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Transformation of organic carbon, trace element, and organo-mineral colloids in the mixing zone of the largest European Arctic river

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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 is 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 using three pore size cutoff (1, 10, and 50 kDa) using an in-situ dialysis procedure. Conventionally dissolved (< 0.22 µm) 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 of concentration seawards. Rather conservative behavior, but with much smaller changes in concentration (variation within ±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 (∼2–5 ‰, Ba, Mn) or intermediate (∼10–15 ‰, 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 $\mathrm{LMW}_{<1\,\mathrm{kDa}}$ 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 µm) pool as the salinity increases. Similarly, the relative proportion of colloidal (1 kDa–0.22 µm) 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 of 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 $HMW_{1\,kDa-0.22\,\mu m}$ portion by the $LMW_{<1\,kDa}$ 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, $LMW_{<1\,kDa}$ 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 vs. 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 a 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 in high latitudes is likely to intensify the production of $LMW_{<1\,kDa}$ 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 the geochemistry of trace elements 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). As a general scheme, 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), 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.

However, until now, there were only occasional studies concerning the arctic river estuaries, and these studies were normally 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 the full hydrological year 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 (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 ($\mathrm{LMW}_{<1\,\mathrm{kDa}}$) 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. Addressing these issues should help constrain the biogeochemical response of the arctic estuaries to on-going environmental changes, such as anthropogenic metal pollution and climate change.

2 Sampling and analyses

2.1 Study site

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.

2.2 Sampling and handling

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 the Supplement (ESM-1). These techniques are very similar to the methods used in our previous studies (Pokrovsky et al., 2006, 2012a; 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 to assess the proportion of colloidal forms operationally defined as the fraction of 1 kDa–0.22 µm.

Filtered and ultrafiltered solutions for the major cation and trace element analyses were acidified (pH 2) with ultrapure double-distilled HNO_3 and stored in HDPE bottles that had been previously washed with ultrapure 0.1 M HCl and rinsed with MilliQ water. The preparation of the bottles for sample storage was performed in a clean room. The samples for the DOC analyses were collected in sterile pyrolyzed Pyrex glass tubes. The MilliQ field blanks were collected and processed to monitor for any potential sample contamination introduced by our sampling and handling procedures. The organic carbon blanks of filtrates and ultrafiltrates never exceeded 0.1 mg L^{-1}, which is low for the organic-rich rivers sampled in this study (typically, 5 to 20 mg L^{-1} DOC). For all major and most trace elements, the concentrations in the blanks were below analytical detection limits ($\leq$ 0.1–1 ng L^{-1} for Cd, Ba, Y, Zr, Nb, REE, Hf, Pb, Th, U; 1 ng L^{-1} for Ga, Ge, Rb, Sr, Sb; ~10 ng L^{-1} for Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As). In several cases, however, clear contamination by Zn, Cu, Ni, and Pb was detected in the 15 kD and 50 kDa ultrafiltrates because these elements' concentrations in fractions this size were > 20 % higher than those in < 0.22 µm fraction. These samples were not included during the analysis of results.

