

# Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia)

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## Abstract

The chemical status of major and trace elements (TE) in various boreal small rivers and watershed has been investigated along a 1500-km transect of NW Russia. Samples were filtered in the field through a progressively decreasing pore size (5, 0.8 and 0.22  $\mu\text{m}$ ; 100, 10, and 1 kD) using a frontal filtration technique. All major and trace elements and organic carbon (OC) were measured in filtrates and ultrafiltrates. Most rivers exhibit high concentration of dissolved iron (0.2–4 mg/l), OC (10–30 mg/l) and significant amounts of trace elements usually considered as immobile in weathering processes (Ti, Zr, Th, Al, Ga, Y, REE, V, Pb). In (ultra)filtrates, Fe and OC are poorly correlated: iron concentration gradually decreases upon filtration from 5  $\mu\text{m}$  to 1 kD whereas the major part of OC is concentrated in the < 1–10 kD fraction. This reveals the presence of two pools of colloids composed of organic-rich and Fe-rich particles. According to their behavior during filtration and association with these two types of colloids, three groups of elements can be distinguished: (i) species that are not affected by ultrafiltration and are present in the form of true dissolved inorganic species (Ca, Mg, Li, Na, K, Sr, Ba, Rb, Cs, Si, B, As, Sb, Mo) or weak organic complexes (Ca, Mg, Sr, Ba), (ii) elements present in the fraction smaller than 1–10 kD prone to form inorganic or organic complexes (Mn, Co, Ni, Zn, Cu, Cd, and, for some rivers, Pb, Cr, Y, HREE, U), and (iii) elements strongly associated with colloidal iron in all ultrafiltrates (P, Al, Ga, REE, Pb, V, Cr, W, Ti, Ge, Zr, Th, U). Based on size fractionation results and taking into account the nominal pore size for membranes, an estimation of the effective surface area of Fe colloids was performed. Although the total amount of available surface sites on iron colloids (i.e., 1–10  $\mu\text{M}$ ) is enough to accommodate the nanomolar concentrations of dissolved trace elements, very poor correlation between TE and surface sites concentrations was observed in filtrates and ultrafiltrates. This strongly suggests a preferential transport of TE as coprecipitates with iron oxy(hydr)oxides. These colloids can be formed on redox boundaries by precipitation of Fe(III) from inflowing Fe(II)/TE-rich anoxic ground waters when they meet well-oxygenated surface waters. Dissolved organic matter stabilizes these colloids and prevents their aggregation and coagulation. Estuarine behavior of several trace elements was studied for two small iron- and organic-rich rivers. While Si, Sr, Ba, Rb, and Cs show a clear conservative behavior during mixing of freshwaters with the White sea, Al, Pb and REE are scavenged with iron during coagulation of Fe hydroxide colloids.

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## 1. Introduction

It has been shown for a long time that the chemistry of rivers provide invaluable informations on the biogeochemical cycle of major and trace elements

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because it is the witness of all the processes that control the behavior of these elements on the earth surface: chemical and physical erosion, formation of secondary phases, adsorption and coprecipitation. Such an approach requires comprehensive studies of rivers or catchments issued from pristine environments with different bedrock composition, hydrology, climate, and vegetation. If many studies have been devoted to tropical and temperate environments of various lithology, boreal regions have received much less attention. This paper is aimed at bridging this gap by presenting a geochemical study of major and trace elements behavior along a 1500-km transect of various organic-rich watersheds and rivers of NW Russia.

The swamp and peatland systems from boreal taiga area are believed to play a crucial role in the control of the CO<sub>2</sub> cycle in the biosphere (Thurman, 1985). Indeed, because of low degradation rates of organic matter in these regions compared to tropical zones, pristine peatlands can serve as an important sink of atmospheric CO<sub>2</sub>. In such organic-rich environments, most of weathering products are transported as dissolved species (major elements) and colloids (trace metals). Several recent studies have been devoted to characterize the colloids responsible for the transport of trace elements and the chemical state of these species. Based on size fractionation by ultrafiltration coupled with various chemical and spectroscopic analyses and complexation capacity measurements (Smith, 1976; Buffle et al., 1978; Hoffman et al., 1981; Horowitz et al., 1992; Sholkovitz, 1992; Tanizaki et al., 1992; Benoit, 1995; Pham and Garnier, 1998; Dupré et al., 1999; Eyrolle and Benaim, 1999; Ross and Sherrell, 1999; Hoffmann et al., 2000; Sigg et al., 2000), it is generally believed that most trace carriers in fresh waters consist in organic colloids (that can be associated with iron) and inorganic Fe and Mn oxides and clays. However, the chemical nature of these colloids and the relative contribution of organic matter and iron oxides to the transport of trace elements is still poorly known and a matter of debate. For example, from results of ultrafiltration experiments, Viers et al. (1997) and Dupré et al. (1999) argued that in organic-rich tropical watersheds of Cameroon, Al, Ga, Y, Zr, Hf, REE, and Th are mostly associated with organic colloids, whereas Olivie-Lauquet et al. (1999, 2000), based on spectroscopic analyses, found that the colloids collected in the same waters consisted of both

iron oxides and Fe-organic particles. Sholkovitz (1995) assigns a major role to Fe-organic colloids for the transport of REE in temperate environments while Ingri et al. (2000) showed that in boreal rivers, REE are controlled by an organic phase with associated Al and Fe and by inorganic Fe oxy(hydr)oxides. In this paper, we present the results of a series of in-field filtration experiments associated with ICP-MS analyses of trace elements in the filtrates. We conducted, for the first time, systematic filtrations through 5, 0.8, and 0.2 μm and 100, 10, and 1 kD pore size membranes using a unique and rigorous protocol throughout the whole study. We hope that results of this study will provide new insights on the behavior and status of trace elements in small organic-rich boreal rivers and their estuarine zones.

## 2. Sample area

The investigated area belongs to the North-West part of Russia and the small rivers sampled in this study are located along a 1500-km-long N–S transect from the north of Moscow to the Kola peninsula. A simplified map of the region with sampling points and some geological informations is given in Fig. 1; the list of sampled sites with their bedrock composition is presented in Table 1. Altogether, 4 swamp zones, 3 lakes, and 24 rivers were sampled in July 1999 and August–September 2000. The largest sampled rivers are Kem (drainage basin at the sampling point is 27 600 km<sup>2</sup>), Shuya (8720 km<sup>2</sup>), Keret (2330 km<sup>2</sup>), Tunguda (1820 km<sup>2</sup>), and Pongoma (1220 km<sup>2</sup>). The other rivers have drainage basin areas from 200 to 800 km<sup>2</sup>. Most of the rivers flow through a system of glacial lakes, which greatly stabilizes their discharge during summer and winter. The majority of samples was collected in the northern part of studied area, the so-called “Karelian” region. This region, because of its limited accessibility and the absence of any agricultural and industrial activity, can be considered as a pristine environment with natural levels of dissolved components in rivers. Only in lake sample (No. 4) of Kola peninsula, contamination from industrial smelters is possible.

The whole studied area is situated at 0–200 m above sea level. The bedrock composition is dominated by the Belomorian metamorphic complex composed of archean amphibole and biotite–amphibole

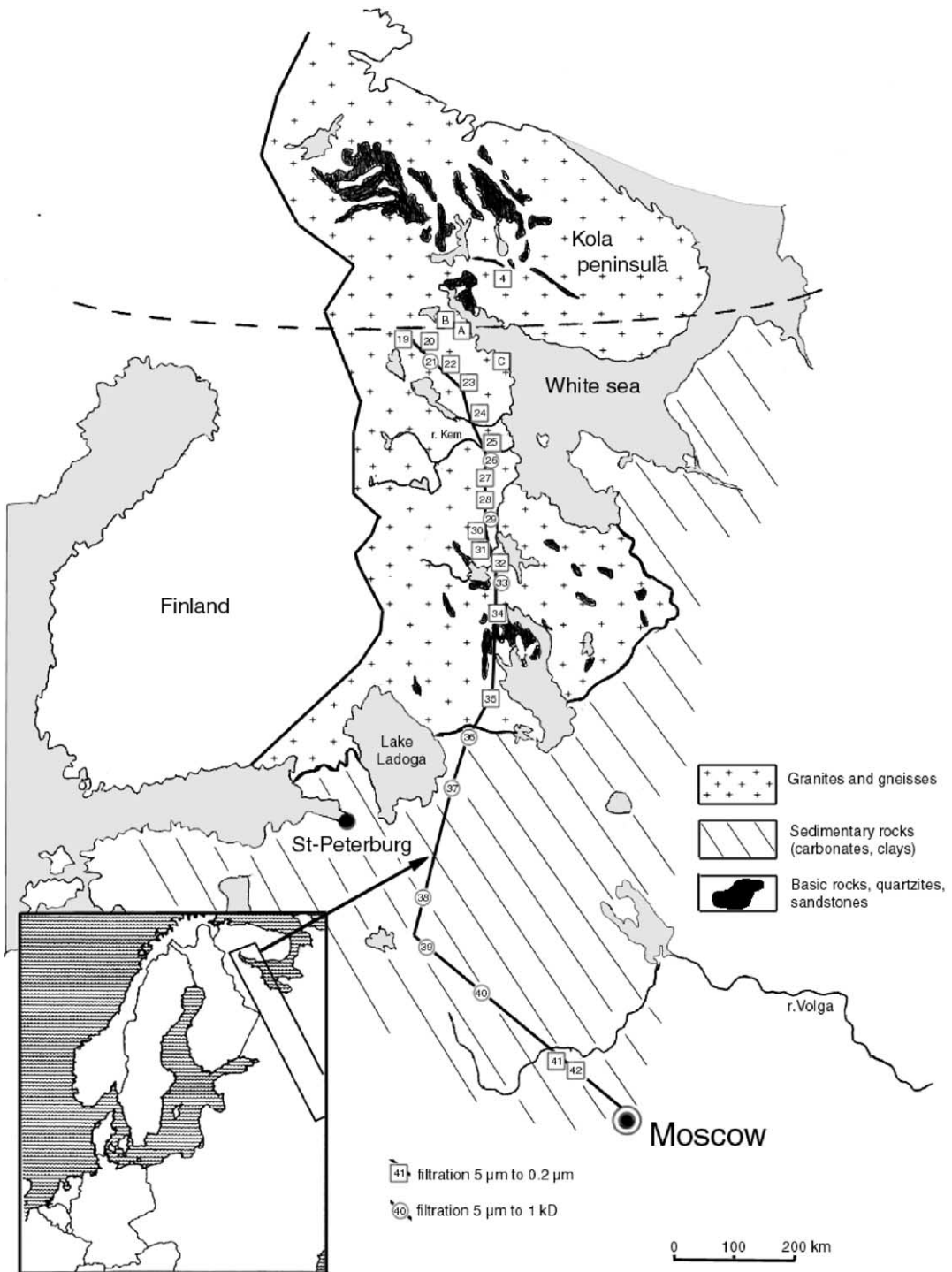


Fig. 1. The simplified map of the region. The sampling points where filtration was performed through 5, 0.8 and 0.2 μm are shown as black squares but the points of full filtration from 5 μm to 1 kD are shown as circles.

Table 1  
Rivers and lakes studied and their bedrock composition

No.	Name	Lake or watershed area (km <sup>2</sup> )	Discharge (m <sup>3</sup> /s)	Bedrock composition of the watershed
A	r. Kalga	500	1	Archean gneisses and amphibolites
B	Swamp lake	0.01	–	Archean gneisses and amphibolites
C	r. Unduksa	250	0.1	Archean gneisses and amphibolites
1	r. Pongoma	1220	5	Gneisses and amphibolite (Belomorian complex)
2	Spring from the swamp	–	0.001	Gneisses and amphibolites
3	r. Keret	2560	12	Gneisses and amphibolites; Tonalites and trondhjemites
4	Small lake	0.02	–	Nepheline syenites
19	Lake Nilmozero	3	–	Gneisses and amphibolites
20	Lake Kotozero	5	–	Gneisses and tonalites
21	r. Kuzema	800	–	Gneisses and amphibolite
22	Lake Khatomzero	2	–	Gneisses and amphibolites
23	Peat swamp	0.01	–	Gneisses and tonalites
24	r. Letniya N.	960	–	Gneisses, tonalites and trondhjemites
25	r. Kem	27 600	130	Granites, Gneisses, amphibolites
26	r. Shuya	8720	25	Sandstones, quartzites, conglomerates, Gneisses and tonalites
27	r. Letniya S.	570	3	Sandstones, quartzites, arkoses
28	r. Tunguda	1820	7	Granites, diorites, granodiorites, Gneisses, amphibolites
29	r. Idel	530	2.2	Gneisses, amphibolites, quartzites
30	r. Onigma	349	2	Gneisses, granites
31	r. Onda	718	4	Migmatite–granites, tonalite–trondhjemites
32	r. Pezega	360	2.4	Lopian complex: granites, leucogranites, tonalite–trondhjemites
33	r. Kumsa	735	5.3	Sandstones, quartzites, granodiorites, amphibolites
34	r. Unitza	340	1.7	Plagiogranites and tonalites, amphibolites, quartzites, sandstones, gabbros, diabases
35	r. Chebinka	280	1.3	Sandstones, siltstones, quartzites
36	r. Svyat	355	2	Gneisses, granites, clay, argillites, sandstones
37	r. Cherniya	50	1.0	Clays, argillites, sandstones, sand
38	r. Sobakina	300	1.5	Limestones, clays, gypsum
39	r. Yaryniya	350	–	Sandstones, siltstones, dolomites
40	r. Belukha	250	–	Limestones, clays
41	r. Doibitza	300	–	Limestones, dolomites, clays
42	r. Yamuga	200	–	Limestones, dolomites, clays

gneisses and middle and low-proterozoic granites. On the seacoast, this complex is presented by biotite and amphibole–biotite gneiss, trondhjemite, and tonalite. Small intrusions of late Lopian complex of ultramafite (olivine, harzburgite, pyroxenite and serpentine) are located in the central part of these metamorphites. In the central and western part of Karelia, middle and low-proterozoic granites are ubiquitous, whereas, in the southern part of studied region, sandstones, quartzites, siltstones, limestones, carbonate–sericite–chlor-

ite schists associated with dykes and sills of diabase and gabbro–diabase are abundant. Quaternary deposits consist primarily of coarse-grained and sandy till or glaciofluvial deposits showing well-developed podzol profiles.

Approximately 20% of the territory is covered by swamps developed on a thick peat and gley-podzol soils. The soil depths vary from 30–40 to 60–85 cm in the northern and southern part of Karelia, respectively. On the hill tops (100–200 m), soils depths do not

exceed 10–20 cm. Large amount of peatlands located in small glacial depressions throughout the whole area provide high concentrations of dissolved organic carbon (OC) in surface waters. The vegetation is represented by spruce and pine forests mixed with some birch trees that cover more than 80% of the territory. All rivers are ice-covered from early November to April. The mean annual temperature of the region varies from 0 to 3 °C depending on latitude. Maximum melt-water discharge occurs in May–June on the north and in April–May on the south. The influence of groundwater feeding reaches a maximum in summer. However, the presence of numerous lakes of various size can significantly diminish this contribution.

Rivers Chernya, Sobakina, Yaruniya, Belukha, Doibitza and Yamuga (samples 37 to 42) flow in the southern part of studied area on podzol and grey soils developed under mixed spruce and birch forests over the Paleozoic and Mesozoic sedimentary rocks (clays and limestones) with some amount of glacial till. Unlike the Karelian region, this area is subjected to some industrial and agricultural load; as a result, water chemistry of these samples can bear an anthropogenic signature.

Two contrasting Karelian rivers, Kalga and Unduksa, and their estuarine zones in the White Sea have been sampled in July–August 1999 for dissolved major and trace elements. The Kalga river is characterized by relatively low content of dissolved organic carbon ( $OC \leq 10$  mg/l), a high discharge ( $\sim 2\text{--}3$  m<sup>3</sup>/s) and a long estuarine zone ( $\sim 10$  km) formed by several similar rivers. The estuary of Kalga is well mixed without important influence of tidal events. In contrast, Unduksa is a typical «black river» with high OC (15–25 mg/l), low discharge ( $\sim 0.1$  m<sup>3</sup>/s), and a very short (<500 m) estuary without influence of other tributaries. The hydrochemistry of Unduksa estuary is characterized by strong temporal variability due to poor mixing and tide inferences. Both of these rivers flow in unpopulated region without any industrial or agricultural activities and therefore exhibit a minimal anthropogenic influence.

### 3. Sampling and analyses

Water temperature and pH were measured in the field. The pH was measured using a combined

Schott–Geräte electrode calibrated against NIST buffer solutions (pH=4.00 and 6.86 at 25 °C). The accuracy of pH measurements was  $\pm 0.02$  pH units. Samples were collected from the beach near the middle of the flow in 1-l high-density polyethylene (HDPE) containers held on a nonmetallic stick. Plastic gloves were always used during all manipulations. The collected waters were immediately filtered through sterilized, single-used filter units Minisart® (Sartorius, acetate cellulose filter) having a diameter of 25 mm and pore sizes of 5 and 0.8  $\mu$ m. First, 100–200 ml of filtrate was always discarded. Filtration through 0.2  $\mu$ m membranes was performed using a Sartorius polycarbonate filter holder and nitrate cellulose Sartorius single-used filters having a diameter of 47 mm. Filtrations were carried out using a MITYVAC® manual vacuum pump. The first 200–400 ml of the filtrate was systematically rejected. Frontal ultrafiltrations (UF) were performed using a 50-ml polycarbonate cell (Amicon 8050) equipped with a suspended magnet stirring bar located beneath the filter to prevent its clogging during filtration. Its major advantage over the more frequently used tangential filtration in hydrochemistry is the very small size of the filter and low amount of pore space, which minimizes the adsorption inside the filter during filtration. Argon pressure (3 bars) was provided by a portable bottle. Filtration was performed with 100, 10, and 1 kD membranes (Amicon, regenerated cellulose, 200- $\mu$ m thickness, 44.5-mm diameter). Before each filtration, the system was cleaned by flushing MilliQ water, then  $\sim 0.1$  M ultrapure HNO<sub>3</sub>, and finally, MilliQ water. During filtration, the first 30–50 ml of solution were discarded, thus allowing the saturation of the filter surface prior collecting the filtrate. Each filter was washed in MQ water before the experiment and used only once. This greatly decreased the probability of cross-contamination during sample filtration, improved OC blank, provided unique conditions of filtration for all samples and allowed high recovery of colloidal particles.

Because of the UF procedure employed in the present study, we could not perform a mass balance verification between the filtrate and retentate. However, as the same material was used for all three filters (100, 10 and 1 kD) with the highest surface area in the lowest pore size filter (1 kD) while the highest retention of colloids was achieved by the largest size

filters (10 and 100 kD, see below), we think that molecular size exclusion rather than adsorption on and inside the filter controls the colloid distributions between ultrafiltrates. A reproducibility check for OC and trace elements concentration in the ultrafiltrate was performed with sample No. 39; two filtrations (1–100 kD) were performed within a 3-day interval and no major difference was found. We also analyzed the first and the last portion of the 10 kD ultrafiltrate for Svyat river (No. 36) and have not found any difference for dissolved Fe, Al, Mn and OC within the analytical uncertainties. Finally, we conducted several batch experiments on TE adsorption from 5  $\mu\text{m}$  filtered river water (river Chernyaya, sample No. 37) on filter materials. It was found that, within the analytical uncertainties, the adsorption of iron and 60 trace elements on 0.22  $\mu\text{m}$  and 100 and 10 kD filter membranes is negligible.

Filtered solutions for cations and trace element analyses were acidified (pH=2) with ultrapure double-distilled  $\text{HNO}_3$  and stored in HDPE bottles previously washed with ultrapure 0.1 M HCl and rinsed with MilliQ deionized water. The preparation of bottles for samples was performed in a clean bench room. The samples for OC analyses were collected in a pyrolyzed Pyrex glass tubes in which  $\text{HgCl}_2$  (10 mg/l) was added to prevent bacterial development. Blanks were performed to control the level of pollution induced by sampling and filtration. The organic carbon blanks of filtrate and ultrafiltrates never exceeded 0.1 mg/l, which is quite low for the organic-rich rivers sampled in this study (i.e., 5–20 mg/l OC). For all major and most of trace elements, concentrations in blanks were below the detection limits. In several cases, however, clear contamination by Zn, Cu, Ni, and Pb was detected in 10 and 1 kD ultrafiltrates. These samples were not considered in the analysis of results.

Aqueous silica concentrations were determined colorimetrically (molybdate blue method) with an uncertainty of 2% using a Technicon automated analyzer. In ultrafiltrates, the total dissolved silica was also analyzed by ICP-MS. No difference was found within the uncertainty of the analysis. Alkalinity was measured by potentiometric titration with HCl to pH=4.2 using a Gran method with a detection limit of  $10^{-5}$  M and an uncertainty of 2%. OC was analyzed using a Carbon Total Analyzer (Shimadzu TOC 5000) with an

uncertainty better than 3%. Major anion concentrations (Cl,  $\text{SO}_4$ , F,  $\text{NO}_3$ ) were measured by ion chromatography (HPLC, Dionex 2000i) with an uncertainty of 2%. Calcium, magnesium, sodium, and potassium concentrations were determined using an atomic absorption Perkin Elmer 5100PC spectrometer with an uncertainty of 1–2%. High concentrations of dissolved iron (i.e., >0.5 mg/l) were measured by flame AAS whereas the lower concentrations were analyzed by ICP-MS (Elan 6000, Perkin Elmer). Trace elements (TE) were measured without preconcentration by ICP-MS. For several ultrafiltrates having very low TE concentration, an automated desolvator was used, which allowed to increase the detection limit by a factor of 5. Indium was used as an external standard and corrections for oxide and hydroxide ions were made for REEs and metals (Ariés et al., 2000). 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 the analyses. Recently, the list of certified trace elements in this standard was extended, thanks to analytical studies performed in several French laboratories (Yeghicheyan et al., 2001). This allowed to include new elements such as B, Cs, Ga, Ge, Li, P, Rb, Si, Th, Ti, W, Y, Zr and REEs. A good agreement between our replicated measurements of SLRS-4 and the certified values was obtained (relative difference < 10%) except for B and P (30%). For several samples of this study, high concentration of dissolved iron (up to 20 mg/l) could cause interferences for trace elements. To check for this effect, SLRS-4 certified samples containing various amount of added iron were analyzed. Up to 2 mg/l of Fe, no effect for all trace elements was found but at higher Fe concentrations, large disagreement (30–50%) between certified and measured values for Cr, Zn and Ge was observed. Therefore, these elements were not analyzed in samples containing >2 mg/l of Fe.

