



Fate of colloids during estuarine mixing in the Arctic

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Abstract. The estuarine behavior of organic carbon (OC) and trace elements (TE) was studied for the largest European sub-Arctic river, which is the Severnaya Dvina; this river has a deltaic estuary covered in ice during several hydrological seasons: summer (July 2010, 2012) and winter (March 2009) baseflow, and the November–December 2011 ice-free period. Colloidal forms of OC and TE were assessed for three pore size cutoffs (1, 10, and 50 kDa) using an in situ dialysis procedure. Conventionally dissolved ($< 0.22 \mu\text{m}$) fractions demonstrated clear conservative behavior for Li, B, Na, Mg, K, Ca, Sr, Mo, Rb, Cs, and U during the mixing of freshwater with the White Sea; a significant (up to a factor of 10) concentration increase occurs with increases in salinity. Si and OC also displayed conservative behavior but with a pronounced decrease in concentration seawards. Rather conservative behavior, but with much smaller changes in concentration (variation within $\pm 30\%$) over a full range of salinities, was observed for Ti, Ni, Cr, As, Co, Cu, Ga, Y, and heavy REE. Strong non-conservative behavior with coagulation/removal at low salinities ($< 5\%$) was exhibited by Fe, Al, Zr, Hf, and light REE. Finally, certain divalent metals exhibited non-conservative behavior with a concentration gain at low ($\sim 2\text{--}5\%$, Ba, Mn) or intermediate ($\sim 10\text{--}15\%$, Ba, Zn, Pb, Cd) salinities, which is most likely linked to TE desorption from suspended matter or sediment outflux.

The most important result of this study is the elucidation of the behavior of the “truly” dissolved low molecular weight $\text{LMW}_{< 1 \text{ kDa}}$ fraction containing Fe, OC, and a number of

insoluble elements. The concentration of the LMW fraction either remains constant or increases its relative contribution to the overall dissolved ($< 0.22 \mu\text{m}$) pool as the salinity increases. Similarly, the relative proportion of colloidal (1 kDa– $0.22 \mu\text{m}$) pool for the OC and insoluble TE bound to ferric colloids systematically decreased seaward, with the largest decrease occurring at low ($< 5\%$) salinities.

Overall, the observed decrease in the colloidal fraction may be related to the coagulation of organo-ferric colloids at the beginning of the mixing zone and therefore the replacement of the $\text{HMW}_{1 \text{ kDa} - 0.22 \mu\text{m}}$ portion by the $\text{LMW}_{< 1 \text{ kDa}}$ fraction. These patterns are highly reproducible across different sampling seasons, suggesting significant enrichment of the mixing zone by the most labile (and potentially bioavailable) fraction of the OC, Fe and insoluble TE. The size fractionation of the colloidal material during estuarine mixing reflects a number of inorganic and biological processes, the relative contribution of which to element speciation varies depending on the hydrological stage and time of year. In particular, $\text{LMW}_{< 1 \text{ kDa}}$ ligand production in the surface horizons of the mixing zone may be linked to heterotrophic mineralization of allochthonous DOM and/or photodestruction. Given the relatively low concentration of particulate versus dissolved load of most trace elements, desorption from the river suspended material was less pronounced than in other rivers in the world. As a result, the majority of dissolved components exhibited either conservative (OC and related elements such as divalent metals) or non-conservative,

coagulation-controlled (Fe, Al, and insoluble TE associated with organo-ferric colloids) behavior. The climate warming at high latitudes is likely to intensify the production of $\text{LMW} < 1 \text{ kDa}$ organic ligands and the associated TE; therefore, the delivery of potentially bioavailable trace metal micronutrients from the land to the ocean may increase.

1 Introduction

Over the past several decades, a comprehensive picture of organic carbon and trace element geochemistry in the mixing zone of the river mouths has been completed for many major and “model” rivers around the world (Bianci, 2007; Bianci and Allison, 2009; Gordeev, 2012). Several main processes control the concentration patterns of OC, Fe, and TE in the estuaries: coagulation of organic and organo-mineral colloids (Sholkovitz, 1976; Boyle et al., 1977; Sigleo and Helz, 1981; Benoit et al., 1994; Lisitsyn, 1995; Guieu et al., 1996; Benoit et al., 1994), desorption from river-suspended matter or sediments (Dai et al., 1995; Guieu and Martin, 2002), diffusive flux from sediments (Shiller, 1996; Audry et al., 2006, 2007), and biological uptake (Redfield et al., 1963; Shiller and Boyle, 1991). The relative importance of each of these processes defines the degree of river flux transformation in the mixing zone and net elemental input from the land to the ocean. In this regard, physicochemical and biological mechanisms operating within the mixing zone of the Arctic Ocean are especially important given the following: (1) extremely high contributions of dissolved flux relative to the surface and ocean volume compared to the other oceans (Holmes et al., 2012); (2) dominance of dissolved and colloidal flux over the suspended flux for most major and trace elements of the river water (Gordeev et al., 1996; Pokrovsky et al., 2010); (3) high vulnerability of Arctic river and sea ecosystems to both anthropogenic pollution and ongoing climate change.

The majority of studies of the Arctic estuaries were carried out during summer baseflow periods (MacDonald and Yu, 2006; Gobeil, 2006; Kuzyk et al., 2008, and McClelland et al., 2012, for a review). Although this season in the Arctic is very important due to the biological activity in the water column, it does not allow the other major controlling factors of element transformation in the estuary, such as photodestruction of DOM-related colloidal forms of TE, desorption from river-suspended matter and redox exchange with the sediments, to be tested. The relative importance of the various driving mechanisms fluctuates depending on the season; therefore, systematic studies over several seasons are required. These studies constitute the first objective of the present study, which is aimed at assessing the estuarine profiles of both major and trace elements, including organic carbon, in the largest European Arctic River, the Severnaya Dvina. These profiles will be based on several sampling campaigns performed in the Severnaya Dvina's mouth zone during the main hydrological seasons:

summer baseflow (July), beginning of winter and ice formation (November–December) and end of winter baseflow (March).

All boreal rivers of the European Arctic, particularly the Severnaya Dvina River, are major carriers of organic and organo-mineral colloids from the land to the ocean. For example, 20 to 30 % of Mn, Zn, and Cu, 30 to 50 % of Fe and REEs, and up to 80 % of C_{org} and U are transported in colloidal form from the total (dissolved + suspended) flux of this river (Pokrovsky et al., 2010). Despite the importance of the colloidal form in the overall elemental transport from the land to the ocean, the transformation of colloids in the mixing zone is still very poorly studied. The main reason for knowledge gap is the lack of uniform and standardized techniques allowing in situ or on site size fractionation of the dissolved load along the salinity gradient. Until now, tangential cross-flow and frontal ultrafiltration, along with diffusive gradients in thin films, have remained the basic techniques used to assess the colloidal distribution in estuarine zones all over the world (Dai and Martin, 1995; Greenamoyer and Moran, 1997; Ingri et al., 2004; Forsberg et al., 2006; Howell et al., 2006; Waeles et al., 2008; Österlund et al., 2012). The use of these techniques, however, requires significant precautions against experimental artifacts, such as charge separation, filter clogging and polarization, thorough calibration and assumptions on the diffusion efficiency in the gels and, most importantly, the use of a trace-clean procedure during sampling, handling and filtration. These issues are sometimes difficult to control under the field conditions of the Arctic environments; as a result, no systematic studies of colloidal size fractionation over different seasons in Arctic estuaries have been performed so far. The in situ dialysis techniques commonly used in boreal rivers and lakes by our group allow for passive, but adequate separation of colloidal (1 kDa–0.22 μm) and truly dissolved (< 1 kDa) fractions, as well as separation by size distribution within the colloidal pool itself (Pokrovsky et al., 2005, 2011, 2012a; Vasyukova et al., 2010). To date, dialysis has been used to assess the size fractionation in freshwaters (Alfaro-De la Torre et al., 2000; Gimpel et al., 2003; Vasyukova et al., 2012), but has only occasionally been applied under estuarine conditions (cf. Hamilton-Taylor et al., 2002); the second objective of this study was to apply this dialysis technique toward studying the Arctic estuary along the full salinity profile. The specific goals here were as follows: (i) to quantify the distribution of organic carbon and TE among the major pools of colloids and truly dissolved fraction and (ii) to trace the evolution of the colloidal fraction along the salinity gradient. Our working hypothesis states that the coagulation of organic and organo-mineral colloids increases the relative proportion of potentially bioavailable, low molecular weight ($\text{LMW} < 1 \text{ kDa}$) fractions while decreasing the proportions of the total dissolved (< 0.22 μm) and colloidal (1 kDa–0.22 μm) fractions. Testing this scenario during different seasons along

the salinity gradient of the Severnaya Dvina River constituted an important objective in this work.

2 Sampling and analyses

The sampling area is located in the northern part of NW Russia within the delta of the Severnaya Dvina River, which belongs to the White Sea basin of the Arctic Ocean (Fig. 1). The field work was performed during several hydrological seasons: winter baseflow in March 2009, summer baseflow in July 2010 and 2012 and the start of ice formation/beginning of winter baseflow in November–December 2011 while the water was still free of ice. Detailed geological, climatic and geographic descriptions of the region are presented elsewhere (Shevchenko et al., 2004, 2010; Pokrovsky et al., 2010; Koukina et al., 2001). Sampling was performed from the surface (0.5 m) horizon using a horizontal water sampler made of polycarbonate/PVC (Aquatic Research Co) hung with nylon cord from the PVC motor boat (July) or from the ice (March). During the ice formation period in December 2011, a coastal pilot ship was used during water sample collection.

In total, 74 samples were collected from the Severnaya Dvina River and its mixing zone using filtration through 0.22 μm acetate cellulose filters. Approximately 80 % of these samples were processed additionally using in situ dialysis (1 kDa or 1, 15 and 50 kDa membranes). The trace metal sampling, filtration, and dialysis, as well as the chemical analyses, are presented in Sect. 1 in the Supplement. These techniques are very similar to the methods used in our previous studies (Pokrovsky et al., 2006, 2011, 2012a; Shirokova et al., 2013; Vasyukova et al., 2010). In situ dialysis was performed using a large volume (5 to 10 L) of unfiltered estuarine surface water placed in a dark room at the temperature at which the sampled water was collected. Regular agitation of the dialysis vessels was ensured. The equilibrium dialysis was performed at a very high ratio of external solution/internal reservoir without any correction for the external reservoir dilution, which allowed assessing of the proportion of colloidal forms operationally defined as the fraction of 1 kDa–0.22 μm . The methodology of dialysis procedure as well as various dialysis artifacts are thoroughly described in Sect. S1 in the Supplement.

3 Results

3.1 Elemental concentration as a function of salinity

Major and trace element concentrations at different salinities and size fraction are listed in Table S1 in the Supplement. Several groups of elements could be distinguished according to their concentration profiles, which were maintained throughout all of the studied seasons:

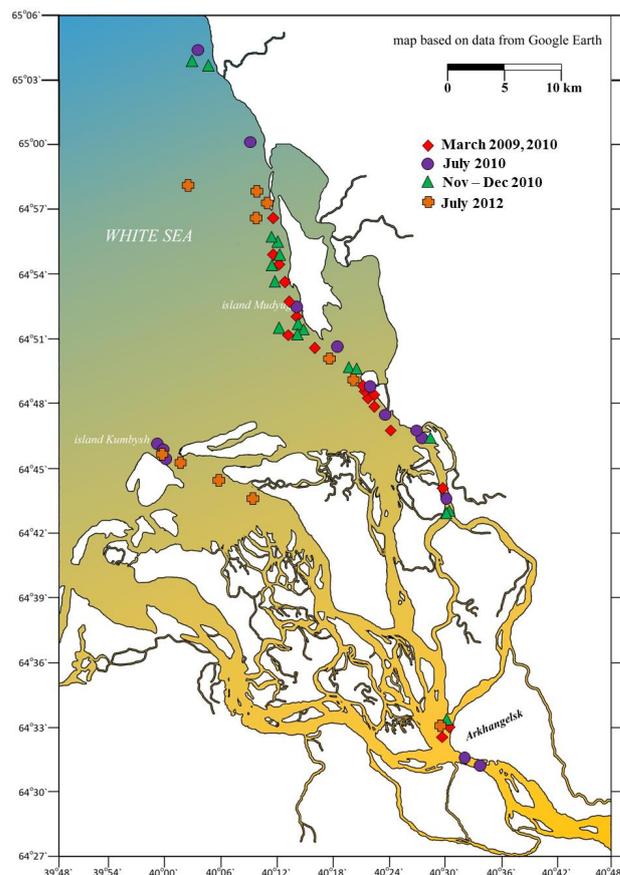


Fig. 1. Schematic map of sampling sites during different seasons. Diamonds, March 2010, 2009; Circles, July 2010, 2012; Triangles, November–December 2011.

1. Elements exhibiting conservative behavior with a strong (up to a factor of 10) linear increase with salinity both in the LMW $< 1 \text{ kDa}$ and the total dissolved ($< 0.22 \mu\text{m}$) fractions: Li, B, Na, Mg, K, Ca, Sr, Rb, Cs, Mo and U, illustrated for B, Mo and U in Fig. 2a–d.
2. Quasi-conservative behavior with a slight or moderate (\leq factor of 3) concentration increase with salinity: V, As, Cr, and Sb, illustrated for the first two elements in Fig. 3a, b.
3. Conservative behavior with strong ($>$ factor of 3) decreases in concentration with the increase in salinity is observed for DOC, Si and Mn (in March), as illustrated in Fig. 4a–c.
4. Conservative behavior with a weak (\leq factor of 2) concentration change or constant level over the full range of salinities, with relative variations within $\pm 30\%$: Ni, Cr, As, Co (in March), Cu, Zn, Ga, Ge, Y, heavy REEs (Gd–Yb), as illustrated in Fig. 5a–d for Ni, Zn, Cu and Cr.

