



## Dissolved, suspended, and colloidal fluxes of organic carbon, major and trace elements in the Severnaya Dvina River and its tributary

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### ABSTRACT

The chemical status of major and trace elements (TE) and organic carbon (OC) has been studied in the Severnaya Dvina and Pinega rivers draining granitic moraine, carbonate and sedimentary deposits of the Arkhangelsk region (NW Russia, the White Sea basin of the Arctic Ocean). Sampling was performed during winter and summer baseflow seasons and during the spring flood (2007–2008). Size separation procedure included on-site filtration through 5  $\mu\text{m}$ , 0.22  $\mu\text{m}$ , 100, 10 and 1 kDa, and dialysis through 1 kDa and 10 kDa pore-size membranes. The organic carbon concentration in “truly” dissolved form (<1 kDa) does not depend on rock lithology or season, being on average equal to  $5.0 \pm 1.4$  mg/L. Our observations may suggest the presence of two types of organic matter pool: i) allochthonous large-size colloids formed by lixiviation from upper soil horizons and ii) autochthonous (aquatic) small molecular-size substances, probably linked to bacterial and phytoplankton exudates. The total dissolved concentration of colloidal TE correlates with OC and Fe contents, being highest during the spring flood and lowest in winter time. There are two different patterns of TE colloidal status during different periods of the year, depending on their association with the organic or organo-mineral constituents of the colloidal matter pool.

Trace and major element concentrations in the suspended matter of the River Severnaya Dvina were measured during different seasons over three years of observation. Based on collected data, we evaluate here, for the first time, the seasonal fluxes of major and trace elements in the suspended (>0.22  $\mu\text{m}$ ), total dissolved (<0.22  $\mu\text{m}$ ) and colloidal (1 kDa–0.22  $\mu\text{m}$ ) forms. On an annual basis, there is a significant contribution ( $\geq 30\%$ ) of conventionally dissolved species (<0.22  $\mu\text{m}$ ) to the overall flux of usually weakly mobile elements such as the divalent transition metals, Cd, Pb, V, Y, all REEs, Zr, Hf and Th. The transport of these insoluble elements occurs essentially in colloidal form. The spring flood occurring in May provides between 30 and 60% of the total annual dissolved and suspended flux of many insoluble trace elements (Fe, Co, Ni, Cr, Y, all REEs, Cd, Pb, Zr, Hf and Th). We argue that trace element fluxes in Arctic rivers are often characterized by a high proportion of total dissolved matter (<0.22  $\mu\text{m}$ ) compared to suspended particulates, due mostly to the large contribution of organically-bound colloidal forms.

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### 1. Introduction

The geochemistry of trace elements (TE) in boreal regions attracts the attention of researchers in view of on-going environmental changes that can affect the fluxes of these elements to the ocean, as well as their speciation and thus their bioavailability. This becomes especially important in the light of the predicted summer sea ice-free conditions of the Arctic Ocean within the next 30–50 years (Wang and Overland, 2009). The high concentration of Dissolved Organic Matter (DOM), and, hence, the organo-mineral colloidal status of most metals, is one of the most important characteristic features of the biogeochemistry of the

European Russian Arctic zone. Most trace elements in boreal zone waters are transported via organic and organo-mineral colloids, whose relative role changes during the year (Ingri et al., 2000; Pokrovsky and Schott, 2002; Shiller, 2003; Andersson et al., 2006; Dahlqvist et al., 2007; Björkvald et al., 2008). There are few investigations of colloidal vs. dissolved forms or the transport of TE in organic-rich waters from pristine catchment areas around the Arctic Ocean basin, apart from some studies addressing soil and river solute migration in Alaska (Brown et al., 1962; Ugolini et al., 1987; Shiller, 2003; Rember and Trefry, 2004) and Canada (Millot et al., 2003) and occasional trace element measurements in the Siberian Arctic (Dai and Martin, 1995; Guieu et al., 1996; Moran and Woods, 1997; Zhulidov et al., 1997; Pokrovsky et al., 2006). A specific feature of all boreal catchments is the large flux of dissolved and particulate matter and especially organic carbon occurring during relatively short high-flow period of snowmelt