#### 4. Results and discussion

Measured major and trace elements concentrations are reported in Appendix A. In the following section, we will discuss the behavior of major and trace elements during filtration/ultrafiltration experiments.

#### 4.1. Major components

The only source of information on Russian rivers of this region are the annual hydrochemical reports of the Russian Hydrometeorological Survey, which are available for the public from 1936 to 1975 (cf. *Annual Reports, 1965–1975*). In these reports, monthly measured values for dissolved Ca, Mg, Na+K, Fe, Si, HCO<sub>3</sub>, SO<sub>4</sub>, Cl, NO<sub>3</sub>, NO<sub>2</sub>, PO<sub>4</sub> and organic carbon for 50–60 rivers of the region are listed. Some of these rivers match our sampling points, which will allow us to compare the obtained hydrochemical features with typical values of element concentrations in rivers of this region. On a global scale, the total inorganic dissolved solid flux for Karelia region is 5–10 tons/km<sup>2</sup>/year (*Hydrochemical map, 1990*), which is comparable with values for Siberian rivers (Gordeev et al., 1996). For the southern part of studied region, composed of sedimentary rocks, the inorganic dissolved flux is about 30–40 tons/km<sup>2</sup>/year. Note that dissolved organic matter flux (C<sub>org</sub>) in Karelia region is very high, about 10 tons/km<sup>2</sup>/year, and comparable with those for large boreal rivers (Onega, N. Dvina and Pechora).

##### 4.1.1. pH and organic carbon

The studied waters are essentially neutral with pH varying from 6 to 7. In organic-rich water (Pezega, No. 32), pH decreases to 5.5 whereas it can increase to 7.5–7.9 in the southern catchments located on sedimentary bedrocks. No difference was detected between pH values of filtrates and ultrafiltrates within ± 0.1 pH units. The pH values for the Karelia region are quite comparable to those reported in neighboring Finnish lakes and streams (around 6, Lahermo et al., 1995) but they are higher than those for Cameroon streams draining granitic bedrock and having similar OC content (4.8 < pH < 6.6; Viers et al., 1997, 2000). This may reflect differences in the acid–base properties of dissolved organic matter in tropical and boreal regions.

All rivers exhibit a high concentration of dissolved organic carbon, from 10 to 30 mg/l, which is typical for rivers draining peatland areas; the average DOC values for two Russian boreal rivers, Sev. Dvina and Pechora, are 21 and 13 mg/l, respectively (Gordeev et al., 1996). Lahermo et al. (1995) reported 10–11 mg/l of DOC as an average for lakes and streams of Finland whereas a value of ~ 30 mg/l is frequently

reported for Suwannee river (Oliver et al., 1983) and other rivers of southeast Georgia (Beck et al., 1974). The inorganic nonbalanced charge calculated for all studied rivers varies from 0 to 0.05 mM ( $(\Sigma^+ - \Sigma^-)/\Sigma^+ < 0.1$ ). Only the organic-rich river Pezega (29 mg/l OC) exhibits an important nonbalanced anions deficit (0.14 mM or  $(\Sigma^+ - \Sigma^-)/\Sigma^+ = 0.7$ ).

Typical OC distributions among filtrates of various pore size are shown in Fig. 2. Usually, more than 90% of OC is concentrated in the <10 kD fraction with 50% of OC being in the <1 kD fraction. This is in contrast with the results of Viers et al. (1997) who observed almost complete removal of OC upon filtration down to the 5 kD pore size. However, Eyrolle et al. (1996) reported that in Parana basin the major part (54–82%) of DOC has a low molecular weight (<5 kD). Similar results for temperate and boreal rivers were reported by Sholkovitz (1995) and Porcelli et al. (1997). Note also that previous Russian studies on podzol soils draining boreal and temperate streams (Varshal, 1973; Varshal et al., 1973) indicate that low-molecular weight fulvic acids constitute at least 50% of DOC in river waters.

##### 4.1.2. Dissolved and colloidal iron

Iron, unlike OC, is strongly affected by ultrafiltration, as shown in Fig. 2. It is very often present as large-size colloids (0.22–5 μm) and is almost completely removed from solution before filtration through 10- and 1-kD membranes. In all filtrates and ultrafiltrates, the correlation between Fe and OC concentrations is very poor (Fig. 3). One can conclude, therefore, that Fe and OC behave independently during the ultrafiltration (UF) and represent two distinct types of colloids. Operationally, we define these colloids as iron-rich and fulvic(humic)-rich. Similar to Finnish and Swedish lakes and streams (Lahermo et al., 1995; Åström et al., 2001; Ingri et al., 2000) and organic-rich USA southeastern rivers (Beck et al., 1974), dissolved iron concentration in Karelian rivers reaches 2–4 mg/l with values as high as 20 mg/l in peatlands creeks (sample No. 2). The variation of iron concentration between different seasons is not significant: for 10 Karelian rivers sampled between 1958 and 1969, it is the lowest in May (0.5 mg/l) and the highest in summer and winter (0.8–1 mg/l; *Annual Reports, 1965–1975; Resources, 1966*). Note that these values are about 100 times higher than the world

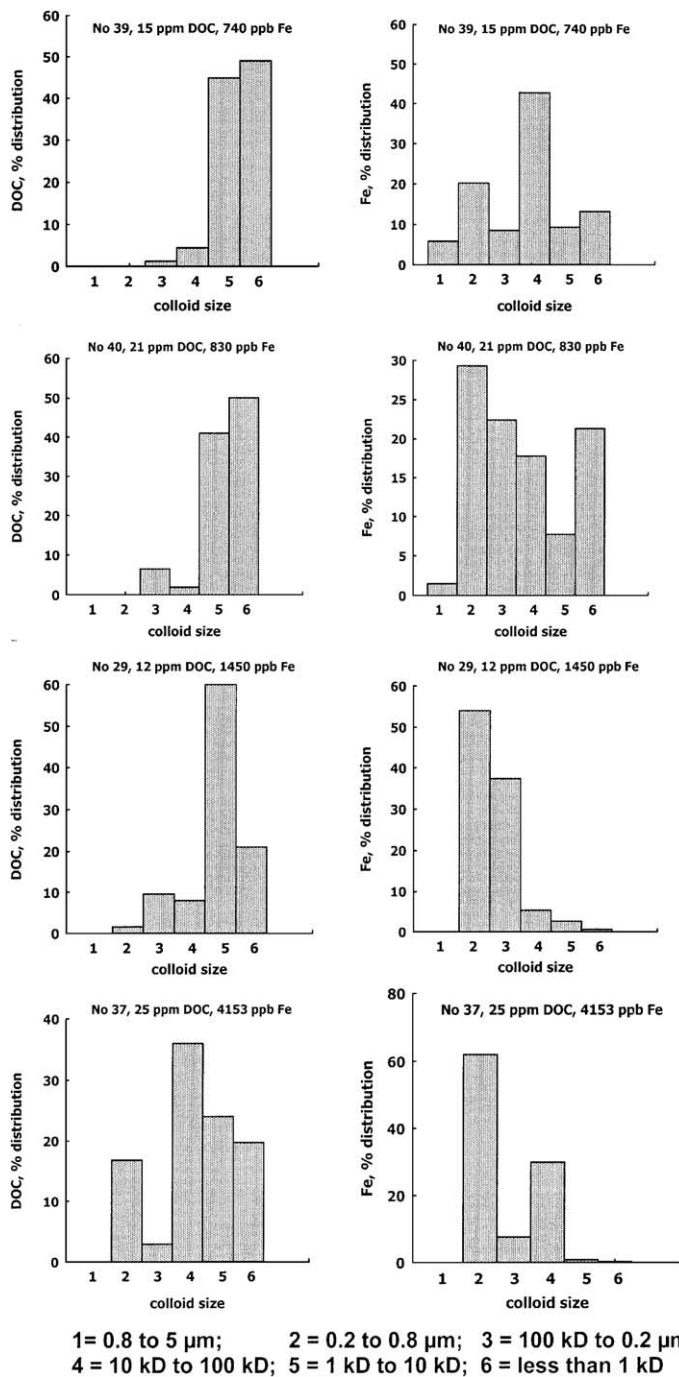


Fig. 2. The OC and Fe distribution among filtrates of various pore size. Concentrations reported on the top of figures were measured in 5  $\mu\text{m}$  filtrates. Note the important difference between Fe and OC distribution for a given river. This strongly suggest the existence of two colloidal pools.



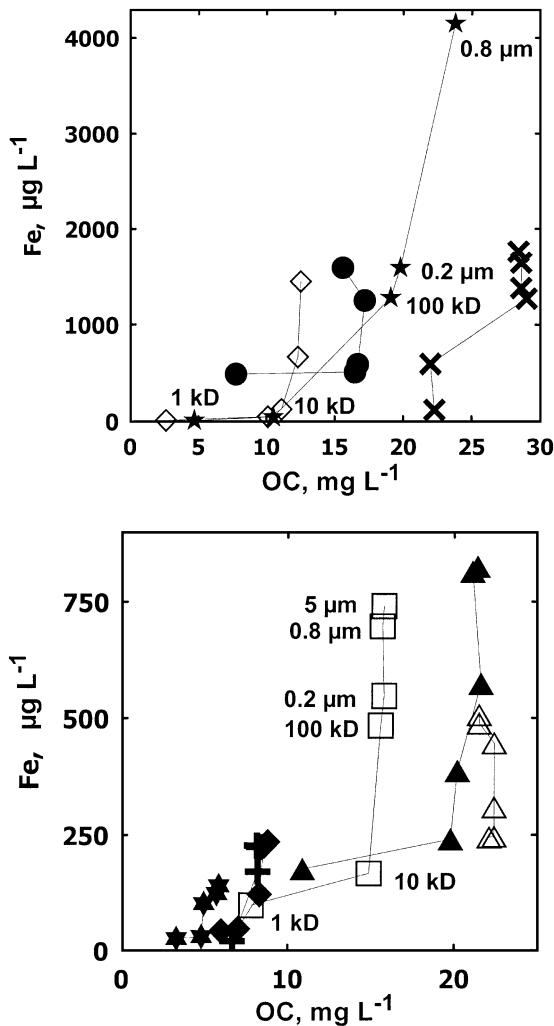


Fig. 3. Correlation between Fe and OC concentration in various filtrates. The significance of the symbols used in this figure and below is the following—○: No. 1, Pongoma; ▽: No. 3, Keret; ◆: No. 21, Kuzema; ★: No. 26, Shuya; ◇: No. 29, Idel; ✕: No. 32, Pezega; †: No. 33, Kumsa; ●: No. 36, Svyat; ★: No. 37, Chernaya; △: No. 38, Sobakina; □: No. 39, Yarynia; ▲: No. 40, Belukha. For each filtration experiment, the first (upper) symbol corresponds to 5 or 0.8  $\mu\text{m}$  pore size and the last (lower) one corresponds to 10 or 1 kD.

average and those measured in large boreal rivers such as Ob and Yenisei (Dai and Martin, 1995). As a result, iron colloids should be considered as a major component of these river waters, which can control, along with OC, the transport of many trace elements.

We will show below how different trace elements follow Fe or OC colloids during successive filtration.

#### 4.1.3. Major ions and silica

The composition of the dissolved load of most rivers reflects the weathering of silicate rocks. The total dissolved solids ( $\text{TDS} = \text{Na} + \text{Ca} + \text{K} + \text{Mg} + \text{Al} + \text{Fe} + \text{H}_4\text{SiO}_4 + \text{Cl} + \text{NO}_3 + \text{SO}_4$ ) measured in summer is around 10–20 mg/l (av. 16 mg/l), which is quite comparable with typical values of 15–30 mg/l for this region (Maksimova, 1967; Annual Reports, 1965–1975). These values are comparable to those reported for organic-rich tropical (Gaillardet et al., 1995; Dupré et al., 1996; Viers et al., 1997) and boreal (Millot et al., 2001) rivers and are among the lowest for world rivers (Meybeck, 1988). It is noteworthy that, although the weathering of granites and gneisses occurs in Karelia at much lower temperatures and weaker biological activity than in Cameroon, the flux of weathering products (and, consequently, chemical weathering rate) for these two regions are close. This can be explained by differences in soil depth: several meter thick soils of Cameroon prevent intensive weathering by screening fresh rocks from penetrating surface waters whereas in Karelia relatively thin soils let the bedrocks easily exposed to main weathering agents.

Unlike in tropical rivers, where TDS is dominated by silica, Karelian rivers analyzed in the present work have an average  $\text{H}_4\text{SiO}_4$  concentration of 5 mg/l, which constitutes only 30% of TDS. It is interesting to note that the average concentrations of dissolved silica is very stable throughout the year: based on published measurements for 10 rivers during 1950–70 (Resources, 1966; Annual Reports, 1965–1975), we calculated the average values of 9 mg/l for summer, 12 mg/l for winter, and 11 mg/l in May when the maximal snowmelt occurs and the discharge increases by a factor of 10–50. Among major elements, dissolved silica is the least affected by ultra-filtration: within analytical uncertainty (better than 2%), we have not found any difference between Si concentration in various filtrates, from 5  $\mu\text{m}$  to 1 kD. This indicates the absence of small-size phytolites or silica-rich organic debris in these waters and confirms that aqueous silica is not complexed by organic acids (Pokrovsky and Schott, 1998). Another important conclusion inferred from this observation is the ab-

sence of any suspended clay minerals and silicate rock debris even in 5  $\mu\text{m}$  filtrates. This allows us to discuss the whole range of filtration experiments solely in terms of colloidal fraction, without interferences from suspended silicate materials.

The concentration of dissolved bicarbonate, 0.3 mM for most karelian rivers as inferred from our data and reports from the Russian Hydrological Survey (Resources, 1966), is very close to that reported for Finnish streams (Lahermo et al., 1995). For most rivers of the region, seasonal variation of carbonate alkalinity is within 0.2–0.3 mM with alkalinity being the highest in winter and the lowest during the spring flood.

#### 4.2. Major and trace element composition in filtrates and ultrafiltrates

In the present work, we define colloids as the aggregates of molecular size between 1 nm (1 kD) and 5  $\mu\text{m}$ . We select this size domain because there is a gradual change of the size of Fe oxy(hydr)oxides present in solution filtered through 5  $\mu\text{m}$  with up to 60% of Fe being concentrated in the fraction 0.22–0.8  $\mu\text{m}$  (see Fig. 2).

##### 4.2.1. Alkali and alkaline-earth metals

Na, Mg, Ca, K, Li, Rb, Cs, Sr, Ba are mostly present in the dissolved pool and their concentrations are within the range reported for other world rivers (Kharkar et al., 1968; Dupré et al., 1996; Edmond et al., 1996; Huh et al., 1998). Cesium exhibits the largest variation among different rivers, which can be related to its strong retention by vermiculate minerals in the soils (Sawhney, 1972). Strontium and barium concentrations markedly increase in rivers draining the carbonate rocks of the southern area. Unlike for tropical organic-rich rivers (Viers et al., 1997), no significant enrichment in Sr, Rb and Ba was detected in colored rivers compare to organic- and iron-depleted rivers. For most rivers, the concentration of all major cations (Na, Mg, K, Ca) and trace elements (Li, Rb, Cs, Sr, Ba) does not change during filtration. In organic-rich rivers Idel and Chernaya, however, Ca, Mg, Sr and Ba concentrations decreased by a factor of 1.5–2 upon filtration from 5  $\mu\text{m}$  to 1 kD. Good correlation between [Ca] and OC in these samples and the absence of such correlation for Fe

indicate that Ca is associated with organic colloids. Organic complexes of Ca and Mg with natural fulvic acids have been identified for temperate (Shapiro, 1958) and boreal (Varshal et al., 1973) waters. Strong effect of ultrafiltration on Ca and Mg concentrations has been earlier reported for organic-rich waters of Cameroon and Brazil (Eyrolle et al., 1996; Viers et al., 1997; Dupré et al., 1999) and was attributed to the sorption of these metals on phytoliths and high molecular weight DOC fractions represented by plant debris. This process is not likely to be significant for boreal rivers probably because of a much lower biological activity and the limited production of phytoliths and organic debris.

##### 4.2.2. Heavy metals: Mn, Co, Ni, Cu, Zn, Cd, Pb

The concentrations of Mn and Co vary significantly, from 3 to 150 and 0.01 to 0.2  $\mu\text{g l}^{-1}$ , respectively, being the highest in Fe and OC-rich streams or in peat creeks where they can achieve 200  $\mu\text{g l}^{-1}$  for Mn and 0.9  $\mu\text{g l}^{-1}$  for Co (sample No. 2). The range of concentration of these elements is similar to those reported in tropical organic-rich rivers (Viers et al., 1997) and other world rivers (Kharkar et al., 1968). However, no direct correlation is observed between Mn and OC or Fe in 0.22  $\mu\text{m}$  filtered waters. Upon ultrafiltration, Mn concentration

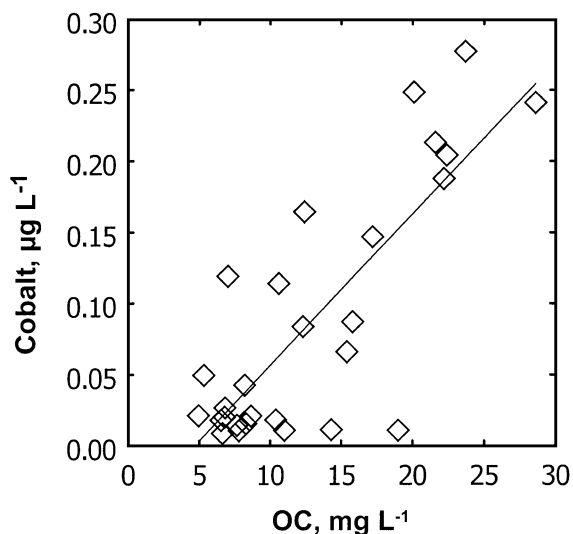


Fig. 4. Cobalt–OC correlation in 0.22  $\mu\text{m}$  filtrates.

slightly decreases and correlates with that of iron, suggesting that not more than 30% of Mn is associated with iron colloids. This is in accord with [Ponter et al. \(1992\)](#) who argued that Fe colloids do not exert an important control on Mn transport in boreal rivers. Colloidal Mn oxyhydroxides and vernadite are present in the sediments of Karelian lakes and, therefore, can contribute significantly to colloidal Mn transport. Besides, a significant part of dissolved manganese can be in the form of  $\text{Mn}^{2+}$  aquo ions as it is often observed in oxic freshwaters ([Laxen et al., 1984](#)).

Clear positive correlation between Co and OC is observed ([Fig. 4](#)), indicating a possible mobilization

of this element by organic colloids or its participation in the soil biochemical processes. Strong complexation of Co with natural organic ligands is well known ([Qian et al., 1998](#)). Results of ultrafiltration show that Co has a tendency to be concentrated in the 1–10 kD organic colloids fraction; for rivers Kumsa, Chernaya, and Belukha, such organic complexes represent more than 50% of total Co. However, for rivers Idel, Pezega and Yarynia, small-size Fe colloids (1–100 kD) control >50% of total Co.

Concentrations of Ni, Cu, and Zn in all rivers (from 0.2 to  $6 \mu\text{g l}^{-1}$ ) are well within the range measured in other world rivers such as Mackenzie ([Reeder et al.,](#)

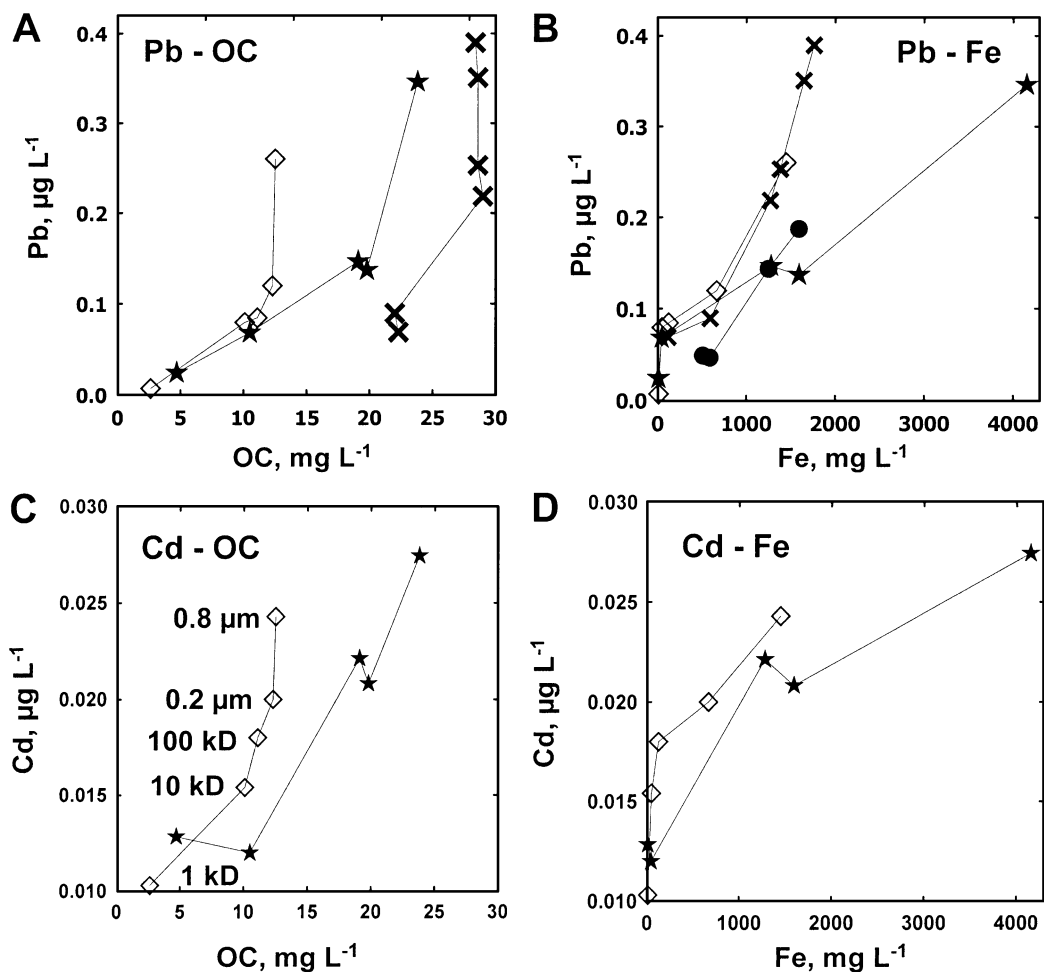


Fig. 5. Change of Pb and Cd concentration as a function of OC (A and C, respectively) and Fe (B and D, respectively) concentration in the successive filtrates from 5  $\mu\text{m}$  to 1 kD.

