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Abstract

The objective of this thesis was to study element speciation and migration in the boreal environments (Karelia and Central Russia). Specific goals were to *i)* characterize the molecular weight distribution of trace elements and organic matter (OM) in various types of natural waters, *ii)* reveal the TE colloidal forms dependence in the continuum soil solution – bog – stream – feeding and terminal lakes in the surface waters of boreal watersheds, and *iii)* quantify the dependence of stable and radiogenic element isotopic composition on the size fraction, element speciation and physico-chemical conditions of surface waters. The main originality of the work is to apply the method of cascade filtration to study the molecular weight distribution of trace elements in surface waters and to combine the geochemical and isotope techniques, for the first time on the same natural objects, and particularly within the watershed continuum soil solution – bog – stream – feeding and terminal lakes, in order to better understand the factors that control biogeochemical cycling of elements in the subarctic region.

The first part is devoted to general introduction and the insight into the problems. The second chapter is aimed at studying natural organic matter size distribution in the natural waters with different redox and hydrodynamic conditions in the continuum soil solution – bog – stream – feeding and terminal lakes for a small watershed with homogeneous bedrock composition. In particular, we investigate organic matter concentrations, weight-average molecular weights, optical properties and carbon/nitrogen ratios to get the information about the origin of DOM (autochthonous / allochthonous), its aromaticity, and its hydrophility / hydrophobicity. The third chapter describes the study the molecular weight distribution of trace elements and it provides quantitative characterization of TE colloidal speciation in pristine, organic-rich rivers and surface waters. We demonstrate that, using TE correlations with iron and OM in the filtrates, one can characterize colloids distribution and compare partition coefficients in the continuum soil solution – bog – stream – feeding and terminal lakes, and also compare natural and modeling data. The fourth chapter describes the results of variations of stable (Cu, Mg) and radiogenic (Sr, Nd) isotopic composition in filtrates and ultrafiltrates of various size fraction in the different types of natural waters of south and north of European Russia boreal zone allowing to identify the factors influencing the isotopic composition variation along the landscape continuum in different size fractions. Finally, the fifth part is devoted to study the variations of iron isotopic composition of different water types and colloidal size fractions. In particular, we investigate the dependence of isotopic composition of filtrates and ultrafiltrateson iron and OM concentrations, pH and other physico-chemical factors. The sixth chapter presents the main conclusions and perspectives.

Investigations carried out in this study should contribute to the prediction of TE and OM behavior in the Arctic and boreal regions due to climate warming mostly pronounced in these latitudes.

Keywods : boreal zone, trace elements, organic matter, colloids, speciation, natural waters, filtration, isotopes.

Résumé

Cette thèse vise à étudier la spéciation des éléments et leur migration dans le milieu boréal (Karélie et Russie Centrale). Les objectifs principaux de ce travail sont : *i)* de caractériser la distribution de taille moléculaire des éléments traces et de la matière organique, *ii)* révéler la régularité de distribution des formes colloïdales des éléments traces dans les eaux naturelles le long du continuum sols – marécages– cours d'eau – lacs intermédiaires et terminaux des bassins versants boréaux, et *iii)* révéler la dépendance de la composition isotopique en fonction de la taille moléculaire, de la spéciation des éléments et des conditions physico-chimiques des eaux. L'originalité de cette thèse est d'appliquer la méthode de la filtration en cascade pour étudier la distribution de taille moléculaire des éléments traces dans les eaux naturelles et de combiner les techniques géochimiques et isotopiques pour la première fois sur les mêmes objets naturels afin de mieux comprendre les facteurs qui contrôlent les cycles biogéochimiques des éléments dans les régions boréales.

La première partie de la thèse consiste en une introduction générale de la problématique. Le deuxième chapitre est consacré à l'étude de la distribution de la matière organique naturelle dans les différentes fractions granulométriques des eaux naturelles présentant des conditions redox et hydrodynamiques variables au sein des micro-systèmes (solution de sols – marécage – cours d'eau – lacs intermédiaires et terminaux) de petits bassins versants à substratum homogène. En particulier, nous avons étudié les concentrations du carbone organique dissous, son poids moléculaire, ses caractéristiques optiques et ses rapports carbone/nitrogène pour obtenir des informations précieuses sur l'origine (allochtone *versus* autochtones), l'aromaticité, l'hydrophilie / l'hydrophobie de la matière organique. La troisième partie de la thèse est consacrée à l'étude de la distribution de taille moléculaire des éléments traces et à la caractérisation quantitative des formes colloïdales des éléments dans les rivières et les eaux de surface de ces milieux qui sont très riches en matière organique et pas soumis à l'impact humain. Dans cette partie il est notamment montré l'existence de corrélations des éléments traces avec le fer et la matière organique dans les filtrâts ; également un intérêt particulier est porté à la distribution des colloïdes et aux coefficients de partition des éléments dans les différents micro-systèmes (solution des sols – marais de source – cours d'eau – lacs intermédiaires et terminaux). Le quatrième chapitre rapporte les résultats des compositions isotopiques en strontium (Sr), néodyme (Nd), cuivre (Cu) et magnésium (Mg) au sein des différentes fractions colloïdales des eaux naturelles du sud et du nord de la zone boréale de la Russie Européenne. Ces derniers travaux conduits sur des isotopes stables (Cu, Mg) et radiogéniques (Sr, Nd) nous permettent de définir les facteurs qui influencent le changement de la composition isotopique. Le cinquième chapitre est consacré à l'étude du fractionnement isotopique du fer dans les types différents d'eaux naturelles sur les fractions granulométriques. En particulier, nous avons étudié la composition isotopique dans les filtrats et ultrafiltrats en fonction des concentrations en fer et en matière organique, du pH et des autres paramètres physico-chimiques. Dans le sixième chapitre il est formulé les conclusions principales et les perspectives de la thèse.

L’étude menée dans cette thèse vise à contribuer à la prévision de l’évolution de la spéciation et des flux des éléments traces et de la matière organique dans les régions Arctiques en réponse au réchauffement climatique global.

Mots Clés : zone boréale, éléments traces, matière organique, colloïdes, spéciation, eaux naturelles, filtration, isotopes.

Резюме

Данная диссертация направлена на изучение форм нахождения и миграции элементов в бореальных ландшафтах (Карелия и Центральная Россия). В рамках работы были поставлены следующие задачи: *i)* охарактеризовать молекулярно-массовое распределение микроэлементов и органического вещества (ОВ) в различных типах природных вод, *ii)* выявить закономерности распределения коллоидных форм отдельных микроэлементов по профилю почвенный раствор – питающие болота – водоток – промежуточные и депонирующие озера в поверхностных водах бореальных водосборных бассейнов, и *iii)* выявить зависимость изотопного состава от размера фракции, форм нахождения элементов и от физико-химических условий вод. Научная новизна диссертации заключается в применении метода каскадной фильтрации как способа исследования молекулярно-массового распределения микроэлементов в поверхностных водах и объединении геохимического и изотопного методов исследований, примененных впервые на одних и тех же природных объектах, в том

числе в системе почвенный раствор – питающие болота – водоток –промежуточные и депонирующие озера, с целью выявления факторов, контролирующих биогеохимические циклы элементов в бореальной зоне.

В первой части работы дается общее введение в проблематику. Вторая глава посвящена изучению распределения природного ОВ по фракциям крупности в природных водах с различными окислительно-восстановительными и гидродинамическими условиями по профилю почвенный раствор – питающие болота – водоток –промежуточные и депонирующее озера для малого водосборного бассейна с однородной геологической подложкой. В частности, мы исследовали содержание растворенного ОВ, его средневесовые молекулярные массы, оптические характеристики, а также отношение углерод/азот для получения информации о происхождении (аллохтонное/автохтонное), содержании ароматических веществ, гидрофильности/гидрофобности ОВ. Третья глава направлена на изучение молекулярно-массового распределения микроэлементов, а также на количественную оценку коллоидных форм микроэлементов в реках и поверхностных водах, богатых органическим веществом и неподверженных антропогенному воздействию. В этой части выявляются корреляции микроэлементов с железом и ОВ в сериях фильтратов, рассматривается распределение коллоидов и сравнение коэффициентов соосаждения по профилю почвенный раствор – водоток –промежуточные и депонирующее озера. В четвертой главе представлены результаты изменения изотопного состава радиогенных (Sr, Nd) и стабильных (Cu, Mg) изотопов по фракциям крупности для различных типов природных вод севера и юга бореальной зоны Европейской части России с целью выявления факторов, влияющих на изменение изотопного состава. Пятая глава посвящена изучению изотопного фракционирования железа в различных типах природных вод по фракциям крупности. В частности, мы исследовали изотопный состав в фильтратах и ультафильтратах как функцию от концентраций железа и ОВ, величины pH и других физико-химических показателей. В шестой главе сформулированы основные выводы и перспективы диссертации.

Исследования, проведенные в этой работе, призваны внести вклад в прогнозирование поведения микроэлементов и ОВ природных вод в арктических регионах вследствие глобального потепления климата.

Ключевые слова: бореальная зона, микроэлементы, органическое вещество, коллоиды, формы нахождения, природные воды, фильтрация, изотопы.

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Letter combinations and abbreviations

Alk	Alkalinity (concentration)
DOC	Dissolved Organic Carbon (concentration)
TOC	Total Organic Carbon
OC	Organic Carbon
NOM	Natural Organic Matter
DOM	Dissolved Organic Matter
OM	Organic Matter
FA	Fulvic Acid
HA	Humic Acid
HS	Humic substances
TE	Trace Elements
REE	Rare Earth Elements
IC	Ion chromatography
HPLC	High Performance Liquid Chromatography
SEC	Size Exclusion Chromatography
ICP-MS	Inductively-Coupled Plasma Mass Spectrometer
MC-ICP-MS	Multi Collector-Inductively Coupled plasma Mass Spectrometry
TIMS	Thermal Ionization Mass Spectrometry
UF	Ultrafiltration
NIST	National Institute of Standards and Technology
K_d	Iron-normalized trace element partition coefficient between dissolved and colloidal fraction
SUVA	Specific Ultra Violet absorbance

Chapter 1

General introduction

1.1. Background of the study

1.1.1. Speciation of elements in boreal zone

One of the major goals of the geochemistry is to quantify the element fluxes occurring between different reservoirs represented by continents, oceans and atmosphere, and to identify the mechanisms which control these fluxes. This exchange takes place at all scales, from the globe surface to a smaller scale of a soil or soil horizon. Figure 1.1 (after Viers et al., 2007) illustrates these matter transfer processes at a river basin scale, and defines the main processes which control these exchanges.

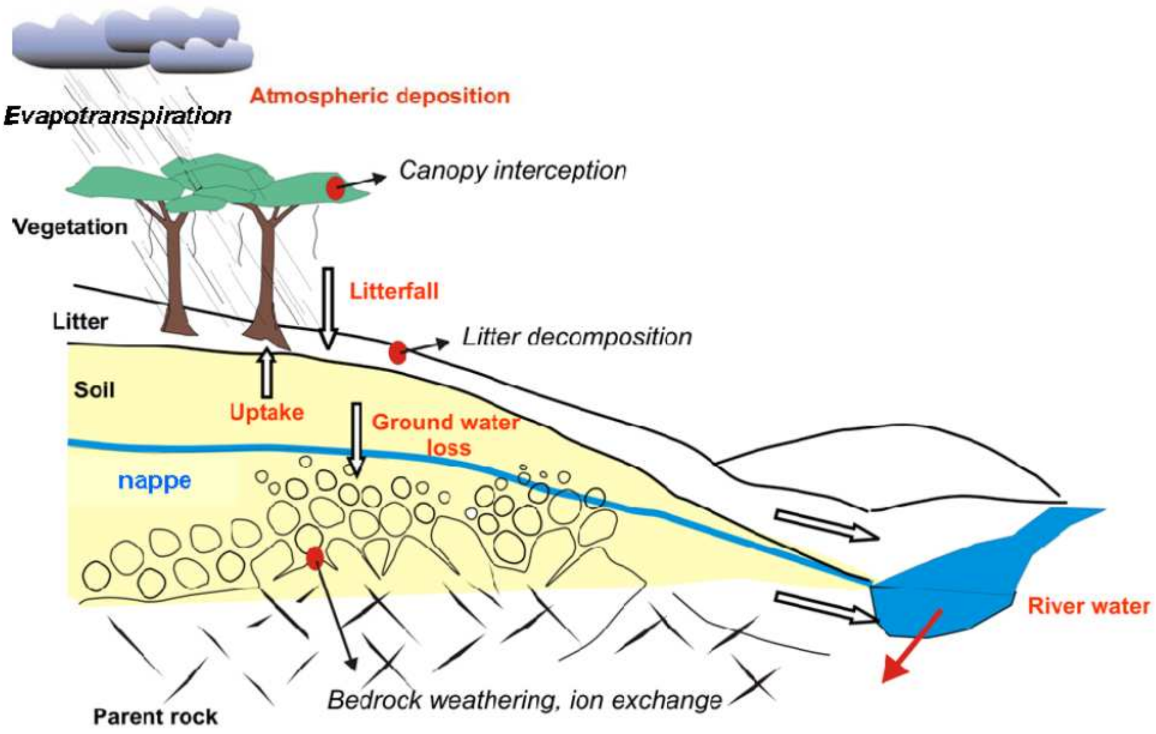

Figure 1.1. Scheme describing the main matter exchange between different reservoirs (soil-rock system, vegetation, and atmosphere) of a watershed (after Viers et al., 2007).

Boreal regions of the Russian Arctic play a crucial role in transport of elements from continents to the ocean at high latitudes. In view of the importance of these circumpolar zones for our understanding of ecosystem response to global warming, it is very timely to carry out detailed regional studies of trace elements (TE) geochemistry in boreal landscapes. Arctic and subarctic regions are among the most fragile zones in the world due to their low resistance to industrial impact, low productivity of terrestrial biota and limited biological activity over the year. Changing climatic conditions for the boreal and arctic regions means that 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 (Dahlqvist et al., 2007). These zones represent one of the most important organic carbon reservoirs in the form of peat bogs, wetlands and soils very rich in organic matter and iron. As a consequence, trace elements in water are likely to be transferred in the form of organic colloids (humic and fulvic acids, microbial exudates, polysaccharides) and organo-mineral entities (Fe and Al hydroxide stabilized by organic matter) (Allard, 2006; Allard and Derenne, 2007; Dahlqvist et al., 2004, 2007; Viers et al., 1997; Ingri and Widerlund, 1994; Gustafsson and Gschwend, 1997; Gustafsson et al., 2000; Andersson et al., 2001; Pokrovsky et al., 2005, 2006, Filella, 2007).

1.1.2. Nature of colloids and their role in mobilisation of trace elements

In order to understand the role of colloids in aquifer systems, it is important first to characterize their occurrence and origin.

The size spectrum of chemical species in aquatic systems is presented in Figure 1.2. The upper size limit for a colloidal suspension can be considered the point at which Brownian motions is no longer the dominant process for particle – particle interactions. In some cases, small living organisms such as viruses, bacteria, protozoa and algae frequently termed hydrophilic biocolloids, may be included in the colloidal fraction (Ogura, 1977). The lower limit for colloids is less well defined (Prost and Rondelez, 1991), with a vague bonduary between dissolved and colloidal phases depending on the chemical species. Thus, the types of organic colloids present in aquatic environments include macromolecular organic matter, microorganisms, viruses, biocolloids, aggregates of exudates and nanoparticles, such asclay minerals and oxides of iron, aluminium and manganese coated with or sorbed on organic matter (Tipping, 1988; Guo and Santschi, 1997; Buffle et al., 1998; Gustafsson et al., 2000; Gaillardet et al., 2003). Depending on research purposes, it is difficult to reach an universal definition for aquatic colloids (Guo and Santschi, 2007).

Colloids in surface water (Gustaffson and Gschwend, 1997) originate, in general, from the soil horizons, and can be organic, inorganic and organo-mineral (Ingri and Widerlund, 1994; Gustafsson and Gschwend, 1997; Viers et al., 1997; Gustafsson et al., 2000; Dahlqvist et al., 2004, 2007; Pokrovsky et al., 2005a, 2006a; Allard, 2006; Andersson et al., 2006; Allard and Derenne, 2007). Degradation of plant litter on the soil’s surface yields a family of organic colloids (soluble humic substances, i.e., humic and fulvic acids) which constitute, in an insoluble form, the upper mineral soil horizon.

These organic colloids are usually combined with mineral soils particles creating either organo-mineral clay-humic complexes (i.e., Fe and Al hydroxides stabilized by organic matter) in well drained environments, or dispersed complexes if the soil is not drained enough. In this upper horizon, trace elements are also present in colloidal form, being released during the decomposition of the plant litter. In boreal regions, the presence of wetlands, abundant precipitation and sufficient plant production creates favorable conditions for formation of organic rich soils, providing high concentrations of organic matter in surficial waters and thus, colloidal status of many elements in waters.

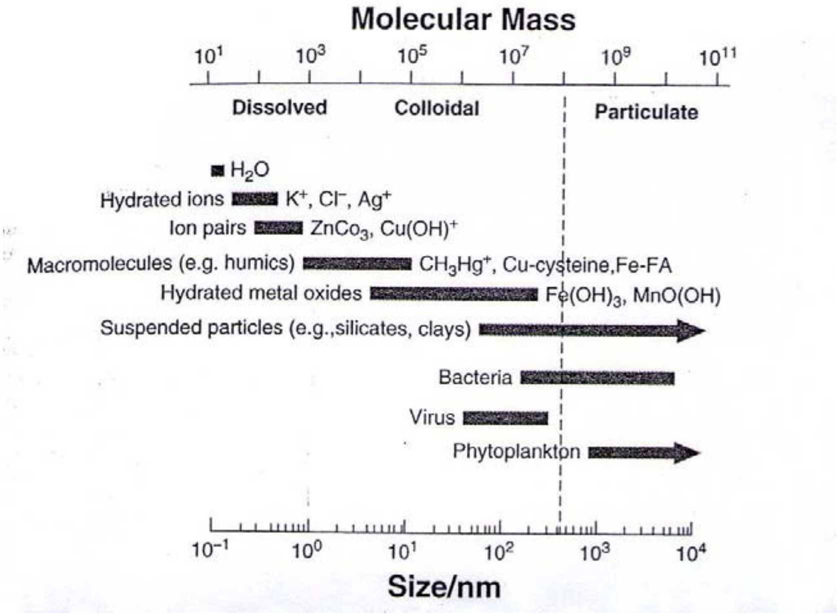

Figure 1.2. Size spectrum of chemical species in aquatic systems. Taken from Guo and Santschi (2007).

Mineral inorganic colloids are most commonly represented by metal oxyhydroxides (e.g., iron-, aluminium- and manganese-oxyhydroxides), siliceous phases and clays. They are formed during intensive chemical weathering of primary soil minerals (silicates and multiple oxides) in the upper soil horizon. This process is usually called “podzolisation” (e.g., Duchaufour, 1951, 1997; Buurman and Jongmans, 2005). It takes place in an aggressive acid medium created by plant litter decomposition products, and is controlled by the influence of a mixture of organic acids and complexing agents. Cations Ca^{2+}, Mg^{2+}, K^+, Na^+ are removed together with iron and aluminium. This leaching is accompanied by migration and subsequent accumulation of iron and/or aluminium organo-mineral complexes in a soil horizon B called podzolic.

One of the colloids’ properties is strong scavenging capacities towards cations. They play a major role in the mobilization of trace elements in soils and waters affecting elemental distribution in natural systems through interfacial adsorption or complexation processes (Buffle, 1988). Quantitative modeling of migration and bioavailability of TE requires the knowledge of stability constants for complexation reactions of trace metals with colloidal organic matter. The most powerful and precise method of assessing these constants is voltammetry and potentiometry; however, their use is restricted by very low number of transition metals (Zn, Cu, Cd, Pb) and some rare earth elements (Stevenson and Chen, 1991; Johannesson et al., 2004; Chang Chien et al., 2006; Prado et al., 2006). Up to present time, large number of trace elements, including trivalent and tetravalent elements, remains unexplored and the quantification of their stability constants with natural colloidal matter is not possible.

1.1.3. Methods of colloids' separation

There is a whole range of currently available strategies for separation and analysis of colloids in natural water. An important progress in characterizing the behaviour of TE in aquatic environments has been done thanks to development of high resolution analytical instrumentation and techniques (see Gaillardet et al., 2003 for review). Techniques like dialysis, voltammetry, gels diffusion (DET and DGT) are routinely used to obtain in situ information for small colloids, whereas a combination of rapid fractionation procedures, including filtration, field-flow fractionation, split-flow lateral transport thin (SPLITT) separation cells, and cross-flow ultrafiltration (CFF) can be used for the ex-situ characterization of TE association with colloids.

Ultrafiltration is most often used to characterize the proportion of dissolved and colloidal forms in surficial rivers, lakes, groundwater and seawater (Hoffman et al., 1981, 2000; Guo and Santschi, 1996; Viers et al., 1997; Dupré et al., 1999; Eyrolle and Benaim, 1999; Olivié-Lauquet et al., 1999, 2000; Ingri et al., 2000, 2004; Pokrovsky and Schott, 2002; Pokrovsky et al., 2005a, 2006a, 2006b; Dia et al., 2000; Pourret et al., 2007; Pédrot et al., 2008). In practice, there are a number of complications associated with concentration polarisation and the formation of a gel layer (the increase in colloid concentration directly above the membrane surface due to the slow back diffusion of colloids compared to their movement, under pressure, towards the membrane) (see Buffle el al., 1992). These effects may result in fractionation occurring in a different size range to that expected from the nominal pore size of the filter. Furthermore, the actual size range separated may alter over the course of the filtration and is dependent on filter manufacturer and surface area (Horowitz et al., 1996). Choice of appropriate filters and filtration conditions, in particular flow rates, can help to reduce these problems. The separation by membranes may, however, be dependent on molecular structures in NOM as well as the size (Assemi et al., 2004). The separation of molecules according to size and shape by membrane filtration is also influenced by the methodical conditions.

When more than one size fraction is required, cascade or parallel filtration may be used to study the colloidal size range in detail. In cascade filtration, the same sample is filtered successively through filters of different pore sizes. In parallel filtration, a series of aliquots are taken from the same sample and filtered separately through filters of different pore sizes. Both parallel (Laxen and Chandler, 1983 and 1982) and cascade filtration (Douglas et al., 1993; Moran and Moore, 1989) have been widely used. However, we recommend cascade filtration because it minimizes aggregation of colloids which occur during storage of the sample and at the membrane surface (Buffle et al., 1992).

Ultrafiltration usually requires an initial pre-filtration step at a pore size of 0.45 µm (Tanizaki et al., 1992; Sigleo and Helz, 1981; Sigleo et al., 1982). Recently ultrafiltration has been performed in cross-flow mode (Martin et al., 1995 for fresh- waters; Moran and Moore, 1989; Sempere et al., 1994 for seawater; Swarzenski et al., 1995 for estuarine waters). Cross- or tangential flow filtration, where the suspension is passed across the filter surface, may have certain advantages over traditional ultrafiltration, such as reducing concentration polarisation and increasing the flow rate (Moran and Buessler, 1993; Yeats and Strain, 1990). Therefore, filtration is best used simply to reduce the polydispersity of natural particles before applying other methods of particle size analysis. When filtration is used for accurate fractionation, filtration conditions, in particular flow rate, need to be optimized.

Some authors used dialysis as an in situ technique of colloid characterization (Benes and Steiness, 1974; Borg and Andersson, 1984; Berggren, 1989; Alfaro-De la Torre et al., 2000; Gimpel et al., 2003; Nolan et al., 2003; Buschmann and Sigg, 2004; Pokrovsky et al., 2005a). Dialysis is related to filtration, but no pressure is applied, the movement of solutes being driven solely by diffusion. The long times required to achieve equilibration (typically days or weeks), has resulted in a limited use of dialysis in the laboratory, although it has been used extensively for in situ measurement of dissolved species in waters (Holm et al., 1995; Borg and Andersson, 1984; Benes and Steinnes, 1974), for example in sediment pore waters (Carignan et al., 1985). Separation is based on the nominal size of the membrane, although the slow diffusion of colloids precludes straight forward size discrimination. Dialysis has been used in conjunction with other fractionation techniques, primarily filtration, either for comparative purposes or to fractionate material into dissolved, colloidal and particulate components in preference to ultrafiltration (Gasser et al., 1994; Apte and Rogers, 1993). Using filtration with dialysis, however, removes one of the main advantages of dialysis i.e. that it can be used in situ.

Generally speaking, chemical composition of the most of surface and ground waters is a result of the rain-water-rock interaction on the earth surface and in the soil zone (Drever, 1982). From ultrafiltration experiments in tropical environment (Cameroon), Dupré et al. (1999) demonstrated the key role of organic colloids in the transport of elements such as Al and Fe, the major constituents of the soil minerals.

Experimental study of the TE speciation in waters of boreal forest landscapes performed by Dobrovolsky (1983) demonstrated an important role of complex organic compounds of metals, as well as colloidal particles. Forms of monatomic ions of iron participating in water migration in boreal zones play here a subordinate role, whereas organic complexes can constitute up to 80% of the overall soluble metals in soil. Notably, the percentage of these forms increases in more boreal landscapes, i.e., proportion of organic complexes depends on the proportion of wetlands of a territory (Laudon et al., 2004; Frey and Smith, 2005). Hence, the first goal of this thesis consists in quantitative study of TE fractionation in colloids of boreal waters using a technique of cascade filtration and ultrafiltration.

1.1.4. Isotopical aproches

Processes controlling the chemical composition of natural waters are of major interest for geochemists because they are the main pathways for the transport of elements and particles from the earth surface and subsurface to the oceans. Chemical and mechanical alteration of the continental crust leads to the disaggregation of rocks and minerals, the formation of soil systems and also allows the removal of chemical elements as well as of larger and smaller particles from altered rocks and soils by rain, pore, spring and river water.

Several geochemical and isotopic studies focused especially on suspended particulate and dissolved river loads in order to provide information about their origin and to examine elemental fractionation between colloidal and solution phases. Strontium-isotope ratios vary in nature because one of the strontium isotopes (^{87}Sr) is formed by the radioactive decay of the naturally occurring element rubidium (^{87}Rb). The ^{87}Sr/^{86}Sr ratios are mainly used as tracers of water–rock interaction (Blum et al., 1994; Négrel et al., 2001). The primary sources of Sr in natural water are atmospheric input, dissolution of Sr-bearing minerals, and anthropogenic input (Négrel and Petelet-Giraud, 2005).

Dissolved ^{87}Sr/^{86}Sr ratios have often been used to trace weathering patterns, water flow paths, erosion sources, and biological processes in groundwater, watershed/lake, riverine, and oceanic systems (Palmer and Edmond, 1989, 1992; Négrel et al., 1993; Yang et al., 1996; Bullen and Kendall, 1998; Chesney et al., 1998; Leung and Jiao, 2006). The ^{87}Sr/^{86}Sr ratio in sediments and suspended matter has also been used to identify sediment provenance in freshwater, estuarine, and marine systems (Faure, 1986; Douglas et al., 1995; Rachold et al., 1997; Négrel et al., 2000; Ingramand Lin, 2002; Singh and France-Lanord, 2002; Douglas et al., 2003; Bayless et al., 2004). Little attention, however, has been paid to the reasons for the distinct and often large differences in the strontium isotopic composition (and geochemistry, Douglas, 1993) between the particulate (> l µm), colloidal (< 1 µm), and dissolved (<0.003 µm) phases. These differences are potentially important to an understanding of the origin and geochemistry of the various suspended particulate and dissolved fraction entering the ocean.

Weathering is the most important factor determining the Nd concentration and isotopic composition in river water. Starting with the studies by Balashov et al. (1964) a number of investigations have recognized that rare earth elements (REE) are mobile during weathering (Fleet, 1984). Detailed studies of till profiles in northern Sweden showed that besides REE mobilization there is also a fractionation between light REE (LREE) and heavy REE (HREE) during till weathering (Ohlander et al., 1991; 1996; Land et al., 1999). This suggests that the Sm/Nd ratio in a soil profile change during weathering causing the isotopic composition of the released Nd to be different from that of the bulk soil. Changes in Nd isotopic composition during till weathering was clearly demonstrated in a study in northern Scandinavia (Ohlander et al., 2000) and these results suggest that selective weathering of the REEs might be an important factor governing the isotopic composition of aqueous transported Nd.

The aquatic geochemistry of REE in rivers and estuaries has been summarized in Sholkovitz (1995). However, despite several studies of river water REEs, there are few investigations on the temporal variations in REE concentrations in river water. A detailed study of river water transport of REE demonstrated large seasonal variations for La with the concentration varying by a factor of seven, and that the major fraction of the REE transport is with colloidal particles rich in organic C and Fe (Ingri et al., 2000). Although the relative proportions of aeolian and river introduced Nd to the oceans are not fully understood (Jeandel et al., 1995), rivers are an important pathway for Nd. Therefore a detailed understanding of the river transport is necessary to be able to understand how the Nd isotopic signal is transformed between its continental sources and final terminus, i.e., seawater and sediments.

Mg isotopes were reported to be particular useful for deciphering fractionation between plants and soils/solutions (Bolou-Bi et al., 2010), silicate (De Villiers et al., 2005; Pogge von Strandmann et al., 2008), and carbonate (Brenot et al., 2008; Jacobson et al., 2010) rock weathering including paleoenvironments (Pokrovsky et al., 2011) and during biotic and abiotic carbonate mineral precipitation (Shirokova et al., 2011; Mavromatis et al., 2012). In all these studies, Mg in aqueous solution is considered to be present as ionic or inorganic complexes of homogeneous isotopic composition. However, in various natural settings Mg may form complexes with organic matter and whose isotope fractionation factor is still very poorly known, except for chlorophyll (Black et al., 2006). The organic-rich boreal waters selected in this work having significant proportion of Mg in colloidal (1 kDa-0.22 µm) form offer an unique opportunity to test the hypothesis of two pools of dissolved Mg (colloidal and ionic) and to check the existence of isotopic equilibrium between colloidal and truly dissolved fractions.

In contrast to magnesium, copper is known to be present in the organic species both allochthonous soil-derived colloidal (1 kDa - 0.22 µm) and autochthonous, phytoplankton-derived Low Molecular Weight (< 1 kDa) complexes (McKnight and Morel, 1979, 1980; Ito and Butler, 2005) having presumably different stability constants (Hoffmann et al., 2007). The isotopic composition of copper is fairly well studied in river waters (Vance et al., 2008), soils (Bigalke et al., 2010 a, b; 2011) and plants (Weinstein et al., 2011). Provided that *i*) the isotopic equilibrium is attained and *ii*) no reduction of Cu(II) → Cu(I) occurs in natural colloids, the Cu^{2+} complexed with strong organic chelates may be expected to be enriched in heavy isotope relative to uncomplexed dissolved Cu^{2+} similar to that of Fe^{3+} (Dideriksen et al., 2008) and Zn^{2+} (Gélabert et al., 2006; Jouvin et al., 2009). The latter finding is in accord with the quantum mechanical calculations which predict that the heavier isotope should concentrate in the species in which it is most strongly bounded (Criss, 1999), as also proved in the case of other metal complexation with organic matter. The difficulties in applying these principles to natural waters lay in distinguishing between different types of ligands and colloids. Ultrafiltration through progressively decreasing pore size offers an elegant way of quantifying copper isotopic composition in high and low molecular weight colloids and organic ligands which will be applied, for the first time, to boreal stream and bog water.

Evidence from Fe isotope investigations has shown that transition metal isotopic signatures can be dynamic in rivers and streams. For example, Fantle and DePaolo (2004) demonstrated that streams with high concentrations of dissolved Fe relative to the concentration of Fe in the suspended load had δ^{56}Fe values that were ~1.0‰ lighter than those for average igneous rocks (~0‰, e.g., Beard and Johnson, 2006). The work by Bergquist and Boyle (2006) on Fe isotopes in the Amazon River system revealed that δ^{56}Fe values varied substantially among several of the river tributaries. Moreover, Ingri et al. (2006) showed that bulk Fe isotopic signatures in streams vary seasonally, probably due to differences in isotopic fractionation among distinct colloidal phases. Among the most important mechanisms that control Fe isotope fractionation are: modification of the oxidation-reduction state, complexation with organic matter, dissolution and precipitation of Fe minerals (Fekiacova et al., 2010). Hence, it is clear that Fe isotopic signatures in river waters provide novel, yet poorly understood, biogeochemical and source information. In order to use Fe isotopic signatures to unravel the geochemistry of Fe, we must first investigate how Fe isotopes are mobilized, transported, and fractionated between dissolved and colloidal phases.

1.1.5. Change of trace elements speciation in the context of the global climate warming

Metals speciation in natural waters is of increasing interest and importance because toxicity, bioavailability, environmental mobility, biogeochemical behavior, and potential risk in general are strongly dependent on the chemical species of metals (Fytianos, 2001). To allow an explanation of the diverging degrees of bioavailability and toxicity of different elements, enhanced knowledge is needed about the chemical forms in which the trace elements are present in water.

Arctic and subarctic regions are among the most fragile zones in the world due to their low resistance to the industrial impact, low productivity of terrestrial biota, limited biological activity over the year, and thus, low ability of the ecosystem for selfrecovering. In view of the importance of these circumpolar zones for our understanding of ecosystems response to the global warming, detailed regional studies of trace elements geochemistry in the boreal landscapes are very timely. Mobility of the organic carbon (OC) and associated TE during permafrost thawing caused by the climate warming is the main change happening in boreal zones and one of the principal environmental and scientific challenges nowadays. Continuous increase of the runoff of Russian arctic rivers during the last several decades (Serreze et al., 2002) together with the liberation of carbon and metals scavenged to present day by this permafrost (Guo et al., 2004) can modify fluxes of elements exported to the oceans (Hölemann et al., 2005), as well as their speciation in river water and soil solutions.

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 (Dahlqvist et al., 2007).

1.2. Description of the region

1.2.1. Characteristics of the boreal zone

The study of pristine river geochemistry, apart of some undeveloped tropical regions and temperate areas of the southern hemisphere, has a tendency to be more and more limited to the subarctic regions. The boreal zone’s remoteness and harsh winter climate have led too much of it being sparsely populated by people. Although not completely isolated from anthropogenic influence, the subarctic environments are relatively pristine which is significant for the studies of basic biogeochemical mechanisms operating in the terrestrial biosphere.

Covering most of inland Russia (especially Siberia), Sweden, Finland, Norway, Alaska and Canada, as well as parts of the extreme northern continental United States, northern Kazakhstan and Japan (Fig. 1.3), the **taiga** or **boreal forest** is the world's largest terrestrial biome extending throughout the middle and high latitudes (from 55°N up to the North Pole Circle) (Sayre, 1994).

Figure 1.3. Geographical distribution of the taiga (boreal) zone (after the Köppen-Geiger climate classification world map), http://fr.wikipedia.org/wiki/Image:Taiga.png.

Taiga zone has a harsh continental climate with a very large temperature range between summer and winter varying from -50°C to 30°C throughout the whole year. Aside from the tundra and permanent ice caps, it is the coldest biome on Earth. The zone experiences relatively low precipitation throughout the year (300-850 mm annually on average), primarily as rain during the summer months, but also as fog and snow; as evaporation is also low for most of the year, precipitation exceeds evaporation and is sufficient for the dense vegetation growth (Sayre, 1994). The forests of the taiga are largely coniferous, dominated by larch, spruce, fir, and pine, but some broadleaf trees also occur, notably birch, aspen, willow, and rowan.

Rocks of the NW Russia boreal zone are very heterogeneous and presented by Archean granites, basalts, ultramafic rocks. Much of the area was glaciated about 10-15 thousand years ago. As the glaciers receded, they left depressions that have since filled with water, creating lakes and bogs (especially muskeg soil). Elsewhere the rocks are covered by granitic moraine released by glaciers in retreat.

Boreal soils tend to be geologically young and poorly developed varying in depth from 30-40 cm in the north to 60-85 cm in the south and mostly presented by podzols in the European zone. They tend to be acidic due to the decomposition of organic materials (e.g., plant litter) and either nutrient-poor or have nutrients unavailable because of low temperatures (Sayre, 1994).

1.2.2. Study site

A part of the boreal region considered in this work is situated between latitudes 67°N and 56°N and longitudes 30°E and 38°E in European part of Russia. The natural waters of the north of boreal region, North Karelia (1) and the south of boreal region, Central Russia (2) were chosen as the objects of the study (Fig. 1.4). There are basins of the Vostochniy Stream, Palojoki River, Senga River, Ignatkovo Lake and the bog of Tsipringa lake basin.

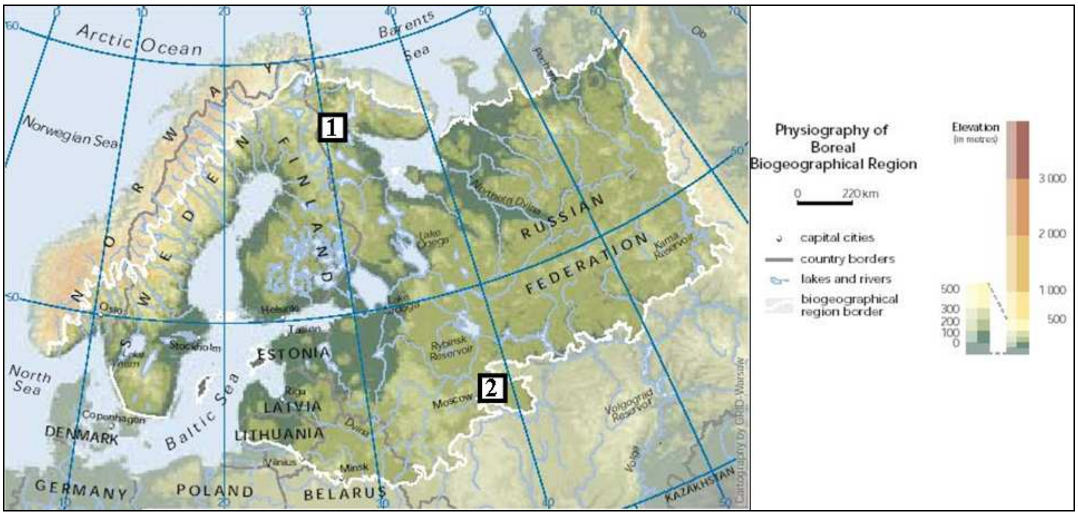

Figure 1.4. Map of the European boreal zone (*Source: EEA. UNEP/GRID Warsaw final map production from http://www.eea.europa.eu)* with the studied Karelia area (1) and Central Russia area (2).

The river Palojoki flows out of Kivakkalampi Lake, it drains the rocky massif Kivakka from the south and empties into Pyaozero Lake. The river has a rapid current; its length is about 9 km and relative altitude of 155 m. The bedrock composition of the catchement are micro-pegmatic granites, granosyenites, syenites, syenit-diorites of the low-Proterozoic, biotite garanitogneisses and tributary biotite, biotite-amphibolite and amphibolite gneisses and amphibolites of the low-Archean ang glassial deposits of Quarternary.

The stream Vostochniy flows from west to east and empties into the lake Tsipringa. Its length is about 1 km and relative altitude of 50 m, the catchment area is of 0.95 km^2. The bedrock of the catchment is amphibolitic gabbroids of the low-Proterozoic of the Olanga groupe intruzive.

The bog (ZPBL) empties into the lake Tsipringa. Its relative altitude of 30 m, the catchment area is of 1.19 km^2. The bedrock of the catchment is Biotite garanitogneisses and tributary biotite, biotite-amphibolite and amphibolite gneisses and amphibolites of the low-Archean.

The river Senga is the right tributary of the Klyazma River. Its length is about 32 km; the catchment area is of 163 km^2. The bedrock of the catchment is alluvial flat deposits of Holocene.

The lake Ignatkovo is an oligotrophic bog lake of 0.3 km^2. The bedrock of the catchment is bog deposits of Holocene.

1.3. Methods using in the study

1.3.1. Cascade filtration and ultrafiltration

The main technique used in this study is a cascade filtration. Large volumes (20–30 L) were collected in pre-cleaned light-protected PVC bottles for size fractionation procedure employing 100, 20, 10, 5, 0.8, 0.4, 0.22, 0.1, 0.046, 0.0066 (100 kDa), 0.0031 (10 kDa), and 0.0014 µm (1 kDa) cascade filtration and ultrafiltration conducted directly in the field conditions using specially prepared polyethylene-covered clean space. The main characteristics of the filtration are listed in the scheme of the procedure is given in Figure 1.5.

Filtration through 100 µm or pre-filtration was performed using nylon net “Fisherbrand”. Cascade frontal filtration with the decreasing pore size from 20 to 0.1 µm was performed using a 250-ml vacuum polycarbonate cell (Nalgene) and nylon membranes (Osmonics). Frontal ultrafiltration (UF) in the series 100 – 10 – 1 kDa was performed using a 400-ml polycarbonate cell (Amicon 8400) equipped with a suspended magnet stirring bar located beneath the filter to prevent clogging during filtration. Vacuum filtration was performed using a portative hand-pump, and the ultrafiltration was performed using a portative automobile pomp. The large volumes of the samples were passed through the

Lavsan (polyethylene tereph-thalate, PETP) filters of 0.4 µm pore size and 500 cm² surface area. The filtration occurred via gravitational flow (0.3-0.5 kPa).

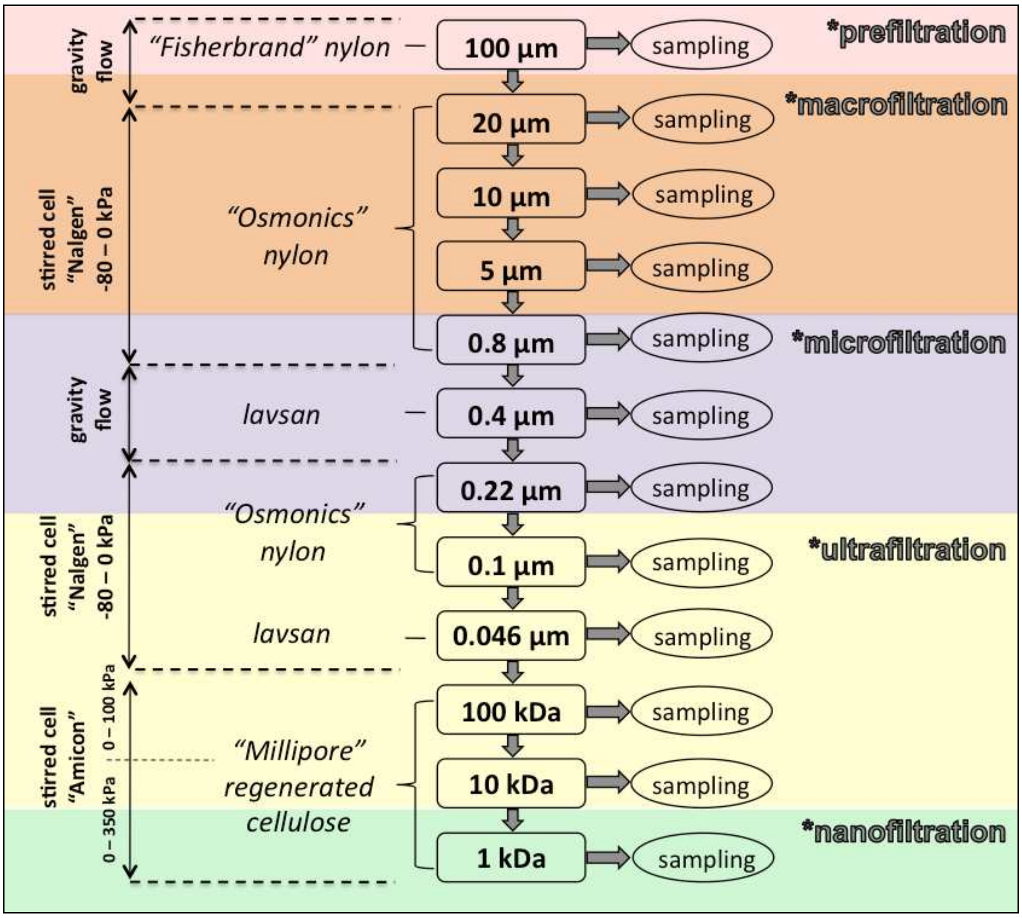

Figure 1.5. The scheme of cascade filtration used in this study.

Between each sample, the filtration system was cleaned by flushing EasyPure water, then 3% ultrapure HNO_3, and finally, EasyPure water. Each filter was soaked in EasyPure water during at least 1 day before the experiment and used only once. During filtration, the first 50 ml of sample solution were discarded, thus allowing saturation of the filter surface prior to recovery of the filtrate. Discussions of this technique and precautions against possible filtration artifacts are given in Viers et al. (1997), Dupré et al. (1999), Pokrovsky and Schott (2002), Pokrovsky et al. (2005, 2006), Alekhin et al. (2010).

Dialysis experiments were performed using 20-50 ml precleaned dialysis bags placed directly in the river or bog water (in-situ dialysis). The duration of this dialysis procedure was between 72 and 120h. For dialysis experiments, EDTA-cleaned trace-metal pure SpectraPor 7® dialysis membranes made of regenerated cellulose and having pore sizes of 1 kDa were thoroughly washed in EasyPure water, filled with ultrapure Milli-Q deionized water and then placed into natural water. The efficiency of the dialysis procedure was evaluated by comparing major anion concentrations. These concentrations were always identical to within

± 10%, suggesting an equilibrium distribution of dissolved components. Further details of dialyses experiments procedure are described in Vasyukova et al., 2010 and Pokrovsky et al., 2011, 2012.

1.3.2. Chemical analysis

Water temperature, pH, dissolved oxygen concentration and conductivity were measured in the field. The pH was measured using a combination glass electrode calibrated against NIST buffer solutions. Dissolved oxygen were measured using analizator of liquids «Expert-001» with termooxymeter (Clark oxygen sensor) with uncertainty of 5%. Major anion concentrations (Cl^-, SO_4^{2-}, NO_3^-) were measured by ion chromatography (Dionex 2000i) with an uncertainty of 2%. Alkalinity was measured in situ by Gran titration with HCl using phenolphthalein as indicator. The dissolved organic carbon (DOC) was determined using Shimadzu SCN Analyzer (Toulouse) and Elementar TOC analyzer (Moscow) with an uncertainty of 3% and a detection limit of 0.1 mg/L.

To study the spectrophotometric characteristics of the water samples directly in the field the absorption in the wavelength range 375-655 nm on photometer "Expert-003" were measured. The cartridges with working wavelengths 375, 400, 430, 470, 505, 525, 572, 590, 655 nm and the glass cell of the length 30.01 mm were used. Absorption spectra (resolution 1 nm) of the filtrates over the wavelength range 200-700 nm were measured with the spectrophotometer Specord 50 in the laboratory.

Weight average molecular weights were measured by size exclusion chromatography (SEC) using chromatographic system Agilent 1100 (Agilent Technologies, USA) with diode array detector and Ultropac column TSK G2000SW 7.5x300mm (LKB, Sweden). Solution of 0.1 M Na–phosphate buffer (pH 7) and 0.1% sodium dodecyl sulfate was used as an effluent. All samples were purified from low molecular weight contaminants by elution through a Sephadex G-10 column. Calibration was made by globular proteins.

Major and trace elements (TE) were measured without preconcentration by ICP-MS (7500ce, Agilent Technologies). Indium and rhenium were used as internal standards. The international geostandard SLRS-4 (Riverine Water Reference Material for Trace Metals certified by the National Research Council of Canada) was used to check the validity and reproducibility of each analysis. A good agreement between our replicated measurements of SLRS-4 and the certified values was obtained (relative difference < 5%).

1.3.3. Isotope analysis

Prior the isotopic separation using chromatographic column, filtered acidified water samples were evaporated in wide mouth Teflon containers (300 mL volume) placed on teflon-coated hotplate at 80°C located within the isolated polycarbonate box (internal air filtered class A 100). Blank Milli-Q water (apparatus Milli-Q Element Merck Millipore) was routinely evaporated using the same procedure. Precipitates formed at the bottom of containers were digested using the mixture of HNO_3, H_2O_2 and HF following standard procedure of organic-rich solid samples digestion (Viers et al., 2007). The digestion products were evaporated and dissolved in HCl or HNO_3 ultrapure bidistilled acids before introduction to the column. All sample preparation manipulations were performed in clean room class A10000 and the chromatographic separation was conducted in the laminar hood box class A100 located in the clean room.

1.3.3.1. Strontium

Strontium isotopic ratios were measured by thermal ionization mass spectrometry (Finnigan Mat 261) preceded by chemical separation and chemical extraction of Sr by ion exchange chromatography using chromatographic material Sr.Spec and HF, HNO_3 and HCl acids in a clean room. Data correction was based on the systematic analysis of the NBS 987 standard. The average value of $^{87}Sr/^{86}Sr$ for NBS 987 standard (0.710248) was found to be 0.710250 ± 0.000010 (n = 10).

1.3.3.2. Neodymium

Nd isotopic ratios were carried out by thermal ionization mass spectrometry (Isoprobe-T, GV Instrument) at the Laboratory of analytical development for isotopic and elementary analysis and by multicollector inductively coupled plasma mass spectrometry (Neptune Plus, Thermo Fisher Scientific) at the LSCE (Laboratoire des Sciences du Climat et de l'Environnement) laboratory.

Nd was isolated from the bulk sample using two different methods. In the first one (for the samples analysed by TIMS) the protocol followed the method already described by Pin et al. (1994, 1997). The second one isolated the rare earth element using a Tru-Spec resin (Quidelleur et al., 2009) followed by a high performance liquid chromatography using a Luna SCX (Strong Cation Exchange) analytical column with 2-hydroxy-2-methylbutyric acid (HMBA, Sigma–Aldrich) complexing agent (Goutelard et al., 2009, Bourgeois et al., 2011).

For TIMS measurements, Nd was acquired in multistatic mode and using the total evaporation method (Dubois et al., 1992). This method was adapted to allow measurements of low quantity of Nd, between 1 and 5ng (Mialle et al., 2011). The average value for ^{143}Nd/^{144}Nd for the JNd-1 was found to be 0.51204 ± 0.00089 (n=20).

For MC-ICP-MS measurements, the instrument was equipped with an Apex system to increase the sensibility at a value of 420V/ppm. Nd sample were analysed at concentration around 2 ng·g^{-1}. Data are corrected from mass bias using JNdi-1 and standard bracketing method. Data were also corrected from an residual Sm contamination using the ratio ^{147}Sm/^{149}Sm=1.08680 ± 0.00016 (Isnard, 2005). $\varepsilon_{Nd}(0)$ was determined using the value $(^{143}\mathrm{Nd}/^{144}\mathrm{Nd})_{CHUR}$=0.512638.

1.3.3.3. Copper

Cu isotopic composition was measured on the Neptune MC-ICP-MS (ThermoFinnigan) at GET (Toulouse). Cu has two stable isotopes of mass 63 and 65, which have average abundances of 69.17% and 30.83%, respectively. Cu was isolated from the bulk sample using the purification procedure of Marechal et al. (1999) on the AGMP-1 anion exchange resin (Bio-Rad, USA). Poly-Prep chromatography columns (0.8 * 4 cm) (Bio-Rad, USA) were used for the elemental separation. After the resin was cleaned (1.6 mL) with MilliQ deionized water (18.2 X) and 0.5 N HNO_3, the conditioning of the resin (6 mL) and the loading of the sample (300 ng of Cu in 1 mL) were performed with 7 N HCl. The hydrogen peroxide was added into the acid solution at a 0.001% concentration to avoid the presence of Cu in a different redox state. The matrix was eluted with 10 mL of 7 N HCl and Cu was collected in the next fraction (20 mL of 7 N HCl). Because isotopic fractionation may occur during the elemental separation on the ion-exchange resin (Marèchal and Albarède, 2002), we analyzed only the samples for which the separation procedure produced a 100% yield, taking into account the analytical uncertainties (Pokrovsky et al., 2008). Instrumental mass fractionation effects were corrected using sample-standard bracketing method or internal Zn standard and an exponential law; all data are presented in delta notation with respect to NIST 976 international reference material (Marechal et al. 1999):

$$\delta^{65}\mathrm{Cu}\ (‰) = \left(\frac{(^{65}Cu/^{63}Cu)_{sample}}{(^{65}Cu/^{63}Cu)_{JMC}} - 1 \right) *1000$$

1.3.3.4. Magnesium

Magnesium separation from matrix elements (mainly Ca) was performed using the protocol defined by Teng et al. (2007), in which ~15 µg of Mg were evaporated to dryness and re-dissolved in 2 ml 1 N HNO3 solution. Later, samples were loaded onto Bio-Rad poly prop 10 ml columns containing AG50W-X12 resin. Mg isotopes were measured with a Thermo-Finnigan 'Neptune' Multi Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP- MS) at GET (Toulouse, France). All solutions were prepared in 0.32 M HNO_3 and were introduced into the Ar Plasma using a standard spray chamber. Instrumental mass fractionation effects were corrected using sample-standard bracketing, and all data are presented in delta notation with respect to DSM3 international reference material (Galy et al., 2001):

$$\delta^{x}\text{Mg (‰)} = \left(\frac{({}^{x}Mg/{}^{24}Mg)_{sample}}{({}^{x}Mg/{}^{24}Mg)_{DSM3}} - 1 \right) *1000$$

The reproducibility of δ^{26}Mg analyses was typically <0.07 ‰ as confirmed by replicate analyses of three international Mg reference standards (DSM-3, CAM-1 and OUMg).

1.3.3.5. Iron

Filtered and acidified water samples were evaporated in the clean room of class 10 000 and iron was purified using anion exchange chromatography in a HCl medium (Strelow, 1980), as outlined in Poitrasson et al. (2004). We used 0.5 ml of Bio Rad AG1 X4, 200–400 mesh anionic resins loaded in thermoretractable Teflon columns having an internal diameter of 4 mm. After resin wash using the elution reagents and preconditioning, samples were loaded in 0.5 ml of 6M HCl and the matrix was eluted in 3 ml of the same acid. Iron was quantitatively eluted with 2 ml of 0.05M HCl. Purified iron samples were analyzed in a 0.05M HCl solution. Iron and the internal standard, Ni, were set to a concentration of 1 and 3 ppm respectivly.

Iron isotope measurements were performed at GET-CNRS in Toulouse using a Thermo Electron Neptune MC-ICP-MS (Bremen, Germany) following the methods described in Poitrasson et al. (2005). All analyses are reported in the delta notation relative to the IRMM-014 standard, expressed as δ^{57}Fe, which represents the deviation in per mil relative to the reference material:

$$\delta^{57}\text{Fe (‰)} = \left(\frac{({}^{57}Fe/{}^{54}Fe)_{sample}}{({}^{57}Fe/{}^{54}Fe)_{IRMM-014}} - 1 \right) *1000$$

We also obtained δ^{56}Fe values but, since the relationships between δ^{56}Fe and δ^{57}Fe of the samples plot on a single mass fractionation line, only δ^{57}Fe values are discussed in this paper. Data quality was checked by reported analyses of our house hematite standard every 5 samples in the analytical sequence.

1.4. Objectives and scope of the study

This study is aimed at improving our understanding of trace element speciation and migration under typical conditions of boreal aquatic environment.

The main objectives of the study are:

1) To describe the molecular weight distribution of trace elements and organic matter in various types of natural waters representative of boreal watersheds;
2) To characterize trace elements, their colloidal forms and organic matter speciation in the continuum soil solution – bog – stream – feeding and terminal lakes in the surface subarctic waters;
3) To test the dependence of isotopic composition on fraction size, speciation and physico-chemical conditions of the waters and to compare their isotopic ratios for the south and the north of Russian European boreal zone.

The main originality of the work is to apply the method of cascade filtration to study the molecular weight distribution of trace elements in surface waters and to combine the geochemical and isotope techniques, for the first time on the same natural objects, and particularly on the system soil solution – bog – stream – feeding and terminal lakes.

1.5. Thesis organisation

The manuscript is composed of the main thesis based on publications, submitted or in preparation, addressing the above mentioned objectives, and the supplementary information which comprises several extended annexes presenting analytical results.

The principal part of the manuscript comprises four chapters organized in the form of scientific articles all devoted to geochemical behaviour and forms of migration of elements in natural waters of European boreal zone, comprising a thorough study of size fractionation along the progressively decreasing pore size from 100 µm to 1 kDa.

- **Chapter 2: Size fractionation and optical properties of dissolved organic matter in the continuum soil solution-bog-river and terminal lake of a boreal watershed**

(North Karelia, Russia). This manuscript (Ilina et al., 2012c, in preparation for *Biogeosciences*) is aimed at assessing the change of size fractionation of dissolved organic carbon and its chemical and optical properties in series of filtrates and ultrafiltrates of progressively decreasing pore size, investigated over 5 orders of magnitude, from 100 µm to 1 kDa, along the landscape transect from the source (feeding) soil solution and humic bog lake to the stream and to the terminal lake.

- **Chapter 3: Speciation, size fractionation and transport of trace elements in a boreal watershed (North Karelia, Russia).** This paper (Ilina et al., 2012d, in preparation for *Chemical Geology*), is aimed at assessing the change of concentration and element ratio change in the series of cascade filtrates and ultrafiltrates from 100 micron to 1 kDa, and estimation the degree of transformation of TE speciation and size distribution of colloids along the gradient soil solution – feeding bog and lake – stream – terminal lake.
- **Chapter 4: Stable (Cu, Mg) and radiogenic (Sr, Nd) isotope fractionation in colloids of boreal organic-rich waters.** This manuscript (Ilina et al., 2012b, submitted to *Chemical Geology*) describes the results of the isotopic composition radiogenic and stable elements, their association with organic matter that depends on the type of surface waters (bog and soil solutions, lake and river) and degree the association of trace element with colloidal fraction control the variation of its isotopic composition during filtration and ultrafiltration from 100 µm to 1 kDa.
- **Chapter 5: Extreme iron isotope fractionation between different size colloids of boreal organic-rich waters.** This part contains a publication (Ilina et al., 2012a, submitted to *Geochimica et Cosmochimica Acta*) which is aimed to test the possibility of the presence of different pools of Fe colloids having distinct isotopic signatures in different size fractions; to characterize the transformation of stable isotopic composition of colloidal Fe in various environments within the same watershed and to compare isotopic signatures of filtrates and ultrafiltrates in organic-rich rivers and lakes between the arctic and temperate zone at otherwise similar hydrochemical and lithological environments.
- In **Chapter 6**, **conclusion**s of the principle results are synthesised and **perspectives** of further research are outlined.

Chapter 2

Size fractionation and optical properties of dissolved organic matter in the continuum soil solution-bog-river and terminal lake of a boreal watershed (North Karelia, Russia)

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Size fractionation and optical properties of dissolved organic matter in the continuum soil solution-bog-river and terminal lake of a boreal watershed (North Karelia, Russia)

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Abstract

Size distribution and speciation of organic matter in natural waters between soil solution, bog, stream and feeding and terminal lake have been investigated in the basin of the Vostochniy Stream of north boreal zone in the Karelia region of North-West Russia during the summer base-flow period. The samples were filtrated directly in the field using cascade filtration as the mode of size fractionation procedure with a progressively decreasing pore size (100, 20, 10, 5, 0.8, 0.4, 0.22, 0.1, 0.046, 0.0066 (100 kDa), 0.0031 (10 kDa), and 0.0014 µm (1 kDa)) followed by dissolved organic carbon analysis, UV-vis and size exclusion chromatography measurements. The surrogate parameters such as SUVA, E_{254}/E_{436}, E_{280}/E_{350}, E_{254}/E_{365}, E_{365}/E_{470} and E_{470}/E_{655} were applied for the characterization of OM in the natural waters of soil solution, bog, river and lake.

In < 0.22 µm filtrates, there is a systematic decrease of DOC concentration, C/N ratio, SUVA (hydrophobicity and aromaticity) and proportion of colloidal (1 kDa – 0.22 µm) organic carbon along the watershed profile, from peat bog soil solution, feeding humic lake to the middle course of the stream and the terminal oligotrophic lake. Within the filtrates and ultrafiltrates of soil solution and terminal lake, the C/N ratio increases from 100 to 140 and from 7 to 25 for fractions of 0.22-10 µm and < 1 kDa, respectively. The SUVA, degree of humification, and hydrophobicity and aromaticity generally increase from HMW to LMW fractions being the highest in < 1 kDa fraction. The obtained results allow for comprehensive view of DOM transport and transformation among various size fractions within a small boreal watershed that can serve as an analogue of small rivers discharge to the Arctic Ocean. It follows that, during the summer baseflow season, the infleunce of organic-rich interstitial soil solutions originated in a typical peat bog zone can be completely masked by the processes occurrirng in adjacent bog surface waters, feeding lakes as well as in the stream itself. As such, depending on local physico-geographic settings, one may expect extremely high variability of both chemical nature and molecular weight of DOM delivered by small coastal watersheds to the Arctic Ocean during summer baseflow period.

2.1. Introduction

Dissolved organic carbon (DOC) in aquatic environments represents one of the largest active organic carbon reservoirs in the biosphere, with the amount of DOC in the oceans alone being comparable to the amount of CO_2 carbon in the atmosphere (Mannino and Harvey, 2000). It is a vital resource (Sun et al., 1997; Wetzel et al., 1995), affecting food webs either directly, by uptake from organisms, or indirectly by mechanisms such as turbidity, pH, metal chelation, and transport of contaminants (McDonald et al., 2004).

The diversity of DOC within a specific reach of a stream is dependent on the potential number of sources (Koetsier et al., 1997), the quality, and availability of the DOC to organisms. Sources of carbon can come from a variety of places with respect to a river, including autochthonous sources, or sources of carbon that arise from in-stream processes, and allochthonous sources, or sources of carbon that enter the stream and are external to the stream. Autochthonous sources may include leachate from dead organisms, phytoplankton, exudates etc., while allochthonous sources may include leachate from surrounding soils, grasses and inputs from riparian trees (Graça, 1993).

Natural organic matter (NOM) is found in all surface, ground and soil waters. NOM is a complex mixture of organic compounds present in all fresh water, particularly surface waters. NOM consists of a range of different compounds, from largely aliphatic to highly colored aromatics. NOM present in waters consists of both hydrophobic and hydrophilic components (Matilainen et al., 2011). The hydrophobic part is rich in aromatic carbon, having phenolic structures and conjugated double bonds, while hydrophilic NOM contains a higher proportion of aliphatic carbon and nitrogenous compounds, such as carbohydrates, proteins, sugars and amino acids. Hydrophobic acids constitute the major fraction of aquatic NOM, accounting for more than half of the dissolved organic carbon (DOC) in water (Thurman, 1985; Swietlik et al., 2004).

A major fraction of NOM present in surface or ground waters is composed of humic substances, which are complex macromolecular products of the chemical and biological degradation of plant and animal residues including lignin, carbohydrates and proteins (Uyguner and Bekbolet, 2005).

Humic substances (HS) are ubiquitous in water, soil and sediments, being one of the most widely distributed classes of natural products on earth (Ikan et al., 1990). They represent about 25% of the total organic carbon on earth and comprise 50–75% of the DOC in waters (Robards et al., 1994; Hertkorn et al., 2002) and, as such, they play an important role in the riverine ecosystem. HS are formed in the process of humification from different structural precursors of biotic origin and have irregular structure and varying composition (Zavarzina et al., 2002). HS can be further separated into three components, according to solubility as humic acids, fulvic acids and humin. Humic acids are defined as the fraction of humic substances that are not soluble in water under acid conditions (below pH 2), but become soluble at greater pH. They are often referred to as being the high molecular weight fraction, with weights being estimated to range from 1500 to 5000 Da in streams, and from 50,000 to 500,000 Da in soils (Malcolm, 1990). Fulvic acids are the fraction of humic substances that are soluble under all pH conditions and are referred to as moderate molecular weight substances ranging from 600 to 1000 Da in streams and 1000 to 5000 Da in soils (Malcolm, 1990). The third fraction, humin, is defined as the fraction that is not soluble in water at any pH value. Although the classification of humic substances into humic and fulvic acids is based on soil chemistry, the same terminology is adopted for aquatic organic matter.

Some of the molecules of which DOM is comprised contain chromophores and fluorophores, through which DOM interacts with UV and visible radiation. DOM contains many nonidentical chromophores, whose collective attenuation of incident UV and visible light causes the absorbance of DOM to decrease with increasing wavelength (Perdue and Ritchie, 2003).

The organic carbon content in water is used as a surrogate parameter to represent NOM concentration. Additionally, UV absorbance at 254 nm (UV254) is interchangeably measured with total organic carbon (TOC) to represent the NOM content in natural waters (Najm et al., 1994). SUVA (UV-adsorption A254nm(1cm)/mg C L^{-1}) is defined as the UV absorbance of a given sample at 254 nm divided by the DOC concentration of the sample. This ratio describes the nature of NOM in the water in terms of hydrophobicity and hydrophilicity; a SUVA >4 indicates mainly hydrophobic and especially aromatic material whilst a SUVA <3 illustrates mainly hydrophilic material (Edzwald and Tobiason, 1999).

Several researchers have emphasised that a good agreement may exist between the ability for NOM removal by coagulation and a high SUVA-value (Archer and Singer, 2006; Bose and Reckhow, 2007). Ratios between two different wavelengths such as: A254/A204, A254/A436, or A250/A365, have also been reported to be useful in NOM characterisation (Hur et al., 2006; Spencer et al., 2007; Li et al., 2009). The UV absorptivity at 280 nm was also introduced to represent total aromaticity because *n-n** electron transition occurs in this UV region (ca. 270-280 nm) for phenolic arenes, benzoic acids, aniline derivatives, polyenes and polycyclic aromatic hydrocarbons with two or more rings (Traina et al., 1990; Chin et al., 1994).

Towards a better understanding of the main features of DOM transformation during its transfer from the soil to the river, within a continuum soil solution – stream-terminal lake, we selected a small pristine boreal (subarctic) watershed. Over past decade, there is significant rise of the interest to boreal and subarctic zone which stems from to the governing role of these landscapes in carbon cycle regulation in high latitudes and overall for the planet (IPCC, 2007). This is mostly due to 1) high stock of organic carbon in soils of northern hemisphere that can be delivered as CO_2 to the atmosphere due to various transformation reactions in the aqueous phase, and, 2) at the same time, high vulnerability of boreal regions to climate warming. In particular, the increase of DOC concentration in surface waters due to global warming as it is observed in Nordic Countries, British Isles, and Northern and Eastern United States (by approx. 10 % over 10 years, Evans et al., 2005) and on-going acidification of boreal surface waters (Reuss et al., 1987, Borg et al., 1989; Skjelkvåle et al., 2001; Davies et al., 2005; Neal et al., 2008) should inevitably alter both the chemical nature of DOM and its bioavailability. In order to assess the main biogeochemical features of dissolved organic matter, we used frontal cascade filtration / ultrafiltration aiming to answer the following questions:

1) Is there a trend of DOM concentration and its chemical composition (C/N ratio, SUVA, light absorbance in visible range) from the source (feeding) soil solution and humic bog lake to the stream and to the terminal lake, and how it may reflect the relative contribution of allochthonous (soil humic) and autochthonous reservoirs?
2) What is the size fractionation of dissolved organic carbon along the progressively decreasing pore size, over 5 orders of magnitude, from 100 µm

to 1 kDa, along the landscape transect?

3) How variable are chemical and optical properties of DOM among the size fractions of various water samples, from soil solution to the terminal lake, and what are the main physico-chemical and biological processes responsible for this transformation?

4) Can the chemical and molecular size parameters of DOM in soil solutions serve as approximation for the nature of DOM delivered by small coastal organic-rich rivers to the Arctic Ocean?

It is anticipated that addressing these questions will provide new insights in the mechanisms of dissolved organic matter migration within the typical small watersheds of the subarctic zone and allow to establish the links between the physico-chemical properties and bioavailability of DOM and its possible transformation reactions in the estuarine zone.

2.2. Object description (climate, geology and hydrology)

The climate of the region is mild-cold, transitional between oceanic and continental, with a determinant influence of the Arctic and Northern Atlantics. Winter is long and soft, summer is short and cool. Average temperature in January is -13°C, and +15°C in July, but extremes can reach -45° to +35°C in winter and summer periods, respectively. The dominant wind direction is South-West in winter and North-East in summer. Average annual precipitation amount is between 450 and 550 mm/yr. Snow period lasts from October to April-May with the average thickness of snow cover 70 – 80 cm, but often over than 1 m. The territory is under the influence of the warm Gulf Stream, but microclimatic conditions differ dramatically because of the large cross-country. In summer in the deep and sheltered valleys it's much warmer than on the mountain tops, whereas in winter it's much colder in the valleys where the mountains cold air accumulates. Our study area is located in the most elevated part of Karelia, in the central part of Maanselkya. It is a landscape of tectonic denudation hills, plateaus and ridges with an average altitude of 300-400 meters with separate insulated massifs (Tunturi).

The region has a well-developed river network that flows via a system of glacial lakes. The water of small and medium-sized lakes gets a warm up to 22-25°C in summer. Water is soft, low mineralized, and rich in dissolved organic matter originated from feeding bogs. Karelian rivers are fed by rainfall, swamps, groundwater and snowmelt. The rivers break up earlier than their conjugated lakes and some full of rapids reaches don't freeze at all. The average date of floods in North Karelia is April 25 – May 5. The rivers freeze in November – December. Natural fluctuations of water level don't exceed 1.5-2 m.

Due to influence of past glaciation, the rivers of Karelia are comparably short. But a large part of length (up to 50%) cans consist of the flowage lakes. There are « lake-river » systems, consisting of a chain of lakes connected by rapids channels. The accumulative systems when the lake collects drain of many rivers giving its waters to one big river are also charactered for Karelia. There is another peculiar phenomenon – this is a bifurcation (splitting) of the water flow. The average gradient of rivers is about 1 m/km, and up to 3-5 m/km in the rapids channels. Rivers of Karelia are very young geologically, their beds are composed of hard rocks, and they just started to make the longitudinal profile and the valley with not wide floodplains, without high terraces.

Chemical composition of river water in Karelia is determined by the chemical weathering of silicate parent rocks of the Baltic crystalline shield and quaternary deposits, and the presence of numerous peatlands. Typical values of total discharge of solids (TDS) for this region are 15-30 mg/l (Maksimova, 1967; Zakharova et al., 2007), and the concentration of river suspended matter is very low. The adjacent lakes between the rivers tremendously decrease the size of actual watershed feeding the given rivers that are being stored in the sediments with chemical elements and OM.

The soil cover of the region is very young and it is often absent on ledges of bedrock and steep slopes. Low temperature in combination with high humidity is responsible for the slow humification and mineralization of plant residues. Therefore, a lot of organic matter is accumulated in the form of peaty horizons, and on better drained sites – in the form of coarse humus. Predominant soils are illuvial-humic and illuvial-ferruginous-humic podzols. All types of podzols exhibit a highly acidic reaction and low base saturation of the upper layers.

Coniferous forests dominate the vegetation of the region. The main conifers are pine and spruce. The common deciduous are birch, aspen, alder. The sphagnum pine occurs on the plains, depressions and swamps. Sparse understory consists of mountain ash and juniper. It is dominated by blueberries and cranberries in the shrub layer, and green mosses in the lower layer. The rocks are usually covered with patches of black, gray, yellow, red, brown crustose lichens.

The basin of the Vostochniy Stream was chosen as the object of the study. It is located in the Northen Karelia (N 66°, E 30°) near the border with Finland and about 40-60 km south from the Arctic Circle. The stream Vostochniy flows from west to east and empties into the lake Tsipringa. Its length is about 1 km and relative altitude of 50 m, the catchment area is of 0.95 km^2. The bedrock of the catchement is amphibolitic gabbroids of the low-Proterozoic of the Olanga groupe intruzive. Tsipringa and Pyaozero lakes are the part of the Kuma reservoir system.

2.3. Materials and methods

2.3.1. Sampling, filtration, dialysis

The basin of the Vostochniy Stream was chosen as the object of study. The feeding humic lakes of the bog zone (OR-4, OR-5, OR-6), waterlogged shores of the feeding lake (OR-2, OR-3), middle course of the stream (OR-7), mouth reach (OR-1) of the stream, interstitial soil solution (OR-9), and large clear water terminal lake (OR-8) were sampled in July 2010 during base-flow period. Soil solution (OR-9) of the peat bog zone of this watershed was collected from the depth of 5-10 cm in a piezometer.

Figure 2.1 presents a simplified scheme of the sites along with sampling points, whereas the list of collected waters is given in Table 2.1. Large volumes (20–30 L) were collected in pre-cleaned light-protected PVC bottles for size fractionation procedure employing 100, 20, 10, 5, 0.8, 0.4, 0.22, 0.1, 0.046, 0.0066 (100 kDa), 0.0031 (10 kDa), and 0.0014 µm (1 kDa) cascade filtration and ultrafiltration conducted directly in the field conditions using specially prepared polyethylene-covered clean space. The main characteristics of the filtration are listed in Table 2.2 and the scheme of the procedure is given in Fig. ESM-2.1.

Filtration through 100 µm or pre-filtration was performed using nylon net “Fisherbrand”. Cascade frontal filtration with the decreasing pore size from 20 to 0.1 µm was performed using a 250-ml vacuum polycarbonate cell (Nalgene) and nylon membranes (Osmonics). Frontal ultrafiltration (UF) in the series 100 – 10 – 1 kDa was performed using a 400-ml polycarbonate cell (Amicon 8400) equipped with a suspended magnet stirring bar located beneath the filter to prevent clogging during filtration. Vacuum filtration was performed using a portative hand-pump, and the ultrafiltration was performed using a portative automobile pomp. The large volumes of the samples were passed through the Lavsan (polyethylene tereph-thalate, PETP) filters of 0.4 µm pore size and 500 cm² surface area. The filtration occurred via gravitational flow (0.3-0.5 kPa).

Before each filtration, the system was cleaned by flushing EasyPure water, then 3% ultrapure HNO_3, and finally, abundant EasyPure water. Each filter was soaked in EasyPure water at least 1 day before the experiment and used only once. Preliminary experiments demonstrated that flushing 50 ml of MilliQ water (after 1 day soaking) through Amicon UF and Nalgen filtration cell with a membrane is sufficient to decrease the blank of OC to as low as 0.2-0.5 mg/L which is at least an order of magnitude lower than the typical concentrations in filtrates and ultrafiltrates.

During filtration, the first 50 ml of sample solution were discarded, thus allowing saturation of the filter surface prior to recovery of the filtrate. This greatly decreased the probability of cross-contamination during sample filtration, while improving the OC blank. It also provided identical conditions of filtration for all samples and allowed a high recovery of colloidal particles. Discussions of this technique and precautions against possible filtration artifacts are given in Viers et al. (1997), Dupré et al. (1999), Pokrovsky and Schott (2002), Pokrovsky et al. (2005, 2006), Alekhin et al. (2010).

2.3.2. Analytical techniques

Water temperature, pH, and conductivity were measured in the field. The pH was measured using a combination glass electrode calibrated against NIST buffer solutions. Major anion concentrations (Cl^-, SO_4^{2-}, NO_3^-) were measured by ion chromatography (Dionex 2000i) with an uncertainty of 2%. Alkalinity was measured in situ by Gran titration with HCl using phenolphthalein as indicator. The dissolved organic carbon concentration (DOC) was determined using Shimadzu SCN Analyzer (Toulouse) and Elementar TOC analyzer (Moscow) with an uncertainty of 3% and a detection limit of 0.1 mg/L.

To study the spectrophotometric characteristics of the water samples directly in the field the absorption in the wavelength range 375-655 nm on photometer “Expert-003” was measured. The cartridges with working wavelengths 375, 400, 430, 470, 505, 525, 572, 590, 655 nm and the the 30.01 mm glass cell were used. Absorption spectra of the filtrates over the wavelength range 200-700 nm with 1 nm resolution were also measured with the spectrophotometer Specord 50 in the laboratory.

Specific UV-absorbance, SUVA (UV-adsorption A254nm(1cm)/mg C L^{-1}) is defined as the UV absorbance of a given sample at 254 nm divided by the DOC concentration of the sample. This ratio describes the nature of NOM in the water in terms of hydrophobicity and hydrophilicity; a SUVA >4 indicates mainly hydrophobic and especially aromatic material whilst a SUVA <3 illustrates mainly hydrophilic material (Edzwald and Tobiason, 1999, Matilainen et al., 2011).

Weight average molecular weights were measured by size exclusion chromatography (SEC) using chromatographic system Agilent 1100 (Agilent Technologies, USA) with diode array detector and Ultropac column TSK G2000SW 7.5x300mm (LKB, Sweden). Solution of 0.1 M Na–phosphate buffer (pH 7) and 0.1% sodium dodecyl sulfate was used as an effluent.

All samples were purified from low molecular weight contaminants by elution through a Sephadex G-10 column. Calibration was made by globular proteins.

2.4. Results and discussion

Measured dissolved organic carbon, nitrogen and major elements concentrations, C/N ratios, weight-average molecular weights, alkalinity, pH and conductivity values in the water samples are reported in the Table 2.3. The studied waters of the Vostochniy stream and the terminal Tsipringa Lake are neutral with pH ranging from 6.3 to 7.5 where as the waters of waterlogged humic lake and soil solution are acidic with pH of 5.8 and 3.6, respectively. All waters are low mineralized (≤ 30 mg/L) with the dominance of Ca and HCO_3^- ions or Ca, Cl and Na ions (soil solution). The inorganic ion charge balance $((\sum^{+}-\sum^{-})/\sum^{+})$ is below 0.1 for all samples except soil solution having a deficit of anions of 0.4-0.5. This deficit is correlated with DOC concentration in filtrates and ultrafiltrates similar to those reported in other surface waters of North Karelia (Vasyukova et al., 2010) typical for organic-rich boreal surface waters (DOC concentration equals to 16-19, 7 and 75 mg/L in stream, terminal lake and soil solution, respectively).

