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Temporal variations of colloidal carrier phases and associated trace elements in a boreal river

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Abstract

Elemental size distributions, from truly dissolved through colloidal to particulate, have been studied in a subarctic boreal river. The measurements, carried out during 2002, ranged from winter to summer conditions, including an intense spring flood event. Results are reported for a total of 42 elements. Size distributions were characterised using a combination of cross-flow (ultra)filtration (CFF), flow field-flow fractionation (FlFFF), and diffusive gradients in thin-films (DGT). The three techniques showed similar trends, but quantitative comparisons reveal some important differences that warrant further investigation.

Previous work has identified two colloidal carrier phases in fresh waters, dominated by iron and carbon, respectively. The majority of the elements studied are associated with one or both of these colloidal carrier phases. The exceptions are the alkali metals and several anions that are only very weakly associated with colloidal material, and which therefore occur mainly as truly dissolved material (<1 kDa in molecular weight). We discuss the likely origin for the two colloidal carrier phases and consider how associated trace elements fit into the geochemical framework. The relative affinities of the elements for iron and carbon colloidal carrier phases are related to their chemistries, and are compared with earlier data from the Delsjö Creek in southern Sweden.

Elemental colloidal concentrations show strong seasonal variations related to changes in the colloidal carrier phase(s) with which they associate. In particular, many elements show a strong spring maximum in colloidal concentrations associated with the strong maximum in colloidal carbon concentration during the spring flood.

1. INTRODUCTION

Assessment of colloidal material presents a series of challenges to the aquatic geochemist: it covers a wide size range (nominally 1 nm–1 μm), and is chemically and physically heterogeneous (Gustafsson and Gschwend, 1997). Despite significant methodological advances in recent years, no method for physico-chemical fractionation in the colloidal size range is without potential artifacts. It is therefore advantageous to use several different methods in parallel, in order to minimize the risk of interpreting artifacts as natural variations (Buffle et al., 1998).

Along with aeolian dust, a major input of trace elements to the ocean is through river discharge. The fate of trace elements in estuarine processes and in the ocean is largely dependent on how the elements are associated to particles and colloids, and/or are present as dissolved species. These characteristics are shaped during terrestrial low tempera-

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ture geochemical processes in fresh water solutions, carrying solute species and colloidal and particulate material. Hence, the study of trace elements and their physicochemical properties in fresh water systems, such as rivers, is important for understanding their fate in the ocean.

The major annual hydrological event for rivers located in the boreal and arctic zones is snowmelt in spring, which causes a dramatic increase in discharge. For instance, most rivers at this latitude draining their water to the Arctic Ocean deliver 40–80% of the annual volume during the spring flood (Arnborg et al., 1967; Gordeev et al., 1996). The load of total suspended matter, organic carbon, and major and trace elements often show large variations in concentration during this episode (e.g. Rember and Trefry, 2004; Ingri et al., 2005; Neff et al., 2006), which not only indicates the importance of performing temporal scale studies with frequent sampling to cover seasonal variations, but also that there still remains much to learn about the nature of the matter transported in river water during such changing conditions.

The studied river, Kalix River, is in many aspects similar to several Russian rivers. It represents an unregulated pristine medium-sized boreal river, draining a till-covered bedrock with mainly granitic origin, and has previously been well characterized in several studies of major and trace elements and isotopes (Pontér et al., 1990; Öhlander et al., 1991, 1996, 2000; Ingri and Widerlund, 1994; Ingri et al., 1997, 2000, 2005, 2006; Porcelli et al., 1997; Land and Öhlander, 1997; Andersson et al., 1998, 2001; Land et al., 1999, 2000a,b; Dahlqivst et al., 2004, 2005). It has been indicated that temporal variations in river runoff is highly correlated to different hydro-geological pathways; a topic which has been highlighted by e.g. Andersson et al. (2006), Neff et al. (2006) and Pokrovsky et al. (2006). Thus, intensity and duration of precipitation and/or snowmelt episodes will control residence times and pathways for soil and ground water, and so have a direct influence on the geochemical imprint of river water, including the chemical composition of the colloidal material.

Arctic and boreal regions holds some of the most important reservoirs for organic carbon (Post et al., 1982; Botch et al., 1995). Peatlands along with organic-rich soils are common features of the boreal and arctic regions on the Eurasian and North-American continents. An increasing global warming at high latitudes in the boreal and arctic zones will most likely change both the amount and character of released organic carbon, including the colloidal fraction. In turn, the changes are likely to also affect transport of elements associated to the released organic material.

The chemical composition and concentration of colloidal particles in river water seems to be a highly variable and affected by variations in hydro-geological pathways. Two different colloidal phases have been identified in recent publications. In Dahlqivst et al. (2004) and Andersson et al. (2006) direct measurements showed the presence of two different colloidal carrier phases; one organic-rich and another Fe-rich component. These two carrier phases were also distinctly different in size. A study in a southern Swedish creek also identified the same two carrier phases in the colloidal size range (Lyvén et al., 2003).

Another study identifying specific colloidal particles is Allard et al. (2004), where spectroscopic and microscopic techniques were applied to characterize Fe-rich colloidal matter in Amazonian rivers. However, direct measurements of the chemistry and size of colloidal particles are rare, and studies on temporal variations of these are even more scarce.

In this paper, we present major and trace element data obtained using several techniques for physicochemical characterization of sampled species, ranging in size from diffusible ions to particles <100 μm. The study show the temporal variation of 42 elements in these fractions from winter conditions, through a distinct spring flood event, and into summer conditions, with focus on assessing the colloidal chemistry and size distribution. The colloidal carrier phases previously identified in the Kalix River (Dahlqivst et al., 2004; Andersson et al., 2006) are used to categorize the trace elemental composition and deduce a likely source for the colloidal material.

The methods used during the study include Cross-Flow (ultra)Filtration (CFF), Flow Field-Flow Fractionation coupled on-line to Inductively Coupled Plasma – Mass Spectrometry (FlFFF-ICP-MS), and Diffusive Gradients in Thin films (DGT). Each of these techniques has limitations regarding resolution in size and/or other operational restraints. However, in many respects they complement each other. Using them together provide more detailed information for interpretation of speciation/fractionation data, and a welcome opportunity to critically assess the data and to identify possible artifacts.

A detailed chemical and physical description of aqueous colloids and particles in terrestrial surface and ground waters may be of great relevance for future studies in the light of global climate change and warming. Changing climatic conditions are likely to significantly affect annual mean temperatures in the boreal and arctic regions and modify both type and amount of precipitation, thus directly affecting hydro-geological pathways. A longer growth period for terrestrial plants will enhance organic production and cycling and possibly increase the reservoir of organic carbon in soils, which is a likely source for organic colloids in surface waters. At the same time thawing permafrost will release large quantities of organic carbon to stream waters. It is difficult to assess how global climatic changes will affect regional hydro-geochemistry. It can be argued that ground waters with long residence times are sources for surface waters with high concentrations of Fe-rich colloids. In contrast to this are soil waters rapidly washing the uppermost organic-rich layers, e.g. during episodes of intense snowmelt or rainstorms, acting as a source for organic-rich colloids. However, it is clear that the colloidal fraction will continue to be a significant component in surface waters and a carrier for other trace elements. It is therefore important to understand current processes and conditions under which certain types of colloids are present and of significance for the total transport of major and trace elements from the terrestrial environment to the ocean.