1972), Mississippi (Shiller and Boyle, 1987; Shiller, 1997), Amazon (Boyle et al., 1982), Ob, Yenisei, and Lena (Martin et al., 1993; Dai and Martin, 1995). Significant increase of Ni and Cu concentration in sample No. 4 (small lake in Kola peninsula) is due to atmospheric deposition from nickel smelters located within 10–50 km from the sampling point. At the same time, Ni and Cu concentrations in all Karelian rivers are two to five times lower than those in organic-rich streams of Cameroon draining the same type of bedrocks. This could be explained by lower concentrations of low-molecular weight extracellular

organic ligands compared to tropical regions as a result of weak biochemical and phytoplanktonic activity in boreal rivers. These metals are known to form much stronger complexes with such ligands than with large-size humic and fulvic acids (Xue et al., 1995; Xue and Sunda, 1997; Sigg et al., 2000). None of these three elements is affected by the presence of iron or organic colloids: Ni, Cu, and Zn concentrations only slightly change upon filtration from 5  $\mu\text{m}$  to 1 kD and are not related to Fe or OC concentrations.

Concentrations of Cd and Pb in all studied streams vary from 0.001 to 0.02 and 0.01 to 0.2  $\mu\text{g l}^{-1}$ ,

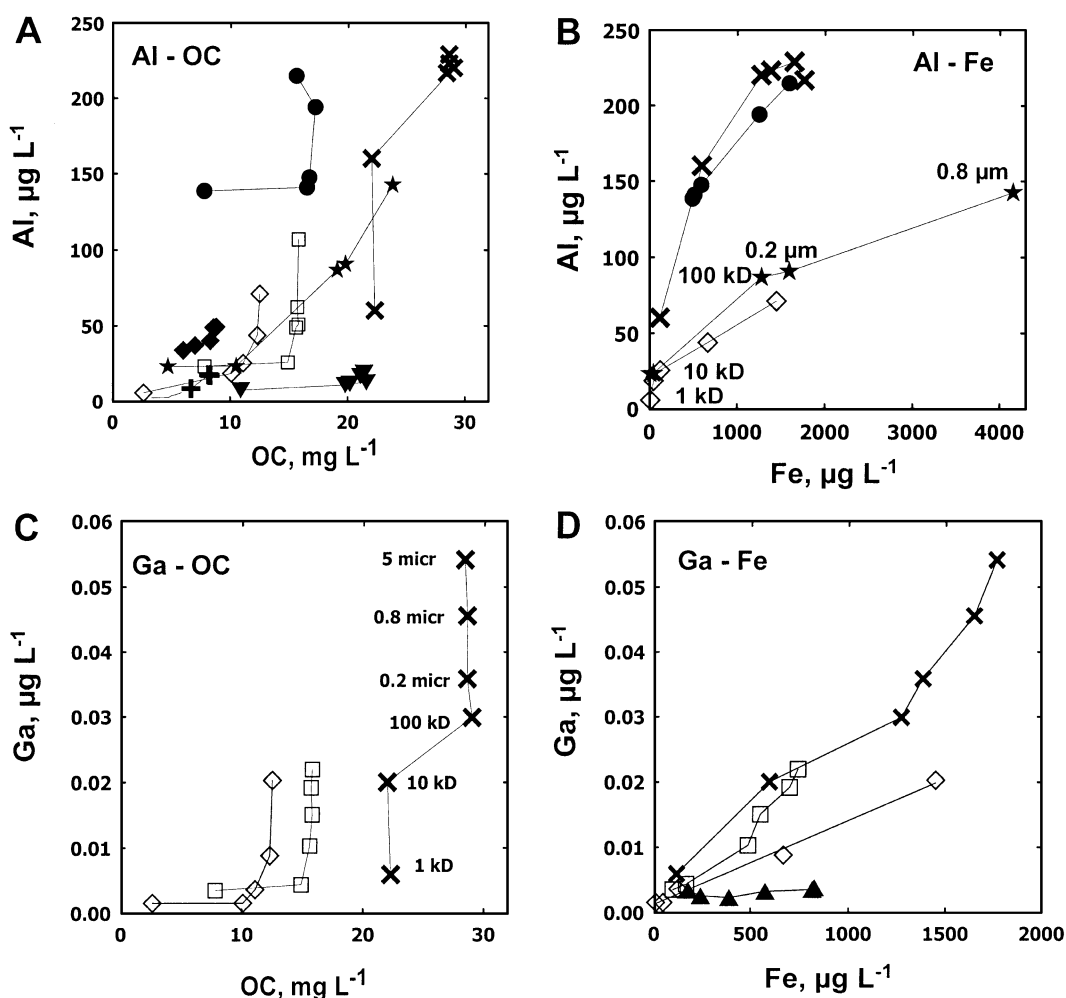


Fig. 6. Change of Al and Ga concentration as a function of OC (A and C, respectively) and Fe (B and D, respectively) concentration in the successive filtrates from 5  $\mu\text{m}$  to 1 kD.

respectively. Dissolved Cd concentration is close to the world river average ( $0.01 \mu\text{g l}^{-1}$ ; Martin et al., 1993) whereas dissolved lead is about 10 times higher than that in Ob, Yenissei and Lena or the world average ( $0.03 \mu\text{g l}^{-1}$ ; Martin et al., 1993; Dai and Martin, 1995). Such high Pb concentrations in Karelian rivers likely result from its colloidal status. Pb-bearing colloids mainly consist of iron oxy(hydr)oxides as shown by a positive trend between Pb and Fe concentrations. Moreover, during filtration, Pb rather follows Fe than OC in most samples (Fig. 5A,B). Only for organic-rich rivers Chernaya and Idel, Pb control by low-molecular-weight organic complexes (1–10 kD) can be important as its concentration sharply decreases during filtration through 1–10 kD filters and correlates with that of OC (Fig. 5A). In these rivers, cadmium is affected both by medium-size organic complexes (<1–10 kD) and large-size iron colloids (5–0.2  $\mu\text{m}$ ) (Fig. 5C,D).

To summarize, the seven investigated heavy metals exhibit different speciation in organic-rich boreal waters: Ni, Cu, and Zn are associated with <1 kD organic colloids or present as true dissolved species whereas Co, Cd, and Pb are associated with medium-size organic molecules (1–10 kD) and large-size (5  $\mu\text{m}$ –100 kD) iron colloids. A polarographic study of ultrafiltrates like that performed by Eyrolle et al. (1996) and Sigg et al. (2000) would allow a direct confirmation of this speciation scheme.

#### 4.2.3. Trivalent metals: Al, Ga, Y, REE

Al concentration is within the range of 5 to 200  $\mu\text{g l}^{-1}$ , which is comparable with that in tropical (Konhauser et al., 1994; Dupré et al., 1996; Eyrolle et al., 1996; Viers et al., 1997) and temperate (Beck et al., 1974) “black” rivers. All sampled waters show a strong dominance of Fe over dissolved Al, with the Fe/Al ratios as high as 150–200. In all streams, Al concentration is well correlated with that of Fe and is only weakly dependent on OC. This indicates a control of Al by inorganic mixed Fe–Al oxyhydroxides colloids. Indeed, Al concentration in rivers is strongly affected by filtration. In particular, at high Al and Fe concentrations (i.e., 50–200 and 800–4000  $\mu\text{g l}^{-1}$ , respectively), Al was found to be essentially bounded to Fe colloids (Fig. 6B) which carry 80–90% of total (<5  $\mu\text{m}$ ) Al whereas at low Al and Fe concentration (Al < 60  $\mu\text{g l}^{-1}$  and Fe < 700  $\mu\text{g l}^{-1}$ ),

these colloids contribute only to 30–70% of dissolved Al. No correlation between Al and OC in filtrates and ultrafiltrates was observed, thus indicating that organic colloids do not exert an important control on Al speciation in studied rivers (Fig. 6A). However, we do not exclude the possibility of Al being partially bound to organic complexes smaller than 10 kD as it is observed for rivers Chernaya and Idel (Fig. 6A). Gallium follows closely aluminum, being mostly controlled by iron colloids. Its concentration strongly decreases with the decrease of Fe concentration in the filtrates (Fig. 6D) whereas it does not depend on OC (Fig. 6C). However, at low Ga concentration (i.e., <0.005  $\mu\text{g l}^{-1}$ , samples 4, 36, 33, 38), speciation of this element does not seem to be affected by the presence of Fe or OC colloids. Ga concentration (from 3 to 20 ppt) is within the range reported for Cameroon streams (Viers et al., 1997) and some US rivers (Shiller, 1988). It has been argued (Shiller, 1988) that Ga/Al ratio in fluvial waters reflects the different affinities of these two elements for iron oxides and OC. However, in all studied rivers, the Ga/Al ratio is essentially independent of Fe/OC ratio, thus indicating that these two elements behave similarly. This contrasts with the control of Al and Ga by organic matter in tropical “black” rivers (Viers et al., 1997; Dupré et al., 1999).

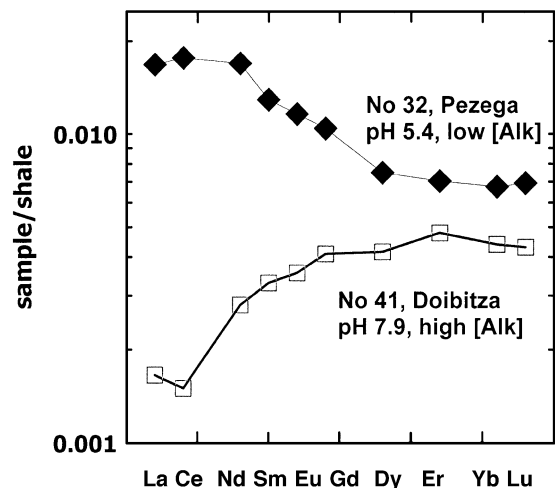


Fig. 7. Shale-normalized REE pattern of 0.22  $\mu\text{m}$  filtrates for Pezega and Doibitza rivers.

All Karelian rivers are enriched in Y and REE compared to large world rivers like Amazon or Mississippi. La and Ce concentrations in Fe- and OC-rich waters vary from 0.1 to  $1.3 \mu\text{g l}^{-1}$ , which is very close to those measured in Cameroon rivers (Dupré et al., 1996; Viers et al., 1997). Dissolved Y and REE concentrations are correlated with both Fe and OC. Association Fe–La(Ce) is stronger than OC–La(Ce), whereas, for HREE, complexation with dissolved organic matter seems to be dominant. This agrees with the general tendency of LREE and HREE to form

adsorbed complexes on inorganic phases (oxides) and aqueous complexes with organic ligands, respectively (Sholkovitz, 1995). The shale-normalized REE pattern of two contrasting rivers is shown in Fig. 7. It can be seen that low pH, low Alk, Fe, organic-rich waters (No. 32, Pezega) are strongly enriched in LREE, which are transported as colloids whereas more alkaline, carbonate-bearing waters (No. 41, Doibitza) are enriched in HREE probably in the form of aqueous carbonate complexes. Again, this is in agreement with LREE-enriched (or flat) patterns for organic-rich riv-

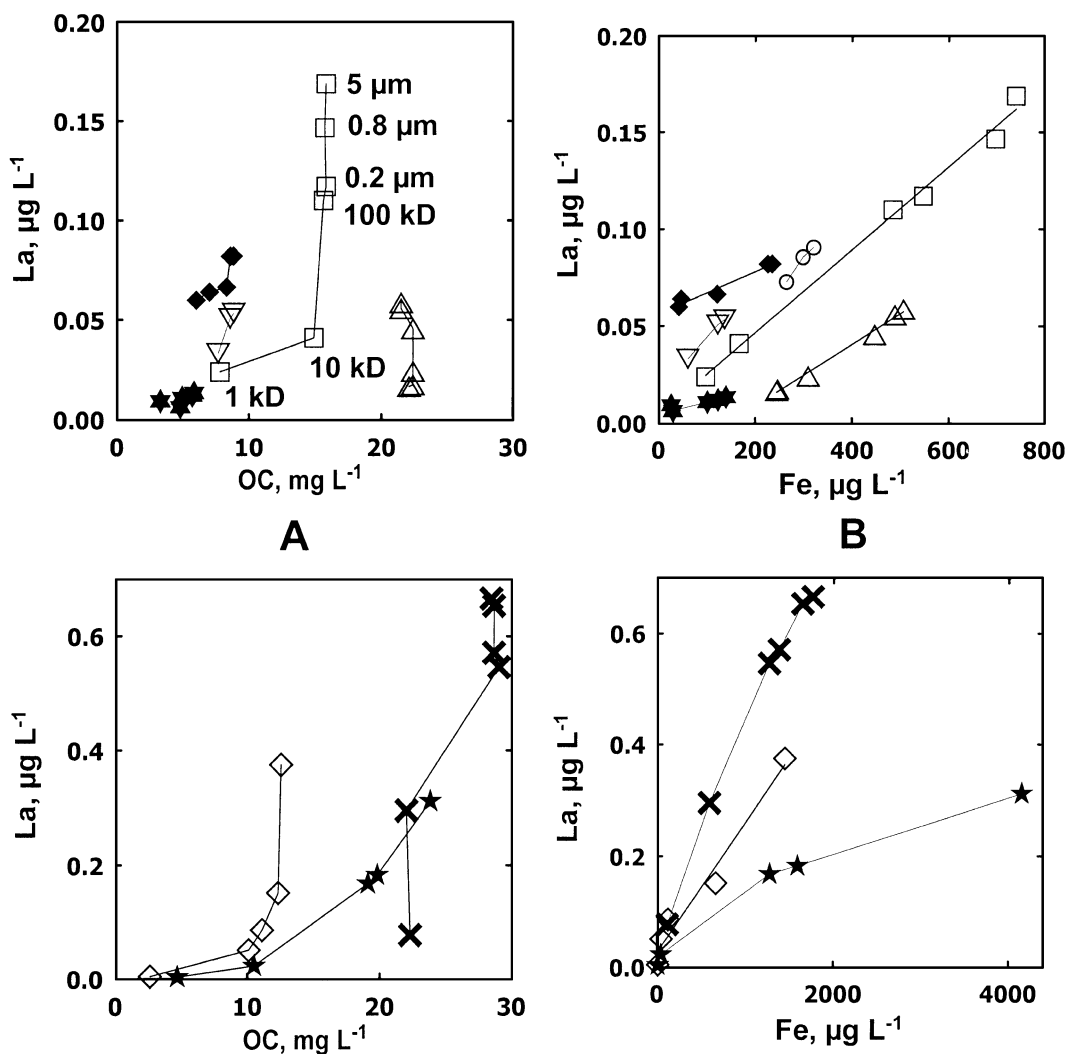


Fig. 8. Lanthanum concentration as a function of OC (A) and Fe (B) concentration in the successive filtrates from 5  $\mu\text{m}$  to 1 kD.

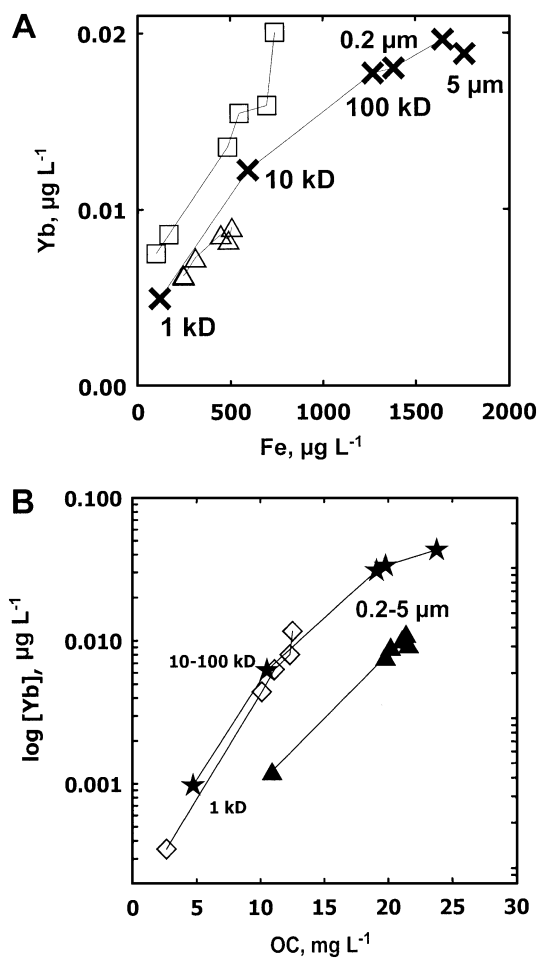


Fig. 9. Ytterbium concentration as a function of Fe (A) and OC (B) concentration in the successive filtrates from 5 μm to 1 kD.

ers draining granitic and metamorphic bedrocks and HREE-enriched patterns for rivers draining carbonate/sedimentary bedrocks (Sholkovitz, 1995).

Yttrium and REE are also strongly affected by filtration: in some cases, their concentration decreases 10–100 times upon filtration from 0.8–5 μm to 1–10 kD. In most rivers, Y has been found to be strongly associated with OC in ultrafiltrates whereas for others

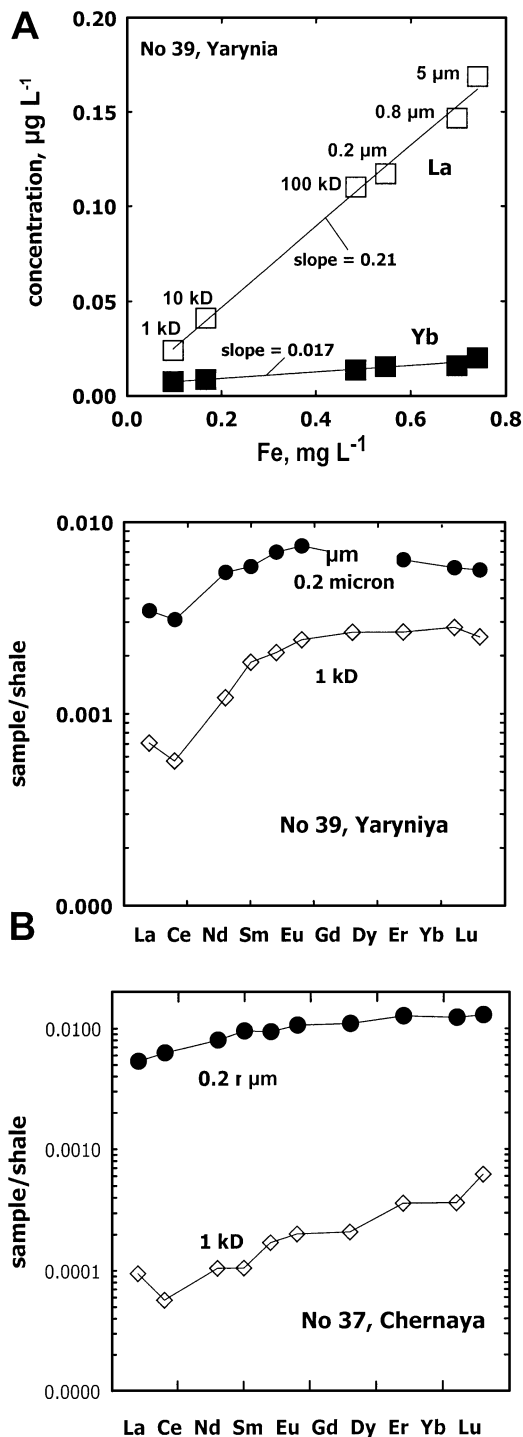


Fig. 10. (A) Evolution of La and Yb concentration as a function of Fe concentration during filtration from 5 μm to 1 kD for r. Yarynia. (B) Shale-normalized pattern of REE in filtrates and ultrafiltrates of rivers Yarynia and Chernaya.