2.4.1. Spatial variations of OC characteristics

2.4.1.1. DOC

The distribution of DOC concentration (< 0.22 µm filtrate) along the landscape profile of the Vostochniy stream is plotted in Fig. 2.2. There is a systematic decrease of [DOC] downward the catchment, from soil solution (OR-9) through the feeding bog (OR-6) and small feeding lakes (OR-5, OR-4, OR-3, OR-2), along the stream itself (OR-7, OR-1) and finally to the terminal Tsipringa lake (OR-8). The largest decrease occurs between soil solution (OR-9) and bog lake (OR-6) and between the mouth of the spring and the terminal clear water lake; the variations of [DOC] within the upper humic lakes and within the stream are rather small (< 10 %).

2.4.1.2. C/N

The concentration of DON and the C/N ratio systematically decrease along the watershed profile, from soil solution through stream and to the terminal lake (Table 2.3, Fig. 2.3 A), and the higher the [DOC], the higher the C/N ratio (Fig. 2.3 B). The C/N value in soil solution is equal to 104 which is similar to the biomass of coniferous trees thus confirming the dominant role of lingo-cellulose complex of pine and birch litter in formation of aqueous organic matter of peat bog soil waters (Guggenberg et al., 1994; See and Bronk, 2005; Tremblay and Benner, 2006).

The samples of the upper lakes (OR-6 to OR-3) and the waters of the stream (OR-2 to OR-1) are very similar between each other but drastically different from bog soil waters. As such, the dominant source of OM in the stream waters should be bog lakes rather than interstitial peat soil solutions.

The water of the Lake Tsipringa exhibits the lowest C/N ratio of 24, typical for aquatic phytoplankton and macrophytes and their humification products (Wolfe et al., 2002). Therefore, the contribution of allochthonous river and bog waters to the DOM pool of large oligotrophic lake is rather small.

2.4.1.3. Optical characteristics

The value of SUVA for water samples of the Vostochniy watershed profile ranges from 0.01 to 0.055 being the maximal for soil solution and the minimal for oligotrophic lake (Fig. 2.4). The coefficient E_{365}/E_{470} is used for characterizing the functional group absorbances in UV and visible range (Uyguner and Bekbolet, 2005). The values of E_{365}/E_{470} along the watershed profile sustematically increase from soil solution towards the terminal lake (Fig. 2.5). A similar trend is observed for the ratio of E_{470}/E_{655} that increases by a factor of 2 from OR-9 to OR-8 (Fig. 2.5). This ratio correlates with the degree of condensation of DOM aromatic groups, or the humification (Chin et al., 1994, Stevenson, 1994, Hur et al., 2006). The lowest value of E_{470}/E_{655} coefficient is encountered for soil solution and waterlogged bog lakes feeding the stream (OR-2 и OR-3). These values are similar to those reported for soil humic acids (Schnitzer and Calderoni, 1985; Adani et al., 2006). For other samples, the coefficient E_{470}/E_{655} is significantly higher which may be linked to the presence of high concentration of LMW fulvic acids (Fig. 2.5) – similar to Chen et al. (1977); Uyguner and Bekbolet (2005).

2.4.2. Results of size fractionation

2.4.2.1. DOC

The relative proportion of various size fraction of organic carbon, from 100 µm to 1 kDa for 5 most representative samples (soil solution OR-9, humic feeding lake at the top of the watershed OR-6, waterlogged shore of another lake OR-2, the mouth reach of the stream

OR-1 and the terminal clear water lake OR-8). In all samples, the mass fraction of LMW DOM (< 1-10 kDa) dominates the dissolved organic carbon with significant proportion of HMW (10 – 100 kDa) colloids (Fig. 2.6). It is important to note that the molar fractions distribution of different size organic molecules is dramatically different from that of the mass fraction. Since the molar weight is proportional to the third degree of molecule diameter, the difference in molecular mass between the associate of molecules of 0.2 µm diameter and the molecule of 10 kDa diameter (approx 3 nm) achieves 6 orders of magnitude being equal to 8×10^{-3} and 8×10^{-9} μm^3, respectively. As a result, the molar concentration of low molecular weight fulvic acids is several orders of magnitude higher that of the HMW organic matter. This should be taken into account during analysis of organic colloids complexation with trace elements (TE). The molar fractions and molar concentrations of LMW (<1-10 kDa) fulvic acids dominate the OC in studied boreal waters. At the same time, the majority of insoluble trace elements is removed from solution after filtration through 100-10 kDa (Pokrovsky and Schott, 2002; Vasyukova et al., 2012). This corroborates the hypothesis of TE presence in the form of HMW (0.22 µm – 100 kDa) organo-ferrric colloids formed by coprecipitation with Fe(III) oxyhydroxide (Olivié-Lauquet et al., 1999, 2000; Ingri et al., 2000; Pokrovsky and Schott, 2002; Pokrovsky et al., 2006; Dahlqvist et al., 2007)

Along the landscape profile of Vostochniy stream, the proportion of LMW (< 1 kDa) organic carbon significantly increases from soil solution to stream and finally, terminal clear water lake, following the decrease of the concentration of conventionally dissolved $DOC_{<0.22\ \mu m}$ (Fig. 2.7). Such an evolution is in agreement with previous observation of allochthonous vs. autochthonous organic carbon, C/N ratio, hydrophobicity and the aromaticity. It corresponds to progressive depolymerization of HMW soil humic acids whether via heterotrophic aerobic bacterioplankton activity like it is known for other boreal landscapes (Tranvik, 1988; Pokrovsky et al., 2011) or due to photodegradation in the feeding lakes and the stream channel (De Haan, 1993; Zuo and Jones, 1997; Wang et al., 2001; Albinet et al., 2010; Thorn at al., 2010). The increase of the proportion of mineralized products of allochthonous HMW organics or the products of photodegradation may be responsible for the increase of proportion of LMW ligands in the continuum soil solution – feeding humic lake – stream – terminal oligotrophic lake. It can be expected that, after leaving soil, the longer the residence time of allochthonous DOM in the system the higher the proportion of LMW products of photo- and bacterioplankton DOM transformation. Additional factor responsible for the trend observed in Fig. 2.7 may be the phytoplankton activity which produces LMW exometabolites dominating the speciation of OC in open water systems and especially in the large clear water lake. Note that the mouth reach of the stream Vostochniy (OR-1) exhibits around 50% of DOC in < 1 kDa form, a typical value for other boreal landscapes (Guo et al., 2004; Prokushkin et al., 2011).

2.4.2.2. Size Exclusion Chromatography

In accord with data on molecular size distribution, results of SEC analysis demonstrate the absolute molar dominance of 1 kDa size molecules (Fig. 2.8, Table 2.3). Within the range of 0.2 µm to 10 kDa (2.8 nm) and the concentration of OC equals to 5.2 mg L^{-1}, 8 molecules of the mass 5,200,000 Da are equivalent to the presence of 4.4×10^6 molecules of the mass 10 kDa.

2.4.2.3. C/N

The C/N ratio in the filtrates and ultrafiltrates exhibits systematic variation for two most contrasting studied samples, terminal oligotrophic lake and soil solution (Fig. 2.9). Compared to HMW fractions of 100 kDa – 100 µm, there is a 20-30% increase of the C/N ratio in 1-10 kDa ultrafiltrates of soil solution OR-9. For the oligotrophic lake, this increase from HMW to LMW fractions achieves a factor of 4 to 5. Such an evolution indicates rather homogeneous chemical composition of various size fractions of the soil solution and strongly suggests a sole source of DOM, presumably lixiviates of the plant litter subjected to minimal chemical and microbiological transformation corresponding to C/N of 100 to 140. In contrast, low C/N values (5 to 10) in 0.1 – 10 µm fraction of large lake presumably stem from HMW phytoplankton and aquatic macrophytes exometabolites enriched to organic N compared to soil humus. The LMW fraction of large lake has the C/N value between 20 and 25 thus approaching to the value of the stream (45-50). The LMW soil fulvic acids and photo- and microbial degradation products smaller than 10 kDa may also present in this fraction thus contributing to the increase of N/C with the decrease of the pore size. However, our data do not allow straightforward discrimination between the effect of allochthonous OM transformation and small-size phytoplankton exometabolites on the relative enrichment by organic N in < 1-10 kDa fraction compared to HMW filtrates.

2.4.2.4. Optical characteristics

The color of filtrates and ultrafiltrates progressively decreases from the 100 µm to 1 kDa fraction as it is illustrated for sample of soil solution (OR-9) in Fig. 2.10. Similarly, the SUVA reflecting the degree of hydrophobicity and aromaticity significantly increases (by a factor of 10) with the decrease of the pore size in soil solution OR-9; this increase is much smaller in the low feeding lake OR-2 (a factor of 2.5) and it is the minimal (≤ 30%) in the stream OR-1 and the terminal clearwater lake OR-8 (Fig. 2.11 A, B). These observations suggest that the transformation of DOM via microbial- and photo-degradation, much more pronounced in large lake and spring water compared to the soil solution, is capable homogenizing the distribution of hydrophobic/aromatic carbon among different size fractions presumably via decreasing the proportion of this fraction in the LMW colloidal pool. This pool is most labile and thus most susceptible to the degradation.

The ratio of the light absorbencies in UV/visible range may help to reveal the basic features of OM chemical and source-related fractionation among different filtrates and ultrafiltrates. For example, the ratio of E_{254} to E_{365} was used as a surrogate for DOM average molecular weight, with samples with relatively lower ratios having relatively higher molecular weight DOM (Peuravuori et al., 1997; Baretto et al., 2003; Hiriart-Baer et al., 2008; Berggren et al., 2007; Guo et al., 2011). However, in studied boreal waters, the E_{254}/E_{365} parameter remains rather constant (typically between 4.5 and 5.5) and does not subject to variations between µm and kDa filtrates and ultrafiltrates (not shown). Baretto et al. (2003) have calculated the value E_{254}/E_{365} close to 4 in all water samples from the lake indicating the fulvic nature of the dissolved organic carbon. In Peuravuori et al. (1997) the values 4.52 and 5.72 of parameter E_2/E_3 correspond to number-average molecular weight of 3380 and 1120, respectively for the humic solutes in whole-water samples.

Similarly, the absorbance ratio of E_{280}/E_{350} which may approximate the aromatic carbon content of DOM (Croue et al., 2000) exhibit very constant distribution among different size fractions, slightly increasing in the < 1 kDa ultrafiltrates (see Table ESM-2.2).

An alternative parameter helping to estimate the relative composition of autochthonous versus terrestrial DOM is the absorbance ratio E_{254}/E_{436} (Battin, 1998; Jaffe, 2004; Hur et al., 2006). For the majority of studied samples this coefficient ranges from 10 to 40 with the minimal values observed in soil solution OR-9 and the maximal ones observed in the terminal lake OR-8 (Fig. 2.12). The increase of the E_{254}/E_{436} parameter with the decrease of the pore size is consistent with the evolution of the C/N ratio in filtrates/ultrafiltrates series.

The change of the degree of humification reflected by E_{470}/E_{655} value (Chen et al., 1977; Schnitzer and Calderoni, 1985; Adani et al., 2006) measured in the filtration and ultrafiltration series is illustrated in Fig. 2.13 for soil solution, stream mouth and the terminal lake. The soil solution exhibits very weak increase (c.a., < 5 %) of E_{470}/E_{655} from HMW to LMW fraction; this increase is a factor of 4 for 10 µm – 1 µm fractions of the stream water and a factor of 8 for 100 kDa – 1 kDa fractions of the terminal lake. Similar to the evolution of hydrophobicity and aromaticity degree (see Fig. 2.11), this result suggests the maximally homogenous distribution of the humification degree among different fractions of the soil solution OR-9 bearing exclusively allochthonous plant litter-derived humic material and highly fractionated OM in oligotrophic lake OR-8 containing very low humified fresh phytoplankton exometabolites of high molecular weight (0.1 – 10 µm) and LMW allochthonous OM and its microbial- and photo-degradation products.

Finally, the presence of the UV/vis absorbing functional groups, reflected by the E_{365}/E_{470} ratio (Uyguner and Bekbolet, 2005), exhibits no evolution during the cascade filtration and ultrafiltration of soil solution OR-9 and stream wat er OR-1 but significantly increases after 0.1 µm filtration of terminal lake water OR-8 (Fig. 2.14). Such a difference in ultrafiltration pattern of OR-8 compared to other samples of the watershed reflects the presence of at least two pools of organic , allochthonous soil humic and fulvic acids, and 2) enrichment of the lake water by phytoplankton/macrophytes exometabolites.

2.5. Concluding remarks: role of the intra-watershed transformation processes in changing the chemical and molecular size signature of soil organic carbon

Results of this study demonstrate significant and systematic change of basic chemical (DOC concentration, C/N ratio, SUV and light absorbencies) and molecular size (100 µm – 1 kDa filtrates and ultrafiltrates) parameters of dissolved organic matter in the continuum soil solution – feeding bog and humic lakes – spring – terminal lake as summarized in a scheme shown in Fig. 2.15. These crucial changes of basic DOM parameters occur at the very short distance, less than 2 km of a representative boreal subarctic watershed. Such an evolution reflects the complex process of the interplay between two main sources of DOC – soil humic and fulvic acids from the plant litter and aquagenic exometabolites of phytoplankton and macrophytes – both subjected to bio- and photodegradation, whose degree depends on the residence time of DOM in a given aquatic reservoir. As a result, the knowledge of type of soil and relative distribution of bog within small subarctic watershed is not sufficient to predict the chemical and physical nature of DOM that will be delivered by the stream to the ocean. Local hydrological regime, the presence of stagnant water bodies and feeding lakes can significantly affect the original allochthonous signature of DOM during its transport from the soil solution to the stream mouth. Moreover, the glacial or thermokarst origin of hydrographic network distribution often suggests the presence of large, oligotrophic terminal lakes as terminus of small subarctic watersheds, in contrast to estuarine mixing zone of the large rivers. As such, small streams may deliver to the ocean the organic carbon that is more significantly chemically fractionated among different size fractions and transformed by bio- and photo-degradation processes. This may be especially true for the most labile < 1 kDa fraction, by far dominant in molar concentration of boreal DOM and susceptible to travel through the freshwater – seawater mixing zone without significant coagulation.

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TABLES

Table 2.1. List of the sampled waters within Vostochniy stream watershed.

sample name	description	GPS coordinates	
OR-1	stream « Vostochniy », mouth reach	N 66°18.455´	E 30°42.653´
OR-2	stream « Vostochniy », waterlogged shore of the low feeding lake, surface area about 50 m^2	N 66°18.448´	E 30°41.372´
OR-3	stream « Vostochniy », waterlogged shore of the low feeding lake, surface area about 50 m^2	N 66°18.453´	E 30°41.364´
OR-4	stream « Vostochniy », the low feeding lake, surface about 200 m^2, depth 2.5 m	N 66°18.468´	E 30°41.244´
OR-5	stream « Vostochniy », the middle feeding lake, surface about 210 m^2, depth 3 m	N 66°18.521´	E 30°41.101´
OR-6	stream « Vostochniy », the top feeding lake, surface about 150 m^2, depth 2.6 m	N 66°18.538´	E 30°40.910´
OR-7	stream « Vostochniy », middle course, 600 m from the mouth	N 66°18.460´	E 30°40.973´
OR-8	Tsipringa lake, 50 m from the mouth reach of the stream Vostochniy	N 66°18.449´	E 30°42.952´
OR-9	stream « Vostochniy », soil solution near the top feeding lake	N 66°18.489´	E 30°40.707´

Table 2.2. The main filtration characteristics.

pore size	filer size	filter material	filter producer	filtration pressure	filtration unit
100 µm	300*300 mm	nylon	"Fisherbrand", USA	gravity flow	-
20 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
10 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
5 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
0.8 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
0.4 µm	2×100*250 mm	lavsan	Dubna, Russia	3 - 5 m	-
0.22 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
0.1 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
0.046 µm	Ø 37 mm	lavsan	Dubna, Russia	-80 - 0 kPa	"Nalgen", 250 ml
100 kDa	Ø 76 mm	regenerated cellulose	"Millipore", USA	0 - 100 kPa	"Amicon", 8400
10 kDa	Ø 76 mm	regenerated cellulose	"Millipore", USA	0 - 350 kPa	"Amicon", 8400
1 kDa	Ø 76 mm	regenerated cellulose	"Millipore", USA	0 - 350 kPa	"Amicon", 8400

Table 2.3. Major chemical composition and DOM parameters in non-filtrated and 0.22 µm farctions of surface waters.

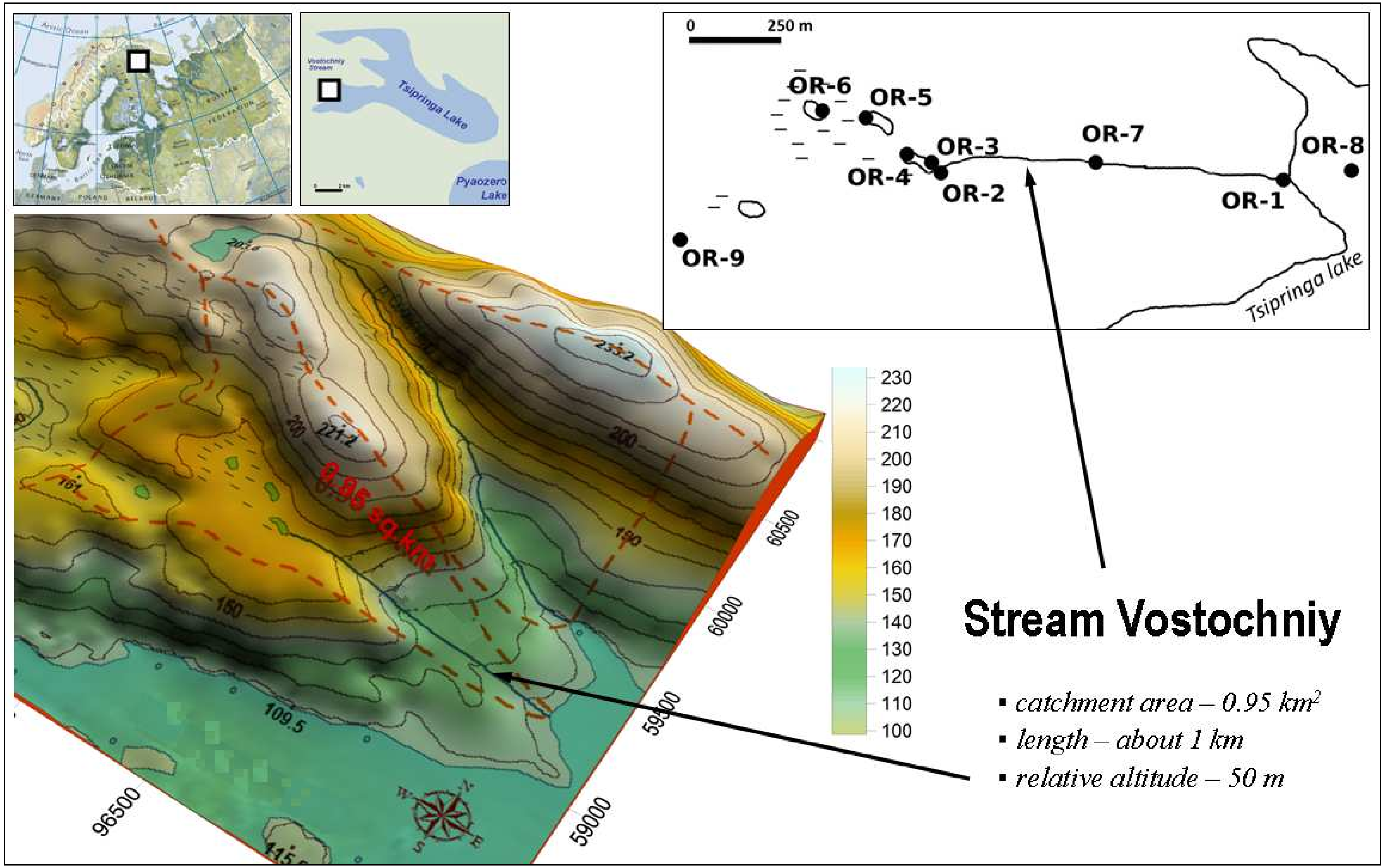
sample	OR-1	OR-2	OR-3	OR-4	OR-5	OR-6	OR-7	OR-8	OR-9	conditions
pH	6.7	6.3	6.59	5.8	6.6	6.3	6.65	7.5	4.3	in-situ
t, °C	12.8	18.9	18.3	19.9	20.1	21.7	15.7	17.8	17.2	in-situ
% of O_2 saturation	90	nd	90	nd	nd	90	nd	100	30	in-situ
R, µSm/cm	14.39	18.1	16.62	15.66	19.09	20.8	14.26	42.5	57.4	in-situ
TDS NaCl, mg/L	8.45	8.22	7.55	8.1	9.71	10.2	7.96	23.3	31.9	in-situ
mg/L										
Na^+	0.9634	0.752	0.7182	0.8443	0.8847	0.9846	0.8772	1.230	1.225	non-filtrated
Mg^{2+}	0.564	0.5128	0.5461	0.5525	0.6071	0.5943	0.5829	1.6338	0.4921	non-filtrated
K^+	0.04015	0.01245	0.0748	0.04011	0.04036	0.0409	0.05556	0.8044	0.3774	non-filtrated
Ca^{2+}	2.166	2.271	2.47	2.024	2.548	3.26	2.038	5.893	1.275	non-filtrated
SO_4^{2-}	0.8945	1.1246	0.2884	0.9714	1.1467	0.32	0.8413	0.0439	0.062	non-filtrated
NO_3^-	0.3932	0.4971	0.1357	0.6149	0.6413	0.0292	0.6417	0.0784	0.116	non-filtrated
Cl^-	0.4207	0.3971	0.3806	0.2795	0.3471	0.325	0.2419	0.640	0.689	non-filtrated
$HCO3^-$	17.40	9.15	9.76	9.00	11.00	13.42	9.50	33.14	0.00	non-filtrated
$(\sum^+-\sum^-)/\sum^+$, %	-3.6	-3.3	5.2	-3.2	3.3	3.8	-3.1	1.3	65.0	
N, mg/L	0.34	nd	nd	nd	nd	0.33	nd	0.18	0.49	non-filtrated
DOC, mg/L	16	18	19	19	18.5	18	16.5	7	144	non-filtrated
C/N	48	nd	nd	nd	nd	58	nd	24	104	non-filtrated
WAMW	1010	nd	nd	nd	nd	1020	nd	960	1260	0.22 µm
SUVA	0.041	0.032	nd	nd	nd	0.042	nd	0.011	0.049	0.22 µm
E_{365} / E_{465}	4.05	3.7	3.7	nd	nd	3.8	3.9	5	2.7	non-filtrated
E_{465} / E_{665}	10	5.7	7.1	nd	nd	8	10.5	12	5.7	non-filtrated

* R – conductivity; ** TDS – salinity; *** WAMW – weight-average molecular weight.

Table 2.4. Compilation of main studied parameters and their evolution in the continuum of the watershed, from soil solution to the terminal lake.

Parameter	Meaning	OR-9 → OR-8	100 µm →0.0014 µm
DOC	Dissolved organic carbon concentration	decrease	decrease
C/N	Autochthonous vs terrestrial DOM	decrease	increase
LMW	Presence of fulvic acids	increase	increase
SUVA	Hydrophobicity and aromaticity	decrease	increase
E_{254}/E_{436}	Autochthonous vs terrestrial DOM	increase	increase
E_{280}/E_{350}	Content of aromatic carbon	stable	stable
E_{254}/E_{365}	DOM average molecular weight	no trend	no trend
E_{365}/E_{470}	UV/vis absorbing functional groups	increase	increase
E_{470}/E_{655}	Degree of humification	increase	increase

FIGURES



Stream Vostochniy

- *catchment area – 0.95 km²*
- *length – about 1 km*
- *relative altitude – 50 m*

Figure 2.1. Sampling scheme.

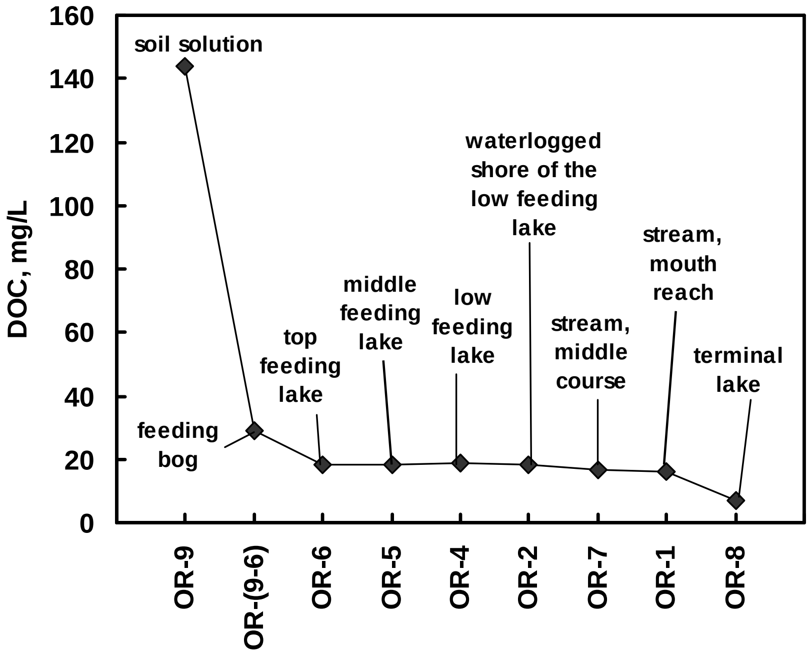


Figure 2.2. DOC concentrations (mg/L) for non-filtrated samples of Vostochniy stream.

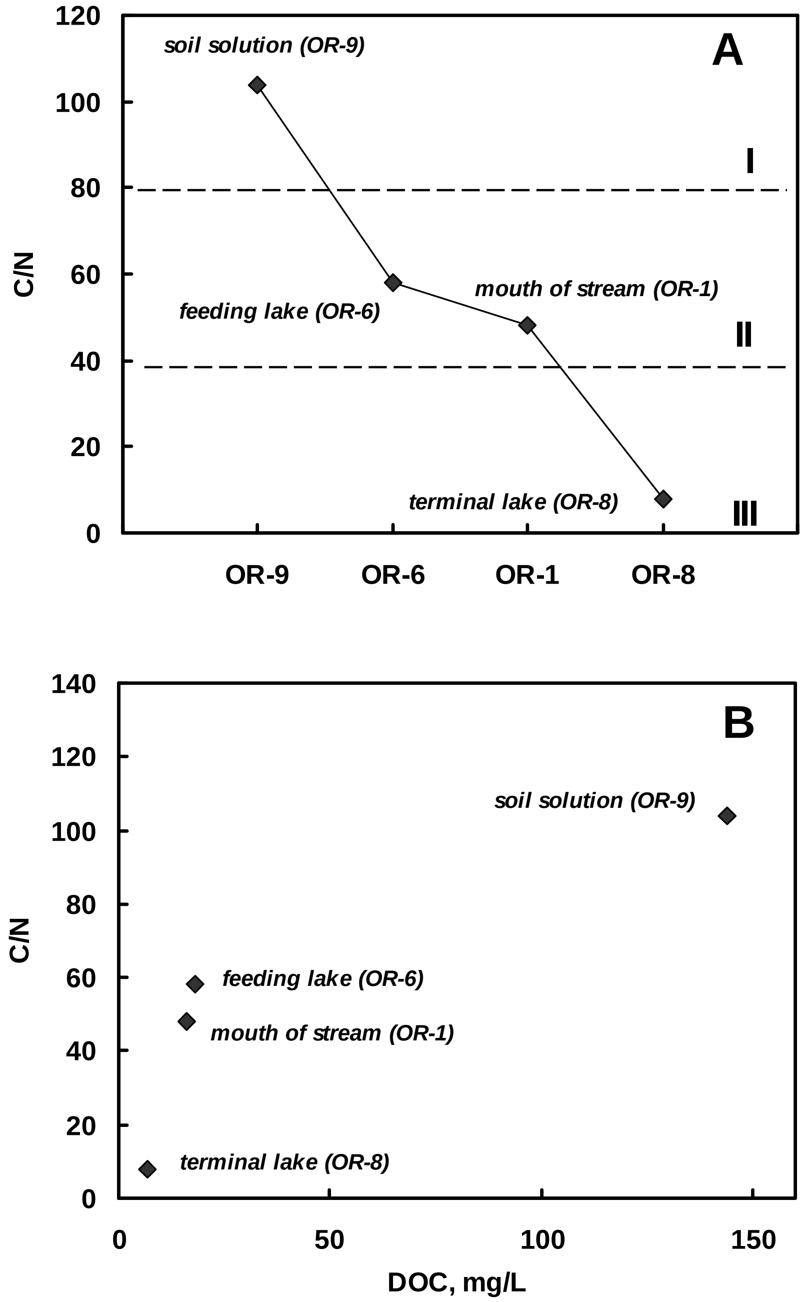


Figure 2.3. C/N ratios for non-filtrated samples of Vostochniy stream.

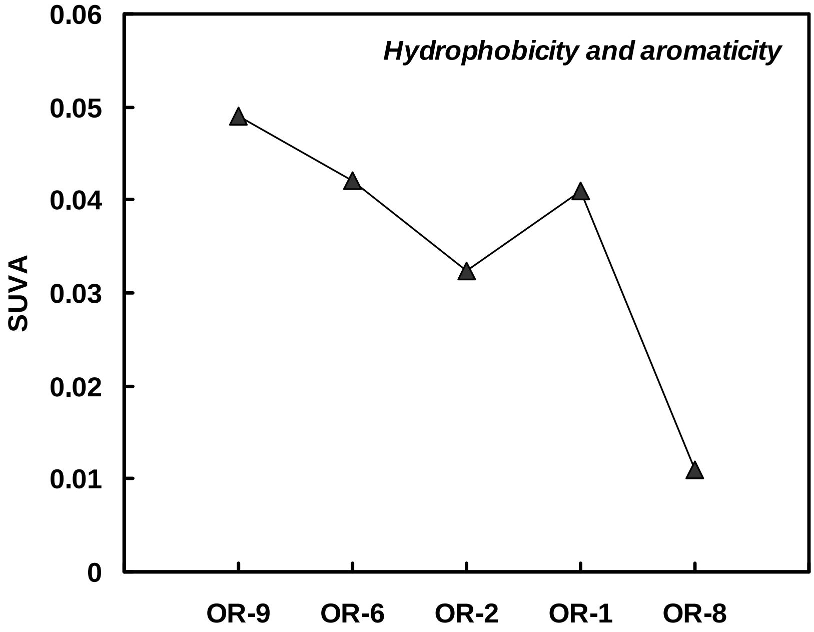


Figure 2.4. SUVA ratios for the fraction 0.22 µm of the samples of Vostochniy stream (OR-9 – soil solution, OR-6 – top feeding lake, OR-2 – waterlogged shore of the low feeding lake, OR-1 – mouth reach of the stream, OR-8 – terminal lake).

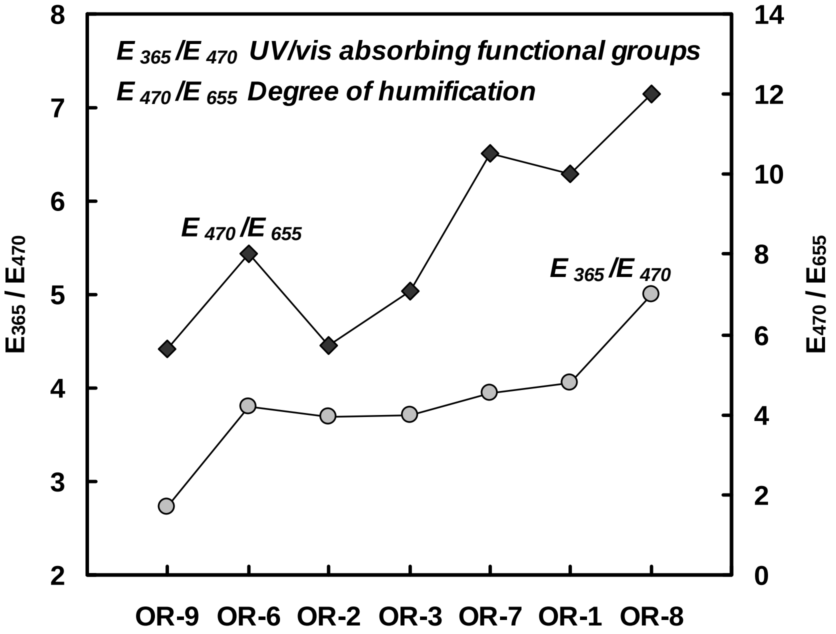


Figure 2.5. E_{365}/E_{470}, E_{470}/E_{655} ratios for the samples of Vostochniy stream (OR-9 – soil solution, OR-6 – top feeding lake, OR-2, OR-3 – waterlogged shore of the low feeding lake, OR-7 – middle course of the stream, OR-1 – mouth reach of the stream, OR-8 – terminal lake), measured in-situ in non-filtrated waters.

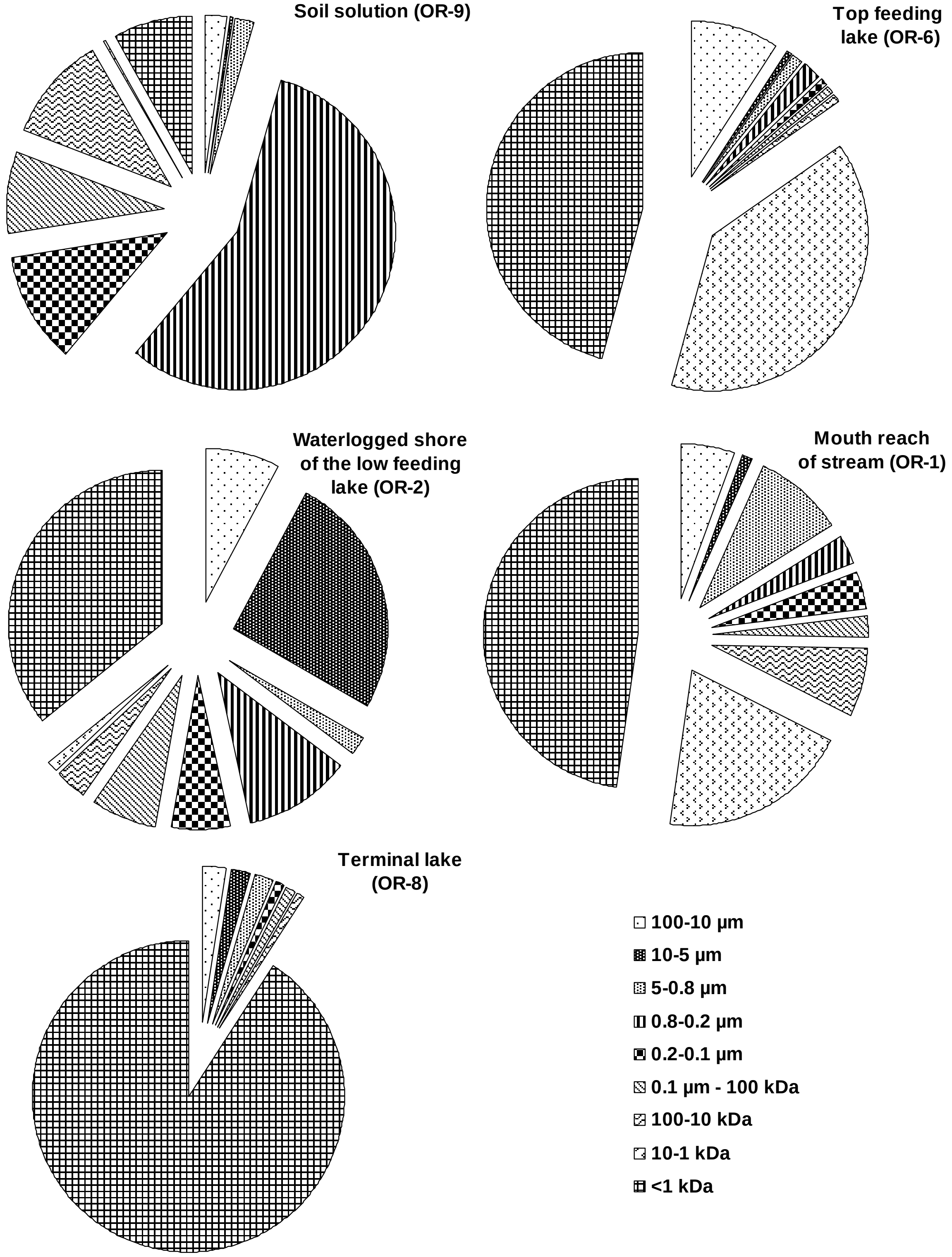


Figure 2.6. DOC fractionation in the samples of Vostochniy stream.

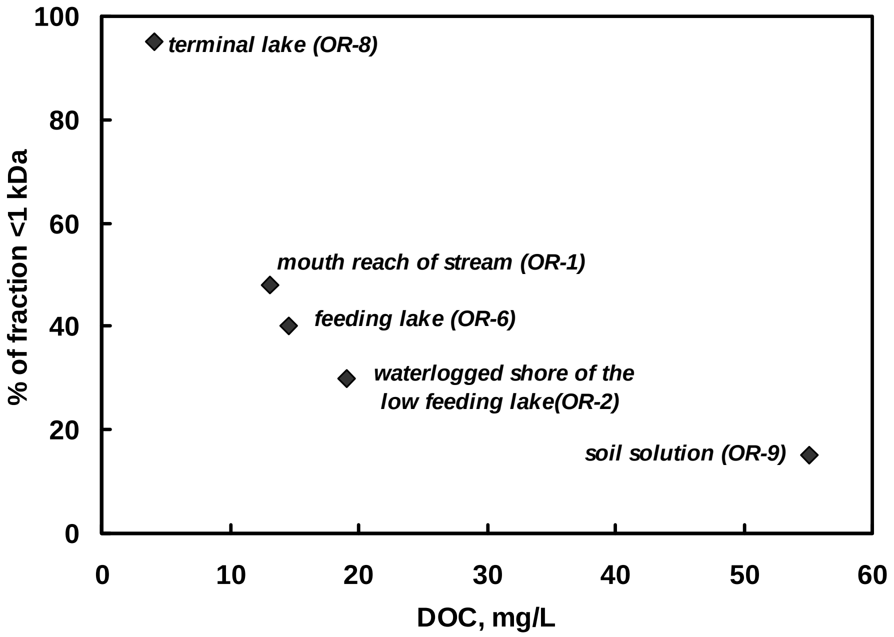


Figure 2.7. Plot the % of < 1 kDa form as a function of DOC in 0.22 µm fraction.

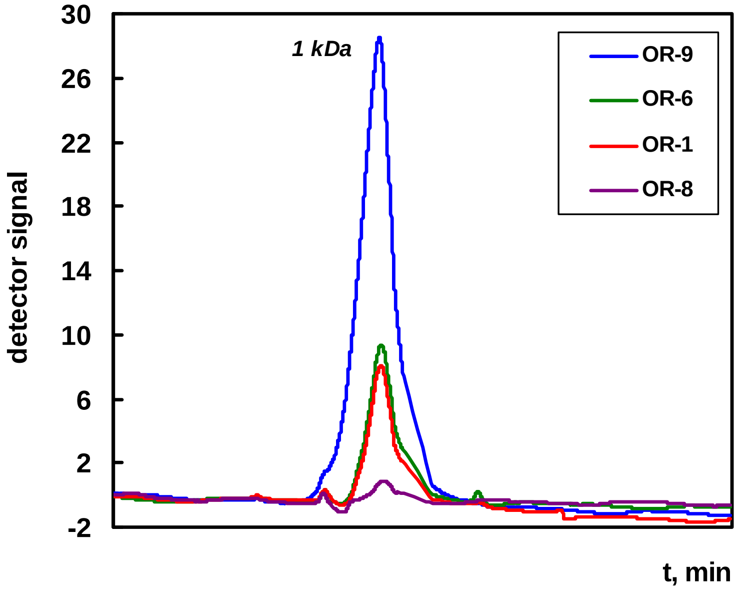


Figure 2.8. Weight-average molecular weight distribution in filtrates (0.22 µm) of Vostochniy stream watershed (OR-9 – soil solution, OR-6 – top feeding lake, OR-1 – mouth reach of the stream, OR-8 – terminal lake), determined by the method of Size Exclusion Chromatography.

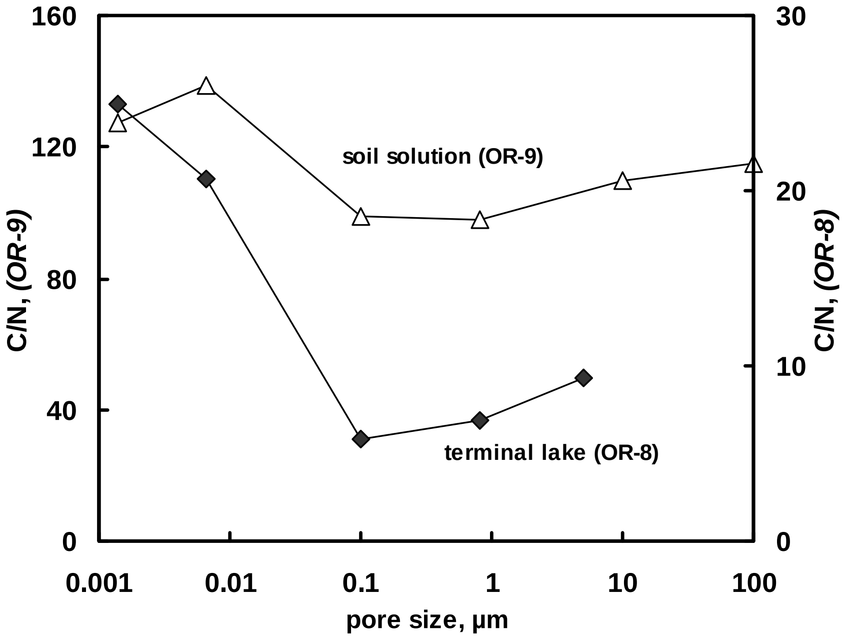


Figure 2.9. C/N ratios with respect to molecular size fractions for the samples of Vostochniy stream.

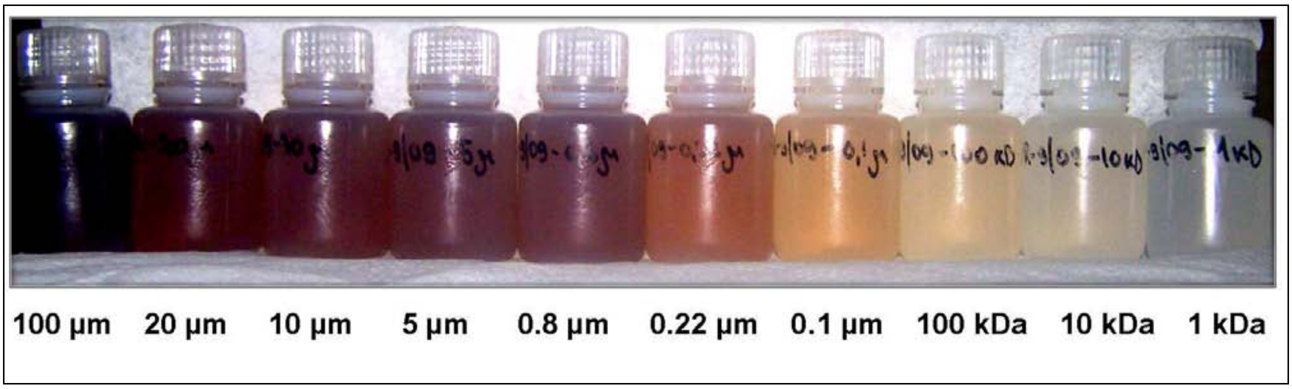


Figure 2.10. Filtrates (100, 20, 10, 5, 0.8, 0.22, 0.1 µm) and ultrafiltrates 100, 10 and 1 kDa) of the soil solution sample (OR-9) of Vostochniy stream.

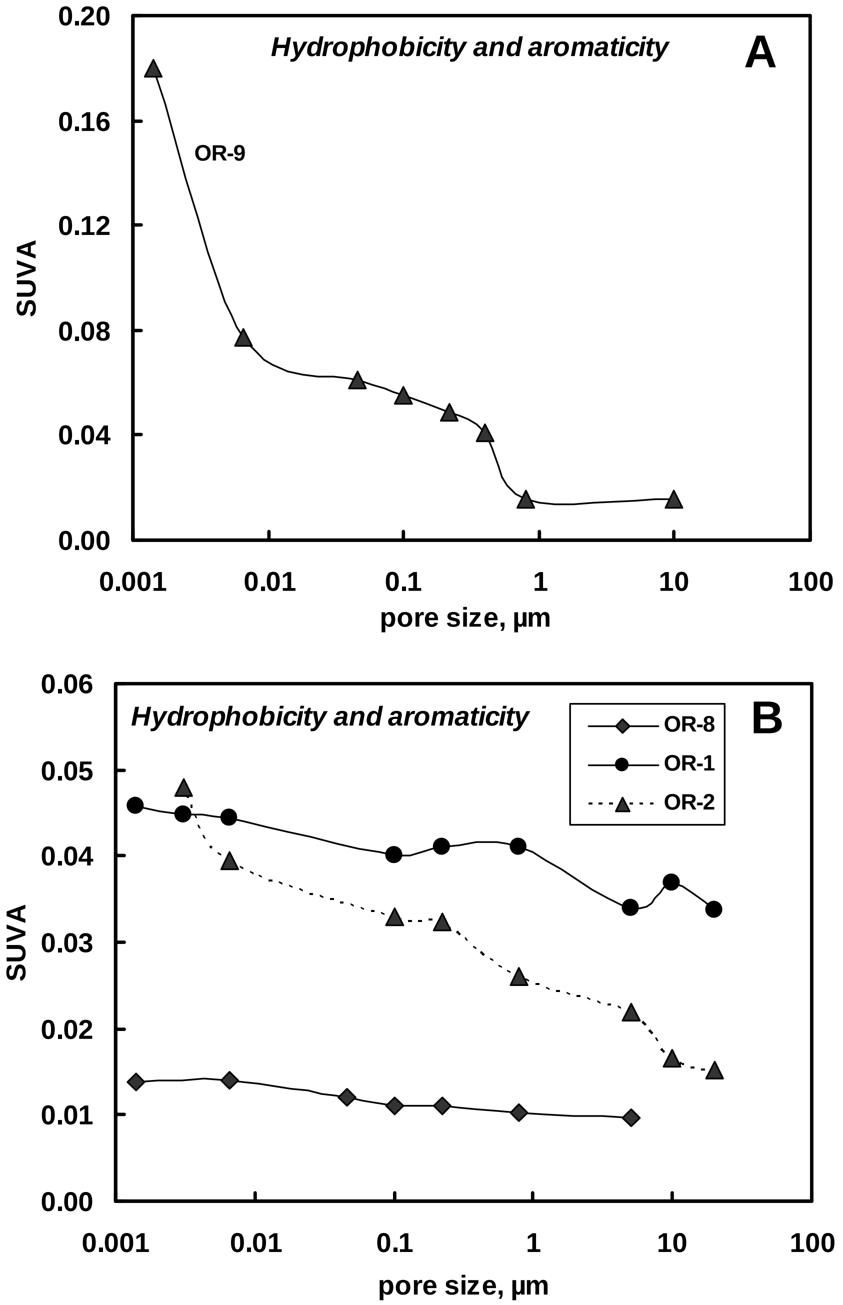


Figure 2.11. SUVA ratios with respect to molecular size fractions for the samples of Vostochniy stream (OR-9 – soil solution, OR-6 – top feeding lake, OR-2 – waterlogged shore of the low feeding lake, OR-1 – mouth reach of the stream, OR-8 – terminal lake).

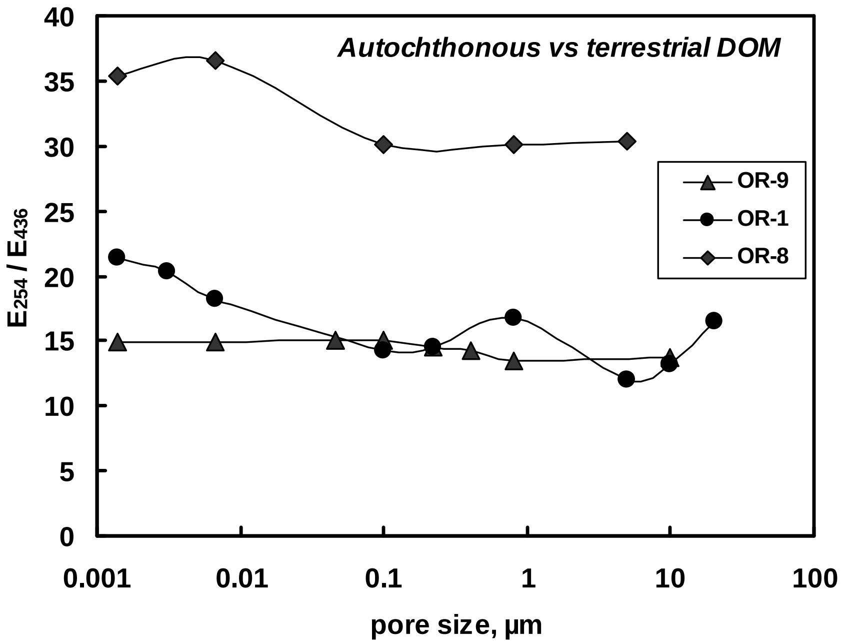


Figure 2.12. E_{254}/E_{436} ratios as a function of pore size of filtrates and ultrafiltrates for the samples of Vostochniy stream (OR-9, soil solution; OR-1, mouth reach of the stream, and OR-8, terminal lake).

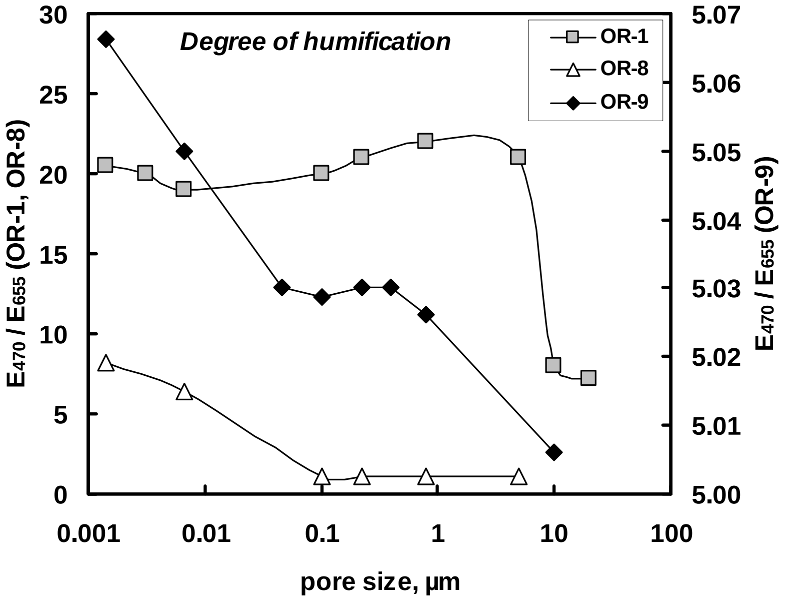


Figure 2.13. E_{470}/E_{655} ratio reflecting the degree of humification plotted as a function of pore size for the samples of Vostochniy stream.

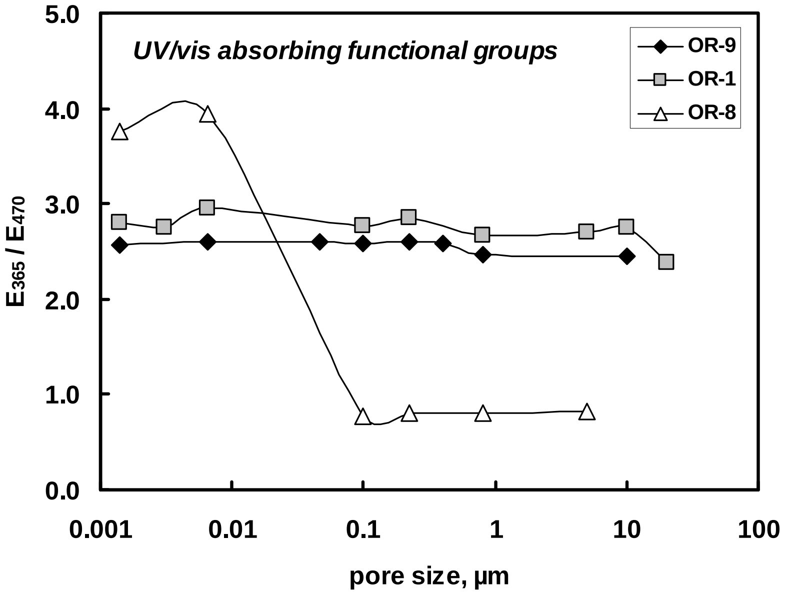


Figure 2.14. E_{365}/E_{470} ratio reflecting the UV/vis absorbing functional groups plotted as a function of pore size of filtrates and ultrafiltrates for the samples of Vostochniy stream watershed.

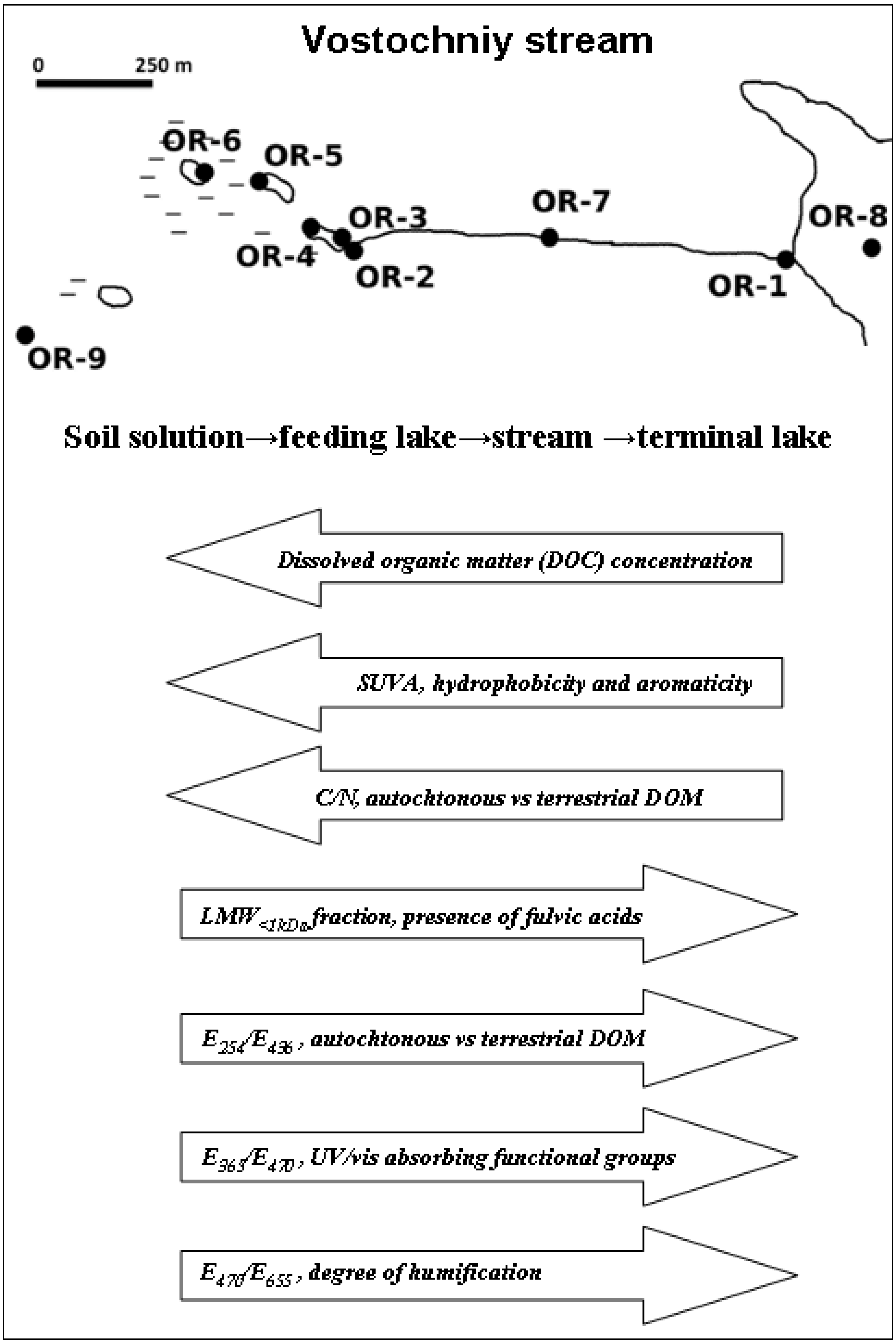


Figure 2.15. A scheme of DOM parameters evolution along the watershed profile, from the soil solution to the terminal lake.

ELECTRONIC ANNEX

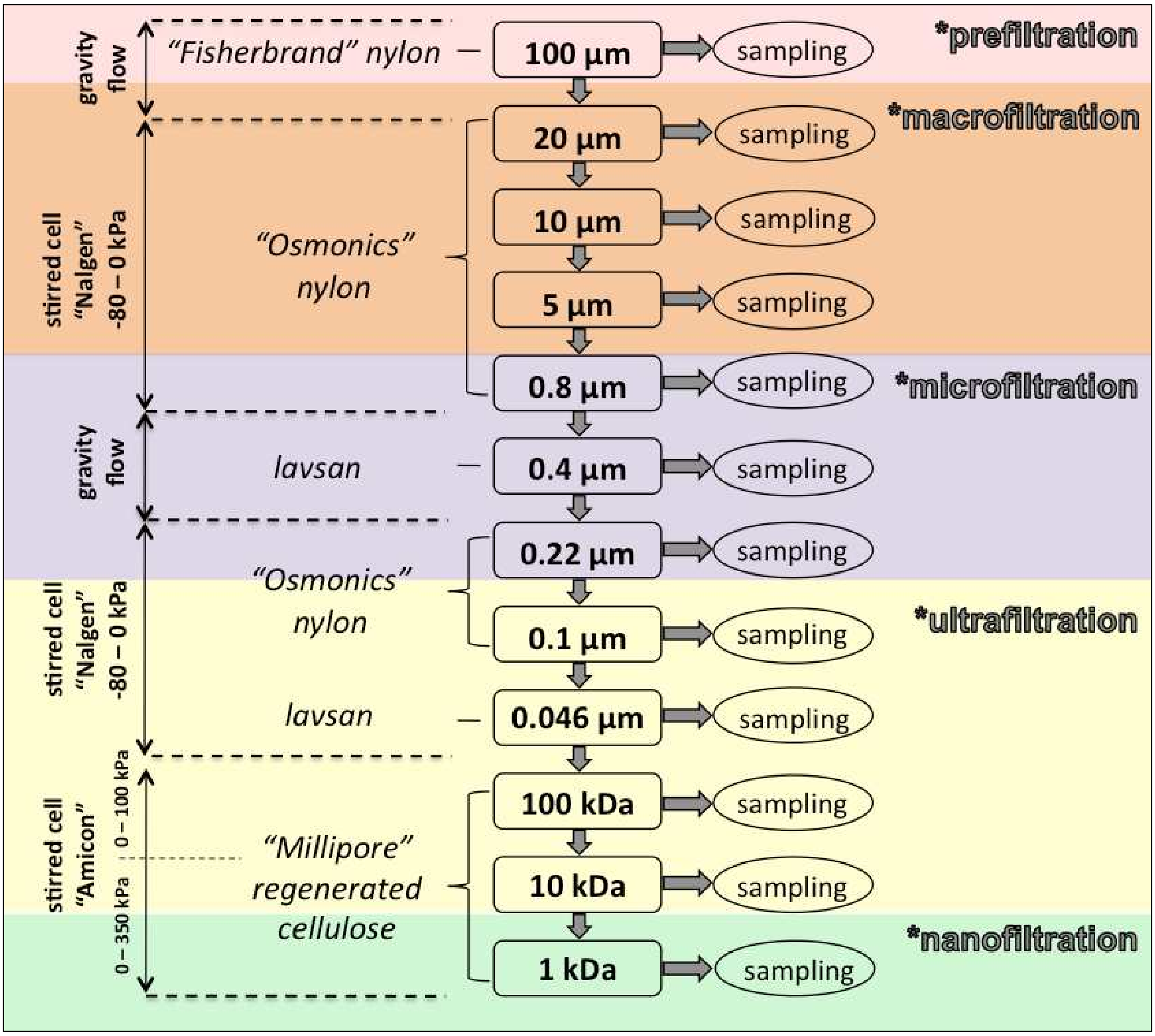


Figure ESM-2.1. The scheme of cascade filtration used in this study.

Table ESM-2.2. DOC, C/N and optical characteristics of filtrates and ultrafiltrates.

sample point	pore size, µm	DOC, mg/L	C/N	SUVA	E_{254}/E_{436}	E_{280}/E_{350}	E_{254}/E_{365}	E_{365}/E_{470}	E_{470}/E_{655}
OR-9	10	138.2	109.6	0.016	13.7	2.65	4.43	2.45	5.01
	0.8	135.2	97.8	0.015	13.5	2.65	4.43	2.47	5.03
	0.4	56.3	nd	0.041	14.2	2.68	4.46	2.59	5.03
	0.22	55.1	nd	0.049	14.5	2.70	4.50	2.60	5.03
	0.1	38.8	99.0	0.055	15.1	2.69	4.66	2.58	5.03
	0.046	34.2	nd	0.061	15.1	2.70	4.60	2.60	5.03
	0.0066	27.1	138.8	0.077	14.9	2.70	4.61	2.61	5.05
	0.0014	11.3	127.6	0.180	15.0	2.70	4.60	2.57	5.07
OR-6	10	15.2	nd	0.044	9.8	2.60	4.13	2.37	2.54
	0.8	14.9	nd	0.047	11.5	2.70	4.36	2.64	3.45
	0.22	14.6	nd	0.042	16.5	2.90	4.86	3.40	5.74
	0.1	14.5	nd	0.046	16.0	2.95	4.95	3.24	6.68
	0.0066	14.3	nd	0.038	12.7	2.89	4.56	2.79	3.18
	0.0031	14.2	nd	0.050	14.1	3.30	5.20	2.70	2.93
	0.0014	7.7	nd	0.044	14.9	3.43	5.34	2.78	3.25
OR-2	20	17.9	nd	0.015	17.1	2.87	4.84	2.80	5.10
	10	17.1	nd	0.017	17.8	2.95	4.95	2.73	4.67
	5	17.0	nd	0.022	14.8	2.80	4.66	2.40	3.60
	0.8	16.3	nd	0.026	12.9	2.93	4.62	2.26	2.75
	0.22	16.1	nd	0.032	14.0	2.84	5.00	2.22	2.12
	0.1	15.0	nd	0.033	16.3	2.87	4.78	2.94	5.68
	0.0066	14.5	nd	0.039	13.9	2.81	4.61	2.50	3.78
	0.0031	13.3	nd	0.048	14.0	2.94	5.14	2.26	3.00
OR-1	20	15.8	nd	0.034	16.5	3.07	5.17	2.38	7
	10	15.0	nd	0.037	13.2	2.93	4.82	2.75	8
	5	14.8	nd	0.034	12.0	2.68	4.38	2.70	21
	0.8	13.3	nd	0.041	16.8	3.01	4.99	2.67	22
	0.22	13.1	nd	0.041	14.5	2.85	4.71	2.85	21
	0.1	12.9	nd	0.040	14.3	2.81	4.69	2.76	20
	0.0066	11.8	nd	0.044	18.2	3.02	5.24	2.95	19
	0.0031	10.7	nd	0.045	20.4	3.10	5.34	2.75	20
	0.0014	7.6	nd	0.046	21.4	4.18	6.52	2.80	21
OR-8	5	5.3	9.4	0.010	nd	nd	nd	0.83	1.10
	0.8	5.2	6.9	0.010	nd	nd	nd	0.80	1.09
	0.22	5.1	nd	0.011	nd	nd	nd	0.80	1.10
	0.1	5.1	5.8	0.011	nd	nd	nd	0.76	1.11
	0.046	5.0	nd	0.012	nd	nd	nd	nd	nd
	0.0066	5.0	20.7	0.014	36.6	4.3	8.4	3.94	6.41
	0.0014	5.0	25.0	0.014	35.4	4.3	8.4	3.77	8.16

Chapter 3

Speciation, size fractionation and transport of trace elements in a boreal watershed (North Karelia, Russia)

S.M. Ilina, Yu.V. Alekhin, S.A. Lapitskiy, J. Viers, O.S. Pokrovsky

In preparation for *Chemical Geology*

Speciation, size fractionation and transport of trace elements in a boreal watershed (North Karelia, Russia)

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Keywords: cascade filtration, ultrafiltration, dialysis, organic matter, trace elements, colloids, natural waters, boreal zone

Abstract

Concentration and size fractionation of major and trace elements (TE) linked to organo-mineral colloids along the landscape gradient soil water – peat bog- river – terminal lake have been investigated in the basin of the Vostochniy stream and Palojoki river of north boreal zone (Karelia region, North-West Russia) in July of 2008 – 2010 corresponding to summer base-flow period. Large volume of natural waters were filtered in the field using cascade filtration and ultrafiltration employing progressively decreasing pore size (100, 20, 10, 5, 0.8, 0.4, 0.22, 0.1, 0.046, 0.0066 (100 kDa), 0.0031 (10 kDa), and 0.0014 µm (1 kDa)) followed by multi-elemental ICP-MS and dissolved organic carbon analysis. In addition, in-situ dialysis with 10 and 1 kDa membranes was also conducted. According to TE distribution among different size fractions in the continuum soil (bog) – feeding humic lakes - river – terminal (oligotrophic) lake, several groups of elements could be distinguished: (*i*) elements significantly bound to colloidal (1 kDa – 0.22 µm) fraction and decreasing the proportion of this fraction from the feeding lake and the stream to the terminal oligotrophic lake (Fe, Ti, U);

(*ii*) colloidally-dominated (>80 %) elements exhibiting similar size fractionation in all studied settings (Y, REEs, Zr, Hf and Th); (*iii*) elements appreciably bound to colloids (20 to 40%) in organic-rich soil and bog waters and decreasing their colloidal fraction to c.a. 10% in the oligotrophic lake (Mg, Ca, Sr, Rb, Mo), and, finally (*iv*) elements significantly linked to colloidal fraction (40 to 80%) and not demonstrating any systematic variation between different landscape context (Ni, Co, Cu, Cd, Cr, Mn, Zn, Pb). In-situ dialysis technique produced similar picture of colloidal size fractionation with generally lower proportions of elements in colloidal fraction compared to the UF. It follows from results of this study that the internal processes of organic matter fractionation during 1) transformation of initially allochtonous soil-derived colloids via photo- and bio-degradation or 2) new organic ligands production by plankton are not capable appreciably affect the distribution trace elements among various size fractions. As such, even crucial changes in environmental conditions such as river regime and relative lake versus bog coverage, surface water pH, pCO_2, and DOC change likely to occur according “extreme” scenario of the climate warming in the Arctic, should not affect the potential aquatic lability and biodisponibility of trace element present as organic (divalent transition metals, alkaline-earth metals) and organo-mineral (Fe, Al, insoluble trivalent and tetravalent elements and U) colloids.

3.1. Introduction

Boreal regions of the Russian Arctic play a crucial role in the transport of elements from continents to the ocean at high latitudes. In view of the importance of these circumpolar zones for our understanding of ecosystem response to global warming, it is very timely to carry out detailed regional studies of trace elements (TE) geochemistry in boreal landscapes. Arctic and subarctic regions are among the most fragile zones in the world due to their low resistance to industrial impact, low productivity of terrestrial biota and limited biological activity over the year. Changing climatic conditions for these regions means that 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 (Dahlqvist et al., 2007). Indeed, increase of dissolved organic carbon concentration in boreal surface waters is among the major consequences of human-induced climate change (by approx. 10 % over 10 years, Evans et al., 2005).

These zones represent one of the most important organic carbon reservoirs in the form of peat bogs, wetlands and soils very rich in organic matter and iron. As a consequence, trace elements in water are likely to be transferred in the form of organic colloids (humic and fulvic acids, microbial exudates, polysaccharides) and organo-mineral entities (Fe and Al hydroxide stabilized by organic matter) (Ingri and Widerlund, 1994; Gustafsson and Gschwend, 1997; Viers et al., 1997; Gustafsson et al., 2000; Andersson et al., 2001; Dahlqvist et al., 2004, 2007; Pokrovsky et al., 2005, 2006; Allard, 2006; Allard and Derenne, 2007; Filella, 2008). Colloids have received special attention because of their small size (1 nm – 1 µm) and large specific surface area, and thus their high reactivity toward contaminants as well as high diffusibility and mobility (Buffle and van Leeuwen, 1992, Pham and Garnier, 1998; Babiarz et al., 2000; Ran et al., 2000; Wang and Guo, 2000; Mosley and Hunter, 2003; Baalousha et al., 2006; Singhal et al., 2006; Guo and Santschi, 2007; Baalousha and Lead, 2007; Seredyn´ska-Sobecka et al., 2007, Ren et al., 2010). Thus, they are thought to play a very important role in controlling the speciation and the cycling of many elements in natural waters (Salomons and Forstner, 1984; Buffle and van Leeuwen, 1992, Waeles et al., 2008).

Colloidal status of trace elements in high latitude rivers is fairly well established feature. It was assessed both as a function of lithology (Vasyukova et al., 2010), in the latitude transect (Pokrovsky and Schott, 2002) and as a function of season on small (Ingri et al., 2000; Andersson et al., 2001, 2006; Pokrovsky and Schott, 2002; Dahlqvist et al., 2004, 2007; Shiller, 2010) and large arctic rivers (Pokrovsky et al., 2010). These results allowed i) emerging a comprehensive picture of trace element migration in the form of colloids and ii) describing the complex size fractionation and TE distribution coefficients between different colloidal fractions, suspended and dissolved forms. The present study is aimed at quantitative characterization, within the landscape continuum, of trace element speciation in pristine, organic-rich rivers and surface waters of the Karelia region sampled during the base flow in summer.

In order to obtain more detailed information on the natural concentrations and transport of major and some trace elements in the studied region, we sampled the feeding bogs, soil water, river, stream, terminal and feeding lakes in the basin of the Vostochniy Stream and Palojoki River. Presented in this study data corroborate those previously published for the Karelian region (Pokrovsky and Schott, 2002; Feoktistov, 2004; Zakharova et al., 2007; Vasyukova et al., 2010). However, despite these recent works on NW Russia, the transformation of colloidal distribution between the sources of colloids (soil solutions, bog waters), the transporters (rivers and streams) and the receptor zones (lakes) still remains very poorly characterized. The lack of this knowledge does not allow to address the changes in bioavailability, relative colloidal stability, their vulnerability to bio- and photo-degradation and transformation processes in the mixing zone river – Arctic Ocean. For this, systematic studies within the continuum soil-bog-river and lake are necessary.

The main issues we attempted to address in this study are: *i*) assessing the change of concentration and element ratio change in the series of cascade filtrates and ultrafiltrates from 100 µm to 1 kDa, and *ii*) estimate the degree of transformation of TE speciation and size distribution of colloids along the landscape gradient soil solution – feeding bog and lake – stream – terminal lake. The main hypothesis to be tested was that the change of colloidal size fractionation and TE speciation is primarily controlled by landscape setting, that is, by pH, DOC, Fe concentration and redox conditions. If this control can be rationalized in the form of multi-parametric equation representing the percentage of colloidal metal as a function of environmental conditions, or, simply, bulk chemical composition of surface waters, then, via the extrapolation of these dependencies to other subarctic watersheds quantitative prediction of TE speciation across the boreal and subarctic zone may become possible.

Towards these goals, we followed, in a two-year sampling during summer baseflow period, major and trace element and organic carbon in large and small fraction of filtered and ultrafiltrated waters performed using on-site size fractionation technique. It is anticipated that addressing these issues will provide us a possibility for straightforward discrimination of the element sources and TE fractionation during transport by surficial fluids in similar small watersheds of the subarctic zone under various climate warming scenario.

3.2. Geological and geographical settings

3.2.1. Climate, topography, soil, vegetation

The climate, topography, soil and vegetation of the region are described in the Electronic Annex (ESM-3.1).

3.2.2. Objects of study

Two small subarctic streams of the NW Russian boreal zone were selected (Fig. 3.1). The basin of the Vostochniy Stream is located in the Northern Karelia (N 66°, E 30°) near the border with Finland and about 40-60 km south from the Arctic Circle. Its length is about 1 km and relative altitude of 50 m, the catchment area is of 0.95 km^2. The river Palojoki with 32 km^2 watershed area is 9 km long; it flows out of Kivakkalampi lake (KAR-7), drains the rocky massif Kivakka from the south and empties into Pyaozero lake having a relative altitude of 155 m. It was sampled in the mouth zone 10 m above the terminal Pyaozero lake (KAR-3), in the middle part of the flow (KAR-1, 80 m above the point KAR-3), in the mouth zone of tributaries (KAR-4 and KAR-5) and in the superior small lake lake (KAR-6). In the upper reaches of this river, it is fed by a minero-trophic bog (KAR-2) of 1.2 km^2 surface area. The bedrock composition of the catchement are micro-pegmatic granites, granosyenites, syenites, syenit-diorites of the low-Proterozoic, biotite garanitogneisses and biotite, biotite-amphibolite and amphibolite gneisses and amphibolites of the low-Archean ang glassial deposits of Quarternary (Fig. 3.1).

The stream Vostochniy originates from the system of interconnected humic lakes (such as OR-6) located within the bog zone and empties into the lake Tsipringa (OR-8). The bedrock of the catchment is represented by low-Proterozoic amphibolitic gabbroids (Fig. 3.1). The Vostochniy stream was sampled in the mouth reach, 1 m above the mixing with Tsipringa lake (OR-1), in the middle part of the flow (OR-7, 30 m above the point OR-1), in the feedings lakes (OR-4, OR-5 and OR-6) and their waterlogged shores (OR-2 and OR-3). Soil solution of the peat bog zone of this watershed was collected from the depth of 5-10 cm in a piezometer (OR-9).

The feeding bogs and lakes, average flows, mouths and tributaries of streams and rivers, feeding and terminal lakes, and soil solutions were sampled in July 2007 – 2010 during the summer base-flow period (Table ESM-3.2). Figure 3.1 presents a simplified scheme of the sites along with sampling points, whereas the list of sampled waters and their bedrock compositions are presented in Table 3.1.

3.3. Materials and methods

3.3.1. Sampling, filtration, dialysis

Large volumes (20–30 L) were collected in pre-cleaned light-protected PVC bottles for size fractionation procedure with 100, 20, 10, 5, 0.8, 0.4, 0.22, 0.1, 0.046, 0.0066 (100 kDa), 0.0031 (10 kDa), and 0.0014 µm (1 kDa pore size) using cascade filtration and ultrafiltration conducted directly in the field conditions using specially prepared polyethylene-covered clean space (Fig. ESM-3.3). The main characteristics of the filtration are listed in Table 3.2 and the scheme of the size fractionation procedure is given in Fig. 3.2.

Filtration through 100 µm or pre-filtration was performed using nylon net “Fisherbrand”. Cascade frontal filtration with the decreasing pore size from 20 to 0.1 µm was performed using a 250-ml vacuum polycarbonate cell (Nalgene) and nylon membranes (Osmonics). Frontal ultrafiltration (UF) of the series 100 – 10 – 1 kDa was performed using a 400-ml polycarbonate cell (Amicon 8400) equipped with a suspended magnet stirring bar located beneath the filter to prevent clogging during filtration. Vacuum filtration was performed using a portative hand-pump, and the ultrafiltration was performed using a portative air pomp. The large volumes of the samples were passed through the Lavsan (polyethylene tereph-thalate, PETP) filters of 0.4 µm pore size and 500 cm² surface area. The filtration occurs via gravitational flow (0.3-0.5 kPa).

Between each sample, the filtration system was cleaned by flushing EasyPure water, then 3% ultrapure HNO_3, and finally, EasyPure water. Each filter was soaked in EasyPure water during at least 1 day before the experiment and used only once. During filtration, the first 50 ml of sample solution were discarded, thus allowing saturation of the filter surface prior to recovery of the filtrate. Discussions of this technique and precautions against possible filtration artifacts are given in Viers et al. (1997), Dupré et al. (1999), Pokrovsky and Schott (2002), Pokrovsky et al. (2005, 2006), Alekhin et al. (2010).

Dialysis experiments were performed using 20-50 ml precleaned dialysis bags placed directly in the river or bog water (in-situ dialysis). The duration of this dialysis procedure was between 72 and 120h. For dialysis experiments, EDTA-cleaned trace-metal pure SpectraPor 7® dialysis membranes made of regenerated cellulose and having pore sizes of 1 kDa were thoroughly washed in EasyPure water, filled with ultrapure Milli-Q deionized water and then placed into natural water. The efficiency of the dialysis procedure was evaluated by comparing major anion concentrations. These concentrations were always identical within ± 10%, suggesting an equilibrium distribution of dissolved components. Blank dialysis experiments performed with precleaned 1 kDa bags filled with MilliQ water in 9 replicates in a clean room (class A 10,000) revealed negligible contamination (< 10% of the typical concentration in < 1 kDa dialysates). Further details of dialysis experiments procedure are described in Vasyukova et al., 2010 and Pokrovsky et al., 2011, 2012.

3.3.2. Analytical techniques

Water temperature, pH, and conductivity were measured in the field. The pH was measured using a combination glass electrode calibrated against NIST buffer solutions. Major anion concentrations (Cl^-, SO_4^{2-}, NO_3^-) were measured by ion chromatography (Dionex 2000i) with an uncertainty of 2%. Alkalinity was measured in the field by Gran titration with HCl using phenolphthalein as indicator. The dissolved organic carbon (DOC) was determined using Shimadzu SCN Analyzer (Toulouse) and Elementar TOC analyzer (Moscow) with an uncertainty of 3% and a detection limit of 0.001 mMol/L.

