; Blake et al., 2003).

There are three aims of this study. The first aim is to make a detailed assessment of the variability in dissolved metal concentrations in peatland headwater streams in the Peak District National Park during baseflow and stormflow conditions. This will be achieved by collecting stream water samples under different hydrological conditions. The second aim is to determine the source of metals in the headwater streams. Dissolved metals in peat waters and mixed waters are compared to elucidate metal source. The final aim is to determine the role of DOC in the mobilisation and transport of metals using stepwise multiple linear regression analyses. Key findings of this study are compared to those of other similar studies in peatland catchments. Overall, this study will add to our understanding of the processes controlling dissolved metal concentrations in peat moorland fluvial systems. In the following text, all metals are referred to as concentrations in the dissolved phase.

Methods

Study area

Previous work in the Peak District National Park in the southern Pennines, UK, has revealed that there are high concentrations of atmospherically derived metals stored in the near-surface layer (top 15 cm) of peat soils of this region due its close proximity to the industrial towns of Manchester, Sheffield, Bradford and Leeds (Livett et al., 1979; Markert and Thornton, 1990; Jones and Hao, 1993; Smith et al., 2005; Rothwell et al., 2007a). The southern Pennines have also received significant inputs of industrially-derived acid deposition over the last few hundred years (Evans et al., 2000). The low buffering capacity of the Millstone Grit sandstones of the region (McNish et al., 1997), combined with contemporary deposition of NH_4 and NO_3 (Fowler et al., 2005) and leaching of organic and industrially-derived