(i.e., rivers Idel, Pezega and Yarynia) Fe colloids were also important. LREE are clearly associated with medium size iron oxides and not with organic colloids as it is shown in Fig. 8 for lanthanum. In contrast, dissolved ytterbium and HREE are very often concentrated in the low-molecular weight (1–10 kD) fraction correlated with OC. In agreement with this speciation scheme, it can be seen in Fig. 9 that large Fe colloids (100 kD–5  $\mu\text{m}$ ) do not contribute significantly to Yb speciation as only a weak decrease of Yb concentration occurs during filtration from 5  $\mu\text{m}$  to 100 kD. This point is further illustrated in Fig. 10A, which presents typical filtration results for r. Yarynia (No. 39). In this figure,

La and Yb concentration in various filtrates are plotted as a function of Fe concentration. The slope of this linear correlation is much higher for La (0.21) than for Yb (0.017), thus confirming that Fe colloids exerts a strong control on La transport but not on Yb. In full agreement with these findings, the shale-normalized REE pattern was found to be sensitive to the size of colloids that bear REE. Yaryniya and Chernaya rivers pattern is presented in Fig. 10B. An enrichment of HREE in 1 kD ultrafiltrates compared to 0.2  $\mu\text{m}$  filtrates can be seen. This observation is in good accord with the results of Sholkovitz (1995) for temperate USA rivers. Similar to the results of this study, he

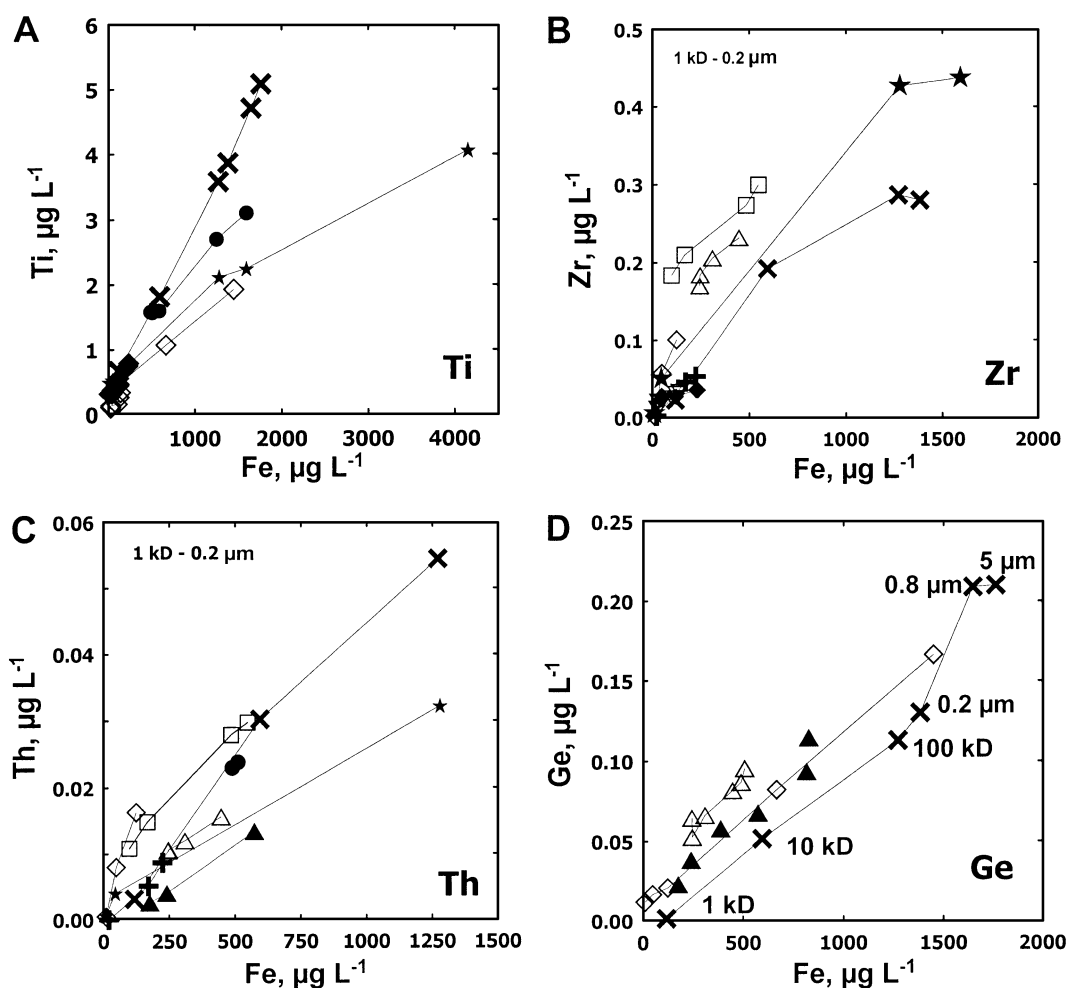


Fig. 11. Change of Ti (A), Zr (B), Th (C), and Ge (D) concentration as a function of Fe concentration in the successive filtrates from 5  $\mu\text{m}$  to 1 kD.



found that Fe and color decrease during ultrafiltration whereas OC kept essentially constant. This indicates that  $>1\text{--}10$  kD inorganic Fe colloids (for all REE) and low-molecular weight ( $1\text{--}10$  kD) organic ligands (for HREE) compete for the control of REE in these waters. This is also confirmed by the results of Ingri et al. (2000) who showed that the REE present in the colloidal (and particulate) fraction were linked to an organic-rich phase (with associated Al–Fe) and a Fe-rich (Fe-oxyhydroxide) inorganic phase.

#### 4.2.4. Tetravalent elements: Ti, Zr, Th, Ge

These elements are generally known to be immobile during weathering, accumulating in mineral altered layers. However, migration of these elements is possible in organic- and iron-rich boreal rivers. Titanium concentration in these rivers ranges from  $0.2$  to  $1\ \mu\text{g l}^{-1}$  but it can reach  $4\ \mu\text{g l}^{-1}$  in some black rivers and peat creeks. Similar values were reported for Mengong, Sanaga, and Nyong rivers of Cameroon (Viers et al., 1997). From the analysis of bulk water samples, it is difficult to assess the relative control of Fe/organic colloids on Ti speciation in these rivers since Ti concentration is positively correlated with both Fe and organic colloids in  $0.22\ \mu\text{m}$  filtrates (not shown). Results of filtration and ultrafiltration experiments, however, unambiguously prove the dominant role of iron colloids in Ti speciation: a very good positive correlation is observed between  $[\text{Ti}]$  and  $[\text{Fe}]$  in filtrates (Fig. 11A).

Dissolved Zr and Th concentration varies from  $0.01$  to  $0.4\ \mu\text{g l}^{-1}$ , and  $0.003$  to  $0.05\ \mu\text{g l}^{-1}$ , respectively, being positively correlated both with Fe and OC. This range of concentration is well above the average values for world rivers but is close to that reported in organic-rich tropical waters of Cameroon (Dupré et al., 1996; Viers et al., 1997). In Karelian rivers, inorganic Fe colloids are essentially responsible for these concentrations as it is demonstrated in Fig. 11B,C that reports results of ultrafiltration experiments. Again, like for trivalent elements, this is a striking difference with the results of Viers et al. (1997) for tropical rivers where these elements were found to be entirely transported in the form of organic colloids. Germanium is strongly controlled by iron oxides as shown by ultrafiltration results (Fig. 11D). Ge concentration range in these waters ( $0.01\text{--}0.2\ \mu\text{g l}^{-1}$ ) is similar to that observed in Cameroon “black” rivers (Viers et al., 1997).

#### 4.2.5. Oxyanions B, V, Cr, Mo, W, As, Sb, P

Boron concentration varies significantly among the rivers with a span of concentration ( $2\text{--}50\ \mu\text{g l}^{-1}$ ) being well within the world average ( $21\ \mu\text{g l}^{-1}$ ; Johannesson et al., 2000). The B/Cl molar ratio in Karelian rivers varies from  $0.001$  to  $0.01$  showing the absence of significant source of boron enriched rocks or hydrothermal input. No correlation between B and Fe or OC is observed in our samples. The high variability of clay minerals concentration and soil thickness among various watersheds may be responsible for the large variations on B concentrations as it is known that this element is readily sorbed onto clay minerals

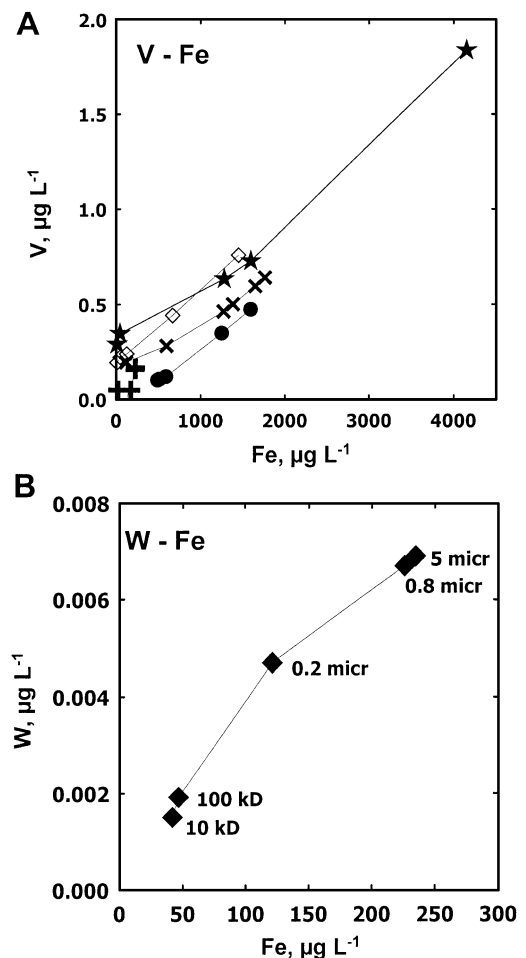


Fig. 12. Change of V (A) and W (B) concentration as a function of Fe concentration in the successive filtrates from  $5\ \mu\text{m}$  to  $1\text{--}10$  kD.

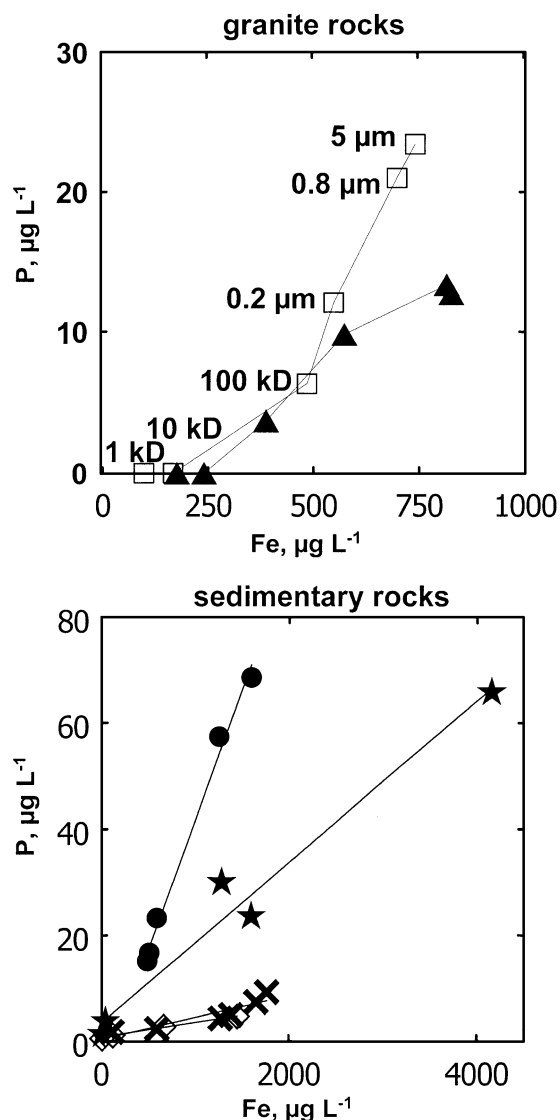


Fig. 13. Phosphorus concentration as a function of Fe concentration in the successive filtrates from 5  $\mu\text{m}$  to 1–10 kD.

(Harder, 1970). B concentration does not change during ultrafiltration.

The ranges of V, Cr, Mo and W concentrations (0.1–1.5, 0.1–0.75, 0.05–0.4, and 0.003–0.02  $\mu\text{g l}^{-1}$ , respectively) are similar to those reported for average world's rivers (0.75  $\mu\text{g l}^{-1}$  for V, 1.4  $\mu\text{g l}^{-1}$  for Cr, 0.49  $\mu\text{g l}^{-1}$  for Mo, and 0.03  $\mu\text{g l}^{-1}$  for W; Kharkar et al., 1968; Johannesson et al., 2000). Among these elements, only Cr showed a clear

correlation with dissolved Fe and OC in 0.22  $\mu\text{m}$  filtrates, thus suggesting that redox reactions can be involved in Cr adsorption on these colloids. Cr concentration is affected by ultrafiltration only in organic- and Fe-rich rivers (Pezega, Chernaya and Belukha). In these rivers, it is associated either with small-size (< 10 kD) organic colloids (r. Pezega and Chernaya) or with Fe colloids (10 kD–0.8  $\mu\text{m}$ ), which can contribute up to 50% of dissolved Cr (r. Belukha).

Molybdenum, which is mostly present as  $\text{MoO}_4^{2-}$ , was not affected by filtration and ultrafiltration experiments. Dissolved vanadium and tungsten were found

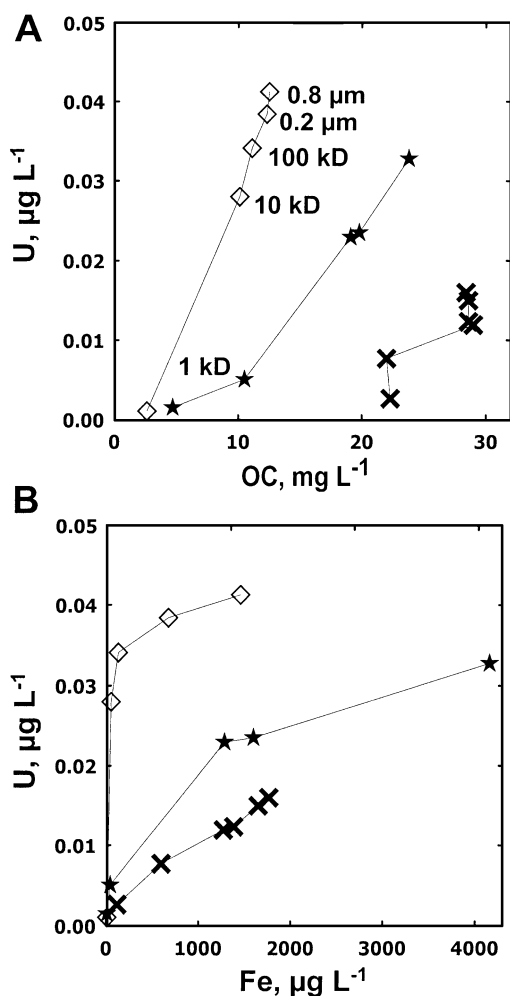


Fig. 14. Uranium concentration as a function of OC (A) and Fe (B) concentration in the successive filtrates from 5  $\mu\text{m}$  to 1 kD.

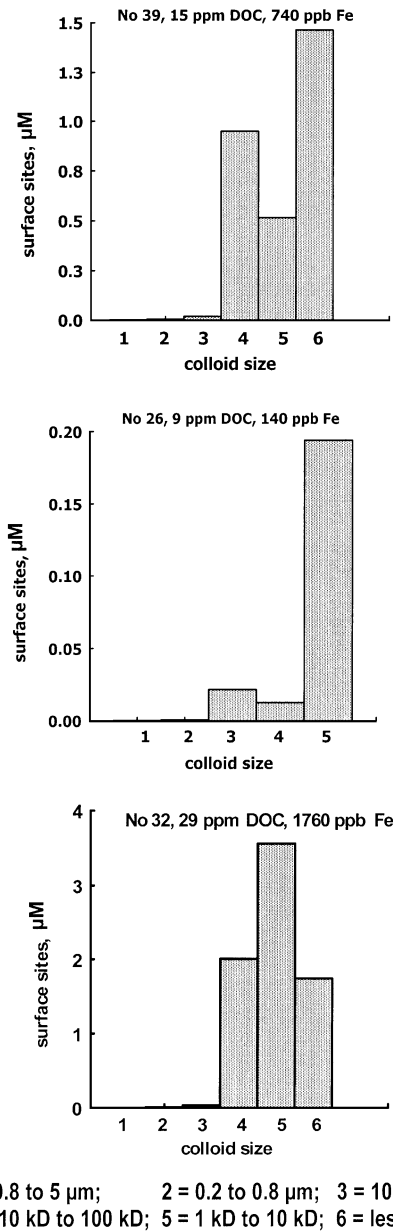


Fig. 15. The surface sites distribution among iron colloids of various sizes. Note that this surface site distributions are remarkably different from that of total dissolved iron (Fig. 2).

to be essentially associated with Fe colloids as their concentrations sharply decrease with decreasing pore size from 0.8 µm to 1 kD (Fig. 12). It has been argued that dissolved V in rivers draining silicate rocks

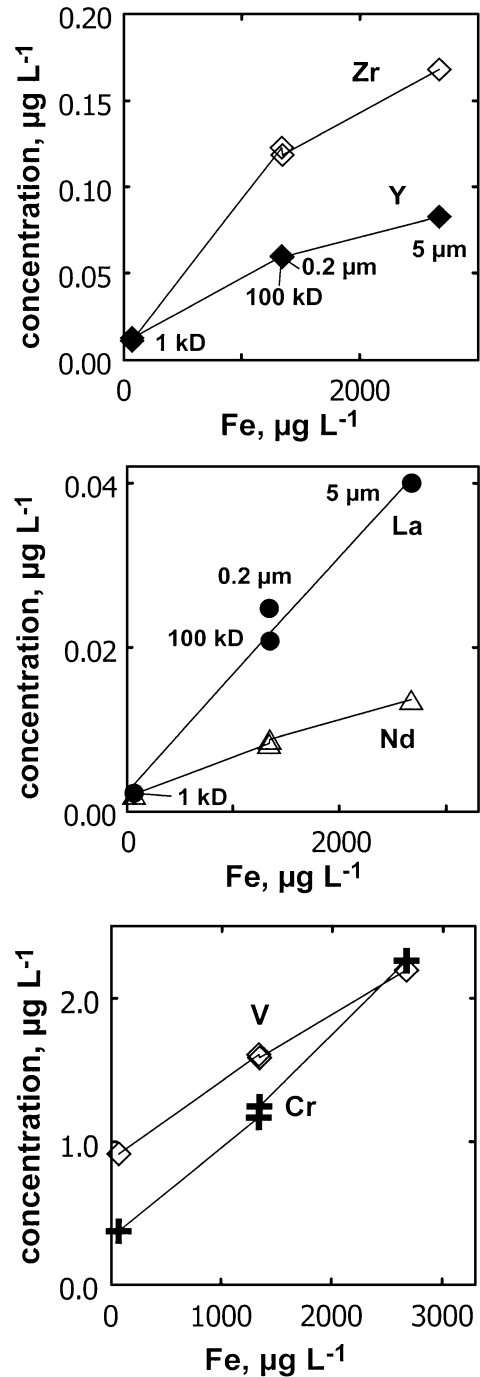


Fig. 16. Plots of several trace element concentrations as a function of Fe concentration in the successive filtrates from 5 µm to 1 kD for Tolbachik river (6.5 mg/l COD, 2.9 mg/l Fe) of Central Kamchatka (Pokrovsky and Schott, unpublished results).

originates from silicate weathering (Shiller and Mao, 2000). However, we have not found any correlation between dissolved Si and V in Karelian rivers. The presence of high amounts of colloidal Fe in these rivers, which serves as V carrier, is likely to hide the different silicate sources.

Antimony and arsenic concentrations in Karelian rivers draining granitic bedrocks ( $0.02$ – $0.07$  and  $0.01$ – $0.5 \mu\text{g l}^{-1}$ , respectively) are significantly lower than average values for world rivers ( $1.1$  and  $1.7 \mu\text{g l}^{-1}$  for Sb and As, respectively; Kharkar et al., 1968; Martin et al., 1993). Low concentrations of these elements were also reported in organic-rich tropical rivers (Konhauser et al., 1994; Viers et al., 1997) and Finnish streams (Åström, 2001). However, As concentration increases to  $1$ – $2 \mu\text{g l}^{-1}$  in rivers draining sedimentary rocks in the southern part of the territory investigated in this study. In all studied rivers, arsenic is never associated with Fe or organic colloids. A

positive correlation is observed between Sb and OC concentrations in  $0.22 \mu\text{m}$  filtrates. It can be related to the presence of organic colloids  $<10$  kD. Indeed, ultrafiltration of organic-rich rivers (Idel, Chernaya, and Belukha) suggest more than 50% of Sb is present as small organic complexes.

Dissolved phosphorus concentration abruptly changes during filtration being strongly correlated with iron (Fig. 13). This supports the hypothesis of P transport adsorbed on or coprecipitated with Fe hydroxides (Fox, 1989). Strong association of phosphate with colloidal iron oxy(hydr)oxide particles isolated from the redox transition boundary layer in an eutrophic lake has been reported by Buffle et al. (1989).

#### 4.2.6. Uranium

Uranium concentration exhibits large variations among different rivers. Generally, it increases from  $0.002$ – $0.06 \mu\text{g l}^{-1}$  in Karelian rivers with silicate

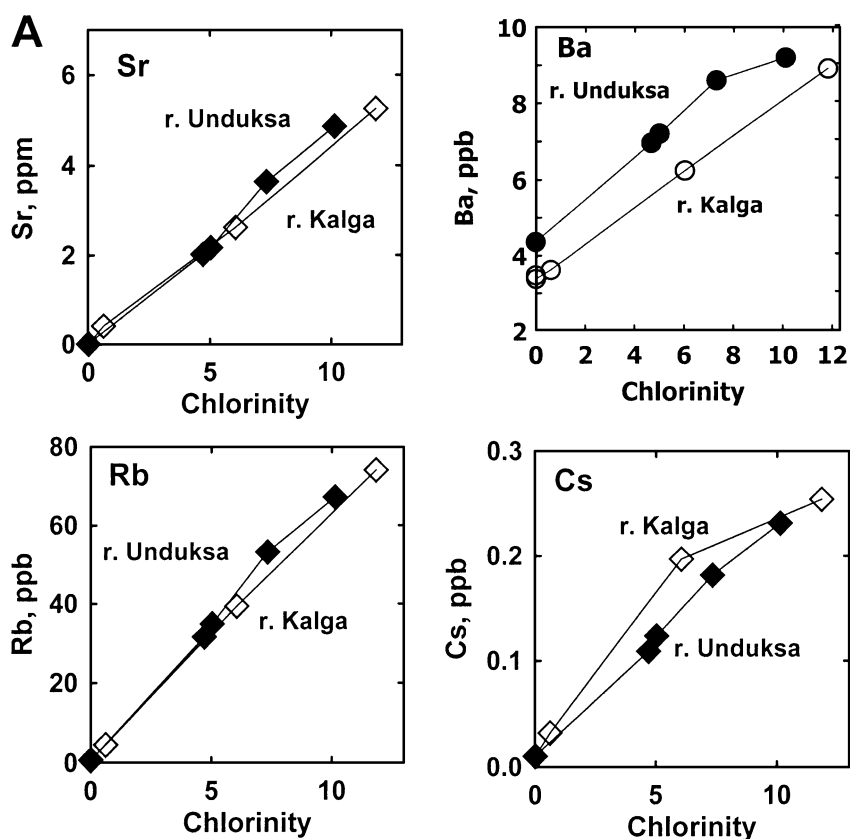


Fig. 17. Distribution of Sr, Ba, Rb, and Cs (A) and Si, Fe, Al, Pb, La and Ce (B) in Unduksa and Kalga rivers.