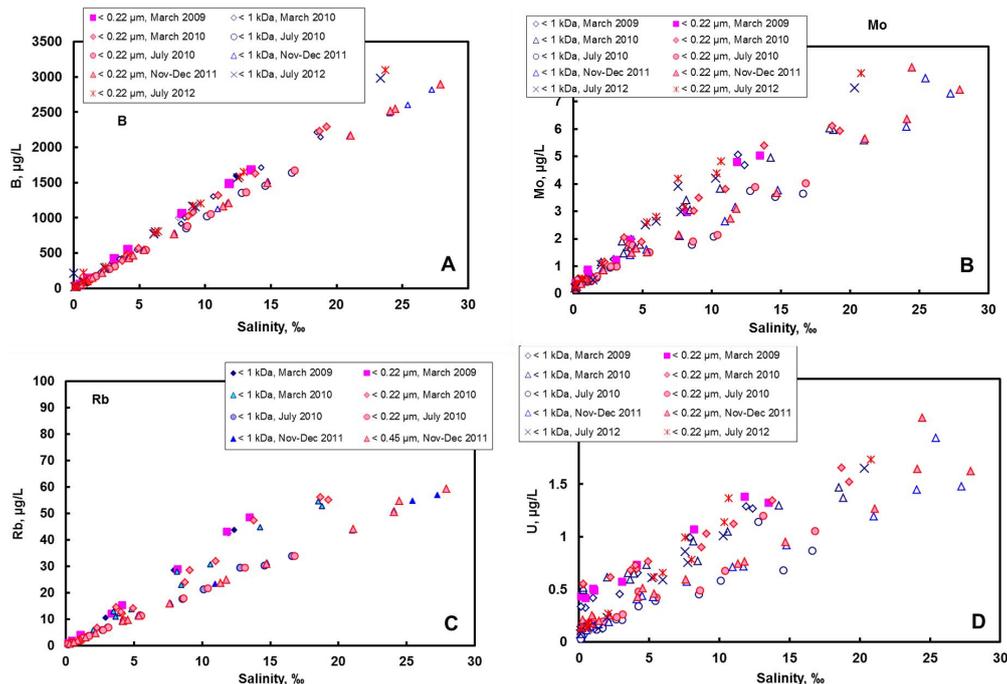


Fig. 2. Boron (A), molybdenum (B), rubidium (C), and uranium (D) concentrations in the estuary.

5. Non-conservative behavior with pronounced coagulation and element removal at low (< 5 ‰) salinities: Ti, Fe, Al, Zr, Hf, LREEs (La-Eu), illustrated in Fig. 6a–c for Al, Fe and Zr, respectively.

6. Non-conservative behavior with a concentration gain at low (~2–5 ‰, Ba, Mn) or intermediate (~10–15 ‰, Cd, Zn, Pb) salinities, illustrated for Ba, Cd and Pb in Fig. 7a, b, and c, respectively.

Note that this classification is not exhaustive and the same element, depending on the season, may belong to several groups. For example, V increases linearly with salinity in March but remains constant or only slightly increases during the other seasons; Al increases its concentration in July 2012; REEs that exhibit rather stable concentrations with salinity increase in March; Mn and Ti show both conservative and non-conservative behavior. Note the pronounced fractionation between the light REE and heavy REE in the estuarine mixing zone because it is illustrated by the concentration ratio of La to Yb (Fig. 8): this ratio decreases by almost one order of magnitude from the freshwater to the seawater zone.

3.2 Behavior of colloidal fraction of organic carbon and trace metals along the salinity gradient

Most elements studied in Sect. 3.1 exhibited similar salinity–concentration profiles for < 0.22 μm and < 1 kDa fractions. However, several typical colloid-borne TE and organic carbons demonstrated decoupling in the salinity profiles of the

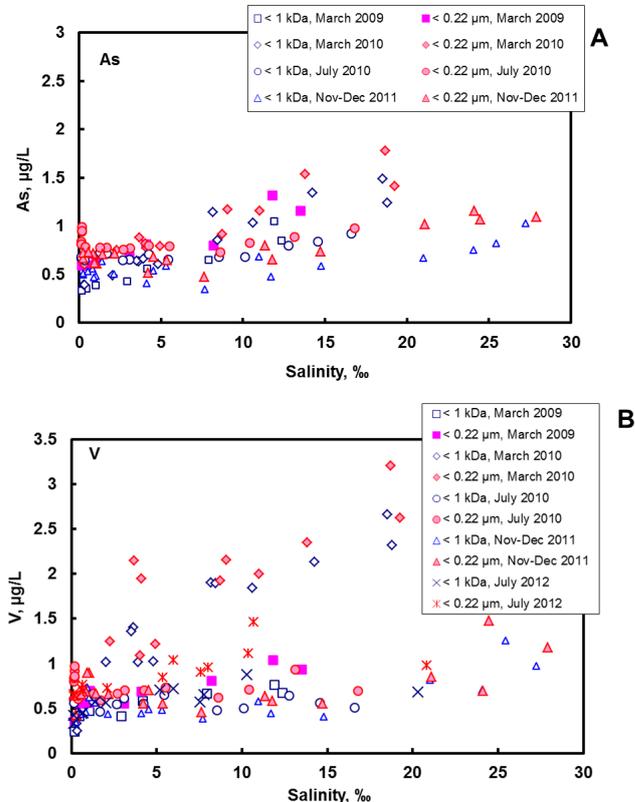


Fig. 3. Arsenic (A) and vanadium (B) concentrations in the estuary.

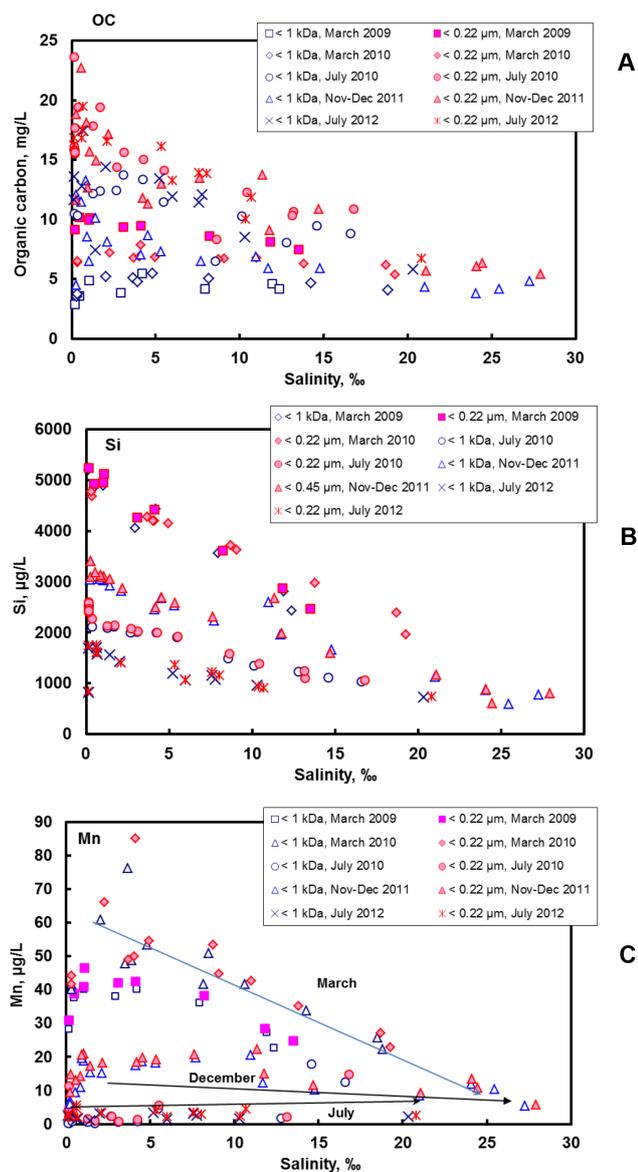


Fig. 4. Organic carbon (A), Si (B) and Mn (C) concentrations as a function of salinity.

total dissolved and LMW_{<1 kDa} fractions. The proportion of colloidal organic carbon as a function of the salinity measured over two summers, two winters and one ice formation period is depicted in Fig. 9. The gradual decrease in colloidal OC with increasing salinity occurred during March and November–December, but the concentration of colloids remained rather constant in the estuary during the summer. There was a sharp drop in colloidal carbon within the first 2–3 ‰ in the summer; at higher salinities, the proportion of colloidal OC was the smallest during this period.

The strongest decrease in the colloidal fraction along the salinity gradient was observed for the insoluble trivalent and tetravalent hydrolysates, as illustrated for Al, Fe, Ti and Zr in

Fig. 10. This decrease in the colloidal fraction, from ca. 80–90 % of the total dissolved concentration in the freshwater, to 10–20 % at 20–15 ‰ salinity, is the most pronounced for Fe, as recorded through all seasons. Similar to organic carbon, this decrease is the largest in the summer and the smallest during winter-ice formation periods. Large decreases in the colloidal fraction with increasing salinity are also recorded for Mn and Pb; the major changes occurred at low salinities (<5 ‰), as shown in Fig. 11a and d. In contrast, the decrease was much smaller for Cu and Ni (Fig. 11b and c, respectively), which exhibited a somewhat constant proportion of colloids or only a 10 % decrease over the full range of salinities, respectively. Similarly, oxyanions and neutral molecules linked to colloids, such as V, Cr, As and Sb, demonstrated a general decrease in the % colloids with salinity (Fig. 12), although this decrease was different across the different seasons and most pronounced for As and Cr (Fig. 12b, c). The colloidal fraction of trivalent REEs (Fig. 13) followed the pattern of Fe (for LREEs) and OC (for HREEs). Finally, U strongly decreased its colloidal fraction in the range of low salinities and then remained mostly in dissolved form during all of the studied seasons (Fig. 13). Taken together, the rather uniform distribution of the colloidal fraction versus salinity during the different seasons shown in Figs. 9–13 allows for the size fractionation of major and trace elements to be approximated with an average value calculated for the range of low salinities (0 to 5 ‰, 36 samples) and for the intermediate to high salinities (5 to 30 ‰, 29 samples), as illustrated in the form of a stack diagram (Fig. 14). Despite the significant uncertainty that stems from the high dispersity of the data points across the different seasons, it is still apparent that both for low- and high-salinity ranges, there are three groups of chemical elements dependent upon their affinity for colloids: (1) <10–20 % in colloidal fraction: Li, Na, K, Si, Ca, Sr, Rb, Mg, B, Mo, Ba, Cs, P, and U; (2) from 20 to 40 % in colloids: Sb, Mn, Zn, As, V, Y, Ni, Cd, Co, Cr, Ga, OC, Cu, Ti, and Al, and (3) 40–80 % present in colloidal form: Hf, Pb, Zr, all REEs, and Fe. A second important observation is the systematically lower proportion of colloidal material in the 5–30 ‰ saline waters compared to the beginning of the estuary (0–5 ‰). This difference ranges from 5 to 20 % among the different trace elements, with the largest shift being observed for Co and Pb.

3.3 Size fractionation of trace elements among major colloidal pools along the salinity gradient

The use of dialysis membranes with different pore sizes (1, 15, and 50 kDa) during all three studied seasons allowed the quantification of the OC and TE size fractionation along the salinity gradient, from freshwater to seawater as the endpoint. Examples of dissolved component size fractionation along the salinity gradient in November–December, July, and March are presented in Figs. 15, 16, and 17, respectively. For this illustration, we have chosen organic carbon, two

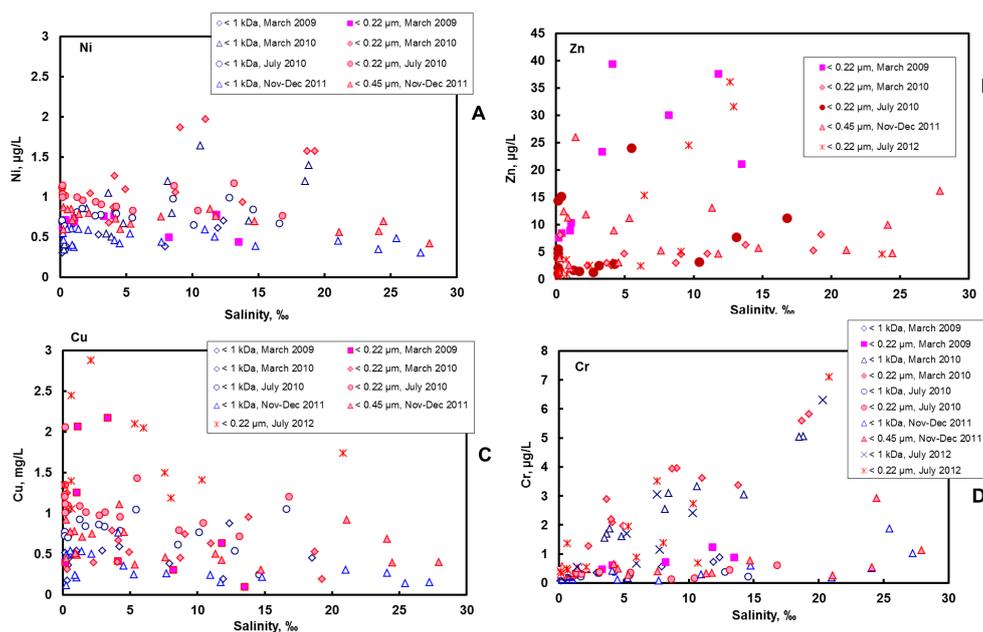


Fig. 5. Ni (A), Zn (B), Cu (C) and Cr (D) concentrations as a function of salinity.

insoluble colloidal elements Al and Fe, which also act as carriers of other TE in the form of organo-mineral colloids, U because it changes its speciation from organic colloids to truly dissolved uranyl carbonate complexes, and two metal micronutrients – Cu and Ni.

In November–December, the organic carbon is dominated by LMW < 1 kDa complexes (60 %) and large colloids (50 kDa–0.22 μm) in the freshwater zone. There is a systematic decrease in the large colloids and an increase in the LMW < 1 kDa forms with the appearance of a non-negligible fraction of small colloids (1–15 kDa) in saline environments. In March, the LMW < 1 kDa progressively increases seaward, whereas the HMW_{50 kDa–0.22 μm} colloidal fraction remains similar between the freshwater and the seawater end point (Fig. 17).