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in April to June. This is very different from hydrogeochemical situation of most studied glacial mountain watersheds (cf. Blum et al., 1998; Jacobson et al., 2002). Concerning the boreal European Russian zone, in common with the Siberian Arctic and Canada (Reeder et al., 1972; Huh et al., 1998; Huh and Edmond, 1999), all previous studies have dealt with the analysis of samples collected during the summer baseflow period (Pokrovsky and Schott, 2002; Pokrovsky et al., 2005, 2006; Vasyukova et al., 2010). Seasonally-resolved fluxes have only been assessed for major elements in the Karelia Region (Zakharova et al., 2007) and, at a rather lower resolution, in the Mackenzie, Yukon, Kolyma, Lena, Yenisei and Ob rivers via the PARTNERS project (<http://ecosystems.mbl.edu/partners>) in 2003–2004. However, this latter project is only concerned with total dissolved (<0.22  $\mu\text{m}$ ) and suspended fractions. At the same time, Swedish researchers have devoted a significant effort to understanding the geochemistry of major and trace elements in small boreal catchments of the Baltic Sea basin, notably the Kalix river (Öhlander et al., 1996; Land and Öhlander, 1997, 2000; Land et al., 2000; Ingrid et al., 2000, 2005, 2006). It has been demonstrated that the main flux of usually insoluble elements occurs during the spring melt, and that both organic and organo-mineral colloids exert a strong control on TE speciation in the river water.

The main difference with the Kalix river system, although occurring under similar climatic conditions, is the much larger size of the Severnaya Dvina catchment (348,000  $\text{km}^2$ , which corresponds to ~80% of the surface-area of Sweden) and the different lithological context. In the case of the Severnaya Dvina–Pinega catchment, the granitic till with a spodosol soil profile is picked out essentially by carbonate and, to a lesser extent, gypsum-bearing sedimentary rocks. Another important difference between the well-studied small Scandinavian and Karelian catchments, on the one hand, and the Severnaya Dvina River, on the other hand, is much weaker influence of lakes on the latter river's hydrology and chemical composition; however, the effect of bogs and mires is quite important in the case of the Severnaya Dvina basin.

To summarize, despite data from a small river of the Baltic Sea basin and occasional measurements of the total dissolved load of major Arctic rivers, the seasonal flux and speciation of trace metals in rivers discharging to the Arctic Ocean remain largely unknown. This study is aimed at extending our knowledge to the largest unregulated European river, the Severnaya Dvina and its tributary (Pinega River). Following the work of Russian hydrochemists (Alekin and Brazhnikova, 1961, 1964; Voronkov et al., 1966; Voronkov, 1970), it is established that the geochemistry of major ions in boreal zone rivers is controlled by predominantly groundwater input (water/bedrock interaction) during the baseflow season and surficial flow input (leaching from surface horizons and plant litter degradation) during the high-flow season. In the present study, we attempt to apply these principles to the geochemistry of trace elements in two boreal rivers. For this purpose, we characterize the size of colloids and quantify the fluxes of TE in the largest European Subarctic river, Severnaya Dvina, in an attempt to address the following questions:

- i) What is the relative proportion of each of the three pools of TE (suspended, colloidal and truly dissolved) contributing to the seasonal and annual fluxes?
- ii) Does colloidal speciation of organic carbon and trace metals in the river water depend on season and catchment lithology?
- iii) Can we distinguish the main sources of major and trace elements in Subarctic rivers according to the hydrological season (i.e. rock, soil minerals and plant litter, and underground water)?