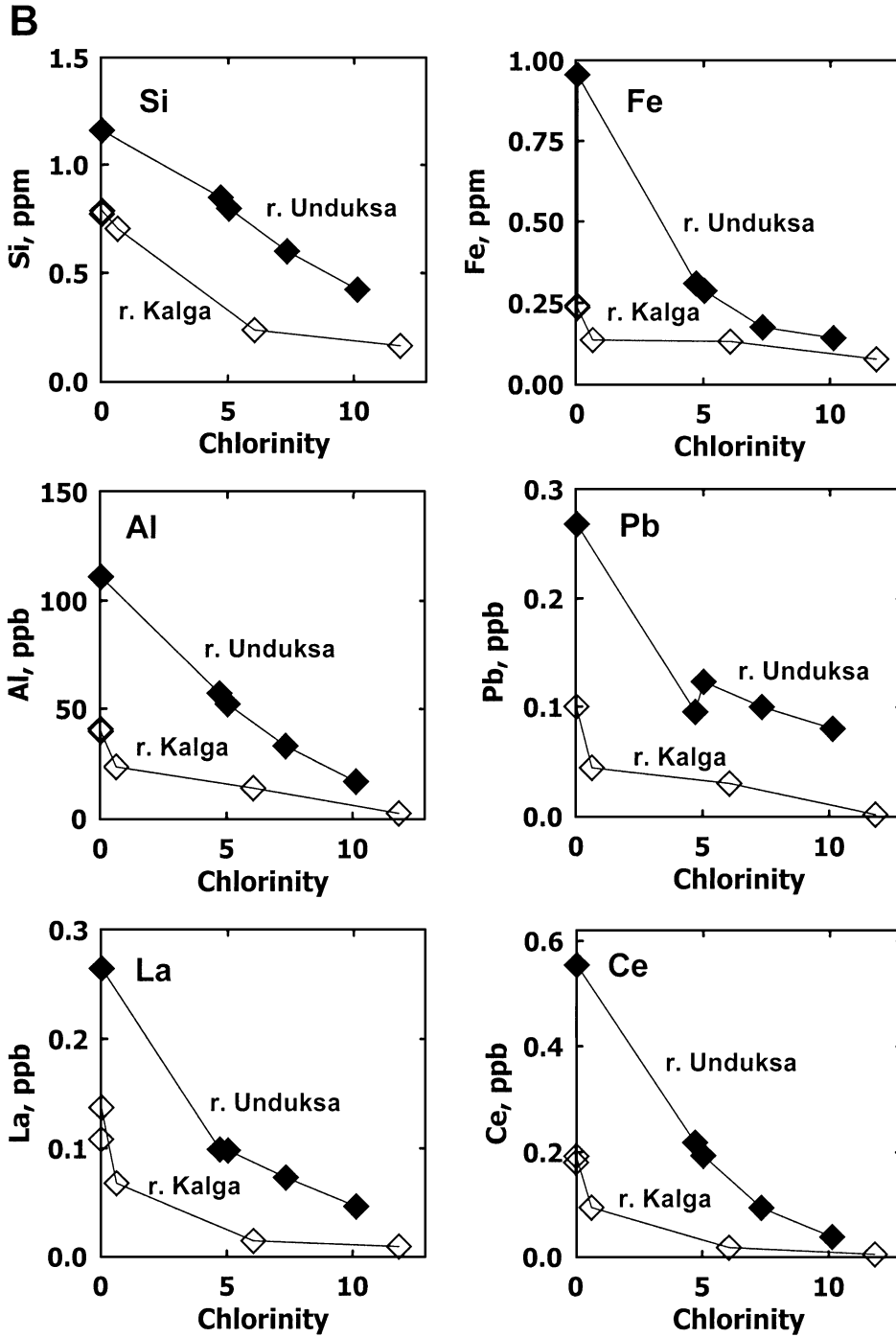


Fig. 17 (continued).

bedrocks to  $0.3\text{--}1.4\ \mu\text{g l}^{-1}$  in southern rivers draining sedimentary (carbonate) basins. These values are in general agreement with the world average and with data reported for organic-rich tropical and boreal rivers (Palmer and Edmond, 1993; Porcelli et al., 1997; Viers et al., 1997). In none of our samples, dissolved ( $<0.22\ \mu\text{m}$ ) U clearly correlates with Fe or OC. Transport of U by organic colloids in boreal rivers (Porcelli et al., 1997) is confirmed by the results of our ultrafiltration experiments on Fe-organic-rich Karelian rivers draining granitic bedrock. Highly alkaline southern rivers of sedimentary basins containing high U concentrations do not exhibit any control of colloids on U transport. In Karelian rivers, dissolved U is present both in organic complexes having molecular weight between 1 and 100 kD (r. Idel and Chernaya, Fig. 14A) and large size Fe-rich colloids (r. Chernaya, Idel, and Pezega, Fig. 14B). Besides, one should not exclude the important role of organic matter for U adsorption on iron oxides via the formation of ternary surface complexes (Murphy et al., 1999). Rivers containing both low concentrations of U ( $<0.01\ \mu\text{g l}^{-1}$ ), Fe ( $<500\ \mu\text{g l}^{-1}$ ) and OC ( $<10\ \text{mg/l}$ ) in  $<0.2\ \mu\text{m}$  fractions, such as Kuzema (No. 21), Shuya (No. 26), and Svyat (No. 36), do not show detectable decrease of U concentration in the 1 kD fraction compare to the  $0.2\text{--}5\ \mu\text{m}$  fractions (not shown). In these rivers, dissolved uranium is present in small inorganic (carbonate) or organic (humic and fulvic) complexes.

#### 4.3. Distinguishing between adsorbed and coprecipitated forms of trace elements in iron colloids

In order to get some insights on the surface area of iron colloids present in investigated waters and the relative importance of metal adsorption on Fe colloids versus coprecipitation with  $\text{Fe}^{3+}$ , we have estimated the surface area of colloids in each filtrate. For this calculation, we used the concentration of Fe in each fraction and the average pore size of colloids retained by specific filter. Assuming that the surface sites concentration for iron oxide is about  $10\ \mu\text{mol/m}^2$  (Dzombak and Morel, 1990), the total amount of available surface sites for different samples is found to range between  $0.3$  and  $18\ \mu\text{M}$ , which is two to three orders of magnitude higher than the typical concentrations of trace elements (nM). Examples of the calculated distribution of surface sites as a func-

tion of Fe colloids size is shown in Fig. 15 for different Fe and OC concentrations. It can be seen that most Fe oxide surface sites are concentrated in the 10–100 and 1–10 kD size fractions or the  $<1$  kD colloids. However, results of our filtration experiments show that many trace elements (Al, Ga, REE, Pb, Ti, Ge, Zr, Th, V) are mostly concentrated in large Fe colloids ( $>100$  kD), which exhibit negligible surface areas. This demonstrates preferential incorporation of these TE in the bulk of large colloids (i.e., coprecipitation) rather than their sorption on Fe colloid surfaces. This coprecipitation of TE with Fe colloids occurs on the oxic/anoxic front frequently found in boreal environment on podzol soils (Perelman, 1982). The dominant size of iron colloids found in studied boreal rivers is between  $0.8\ \mu\text{m}$  and 100 kD (Fig. 2), which matches the value  $0.05\text{--}0.2\ \mu\text{m}$  measured by Buffle et al. (1989) on the redox boundary in an eutrophic lake. According to Ingri et al. (2000), colloidal Fe oxy(hydr)oxides in Kalix river and Sweden mires are formed by precipitation of Fe from inflowing oxygen-depleted ground water. In this study, we observed precipitation of iron hydroxide at the contact between anoxic waters from a swamp creek ( $20\ \text{mg/l}$  of Fe, sample No. 2) and oxygenated surface waters (r. Pongoma). The granitic groundwaters from boreal regions contain up to several  $\mu\text{g/l}$  of Ce or La as observed in Norway (Banks et al., 1999) and in Kola peninsula (Pokrovsky et al., unpublished results). Such high concentrations favor TE coprecipitation with iron hydroxide as shown by scavenging experiments performed with various trace metals (Martinez and Mc Bride, 1998; Bau, 1999). Note also that natural dissolved organic matter adsorbs on the surface of iron oxyhydroxides in the form of humic and fulvic acid, which can help to stabilize iron colloids and prevents their aggregation and coagulation (Deb, 1949; Shapiro, 1964).

The chemical nature of iron colloids formed in organic-rich surficial waters is not well known. Recently, using a set of spectroscopic techniques (Electronic Paramagnetic Resonance, Infrared Spectroscopy), Olivie-Lauquet et al. (1999) showed that Fe(III) occurred in colloidal materials from Cameroon rivers both as organic complexes and inorganic (hydr)oxides and that the proportion of Fe inorganic colloids in colored organic-rich waters is generally underestimated. Amorphous iron hydroxides whose

large sorption capacities are well known can thus serve as important TE carriers both in organic-rich tropical waters (Olivié-Lauquet et al., 2000) and DOC-poor groundwaters (Dia et al., 2000). However, a spectroscopic study of the organic and inorganic forms of iron in boreal river colloids would be necessary to further elaborate this issue.

How general could be TE transport as Fe colloids in natural waters? Apparently, all iron-rich waters ( $[\text{Fe}] > 1 \text{ mg/l}$ ) can accommodate important amount of TE via adsorption on and/or coprecipitation with colloids. In river Tolbachik (Central Kamchatka) that contains 2.6 mg/l Fe and 7 mg/l OC, we found that concentrations of many trace elements (V, Cr, Zr, Y, REE, Ge) almost linearly correlates with Fe concentration but not OC upon filtration/ultrafiltration from 5  $\mu\text{m}$  to 1 kD (Fig. 16; Pokrovsky and Schott, unpublished results).

#### 4.4. Estuarine distribution of trace elements

Distribution of TE has been investigated in Kalga and Unduksa estuaries. Rb, Cs, Sr and Ba exhibit typical conservative behavior in the estuarine zones (Fig. 17A); their concentrations linearly increase with salinity seaward. This indicates that these elements are not affected by colloids coagulation and biochemical uptake in the estuaries. Silica concentration decreases almost linearly seaward, exhibiting nearly conservative behavior (dilution by seawater) or partial uptake by marine plankton (Fig. 17B). Dissolved ( $< 0.2 \mu\text{m}$ ) Fe, Al, Pb, and REE exhibit different behaviors in these two estuaries (Fig. 17B). In the Kalga river estuary, there is a nonconservative behavior of these elements with a sharp decrease of their concentration occurring at the beginning of salinity increase. This results from the coagulation of the Fe(organic?) carriers of these elements (Sholkovitz, 1976; Boyle et al., 1977; Sigleo and Helz, 1981; Hoyle et al., 1984; Andersson et al., 1994; Guieu et al., 1996). Based on our data, we cannot distinguish between Fe and organic colloids because OC was not measured in these samples. However, a close correlation between dissolved Fe and TE both in filtrates of rivers and the estuarine zones implies a strong control of Fe colloids on TE scavenging. In the small estuary of organic-rich Unduksa river, Al, Fe, and REE exhibit a quite conservative behavior, their concen-

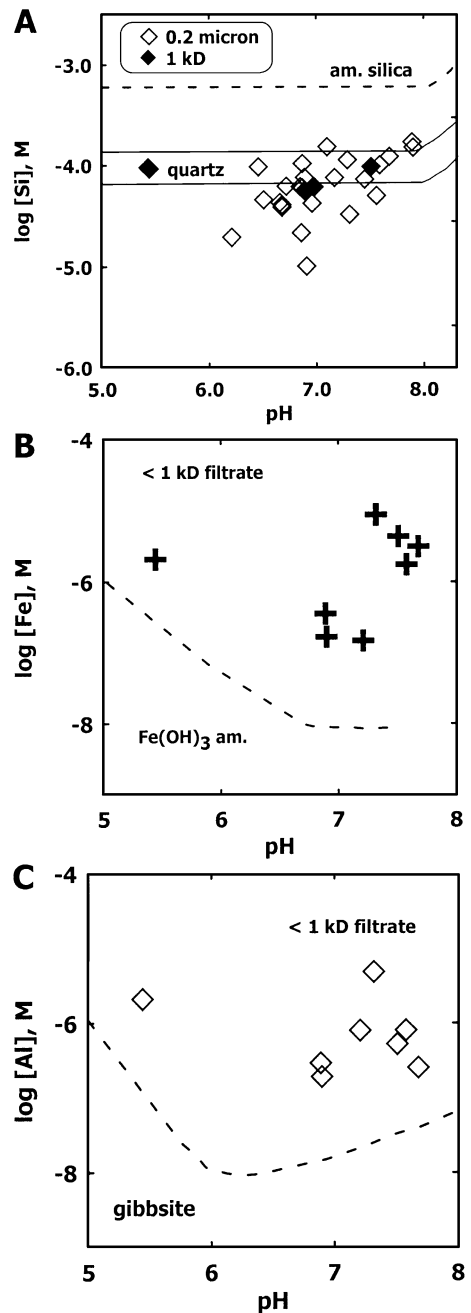


Fig. 18. Saturation state of filtrates and ultrafiltrates with respect to quartz (A), amorphous iron hydroxide (B) and gibbsite (C) at 15 °C. Values of thermodynamic parameters are from Rimstidt (1997) and Walther and Helgeson (1977) (quartz), Diakonov (1995) (Fe(OH)<sub>3</sub>) and Verdes et al. (1992) (gibbsite).



trations decreasing almost linearly with salinity increase. This contrasting behavior can be explained by slow removal of dissolved organic carbon and weak influence of chemical coagulation in a small poorly mixed estuary. In other words, the short residence time of river colloids in a small estuary does not allow iron/organic colloids to coagulate and thus prevents rapid scavenging of TE. Therefore, small estuaries can serve as a model for direct groundwater discharge into the sea.

#### 4.5. Control of element concentrations by mineral phases

All Karelian rivers are 10–100 times and 100–1000 times supersaturated with respect to amorphous Fe oxy(hydroxide) and gibbsite, and kaolinite, respectively. After ultrafiltration, Al and Fe concentrations decrease 10 times, leaving the solutions still strongly supersaturated with respect to these phases. A plot of “true dissolved” (<1 kD) Al and Fe concentration as a function of sample pH is presented in Fig. 18B,C. Apparently, small polymers and organic complexes present in these ultrafiltrates can significantly contribute to the speciation of dissolved Al and Fe. Si concentration in ultrafiltrates is reported as a function of pH in Fig. 18A; it can be seen that most of studied samples are close to equilibrium or slightly undersaturated with respect to quartz or clay minerals assemblages (vermiculate, montmorillonite).

## 5. Conclusions and perspectives

(1) Karelian boreal rivers draining granitic/gneiss bedrocks on podzol and peat soils exhibit high concentration of dissolved Fe, OC, and a number of usually insoluble trace elements (Al, Mn, Ti, Ga, Ge, Zr, Y, REE, U, Th). These traces can be carried either as organic or Fe oxy(hydr)oxides colloids.

(2) Correlations between dissolved Fe, OC and trace elements concentration in filtered (0.22  $\mu\text{m}$ ) samples of various streams and lakes do not allow to distinguish between their organic and inorganic carriers. Indeed, because of (i) various sources of TE, Fe colloids and OC, (ii) strong dilution effect by atmospheric precipitation, (iii) groundwater input

and (iv) regulation by lakes in various catchments, direct correlation between Fe(or OC) and TE concentration for all set of rivers do not make sense.

(3) Ultrafiltration experiments show that several transition metals (Cu, Zn, Ni, Co, Cd), Y, HREE and U can be partially transported by low-molecular weight (<1–10 kD) organic acids. All other trace elements are incorporated in Fe-colloids.

(4) In filtrates and ultrafiltrates, TE concentration correlates with total iron concentration but not the surface area of Fe colloids. This strongly suggests that coprecipitation (bulk incorporation) rather than surface adsorption controls the transport in surface waters of TE released by weathering. Fe(II) oxidation followed by massive precipitation of Fe(OH)<sub>3</sub>(am) on redox boundaries when anoxic groundwaters meet oxygen-saturated surface waters explains such a “colloidal mobilization” of TE.

Several issues should be addressed in the future for a better knowledge of the mechanisms of transport of trace elements in boreal surficial waters. It is important to compare the results of filtration experiments performed in summer, when, due to high phytoplankton activity, there are many low-molecular-weight organic ligands available to strongly complex TE and in spring floods, when OC is dominated by soil-derived organics, high-molecular weight humic and fulvic acids, organic debris and phytolites. An ultrafiltration study of soil and groundwater solutions could give insights on the successive processes controlling TE migration from the rocks to the riverwaters. A direct method to assess the relative role of organic and inorganic colloids in trace elements transport would be an ultrafiltration study following in situ UV-radiation decomposition of organic matter.

## Acknowledgements

We acknowledge the insightful and constructive reviews of J. Gaillardet, J. Ingri and an anonymous reviewer. The authors are grateful to R. Freydieier for careful technical assistance during the analytical part of this study. We thank A.A. Pokrovskaya for participation in the fieldwork and for providing the geological information. J. Viers is thanked for helpful discussions. [EO]



## Appendix A

Measured major and trace element concentrations in all filtrates and ultrafiltrates. All concentrations are in  $\mu\text{g/l}$  except Alkalinity (mM)

Filter	Swamp B	Kalga	Unduksa	No. 1	No. 1	No. 1	No. 2	No. 2
	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$	5 $\mu\text{m}$	0.8 $\mu\text{m}$	0.22 $\mu\text{m}$	5 $\mu\text{m}$	0.8 $\mu\text{m}$
pH	nd	nd	nd			6.91		
Na	1960	2960	9300			1900		
K	86	711	821			396		
Mg	334	551	672			414		
Ca	307	863	1020	515	519	488	2597	
[Alk]	nd	nd	nd			0.086		
Cl	nd	nd	nd			1380		
SO <sub>4</sub>	nd	nd	nd			1290		
F	nd	nd	nd			30		
Si	50	771	1160	290	285	282	600	590
P	nd	nd	nd	0.00	0.00	0.00	0.00	0.00
DOC	23.0	8.2	15.4	7.6	7.9	6.8	26.7	24.9
Al	30	40	111	36	34	28	79	79
Mn	4.8	6.0	5.2	5.9	5.4	4.1	211	206
Fe	107	239	956	320	298	264	20100	18200
Li	nd	nd	nd	0.560	0.606	0.568	1.87	2.00
B	nd	nd	nd	<0.5	<0.5	<0.5	9.7	nd
Ti	nd	nd	nd	0.523	0.440	0.395	4.00	3.40
V	0.282	0.255	0.197	0.096	0.065	0.014	2.90	2.68
Cr	0.401	0.473	0.582	0.260	0.237	0.211	1.690	1.580
Co	0.042	0.0427	0.0661	0.0328	0.0354	0.0268	0.960	0.953
Ni	0.345	0.584	0.616	0.179	0.157	0.146	0.444	0.496
Cu	0.261	0.743	0.257	0.256	0.303	0.272	0.127	0.117
Zn	nd	1.35	1.10	1.15	1.22	1.15	2.242	2.570
Ga	nd	nd	nd	0.0044	0.0036	0.0039	0.0267	0.0236
Ge	nd	nd	nd	nd	nd	nd	nd	nd
As	0.277	0.209	0.253	nd	nd	nd	0.486	0.412
Rb	0.064	0.788	0.613	0.623	0.620	0.592	0.252	0.261
Sr	2.7	8.2	10.0	6.0	6.0	5.5	25.9	26.2
Y	0.013	0.052	0.125	0.047	0.044	0.040	0.467	0.476
Zr	nd	nd	nd	0.029	0.030	0.023	0.484	0.509
Mo	nd	nd	nd	nd	nd	nd	0.006	0.007
Cd	nd	0.0086	0.0067	nd	nd	nd	0.0041	0.0042
Sb	nd	nd	nd	nd	nd	nd	0.015	0.014
Cs	nd	0.010	0.010	0.0064	0.0060	0.0055	0.0071	0.0074
Ba	0.62	3.43	4.36	2.46	2.45	1.96	11.2	10.5
La	0.0097	0.123	0.264	0.091	0.086	0.073	0.854	0.802
Ce	0.0250	0.186	0.554	0.172	0.170	0.142	1.83	1.70
Pr	0.0037	0.027	0.068	0.023	0.0224	0.0181	0.232	0.223
Nd	0.0121	0.112	0.270	0.089	0.0836	0.0725	0.982	0.949
Sm	0.0044	0.019	0.0467	0.014	0.0134	0.0121	0.161	0.160
Eu	0.0009	0.0041	0.0097	0.0028	0.0025	0.0026	0.0276	0.0292
Gd	0.0023	0.014	0.038	0.013	0.0119	0.0101	0.136	0.122
Tb	0.0004	0.0017	0.0040	0.0014	0.0015	0.0011	0.0149	0.0150
Dy	0.0026	0.0086	0.023	0.0083	0.0074	0.0071	0.0829	0.0815
Ho	0.0002	0.0016	0.0041	0.0017	0.0015	0.0013	0.017	0.017
Er	0.0015	0.0048	0.0137	0.0041	0.0038	0.0039	0.045	0.044
Tm	0.0002	0.0006	0.0019	0.0005	0.0005	0.0003	0.0073	0.0072
Yb	0.0009	0.0045	0.0113	0.0037	0.0041	0.0037	0.041	0.039

(continued on next page)