Major and trace elements (TE) including Fe were measured without preconcentration by ICP-MS (7500ce, Agilent Technologies). Indium and rhenium were used as internal standards. The international geostandard SLRS-4 (Riverine Water Reference Material for Trace Metals certified by the National Research Council of Canada) was used to check the validity and reproducibility of each analysis. A good agreement between our replicated measurements of SLRS-4 and the certified values was obtained (relative difference < 5%).

3.4. Results and Discussion

3.4.1. pH, major components, and DOC

Measured dissolved organic carbon, trace and major elements concentrations, alkalinity, pH and conductivity values in the water samples are reported in the Table A3.1 of Annex A.

The studied waters of the Vostochniy stream, the terminal Tsipringa Lake and Palojoki river are neutral with pH ranging from 6.3 to 7.5 where as the waters of bog, waterlogged humic lake and soil solution are acidic with pH of 4.1, 5.8 and 3.6, respectively. There is a decrease of pH value by 0.5 units during filtration from 20 µm to 1 kDa (Fig. 3.3). All waters are low mineralized (≤ 30 mg/L) with the dominance of Ca and HCO_3^- ions or Ca, Cl and Na ions (soil solution). The inorganic ion charge balance $((\sum^+-\sum^-)/\sum^+)$ is below 0.1 for all samples except soil solution having a deficit of anions of 0.4-0.5. This deficit is correlated with DOC concentration in filtrates and ultrafiltrates similar to those reported in other surface waters of North Karelia (Vasyukova et al., 2010) typical for organic-rich boreal surface waters (DOC concentration equals to 10-20, 5-20, 20-60 and 120-150 mg/L in river and stream, lakes, bog and soil solution, respectively). The distribution of DOC concentration (< 0.22 µm filtrate) along the landscape profile of the Vostochniy stream demonstrates a systematic decrease of [DOC] downward the catchment, from soil solution (OR-9) through the feeding bog (OR-6) and small feeding lakes (OR-5, OR-4, OR-3, OR-2), along the stream itself (OR-7, OR-1) and finally to the terminal Tsipringa lake (OR-8). The largest decrease occurs between soil solution (OR-9) and bog lake (OR-6) and between the mouth of the spring and the terminal clear water lake; the variations of [DOC] within the upper humic lakes and within the stream are rather small (< 15 %).

3.4.2. Major and trace elements

3.4.2.1. Concentration distribution within the catchment profile

3.4.2.1.1. Iron

There is two orders of magnitude decrease of Fe concentration (< 0.22 µm) along the stream Vostonychiy profile, from soil solution (2600 µg/L, OR-9), through the feeding lake (125 µg/L, OR-6), downstream (170 µg/L, OR-2, OR-1) towards the terminal lake (10 µg/L, OR-8). Extremely high concentration of total dissolved Fe in soil solution probably reflects the presence of soluble Fe(II) in this partially anoxic solution. The most pronounced concentration decreases occur between OR-9 and OR-6 and between OR-1 to OR-8. The variations of Fe concentration between sampling points OR-6 and OR-1 are insignificant. The pattern of Fe concentration in the Palojoki river is more complex due to the larger area of its watershed and the presence of numerous tributaries. Clearwater oligotrophic lake Kivakkalampi located at the upper reaches of the stream exhibits the lowest concentrations (80 µg/L, KAR-7), whereas the concentrations in the feeding humic lake (750 µg/L, KAR-6) and the river mouth (180 µg/L, KAR-3) are significantly lower compared to the Fe-and OC-rich tributaries (4500 µg/L, KAR-4, 3000 µg/L, KAR-5) and the feeding bog (3700 µg/L, KAR-2).

3.4.2.1.2. Alkali and alkaline-earth metals, neutral molecules and oxyanions.

Behavior of all alkali Na, K, Rb along the profile of Vostochniy stream is quite uniform with the maximal concentrations observed in large terminal lake (OR-8), and soil solution (OR-9), and the minimal concentrations observed in the feeding bog lake (OR-2). Downward the landscape profile there is a decrease of concentrations from OR-9 to OR-2, followed by the increase from OR-2 to OR-8. Unlike other alkali, Cs concentration decreases from OR-1 to OR-8. The concentrations of these elements in the Palojoki watershed profile are rather small, with the maximal values observed in the feeding bog. Likewise alkali, Ca, Mg, Sr and Ba concentrations decrease from soil solution and bogs towards the terminal lake; there is pronounced increase in the river mouth probably reflecting the feeding by the groundwaters.

The evolution of concentration of the elements present as neutral molecules and oxy-anions in both studied watersheds profile does not demonstrate any systematic trend within the watershed continuum; the concentrations vary by a factor of 3 to 10 without any detectable influence of the landscape context, DOC and Fe concentration.

3.4.2.1.3. Insoluble trivalent and tetravalent elements

Within the Vostochniy watershed, Al concentration steadily decreases by a factor of 2 downstream from soil solution (OR-9) until the river mouth (OR-1) and further by a factor of 6 towards the terminal lake (OR-8). Ga concentration varies non-systematically between 0.004 and 0.02 µg/L with the minimal values observed in humic lakes (OR-2, OR-6). Likewise, REE concentrations are similar among all samples with the values in the terminal lake OR-8 being a factor of 4 to 5 smaller than in the others. Along the Palojoki profile, concentrations of Al, Ga, Y, REEs change systematically, increasing from the upper clear water Kivakkalampi lake (KAR-7), through intermediate lake (KAR-6) towards the feeding bog (KAR-2), and further decreasing from the middle course (KAR-1) towards the river mouth (KAR-3). Similar to Fe, the tributary KAR-4 likely fed by the groundwaters exhibits the highest Al, Ga, Y, and REEs concentrations.

The tetravalent elements (Ti, Zr, Hf, Th) exhibit the evolution of the concentration that is similar to that of REEs both within the components of Palojoki river (KAR series) and Vostochniy stream (OR series). The tetravalent elements (Ti, Zr, Hf, Th) concentrations remain fairly constant (±10%) between OR-9 and OR-1 decreasing by 30-50% in the terminal lake OR-8. Similar to Fe, variations of tetravalent element concentrations in the Palojoki stream are significant, increasing from KAR-7 to KAR-2 by a factor of 3 to 5, and further decreasing, by a factor of 1.5 to 2.0, towards the middle course (KAR-2) and the river mouth (KAR-3).

3.4.2.1.4. Other trace elements: V, Mn, Ni, Cr, Co, Cu, Zn, Pb, Cd, U

The change of V, Ni, Cr, Co, Cu, and Mn concentration along the watershed of Vostochniy stream is rather similar: they decrease by 30-80 % from OR-9 to OR-6 and then remain constant until the stream mouth (OR-1), finally decreasing towards the terminal lakes OR-8, thus generally following the behavior of Fe. The uranium concentration systematically increases, by a factor of 8 along the profile of Vostochniy stream, from soil solution to terminal lake. Concentrations of Cd, Zn, Co, Mn and Pb do not exhibit any systematic variations along the Vostochniy watershed profile. Other metal micronutrients or biologically relevant elements (V, Ni, Cr, Cu, Zn) exhibit rather small evolution of total dissolved concentration. For the Palojoki watershed, U concentration significantly increases, by a factor of 4 where as Cd, Co, Mn and Pb do not exhibit any systematic trend ranging by a factor of 5 to 100 among different landscape components of the Palojoki river.

3.4.2.2. Element distribution among different size fractions

Measured trace and major elements and dissolved organic carbon concentrations in filtrates and dialysates are reported in the Table A3.2 and A3.3 of Annex A. Correlation coefficients (R^2) of TE with Fe and OC in filtrates and ultrafiltrates are reported in the Table 3.3.

3.4.2.2.1. Comparison between dialysis and ultrafiltration

Rigorous comparison between dialysis and ultrafiltration could be performed for 4 contrasting samples of the Vostochniy stream watershed (soil solution OR-9, humic lake OR-6, the mouth of the stream OR-1 and the terminal clearwater lake OR-8) and 2 samples of the Palojoki river (feeding bog KAR-2 and the middle course KAR-1). A number of major and trace elements do not exhibit statistically significant difference between dialysis and ultrafiltration in all four samples including K, Na, Mg, Ca, Si, Sc, V, Cr, Mn, Co, Ni, Ga, Ge, Sr, Mo, Cd, Ba, Pb. At the same time, concentrations of Al, Fe, Ti, Cu, Zn, As, Rb, Y, Zr, Cs, REE, Hf, W, Th, U in < 1 kDa dialysates were systematically lower compared to 1 kDa ultrafiltrates, producing a noticeably smaller proportion of colloidal metals (from 10 to 40%) in ultrafiltrates compared to dialysates. This result is in full agreement with previous data from the NW Russian boreal zone, obtained in other type of surface waters using different ultrafiltration setup (Vasyukova et al., 2010).

3.4.2.2.2. Iron

The removal of Fe during cascade filtration and ultrafilration occurs in two steps, with the maximal decrease happening between 1 and 0.1 µm and below 100 kDa which may correspond to the size of Fe-rich coarse colloids and LMW organic complexes, respectively (Fig. 3.4). Correlation of Fe with DOC is in ultrafiltrates series is not significant (not shown). Typically, significant drop in Fe concentration, notably in the region of coarse colloids, is not accompanied by any significant DOC concentration change and even in the region of LMW complexes, the DOC concentration decreases only by a factor of 1.5-2 with up to 1 order of magnitude Fe concentration decrease.

3.4.2.2.3. Elements not affected by filtration and ultrafiltration procedure (<10-20 % in colloids)

The alkaline metals (Na, K, Rb, Cs) are not affected by the ultrafiltration and do not exhibit any meaningful correlation with Fe or DOC, being largely present as ionic, non complexed species. The alkaline-earth metals also do not change the concentration during filtration or decrease their concentration by 10-20 % after filtration through 1-10 kDa. The latter decrease often coincide with that of organic carbon rather than Fe thus suggesting the presence of colloidal organic complexes of these elements.

Neutral molecules and oxyanions (Si, Ge, As, Mo, Sb, W) demonstrate the lack of concentration variation in the full series of filtrates and ultrafilatres, over 5 orders of magnitude in the size fraction, from 100 µm to 1 kDa. There is no correlation of these elements concentration with Fe or OC in the ultrafiltrates. This strongly suggests the absence of not only colloids and LMW complexes but also of large size silicate particles, suspended mineral material or phytoliths capable transporting these elements in surface waters.

3.4.2.2.4. Elements affected by size separation procedure: trivalent and tetravalent metals

In the course of filtration and ultrafiltration procedure, aluminum concentration is highly correlated with that of Fe whereas the correlation with OC is detectable only in fractions < 0.22 µm. It is fairly possible that this reflects the presence of both inorganic Fe-Al-rich oxyhydroxides (stabilized by organic matter) and Al- organic matter colloids and LMW complexes; the latter is also demonstrated by Dia et al., 2000. The correlation between Ga and Fe is rather poor in the filtrates of river waters but much better in the feeding bog (KAR-2); the correlation of this element with OC is rather weak. Yttrium and Light Rare Earth Elements (LREEs) such as Y, La-Sm exhibit very good correlation with Fe; this correlation decreases for medium REEs (Eu-Er) and becomes absent for Heavy Rare Earth Elements (HREEs) such as Tm-Lu. At the same time, HREE are better correlated with organic carbon, notably in the LMW fraction. This observation, documented both for Vostochniy stream and Palojoki river nicely corroborates the previous results of the high affinity of the LREEs to mineral surfaces and HREEs to the organic ligands known both from laboratory experiments (Byrne and Kim, 1990; Koeppenkastrop and De Carlo, 1992, 1993; De Carlo, 1998; Bau, 1999) and natural observations (Sholkovitz, 1995; Tyler, 2004; Pokrovsky et al., 2006; Pourret et al., 2007; Pédrot et al., 2008).

Among insoluble tetravalent elements, Ti, Zr and Th are well correlated with Fe in filtrates and ultrafiltrates, especially in soil solution; Th is also correlated with OC although this dependence is less pronounced than that with Fe. Good correlation of Th with DOC in different size fraction filtrates was also demonstrated by Dia et al. (2000).

3.4.2.2.5. Other Trace elements: V, Mn, Ni, Cr, Co, Cu, Zn, Pb, Cd, U

In filtrates and ultrafiltrates, Mn, Co and V are much better correlated with Fe compared to DOC. Cr, Ni, Cu, Zn, Cu, Cd do not exhibit any significant correlation with Fe or DOC. A link between Fe and Pb can be evidenced for the feeding bog of Palojoki river (KAR-2) as well as in soil solution and Vostochniy stream and the lake (OR-1, OR-8, OR-9). Vanadium is also linked to Fe in samples OR-1, OR-6, OR-9 which do not exhibit any connection to DOC concentration in filtrates and ultrafiltrates. Similar to numerous previous works (Andersson et al., 1998; Dia et al., 2000; Pokrovsky and Schott, 2002), uranium is strongly correlated with Fe but in less degree with OC in all samples of Palojoki watershed.

3.4.3. Geochemistry and size fractionation of Rare Earth Elements

The ratio of La/Yb does not exhibit significant evolution in the series of filtrates and ultrafiltrates from 100 μm to 1 kDa although some enrichment of heavy versus light REE in LMW filtrates is clearly observed for humic lake (OR-6) and soil solution of Vostochniy stream (OR-9), for Palojoki mouth (KAR-3) and the feeding bog of the river (KAR-2) as it is illustrated in Fig. 3.5 A and B, respectively. The slope of the dependence between La and Fe concentration in filtrates and ultrafiltrates systematically decreases along the watershed profile of Vostochniy stream, being equal to $3 \cdot 10^{-5}$, $6 \cdot 10^{-4}$, $3 \cdot 10^{-4}$ and $3.2 \cdot 10^{-3}$ for samples OR-9, OR-6, OR-1 ad OR-8, respectively (Fig. 3.6).

Further insights on size fractionation of REE can be assessed from REE spectra (concentrations normalized to NASC) for various filtrates and ultrafiltrates of both studied watersheds (Fig. 3.7 A-E). The following typical features can be noted. The REE spectra of soil solution (OR-9, Fig. 3.7 A) is flat without Ce minimum, typical for anoxic or suboxic aquatic environments (Sholkovitz et al., 1992; Sholkovitz, 1992, 1993, 1994; German et al., 1995; Sultan and Shazili, 2009). Oxygenated humic lake (OR-6) also exhibits flat spectrum but the Ce minimum becomes visible in HMW colloids > 10 kDa (Fig. 3.7 B). Vostochniy stream filtration series (OR-1) demonstrates strongly pronounced Ce minimum detectable down to < 1 kDa ultrafiltrates and Eu maximum, the latter is also visible in all filtrates of the terminal Tsipringa lake (OR-8, see Fig. 3.7 D). The feeding bog of the Palojoki river (KAR-2) demonstrates an enrichment of filtrates by LREEs without the presence of Ce minimum. This minimum appears for HMW (> 10 kDa) ultrafiltrates only in the river Palojoki itself.

It is known that the presence of Ce minimum is tightly linked to its oxidation on Fe oxyhydroxide colloids and particles as follows from numerous previous studies (Sholkovitz, 1992, 1993, 1994; Ingri et al., 2000; Pourret et al., 2008). For this minimum to be pronounced in all filtration and ultrafiltration series, high dissolved Fe concentrations and O_2-saturated environments are necessary. These conditions are met for samples OR-1, OR-6, OR-8 and KAR-3. Partially suboxic waters with high concentration of colloidal and suspended Fe do not show Ce anomaly but demonstrate the enrichment of HMW (> 10 kDa) filtrates in LREEs (KAR-2, Fig. 3.7 E). The Ce minima disappears in $LMW_{<1\ kDa}$ ultrafiltrates of the Palojoki river (KAR-3, Fig. 3.7 F) but clearly persists in 1 kDa ultrafiltrates of Vostochniy stream

(OR-1, Fig. 3.7 C). The reason for such a striking difference between two oxygenated streams is that 1 kDa fraction of OR-1 exhibits an order of magnitude higher Fe concentration than that of KAR-3. This confirms the importance of Fe-rich colloidal and dissolved carriers in creating Ce anomaly in oxygenated surface waters. Note that the fractionation between HREE and LREE disappears for all $\text{LMW}_{< 1\ \text{kDa}}$ fractions having Fe concentration lower than 100 µg/L.

Compared to bog soil solution (OR-9), the humic lake feeding the stream Vostochniy and receiving its water from adjacent bogs (OR-6) exhibit much lower REE concentrations in LMW fraction and the absence of Ce anomaly in 1 kDa ultrafiltrates (Fig. 3.7 B). The most likely cause for such a transformation of REE spectrum between bog water and lake waters is the deposition of Fe oxy(hydr)oxides in this oxygenated lake via coagulation induced by gravitational sedimentation, photo- and bio-degradation of organo-mineral colloids. Because colloidal Fe oxy(hydr)oxides are the main carriers of REE in studied waters, Fe-poor LMW organic fraction does not have Ce anomaly and exhibits an order of magnitude lower concentration of all REE.

Strong positive Eu anomaly in all filtrates and ultrafiltrates of large terminal clear water lake (OR-8, Fig. 3.7 D) may be linked to its feeding by groundwaters bearing the signature of basic rocks. Note that this Eu anomaly is also visible in soil waters located within the basic rocks (OR-9, Fig. 3.7 A). Finally, very high concentration of HMW and subcolloidal Fe in the Palojoki stream and feeding bog (samples KAR-2, KAR-3) leads to significant enrichment of > 1 µm filtrates by LREEs (Fig. 3.7 E and F), in full agreement with experimentally established higher affinity of LREE compared to HREEs to minerals surfaces (Bau, 1999), also proven from the analysis of filtrates and ultrafiltrates of natural Fe and OC-rich samples (Sholkovitz, 1994 for Hudson river filtrates 0.025 µm, 50 kDa and 5 kDa and Pédrot et al., 2008 for soil solution filtrates 0.22µm, 30, 5 and 2 kDa).

3.4.4. Proportion of colloidal fraction

Proportion of colloidal fraction of a trace element can be evaluated using the equation (Pokrovsky et al., 2010; Vasyukova et al., 2010):

$$\%\ \text{colloidal} = ([C_{0.22\ \mu\text{m}}]-[C_{1\ \text{kDa}}])/[C_{0.22\ \mu\text{m}}] \times 100\%$$

The average percentage of colloidal fraction calculated among all studied settings is given in Table 3.4 and illustrated in Fig. 3.8.

According to the evolution of colloidal fractions in the continuum soil (bog) – feeding humic lakes - river – terminal (oligotrophic) lake of Vostochniy stream watershed, several groups of elements could be distinguished: (*i*) elements significantly bound to colloidal (1 kDa – 0.22 µm) fraction and decreasing the proportion of this fraction from the feeding lake and the stream to the terminal oligotrophic lake (Fe, Ti, U); (*ii*) colloidally-dominated (>80 %) elements exhibiting similar size fractionation in all studied settings (Y, REEs, Zr, Hf, and Th); (*iii*) elements appreciably bound to colloids (20 to 40%) in organic-rich soil and bog waters and decreasing their colloidal fraction to c.a. 10% in the oligotrophic lake (Mg, Ca, Sr, Rb) and, finally (*iv*) elements significantly linked to colloidal fraction (40 to 80%) and not exhibiting any systematic variation between different landscape context (Ni, Co, Cu, Cd, Cr, Mn, Zn, Pb).

The majority of TE exhibit the proportion of colloidal fraction that is similar to those assessed previously in other boreal and temperate settings using ultrafiltration (Dahlqvist et al., 2004; Stolpe et al., 2005; Pourret et al., 2007; Pédrot et al., 2008; Pokrovsky et al., 2010; Vasyukova et al., 2012). Among all studied landscape settings, only suboxic Fe(II)- and organic-rich peat soil solution (OR-9) exhibit significantly different proportion of colloidal fraction notably for elements normally weakly affected by colloids in oxygenated surface waters of lakes and streams. Neglecting this soil sample, the other 6 samples do not demonstrate statistically significant difference in the percentage of colloidal TE as a function of landscape context.

This can be further assessed from a plot of the percentage of TE in colloids as a function of total dissolved TE concentration in 0.22 µm fraction (Fig. 3.9). It can be seen from these plots that, disregarding the soils solution sample, none of the element presented in this graph exhibit a clear trend of the percentage in colloids with the concentration increase. As such, the values of colloidal proportion recommended in this work may be considered, within the uncertainties associated with these values, as universal characteristics of all the boreal surficial aquatic environments.

It follows from this comparison that the transformation of allochthonous humic –rich soil colloids by autochthonous DOM does not bring about measurable change in TE size fractionation. What can be expected is that soil colloids, once delivered to the lake or bog waters and further to the stream will be subjected to photodegradation and bio-mineralisation by heterotrophic bacterioplankton and will be progressively replaced, along the watershed profile, by their degradation products and, at the same time, will be enriched by authochtnous exometabolites of phytoplankton and peryphyton. Apparently, these transformation processes, certainly occurring in studied aquatic systems, are neither capable of changing dramatically the partitioning of TE between different size fractions nor affecting the element fractionation with respect to Fe and organic carbon, the main colloidal constituents.

Further insights on sub-colloidal versus truly dissolved (LMW) fraction evolution among different types of the studied ecosystems can be assessed from the analysis of the ratio [20–0.22 µm] fraction to [0.22 µm - 1 kDa] fraction. This ratio reflects the relative contribution of the suspended, non-silicate (particulate) fraction to the truly dissolved (low molecular weight) element fraction. However, the values of the ratio of particles to colloids is smaller than 0.01 for the majority of elements in the stream and the feeding lake (not shown). The exceptions are Fe, Sr and Ti in the lake Tsipringa exhibiting significant amount of particulate forms of these elements of non-silicate nature.

3.4.5. Partition coefficient K_d

Because the decrease of Fe concentration initiates at the 1 µm filter size (chapter 3.4.2.2.2, Fig. 3.4) it is reasonable to define the iron-normalized TE partition coefficient between LMW (< 1 kDa) and HMW colloidal fraction (1 kDa – 1 µm) fractions as:

$$K_d = (\mathrm{TE/Fe})_{1\ \mu\mathrm{m} - 1\ \mathrm{kDa}} / (\mathrm{TE/Fe})_{< 1\ \mathrm{kDa}}$$

The calculated K_d values (see Table ESM-3.4) in surface waters of Vostochniy watershed (samples OR-6 and OR-1) are very similar to those measured in other boreal zone (Vasyukova et al., 2010). The calculation of K_d can be performed only for those samples where the concentration of Fe is sufficiently high, typically this is above 100 µg/L. This threshold stems from the principle of sufficiently high dilution (minimum a factor of 10) of TE in Fe-organic matrix; it thus requires maximum 10% content of TE in organo-ferric colloids.

The values of K_d for alkali and Si are close to zero for all sampling points of both watersheds. For alkaline earth metals in Palojoki river, the K_d decreases from bog to the river where these values approach zero. The K_d values of elements strongly bound to colloids such as Ti, Y, REEs change in a similar manner: they decrease from the feeding bog towards the mouth of Palojoki stream and, from the soil solution to intermediate lake and afterwards they remain constant until the river mouth. Similarly, we observe progressive decrease of K_d for Cu, Ni, Cd, Ga, Th along the Palojoki watershed, from feeding bog to the middle course and along the Vostochniy stream, from he soil solution and humic lake towards the stream following the further decrease in the terminal lake.

For both studied streams, the better the correlation of TE with Fe concentration in filtrates and UF series, the higher the K_d coefficients. Note for example, significantly higher values of K_d for LREE (La) compared to HREE (i.e., Yb). This is in full accord with much higher affinity of LREE to Fe oxy(hydr)oxide surfaces and strong complexation of HREE with dissolve organic ligands discussed in section 3.4.3 above.

Such a progressive decrease of the degree of TE association with ferric colloids from soil solution towards the terminal lake, also reflected in the decrease of colloidal Fe concentration, may reflect significant transformation of colloids consisting in 1) photo- and bio-degradation of allochthonous colloids leading to sedimentation of Fe-rich phases and 2) progressive enrichment of dissolved pool by autochthonous organic-rich, Fe-poor dissolved organic matter of periphyton and plankton exometabolites.

3.5. Conclusions and prospectives for climate warming

Systematic size fractionation study of boreal surface water colloids using unified on-site cascade filtration/ultrafiltration and dialysis procedure conducted within the continuum soil solution – bogs – humic lakes – streams – terminal clear water lake allowed first order assessment of the degree of major and TE binding to various colloidal pools in basic aquatic settings of the region. The transformation of allochthonous humic–rich soil colloids and progressive enrichment of waters by autochthonous DOM within the sequence from soil solution to the stream and further to the terminal lakes does not bring about measurable change in TE size fractionation. It follows that both photo-and biodegradation processes occurring in studied water systems cannot significantly modify the relative percentage of TE in colloidal (1 kDa – 0.22 µm) fraction. At the same time, we observe a progressive decrease of the degree of TE association with ferric colloids from soil solution towards the terminal lake, also reflected in the decrease of colloidal Fe concentration. This may reflect significant transformation of colloids consisting in *i)* photo- and bio-degradation of allochthonous colloids leading to sedimentation of Fe-rich phases and *ii)* progressive enrichment of dissolved pool by autochthonous organic-rich, Fe-poor dissolve organic matter of periphyton and plankton exometabolites.

Given that the climate warming in high latitudes will produce higher water temperatures and as such will intensify 1) primary productivity of phytoplankton, notably dominance of cyanobacteria over other phytoplankton (Carey et al., 2012); 2) rate of DOM mineralization of heterotrophic bacterioplankton and 3) photo-degradation of colloidal material, the following changes in colloidal size distribution and chemical composition may occur. First, proportion of HMW organic-rich humic-like soil – borne colloids will decrease at the expense of LMW phytoplankton exometabolites. Second, enhanced mineralization of organo-ferric colloids will decrease the ability of insoluble trivalent and tetravalent element to migrate from the soil and riparian/hyporheic zone to the terminal lake. Note that, unlike the permafrost zone, where the rise of air and soil temperature will increase the thickness of thawing depth and will intensify the input of colloids from mineral horizons (cf., Bagard et al., 2011), boreal non-permafrost zone will be much less affected by the change of groundwater regime.

All these aforementioned processes will inevitably increase the flux of LMW, Fe-poor organic colloids to the ocean and as such will potentially deliver more labile and bioavailable DOC and related trace elements, including metal micronutrients, to the coastal biota. As a result of the change of the structure of colloidal flux to the ocean, significant increase of productivity of both autotrophic (nutrients) and heterotrophic (organic matter) components of the food chain may occur. During the open water summer base-flow period, the flux of divalent metals such as Cu, Zn, Pb, Cd, Ni, Co which are present in LMW organic complexes, much more labile through the estuarine mixing zone, will therefore increase. In contrast, the delivery from the land to the ocean of insoluble trivalent, tetravalent elements (Al, Ga, Y, REEs, Ti, Zr, Hf, Th) and U present as large-size organo-ferric colloids will decrease. However, the magnitude of these possible changes are impossible to foresee at the present time.

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TABLES

Table 3.1. List of sampled waters and their bedrock compositions.

sample name	description	GPS coordinates		bedrock composition	Age
KAR-3	Palojoki river, mouth reach, the zone of mixing river and Pyaozero lake	N 66°11.037´	E 30°34.520´	Biotite garanitogneisses and tributary biotite, biotite-amphibolite and amphibolite gneisses and amphibolites	AR$_1$
KAR-1	Palojoki river, middle course	N 66°12.096´	E 30°28.639´	Micro-pegmatic granites, Granosyenites, Syenites, Syenit-diorites	Pt$_1$
KAR-2	Watershed of Palojoki river, the feeding swamp, surface area about 1.2 km^2	N 66°12.483´	E 30°29.279´		
KAR-4	Palojoki river, the second right tributary				
KAR-5	Palojoki river, the first right tributary				
KAR-6	Palojoki river, the feeding lake, surface area about 80 m^2				
KAR-7	Kivakkalampi lake, surface area about 3.4 km^2				
OR-1	stream « Vostochniy », mouth reach, the zone of mixing river and Tsipringa lake	N 66°18.455´	E 30°42.653´	Meta-gabbro	
OR-2	Watershed « Vostochniy », the low feeding lake, surface area about 50 m^2	N 66°18.448´	E 30°41.372´		
OR-3	Watershed « Vostochniy », the low feeding lake, surface area about 50 m^2	N 66°18.453´	E 30°41.364´		
OR-4	Watershed « Vostochniy », the low feeding lake, surface about 200 m^2, depth 2.5 m	N 66°18.468´	E 30°41.244´		
OR-5	Watershed « Vostochniy », the middle feeding lake, surface about 210 m^2, depth 3 m	N 66°18.521´	E 30°41.101´		
OR-6	Watershed « Vostochniy », the top feeding lake, surface about 150 m^2, depth 2.6 m	N 66°18.538´	E 30°40.910´		
OR-7	stream « Vostochniy », middle course, 600 m from the mouth	N 66°18.460´	E 30°40.973´		
OR-8	Tsipringa lake, 50 m from the mouth of the stream Vostochniy	N 66°18.449´	E 30°42.952´		
OR-9	stream « Vostochniy », soil solution near the top feeding lake	N 66°18.489´	E 30°40.707´		

Table 3.2. The main filtration characteristics.

pore size	filer size	filter material	filter producer	filtration pressure	filtration unit
100 µm	300*300 mm	nylon	"Fisherbrand", USA	gravity flow	-
20 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
10 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
5 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
0.8 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
0.4 µm	2×100*250 mm	lavsan	Dubna, Russia	3 - 5 m	-
0.22 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
0.1 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
0.046 µm	Ø 37 mm	lavsan	Dubna, Russia	-80 - 0 kPa	"Nalgen", 250 ml
100 kDa	Ø 76 mm	regenerated cellulose	"Millipore", USA	0 - 100 kPa	"Amicon", 8400
10 kDa	Ø 76 mm	regenerated cellulose	"Millipore", USA	0 - 350 kPa	"Amicon", 8400
1 kDa	Ø 76 mm	regenerated cellulose	"Millipore", USA	0 - 350 kPa	"Amicon", 8400

Table 3.3. Correlation coefficients (R^2) of TE with Fe and OC in filtrates and ultrafiltrates.

	TE-Fe (R^2)							TE-DOC (R^2)						
	OR-9	OR-6	OR-1	OR-8	KAR-2	KAR-1	KAR-3	OR-9	OR-6	OR-1	OR-8	KAR-2	KAR-1	KAR-3
Al	0.99	0.76	0.99	0.81	0.85	0.88	0.8	<0.60	0.91	0.51	<0.60	0.63	0.93	0.75
Ti	0.97	0.82	0.95	<0.60	0.97	0.98	0.98	<0.60	0.87	0.6	<0.60	<0.60	0.87	<0.60
V	0.97	0.82	0.95	<0.60	0.97	0.98	0.98	<0.60	0.68	<0.60	<0.60	<0.60	0.73	<0.60
Cr	0.63	<0.60	0.71	<0.60	0.74	0.92	<0.60	<0.60	0.79	<0.60	<0.60	0.65	0.63	0.7
Mn	0.69	0.88	0.98	<0.60	0.96	<0.60	0.97	<0.60	0.87	0.64	<0.60	<0.60	<0.60	<0.60
Fe	-	-	-	-	-	-	-	<0.60	0.83	<0.60	0.77	<0.60	0.82	<0.60
Co	0.87	<0.60	0.94	<0.60	0.86	0.7	0.94	<0.60	0.7	<0.60	0.82	0.6	<0.60	<0.60
Ni	0.88	0.6	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	0.88	<0.60	<0.60	0.78	<0.60	0.84
Cu	0.72	<0.60	0.72	<0.60	<0.60	<0.60	<0.60	<0.60	0.88	<0.60	<0.60	<0.60	<0.60	0.64
Zn	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60
Ga	0.8	<0.60	<0.60	<0.60	0.99	0.89	0.94	<0.60	<0.60	<0.60	<0.60	<0.60	0.92	<0.60
Ge	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60
As	<0.60	<0.60	0.73	<0.60	<0.60	<0.60	<0.60	<0.60	0.75	0.84	<0.60	<0.60	<0.60	<0.60
Rb	<0.60	<0.60	<0.60	<0.60	0.93	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60
Sr	0.88	0.69	<0.60	0.6	<0.60	<0.60	<0.60	<0.60	0.89	<0.60	<0.60	0.87	<0.60	0.6
Y	0.97	0.83	0.89	0.71	0.82	0.87	0.62	<0.60	0.95	<0.60	<0.60	0.66	0.96	0.89
Zr	0.81	<0.60	0.78	<0.60	<0.60	<0.60	<0.60	<0.60	0.84	0.68	<0.60	0.96	0.88	0.91
Mo	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60
Cd	<0.60	0.91	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	0.74	<0.60	<0.60	<0.60	<0.60	<0.60
Sn	0.76	<0.60	<0.60	<0.60	0.87	0.99	0.97	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60
Cs	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60
Ba	0.96	0.75	<0.60	<0.60	0.7	0.976	0.67	<0.60	0.88	<0.60	<0.60	0.8	0.65	0.86
La	0.97	0.88	0.94	0.81	0.9	0.93	0.78	<0.60	0.9	0.67	0.65	<0.60	0.94	0.77
Ce	0.99	0.87	0.96	0.85	0.86	0.93	0.9	<0.60	0.89	0.72	0.69	0.62	0.94	0.64
Pr	0.94	0.85	0.96	0.8	0.85	0.94	0.86	<0.60	0.87	0.73	0.63	0.64	0.93	0.72
Nd	0.97	0.83	0.91	0.76	0.81	0.93	0.86	<0.60	0.9	0.71	0.64	0.65	0.93	0.7
Sm	0.82	0.78	0.93	0.6	0.76	0.92	0.8	<0.60	0.86	0.83	<0.60	0.71	0.96	0.74
Eu	0.68	0.76	0.71	<0.60	0.68	0.79	0.68	<0.60	0.81	0.7	<0.60	0.82	0.96	0.77
Gd	0.66	0.6	0.69	<0.60	0.8	0.91	0.71	<0.60	<0.60	0.75	<0.60	0.69	0.94	0.79
Tb	0.76	0.75	0.62	<0.60	<0.60	0.9	0.75	<0.60	0.85	<0.60	<0.60	0.8	0.95	0.78
Dy	0.75	0.84	0.72	<0.60	0.85	0.9	0.67	<0.60	0.88	<0.60	<0.60	0.6	0.93	0.84
Ho	0.66	0.75	<0.60	<0.60	0.77	0.86	<0.60	<0.60	0.8	0.6	<0.60	0.7	0.99	0.78
Er	0.8	0.81	0.64	<0.60	0.76	0.69	<0.60	<0.60	0.94	<0.60	<0.60	0.73	0.83	0.89
Tm	<0.60	<0.60	0.7	<0.60	0.73	0.8	<0.60	<0.60	0.86	<0.60	<0.60	0.76	0.84	0.81
Yb	<0.60	<0.60	<0.60	<0.60	0.77	<0.60	<0.60	<0.60	0.89	<0.60	<0.60	0.68	0.9	0.84
Lu	<0.60	<0.60	<0.60	<0.60	0.82	<0.60	<0.60	<0.60	0.78	<0.60	<0.60	0.63	0.69	0.83
Hf	<0.60	<0.60	<0.60	<0.60	<0.60	0.96	<0.60	<0.60	<0.60	<0.60	<0.60	0.66	0.74	<0.60
W	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60
Pb	0.79	<0.60	0.95	0.97	0.81	0.78	<0.60	<0.60	0.72	0.75	0.7	<0.60	0.79	0.67
Th	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	0.91	<0.60	<0.60	0.93	0.77	0.76
U	<0.60	<0.60	0.68	<0.60	<0.60	<0.60	<0.60	<0.60	0.92	<0.60	<0.60	0.89	0.89	0.94

Table 3.4. Means values of colloidal proportion calculated using data of ultrafiltration (UF) 1 kDa and dialysis (D) 1 kDa for 4 samples of Vostochniy stream and 3 samples of Palojoki river basins.

sample	OR-9		OR-6		OR-1		OR-8		KAR-2		KAR-1		KAR-3
separ. tech.	UF	D	UF	D	UF	D	UF	D	UF	D	UF	D	UF
Na	27	35	0	31	0	0	0	0	0	31	0	0	0
Mg	77	68	19	31	22	0	0	2	7	57	0	21	0
Al	80	91	73	93	67	94	0	21	33	85	52	90	73
Si	0	0	0	50	10	0	0	8	0	0	0	0	0
K	34	22	10	0	35	0	0	0	0	75	0	20	0
Ca	84	71	31	38	32	0	2	7	14	54	2	13	2
Ti	91	86	68	79	73	60	18	12	70	84	47	55	48
V	0	87	20	0	33	75	25	0	26	35	14	57	22
Cr	78	66	64	71	49	78	7	nd	26	62	17	42	33
Mn	79	61	31	82	50	nd	0	44	14	50	9	35	9
Fe	88	91	94	97	95	91	15	63	67	96	92	97	96
Co	83	65	71	71	87	40	0	50	23	67	10	66	29
Ni	83	72	55	73	43	57	0	63	27	76	4	65	33
Cu	80	85	53	73	38	44	0	66	25	72	8	42	38
Zn	95	96	11	61	nd	nd	38	98	0	51	0	nd	16
Ga	86	86	93	45	86	71	0	33	55	70	40	66	80
Ge	76	75	33	0	56	nd	0	75	20	65	71	86	17
As	62	69	25	44	30	40	nd	nd	23	nd	55	nd	44
Rb	37	72	0	nd	23	nd	0	0	0	60	0	8	0
Sr	81	55	31	40	32	nd	5	12	24	59	6	24	12
Y	84	89	75	94	71	94	50	80	54	90	67	95	76
Zr	84	90	79	99	77	95	0	76	67	94	60	98	79
Mo	90	60	nd	nd	nd	54	0	9	87	nd	10	40	0
Cd	65	5	70	65	50	25	0	43	28	60	14	29	53
Cs	43	86	50	50	0	nd	55	99	82	nd	23	38	46
Ba	90	58	48	54	47	24	50	40	49	23	14	nd	23
La	94	91	85	95	78	95	67	80	70	94	71	96	83
Ce	90	90	87	94	77	96	53	80	67	94	76	96	83
Pr	90	90	87	95	78	94	50	83	57	93	70	65	87
Nd	86	89	80	94	73	94	60	84	60	93	67	97	85
Sm	89	89	82	94	73	93	42	67	58	91	79	98	80
Eu	84	82	75	95	75	92	43	98	60	90	75	75	80
Gd	90	93	67	94	50	89	40	82	60	89	60	97	88
Tb	89	89	91	100	75	92	25	93	70	88	56	nd	92
Dy	87	90	79	98	67	90	43	93	55	90	56	94	79
Ho	87	88	75	98	67	85	17	92	64	90	60	nd	71
Er	84	89	71	89	67	83	0	64	50	95	67	nd	83
Tm	83	93	80	90	72	84	nd	nd	64	82	70	nd	91
Yb	76	88	75	94	65	82	25	90	20	90	83	nd	77
Lu	79	92	83	92	60	80	0	nd	62	86	75	nd	67
Hf	67	90	50	98	71	94	0	nd	66	88	36	89	87
W	nd	60	nd	nd	nd	nd	0	91	40	40	0	70	0
Pb	97	93	nd	80	nd	nd	0	83	95	nd	nd	nd	nd
Th	90	92	90	95	88	96	0	85	82	89	60	94	83
U	75	90	87	93	75	93	5	50	59	91	53	97	97

Table 3.5. Ratio of coarse colloids/particle (%), calculated by formula ([20 µm]-[0.22µm])/([0.22 µm]-[1 kDa]), nd – non determinated.

	OR-9	OR-6	OR-1	OR-8
Na	0.00	0.00	0.00	0.00
Mg	0.08	0.00	0.00	0.00
Al	0.43	0.00	0.00	0.00
Si	0.00	0.00	0.00	0.00
K	0.45	0.00	0.00	0.00
Ca	0.07	0.00	0.00	1.00
Ti	0.85	0.21	0.45	3.00
V	0.26	0.50	1.13	0.00
Cr	0.62	0.11	0.00	0.00
Mn	0.13	0.00	0.21	0.00
Fe	0.54	0.22	0.67	2.78
Co	0.25	0.00	0.00	0.00
Ni	0.40	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00
Zn	0.94	1.50	nd	0.00
Ga	2.00	0.00	0.00	0.00
Ge	0.33	0.00	0.20	0.00
As	0.56	0.00	0.67	nd
Rb	0.00	0.00	0.00	0.00
Sr	0.54	0.00	0.00	1.45
Y	0.44	0.00	0.08	0.00
Zr	0.36	0.00	0.00	0.00
Mo	0.37	nd	nd	0.00
Cd	1.54	0.00	0.00	0.00
Cs	0.33	0.00	0.00	0.00
Ba	0.42	0.00	0.00	0.00
La	0.60	0.00	0.14	0.50
Ce	0.55	0.00	0.09	0.63
Pr	0.53	0.00	0.14	0.67
Nd	0.52	0.00	0.17	0.53
Sm	0.44	0.00	0.00	0.26
Eu	0.53	0.00	0.00	0.00
Gd	0.56	0.17	0.00	0.50
Tb	0.43	0.00	0.00	1.00
Dy	0.38	0.00	0.00	0.77
Ho	0.38	0.00	0.00	0.00
Er	0.38	0.20	0.00	0.00
Tm	0.40	0.00	0.00	nd
Yb	0.54	0.00	0.00	0.00
Lu	0.32	0.00	0.00	0.00
Hf	0.25	0.00	0.00	0.00
W	nd	nd	nd	0.00
Pb	0.49	nd	nd	0.00
Th	0.40	0.00	0.00	0.00
U	0.00	0.00	0.00	0.00

FIGURES

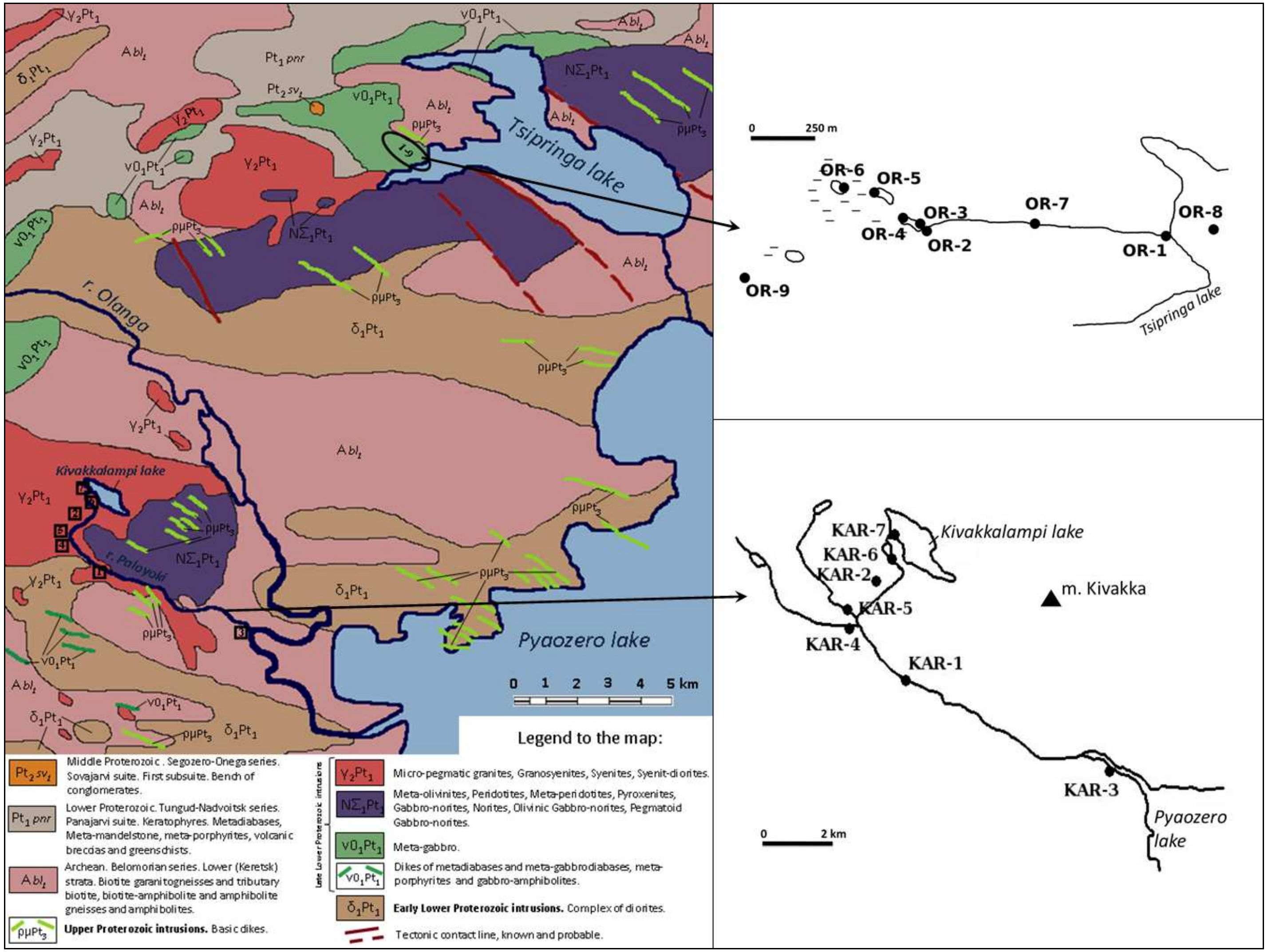

Figure 3.1. Geological map and sampling scheme

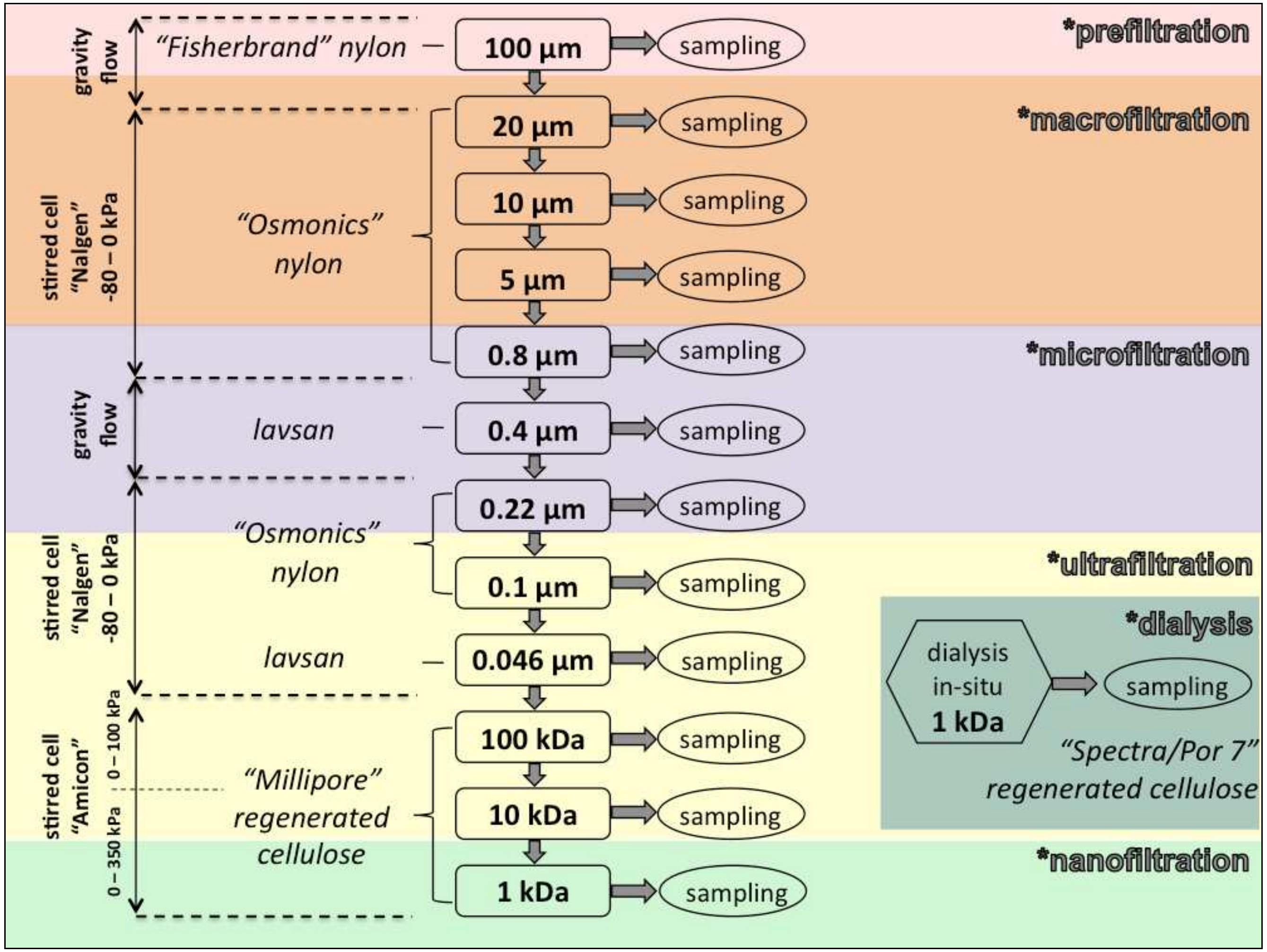

Figure 3.2. The scheme of cascade filtration.

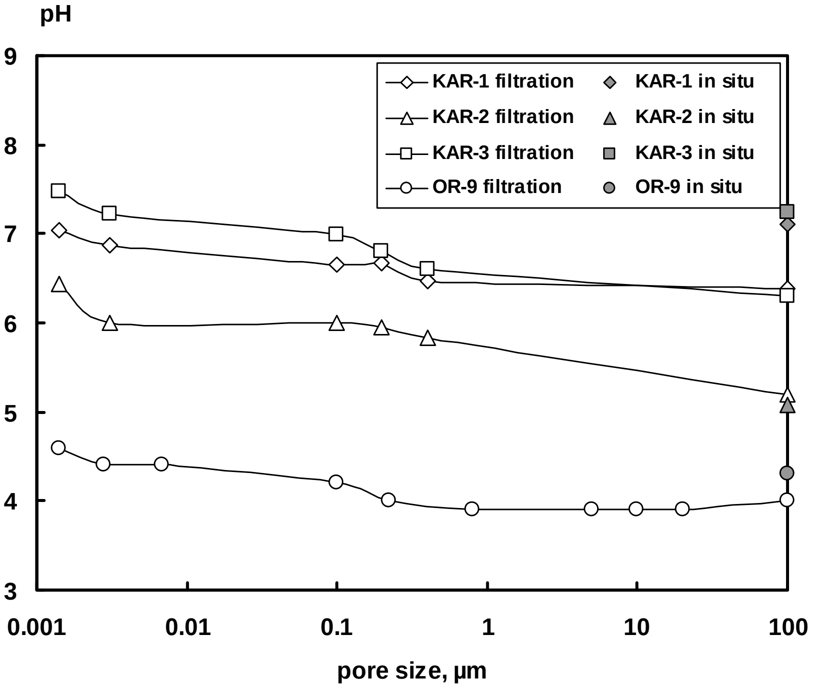

Figure 3.3. pH values measured in filtrates and in-situ in the samples of Palojoki river (KAR-1 – middle course of the river, KAR-2 – feeding bog, KAR-3 – mouth reach) and Vostochniy stream (OR-9 – soil solution) watersheds.

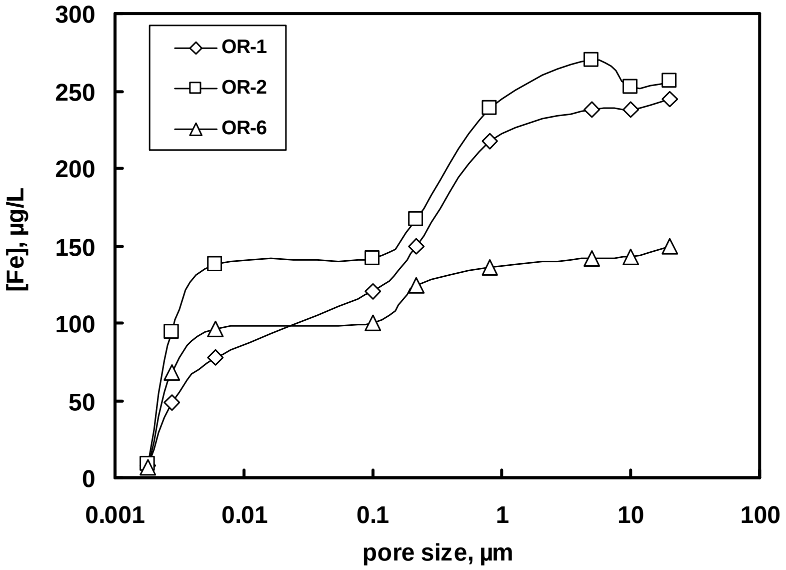

Figure 3.4. Iron distribution in the filtrates of Vostochniy stream watershed (OR-1 – middle course of the stream, OR-2 – waterlogged shore, OR-6 – upper feeding lake).

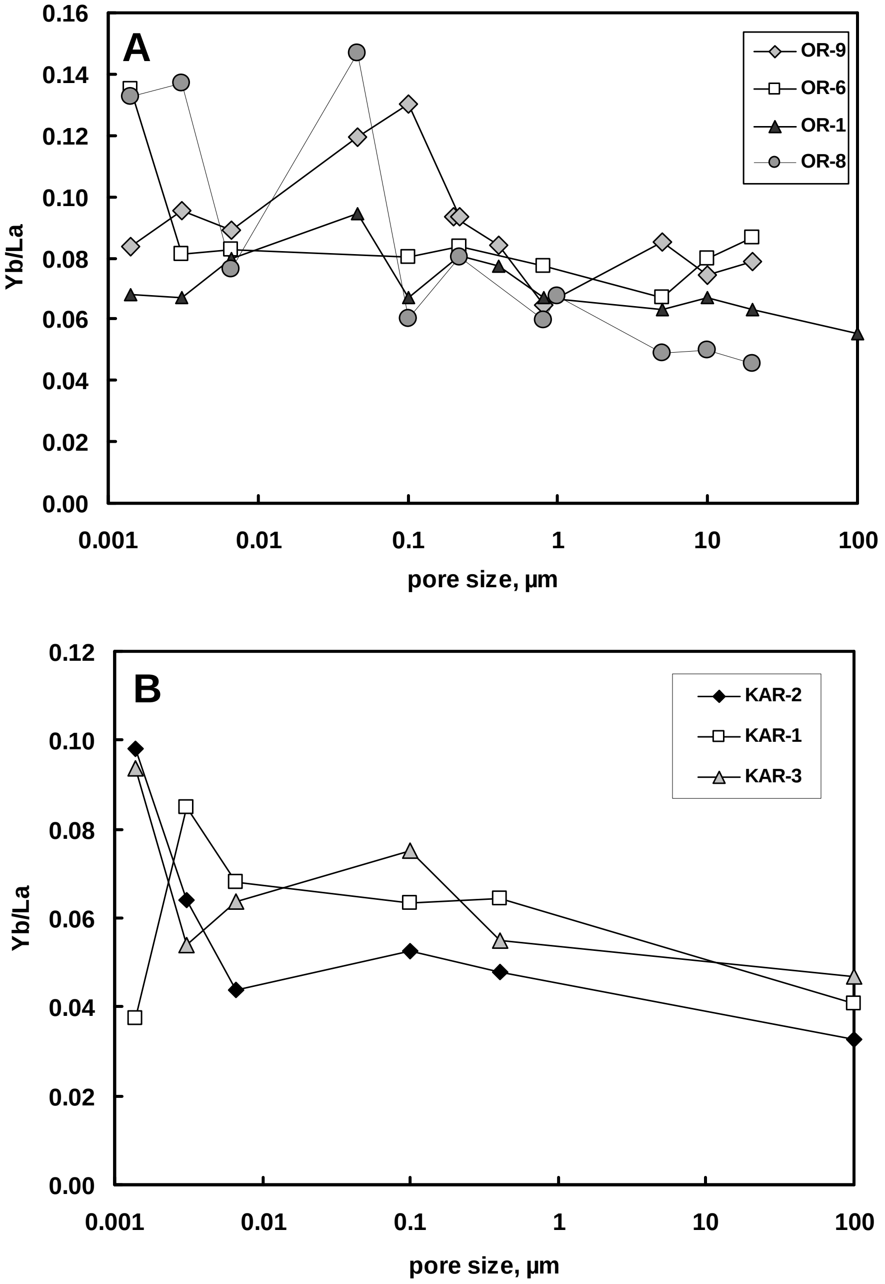

Figure 3.5. La/Yb ratio of filtrates and ultrafiltrates from 100 μm to 1 kDa of Vostochniy stream (A) and Palojoki river (B) watersheds.

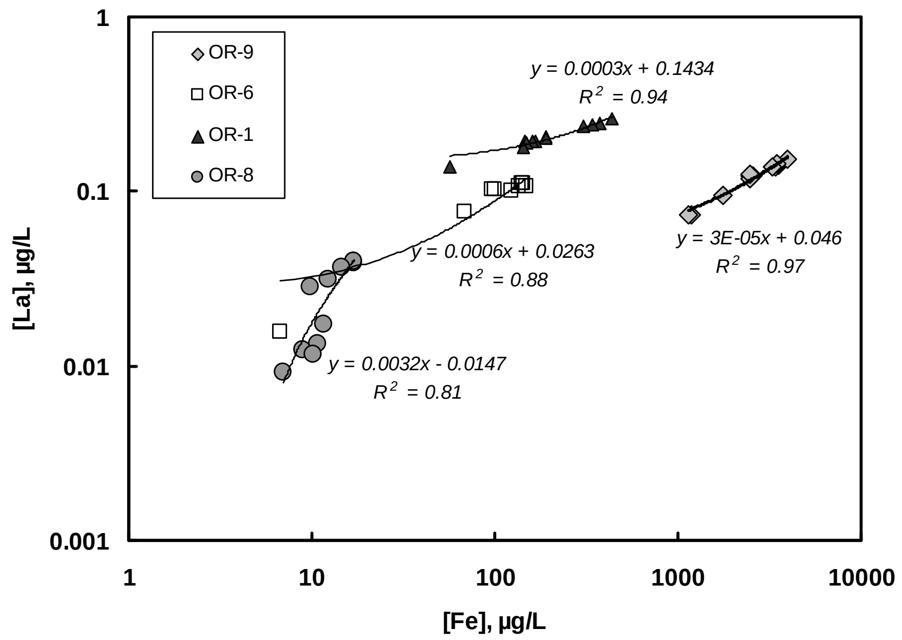

Figure 3.6. Dependence between La and Fe concentration in filtrates and ultrafiltrates of Vostochniy stream watershed (OR-9 – soil solution, OR-6 – upper feeding lake, OR-1 – middle course of the stream, OR-8 – terminal lake Tsipringa).

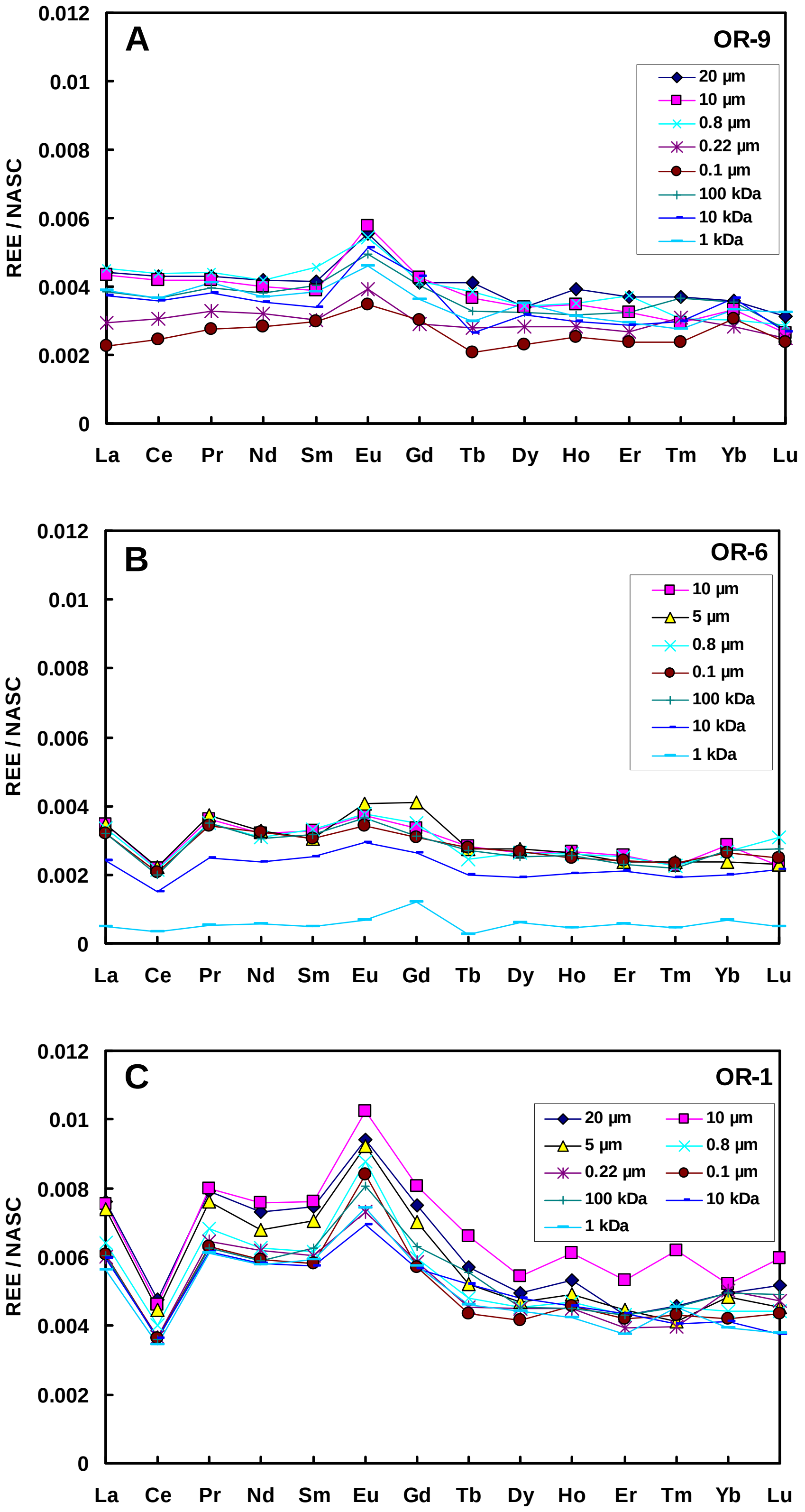

Figure 3.7. REE patterns normalized to NASC for filtrates and ultrafiltrates of Vostochniy stream watershed (A – soil solution, B – upper feeding lake, C – middle course of the stream).

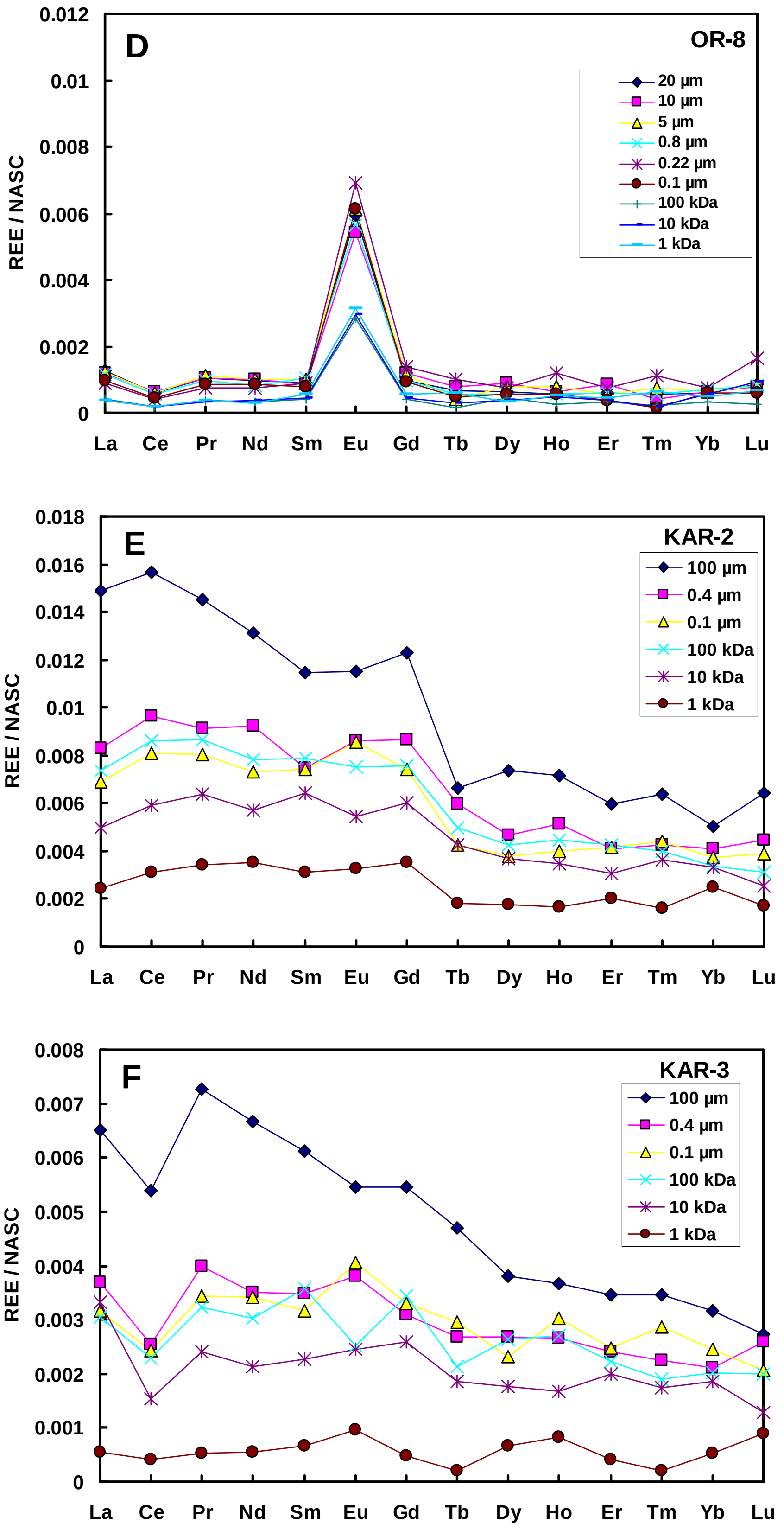

Figure 3.7 continued. REE patterns normalized to NASC for filtrates and ultrafiltrates of Vostochniy stream watershed (D – terminal lake Tsipringa) and Palojoki river watershed (E – feeding bog, F – mouth reach of the river).

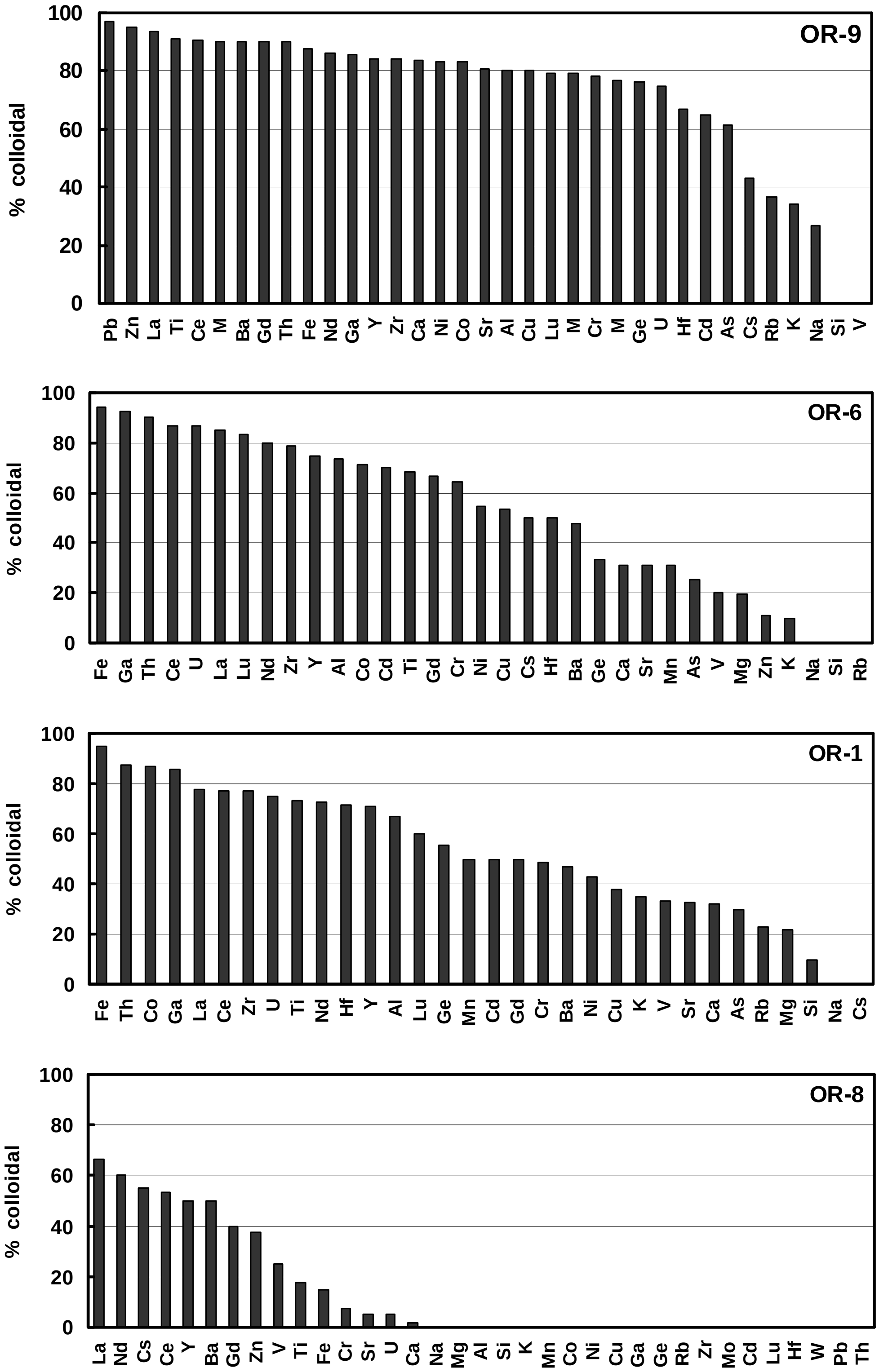

Figure 3.8. Proportion of colloidal fraction of trace elements in Vostochniy stream watershed for soil solution (OR-9), upper feeding lake (OR-6), middle course of the stream (OR-1), and terminal lake Tsipringa (OR-8).

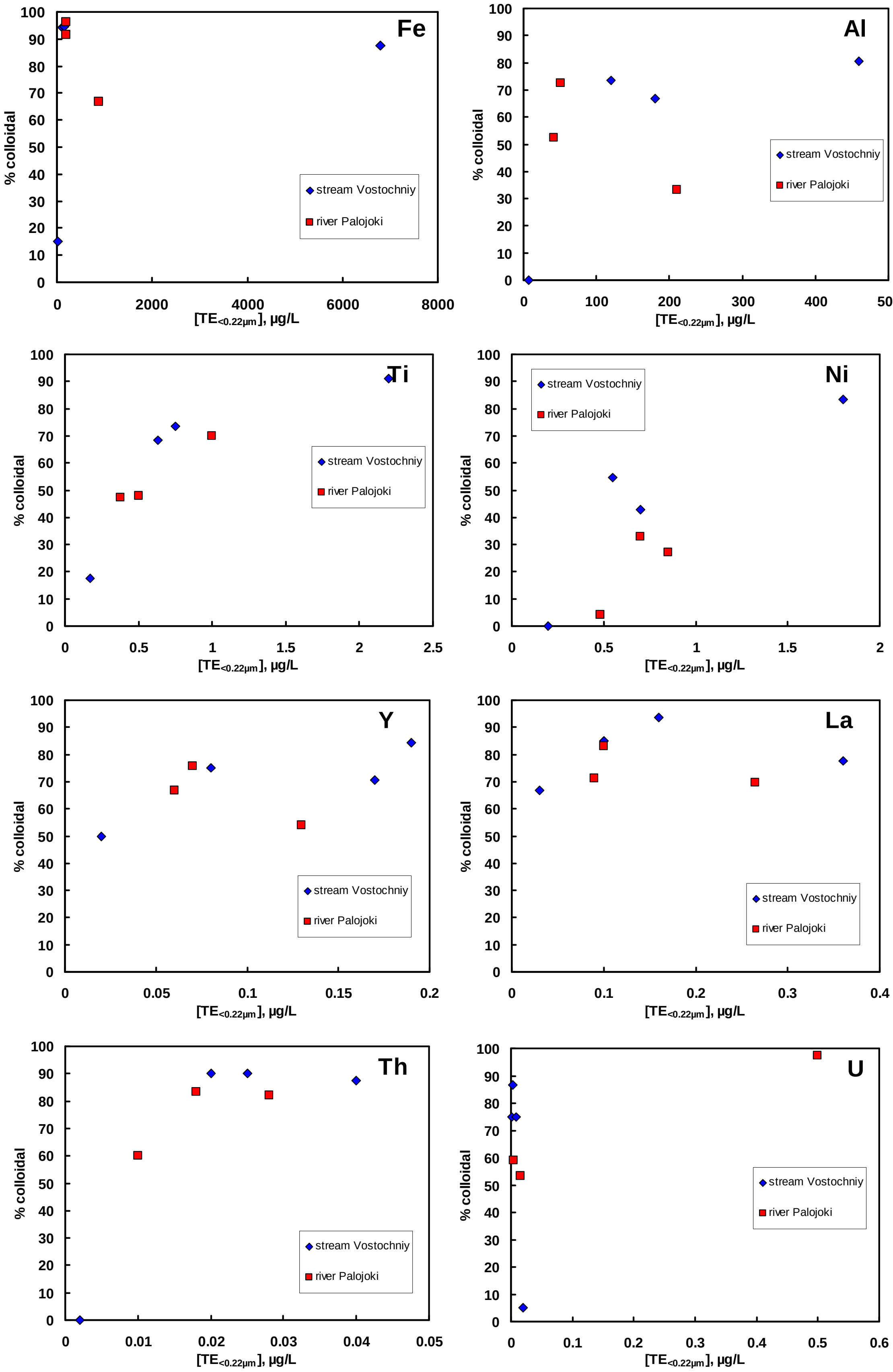

Figure 3.9. The percentage of colloidal metal as a function of metal concentration in < 0.22 µm in Vostochniy stream and Palojoki river watersheds.

ANNEX A

Table A3.1. Trace and major elements (µg/L), dissolved organic carbon (mg/L), anions (mg/L) concentrations measured in the samples (0.22 µm), alkalinity (mMol/L), temperature (°C), pH, salinity (TDS, mg/L), conductivity (R, µSm/cm) and oxygen saturation (%) values measured in-situ in water samples of the study, 2009, nd – non determined, cont – contamination, trace – trace concentrations.