2.3 Analyses

The concentration of aqueous silica was determined colorimetrically (molybdate blue method) with an uncertainty of 2 % using a Technicon automated analyzer. Alkalinity was measured via potentiometric titration with HCl to pH = 4.2 using the Gran method, with a detection limit of 10^{-5} M and an uncertainty of 2 %. The DOC was analyzed using a Carbon Total Analyzer (Shimadzu CSN) with an uncertainty better than 3 %. The major anion concentrations (Cl, SO_4) were measured using ion chromatography (HPLC, Dionex ICS 2000i) HPLC, with an uncertainty of 2 %. Calcium, magnesium, sodium, and potassium concentrations were determined using atomic absorption spectroscopy (AAS; Perkin Elmer 5100PC analyzer) with an uncertainty of 1–2 %. The trace elements (TE) were measured without preconcentration with an ICP-MS Agilent 7500 ce using both Ar and He modes to diminish the interference. Indium and rhenium were used as internal standards at concentrations of ~3 $\mu g\,L^{-1}$ and corrections for oxide and hydroxide ions were made for the REEs and the other trace elements (Aries et al., 2000). The typical uncertainty for elemental concentration measurement ranged from 5–10 % at 1–1000 $\mu g\,L^{-1}$ to 20–30 % at 0.001–0.1 $\mu g\,L^{-1}$. In the latter case, the high uncertainties stemmed from the significant dilution (factor of 20 to 100 depending on salinity) of the initial sample. For many samples of filtrates and dialysates collected at > 10 ‰ salinity with very low concentrations of TE (on the order of 0.001 $\mu g\,L^{-1}$, comparable with detection limits), such as Cd, Hf, Ge, Cs, Ga, and W, the minimal estimated uncertainty was 30 %. During the ICP-MS analyses, the international geostandards SLRS-4 and SLRS-5 (Riverine Water References Material for Trace Metals certified by the National Research Council of Canada) and 15 ‰ estuarine standard SLEW-3 were measured after each 20 samples to assess the validity and reproducibility of the analyses. Good agreement between our replicated measurements of SLRS-4 and the certified values (e.g., Yeghicheyan et al., 2001) was obtained (relative difference < 10 %) except for B and P (30 %). All certified major (Ca, Mg, K, Na, Si) and trace element (Al, As, B, Ba, Co, Cr, Cu, Fe, Ga, Li, Mn, Mo, Ni, Pb, all REEs, Sb, Sr, Th, Ti, U, V, Zn) concentrations of the SLRS-5 standard (e.g., Heimburger et al., 2012) and the measured concentrations agreed with an uncertainty of 10–20 %. The agreement for Cd, Cs and Hf was between 30 and 50 %. For several dialysates with very low TE concentrations, an automated desolvator was used to decrease the detection limit by a factor of five. For the SLEW-3 estuarine standard, the agreement between the measured and certified values was within 20 % for As, Cr, Cu, Mo, Ni, V, Mn and U. The agreement for Cd was only 30 %, whereas strong dilution of SLEW-3 could not facilitate the quantification of Pb, Zn, Fe and Co using the Agilent 7500 ce. While for As, Cd, Cr, Co, Cu, Mo, Ni, U and V the concentration in SLEW-3 and in the Severnaya Dvina estuary at ∼15 ‰ salinity are comparable within 30–50 %, the concentrations of Mn, Fe, Pb and Zn are 10–100 times higher in the Severnaya Dvina site relative to SLEW-3. As a result, one cannot judge the validity of our measurements of Fe, Pb and Zn based on the analysis of a strongly diluted SLEW-3 standard. On a related note, verification of the analysis of trivalent and tetravalent insoluble hydrolyzates (Ti, Zr, Hf, Th, Ga, REEs, etc) could not be performed because these elements are not certified in a SLEW standard. However, a particular feature of the organic-rich Severnaya Dvina River made the analysis of these and other insoluble trace components, such as Fe and Al, possible, even after very strong dilution. Essentially, the colloidal transport of TE in this river is responsible for the high concentrations of insoluble trace components in the freshwater zone; for example, average Al, Ti, Fe, Zr, and La concentrations (Pokrovsky et al., 2010) are a factor of 4, 5, 6, and 10 higher than those of the world river average, respectively (Gaillardet et al., 2003).

In addition to using the Agilent 7500ce, the samples were analyzed with an Element XR ICP MS. The dilution factor of the estuarine samples ranged from 10 to 500 depending on the salinity. The instrument was usually operated in low or medium resolution mode to allow adequate peak separation, even in the presence of 50–100 mg L^{-1} of total seawater salts, particularly for ^{56}Fe and CaO, as well as for other intermediate and heavy elements. Using this ICP-MS instrument greatly increased the detection limits of a number of elements and improved the precision of the analyses while avoiding interference. The uncertainty of the Element XR analysis was ≤ 5 %, while its detection limit was a factor of 100 lower than the traditional (Agilent) instrument. The Element XR operated in three modes depending on the elements measured: low resolution for B, Rb, Sr, Zr, Mo, Cd, Sb, Cs, Ba, REEs, Hf, W, Pb, Th, U; medium resolution for Na, Mg, Al, Si, P, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Sr, and high resolution for K and As.