Al, Fe and other tri- and tetravalent insoluble elements mostly appeared as HMW_{50 kDa–0.22 μm} colloids in the low-salinity zone; this fraction almost disappears (Al) or decreases significantly (Fe) in the high-salinity samples, whereas the LMW < 1 kDa fraction becomes dominant above 9.5 ‰ salinity, which was observed for November–December and July (Figs. 15 and 16). Notably, while the fractions for 1–15 kDa and 15–50 kDa of Fe are minor in the low-salinity range, they constitute 13–19 % of the total dissolved metal at 9.5–24 ‰ salinity.

Uranium exhibits a rapid decrease in the proportion of both medium (1–15 kDa) and high (50 kDa–0.22 μm) molecular weight forms at low-salinity ranges in November–December and in March. During the summer period, this decrease is less pronounced; ca. 10 % of U is still present as 50 kDa–0.22 μm colloids at 10 ‰ salinity.

Divalent metals exhibit a complex pattern of size fractionation as a function of salinity, which resembles neither the organic carbon nor the iron profile. For Ni, the HMW_{50 kDa–0.22 μm} fraction achieves its maximum in November–December, and in March, the maximum is at 9.0 ± 0.5 ‰; for medium size fractions (15–50 kDa or 1–50 kDa), however, this maximum occurs at 24 ‰ in November–December and at 3.7 ‰ in March. The summer period is characterized by the presence of ~ 40 % of HMW colloids in the freshwater zone and their disappearance with rising salinity at the expense of approximately equal amounts of 1–15 kDa and 15–50 kDa fractions. In contrast to Ni, the HMW of copper disappears above 1.2 ‰ salinity and the medium-size fraction (15–50 kDa) becomes dominant in highly saline water.

4 Discussion

4.1 Conservative versus non-conservative behavior controlled by colloidal coagulation in the estuary

This work demonstrates rather “classic” behavior of major and trace elements in conventionally dissolved (< 0.22 μm) fractions in the mixing zone of the Severnaya Dvina River and the White Sea. The spatial resolution of our measurements does not allow the detection of the flocculation of DOC that is reported to occur within the 2 to 4 ‰ salinity range in the Severnaya Dvina estuary (Artemyev and Romankevich, 1988). A linear decrease in the dissolved organic carbon with salinity increase in the major Arctic estuaries is fairly well known (Kattner et al., 1999; Koehler et al.,

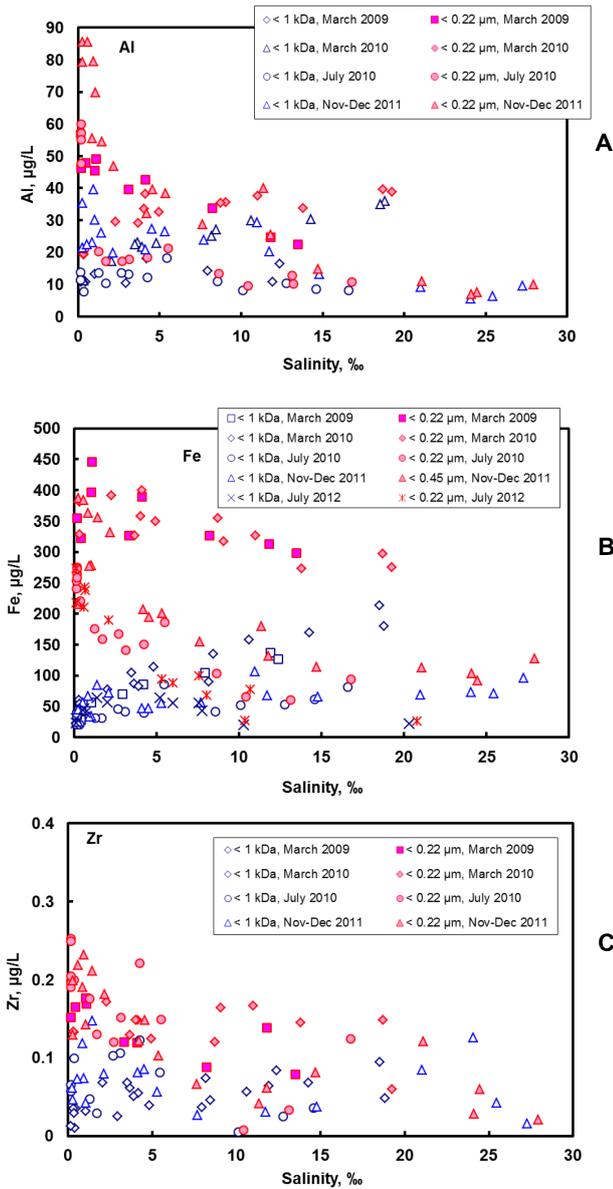


Fig. 6. Al (A), Fe (B) and Zr (C) concentrations as a function of salinity in the estuary.

2003; Amon et al., 2012). This phenomenon is linked to the rather refractory nature of DOM in the subarctic rivers and the large proportion of LMW_{<1 kDa} that was not subjected to coagulation compared to large colloids (see Sect. 4.2). In contrast to a productive temperate estuary (i.e., McKenna, 2004), it is very unlikely that the coupled DOC addition and removal may explain the semi-linear dependence of DOC_{<0.22 µm} on salinity. The preservation of this highly conservative behavior takes place during both summer and the glacial season in the Severnaya Dvina estuary (Figs. 4a and 9).

Other examples of the highly conservative behavior observed during the estuarine mixing in the Arctic are boron

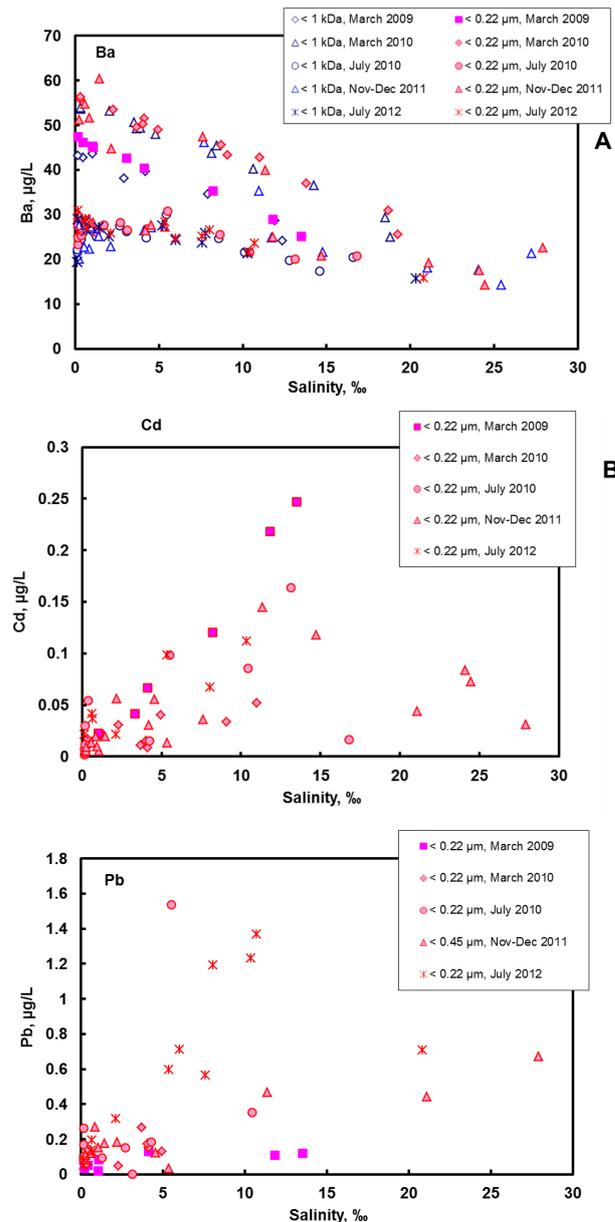


Fig. 7. Ba (A), Cd (B) and Pb (C) concentrations as a function of salinity in the estuary.

(Savenko et al., 2003), molybdenum, rubidium, and uranium, the concentrations of which in the seawater are an order of magnitude higher than the content of the freshwater end member. Whereas B, Rb and Mo are unlikely to be affected by colloidal forms (Fig. 2a, b), U does appear in HMW_{50 kDa–0.22 µm} colloids in the freshwater zone (Figs. 13 and 15–17). However, strong uranyl carbonate complexes start to appear at the beginning of mixing with the seawater, which decreases the affinity of this element for organo-mineral colloid formation and renders it mainly to its truly dissolved form. The removal of dissolved U in the very

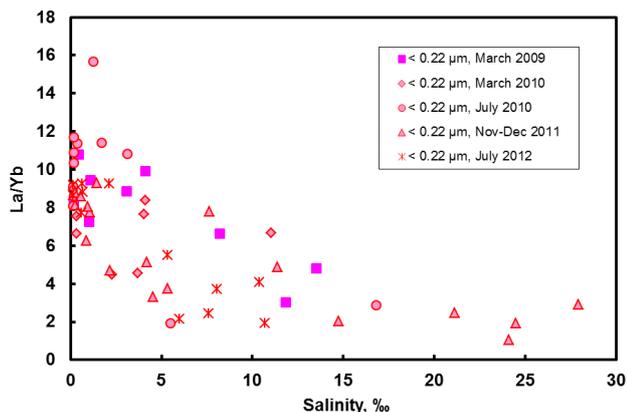


Fig. 8. Plot of the La/Yb $0.22 \mu\text{m}$ fraction concentration ratio as a function of salinity during different seasons in the Severnaya Dvina estuary.

low-salinity zone by the Fe- and organo-rich colloids observed in the Severnaya Dvina River estuary (Figs. 13, 15a, 16) corroborates numerous observations in the Kalix River–Baltic Sea mixing zone (Porcelli et al., 1997; Andersson et al., 1998, 2001), as well as reports for small rivers on the NW German coast (Beck et al., 2012).

Other neutral molecules and oxyanions, such as As, Sb, V, and Cr, demonstrate systematic concentration increases toward the seawater end member (Fig. 3a, b) because these elements are more concentrated in seawater than in the freshwater. This behavior is quite typical for anionic species in the temperate estuaries (i.e., Van der Sloot et al., 1985; Strady et al., 2009). Despite the fact that these elements are bound to 10–30 % in HMW organo-ferric colloids in the Severnaya Dvina River (Pokrovsky et al., 2010), this speciation feature does not influence their concentration pattern, which remains independent for the Fe above ~ 2 ‰ salinity. Only at the very beginning of the estuarine mixing does a measurable drop (20 to 30 % from the freshwater concentration) occur, as illustrated for As and V in Fig. 3a, b. This drop can be linked to the coagulation of the majority of HMW_{50 kDa–0.22 μm} Fe colloids at the beginning of the mixing zone, because the proportion of colloidal forms in total dissolved concentration of As and V achieves 20–25 % (Fig. 14). Chromium is different from other oxyanions, because, as it can be seen in Fig. 5, in addition to the general increase in concentration with increasing salinity, Cr also shows a mid-salinity maximum similar to Ni and Cu. This result is consistent with occurrence of both Cr(III) and Cr(VI) in natural waters (Schroeder and Lee, 1975). The appearance of this maximum may be linked to Cr(III) association with humic substances similar to Ni and Cu or Cr(III) desorption from river-suspended matter similar to other cations.

As expected, Si presents quite conservative behavior during all three studied seasons (Fig. 4b), with the seawater

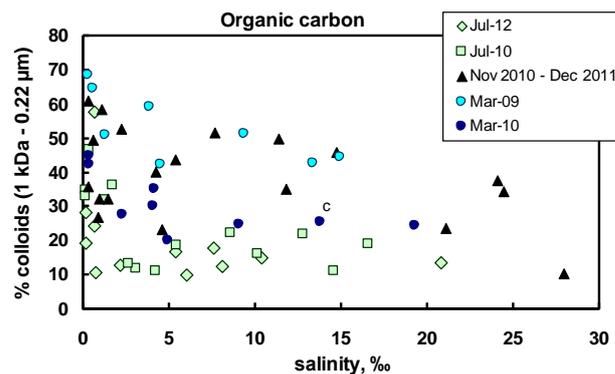


Fig. 9. Relative proportion of colloidal organic carbon as a function of salinity during different seasons in the Severnaya Dvina estuary.

end member being equal to $900 \pm 100 \mu\text{g L}^{-1}$ during all seasons and the riverine component ranging from 1800 to $5100 \mu\text{g L}^{-1}$. This behavior agrees with numerous previous observations (i.e., Boyle et al., 1974) in the Severnaya Dvina estuary in particular (Savenko and Shevchenko, 2005), and the reported minimal removal of silica in the brackish bay mixing zone of the Baltic Sea (Gustafsson et al., 2000). This result strongly suggests the lack of any active uptake of Si by the diatoms in the mixing zone, as well as a negligible effect on the dissolution of sediments or diagenetic flux. In agreement with the majority of the previous experiments using dialysis and ultrafiltration (Pokrovsky and Schott, 2002; Vasyukova et al., 2010), colloidal Si does not appear in these waters.