	OR-9	OR-6	OR-2	OR-1	OR-8	KAR-7	KAR-6	KAR-2	KAR-5	KAR-4	KAR-1	KAR-3
T°C	17.2	21.7	18.9	12.8	17.8	19	26	17.2	16	16.4	17.9	16.3
pH	4.3	6.3	6.3	6.7	7.5	6.95	7.01	5.54	6.92	7.35	7.27	6.87
R	57.4	20.8	18.1	14.39	42.5	10.7	23.5	35.3	32.2	24.1	23.0	23.7
TDS	31.9	10.2	8.22	8.45	23.3	5.42	10.5	19.5	18.2	13.4	12.4	12.9
O_2 sat.	40	85	nd	90	100	90	90	75	95	100	100	100
Alk.	0.00	0.22	0.15	0.28	0.54	nd	nd	0.11	nd	0.25	0.27	0.33
Cl^-	0.689	0.325	0.3971	0.4207	0.640	nd	nd	0.089	nd	0.089	3.69	0.082
SO_4^{2-}	0.062	0.32	1.1246	0.8945	0.0439	nd	nd	0.056	nd	0.023	0.026	trace
NO_3^-	0.116	0.0292	0.4971	0.3932	0.0784	nd	nd	nd	nd	nd	nd	nd
DOC	144	18	18	16	7	20	27	16	32	29	11	11
Na	980	984	834	1041	1212	878	707	7110	1024	1496	1017	1132
Mg	264	591	498	923	1736	535	693	616	1250	1421	947	1166
K	315	37	5	249	843	208.4	48.38	627.5	194.2	419.1	186.8	272.4
Ca	708	3237	2178	3275	5902	1787	2725	2597	5446	5846	3540	3300
Si	1863	1870	1070	2862	1280	1697	652.7	2816	2669	3624	2308	2505
Al	168	117	134	89	14	56	228	352	83	160	111	52
Ti	1.28	0.63	0.48	0.64	0.36	0.40	1.32	1.98	0.86	1.69	0.95	0.58
V	0.28	0.12	0.13	0.11	0.09	0.09	0.27	1.68	0.32	0.50	0.32	0.09
Cr	0.45	0.28	0.31	0.31	0.06	0.15	0.23	0.84	0.30	0.60	0.32	0.34
Mn	28.5	13.3	5.9	30.0	0.2	3.41	19.75	14.09	65.59	425.2	83.86	12.08
Fe	2580	123.9	167	167.6	9.6	80.73	757.3	3695	3081	4575	1998	181.5
Co	0.61	0.06	0.09	0.18	0.01	nd	0.20	0.24	0.36	2.31	0.48	0.08
Ni	1.16	0.56	0.57	0.63	0.20	0.236	0.433	1.100	0.438	0.945	0.619	0.703
Cu	1.50	0.45	0.46	0.86	0.60	0.559	0.411	2.244	0.328	0.816	0.691	1.260
Zn	23.2	1.8	1.4	15.6	1.7	2.6	6.1	5.1	3.2	6.9	4.3	5.2
Ga	0.020	0.002	0.002	0.005	0.004	0.004	0.026	0.035	0.011	0.049	0.016	0.005
Ge	0.006	0.002	0.002	0.006	0.002	0.002	0.004	0.012	0.007	0.014	0.004	0.006
As	0.396	0.104	0.121	7.407	0.067	0.088	0.208	0.320	0.169	0.335	0.357	0.316
Rb	0.844	0.245	0.142	0.917	0.938	0.510	0.196	0.870	0.531	0.886	0.540	0.515
Sr	6.7	7.9	6.3	9.4	11.3	9.8	15.6	18.7	34.5	43.8	22.2	17.2
Y	0.102	0.077	0.093	0.126	0.016	0.042	0.141	0.283	0.108	0.197	0.110	0.070
Zr	0.056	0.058	0.062	0.117	0.035	0.042	0.072	0.178	0.090	0.186	0.092	0.074
Mo	0.008	0.002	0.003	0.006	0.072	0.046	0.016	0.065	0.143	0.090	0.107	0.076
Cd	0.063	0.010	0.018	0.005	0.015	0.012	0.016	0.036	0.006	0.226	0.020	0.146
Cs	0.006	0.001	0.000	0.021	0.001	0.004	0.002	0.005	0.004	0.008	0.005	0.001
Ba	13.9	5.9	7.3	9.0	5.5	2.2	7.3	4.2	6.9	12.2	5.7	3.8
La	0.122	0.101	0.146	0.192	0.032	0.090	0.328	0.571	0.236	3.391	0.524	0.101
Ce	0.270	0.144	0.287	0.268	0.038	0.143	0.635	1.565	0.413	5.103	0.753	0.177
Pr	0.031	0.026	0.037	0.051	0.006	0.023	0.097	0.160	0.060	0.545	0.098	0.027
Nd	0.122	0.099	0.147	0.204	0.023	0.084	0.371	0.624	0.221	1.592	0.329	0.113
Sm	0.022	0.018	0.023	0.034	0.004	0.014	0.058	0.104	0.035	0.070	0.037	0.018
Eu	0.005	0.004	0.005	0.009	0.001	0.003	0.013	0.022	0.009	0.017	0.009	0.005
Gd	0.020	0.031	0.038	0.030	0.004	0.012	0.043	0.093	0.033	0.119	0.038	0.017
Tb	0.003	0.002	0.003	0.004	0.000	0.001	0.004	0.010	0.003	0.007	0.004	0.003
Dy	0.017	0.013	0.014	0.023	0.002	0.008	0.026	0.058	0.020	0.045	0.023	0.012
Ho	0.003	0.003	0.003	0.005	0.000	0.001	0.005	0.010	0.004	0.007	0.004	0.003
Er	0.010	0.007	0.010	0.013	0.001	0.004	0.014	0.030	0.012	0.022	0.011	0.008
Tm	0.001	0.001	0.001	0.002	0.000	0.001	0.002	0.004	0.002	0.003	0.002	0.001
Yb	0.011	0.008	0.009	0.016	0.001	0.004	0.014	0.026	0.011	0.021	0.011	0.008
Lu	0.001	0.001	0.001	0.002	0.000	0.001	0.002	0.004	0.002	0.003	0.002	0.001
Hf	0.002	0.005	0.004	0.004	0.002	0.003	0.005	0.008	0.005	0.010	0.006	0.004
W	0.003	0.002	0.001	0.003	0.001	0.001	0.004	0.011	0.001	0.006	0.004	0.010
Pb	0.476	0.013	0.008	0.025	0.028	0.098	0.313	0.986	0.090	0.352	cont	0.098
Th	0.010	0.019	0.019	0.031	0.003	0.007	0.015	0.036	0.021	0.035	0.021	0.018
U	0.003	0.003	0.002	0.008	0.024	0.013	0.004	0.022	0.017	0.013	0.019	0.048

Table A3.2. Trace elements (µg/L) and dissolved organic carbon (mg/L) concentrations in filtrates (2009) and dialysate 1 kDa (2010, D1) of the soil solution (OR-9) of Vostochniy stream watershed, nd – non determined, cont – contamination.

OR-9	20 µm	10 µm	5 µm	0.8 µm	0.22 µm	0.1 µm	100 kDa	10 kDa	1 kDa	D1
Na	1200	1200	1200	1200	1200	1200	1200	980	880	780
Mg	500	500	500	470	470	470	205	155	110	150
Al	620	620	620	490	460	460	270	190	90	40
Si	2000	2000	2000	2000	2000	2000	2000	2000	1800	2000
K	370	370	370	320	320	320	320	240	210	250
Ca	1270	1270	1270	1200	1200	1000	430	430	195	350
Ti	3.9	3.9	3.9	3.2	2.2	1.8	0.5	0.3	0.2	0.3
V	1.1	1.1	1.1	0.99	0.93	0.85	0.6	0.37	0.28	0.12
Cr	1.1	1.1	1.1	0.95	0.74	0.65	0.4	0.26	0.16	0.25
Mn	33	33	33	30	30	26	11.3	8.3	6.3	11.8
Fe	10000	10000	10000	8600	6800	5200	1850	1030	842	585
Co	1.15	1.15	1.15	1.00	0.95	0.8	0.33	0.23	0.16	0.33
Ni	2.4	2.4	2.4	2.3	1.8	1.6	0.65	0.55	0.3	0.5
Cu	1.4	1.4	1.4	1.4	1.4	0.92	0.38	0.28	0.28	0.21
Zn	13.66	10.97	10.95	10.44	8.5	8.379	5.6	4.97	3.86	3.35
Ga	0.095	0.095	0.095	0.045	0.035	0.035	0.03	0.02	0.005	0.005
Ge	0.01	0.01	0.01	0.009	0.008	0.0065	0.0058	0.0035	0.0019	0.002
As	0.70	0.69	0.67	0.65	0.52	0.44	0.27	0.20	0.20	0.16
Rb	0.95	0.95	0.95	0.95	0.95	0.95	0.75	0.70	0.60	0.27
Sr	9.6	9.6	9.6	9.6	6.7	6.7	2.8	1.9	1.3	3
Y	0.26	0.26	0.26	0.26	0.19	0.14	0.06	0.04	0.03	0.02
Zr	0.13	0.13	0.13	0.12	0.1	0.09	0.035	0.017	0.016	0.01
Mo	0.02	0.02	0.02	0.02	0.015	0.015	0.005	0.005	0.0015	0.006
Cd	0.04	0.04	0.04	0.04	0.02	0.02	0.012	0.01	0.007	0.019
Cs	0.008	0.008	0.008	0.008	0.007	0.006	0.006	0.004	0.004	0.001
Ba	11	11	11	11	8	6	2.3	1.5	0.8	3.4
La	0.25	0.25	0.25	0.25	0.16	0.12	0.03	0.026	0.01	0.014
Ce	0.63	0.63	0.63	0.63	0.42	0.31	0.1	0.06	0.04	0.04
Pr	0.071	0.071	0.071	0.071	0.048	0.035	0.012	0.008	0.005	0.005
Nd	0.26	0.26	0.26	0.26	0.18	0.15	0.05	0.035	0.025	0.02
Sm	0.05	0.05	0.05	0.05	0.036	0.025	0.01	0.006	0.004	0.004
Eu	0.013	0.013	0.013	0.013	0.009	0.006	0.003	0.0014	0.0014	0.0016
Gd	0.09	0.09	0.09	0.09	0.06	0.025	0.01	0.006	0.006	0.004
Tb	0.0065	0.0065	0.0065	0.0065	0.0047	0.0035	0.0012	0.0009	0.0005	0.0005
Dy	0.04	0.04	0.04	0.04	0.03	0.02	0.009	0.005	0.004	0.003
Ho	0.008	0.008	0.008	0.008	0.006	0.005	0.0017	0.0012	0.0008	0.0007
Er	0.025	0.025	0.025	0.025	0.019	0.0157	0.0068	0.004	0.003	0.002
Tm	0.004	0.004	0.004	0.004	0.003	0.002	0.001	0.0006	0.0005	0.0002
Yb	0.024	0.024	0.024	0.024	0.017	0.015	0.008	0.004	0.004	0.002
Lu	0.003	0.003	0.003	0.003	0.0024	0.0024	0.0013	0.0005	0.0005	0.0002
Hf	0.007	0.007	0.007	0.007	0.006	0.005	0.003	0.002	0.002	0.0006
W	0.01	0.01	0.01	0.009	0.005	0.005	0.005	0.0003	nd	0.002
Pb	1.4	1.4	1.4	1.4	0.95	0.53	0.11	0.05	0.03	0.07
Th	0.034	0.034	0.034	0.03	0.025	0.019	0.006	0.0025	0.0025	0.002
U	0.002	0.002	0.002	0.002	0.002	0.001	0.0005	0.0005	0.0005	0.0002
DOC	141.44	138.22	137.89	135.20	55.10	38.75	27.14	11.87	11.33	

Table A3.2 continued. Trace elements (µg/L) and dissolved organic carbon (mg/L) concentrations in filtrates (2009) and dialysate 1 kDa (2010, D1) of the upper feeding lake (OR-6) of Vostochniy stream watershed, nd – non determined, cont – contamination.

OR-6	20 µm	10 µm	5 µm	0.8 µm	0.22 µm	0.1 µm	100 kDa	10 kDa	1 kDa	D1
Na	980	980	980	980	980	980	980	980	980	680
Mg	590	590	590	590	590	590	590	590	475	410
Al	120	120	120	120	120	120	120	110	32	9
Si	2000	2000	2000	2000	2000	2000	2000	2000	1900	1000
K	41	41	41	41	41	41	41	41	37	100
Ca	3200	3200	3200	3200	3200	3200	3200	3200	2200	2000
Ti	0.72	0.72	0.72	0.65	0.63	0.63	0.62	0.48	0.2	0.13
V	0.11	0.11	0.11	0.10	0.10	0.10	0.10	0.095	0.08	0.1
Cr	0.3	0.3	0.3	0.3	0.28	0.28	0.28	0.28	0.1	0.08
Mn	13	13	13	13	13	12	12	12	9	2.4
Fe	150	142	142	136	124	100	96	68	7	3.7
Co	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.02	0.02
Ni	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.25	0.15
Cu	0.45	0.45	0.45	0.45	0.45	0.45	0.44	0.44	0.21	0.12
Zn	2.1	2.1	1.9	1.8	1.8	1.8	1.8	1.8	1.6	0.7
Ga	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.0038	0.0003	0.0022
Ge	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.002	0.0025
As	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.082	0.062
Rb	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.32
Sr	8	8	8	8	8	8	8	8	5.5	4.8
Y	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.07	0.02	0.005
Zr	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.015	0.001
Mo	nd	nd	nd	nd	nd	nd	nd	nd	0.005	0.006
Cd	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.006	0.003	0.0035
Cs	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001
Ba	6.3	6.3	6.3	6.3	6.3	6.3	6.3	5.8	3.3	2.9
La	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.077	0.015	0.005
Ce	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.11	0.02	0.009
Pr	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.004	0.0015
Nd	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.08	0.02	0.006
Sm	0.017	0.017	0.017	0.017	0.017	0.017	0.017	0.015	0.003	0.001
Eu	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.003	0.001	0.0002
Gd	0.02	0.02	0.02	0.018	0.018	0.016	0.016	0.014	0.006	0.001
Tb	0.0023	0.0023	0.0023	0.0023	0.0023	0.0023	0.0023	0.0017	0.0002	0.00001
Dy	0.014	0.014	0.014	0.014	0.014	0.014	0.013	0.01	0.003	0.0003
Ho	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.0005	0.00005
Er	0.008	0.008	0.008	0.008	0.007	0.007	0.007	0.007	0.002	0.0008
Tm	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.0002	0.0001
Yb	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.006	0.002	0.0005
Lu	0.0012	0.0012	0.0012	0.0012	0.0012	0.0012	0.0012	0.001	0.0002	0.0001
Hf	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.002	0.0001
W	nd	nd	nd	nd	nd	nd	nd	0.004	0.0015	0.001
Pb	0.02	0.02	0.02	0.02	0.02	0.02	0.02	nd	nd	0.004
Th	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.017	0.002	0.001
U	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.0004	0.0002
DOC	16.71	15.10	15.20	14.88	14.56	14.45	16.28	14.45	7.68	nd

Table A3.2 continued. Trace elements (µg/L) and dissolved organic carbon (mg/L) concentrations in filtrates (2009) and dialysate 1 kDa (2010, D1) of the middle course (OR-1) of Vostochniy stream watershed, nd – non determined, cont – contamination.

OR-1	20 µm	10 µm	5 µm	0.8 µm	0.22 µm	0.1 µm	100 kDa	10 kDa	1 kDa	D1
Na	900	900	900	900	900	900	900	900	900	990
Mg	550	550	550	550	550	550	550	550	430	890
Al	180	180	180	180	180	180	180	160	60	11
Si	2100	2100	2100	2100	2100	2100	2100	2100	1900	2550
K	40	40	40	40	40	40	39	38	26	275
Ca	2100	2100	2100	2100	2100	2100	2100	2020	1430	2700
Ti	1	1	1	0.93	0.75	0.7	0.6	0.5	0.2	0.3
V	0.165	0.14	0.14	0.137	0.12	0.105	0.09	0.086	0.08	0.03
Cr	0.41	0.41	0.41	0.41	0.41	0.4	0.37	0.35	0.21	0.09
Mn	9.3	8.8	8.8	8.7	8.4	8.3	6.1	5.5	4.2	17
Fe	245	238	237	220	150	120	78	48	8	13
Co	0.1	0.1	0.1	0.1	0.1	0.1	0.08	0.06	0.013	0.06
Ni	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.65	0.4	0.3
Cu	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.7	0.5	0.45
Zn	nd	nd	nd	nd	nd	nd	nd	nd	nd	2.6
Ga	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.004	0.001	0.002
Ge	0.005	0.005	0.005	0.005	0.0045	0.0045	0.0045	0.0035	0.002	0.005
As	0.12	0.11	0.11	0.1	0.1	0.1	0.1	0.1	0.07	0.06
Rb	0.26	0.26	0.26	0.26	0.26	0.25	0.25	0.25	0.2	1
Sr	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.6	4.6	8.1
Y	0.18	0.18	0.18	0.18	0.17	0.17	0.16	0.13	0.05	0.01
Zr	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.12	0.03	0.007
Mo	0.014	0.014	0.014	0.014	0.013	0.007	0.003	0.002	nd	0.006
Cd	0.004	0.004	0.004	0.004	0.004	0.004	0.0035	0.0035	0.002	0.003
Cs	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.004
Ba	9	9	9	9	9	9	9	8	4.8	6.8
La	0.4	0.4	0.4	0.4	0.36	0.36	0.36	0.3	0.08	0.01873
Ce	0.75	0.75	0.75	0.7	0.7	0.7	0.6	0.5	0.16	0.025
Pr	0.1	0.1	0.1	0.09	0.09	0.09	0.09	0.07	0.02	0.005
Nd	0.37	0.37	0.37	0.37	0.33	0.32	0.32	0.26	0.09	0.02
Sm	0.06	0.06	0.06	0.06	0.06	0.06	0.05	0.04	0.016	0.004
Eu	0.012	0.012	0.012	0.012	0.012	0.011	0.01	0.009	0.003	0.001
Gd	0.05	0.05	0.05	0.05	0.05	0.05	0.046	0.04	0.025	0.0055
Tb	0.006	0.006	0.006	0.006	0.006	0.006	0.0055	0.005	0.0015	0.0005
Dy	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.025	0.01	0.003
Ho	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.005	0.002	0.0009
Er	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.015	0.006	0.003
Tm	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.002	0.002	0.0007	0.0004
Yb	0.017	0.017	0.017	0.017	0.017	0.017	0.015	0.014	0.006	0.003
Lu	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.002	0.002	0.001	0.0005
Hf	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.002	0.0004
W	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.0005
Pb	0.03	0.03	0.03	0.03	0.01	0.01	0.01	0.01	nd	0.02
Th	0.04	0.04	0.04	0.04	0.04	0.04	0.03	0.03	0.005	0.0017
U	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.007	0.002	0.0006
DOC	11.82	14.96	11.8	14.76	13.2	12.77	12.2	10.68	7.5	

Table A3.2 continued. Trace elements (µg/L) and dissolved organic carbon (mg/L) concentrations in filtrates (2010) and dialysate 1 kDa (2010, D1) of the terminal lake Tsipringa (OR-8) of Vostochniy stream watershed, nd – non determined, cont – contamination.

OR-8	20 µm	10 µm	5 µm	0.8 µm	0.4 µm	0.22 µm	0.1 µm	0.046 µm	100 kDa	10 kDa	1 kDa	D1
Na	1200	1200	1200	1200	1200	1200	1200	1200	1200	1200	1200	1200
Mg	1700	1700	1700	1700	1700	1700	1700	1700	1700	1700	1700	1670
Al	9.0	9.0	9.0	8.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	5.5
Si	1300	1300	1300	1300	1300	1300	1300	1300	1300	1300	1300	1200
K	820	820	820	820	820	820	820	820	820	820	820	820
Ca	6200	6200	6200	6200	6100	6100	6000	6000	6000	6000	6000	5700
Ti	0.26	0.26	0.26	0.24	0.17	0.17	0.15	0.14	0.14	0.14	0.14	0.15
V	0.1	0.1	0.1	0.1	0.1	0.1	0.09	0.075	0.075	0.075	0.075	0.1
Cr	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.065	0.1
Mn	0.92	0.92	0.92	0.92	0.82	0.82	0.82	0.82	0.82	0.82	0.82	0.46
Fe	17	16.5	16	14	12	12	12	10.2	10.2	10.2	10.2	4.4
Co	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.005
Ni	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.075
Cu	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.24
Zn	40	40	40	40	40	40	40	25	25	25	25	0.9
Ga	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.002
Ge	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.0005
As	cont	cont	cont	cont	cont	cont	cont	cont	cont	cont	cont	0.07
Rb	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
Sr	12.9	12.9	12.06	12.12	11.9	11.9	11.82	11.32	11.32	11.25	11.21	10.51
Y	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.004
Zr	0.009	0.009	0.009	0.009	0.0085	0.0085	0.0085	0.0085	0.0085	0.0085	0.0085	0.002
Mo	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.073
Cd	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.0017
Cs	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.045	0.045	0.045	0.045	0.0006
Ba	8.0	8.0	8.0	8.0	8.0	8.0	8.0	4.0	4.0	4.0	4.0	4.8
La	0.04	0.04	0.04	0.04	0.03	0.03	0.03	0.01	0.01	0.01	0.01	0.006
Ce	0.04	0.04	0.04	0.04	0.03	0.03	0.03	0.014	0.014	0.014	0.014	0.006
Pr	0.008	0.008	0.008	0.007	0.006	0.006	0.006	0.003	0.003	0.003	0.003	0.001
Nd	0.033	0.033	0.033	0.025	0.025	0.025	0.025	0.01	0.01	0.01	0.01	0.004
Sm	0.005	0.005	0.005	0.005	0.0045	0.0045	0.0045	0.0026	0.0026	0.0026	0.0026	0.0015
Eu	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.0045	0.004	0.004	0.004	0.0001
Gd	0.006	0.006	0.006	0.005	0.005	0.005	0.005	0.003	0.003	0.003	0.003	0.0009
Tb	0.0005	0.0005	0.0005	0.0005	0.0004	0.0004	0.0004	0.0004	0.0003	0.0003	0.0003	0.00003
Dy	0.004	0.004	0.004	0.003	0.003	0.003	0.003	0.002	0.002	0.002	0.0017	0.0002
Ho	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0005	0.0005	0.0005	0.0005	0.00045
Er	0.002	0.002	0.002	0.002	0.0014	0.0014	0.0014	0.0014	0.0014	0.0014	0.0014	0.0005
Tm	0.0002	0.0002	0.0002	0.0002	0.0001	0.0001	0.0001	0.0001	0.0001	nd	nd	nd
Yb	0.002	0.002	0.002	0.002	0.002	0.002	0.0018	0.0015	0.0015	0.0015	0.0015	0.0002
Lu	0.0004	0.0004	0.0004	0.0004	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	nd
Hf	0.0006	0.0006	0.0006	0.0006	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	nd
W	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.0007
Pb	0.021	0.021	0.021	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.0017
Th	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.0003
U	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.019	0.01
DOC	5.20	5.20	5.20	5.20	5.20	5.10	5.10	5.10	5.10	5.10	5.10	8.46

Table A3.3. Trace elements (µg/L) and dissolved organic carbon (mg/L) concentrations in filtrates (2008) and dialysate 1 kDa (2009, D1) of the feeding bog (KAR-2) of Palojoki river watershed, nd – non determined, cont – contamination.

KAR-2	100 µm	0.4 µm	0.1 µm	100 kDa	10 kDa	1 kDa	D1
Na	800	800	800	800	800	800	550
Mg	460	460	460	460	450	430	200
Al	285	210	210	205	165	140	31
Si	2200	2200	2200	2200	2200	2200	2200
K	110	110	110	110	110	110	28
Ca	1250	1250	1250	1250	1150	1070	580
Ti	2.2	1.0	1.0	0.86	0.5	0.3	0.16
V	1.5	0.23	0.23	0.2	0.17	0.17	0.15
Cr	0.75	0.66	0.62	0.58	0.51	0.49	0.25
Mn	48	36	36	36	35	31	18
Fe	3330	876	835	815	520	290	31
Co	0.58	0.48	0.45	0.45	0.44	0.37	0.16
Ni	0.86	0.85	0.85	0.85	0.75	0.62	0.2
Cu	1.6	1.6	1.6	1.6	1.3	1.2	0.45
Zn	10	10	10	10	10	10	4.9
Ga	0.03	0.01	0.01	0.01	0.007	0.0045	0.003
Ge	0.02	0.02	0.02	0.02	0.02	0.016	0.007
As	0.3	0.3	0.3	0.3	0.23	0.23	cont
Rb	0.15	0.15	0.15	0.15	0.15	0.15	0.06
Sr	8.9	8.5	8.5	8.5	7.4	6.5	3.5
Y	0.19	0.13	0.12	0.12	0.1	0.06	0.013
Zr	0.13	0.12	0.12	0.11	0.08	0.04	0.007
Mo	0.026	0.015	0.015	0.015	0.015	0.002	0.02
Cd	0.08031	0.1245	0.1536	0.1477	0.1165	0.09	0.05
Cs	0.0007	0.00068	0.00013	0.00013	0.00013	0.00012	0.0008
Ba	8.1	6.1	6.1	5.9	4.7	3.1	4.7
La	0.4763	0.2648	0.2207	0.2365	0.1601	0.08	0.016
Ce	1.15	0.7	0.6	0.6	0.43	0.2281	0.045
Pr	0.11	0.07	0.07	0.07	0.05	0.03	0.005
Nd	0.43	0.3	0.25	0.25	0.19	0.12	0.02
Sm	0.065	0.043	0.043	0.043	0.037	0.018	0.004
Eu	0.014	0.01	0.01	0.009	0.007	0.004	0.001
Gd	0.064	0.045	0.04	0.04	0.03	0.018	0.005
Tb	0.0056	0.005	0.004	0.004	0.004	0.0015	0.0006
Dy	0.04	0.02	0.02	0.02	0.02	0.009	0.002
Ho	0.007	0.005	0.004	0.004	0.0036	0.0018	0.0005
Er	0.02	0.014	0.014	0.014	0.01	0.007	0.0007
Tm	0.003	0.0022	0.0022	0.002	0.0018	0.0008	0.0004
Yb	0.015	0.01	0.01	0.01	0.01	0.008	0.001
Lu	0.0031	0.0021	0.0018	0.0015	0.0012	0.0008	0.0003
Hf	0.005	0.005	0.005	0.0048	0.0037	0.0017	0.0006
W	0.005	0.005	0.005	0.004	0.003	0.003	0.003
Pb	0.4	0.14	0.14	0.12	0.04	0.007	nd
Th	0.03	0.028	0.02	0.02	0.015	0.005	0.003
U	0.0058	0.0044	0.0044	0.0044	0.0039	0.0018	0.0004
DOC	16.68	16.67	16.57	15.7	14.28	11.29	

Table A3.3 continued. Trace elements (µg/L) and dissolved organic carbon (mg/L) concentrations in filtrates and dialysate 1 kDa (D1) of the middle course (KAR-2) of Palojoki river watershed, nd – non determined, cont – contamination.

KAR-1	100 µm	0.4 µm	0.1 µm	100 kDa	10 kDa	1 kDa	D1
Na	900	900	900	900	900	900	900
Mg	820	820	820	820	820	820	650
Al	70	42	40	40	29	20	4
Si	2000	2000	2000	2000	2000	2000	2000
K	200	200	200	200	200	200	160
Ca	3000	3000	3000	3000	3000	2950	2620
Ti	0.83	0.38	0.36	0.35	0.2	0.2	0.17
V	0.25	0.07	0.06	0.06	0.06	0.06	0.03
Cr	0.34	0.24	0.2	0.2	0.2	0.2	0.14
Mn	71	66	65	65	62	60	43
Fe	1363	200	200	200	50	17	7
Co	0.34	0.29	0.26	0.26	0.26	0.26	0.1
Ni	0.48	0.48	0.48	0.48	0.48	0.46	0.17
Cu	1.4	1.2	1.2	1.2	1.2	1.1	0.7
Zn	6	6	6	6	6	6	nd
Ga	0.009	0.005	0.004	0.004	0.004	0.003	0.0017
Ge	0.007	0.007	0.005	0.005	0.0035	0.002	0.001
As	0.4	0.4	0.2	0.2	0.18	0.18	cont
Rb	0.4	0.4	0.4	0.4	0.4	0.4	0.37
Sr	18	17	16	16	16	16	13
Y	0.09	0.06	0.05	0.05	0.04	0.02	0.003
Zr	0.07	0.05	0.05	0.05	0.04	0.02	0.001
Mo	0.11	0.1	0.09	0.09	0.09	0.09	0.06
Cd	0.07	0.07	0.07	0.07	0.07	0.06	0.05
Cs	0.0013	0.0013	0.0013	0.0013	0.0013	0.001	0.0008
Ba	4.5	3.7	3.7	3.7	3.5	3.2	cont
La	0.21	0.09	0.085	0.085	0.05	0.026	0.004
Ce	0.39	0.17	0.16	0.16	0.09	0.04	0.007
Pr	0.05	0.02	0.02	0.02	0.01	0.006	0.007
Nd	0.2	0.09	0.085	0.085	0.045	0.03	0.003
Sm	0.03	0.014	0.014	0.014	0.01	0.003	0.0003
Eu	0.006	0.004	0.003	0.003	0.002	0.001	0.001
Gd	0.03	0.015	0.015	0.015	0.009	0.006	0.0005
Tb	0.0032	0.0016	0.0016	0.0014	0.0009	0.0007	nd
Dy	0.017	0.009	0.009	0.009	0.005	0.004	0.0005
Ho	0.0035	0.002	0.002	0.0017	0.0016	0.0008	nd
Er	0.01	0.006	0.006	0.006	0.004	0.002	nd
Tm	0.0015	0.001	0.001	0.001	0.0004	0.0003	nd
Yb	0.009	0.006	0.005	0.005	0.004	0.001	nd
Lu	0.001	0.0008	0.0008	0.0008	0.0003	0.0002	nd
Hf	0.0033	0.0028	0.0022	0.0019	0.0018	0.0018	0.0003
W	0.01	0.01	0.01	0.01	0.01	0.01	0.003
Pb	0.12	0.05	0.05	0.05	nd	nd	nd
Th	0.012	0.01	0.01	0.01	0.007	0.004	0.0006
U	0.02	0.015	0.015	0.015	0.014	0.007	0.0004
DOC	12.62	10.93	10.89	10.71	10.5	9.44	

Table A3.3 continued. Trace elements (µg/L) and dissolved organic carbon (mg/L) concentrations in filtrates of the middle course (KAR-2) of Palojoki river watershed, nd – non determined, cont – contamination.

KAR-3	100 µm	0.4 µm	0.1 µm	100 kDa	10 kDa	1 kDa
Na	1100	1100	1100	1100	1100	1100
Mg	1100	1100	1100	1100	1100	1100
Al	88	51	51	51	39	14
Si	2500	2500	2500	2500	2500	2500
K	270	270	270	270	270	270
Ca	3100	3100	3100	3100	3100	3030
Ti	1.2	0.5	0.5	0.4	0.4	0.26
V	0.3	0.09	0.09	0.09	0.075	0.07
Cr	0.32	0.3	0.3	0.3	0.3	0.2
Mn	22	11	11	11	11	10
Fe	944	183	181	148	64	6.8
Co	0.15	0.085	0.085	0.085	0.085	0.06
Ni	0.7	0.7	0.7	0.63	0.62	0.47
Cu	1.2	1.2	1.2	1.2	1.1	0.74
Zn	5	5	5	5	5	4.2
Ga	0.009	0.005	0.005	0.0029	0.0028	0.001
Ge	0.006	0.006	0.006	0.006	0.005	0.005
As	0.32	0.32	0.32	0.25	0.22	0.18
Rb	0.53	0.53	0.53	0.53	0.53	0.53
Sr	17	17	17	17	16	15
Y	0.1	0.07	0.07	0.07	0.05	0.017
Zr	0.1	0.08	0.08	0.08	0.07	0.017
Mo	0.08	0.08	0.08	0.08	0.08	0.08
Cd	0.15	0.15	0.14	0.13	0.13	0.07
Cs	0.0013	0.0013	0.0011	0.0007	0.0007	0.0007
Ba	4.5	3.9	3.8	3.8	3.8	3
La	0.2	0.1	0.1	0.1	0.1	0.017
Ce	0.39	0.18	0.17	0.16	0.11	0.03
Pr	0.057	0.031	0.027	0.025	0.019	0.004
Nd	0.22	0.12	0.11	0.1	0.07	0.018
Sm	0.035	0.02	0.02	0.02	0.013	0.004
Eu	0.007	0.005	0.005	0.003	0.003	0.001
Gd	0.028	0.017	0.017	0.017	0.013	0.002
Tb	0.004	0.0025	0.0025	0.0018	0.0016	0.0002
Dy	0.02	0.014	0.013	0.013	0.009	0.003
Ho	0.0038	0.0028	0.0028	0.0028	0.0017	0.0008
Er	0.012	0.008	0.008	0.0076	0.0068	0.0014
Tm	0.0017	0.0011	0.0011	0.00095	0.0009	0.0001
Yb	0.01	0.007	0.007	0.0062	0.0057	0.0016
Lu	0.0013	0.0012	0.001	0.001	0.0006	0.0004
Hf	0.003	0.003	0.003	0.003	0.003	0.0004
W	0.005	0.005	0.005	0.005	0.005	0.005
Pb	0.1	0.08	0.08	0.08	0.025	nd
Th	0.018	0.018	0.018	0.018	0.008	0.003
U	0.6	0.5	0.5	0.5	0.04	0.013
DOC	10.92	10.82	10	9.92	9.71	7.6

ELECTRONIC ANNEX

ESM-3.1. Description of climate, topography, soil and vegetation of the regions.

3.1.1. North Karelia, NW Russia

3.1.1.1. Climate

The climate of the region is mild-cold, transitional between oceanic and continental, with a determinant influence of the Arctic and Northern Atlantics. Winter is long and soft, summer is short and cool. Average temperature in January is -13°C, and +15°C in July, but extremes can reach -45° to +35°C in winter and summer periods, respectively. The dominant wind direction is South-West in winter and North-East in summer. Average annual precipitation amount is between 450 and 550 mm/yr. Snow period lasts from October to April-May with the average thickness of snow cover 70 - 80 cm, but often over than 1 m. The territory is under the influence of the warm Gulf Stream, but microclimatic conditions differ dramatically because of the large cross-country. In summer in the deep and sheltered valleys it's much warmer than on the mountain tops, whereas in winter it's much colder in the valleys where the mountains cold air accumulates.

3.1.1.2. Topography

Tectonics and glaciation shaped the terrain of Karelia. Crustal snaps and step faults, reaching in two mutually perpendicular directions: the north-west to south-east and south-west to north-east have formed as a result of tectonic processes. Traces of glaciation occur in the glacial landforms that presented in moraine ridges extended from the north-west to south-east.

Much part of the region is a hilly plain with elevations of 200 m. Along the White Sea coast there is a wide zone of lowland Pribelomorskaya with elevations less then 100 m. In the western part, on the border with Finland, moraine ridge Maanselkya is located, it represents a watershed between the basins of the Baltic and White Seas.

Our study area is located in the most elevated part of Karelia, in the central part of Maanselkya. It is a landscape of tectonic denudation hills, plateaus and ridges with an average altitude of 300-400 meters with separate insulated massifs (Tunturi).

3.1.1.3. Hydrology

The region has a well-developed river network that flows via a system of glacial lakes. The water of small and medium-sized lakes warms up to 22-25 °C in summer. Water is soft, low mineralized, often with a brown hue because of feeding swamps.

The large number of wetlands is typical feature of North Karelia. The small marshes with area from 3-5 to 30-50 hectares are dominated. A kind of "hanging" (omrotrophic) bogs is formed on the steep slopes. By the nature of their feeding, Karelian rivers belong to the mixed type, fed by rainfall, bogs, groundwater and snowmelt. The rivers break up earlier than their conjugated lakes and some full of rapids reaches don't freeze at all. The average date of floods in North Karelia is April 25 - May 5. The rivers freeze in November - December. Natural fluctuations of water level do not exceed 1.5-2 m.

Rivers of Karelia are comparably short. Significant part of their length (up to 50%) may consist of the flowage lakes. There are « lake-river » systems, consisting of a chain of lakes connected by rapids channels. The accumulative systems are represented by a lake that collects the water of many rivers and serves as outlet of one larger river are also typical for Karelia. Another peculiar phenomenon is a bifurcation (splitting) of the water flow. The average gradient of rivers is about 1 m/km, and up to 3-5 m/km in the rapids channels. Rivers of Karelia are very young geologically, and their beds are composed of hard rocks. Because the rivers are, just started to make the longitudinal profile, their valleys are not wide floodplains, and they almost do not have high terraces.

Chemical composition of river waters in Karelia is determined by the chemical weathering of silicate parent rocks of the Baltic crystalline shield and quaternary deposits, and the presence of numerous peatlands. Typical values of total discharge of solids (TDS) for this region are 15-30 mg/l (Maksimova, 1967; Zakharova et al., 2007), and the concentration of river suspended matter is very low. The adjacent lakes between the rivers significantly decrease the size of actual feeding watershed of a given river.

3.1.1.4. Soil, vegetation

The soil cover of the region is very young and it is often absent on ledges of bedrock and steep slopes. Low temperature in combination with high humidity is responsible for the slow humification and mineralization of plant residues. Therefore, a lot of organic matter is accumulated in the form of peaty horizons, and on better drained sites - in the form of coarse humus. Predominant soils are illuvial-humic and illuvial-ferruginous-humic podzols. All types of podzols exhibit a highly acidic reaction and low base saturation of the upper layers.

Coniferous forests dominate the vegetation of the region. The main conifers are pine and spruce. The common deciduous trees are birch, aspen, alder. The sphagnum pine occurs on the plains, depressions and swamps. Sparse understory consists of mountain ash and juniper. It is dominated by blueberries and cranberries in the shrub layer, and green mosses in the lower layer. The rocks are usually covered with patches of black, gray, yellow, red, brown crustose lichens. Herbaceous plants are rare. The main mushrooms are aspen and boletus. There are poisonous plants in Karelia such as, hemlock, cowbane, mezereon.

Table ESM-3.2. The weather characteristics of the samplings periods by the data of meteostation 22217 KANDALAKSHA (25m - 67 09N - 32 21E), www.mundomanz.com

Precipitations, mm	*2007*	*2008*	*2009*	*2010*
june	42.3	99.0	68.4	72.8
july	102.8	69.7	79.7	37.6
august	38.8	99.3	105.5	65.0
year	602.2	631.8	562.2	506.4
Temperature, °C	*2007*	*2008*	*2009*	*2010*
june	11.1	11.2	10.6	10.4
july	14.4	13.7	13.5	16.3
august	14.0	10.7	13.4	11.9
year	1.7	1.2	0.9	0.1

Figure ESM-3.3. Field clean room.

Table ESM-3.4. Iron-normalized TE partition coefficients (K_{d1} and K_d) for the samples of Vostochniy stream basin and (K_d) for the samples of Palojoki river basin.

TE	OR-9		OR-6		OR-1		KAR-2	KAR-1	KAR-3
	K_{d1}	K_d	K_{d1}	K_d	K_{d1}	K_d	K_d	K_d	K_d
Na	0.04	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.36	0.46	0.01	0.01	0.01	0.02	0.03	0.00	0.00
Al	0.48	0.58	0.15	0.16	0.08	0.11	0.25	0.10	0.10
Si	0.01	0.02	0.00	0.00	0.00	0.01	0.00	0.00	0.00
K	0.06	0.07	0.01	0.01	0.02	0.03	0.00	0.00	0.00
Ca	0.56	0.73	0.02	0.03	0.02	0.03	0.08	0.00	0.00
Ti	1.63	1.41	0.12	0.13	0.14	0.15	1.15	0.08	0.04
V	0.28	0.33	0.01	0.01	0.03	0.03	0.17	0.02	0.01
Cr	0.54	0.51	0.11	0.11	0.04	0.05	0.17	0.02	0.02
Mn	0.41	0.53	0.02	0.03	0.04	0.06	0.08	0.01	0.00
Fe	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Co	0.57	0.70	0.14	0.15	0.25	0.38	0.15	0.01	0.02
Ni	0.72	0.71	0.07	0.07	0.03	0.04	0.18	0.00	0.02
Cu	0.43	0.57	0.06	0.07	0.02	0.03	0.16	0.01	0.02
Zn	0.19	2.60	0.01	0.01	nd	nd	0.00	0.00	0.01
Ga	0.87	0.85	0.67	0.74	0.23	0.34	0.60	0.06	0.15
Ge	0.41	0.45	0.03	0.03	0.06	0.07	0.12	0.23	0.01
As	0.24	0.23	0.02	0.02	0.02	0.02	0.15	0.11	0.03
Rb	0.06	0.08	0.00	0.00	0.01	0.02	0.00	0.00	0.00
Sr	0.69	0.59	0.02	0.03	0.02	0.03	0.15	0.01	0.01
Y	0.83	0.75	0.16	0.18	0.10	0.14	0.58	0.19	0.12
Zr	0.71	0.74	0.20	0.22	0.13	0.19	0.99	0.14	0.14
Mo	1.34	1.27	nd	nd	nd	nd	3.22	0.01	0.00
Cd	0.51	0.26	0.13	0.14	0.04	0.06	0.19	0.02	0.04
Cs	0.11	0.11	0.05	0.06	0.00	0.00	2.31	0.03	0.03
Ba	1.38	1.27	0.05	0.05	0.03	0.05	0.48	0.01	0.01
La	2.60	2.12	0.31	0.34	0.15	0.20	1.14	0.23	0.19
Ce	1.60	1.34	0.35	0.39	0.13	0.19	1.02	0.30	0.19
Pr	1.43	1.22	0.35	0.39	0.13	0.20	0.66	0.22	0.26
Nd	1.02	0.88	0.22	0.24	0.12	0.15	0.74	0.19	0.22
Sm	1.25	1.13	0.25	0.28	0.10	0.15	0.69	0.34	0.15
Eu	0.90	0.77	0.16	0.18	0.11	0.17	0.74	0.28	0.15
Gd	1.52	1.27	0.11	0.12	0.04	0.06	0.74	0.14	0.29
Tb	1.30	1.19	0.57	0.63	0.11	0.17	1.15	0.12	0.44
Dy	0.98	0.92	0.20	0.22	0.08	0.11	0.60	0.12	0.14
Ho	0.98	0.92	0.16	0.18	0.08	0.11	0.88	0.14	0.10
Er	0.80	0.75	0.16	0.15	0.08	0.11	0.49	0.19	0.18
Tm	0.76	0.71	0.22	0.24	0.10	0.14	0.87	0.22	0.39
Yb	0.54	0.46	0.16	0.18	0.07	0.10	0.12	0.46	0.13
Lu	0.54	0.54	0.27	0.30	0.06	0.08	0.80	0.28	0.08
Hf	0.27	0.28	0.05	0.06	0.09	0.14	0.96	0.05	0.25
W	nd	nd	nd	nd	nd	nd	0.33	0.00	0.00
Pb	4.96	4.33	nd	nd	nd	nd	9.40	nd	nd
Th	1.19	1.27	0.49	0.54	0.26	0.39	2.28	0.14	0.19
U	0.33	0.42	0.35	0.39	0.11	0.17	0.71	0.11	1.45

Chapter 4

Stable (Cu, Mg) and radiogenic (Sr, Nd) isotope fractionation in colloids of boreal organic-rich waters

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Stable (Cu, Mg) and radiogenic (Sr, Nd) isotope fractionation in colloids of boreal organic-rich waters

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Abstract

Variations of stable (Cu, Mg) and radiogenic (Sr, Nd) isotopic composition in filtrates and ultrafiltrates of various size fraction have been measured in waters of subarctic watersheds (NW Russia) and in temperate river and lake of South boreal zone. Large volume of samples were filtered in the field using cascade filtration and ultrafiltration employing progressively decreasing pore size (100, 20, 10, 5, 0.8, 0.4, 0.22, 0.1, 0.046, 0.0066 (100 kDa), 0.0031 (10 kDa), and 0.0014 µm (1 kDa)) followed by element isotopic analysis using Thermal Ionization Mass Spectrometers and a Neptune multicollectror ICP-MS. In boreal watershed underlined by archean and proterozoic rocks, the $^{87}Sr/^{86}Sr$ ratio decreases during ultrafiltration through 1-100 kDa and dialysis by 0.0001 - 0.0004 compared to usual 0.45 µm filtered water. Despite the dominance of colloids in Nd speciation in surface waters, the isotopic value of Nd (ε) in filtrates and ultrafiltrates remains constant within the uncertainty of measurements. This indicates the absence of atmospheric input of silicate dust for Nd but the

presence of marine aerosols for Sr and strongly suggest the small residence time of Sr in studied surface waters compared to the time of achieving the isotopic equilibrium between colloidal (1 kDa - 0.22 µm) and truly dissolved (< 1 kDa) pools. The stable isotope composition of Cu in streams remains constant within ±0.1 ‰ during filtration through 100 µm to 1 kDa despite the fact that 40-60% of Cu was in colloidal (1 kDa - 0.22 µm) fraction. This suggests either the homogeneity of Cu isotopic composition with colloidal and truly dissolved pool or the very fast isotopic exchange rate of aqueous Cu between fulvic complexes of different molecular weight compared to the rate of Cu renewal in the river water. Finally, stable isotope composition of Mg bound in colloidal fraction to 70 % for soils solution and bog surface water demonstrate very slight enrichment of 1 kDa fraction in heavy isotope by only 0.03 and 0.08 ‰ which is comparable with the analytical uncertainty.

Despite dramatically different structure of metal - dissolved organic matter (DOM) complexes for Cu^{2+} and Mg^{2+}, results of the present work witness high homogeneity of stable isotope composition among filtered (0.22 µm) and ultrafiltered (1 kDa) fractions, presumably due to high rate of isotopic exchange between colloidal and ionic form of metals. Contrasting isotopic composition of Sr in ultrafiltered (1 kDa) compared to conventionally filtered (0.22 µm) fractions is a new feature allowing to reconstruct the degree of atmospheric input in chemical composition of surface waters which also provides new important constraints on the isotopic composition of Sr carried by small organic-rich boreal rivers to the Arctic ocean.

4.1. Introduction

Traditionally, radiogenic isotopes have been used as a very powerful tool for unraveling the source of material in rivers helping to characterize the reservoirs of elements at the Earth surface (Négrel et al., 1993; Cameron et al., 1995; Viers et al., 2000; Derry et al., 2006). In particular, measuring Sr isotopes in rivers allowed rigorously tracing the contribution of carbonate versus silicate rock in the cationic river water load (Palmer and Edmond, 1992; Gaillardet et al., 1999) where as Nd was reported to be particularly useful in revealing the relative contribution of desert dust in large river chemical composition (Viers and Wasserburg, 2004) or in the role of different water masses in the oceanic water mass balance (Porcelli et al., 2009). A powerful method for distinguishing different sources of dissolved material in the river water is measuring radiogenic isotopes in both conventionally dissolved (< 0.22 µm) and ultrafiltered, colloid-free fraction (Viers and Wasserburg, 2004; Bagard et al., 2011). Up to present time, however, this method has been only occasionally used on monolithological terrain and it certainly requires a rigorous calibration for different ultrafiltered fractions. It can be assumed that, provided that the source of material is unique and no fractionation of radiogenic isotopes is possible due to physico-chemical processes, all filtered and ultrafiltered fractions of the surface waters should have the same isotopic ratio of Sr or Nd, regardless of the degree of metal association with colloids. However, if there are several sources of dissolved material in the water, and the income flux (groundwater, atmospheric precipitation) is higher than the rate of isotopic exchange in the system, i.e., the residence time of Sr or Nd in the water reservoir is small, then the different colloidal and ultrafiltered fractions will exhibit different isotopic ratio. Therefore, the first objective of this study was to test the hypothesis of Sr and Nd isotopic equilibrium among different colloidal fractions and to trace the different sources of dissolved load (rocks, marine aerosols, dust) in waters of boreal catchments.

The second part of this work is devoted to the fractionation of stable isotopes of major (Mg) and trace (Cu) elements among different fractions of boreal colloids. Mg isotopes were reported to be particular useful for deciphering fractionation between plants and soils/solutions (Bolou-Bi et al., 2010), silicate (De Villiers et al., 2005; Pogge von Strandmann et al., 2008), and carbonate (Brenot et al., 2008; Jacobson et al., 2010) rock weathering including paleoenvironments (Pokrovsky et al., 2011) and during biotic and abiotic carbonate mineral precipitation (Shirokova et al., 2011; Mavromatis et al., 2012). In all these studies, Mg in aqueous solution is considered to be present as ionic or inorganic complexes of homogeneous isotopic composition. However, in various natural settings Mg may form complexes with organic matter whose isotope fractionation factor is still very poorly known, except for chlorophyll (Black et al., 2006). The organic-rich boreal waters having significant proportion of Mg in colloidal (1 kDa-0.22 µm) form offer an unique opportunity to *i*) test the hypothesis of two pools of dissolved Mg (colloidal and ionic) and *ii*) check the existence of isotopic equilibrium between colloidal and truly dissolved fractions.

In contrast to magnesium, copper is known to be present in the organic species both allochthonous soil-derived colloidal (1 kDa - 0.22 µm) or heavy molecular weight (HMW) and autochthonous, phytoplankton-derived Low Molecular Weight (LMW, < 1 kDa) complexes (McKnight and Morel, 1979, 1980; Ito and Butler, 2005) having presumably different stability constants (Hoffmann et al., 2007). Different stability constants for Cu-organic ligand complexes in LMW and HMW fractions have been also reported in soil solutions (Bravin et al., 2012) and in DOM originated from chicken manure (Wang et al., 2010). The isotopic composition of copper is fairly well studied in river waters (Vance et al., 2008), soils (Bigalke et al., 2010 a, b; 2011) and plants (Weinstein et al., 2011). Provided that *i*) the isotopic equilibrium is attained among different colloidal pools and *ii*) no reduction of Cu(II) $\rightarrow$ Cu(I) occurs in natural colloids, the Cu^{2+} complexed with strong organic chelates will be enriched in heavy isotope relative to uncomplexed dissolved Cu^{2+} similar to that of Fe^{3+} (Dideriksen et al., 2008) and Zn^{2+} (Gélabert et al., 2006; Jouvin et al., 2009). The latter finding is in accord with the quantum mechanical calculations which predict that the heavier isotope should concentrate in the species in which it is most strongly bounded (Criss, 1999), as also proved in the case of other metal complexation with organic matter. The difficulties in applying these principles to natural waters lay in distinguishing between different types of ligands and colloids. Ultrafiltration through progressively decreasing pore size offers an elegant way of quantifying copper isotopic composition in high and low molecular weight colloids and organic ligands which will be applied, for the first time, to boreal stream and bog water.

To sum up, the main research questions we attempted to answer in this study are: *i*) to which degree the association of trace elements with colloidal fractions control the variation of their isotopic composition during filtration and ultrafiltration from 100 µm to 1 kDa, ii) how the isotopic ratio of radiogenic and stable isotopes associated with organic matter depends on the type of surface waters (bog and soil solutions, lake and river). It is anticipated that, thanks to the selection of several contrasting elements in terms of speciation in solution (ionic Sr^{2+} and colloidal Nd for radiogenic isotopes and covalent-bound Cu^{2+} and electrostatically bound Mg^{2+} for stable isotopes) it will be possible to provide new constraints on preservation of isotopic signature during radiogenic elements transfer in rivers and to reveal specific physico-chemical processes responsible for stable isotopes fractionation during colloids formation in surface waters.

4.2. Study sites

The surface waters of the north of boreal region (North Karelia, subarctic zone) and the south of the boreal region (Central Russia, temperate zone) were investigated in this study (Fig. 4.1). Both sites are pristine in terms of local industrial or agricultural pollution and receive only long-range atmospheric impact of metals. In the subarctic zone, we studied the basins of the Vostochniy stream and the Palojoki river (Fig. 4.1 A), comprising several samples of river and stream, the feeding bog or lake and the soil solution (Vostochniy stream watershed, Fig. 4.1 C and Fig. ESM-4.1). In the temperate zone, the Senga river and the Ignatkovo lake were sampled (Fig. 4.1 D, Fig. ESM-4.2). Both sites are similar in the sense that the chemical composition of rivers is controlled by high amount of bog and peat soils present within the watershed. As a result, the waters are rich in dissolved organic carbon (DOC), from 10 to 50 mg/L, originated from organic-rich bog waters and peat soil solutions, the latter having from 60 to 140 mg/L of DOC. At the same time, the sites are different in latitude position (1500 km from north to south), climate and vegetation primary productivity.

The subarctic river Palojoki has a watershed of 32 km² and drains the intrusive rocky massif Kivakka. It was sampled in the mouth zone 10 m above the terminal Pyaozero lake (KAR-3) and in the middle part of the flow (KAR-1, 800 m above the point KAR-3). In the upper reaches of this river, it is fed by a minero-trophic bog (KAR-2). The bedrock composition of the watershed is represented by micro-pegmatic granites, granosyenites, syenites, syenit-diorites of the low-Proterozoic, biotite granito-gneisses and biotite, biotite-amphibolite and amphibolite gneisses and amphibolites of the low-Archean and glacial deposits of Quarternary (Fig. ESM-4.1). The stream Vostochniy originates from the system of interconnected humic lakes (such as OR-6) located within the bog zone and empties into the lake Tsipringa. Its length is about 1 km and relative altitude of 50 m, the catchment area is of 0.95 km^2. The bedrock of the catchment is represented by low-Proterozoic amphibolitic gabbroids (Fig. ESM-4.1). The Vostochniy stream was sampled in the mouth reach, 1 m above the mixing with Tsipringa lake (OR-1). Soil solution of the peat bog zone of this watershed was collected from the depth of 5-10 cm in a piezometer (OR-9). Another example of organic-rich river feeding fluid is a bog zone adjacent to the lake Tsipringa (ZPBL, Fig. 4.1 B). This bog of 1.19 km² area has a relative altitude of 30 m and it is underlained by early-Archean biotite granito-gneisses with biotite, biotite-amphibolite and amphibolite gneisses and amphibolites (Fig. ESM-4.1).

The temperate river Senga is the right tributary of the Klyazma river, a tributary of Oka, one of the largest right tributary of the Volga river. The length of Senga river is about 32 km, and the catchment area is of 163 km^2. The bedrock of the catchment is alluvial flat deposits of the Holocene represented by granite moraine deposits (Fig. ESM-4.2). The lake Ignatkovo is a humic lake of 0.3 km^2 located within the bog area covered by peat deposits of the Holocene (Fig. ESM-4.2). Further details of climate, topography, soil and vegetation of the two regions are described in the Electronic Annex (ESM-4.3).

4.3. Materials and methods

4.3.1. Sampling and filtration

Water samples of the subarctic zone (Vostochniy stream, Palojoki river, bog of Tsipringa lake basin of the North boreal zone, Karelia, were sampled in July 2008 and 2009 and waters of the temperate zone (Senga river and Ignatkovo lake of South boreal zone (Meschera, Vladimir region, Central Russia)) were sampled in November 2008.

Figure 4.1 presents a simplified scheme of the sites along with sampling points, whereas the list of sampled waters and their bedrock compositions are presented in Table 4.1. Large volumes (20-30 L) were collected in pre-cleaned light-protected PVC bottles for size fractionation procedure of 100, 20, 10, 5, 0.8, 0.4, 0.22, 0.1, 0.046, 0.0066 (100 kDa), 0.0031 (10 kDa), and 0.0014 µm (1 kDa) using cascade filtration and ultrafiltration conducted directly in the field conditions using specially prepared polyethylene-covered clean space (Fig. ESM-4.4). The main characteristics of the filtration are listed in Table ESM-4.5 and the scheme of the size fractionation procedure is given in Fig. 4.2.

Filtration through 100 µm or pre-filtration was performed using nylon net "Fisherbrand". Cascade frontal filtration with the decreasing pore size from 20 to 0.1 µm was performed using a 250-ml vacuum polycarbonate cell (Nalgene) and nylon membranes (Osmonics). Frontal ultrafiltration (UF) of the series 100 - 10 - 1 kDa was performed using a 400-ml polycarbonate cell (Amicon 8400) equipped with a suspended magnet stirring bar located beneath the filter to prevent clogging during filtration. Vacuum filtration was performed using a portative hand-pump, and the ultrafiltration was performed using a portative automobile leg-pump. The large volumes of the samples were passed through the Lavsan (polyethylene tereph-thalate, PETP) filters of 0.4 µm pore size and 500 cm² surface area; in this case, the filtration occurred via gravitational flow (0.3-0.5 kPa).

Between each sample, the filtration system was cleaned by flushing EasyPure water, then 3% ultrapure HNO_3, and finally, EasyPure water. Each filter was soaked in EasyPure water during at least 1 day before the experiment and used only once. During filtration, the first 50 ml of sample solution were discarded, thus allowing saturation of the filter surface prior to recovery of the filtrate. Discussions of this technique and precautions against possible filtration artifacts are given in Viers et al. (1997), Dupré et al. (1999), Pokrovsky and Schott (2002), Pokrovsky et al. (2005, 2006, 2010) and Alekhin et al. (2010).

Dialysis experiments were performed using 20-50 ml precleaned dialysis bags placed directly in the river or bog water (in-situ dialysis). The duration of this dialysis procedure was between 72 and 120 h. For dialysis experiments, EDTA-cleaned trace-metal pure SpectraPor $7^{®}$ dialysis membranes made of regenerated cellulose and having pore sizes of 1 kDa were thoroughly washed in EasyPure water, filled with ultrapure Milli-Q deionized water and then placed into natural water. The efficiency of the dialysis procedure was evaluated by comparing major anion concentrations. These concentrations were always identical to within ± 10%, suggesting an equilibrium distribution of dissolved components. Further details of dialyses experiments procedure are described in Vasyukova et al. (2010) and Pokrovsky et al. (2010, 2012).

4.3.2. Chemical analysis

Water temperature, pH, and conductivity were measured in the field. The pH was measured using a combined glass electrode calibrated against NIST buffer solutions. Major anion concentrations (Cl^-, SO_4^{2-}, NO_3^-) were measured by ion chromatography (Dionex 2000i) with an uncertainty of 2%. Alkalinity was measured in-situ by acid titration with HCl using phenolphthalein as indicator followed by Gran treatment method. The dissolved organic carbon (DOC) was determined using Shimadzu SCN Analyzer (Toulouse) and Elementar TOC analyzer (Moscow) with an uncertainty of 3% and a detection limit of 0.1 mg/L.

Major and trace elements (TE) including Fe were measured without preconcentration by ICP-MS (7500ce, Agilent Technologies). Indium and rhenium were used as internal standards. The international geostandard SLRS-4 (Riverine Water Reference Material for Trace Metals certified by the National Research Council of Canada) was used to check the validity and reproducibility of each analysis. A good agreement between our replicated measurements of SLRS-4 and the certified values for Sr, Nd, Mg and Cu was obtained (relative difference < 5%).

4.3.3. Isotope analysis

Prior the isotopic separation using chromatographic column, filtered acidified water samples were evaporated in wide mouth Teflon containers (300 mL volume) placed on teflon-coated hotplate at 80°C located within the isolated polycarbonate box (internal air filtered class A 100). Blank Milli-Q water (apparatus Milli-Q Element Merck Millipore) was routinely evaporated using the same procedure. Precipitates formed at the bottom of containers were digested using the mixture of HNO_3, H_2O_2 and HF following standard procedure of organic-rich solid samples digestion (Viers et al., 2007). The digestion products were evaporated and dissolved in HCl or HNO_3 ultrapure bidistilled acids before introduction to the column. All sample preparation manipulations were performed in clean room class A10000 and the chromatographic separation was conducted in the laminar hood box class A100 located in the clean room.

4.3.3.1. Strontium

Strontium isotopic ratios were measured by thermal ionization mass spectrometry (Finnigan Mat 261) preceded by chemical separation and chemical extraction of Sr by ion exchange chromatography using chromatographic material Sr.Spec and HF, HNO_3 and HCl acids in a clean room. Data correction was based on the systematic analysis of the NBS 987 standard. The average value of $^{87}Sr/^{86}Sr$ for NBS 987 standard (0.710248) was found to be 0.710250 ± 0.000010 (n = 10).

4.3.3.2. Neodymium

Nd isotopic ratios were carried out by thermal ionization mass spectrometry (Isoprobe-T, GV Instrument) at the Laboratory of analytical development for isotopic and elementary analysis and by multicollector inductively coupled plasma mass spectrometry (Neptune Plus, Thermo Fisher Scientific) at the LSCE (Laboratoire des Sciences du Climat et de l’Environnement) laboratory.

Nd was isolated from the bulk sample using two different methods. In the first one (for the samples analysed by TIMS) the protocol followed the method already described by Pin et al. (1994) and Pin (1997). The second one isolated the rare earth element using a Tru-Spec resin (Quidelleur et al., 2009) followed by a high performance liquid chromatography using a Luna SCX (Strong Cation Exchange) analytical column with 2-hydroxy-2-methylbutyric acid (HMBA, Sigma–Aldrich) complexing agent (Goutelard et al., 2009, Bourgeois et al., 2011).

For TIMS measurements, Nd was acquired in multistatic mode and using the total evaporation method (Dubois et al., 1992). This method was adapted to allow measurements of low quantity of Nd, between 1 and 5ng (Mialle et al., 2012). The average value for $^{143}Nd/^{144}Nd$ for the JNd-1 was found to be 0.51204 ± 0.00089 (n=20).

For MC-ICP-MS measurements, the instrument was equipped with an Apex system to increase the sensibility at a value of 420V/ppm. Nd sample were analysed at concentration around 2 $ng\cdot g^{-1}$. Data were corrected from mass bias using JNdi-1 and standard bracketing method. Data were also corrected from an residual Sm contamination using the ratio $^{147}Sm/^{149}Sm$ of 1.08680 ± 0.00016 (Isnard, 2005). The parameter $\varepsilon_{Nd}(0)$ was determined using the value $(^{143}Nd/^{144}Nd)_{CHUR}$ of 0.512638.

4.3.3.3. Copper

Cu isotopic composition was measured on the Neptune MC-ICP-MS (ThermoFinnigan) at GET (Toulouse). Cu has two stable isotopes of mass 63 and 65, which have average abundances of 69.17% and 30.83%, respectively. Cu was isolated from the bulk sample using the purification procedure of Marechal et al. (1999) on the AGMP-1 anion exchange resin (Bio-Rad, USA). Poly-Prep chromatography columns (0.8 * 4 cm) (Bio-Rad, USA) were used for the elemental separation. After the resin was cleaned (1.6 mL) with MilliQ deionized water (18.2 X) and 0.5 N HNO_3, the conditioning of the resin (6 mL) and the loading of the sample (300 ng of Cu in 1 mL) were performed with 7 N HCl. The hydrogen peroxide was added into the acid solution at a 0.001% concentration to avoid the presence of Cu in a different redox state. The matrix was eluted with 10 mL of 7 N HCl and Cu was collected in the next fraction (20 mL of 7 N HCl). Because isotopic fractionation may occur during the elemental separation on the ion-exchange resin (Marèchal and Albarède, 2002), we analyzed only the samples for which the separation procedure produced a 100% yield, taking into account the analytical uncertainties (Pokrovsky et al., 2008). Instrumental mass fractionation effects were corrected using sample-standard bracketing method or internal Zn standard and an exponential law; all data are presented in delta notation with respect to NIST 976 international reference material (Marechal et al. 1999):

$$\delta^{65}Cu\ (‰) = \left(\frac{(^{65}Cu/^{63}Cu)_{sample}}{(^{65}Cu/^{63}Cu)_{JMC}} - 1\right) *1000$$

4.3.3.4. Magnesium

Magnesium separation from matrix elements (mainly Ca) was performed using the protocol defined by Teng et al. (2007), in which ~15 µg of Mg were evaporated to dryness and re-dissolved in 2 ml 1 N HNO3 solution. Later, samples were loaded onto Bio-Rad poly prop 10 ml columns containing AG50W-X12 resin. Mg isotopes were measured with a Thermo-Finnigan ‘Neptune’ Multi Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP- MS) at GET (Toulouse, France). All solutions were prepared in 0.32 M HNO_3 and were introduced into the Ar Plasma using a standard spray chamber. Instrumental mass fractionation effects were corrected using sample-standard bracketing, and all data are presented in delta notation with respect to DSM3 international reference material (Galy et al., 2001):

$$\delta^{x}\mathrm{Mg}\ (‰) = \left(\frac{({}^{x}Mg/{}^{24}Mg)_{sample}}{({}^{x}Mg/{}^{24}Mg)_{DSM3}} - 1\right) * 1000$$

The reproducibility of δ^{26}Mg analyses was typically <0.07 ‰ as confirmed by replicate analyses of three international Mg reference standards (DSM-3, CAM-1 and OUMg).

4.4. Results and discussion

4.4.1. Radiogenic Strontium

4.4.1.1. Raio ^{87}Sr/^{86}Sr along the watershed profile within the different lithological and climatic settings

All obtained results on Sr isotopes (Table 4.2) demonstrate that the most radiogenic Sr is found in subarctic stream Vostochniy (OR-1) and river Palojoki (samples KAR series) draining Archean and Low Proterozoic granites and basic intrusives. The range of ^{87}Sr/^{86}Sr values (0.718-0.735) measured in the surface waters are similar to those reported for the soils of Kivakka intrusion (0.720-0.725) and local granito-gneisses (Revyakovo et al., 2007). The temperate river and lake of the Central part of Russia (samples Seng series) underlained by young Phanerozoic sedimentary rocks and quaternary deposits exhibit significantly lower values of ^{87}Sr/^{86}Sr reflecting both the effect of younger rocks and the importance of atmospheric precipitation, pronounced at the scale of a large watershed (^{87}Sr/^{86}Sr$_{snow}$ =0.708) similar to other regions (Douglas et al., 1995; Probst et al., 2000; Pierson-Wickmann et al., 2009; De Souza et al., 2010).

Along the watershed profile of small subarctic stream Vostochniy, the isotopic ratio of radiogenic Sr in the 0.22 or 0.40 µm filtrates systematically increases from soil solution (OR-9) to feeding lake (OR-6) and further to the stream mouth (OR-1) with values of 0.724, 0.730 and 0.735, respectively. Given the similarity of the silicate mineral substrate at such a small distances within the watershed, these differences are significant and they certainly indicate the presence of different sources of Sr in the surface waters. It could reflect the input of highly radiogenic Sr present in archean rock-hosted groundwaters to the river channel at OR-1 and influence of atmospheric precipitation via vegetation uptake and release in bog soil profile (OR-9) and peat bog-hosted shallow lake (OR-6). The increase of the Sr isotopic ratio from OR-6 and OR-9 to OR-1 may reflect an increase of the contribution of high radiogenic Archean-hosted groundwaters to the surface waters. It is unlikely this trend to be related to the effect of atmospheric deposits on bog area because these deposits should have an isotopic ratio lower than that of the geological background (Probst et al., 2000; De Souza et al., 2010). An alternative hypothesis would be the preferential dissolution of radiogenic soil minerals as it is known that significant quantities of of radiogenic Sr may be leached from K-feldspar during weathering of granitoids (Bullen et al., 1997). Similarly, for the larger subarctic river Palojoki the $^{87}Sr/^{86}Sr$ value of feeding bog waters is 0.7185 and it increases to 0.7218 for the river mouth (see Table 4.2). These observations corroborates the previous data of Probst et al. (2000) who reported the values of $^{87}Sr/^{86}Sr$ equal to 0.721 and 0.724 for soil solution and stream waters, respectively.

The temperate Senga River exhibits the same values of $^{87}Sr/^{86}Sr$ at the different sampling sites (Seng-1 and Seng-2) whereas the adjacent lake Ignatkovo (Ign) appears to be significantly more radiogenic (0.709 and 0.710, respectively). A possible explanation of this difference of isotopic signature between the lake ad the adjacent river could be the discharge of deep groundwaters at the lake's bottom; these groundwaters should be more radiogenic than surface waters because of their interaction with radiogenic old rocks constituting the geological substratum. By contrast, the river is fed essentially by atmospheric deposits during sampling period and, consequently, exhibit a Sr isotope ratio close to that of the snow. Note that such a difference between river and lake is not observed in smaller watershed of Vostochniy stream of the subarctic zone (OR-1 and OR-6 samples) because of shallower depth and smaller size of the lake that feds the outlet stream. This lake is located within the raised bog landscape and as such receives minimal input of deep groundwaters interacting with old intrusive rocks.

4.4.1.2. Ratio $^{87}Sr/^{86}Sr$ in the filtrates and ultrafiltrates

Upon filtration and ultrafiltration of all rivers, streams and subarctic bog lake, there is a measurable and significant decrease of $^{87}Sr/^{86}Sr$ ratio, ranging from $3.4 \cdot 10^{-5}$ to $2 \cdot 10^{-4}$ between the largest (10-100 µm) and the smallest fraction (1 kDa). The main change in Sr isotopic composition occurs between the size fractions where the most significant change in Sr concentration occurs (0.4 µm - 100 kDa and 1 - 10(100) kDa). Plotted in Fig. 4.3 is the difference in $^{87}Sr/^{86}Sr$ value between low molecular weight or LMW fraction (1 or 10 kDa) and high molecular weight or HMW colloidal fraction (10 kDa or 100 kDa) as a function of the percentage of colloidal Sr concentrated in these fractions. It can be seen that the largest shift towards less radiogenic Sr occurs in samples exhibiting the smallest fraction of colloidal Sr. Moreover, with the increase of the degree of Sr association with colloids the difference in isotopic ratio vanishes (Fig. 4.4 A-E). Indeed, soil solution of the Vostochniy stream (OR-9) exhibits the minimal variations of $^{87}Sr/^{86}Sr$ along the filtration and ultrafiltration series (see Table 4.2, Fig. 4.4 F).

Three possible reasons can be responsible for systematic decrease of $^{87}Sr/^{86}Sr$ value in cascade filtration and ultrafiltration series of subarctic rivers (Fig. 4.4 C) and streams (Fig. 4.4 A, B), all linked to the hypothesis of various sources at the conditions of lack of isotopic equilibrium in aqueous phase: (*i)* the presence of silicate river suspended matter from young quaternary deposits, *ii)* the influence of atmospheric dust deposits, and *iii)* the influence of marine aerosols. The first hypothesis involves the presence of silicate river suspended matter originating from young quaternary deposits. In this case the $^{87}Sr/^{86}Sr$ would increase from large to small fraction, the latest fraction reflecting the truly dissolved Sr originated from groundwater - base rocks interaction. This hypothesis would be consistent with the data of Douglas et al. (1995) who reported the increase of $^{87}Sr/^{86}Sr$ value in suspended particulate matter of the Murray-Darling River from large fraction to smaller fraction. However, this explanation does not stand because of the lack of both suspended (> 0.22 µm) and colloidal (< 0.22 µm) silicate particles as the concentration of total dissolved silica measured by ICP-MS in different size fractions remains constant within ± 10-20% (Pokrovsky and Schott, 2002; Vasyukova et al., 2010; Ilina, 2012). The second hypothesis also requires non-negligible amount of atmospheric silicate dust younger than AR-PR host rocks of watershed which is still incompatible with constant Si concentration in all fractions and the remoteness of the study site from the desert provinces. It is also unsupported by high stability of Nd isotope ratios (see next section), a criteria of the effect of desert aeolian deposit (Viers and Wasserburg, 2004; Grousset and Biscaye, 2005). By contrast, the hypothesis of marine aerosols deposition allows a first order explanation of the observed change in Sr isotopic ratio along the ultrafiltration series and the difference of this ratio between rivers and soils solutions. Indeed, the deposition of marine aerosols from the adjacent Barents Sea, White Sea and Baltic Sea would shift the Sr ratio towards less radiogenic values thus decreasing the signature of AR-PR intrusive rocks. If the residence time of water in small spring and humic lakes is short then the isotopic equilibrium could not be attained and one would observe more radiogenic HMW colloids and subcolloidal material and less radiogenic "truly dissolved" (< 1 kDa) fraction. This is what we observe in the present study with a difference much less pronounced for soil solutions (OR-9) exhibiting the minimal difference in Sr isotopic ratio between different fractions (see Fig. 4.4 F and Table 4.2). Moreover, the higher the proportion of uncomplexed Sr the higher the shift towards the isotopic disequilibrium or the more pronounced the effect of low-radiogenic marine aerosols-borne Sr. Therefore, high concentration of colloidal Sr such as that in interstitial soil solution and sufficiently long residence time of fluids in the peatbog allows the achievement of minimal difference in $^{87}Sr/^{86}Sr$ in a series of ultrafiltrates. In constrast, relatively large temperate lake Ignatkovo (sample Ign) exhibits an increase of $^{87}Sr/^{86}Sr$ in the LMW ultrafiltrates (Fig. 4.4 D). In accord with what is stated in previous section, the ultrafiltered (ionic) fraction of waters of this temperate lake may have a signature of older rocks compared to the majority of "surface" Sr originated from quaternary deposits and marine aerosols. The discharge of deep groundwaters at the lake's bottom originated from water - Cretaceous rock (aleurites and sands) interaction at some depth may well provide the uncomplexed less radiogenic fraction detectable by ultrafiltration.

Interestingly that, in this regard, the difference between ultrafiltered (< 1 kDa) and conventionally filtered (< 0.22 µm) fractions assessed in this study is analogous to the comparison of Sr isotopic ratio of less radiogenic soil exchangeable Sr to the more radiogenic bulk Sr in soils (i.e., Poszwa et al., 2004). Note that the variation of Sr isotopic ratio among filtrates and ultrafiltrates of boreal European zone is different from that recently reported in permafrost-bearing basaltic watershed of Central Siberia (Bagard et al., 2011). In the latter study, the ultrafiltered (< 10 kDa) fraction exhibited c.a. 0.0002 units higher $^{87}Sr/^{86}Sr$ compared to < 0.22 µm fraction. For large Siberian rivers exhibiting significant discharge during the spring melt, the lower value in < 0.22 µm fraction may reflect the influence of colloids and plant litter lessivates whereas the higher value in LMW fraction corresponds to the influence of deep underground waters (Bagard et al., 2011). In this regard, short residence time of Sr in the system during the freshet does not allow the achievement of isotopic equilibrium between HMW organic (colloidal) phase and LMW ionic Sr^{2+} forms. Thus the fundamental mechanisms responsible for such a difference are the same in boreal subarctic permafrost –free settings and sites with under continuous permafrost of Central Siberia.

4.4.2. Nd isotopes

The isotopic composition of Nd remains constant, within the uncertainty of analyses in filtrates and ultrafiltrates of the subarctic Vostochniy stream (OR-1) and the Palojoki river (KAR-1) as illustrated in Fig. 4.5. At the same time, the majority of Nd is concentrated in colloidal form (70 to 90 %). This last result is in agreement with that of Andersson et al. (2001) for the Kalix River. According to these authors, the Nd in the Kalix River is mainly transported in a colloidal phase, dominated by organic C and Fe, with less than 5% of the Nd being present in the <3 kD fraction "truly dissolved" fraction. In accord with our data, the temporal variations in the $\xi_{Nd}(0)$ in filtered Kalix River water are small (<2.3 ξ-units) showing no obvious relationship with the observed large variation in C_{Nd} (Anderson et al., 2001). The values $\xi_{Nd}(0)$ in the Kalix River are significantly lower than those in the unweathered till and average bedrock (from -27 to -25 and -22 units, respectively) and show a closer resemblance with the $\xi_{Nd}(0)$ found in humic and plant material (from -27 to -24 units). The values measured in the Kalix River catchment are higher than those measured in the Karelian streams in this work ($\xi_{Nd}(0)$ = -31 to -40, Table 4.3). Such low values of this study match those reported in waters draining the Precambrian shields (-26 in the Baffin Bay, Stordal and Wasserburg, 1986) being much lower compared to the major arctic rivers (from -5 to -14, Guo et al., 2004; Zimmerman et al., 2009; Porcelli et al., 2009). The temperate Senga river, draining younger silicate and carbonate rocks exhibit significantly smaller value of $\xi_{Nd}(0)$, 13±2, and also does not show any pronounced trend in Nd isotopic composition as a function of the pore size (Fig. 4.5 C).

At the same time, isotopic systematics of Nd in fluids of boreal zone is different from that in tropical regions. Viers and Wasserburg (2004) reported the value $\xi_{Nd}(0)$ different by 5 units for 0.22 µm and 5 kDa filtrates of Mengong river, (-18.73 and -13.30 respectively). These authors explained the observed difference by the presence of another source of more radiogenic Nd in ultrafiltrable form, presumably originated from the Sahara dust (carbonates dissolution). This non homogeneous isotopic composition was explained by the fact that exchange rate with colloidal Nd originated from the bedrock and saprolite weathering was too slow compared to the rate of water exchange in the river watershed. The most likely cause for this difference between Scandinavian and African surface waters may be the proximity of the Sahara desert supplying significant amount of dust soluble material in the latter setting. In contrast, the effect of marine aerosols, well pronounced for Sr (see previous section) is not visible for Nd due to relatively high concentration of colloidal Nd in organic–rich waters compared to low Nd concentration in the seawater and marine aerosols.

4.4.3. Copper isotopes

The value of δ^{65}Cu in 0.40 µm filtrates for the Palojoki River (+0.46 ± 0.05 ‰) coincides, within the uncertainty, with that of the Kalix River, Ottawa River, Tocantins and Nile. These values are higher than those reported for the Missouri River (from -0.04 to +0.3 ‰) but lower than those of the Amazon River (from +0.64 to +0.7 ‰), the Brahmaputra River (+0.64 ‰), the Chang Jang River (from +1.18 to +1.55 ‰) and the Volga River (+0.65 ‰) (Vance et al., 2008). There is no systematic and significant difference in δ^{65}Cu among two sampling points of the Palojoki River and the feeding bog.

In the two sampling points of the Palojoki River, the concentration of copper remains essentially constant in a series of filtrates and ultrafiltrates (from 100 µm to 10 kDa) and only the smallest (< 1 kDa) dialysate fraction demonstrate significant, (c.a., 65-45 %) decrease of Cu concentration relative to the previous filtrates. Therefore, it was important to assess the possibility of isotopic fractionation between different fractions. However, within the uncertainty of ±0.05 ‰ we did not detect any difference in isotopic composition of copper among different filtrates and ultrafiltrates (Table 4.4, Fig. 4.6).

The possible reason of constant Cu isotopic composition in each studied ultrafiltration series may be the presence of a single source of this metal (soils and vegetation) and the weak fractionation between HMW organo-ferric colloids and "truly" dissolved LMW organic ligands (< 1 kDa). Since the concentration of dissolved copper in studied waters are rather pristine, on the order of 1 µg/L, which is similar to those in large boreal rivers (0.4-0.6 µg/L, Guay et al., 2010), the atmospheric deposition from Cu-Zn smelters of the Kola peninsula is unlikely. Therefore the weak fractionation of copper between > 1 kDa and < 1 kDa fractions may stem from i) the similarity of the nature of Cu-fulvic complexes of different molecular size (cf., Vasyukova et al., 2012) and ii) the absence of specific Cu-binding LMW ligands originated from phytoplankton exometabolites (e.g., Hoffmann et al., 2007). It is known that the separation through 1-kDa membrane is used to assess the proportion of colloidal (i. e. >1 kDa) forms compared to total dissolved content of trace metals (Buffle and van Leeuwen, 1992; Marsac et al., 2010). However, given that the fulvic acids are just a few nm in size (e.g., 1.5-2.5 nm, Lead et al., 2000), significant part of soil-derived organic matter can be found in the 1-kDa dialysate. In all our samples we checked by HPLC analysis that the concentration of low molecular weight organic acids (formic, acetic acids etc.) was negligible compared to total DOC concentration. As such, the most likely cause of similarity of Cu isotopic composition among all filtrates and ultrafiltrates is the similarity of LMW and HMW Cu-fulvic complexes controlling the speciation of these elements in boreal surface waters.

Noteworthy that the isotopic results obtained in this study strongly suggest the presence of Cu exclusively in Cu(II) form, with negligible amount of reduced Cu(I) or Cu-S groups in the organic matter. In the latter cases, the enrichment of the reduction product or the sulphydryl moieties of the fulvic acid would produced a 1 to 4 ‰ impoverishment in heavy isotope as it is known for soil bacteria (Pokrovsky et al., 2008; Navarrete et al., 2011), and S-bearing proteins (Zhu et al., 2002). The lack of Cu photoreduction contrasts that to Fe^{3+} which may be subjected to photoreduction producing heavy-isotope enriched LMW organic complexes (Ilina et al., 2012, submitted).