For both ICP MS instruments, the internal uncertainties of the TE analysis in samples within the dialysis and filtration series (1 kDa, 15 kDa, 50 kDa, and 0.22 µm at a given salinity) are much smaller than the external uncertainties due to the uniform effect of background dissolved components on interference and signal stability within the series of dialysis and ultrafiltration, which have very similar concentrations of major seawater ions present in the form of < 1 kDa ions and inorganic complexes. Therefore, the fine (< 10 %) differences in the insoluble (colloidal) TE concentrations between the LMW fractions and colloids within a dialysis UF^{-1} series could be adequately detected by ICP MS, even at high ionic charges (300–500 $\mathrm{mg\,L^{-1}}$) or/and after significant dilution of samples.

In the range of low salinities (0–5 ‰), the agreement between the two ICP MS methods was within 10 %. In the range of intermediate (5 to 15 ‰) and high (15–25 ‰) salinities, the typical agreement between two instruments was within 20 %; however, many heavy elements were below the detection limit of the Agilent 7500 ce and therefore, the results from the Element XR were used primarily for this salinity range. Some heavy elements, including HREE, Th, and Hf, could not be measured in the dialysates due to detection limit restrictions.

Finally, half of the samples measured by both ICP MS instruments were analyzed for dissolved Fe using graphite furnace AAS. This technique is much less susceptible to interference from salt ions because several calibrations have been performed in seawater solutions diluted to different degrees to match the estuarine salinity profile. The typical uncertainty of the Fe analysis performed by GF AAS, which had a detection limit of 2 $\mathrm{\mu g\,L^{-1}}$, was 5 % in the low salinity range and 10 % within the 5–25 ‰ salinity range.

3 Results

3.1 Methodology of dialysis procedure

Although the methodological aspects of the in-situ dialysis have been thoroughly addressed concerning freshwater objects (Vasyukova et al., 2010; Pokrovsky et al., 2011, 2012a, b; Shirokova et al., 2013), in this study it was used for the first time along a salinity gradient. To compare the rates of dialysis equilibrium attainment in the saline vs. the freshwater zone, several dialysis bags (20 mL volume) were placed in large (approx. 20 L) volumes of river water and 6 ‰ estuarine water; these bags were sampled regularly over a period of two days. Figure 2 presents examples of the concentrations of OC and TE inside the dialysis bag (1 kDa) as a function of elapsed time. Note that higher concentrations of $\text{LMW}_{<1\,\text{kDa}}$ fraction in saline waters were observed compared to the freshwater end member; this disparity is thoroughly discussed below (Sects. 3.3, 3.4 and 4.2). It can be observed from Fig. 2 that for many trace elements, a stable concentration is attained after 40 h of exposure. Therefore, during routine application of the dialysis procedure used in this study, an exposure time of 72 h was chosen, which was also in agreement with the previous kinetic studies in continental waters.

3.2 Elemental concentration as a function of salinity

Several groups of elements could be distinguished according to their concentration profiles, which were maintained throughout all of the studied seasons:

(1) Elements exhibiting a conservative behavior with a strong (up to a factor of 10) linear increase with salinity both in the $\text{LMW}_{<1\,\text{kDa}}$ and the total dissolved (< 0.22 µm) fractions: Li, B, Na, Mg, K, Ca, Sr, Rb, Cs, Mo and U, illustrated for B, Mo and U in Fig. 3a–c;

(2) Quasi-conservative behavior with a slight or moderate (≤ factor of 3) concentration increase with salinity: V, As, Cr, and Sb, illustrated for first two elements in Fig. 4a and b;

(3) Conservative behavior with strong (> factor of 3) decreases in concentration with the increase of salinity is observed for DOC, Si and Mn (in March), as illustrated in Fig. 5a–c;

(4) Conservative behavior with a weak (≤ factor of 2) concentration change or constant level over the full range of salinities, with relative variations within ±30 %: Ni, Cr, As, Co (in March), Cu, Zn, Ga, Ge, Y, heavy REEs (Gd-Yb), as illustrated in Fig. 6a–d for Ni, Zn, Cu and Cr;

(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. 7a–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. 8a, 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. 9): this ratio decreases by almost an order of magnitude from the freshwater to the seawater zone.