## Appendix A (continued)

Filter	Swamp B	Kalga	Unduksa	No. 1	No. 1	No. 1	No. 2	No. 2
	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$	5 $\mu\text{m}$	0.8 $\mu\text{m}$	0.22 $\mu\text{m}$	5 $\mu\text{m}$	0.8 $\mu\text{m}$
Lu	0.0001	0.0007	0.0019	0.0006	0.0007	0.0006	0.0070	.0075
W	nd	nd	nd	nd	nd	nd	< dl	nd
Pb	0.412	0.103	0.268	0.132	0.115	0.096	0.173	0.144
Th	0.0000	0.0027	0.019	0.0043	0.0040	0.0028	0.0943	0.0947
U	0.0009	0.0061	0.0161	0.0051	0.0042	0.0046	0.0127	0.0120
	Swamp	Kalga	Unduksa	1–5 $\mu\text{m}$	1–0.8 $\mu\text{m}$	1–0.2 $\mu\text{m}$	No. 2–5 $\mu\text{m}$	2–0.8 $\mu\text{m}$
Filter	No. 2	No. 3	No. 3	No. 3	No. 4	No. 19	No. 20	No. 21
	0.22 $\mu\text{m}$	5 $\mu\text{m}$	0.8 $\mu\text{m}$	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$	5 $\mu\text{m}$
pH	6.86			6.68	7.11	6.96	6.89	
Na	13 100			1550	3190	2700	1500	
K	280			515	1100	809	542	
Mg	1640			890	1370	1440	913	
Ca	1800	1650	1606	1390	7120	2110	1380	510
[Alk]	nd			0.145	0.265	0.182	0.115	
Cl	nd			1340	8280	4040	1710	
SO <sub>4</sub>	nd			1350	6100	2570	1570	
F	< dl			10	20	< dl	< dl	
Si	600	1070	1075	1070	357	1170	2110	1110
P	0.00	0.00	0.00	0.00	1.35	0.00	0.00	0.00
DOC	16.2	8.8	8.6	7.7	7.0	10.4	8.6	8.1
Al	61	19	16	9.0	46.4	32.1	62.9	49.3
Mn	172	4.38	2.46	1.21	2.12	2.96	7.81	8.4
Fe	11271	136.5	122.2	61	64	142	244	235
Li	2.06	0.476	0.493	0.482	0.358	0.636	0.456	0.415
B	12.1	< 0.5	< 0.5	< 0.5	0.9	3.1	1.5	< 0.5
Ti	2.58	0.590	0.488	0.182	0.431	0.435	0.560	0.786
V	1.50	< dl	< dl	< dl	0.396	0.000	0.000	0.230
Cr	1.268	0.181	0.216	0.158	0.470	0.420	0.313	0.232
Co	0.844	0.025	0.022	0.015	0.1190	0.0182	0.0210	0.0223
Ni	0.455	0.291	0.237	0.280	5.670	1.108	0.375	0.239
Cu	0.119	0.346	0.363	0.341	5.010	0.539	0.482	0.245
Zn	2.160	0.756	0.660	0.219	2.78	0.57	3.11	3.6
Ga	0.0212	0.0039	0.0023	0.0007	nd	< dl	0.0003	0.0052
Ge	nd	nd	nd	nd	nd	< dl	0.0186	< dl
As	nd	nd	nd	nd	nd	0.081	0.113	0.073
Rb	0.246	0.905	0.897	0.886	0.992	1.840	1.203	0.681
Sr	25.3	13.7	13.7	13.7	25.1	17.3	11.5	5.69
Y	0.378	0.027	0.027	0.021	0.118	0.073	0.091	0.039
Zr	0.386	0.032	0.028	0.019	0.026	0.070	0.066	0.036
Mo	nd	nd	nd	nd	nd	0.058	0.011	0.011
Cd	nd	nd	nd	nd	nd	0.0010	0.0021	< dl
Sb	nd	nd	nd	nd	nd	0.018	0.017	0.018
Cs	0.0065	0.0034	0.0034	0.0029	0.0069	0.0067	0.0042	0.0073
Ba	9.2	3.67	3.55	3.42	7.42	6.18	5.35	2.88
La	0.546	0.0535	0.0508	0.0333	0.252	0.179	0.270	0.0822
Ce	1.18	0.0818	0.0756	0.0462	0.282	0.305	0.430	0.133
Pr	0.153	0.0124	0.0116	0.0072	0.056	0.042	0.064	0.0208
Nd	0.666	0.0448	0.0425	0.0253	0.207	0.172	0.245	0.0776
Sm	0.118	0.0090	0.0079	0.0049	0.034	0.027	0.042	0.0112
Eu	0.0197	0.0016	0.0011	0.0008	0.0077	0.0034	0.0021	0.0024

## Appendix A (continued)

Filter	No. 2	No. 3	No. 3	No. 3	No. 4	No. 19	No. 20	No. 21
	0.22 $\mu\text{m}$	5 $\mu\text{m}$	0.8 $\mu\text{m}$	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$	5 $\mu\text{m}$
Gd	0.097	0.0061	0.0060	0.0042	0.0320	0.0192	0.0263	0.0087
Tb	0.0118	0.0006	0.0007	0.0006	0.0037	0.0020	0.0029	0.0014
Dy	0.0631	0.0047	0.0042	0.0034	0.0190	0.0121	0.0171	0.0062
Ho	0.013	0.0008	0.0008	0.0006	0.0033	0.0017	0.0026	0.0015
Er	0.038	0.0026	0.0028	0.0019	0.0091	0.0060	0.0085	0.0038
Tm	0.0051	0.0003	0.0003	0.0002	0.0012	0.0006	0.0009	0.0005
Yb	0.034	0.0030	0.0024	0.0017	0.0075	0.0048	0.0069	0.0033
Lu	0.0059	0.0003	0.0003	0.0002	0.0011	0.0006	0.0012	0.0006
W	nd	nd	nd	nd	nd	<dl	<dl	0.0069
Pb	0.079	0.029	0.022	0.017	0.185	<dl	0.0094	0.0665
Th	0.0765	0.0050	0.0052	0.0012	0.0168	0.0164	0.0076	0.0077
U	0.0098	0.0104	0.0110	0.0097	0.105	0.0190	0.0233	0.0050
	2–0.2 $\mu\text{m}$	3–5 $\mu\text{m}$	3–0.8 $\mu\text{m}$	3–0.2 $\mu\text{m}$	No. 4-Kola	No. 19	No. 20	21–5 $\mu\text{m}$
Filter	No. 21	No. 21	No. 21	No. 21	No. 22	No. 23	No. 24	No. 25
	0.8 $\mu\text{m}$	0.22 $\mu\text{m}$	100 kD	10 kD	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$
pH		6.68			6.66	6.86	6.87	6.51
Na		1535			1720	8730	8400	4580
K		377			450	447	858	1386
Mg		384			503	382	1010	1290
Ca	505	511	489	479	690	437	1420	2250
[Alk]		0.065			0.100	0.296	0.378	0.300
Cl		1210			1000	3010	4700	3590
SO <sub>4</sub>		1130			1030	878	752	2760
F		0			<dl	<dl	220	<dl
Si	1125	1130	1120	1115	1190	605	2900	1270
P	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DOC	8.6	8.3			7.8	10.6	14.3	5.3
Al	48.9	40.3	37.1	33.9	45.8	50.6	34.5	10.1
Mn	8.1	5.7	4.4	4.1	5.8	9.3	1.6	30.6
Fe	226	121	47	42	203	188	174	64
Li	0.421	0.436	0.446	0.419	0.575	0.780	1.783	0.932
B	<0.5	<0.5	<0.5	<dl	0.8	5.2	7.7	4.7
Ti	0.749	0.445	0.368	0.318	0.334	0.302	0.631	0.149
V	0.220	0.171	0.159	0.160	0.000	0.000	0.000	0.000
Cr	0.235	0.219	0.227	0.214	0.184	0.336	0.467	0.187
Co	0.0226	0.0156	0.0115	0.0117	0.0107	0.1140	0.0113	0.0495
Ni	0.228	0.232	0.218	0.291	0.025	0.000	0.000	0.294
Cu	0.250	cntd	0.265	0.252	0.206	0.225	0.000	0.666
Zn	3.2	2.0	cntd	cntd	1.1	2.1	2.5	9.4
Ga	0.0038	0.0027	0.0012	0.0006	0.0000	0.0000	0.0000	0.0003
Ge	<dl	<dl	<dl	<dl	0.0000	0.0000	0.0000	0.0000
As	0.063	0.057	0.064	0.055	0.000	0.044	0.053	0.032
Rb	0.681	0.678	0.679	0.646	0.670	0.498	0.518	1.518
Sr	5.73	5.68	5.53	5.27	6.63	4.22	12.9	16.5
Y	0.037	0.031	0.028	0.027	0.055	0.054	0.110	0.050
Zr	0.036	0.027	0.028	0.023	0.036	0.064	0.169	0.043
Mo	0.009	0.009	0.007	0.009	0.012	0.025	0.134	0.082
Cd	<dl	<dl	<dl	<dl	0.0010	0.0053	0.0000	0.0029
Sb	0.019	0.019	0.023	0.019	0.017	0.019	0.014	0.023
Cs	0.0061	0.0063	0.0067	0.0065	0.0021	0.0018	0.0009	0.0000

(continued on next page)

## Appendix A (continued)

Filter	No. 21	No. 21	No. 21	No. 21	No. 22	No. 23	No. 24	No. 25
	0.8 $\mu\text{m}$	0.22 $\mu\text{m}$	100 kD	10 kD	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$
Ba	2.83	2.65	2.47	2.2	3.2	1.7	4.4	3.5
La	0.0820	0.0665	0.0641	0.0600	0.117	0.0862	0.0933	0.0827
Ce	0.131	0.104	0.0961	0.0849	0.197	0.179	0.175	0.150
Pr	0.0202	0.0159	0.0147	0.0135	0.0289	0.0255	0.0259	0.0198
Nd	0.0742	0.0604	0.0550	0.0487	0.113	0.0948	0.113	0.0832
Sm	0.0136	0.0103	0.0100	0.0078	0.0185	0.0152	0.0216	0.0160
Eu	0.0017	0.0017	0.0012	0.0017	0.0008	0.0022	0.0040	0.0030
Gd	0.0095	0.0073	0.0071	0.0067	0.0125	0.0109	0.0205	0.0121
Tb	0.0011	0.0011	0.0008	0.0008	0.0011	0.0012	0.0025	0.0011
Dy	0.0064	0.0050	0.0046	0.0050	0.0082	0.0092	0.0172	0.0072
Ho	0.0012	0.0010	0.0012	0.0008	0.0016	0.0014	0.0029	0.0012
Er	0.0036	0.0032	0.0028	0.0027	0.0057	0.0060	0.0104	0.0046
Tm	0.0005	0.0005	0.0004	0.0005	0.0004	0.0004	0.0012	0.0004
Yb	0.0037	0.0029	0.0026	0.0025	0.0045	0.0052	0.0113	0.0044
Lu	0.0007	0.0005	0.0004	0.0004	0.0012	0.0006	0.0015	0.0006
W	0.0067	0.0047	0.0019	0.0015	< dl	< dl	< dl	< dl
Pb	0.0623	0.0424	0.0309	cntd	< dl	< dl	< dl	< dl
Th	0.0069	0.0057	0.0065	0.0049	< dl	< dl	< dl	< dl
U	0.0041	0.0038	0.0039	0.0043	0.0020	0.0022	0.0049	0.0302
	21–0.8 $\mu\text{m}$	21–0.2 $\mu\text{m}$	21–100 kD	21–10 kD	No. 22	No. 23	No. 24	No. 25
Filter	No. 26	No. 26	No. 26	No. 26	No. 26	No. 27	No. 28	No. 29
	5 $\mu\text{m}$	0.8 $\mu\text{m}$	0.22 $\mu\text{m}$	100 kD	10 kD	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$	0.8 $\mu\text{m}$
pH			6.87			7.56	7.31	6.90
Na			1640			1720	1330	
K			631			518	576	
Mg			1400	1400	1390	1790	858	977
Ca		5955	6020	5900	5740	5750	2530	2355
[Alk]			0.422			0.429	0.210	
Cl			2030			1820	765	
SO <sub>4</sub>			1630			1500	940	
F			< dl			< dl	< dl	
Si	1700	1690	1670	1680	1640	1390	907	1700
P	0.76	0.07	0.00	0.00	0.00	0.00	0.00	4.63
DOC	5.9	5.7	5.0	4.8	3.3	6.5	6.6	12.5
Al	5.6	5.2	3.4	2.5	2.1	4.17	14.3	71.3
Mn	12.6	7.9	7.6	7.5	7.5	29.3	12.0	34.3
Fe	140	123	101	30	26	165	304	1449
Li	0.530	0.538	0.555	0.553	0.503	0.475	0.549	0.786
B	2.3	2.2	2.3	2.3	2.3	0.92	0.54	40
Ti	0.339	0.260	0.155	0.133	0.104	0.127	0.385	1.93
V	0.032	0.000	0.000	0.000	0.000	0.000	0.000	0.759
Cr	0.142	0.158	0.163	0.135	0.139	0.110	0.156	1.100
Co	0.0212	0.0185	0.0212	0.0192	0.0207	0.018	0.0088	0.115
Ni	0.128	0.155	0.161	0.171	0.161	0.040	0.048	0.336
Cu	0.488	0.463	0.468	0.502	0.463	0.265	0.184	0.364
Zn	1.7	1.3	1.0	cntd	cntd	0.437	2.496	6.243
Ga	0.0011	0.0008	< dl	< dl	< dl	< dl	< dl	0.0203
Ge	0.0168	0.0133	0.0140	0.0126	0.0098	0.0000	0.0000	0.1663
As	0.358	0.353	0.346	0.340	0.302	0.000	0.267	0.234
Rb	0.832	0.826	0.823	0.818	0.786	0.826	0.850	0.904
Sr	19.8	19.8	19.5	19.7	19.0	17.9	14.5	16.7

## Appendix A (continued)

Filter	No. 26 5 µm	No. 26 0.8 µm	No. 26 0.22 µm	No. 26 100 kD	No. 26 10 kD	No. 27 0.22 µm	No. 28 0.22 µm	No. 29 0.8 µm
Y	0.014	0.013	0.013	0.009	0.008	0.015	0.032	0.124
Zr	0.033	0.030	0.025	0.020	0.011	0.028	0.038	0.137
Mo	0.068	0.060	0.052	0.055	0.051	0.046	0.112	0.119
Cd	0.0061	0.0061	0.0056	0.0066	0.0045	0.0000	0.0044	0.0243
Sb	0.024	0.026	0.024	0.022	0.024	0.015	0.018	0.025
Cs	0.0053	0.0039	0.0038	0.0032	0.0027	0.0014	0.0039	0.0113
Ba	15.5	15.3	15.2	15.0	14.4	13.2	6.7	5.3
La	0.0135	0.0121	0.0109	0.0063	0.0092	0.0181	0.0554	0.3750
Ce	0.0223	0.0207	0.0189	0.0089	0.0083	0.0280	0.0900	0.4263
Pr	0.0033	0.0027	0.0026	0.0012	0.0012	0.0043	0.0137	0.0619
Nd	0.0130	0.0127	0.0115	0.0063	0.0062	0.0188	0.0516	0.2357
Sm	0.0067	0.0052	0.0022	0.0010	0.00076	0.0035	0.0090	0.0385
Eu	0.0020	0.0021	0.0016	0.0016	0.00112	0.0008	0.0009	0.0065
Gd	0.0028	0.0025	0.0021	0.0022	0.0020	0.0031	0.0079	0.0306
Tb	0.0003	0.0000	0.0004	0.0000	0.0000	0.0000	0.0005	0.0038
Dy	0.0025	0.0022	0.0024	0.0015	0.0013	0.0021	0.0050	0.0210
Ho	0.0003	0.0002	0.0003	0.0001	0.0002	0.0001	0.0006	0.0039
Er	0.0008	0.0012	0.0010	0.0006	0.0006	0.0017	0.0028	0.0122
Tm	0.0001	0.0001	0.0001	0.0001	0.0000	0.0000	0.0000	0.0019
Yb	0.0014	0.0014	0.0013	0.0011	0.0010	0.0015	0.0032	0.0115
Lu	0.0002	0.0002	0.0001	0.0001	0.0000	0.0003	0.0002	0.0020
W	<dl	<dl	<dl	<dl	<dl	<dl	<dl	<dl
Pb	nd	nd	nd	nd	nd	0.0000	0.0091	0.2603
Th	0.0061	0.0028	0.0010	0.0006	0.0005	0.0000	0.0000	0.0269
U	0.0082	0.0085	0.0078	0.0076	0.0075	0.0517	0.0189	0.0413
	26–5 µm	26–0.8 µm	26–0.2 µm	26–100 kD	26–10 kD	No. 27	No. 28	29–0.8 µm
Filter	No. 29 0.22 µm	No. 29 100 kD	No. 29 10 kD	No. 29 1 kD	No. 30 0.22 µm	No. 31 0.22 µm	No. 32 5 µm	No. 32 0.8 µm
pH	6.85	6.92			6.46	6.21	5.48	
Na	2475				2400	1190		
K	684				729	501		
Mg	958	959	913	581	1210	674	nd	629
Ca	2350	2271	2130	1246	2310	1530	1300	1332
[Alk]	0.214				0.269	0.150		
Cl	1870				1310	665		
SO <sub>4</sub>	1130				1030	1120		
F	10				<dl	<dl		
Si	1710	1720	1700	1700	2700	544	2710	2680
P	2.67	1.05	1.17	0.45	0.00	0.00	9.22	7.34
DOC	12.3	11.1	10.1	2.6	11.0	6.8	28.4	28.6
Al	43.8	25.4	18.5	5.59	22.1	23.6	217	229
Mn	22.8	14.9	13.4	12.12	2.65	2.64	23.5	22.7
Fe	666	124	47.1	9.4	360	356	1763	1648
Li	0.795	0.761	0.771	0.630	0.740	0.796	0.764	0.765
B	39	38	37	36	1.7	<0.5	2.6	2.4
Ti	1.07	0.467	0.374	0.315	0.705	0.800	5.09	4.71
V	0.442	0.239	0.222	0.194	0.000	0.108	0.641	0.596
Cr	1.070	1.000	0.943	0.764	0.295	0.455	0.915	0.907
Co	0.084	0.049	0.042	0.036	0.011	0.020	0.238	0.231
Ni	0.348	0.327	0.330	0.261	0.000	0.210	0.500	0.470

(continued on next page)

## Appendix A (continued)

Filter	No. 29	No. 29	No. 29	No. 29	No. 30	No. 31	No. 32	No. 32
	0.22 $\mu\text{m}$	100 kD	10 kD	1 kD	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$	5 $\mu\text{m}$	0.8 $\mu\text{m}$
Cu	0.456	0.629	0.624	0.191	0.049	0.217	0.283	0.238
Zn	6.296	6.887	cntd	cntd	0.652	0.953	6.3	5.7
Ga	0.0088	0.0036	0.0015	0.0015	< dl	0.0582	0.0542	0.0456
Ge	0.0824	0.0207	0.0165	0.0117	< dl	< dl	0.2100	0.2089
As	0.206	0.155	0.132	0.060	0.020	< dl	0.339	0.295
Rb	0.955	0.928	0.873	0.677	0.762	0.659	0.415	0.387
Sr	16.8	16.1	15.1	9.20	17.9	15.9	14.9	14.0
Y	0.092	0.063	0.042	0.002	0.068	0.060	0.225	0.216
Zr	0.130	0.101	0.057	0.002	0.109	0.113	0.293	0.268
Mo	0.112	0.096	0.100	0.063	0.200	nd	0.039	0.036
Cd	0.0200	0.0180	0.0154	0.0103	0.0000	nd	0.0142	0.0170
Sb	0.027	0.023	0.023	0.015	0.016	nd	0.033	0.033
Cs	0.0112	0.0112	0.0101	0.0078	0.0029	0.0068	0.0067	0.0065
Ba	4.9	4.5	4.1	3.0	4.25	3.65	9.15	9.15
La	0.1514	0.0860	0.0505	0.0041	0.106	0.088	0.666	0.653
Ce	0.2429	0.1270	0.0744	0.0060	0.179	0.156	1.39	1.33
Pr	0.0368	0.0202	0.0127	0.0007	0.0254	0.0227	0.160	0.151
Nd	0.1413	0.0828	0.0472	0.0034	0.0991	0.0988	0.582	0.554
Sm	0.0240	0.0153	0.0098	0.0008	0.0177	0.0181	0.0855	0.0856
Eu	0.0039	0.0035	0.0017	0.0002	0.0040	0.0041	0.0166	0.0150
Gd	0.0190	0.0126	0.0084	0.0007	0.0155	0.0111	0.0619	0.0568
Tb	0.0025	0.0018	0.0012	0.0002	0.0014	0.0014	0.0073	0.0068
Dy	0.0131	0.0096	0.0061	0.0006	0.0100	0.0087	0.0392	0.0383
Ho	0.0027	0.0021	0.0015	0.0002	0.0021	0.0018	0.0077	0.0077
Er	0.0084	0.0062	0.0047	0.0003	0.0071	0.0064	0.0220	0.0220
Tm	0.0015	0.0008	0.0007	0.0002	0.0006	0.0007	0.0032	0.0032
Yb	0.0079	0.0063	0.0044	0.0003	0.0058	0.0057	0.0188	0.0196
Lu	0.0015	0.0012	0.0008	0.0001	0.0011	0.0009	0.0030	0.0031
W	< dl	< dl	< dl	< dl	< dl	nd	< dl	< dl
Pb	0.1194	0.0844	0.0793	0.0070	0.0000	0.0510	0.390	0.351
Th	0.0224	0.0163	0.0080	0.0004	0.0038	0.0147	0.051	0.055
U	0.0384	0.0341	0.0280	0.0010	0.0430	0.0346	0.0170	0.0150
	29–0.2 $\mu\text{m}$	29–100 kD	29–10 kD	29–1 kD	No. 30	No. 31	32–5 $\mu\text{m}$	32–0.8 $\mu\text{m}$
Filter	No. 32	No. 32	No. 32	No. 32	No. 33	No. 33	No. 33	No. 33
	0.22 $\mu\text{m}$	100 kD	10 kD	1 kD	5 $\mu\text{m}$	0.8 $\mu\text{m}$	100 kD	
pH	5.43		5.51	5.44	6.72	6.77	6.79	
Na	1830					1320		
K	248					629		
Mg	612	543	569	301		2240	2350	
Ca	1310	1310	1291	619		4240	4330	
[Alk]	0.010					0.340		
Cl	1454					2250		
SO <sub>4</sub>	503					2190		
F	50					< dl		
Si	2660	2660	2690	2580	1620	1580	1570	
P	4.88	4.25	2.24	1.72	nd	nd	< dl	
DOC	28.6	29.0	22.0	22.3	8.2	8.3	8.2	
Al	223	220	160	60	17.8	17.3	17.6	
Mn	24.6	25.2	22.1	17.9	7.36	4.80	2.65	
Fe	1382	1271	594	117	227	224	170	
Li	0.693	0.746	0.694	0.565	0.695	0.698	0.715	