4.4.4. Mg isotopes

The negative values of δ^{26}Mg measured in this study (c.a. -0.6 ‰, Table 4.5) are typical for soils and soil solutions (Tipper et al., 2010) and lay within the range of river waters draining basic rocks (-0.96 to +0.64 ‰, Pogge von Strandmann et al., 2008). In the latter study of organic-poor rivers, the proportion of colloidal Mg fraction ranged between 2 and 8 % and the isotopic signature of different soluble fractions could not be assessed. In Karelian surface waters, the concentration of colloidal (1 kDa - 0.22 µm) Mg was significant only for samples of soil solution (OR-9) and bog waters (ZPBL) of the subarctic zone (74 and 66 %, respectively). The other studied river water samples exhibited less than 20% of colloidal Mg and thus could not be used for isotopic fractionation study. For the soil solution and the bog water, the 1 kDa ultrafiltrate fraction is 0.03 and 0.08 ‰, respectively, heavier than the 0.22 µm fraction. This difference is within the uncertainty of analysis (Fig. 4.7) and it is much smaller compared to reported variations of Mg isotopic composition in rivers, soils and plants. Although we have not assessed δ^{26}Mg in possible sources of Mg in studied watersheds (atmospheric precipitation, rocks, soils and plant litter) it follows that *1)* the isotopic exchange of Mg between colloidal and LMW $_{<1\ kDa}$ fractions is faster than the Mg exchange within the soil and bog surface waters and incoming sources (precipitation, groundwater…) and/or *2)* the physico-chemical nature (structure and stability of Mg-organic ligand complexes and $Mg(H_2O)_6^{2+}$ aqua-ion) is very similar between colloidal and LMW$_{<\ 1kDa}$ fraction. The latter hypothesis is indirectly supported by essentially electrostatic (non-covalent) bonding of Mg to NOM (Tipping, 1994, 1998; Gustafsson, 1999) that implies the preservation of the first hydration sphere of organically-bound Mg.

4.5. Concluding remarks

The radiogenic and stable isotope composition of subarctic and temperate organic-rich surface waters measured in this study for a series of cascade filtrates, ultrafiltrates and dialysates allow a systematic look on the origin and fractionation of contrasting elements in boreal landscapes. Due to high concentration of organo-ferric and organic colloids controlling the speciation of soluble (Mg, Sr), insoluble (Nd) and organic-(Cu) elements, we could assess the isotopic signatures in both conventionally dissolved (< 0.4-0.22 µm) and "truly" dissolved (< 1 kDa) fractions. The difference in isotopic composition in various filtrates allowed tracing the possible presence of marine aerosols (Sr) but the absence of solid dust deposition (Nd). Colloidal and dissolved Cu and Mg exhibit negligible difference in isotopic composition in the full series of ultrafiltrates down to < 1 kDa fraction which strongly suggest the similarity of the structure and stability of organic complexes binding these metals in different fractions. Since organic and organo-mineral colloids may coagulate in the mixing zone of the river water with the seawater (Porcelli et al., 1997; Gustafsson et al., 2000; Pokrovsky and Schott, 2002; Stolpe and Hassellov, 2007), obtained results shed new light on the degree of transformation of isotopic composition of dissolved element flux from the land to the Arctic ocean. In terms of element transfer by small Arctic rivers to the ocean, it follows that the isotopic signature of riverine Sr flux to the Arctic ocean may be measurably affected by colloids since the $\mathrm{LMW}_{<1\ \mathrm{kDa}}$ "ionic" fraction is up to 0.0002 units of $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ less radiogenic compared to usual < 0.22 µm fraction; despite the dominance of colloidal Nd in the river water, the isotopic signature of all filterable fractions including most labile LMW<1 kDa species remains essentially the same and unaffected by colloids. Organic and organo-mineral colloids controlling the speciation of Cu^{2+} and Mg^{2+} in river waters and soils/bog waters do not produce any measurable isotope fractionation compared to $\mathrm{LMW}_{<\ 1\ \mathrm{kDa}}$ fraction and as such the isotopic ratio of these metals is unlikely to be modified by colloidal coagulation in the mixing zone of the river mouth.

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TABLES

Table 4.1. List of sampled waters and their bedrock compositions.

sample name	description	surface of watershed, km^2	GPS coordinates		bedrock composition	Age
KAR-1	Palojoki river, middle course, North Karelia	32	N 66°12´	E 30°28´	Micro-pegmatic granites, Granosyenites, Syenites, Syenite-diorites	Pt_1
KAR-2	Feeding bog of Palojoki river, North Karelia		N 66°12´	E 30°29´		
KAR-3	Palojoki river, mouth reach, the zone of mixing river and Pyaozero lake, North Karelia		N 66°11´	E 30°34´	Biotite garanitogneisses and tributary biotite, biotite-amphibolite and amphibolite gneisses and amphibolites	AR_1
ZPBL	Bog of the Tsipringa lake basin, North Karelia	1.19	N 66°17´	E 30°53´		
OR-1	Stream Vostochniy, mouth reach, the zone of mixing river and Tsipringa lake, North Karelia	0.95	N 66°18´	E 30°42´	Meta-gabbro	Pt_1
OR-6	Top feeding lake of stream Vostochniy basin, North Karelia		N 66°18 ´	E 30°40´		
OR-9	Soil solution of stream Vostochniy basin, about 500 m from the top feeding lake, North Karelia		N 66°18´	E 30°40´		
Seng-1	Senga river, mouth reach, Central Russia	163	N 55°52´	E 39°31´	Cretaceous: aleurite, sand with layers of clays and sandstones; Quarternary alluvial flat deposits: sand with gravel and pebble, clay loam, sandy clay (to 20 m).	K_{1g2-br} Q_{IV}
Seng-2	Senga river, middle course, Central Russia		N 55°50´	E 39°24´		
Ign	Ignatkovo lake, Central Russia	0.76	N 55°53´	E 39°26´	Cretaceous: aleurite, sand with layers of clays and sandstones; Quarternary bog deposits: peat, sandy clay (to 5 m).	

Table 4.2. Chemical and Sr isotopic composition of filtrates and ultrafiltrates.

Sample	pore size, µm	^{87}Sr/^{86}Sr	2σ	[Sr], µg/L	DOC, mg/L	[Fe], µg/L
Ign/100 µm	100	0.710768	0.000012	3.41	73.0	191
Ign/0.4 µm	0.4	0.710748	0.000027	3.4	48.1	164
Ign/100 kDa	0.0066	0.710740	0.000031	3.357	17.2	142
Ign/10 kDa	0.0031	0.710813	0.000099	3.175	15.7	105.
Ign/1 kDa	0.0014	0.710838	0.000037	2.14	12.5	20.42
Seng-2/100 µm	100	0.709237	0.000020	124.6	78.9	5385
Seng-2/0.4 µm	0.4	0.709262	0.000028	122	44.4	743
Seng-2/100 kDa	0.0066	0.709142	0.000018	119.1	40.7	430
Seng-2/10 kDa	0.0031	0.709145	0.000027	118.1	31.7	92.4
Seng-2/1 kDa	0.0014	0.709125	0.000026	115.2	23.8	14.5
Seng-1/100 µm	100	0.709361	0.000017	100.2	60.8	4337
Seng-1/0.4 µm	0.4	0.709366	0.000017	95.5	55.9	1076
Seng-1/100 kDa	0.0066	0.709373	0.000016	94.75	51.8	453.4
Seng-1/10 kDa	0.0031	0.709406	0.000024	94.67	35.0	76.0
Seng-1/1 kDa	0.0014	0.709331	0.000008	86.33	30.1	16.0
Snow from the Senga basin	100 0.22	0.708561 0.708476	0.000008 0.000019	3.934 2.398	12.3 8.4	14.6 9.68
KAR-1/100 µm	100	0.721109	0.000019	17.82	12.6	1363
KAR-1/0.4 µm	0.4	0.721217	0.000022	17.51	10.9	203
KAR-1/0.1 µm	0.1	0.721126	0.000020	16.72	10.9	199
KAR-1/100 kDa	0.0066	0.720949	0.000015	16.57	10.7	192
KAR-1/10 kDa	0.0031	0.721020	0.000029	16.22	10.5	51.2
KAR-1/1 kDa	0.0014	0.720983	0.000020	14.12	9.4	17.3
KAR-3/100 µm	100	0.721815	0.000021	17.21	10.9	943.9
KAR-3/0.4 µm	0.4	0.721805	0.000013	16.94	10.8	182.8
KAR-3/0.1 µm	0.1	0.721611	0.000017	16.78	10.0	181.5
KAR-3/100 kDa	0.0066	0.721676	0.000023	16.63	9.9	148.2
KAR-3/10 kDa	0.0031	0.721605	0.000022	16.48	9.7	64.49
KAR-3/1 kDa	0.0014	0.721604	0.000013	15.38	7.6	6.804
KAR-3/D1	0.0014	0.720857	0.000016	14.38	5.3	13.38
OR-9/10 µm	10	0.723986	0.000011	9.778	138.2	9863
OR-9/0.22 µm	0.22	0.723956	0.000014	7.901	55.1	6821
OR-9/100 kDa	0.0066	0.723958	0.000011	2.802	27.1	1851
OR-6/10 µm	10	0.729898	0.000012	8.336	15.2	142.3
OR-6/0.22 µm	0.22	0.729892	0.000017	8.303	14.6	12.9
OR-6/100 kDa	0.0066	0.729843	0.000010	7.998	14.3	95.86
OR-6/10 kDa	0.0031	0.729825	0.000009	7.927	14.2	67.9
OR-6/1 kDa	0.0014	0.729811	0.000013	5.502	7.7	6.73
OR-1/10 µm	10	0.735015	0.000009	6.918	15.0	238
OR-1/0.22 µm	0.22	0.735005	0.000014	6.875	12.8	149.7
OR-1/100 kDa	0.0066	0.734996	0.000014	6.577	11.8	77.7
OR-1/10 kDa	0.0031	0.734998	0.000009	6.564	10.7	48.4
OR-1/1 kDa	0.0014	0.734981	0.000012	4.649	7.6	7.89
KAR-1/100 kDa	100	0.720988	0.000021	22.4	10.5	165
KAR-1/10 kDa	0.0066	0.721018	0.000037	22.21	9.7	38.3
KAR-1/1 kDa	0.0031	0.720961	0.000018	20.38	8.3	18.9

Table 4.3. Chemical and Nd isotopic composition of filtrates and ultrafiltrates.

	pore size. µm	$^{143}Nd/^{144}Nd$	2σ	$\xi_{Nd}(0)$	[Nd], µg/L	DOC, mg/L	[Fe], µg/L
Seng-1/100 µm**	100	0.511988	0.000096	-12.7±1	0.161	60.81	4337
Seng-1/10 kDa**	0.0031	0.511910	0.000032	-14.2±0.6	0.029	35.03	76

2009	pore size. µm	$^{143}Nd/^{144}Nd$	2σ	$\xi_{Nd}(0)$	[Nd], µg/L	DOC, mg/L	[Fe], µg/L
OR-1/0.1 µm**	0.1	0.511050	0.000017	-31±0.6	0.328	12.19	120.2
OR-1/100 kDa**	0.0066	0.511056	0.000020	-30.9±0.6	0.326	11.80	77.7
OR-1/10 kDa**	0.0031	0.511045	0.000059	-31±0.6	0.260	10.69	48.4
OR-1/1 kDa**	0.0014	0.511069	0.000072	-30.6±0.6	0.087	7.57	7.9
KAR-1/100 µm*	100	0.510750	0.000278	-37±2	0.190	17.68	1882
KAR-1/20 µm*	20	0.510720	0.000754	-37±6	0.139	17.72	1708
KAR-1/0.8 µm*	0.8	0.510817	0.000119	-36±3	0.092	10.85	743
KAR-1/100 kDa*	0.0066	0.511048	0.000189	-31±3	0.052	10.50	165.4
KAR-1/10 kDa*	0.0031	0.510574	0.000422	-40±4	0.032	9.72	38.3

* TIMS
** MC-ICPMS

Table 4.4. Chemical and Cu isotopic composition of filtrates and ultrafiltrates.

2008	pore size. µm	$\delta^{65}Cu$, ‰	2σ	[Cu], µg/L	DOC, mg/L	[Fe], µg/L
KAR-1/100 µm	100	0.39	0.03	1.37	12.62	1363
KAR-1/0.4 µm	0.4	0.46	0.05	1.24	10.93	203.3
KAR-1/10 kDa	0.0031	0.41	0.02	1.18	10.50	51.24
KAR-1/D1*	0.0014	0.46	0.04	0.66	9.44	7.07
KAR-2/0.4 µm	0.4	0.44	0.04	1.33	16.67	876.2
KAR-2/10 kDa	0.0031	0.34	0.05	1.30	14.28	517.3
KAR-2/D1*	0.0014	0.44	0.03	0.45	4.13	30.89
KAR-3/100 µm	100	0.50	0.05	1.26	10.92	943.9
KAR-3/0.4 µm	0.4	0.36	0.05	1.11	10.82	182.8
KAR-3/10 kDa	0.0031	0.40	0.06	1.05	9.71	64.49

*D1 – dialysis 1 kDa

Table 4.5. Chemical and Mg isotopic composition of filtrates and ultrafiltrates.

Sample	pore size. µm	$\delta^{25}Mg$	$\delta^{26}Mg$	[Mg], µg/L	DOC, mg/L	[Fe], µg/L
OR-9/0.22 µm	0.22	-0.353	-0.680	410.1	55.1	6821
OR-9/1 kDa	0.0014	-0.342	-0.647	107.2	11.3	842
ZPBL/0.22 µm	0.22	-0.333	-0.645	1144	34.9	9348
ZPBL/1 kDa	0.0014	-0.294	-0.560	392.8	9.96	484

FIGURES

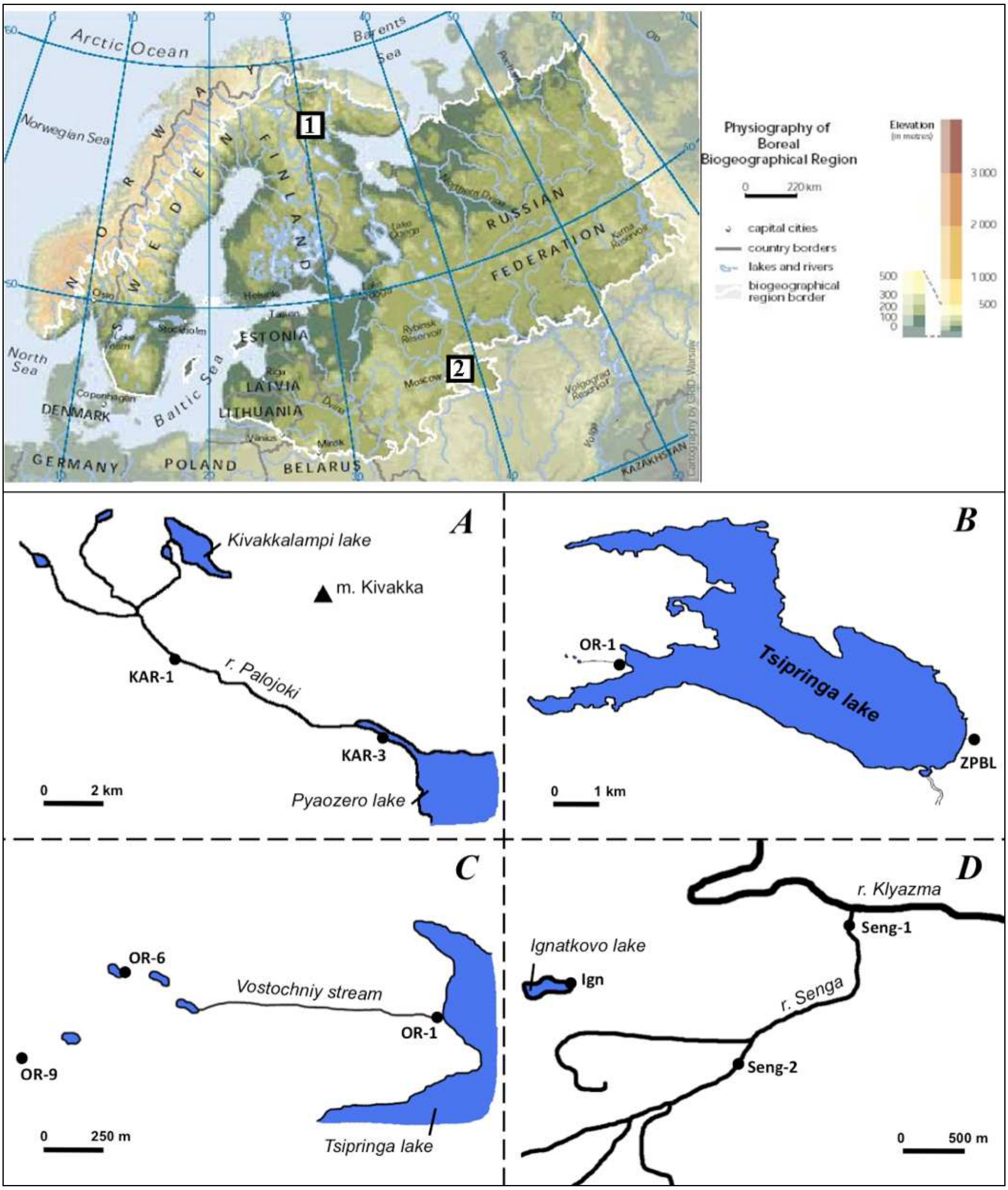

Figure 4.1. Map of boreal zone (*Source: EEA. UNEP/GRID Warsaw final map production from http://www.eea.europa.eu)* with the studied area and sampling sites of the Palojoki river (*A*), the bog ZPBL of Tsipringa lake watershed (*B*), Vostochniy stream watershed (*C*) of Karelia region (1) and Senga river (*D*) watershed of Central Russia (2).

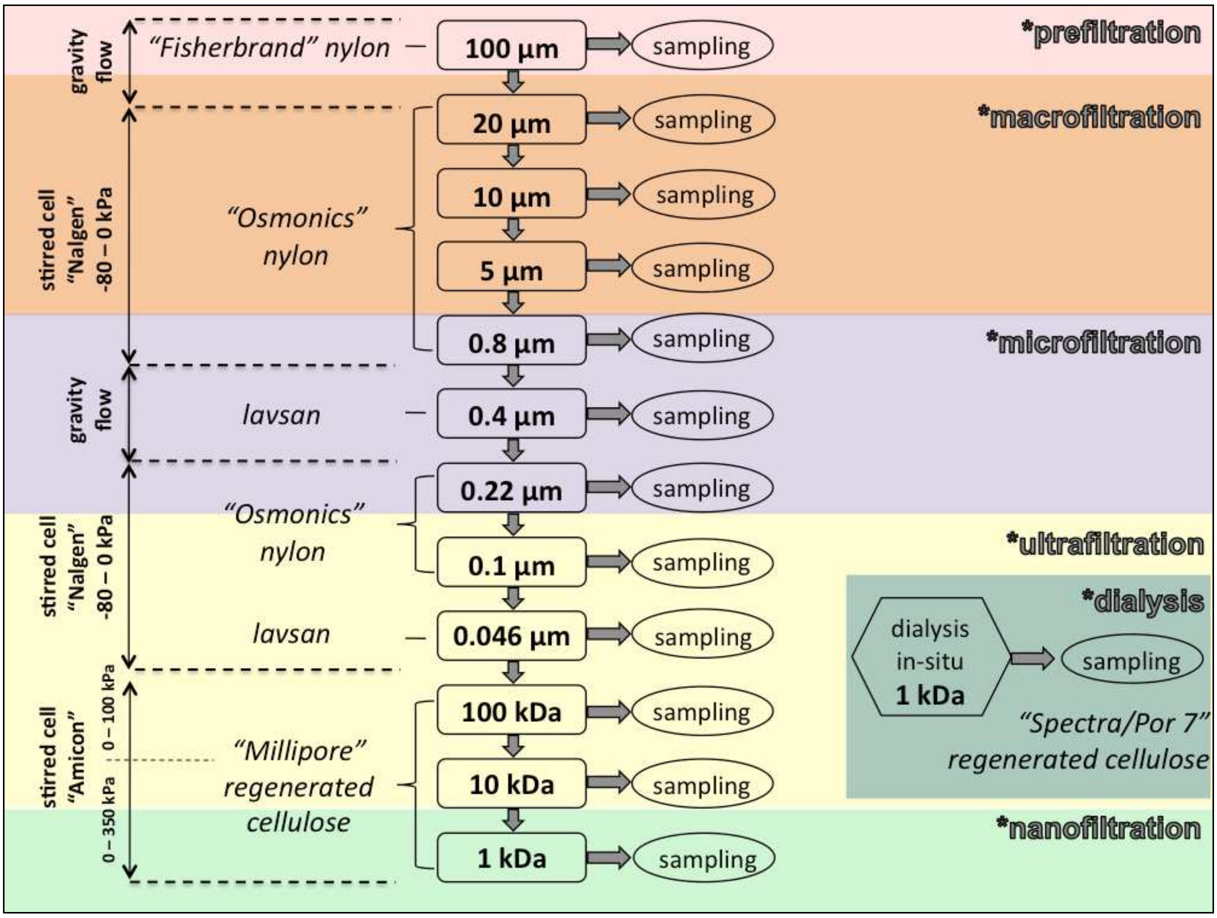

Figure 4.2. The scheme of cascade filtration used in this study.

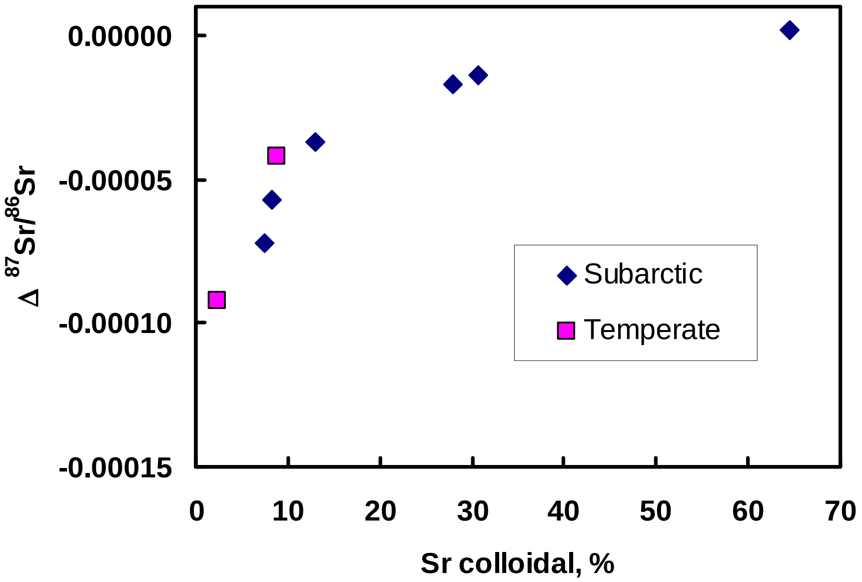

Figure 4.3. Plot of the difference in $^{87}Sr/^{86}Sr$ value between LMW and HMW fraction as a function of % of colloidal Sr in these fractions: 1-10 kDa (OR-1, OR-6, KAR-1); 1-100 kDa (Seng-1 and KAR-3) and 100 kDa - 0.4 µm (Seng-2). These are the fractions where the maximal change in Sr isotopic ratio and concentration occurs during ultrafiltration procedure. Blue dimonds correspond to streams and lake of subarctic zone and pink squares represent the temperate zone. The uncertainty of analysis is within the symbol size.

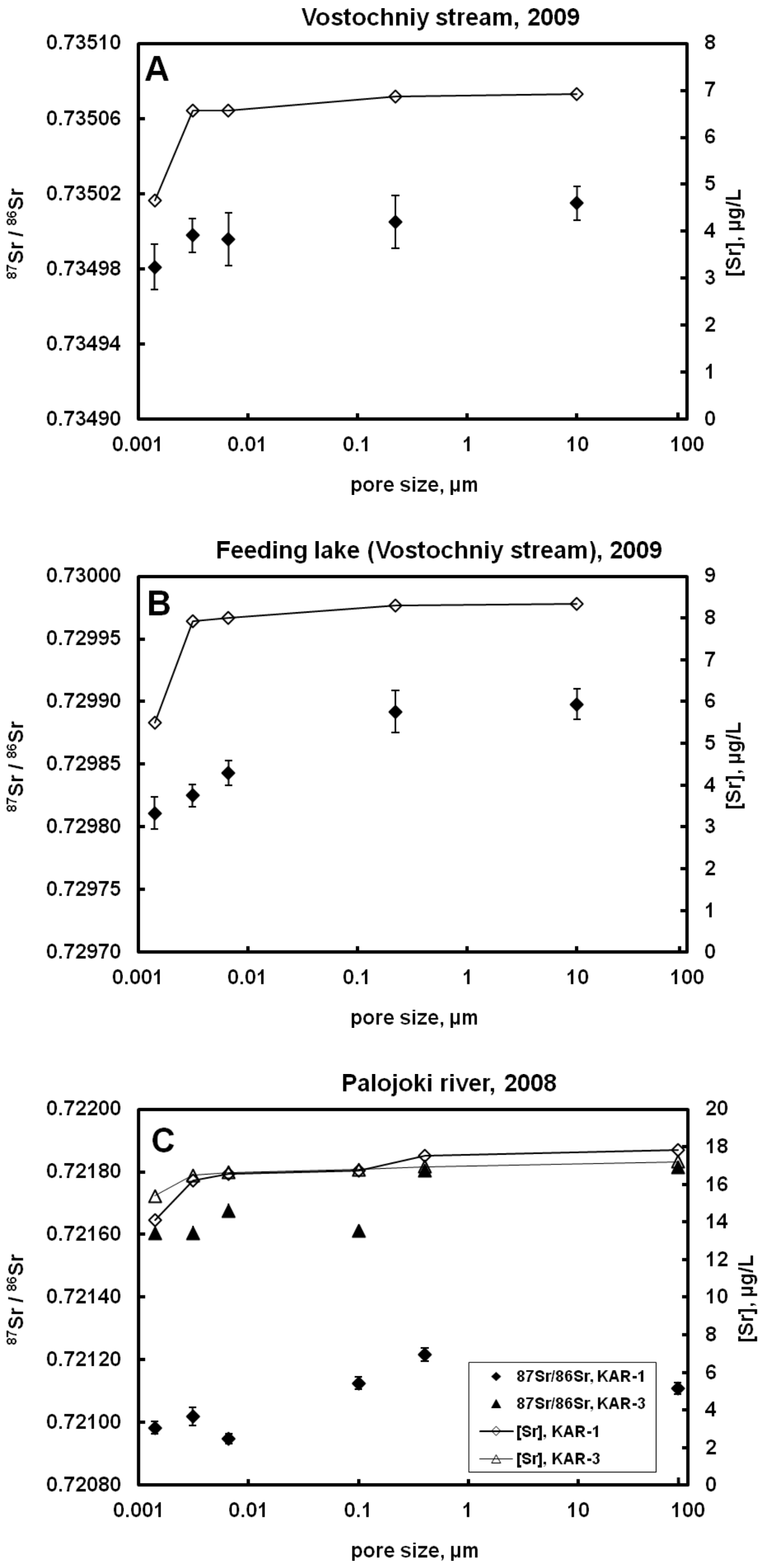

Figure 4.4. ^{87}Sr/^{86}Sr and Sr concentration as a function of pore size in river waters, A: a mouth reach of Vostochniy stream (OR-1), Karelia; B: feeding lake of Vostochniy stream basin (OR-6), Karelia; C: middle course (KAR-1) and mouth reach (KAR-3) of Palojoki river, Karelia;

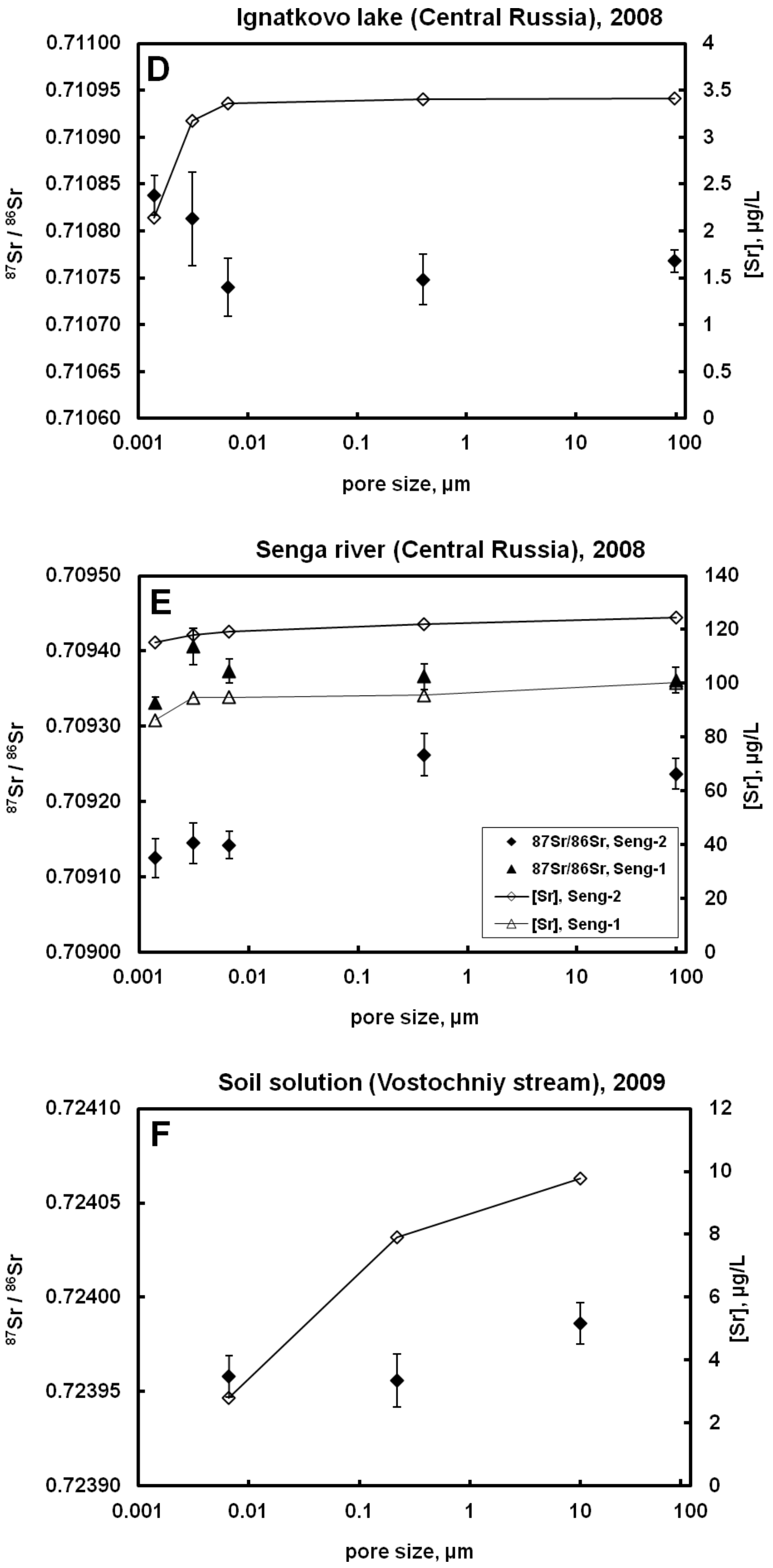

Figure 4.4 continued. $^{87}Sr/^{86}Sr$ and Sr concentration as a function of pore size in river waters, D: Ignatkovo lake (Ign), Central Russia; E: middle course (Seng-2) and mouth reach (Seng-1) of Senga river, Central Russia; F: soil so lution of Vostochniy stream basin (OR-9), Karelia. Open symbols – concentrations, closed symbols – isotopic ratios.

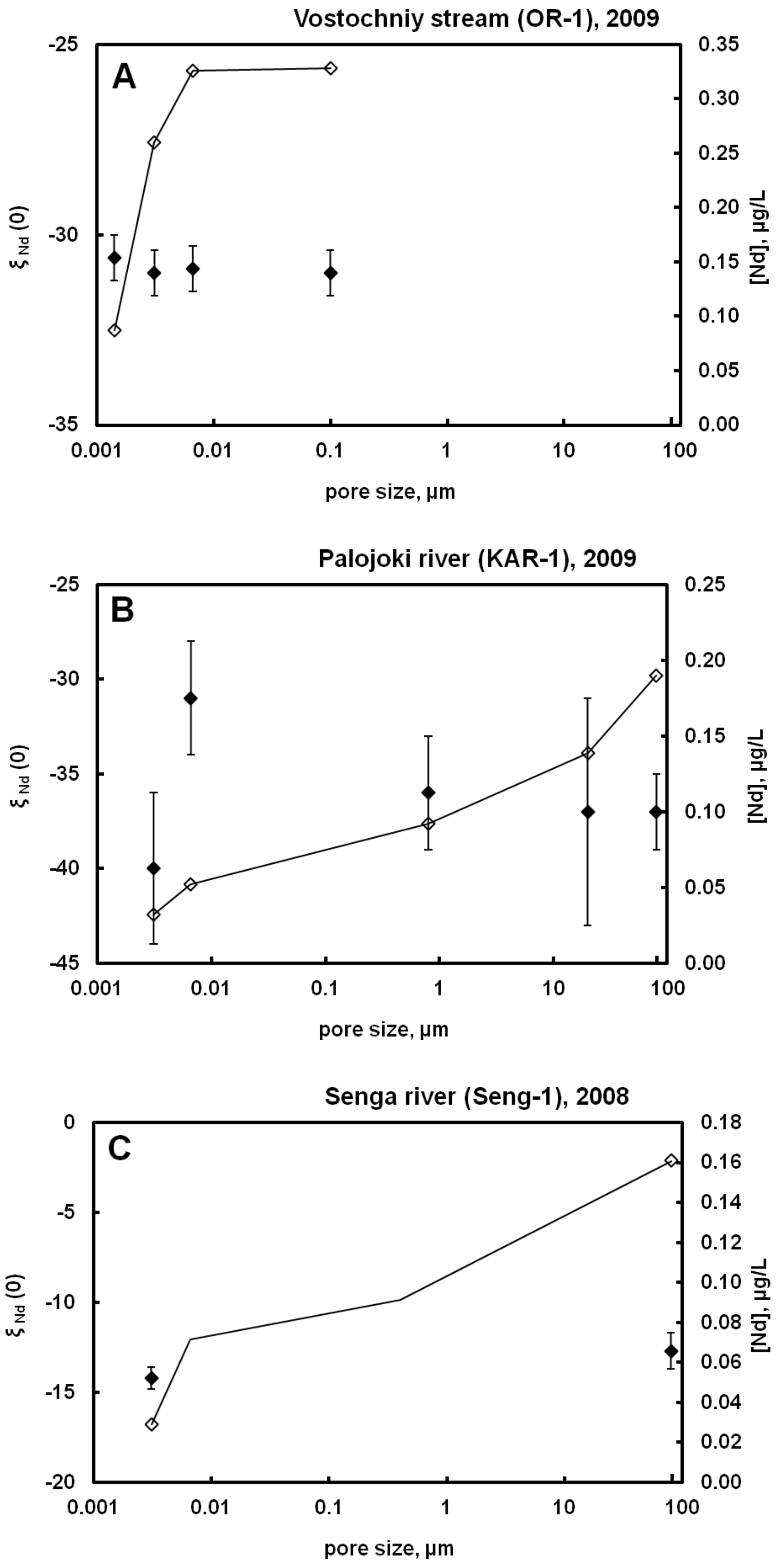

Figure 4.5. ξ_{Nd} (0) and Nd concentration as a function of pore size in river waters, A: a mouth reach of Vostochniy stream (OR-1), Karelia; B: middle course (KAR-1) of Palojoki river, Karelia; C: mouth reach (Seng-1) of Senga river, Central Russia. Open symbols – concentrations, closed symbols – isotopic ratios.

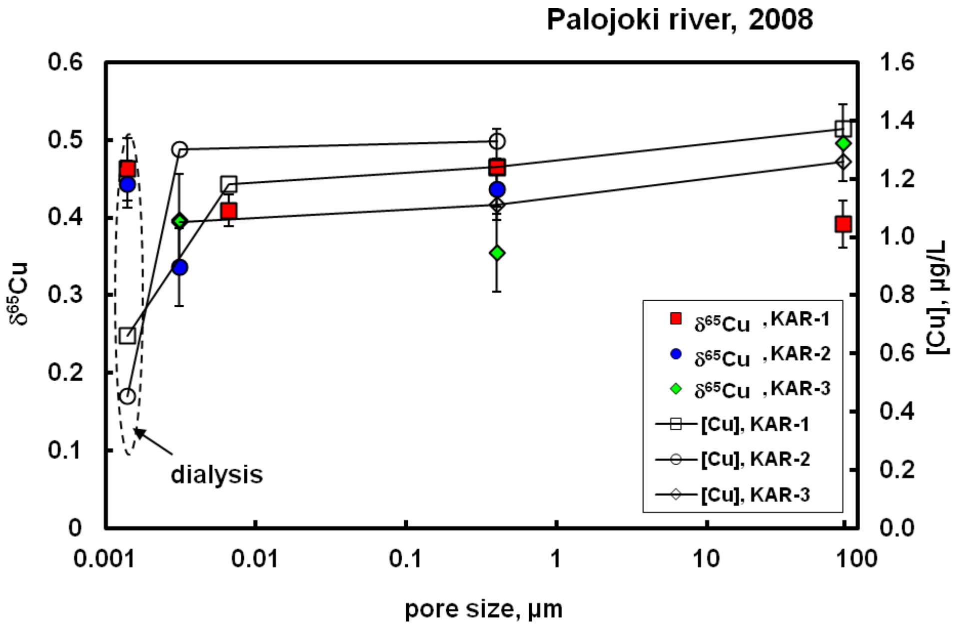

Figure 4.6. δ^{65}Cu and Cu concentration as a function of pore size in Palojoki river waters, KAR-3: a mouth reach, KAR-1: middle course, KAR-2: feeding bog, Karelia. Open symbols – concentrations, closed symbols – isotopic ratios.

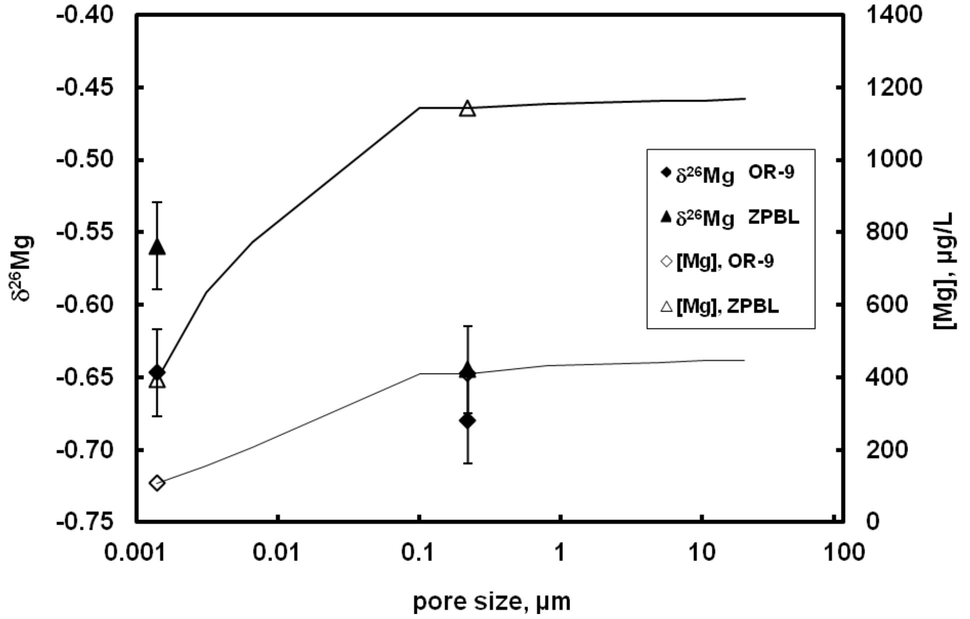

Figure 4.7. δ^{26}Mg and Mg concentration as a function of pore size in a soil solution of Vostochniy stream basin (OR-9) and bog (ZPBL) of Tsipringa lake basin, Karelia. Open symbols – concentrations, closed symbols – isotopic ratios.

ELECTRONIC ANNEX

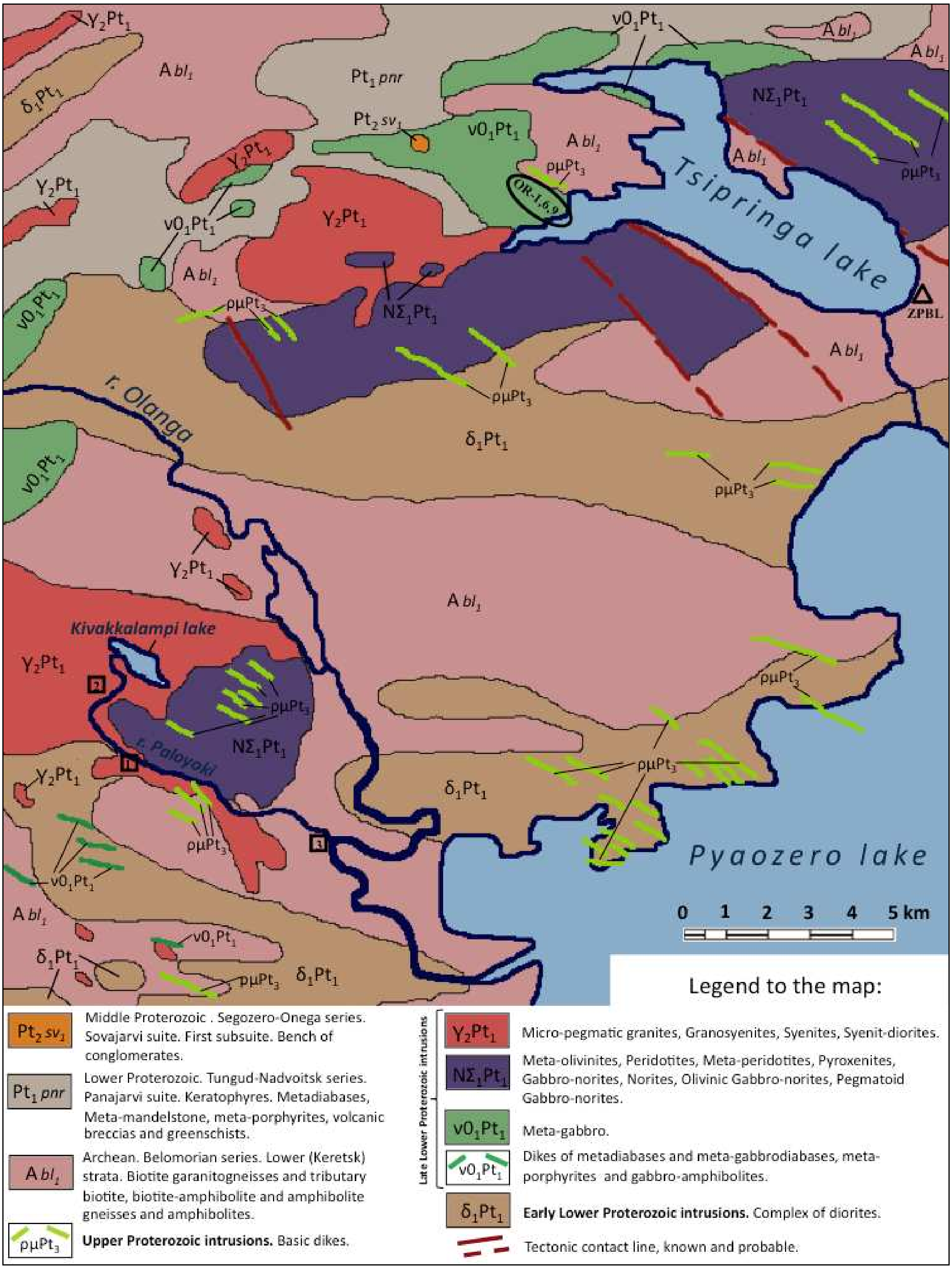

Figure ESM-4.1. Geological map of Karelia region (NW Russia) with sampling points.

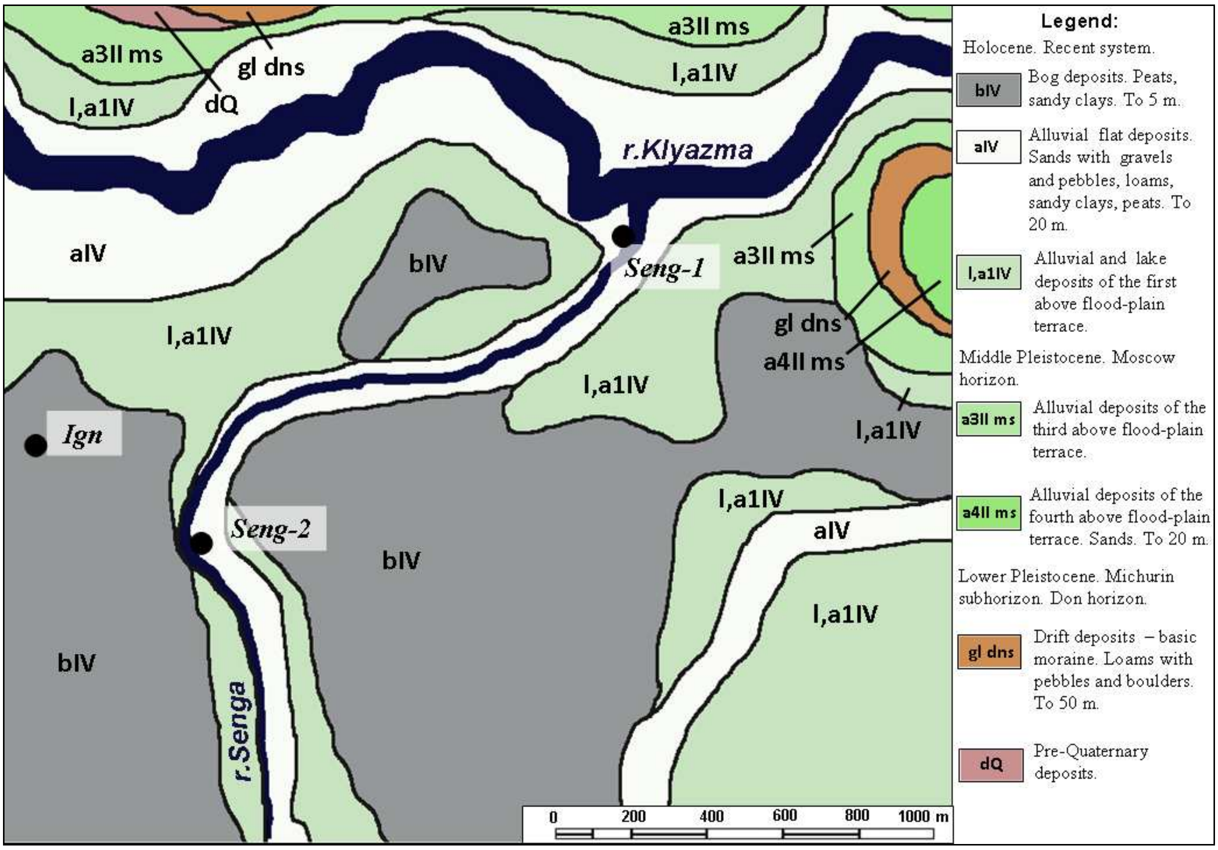

Figure ESM-4.2. Quarternary deposits map of Vladimir region (Central Russia) with sampling points.

ESM-4.3. Description of climate, topography, soil and vegetation of the regions.

4.3.1. North Karelia, NW Russia

4.3.1.1. Climate

The climate of the region is mild-cold, transitional between oceanic and continental, with a determinant influence of the Arctic and Northern Atlantics. Winter is long and soft, summer is short and cool. Average temperature in January is -13°C, and +15°C in July, but extremes can reach -45° to +35°C in winter and summer periods, respectively. The dominant wind direction is South-West in winter and North-East in summer. Average annual precipitation amount is between 450 and 550 mm/yr. Snow period lasts from October to April-May with the average thickness of snow cover 70 - 80 cm, but often over than 1 m. The territory is under the influence of the warm Gulf Stream, but microclimatic conditions differ dramatically because of the large cross-country. In summer in the deep and sheltered valleys it's much warmer than on the mountain tops, whereas in winter it's much colder in the valleys where the mountains cold air accumulates.

4.3.1.2. Topography

Tectonics and glaciation shaped the terrain of Karelia. Crustal snaps and step faults, reaching in two mutually perpendicular directions: the north-west to south-east and south-west to north-east have formed as a result of tectonic processes. Traces of glaciation occur in the glacial landforms that presented in moraine ridges extended from the north-west to south-east.

Much part of the region is a hilly plain with elevations of 200 m. Along the White Sea coast there is a wide zone of lowland Pribelomorskaya with elevations less then 100 m. In the western part, on the border with Finland, moraine ridge Maanselkya is located; it represents a watershed between the basins of the Baltic and White Seas.

Our study area is located in the most elevated part of Karelia, in the central part of Maanselkya. It is a landscape of tectonic denudation hills, plateaus and ridges with an average altitude of 300-400 meters with separate insulated massifs (Tunturi).

4.3.1.3. Hydrology

The region has a well-developed river network that flows via a system of glacial lakes. The water of small and medium-sized lakes warms up to 22-25°C in summer. Water is soft, low mineralized, often with a brown hue because of feeding swamps.

The large number of wetlands is typical feature of North Karelia. The small marshes with area from 3-5 to 30-50 hectares are dominated. A kind of "hanging" (omrotrophic) bogs is formed on the steep slopes. By the nature of their feeding, Karelian rivers belong to the mixed type, fed by rainfall, bogs, groundwater and snowmelt. The rivers break up earlier than their conjugated lakes and some full of rapids reaches don't freeze at all. The average date of floods in North Karelia is April 25 - May 5. The rivers freeze in November - December. Natural fluctuations of water level do not exceed 1.5-2 m.

Rivers of Karelia are comparably short. Significant part of their length (up to 50%) may consist of the flowage lakes. There are « lake-river » systems, consisting of a chain of lakes connected by rapids channels. The accumulative systems are represented by a lake that collects the water of many rivers and serves as outlet of one larger river are also typical for Karelia. Another peculiar phenomenon is a bifurcation (splitting) of the water flow. The average gradient of rivers is about 1 m/km, and up to 3-5 m/km in the rapids channels. Rivers of Karelia are very young geologically, and their beds are composed of hard rocks. Because the rivers are~~,~~ just started to make the longitudinal profile, their–valleys are not wide floodplains, and they almost do not have high terraces.

Chemical composition of river waters in Karelia is determined by the chemical weathering of silicate parent rocks of the Baltic crystalline shield and quaternary deposits, and the presence of numerous peatlands. Typical values of total discharge of solids (TDS) for this region are 15-30 mg/l (Maksimova, 1967; Zakharova et al., 2007), and the concentration of river suspended matter is very low. The adjacent lakes between the rivers significantly decrease the size of actual feeding watershed of a given river.

4.3.1.4. Soil, vegetation

The soil cover of the region is very young and it is often absent on ledges of bedrock and steep slopes. Low temperature in combination with high humidity is responsible for the slow humification and mineralization of plant residues. Therefore, a lot of organic matter is accumulated in the form of peaty horizons, and on better drained sites - in the form of coarse humus. Predominant soils are illuvial-humic and illuvial-ferruginous-humic podzols. All types of podzols exhibit a highly acidic reaction and low base saturation of the upper layers.

Coniferous forests dominate the vegetation of the region. The main conifers are pine and spruce. The common deciduous trees are birch, aspen, alder. The sphagnum pine occurs on the plains, depressions and swamps. Sparse understory consists of mountain ash and juniper. It is dominated by blueberries and cranberries in the shrub layer, and green mosses in the lower layer. The rocks are usually covered with patches of black, gray, yellow, red, brown crustose lichens. Herbaceous plants are rare. The main mushrooms are aspen and boletus. There are poisonous plants in Karelia such as, hemlock, cowbane, mezereon.

4.3.2. Meschera lowland, Vladimir region, Central Russia

4.3.2.1. Climate

The climate of the region is temperate continental with very cold long winters and warm humid summers. Winter is long and soft, summer is short and cool. Average temperature in January is -10.1°C, and +18.2°C in July, average annual temperature is +4.4°C. Annual average surface temperature is 4.8°C, an amplitude of annual variations is 33.9°C. The frost-free period lasts from May 20 to September 20. Average annual precipitation amount is about 700 mm/yr. About 55% (387.5 mm) of precipitation falls in the warm season.

4.3.2.2. Topography

Meshchera lowland is one of the largest woodlands of the Russian Plain. The Northern boundary of lowland is r. Klyazma, the West one is r. Moskva, the South one is r. Oka and the East one is the Oka-Tsninsky shaft.

Senga river is a small river; this is a right tributary of the r. Klyazma that drains bogs of Meshchera lowland.

Ignatkovo Lake is a closed lake with marshy shores.

Much of Meschera surface is waterlogged. Klyazma has a terraced surface. Among the marshes there are a lot of overgrown lakes, creeks, oxbow lakes, etc. The average elevations are in the range 100 - 140 m. Terraces, gullies and ravines network, eolian mounds, depressions and lakes lowers of Klyazma valley make a significant variety among the generally flat topography.

4.3.2.3. Hydrology

By the nature of feed r. Klyazma refers to typical lowland rivers of European Russia. The river depth is 1.5 - 2.5 m; flow rate is 0.3 - 0.6 m/sec. The main feeding source in spring period is snowmelt, in summer-autumn period is rain, and in winter is groundwater. The level fluctuations of the river (rises to 2.0 - 3.5 m in spring period) are associated with variation of feeding source.

Lakes are numerous within Meshchera lowland. The larger ones have a surface area of 25 km^2. The amplitude of level fluctuations of lakes is smaller than of rivers (0.8 - 1.5 m). The thicknesses of silt and peat consider about recent sedimentation in lakes and rivers.

Bogs of Meshchera lowland are difficult or quite impassable; they occupy about 35% of the territory. They are located in areas of low relief in the river valleys and low watersheds (with an altitude of up to 125 m). The surface of bogs is almost everywhere forested on 50 - 60%.

4.3.2.4. Soil, vegetation

Meshchera lowland belongs to the southern part of the forest zone, it is characterized by mixed coniferous and deciduous forests; marsh and meadow vegetation is also widely distributed.

Low-lying bogs occupy more than half the area of Meschera lowland, covered by birch, aspen and alder trees. Peat of these bogs is of low quality, the degree of decomposition is 20 - 30% and the ash content is 8 - 16%.

Soils substratum is outwash sands fanned and rewashed during geological history. The soils of the region are mainly sod-podzolic, podzolic-gley and podzolic. All types of podzols exhibit a highly acidic reaction.

Figure ESM-4.4. Field clean room.

Table ESM-4.5. The main filtration characteristics.

pore size	filer size	filter material	filter producer	filtration pressure	filtration unit
100 µm	300*300 mm	nylon	"Fisherbrand", USA	gravity flow	-
20 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
10 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
5 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
0.8 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
0.4 µm	2*100*250 mm	lavsan	Dubna, Russia	3 - 5 m	-
0.22 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
0.1 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
0.046 µm	Ø 37 mm	lavsan	Dubna, Russia	-80 - 0 kPa	"Nalgen", 250 ml
100 kDa	Ø 76 mm	regenerated cellulose	"Millipore", USA	0 - 100 kPa	"Amicon", 8400
10 kDa	Ø 76 mm	regenerated cellulose	"Millipore", USA	0 - 350 kPa	"Amicon", 8400
1 kDa	Ø 76 mm	regenerated cellulose	"Millipore", USA	0 - 350 kPa	"Amicon", 8400

Chapter 5

Extreme iron isotope fractionation between different size colloids of boreal organic-rich waters

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Extreme iron isotope fractionation between different size colloids of boreal organic-rich waters

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Keywords: ultrafiltration, iron isotopes, river, bog, lake, boreal zone, colloids

Abstract

Significant and systematic variations of iron isotopic composition of different water sample fractions obtained by frontal cascade filtration and ultrafiltration have been recorded in 1) subarctic organic-rich waters of boreal river and stream, bogs and lakes feeding these streams and soil solutions in northern taiga zone (Karelia, NW Russia) in July 2008 - 2009 and 2) temperate river and lake water of the southern boreal zone (Central Russia) in November 2008. Large volume of samples were filtered in the field employing progressively decreasing pore size (100, 20, 10, 5, 0.8, 0.4, 0.22, 0.1, 0.046, 0.0066 (100 kDa), 0.0031 (10 kDa), and 0.0014 µm (1 kDa)) followed by major and trace element, organic carbon and iron isotope analysis. The latter was performed using an inductively coupled plasma mass spectrometry multicollector. In all 5 river samples, there was a gradual increase of δ^{57}Fe relative to IRMM-14 with decrease of the pore size, from +0.4±0.1 ‰ at 100 µm up to +4.2±0.1 ‰ at 1 kDa fraction in the subractic zone and from +0.5±0.2 ‰ at 100 µm up to +1.2±0.2 ‰ at 10 kDa in temperate zone. Peat soil solution yielded constant negative δ^{57}Fe (-0.3 ‰) for fraction 20 µm – 10 kDa with further decrease to –0.8 ‰ in < 1 kDa ultrafiltrates. Within the watershed of a subarctic stream in 0.22 µm fraction, there is a strong increase of δ^{57}Fe from negative values in soil solutions and bog waters (-0.3 ‰) to strongly positive values in feeding lake and terminal river zone (+2.6 ‰). In well oxygenated rivers and lakes, total dissolved Fe concentration strongly anticorrelates with δ^{57}Fe. In the series of filtrates/ultrafiltrates of subarctic and temperate streams and rivers, the δ^{57}Fe value decreases with the increase of the molar ratio Fe/DOC (iron/ dissolved organic carbon).

The results obtained are consistent with available information on mechanisms of Fe isotope fractionation between aqueous solution, organic matter and solid oxy(hydroxides) and the basic principles of stable isotope fractionation. The nature of organo-ferric colloids and the relative concentration of organic carbon versus dissolved Fe in filtrates determine the pattern of δ^{57}Fe evolution as a function of filter pore size. The studied rivers are dominated by high concentration of colloidal and particulate (< 100 µm) Fe oxy(hydr)oxide and thus bulk waters exhibit similar values of δ^{57}Fe close to +0.5 ‰, significantly higher than the continental crust value (0.1 ‰). This values increase by 1.5-2‰ depending on the relative enrichment of organically-bound Fe(III) in low molecular weight (LMW) fraction of well oxygenated waters. The relative enrichment of 1-10 kDa ultrafiltrates in heavy isotope suggests that low molecular weight ligands bind Fe more strongly than Fe(III)oxy(hydr)oxides, in accord with quantum mechanics principles. Overall, results of this work dismiss the previous hypothesis of the dominance of isotopically heavy Fe(III)-rich mineral colloids and isotopically light Fe-organic complexes in boreal waters. Highly positive δ^{57}Fe of the LMW (< 1 kDa) fraction of labile and potentially bioavailable Fe in small subarctic rivers may turn out to be a very important source of isotopically heavy Fe in the Arctic Ocean.

5.1. Introduction

Over past decade, there has been an increased attention to the biogeochemistry of arctic and subarctic zones, mainly linked to: 1) their vulnerability to both local (pollution) and global (climate warming) impacts and, more importantly, 2) their pivotal role in the regulation of the carbon cycle in Earth's Northern hemisphere, notably of the organic carbon flux to the Arctic ocean and CO_2 exchange between the soil, hydrosphere and the atmosphere (Fransson et al., 2001; IPCC, 2007; Bates and Mathis, 2009; Jutterström and Anderson, 2010). In contrast to overwhelming number of studies devoted to biogeochemistry of greenhouse gazes in the boreal zone (Duchemin et al., 1995; Whiting and Chanton, 2001; Huttunen et al., 2003; Liikanen et al., 2003), the studies of metal transport and speciation remain restricted to a small number of "pilot" sites with relatively little information on aqueous geochemistry of metals and their isotopes in the boreal and subarctic zones.

A typical feature of all boreal surface waters is their high concentration of dissolved (< 0.22 µm) organic matter (DOM) and iron, notably in the form of Fe(III)-OM complexes and colloids (Ingri and Widerlund, 1994; Gustafsson and Gschwend, 1997; Gustafsson et al., 2000; Ingri et al., 2000; Andersson et al., 2001; Pokrovsky and Schott, 2002; Dahlqvist et al., 2004, 2007; Pokrovsky et al., 2005, 2006; Bjorkvald et al., 2008; Porcal et al., 2009). Until up to the present time, the majority of studies of colloids in boreal zone were dealing with trace elements and radiogenic isotopes (Ingri and Widerlund, 1994; Porcelli et al., 1997; Andersson et al., 1998, 2001, 2006; Gustafsson et al., 2000; Ingri et al., 2000; Porcelli, 2001; Pokrovsky and Schott, 2002; Dahlqvist et al., 2004, 2007; Pokrovsky et al., 2006, 2010, 2012; Vasyukova et al., 2010). Novel "non-traditional" stable isotope of metals, and notably iron, offer a new look on the origin and transformation of organo-ferric colloids in the continuum soil solution - bog - river - lake, a typical landscape setting of subarctic and boreal regions. Despite the importance of colloidal Fe as a vector of trace elements (TE) transport in continental waters (Pokrovsky and Schott, 2002; Gaillardet et al., 2003; Pokrovsky et al., 2005; Dahlqvist et al., 2007; Hassellov and Von Der Kammer, 2008) attempts to quantify Fe isotope compositions in surface waters are scarce. Ingri et al. (2006) measured isotopic compositions in the particulate fraction of Fe-, organic-rich boreal river and hypothesized at the basis of soil data (Emmanuel et al., 2005) and water data (Bullen et al., 2001) that small-size Fe-C colloids should have a negative δ^{56}Fe value whereas large-size Fe-oxyhydroxide colloids should be enriched in heavy isotope. In contrast, Escoube et al. (2009) measured filtered (0.22 and 0.025 µm) and suspended (> 0.22 µm) fraction of large, Fe, C-poor temperate river and observed little variation of δ^{56}Fe during filtration and ultrafiltration with colloids being generally more positive than particulate material. Based on available physico-chemical experimental and modeling data (see Brantley et al., 2001; Wiesli et al., 2004; Hill et al., 2009; Beard et al., 2010), one can expect that solid (and, presumably, colloidal) Fe oxy(hydro)xide formed by Fe(II) oxidation by biotic or abiotic pathways in surface waters will be enriched in heavy isotope with a fractionation factor relative to aqueous Fe from 1 ‰ to 4.5 ‰ (Bullen et al., 2001; Croal et al., 2004; Anbar et al., 2005; Beard et al., 2010) whereas Fe(III) complexed with strong organic chelates will be enriched in heavy isotope relative to uncomplexed dissolved Fe (i.e., by +0.6 ‰, Dideriksen et al., 2008). The latter finding is in accord with the quantum mechanical calculations which predict that the heavier isotope should concentrate in the species in which it is bounded most strongly (Criss, 1999), as also proved in the case of other metal complexation with organic matter (Gélabert et al., 2006; Jouvin et al., 2009). However, applying these basic principles for natural colloids is hindered by the complex nature of Fe-rich organic colloids. First, high resolution spectroscopic measurements demonstrated the presence, within the Fe^{III}-O_6 octahedra of ferric colloids, of carboxylate groups that prevents the polymers to coagulate and form particulate oxy(hydr)oxide (Rose et al., 1998). Second, the chemical structure of Fe(III) - LMW complexes (<1-10 kDa) represented by both soil fulvic OM and autochthonous microbial exometabolites or DOM transformation products, remains virtually unknown. And third, the photoreduction of organic-bound Fe(III) resulting in an increase of both Fe^{2+} and total dissolved Fe in oxygenated surface waters notably during the arctic summer (McKnight et al., 1988; Kelton et al., 2007) may lead to additional and yet unknown isotope fractionation. However, as a working hypothesis, we assume that the large Fe(III)oxyhydroxide colloids and particles will be enriched in heavy isotope relative to small-size Fe(III) organic complexes whereas Fe(II)-bearing anoxic groundwater/bog/soil solutions solutions will be significantly lighter compared to Fe(III)-bearing oxygenated surface waters.

With the goal of testing the hypothesis of light Fe isotope in the organic-reach LMW pool and heavy Fe isotope in Fe-rich colloidal oxy(hyd)oxide, this work addresses isotope fractionation and colloidal speciation of Fe using conventional size separation technique, on-site frontal filtration and ultrafiltration. Specifically, we aimed to 1) test the possibility of the presence of different pools of Fe colloids having distinct isotopic signatures in different size fractions 2) characterize the transformation of stable isotopic composition of colloidal Fe in various environments within the same watershed and 3) compare isotopic signatures of filtrates and ultrafiltrates in organic-rich rivers and lakes between the arctic and temperate zone in otherwise similar hydrochemical and lithological environments. We demonstrate distinct isotopic signatures of dissolved and colloidal iron and systematic evolution of Fe isotopic composition in subarctic streams in series of cascade filtrates and ultrafiltrates from 100 µm down to 1 kDa. Through detailed analysis of possible experimental artifacts and comparison with available literature data, we revealed new features of Fe isotopic fractionation that can be potentially applied to a wide range of boreal surface waters and help to constrain the isotopic signature of continental Fe discharged to the Arctic Ocean.

5.2. Study area

The surface waters of the north of boreal region (North Karelia, subarctic zone) and the south of the boreal region (Central Russia, temperate zone) were chosen for this study (Fig. 5.1). Both sites are pristine in terms of local industrial or agricultural pollution and receive only long-range atmospheric impact of metals. In the subarctic zone, we studied the basins of the Vostochniy stream and the Palojoki river (Fig. 5.1 A), comprising several rivers and streams, the feeding bog or lake and soil solution (Fig. 5.1 C and Fig. ESM-5.1). In the temperate zone, the Senga river and the Ignatkovo lake were sampled (Fig. 5.1 D, Fig. ESM-5.2). Both sites are similar in the sense that the chemical composition of rivers is controlled by high amount of bog and peat soils present within the watershed. As a result, the waters are rich in dissolved organic carbon (DOC, from 10 to 50 mg/L) originating from organic-rich bog waters and peat soil solutions, the latter having from 60 to 140 mg/L of DOC. At the same time, the sites are different in latitude position (1500 km from north to south), climate and vegetation. As a result, they can be used for testing the climate warming scenario in the boreal taiga zone applying the well established approach of substitution "space for time" (e.g., Frey et al., 2007; Walter et al., 2007).

The subarctic river Palojoki flows out of Kivakkalampi lake, it drains the rocky massif Kivakka from the south and empties into Pyaozero lake. The river watershed's area is 32 km^2; its length is about 9 km and relative altitude of 155 m. It was sampled in the middle part of the flow (KAR-1) and in the mouth zone 90 m above the Pyaozero lake (KAR-3). The bedrock composition of the watershed is represented by micro-pegmatitic granites, granosyenites, syenites, syeno-diorites of the lower-Proterozoic, biotite granito-gneisses and biotite-amphibolite and amphibolite gneisses and amphibolites of the lower-Archean ang glacial deposits of Quarternary (Fig. ESM-5.1). The stream Vostochniy flows from a system of interconected humic lakes (such as OR-6) located within the bog zone and empties into the lake Tsipringa. Its length is about 1 km and relative altitude of 50 m, the catchment area is of 0.95 km^2. The bedrock of the catchment is represented by lower-Proterozoic amphibolitic gabbro (Fig. ESM-5.1). The Vostochniy stream was sampled in the mouth reach, 30 m above the mixing zone with Tsipringa lake (OR-1). Soil solution of the peat bog zone of this watershed was collected from the depth of 5-10 cm in a piezometer (OR-9). Another example of organic-rich river feeding water is a bog zone adjacent to the lake Tsipringa (ZPBL, Fig. 5.1 B). This bog of 1.19 km² area has a relative altitude of 30 m and underlain by Early-

Archean biotite granito-gneisses with biotite-amphibolite and amphibolite gneisses and amphibolites (Fig. ESM-5.1).

The temperate river Senga is the right tributary of the Klyazma river, a tributary of Oka, one of the largest right tributary of the Volga River. The length of Senga river is about 32 km, and the catchment area is of 163 km^2. The bedrock of the catchment is alluvial flat deposits of the Holocene represented by granite moraine deposits (Fig. ESM-5.2). The lake Ignatkovo is an oligotrophic lake of 0.3 km^2 located within the bog area covered by peat deposits of the Holocene (Fig. ESM-5.2). Further details of climate, topography, soil and vegetation of two regions are described in the Electronic Annex (ESM-5.3).

5.3. Materials and methods

5.3.1. Sampling, filtration, dialysis

Water samples of the subarctic zone (Vostochniy stream, Palojoki river, Bog of Tsipringa lake basin of North boreal zone (Karelia, NW Russia)) were sampled in July 2008 and 2009 and the waters of the temperate zone (Senga river and Ignatkovo lake of South boreal zone (Meschera, Vladimir region, Central Russia)) were sampled in November 2008. The list of sampled waters and their bedrock compositions is given in Table 5.1. Large volumes (20-30 L) were collected about 0-20 cm below surface in pre-cleaned light-protected PVC bottles for size fractionation procedure of 100, 20, 10, 5, 0.8, 0.4, 0.22, 0.1, 0.046, 0.0066 (100 kDa), 0.0031 (10 kDa), and 0.0014 µm (1 kDa) using cascade filtration and ultrafiltration conducted directly in the field using specially prepared polyethylene-covered clean space (Fig. ESM-5.4). The main characteristics of the filtration are listed in Table ESM-5.5 and the scheme of the procedure is given in Fig. 5.2.

Filtration through 100 µm or pre-filtration was performed using nylon net "Fisherbrand". Cascade frontal filtration with the decreasing pore size from 20 to 0.1 µm was performed using a 250-ml vacuum polycarbonate cell (Nalgene) and nylon membranes (Osmonics). Frontal ultrafiltration (UF) of the series 100 - 10 - 1 kDa was performed using a 400-ml polycarbonate cell (Amicon 8400) equipped with a suspended magnet stirring bar located beneath the filter to prevent clogging during filtration. Vacuum filtration was performed using a portative hand-pump, and the ultrafiltration was performed using a portative air pump. The large volumes of the samples were passed through the Lavsan (polyethylene tereph-thalate, PETP) filters of 0.4 µm pore size and 500 cm² surface area. The filtration occurred via gravitational flow (0.3-0.5 kPa).

Between each sample, the filtration system was cleaned by flushing EasyPure water, then 3% ultrapure HNO_3, and finally, EasyPure water. Each filter was soaked in EasyPure water during at least 1 day before the experiment and used only once. During filtration, the first 50 ml of sample solution were discarded, thus allowing saturation of the filter surface prior to recovery of the filtrate. Discussions of this technique and precautions against possible filtration artifacts are given in Viers et al. (1997), Dupré et al. (1999), Pokrovsky and Schott (2002), Pokrovsky et al. (2005, 2006, 2010), Vasyukova et al. (2010).

In the sample of soil solution (OR-9) both filtrates and retentates of all pore sizes (20, 5, 0.8 and 0.1 µm and 100, 10 and 1 kDa) were analyzed for Fe isotopic composition. A river sample KAR-1 was 1 kDa-ultrafiltered following traditional cascade scheme (Fig. 5.2) and also ultrafiltered from 0.4 µm fraction without cascade mode to check for eventual filtration artifacts on Fe isotope analysis.

For quality control, MilliQ water was filtered and ultrafiltered in the field following exactly the same procedure as that employed for samples fractionation. Iron concentration in blanks has never exceeded 1 % of the minimal value observed in the ultrafiltrates of natural waters.

5.3.2. Chemical analysis

Water temperature, pH, dissolved oxygen concentration and conductivity were measured in the field. The pH was measured using a combination glass electrode calibrated against NIST buffer solutions. Dissolved oxygen were measured using oxymeter «Expert-001» with Clark oxygen sensor and uncertainty of 5%. Major anion concentrations (Cl^-, SO_4^{2-}, NO_3^-) were measured by ion chromatography (Dionex 2000i) with an uncertainty of 2%. Alkalinity was measured in situ by Acid titration and Gran treatment method. The dissolved organic carbon (DOC) was determined using Shimadzu SCN Analyzer (Toulouse) and Elementar TOC analyzer (Moscow) with an uncertainty of 3% and a detection limit of 0.1 mg/L.

Major and trace elements including Fe were measured without preconcentration by ICP-MS (7500ce, Agilent Technologies). Indium and rhenium were used as internal standards. The international geostandard SLRS-4 (Riverine Water Reference Material for Trace Metals certified by the National Research Council of Canada) was used to check the validity and reproducibility of each analysis. A good agreement between our replicated measurements of SLRS-4 and the certified values was obtained for the elements of interest (relative difference < 5%).

5.3.3. Iron isotope analysis

Filtered and acidified water samples were evaporated in the clean room of class 10 000 and iron was purified using anion exchange chromatography in a HCl medium (Strelow, 1980), as outlined in Poitrasson et al. (2004). We used 0.5 ml of Bio Rad AG1 X4, 200-400 mesh anionic resins loaded in thermoretractable Teflon columns having an internal diameter of 4 mm. After resin wash using the elution reagents and preconditioning, samples were loaded in 0.5 ml of 6M HCl and the matrix was eluted in 3 ml of the same acid. Iron was quantitatively eluted with 2 ml of 0.05M HCl. Purified iron samples were analyzed in a 0.05M HCl solution. Iron and the internal standard, Ni, were set to a concentration of 1 and 3 ppm respectively.

Iron isotope measurements were performed at GET-CNRS in Toulouse using a Thermo Electron Neptune MC-ICP-MS (Bremen, Germany) following the methods described in Poitrasson and Freydier (2005). All analyses are reported in the delta notation relative to the IRMM-014 standard, expressed as δ^{57}Fe, which represents the deviation in per mil relative to the reference material:

$$\delta^{57}\text{Fe (‰)} = \left(\frac{(^{57}Fe/^{54}Fe)_{sample}}{(^{57}Fe/^{54}Fe)_{IRMM-014}} - 1 \right) * 1000$$

We also obtained δ^{56}Fe values but, since the relationships between δ^{56}Fe and δ^{57}Fe of the samples plot on a single mass fractionation line, only δ^{57}Fe values are discussed in this paper. Data quality was checked by reported analyses of our house hematite standard every 5 samples in the analytical sequence.

5.4. Results

Selected chemical and all Fe isotope results are reported in Table 5.2. The studied waters of the Vostochniy stream, Palojoki River, Senga River and Ignatkovo lake are neutral with pH ranging from 6.3 to 7.1 whereas the waters of bog and soil solution are acidic with pH of 4.9 and 3.9, respectively. All waters are low mineralized (≤ 100 mg/L) with the dominance of Ca and HCO_3^- ions or Ca, Cl and Na ions (soil solution). The inorganic ion charge balance ($(\sum^+ - \sum^-)/\sum^+$) is below 0.1 for all samples except soil solution having a deficit of anions of 0.4-0.5. This deficit is correlated with DOC concentration in filtrates and ultrafiltrates similar to those reported in other surface waters of North Karelia (Vasyukova et al., 2010) typical for organic-rich boreal surface waters (DOC concentration equals to 10-20, 5-20, 20-60, 120-150, 30-80, 15-50 mg/L in Arctic river and stream, lake, bog and soil solution and temperate river and lake, respectively).

5.4.1. Evolution of δ^{57}Fe as a function of the pore size

5.4.1.1. Soil solutions and bog waters (subarctic zone)

The values of δ^{57}Fe within the filtrates and ultrafiltrates of soil solution (OR-9) ranged between -0.2 and -0.3 ‰ for the size fraction of 20 µm to 10 kDa without any significant dependence on the pore size. The values of δ^{57}Fe measured in the filter retentates ranged between -0.20 and -0.46 ‰ showing a slight decrease (c.a., by 0.1-0.2 ‰) for the fraction of < 0.1 µm (Fig. 5.3).

Similar to the soil solution from Vostochniy stream watershed (OR-9), the evolution of δ^{57}Fe within the filtration series for the bog zone (ZPBL) does not show any systematic trend, although more scattered. With the exception of the fraction < 1 kDa (Fig. 5.4) the bog zone is isotopically heavier than the reference continental crust value (0.1 ‰, Poitrasson, 2006), whereas the soil solution are much lighter (Fig. 5.3).

5.4.1.2. Rivers, stream and lakes

All studied rivers, streams and lake of the subarctic zone exhibit a very similar trend in their δ^{57}Fe evolution as a function of the filter pore size. They show a strong increase of δ^{57}Fe from +0.4…+1 ‰ for the 1–100 µm fraction up to +4‰ for the smallest, < 1 kDa fraction. Figure 5.5 A, B, C and D show this systematic trend for OR-1, OR-6, and KAR-1, respectively. Note the similarity of δ^{57}Fe – size fraction dependence for the same river Palojoki (KAR-1) sampled in 2008 and 2009 (Fig. 5.5 C). The ultrafiltrates of 1 and 10 kDa of KAR-1 sample collected in 2009 exhibit noticeable deviation from the general trend, likely reflecting different processes controlling Fe isotopic composition in different size fractions.

A similar evolution of both δ^{57}Fe and [Fe] as a function of the filter pore size for the temperate Senga River is shown in Fig. 5.6. Likewise the subarctic zone, δ^{57}Fe values in temperate river are above the continental crust reference but the smallest fraction of 10 kDa shows only 0.3–0.4 ‰ increase compared to 100 kDa – 0.4 µm filtrates. Finally, the temperate lake (sample Ign) exhibit constant value of δ^{57}Fe equals to 0.60 ± 0.05‰ with no distinct trend between 0.4 µm and 10 kDa filtrates (see Table 5.2), similar to subarctic peat bog and soil solution.