## 2. Sampling and analyses

The sampling area is located in the northern part of NW Russia, within the catchment of the Severnaya Dvina River that belongs to the

White Sea basin of the Arctic Ocean (Fig. 1). The field work was performed in several hydrological seasons: winter baseflow in February 2007 and March 2008, spring flood in May 2007 and April–June 2008 and summer baseflow in August 2007. Detailed geological, climatic and geographic descriptions of the region and sample description are given in the [Electronic Supplementary Material \(ESM-1\)](#). Altogether, 30 samples were collected from the Severnaya Dvina River, 20 samples from the Pinega River and its three tributaries, as well as a typical ombrotrophic bog feeding the large river in spring, using filtration through different pore-sizes (5  $\mu\text{m}$  and 0.22  $\mu\text{m}$  acetate cellulose filters). The sampling, filtration, ultrafiltration and dialysis as well as the chemical analyses, are presented in the [Electronic Supplementary Materials \(ESM-2\)](#). These techniques are very similar to those used in our previous studies (Pokrovsky and Schott, 2002; Pokrovsky et al., 2006).

For several samples, ultrafiltration (100, 10 and 1 kDa Amicon YM Regenerated cellulose filters installed in a portable stirred ultrafiltration cell “Amicon 8050” having 50 mL volume) and dialysis experiments (1 and 10 kDa membranes) were performed within one day after sampling. Detailed description of ultrafiltration and dialysis procedure is given in [Electronic Supporting Information 2 \(ESM-2\)](#). Results of ultrafiltration and dialysis are in general agreement with each other with not more than 50% difference between the concentration of dialyzed and ultrafiltered samples for the nominal membrane cut-off of 1 kDa. In contrast, the size separation procedure through 10 kDa nominal cut-off yields factor of 2 to 5 higher concentration in the ultrafiltrates compared to dialysates of elements strongly affected by the presence of colloids (Al, Ti, Fe, Co, Y, Zr, REEs, Hf, Th, and U). The agreement between two methods is better for winter samples than for the spring flood period (not shown). This suggests that both Fe and DOC concentration determine the efficiency of the size separation procedure. The largest disagreement is observed for Fe, Zr, Hf, Th and REEs in 10 kDa fractions (Fig. ESM-2) since these elements are tightly linked to Fe(III) colloids (Pokrovsky and Schott, 2002). The previous methodological work performed in NW boreal Russian region on basalt and granitic watersheds (Vasyukova et al., 2010) also demonstrated a factor of 3 enrichment in ultrafiltrates compared to dialysates. Since equilibrium dialysis performed at a very high ratio of external solution/internal reservoir should be much less affected by the various artefacts of size separation, we use the results of dialysis through 1 kDa to assess the proportion of colloidal forms. However, we should point out that the 1 kDa separation, routinely used in this work to define colloidal (1 kDa–0.22  $\mu\text{m}$ ) versus truly dissolved (<1 kDa) fractions, is statistically equivalent for both ultrafiltration and dialysis. Note that, since the evaluation of colloidal fraction is strictly related to the method that we are using, these are operationally defined colloids.

Samples of river suspended matter were collected during 2004–2006 in the freshwater mouth zone of the Severnaya Dvina River, always during the ebb tide. To sample this suspended matter, 50 to 80 L volumes of surface river water were left to settle over 3 to 5 days (Shevchenko et al., 2004, 2005). The remaining suspension was dried at 90 °C.

## 3. Results and discussion

### 3.1. Dissolved major elements

The data on major element composition and discharges were obtained from systematic surveys by the Hydrometeorological State Committee of the former USSR Goskomgidromet and Roskomgidromet (State Water Cadastre Hydrological Yearbooks of Arkhangelsk region, generalized in the “Resources of [Surface Waters USSR, 1972](#)”). The data of Russian Hydrological Survey (RHS) were collected using certified procedure of sampling and analysis (Semenov, 1977; Soyer and Semenov, 1971). These are robust values, at least for major

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