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Landscape control on the hydrogeochemistry of As, Co and Pb in a boreal stream network

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Abstract

In a boreal stream network, stream water concentrations of As, Co and Pb (filtered, <0.4 μm) of 10 nested streams were studied during two consecutive years in order to evaluate the influence of land cover on the temporal and spatial variability of metal concentrations and speciation. Mean concentrations of Co and Pb showed significant but contrasting relationship to landscape type, while As concentrations were not related to landscape type. Highest concentrations of Pb were found in the wetland dominated streams (>30% wetland), which was suggested to be controlled by atmospheric deposition in combination with high DOC release from the wetlands. For Co, the highest concentrations were found in the forest dominated sites (>98% forest), which were attributed to the weathering of minerogenic sources. Contrasting response to runoff events could also be related to landscape type; during the spring flood, decreasing concentrations of As, Co and Pb were observed in the wetland dominated catchments due to dilution, while increasing concentrations during spring flood were observed in the mixed catchments (2–30% wetland) and to some degree in the forested catchments, probably due to flushing of the organic-rich riparian sources. Further, metal speciation was calculated using the geochemical equilibrium model Visual MINTEQ. This suggests that dissolved inorganic species of As and Co dominated in headwater streams with low pH while DOC had a major influencing role for Pb. In the larger mixed streams where pH was higher and precipitation of e.g. colloidal Fe and Mn (hydr)oxides was favoured, the major influencing factor was instead adsorption to colloidal Fe for As and Pb, while association to organic matter and colloids of e.g. Mn influenced the concentrations of Co. We thus conclude that landscape type and the magnitude of the runoff events are of great importance for the spatial and temporal variations of As, Co and Pb in this boreal stream network. Projected climate change, with increasing runoff, may therefore influence riverine concentrations and fluxes differently, depending on the prevailing landscape type.

Keywords: Metal geochemistry; Geochemical modelling; Visual MINTEQ; Speciation; DOC; Iron

1. INTRODUCTION

Although the concentrations of trace metals in atmospheric deposition in Europe have decreased significantly during the past decades (Rühling and Tyler, 2001; Harmens et al., 2008), there is an increasing concern that trace metals that have accumulated in soils (Brännvall

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et al., 2001; Kaste et al., 2003; Klaminder et al., 2006; Bindler, 2011) can potentially be leached to groundwater and surface waters. Of particular concern is mobilisation and transport of previously atmospherically deposited trace metals of anthropogenic origin from soils to surface waters. In the perspective of climate change the mobility of trace metals can become an important issue, especially in organic-rich environments such as in the boreal region (Lawlor and Tipping, 2003; Graham et al., 2006; Klaminder et al., 2006, 2010; Rothwell et al., 2007; Bindler, 2011; Bohdalkova et al., 2014).

Previous studies of trace metals in stream water have mostly focused on forested catchments (e.g. Shafer et al., 1997; Sherrell and Ross, 1999; Pokrovsky and Schott, 2002), regions with acid-sulphate soils (e.g. Åström and Spiro, 2005) or polluted sites (e.g. Nagorski et al., 2003; Rothwell et al., 2007). In regions where the spring snowmelt is the major hydrological event, increasing concentrations of organic matter (Laudon et al., 2004; Finlay et al., 2006) as well as Fe, Mn and Al (Cory et al., 2006; Björkvald et al., 2008) have been observed during the event, all of which act as important carriers for trace elements. As a consequence, increasing concentrations of associated trace metals have also been observed during spring flood events (Rember and Trefry, 2004; Dahlqvist et al., 2007).

Only a few studies have reported on the spatial variation of trace metals in small to meso-scale catchments, although some studies have addressed the importance of suspended particulate matter, dissolved organic carbon (DOC) and catchment hydrology for trace metal concentrations in stream water (e.g. Lazerte et al., 1989; Dillon and Molot, 1997; Shafer et al., 1997; Rember and Trefry, 2004; Temnerud et al., 2013; Köhler et al., 2014; Lidman et al., 2014). Studies of stream water chemistry from a landscape perspective are scarce and the importance of wetlands, which cover 10–50% of the land area in Fennoscandia (Pakarinen, 1995), for trace metal concentrations has not been thoroughly investigated. However, some of the studies that have been done point to the fact that wetlands have an important influence on metal transport and concentrations (Cory et al., 2006; Björkvald et al., 2007; Lidman et al., 2012, 2014; Köhler et al., 2014).