5.4.2. Possible artifacts of filtration on isotope compositions

The main source of possible artifacts of filtration and ultrafiltration in the cascade mode adopted in this study is gradual transformation of filtrates after prolonged exposure to atmospheric air, light, and the presence of aerobic microorganisms. In addition, filter clogging and modification of the effective pore size is a usual problem of ultrafiltration (e.g., Viers et al., 1997; Burba et al., 1998; Benoit and Rozan, 1999; Dupré et al., 1999; Nifant'eva et al., 1999; Alekhin et al., 2010) that may significantly affect iron isotope fractionation. Whereas the first process is expected to be mostly pronounced for partially anoxic and thus "unstable" soil solutions and bog waters, the second process may occur for all studied samples.

These artifacts has been addressed via 1) comparison of direct and cascade ultrafiltration through 1 kDa filter (Fig. 5.5 C) and 2) analyses of filter retentates in soil solution sample (Fig. 5.3). It can be seen from the Table 5.2 that the value of <1 kDa ultrafiltrate of KAR-1 sample collected in non-cascade mode (from 0.4 µm filtrate) is equal to that of the cascade ultrafiltrate within the analytical uncertainty (1.77±0.05 and 1.80±0.18 ‰, respectively). This strongly suggests negligible isotopes separation due to filtration effects and the absence of systematic transformation and coagulation of colloids during to cascade filtration from 20 µm to 10 kDa.

Similarly, soil solution filtrates and ultrafiltrates (sample OR-9) exhibiting partially anoxic conditions ($[O]_2$= 40 % saturation) demonstrate an agreement between the values of δ^{57}Fe of retentates and those of filtrates and ultrafiltrates within ±0.1…0.2‰ (Fig. 5.3). This important result demonstrates the absence of significant precipitation of Fe oxy(hydr)oxide on filters during cascade filtration. Indeed, a formation of solid insoluble Fe(III)oxyhydroxide on the filters could be expected here due to oxydation of Fe(II) initially present in this partially anoxic sample. This should have brought an enrichment of retentates in heavy ~~isotopes~~ relative to filtrates by a minimum of 2.25±0.3 ‰ (Beard et al. (2010) following results of Bullen et al. (2001) on $FeCl_2$ oxydation). This is not observed in our experiments. Hence, Fe(II) oxydation with Fe(III) oxy(hydr)oxide formation is very unlikely during the filtration and ultrafiltration procedure used in this study. Overall, we take these experiments and observations as an indication that no filtration biases >0.2 ‰ is induced by our water treatment procedures.

5.4.3. Effect of dissolved Fe, organic carbon and Fe/C ratio in colloids

The values of δ^{57}Fe exhibit significant correlation with Fe concentration in filtrates and ultrafiltrates in rivers, streams and lakes with correlation coefficient (R^2) ranging from 0.83 to 0.98 (Fig. 5.7 A and B). It can be seen from these figures that the lower the Fe concentration, the higher the enrichment of filtrates in heavy isotope. At the same time, the slope of [δ^{57}Fe, ‰] – [Fe, µg/L] relationship ranges from -0.021 for Vostochniy stream and feeding lake to -0.0006 for Palojoki and Senga Rivers. In contrast, there is no dependence between δ^{57}Fe and [Fe] for filtrates and ultrafiltrates of soil solution (OR-9) and bog water (ZPBL) as the correlation coefficient is less than 0.35. The Ignatkovo lake also shows lighter δ^{57}Fe despite moderate Fe concentrations (Fig. 5.7 A) and does not follow the general trend.

The correlation of δ^{57}Fe with DOC concentration is less pronounced than that with [Fe] for subarctic rivers and streams because of outlying samples (R^2 of 0.55 to 0.90, Fig. ESM-5.6 A) but significant for temperate river Senga ($R^2 = 0.997$-0.998, see Fig. ESM-6 B). Similar to what is observed for Fe concentration, there is no correlation between δ^{57}Fe and [DOC] for filtrates and ultrafiltrates of soil solution and bog waters (R^2=0.12-0.40, not shown).

We found that the molar ratio of Fe/C in ultrafiltrates can serve as a useful proxy for Fe isotopic ratio as it is illustrated for subarctic watershed Vostochniy in Fig. 5.8. It can be seen from this figure that there is a gradual decrease of δ^{57}Fe from +4 ‰ to +1 ‰ when Fe/C changes from 0.0035 to 0.001. Considering all sampled rivers and streams, for a much larger range of the (Fe/C) parameter, there are two clusters of isotopic trends with temperate rivers being approx 1‰ isotopically lighter compared to subarctic rivers and lakes at a given Fe/C ratio (Fig. 5.9).

5.4.4. δ^{57}Fe as a function of pH, redox conditions and landscape setting.

The dependence of δ^{57}Fe on the pH value in all measured filtrates and ultrafiltrates revealed a tendency of the depletion of acidic (pH < 6) fluids in heavy isotopes compared to neutral waters (Fig. ESM-5.7). However, this observation may be due to the lower isotopic signature of organic-rich, partially anoxic bog waters and soil solutions bearing, presumably, significant amounts of Fe(II) having lighter isotopic composition compared to Fe(III) colloids and oxy(hydroxides). For well oxygenated surface streams and lakes, there is no statistically significant dependence between Fe isotopic composition and pH.

The evolution of δ^{57}Fe within different landscape settings, soil solution – feeding lake – stream demonstrates a clear trend with the minimal values of δ^{57}Fe are observed in soil solution and the maximal ones in the intermediate feeding lake (Fig. 5.10). All size fractions of the soil solution have the negative values of δ^{57}Fe, less than continental crust reference.

Note that the δ^{57}Fe values of 0.22 and 5 µm filtered water of the feeding lake located at the upper reaches of Vostochniy stream (OR-6) are 0.4-1.1 ‰ more positive than those in the stream itself (OR-1). This observation is consistent with the trend of increasing δ^{57}Fe with the decrease of the pore size (see section 5.4.1.2). It can be suggested that the coarse subcolloidal particles (> 0.22 µm) have been gravitationally precipitated in the lake; as a result, the lakewater has acquired more positive isotopic signature compared to the stream.

5.5. Discussion

5.5.1. Size fractionation in different samples and the magnitude of isotopic variations

Conventional filtration and ultrafiltration of small boreal rivers and streams used in this study revealed unusually large variation of Fe isotopic composition (δ^{57}Fe) between different size fractions of water samples with a maximal amplitude of 5.1 ‰ leading for one of the highest δ^{57}Fe values reported in nature so far (δ^{57}Fe = 4.2 ‰). At the same time, the difference of δ^{57}Fe in dissolved fraction (< 0.22-0.4 µm) between different types of surface waters reaches 3 ‰. This range is larger than that reported in other natural settings from lower latitudes, such as lake and river suspended matter (2.0 ‰) for particles in Aha lake, China (Song et al., 2011); dissolved fraction of Fe-rich lake (2.7 ‰) for Lake Nyos, Cameroon (Teutsch et al., 2009), and Fe isotopic variation in the Amazon basin (2.25 ‰) (Bergquist and Boyle, 2006). Moreover, the range of isotopic variations in subarctic surface waters of this study is significantly larger than that of boreal river and the Baltic Sea suspended matter (0.03, 0.66 and 0.3 ‰, Beard et al., 2003b, Ingri et al., 2006 and Gelting et al., 2010, respectively), sediments porewaters of the subterranean estuaries (from -3.5 to -7.5 ‰, Rouxel et al., 2008) and a temperate river (from -1.7 to -0.3 ‰ and 0.55-0.78 ‰, Fantle and DePaolo, 2004, and Escoube et al., 2009, respectively).

A systematic enrichment of filtrates in heavy isotope with the decrease of the size fraction and Fe/C_{org} ratio strongly suggests that the small size organic-rich colloids are isotopically heavy and the large size mineral-rich colloids are lighter. This result contrasts the previous conclusion reached from the analysis of river suspended material (Ingri et al., 2006). It can be linked to the combination of several processes occurring in boreal aquatic environments as discussed below.

5.5.2. Mechanisms of colloid formation and evolution within the watershed

It is generally accepted that in boreal, non-permafrost zone, formation of Fe(III)-bearing organic colloids occurs at the redox front during the mixing of anoxic Fe(II)-bearing groundwaters or in deep soil waters with well oxygenated DOC-rich surface bog waters or surface soil horzons; this may also occur in the hyporheic zone of the stream (Pokrovsky and Schott, 2002; Ingri et al., 2006; Bjorkvald et al., 2008; Vasyukova et al., 2010). Results of the present work support this general scheme as soil solution and bogs exhibiting partially anoxic conditions have distinctly lower value of δ^{57}Fe compared to well oxygenated river, stream and lake. Formation of inorganic Fe(III) oxy(hydr)oxides from Fe(II) aqueous solution brings about an enrichment of solid phase in 1.5 to 4-5 ‰ relative to the fluid (Bullen et al., 2001; Johnson et al., 2002; Skulan et al., 2002; Welch et al., 2003; Beard et al., 2010), as also supported by natural observations (Bullen et al., 2001; Teutsch et al., 2009; Song et al., 2011). The Fe(III)-bearing particles (1-100 µm) and colloids sampled in well oxygenated waters in this study are indeed, 1 to 2 ‰ heavier compared to the source material (groundwaters, soil solution or rocks). However, in conventionally filtered fractions (0.22 and 5 µm), the largest isotopic change occurs between the soil solution (OR-9) or analogous bog/groundwaters (ZPBL) and stream-feeding humic lake (OR-6, Fig. 5.10). This lake is located within the bog zone but subjected to strong insolation during the arctic summer, oxygenation and (presumably) heterotrophic microbial respiration and phytoplankton development. These processes, as described in sections 5.5.3.1-5.5.3.2 below may bring about the enrichment of water in small-size organic Fe(II, III) complexes having distinctly different isotopic signature compared to the source Fe(III). This signature is then preserved in the stream until the terminal large oligotrophic Tsipringa lake where the new processes of colloid transformation may initiate. An additional reason for heavy Fe isotope enrichment in stagnant lake water (OR-6) compared to stream water (OR-1) may be gravitational sedimentation of large 1-100 µm Fe oxy(hydr)oxide particles having lower δ^{57}Fe value compared to smaller particles and colloids (< 1 µm) given that recent experimental results suggest that nanoparticles may exhibit larger Fe isotope fractionation (Beard et al., 2010).

5.5.3. Mechanisms of Fe isotopic fractionation

5.5.3.1. Fe(III) oxyhydroxides formed by Fe(II) oxydation

The δ^{57}Fe values of soil solution (OR-9) and peat bog (ZPBL) are lighter than the continental crust and exhibit similar evolution of δ^{57}Fe and dissolved Fe concentration in filtrates and ultrafiltrates series (Fig. 5.3) thus suggesting partially anoxic conditions. Part of the Fe^{2+} of those waters would oxidize to form Fe(III) solid oxy(hydr)oxides and leading the remaining solution enriched in light isotopes. This is in accord both with natural observations (Bergquist et al., 2006; Wiederhold et al., 2007; Escoube et al., 2009; Teutsch et al., 2009), and with numerous laboratory measurements of Fe fractionation during Fe(II) oxidation (e.g. Bullen et al., 2001; Beard et al., 2010). Note that the absence of the dependence between δ^{57}Fe and [Fe] for filtrates and ultrafiltrates of soil solution (OR-9) and bog (ZPBL) suggests that the values result from the combination of more than one single process.

In contrast to peat soil solution and bog, the absence of divalent Fe in well oxygenated surface rivers, streams and lakes is supported by the observed anticorrelation between Fe concentration in filtrates and δ^{57}Fe (Fig. 5.7 A and B). This relationship contrasts with a positive correlation reported between δ^{57}Fe and Fe(II) concentration in reduced groundwaters and interpreted as Fe(II) adsorption on newly formed Fe(III)(hydr)oxide surfaces produced by injection of oxygen-rich waters (Teutsch et al., 2005). Therefore, the presence of inorganic species of Fe(II) can not be responsible for observed iron isotopic composition in well oxygenated boreal surface waters sampled in this study.

The decrease of δ^{57}Fe with the increase of Fe/C in colloids allow extrapolation of this dependence to C/Fe = 0 corresponding to C_{org}-free ferric colloids (Fig. ESM-5.8). This extrapolation yields the values of δ^{57}Fe = +0.30±0.18 ‰ for Vostochniy stream and its feeding lake (OR-1 and OR-6) and δ^{57}Fe = +0.40±0.10 ‰ for the Senga river (Seng-1, 2). These relatively low values of pure inorganic Fe(III) oxyhydroxides compared to δ^{57}Fe = -0.8-0.9 ‰ in lowest molecular weight fraction of soil solution and bog waters (OR-9, ZPBL), which most likely reflect dissolved Fe(II) pool, allow to calculate a minimal fractionation factor between $Fe(II)_{aqueous}$ and Fe(III) oxyhydroxide occurring at the redox front during the formation of colloids. Our calculated values range from +0.7 to +1.3 ‰ and is broadly consistent with the minimal value of +1.3 ‰ measured in laboratory experiments (Beard et al., 1999, 2003a; Bullen et al., 2001; Croal et al., 2004).

5.5.3.2. Low molecular weight (< 1 kDa) organic complexes of Fe

Compared to temperate and tropical rivers, all boreal and subarctic rivers exhibit elevated proportion of LMW (< 1 kDa) fraction of organic carbon achieving 30-50 % of total dissolved (< 0.22 µm) DOC (Guo and Macdonald, 2006; Pokrovsky et al., 2010). Moreover, in large Siberian rivers during summer baseflow, the LMW (<1 kDa) fraction constitutes from 60 to 90% of DOC (Prokushkin et al., 2011).

The appearance of low molecular weight autochthonous organic complexes of Fe bearing highly positive isotopic signature in oxygenated surface waters of the subarctic zone may stem from *i*) phytoplankton exometabolites production, *ii*) heterotrophic respiration (mineralization) of organo-ferric colloids by bacterioplankton, known for other boreal lakes (Tranvik, 1988, 1994; Pokrovsky et al., 2011), and *iii*) photoreduction of Fe(III). Phytoplankton has been shown to fractionate Fe towards the enrichment of cells by heavy isotope relative to aqueous solution, upon adsorption of iron at the cell surfaces. Depending on the phytoplankton species and the composition of the culture medium, the cell surface was found to be enriched by 2.4±0.6 ‰ to 2.9±0.1 ‰ for Fe^{2+} containing solution and 0.4±0.2 to 1.0±0.2 ‰ for Fe^{3+} solution (Mulholland et al., 2010). However, the fractionation of Fe between cells, colloids and exometabolites remains unknown. Assuming that the cell surface may serve as analogue for cell exometabolites in terms of Fe local structure, we infer that adsorbed Fe(III) present in the form of individual $Fe\text{-}O_6$ octahedra linked to the phosphoryl or carboxyl groups of the cell wall (Gonzalez et al., 2009, 2010), also should form strong bonds with C, N or P as second neighbor of LMW phytoplankton exometabolites. Similar to zinc, the enrichment of cell surface (and cell exometabolites) by heavy isotopes may be linked to shortening of Me-O bonds and decreasing metal's coordination number (e.g., Gélabert et al., 2006).

The complexation of aqueous Fe(III) with strong organic chelates such as desferrioxamine-B (DFO-B) is known to enrich the Fe-organic complexes in heavy isotope compared $Fe^{3+}(H_2O)_6$ species with an isotopic shift of 0.90±0.23 ‰ (Dideriksen et al., 2008). This is in accord with quantum mechanical calculations which predict that the heavier isotope should concentrate in the species in which it is bounded most strongly (Criss, 1999). However, the relative enrichment of LMW organic-rich fraction (< 1 kDa) compared to Fe-rich colloids (< 0.22 µm) measured in this study is between 1.5 and 4.0 ‰ which is still higher than that known for strongest chelates. Possible explanations for this a priori disagreement may include: 1) the relative stability of LMW Fe(III)-fulvic complexes exceeds that of the synthetic chelates or 2) the conformational changes of Fe local structure, and the dissymmetry of the octahedral environment of Fe bound with organic ligands in LMW fraction is different from Fe chelates. These factors may lead to additional enrichment of organic complexes by heavy isotope.

In summertime, the photoreaction of Fe(III) under the visible range of light and UV may produce labile (< 100 Da) Fe, as shown in experiments on boreal stream waters (Kelton et al., 2007). This photoreduction, which exhibits a diurnal pattern (Emmenegger et al., 2001), may lead to a replacement of essentially allochthonous large-size humic and fulvic complexes at nighttime by LMW ligands of phytoplankton exometabolites appearing during daytime photosynthesis especially pronounced in lake setting (Shirokova et al., 2010). All studied subarctic surface waters were sampled in July during the Arctic summer, then the solar illumination was the highest. The photoreduction of Fe(III)organo-ferric colloids remain the last and virtually unknown possibility of acquiring highly positive values of δ^{57}Fe in LMW fraction and increasing of δ^{57}Fe during progressively decreasing filtrates and ultrafiltrates. If we hypothesize that the small-size organic complexes of photoreduced Fe are enriched in heavy isotope with the fractionation factor relative to Fe(III) source colloids between 1.003 and 1.004, then the progressive increase of filtrates and ultrafiltrates in isotopically heavy Fe relative to retentates (or large-size filtrates) will produce the observed increase of δ^{57}Fe with decrease of *i*) size fraction, *ii*) Fe concentration and *iii*) Fe/C ratio.

5.5.4. Climate and lithological effects on subarctic versus temperate watersheds and consequences for Fe transport to the Arctic Ocean.

The trend of isotopic composition change in the course of filtration and ultrafiltration is similar between subarctic and temperate rivers and streams (Fig. 5.9). However, at otherwise close Fe/C ratios, the absolute values of δ^{57}Fe are distinctly shifted by -1 ‰ in temperate Senga River draining podzol soils developed on quaternary sand alluvial deposits compared to subarctic Palojoki River draining Archaen and Proterozoic acidic and basic magmatic rocks overlaid by thin (less than 10 cm) podzol soils. It is possible that the difference in lithological substrate and the regime of groundwaters define the initial composition of surface waters. First, the role of groundwater discharge of presumably isotopically light anoxic waters should be more important in large Senga River compared to small Vostochniy stream fed by humic lake (OR-6) and by surface soil runoff waters. Second, the concentration of river suspended matter in large Senga River (50 - 150 mg/L, Sidorenko, 1966) is significantly higher than that in small Palojoki River and Vostochniy stream (< 10 mg/L, this study). Therefore, the signature of isotopically light silicate material present in river-borne particles compared to more positive value of riverine colloids (e.g., Escoube et al., 2009) may explain the difference between small subarctic streams and large temperate river. And finally, production of Fe isotopically-heavy LMW organic ligands via photoreduction, heterotrophic bacterioplankton respiration and phytoplankton metabolism may be different between small subarctic stream and large temperate river.

Overall, significantly heavier isotopic composition of small subarctic streams compared to previously reported large temperate and tropical rivers (Beard et al., 2003b; Fantle and DePaolo, 2004; Bergquist and Boyle, 2006; Escoube et al., 2009) or as it is inferred from boreal river particle analysis (Ingri et al., 2006), suggest that the dissolved load of other large rivers cannot serve as a proxy for Fe isotopic composition in the river discharge from the land to the Arctic ocean. Moreover, even higher enrichment by heavy isotope of LMW fractions (< 1 kDa) may add very important constrains on terrestrial isotopic signature of Fe transport to the Arctic Ocean. This small, previously overlooked soluble fraction is: *i*) less likely to coagulate in the estuarine zone and *ii*) potentially more bioavailable for aquatic microorganisms compared to usually considered < 0.22 µm fraction. Indeed, it has been recently shown that the isotopic fractionation of Fe during estuarine mixing is negligible (De Jong et al., 2007; Escoube et al., 2009), even when there is a coagulation of Fe oxy(hydr)oxide (Bergquist and Boyle, 2006). In estuarine mixing experiments, it was also shown that the iron oxyhydroxide colloids of the river water aggregate into much larger particles while the organic colloidal phase remained virtually unaffected (Stolpe and Hassellov, 2007). Therefore, it is not excluded that the isotopic signature of most labile and potentially bioavailable Fe fraction in the Arctic Ocean will be up to +4 ‰ heavier compared to the silicate terrestrial source material transported in the form of river suspended matter. This is constituent with increasingly heavier δ^{57}Fe delivered by rivers to the ocean as latitude increases as inferred from soil studies (Poitrasson et al., 2008). The climate warming in high latitudes should intensify both photoreduction and plankton exometabolite production due to the water temperature increase and as such, the relative input of isotopically heavy Fe to the Arctic ocean will further increase in the next decades, thereby providing an other, new tracer of global warming.

5.6. Conclusions

During filtration and ultrafiltration of organic- and Fe-rich surface waters of small boreal watersheds we observed unprecedentedly large variations of Fe isotopic composition (with δ^{57}Fe relative to IRMM-14 ranging from -0.9 to +4.2 ‰. The suboxic groundwater, soil solutions and bog waters exhibit close to zero, and therefore similar to the continental crust value, or slightly negative isotopic signature (δ^{57}Fe from -0.5 to 0‰). In contrast, the oxygenated rivers and streams contain HMW colloids (1 µm – 10 kDa) and subcolloidal particles (40 µm to 0.1 µm) having positive δ^{57}Fe (from 0.5 to 2.0 ‰). A novel and unexpected finding is that small size, Fe-poor, C-rich colloids and conventionally dissolved LMW fraction (< 1 kDa) exhibit even higher enrichment in heavy isotope with δ^{57}Fe value reaching up to +4.2 ‰. This result does not support the common view, established from analysis of filter particulate material, that boreal C-rich soluble fraction should be isotopically light and colloidal Fe(III)oxyhydroxide should be isotopically heavy. Contrary to what is expected from laboratory Fe(III) oxy(hydr)oxide precipitation from Fe(II)-bearing aqueous solutions in inorganic systems, the natural organo-ferric colloids are getting progressively enriched in heavy isotope with the decreasing of their molecular size, i.e., when moving in the direction "particulate Fe oxy(hydr)oxide → dissolved Fe”. The ratio Fe/C in colloids seems to be one of the major factors controlling their isotopic composition; however, there is a systematic difference in δ^{57}Fe dependence on Fe/C between subarctic and temperate surface waters, possibly, linked to the different nature of initial mineral substrate and bog/soil water regime.

Tentatively, the observed results could be explained by a sequence of the following processes: 1) Fe(II)-bearing bog and soil solution oxidation with formation of isotopically heavy Fe(III) large-size organic-rich colloids and particles at the redox front between anoxic soil and groundwaters and organic-rich surface bog waters, 2) transformation of organo-ferric colloids in open-water small lakes and bog water surface or within the stream flow which may include but not limited to: *i*) photoreduction of Fe(III) with formation of Fe(II)-organic complexes, *ii*) microbial heterotrophic respiration of dissolved organic matter, producing small size organic ligands complexing Fe(III) and *iii*) appearance of phytoplankton LMW exometabolites complexing Fe(III). These processes should destabilize the original Fe(III), C-bearing colloids and produce more stable autochthonous Fe complexes and colloids. All three possible pools of autochthonous Fe-organic complexes where Fe is bound stronger than in the Fe(III) oxy(hydr)oxide polymers are likely to have heavier isotopic composition compared to the source material, as it is known from the basic principles of quantum mechanics. However, at present, none of the mentioned processes has been subjected to laboratory quantification for Fe isotopic fractionation and as such the future experimental work is needed to calibrate Fe isotopic fractionation in boreal organic-rich waters. The importance of LMW isotopically heavy fraction for Fe transport from the land to the Arctic Ocean stems from its higher mobility through the estuarine mixing zone and its potentially high bioavailability. As a result, the small-size, Fe- and organic carbon rich coastal rivers and streams may play very important and yet underestimated role in the overall Fe chemical and isotopic budget of the Arctic Ocean.

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TABLES

Table 5.1. List of sampled waters and their bedrock compositions.

sample name	description	GPS coordinates		bedrock composition	Age
KAR-1	Palojoki river, middle course, North Karelia	N 66°12´	E 30°28´	Micro-pegmatic granites, Granosyenites, Syenites, Syeno-diorites	PR_1
KAR-3	Palojoki river, mouth reach, the zone of mixing river and Pyaozero lake, North Karelia	N 66°11´	E 30°34´	Biotite granitogneisses and biotite, biotite-amphibolite and amphibolites	AR_1
ZPBL	Bog of the Tsipringa lake basin, North Karelia	N 66°17´	E 30°53´		
OR-1	Stream Vostochniy, mouth reach, the zone of mixing river and Tsipringa lake, North Karelia	N 66°18´	E 30°42´	Meta-gabbro	PR_1
OR-6	Top feeding lake of stream Vostochniy, North Karelia	N 66°18 ´	E 30°40´		
OR-9	Soil solution of stream Vostochniy basin, about 500 m from the top feeding lake, North Karelia	N 66°18´	E 30°40´		
Seng-1	Senga river, mouth reach, Central Russia	N 55°52´	E 39°31´	Cretaceous: aleurite, sand with layers of clays and sandstones; Quarternary alluvial flat deposits: sand with gravel and pebble, clay loam, sandy clay (to 20 m).	$K_{1g2\text{-}br}$ Q_{IV}
Seng-2	Senga river, middle course, Central Russia	N 55°50´	E 39°24´		
Ign	Ignatkovo lake, Central Russia	N 55°53´	E 39°26´	Cretaceous: aleurite, sand with layers of clays and sandstones; Quarternary bog deposits: peat, sandy clay (to 5 m).	

Table 5.2. Chemical and isotopic composition of filtrates and ultrafiltrates.

sample	δ^{57}Fe (‰)	2SE	[Fe], µg/L	DOC, mg/L	pH	HCO_3^-, mg/L	Mineralization, mg/L	O_2, %
2009								
OR-9/20µm	-0.253	0.127	9863	141	3.9	0	14	40
OR-9/5µm	-0.318	0.058	9794	138	3.9			
OR-9/0.8µm	-0.317	0.033	8613	135	3.9			
OR-9/0.22µm	-0.288	0.123	6821	55	4.2			
OR-9/100kDa	-0.154	0.089	1851	27	4.4			
OR-9/10kDa	-0.311	0.019	1034	12	4.4			
OR-9/1kDa	-0.833	0.024	842	11	4.6			
OR-9/F20µm	-0.210	0.085						
OR-9/F5µm	-0.202	0.052						
OR-9/F0.8µm	-0.320	0.053						
OR-9/F0.22µm	-0.311	0.030						
OR-9/F100kDa	-0.459	0.017						
OR-9/F10kDa	-0.422	0.097						
OR-9/F1kDa	-0.377	0.137						
OR-1/5µm	0.844	0.028	238	14.7	7.1	17.4	13.5	100
OR-1/0.8µm	1.149	0.031	218	13.2	7.1			
OR-1/0.22µm	2.212	0.067	150	12.7	7.2			
OR-1/0.1µm	2.427	0.111	120	12.2	7.2			
OR-1/100kDa	3.486	0.149	78	11.8	7.2			
OR-1/10kDa	4.186	0.111	48	10.7	7.2			
OR-6/20µm	1.857	0.168	150	16.7	6.3	13.42	10.6	100
OR-6/5µm	1.923	0.174	142	15.1	6.3			
OR-6/0.8µm	1.939	0.143	136	14.9	6.3			
OR-6/0.22µm	2.666	0.261	124	14.6	6.3			
OR-6/0.1µm	2.922	0.068	100	14.5	6.3			
OR-6/100kDa	3.215	0.109	96	14.3	6.4			
OR-6/10kDa	3.400	0.150	68	14.2	6.4			
ZPBL/20µm	-0.045	0.320	7651	58.	4.9	25.3	79.7	50
ZPBL/5µm	0.663	0.045	8306	48	4.9			
ZPBL/0.8µm	0.080	0.105	9694	41	4.9			
ZPBL/0.22µm	0.238	0.007	9348	35	5			
ZPBL/0.1µm	0.121	0.100	9743	32	5			
ZPBL/100kDa	0.302	0.037	1257	11	5.1			
ZPBL/1kDa	-0.909	0.099	49	10	5.3			
KAR-1/20µm	0.487	0.177	1708	17.7	6.9	16.4	12.4	100
KAR-1/5µm	0.550	0.069	1621	11.1	6.9			
KAR-1/0.8µm	1.054	0.106	743	10.9	6.9			
KAR-1/0.4µm	1.251	0.089	243	10.8	7			
KAR-1/0.22µm	1.350	0.089	215	10.7	7			
KAR-1/0.1µm	1.320	0.057	287	10.6	7			
KAR-1/100kDa	1.256	0.080	165	10.5	7			
KAR-1/10kDa	1.971	0.119	38	9.7	7.1			
KAR-1/1kDa	1.804	0.180	19	8.3	7.1			
KAR-1/0.4µm-1kDa	1.773	0.046						

Table 5.2, continued.

2008								
KAR-1/100µm	0.518	0.081	1363	12.6	6.4	16.41	29.03	100
KAR-1/0.4µm	1.746	0.086	192	10.9	6.5			
KAR-1/10kDa	2.259	0.123	51	10.5	6.9			
KAR-1/1kDa	2.220	0.097	17	9.4	7			
KAR-3/100µm	0.382	0.083	944	10.9	6.3	20.31	31.26	
KAR-3/0.4µm	1.642	0.091	183	10.8	6.6			
KAR-3/1kDa	2.437	0.020	7	7.6	7.5			
Seng-1/0.4µm	0.637	0.054	1076	55	7.0		76.40	100
Seng-1/100kDa	0.785	0.058	453	52	7.0			
Seng-1/10kDa	1.240	0.113	76	35	7.0			
Seng-2/100µm	-0.024	0.136	5385	79	7.0	86.99	93.10	100
Seng-2/0.4µm	0.422	0.136	743	44	7.0			
Seng-2/100kDa	0.628	0.101	430	41	7.0			
Seng-2/10kDa	0.970	0.051	92	32	7.0			
Ign/0.4µm	0.547	0.110	164	48	5.4		6.02	50
Ign/100kDa	0.600	0.065	142	17	5.4			
Ign/10kDa	0.639	0.043	105	16	5.4			

"F" before size fraction stands for filter retentates (samples from the OR-9 series).

FIGURES

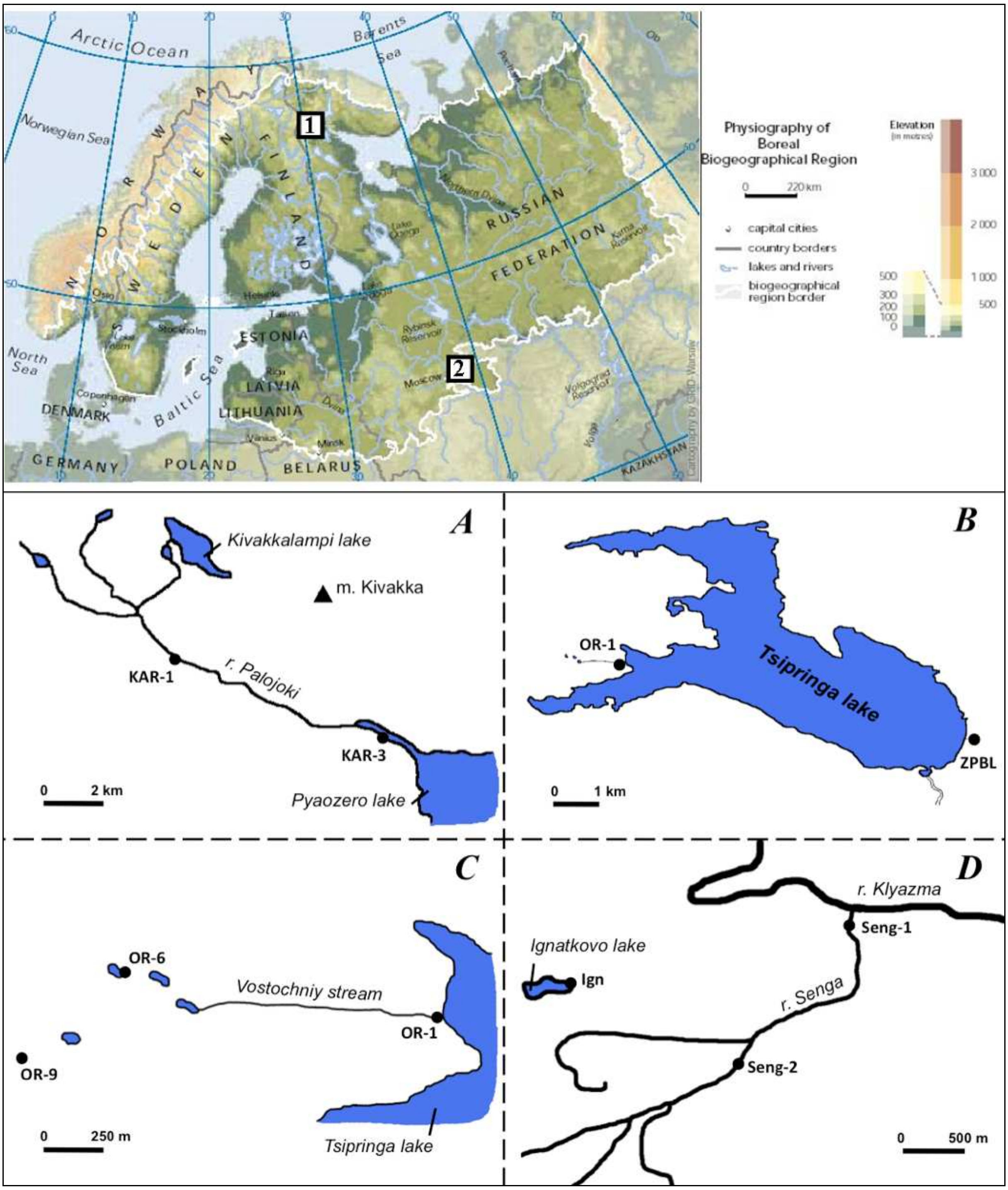


Figure 5.1. Map of boreal zone (*Source: EEA. UNEP/GRID Warsaw final map production from http://www.eea.europa.eu)* with the studied area and sampling sites of the Palojoki river (*A*), the bog ZPBL of Tsipringa lake watershed (*B*), Vostochniy stream watershed (*C*) of Karelia region (1) and Senga river (*D*) watershed of Central Russia (2).

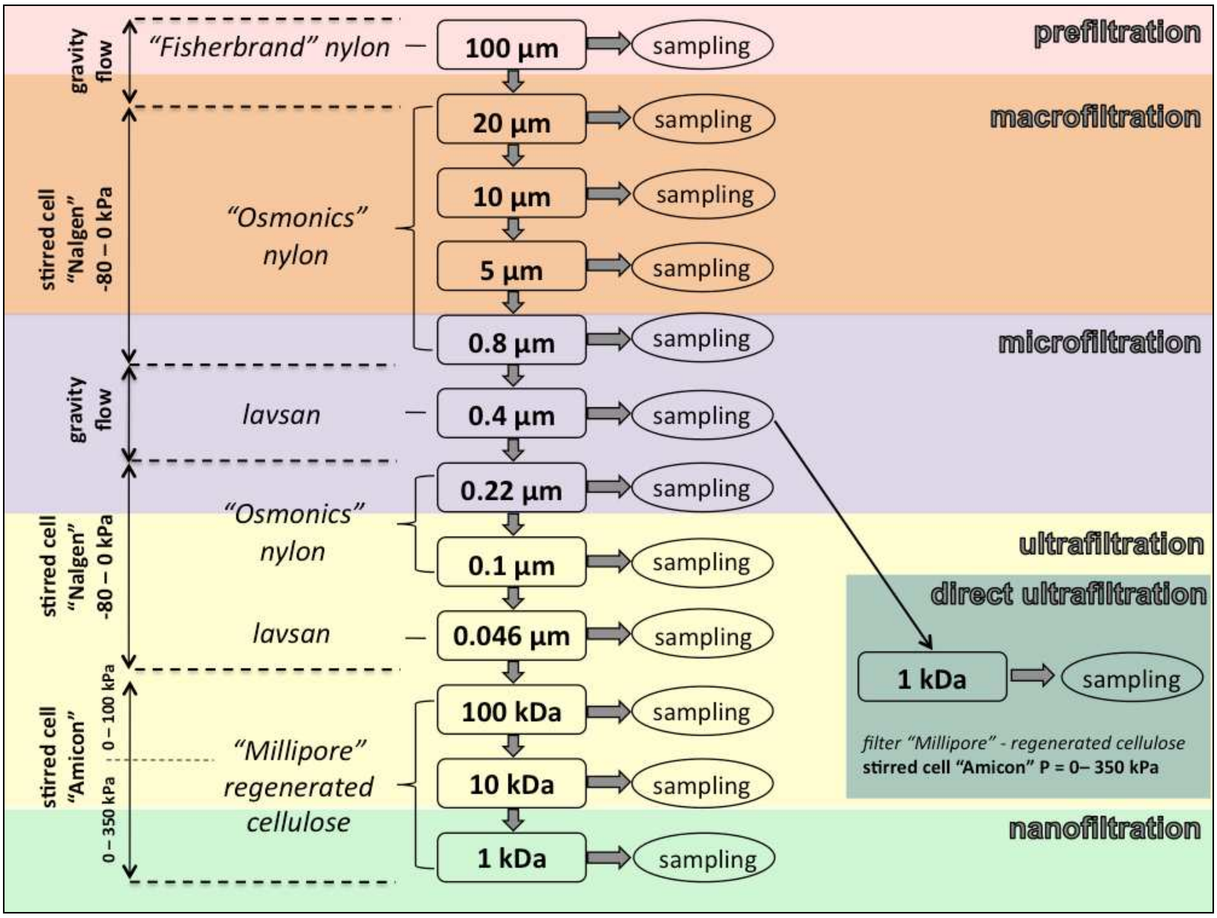


Figure 5.2. The scheme of cascade filtration used in this study. Lavsan is the trade name for polyethylene terephthalate fibers.

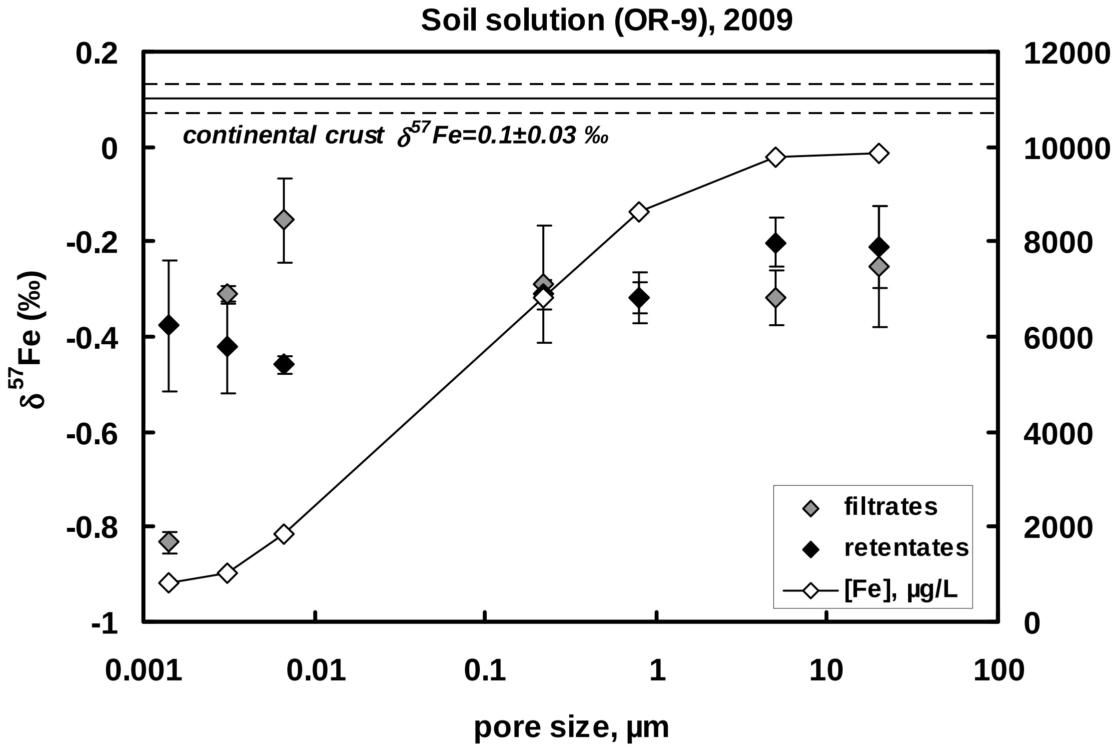


Figure 5.3. δ^{57}Fe (closed symbols) and Fe concentration (open symbols) as a function of pore size in a soil solution (OR-9) filtrates and retentates of Vostochniy stream basin. The isotopic composition of the continental crust (δ^{57}Fe = 0.1 ±0.03 ‰; Poitrasson, 2006) is shown for reference.

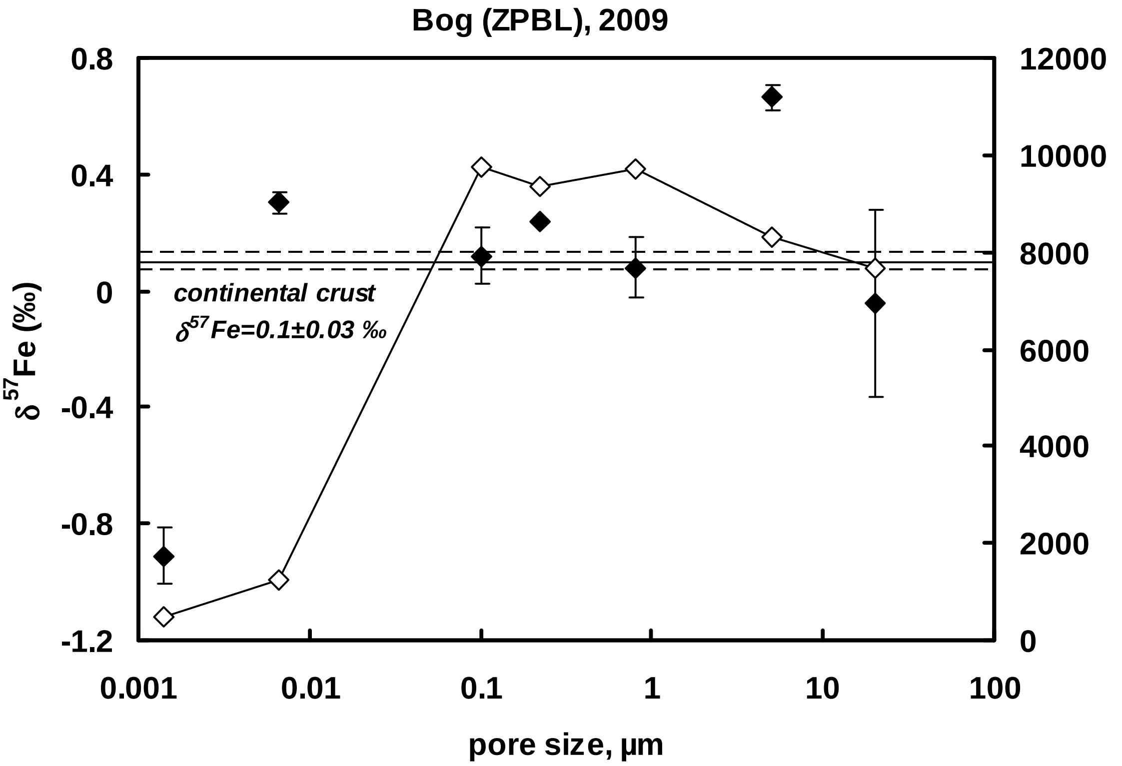


Figure 5.4. δ^{57}Fe (closed symbols) and Fe concentration (open symbols) as a function of pore size in a bog (ZPBL) filtrates of Tsipringa lake basin.

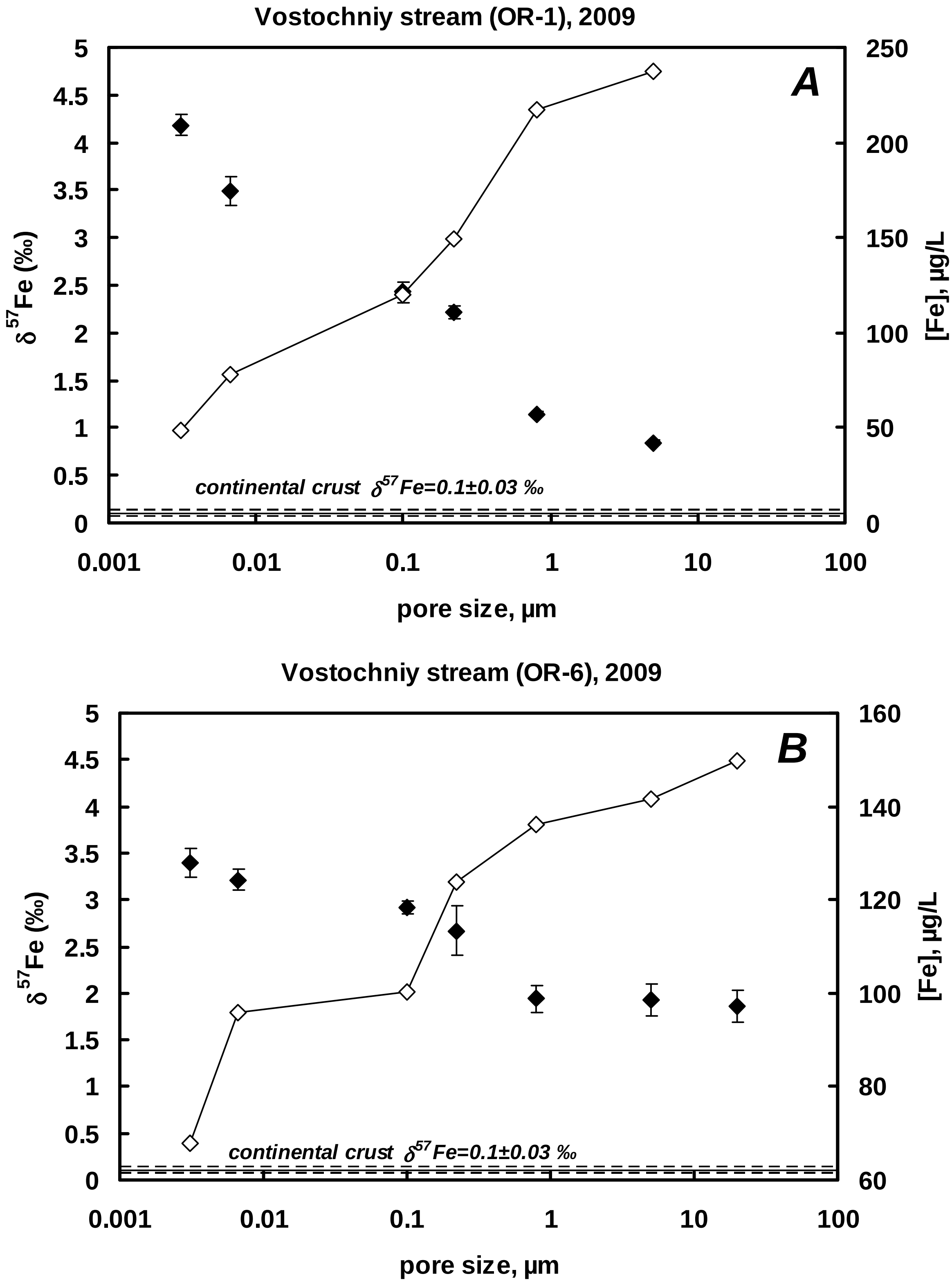
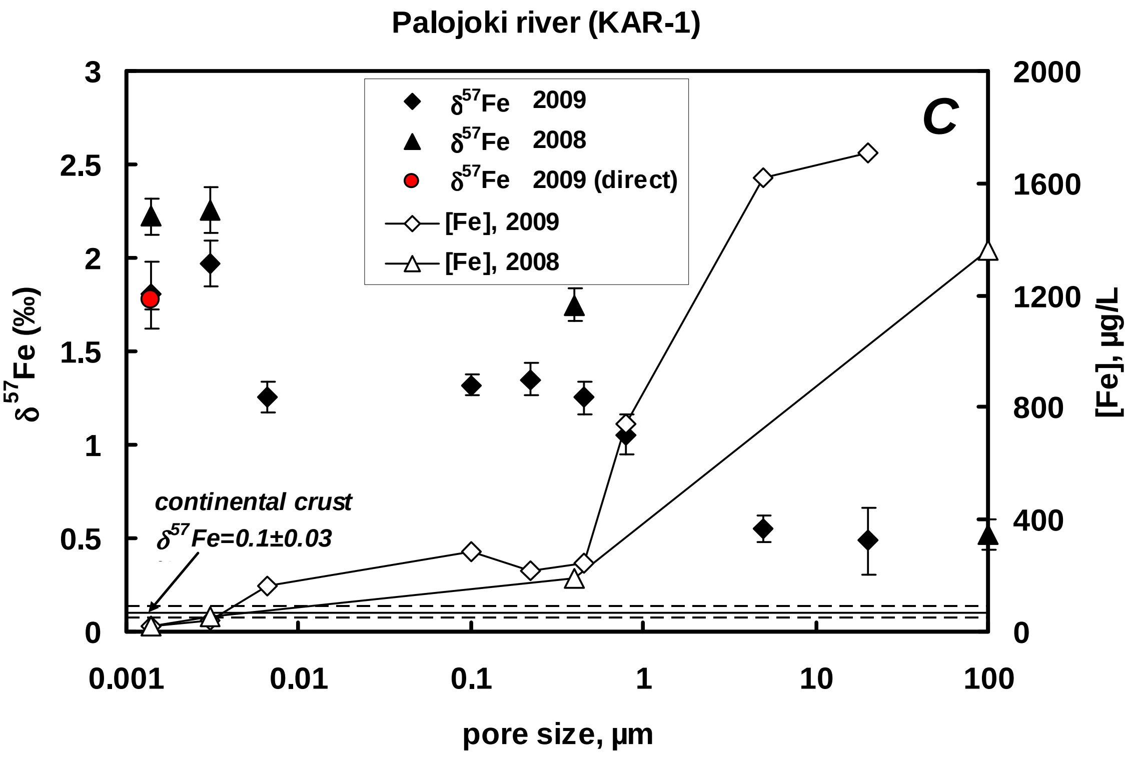


Figure 5.5. δ^{57}Fe (closed symbols) and Fe concentration (open symbols) as a function of pore size in subarctic surface waters, A: mouth reach of Vostochniy stream (OR-1), B: feeding lake of Vostochniy stream basin (OR-6),



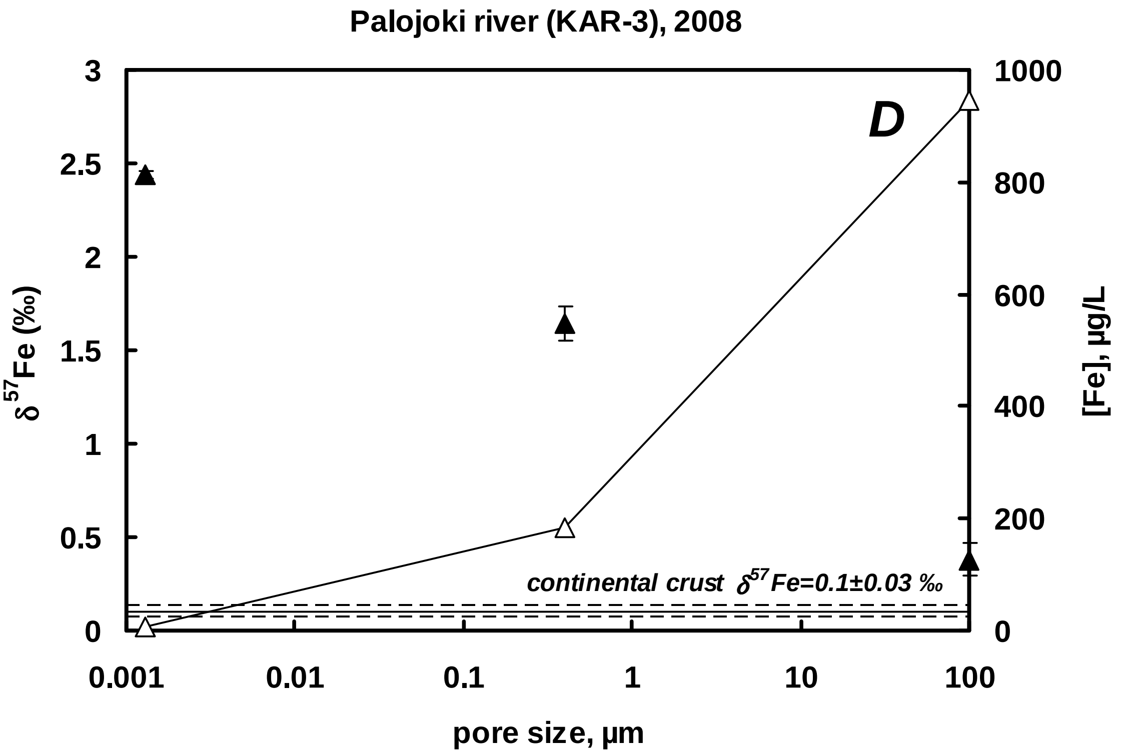


Figure 5.5, continued. δ^{57}Fe (closed symbols) and Fe concentration (open symbols) as a function of pore size in subarctic waters, C: middle course of Palojoki River (KAR-1), D: mouth reach of Palojoki River (KAR-3).

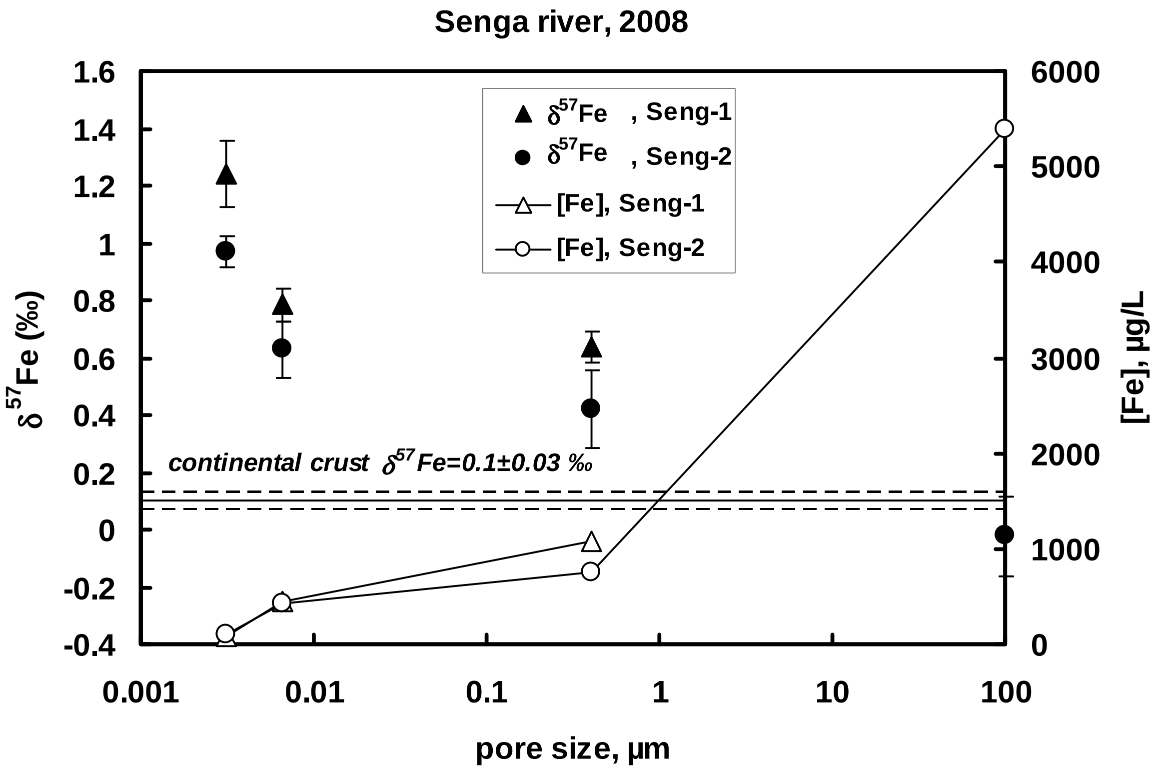


Figure 5.6. δ^{57}Fe (closed symbols) and Fe concentration (open symbols) as a function of pore size in filtrates of temperate Senga River, Seng-1 represents the mouth reach, and Seng-2 represents the middle course flow.

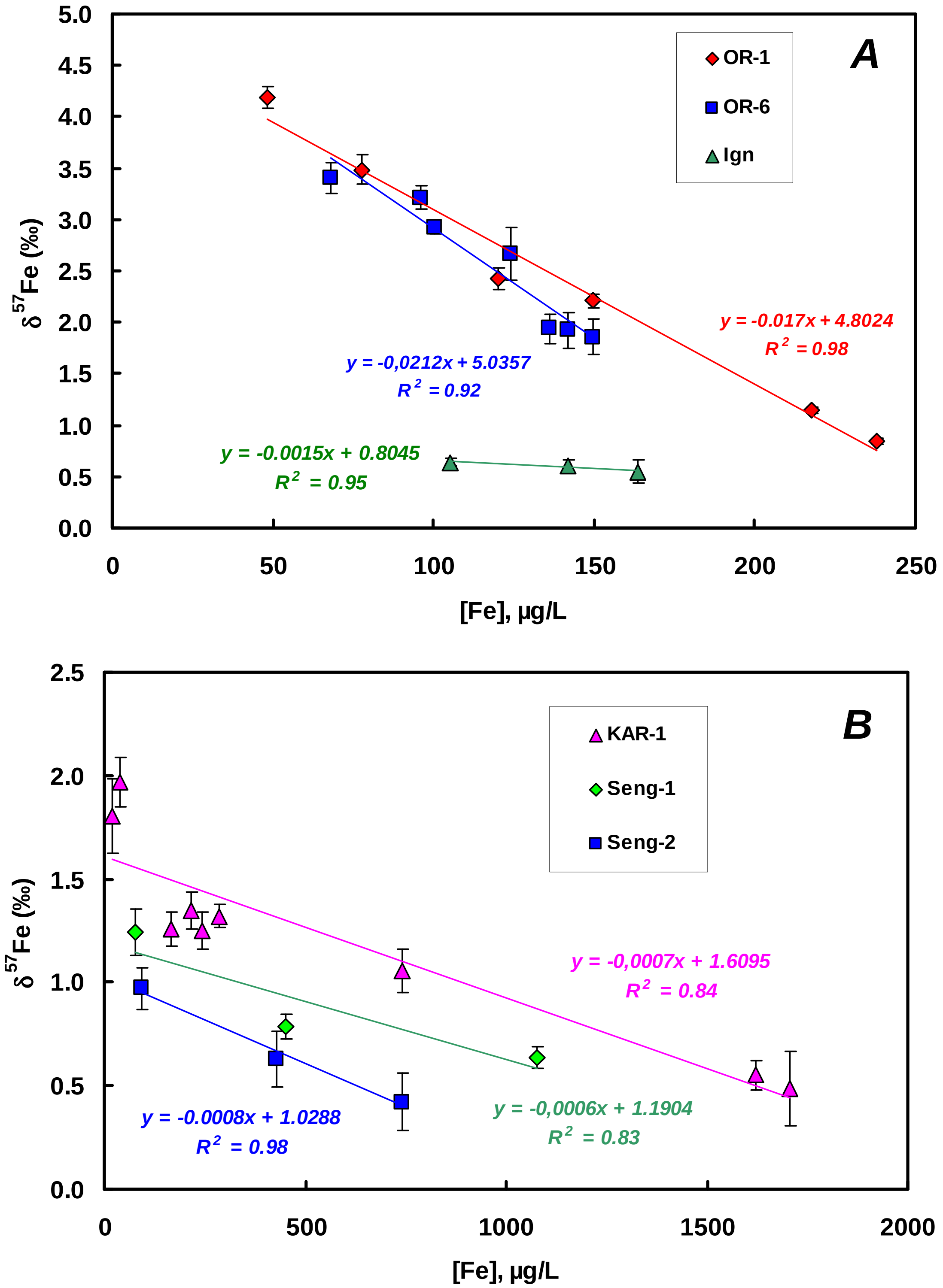


Figure 5.7. δ^{57}Fe as a function of Fe concentration in filtrates of iron-poor waters (A) and iron-rich waters (B). OR-1 is mouth reach of Vostochniy stream, OR-6 is feeding lake of Vostochniy stream basin, Ign is Ignatkovo lake, KAR-1 is middle course of Palojoki River, Seng-1 is mouth reach of Senga River, Seng-2 is the middle course of Senga River.

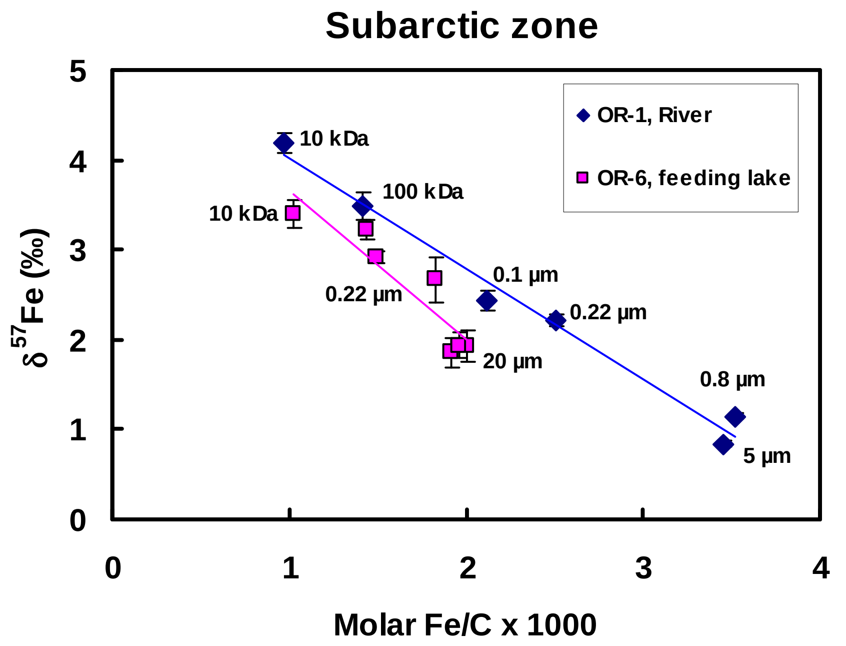


Figure 5.8. δ^{57}Fe as a function of molar Fe/C ratio in filtrates and ultrafiltrates of Vostochniy stream and its feeding lake.

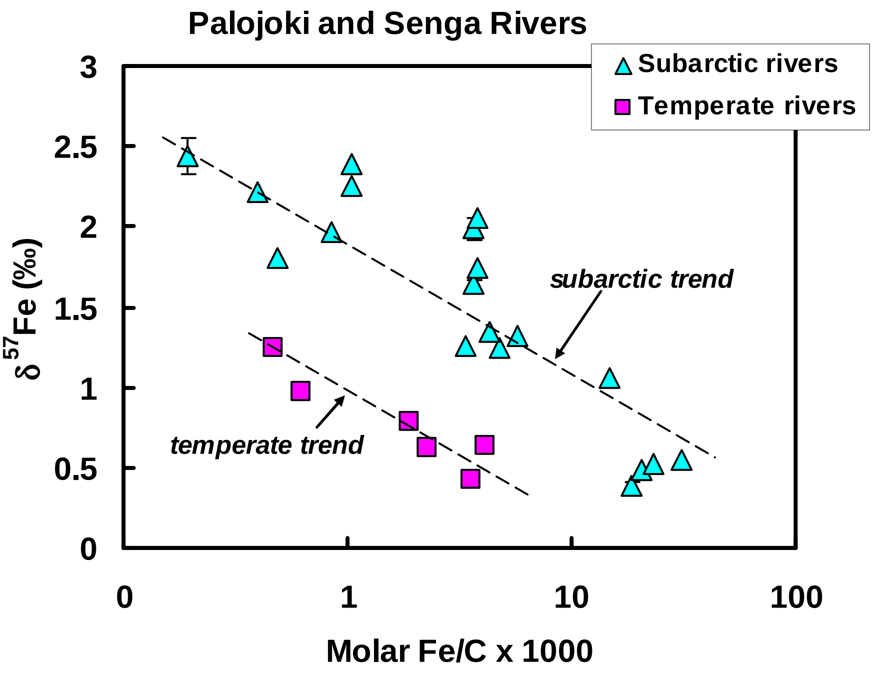


Figure 5.9. δ^{57}Fe as a function of molar Fe/C_{org} ratio in filtrates and ultrafiltrates of temperate and subarctic rivers (samples Seng and KAR, respectively).

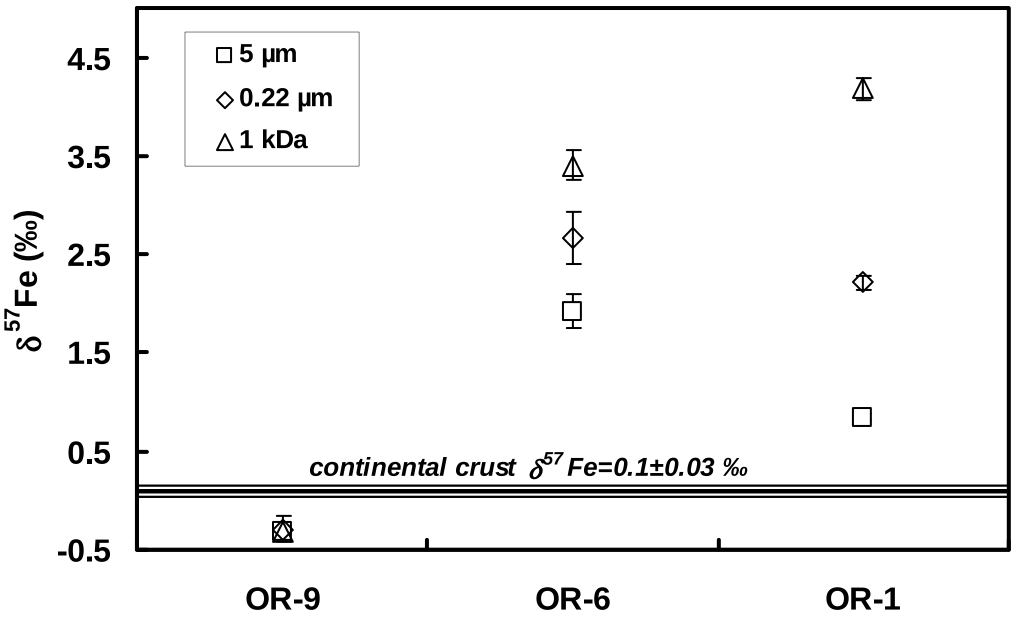


Figure 5.10. The variation of Fe isotopic composition in 0.22 and 5 µm filtrates among soil solution (OR-9), feeding lake (OR-6) and Vostochniy stream (OR-1) mouth of subarctic site.

ELECTRONIC ANNEX

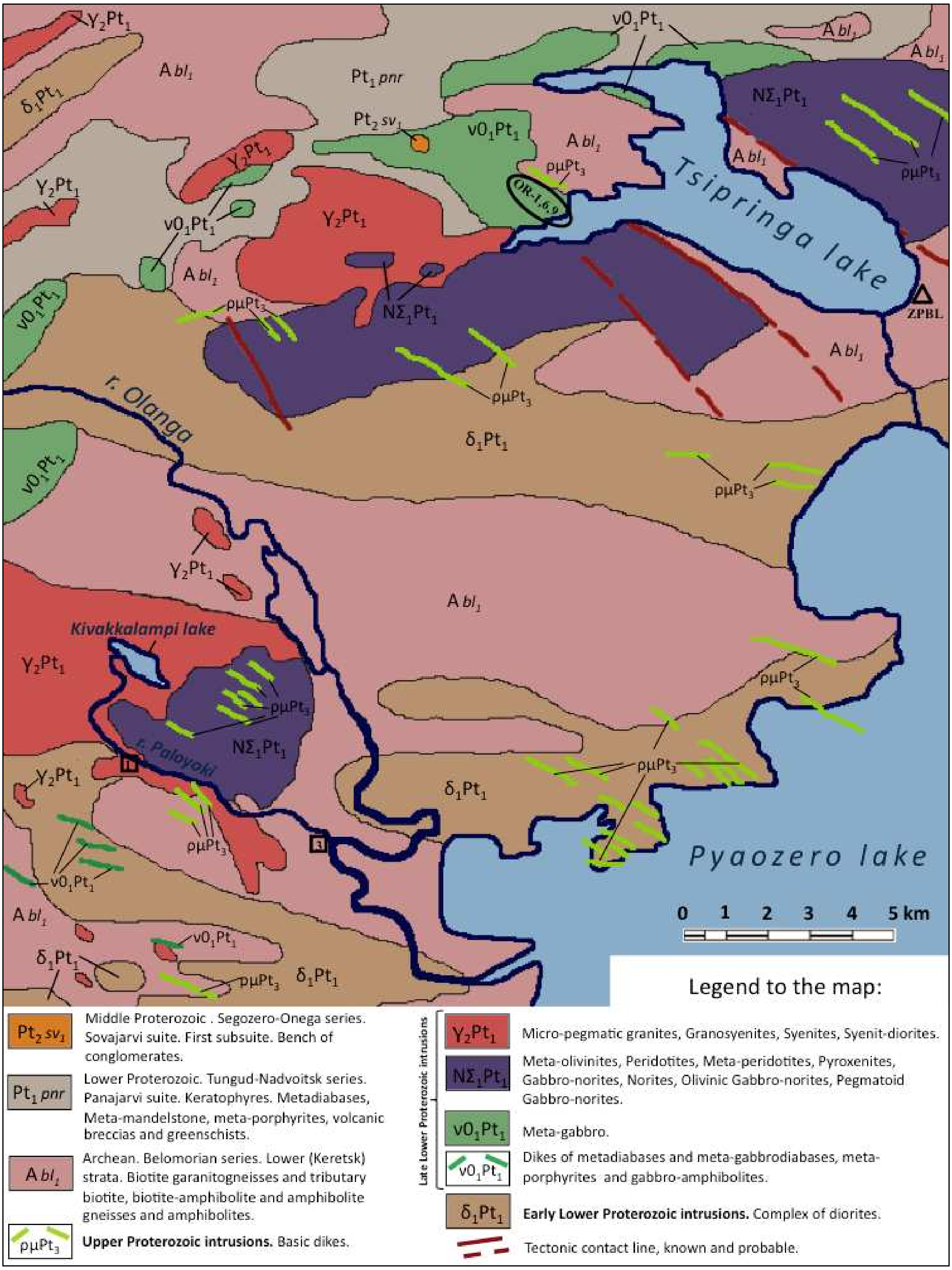


Figure ESM-5.1. Geological map of Karelia region (NW Russia) with sampling points.

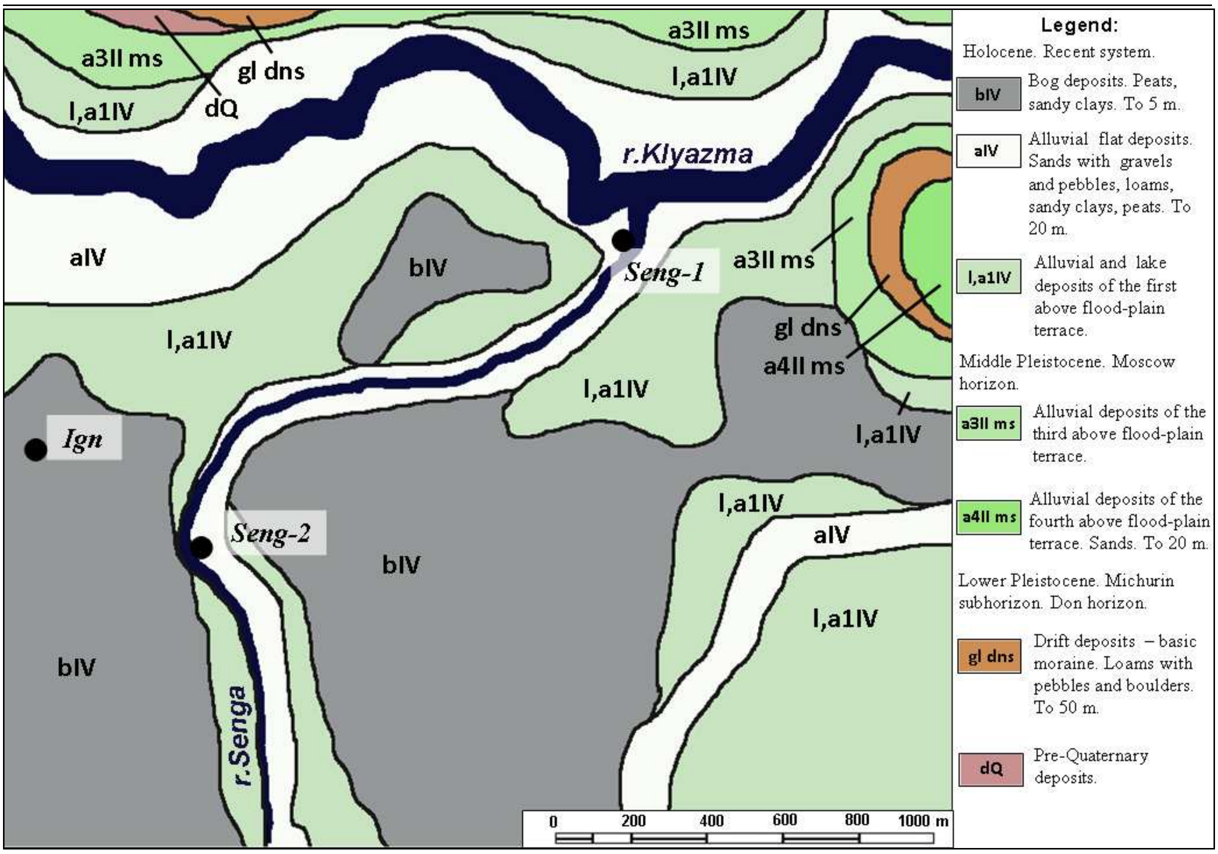


Figure ESM-5.2. Quarternary deposits map of Vladimir region (Central Russia) with sampling points.

ESM-5.3. Description of climate, topography, soil and vegetation of the regions.

5.3.1. North Karelia, NW Russia

5.3.1.1. Climate

The climate of the region is mild-cold, transitional between oceanic and continental, with a determinant influence of the Arctic and Northern Atlantics. Winter is long and soft, summer is short and cool. Average temperature in January is -13°C, and +15°C in July, but extremes can reach -45° to +35°C in winter and summer periods, respectively. The dominant wind direction is South-West in winter and North-East in summer. Average annual precipitation amount is between 450 and 550 mm/yr. Snow period lasts from October to April-May with the average thickness of snow cover 70 - 80 cm, but often over than 1 m. The territory is under the influence of the warm Gulf Stream, but microclimatic conditions differ dramatically because of the large cross-country. In summer in the deep and sheltered valleys it's much warmer than on the mountain tops, whereas in winter it's much colder in the valleys where the mountains cold air accumulates.

5.3.1.2. Topography

Tectonics and glaciation shaped the terrain of Karelia. Crustal snaps and step faults, reaching in two mutually perpendicular directions: the north-west to south-east and south-west to north-east have formed as a result of tectonic processes. Traces of glaciation occur in the glacial landforms that presented in moraine ridges extended from the north-west to south-east.

Much part of the region is a hilly plain with elevations of 200 m. Along the White Sea coast there is a wide zone of lowland Pribelomorskaya with elevations less then 100 m. In the western part, on the border with Finland, moraine ridge Maanselkya is located, it represents a watershed between the basins of the Baltic and White Seas.

Our study area is located in the most elevated part of Karelia, in the central part of Maanselkya. It is a landscape of tectonic denudation hills, plateaus and ridges with an average altitude of 300-400 meters with separate insulated massifs (Tunturi).

5.3.1.3. Hydrology

The region has a well-developed river network that flows via a system of glacial lakes. The water of small and medium-sized lakes warms up to 22-25°C in summer. Water is soft, low mineralized, often with a brown hue because of feeding swamps.

The large number of wetlands is typical feature of North Karelia. The small marshes with area from 3-5 to 30-50 hectares are dominated. A kind of "hanging" (omrotrophic) bogs is formed on the steep slopes. By the nature of their feeding, Karelian rivers belong to the mixed type, fed by rainfall, bogs, groundwater and snowmelt. The rivers break up earlier than their conjugated lakes and some full of rapids reaches don't freeze at all. The average date of floods in North Karelia is April 25 - May 5. The rivers freeze in November - December. Natural fluctuations of water level do not exceed 1.5-2 m.

Rivers of Karelia are comparably short. Significant part of their length (up to 50%) may consist of the flowage lakes. There are « lake-river » systems, consisting of a chain of lakes connected by rapids channels. The accumulative systems are represented by a lake that collects the water of many rivers and serves as outlet of one larger river are also typical for Karelia. Another peculiar phenomenon is a bifurcation (splitting) of the water flow. The average gradient of rivers is about 1 m/km, and up to 3-5 m/km in the rapids channels. Rivers of Karelia are very young geologically, and their beds are composed of hard rocks. Because the rivers are~~,~~ just started to make the longitudinal profile, their–valleys are not wide floodplains, and they almost do not have high terraces.

Chemical composition of river waters in Karelia is determined by the chemical weathering of silicate parent rocks of the Baltic crystalline shield and quaternary deposits, and the presence of numerous peatlands. Typical values of total discharge of solids (TDS) for this region are 15-30 mg/l (Maksimova, 1967; Zakharova et al., 2007), and the concentration of river suspended matter is very low. The adjacent lakes between the rivers significantly decrease the size of actual feeding watershed of a given river.

5.3.1.4. Soil, vegetation

The soil cover of the region is very young and it is often absent on ledges of bedrock and steep slopes. Low temperature in combination with high humidity is responsible for the slow humification and mineralization of plant residues. Therefore, a lot of organic matter is accumulated in the form of peaty horizons, and on better drained sites - in the form of coarse humus. Predominant soils are illuvial-humic and illuvial-ferruginous-humic podzols. All types of podzols exhibit a highly acidic reaction and low base saturation of the upper layers.