The significant coagulation of Al, Fe, and trivalent (REEs) and tetravalent (Ti, Zr, Hf, Th) hydrolysates is pronounced mostly at the very beginning of the estuarine mixing (Figs. 10 and 13) because these elements normally appear as large-size colloids (Figs. 15–17) that are quite unstable in aqueous solution with an elevated ionic strength, as confirmed by numerous observations of the flocculation and removal of colloidal material with increasing salinity in the estuaries (Sholkowitz, 1976, 1978; Sigleo and Helz, 1981). The decrease in the proportion of colloidal Fe with the concomitant increase in salinity is well established from size-fractionation techniques (Kuma et al., 1998; Sañudo-Wilhelmy et al., 1996; Stolpe and Hasselöv, 2007). Insoluble, less mobile elements follow the pattern of Fe tightly, with maximal removal occurring in the low (0–5‰) salinity zone. These results are consistent with the dominant status of the trivalent and tetravalent elements in the White Sea watersheds, which occur in the form of large organo-ferric colloids rather than organic complexes capable of controlling the speciation of these elements in the surface boreal waters (Pokrovsky and Schott, 2002; Vasyukova et al., 2010; Pokrovsky et al., 2010, 2012b). The decrease in the La/Yb ratio in the $<0.22 \mu\text{m}$ fraction with rising salinity (Fig. 8) may reflect the removal of the Fe-rich colloids, binding LREE via surface adsorption or

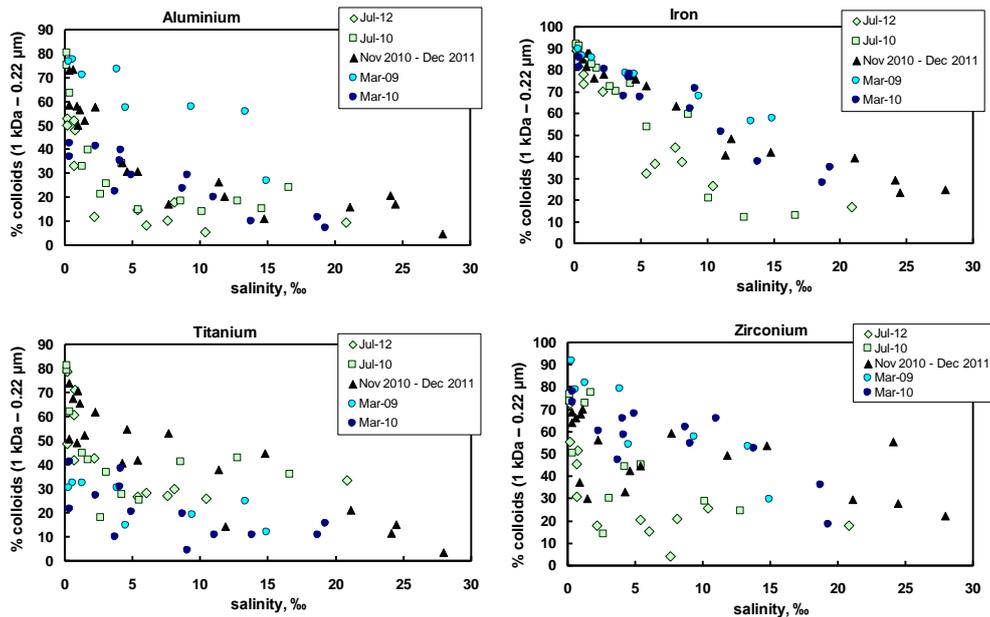


Fig. 10. Proportion of colloidal Al, Fe, Ti and Zr as a function of salinity during different seasons in the Severnaya Dvina estuary.

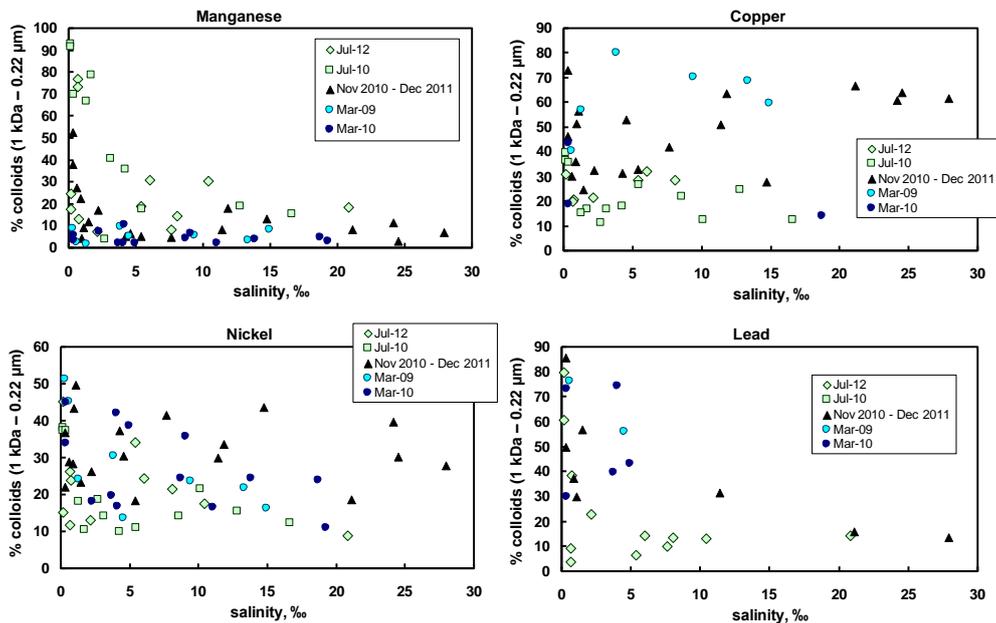


Fig. 11. Proportion of colloidal Mn, Cu, Ni and Pb as a function of salinity during different seasons in the Severnaya Dvina estuary.

incorporation, and the appearance of LMW organic ligands forming strong complexes with HREE. Preferential removal of the light REE was already observed in temperate estuaries (Sholkovitz and Elderfield, 1988; Elderfield et al., 1990) and LREE are known to be removed more efficiently than HREE in small estuaries (Lawrence and Kamber, 2006; Åström et al., 2012). The affinity of light REE for mineral and colloidal surfaces such as HMW organo-ferric colloids,

and HREE for soluble organic ligands such as LMW < 1 kDa complexes, is fairly well known both from experimental studies (Bau, 1999) and natural observations in the boreal zone (Pokrovsky et al., 2006). This is also proven from the analysis of filtrates and ultrafiltrates of natural Fe and OC-rich samples (Sholkovitz, 1995, for Hudson river filtrates 0.025 μm , 50 kDa and 5 kDa and Pédrot et al., 2008, for soil solution filtrates 0.22 μm , 30, 5 and 2 kDa).

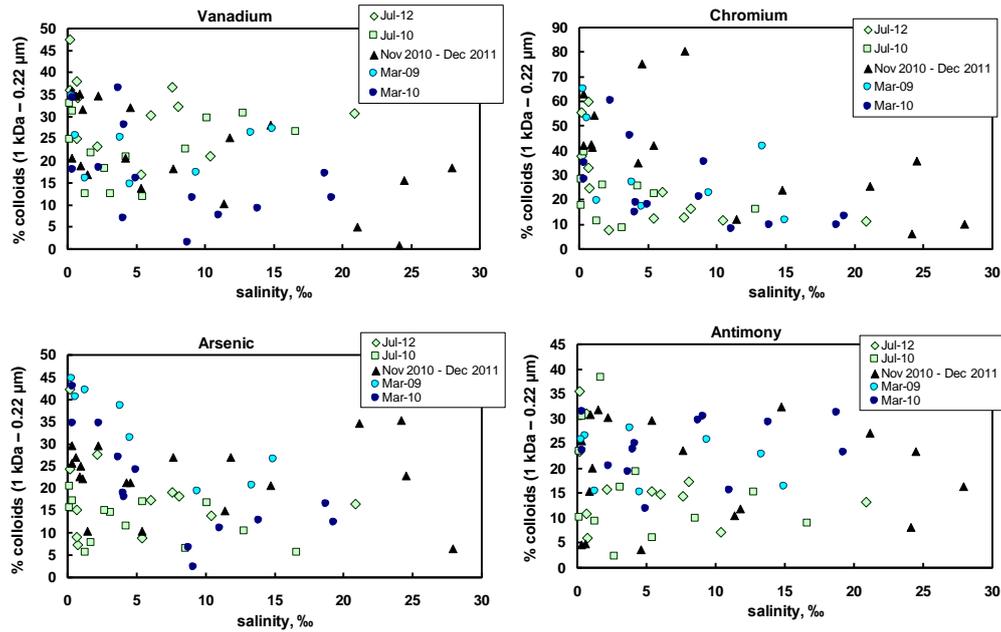


Fig. 12. Proportion of colloidal V, Cr, As and Sb as a function of salinity during different seasons in the Severnaya Dvina estuary.

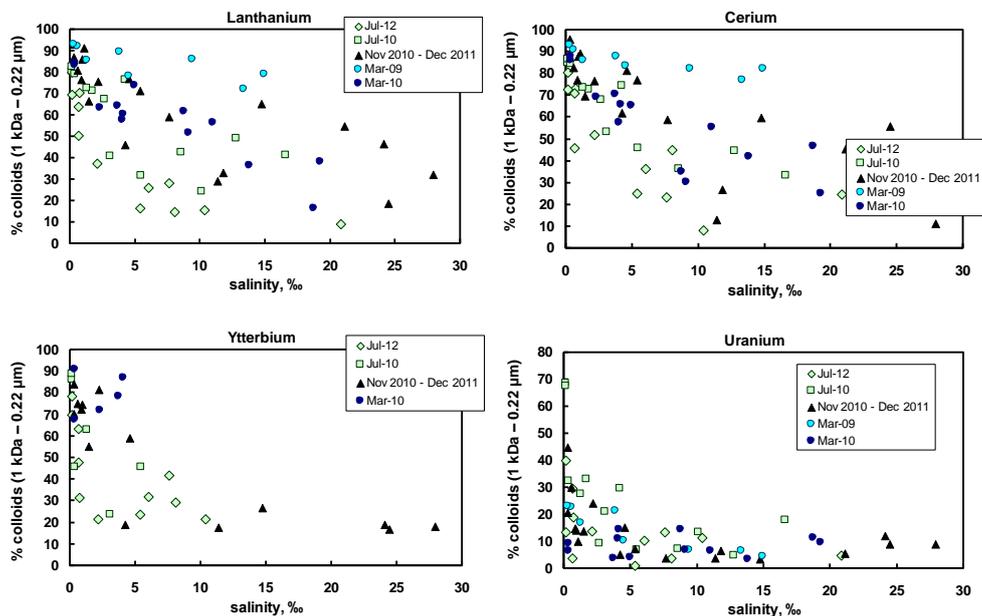


Fig. 13. Proportion of colloidal La, Ce, Yb, and U as a function of salinity during different seasons in the Severnaya Dvina estuary.

The behavior of the divalent transition metals (Ni, Cu, Zn) reflects both seasonal variation in elemental concentration in the freshwater end member, as well as their affinity for organic matter. The concentration–salinity pattern of these elements is quite complex, with generally flat or seaward-decreasing concentration lines with pronounced maxima in the medium-salinity (10–15 ‰) range (Fig. 5a–c). The phytoplankton uptake of these elements is not strongly

pronounced in the Severnaya Dvina estuary because the summer-period element concentrations are comparable to the winter time measurement. For the same reason, the desorption of these divalent micronutrients from the river suspended matter (RSM) and bed sediments, which is induced by the inorganic complexation of the metals by seawater anions and also known to occur in the estuaries (Kraepiel et al., 1997; Takata et al., 2012), cannot be proved from our data. Indeed,

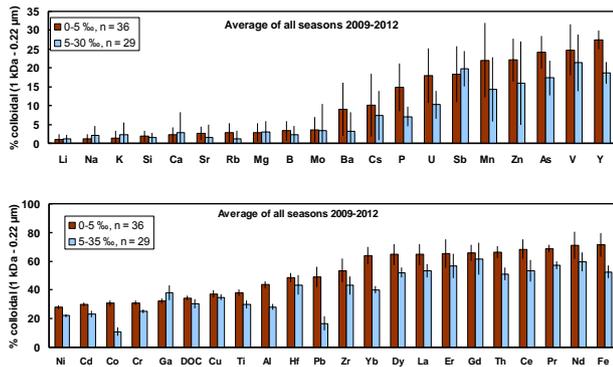


Fig. 14. A stack diagram of colloidal fractions of TE as an average of all seasons in low-salinity and high-salinity zones (dark and light columns, respectively).

the RSM concentration in March is a factor of 2 to 3 lower than that which was observed in the summer (Shevchenko et al., 2004, 2010), yet the concentrations of these three elements exhibit the maximum value in the range of medium salinities during winter baseflow. At the same time, the diffusion flux from the sediments, similar to what is reported for these elements from other world estuaries (Boughriet et al., 1992; Audry et al., 2006, 2007; Point et al., 2007), cannot be excluded because of the existence of several maxima of heavy metal distribution in the sediments of the Severnaya Dvina estuary along the salinity profile (Koukina et al., 2001).

Manganese should be considered separately from other divalent metals because of the following: its concentration (1) strongly varies across the different seasons, reflecting strong accumulation in the winter under the ice because of the enhanced discharge of anoxic groundwater or Mn-rich tributary (Gordeev et al., 2007; Pokrovsky et al., 2010) and (2) depends on the light and oxygen due to the multiple redox states of Mn in boreal waters during the summer (Ingri et al., 2011; Pokrovsky and Shirokova, 2013). The first mechanism is consistent with the peaks of the concentration observed at low (0–5‰) salinity ranges that follow the order of March > November–December > July (Fig. 4c). This order also supports the hypothesis that the Mn concentration in the estuary is being controlled by diffusion from the sediments, which is likely to be most pronounced during the winter period. Remobilization of the Mn from the sediments due to strong Mn reductions taking place directly below the sediment–water interface is fairly well established for other Arctic river delta settings (i.e., Nolting et al., 1996) and was also suggested for the Baltic Sea coastal zone (Ingri et al., 2004). The reduction of Mn oxides in the water column itself cannot be excluded either (Klinkhammer and McManus, 2001).