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

Most elements studied in Sect. 3.2 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 total dissolved and LMW$_{<1\,\mathrm{kDa}}$ 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. 10. The gradual decrease in colloidal OC with increasing salinity occured during March and November–December, but the concentration of colloids remained rather constant in the estuary during the summer. There was a sharp drop of 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. 11. This decrease from ca. 80–90 % of the colloidal fraction 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. 12a and d. In contrast, the decrease was much smaller for Cu and Ni (Fig. 12b 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 of the % colloids with salinity (Fig. 13), although this decrease was different across the different seasons and most pronounced for As and Cr (Fig. 13 b, c). The colloidal fraction of trivalent REEs 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. 14d). Taken together, the rather uniform distribution of the colloidal fraction vs. salinity during the different seasons shown in Figs. 10–14 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. 15). Despite the significant uncertainty that stems from the high dispersity of the data points across the

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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 to 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, DOC, 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.

3.4 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. 16, 17 and 18, respectively. For this illustration, we have chosen organic carbon, two 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$_{<1\,\mathrm{kDa}}$complexes (60 %) and largee 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$_{<1\,\mathrm{kDa}}$ forms with the appearance of a non-negligible fraction of small colloids (1–15 kDa) in saline environments. In March, the LMW$_{<1\,\mathrm{kDa}}$ progressively increases seaward, whereas the HMW$_{50\,\mathrm{kDa}-0.22\,\mu\mathrm{m}}$ colloidal fraction remains similar between the freshwater and the seawater end point (Fig. 18).

Al, Fe and other tri- and tetravalent insoluble elements mostly appeared as $\text{HMW}_{50\,\text{kDa}-0.22\,\mu\text{m}}$ colloids in the low-salinity zone; this fraction almost disappears (Al) or decreases significantly (Fe) in the high salinity samples whereas the $\text{LMW}_{<1\,\text{kDa}}$ fraction becomes dominant above 9.5 ‰ salinity, which was observed for November/December and July (Figs. 16 and 17). 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 $\text{HMW}_{50\,\text{kDa}-0.22\,\mu\text{m}}$ fraction achieves its maximum in November/December, and in March, the maximum is at 9.0 ± 0.5 ‰; for medium size fraction (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 vs. 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 in the major arctic estuaries is fairly well known (Kattner et al., 1999; Koehler et al., 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 $\text{LMW}_{<1\,\text{kDa}}$ 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 $\text{DOC}_{<0.22\,\mu\text{m}}$ on salinity. The preservation of this highly conservative behavior takes place during both during summer and the glacial season in the Severnaya Dvina estuary.

Other examples of the highly conservative behavior observed during the estuarine mixing in the Arctic are boron (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, U does appear in $\text{HMW}_{50\,\text{kDa}-0.22\,\mu\text{m}}$ colloids in the freshwater zone. 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 render it mainly to its truly dissolved form. The removal of dissolved U in the very low salinity zone by the Fe- and organo-rich colloids observed in the Severnaya Dvina River estuary (Fig. 14, 16a and 17) 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, Cr, demonstrate systematic concentration increases toward the seawater end member (Fig. 4a and 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. 4a, b. This drop can be linked to the coagulation of the majority of $\text{HMW}_{50\,\text{kDa}-0.22\,\mu\text{m}}$ Fe colloids at the beginning of the mixing zone (Fig. 15, 16) because these colloids contain significant amount of oxyanions.

Interestingly, Si presents quite conservative behavior, with seawater end member being equal to 900±100 $\mu g\,L^{-1}$ during all seasons and riverine component ranging from 1800 to 5100 $\mu g\,L^{-1}$. However, the mixing line remains conservative during all three studied seasons (Fig. 5b), in accordance with numerous previous observations (i.e., Boyle et al., 1974) in 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, trivalent (REEs) and tetravalent (Ti, Zr, Hf, Th) hydrolysates is pronounced mostly at the very beginning of the estuarine mixing because these elements normally appear as large-size colloids that are quite unstable in aqueous solution with an elevated ionic strength, as confirmed by numerous observations on the flocculation and removal of colloidal material with increasing salinity in the estuaries (Sholkowitz, 1976, 1978; Sigleo and Helz, 1981). The decrease of the proportion of colloidal Fe with the concomitant increase in salinity is well established from size-fractionation techniques (Kuma et al., 1998; Sanudo-Wilhelmy et al., 1996; Stolpe and Hassellöv, 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; Pokrovsky et al., 2010, 2012b). The decrease in the La/Yb ratio in the $< 0.22\,\mu$m fraction with rising salinity (Fig. 9) may reflect the replacement of the Fe-rich colloids, binding LREE via surface adsorption or incorporation, by 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 toward mineral and colloidal surfaces, such as HMW organo-ferric colloids, and HREE to soluble organic ligands such, as $\text{LMW}_{<1\,\text{kDa}}$ 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, 1994 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).