Coniferous forests dominate the vegetation of the region. The main conifers are pine and spruce. The common deciduous trees are birch, aspen, alder. The sphagnum pine occurs on the plains, depressions and swamps. Sparse understory consists of mountain ash and juniper. It is dominated by blueberries and cranberries in the shrub layer, and green mosses in the lower layer. The rocks are usually covered with patches of black, gray, yellow, red, brown crustose lichens. Herbaceous plants are rare. The main mushrooms are aspen and boletus. There are poisonous plants in Karelia such as, hemlock, cowbane, mezereon.

5.3.2. Meschera lowland, Vladimir region, Central Russia

5.3.2.1. Climate

The climate of the region is temperate continental with very cold long winters and warm humid summers. Winter is long and soft, summer is short and cool. Average temperature in January is -10.1°C, and +18.2°C in July, average annual temperature is +4.4°C. Annual average surface temperature is 4.8°C, an amplitude of annual variations is 33.9°C. The frost-free period lasts from May 20 to September 20. Average annual precipitation amount is about 700 mm/yr. About 55% (387.5 mm) of precipitation falls in the warm season.

5.3.2.2. Topography

Meshchera lowland is one of the largest woodlands of the Russian Plain. The Northern boundary of lowland is r. Klyazma, the West one is r. Moskva, the South one is r. Oka and the East one is the Oka-Tsninsky shaft.

Senga river is a small river; this is a right tributary of the r. Klyazma that drains bogs of Meshchera lowland.

Ignatkovo Lake is a closed lake with marshy shores.

Much of Meschera surface is waterlogged. Klyazma has a terraced surface. Among the marshes there are a lot of overgrown lakes, creeks, oxbow lakes, etc. The average elevations are in the range 100 - 140 m. Terraces, gullies and ravines network, eolian mounds, depressions and lakes lowers of Klyazma valley make a significant variety among the generally flat topography.

5.3.2.3. Hydrology

By the nature of feed r. Klyazma refers to typical lowland rivers of European Russia. The river depth is 1.5 - 2.5 m; flow rate is 0.3 - 0.6 m/sec. The main feeding source in spring period is snowmelt, in summer-autumn period is rain, and in winter is groundwater. The level fluctuations of the river (rises to 2.0 - 3.5 m in spring period) are associated with variation of feeding source.

Lakes are numerous within Meshchera lowland. The larger ones have a surface area of 25 km^2. The amplitude of level fluctuations of lakes is smaller than of rivers (0.8 - 1.5 m). The thicknesses of silt and peat consider about recent sedimentation in lakes and rivers.

Bogs of Meshchera lowland are difficult or quite impassable; they occupy about 35% of the territory. They are located in areas of low relief in the river valleys and low watersheds (with an altitude of up to 125 m). The surface of bogs is almost everywhere forested on 50 - 60%.

5.3.2.4. Soil, vegetation

Meshchera lowland belongs to the southern part of the forest zone, it is characterized by mixed coniferous and deciduous forests; marsh and meadow vegetation is also widely distributed.

Low-lying bogs occupy more than half the area of Meschera lowland, covered by birch, aspen and alder trees. Peat of these bogs is of low quality, the degree of decomposition is 20 - 30% and the ash content is 8 - 16%.

Soils substratum is outwash sands fanned and rewashed during geological history. The soils of the region are mainly sod-podzolic, podzolic-gley and podzolic. All types of podzols exhibit a highly acidic reaction.

Figure ESM-5.4. Field clean room.

Table ESM-5.5. The main filtration characteristics.

pore size	filer size	filter material	filter producer	filtration pressure	filtration unit
100 µm	300*300 mm	nylon	"Fisherbrand", USA	gravity flow	-
20 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
10 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
5 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
0.8 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
0.4 µm	100*250 mm	lavsan	Dubna, Russia	3 - 5 m	-
0.22 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
0.1 µm	Ø 37 mm	nylon	"Osmonics", GE, USA	-80 - 0 kPa	"Nalgen", 250 ml
0.046 µm	Ø 37 mm	lavsan	Dubna, Russia	-80 - 0 kPa	"Nalgen", 250 ml
100 kDa	Ø 76 mm	regenerated cellulose	"Millipore", USA	0 - 100 kPa	"Amicon", 8400
10 kDa	Ø 76 mm	regenerated cellulose	"Millipore", USA	0 - 350 kPa	"Amicon", 8400
1 kDa	Ø 76 mm	regenerated cellulose	"Millipore", USA	0 - 350 kPa	"Amicon", 8400

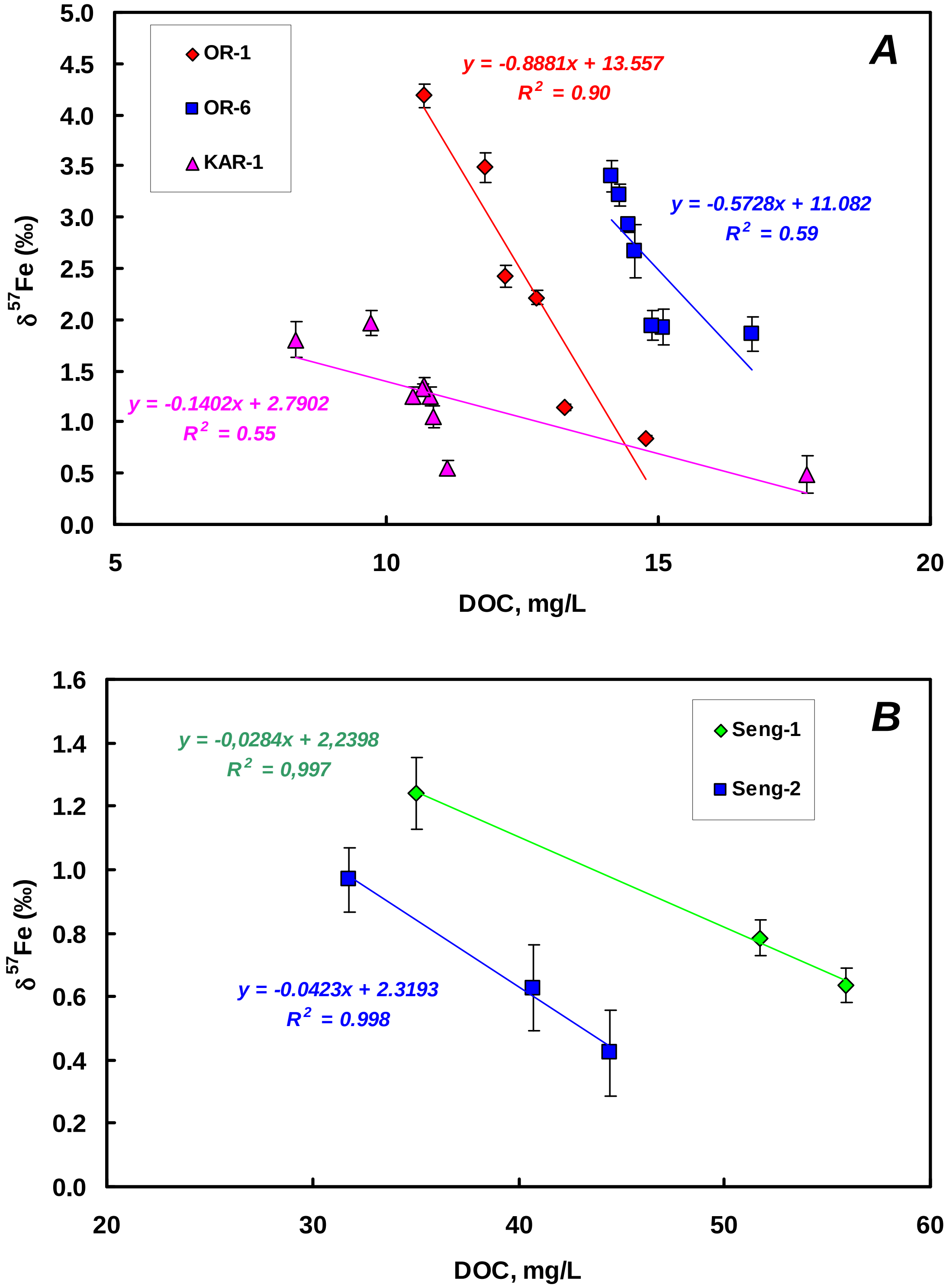


Figure ESM-5.6. δ^{57}Fe as a function of DOC concentration in filtrates of organic-poor waters (A) and organic-rich waters (B). OR-1 is mouth reach of Vostochniy stream, OR-6 is feeding lake of Vostochniy stream basin, KAR-1 is middle course of Palojoki river, Seng-1 is mouth reach of Senga river, and Seng-2 is middle course of Senga river.

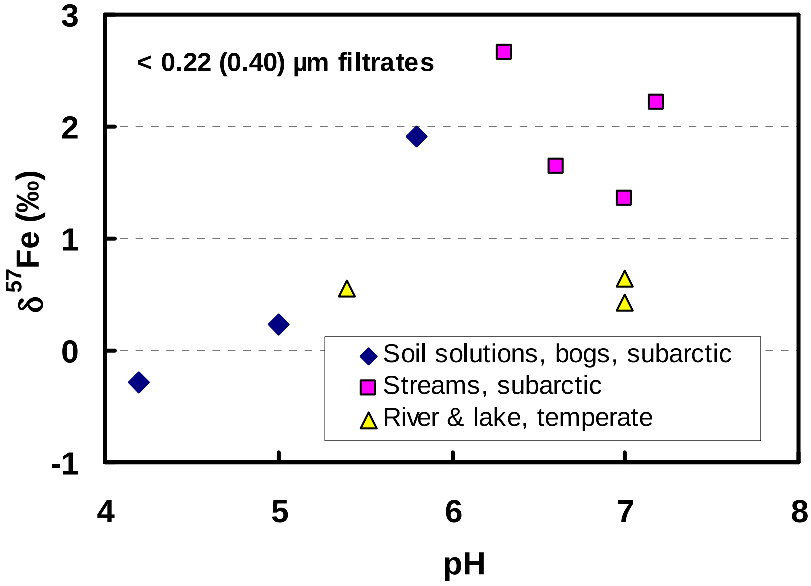


Figure ESM-5.7. A plot of δ^{57}Fe as a function of pH in conventionally filtered (<0.22 or < 0.40 µm) fractions.

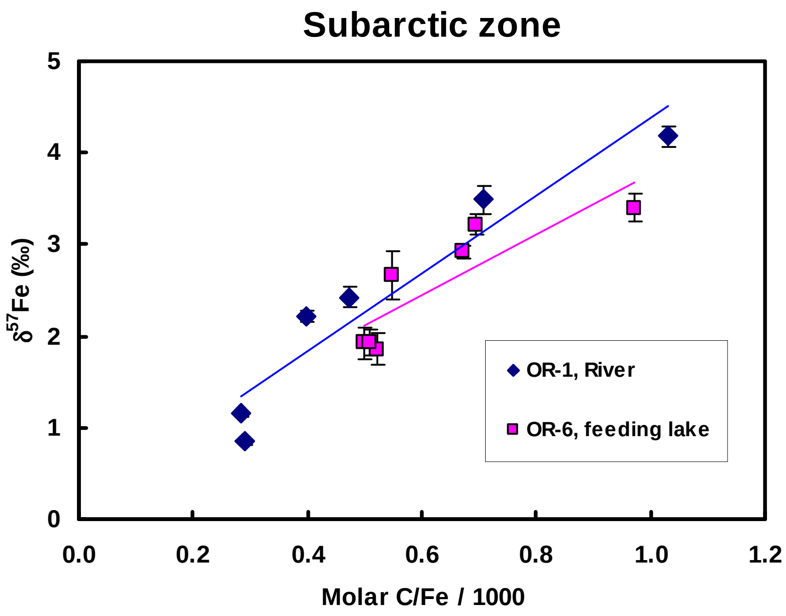


Figure ESM-5.8. Values of δ^{57}Fe as a function of molar C/Fe ratio in filtrates and ultrafiltrates of Vostochniy stream and its feeding lake.

Chapter 6

Conclusions and perspectives

6.1. Conclusions

Following conclusions emerge from this study:

- First part of this thesis was aimed at studying natural organic matter size distribution in the natural waters with different redox and hydrodynamic conditions in the continuum soil solution – bog – stream – feeding and terminal lakes for a small watershed with homogeneous bedrock composition. The significant and systematic changes of basic DOM and molecular size parameters occur in the continuum at the very short distance, less than 2 km of a representative boreal subarctic watershed. Such an evolution reflects the complex process of the interplay between two main sources of DOC – soil humic and fulvic acids from the plant litter and aquagenic exometabolites of phytoplankton and macrophytes – both subjected to bio- and photodegradation, whose degree depends on the residence time of DOM in a given aquatic reservoir.

  Local hydrological regime, the presence of stagnant water bodies and feeding lakes can significantly affect the original allochthonous signature of DOM during its transport from the soil solution to the stream mouth. Moreover, the glacial or thermokarst origin of hydrographic network distribution often suggests the presence of large, oligotrophic terminal lakes as terminus of small subarctic watersheds, in contrast to estuarine mixing zone of the large rivers. As such, small streams may deliver to the ocean the organic carbon that is significantly chemically fractionated among different size fractions and transformed by bio- and photo-degradation processes.

- In the second part of this work, we investigated the molecular weight distribution and colloidal speciation of trace elements in boreal waters from Northern Karelia. The transformation of allochthonous humic–rich soil colloids and progressive enrichment of waters by autochthonous DOM within the sequence from soil solution to the stream and further to the terminal lakes does not bring about measurable change in TE size fractionation. It follows that both photo-and biodegradation processes occurring in studied water systems cannot significantly modify the relative percentage of TE in colloidal (1 kDa – 0.22 µm) fraction. At the same time, we observe a progressive decrease of the degree of TE association with ferric colloids from soil solution towards the terminal lake, also reflected in the decrease of colloidal Fe concentration. This may reflect significant transformation of colloids consisting in *i)* photo- and bio-degradation of allochthonous colloids leading to sedimentation of Fe-rich phases and *ii)* progressive enrichment of dissolved pool by autochthonous organic-rich, Fe-poor dissolve organic matter of periphyton and plankton exometabolites.

Given that the climate warming in high latitudes will produce higher water temperatures and as such will intensify 1) primary productivity of phytoplankton, notably dominance of cyanobacteria over other phytoplankton (Carey et al., 2012); 2) rate of DOM mineralization of heterotrophic bacterioplankton and 3) photo-degradation of colloidal material, the following changes in colloidal size distribution and chemical composition may occur. First, proportion of HMW organic-rich humic-like soil – borne colloids will decrease at the expense of LMW phytoplankton exometabolites. Second, enhanced mineralization of organo-ferric colloids will decrease the ability of insoluble trivalent and tetravalent element to migrate from the soil and riparian/hyporheic zone to the terminal lake. Note that, unlike the permafrost zone, where the rise of air and soil temperature will increase the thickness of thawing depth and will intensify the input of colloids from mineral horizons (cf., Bagard et al., 2011), boreal non-permafrost zone will be much less affected by the change of groundwater regime.

All these aforementioned processes will inevitably increase the flux of LMW, Fe-poor organic colloids to the ocean and as such will potentially deliver more labile and bioavailable DOC and related trace elements, including metal micronutrients, to the coastal biota. As a result of the change of the structure of colloidal flux to the ocean, significant increase of productivity of both autotrophic (nutrients) and heterotrophic (organic matter) components of the food chain may occur. During the open water summer base-flow period, the flux of divalent metals such as Cu, Zn, Pb, Cd, Ni, Co which are present in LMW organic complexes, much more labile through the estuarine mixing zone, will therefore increase. In contrast, the delivery from the land to the ocean of insoluble trivalent, tetravalent elements (Al, Ga, Y, REEs, Ti, Zr, Hf, Th) and U present as large-size organo-ferric colloids will decrease. However, the magnitudes of these possible changes are impossible to foresee at the present time.

- The radiogenic and stable isotope composition of subarctic and temperate organic-rich surface waters measured in this study for a series of cascade filtrates, ultrafiltrates and dialysates allow a systematic look on the origin and fractionation of contrasting elements in boreal landscapes. Due to high concentration of organo-ferric and organic colloids controlling the speciation of soluble (Mg, Sr), insoluble (Nd) and organic-borne (Cu) elements, we could assess the isotopic signatures in both conventionally dissolved (< 0.4-0.22 µm) and "truly" dissolved (< 1 kDa) fractions. The difference in isotopic composition in various filtrates allowed tracing the possible presence of marine aerosols (Sr) but the absence of solid dust deposition (Nd). Colloidal and dissolved Cu and Mg exhibit negligible difference in isotopic composition in the full series of ultrafiltrates down to < 1 kDa fraction which strongly suggest the similarity of the structure and stability of organic complexes binding these metals in different fractions.

In terms of element transfer by small Arctic rivers to the ocean, it follows that the isotopic signature of riverine Sr flux to the Arctic ocean may be measurably affected by colloids since the $LMW_{<1\ kDa}$ "ionic" fraction is up to 0.0002 units of $^{87}Sr/^{86}Sr$ less radiogenic compared to usual < 0.22 µm fraction; despite the dominance of colloidal Nd in the river water, the isotopic signature of all filterable fractions including most labile $LMW_{<1\ kDa}$ species remains essentially the same and unaffected by colloids. Organic and organo-mineral colloids controlling the speciation of Cu^{2+} and Mg^{2+} in river waters and soils/bog waters do not produce any measurable isotope fractionation compared to $LMW_{<1\ kDa}$ fraction.

- During filtration and ultrafiltration of organic- and Fe-rich surface waters of small boreal watersheds we observed unprecedentedly large variations of Fe isotopic composition (with $\delta^{57}Fe$ relative to IRMM-14 ranging from -0.9 to +4.2 ‰). The suboxic groundwater, soil solutions and bog waters exhibit close to zero, and therefore to the continental crust value, or slightly negative isotopic signature ($\delta^{57}Fe$ from -0.5 to 0‰). In contrast, the oxygenated rivers and streams contain large-size colloids and subcolloidal particles (20 µm to 0.1 µm) having positive $\delta^{57}Fe$ (from 0.5 to 2.0 ‰).

A novel and unexpected finding is that small size, Fe-poor, C-rich colloids and conventionally dissolved LMW fraction (< 1 kDa) exhibit even higher enrichment in heavy isotope with $\delta^{57}Fe$ value reaching up to +4.2‰. This result does not support the common view, the natural organo-ferric colloids are getting progressively enriched in heavy isotope with the decreasing of their molecular size, i.e., when moving in the direction “particulate Fe oxy(hydr)oxide → dissolved Fe”.

The ratio Fe/C in colloids seems to be one of the major factors controlling their isotopic composition; however, there is a systematic difference in $\delta^{57}Fe$ dependence on Fe/C between subarctic and temperate surface waters, possibly, linked to the different nature of initial mineral substrate and bog/soil water regime.

- The observed results could be explained by a sequence of the following processes: 1) Fe(II)-bearing bog and soil solution oxidation with formation of isotopically heavy Fe(III) large-size organic-rich colloids and particles at the redox front between anoxic soil and groundwaters and organic-rich surface bog waters, 2) transformation of organo-ferric colloids in open-water small lakes and bog water surface or within the stream flow which may include but not limited to: *i*) photoreduction of Fe(III) with formation of Fe(II)-organic complexes, *ii*) microbial heterotrophic respiration of dissolved organic matter, producing small size organic ligands complexing Fe(III) and *iii*) appearance of phytoplankton LMW exometabolites complexing Fe(III). These processes should destabilize the original Fe(III), C- bearing colloids and produce more stable autochthonous Fe complexes and colloids.

- As a result, the small-size, Fe- and organic carbon rich coastal rivers and streams may play very important and yet underestimated role in the overall Fe chemical and isotopic budget of the Arctic Ocean.

6.2. Perspectives

In the course of this study, a number of new scientific challenges have been identified. Like any multidisciplinary study, while providing the answers to the preidentified objectives, it opens a number of new frontiers and provides the necessary background to tackle new questions. In the near next future, in order to further advance in our understanding of biogeochemistry of boreal systems, several new issues have to be addressed:

- To get further insights in the structure of organo-mineral colloids collected in natural waters detailed microscopic/spectroscopic study is necessary. The size of colloids subjected to different treatment can be assessed via laser granulometry, while the chemical structure of organo-mineral associates can be characterized using X-ray Synchrotron microscopy (NEXAFS for C and Fe).

- Further progress can still be done for the understanding the origin of element in the rivers. In addition to the effect of soil minerals and rocks dissolution and the groundwater input, surface soil water transport of plant litter degradation products can be better assessed. For this, thorough measurements of major group of plants litter chemical composition, its degradation in soil and further transport to the rivers via subsurface and surface flow should be assessed. According to the balance calculation by Zakharova et al. (2007) for Karelia region, up to 30-40% of major elements and silica in the river water may be originated from the plant litter degradation. At present, we have no evaluation for the role of plant litter in the transport of other major and trace elements, notably those present in the form of colloids and further in-situ and laboratory experiments are necessary.

- In order to better distinguish the influence of UV irradiation in OM transformation and the relative role of organic part of colloids in the binding of trace metals during migration from the feeding bogs and lakes to the river flow some experimental studies can be performed. This can be achieved via exposing of the natural organic-rich boreal waters in UV-irradiation for the different time periods followed by split sampling and standard ultrafiltration procedure in-situ as well as specially designed laboratory experiments. It will allow quantifying the impact of photodegradation processes on organo-mineral colloids distribution.

- The the next step would be to study the impact of microbial activity (i.e., organic matter mineralization by typical soil aerobic bacteria such as *Pseudomonas*) on biogeochemical cycles of elements through the applying parallel geochemical, physico-chemical and microbiological tools is required. Detailed study of the physico-chemical processes will be achieved via experimental modeling of the degradation of dissolved and particulate (bacterial-plankton by heterotrophic soil solution extracts) organic matter. It will allow answering the questions: 1) How the carbon flux can be changed by the biodegradation of dissolved humic and fulvic acids? and 2) What are the quantitative relationships between the organic matter degradation by aerobic bacteria (ex. *Pseudomonas*) and the modification of speciation and distribution among different colloidal pools of associated elements?

- Finally, quantitative thermodynamic or, rather, chemodynamic modeling of colloid formation of different size using the results of cascade filtration and comparison of the acquired data with natural observations will allow to ascertain the mechanism of TE interaction with organo-mineral colloids of the boreal zone.

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ANNEX 2

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Results of a Study of Co-Migration of Trace Elements and Organic Matter in a River Flow in a Boreal Zone

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Abstract—This work describes the evolution of migration forms of true dissolved compounds and colloidal entities using an integrated approach with molecular mass distribution and differences in the association of trace elements with organic matter and Fe-oxide colloids in the soil water–bog–river–lake system. One major problem is obtaining reliable information on the processes of redistribution deposited forms and trace element complexes during the phase transformation of organic humic compounds in a series of high-molecular-weight organic matter of bog soils to colloidal and truly dissolved forms, as well as to the river and lake fine sediment (suspension) as a transit zone and deposit region.

Keywords: filtration, ultrafiltration, migration, trace elements, organic matter.

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INTRODUCTION

Concepts about the practically complete complexation of dissolved heavy metals (HM) with humic organic matter (HOM) and their export to bottom sediments during joint coagulation of HOM and iron hydroxides, especially in northern rivers with bog nutrition, which are mostly enriched with humic acids, are common and have been explained in detail [3, 4, 6]. Along the feeding bog–stream and river–deposited pond water route a change in the predominant forms of transfer is observed. The fraction of the largest molecules of HOM in the molecular mass distribution is always variable, does not exceed 20% (by weight), and drastically depends on the hydrological regime of the season, conditions of soil nutrition, and rain.

These fractions (100–0.2 μm) effectively accumulate as early as in bog soils and easily sedimentate with a slow flow rate. In their content, especially in gutters, the fraction of colloidal particles of different natures may be observed, iron (hydr)oxides and silicate (clay), which are mainly present in the largest fractions (>1 μm) together with aggregates of molecules of humic acids. The distribution of substances by fractions is always specific; it can be studied in detail by means of cascade filtration, disturbance of the stationary state during hyperfiltration, and spectrophotometrically during the determination of the fraction of humic acids in the total balance of organic matter. This study of the distribution of trace elements by analytical mass spectrometry with inductively-coupled plasma (ICP-MS) was performed to search for a correlation between the contents of organic matter of waters and colloids of iron (hydr)oxide in a series of consecutive filtrates.

METHODS OF INVESTIGATION

The drainage area of the Vostochniy Stream, Palojoki River (North Karelia, Kumsk system of reservoirs), and for comparison, the Sen'ga River and Lake Ignatkovo (Vladimir Region, river basin of the Klyazma) were chosen as the objects of investigation. The sampling points were feeding bogs, average flows and creeks of streams and rivers, streaming and depositing lakes, and soil solutions. Large volume samples (50–100 l) were taken using cascade filtration, ultrafiltration, and hyperfiltration of the samples directly in field conditions consecutively through filters of 100, 20, 10, 5, 0.8, 0.4, 0.2, 0.1, 0.0059, 0.0027, and 0.0013 μm with the accumulation and isolation of organic matter, coarse suspensions, and fine colloids on different bilayer membrane and nuclear (track) filters.

The ICP-MS method was used for the analysis of the isolated fractions of filtrates and precipitates on a wide variety of macro- and trace elements, (Element-2, Department of Geology, MSU; Plasma Quard-2, IMT RAS; Agilent 7500; LMTG, Toulouse). A comparison of the analysis results of 11 samples in three laboratories was carried out for the following elements: Li; Na; Mg; Si; Rb; Sr; Y; Zr; Mo; Cd; Sn; Sb; Cs; Ba; La; Ce; Pr; Nd; Sm; Eu; Gd; Tb; Dy; Ho; Er; Tm; Yb; Lu; Hf; W; Re; Al; Ca; Ti; V; Cr; Mn; Fe; Co; Ni; Cu; Zn; Ge; K; and As. These results showed that differences were absent in the analyses of these laboratories for Sr, Y, Zr, Mo, Cd, Sn, Sb, La, Ba, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, W, Zn, Ge, K, Al, V, Mn, Co, Cu at the 99% probability level.

The amount of non-purgeable organic carbon was measured by catalytic combustion with detection on a Shimadzu analyzer (LMTG, Toulouse), as well as spectrophotometrically (Expert 003, Department of Geology, MSU, and Specord-50, Analytical Center of the Institute of Ecological Pedology, MSU). Spectrophotometry is important in this study, because it solves several problems. The color of the samples and optical density (D) in the visible range of wavelengths are proportional to the concentration of humic and fulvic acids and are not sensitive to the total content of C_{org} in filtrates and natural waters. The HOM of a cellulose nature and low-molecular weight carboxylic acids are not optically active in the visible range of the spectrum. When plotting the calibration dependence between the optical density and the amount of dissolved carbon we only used the data from filtrates that did not contain soluble cellulose organics: a calibration graph was plotted for 22 samples that were passed through lavsan (0.2 and 0.4 μm) and teflon (0.1 μm) filters (Fig. 1), by which the real contents of predominant natural organic (humic) carbon in residual filtrates were evaluated.

EXPERIMENTAL

1. Cascade (consecutive) filtration was used for the study of the molecular mass distributions of dissolved and suspended HOM, as well as the preparation of the analytical information about the correlations of the contents of HOM and other elements in a series of consecutive filtrates. In this case, the "export curve" method is effective, while for the series of consecutive filtrates (*table*) the trends of the changes in the concentrations of microcomponents and their values, which were normalized for the total and variable amounts of macrocomponents, complexing agents, and potential sorbents were compared. Fresh and ultrafresh river waters of the boreal zone, where bog nutrition usually predominates, as well as small rivers of the taiga–forest humid zone, are characterized, as a rule, by the fact that humic HOM predominate among macrocomponents, as well as complexes and ashes of iron hydroxides [7], A relatively small amount of suspended clay particles are present as well. For the separation of such mixtures by size fractions in such a way that the last filtrate definitely contains only dissolved forms, a combination of filtration, ultrafiltration, and hyperfiltration is required. The total cascade of consecutive filters (technologically and chemically of various natures) usually contains not more than 7–10, but the main and principal ones are the procedures for the separation of the coarse, i.e., sedimentationally unstable, fraction >0.2–0.4 μm (filtration), separation of humic and fulvic acids by ultrafiltration, and the isolation of narrow molecular fractions of dissolved HOM in the 1–100 kDa interval of molecular mass by hyperfiltration.[1]

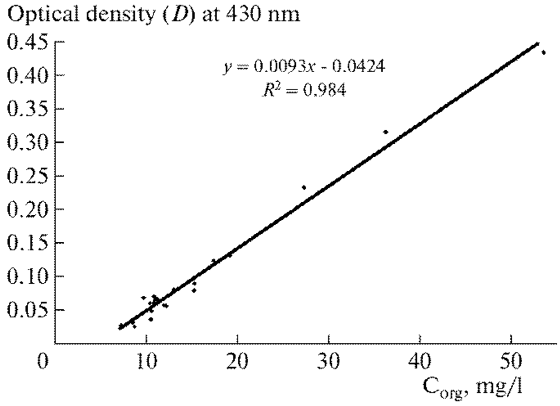

Fig. 1. Calibration graph of the optical density at 430 nm vs. the humic C_{org} content.

Hyperfiltration as a type of reverse-osmotic filtration is widely used during desalination of waters [2], but is far from the filtration and ultrafiltration by the main physiochemical mechanism of the separation of the solution components [1]. The two latter processes are counterparts of typical sieving by the mechanism of separation, where steric restrictions predominate and the ratio of particle and pore sizes. Hyperfiltration of natural waters, especially solutions with HOM in a wide spectrum of molecular masses, always combine the processes of reverse-osmotic and sieve separation. Membranes with a pore diameter of 1–10 kDa are close to the limit of 10–20 Å, after which the filtrate is considered to contain only dissolved substances without ultracolloidal particles.

The basis of this approach is obvious, since for molecules of humic acids of formally colloidal sizes with masses of 100 kDa and more, the condition of sedimentation stability is realized and they are "truly dissolved" until their aggregation and sedimentation is intentionally caused by changes in pH. The range of 1–100 kDa in all respects is the most interesting for the detailed study of the properties of natural HOM of a humic nature, since fulvic acids with molecular masses <10 kDa absolutely predominate in the molar fraction of the HOM of each type of waters. It should be noted that cascade filtration as a modern method for the isolation of very narrow fractions of HOM and the determination of the accompanying concomitant microelement composition has an important advantage compared to the methods for studying molecular mass distributions that are common in the chemistry of soils.

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[1] The nomenclature of "kilodalton" filters for hyperfiltration is based on the molecular density of spherical protein molecules; it is accepted that pores with a diameter of 0.0059 μm are responsible for passing molecules with a mass of 100 kDa; 10 kDa, 0.0027, and 1 kDa, 0.0013 μm, respectively.

Results of the determination of the composition (μg/l) of consecutive filtrates of the sample KAR-2 (a feeding bog of the Palojoki River, 2008) by ICP-MS

Elements	Pore diameter of filters					
	100 μm	0.4 μm	0.1 μm	100 kDa	10 kDa	1 kDa
Na	749.6	773.7	809.3	814.5	818.6	865.6
Mg	469	446	456.2	460.5	446	431.9
Al	284.5	204.1	211.1	204.9	164.3	140.3
Si	2224	2180	2238	2256	2253	2302
K	55.09	100	112.1	110.9	119.6	124
Ca	1256	1223	1287	1262	1153	1072
Ti	2.19	0.94	1.05	0.86	0.50	0.30
V	1.54	0.23	0.26	0.20	0.17	0.17
Cr	0.75	0.66	0.62	0.58	0.51	0.50
Mn	48.27	36.41	35.94	37.21	34.8	31.17
Fe	3328	876.2	835	814.1	517.3	289.8
Co	0.58	0.48	0.45	0.46	0.44	0.37
Ni	0.86	0.76	0.83	0.85	0.75	0.62
Cu	1.45	1.33	1.80	1.66	1.30	1.23
Zn	8.98	10.56	11.93	12.41	12.78	10.89
Rb	0.11	0.15	0.17	0.17	0.18	0.18
Sr	8.97	8.11	8.65	8.48	7.42	6.56
Y	0.19	0.13	0.12	0.12	0.10	0.06
Zr	0.13	0.12	0.13	0.11	0.08	0.04
Mo	0.026	0.012	0.018	0.016	0.017	0.002
Cs	0.00075	0.00068	0.00115	0.00031	0.00013	0.00013
Ba	8.09	6.11	6.10	5.95	4.71	3.13
La	0.48	0.26	0.22	0.24	0.16	0.08
Ce	1.15	0.70	0.59	0.63	0.43	0.23
Pr	0.115	0.072	0.064	0.068	0.050	0.027
Nd	0.433	0.305	0.241	0.259	0.188	0.117
Sm	0.0655	0.0425	0.0422	0.0450	0.0366	0.0177
Eu	0.0143	0.0107	0.0106	0.0093	0.0067	0.0041
Gd	0.0639	0.0452	0.0386	0.0393	0.0313	0.0182
Tb	0.0057	0.0051	0.0036	0.0042	0.0036	0.0015
Dy	0.0383	0.0243	0.0196	0.0222	0.0192	0.0093
Ho	0.0074	0.0053	0.0042	0.0046	0.0036	0.0018
Er	0.0203	0.0139	0.0141	0.0145	0.0105	0.0068
Tm	0.0032	0.0021	0.0022	0.0020	0.0018	0.0008
Yb	0.0156	0.0127	0.0116	0.0104	0.0103	0.0077
Lu	0.0031	0.0021	0.0019	0.0015	0.0012	0.0008
Hf	0.0035	0.0046	0.0058	0.0048	0.0037	0.0017
W	0.0021	0.0009	0.0050	0.0038	0.0035	0.0033
Th	0.0306	0.0277	0.0230	0.0242	0.0159	0.0054
U	0.0058	0.0044	0.0052	0.0044	0.0039	0.0018

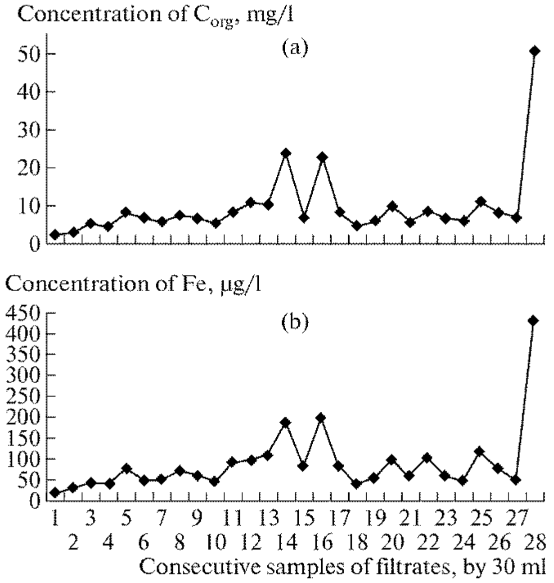

Fig. 2. Variations of the content of (*A*) C_{org} ($R = 0.45$) and (*B*) Fe ($R = 0.9$) during filtration of the KAR-2/08 sample (R is the integral rejection coefficient).

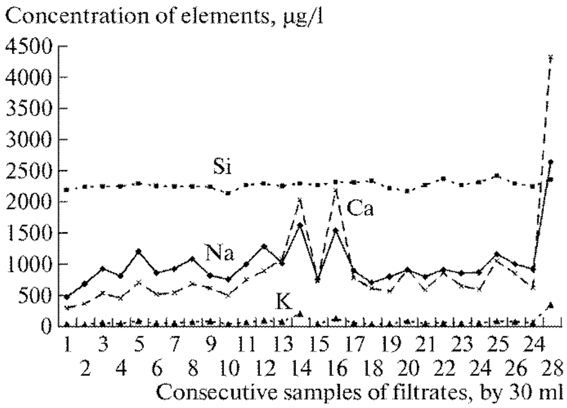

Fig. 3. Variations of the Na content ($R = 0.24$), Si ($R = 0.0$), K ($R = 0.12$), and Fe ($R = 0.3$) during filtration of the KAR-2/08 sample (R is the integral rejection coefficient).

For example, methods of chromatographic separation are always complicated with the adsorption losses of trace elements and for optimization of the conditions of the isolation of the fractions of HOM, along with the necessity of correcting the initial composition. However, the use of filters for hyperfiltration as a method for the separation of fractions has not been completely methodologically explained and is not based on the electrokinetical theory of reverse-osmotic desalination; i.e., it only formally studies sieving methods. Ionic concentration polarization and increases in the concentration of a solution during reverse-osmotic desalination are not accompanied by the export of these components into the precipitate and their sedimentation. For HOM on a filter, this is a natural phenomenon, where aggregation is possible during the concentration and shifting of adsorption equilibria. Therefore, the use of membranes for hyperfiltration for accurate investigations of molecular mass distribution requires several conditions, a decrease in concentration polarization and a delay by the mechanism of reverse osmosis.

2. Use of the disturbance of the stationary state during hyperfiltration. It is important to note that the attainable stationary state may be controlled during hyperfiltration, i.e., the phenomena of the differential transfer of macromolecules of HOM and microcomponents; it is sufficient to create disturbances in the conditions of stationary separation during filtration. The results of the analysis of filtration experiments make it possible to determine the objective properties of separating membranes for hyperfiltration (Millipore, 1–100 kDa). With respect to dissolved organic materials (DOM) of fulvic and humic natures, membranes exhibit specific reverse-osmotic properties, which involve concentrating the solution before filtering by the mechanism of the retention of dissolved components in the filtrate. On such membranes, filtration is not limited to molecular mass separation by the sieve effect with a predominant role of exceptional size and steric restrictions. For membranes with small pores (1–10 kDa), the desalination of a filtrate (i.e., the retention of electrolytes by the reverse-osmotic mechanism) is observed for components that are not bonded to complexes with HOM, for instance, for sodium. The stationary state that is attained during reverse-osmotic filtration can be controlled with respect to the composition of the filtrate and the concentration polarization; this makes it possible to create a new method for the study of the degree of complexation of trace elements with HOM of natural waters by disturbance of the stationary state during filtration.

As is known from the research on the reverse-osmotic filtration and filtration effect [1], the rejection coefficient:

$$R = 1 - (C_2/C_1)$$

depends on the ratio of concentrations “on the inlet—C_1” and “on the exit—C_2” of the membrane, which are determined by the conditions of stirring, the rate of filtration, and the flow potential. Changes in these conditions result in consistent changes in the concentrations of many elements in a series of consecutive filtrates as natural concentrations according to their pulsation values. These fluctuations, rather than smooth changes in the concentration from one sample to another during disturbances of the stationary state, are correlated (Figs. 2–4) for most dissolved components and are related not only to the hydrodynamic features

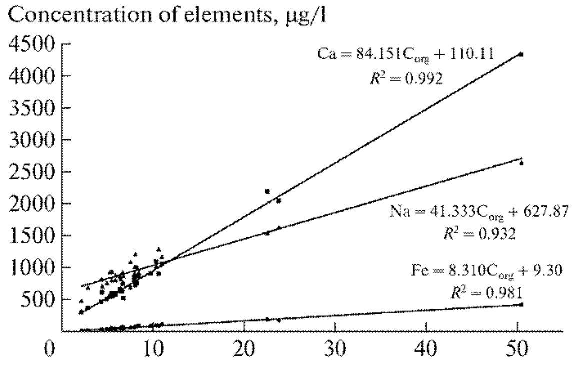

Fig. 4. Pair correlations of the contents of consecutive samples during hyperfiltration 4000, 12.7 Å for a set of elements with C_{org}.

of diffusion and filtration flows during changes of the conditions of filtration and the values of delay coefficients, but also by sedimentation export with HOM and colloids $Fe(OH)_3$ on a membrane.

3. Spectrophotometric study of the initial samples and filtrates. The study of the optical characteristics of all the solutions was carried out by spectrophotometry in the visible range of the spectrum and partially in the ultraviolet range on a Specord-50 stationary spectrophotometer. Monitoring of the coagulation processes and the retention of humic dissolved carbon in initial samples and consecutive filtrates was performed under field conditions. These investigations of spectrophotometric characteristics were conducted during the measurement of the optical density in the wavelength interval from 400 to 655 nm on an Expert-003 photometer. The correlations of the optical density with the C_{org} content, which was determined in parallel using high-temperature oxidation in all samples, were studied at a wavelength of 430 nm. The spectra of organic matter in the initial samples and filtrates during the sampling were obtained for 6 samples taken in 2008 and 14 samples taken in 2009. In all cases, the optical density of the initial samples and filtrates shows natural changes in the entire range of wavelengths for a series of consecutive filtrates (Fig. 5) with a decrease in the fraction of DOM. These optical characteristics (optical densities) served as the analytical basis for the determination of the weight fraction of the humic organic matter in filtrates and initial samples.

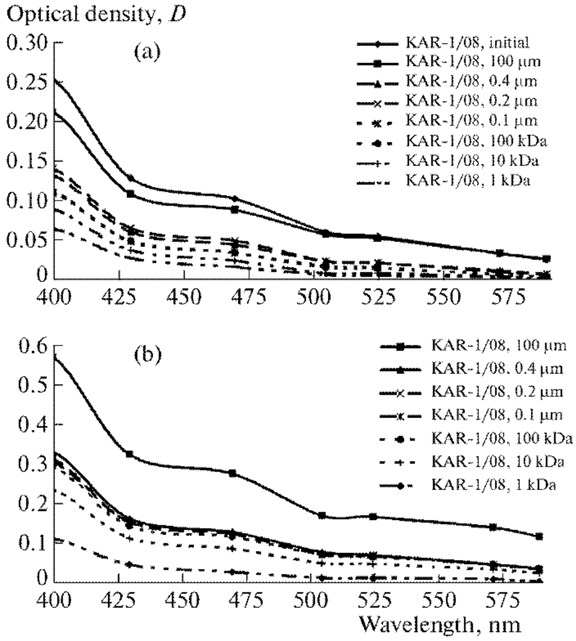

Fig. 5. Distribution of absorption spectra of the dissolved organic matter during cascade filtration (*A* is the average flow of the Palojoki River, *B* is the feeding bog of the Palojoki River).

RESULTS AND DISCUSSION

For soil solutions (point OR-9), the mineralization was 32 mg/l; this sample was characterized by an acidic pH of 3.6. In feeding lakes and bogs, the pH changed from 5.9 to 6.5. In samples from the Vostochniy stream, the pH oscillated from 6.5 to 7.0. The stream flows into Lake Tsipringa (OR-8), which is characterized by a mineralization of 23.3 mg/l and a pH of 7.4. Thus, from the feeding area and soil solutions to the area of the inflow of the stream, the mineralization decreases from 32 to 23.3 mg/l and pH increases from 3.6 to 7.4. Waters of the Sen'ga River, the right tributary, draining the background territories of the swampy part of Mescherskaya lowland, are ultrafresh, with neutral pH. The mineralization was 74 mg/l; this is slightly higher than in Karelia. In Lake Ignatkovo, pH 5.44 and the mineralization is ~5 mg/l.

The changes in the acidity and oxidation–reduction conditions [5] determine the rate of formation of colloids of iron (hydr)oxides, adsorption of trace elements and large molecules of HOM, and their complexation degree with humic substances. For the KAR-1 (average flow of the Palojoki River) and OR-9 samples, a high weight percent of the export of organic matter on filters with pore diameters of 0.4 and 0.1 μm is intrinsic; (Fig. 6), however, after the 1 kDa filter, the content of organic matter in these samples was 47 and 8 wt %, respectively.

In Fig. 7, diagrams of the weight distribution of organic matter for the percent ratio of its total contents in the KAR-1 (average flow of the Palojoki River, August of 2008 and July of 2009) and KAR-2/08 (feeding bog) samples are given. In both cases, the fraction of the low-molecular weight DOM is high and a significant weight fraction of high-molecular weight HOM is also present; this is determined by the high contribution of rain into the mass balance.

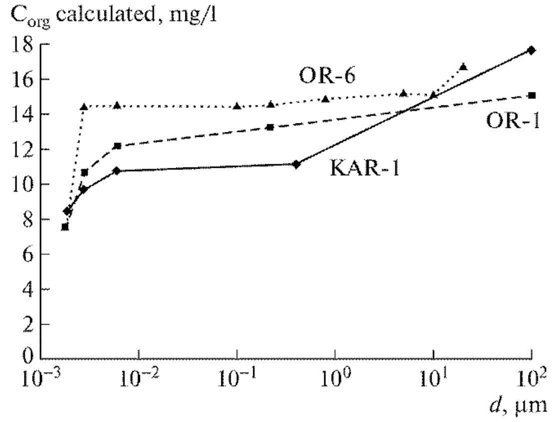

Fig. 6. Distribution of C_{org} by the filtrates of the samples: KAR-1 is the average flow of the Palojoki River; OR-1 is the mouth of the Vostochniy Stream; OR-6 is the upper lake of the Vostochniy Stream (2009).

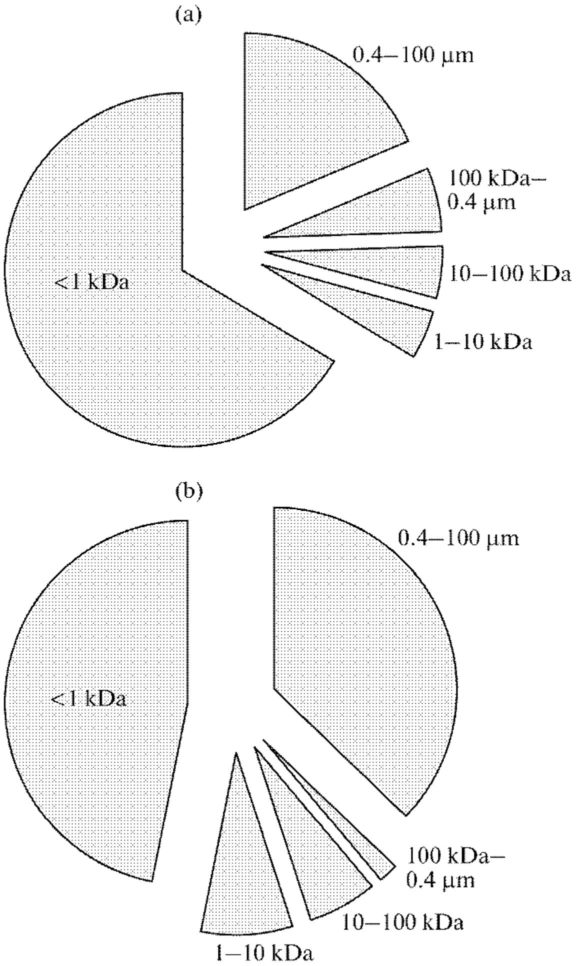

Fig. 7. Distribution of C_{org} in selected filtrates of the sample of the average flow of the Palojoki River: (a) KAR-1/08, July, 2008; (b) KAR-2/09, August, 2009.

Notably, the pie diagrams of the weight portion of the fractions of various dimensions clearly demonstrate the weight portions of the fractions, but not the molar fractions of the molecules of various sizes. Since the molecular weight values are proportional to the cubic diameters of molecules, the difference in the molecular masses is six orders for molecules with a diameter of 0.2 μm and for molecules with a mass of 10 kDa and diameters it is close to 2 nm (2×10^{-3} μm): 8×10^{-3} and 8×10^{-9} μm^3, respectively. As is seen from this comparison, the weight fractions for the molecules of various sizes create the illusion of similar occurrences of molecules of various sizes. Actually, the molar concentration of the low-molecular weight fulvic acids is many orders higher; this should be taken into account when considering complexation and their joint transport with trace elements. The molar portion of fulvic acids and concentrations of their molecules in all types of natural waters, even in swampy ones, absolutely predominate, and the main complexation is related to them (Fig. 8a).

Another form has the export curves of iron and trace elements (Fig. 8b and 8c), associating with colloids of the iron hydroxides, first of all, rare-earth elements, V, Ti, Zr, and other types.

Four groups of elements were chosen according to their correlations with the export curves of HOM and iron. The elements that are adsorptionally bonded with colloids of Fe-hydroxides belong to the first group. These are primarily rare-earth elements and elements–hydrolyzers: Al, Ti, Zr, and V. Up to 50–80% iron is in the high-molecular weight colloidal form in the river and partially boggy waters and it was effectively exported on filters with a pore sizes >0.1 μm.

The second group includes trace elements that forming high-molecular weight complexes together with iron-organic complex: Fe; Ti; Cd; Al; V; Cr; Mn; Co; Ni; Cu; Ga; As; Y; Ce; Ho; and Tm. In this case, the distribution of the elements in the consecutive filtrates correlates well with their contents of HOM. During filtration, their joint export on filters takes place, the main part of the elements is bonded to DOM, and their main part is bonded to high-molecular weight DOMs adsorptionally.

The third group is represented by the elements that have another character of export during cascade filtration complexed with low-molecular HOM (Cr, Cu, Ni, Co, Hf, Lu, Eu, Tm, and U). They almost do not precipitate during the first filtration steps. The highest decrease in concentrations is observed in the last filtrates (1–10 kDa) (Fig. 8a and 8b). This means that the main part of these trace elements occur in complexes with low-molecular HOM (fulvic acids); however, adsorption export with colloids of Fe hydroxides is partially observed for them.

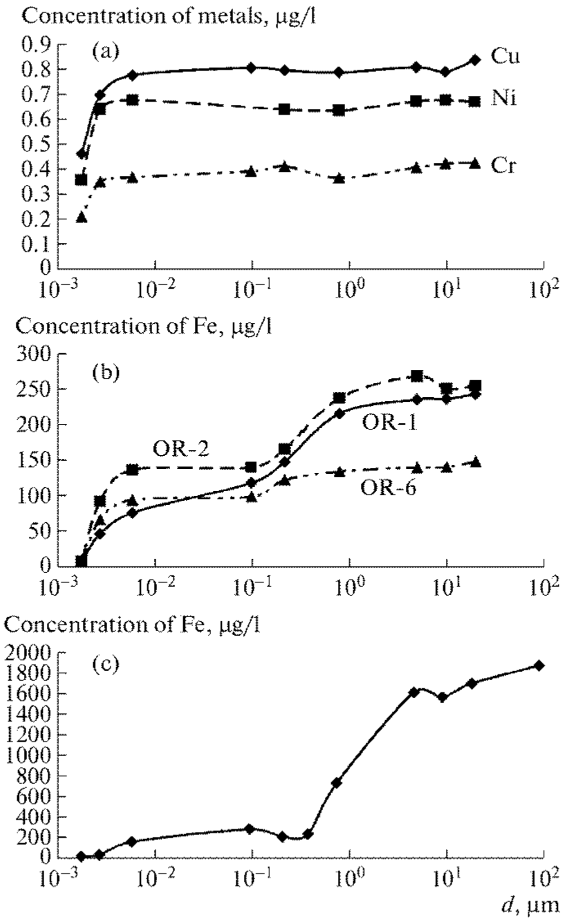

Fig. 8. Distribution of elements in filtrates, d is the pore diameter, μm; (a) Cu, Ni, Cr; mouth of the Vostochniy stream; (b) Fe; OR-1, the mouth of the Vostochniy Stream; OR-2, the lower lake of the Vostochniy Stream; OR-6, the upper lake of the Vostochniy Stream; (c) Fe; KAR-1, the average flow of Palojoki River.

The elements of the fourth group (Si, K, Na, Zn, Rb, Cs, and Sc) are not complexed with HOM and are not exported during cascade filtration. This group also includes complexes with low-molecular weight organic acids. It is obvious that the export of the silica with HOM does not take place, because the predominant form is true dissolved nonpolymerized silicic acid (up to 4.5 mg SiO_2/l), with which the waters are not saturated.

CONCLUSIONS

No matter what the long-term predictions and climate changes scenarios are for the northern hemisphere, the scientific-methodological study of the migration forms of organic matter and trace elements in rivers of different climatic zones is topical in all cases. Only on this basis the objective information be obtained on the changes in the scale and transfer form of trace elements in river flows. The complexity and variability of the compositions of natural waters over time determines the methodological difficulties that occur during the study of the principles of migration and forms of heavy metals and other trace elements in river flows. Various inorganic and organic compounds in natural waters that contain ionic, molecular, surface-active, and coarse solid as well as colloidal particles, which can adsorb chemical elements, govern the behavior of trace elements in river flows.

In our opinion, only the use of separate (or fractional) isolation phases that are carriers of heavy metals makes it possible to determine separate fractions of the migration forms, the distribution coefficients between different forms of existence, and determine the causes of their changes in mixing zones, during transfer, and deposition.

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ОПЫТ СРАВНИТЕЛЬНОГО АНАЛИЗА ОТДЕЛЬНЫХ СОСТАВЛЯЮЩИХ РЕЧНОГО СТОКА МАЛЫХ РЕК СЕВЕРНОЙ ЗОНЫ И СРЕДНЕЙ ПОЛОСЫ РОССИИ

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Рассматривается изменение форм нахождения и миграции истинно растворенных соединений и коллоидных образований посредством сравнения отдельных составляющих речного стока северной зоны и средней полосы России в системе почвенный раствор—болото—река—озеро. Главным инструментом изучения послужила каскадная фильтрация с последующим анализом водных проб, что позволило комплексно исследовать трансформации молекулярно-массового распределения и эколого-геохимические особенности миграции микроэлементов с органическим веществом и коллоидами гидроксидов железа.

Ключевые слова: речной сток, каскадная фильтрация, органическое вещество, микроэлементы, коллоиды и ультраколлоиды.

Получение достоверной информации о процессах изменения форм переноса, т.е. комплексов и адсорбционно-депонированных форм тяжелых металлов и других микроэлементов при фазовой трансформации органических гуминовых соединений речного стока, последовательно от высокомолекулярных органических веществ (ОВ) болотных почв к коллоидным и истинно растворенным формам, а также к тонким взвесям (суспензиям) реки как зоны транзита и озера как области депонирования является важной задачей экологической геохимии. Изучение особенностей и различий в миграции в виде металлорганических комплексов и коллоидов в малых реках средней полосы России и северной зоны с различающимися гидрологическими и гидрохимическими особенностями позволяет обосновать количественные модели трансформации вещества речного стока при изменении природных обстановок.

Объекты исследования

Для северной зоны (Северная Карелия) в качестве первого автономного объекта была выбрана р. Палойоки бассейна Пяоозера Кумской системы. В качестве второго объекта выбран водосборный бассейн оз. Ципринга — небольшого сателлитного оз. Кумской системы водохранилищ (66°20′ с.ш., 30°45′ в.д.) площадью около 50 км^2 и средней глубиной 7 м (до 36 м), соединенного узкой протокой длиной 1 км с остальной системой, разгружающейся в Кандалакшский залив Белого моря. Этот водосборный бассейн, как и вся Кумская система, имеет для рек устойчивую устьевую уровневую отметку 109 м. Ультрапресные воды бассейна разгружаются в озера, дренируя почвы, в которых развиты типичные омброфильные биоценозы (Заварзин, 2009), характерные для болот. Подпочвенным субстратом в основном являются протерозойские кристаллические сланцы и гнейсы. В качестве третьего объекта как объекта сравнения были выбраны р. Сеньга, дренирующая Мещерскую низменность, и заболачиваемое оз. Игнатково. При выборе объекта сравнения мы учитывали подобие литохимического состава подпочвенного субстрата флювиогляциальных отложений QIV, принесенных ледниками из Фенноскандии, и однотипность хвойных лесов. Принципиальные различия заключались лишь в разнице климатических условий и гидрологических режимов при сходстве типа питания болотными водами. Помимо детально исследованных и использованных при проведении экспериментов 11 основных точек отбора проб и их последовательных фильтратов изучены также более 20 водотоков водосборного бассейна оз. Ципринга, аналитические данные по которым здесь не обсуждаются.

Методология исследований

Для успешного решения комплекса поставленных задач ключевым является выбор эталонных объектов. Они должны отвечать следующим консервативным требованиям: 1. Площадь водосборного бассейна должна быть сопоставима с площадью озера депонированных вод при неразветвленной и короткой сети питающих потоков (малых рек и ручьев). 2. Система питающих болот, коротких рек и ручьев и принимающего озера должна быть гидрологически и гидрохимически достаточно автономной с незначительными вариациями сезонного уровня вод озера. 3. Водосборный бассейн должен отличаться устойчивой водообильностью болот и влажностью почв. 4. В региональном плане объект должен быть достаточно удален от источников сосредоточенного техногенного загрязнения. 5. Климатически районы сравниваемых объектов должны характеризоваться стационарно избыточной влажностью почв.

Этим требованиям, но в разной степени, отвечают многие объекты вплоть до арктической зоны России. Дополнительным требованием является условие литохимической однородности подстилающего субстрата и типового однообразия почв сравниваемых водосборных бассейнов. Только при выполнении этих условий можно постулировать относительную стационарность системы, т.е. объективно исследовать устойчивые закономерности трансформации форм миграции в системе болото—река—озеро. Необходимо подчеркнуть, что почвенные растворы, воды болот и торфяников вместе с особенностями процессов в водах рек и озер редко изучаются комплексно в рамках единой программы исследования, в отличие от большого количества работ, посвященных изучению процессов в зоне смешения река—море. Мы полагаем, что комплексный подход позволяет выйти на новый уровень понимания процессов водной миграции в водах этих климатических зон, а также обосновать механизмы и балансы поступлений и выведений широкого круга химических элементов для подобных автономных систем.

При необходимости исследования главных составляющих речного стока всегда возникает вопрос оптимизации работ в отношении количества фильтратов и выделенных на фильтре осадков. К сожалению, получение аналитически представительных объемов осадков требует фильтрования проб большого объема. Способом решения поставленной задачи являлся отбор проб большого объема (до 20—40 л), с использованием непосредственно в полевых условиях методов последовательной и параллельной фильтрации и ультрафильтрации проб через фильтры 100; 20; 10; 5; 0,8; 0,4; 0,2; 0,1 мкм; 100 (0,0065 мкм); 10 (0,0027 мкм) и 1 (0,0013 мкм) кДа с выделением органического вещества, грубой взвеси и тонких коллоидов на различных видах фильтров, как мембранных, так и трековых. Ключевым при анализе выделенных фракций фильтратов и осадков на широкий круг макро- и микроэлементов было использование метода аналитической масс-спектрометрии с индуктивно связанной плазмой (ИСП-МС) и каталитического сжигания с детектированием органического вещества, а также методов ионометрии, кондуктометрии и спектрофотометрии в полевом и лабораторном вариантах. Основным приемом при обработке результатов анализов был метод поиска парных корреляций между содержанием микроэлементов и потенциальных депонирующих фаз-адсорбентов. От питающих болот к транзитным ручьям и рекам до депонирующего водного бассейна наблюдается закономерное изменение доминирующих форм переноса: взвесей и растворенных форм ОВ, коллоидов гидроксидов железа и коллоидной фракции силикатных частиц. Для водотоков первичной гидрологической сети в бореальной зоне количество силикатных коллоидов обычно невелико. Таким образом, главной задачей было исследование перераспределений микроэлементов между ОВ гуминовой природы и гидроокислами железа, выводимых на серии последовательных фильтров совместно с этими депонирующими фазами. Доля наиболее крупных молекул ОВ в молекулярно-массовом распределении всегда переменна, не превышает 20% (по массе) и радикально зависит от гидрологического режима сезона, условий почвенного питания и плоскостного смыва. Эти фракции (100—0,2 мкм) эффективно задерживаются уже в болотных почвах и седиментируют при малых скоростях течения. Распределение вещества по фракциям всегда специфично и может быть детально изучено методами каскадной и параллельной фильтрации при поиске корреляций с содержанием органического вещества вод и коллоидов (гидр)оксидов железа в серии последовательных фильтратов.

Общепринятой идеей (Варшал, 1994; Линник, Зубко, 2007; Pokrovsky, Schott, 2002; Pokrovsky et al., 2006) являются представления о переносе растворенной части тяжелых металлов (ТМ) в виде комплексов с органическим веществом гуминовой природы и выведении их в донные осадки при совместной коагуляции ОВ и гидроокислов железа, особенно в северных реках с болотным питанием, наиболее богатых гуминовыми кислотами. В химии почв, при анализе водных вытяжек, а также в химии гуминовых соединений рек достигнут значительный прогресс в понимании комплексообразующей роли этих соединений (McDonald et al., 2004; Pokrovsky, Schott, 2002). В последнее десятилетие появилось большое количество публикаций, детализирующих особенности поведения органометаллических комплексов в речном стоке (López et al., 2001; Pokrovsky et al., 2006; Sharma et al., 2005; Vasyukova et al., 2010; Xiaoxia et al., 2009; Zhang, Buffle, 2009). Однако климатические воздействия на компоненты окружающей среды в локальных ситуациях многообразны и оцениваются по-разному в силу своей недостаточной изученности. Локальные вклады в циклы ряда элементов в результате пре-

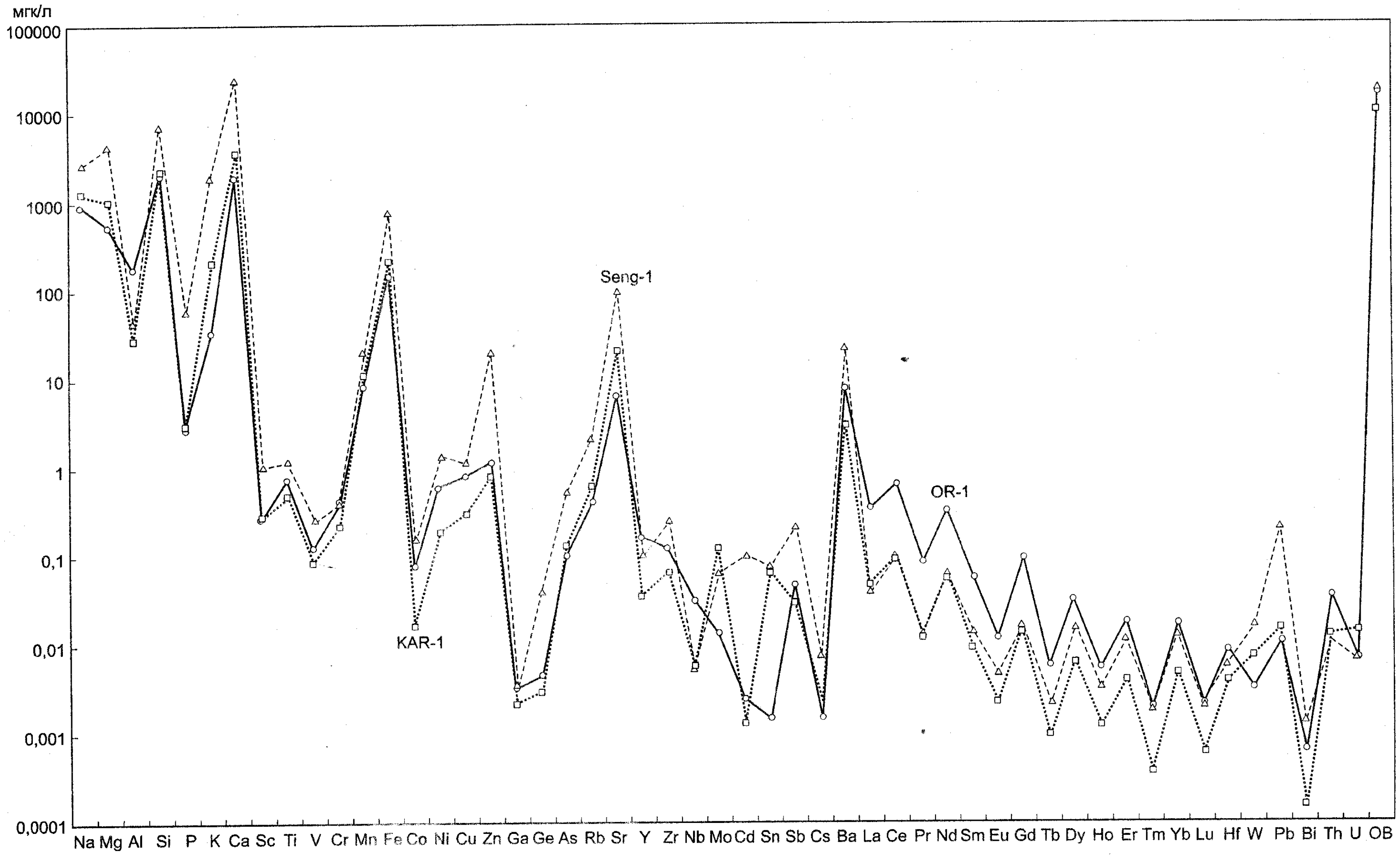

Рис. 1. Сравнение содержания элементов в фильтратах 0,2 мкм речного стока двух регионов:
KAR-1 — р. Палойоки; OR-1 — руч. Восточный (бореальная зона) и Seng-1 — р. Сеньга (Мещерская низменность)

образования биосферы (почвы, растительность, атмосферные выпадения и др.) резко меняются, но конкретные физико-химические механизмы этих изменений, проявляющиеся лишь в балансе глобальных циклов, на региональном и локальном уровнях в большинстве случаев плохо изучены. Динамическое состояние биосферы реализуется в том числе в форме различных по длительности и охватываемому пространству круговоротов вещества и энергии, называемых циклами. Так, для ряда биогенных элементов они практически замкнуты, а для ряда микроэлементов (особенно техногенных) извлечение из недр приводит к накоплению и рассеянию при незамкнутости циклов. Отсутствие необходимой информации о физико-химических особенностях циклов для ряда микроэлементов, наиболее технофильных, и механизмах их резервуарного депонирования — один из важнейших сдерживающих факторов. Наши знания о важнейшей динамической характеристике циклов — плотности (интенсивности) обменных потоков и природо- и техногенно-обусловленных вариациях этой величины, из которой может быть получена информация о мощности процессов межрезервуарного обмена, еще недостаточны. В современной эколого-геохимической литературе в качестве меры антропогенного воздействия на глобальные геохимические циклы элементов используется соотношение двух величин: наиболее мощного естественного потока — речного стока и мировой добычи элемента. При этом для ряда экологически важных элементов результаты не согласуются. Для речного стока это в значительной степени связано со сложностью выделения в суммарном миграционном потоке вкладов, связанных с истинно растворенными формами, коллоидами и взвесями при быстрых взаимных переходах доминирующих форм транспорта (Линник, Зубко, 2007; Alekhin et al., 2009; Appelo et al., 1999; Jones, Bryan, 1998). Неопределенности, возникающие при выделении этих вкладов, достаточно принципиальны (Ильина и др., 2008) не только для экологических прогнозов, но и для количественного решения задач массообмена на локальном и региональном уровнях. Так, в работе "Антропогенные модификации экосистемы озера Имандра" (Моисеенко и др., 2002) для этого озера, одного из немногочисленных водоемов России (Кольский полуостров, 150 км севернее оз. Ципринга), по которому имеются многолетние наблюдения, позволяющие проследить его антропогенную динамику по основным звеньям водной системы, есть указания, что лишь самый северный плес характеризуется мезотрофными процессами, а для южной части этого ультрапресного водоема до настоящего времени сохраняется олиготрофный характер. Для оз. Ципринга в полном объеме сохранен олиготрофный характер при незначительном вкладе аэральной контаминации при северных ветрах со стороны Кольского п-ова, Мончегорского, Оленегорского комбинатов и апатит-нефелиновых обогатительных фабрик г. Кировска. Для наших объектов в северной зоне до настоящего времени условия близки к фоновым для Фенноскандии.

В речном стоке вклад растворенных форм (< 0,2 мкм) микроэлементов характеризуется переменными, но наиболее низкими концентрациями (рис. 1). В ряду значений коэффициентов водной миграции взвеси и донные осадки отличаются наибольшими концентрациями, меньшими скоростями переноса и демонстрируют динамику изменения содержания элементов и их форм за большие интервалы времени. Еще меньшие значения коэффициентов миграции характерны для почв как среды депонирования, и в этом случае динамика поступления загрязнителей в водотоки и реки определяется гидрологическими особенностями плоскостного смыва с территорий, дренируемых притоками высоких порядков. Однако водорастворенные формы, отличаясь по ряду низкокларковых элементов наименьшими концентрациями, тем не менее могут обеспечивать сопоставимый вклад в потоки рассеяния при максимальных скоростях миграции. Именно поэтому задача достоверного определения концентраций растворенных веществ, в том числе в форме металлоорганических комплексов, и их количеств, переносимых в других формах, остается принципиальной. Наиболее сложными остаются проблемы динамики перераспределения форм элементов между наиболее важными адсорбентами — коллекторами микроэлементов: гидроокислами железа и гуминовым веществом, и механизма оксидогенеза с образованием коллоидов $Fe(OH)_3$ при поступлении болотных вод в водотоки.

Обсуждение результатов

Обсуждение результатов проводится нами с использованием значительного массива аналитических данных (Приложение *А*), которые имеют самостоятельную ценность, так как являются редким примером сравнительного анализа различий в содержании широкого круга элементов по отдельным фракциям крупности коллоидных и взвешенных частиц. В этой статье мы сможем обсудить только главные выявленные закономерности и проиллюстрировать их кривыми выведения (задержки, *R*) в зависимости от логарифма диаметра пор фильтров (lg *d*), а также графиками парных корреляций содержания микроэлементов с концентрациями их потенциальных коллекторов. Математическое обоснование приемов построения таких зависимостей и физический смысл угловых коэффициентов и свободных членов в уравнениях линейной корреляции рассмотрены в приложении *Б*. Этот аппарат имеет также самостоятельную ценность, но не является необходимым при обсуждении геохимических особенностей поведения ряда элементов в составляющих речного стока. Тем не менее все обсуждение построено на результатах обработки данных Приложения *А* с помощью аппарата, развитого в Приложении *Б*.

Сравнение графиков изменения концентраций растворенных компонентов (конвенционально растворенные формы, обычно <0,2 мкм) трех типичных водотоков двух выбранных регионов демонстрирует удивительное согласие. Выбор р. Сеньга (рис. 1), дренирующей болота Мещерской низменности, в качестве объекта сравнения оказался правомерным. В настоящее время хорошо известны региональные различия, обусловленные: 1) видами техногенного воздействия на природные воды, в зависимости от источников поступления загрязнителей; 2) разными мощностями источников поступления в воды растворенного и коллоидного ОВ; 3) разными интенсивностями разложения органического вещества в питающих водах болот и в почвах первичной гидрографической сети; 4) скоростями взаимодействия тяжелых металлов и микроэлементов с ОВ в зависимости от положения зоны основного взаимодействия (транзитной или депозитной); 5) спецификой молекулярно-массового распределения коллоидов, в том числе полигенных, отличающихся источниками, химической природой и возрастом (соотношение гидроокислов железа и алюминия, а также ОВ). Однако все эти особенности не проявлены в фильтратах <0,2 мкм, и детализация возможна только при сравнении составов последовательных фильтратов как фракций речного стока.

Содержание ОВ болотного генезиса в р. Сеньга, р. Палойоки и руч. Восточный однотипно, так же как и высокое (но разное) содержание гидроксидов железа в коллоидной форме. Отчетливо проявлено техногенное загрязнение вод р. Сеньга свинцом, цинком, кадмием и медью. При близости концентраций для большинства элементов и подобии графиков содержания наблюдается отчетливое различие в уровнях накопления (выведения) редкоземельных элементов (TR) и элементов-гидролизатов с поведением, аналогичным поведению коллоидов $Fe(OH)_3$. Высокие концентрации легких TR лантанцериевой группы в руч. Восточном демонстрируют незавершенность процесса их выведения вместе с гидроксидом железа. Причиной близости концентраций низкокларковых тяжелых TR в р. Сеньга и руч. Восточный является их большая способность к адсорбции на $Fe(OH)_3$ и ОВ гуминовой природы. Это еще лучше проявлено (рис. 2) при сравнении спектров содержания TR в консервативном и заболачиваемом торфяном оз. Игнатково и р. Палойоки северной зоны, однотипно нормализованных на содержание редких земель в хондритах (Boynton, 1984). Спектр редких земель с преобладанием легких в р. Палойоки типичен и демонстрирует их интенсивное вымывание из вмещающих пород и почв. Для оз. Игнатково характерно поступление TR из почв Q_{IV}, в которых процесс выведения легких TR из ледниковых отложений практически завершен. Спектры тяжелых TR демонстрируют в обоих случаях значительное адсорбционное выведение в коллоиды при существенно более низкой концентрации в случае озера средней полосы России. Эти же выводы подтверждаются отсутствием европиевого максимума для вод средней полосы, так как частично двухвалентный европий вынесен из подпочвенного субстрата и почв в течение длительной геологической истории эволюции состава ледниковых отложений. Для рек северной зоны, напротив, наблюдается европиевый (и для соседнего Gd) максимум, так как процесс его экстракции не завершен и он более подвижен в двухвалентной форме, характерной для восстановительных условий болотной обстановки. В этих же водоемах обратные соотношения наблюдаются для церия, частичное присутствие которого в 4-валентном состоянии предопределяет его накопление (слабый максимум) в породах средней полосы в течение геологической истории и меньшую миграционную подвижность в северной зоне в современную эпоху. На этом фоне отчетливо проявлено значительное адсорбционное связывание (меньшая подвижность) тяжелых TR в обоих случаях.

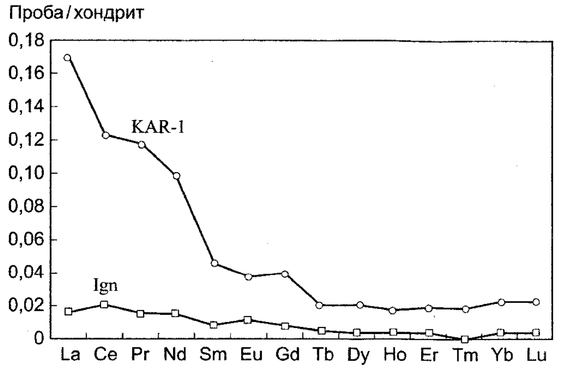

Рис. 2. Нормализованные спектры распределения редкоземельных элементов, растворенных (0,2 мкм) в водных пробах сравниваемых регионов:
KAR-1 — р. Палойоки (бореальная зона) и Ign — оз. Игнатково (Мещерская низменность)

Достаточно типичны кривые выведения отдельных фракций ОВ от области питания к области транзита и депонирующему озеру (рис. 3, *А*, KAR-2, KAR-1 и KAR-3). Для области питания (KAR-2) характерны неоднородность распределения молекул ОВ по крупности и их более высокие концентрации. В водотоке (р. Палойоки) происходит существенная сортировка размеров молекул в резуль-

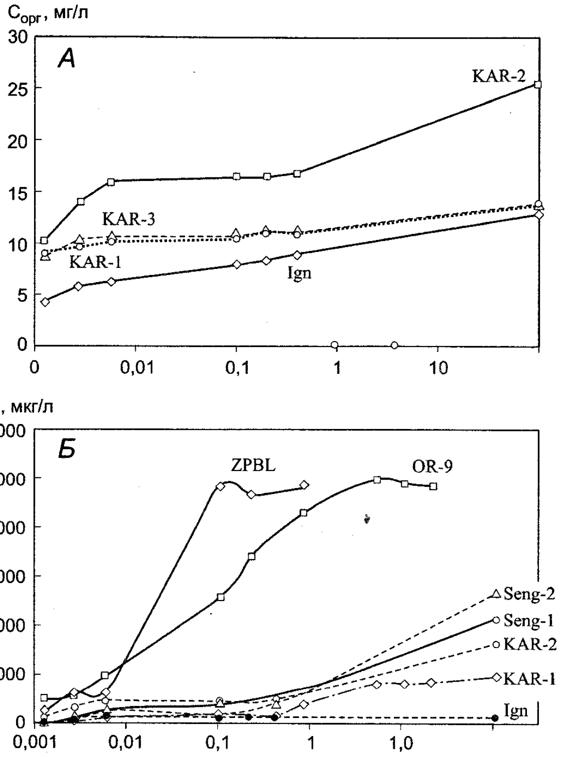

Рис. 3. Распределение $C_{орг}$ (*А*) и Fe (*Б*) по фракциям крупности в водах сравниваемых регионов:
KAR-1 — р. Палойоки, среднее течение; KAR-2 — р. Палойоки, питающее болото; KAR-3 — р. Палойоки, приустьевая часть; OR-9 — почвенный раствор водосборного бассейна руч. Восточный; ZPBL — водоток болотных вод, непосредственно разгружающихся в оз. Ципринга (Северная Карелия); Seng-1 — р. Сеньга, приустьевая часть; Seng-2 — р. Сеньга, среднее течение; Ign — оз. Игнатково (Мещерская низменность)

тате процессов их седиментации и дезинтеграции. Вплоть до устьевой части (KAR-3) тренды распределения молекул по крупности существенно линеаризируются с почти постоянным угловым коэффициентом их массовых долей, вплоть до молекул, представленных в самых тонких фракциях фульвокислотами. Для сравнения здесь же отображены данные по оз. Игнатково, в водах которого ОВ консервативно находится в состоянии равновесного стоксовского распределения молекул по крупности. Для таких случаев медленное седиментационное выведение реализуется в форме линейных зависимостей массовых долей молекул ОВ при более низкой общей концентрации. Таким образом, случаи нелинейных трендов выведения ОВ на фильтрах всегда характеризуют полигенность источников (смешение вод реки и притоков) или резкие изменения гидрологического режима, при которых возможна как дезинтеграция ассоциатов молекул ОВ, так и их агрегация в условиях медленного течения. Аналогичные закономерности наблюдаются и в распределении по крупности коллоидов гидроксидов железа, но с некоторыми особенностями (рис. 3, *Б*). В водах почвенных растворов и болот наблюдаются самые высокие исходные концентрации железа, практически не уменьшающиеся при фильтрации через грубопористые мембраны. Процесс выведения железа из этих растворов с резким падением концентрации наблюдается при достижении размера пор аналогичного коллоидным частицам максимального размера. Только в этих системах на кривых выведения наблюдается горизонтальный участок в области максимальных концентраций железа. Отметим, что для этих растворов в этой же области размеров пор не наблюдается значимого выведения и других элементов-гидролизатов, сопровождающих коллоиды гидроксида железа. Во всех остальных случаях (реки и озера) тренды выведения коллоидных частиц разной размерности достаточно линейны, но в различных интервалах (от 5 до 0,1—0,01 мкм). Для кривых выведения железа характерны также практически горизонтальные участки в области пор самого малого размера. Эти области характеризуются преобладанием истинно растворенных комплексов железа с ОВ гуминовой природы после практически полного извлечения коллоидной составляющей. Известно, что наибольшей агрегативной устойчивостью обладают коллоиды $Fe(OH)_3$ с максимумом в интервале 1—0,1 мкм. Более тонкие быстро укрупняются, а крупные седиментируют и присутствуют в значимых количествах только в почвенных растворах и застойных болотных водах.