Finally, two indifferent/toxic heavy metals – Cd and Pb – as well as Ba, demonstrated the typical maxima of

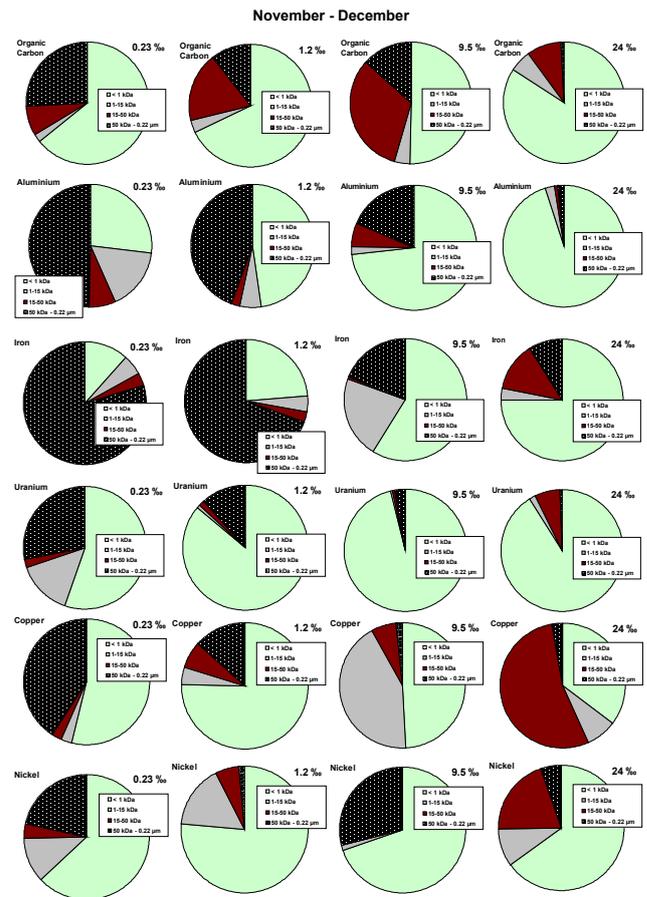


Fig. 15. A diagram of relative fraction of colloidal material in the Severnaya Dvina River estuary during the November–December ice formation period.

concentration at moderate (Cd, Pb) and low (Ba) salinities (Fig. 7), which is most likely linked to desorption from the river suspended matter (Shiller and Boyle, 1991; Dai et al., 1995; Elbaz-Poulichet et al., 1996; Shulkin and Bogdanova, 2003), sediments (Stecher III and Kogut, 1999) and/or diffusion flux from the sediments (Point et al., 2007; Du Laing et al., 2009). The particle desorption or the influx from the sediments is known to increase the Cd concentration in the high-salinity zone of temperate estuaries to as much as 360 % of its riverine end member (Waelles et al., 2004) because the seawater Ca^{2+} replaces the Cd^{2+} in the iron/manganese oxide-associated fraction (Waelles et al., 2005a, b). In the case of the Severnaya Dvina estuary, the desorption from the RSM occurring at low salinities is more pronounced in the $\text{LMW} < 1 \text{ kDa}$ fraction (Fig. 7b), demonstrating the importance of the exchangeable (ionic) form of this metal to the estuarine behavior. Despite the high affinity of Pb^{2+} toward the large Fe-rich colloids demonstrated in the boreal waters of the White Sea watershed (Pokrovsky and Schott, 2002; Vasyukova et al., 2010), some temperate rivers (Stolpe et al., 2010) and boreal estuaries (Stolpe and Hassellöv, 2007),

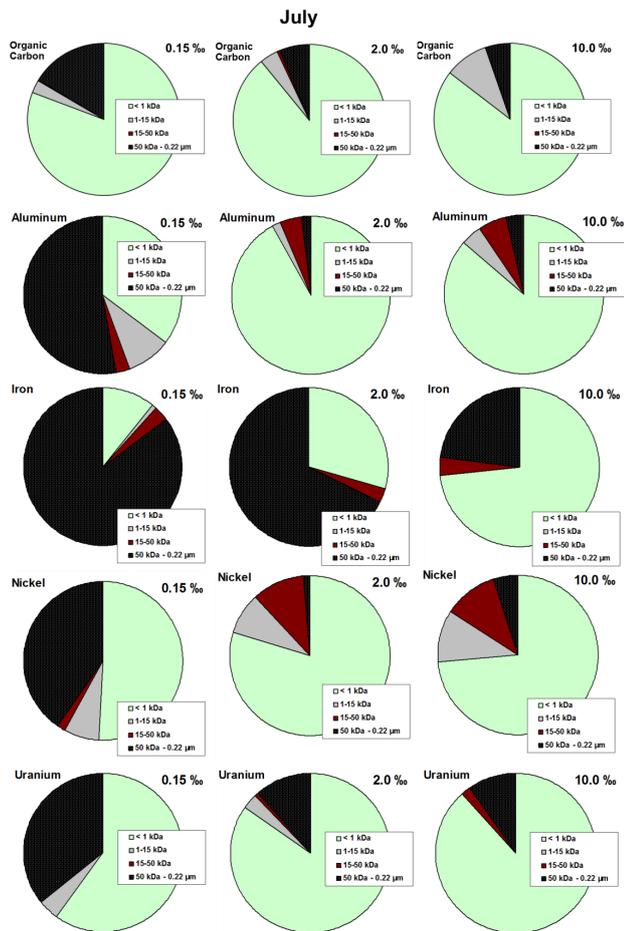


Fig. 16. A diagram of relative fraction of colloidal material in the Severnaya Dvina River estuary during July.

the co-precipitation of Pb with coagulates of organo-ferric colloids at a lower salinity range known for other estuaries (Breuer et al., 1999) is not pronounced in the Severnaya Dvina estuary. Instead we observed an enrichment of the mixing zone in Pb (Fig. 7) likely due to both RSM desorption and sediment mobilization. This effect is most likely due to the low Pb concentration in the riverine end member; however, anthropogenic contamination of estuarine sediments cannot be ruled out, given the highest Pb concentration in clays of the Severnaya Dvina compared to other neighboring sub-arctic rivers such as the Mezen and Pechora (Kukina et al., 2002).

4.2 Increase in the proportion of LMW < 1 kDa of OC, trace elements and metal micronutrients during estuarine mixing

The first and most significant result is the difference in the degree of conservative or non-conservative behavior between traditional “total” (< 0.22 μm) and “truly” dissolved LMW < 1 kDa fractions. For the majority of studied metals

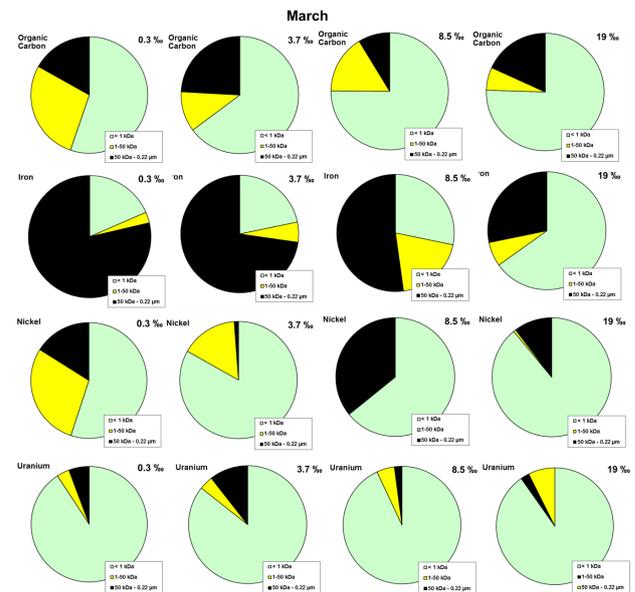


Fig. 17. A diagram of relative fraction of colloidal material in the Severnaya Dvina River estuary during March (winter baseflow).

this result was not counterintuitive because it was demonstrated in earlier studies that the colloidal fraction in the estuary is subjected to the largest degree of coagulation (Dai and Martin, 1995). Additionally, a much smaller decrease in the truly dissolved (< 1 kDa) form of Fe and Cu compared to the < 0.22 μm fraction when the salinity increases in the coastal zone has been already reported across the range of high salinities (Wells et al., 2000). However, the less expected result is the enrichment of the LMW fraction in many insoluble metals and OC with increased salinity. For example, organic carbon demonstrates an increase in the LMW < 1 kDa fraction in July 2012 and 2010 at approximately 5‰ salinity; otherwise, it exhibits a rather flat concentration pattern along the estuary (Fig. 5a). No loss of this fraction occurs; rather, there is some gain in the LMW < 1 kDa fraction at ca. 2‰ salinity, presumably due to the autochthonous process of OC transformation/production within the water column. An organic-rich subtropical river in the southeastern US also demonstrated an increase in the LMW fraction of OC at low salinity and relatively flat concentrations towards the seawater end member (Powell et al., 1996); a boreal estuary demonstrated the unchanged concentration of small (0.5–3 nm) fluorescent OM with increasing salt concentrations up to 25‰ salinity (Stolpe and Hassellöv, 2007). DOC production during an August phytoplankton bloom in the estuaries is also fairly well known (McKenna, 2004).

Because the increase in the organic carbon LMW < 1 kDa in the Severnaya Dvina River estuary is much stronger and pronounced in July than in winter (Figs. 4a and 9), three main processes may be responsible for it: (i) photochemical oxidation of allochthonous organic matter that produces LMW

complexes because it is fairly well known for a number of other boreal and temperate settings (cf. Amon and Benner, 1996; Bertilsson and Tranvik, 2000; Moran et al., 2000; Jonsson et al., 2001; Anesio and Graneli, 2004; Kopáček et al., 2006a, b; Kelton et al., 2007), (ii) heterotrophic mineralization of DOM by aerobic bacterioplankton known for their effect on boreal lakes (cf. Tranvik, 1988; Tranvik and Jørgensen, 1995; Jansson et al., 2000, 2007; Kritzberg et al., 2004; Ask et al., 2008), subtropical marshes (Moran and Hodson, 1990), and temperate estuaries (Raymond and Bauer, 2000), and (iii) the exometabolites of the phytoplankton, whose presence is mostly pronounced at the beginning of the Severnaya Dvina estuarine mixing, in the zone where both marine and freshwater species co-exist (T. Y. Vorobieva, unpublished data); exometabolite production by gram-negative bacteria in the marine zone cannot be ruled out (Wells et al., 1998). The photo degradation of dissolved organic matter is known to produce LMW organic compounds that can significantly stimulate bacterial biomass production (Moran and Zepp, 1997). For example, production of the lower molecular weight species of OC, Fe and metals at higher salinities has been detected in the Trinity Estuary (Galveston Bay, Gulf of Mexico) and suggested to be induced by some photochemical and microbiological reactions (Wen et al., 1999). However, the degree of the increase in the LMW fraction in this tropical organic-poor river (6 mg L^{-1} DOC in the freshwater zone) was significantly smaller than the organic-rich Severnaya Dvina River estuary.

The most crucial changes in the size fractionation pattern over the estuarine zone occurred with Fe, which is normally present in the freshwater end member of this river as organo-ferric HMW colloids (Pokrovsky et al., 2010), which is consistent with other rivers' speciation studies (Stolpe et al., 2010). It can be observed from Fig. 6b that a clear enrichment of the mixing zone by $\text{LMW}_{< 1 \text{ kDa}}$ Fe complexes occurred, with a relative increase between freshwater and $10 \pm 5\%$ salinity as high as a factor of 5. This suggests higher stability of LMW Fe complexes during river water migration through the mixing zone. Indeed, the lifetime of truly dissolved iron in coastal waters is known to be significantly longer than that of colloidal fractions (14 days and < 1 h, respectively, Fujii et al., 2008b). The increase in LMW-reactive Fe fractions at high salinities has been already observed in subtropical, organic-rich estuaries (Powell et al., 1996). On the northwest African coast, LMW ($< 0.02 \mu\text{m}$) colloidal Fe decreased its concentration seaward to a smaller degree than that of dissolved ($< 0.22 \mu\text{m}$) Fe (Ussher et al., 2010). Experimental studies in the Scheldt estuary demonstrated that, in the range of 0.3 to 10‰ salinity, Fe concentration decreased much more sharply for the fraction $< 0.2 \mu\text{m}$ compared to the fraction $< 1 \text{ kDa}$ (Gerringa et al., 2007). This analysis demonstrated that, although a smaller degree of coagulation for LMW Fe commonly occurs in the estuary, the increase in this fraction seaward observed in the present study is unprecedented. In the Severnaya Dvina estuary, the

maximal increase of $\text{LMW}_{< 1 \text{ kDa}}$ Fe fraction was detected during the winter baseflow (Figs. 6b and 15–17). This observation rules out the possibility of superoxide-mediated LMW Fe(II) photochemical formation from organically complexed Fe(III), as it is known for coastal waters from the temperate zone (Kuma et al., 1995; Fujii et al., 2008a). The 50–80 cm ice coverage together with an equal amount of overlaying snow during the Arctic winter period should not allow significant photo-reduction processes. Given that phytoplankton activity during glacial periods is also low, we hypothesize that the process responsible for winter-time increase of LMW compounds is heterotrophic mineralization of allochthonous DOM. Indeed, the efficiency of DOC utilization by bacteria is known to increase with the increase in salinity, as shown by in situ incubation experiments in a temperate estuary (Raymond and Bauer, 2000). Concurrently, the relative decrease in the 1 kDa – $0.22 \mu\text{m}$ fraction, i.e., coagulation processes of Fe colloids, is more pronounced during summer, when compared to levels during the winter baseflow (Fig. 10). This result is consistent with the fact that both phytoplankton activity and photo degradation leading to the production of $\text{LMW}_{< 1 \text{ kDa}}$ fractions are much more efficient in summer than in winter. Indeed, in the freshwater temperate settings, an increase in LMW carbohydrates during summer time was reported (Wilkinson et al., 1997). Additionally, bacterial consumption of DOC is known to increase with temperature increase in the estuary (Raymond and Bauer, 2000). Production of the LMW (0.3–1 kDa) Fe(III) siderophores by marine prokaryotes is fairly well known (Reid et al., 1993; Barbeau et al., 2001) and strong LMW complexes of this metal need to be reported in sea surface waters (Wen et al., 2006). The effect of redox processes should not be pronounced for dissolved Fe in the Severnaya Dvina estuary because the majority ($> 95\%$) of this element is present in its trivalent form, as determined from spectrophotometric analysis (Pokrovsky et al., 2010, and references therein). This finding is consistent with the other data, indicating that all dissolved Fe in freshwater appears as Fe-humic complexes or aggregates of Fe hydroxides and humic-Fe (Allard et al., 2004; Lofts et al., 2008; Liu et al., 2013). Another reason for more pronounced total dissolved concentration of OC and Fe decrease in July compared to March is that the river contained a higher concentration of aquatic organic polymers in summer than in winter (i.e., Wilkinson et al., 1997), thus enhancing the aggregation of colloids in July.

The behavior of other insoluble elements linked to organo-ferric colloids (Al, Ti, Zr, REEs, Figs. 10 and 13), as well as As, Cr, Pb and U (Figs. 12 and 13), follows that of Fe with the (i) strong decrease in the colloidal fraction across all seasons, which is linked to coagulation and the mechanical removal of these elements in the form of Fe-rich precipitates; the (ii) intense processes of colloidal transformation during the summer and the appearance of a significant fraction of the $\text{LMW}_{< 1 \text{ kDa}}$ forms. This estuarine behavior corroborates with the strong control over the migration of these elements

as organo-ferric colloids, which is known for the freshwater settings of the White Sea watershed in general (Pokrovsky and Schott, 2002) and the Severnaya Dvina River in particular (Pokrovsky et al., 2010). At the same time, the chemical nature of strong metal chelators, including LMW forms, which might serve as transports for bio-available iron in the rivers, estuaries and coastal waters have not yet been identified (cf., Krachler et al., 2005; Boye et al., 2010).