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 toward 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. 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 because the RSM concentration in March is a factor of 2 to 3 lower than that what 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's 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 th concentration observed at low (0–5 ‰) salinity ranges that follow the order of March > November/December > July (Fig. 5c). 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 concentration at moderate (Cd, Pb) and low (Ba) salinities, 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 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 (Waeles et al., 2004) because the seawater Ca^{2+} replaces the Cd^{2+} in the iron/manganese oxide-associated fraction (Waeles 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 $LMW_{<1\,kDa}$ fraction, 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), 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 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 subarctic rivers such as Mezen and Pechora (Kukina et al., 2002).

4.2 Increase of the proportion of $LMW_{<1\,kDa}$ of many trace elements and metal micronutrients during estuarine mixing

An important dimension of TE geochemistry in the mixing zone was achieved because of the new dialysis procedure that was applied for the first time on a wide range of trace elements during this study. 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 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 that 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$_{<1\,\mathrm{kDa}}$ fraction in July 2012 and 2010 at approximately 5 ‰ salinity; otherwise, it exhibits a rather flat concentration pattern along the estuary. No loss of this fraction occurs; rather there is some gain in the LMW$_{<1\,\mathrm{kDa}}$ fraction at ca. 2 ‰ salinity due to the autochthonous process of OC transformation 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 that 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$_{<1\,\mathrm{kDa}}$ in the Severnaya Dvina River estuary is much stronger and pronounced in July than in winter, 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 settings (cf. Amon and Benner, 1996; Bertilsson and Tranvik, 2000; Jonsson et al., 2001; Anesio and Graneli, 2004; Kopáček et al., 2005, 2006; Kelton et al., 2007), (ii) heterotrophic mineralization of DOM by aerobic bacterioplankton known for their effect on boreal lakes (cf. Tranvik, 1988; Tranvik and Jorgensen, 1995; Jansson et al., 2000, 2007; Kritzberg et al., 2004; Ask et al., 2008) and subtropical marshes (Moran and Hodson, 1990), 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 (authors' unpublished data); exometabolite production by gram-negative bacteria in the marine zone cannot be ruled out (Wells et al., 1998). Note that the production of the lower molecular weight species of OC, Fe and metals at higher salinities have been detected in the Trinity Estuary (Galveston Bay, Gulf of

Mexico) and suggested to be I nduced 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 and unexpected 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. 7b 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 ± 5 ‰ salinity as high as a factor of 5. The maximal increase was detected during the winter baseflow. 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., 2008). 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 process. The increase of LMW reactive Fe fractions at high salinities has been already observed in subtropical, organic-rich estuaries (Powell et al., 1996). The processes of heterotrophic mineralization of DOM are most pronounced during this period. Concurrently, the relative decrease of the 1 kDa −0.22 µm fraction, i.e., coagulation processes of Fe colloids, are more pronounced during summer, when compared to levels during the winter baseflow (Fig. 11). This result is consistent with the fact that both phytoplankton activity and photo degradation leading that to the production of $\text{LMW}_{<1\,\text{kDa}}$ fractions are much more efficient in summer than in winter. 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 appear as Fe-humic complexes or aggregates of Fe hydroxides and humic-Fe (Allard et al., 2004; Lofts et al., 2008; Liu et al., 2013).

The behavior of other the insoluble elements linked to organo-ferric colloids (Al, Ti, Zr, REEs), as well as As, Cr, Pb and U, 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 LMW$_{<1\,\mathrm{kDa}}$ 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, which might serve as transports for bio-available iron in the rivers and estuaries have not yet been identified (cf., Krachler et al., 2005).

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 much more gradual decrease in the colloidal forms during the winter period. 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 the seasonal variation of colloidal fraction. 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 der Berg et al., 1987; Muller, 1998; Waeles et al., 2005a; Wen et al., 2011). Strong Cu^{2+} binding to humic complexes across the full range of salinity was 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. 12), 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 phytoplankon exometabolites in the mixing zone.