Достаточно информативны графики скоррелированности изменений коэффициентов задержки ($R = 1 - C_{проб}/C_{исх}$) микроэлементов и элементов-коллекторов (ОВ и коллоиды гидроксида железа). Для среднего течения р. Палойоки (рис. 4, *А*, *Б*) практически отсутствует выведение микроэлементов при двукратном уменьшении концентраций $C_{орг}$ в крупных фракциях речного стока. Это свидетельствует о незначительности доли микроэлементов, адсорбционно связанных с крупными агрегатами молекул ОВ. В дальнейшем, по мере увеличения относительной доли истинно растворенного ОВ (фульвокислот) наблюдается согласованное изменение коэффициентов задержки и доли выводимого $C_{орг}$. Это подобие в значительной степени связано с совместным выведением микроэлементов (и железа) на крутом участке зависимости в виде крупных ассоциатов с ОВ (рис. 4, *А*). Значительное выведение микроэлементов для тонких фильтров также сопровождается аналогичной по величине задержкой ОВ. Это область преобладания комплексов фульвокислот с микроэлементами (на рис. 4, *А* верхние точки). Элементы, подобные Ca (Na, K, Mg), имеют коэффициенты задержки $R = 0$, т.е. не выводятся на фильтрах, вплоть до мембраны 1 кДа. Наблюдается стационарно небольшая задержка стронция. Более закономерны корреляции между коэффициентами задержки железа с $C_{орг}$ и микроэлементами. Значительная скореллированность наблюдается только между железом и элементами-гидролизатами. Связь между коэффициентами задержки $C_{орг}$ и Fe значительно более слабая. Существенное выведение железа в виде коллоида $Fe(OH)_3$ не сопровождается аналогичным по масштабам выведением ОВ. Оно накапливается и выводится главным образом в последних фильтратах. В консервативном объекте сравнения (оз. Игнатково) в процессе седиментационного выведения достигнуто стационарное состояние, при котором доли крупных коллоидных частиц из растворов выведены. Поэтому на кривых корелляций в области крупных размеров пор в фильтратах не наблюдаются значимые коэффициенты задержки как при сравнении с железом (рис. 5, *Б*), так и с $C_{орг}$ (рис. 5, *А*). Существенное выведение наблюдается только для области килодальтонных фильтров. Этот неожиданный вывод приводит нас к очевидному заключению: для сравниваемых регионов спектры концентраций микроэлементов весьма подобны (рис. 1), а распределение элементов по отдельным фракциям крупности целиком определяется различиями в гидрологических режимах. При близких исходных концентрациях взвешенного и растворенного ОВ, а также коллоидов гидроксидов железа, особенности молекулярно-массового распределения (ММР) в отдельных точках пробоотбора обусловлены динамикой водных потоков.

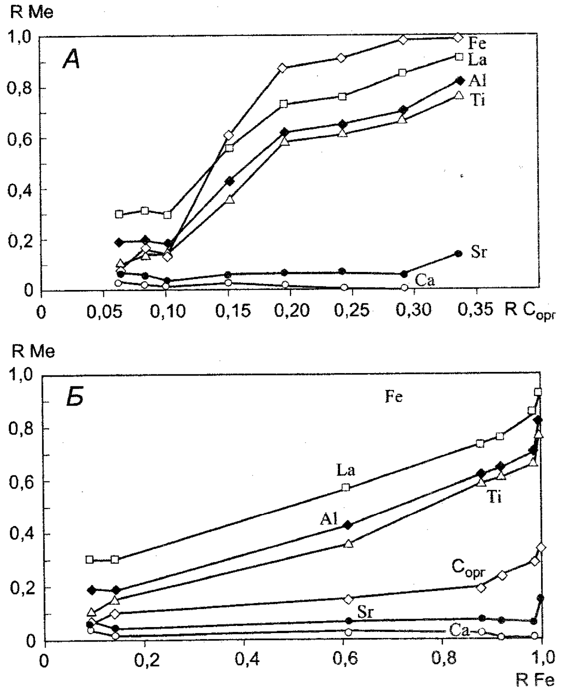

Рис. 4. Парные корреляции коэффициентов интегральной задержки (*R*) микроэлементов — $C_{орг}$ (*А*) и Fe (*Б*) в сериях последовательных фильтратов для среднего течения р. Палойоки

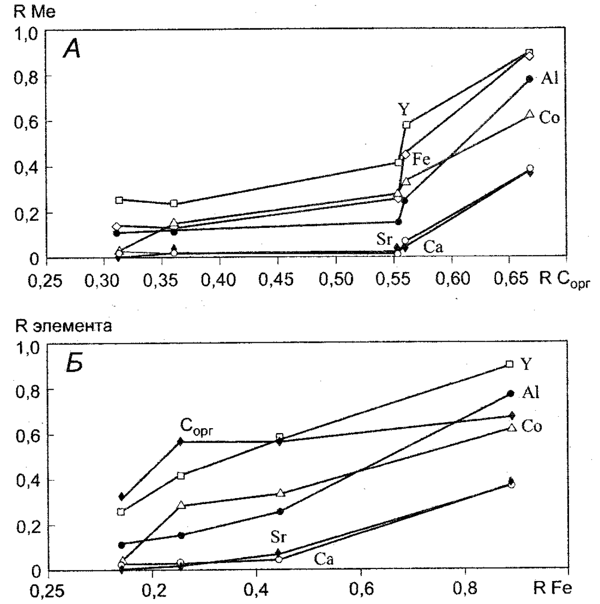

Рис. 5. Парные корреляции коэффициентов интегральной задержки (*R*) микроэлементов — $C_{орг}$ (*А*) и Fe (*Б*) в сериях последовательных фильтратов для оз. Игнатково

Заключение

Нами впервые собран значительный аналитический материал, характеризующий распределение микроэлементов (около 50) по фракциям крупности составляющих речного стока в двух регионах. Их подобие в спектре концентраций микроэлементов нами ожидалось. Однако ожидалось также, что будут выявлены и многие различия в распределении форм миграции отдельных микроэлементов по фракциям крупности, связанные с тем, что сравниваемые районы различаются по модулям стока и особенностям русловых процессов. Тем не менее для равнинной р. Сеньга не выявлено сколько-нибудь значимых отличий по фракциям крупности от аналогичного распределения микроэлементов в р. Палойоки (табл. 6—9 в Приложении *А*). С одной стороны, это ожидаемый результат, так как для всех рек и ручьев сравниваемых районов полностью преобладает питание болотными водами. С другой стороны — несомненно отмечаются значимые отличия в спектрах накопления редкоземельных элементов для этих районов с долгой и разной геологической предысторией. Особенности накопления и адсорбционного выведения индивидуальных элементов редких земель достаточно специфичны и демонстрируют существенно более высокую степень выравненности их спектров в случае Мещёрской низменности. При всей специфичности кривых выведения микроэлементов для всех точек опробования сравниваемых регионов основной причиной различий в молекулярно-массовом распределении является локальная изменчивость гидрологического режима.

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Приложение *А*

Результаты анализов исходных проб и последовательных фильтратов (мкг/л)

Таблица 1

Результаты анализа пробы OR-1 при параллельной фильтрации (устье руч. Восточный)

Элемент	20 мкм	10 мкм	5 мкм	0,8 мкм	0,1 мкм	0,0065 мкм	0,0027 мкм	0,0013 мкм
Na	963,4	782,1	778,6	773,5	775,6	789,5	776,5	(857,9)*
Mg	564	550,4	555	549,5	545,3	560,5	544,9	427,6
Al	189,4	195,1	197,2	194,3	180,8	180,4	157,3	59,18
K	40,15	38,15	38,72	40,26	40,06	38,63	38,13	26,49
Ca	2166	2089	2102	2065	2062	2122	2026	1430
Sc	0,28	0,26	0,27	0,26	0,29	0,28	0,27	0,21
Ti	1,11	0,99	1,03	0,93	0,73	0,61	0,47	0,19
V	0,17	0,14	0,14	0,14	0,11	0,09	0,09	0,08
Cr	0,43	0,43	0,41	0,37	0,40	0,37	0,36	0,22
Mn	9,29	8,82	8,89	8,71	8,34	6,08	5,47	4,21
Fe	245	238,1	237,7	217,7	120,2	77,7	48,44	7,88
Co	0,099	0,104	0,107	0,105	0,106	0,081	0,063	0,013
Ni	0,675	0,681	0,676	0,639	(0,803)	0,681	0,646	0,362
Cu	0,843	0,794	0,814	0,792	0,812	0,781	0,702	0,467
Zn	5,78	2,02	1,57	1,45	2,13	1,87	(5,81)	(3,27)
Ga	(0,0048)	0,0107	0,0096	0,0091	0,0067	0,0069	0,0040	0,0008
Ge	0,0057	0,0053	0,0057	0,0055	0,0044	0,0045	0,0035	0,0019
As	0,120	0,116	0,116	0,109	0,109	0,110	0,100	0,071
Rb	0,274	0,339	0,285	0,266	0,252	0,258	0,250	0,207
Sr	6,72	6,92	6,90	6,85	6,79	6,88	6,58	4,65
Y	0,184	0,182	0,186	0,178	0,167	0,168	0,136	0,056
Zr	0,132	0,134	0,134	0,137	0,134	0,130	0,127	0,034
Mo	(0,0040)	(0,0322)	0,0146	0,0145	0,0073	0,0031	0,0024	ПО**
Sb	(0,0233)	0,0625	0,0396	0,0353	(0,1648)	0,0245	0,0232	0,0096
Cs	(0,0011)	0,0021	0,0018	0,0020	0,0020	0,0016	0,0014	0,0008
Ba	8,81	9,34	9,30	9,18	8,90	8,81	7,98	4,83
La	0,393	0,414	0,416	0,405	0,363	0,363	0,278	0,085
Ce	0,727	0,757	0,755	0,741	0,669	0,648	0,505	0,159
Pr	0,0955	0,1002	0,1011	0,0966	0,0897	0,0873	0,0687	0,0232
Nd	0,353	0,376	0,385	0,368	0,328	0,326	0,260	0,087
Sm	0,0602	0,0591	0,0617	0,0607	0,0581	0,0548	0,0418	0,0165
Eu	0,0126	0,0130	0,0121	0,0125	0,0117	0,0113	0,0090	0,0030
Gd	0,1033	0,0561	0,0537	0,0549	0,0505	0,0463	0,0394	0,0252
Tb	0,0059	0,0065	0,0067	0,0066	0,0058	0,0056	0,0047	0,0015
Dy	0,0340	0,0363	0,0356	0,0341	0,0319	0,0324	0,0256	0,0097
Ho	0,0063	0,0070	0,0069	0,0064	0,0059	0,0061	0,0051	0,0019
Er	0,0187	0,0189	0,0193	0,0183	0,0183	0,0185	0,0150	0,0062
Tm	0,0026	0,0027	0,0024	0,0028	0,0025	0,0024	0,0023	0,0008
Yb	0,0158	0,0186	0,0183	0,0179	0,0169	0,0150	0,0143	0,0057
Lu	0,0024	0,0031	0,0025	0,0023	0,0027	0,0023	0,0019	0,0012
Hf	0,0066	0,0082	0,0069	0,0079	0,0070	0,0074	0,0066	0,0018
W	ПО	(0,0073)	0,0032	0,0020	0,0019	0,0017	0,0001	ПО
Pb	(0,0247)	0,0353	0,0376	0,0272	0,0097	0,0032	(0,0122)	ПО
Th	0,0373	0,0365	0,0360	0,0379	0,0420	0,0378	0,0324	0,0056
U	0,0081	0,0081	0,0087	0,0083	0,0074	0,0080	0,0069	0,0018

*Здесь и далее в скобках приведены аномальные концентрации ввиду мембранного накопления и задержки; **здесь и далее ПО — концентрации ниже предела обнаружения.

Таблица 2

Результаты анализа фильтратов пробы OR-2 при параллельной фильтрации (руч. Восточный, среднее течение)

Элемент	20 мкм	10 мкм	5 мкм	0,8 мкм	0,1 мкм	0,0065 мкм	0,0027 мкм	0,0013 мкм
B	1,43	1,28	1,17	1,17	1,12	1,20	1,26	1,30
Na	752,0	743,8	734,9	734,3	744,1	733,6	731,5	(801,5)
Mg	512,8	509,7	502,3	504,6	499,1	496,8	490,9	376,7
Al	155,1	155,4	152,1	151,9	140,2	140,6	126,7	39,7
Si	1153	1150	1124	1121	1114	1104	1101	(1141)
P	(2,31)	3,81	3,48	2,18	1,14	0,52	(2,33)	(4,56)
K	12,45	12,85	11,4	10,48	(13,25)	8,84	(17,26)	5,71
Ca	2271	2261	2236	2276	2228	2224	2150	1413
Ti	0,643	0,659	0,609	0,623	0,479	0,488	0,355	0,119
V	0,167	0,151	0,155	0,151	0,131	0,129	0,116	0,107
Cr	0,298	0,292	0,259	0,271	0,358	0,305	0,257	0,134
Mn	6,23	6,25	6,26	6,23	5,82	5,71	5,52	3,80
Fe	256,5	252,6	270,3	239,1	141,7	138,3	93,8	9,1
Co	0,124	0,128	0,125	0,127	0,120	0,122	0,115	0,039
Ni	0,563	0,551	0,574	0,562	0,552	0,556	0,524	0,275
Cu	0,466	0,487	0,487	0,474	0,558	0,454	0,417	0,199
Zn	1,44	1,32	1,44	1,40	1,42	(2,82)	(6,87)	1,23
Ga	0,0070	0,0073	0,0064	0,0058	0,0040	0,0043	0,0038	0,0007
Ge	0,0018	0,0022	0,0025	(0,0039)	0,0012	0,0014	0,0011	(0,0053)
As	0,122	0,129	0,125	0,117	0,118	0,119	0,115	0,092
Rb	0,120	0,114	0,108	0,105	0,108	0,099	0,102	(0,141)
Sr	6,73	6,82	6,70	6,74	6,63	6,53	6,37	3,99
Y	0,0970	0,0955	0,0993	0,0957	0,0886	0,0879	0,0739	0,0226
Zr	0,0651	0,0658	0,0663	0,0650	0,0671	0,0650	0,0604	0,0125
Nb	0,0113	0,0077	0,0063	0,0057	0,0056	0,0035	0,0029	(0,0147)
Mo	0,0079	0,0088	0,0051	0,0046	0,0005	0,0012	ПО	(0,0073)
Cd	0,0267	0,0248	0,0224	0,0251	0,0260	0,0238	0,0174	0,0085
Sn	0,0018	0,0028	0,0025	0,0005	0,0010	(0,0022)	(0,0041)	ПО
Sb	0,03408	0,02543	0,02558	0,025	(0,1729)	0,01965	0,0199	0,02927
Cs	0,0016	0,0013	0,0015	0,0011	0,0010	0,0012	0,0013	0,0011
Ba	7,98	7,94	7,94	7,96	7,72	7,71	6,97	3,66
La	0,170	0,172	0,173	0,167	0,148	0,147	0,117	0,024
Ce	0,338	0,336	0,338	0,330	0,292	0,294	0,230	0,052
Pr	0,0428	0,0429	0,0442	0,0430	0,0386	0,0368	0,0298	0,0070
Nd	0,168	0,168	0,166	0,167	0,149	0,141	0,116	0,029
Sm	0,0278	0,0292	0,0282	0,0295	0,0236	0,0263	0,0186	0,0049
Eu	0,0070	0,0062	0,0057	0,0064	0,0063	0,0055	0,0056	0,0012
Gd	0,0239	0,0246	0,0261	0,0225	0,0231	0,0224	0,0176	0,0092
Tb	0,0032	0,0030	0,0030	0,0026	0,0027	0,0027	0,0022	0,0005
Dy	0,0176	0,0178	0,0161	0,0175	0,0157	0,0157	0,0133	0,0035
Ho	0,0034	0,0036	0,0032	0,0036	0,0030	0,0031	0,0025	0,0006
Er	0,0091	0,0113	0,0098	0,0107	0,0095	0,0096	0,0088	0,0023
Tm	0,0015	0,0018	0,0014	0,0013	0,0014	0,0012	0,0012	0,0003
Yb	0,0108	0,0111	0,0112	0,0087	0,0089	0,0096	0,0072	0,0033
Lu	0,0016	0,0016	0,0014	0,0015	0,0013	0,0014	0,0012	0,0003
Hf	0,0044	0,0041	0,0041	0,0033	0,0048	0,0031	0,0035	0,0024
W	0,00199	0,00171	0,00086	0,00055	0,00081	ПО	ПО	(0,00095)
Pb	0,0664	0,0650	0,0707	0,0623	(0,0166)	0,0416	0,0192	ПО
Bi	0,0011	0,0013	0,0008	0,0009	0,0003	0,0005	0,0002	0,0002
Th	0,0182	0,0191	0,0176	0,0185	0,0199	0,0196	0,0171	0,0017
U	0,0027	0,0031	0,0027	0,0022	0,0024	0,0021	0,0020	0,0003

Таблица 3

Результаты анализа пробы OR-6 при параллельной фильтрации (руч. Восточный, промежуточное проточное озеро)

Элемент	20 мкм	10 мкм	5 мкм	0,8 мкм	0,22 мкм	0,1 мкм	0,0065 мкм	0,0027 мкм	0,0013 мкм
B	0,87	1,07	1,09	0,98	1,31	1,03	(1,91)	(1,81)	(1,04)
Na	984,6	818,3	813,0	811,7	983,5	808,2	856,7	869,8	977,5
Mg	594,3	592,3	587,1	585,1	590,8	585,0	585,7	588,1	475,6
Al	121,4	128,8	127,5	125,7	117,0	123,3	122,5	111,7	31,8
Ca	3260	3293	3264	3269	3237	3245	3279	3228	2239
Ti	0,692	0,749	0,718	0,656	0,628	0,631	0,619	0,482	0,194
V	0,125	0,115	0,113	0,105	0,118	0,101	0,104	0,095	0,084
Cr	0,306	0,265	0,349	0,302	0,284	0,229	0,282	0,280	0,106
Mn	13,1	12,6	12,7	12,6	13,3	12,0	11,5	11,7	9,0
Fe	149,8	142,3	141,7	136,1	123,9	100,4	95,9	68,0	6,7
Co	0,0641	0,0732	0,0750	0,0766	(0,0550)	0,0756	(0,0554)	0,0715	0,0224
Ni	0,5461	0,5377	0,5247	0,5401	0,5574	0,5295	0,5233	0,5696	0,2577
Cu	0,4566	0,4872	0,4770	0,4780	0,4521	0,4468	0,4874	0,4408	0,2128
Zn	2,06	2,10	1,94	1,77	1,79	2,01	2,94	(14,93)	1,58
Ga	0,0021	0,0056	0,0051	(0,0044)	(0,0023)	(0,0038)	0,0047	0,0038	0,0003
Ge	0,0014	0,0029	0,0019	0,0016	0,0020	0,0020	(0,0034)	(0,0031)	(0,0020)
As	0,12	0,11	0,11	0,10	0,10	0,11	0,12	0,11	0,08
Rb	0,2030	0,1766	0,1634	0,1571	(0,2453)	0,1537	(0,2561)	0,1923	0,1913
Sr	8,10	8,30	8,27	8,24	7,93	8,14	8,34	8,00	5,50
Y	0,0831	0,0813	0,0835	0,0817	0,0773	0,0768	0,0773	0,0698	0,0173
Zr	0,0632	0,0647	0,0644	0,0635	0,0582	0,0624	0,0713	0,0672	0,0152
Mo	0,0029	0,0034	0,0034	0,0017	0,0024	0,0009	(0,0282)	(0,0195)	(0,0054)
Cd	0,0102	0,0110	0,0109	0,0101	0,0099	0,0091	0,0098	0,0059	0,0033
Sb	0,0212	0,0237	0,0222	0,0230	0,0365	(0,1325)	(0,0664)	(0,0458)	(0,0279)
Ba	6,10	6,45	6,38	6,35	5,94	6,27	6,29	5,78	3,35
La	0,1076	0,1112	0,1104	0,1072	0,1006	0,1023	0,1024	0,0767	0,0158
Ce	0,1522	0,1597	0,1622	0,1565	0,1437	0,1520	0,1459	0,1108	0,0240
Pr	0,0274	0,0284	0,0293	0,0277	0,0261	0,0270	0,0278	0,0197	0,0042
Nd	0,1035	0,1059	0,1083	0,1018	0,0986	0,1062	0,1007	0,0780	0,0182
Sm	0,0168	0,0186	0,0175	0,0188	0,0179	0,0173	0,0180	0,0145	0,0029
Eu	0,0040	0,0046	0,0050	0,0047	0,0042	0,0042	0,0045	0,0037	0,0008
Gd	0,0334	0,0174	0,0214	0,0181	(0,0311)	0,0161	0,0162	0,0136	0,0062
Tb	0,0021	0,0024	0,0023	0,0021	0,0021	0,0024	0,0023	0,0017	0,0002
Dy	0,0135	0,0137	0,0142	0,0137	0,0132	0,0139	0,0132	0,0100	0,0031
Ho	0,0023	0,0028	0,0028	0,0027	0,0027	0,0026	0,0027	0,0021	0,0005
Er	0,0086	0,0086	0,0081	0,0086	0,0075	0,0082	0,0078	0,0071	0,0019
Tm	0,0010	0,0011	0,0012	0,0011	0,0010	0,0012	0,0011	0,0010	0,0002
Yb	0,0093	0,0089	0,0074	0,0083	0,0084	0,0082	0,0084	0,0062	0,0021
Lu	0,0012	0,0011	0,0011	0,0015	0,0012	0,0012	0,0013	0,0010	0,0002
Hf	0,0040	0,0037	0,0041	0,0043	0,0047	0,0037	(0,0073)	(0,0074)	0,0022
W	0,0003	0,0021	0,0015	0,0011	0,0024	0,0006	(0,0079)	(0,0040)	(0,0015)
Pb	0,0200	0,0296	0,0253	0,0269	0,0127	0,0161	0,0217	конт.*	конт.
Th	0,0192	0,0200	0,0191	0,0192	0,0189	0,0192	0,0199	0,0177	0,0023
U	0,0033	0,0029	0,0027	0,0031	0,0031	0,0028	0,0031	0,0029	0,0004

* Здесь и далее “конт.” — аналитический результат недостоверен из-за случайного загрязнения фильтрата пробы.

Таблица 4

Результаты анализа пробы OR-9 при параллельной фильтрации (бассейн руч. Восточный, почвенный раствор)

Элемент	20 мкм	10 мкм	5 мкм	0,8 мкм	0,22 мкм	0,1 мкм	0,0065 мкм	0,0027 мкм	0,0013 мкм
Na	1225	1254	1260	1294	1216	(1760)	1260	981,8	879,3
Mg	492,1	505,2	507,5	431,5	410,1	(471,4)	205,1	153,9	107,2
Al	602,7	612,0	617,9	490,1	380,2	(463)	273,0	189,0	91,0
Si	2484	2571	2614	(1741)	(1966)	2533	2437	2391	1842
P	45,0	46,1	47,4	25,0	17,0	18,0	6,8	5,1	4,4
K	377,4	401,8	403,2	327,6	344,7	(509,5)	319,5	238,9	208,4
Ca	1275	1295	1291	1155	1281	988,2	426,9	489,2	195,4
Sc	0,3583	0,3820	0,3934	0,2732	0,2767	0,3208	0,2837	0,2575	0,2362
Ti	3,95	4,36	3,98	3,23	2,24	1,87	0,50	0,28	0,19
V	1,056	1,049	1,078	0,989	0,925	0,850	0,603	0,371	0,288
Cr	1,037	1,037	1,139	0,949	0,736	0,647	0,393	0,261	0,164
Mn	33,1	33,7	33,8	30,2	(48,6)	26,0	11,3	8,4	6,3
Fe	9794	9863	10010	8613	6821	5176	1851	1034	841,9
Co	1,13	1,14	1,16	1,01	0,95	0,80	0,33	0,23	0,16
Ni	2,43	2,39	2,43	2,26	1,85	1,63	0,65	0,56	0,30
Cu	1,17	1,21	1,43	1,16	1,40	0,92	0,38	0,28	0,39
Zn	13,7	11,0	11,0	10,4	конт.	8,4	5,6	(10,9)	3,9
Ga	0,0950	0,0870	0,0942	0,0453	0,0346	(0,0532)	0,0284	0,0191	0,0053
Ge	0,0101	0,0085	(0,0125)	0,0092	0,0080	0,0065	0,0058	0,0034	0,0019
As	0,704	0,694	0,678	0,658	0,521	0,443	0,276	0,207	0,204
Rb	0,957	0,975	0,974	1,171	1,195	0,935	0,743	0,535	0,634
Sr	9,67	9,78	9,63	9,59	7,90	6,75	2,80	1,97	1,33
Y	0,268	0,268	0,264	0,264	0,190	0,141	0,058	0,040	0,029
Zr	0,125	0,135	0,132	0,127	0,104	0,089	0,035	0,017	0,016
Nb	0,0253	0,0264	0,0269	(0,0511)	0,0154	0,0191	0,0093	0,0053	0,0065
Mo	0,0243	0,0190	0,0177	(0,0310)	(0,0024)	(0,0148)	0,0052	0,0054	0,0016
Cd	0,0439	0,0432	0,0487	0,0444	(0,2046)	0,0328	0,0123	0,0098	0,0070
Sn	0,0735	0,0742	0,0706	0,0527	(0,2248)	0,0264	0,0048	0,0032	ПО
Sb	0,0467	0,0458	0,0504	0,0799	0,1093	(2,504)	0,0270	0,0192	0,0205
Cs	0,0078	0,0070	0,0076	0,0080	0,0074	0,0068	0,0057	0,0043	0,0046
Ba	11,0	11,1	10,9	11,3	7,9	6,2	2,3	1,5	0,8
La	0,250	0,253	0,249	0,259	0,164	0,121	0,034	0,026	0,014
Ce	0,624	0,635	0,627	0,645	0,419	0,312	0,103	0,066	0,044
Pr	0,0698	0,0702	0,0713	0,0718	0,0485	0,0360	0,0128	0,0087	0,0055
Nd	0,267	0,258	0,256	0,269	0,187	0,146	0,055	0,035	0,026
Sm	0,0488	0,0486	0,0519	0,0532	0,0361	0,0259	0,0109	0,0066	0,0045
Eu	0,0130	0,0143	0,0127	0,0134	0,0091	0,0061	0,0030	0,0014	0,0014
Gd	0,0468	0,0521	0,0501	(0,0934)	(0,0683)	0,0253	0,0117	0,0065	0,0097
Tb	0,0064	0,0060	0,0063	0,0065	0,0047	0,0035	0,0012	0,0009	0,0005
Dy	0,0367	0,0391	0,0397	0,0397	0,0291	0,0210	0,0087	0,0052	0,0040
Ho	0,0080	0,0088	0,0076	0,0082	0,0061	0,0049	0,0017	0,0012	0,0008
Er	0,0254	0,0243	0,0221	0,0249	0,0190	0,0157	0,0068	0,0042	0,0034
Tm	0,0040	0,0037	0,0039	0,0037	0,0028	0,0021	0,0010	0,0006	0,0005
Yb	0,0206	0,0207	0,0239	0,0243	0,0170	0,0154	0,0080	0,0041	0,0040
Lu	0,0034	0,0037	0,0031	0,0031	0,0024	0,0024	0,0013	0,0006	0,0006
Hf	0,0067	0,0075	0,0075	0,0082	0,0061	0,0050	0,0027	0,0016	0,0023
W	0,0086	0,0093	0,0110	0,0097	0,0053	0,0054	0,0017	0,0003	ПО
Pb	1,39	1,43	1,42	1,43	0,94	0,53	0,11	0,05	0,03
Bi	0,0175	0,0166	0,0165	0,0142	0,0085	0,0058	0,0015	0,0007	0,0008
Th	0,0318	0,0324	0,0343	0,0307	0,0248	0,0190	0,0062	0,0023	0,0026
U	0,0019	0,0027	0,0022	0,0020	0,0026	0,0014	0,0004	0,0004	0,0005

Таблица 5

Результаты анализа пробы ZPBL при параллельной фильтрации (низинное болото, область высачивания и разгрузки подземных вод на восточном берегу оз. Ципринга)

Элемент	20 мкм	10 мкм	5 мкм	0,8 мкм	0,0065 мкм	0,0027 мкм	0,0013 мкм
Na	983,0	828,5	846,7	783,1	668,8	612,7	708,8
Mg	1167,0	1274,0	1297,0	1229,0	772,5	635,2	392,8
Al	252,1	256,9	277,5	271,4	139,9	87,4	49,9
K	63,7	68,2	73,5	58,6	53,3	43,3	37,2
Ca	1778	1788	1851	1761	1039	810,8	481,4
Sc	0,421	0,427	0,420	0,402	0,321	0,293	0,259
Ti	1,66	1,69	2,09	1,98	0,39	0,28	0,16
V	0,279	0,246	0,342	0,433	0,060	0,099	0,057
Cr	1,62	1,45	1,67	1,62	0,72	0,43	0,21
Mn	47,4	44,4	44,9	45,3	27,8	21,1	13,4
Fe	7651	6168	8306	9694	1257	1202	484,4
Co	0,983	0,883	0,950	0,955	0,510	0,340	0,182
Ni	1,67	1,49	1,62	1,59	0,82	0,50	0,28
Cu	0,109	0,122	0,163	0,165	0,077	0,068	0,024
Zn	5,56	5,38	6,54	6,81	4,56	4,19	2,90
Ga	0,0080	0,0160	0,0216	0,0203	0,0050	0,0038	0,0011
Ge	0,0054	0,0070	0,0069	0,0077	0,0032	0,0033	0,0012
As	0,2885	0,2642	0,3023	0,3024	0,1500	0,1319	0,1050
Rb	0,2886	0,2755	0,2652	0,2504	0,2461	0,2058	0,1778
Sr	8,02	7,81	8,18	7,83	4,67	3,36	2,11
Y	0,3859	0,3580	0,3811	0,3768	0,1928	0,1093	0,0595
Zr	0,3907	0,3770	0,4127	0,4091	0,1462	0,0934	0,0093
Nb	0,0117	0,0144	0,0153	0,0146	0,0163	0,0096	ПО
Mo	0,0077	0,0097	0,0072	0,0084	0,0155	0,0099	ПО
Cd	0,0053	0,0055	0,0102	0,0072	0,0044	0,0046	0,0014
Sb	0,0382	0,0305	0,0313	0,0284	0,0368	0,0359	0,0074
Cs	0,0016	0,0029	0,0024	0,0024	0,0025	0,0021	0,0016
Ba	5,06	4,84	5,33	5,24	2,43	1,34	0,98
La	0,3506	0,3330	0,3769	0,3736	0,1388	0,0692	0,0341
Ce	0,9116	0,8681	0,9764	0,9630	0,4045	0,2029	0,1104
Pr	0,0978	0,0949	0,1069	0,1065	0,0465	0,0235	0,0135
Nd	0,3877	0,3718	0,4167	0,4109	0,1968	0,1041	0,0611
Sm	0,0737	0,0723	0,0756	0,0769	0,0353	0,0228	0,0112
Eu	0,0157	0,0144	0,0163	0,0164	0,0081	0,0047	0,0023
Gd	0,1477	0,0744	0,0773	0,0789	0,0382	0,0190	0,0239
Tb	0,0095	0,0096	0,0104	0,0106	0,0045	0,0026	0,0014
Dy	0,0609	0,0600	0,0674	0,0661	0,0307	0,0178	0,0090
Ho	0,0135	0,0130	0,0140	0,0135	0,0066	0,0041	0,0020
Er	0,0419	0,0412	0,0440	0,0414	0,0215	0,0139	0,0067
Tm	0,0064	0,0063	0,0063	0,0059	0,0036	0,0020	0,0010
Yb	0,0412	0,0393	0,0448	0,0449	0,0230	0,0139	0,0080
Lu	0,0061	0,0060	0,0069	0,0065	0,0036	0,0022	0,0013
Hf	0,0136	0,0122	0,0144	0,0131	0,0069	0,0040	0,0006
Bi	0,0011	0,0011	0,0017	0,0014	0,0002	0,0003	ПО
Th	0,0978	0,0964	0,1054	0,1043	0,0330	0,0186	0,0021
U	0,0112	0,0111	0,0122	0,0122	0,0047	0,0023	0,0010

Таблица 6

Результаты анализа пробы KAR-1/2009 (р. Палойоки) при параллельной фильтрации

Элемент	100 мкм	20 мкм	10 мкм	5 мкм	0,8 мкм	0,4 мкм	0,22 мкм	0,1 мкм	0,0065 мкм	0,0027 мкм	0,0013 мкм
Na	1089	1337	1153	1170	1186	1190	1312	1177	1177	1204	1325
Mg	1114	1060	1187	1189	1194	1187	1035	1190	1182	1202	1010
Al	66,2	53,5	53,1	54,0	37,9	25,3	27,3	29,1	23,5	(76,6)	12,0
K	220,7	219,1	225,7	230,5	236,4	229,9	212,6	229,2	235,4	239,4	220,2
Ca	4265	4121	4163	4186	4146	4187	3841	4042	4239	4255	3762
Sc	0,292	0,318	0,315	0,326	0,305	0,286	0,279	0,291	0,289	0,278	0,293
Ti	0,846	0,756	0,728	0,810	0,542	0,350	0,485	0,399	0,331	0,284	0,200
V	0,290	0,294	0,269	0,272	0,131	0,066	0,087	0,074	0,057	0,055	0,046
Cr	0,292	0,230	0,257	0,281	0,226	0,225	0,221	0,216	0,246	0,234	0,137
Mn	37,7	9,8	9,9	10,6	9,5	16,3	11,6	17,5	17,2	19,5	18,0
Fe	1882	1708	1575	1621	743	242,6	214,8	287,4	165,4	38,3	18,89
Co	0,175	0,025	0,034	0,042	0,026	0,038	0,017	0,043	0,081	0,118	0,058
Ni	0,289	0,189	0,193	0,195	0,197	0,227	0,194	0,222	0,343	0,339	0,334
Cu	0,261	0,303	0,309	0,310	0,319	0,086	0,299	0,457	0,144	0,445	0,117
Zn	5,09	3,35	1,50	2,17	2,34	7,40	0,83	1,77	14,90	32,50	58,65
Ga	0,0084	(0,0026)	0,0070	0,0060	0,0038	0,0025	0,0022	0,0029	0,0022	(0,0084)	0,0018
Ge	0,0046	0,0037	0,0062	0,0052	0,0024	0,0029	0,0030	0,0035	0,0026	0,004448	0,0042
As	0,138	0,166	0,158	0,164	0,144	0,126	0,133	0,133	0,125	0,116	0,122
Rb	0,554	0,557	0,632	0,586	0,580	0,561	0,593	0,551	0,546	0,551	0,736
Sr	23,9	22,2	22,3	22,8	22,3	22,2	20,8	21,7	22,2	22,4	20,4
Y	0,0881	0,0682	0,0656	0,0669	0,0492	0,0395	0,0378	0,0420	0,0368	0,0295	0,0191
Zr	0,0858	0,0704	0,0720	0,0771	0,0779	0,0629	0,0650	0,0688	0,0621	0,0594	0,0353
Nb	(0,0021)	(0,0025)	0,0221	0,0164	0,0139	0,0075	0,0063	0,0061	0,0044	0,0045	(0,0306)
Mo	0,1238	0,1148	0,1591	0,1431	0,1387	0,1334	0,1212	0,1183	0,1294	0,1359	0,1457
Cd	0,0198	0,0016	0,0037	0,0027	0,0054	0,0158	0,0013	0,0022	0,0158	0,0128	0,0100
Cs	0,0032	(0,0017)	0,0030	0,0033	0,0028	0,0025	0,0025	0,0024	0,0024	0,0025	0,0031
Ba	4,55	3,78	3,98	3,99	3,67	3,58	3,10	3,13	3,55	3,39	3,46
La	0,195	0,136	0,134	0,136	0,085	0,052	0,048	0,053	0,047	0,029	0,016
Ce	0,3637	0,2506	0,2590	0,2630	0,1623	0,0999	0,0954	0,1059	0,0891	0,0546	0,0313
Pr	0,0500	0,0340	0,0352	0,0355	0,0223	0,0143	0,0130	0,0150	0,0131	0,0080	0,0040
Nd	0,190	0,139	0,145	0,144	0,092	0,059	0,059	0,064	0,052	0,032	0,019
Sm	0,0306	0,0217	0,0215	0,0229	0,0134	0,0089	0,0093	0,0105	0,0078	0,0052	0,0029
Eu	0,0075	0,0054	0,0052	0,0051	0,0043	0,0028	0,0023	0,0028	0,0024	0,0019	0,0011
Gd	0,0264	0,0349	0,0192	0,0203	0,0128	0,0106	0,0144	0,0111	0,0092	0,0060	0,0073
Tb	0,0030	0,0020	0,0022	0,0023	0,0014	0,0009	0,0010	0,0012	0,0007	0,0008	0,0005
Dy	0,0167	0,0119	0,0134	0,0120	0,0091	0,0066	0,0063	0,0072	0,0058	0,0045	0,0026
Ho	0,0028	0,0024	0,0027	0,0023	0,0018	0,0013	0,0013	0,0013	0,0013	0,0009	0,0007
Er	0,0091	0,0073	0,0082	0,0065	0,0058	0,0041	0,0039	0,0045	0,0037	0,0026	0,0023
Tm	0,0013	0,0009	0,0011	0,0010	0,0008	0,0006	0,0004	0,0007	0,0006	0,0003	0,0004
Yb	0,0089	0,0064	0,0071	0,0074	0,0067	0,0047	0,0047	0,0051	0,0040	0,0031	0,0018
Lu	0,0013	(0,0008)	0,0013	0,0013	0,0009	0,0007	0,0006	0,0005	0,0006	0,0006	0,0001
Hf	(0,0035)	(0,0025)	0,0045	0,0042	0,0048	0,0041	0,0038	0,0037	0,0039	0,0030	(0,0060)
Pb	(0,0836)	(0,0732)	0,1141	0,0913	0,0413	0,0246	ПО	0,0148	(0,0509)	0,02362	0,0195
Bi	(0,0008)	(0,0011)	0,0016	0,0014	0,0011	(0,0003)	(0,00015)	0,0007	0,0004	0,0001	0,0003
Th	0,0174	0,0186	0,0186	0,0210	0,0171	0,0121	0,0131	0,0142	0,0112	0,0082	0,0045
U	0,0231	0,0192	0,0195	0,0193	0,0176	0,0162	0,0140	0,0153	0,0163	0,0150	0,0095

Таблица 7

Результаты анализа пробы KAR-1/2008 в варианте каскадной фильтрации

Элемент	100 мкм	0,4 мкм	0,1 мкм	0,0065 мкм	0,0027 мкм	0,0013 мкм
Na	861	901	717	857	885	884
Mg	824	846	695	811	824	837
Al	69,9	42,1	33,3	40,8	28,9	20,3
Si	1933	2004	1546	1910	1944	1994
K	167	216	151	182	186	206
Ca	3083	3110	2477	2879	2956	2914
Ti	0,833	0,382	0,364	0,346	0,202	0,213
V	0,237	0,067	0,057	0,077	0,058	0,060
Cr	0,335	0,237	0,209	0,230	0,197	0,227
Mn	71,2	66,3	52,0	64,7	62,2	60,1
Fe	1363	192,2	203,3	199,1	51,2	17,3
Co	0,336	0,294	0,237	0,276	0,263	0,261
Ni	0,483	0,549	0,379	0,450	0,426	0,463
Cu	1,37	1,24	1,09	1,37	1,18	1,15
Zn	5,71	5,14	4,74	17,63	14,47	16,38
Ga	0,0088	0,0048	0,0041	0,0043	0,0043	0,0029
Ge	0,0027	0,0067	0,0044	0,0048	0,0035	0,0023
As	0,146	(0,443)	0,128	0,207	0,180	0,184
Rb	0,401	0,447	0,353	0,409	0,413	0,427
Sr	17,8	17,5	14,1	16,7	16,6	16,2
Y	0,0963	0,0582	0,0474	0,0513	0,0374	0,0230
Zr	0,0678	0,0526	0,0455	0,0525	0,0399	0,0203
Mo	0,107	0,097	0,082	0,097	0,088	0,094
Sn	0,170	0,068	0,066	0,070	0,050	0,047
Cs	0,0012	0,0013	0,0012	0,0013	0,0013	0,0012
Ba	4,48	3,59	3,06	3,76	3,46	3,23
La	0,214	0,100	0,082	0,085	0,050	0,027
Ce	0,386	0,169	0,145	0,162	0,091	0,044
Pr	0,054	0,022	0,019	0,023	0,012	0,006
Nd	0,200	0,093	0,081	0,086	0,045	0,030
Sm	0,0335	0,0125	0,0142	0,0144	0,0102	0,0033
Eu	0,0065	0,0042	0,0032	0,0030	0,0024	0,0011
Gd	0,0308	0,0156	0,0139	0,0150	0,0089	0,0059
Tb	0,0032	0,0016	0,0016	0,0014	0,0009	0,0007
Dy	0,0173	0,0088	0,0081	0,0093	0,0051	0,0037
Ho	0,0035	0,0020	0,0020	0,0017	0,0016	0,0008
Er	0,0112	0,0068	0,0048	(0,0081)	0,0042	0,0019
Tm	0,0016	0,0007	0,0007	(0,0011)	0,0004	0,0003
Yb	0,0087	0,0064	0,0052	0,0058	0,0042	0,0010
Lu	0,0011	0,0007	0,0008	(0,0009)	0,0003	0,0003
Hf	0,0033	0,0028	0,0022	0,0019	0,0018	0,0018
Pb	0,1214	0,0343	0,0626	0,0514	ПО	ПО
Th	0,0121	0,0091	0,0085	0,0109	0,0072	0,0041
U	0,0209	0,0151	0,0142	0,0165	0,0143	0,0074

Таблица 8

Результаты анализа пробы KAR-3/2008 (устье р. Палойоки) в варианте каскадной фильтрации и диализатов проб KAR-1/D1, KAR-2/D1, KAR-3/D1, KAR-4/D1 (D1 — диализные мембраны с порами 0,0013 мкм)

Элемент	0,1 мкм	0,0065 мкм	0,0027 мкм	0,0013 мкм	KAR-1/D1	KAR-2/D1	KAR-3/D1	KAR-4/D1
Na	1132	1120	1145	1157	911,9	551,1	1052	1072
Mg	1166	1158	1155	1121	649,4	197,5	934,1	942
Al	52,0	50,7	38,9	13,8	3,481	30,79	7,843	2,389
Si	2505	2494	2509	2516	2012	2199	2201	2652
K	272	273	283	278	166,2	27,49	256,7	210,2
Ca	3300	3265	3206	3029	2625	579	2988	4115
Ti	0,58	0,41	0,41	0,26	0,17	0,17	0,58	0,22
V	0,091	0,089	0,075	0,072	0,032	0,156	0,063	0,016
Cr	0,342	0,301	0,300	0,227	0,136	0,251	0,312	0,089
Mn	12,1	11,7	11,4	10,5	43,7	18,1	3,88	74,4
Fe	181,5	148,2	64,5	6,8	7,1	30,9	13,4	5,9
Co	0,084	0,082	0,085	0,062	0,108	0,160	0,0197	0,121
Ni	0,703	0,626	0,621	0,467	0,166	0,205	0,756	0,188
Cu	1,26	1,21	1,11	0,74	0,66	0,45	0,778	0,51
Zn	5,18	5,26	5,61	4,26	9,86	4,96	13,8	2,37
Ga	0,127	0,121	0,115	0,097	0,653	0,143	1,47	0,254
Ge	0,0201	0,0126	0,0100	0,0051	0,0046	0,0079	0,0060	0,0063
As	0,3160	0,2513	0,2187	0,1837	конт.	конт.	конт.	конт.
Rb	0,5147	0,5132	0,5332	0,5304	0,3725	0,06439	0,5162	0,4903
Sr	17,2	16,9	16,6	15,4	13,1	3,5	14,4	25,4
Y	0,0697	0,0683	0,0520	0,0168	0,0027	0,0130	0,0049	0,0040
Zr	0,0737	0,0800	0,0672	0,0167	0,0010	0,0069	0,0186	0,0018
Cd	0,1457	0,1295	0,1308	0,0762	0,0499	0,0513	0,2006	0,0257
Sn	0,0953	0,0927	0,0739	0,0538	0,1204	0,0538	0,0689	0,0477
Sb	0,0475	0,0451	0,0472	0,0428	0,0388	0,0313	0,0682	0,0225
Cs	0,0011	0,0003	(0,0004)	(0,0007)	0,0008	0,0008	0,0010	0,0038
Ba	3,84	3,86	3,79	3,05	конт.	4,69	конт.	конт.
La	0,1009	0,0979	0,1066	0,0173	0,0039	0,0168	0,0077	0,0029
Ce	0,1773	0,1667	0,1127	0,0298	0,0077	0,0458	0,0105	0,0049
Pr	0,0271	0,0256	0,0190	0,0042	0,0007	0,0055	0,0014	0,0010
Nd	0,1130	0,0996	0,0700	0,0180	0,0037	0,0206	0,0067	0,0053
Sm	0,0181	0,0204	0,0130	0,0038	0,0003	0,0040	0,0015	0,0016
Eu	0,0050	0,0031	0,0030	0,0012	0,0014	0,0012	0,0036	0,0014
Gd	0,0172	0,0178	0,0134	0,0025	0,0005	0,0056	0,0036	0,0021
Tb	0,0025	0,0018	0,0016	0,0002	ПО	0,0007	0,0001	0,0004
Dy	0,0121	0,0137	0,0092	0,0034	0,0005	0,0024	0,0009	0,0007
Ho	0,0032	0,0028	0,0017	0,0008	ПО	0,0006	0,0002	0,0006
Er	0,0084	0,0076	0,0068	0,0014	ПО	0,0007	0,0005	0,0009
Tm	0,0014	0,0010	0,0009	0,0001	ПО	0,0004	0,0001	0,0005
Yb	0,0076	0,0062	0,0057	0,0016	ПО	0,0016	0,0013	0,0014
Lu	0,0010	0,0010	0,0006	0,0004	ПО	0,0003	0,0002	0,0002
W	0,0097	0,0060	0,0056	0,0058	0,0032	0,0029	ПО	0,0027
Th	0,0179	0,0184	0,0081	0,0026	0,0006	0,0028	0,0007	0,0008
U	0,0484	0,0510	0,0400	0,0127	0,0004	0,0005	0,0022	0,0011

Таблица 9

Результаты анализа проб Seng-1/2008 и Seng-2/2008 в варианте каскадной фильтрации (соответственно приустьевая часть и среднее течение р. Сеньга — правого притока р. Клязьма, дренирующего болота Мещерской низменности).

Вторая точка — интервал реки, дренирующий болота Мещерской низменности

Элемент	Seng-1					Seng-2	
	100 мкм	0,4 мкм	0,0065 мкм	0,0027 мкм	0,0013 мкм	100 мкм	0,4 мкм
Na	2852	2826	2721	2602	(2758)	3164	2973
Mg	3790	3696	3549	3541	2285	4564	4287
Al	83,41	46,66	32,93	24,14	15,06	86,98	38,39
K	1698	1675	1625	(1640)	(1730)	1609	1562
Ca	20730	19780	19580	18980	19090	25910	25140
Ti	2,05	1,33	1,18	0,81	1,00	2,32	1,26
V	0,744	0,279	0,186	0,160	0,141	0,907	0,243
Cr	0,720	0,632	0,496	0,472	0,261	0,751	0,565
Mn	56,4	50,2	40,7	38,6	34,9	92,5	80,3
Fe	4337	1076	453,4	76,0	16,1	5385	743,1
Co	0,315	0,270	0,242	0,229	0,175	0,390	0,333
Ni	1,58	1,45	1,43	1,40	1,19	1,80	1,64
Cu	(0,275)	0,413	0,425	0,418	0,376	0,441	0,944
Zn	5,90	4,34	5,75	4,87	4,92	5,92	6,42
Ga	0,860	0,621	0,715	0,728	0,008	1,106	0,756
Ge	1,186	0,301	0,159	0,050	0,021	1,561	0,228
As	1,343	0,794	0,674	0,626	0,536	1,868	0,880
Rb	2,27	2,25	2,24	2,25	2,20	2,06	2,06
Sr	100,2	95,5	94,7	94,8	86,3	119,1	115,2
Y	0,2432	0,1677	0,1370	0,0907	0,0284	0,2538	0,1417
Zr	0,5414	0,4486	0,3953	0,3012	0,0736	0,5674	0,4164
Mo	0,0637	0,0791	0,0828	0,0665	0,0682	0,0797	0,0787
Cd	(0,0265)	(0,0464)	0,0527	0,0348	0,0121	0,0200	0,0269
Sn	(0,0239)	(0,0494)	0,0962	0,0530	0,0437	0,0066	0,0133
Sb	(0,0531)	0,0974	0,0920	0,0844	0,0759	0,0540	0,0796
Cs	0,0096	0,0096	(0,0086)	0,0091	0,0089	0,0097	0,0092
Ba	22,5	17,3	20,2	20,8	12,5	24,8	18,9
La	0,1002	0,0485	0,0338	0,0142	0,0037	0,0921	0,0287
Ce	0,2652	0,1333	0,1005	0,0395	0,0133	0,2477	0,0846
Pr	0,0352	0,0187	0,0136	0,0063	0,0014	0,0330	0,0127
Nd	0,1605	0,0911	0,0714	0,0292	0,0083	0,1446	0,0601
Sm	0,0406	0,0223	0,0169	0,0075	0,0033	0,0383	0,0196
Eu	0,0114	0,0073	0,0060	0,0035	0,0018	0,0092	0,0053
Gd	0,0509	0,0282	0,0213	0,0109	0,0030	0,0440	0,0197
Tb	0,0059	0,0036	0,0028	0,0018	0,0004	0,0053	0,0038
Dy	0,0415	0,0281	0,0206	0,0162	0,0029	0,0365	0,0200
Ho	0,0083	0,0069	0,0045	0,0037	0,0009	0,0090	0,0052
Er	0,0307	0,0220	0,0183	0,0156	0,0038	0,0310	0,0162
Tm	0,0046	0,0032	0,0031	0,0023	0,0005	0,0043	0,0031
Yb	0,0308	0,0224	0,0166	0,0116	0,0044	0,0325	0,0224
Lu	0,0053	0,0036	0,0030	0,0027	0,0007	0,0065	0,0036
Hf	0,0167	0,0167	0,0116	0,0071	0,0048	0,0188	0,0125
Pb	0,2576	0,1790	0,0666	0,0118	0,0226	0,2616	0,2088
Bi	0,0017	0,0004	0,0005	0,0004	ПО	0,0007	0,0004
Th	0,0305	0,0190	0,0178	0,0112	0,0025	0,0287	0,0163
U	0,0173	0,0127	0,0141	0,0108	0,0059	0,0211	0,0185

Таблица 10

Результаты анализа пробы Ign/2008 в варианте каскадной фильтрации (бессточное оторфованное заболачиваемое озеро Мещерской низменности) и сравнение с экспериментальными данными

Элемент	100 мкм	0,4 мкм (1)	0,4 мкм (2)	0,0065 мкм	0,0027 мкм	ср. эксп. 0,0027 мкм	0,0013 мкм
Na	897,5	898,6	898,7	898,8	893,2	1154,0	785,3
Mg	305,6	303,3	277,6	293,4	292,9	248,4	207,5
Al	48,6	43,3	38,2	41,4	36,5	32,2	11,3
K	582,5	577,7	622,2	580,2	582,3	655,7	494,0
Ca	790,2	768,9	765,6	771,1	756,7	749,4	499,8
Ti	0,355	0,263	0,247	0,216	0,183	0,222	0,039
V	0,222	0,189	0,173	0,175	0,171	0,154	0,152
Cr	0,174	0,145	0,142	0,157	(0,187)	0,131	0,084
Mn	23,53	24,35	21,28	30,69	29,56	16,87	19,33
Fe	190,5	163,5	135,3	141,9	105,4	100,5	20,4
Co	0,0718	0,0692	0,0546	0,0519	0,0480	0,0347	0,0271
Ni	0,349	0,291	0,289	0,357	0,333	0,271	0,190
Cu	(0,794)	(1,242)	1,130	1,713	1,330	1,018	0,326
Zn	(9,98)	(10,13)	8,75	13,7	14,83	8,06	10,01
Ga	0,1029	0,0855	0,0059	0,0861	0,0848	0,0049	0,0476
Ge	0,0638	0,0509	0,0027	0,0417	0,0349	0,0027	0,0068
As	0,332	0,352	0,308	0,332	0,343	0,251	0,285
Rb	1,90	1,90	1,88	1,88	1,87	1,84	1,60
Sr	3,40	3,41	3,37	3,36	3,18	3,23	2,14
Y	0,0101	0,0075	0,0081	0,0060	0,0044	0,0082	0,0011
Zr	0,0215	0,0222	0,0241	0,0211	0,0159	0,0260	0,0017
Mo	0,0092	0,0101	0,0047	0,0111	0,0108	0,0062	0,0096
Cd	(0,0299)	(0,0386)	0,0379	0,0824	0,0608	0,0414	0,0336
Sn	(0,0005)	(0,0107)	0,0091	0,0290	0,0312	0,0095	0,0148
Sb	(0,0390)	0,0637	0,0664	0,0531	0,0582	0,0752	0,0551
Cs	0,0302	0,0266	0,0260	0,0258	0,0238	0,0260	0,0217
Ba	2,07	1,68	4,29	1,81	1,61	6,85	0,96
La	0,0096	(0,0062)	0,0050	0,0081	0,0036	0,0035	0,0017
Ce	0,0222	0,0186	0,0171	0,0157	0,0106	0,0150	0,0019
Pr	0,0025	0,0019	0,0019	0,0017	0,0011	0,0020	0,0001
Nd	0,0131	0,0109	0,0090	0,0073	0,0039	0,0082	0,0036
Sm	0,0018	0,0016	0,0016	(0,0024)	0,0016	0,0019	0,0003
Eu	(0,0004)	(0,0001)	0,0008	(0,0005)	ПО	0,0014	(0,0002)
Gd	0,0027	0,0016	0,0019	0,0011	0,0006	0,0023	0,0006
Tb	0,0003	0,0003	0,0002	0,0002	0,0001	0,0004	ПО
Dy	(0,0006)	0,0012	0,0013	0,0009	0,0006	0,0016	ПО
Ho	0,0003	0,0002	0,0003	0,0003	0,0001	0,0004	0,0000
Er	0,0012	0,0010	0,0010	0,0007	0,0009	0,0009	0,0005
Tm	0,0001	ПО	ПО	ПО	(0,0002)	0,0003	(0,0002)
Yb	0,0020	0,0007	0,0009	0,0006	0,0004	0,0011	ПО
Lu	(0,0001)	(0,0001)	0,0001	(0,0004)	(0,0002)	0,0003	(0,0002)
Hf	0,0016	0,0008	0,0008	0,0010	(0,0015)	0,0012	0,0002
Pb	(0,2795)	0,3902	0,352	0,1667	0,1138	0,284	0,0228
Bi	0,0015	0,0014	0,0014	0,0014	0,0012	0,0015	0,0002
Th	0,0030	0,0028	0,0033	0,0023	0,0020	0,0035	ПО
U	(0,0012)	(0,0018)	0,0012	0,0033	0,0034	0,0007	0,0012

Таблица 11

Коэффициенты интегральной задержки (R_Σ) при фильтровании исходных растворов (0,4 мкм) через двуслойные мембраны (1—10 кДа) в режиме обратноосмотического фильтрования с перемешиванием (I) и в режиме фильтрования без перемешивания через обращенную мембрану (II)

Элемент	0,4 мкм → 10 кДа, II	0,4 мкм → 1 кДа, I	Элемент	0,4 мкм → 10 кДа, II	0,4 мкм → 1 кДа, I
Li	0,035	0,108	Cd	0,055	0,718
Na	0,008	0,237	Sn	0,142	0,582
Mg	0,013	0,340	Sb	0,000	0,127
Al	0,078	0,689	Cs	0,020	0,177
Si	0,003	0,010	Ba	0,026	0,256
K	0,028	0,230	La	0,037	0,822
Ca	0,031	0,437	Ce	0,112	0,793
Ti	0,149	0,754	Pr	0,075	0,767
V	0,187	0,544	Nd	0,085	0,763
Cr	0,090	0,653	Sm	0,012	0,710
Mn	0,071	0,453	Eu	0,109	0,735
Fe	0,072	0,923	Gd	0,000	0,582
Co	0,129	0,540	Tb	0,120	0,776
Ni	0,059	0,630	Dy	0,186	0,737
Cu	0,000	0,222	Ho	0,005	0,770
Zn	0,051	0,296	Er	0,086	0,695
Ga	0,015	0,860	Tm	0,018	0,724
Ge	0,00	0,048	Yb	0,008	0,641
As	0,052	0,344	Lu	0,032	0,677
Rb	0,032	0,276	Hf	0,032	0,425
Sr	0,039	0,508	W	0,018	0,312
Y	0,171	0,696	Pb	0,158	0,411
Zr	0,000	0,866	Bi	0,017	0,418
Mo	0,406	0,241	Th	0,132	0,912

Приложение *Б*

Методическое обоснование процедур каскадной фильтрации и способов обработки результатов

При каскадной фильтрации растворов через серию фильтров (Лапицкий и др., 2009) с уменьшающимся диаметром пор (*d*) удобной формой графического отображения аналитических данных по задержке микроэлементов в виде растворенного и коллоидного вещества речного стока являются так называемые "кривые выведения" в координатах $\Delta C/C_{исх}$ – lg *d* и $C_{проб}/C_{исх}$ – lg *d*, где $\Delta C = C_{исх} - C_{проб}$. В практике расчетов мы по нескольким причинам не используем дифференциальную форму соотношения, а первоначально исследуем именно зависимость $C_{проб}/C_{исх}$ – lg *d*. Во-первых, отношение концентраций соответствует доле компонента, выведенной на конкретном фильтре (*n*), где $\Sigma(C_{проб}/C_{исх}) = 1$. Во-вторых, эта нормировка позволяет единообразно, в долях единицы, отображать относительные концентрации всех элементов, присутствующих в водах в концентрациях, различающихся на многие порядки. В-третьих, переход к дифференцированию всегда возможен, но необходим при большой и очевидной нелинейности зависимостей в этих координатах, что наблюдается далеко не во всех интервалах диаметров пор. Эти соотношения по внутренней структуре напоминают выражения для коэффициента задержки $R = 1 - (C_2/C_1)$, в теориях обратноосмотического обессоливания (Дытнерский, 1978) и фильтрационного эффекта (Алехин и др., 1982), где C_1 и C_2 — истинные концентрации до и после фильтра соответственно, и $\varphi = C_2/C_1$ — коэффициент фильтрационного эффекта.

При необходимости они могут быть сведены к ним, но не в полной мере. При описании явлений обратного осмоса широко используется величина кажущегося коэффициента задержки ($\breve{R}$), где изменяющаяся концентрация последовательных фильтратов сравнивается с постоянной исходной. Такой подход неизбежен, когда концентрация над фильтром также непрерывно изменяется в силу концентрирования фильтранта по механизму обратного осмоса. Однако не следует думать, что такие эффекты возникают только на типичных обратноосмотических мембранах 1—10 кДа. Для макромолекул ОВ эффекты увеличения концентрации в растворе до фильтра (фильтранте) возможны в результате процессов агрегации—дезинтеграции в осадке на фильтре. Формирующийся на фильтре осадок редко химически пассивен. Обычно он сам ведет себя как динамически формирующаяся адсорбционно-осадительная хроматографическая мембрана, селективно разделяющая компоненты последующих порций фильтрата. Эти явления можно успешно изучать и учитывать, если в экспериментах, как мы увидим ниже, анализировать один фильтрат в последовательных пробах с добавлением к нему порций исходного раствора известной концентрации. Основанный на этом приеме наш метод возмущения стационарного состояния при фильтрации позволяет исследовать парные корреляции в поведении фильтрующихся компонентов. При этом мы вынуждены использовать весьма полезный интегральный коэффициент кажущейся задержки, $R_\Sigma = \Sigma(C_{проб}V_{проб})/(C_{исх}\,\Sigma V_{исх})$. При фильтровании больших проб затруднительно осуществлять мониторинг концентраций малых компонентов в исходном растворе при изменении в нем концентраций седиментирующих компонентов на грубых фракциях и образующих ассоциаты при концентрировании фильтранта.

Всегда дискретен набор фильтров с выбранными диаметрами пор фильтрующих перегородок, а соотнесение координат точки $\Delta C_1/C_{исх}$ с началом или концом интервала диаметров пор от d_1 до d_2, где d_1 — диаметр пор предыдущего, а d_2 — последующего фильтра имеет элемент произвола, так как в процессе фильтрования поры постепенно забиваются осадком и эффективный диаметр пор становится меньше номинального (заявленного). Однако еще важнее сформулировать некоторый общий закон распределения массовых долей (относительных концентраций) компонента как функцию диаметра молекул (пор), а все случаи отклонения распределения от идеального можно связать с конкретными особенностями его поведения и главными формами нахождения, анализируя кривую ММР. Прежде всего определимся с конкретными физическими ограничениями в отношении пор и диаметров молекул, ионов, коллоидных мицелл и взвесей. Очевидно, что мембрана с диаметром пор 3 Å (0,0003 мкм) не будет пропускать растворенные компоненты, так как для молекулы воды этот диаметр составляет 2,7 Å. Практически используя в своей работе фильтры 1 кДа (0,0013 мкм), мы не так далеки от этого физического предела. Всегда достаточно очевиден и необходимый верхний предел диаметров частиц взвеси. Он определяется условиями седиментации, т.е. радиусами частиц и их плотностью. Для не слишком быстрых течений это условие автоматически следует из решения уравнения Стокса $\upsilon_{sed} = 2/9 \cdot r^2 g \cdot (\rho_c - \rho_w)/\eta$. На практике раствор после предфильтра (фильтрат Ф0, обычно после 100 мкм) редко подвергается фильтрованию через другие фильтры с номиналами 20, 10 и 5 мкм, но в этом есть определенный смысл для быстрых водотоков. Обычно составы таких последовательных фильтратов не демонстрируют аналитически значимого и закономерного выведения элементов с взвесью — ее в норме просто нет и концентрации равны исходным концентрациям практически по всем компонентам, кроме $C_{орг}$. Однако это так в случае каскадного, последовательного фильтрования одной порции предфильтрата через всю линейку фильтров. В грубых фракциях в случае параллельного (одновременного) фильтрования исходного раствора через такие фильтры с порами различных номинальных диаметров всегда велика дисперсия составов, особенно в отношении макрокомпонентов, присутствующих во взвеси: ОВ и коллоидов $Fe(OH)_3$, и реже — от такого же незакономерного попадания алюмосиликатных частиц и минеральных частиц глинистой размерности. Для интервала пор вплоть до 0,2—0,4 мкм только анализ последовательных фильтратов обеспечивает минимальную дисперсию, повторяемость аналитических результатов и необходимую гладкость функций выведения (только тогда выполняется основное требование — на кривых выведения не должно быть максимумов). Для крупных фракций исходный раствор и последующие фильтранты надо интенсивно гомогенизировать взбалтыванием для устранения седиментационных потерь, а пробы для определения больших исходных концентраций $C_{орг}$ в фильтратах необходимо не только стабилизировать подщелачиванием против коагуляции и седиментации, но и консервировать (или стерилизовать). Таким образом, в интервале размерностей пор от 3 до 0,0003 мкм (4 порядка) необходимо иметь 7—8 достаточно равномерно распределенных номиналов фильтров (через 0,5 порядка), чтобы обеспечить 100%-е выведения любого компонента. При линейном тренде выведения это соответствует изменению величины $C_{проб}/C_{исх}$ с угловым коэффициентом 0,25 в координатах $C_{проб}/C_{исх} - \lg d$. Величины угловых коэффициентов достаточно типичны для отдельных групп элементов. Так, для истинно растворенных элементов в простых ионных и молекулярных формах (Na, K, Ca, Mg, Si, Ge и т.д.) угловой коэффициент на трендах выведения равен нулю вплоть до последнего фильтрата. Для элементов-гидролизатов, в том числе адсорбирующихся и соосаждающихся с коллоидами $Fe(OH)_3$, угловые коэффициенты выведения в интервале диаметров 0,05—0,5 мкм близки к угловым коэффициентам выведения железа и наблюдаются устойчивые парные корреляции концентраций Me/Fe в фильтратах. Важно подчеркнуть, что дифференцирование по $\lg d$ представляет удобную форму, так как $\lg V = 1{,}57 \lg d$ и $\lg S = 6{,}28 \lg d$ для сферических молекул и ассоциатов. Эти случаи весьма контрастны по угловым коэффициентам выведения в координатах $C_{проб}/C_{исх} - \lg d$. В первом случае (при объемном выведении микропримесей с депонирующей фазой) угловой коэффициент равен 0,637, а при адсорбционном выведении поверхностью мицелл равен 0,159. В большинстве случаев нами отмечается именно адсорбционное выведение микроэлементов. При мицеллообразовании коллоидов $Fe(OH)_3$ угловые коэффициенты соответствуют объемному выведению железа. В некоторых случаях для элементов-гидролизатов также наблюдается их выведение объемом коллоидных частиц. Третью группу зависимостей с небольшими угловыми коэффициентами в координатах $C_{проб}/C_{исх} - \lg d$ образуют элементы, по общему мнению, связанные в комплексы с ОВ гуминовой природы. Однако главная часть таких комплексов является истинно растворенными формами. Поэтому не наблюдается сколько-нибудь заметного выведения микроэлементов в виде фульватных комплексов вплоть до фильтров 1—10 кДа. В выражениях для констант комплексообразования присутствуют мольные (не весовые!) концентрации ОВ. Так, в интервале 0,2 мкм—10 кДа (0,0028 мкм) при сохранении весовой концентрации на уровне 5,2 мг/л $C_{орг}$ восьми молекулам с массой 5 200 000 а.е. соответствуют 4 400 000 молекул ОВ с массами 10 кДа. Таким образом, именно мольные концентрации фульвокислот и аналогичных органических молекул другой природы ответственны за основной перенос микроэлементов, а не адсорбция на крупных ассоциатах ОВ.

Термодинамические свойства пресных высокогуминовых вод радикальным образом связаны с тем, что поликонденсированные ГК и их комплексы с Ме представляют собой пример ассоциированных растворов, демонстрирующих ряд свойств растворов полимеров (Пригожин, Дефэй, 1966). В этой работе можно найти не устаревший до сих пор аппарат описания свойств подобных систем и соответствующие модельные представления, что не входит в нашу задачу. Следует лишь подчеркнуть, что в теоретических моделях для ассоциированных растворов И. Пригожиным показаны их важные свойства и следствия, необходимые для наших построений. Главное из них — доказательство равенства химических потенциалов мономерных фрагментов и ассоциативных комплексов, т.е. определенное термодинамическое безразличие, неспонтанность процессов полимеризации — деполимеризации, даже случайность соотношений концентраций молекул — ассоциатов разной величины. В моделях последовательный ряд значений констант полимеризации как констант присоединения элементарного фрагмента к ассоциату образует медленно убывающий ряд, так что свободные энергии в такой последовательности ступенчатого комплексообразования для соседних по номеру полимеров n и $n + 1$ фактически одинаковы. Их устойчивость — это скорее дилемма сопоставимости величины энергии присоединения и тепловой (около 600 кал/моль). В нашем случае зависимости $\lg K_n$, $\lg K_{n+1}$, $\lg K_{n+2}$ от $1/n$ не только линейны (Migdisov et al., 2002), но и имеют небольшое уменьшение в энергии связи мономерного фрагмента с увеличивающимся кластером, и в пределе для $1/n \to 0$ эта величина вряд ли далека от 600 кал для ассоциатов с n = 400—700 при молекулярных массах до 200—350 кДа и минимальной молекулярной массе фрагмента фульвокислоты 500 Да. Значительная весовая доля ассоциатов ГК нами отмечена только в почвенных растворах и водах питающих болот. Для речного стока относительная массовая доля крупных молекул не превышает 20% (Алехин и др., 2010) и радикально зависит от скорости течения, однако мольные доли крупных ассоциатов ГК пренебрежимо малы. Таким образом, мы приходим к статистической гипотезе (нулевая гипотеза, H_0), что распределение размеров коллоидов элементов-гидролизатов и особенно ОВ гуминовой природы в интервале их седиментационной устойчивости должно быть нормально (Дмитриев, 1995) распределенной случайной величиной и параметры кривых выведения в конкретных случаях связаны с отклонениями от этого распределения.

Использование обратноосмотических мембран в целях исследования ММР имеет свои специфические особенности. Эти килодальтонные мембраны двуслойны и задерживающий слой с тонкими порами диаметром 10—60 Å в практике фильтрационного разделения расположен со стороны исходного раствора. Для увеличения коэффициента задержки фильтрация производится при перемешивании исходного раствора, т.е. в режиме максимальной концентрационной поляризации. При условии, когда $C_1 >> C_2$ и $C_2/C_1 \to 0$, $R \to 1$, и в таком режиме удается обессоливать фильтрат по всем растворенным компонентам. Эту особую область при каскадном фильтровании мы исследовали в своих экспериментах для того, чтобы оценить доли обратноосмотической задержки и задержки, связанной с отделением крупных молекул и их ассоциатов по обычному механизму ситования. Было очевидно, что интегральный коэффициент кажущейся задержки (R_Σ) есть сумма этих двух эффектов. Для получения информации об истинном ММР необходимо уменьшить обратноосмотическое обессоливание. В двуслойных мембранах, когда радиус пор подложки r_1 = 0,11 мкм, а в задерживающем слое r_2 = 0,0014 мкм, возникает значительное капиллярное противодавление, и в соответствии с законом Лапласа, $\Delta p = 2\sigma(1/r_2 - 1/r_1)$ для мембран 1—10 кДа, оно близко к 3 атм. При обратноосмотическом обессоливании приходится преодолевать это капиллярное противодавление, фильтруя при больших перепадах приложенного давления. Если фильтровать через перевернутую двуслойную мембрану, направление приложенного давления совпадает с направлением капиллярного давления и эффективное фильтрование возможно уже при небольших приложенных давлениях порядка 0,1—0,5 атм. Это не исключает обессоливание, т.е. мембрана менее эффективно, но продолжает разделять растворенные компоненты. Однако если фильтровать в режиме минимальной концентрационной поляризации, т.е. не перемешивать исходный раствор, мы переходим в режим с $R \to 0$, сформировав в рыхлом слое двуслойной мембраны область стационарно высокой концентрации, когда $C_1 = C_2$. Если в этих условиях фильтрования $C_1 \neq C_2$, то этот эффект связан с обычной ситовой задержкой на фильтре. В табл. 11 (Приложение *А*) показано, что фильтрование через обращенную мембрану значительно минимизирует величины интегральных коэффициентов задержки. Заметим, что для компонентов, присутствующих в растворе в виде нейтральных молекул, и в режиме обратноосмотического фильтрования (I) коэффициенты задержки невелики (H_4SiO_4, H_4GeO_4), что свидетельствует в пользу версии об электрокинетическом механизме разделения на таких мембранах. Поэтому в практике процессов фильтрования с минимальным разделением предпочтителен режим тока течения, но не потенциала течения. Фильтрование через обращенную мембрану (слой рыхлой подложки со стороны исходного раствора, без перемешивания, режим II) обладает тремя другими преимуществами: 1) отсутствует ассоциация молекул ОВ и их последующая задержка, вызываемая концентрированием раствора над фильтром; 2) не искажается ММР, так как перемешивание провоцирует разрушение ассоциированных молекул, лишь происходит их задержка в рыхлой подложке; 3) фильтрование при малых приложенных давлениях не вызывает деструкцию молекул в пределах поровых каналов. С учетом всех этих факторов кривые выведения $C_{орг}$ и комплексов микроэлементов с ОВ существенно изменяются в области 60—10 Å, они становятся более пологими вплоть до мембраны 1 кДа.

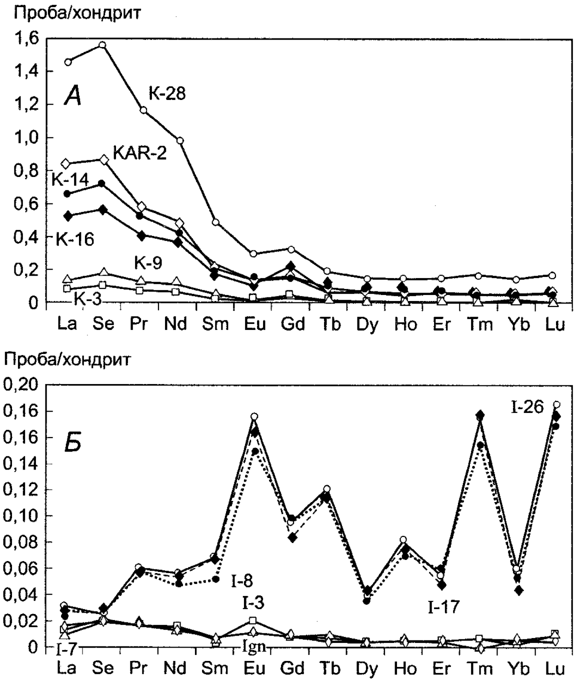

Рис. 6. Изменение нормализованных спектров распределения редкоземельных элементов в серии последовательных (K-3, K-9, K-16 и т.д., KAR-2 — исходный раствор) фильтратов в варианте обратноосмотического разделения (*А*) пробы KAR-2 (0,4 мкм → → 1 кДа) и в варианте обычного фильтрования (*Б*) для пробы Ign (4 мкм → 10 кДа). I-3, I-7, I-8 и т.д. — составы последовательных фильтратов и Ign — исходный спектр распределения

При больших объемах фильтрования сформировавшийся слой осадка может сам выступать в качестве адсорбционно-осадительного барьера с хроматографическим разделением компонентов в этом слое. Наиболее ярким примером такого поведения осадка являются эксперименты с обратноосмотической (рис. 6, *А*) и обращенной мембраной (рис. 6, *Б*). Наблюдается прогрессирующее разделение TR в серии последовательных порций фильтрата. Все спектры TR в фильтратах и исходных растворах нормализованы на их индивидуальную мировую распространенность (Boynton, 1984) для ее сглаживания в пробах континентальных вод. Однако мы видим (рис. 6, *А*), что в первых же пробах фильтратов концентрации легких TR вследствие обратноосмотической задержки существенно ниже, чем в исходных растворах. В случае обращенной мембраны в первых порциях фильтратов (рис. 6, *Б*) содержание и спектр редких земель близки к исходным. Этот факт можно было бы связать с высокими концентрациями коллоидов железа, для р. Палойоки (Ilina et al., 2009), так как для консервативного оз. Игнатково (рис. 6, *Б*) с существенно более низкими концентрациями железа подобный эффект не наблюдается. Однако по мере фильтрования в обоих случаях наблюдается постепенное увеличение концентраций TR в последовательных пробах фильтратов, и к концу экспериментов они не только возрастают в 2—10 раз, но и спектры редких земель полностью искажаются. На фоне общего увеличения их концентраций вследствие ионного обмена с макрокомпонентами в пределах мембраны растворы прогрессивно обогащаются нечетными TR и происходит адсорбционная задержка четных TR. Такое значительное накопление в последних фильтратах нечетных редких земель полностью обращает их обычный спектр — в этих растворах доминируют нечетные элементы с меньшей мировой распространенностью. Этот настораживающий факт требует обязательного выполнения следующего условия: необходимо фильтровать минимальные объемы и контролировать составы последовательных фильтратов. Фильтрация объемов до 1 л допустима только в случае необходимости анализа осадка, и при больших количествах ОВ и коллоидов $Fe(OH)_3$ в водах можно минимизировать объем фильтрата в режиме перевернутой мембраны первыми 50—100 мл. По этим причинам, т.е. по причине проявления эффектов обратноосмотического концентрирования, и в случаях, когда велики хроматографические эффекты разделения компонентов в слое сформировавшегося осадка, в табл. 1—10 Приложения *А* такие результаты нами рассматриваются как аномальные, вызванные условиями фильтрования (такие результаты в таблицах приведены в скобках). В исходных растворах и в некоторых фильтратах после мембран с большим диаметром пор иногда наблюдается значительная дисперсия, что приводит к аномальным максимумам на кривых выведения (такие значения также приведены в скобках).

EXPERIENCE OF COMPARATIVE ANALYSIS OF SEPARATED COMPONENTS IN NORTHERN AND MIDDLE ZONES OF RUSSIA SMALL RIVERS

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The work is aimed at studying the evolution of migration forms of true dissolved compounds and colloidal entities by the comparison of the separated components of the river flow of the northern (boreal) and central regions of the Russia in the system soil water—bog—river—lake. The main tool of the research was the cascade filtration with subsequent analysis of the water samples, which allowed a comprehensive study of transformation of molecular mass distribution and ecological-geochemical features of the trace elements migration with organic matter and iron-hydroxide colloids.

Key words: river flow, cascade filtration, organic matter, trace elements, colloids, ultracolloids.

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