The primary sources for trace metals in streams are weathering of minerals and/or anthropogenic activities. One of the major transport pathways for trace metals in freshwater is through adsorption or complexation to organic molecules and reactive mineral surfaces of suspended sediment and colloids. Several trace metals form stable complexes with organic matter, e.g. DOC (Davis, 1984; Tessier et al., 1996; Gustafsson et al., 2011; Sjöstedt et al., 2013).

Trace elements such as arsenic (As) and lead (Pb) are of particular concern since they are moderately to very toxic for biota (Hutchinson and Meema, 1987). Both As and Pb are present in the lithosphere in trace amounts (Wedepohl, 1995). In natural waters, As is a redox sensitive element and the distribution between As(III) and As(V), is dependent on redox potential (Smith et al., 1998; Smedley and Kinniburgh, 2002). As(V) adsorbs strongly to Fe and Al oxide surfaces, especially at low pH (Manning and Goldberg, 1996; Smedley and Kinniburgh, 2002). In natural waters Pb is, in contrast to As, a redox-stable divalent cation exhibiting a high affinity for both organic compounds and iron (hydr)oxides (Gustafsson et al., 2011). Pb is of special concern since anthropogenic emissions have historically been large and are still a concern in many regions (Brännvall et al., 2001; Bindler, 2011).

Cobalt (Co) is an essential element for many organisms. It is often found in association with Fe oxide minerals (Hamilton, 1994) and is considered as easily mobilised during weathering. In aquatic environments, under oxic conditions and in the pH interval of most natural waters, Co(II) is totally dominating over Co(III) (Collins and Kinsela, 2010). In freshwater environments, Co has been reported to be associated with both natural organic matter (Lyvén et al., 2003; Collins and Kinsela, 2010) and references therein), and with colloids of Fe and Mn (Kay et al., 2001; Lyvén et al., 2003; Grybos et al., 2007). In a marine environment, a strong association between Co and Mn oxide has been demonstrated (Takahashi et al., 2007).

The purpose of this study was to investigate the temporal and spatial variation of As, Co and Pb (filtered <0.4 μm) in stream waters of a boreal stream network. These elements are, as described above, chemically different in terms of e.g. redox and pH sensitivity and to what extent they bind to dissolved organic matter or adsorb to particles and colloids. They are also assumed to be contributed from different main sources, where Co is expected to be contributed mainly from mineral weathering while Pb is known to be contributed mainly from past and present atmospheric deposition (Klaminder et al., 2006). This combination of elements was thus chosen with the aim to address the influence of different landscape types on trace metal transport and concentrations in the boreal landscape. We hypothesise that (1) trace metal concentrations will vary spatially with landscape features, like the proportion of wetlands, e.g. as a result of trace metals complexation with organic matter and since general water chemistry, like pH, generally differ between different catchment types and (2) that trace elements with different origin will show contrasting patterns in terms of landscape influence. For example, Co is presumed to be contributed mainly from weathering and is therefore expected to show high concentrations in forest dominated catchments compared to wetland dominated catchments where the weathering contribution can be expected to be small. Pb on the other hand is assumed to be contributed mainly from atmospheric deposition both in forest dominated and wetland dominated catchments. Since Pb is known to adsorb to organic matter, wetlands can be expected to act as sinks for Pb. Further we hypothesise (3) that the spring flood will result in a considerable temporal variation of these elements since pH, and concentrations of DOC and Fe are changing dynamically during this period. Also in this case we expect different patterns for different elements and landscape types, where e.g. the influence on elements contributed mainly from weathering is expected to differ from the influence on elements contributed mainly from atmospheric deposition.

A geochemical model was also used, with the aim to support the discussion about important factors determining the