Divalent metals (Cu, Ni, Mn, Pb) also exhibit a rapid decrease in their colloidal forms in the summer at the very beginning of the mixing zone and a much more gradual decrease in the colloidal forms during the winter period (Fig. 11). The highly dynamic behavior of the colloidal divalent metals (Cd, Co, Cu, Ni, Pb, Zn) during the summer in the Trinity River estuary has been reported by Wen et al. (1999). The abiotic coagulation of colloids should be similar across the different seasons and thus does not allow explaining of the seasonal variation of colloidal fractions. In contrast, either photo-induced degradation or respiration by bacterioplankton – both being intensified during the ice-free summer period and warmer water temperatures – can be invoked to control the divalent metal speciation in the mixing zone. In addition, the contribution of the LMW phytoplankton exudates to the total dissolved pool of metals can decrease the proportion of the colloidal fraction. This decrease is much smaller for Cu relative to Mn, Pb and Ni (Fig. 11), which is consistent with a very strong complexation of this metal by LMW organic ligands of both terrestrial origin (Shank et al., 2004; Krachler et al., 2005) and from phytoplankton exometabolism (van den Berg et al., 1987; Muller, 1998; Waelles et al., 2005a; Wen et al., 2011). Strong Cu^{2+} binding to humic complexes across the full range of salinity is also known from dialysis mixing experiments (Hamilton-Taylor et al., 2002). In contrast, the similar pattern of % colloids vs. salinity for Mn and Pb (Fig. 11), which are two strongly opposing metals in terms of their biological affinity and the degree of their complexation by DOM (Powell et al., 1996; Kozelka et al., 1997), is not supportive of active biological control of metal complexation due to the LMW phytoplankton exometabolites in the mixing zone.

4.3 Perspective on carbon and trace element delivery to the Arctic Ocean under a climate change scenario

The increase in the concentration of the $\text{LMW}_{<1\text{ kDa}}$ fraction in the seaward direction highlighted for the first time in this work may have significant and unexpected consequences for the biogeochemical functioning of the mixing zone. First, this LMW fraction is potentially bioavailable because the pore sizes of cell wall transport channels and pores of the 1 kDa dialysis membranes are comparable (see discussion in Vasyukova et al., 2012). Therefore, a number of metal micronutrients (Fe, Co, Ni, Mn, Zn, V, etc.) should enrich the coastal zone with their potentially bioavailable fraction and thus affect the primary productivity of the Arctic

Ocean. Second, the LMW fraction of the trace metals in the river water exhibits isotopic signatures drastically different from those of conventionally dissolved $<0.22\ \mu\text{m}$ fraction, as is known for Fe (Ilina et al., 2013a), Sr (Ilina et al., 2013b) and U (Bagard et al., 2011). For example, the $\text{LMW}_{<1\text{ kDa}}$ of the river water is 2 to 4 ‰ enriched in ^{57}Fe relative to the $<0.22\ \mu\text{m}$ fraction. The unusually high mobility of the $\text{LMW}_{<1\text{ kDa}}$ fraction of Fe through the mixing zone is capable of enriching the Arctic Ocean in the heavy isotope of various metals relative to what might be predicted from the flux of the $<0.22\ \mu\text{m}$ fraction.

Upon the climate warming, the ongoing increase in the LMW metal and OC concentration occurring in the White Sea watersheds (cf., Shirokova et al., 2013; Pokrovsky et al., 2013) will be further accentuated in the estuaries because this LMW pool passes through the mixing zone without coagulation. This phenomenon might influence the following: (i) the primary productivity of the coastal zone, leading to CO_2 drawdown from the atmosphere, and (ii) heterotrophic respiration of the allochthonous DOC accompanied by CO_2 release into the atmosphere. However, distinguishing quantitatively between these two processes is not yet possible. For organic carbon, the smallest proportion of colloids (1 kDa– $0.22\ \mu\text{m}$) is observed during summer across the entire salinity zone (Fig. 9). The insoluble elements (Al, Fe, Zr, REEs) and divalent metals (Co, Ni, Cu, Pb) follow this scheme, therefore suggesting that the heating of the surface water and extension of the active (vegetative) ice-free period should decrease the proportion of colloids versus “truly” dissolved components of the $\text{LMW}_{<1\text{ kDa}}$ fraction.

Finally, the majority of annual colloidal flux in the Severnaya Dvina River occurs during the spring flood period (Pokrovsky et al., 2010). The most important transformation processes of the allochthonous organic matter and related elements should therefore occur in May (i.e., Gustafsson et al., 2000), which is the period not yet investigated using this size fractionation technique along the salinity gradient in Russian Arctic rivers. The particularity of colloidal composition during spring flood on the Severnaya Dvina River has been thoroughly described in Pokrovsky et al. (2010). It consists in the higher proportion of colloidal (1 kDa– $0.22\ \mu\text{m}$) fraction compared to winter and summer baseflow and a factor of 2 to 3 higher concentration of $0.22\ \mu\text{m}$ filtered DOC, Fe and a number of insoluble trivalent and tetravalent hydrolysates. As a result, one may expect significantly more pronounced colloidal coagulation in the estuarine zone during the spring flood in May compared to winter and summer baseflow. On the annual scale, consideration the spring flood period would certainly increase the flux of LMW fraction of OC and TE to the Arctic Ocean. Given highly pronounced Arctic summer insolation, low water temperatures and low phytoplankton activity in May, the relative order of the processes controlling the production of $\text{LMW}_{<1\text{ kDa}}$ fraction may be as follows: photodestruction > heterotrophic mineralization > exometabolite production. On the other hand, due to

significantly higher discharge in spring, the water residence time in the estuary becomes shorter and thus the time necessary for colloidal coagulation might be insufficient to ensure the non-conservative behavior of insoluble elements. Thus, Fe-rich HMW colloids may travel further seaward, north of Mud'yug Island (Fig. 1) due to significantly higher freshwater zone influence.

5 Conclusions

Systematic sampling of the Severnaya Dvina River mixing zone within the White Sea (European subarctic) revealed several families of major and trace elements, depending on their conservative or non-conservative behavior, which was in accordance with previous studies of both temperate and tropical estuaries. The *in situ* dialysis of estuarine water performed for the first time with membranes having different pore sizes (1, 15, and 50 kDa) allowed the characterization of the complexity of the colloidal size distribution and allowed us to trace the transformation of HMW into LMW fractions along the estuarine profile during different seasons. The coagulation of HMW_{50 kDa–0.22 μm} colloids at the beginning (< 5 %) of the mixing zone is especially pronounced for the insoluble TE bound to ferric colloids in the river water (Al, Ti, Zr, Hf, Th, REEs, Pb, Mn (in winter), U) and more rarely observed for divalent metals initially present as LMW organic complexes (Cu, Ni) or oxyanions (As, Sb, V, Cr). At the same time, the enrichment of the estuarine surface water in the LMW_{< 1 kDa} organic fraction seaward for most insoluble elements, such as Fe, is a novel and unexpected finding. Therefore, the LMW_{< 1 kDa} fraction of DOC, Fe, Al, and other insoluble trace metals is accumulated in the estuary, despite significant coagulation of the colloidal fraction. The climate warming at high latitudes is likely to accentuate the enrichment of the coastal waters in the LMW_{< 1 kDa} fraction by decreasing the degree of colloidal coagulation in the estuarine mixing zone.

Supplementary material related to this article is available online at <http://www.ocean-sci.net/10/107/2014/os-10-107-2014-supplement.pdf>.

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References

- Alfaro-De la Torre, M. C., Beaulieu, P. Y., and Tessier, A. T.: *In situ* measurement of trace metals in lakewater using the dialysis and DGT techniques, *Anal. Chim. Acta*, 418, 53–68, 2000.
- Allard, T., Menguy, N., Salomon, J., Calligaro, T., Weber, T., Calas, G., and Benedetti, M. F.: Revealing forms of iron in river-borne material from major tropical rivers of the Amazon Basin (Brazil), *Geochim. Cosmochim. Ac.*, 68, 3079–3094, 2004.
- Amon, R. M. W. and Benner, R.: Photochemical and microbial consumption of dissolved organic carbon and dissolved oxygen in the Amazon River System, *Geochim. Cosmochim. Ac.*, 60, 1783–1792, 1996.
- Amon, R. M. W., Rinehart, A. J., Duan, S., Louchouart, P., Prokushkin, A., Guggenberger, G., Bauch, D., Stedmon, C., Raymond, P. A., Holmes, R. M., McClelland, J. W., Peterson, B. J., Walker, S. A., and Zhulidov, A. V.: Dissolved organic matter sources in large Arctic rivers, *Geochim. Cosmochim. Ac.*, 94, 217–237, 2012.
- Andersson, P. S., Porcelli, D., Wasserburg, G. J., and Ingri, J.: Particle transport of ²³⁴U/²³⁸U in the Kalix river and in the Baltic Sea, *Geochim. Cosmochim. Ac.* 62, 385–392, 1998.
- Andersson, P. S., Porcelli, D., Gustafsson, O., Ingri, J., and Wasserburg, G. J.: The importance of colloids for the behavior of uranium isotopes in the low-salinity zone of a stable estuary, *Geochim. Cosmochim. Ac.*, 65, 13–25, 2001.
- Anesio, A. M. and Graneli, W.: Photochemical mineralization of dissolved organic carbon in lakes of different pH and humic content, *Archiv für Hydrobiologie*, 160, 105–116, 2004.
- Artemyev, V. E. and Romankevich, E. A.: Seasonal variations in the transport of organic matter in North Dvina Estuary, *Mitt. Geol.-Paläont. Inst. Univ. Hamburg, SCOPE/UNEP Sonderband Heft*, 66, 177–184, 1988.
- Ask, J., Karlsson, J., Persson, L., Ask, P., Byström, P., and Jansson, M.: Whole-lake estimates of carbon flux through algae and bacteria in benthic and pelagic habitats of clear-water lakes, *Ecology*, 90, 1923–1932, 2008.
- Åström, M. E., Österholm, P., Gustafsson, J. P., Nystrand, M., Pelto, P., Nordmyr, L., and Boman, A.: Attenuation of rare earth elements in a boreal estuary, *Geochim. Cosmochim. Ac.*, 96, 105–119, 2012.
- Audry, S., Blanc, G., Schäfer, J., Chaillou, G., and Robert, S.: Early diagenesis of trace metals (Cd, Cu, Co, Ni, U, Mo, and V) in the freshwater reaches of a macrotidal estuary, *Geochim. Cosmochim. Ac.*, 70, 2264–2282, 2006.
- Audry, S., Blanc, G., Schäfer, J., and Robert, S.: Effect of estuarine sediment resuspension on early diagenesis, sulfide oxidation and dissolved molybdenum and uranium distribution in the Gironde estuary, France, *Chem. Geol.*, 238, 149–167, 2007.
- Bagard, M. L., Chabaux, F., Pokrovsky, O. S., Prokushkin, A. S., Viers, J., Dupré, B., and Stille, P.: Seasonal variability of element fluxes in two Central Siberian rivers draining high latitude per-