## Appendix A (continued)

Filter	No. 32	No. 32	No. 32	No. 32	No. 33	No. 33	No. 33	
	0.22 $\mu\text{m}$	100 kD	10 kD	1 kD	5 $\mu\text{m}$	0.8 $\mu\text{m}$	100 kD	
B	2.3	2.2	2.5	2.5	nd	nd	<0.5	
Ti	3.87	3.58	1.82	0.67	0.849	0.898	0.420	
V	0.501	0.463	0.282	0.195	0.166	0.158	0.048	
Cr	0.877	0.876	0.690	0.340	0.307	nd	0.257	
Co	0.241	0.253	0.195	0.091	nd	nd	0.0560	
Ni	0.524	0.561	0.457	0.426	0.353	0.348	0.333	
Cu	0.284	0.296	0.289	cntd	0.409	0.385	0.408	
Zn	6.4	5.9	5.7	5.8	1.1	1.1	1.4	
Ga	0.0358	0.0299	0.0200	0.0059	0.0029	0.0027	0.0023	
Ge	0.1301	0.1129	0.0517	0.0013	nd	nd	nd	
As	0.367	0.325	0.243	0.119	0.467	0.487	nd	
Rb	0.414	0.416	0.424	0.322	1.460	1.420	1.409	
Sr	15.8	16.2	13.1	6.07	13.7	13.4	13.4	
Y	0.227	0.227	0.150	0.053	0.053	0.053	0.048	
Zr	0.280	0.287	0.192	0.022	0.055	0.053	0.046	
Mo	0.042	0.037	0.034	0.029	0.102	0.113	nd	
Cd	0.0169	0.0138	0.0170	0.0099	nd	nd	nd	
Sb	0.035	0.037	0.033	0.024	0.032	0.028	nd	
Cs	0.0065	0.0067	0.0067	0.0043	0.0137	0.0143	0.0138	
Ba	8.67	8.46	5.73	2.85	9.1	9.0	8.4	
La	0.571	0.546	0.295	0.0774	0.0793	0.0741	0.0619	
Ce	1.18	1.14	0.642	0.175	0.0988	0.0917	0.0747	
Pr	0.137	0.136	0.0795	0.0242	0.0202	0.0178	0.0148	
Nd	0.510	0.483	0.300	0.0994	0.0746	0.0602	0.0581	
Sm	0.0748	0.0777	0.0460	0.0155	0.0108	0.0098	0.0097	
Eu	0.0134	0.0098	0.0076	0.0027	0.0019	0.0018	0.0011	
Gd	0.0533	0.0577	0.0368	0.0113	0.0086	0.0085	0.0083	
Tb	0.0066	0.0064	0.0043	0.0015	0.0012	0.0012	0.0011	
Dy	0.0350	0.0342	0.0225	0.0077	0.0075	0.0074	0.0066	
Ho	0.0071	0.0070	0.0042	0.0016	0.0019	0.0014	0.0012	
Er	0.0192	0.0193	0.0130	0.0047	0.0054	0.0046	0.0042	
Tm	0.0028	0.0025	0.0020	0.0008	0.0007	0.0005	0.0005	
Yb	0.0180	0.0177	0.0122	0.0050	0.0050	0.0052	0.0041	
Lu	0.0028	0.0028	0.0020	0.0008	0.0008	0.0007	0.0006	
W	<dl	<dl	<dl	<dl	0.0032	0.0027	nd	
Pb	0.253	0.218	0.0895	0.0688	0.0656	0.0494	0.0436	
Th	0.051	0.054	0.030	0.0031	0.0085	0.0087	0.0051	
U	0.0121	0.0119	0.0077	0.0026	0.0815	0.0805	0.0800	
	32–0.2 $\mu\text{m}$	32–100 kD	32–10 kD	32–1 kD	33–5 $\mu\text{m}$	33–0.8 $\mu\text{m}$	33–100 kD	
Filter	No. 33	No. 34	No. 34	No. 34	No. 35	No. 36	No. 36	No. 36
	1 kD	5 $\mu\text{m}$	0.8 $\mu\text{m}$	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$	0.8 $\mu\text{m}$	0.22 $\mu\text{m}$	100 kD
pH	6.89			6.72	7.17		7.29	7.39
Na				924	1120		1980	
K				589	354		738	
Mg	2230			2370	1650	1980	1990	
Ca	4250			4200	3670	2810	2820	2840
[Alk]				0.330	0.294		0.248	
Cl				986	1420		2000	
SO <sub>4</sub>				1030	645		1740	
F				<dl	<dl		<dl	

(continued on next page)

## Appendix A (continued)

Filter	No. 33	No. 34	No. 34	No. 34	No. 35	No. 36	No. 36	No. 36
	1 kD	5 $\mu\text{m}$	0.8 $\mu\text{m}$	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$	0.8 $\mu\text{m}$	0.22 $\mu\text{m}$	100 kD
Si	1565	1820	1780	1730	2100	3230	3150	3190
P	<dl	5.7	5.5	3.9	0.00	69	57	23
DOC	6.7	25.8	26.0	23.7	18.0	18.6	17.2	16.7
Al	8.5	108	118	71	13.03	215	194	147
Mn	0.63	162	161	123	2.45	92	89	82
Fe	20	2018	1941	537	145	1594	1250	589
Li	0.754	0.558	0.553	0.556	0.492	0.976	1.02	1.09
B	<0.5	nd	nd	2.1	0.0	<0.5	<0.5	<0.5
Ti	0.210	2.06	1.98	0.824	0.331	3.10	2.70	1.60
V	0.049	0.611	0.578	0.142	<dl	0.474	0.349	0.120
Cr	0.134	0.543	0.519	0.474	0.252	0.543	0.505	0.459
Co	0.0060	0.366	0.379	0.277	0.0110	0.137	0.147	0.124
Ni	nd	0.369	0.350	0.195	0.152	0.689	0.668	0.665
Cu	nd	0.314	0.310	0.249	0.321	0.440	0.403	0.391
Zn	nd	3.1	2.6	1.1	1.1	3.746	4.840	2.628
Ga	0.0026	0.0170	0.0185	0.0062	<dl	0.0221	0.0151	0.0098
Ge	nd	nd	nd	0.0692	nd	nd	nd	nd
As	nd	1.1337	1.1141	0.818	nd	nd	nd	nd
Rb	1.424	1.290	1.299	1.273	0.899	1.32	1.32	1.27
Sr	13.1	16.7	16.5	15.6	12.06	25.2	25.3	24.3
Y	0.013	0.116	0.119	0.088	0.034	0.156	0.144	0.117
Zr	0.002	0.180	0.183	0.145	0.041	0.157	0.145	0.131
Mo	nd	0.1575	0.1605	0.143	nd	nd	nd	nd
Cd	nd	0.0043	0.0040	0.0030	nd	nd	nd	nd
Sb	nd	0.043	0.041	0.038	nd	nd	nd	nd
Cs	0.0125	0.0220	0.0210	0.0184	0.0063	0.0074	0.0073	0.0066
Ba	8.9	12.3	12.0	11.3	4.3	9.5	10.1	8.5
La	0.0310	0.187	0.182	0.145	0.0730	0.238	0.246	0.176
Ce	0.0107	0.330	0.325	0.202	0.0866	0.425	0.427	0.311
Pr	0.0024	0.0464	0.0463	0.0301	0.0148	0.0615	0.0628	0.0465
Nd	0.0110	0.178	0.168	0.113	0.0581	0.235	0.239	0.173
Sm	0.0025	0.0285	0.0228	0.0233	0.0089	0.0427	0.0445	0.0317
Eu	0.0013	0.0056	0.0057	0.0058	0.0015	0.0082	0.0080	0.0077
Gd	0.0022	0.0196	0.0203	0.0167	0.0072	0.0336	0.0349	0.0263
Tb	0.0002	0.00347	0.00306	0.0015	0.0009	0.0042	0.0043	0.0035
Dy	0.0015	0.0185	0.0178	0.0121	0.0052	0.0260	0.0261	0.0208
Ho	0.0003	0.00379	0.00366	0.0027	0.0012	0.0049	0.0053	0.0043
Er	0.0012	0.01022	0.01150	0.0091	0.0034	0.0141	0.0141	0.0123
Tm	0.0001	0.00125	0.00125	0.0011	0.0005	0.0023	0.0022	0.0019
Yb	0.0010	0.01045	0.01170	0.0078	0.0029	0.0133	0.0141	0.0111
Lu	0.0002	0.00204	0.00200	0.0011	0.0005	0.0019	0.0020	0.0016
W	nd	nd	nd	0.0028	nd	nd	nd	nd
Pb	0.0324	0.206	0.265	0.0562	0.0468	0.187	0.143	0.0466
Th	0.0000	0.028	0.026	0.0242	0.0043	0.0276	0.0233	0.0235
U	0.0280	0.030	0.030	0.027	0.016	0.0111	0.0105	0.0093
	33–1 kD	34–5 $\mu\text{m}$	34–0.8 $\mu\text{m}$	34–0.2 $\mu\text{m}$	No. 35–0.2 $\mu\text{m}$	36–0.8 $\mu\text{m}$	36–0.2 $\mu\text{m}$	36–100 kD
Filter	No. 36	No. 36	No. 37	No. 37	No. 37	No. 37	No. 37	No. 38
	10 kD	1 kD	0.8 $\mu\text{m}$	0.22 $\mu\text{m}$	100 kD	10 kD	1 kD	5 $\mu\text{m}$
pH	7.32			7.10	7.12	7.21		
Na				1520				
K				771				



## Appendix A (continued)

Filter	No. 36	No. 36	No. 37	No. 37	No. 37	No. 37	No. 37	No. 38
	10 kD	1 kD	0.8 $\mu\text{m}$	0.22 $\mu\text{m}$	100 kD	10 kD	1 kD	5 $\mu\text{m}$
Mg	2010			1630	1617	1434	1050	
Ca	2810	2704	3816	3660	3737	2783	2005	4920
[Alk]				0.248				
Cl				2190				
SO <sub>4</sub>				1680				
F				<dl				
Si	3160	3120	4290	4250	4250	4200	4200	2780
P	17	15	65.8	23.6	30.0	3.7	1.3	125
DOC	16.5	7.8	23.8	19.8	19.1	10.5	4.7	23.5
Al	141	139	143	91	87	23	23	35.5
Mn	79	77	129	113	120	82	55	28.1
Fe	511	489	4153	1594	1279	44	8.3	506
Li	1.10	1.08	0.814	0.812	0.827	0.808	0.732	3.03
B	<0.5	<0.5	6	6	5	6	5	23
Ti	1.57	1.58	4.060	2.250	2.120	0.530	0.494	3.31
V	0.106	0.101	1.839	0.728	0.634	0.347	0.290	1.61
Cr	0.408	0.425	1.099	1.051	1.019	0.388	0.110	0.739
Co	0.121	0.120	0.298	0.248	0.258	0.124	0.056	0.224
Ni	0.665	0.631	0.700	0.688	0.748	0.426	0.241	1.05
Cu	0.404	0.457	0.719	0.683	0.771	0.561	0.352	1.30
Zn	2.783	3.999	7.591	6.000	6.512	4.077	3.372	4.8
Ga	0.0086	0.0088	0.0245	0.0153	0.0110	0.0080	0.0017	0.0118
Ge	nd	nd	nd	nd	nd	nd	nd	0.096
As	nd	nd	0.245	0.168	0.153	0.110	0.102	1.30
Rb	1.25	1.25	1.118	1.085	1.116	1.020	0.913	3.91
Sr	24.1	23.9	30.0	28.6	28.4	21.7	16.2	287
Y	0.117	0.112	0.494	0.357	0.334	0.052	0.007	0.106
Zr	0.130	0.126	0.492	0.437	0.427	0.051	0.006	0.264
Mo	nd	nd	0.056	0.055	0.058	0.052	0.036	0.235
Cd	nd	nd	0.0274	0.0208	0.0221	0.0120	0.0128	0.0547
Sb	nd	nd	0.048	0.046	0.045	0.037	0.022	0.074
Cs	0.0067	0.0072	0.0066	0.0066	0.0067	0.0059	0.0056	0.0035
Ba	8.9	8.3	28.4	24.0	24.0	15.0	10.0	47.4
La	0.180	0.168	0.312	0.183	0.168	0.0227	0.0032	0.0588
Ce	0.321	0.288	0.713	0.421	0.378	0.0346	0.0038	0.110
Pr	0.0466	0.0435	0.0921	0.0558	0.0493	0.00470	0.00069	0.0174
Nd	0.184	0.161	0.383	0.242	0.214	0.0227	0.0032	0.0742
Sm	0.0334	0.0304	0.086	0.055	0.050	0.0052	0.00061	0.0176
Eu	0.0071	0.0061	0.0198	0.0109	0.0090	0.00098	0.00020	0.0060
Gd	0.0263	0.0225	0.0881	0.0547	0.0501	0.00603	0.00103	0.0180
Tb	0.0036	0.0027	0.0127	0.0080	0.0075	0.00107	0.00020	0.0029
Dy	0.0217	0.0198	0.0747	0.0514	0.0473	0.00685	0.00098	0.0166
Ho	0.0043	0.0037	0.0170	0.0115	0.0104	0.00167	0.00024	0.0035
Er	0.0126	0.0112	0.0498	0.0347	0.0323	0.00551	0.00098	0.0113
Tm	0.0017	0.0015	0.0069	0.0048	0.0045	0.00102	0.00016	0.0017
Yb	0.0112	0.0104	0.0426	0.0330	0.0305	0.00619	0.00097	0.0090
Lu	0.0019	0.0018	0.0073	0.0053	0.0049	0.0012	0.00025	0.0016
W	nd	nd	0.0020	0.0020	0.0026	<dl	<dl	<dl
Pb	0.0488	cntd	0.346	0.137	0.146	0.068	0.024	0.154
Th	0.0238	0.0230	0.0374	0.0321	0.0322	0.0040	0.0006	0.0214
U	0.0091	0.0092	0.0328	0.0235	0.0229	0.0051	0.0015	1.39
	36–10 kD	36–1 kD	37–0.8 $\mu\text{m}$	37–0.2 $\mu\text{m}$	37–100 kD	37–10 kD	37–1 kD	38–5 $\mu\text{m}$

(continued on next page)

## Appendix A (continued)

Filter	No. 38	No. 38	No. 38	No. 38	No. 38	No. 39	No. 39	No. 39
	0.8 $\mu\text{m}$	0.22 $\mu\text{m}$	100 kD	10 kD	1 kD	5 $\mu\text{m}$	0.8 $\mu\text{m}$	0.22 $\mu\text{m}$
pH		7.59	7.48	7.52	7.51	7.49	7.49	7.45
Na		28 200						1890
K		7180						1310
Mg		14 200				2780	2810	2840
Ca	47 800	45 900	44 400	42 700	41 200	12 435		13 090
[Alk]		0.892						0.924
Cl		95 900						890
SO <sub>4</sub>		29 700						2060
F		50						< dl
Si	2800	2800	2750	2660	2700	2010	2000	2020
P	124	115	89	80	76	23	21	12
DOC	22.5	22.4	22.4	22.4	22.1	15.8	15.7	15.8
Al	30.0	19.5	15.7	15.7	15.3	107	63	51
Mn	27.2	26.1	11.5	11.0	10.8	40.4	37.3	34.7
Fe	489	446	309	246	244	740	697	547
Li	2.83	2.74	2.69	2.71	2.67	0.603	0.486	0.474
B	21	20	19	18	17	24	19	6
Ti	2.73	1.15	0.85	0.808	0.786	5.200	2.900	2.500
V	1.44	1.40	1.36	1.38	1.40	0.404	0.407	0.316
Cr	0.644	0.616	0.457	0.420	0.405	0.849	0.738	0.681
Co	0.221	0.204	0.202	0.194	0.189	0.109	0.089	0.087
Ni	1.05	0.94	1.04	1.07	1.01	1.28	1.31	1.24
Cu	1.26	1.21	1.20	1.20	1.25	0.737	0.790	0.759
Zn	5.7	3.7	3.7	3.7	3.7	2.7	2.8	2.4
Ga	0.0097	0.0068	0.0065	0.0061	0.0065	0.0220	0.0192	0.0151
Ge	0.087	0.082	0.066	0.053	0.046	nd	nd	nd
As	1.27	1.15	1.12	1.05	1.01	nd	0.607	0.584
Rb	3.84	3.80	3.80	3.76	3.68	1.69	1.65	1.61
Sr	284	280	279	276	271	76.4	76.6	77.7
Y	0.102	0.099	0.077	0.063	0.060	0.213	0.206	0.171
Zr	0.267	0.232	0.206	0.184	0.170	0.346	0.299	0.300
Mo	0.229	0.215	0.212	0.203	0.223	nd	0.065	0.067
Cd	0.0526	0.0482	0.0360	0.0332	0.0298	nd	0.0092	0.0104
Sb	0.071	0.062	0.066	0.061	0.061	nd	0.0448	0.0444
Cs	0.0030	0.0026	0.0028	0.0025	0.0032	0.0039	0.0034	0.0017
Ba	47.0	46.6	45.9	45.2	45.2	40.8	40.4	40.2
La	0.0558	0.0458	0.0244	0.0176	0.0167	0.169	0.147	0.117
Ce	0.111	0.0871	0.0405	0.0269	0.0279	0.590	0.278	0.206
Pr	0.0178	0.0151	0.0078	0.0056	0.0051	0.052	0.045	0.036
Nd	0.0742	0.0658	0.0391	0.0258	0.0259	0.222	0.194	0.165
Sm	0.0172	0.0163	0.0107	0.0071	0.0071	0.054	0.049	0.034
Eu	0.0060	0.0040	0.0030	0.0013	0.0009	0.0107	0.0092	0.0081
Gd	0.0166	0.0179	0.0115	0.0086	0.0086	0.0525	0.0429	0.0386
Tb	0.0027	0.0028	0.0017	0.0014	0.0014	0.0072	0.0060	0.0051
Dy	0.0164	0.0164	0.0112	0.0094	0.0088	0.0398	0.0353	0.0311
Ho	0.0035	0.0033	0.0026	0.0020	0.0019	0.0076	0.0066	0.0059
Er	0.0101	0.0098	0.0073	0.0063	0.0065	0.0216	0.0193	0.0174
Tm	0.0015	0.0016	0.0011	0.0010	0.0011	0.0030	0.0025	0.0024
Yb	0.0083	0.0086	0.0073	0.0062	0.0063	0.0200	0.0159	0.0155
Lu	0.0015	0.0015	0.0011	0.0009	0.0012	0.0024	0.0023	0.0023
W	< dl	< dl	< dl	< dl	< dl	nd	< dl	< dl
Pb	0.137	0.102	0.130	0.0854	0.0912	0.120	0.120	0.092

## Appendix A (continued)

Filter	No. 38	No. 38	No. 38	No. 38	No. 38	No. 39	No. 39	No. 39
	0.8 $\mu\text{m}$	0.22 $\mu\text{m}$	100 kD	10 kD	1 kD	5 $\mu\text{m}$	0.8 $\mu\text{m}$	0.22 $\mu\text{m}$
Th	0.0189	0.0156	0.0120	0.0106	0.0105	0.0428	0.0280	0.0297
U	1.32	1.36	1.41	1.41	1.40	0.0768	0.0804	0.0760
	38–0.8 $\mu\text{m}$	38–0.2 $\mu\text{m}$	38–100 kD	38–10 kD	38–1 kD	39–5 $\mu\text{m}$	39–0.8 $\mu\text{m}$	39–0.2 $\mu\text{m}$
Filter	No. 39	No. 39	No. 39	No. 40	No. 40	No. 40	No. 40	No. 40
	100 kD	10 kD	1 kD	5 $\mu\text{m}$	0.8 $\mu\text{m}$	0.22 $\mu\text{m}$	100 kD	
pH	7.58	7.58				7.68		
Na						4530		
K						928		
Mg	2800	2826	2810	10240	10200	10100		10100
Ca	12580	12600	12350	45900	46000	45500		49900
[Alk]						3.060		
Cl						6710		
SO <sub>4</sub>						1290		
F						< dl		
Si	1980	1985	1980	3400	3460	3390		3310
P	6	0	0	13	13	10		4
DOC	15.6	14.9	7.8	21.4	21.1	21.6		20.2
Al	49	26	23	19.0	16.7	12.6		11.7
Mn	32.5	3.0	2.7	160	161	160		161
Fe	484	166	98	826	815	573		387
Li	0.467	0.482	0.474	0.553	0.553	0.550		0.499
B	6	8	8	12	10	10		8
Ti	1.800	0.535	0.370	0.652	0.661	0.484		0.273
V	0.280	0.106	0.089	0.144	0.109	0.073		nd
Cr	0.648	0.361	0.399	0.657	0.591	0.561		0.448
Co	0.065	0.047	0.019	0.217	0.222	0.213		0.222
Ni	1.14	1.17	1.13	1.95	1.99	1.96		2.23
Cu	0.801	0.832	0.765	0.523	0.476	0.504		cntd
Zn	2.7	2.8	2.6	0.517	0.512	0.561		cntd
Ga	0.0103	0.0044	0.0035	0.0038	0.0035	0.0033		0.0023
Ge	nd	nd	nd	0.1145	0.0936	0.0678		0.0580
As	nd	nd	nd	0.830	0.818	0.762		0.759
Rb	1.53	1.51	1.59	1.36	1.38	1.36		1.40
Sr	75.8	74.8	77.8	92.1	93.3	93.0		94.5
Y	0.171	0.107	0.082	0.122	0.116	0.111		0.100
Zr	0.274	0.210	0.184	0.278	0.283	0.271		0.269
Mo	nd	nd	nd	0.285	0.294	0.307		0.293
Cd	nd	nd	nd	0.0086	0.0079	0.0081		0.0071
Sb	nd	nd	nd	0.052	0.046	0.048		0.052
Cs	0.0011	< dl	< dl	< dl	< dl	< dl		< dl
Ba	40.1	37.8	38.0	74.6	74.5	73.5		74.1
La	0.110	0.0411	0.0240	0.0552	0.0550	0.0407		0.0338
Ce	0.208	0.0714	0.0380	0.109	0.107	0.0829		0.0692
Pr	0.037	0.014	0.0081	0.0184	0.0179	0.0140		0.0124
Nd	0.156	0.064	0.036	0.0799	0.0805	0.0632		0.0569
Sm	0.033	0.017	0.011	0.0184	0.0189	0.0154		0.0144
Eu	0.0102	0.0077	0.0024	0.0043	0.0042	0.0033		0.0024
Gd	0.0374	0.0202	0.0124	0.0195	0.0206	0.0164		0.0132
Tb	0.0050	0.0027	0.0020	0.0027	0.0031	0.0020		0.0019
Dy	0.0310	0.0151	0.0124	0.0180	0.0192	0.0178		0.0152