- mafrost dominated areas, *Geochim. Cosmochim. Ac.*, 75, 3335–3357, 2011.
- Barbeau, K., Rue, E., Bruland, K., and Butler, A.: Photochemical cycling of iron in the surface ocean mediated by microbial iron (III)-binding ligands, *Nature*, 413, 409–413, 2001.
- Bau, M.: Scavenging of dissolved yttrium and rare earths by precipitating iron oxyhydroxide: Experimental evidence for Ce oxidation, Y-Ho fractionation, and lanthanide tetrad effect, *Geochim. Cosmochim. Ac.*, 63, 67–77, 1999.
- Beck, M., Dellwig, O., Fischer, S., Schnetger, B., and Brumsack, H.-J.: Trace metal geochemistry of organic-rich watercourses draining the NW German coast, *Estuar. Coast. Shelf S.*, 104–105, 66–79, 2012.
- Benoit, G., Oktay-Marshall, S. D., Cantu II, A., Hood, E. M., Coleman, C. H., Corapcioglu, M. O., and Santschi, P. H.: Partitioning of Cu, Pb, Ag, Zn, Fe, Al, and Mn between filter-retained particles, colloids, and solution in six Texas estuaries, *Mar. Chem.*, 45, 307–336, 1994.
- Bertilsson, S. and Tranvik, L. J.: Photochemical transformation of dissolved organic matter in lakes, *Limnol. Oceanogr.*, 45, 753–62, 2000.
- Bianci, T. S.: *Biogeochemistry of Estuaries*, Oxford University Press, Oxford, United Kingdom, 706 pp., 2007.
- Bianci, T. S. and Allison, M. A.: Large-river delta-front estuaries as natural “recorders” of global environmental change, *P. Natl. Acad. Sci. USA*, 106, 8085–8092, 2009.
- Boughriet, A., Ouddane, B., Fischer, J. C., Wartel, M., and Leman, G.: Variability of dissolved Mn and Zn in the Seine estuary and chemical speciation of these metals in suspended matter, *Water Res.*, 26, 1359–1378, 1992.
- Boye, M., Nishioka, J., Croot, P., Laan, P., Timmermans, K. R., Strass, V. H., Takeda, S., and de Baar, H. J. W.: Significant portion of dissolved organic Fe complexes in fact is Fe colloids, *Mar. Chem.*, 122, 20–27, 2010.
- Boyle, E., Collier, R., Dengler, A. T., Edmond, J. M., Ng, A. C., and Stallard, R. F.: On the chemical mass-balance in estuaries, *Geochim. Cosmochim. Ac.*, 38, 1719–1728, 1974.
- Boyle, E., Edmond, J. M., and Sholkowitz, E. R.: The mechanism of iron removal in estuaries, *Geochim. Cosmochim. Ac.*, 41, 1313–1324, 1977.
- Breuer, E., Sañudo-Wilhelmy, S. A., and Aller, R. C.: Trace metals and dissolved organic carbon in an estuary with restricted river flow and a brown tide bloom, *Estuaries*, 22, 603–615, 1999.
- Dai, M. and Martin, J.: First data on trace metal level and behaviour in two major Arctic river-estuarine systems (Ob and Yenisey) and in the adjacent Kara Sea, Russia, *Earth Planet. Sc. Lett.*, 131, 127–141, 1995.
- Dai, M., Martin, J., and Cauwet, G.: The significant role of colloids in the transport and transformation of organic carbon and associated trace metals (Cd, Cu and Ni) in the Rhône delta (France), *Mar. Chem.*, 51, 159–175, 1995.
- Du Laing, G., Rinklebe, J., Vandecasteele, B., Meers, E., and Tack, F. M. G.: Trace metal behavior in estuarine and riverine floodplain soils and sediments: A review, *Sci. Total Environ.*, 407, 3972–3985, 2009.
- Elbaz-Poulichet, F., Garnier, J.-M., Guan, D. M., Martin, J.-M., and Thomas, A. J.: The conservative behaviour of trace metals (Cd, Cu, Ni and Pb) and As in the surface plume of stratified estuaries: example of the Rhône River (France), *Estuar. Coast. Shelf S.*, 42, 289–310, 1996.
- Elderfield, H., Upstill-Goddard, R., and Sholkovitz, E. R.: The rare earth elements in rivers, estuaries, and coastal seas and their significance to the composition of ocean waters, *Geochim. Cosmochim. Ac.*, 54, 971–991, 1990.
- Forsberg, J., Dahlqvist, R., Gelting-Nystrom, J., and Ingri, J.: Trace metal speciation in brackish water using diffusion gradients in thin films and ultrafiltration: comparison of techniques, *Environ. Sci. Technol.*, 40, 3901–3905, 2006.
- Fujii, M., Ito, H., Rose, A. L., Waite, D. T., and Omura, T.: Superoxide-mediated Fe(II) formation from organically complexed Fe(III) in coastal waters, *Geochim. Cosmochim. Ac.*, 72, 6079–6089, 2008a.
- Fujii, M., Ito, H., Rose, A. L., Waite, D. T., and Omura, T.: Transformation dynamics and reactivity of dissolved and colloidal iron in coastal waters, *Marine Chem.*, 110, 165–175, 2008b.
- Gerringa, L. J. A., Rijkenberg, M. J. A., Wolterbeek, H. Th., Verburg, T. G., Boye, M., and de Baar, H. J. W.: Kinetic study reveals weak Fe-binding ligand, which affects the solubility of Fe in the Scheldt estuary, *Mar. Chem.*, 103, 30–45, 2007.
- Gimpel, J., Zhang, H., Davison, W., and Edwards, A. C.: In situ metal speciation in lake surface waters using DGT, dialysis, and filtration, *Environ. Sci. Technol.*, 37, 138–146, 2003.
- Gobeil, C.: Biogeochemistry and chemical contamination in the St. Lawrence Estuary, *The Handbook of Environmental Chemistry*, Pt. H, 5, 121–147, doi:10.1007/698_5_023, 2006.
- Gordeev, V. V.: *Geochemistry of the river-sea system*, Moscow, Russia, 452 pp., 2012.
- Gordeev, V. V., Martin, J.-M., Sidorov, I. S., and Sidorova, M. V.: A reassessment of the Eurasian river input of water, sediment, major elements, and nutrients to the Arctic Ocean, *Am. J. Sci.*, 296, 664–691, 1996.
- Gordeev, V. V., Beeskov, B., and Rachold, V.: Geochemistry of the Ob and Yenisey estuaries: A comparative study, *Berichte zur Polar- und Meeresforschung*, AWI-Bremerhaven, Germany, 565, 235 pp., 2007.
- Greenamoyer, J. M. and Moran, S. B.: Investigation of Cd, Cu, Ni and ²³⁴Th in the colloidal size range in the Gulf of Maine, *Mar. Chem.*, 57, 217–226, 1997.
- Guieu, C. and Martin, J. M.: The level and fate of metals in the Danube River plume, *Estuar. Coast. Shelf S.*, 54, 501–512, 2002.
- Guieu, C., Huang, W. W., Martin, J.-M., and Yong, Y. Y.: Outflow of trace metals into the Laptev Sea by the Lena River, *Mar. Chem.*, 53, 255–267, 1996.
- Gustafsson, O., Widerlund, A., Andersson, P. S., Ingri, J., Roos, P., and Ledin, A.: Colloid dynamics and transport of major elements through a boreal river – brackish bay mixing zone, *Mar. Chem.*, 71, 1–21, 2000.
- Hamilton-Taylor, J., Postill, A. S., Tipping, E., and Harper, M. P.: Laboratory measurements and modelling of metal-humic interactions under estuarine conditions, *Geochim. Cosmochim. Ac.*, 66, 403–415, 2002.
- Holmes, R. M., McClelland, J. W., Peterson, B. J., Tank, S. E., Buliygina, E., Eglinton, T. I., Gordeev, V. V., Gurtovaya, T. Y., Raymond, P. A., Repeta, D. J., Staples, R., Striegl, R. G., Zhulidov, A. V., and Zimov, S. A.: Seasonal and annual fluxes of nutrients and organic matter from large rivers to the Arctic Ocean and sur-

- rounding seas, *Estuar. Coast.*, 35, 369–382, doi:10.1007/s12237-011-9386-6, 2012.
- Howell, K. A., Achterberg, E. P., Tappin, A. D., and Worsfold, P. J.: Colloidal metals in the Tamar Estuary and their influence on metal fractionation by membrane filtration, *Environ. Chem.*, 3, 199–207, 2006.
- Ilna, S. M., Poitrasson, F., Lapitskiy, S. A., Alekhin, Yu. V., Viers, J., and Pokrovsky, O. S.: Extreme iron isotope fractionation between colloids and particles of boreal and temperate organic-rich waters, *Geochim. Cosmochim. Ac.*, 101, 96–111, 2013a.
- Ilna, S. M., Viers, J., Mialle, S., Mavromatis, V., Brunet, P., Lapitskiy, S. A., Alekhin, Y. V., and Pokrovsky, O. S.: Stable (Cu, Mg) and radiogenic (Sr, Nd) isotope fractionation in colloids of boreal organic-rich waters, *Chem. Geol.*, 342, 63–75, 2013b.
- Ingri, J., Nordling, S., Larsson, J., Rönnegård, J., Nilsson, N., Rodushkin, I., Dahlqvist, R., Andersson, P., and Gustafsson, Ö.: Size distribution of colloidal trace metals and organic carbon during a coastal bloom in the Baltic Sea, *Mar. Chem.*, 91, 117–130, 2004.
- Ingri, J., Pekka, L., Dauvalter, V., Rodushkin, I., and Peinerud, E.: Manganese redox cycling in Lake Imandra: impact on nitrogen and the trace metal sediment record, *Biogeosciences Discuss.*, 8, 273–321, doi:10.5194/bg-8-273-2011, 2011.
- Jansson, M., Bergström, A. K., Blomqvist, P., and Drakare, S.: Allochthonous organic carbon and phytoplankton/bacterioplankton production relationship in lakes, *Ecology*, 81, 3250–3255, 2000.
- Jansson, M., Persson, L., De Roos, A. M., Jones, R. I., and Tranvik, L. J.: Terrestrial carbon and intraspecific size-variation shape lake ecosystems, *Trends Ecol. Evol.*, 22, 316–322, 2007.
- Jonsson, A., Meili, M., Bergström, A. K., and Jansson, M.: Whole-lake mineralization of allochthonous organic carbon in a large humic lake (Ortrasket, N. Sweden), *Limnol. Oceanogr.*, 46, 1691–700, 2001.
- Kattner, G., Lobbes, J., Fritznar, H. P., Engbrodt, R., and Lara, R. J.: Tracing dissolved organic substances and nutrients from the Lena River through Laptev Sea (Arctic), *Mar. Chem.*, 65, 25–39, 1999.
- Kelton, N., Molot, L. A., and Dillon, P. J.: Effect of ultraviolet and visible radiation on iron lability in boreal and artificial waters, *Aquat. Sci.*, 69, 86–95, 2007.
- Klinkhammer, G. P. and McManus, J.: Dissolved manganese in the Columbia River estuary: Production in the water column, *Geochim. Cosmochim. Ac.*, 65, 2835–2841, 2001.
- Koehler, H., Meon, B., Gordeev, V. V., Spitz, A., and Amon, R. M. W.: Dissolved organic matter (DOM) in the estuaries of Ob and Yenisei and the adjacent Kara-Sea, Russia, *Proceed. Marine Sci.*, 6, 281–309, 2003.
- Kopáček, J., Klementová, S., and Norton, S. A.: Photochemical production of ionic and particulate aluminium and iron in lakes, *Environ. Sci. Technol.*, 39, 3656–3662, 2006a.
- Kopáček, J., Marešova, M., Norton, S. A., Porcal, P., and Vesely, J.: Photochemical source of metals for sediments, *Environ. Sci. Technol.*, 40, 4455–4459, 2006b.
- Koukina, S. E., Calafat-Frau, A., Hummel, H., and Palerud, R.: Trace metals in suspended particulate matter and sediments from the Severnaya Dvina estuary, Russian Arctic, *Polar Res.*, 37, 249–256, 2001.
- Kozelka, P. B., Sanudo-Wilhelmy, S., Flegal, A. R., and Bruland, K. W.: Physico-chemical speciation of lead in South San Francisco Bay, *Estuar. Coast. Shelf S.*, 44, 649–658, 1997.
- Krachler, R., Jirsa, F., and Ayromlou, S.: Factors influencing the dissolved iron input by river water to the open ocean, *Biogeosciences*, 2, 311–315, doi:10.5194/bg-2-311-2005, 2005.
- Kraepiel, A. M. L., Chiffoleau, J.-F., Martin, J.-M., and Morel, F. M. M.: Geochemistry of trace metals in the Gironde estuary, *Geochim. Cosmochim. Ac.*, 61, 1421–1436, 1997.
- Kritzberg, E. S., Cole, J. J., Pace, M. L., Granéli, W., and Bade, D. L.: Autochthonous versus allochthonous carbon sources of bacteria: results from whole-lake ¹³C addition experiments, *Limnol. Oceanogr.*, 49, 588–596, 2004.
- Kukina, S. E., Sadovnikova, L. K., Kalafat, A., Hummel, H., and Regoli, F.: Distribution of metals in suspended matter and bottom sediments in the estuary of the Northern Dvina, *Oceanology*, 42, 218–227, 2002.
- Kuma, K., Nakabayashi, S., and Matsunaga, K.: Photoreduction of Fe(III) by hydroxycarboxylic acids in seawater, *Water Res.*, 29, 1559–1569, 1995.
- Kuma, K., Katsumoto, A., Nishioka, J., and Matsunaga, K.: Size-fractionated iron concentrations and Fe(III) hydroxide solubility in various coastal waters, *Estuar. Coast. Shelf S.*, 47, 275–283, 1998.
- Kuzyk, Z. A., MacDonald, R. W., Granskog, M. A., Scharien, R. K., Galley, R. J., Michel, C., Barber, D., and Stern, G.: Sea ice, hydrological, and biological processes in the Churchill River estuary region, Hudson Bay, *Estuar. Coast. Shelf S.*, 77, 369–384, 2008.
- Lawrence, M. G. and Kamber, B. S.: The behaviour of the rare earth elements during estuarine mixing-revisited, *Mar. Chem.*, 100, 147–161, 2006.
- Lisitsyn, A. P.: The marginal filter of the ocean, *Oceanology*, 34, 671–682, 1995.
- Liu, R., Lead, J. R., and Zhang, H.: Combining cross flow ultra-filtration and diffusion gradients in thin-films approaches to determine trace metal speciation in freshwaters, *Geochim. Cosmochim. Ac.*, 109, 14–26, 2013.
- Lofts, S., Tipping, E., and Hamilton-Taylor, J.: The chemical speciation of Fe(III) in freshwaters, *Aquat. Geochem.*, 14, 337–358, 2008.
- MacDonald, R. W. and Yu, Y.: The Mackenzie Estuary of the Arctic Ocean, *The Handbook of Environmental Chemistry*, Pt. H, 5, 91–120, doi:10.1007/698_5_027, 2006.
- McClelland, J. W., Holmes, R. M., Dunton, K. H., and MacDonald, R. W.: The Arctic Ocean estuary, *Estuar. Coast.*, 35, 353–368, 2012.
- McKenna, J. H.: DOC dynamics in a small temperate estuary: simultaneous addition and removal processes and implications on observed nonconservative behaviour, *Estuaries*, 27, 604–616, 2004.
- Moran, M. A. and Hodson, R. E.: Bacterial production on humic and nonhumic components of dissolved organic carbon, *Limnol. Oceanogr.*, 35, 1744–1757, 1990.
- Moran, M. A. and Zepp, R. G.: Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter, *Limnol. Oceanogr.*, 42, 1307–1316, 1997.
- Moran, M. A., Sheldon Jr., W. M., and Zepp, R. G.: Carbon loss and optical property changes during long-term photochemical and bi-

- ological degradation of estuarine dissolved organic matter, *Limnol. Oceanogr.*, 45, 1254–1264, 2000.
- Muller, F. L. L.: Colloid/Solution partitioning of metal-selective organic ligands, and its relevance to Cu, Pb and Cd cycling in the Firth of Clyde, *Estuar. Coast. Shelf S.*, 46, 419–437, 1998.
- Nolting, R. F., van Dalen, M., and Helder, W.: Distribution of trace and major elements in sediment and pore waters of the Lena Delta and Laptev Sea, *Mar. Chem.*, 53, 285–299, 1996.
- Österlund, H., Gelting, J., Nordblad, F., Baxter, D. C., and Ingri, J.: Copper and nickel in ultrafiltered brackish water: labile or non-labile?, *Mar. Chem.*, 132–133, 34–43, 2012.
- Pédrot, M., Dia, A., Davranche, M., Coz, M. B.-L., Henin, O., and Gruau, G.: Insights into colloid-mediated trace element release at the soil/water interface, *J. Colloid-Interf. Sci.*, 325, 187–197, 2008.
- Point, D., Monperrus, M., Tessier, E., Amouroux, D., Chauvaud, L., Thouzeau, G., Jean, F., Amice, E., Gall, J., Leynaert, A., Clavier, J., and Donard, O. F. X.: Biological control of trace metal and organometal benthic fluxes in a eutrophic lagoon (Thau Lagoon, Mediterranean Sea, France), *Estuar. Coast. Shelf S.*, 72, 457–471, 2007.
- Pokrovsky, O. and Schott, J.: Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia), *Chem. Geol.*, 190, 141–179, 2002.
- Pokrovsky, O. S. and Shirokova, L. S.: Diurnal variations of dissolved and colloidal organic carbon and trace metals in a boreal lake during summer bloom, *Water Res.*, 47, 922–932, 2013.
- Pokrovsky, O. S., Dupré, B., and Schott, J.: Fe-Al-organic colloids control of trace elements in peat soil solutions, *Aquat. Geochem.*, 11, 241–278, 2005.
- Pokrovsky, O. S., Schott, J., and Dupré, B.: Trace element fractionation and transport in boreal rivers and soil porewaters of permafrost-dominated basic terrain in Central Siberia, *Geochim. Cosmochim. Ac.*, 70, 3239–3260, 2006.
- Pokrovsky, O. S., Viers, J., Shirokova, L. S., Shevchenko, V. P., Filipov, A. S., and Dupré, B.: Dissolved, suspended, and colloidal fluxes of organic carbon, major and trace elements in Severnaya Dvina River and its tributary, *Chem. Geol.*, 273, 136–149, 2010.
- Pokrovsky, O. S., Shirokova, L. S., Kirpotin, S. N., Audry, S., Viers, J., and Dupré, B.: Effect of permafrost thawing on organic carbon and trace element colloidal speciation in the thermokarst lakes of western Siberia, *Biogeosciences*, 8, 565–583, doi:10.5194/bg-8-565-2011, 2011.
- Pokrovsky, O. S., Shirokova, L. S., Zabelina, S. A., Vorobieva, T. Y., Moreva, O. Yu., Chupakov, A., Shorina, N. V., Kokryatskaya, N. M., Andry, S., Viers, J., Zoutien, C., and Freydier, R.: Size fractionation of trace elements in a seasonally stratified boreal lake: control of organic matter and iron colloids, *Aquat. Geochem.*, 18, 115–139, 2012a.
- Pokrovsky, O. S., Viers, J., Dupré, B., Chabaux, F., Gaillardet, J., Audry, S., Prokushkin, A. S., Shirokova, L. S., Kirpotin, S. N., Lapitsky, S. A., and Shevchenko, V. P.: Biogeochemistry of carbon, major and trace elements in watersheds of northern Eurasia drained to the Arctic Ocean: The change of fluxes, sources and mechanisms under the climate warming prospective, *C.R. Geosci.*, 344, 663–677, 2012b.
- Pokrovsky, O. S., Shirokova, L. S., Kirpotin, S. N., Kulizhsky, S. P., and Vorobiev, S. N.: Impact of western Siberia heat wave 2012 on greenhouse gases and trace metal concentration in thaw lakes of discontinuous permafrost zone, *Biogeosciences*, 10, 5349–5365, doi:10.5194/bg-10-5349-2013, 2013.
- Porcelli, D., Andersson, P. S., Wasserburg, G. J., Ingri, J., and Baskaran, M.: The importance of colloids and mires for the transport of uranium isotopes through the Kalix River watershed and Baltic Sea, *Geochim. Cosmochim. Ac.*, 61, 4095–4113, 1997.
- Powell, R. T., Landing, W. M., and Bauer, J. E.: Colloidal trace metals, organic carbon and nitrogen in a southeastern U.S. estuary, *Mar. Chem.*, 55, 165–176, 1996.
- Raymond, P. A. and Bauer, J. E.: Bacterial consumption of DOC during transport through a temperate estuary, *Aquatic Microb. Ecol.*, 22, 1–12, 2000.
- Redfield, A. C., Ketchum, B. H., and Richards, F. A.: The influence of organisms on the composition of seawater, in: *The Sea. Ideas and Observation on Progress in the Study of the Seas*, 2, edited by: Hill, M. N., John Wiley, London, United Kingdom, 26–77, 1963.
- Reid, R., Live, D., Faulkner, D., and Bauer, J.: A siderophore from a marine bacterium with an exceptional ferric ion affinity constant, *Nature*, 366, 455–458, 1993.
- Savenko, A. V. and Shevchenko, V. P.: Seasonal variability of the distribution of dissolved forms of biogenic elements and alkalinity in the Northern Dvina mouth, *Water Resour.*, 32, 417–421, 2005.
- Savenko, A. V., Shevchenko, V. P., Novigatskii, A. N., and Efimova, L. V.: Effect of seasonal variability in the chemical composition of the riverine runoff on the distribution of dissolved forms of strontium, calcium, fluorine, and boron in the mouths of the Severnaya Dvina and Onega rivers, *Oceanology*, 43, 99–107, 2003.
- Sañudo-Wilhelmy, S. A., Rivera-Duarte, I., and Flegal, A. R.: Distribution of colloidal trace metals in the San Francisco Bay estuary, *Geochim. Cosmochim. Ac.*, 60, 4933–4944, 1996.
- Schroeder, D. C. and Lee, F. G.: Potential transformations of chromium in natural waters, *Water Air Soil Pollut.*, 4, 355–365, 1975.
- Shank, G. C., Skrabal, S. A., Whitehead, R. F., and Kieber, R. J.: Strong copper complexation in an organic-rich estuary: the importance of allochthonous dissolved organic matter, *Mar. Chem.*, 88, 21–39, 2004.
- Shevchenko, V. P., Lisitzin, A. P., Belyaev, N. A., Filipov, A. S., Golovkina, E. A., Ivanov, A. A., Klyuvitkin, A. A., Malinkovich, S. M., Novigatsky, A. N., Politova, N. V., Rudakova, V. N., Rusakov, V. Yu., and Sherbak, S. S.: Seasonality of suspended particulate matter distribution in the White Sea, *Berichte zur Polar- und Meeresforschung*, 482, 142–149, 2004.
- Shevchenko, V. P., Pokrovsky, O. S., Filipov, A. S., Lisitsyn, A. P., Bobrov, V. A., Bogunov, A. Yu., Zavernina, N. N., Zolotykh, E. O., Isaeva, A. B., Kokryatskaya, N. M., Korobov, V. B., Kravchishina, M. D., Novigatsky, A. N., and Politova, N. V.: On the elemental composition of suspended matter of the Severnaya Dvina river (White Sea region), *Doklady Earth Sciences*, 430, 228–234, 2010.
- Shiller, A. M.: The effect of recycling traps and upwelling on estuarine chemical flux estimates, *Geochim. Cosmochim. Ac.*, 60, 3177–3185, 1996.
- Shiller, A. M. and Boyle, E. A.: Trace elements in the Mississippi River Delta outflow region: Behavior at high discharge, *Geochim. Cosmochim. Ac.*, 55, 3241–3251, 1991.

- Shirokova, L. S., Pokrovsky, O. S., Moreva, O. Y., Chupakov, A. V., Zabelina, S. A., Klimov, S. I., Shorina, N. V., and Vorobieva, T. Ya.: Decrease of concentration and colloidal fraction of organic carbon and trace elements in response to the anomalously hot summer 2010 in a humic boreal lake, *Sci. Total Environ.*, 463–464, 78–90, 2013.
- Sholkovitz, E. R.: Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater, *Geochim. Cosmochim. Ac.*, 40, 831–845, 1976.
- Sholkovitz, E. R.: The flocculation of dissolved Fe, Mn, Al, Cu, Ni, Co and Cd during estuarine mixing, *Earth Planet. Sc. Lett.*, 41, 77–86, 1978.
- Sholkovitz, E. R.: The aquatic chemistry of rare earth elements in rivers and estuaries, *Aquat. Geochem.*, 1, 1–34, 1995.
- Sholkovitz, E. R. and Elderfield, H.: The cycling of dissolved rare-earth elements in Chesapeake Bay, *Global Biogeochem. Cy.*, 2, 157–176, 1988.
- Shulkin, V. M. and Bogdanova, N. N.: Mobilization of metals from riverine suspended matter in seawater, *Mar. Chem.*, 83, 157–167, 2003.
- Sigleo, A. C. and Helz, G. R.: Composition of estuarine colloidal material: major and trace elements, *Geochim. Cosmochim. Ac.*, 45, 2501–2509, 1981.
- Stecher III, H. A. and Kogut, M. B.: Rapid barium removal in the Delaware estuary, *Geochim. Cosmochim. Ac.*, 63, 1003–1012, 1999.
- Stolpe, B. and Hassellöv, M.: Changes in size distribution of fresh water nanoscale colloidal matter and associated elements on mixing with seawater, *Geochim. Cosmochim. Ac.*, 71, 3292–3301, 2007.
- Stolpe, B., Guo, L., Shiller, A. M., and Hassellöv, M.: Size and composition of colloidal organic matter and trace elements in the Mississippi River, Pearl River and the northern Gulf of Mexico, as characterized by flow field-flow fractionation, *Mar. Chem.*, 118, 119–128, 2010.
- Strady, E., Blanc, G., Schäfer, J., Coynel, A., and Dabrin, A.: Dissolved uranium, vanadium and molybdenum behaviours during contrasting freshwater discharges in the Gironde Estuary (SW France), *Estuar. Coast. Shelf S.*, 83, 550–560, 2009.
- Takata, H., Aono, T., Tagami, K., and Uchida, S.: Influence of dissolved organic matter on particle-water interactions for Co, Cu and Cd under estuarine conditions, *Estuar. Coast. Shelf S.*, 111, 75–83, 2012.
- Tranvik, L.: Availability of dissolved organic carbon for planktonic bacteria in oligotrophic lakes of differing humic content, *Microb. Ecol.*, 16, 311–322, 1988.
- Tranvik, L. J. and Jørgensen, N. O. G.: Colloidal and dissolved organic matter in lake water: Carbohydrate and amino acid composition, and ability to support bacterial growth, *Biogeochemistry*, 30, 77–97, 1995.
- Ussher, S. J., Achterberg, E. P., Sarthou, G., Laan, P., de Baar, H. J. W., and Worsfold, P. J.: Distribution of size fractionated dissolved iron in the Canary Basin, *Marine Environ. Res.*, 70, 46–55, 2010.
- Van den Berg, C., Merks, A., and Duursma, E.: Organic complexation and its control of the dissolved concentrations of copper and zinc in the Scheldt estuary, *Estuar. Coast. Shelf S.*, 24, 785–797, 1987.
- Van der Sloot, H. A., Hoede, D., Wijkstra, J., Duinker, J. C., and Nolting, R. F.: Anionic species of V, As, Se, Mo, Sb, Te and W in the Scheldt and Rhine estuaries and the Southern Bight (North Sea), *Estuar. Coast. Shelf S.*, 21, 633–651, 1985.
- Vasyukova, E. V., Pokrovsky, O. S., Viers, J., Oliva, P., Dupre, B., Martin, F., and Candaudap, F.: Trace elements in organic- and iron-rich surficial fluids of the boreal zone: Assessing colloidal forms via dialysis and ultrafiltration, *Geochim. Cosmochim. Ac.*, 74, 449–468, 2010.
- Vasyukova, E. V., Pokrovsky, O. S., Viers, J., and Dupré, B.: New operational method of testing colloid complexation with metals in natural waters, *Appl. Geochem.*, 27, 1226–1237, 2012.
- Waeles, M., Riso, R. D., Maguer, J.-F., and Le Corre, P.: Distribution and chemical speciation of dissolved cadmium and copper in the Loire estuary and North Biscay continental shelf, France, *Estuar. Coast. Shelf S.*, 59, 49–57, 2004.
- Waeles, M., Riso, R. D., and Le Corre, P.: Seasonal variations of dissolved and particulate copper species in estuarine waters, *Estuar. Coast. Shelf S.*, 62, 313–323, 2005a.
- Waeles, M., Riso, R. D., and Le Corre, P.: Seasonal variations of cadmium speciation in the Penzé estuary, NW France, *Estuar. Coast. Shelf S.*, 65, 143–152, 2005b.
- Waeles, M., Tanguy, V., Lespes, G., and Riso, R. D.: Behaviour of colloidal trace metals (Cu, Pb and Cd) in estuarine waters: An approach using frontal ultrafiltration (UF) and stripping chronopotentiometric methods (SCP), *Estuar. Coast. Shelf S.*, 80, 538–544, 2008.
- Wells, M. L., Kozelka, P. B., and Bruland, K. W.: The complexation of ‘dissolved’ Cu, Zn, Cd and Pb by soluble and colloidal organic matter in Narragansett Bay, RI, *Mar. Chem.*, 62, 203–217, 1998.
- Wells, M. L., Smith, G. J., and Bruland, K. W.: The distribution of colloidal and particulate bioactive metals in Narragansett Bay, RI, *Mar. Chem.*, 71, 143–163, 2000.
- Wen, L.-S., Santschi, P., Gill, G., and Paternostro, C.: Estuarine trace metal distributions in Galverston Bay: importance of colloidal forms in the speciation of the dissolved phase, *Mar. Chem.*, 63, 185–212, 1999.
- Wen, L.-S., Jiann, K.-T., and Santschi, P. H.: Physicochemical speciation of bioactive trace metals (Cd, Cu, Fe, Ni) in the oligotrophic South China Sea, *Mar. Chem.*, 101, 104–129, 2006.
- Wen, L.-S., Santschi, P. H., Warnken, K. W., Davison, W., Zhang, H., Li, H.-P., and Jiann, K.-T.: Molecular weight and chemical reactivity of dissolved trace metals (Cd, Cu, Ni) in surface waters from the Mississippi River to Gulf of Mexico, *Estuar. Coast. Shelf S.*, 92, 649–658, 2011.
- Wilkinson, K. J., Joz-Roland, A., and Buffle, J.: Different roles of pedogenic fulvic acids and aquagenic biopolymers on colloid aggregation and stability in freshwaters, *Limnol. Oceanogr.*, 42, 1714–1724, 1997.