(continued on next page)

## Appendix A (continued)

Filter	No. 39	No. 39	No. 39	No. 40	No. 40	No. 40	No. 40
	100 kD	10 kD	1 kD	5 $\mu$ m	0.8 $\mu$ m	0.22 $\mu$ m	100 kD
Ho	0.0057	0.0035	0.0027	0.0040	0.0035	0.0038	0.0031
Er	0.0168	0.0103	0.0073	0.0116	0.0111	0.0106	0.0104
Tm	0.0020	0.0014	0.0010	0.0013	0.0014	0.0012	0.0010
Yb	0.0136	0.0086	0.0075	0.0110	0.0101	0.0094	0.0090
Lu	0.0022	0.0014	0.0010	0.0017	0.0018	0.0012	0.0013
W	nd	nd	nd	<dl	<dl	<dl	<dl
Pb	0.076	0.077	0.047	0.0206	0.0142	cntd	cntd
Th	0.0279	0.0149	0.0108	0.0201	0.0162	0.0134	<dl
U	0.0709	0.0731	0.0683	0.649	0.648	0.629	0.643
	39–100 kD	39–10 kD	39–1 kD	40–5 $\mu$ m	40–0.8 $\mu$ m	40–0.2 $\mu$ m	40–100 kD
Filter	No. 40		40–1 kD		No. 41		No. 42
	10 kD		1 kD		0.22 $\mu$ m		0.22 $\mu$ m
pH					7.90		7.89
Na					4410		12 550
K					2010		5450
Mg	9940		9450		14 200		20 200
Ca	48 700		45 200		48 400		61 800
[Alk]					3.260		4.390
Cl					6570		22 700
SO <sub>4</sub>					16 100		23 800
F					<dl		<dl
Si	3300		3350		4170		4720
P	0		0		36		88
DOC	19.8		10.9		22.2		12.4
Al	10.8		7.4		44.9		6.2
Mn	156		131		26		21
Fe	240		176		532		299
Li	0.518		0.500		1.927		8.156
B	7		7		16		47
Ti	0.238		0.040		1.000		0.770
V	nd		0.071		0.467		0.801
Cr	0.341		0.121		0.471		0.368
Co	0.203		0.115		0.188		0.165
Ni	2.05		1.64		2.87		2.45
Cu	cntd		cntd		1.11		
Zn	cntd		cntd		1.75		1.13
Ga	0.0026		0.0034		0.0083		0.0063
Ge	0.038		0.0228		0.0631		0.0514
As	0.707		0.606		1.872		2.355
Rb	1.36		1.31		1.52		2.59
Sr	92.7		86.6		147		409
Y	0.082		0.019		0.132		0.033
Zr	0.228		0.041		0.370		0.156
Mo	0.319		0.291		0.478		0.607
Cd	0.0073		0.0078		0.024		0.0047
Sb	0.047		0.030		0.074		0.076
Cs	<dl		<dl		0.0000		0.0000
Ba	69.9		65.2		68.0		66.4
La	0.0284		0.0079		0.0562		0.0069
Ce	0.0469		0.0073		0.1000		0.0140
Pr	0.0078		0.0008		0.0179		0.0020

## Appendix A (continued)

Filter	No. 40	40–1 kD	No. 41	No. 42
	10 kD	1 kD	0.22 $\mu\text{m}$	0.22 $\mu\text{m}$
Nd	0.0415	0.0078	0.0842	0.0125
Sm	0.0106	0.0021	0.0191	0.0033
Eu	0.0009	0.0004	0.0041	0.0008
Gd	0.0118	0.0019	0.0209	0.0043
Tb	0.0017	0.0000	0.0028	0.0004
Dy	0.0116	0.0023	0.0194	0.0043
Ho	0.0023	0.0003	0.0044	0.0006
Er	0.0097	0.0015	0.0131	0.0027
Tm	0.0007	0.0000	0.0016	0.0003
Yb	0.0077	0.0012	0.0117	0.0030
Lu	0.0012	0.0002	0.0018	0.0004
W	<dl	<dl	<dl	<dl
Pb	cntd	cntd	0.0674	0.0747
Th	<dl	0.0026	0.0203	0.0066
U	0.619	0.551	0.674	0.324
	40–10 kD	40–1 kD	No. 41	No. 42

## References

- Andersson, P.S., Wasserburg, G.J., Ingri, J., Stordal, M.C., 1994. Strontium, dissolved and particulate loads in fresh and brackish waters: the Baltic Sea and Mississippi Delta. *Earth Planet. Sci. Lett.* 124, 195–210.
- Annual Reports of Russian Hydrological Survey, 1965–1975. v.1. Karelia and North-West. *Gidrometeoizdat, Leningrad.*
- Ariés, S., Valladon, M., Polvé, M., Dupré, B., 2000. A routine method for oxide and hydroxide interference corrections in ICP-MS chemical analysis of environmental and geological samples. *Geostand. Newsl.* 24, 19–31.
- Åström, M., 2001. The effect of acid soil leaching on trace element abundance in a medium-sized stream, W. Finland. *Appl. Geochem.* 16, 387–396.
- Åström, M., Aaltonen, E.-K., Koivusaari, J., 2001. Impact of ditching in a small forested catchment on concentrations of suspended material, organic carbon, hydrogen ions and metals in stream water. *Aquat. Geochem.* 57, 57–73.
- Banks, D., Hall, G., Reimann, C., Siewerss, U., 1999. Distribution of rare earth elements in crystalline bedrock groundwaters: Oslo and Bergen regions, Norway. *Appl. Geochem.* 14, 27–39.
- Bau, M., 1999. Scavenging of dissolved yttrium and rare earths by precipitating iron oxyhydroxides: experimental evidence for Ce oxidation and lanthanide tetrad effect. *Geochim. Cosmochim. Acta* 63, 67–77.
- Beck, K.C., Reuter, J.H., Perdue, E.M., 1974. Organic and inorganic geochemistry of some coastal plain rivers of the southeastern United States. *Geochim. Cosmochim. Acta* 38, 341–364.
- Benoit, G., 1995. Evidence of the particle concentration effect for lead and other metals in freshwaters based on ultraclean technique analysis. *Geochim. Cosmochim. Acta* 59, 2677–2687.
- Boyle, E.A., Edmond, J.M., Sholkovitz, E.R., 1977. The mechanism of iron removal in estuaries. *Geochim. Cosmochim. Acta* 41, 1311–1324.
- Boyle, E.A., Husteded, S.S., Grant, B., 1982. The chemical mass balance of the Amazon Plume—II. Copper, nickel, and cadmium. *Deep-Sea Res.* 29 (11A), 1355–1364.
- Buffle, J., Deladoey, P., Haerdi, W., 1978. The use of ultrafiltration for the separation and fractionation of organic ligands in fresh waters. *Anal. Chim. Acta* 101, 339–357.
- Buffle, J., De Vitre, R.R., Perret, D., Leppard, G.G., 1989. Physico-chemical characteristics of a colloidal iron phosphate species formed at the oxic–anoxic interface of a eutrophic lake. *Geochim. Cosmochim. Acta* 53, 399–408.
- Dai, M.-H., Martin, J.-M., 1995. First data on trace metal level and behavior in two major Arctic river-estuarine systems (Ob and Yenisey) and in the adjacent Kara Sea, Russia. *Earth Planet. Sci. Lett.* 131, 127–141.
- Deb, B.C., 1949. The movement and precipitation of iron oxides in podzol soils. *J. Soil Sci.* 1, 112–122.
- Dia, A., Gruau, G., Olivie-Lauquet, G., Riou, C., Molénat, J., Curmi, P., 2000. The distribution of rare earth elements in groundwaters: assessing the role of source-rock composition, redox changes and colloidal particles. *Geochim. Cosmochim. Acta* 64, 4131–4151.
- Diakonov, I., 1995. Etude Expérimentale de la Complexation de l'Aluminium avec l'Ion Sodium et de la Spéciation du Gallium et du Fer(III) dans les Solutions Naturelles. PhD Thesis, Université Paul Sabatier, Toulouse, 166 pp.
- Dupré, B., Gaillardet, J., Rousseau, D., Allègre, C.J., 1996. Major and trace element of river-born material: the Congo Basin. *Geochim. Cosmochim. Acta* 60, 1301–1321.
- Dupré, B., Viers, J., Dandurand, J.-L., Polvé, M., Bénézech, P., Vervier, Ph., Braun, J.-J., 1999. Major and trace elements associated with colloids in organic-rich river waters: ultrafiltration of natural and spiked solutions. *Chem. Geol.* 160, 63–80.
- Dzombak, D.A., Morel, F.M.M., 1990. *Surface Complexation Modeling*. Wiley, New York.
- Edmond, J.M., Palmer, M.R., Measures, C.I., Brown, E.T., Huh, Y.,

1996. Fluvial geochemistry of the eastern slope of the north-eastern Andes and its foredeep in the drainage of the Orinoco in Colombia and Venezuela. *Geochim. Cosmochim. Acta* 60, 2949–2976.
- Eyrolle, F., Benaim, J.-Y., 1999. Metal available sites on colloidal organic compounds in surface waters (Brazil). *Water Res.* 33, 995–1004.
- Eyrolle, F., Benedetti, M.F., Benaim, J.Y., Février, D., 1996. The distribution of colloidal and dissolved organic carbon, major elements, and trace elements in small tropical catchments. *Geochim. Cosmochim. Acta* 60, 3643–3656.
- Fox, L.E., 1989. A model for inorganic control of phosphate concentrations in river waters. *Geochim. Cosmochim. Acta* 53, 417–428.
- Gaillardet, J., Dupré, B., Allègre, C.J., 1995. A global geochemical mass budget applied to the Congo Basin rivers: erosion rates and continental crust composition. *Geochim. Cosmochim. Acta* 59, 3469–3485.
- Gordeev, V.V., Martin, J.-M., Sidorov, I.S., Sidorova, M.V., 1996. A reassessment of the Eurasian river input of water, sediment, major elements, and nutrients to the Arctic Ocean. *Am. J. Sci.* 296, 664–691.
- Guieu, C., Huang, W.W., Martin, J.-M., Yong, Y.Y., 1996. Outflow of trace metals into the Laptev Sea by the Lena River. *Mar. Chem.* 53, 255–267.
- Harder, H., 1970. Boron content of sediments as a tool in facies analysis. *Sediment. Geol.* 4, 153–175.
- Hoffman, M.R., Yost, E.C., Eisenreich, S.J., Maier, W.L., 1981. Characterization of soluble and colloidal-phase complexes in river water by ultrafiltration. A mass balance approach. *Environ. Sci. Technol.* 15, 655–661.
- Hoffmann, S.R., Shafer, M.M., Babiarz, C.L., Armstrong, D.E., 2000. A critical evaluation of tangential-flow ultrafiltration for trace metal studies in freshwater systems: 1. Organic carbon. *Environ. Sci. Technol.* 34, 3420–3427.
- Horowitz, A.J., Elrick, K.A., Colberg, M.R., 1992. The effect of membrane filtration artifacts on dissolved trace element concentrations. *Water Res.* 26, 753–763.
- Hoyle, J., Elderfield, H., Gledhill, A., Greaves, M., 1984. The behavior of the rare earth elements during mixing of river and sea waters. *Geochim. Cosmochim. Acta* 48, 143–149.
- Huh, Y., Chan, L.-H., Zhang, L., Edmond, J.M., 1998. Lithium and its isotopes in major world rivers: implications for weathering and the oceanic budget. *Geochim. Cosmochim. Acta* 62, 2039–2051.
- Hydrochemical map of USSR, 1990. *Gidrokhimicheskii atlas SSSR*; Moscow, Gidrokhim. in-t Roskomgidrometa SSSR, 110 pp.
- Ingri, J., Widerlund, A., Land, M., Gustafsson, O., Andersson, P., Ohlander, B., 2000. Temporal variations in the fractionation of the rare earth elements in a boreal river; the role of colloidal particles. *Chem. Geol.* 166, 23–45.
- Johannesson, K.H., Lyons, W.B., Graham, E.Y., Welch, K.A., 2000. Oxyanion concentrations in Eastern Sierra Nevada Rivers—3. Boron, molybdenum, vanadium, and tungsten. *Aquat. Geochem.* 6, 19–46.
- Kharkar, D.P., Turekian, K.K., Bertine, K.K., 1968. Stream supply of dissolved silver, molybdenum, antimony, selenium, chromium, cobalt, rubidium and cesium to the oceans. *Geochim. Cosmochim. Acta* 32, 285–298.
- Konhauser, K.O., Fyfe, W.S., Kronberg, B.I., 1994. Multi-element chemistry of some Amazonian waters and soils. *Chem. Geol.* 111, 155–175.
- Lahermo, P., Mannio, J., Tarvainen, T., 1995. The hydrogeochemical comparison of streams and lakes in Finland. *Appl. Geochem.* 10, 45–64.
- Laxen, D.P.H., Davison, W., Woof, C., 1984. Manganese chemistry in rivers and streams. *Geochim. Cosmochim. Acta* 48, 2107–2111.
- Maksimova, M.P., 1967. Inorganic and organic composition of major ions in rivers of Karelian coast of the White Sea. *Gidrobiologicheskie issledovaniya na Karelskom poberezhie Belogo moray*. Nauka, Leningrad, pp. 9–20 (in Russian).
- Martin, J.M., Guan, D.M., Elbaz-Poulichet, F., Thomas, A.J., Gordeev, V.V., 1993. Preliminary assessment of the distribution of some trace elements (As, Cd, Cu, Fe, Ni, Pb and Zn) in a pristine aquatic environment: the Lena River estuary (Russia). *Mar. Chem.* 43, 185–199.
- Martinez, C.E., Mc Bride, M.B., 1998. Coprecipitates of Cd, Cu, Pb and Zn in iron oxides: solid phase transformation and metal solubility after aging and thermal treatment. *Clays Clay Miner.* 46, 537–545.
- Meybeck, M., 1988. Global chemical weathering from surficial rocks estimated from river dissolved loads. *Am. J. Sci.* 287, 401–428.
- Millot, R., Gaillardet, J., Dupré, B., Allègre, C.J., 2001. Global control of silicate weathering rates and the coupling with physical erosion: new insights from rivers of the Canadian Shield. *Earth Sci. Planet. Lett.* 196, 83–98.
- Murphy, R.J., Lenhart, J.J., Honeyman, B.D., 1999. The sorption of thorium (IV) and uranium (VI) to hematite in the presence of natural organic matter. *Colloids Surf.* 157, 47–62.
- Oliver, B.G., Thurman, E.M., Malcolm, R.L., 1983. The contribution of humic substances to the acidity of colored natural waters. *Geochim. Cosmochim. Acta* 47, 2031–2035.
- Olivé-Lauquet, G., Allard, Th., Benedetti, M., Muller, J.-P., 1999. Chemical distribution of trivalent iron in riverine material from a tropical ecosystem: a quantitative EPR study. *Water Res.* 33, 2726–2734.
- Olivé-Lauquet, G., Allard, Th., Bertaux, J., Muller, J.-P., 2000. Crystal chemistry of suspended matter in a tropical hydro-system, Nyong basin (Cameroon, Africa). *Chem. Geol.* 170, 113–131.
- Palmer, M.R., Edmond, J.M., 1993. Uranium in river water. *Geochim. Cosmochim. Acta* 57, 4947–4955.
- Perelman, A.A., 1982. *Geochemistry of Hypergenesis (Geokhimiya gipergeneza, in Russian)*. Nauka, Moscow.
- Pham, M.K., Garnier, J.-M., 1998. Distribution of trace elements associated with dissolved (<0.45 μm–1 nm) in freshwater using coupled (frontal cascade) ultrafiltration and chromatographic separations. *Environ. Sci. Technol.* 32, 440–449.
- Pokrovski, G.S., Schott, J., 1998. Experimental study of the complexation of silicon and germanium with aqueous organic species: implications for germanium and silicon transport and Ge/

- Si ratio in natural waters. *Geochim. Cosmochim. Acta* 62, 3413–3428.
- Ponter, C., Ingri, J., Bostrom, K., 1992. Geochemistry of manganese in the Kalix River, northern Sweden. *Geochim. Cosmochim. Acta* 56, 1485–1494.
- Porcelli, D., Andersson, P.S., Wasserburg, G.J., Ingri, J., Baskaran, M., 1997. The importance of colloids and mires for the transport of uranium isotopes through the Kalix River watershed and Baltic Sea. *Geochim. Cosmochim. Acta* 61, 4095–4113.
- Qian, J., Xue, H.B., Sigg, L., Albrecht, A., 1998. Complexation of cobalt by natural ligands in freshwater. *Environ. Sci. Technol.* 32, 2043–2050.
- Reeder, S.W., Hitchon, B., Levinson, A.A., 1972. Hydrogeochemistry of the surface waters of the Mackenzie River drainage basin, Canada—I. Factors controlling inorganic composition. *Geochim. Cosmochim. Acta* 36, 826–865.
- Resources of Surface Waters of the USSR. Main Hydrological Characteristics, vol. 2. Karelia and North-West. *Gidrometeorizdat, Leningrad* (in Russian).
- Rimstidt, J.D., 1997. Quartz solubility at low temperature. *Geochim. Cosmochim. Acta* 61, 2553–2558.
- Ross, J.M., Sherrell, R.M., 1999. The role of colloids in trace metal transport and adsorption behavior in New Jersey Pinelands streams. *Limnol. Oceanogr.* 44, 1019–1034.
- Sawhney, B.L., 1972. Selective sorption and fixation of cations by clay minerals: a review. *Clays Clay Miner.* 20, 93–100.
- Shapiro, J., 1958. *Science* 127, 702.
- Shapiro, J., 1964. Effect of yellow organic acids on iron and other metals in water. *Am. Water Works Assoc. J.* 55, 1062–1082.
- Shiller, A.M., 1988. Enrichment of dissolved gallium relative to aluminium in natural waters. *Geochim. Cosmochim. Acta* 52, 1879–1882.
- Shiller, A.M., 1997. Dissolved trace elements in the Mississippi River: seasonal, interannual and decadal variability. *Geochim. Cosmochim. Acta* 61, 4321–4330.
- Shiller, A.M., Boyle, E.A., 1987. Variability of dissolved trace metals in the Mississippi River. *Geochim. Cosmochim. Acta* 51, 3273–3277.
- Shiller, A.M., Mao, L., 2000. Dissolved vanadium in rivers: effects of silicate weathering. *Chem. Geol.* 165, 13–22.
- Sholkovitz, E.R., 1976. Fluctuation of dissolved organic and inorganic matter during the mixing of river water and seawater. *Geochim. Cosmochim. Acta* 40, 831–845.
- Sholkovitz, E.R., 1992. Chemical evaluation of rare-earth elements: fractionation between colloidal and solution phases of filtered river water. *Earth Planet. Sci. Lett.* 114, 77–84.
- Sholkovitz, E.R., 1995. The aquatic chemistry of rare earth elements in rivers and estuaries. *Aquat. Geochem.* 1, 1–34.
- Sigg, L., Xue, H., Kistler, D., Schönenberger, R., 2000. Size fractionation (dissolved, colloidal and particulate) of trace metals in Thur River, Switzerland. *Aquat. Geochem.* 6, 413–434.
- Sigleo, A., Helz, G.R., 1981. Composition of estuarine colloidal material: major and trace elements. *Geochim. Cosmochim. Acta* 45, 2501–2509.
- Smith, J.R.G., 1976. Evaluation of combined applications of ultrafiltration and complexation capacity techniques to natural waters. *Environ. Sci. Technol.* 48, 74–76.
- Tanizaki, Y., Shimokawa, T., Yamazaki, M., 1992. Physicochemical speciation of trace elements in urban streams by size fractionation. *Water Res.* 26, 55–63.
- Thurman, E.M., 1985. *Organic Geochemistry of Natural Waters*. Nijhoff/Junk, Dordrecht, 497 pp.
- Varshal, G.M., 1973. On the mineral components of natural waters. *Methods of Analysis of Natural and Sewage Waters. Problems of Analytical Chemistry*, vol. 7. Nauka, Moscow, pp. 94–107 (in Russian).
- Varshal, G.M., Velukhanova, T.K., Sirotkina, I.S., Yartzeva, P.D., 1973. *Gidrohim. Mater.* 59, 143.
- Verdes, G., Gout, R., Castet, S., 1992. Thermodynamic properties of the aluminate ion and of bayerite, boehmite, diasporite and gibbsite. *Eur. J. Mineral.* 4, 767–792.
- Viers, J., Dupré, B., Polvé, M., Schott, J., Dandurand, J.-L., Braun, J.-J., 1997. Chemical weathering in the drainage basin of a tropical watershed (Nsimi–Zoetele site, Cameroon): comparison between organic-poor and organic-rich waters. *Chem. Geol.* 140, 181–206.
- Viers, J., Dupré, B., Braun, J.-J., Deberdt, S., Angeletti, B., Ngoupayou, J.D., Michard, A., 2000. Major and trace element abundances, and strontium isotopes in the Nyong basin rivers (Cameroon): constraints on chemical weathering processes and elements transport mechanisms in humid tropical environments. *Chem. Geol.* 169, 211–241.
- Walther, J., Helgeson, H.C., 1977. Calculation of the thermodynamic properties of aqueous silica and the solubility of quartz and its polymorphs at high pressures and temperatures. *Am. J. Sci.* 277, 1315–1351.
- Xue, H., Sunda, W.G., 1997. Comparison of  $[Cu^{2+}]$  measurements in lake water determined by ligand exchange and cathodic stripping voltammetry and by ion-selective electrode. *Environ. Sci. Technol.* 31, 1902–1909.
- Xue, H., Kistler, D., Sigg, L., 1995. Competition of copper and zinc for strong ligands in a eutrophic lake. *Limnol. Oceanogr.* 40, 1142–1152.
- Yeghicheyan, D., Carignan, J., Valladon, M., Le Coz, M.B., Aquilina, L., et al., 2001. A compilation of some trace elements measured in the natural river water standard SLRS-4 (NRC-CNRS). *Geostand. Newsl.* 25, 468–474.