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

A systematic decrease in the relative proportion of the colloidal fraction for almost all of the TE and OC in the saline waters compared to the low saline/freshwater zone (Fig. 15) reflects the processes of both physicochemically and biologically induced coagulation occurring in the mixing zone combined with the autochthonous production of LMW organic complexes of trace elements. The increase in the concentration of the $\mathrm{LMW}_{<1\,\mathrm{kDa}}$ 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 (10–30 Å in bacteria, 35–50 Å in plant cells, Carpita et al., 1979; Trias et al., 1992) and pores of the 1 kDa dialysis membranes (1–2 nm) are comparable. For example, studies concerning the Mississippi River plume demonstrated that certain organic complexes of Fe(III) escape the estuarine zone and make essential contributions to the fertility of the coastal waters (Rose and Waite, 2003; Powell and Wilson-Finelli, 2003). Because of their conservative or accumulative pattern in the $\mathrm{LMW}_{<1\,\mathrm{kDa}}$ fraction, the insoluble biologically inert elements are expected to be delivered to the ocean in larger concentrations compared to what one may expect from the conventionally dissolved (< 0.22 µm) concentration profile. Additionally, a number of metal micronutrients (Co, Ni, Mn, Zn...) should enrich the coastal zone with their potentially bioavailable fraction and therefore affect the primary productivity of the Arctic Ocean.

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

The most significant consequence of the discovered increase of the $LMW_{<1\,kDa}$ fraction of metals along the salinity gradient seems to be linked to the effect of climate change on element speciation in boreal and subarctic waters. Recently, based on the available time series of concentration and size fractionation results, we have demonstrated that an increase in the concentration and relative proportions of the $LMW_{<1\,kDa}$ fraction in the lake water was subject to rising temperatures (up to 10 °C above the average) linked to a 2 month heat wave during the summer in two subarctic regions (see Shirokova et al., 2013; Pokrovsky et al., 2013). This increase in the typical metal micronutrients that potentially limit the aquatic biota, such as Ni, Cr, Zn, Mn, Co and Fe, was as high as 2 to 6-fold in the thermokarst lakes in Western Siberia, which developed on the permafrost terrain (Pokrovsky et al., 2013), and 1.5 to 3-fold in boreal stratified humic lakes in the non-permafrost zone in the White Sea watershed (Shirokova et al., 2013). The on-going increase in the LMW metal organic complex concentration occurring in the surface waters on land will be further accentuated in the estuaries because this LMW pool not only passes through the mixing zone without coagulation but also may lead to an increase in concentration of some potentially limiting micronutrients, such as Fe, Mn, V, relative to the freshwater end member. 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 to the atmosphere. However, distinguishing quantitatively between these two processes is not yet possible.

Another foreseen indirect possibility of the consequences of global warming on the TE flux transformation in the Arctic Ocean estuaries is the analysis of seasonal variations in the degree of colloid coagulation in the mixing zone. For organic carbon, the smallest proportion of colloids (1 kDa–0.22 µm) is observed during summer across the entire the salinity zone, whereas both the early (November–December) and late winter (March) fractions vary quite similarly. The insoluble elements (Al, Fe, Zr, REEs) and divalent metals (Co, Ni, Cu, Pb) follow this scheme, therefore suggesting that (i) warmer or ice-free winters (November/December vs. March) should not appreciably affect the size fractionation of most metals in the estuary and (ii) the heating of the surface water and extension of the active (vegetative) ice-free period should certainly decrease the proportion of colloids vs. "truly" dissolved components of the $LMW_{<1\,kDa}$ fraction.

In contrast, Mn may potentially limit phytoplankton bloom in freshwater (cf., Pokrovsky and Shirokova, 2013 and references therein) and therefore exhibits the highest proportion of colloids during summer, followed by early winter and late winter across the full range of salinities. For this element, the intensified processes of photodegradation in warmer waters and the longer ice-free period may actually decrease its ability to travel through the estuarine mixing zone.

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.

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 HMW50 kDa–0.22 µm colloids in 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 in high latitudes is likely to accentuate the enrichment of the surface 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-discuss.net/10/1707/2013/osd-10-1707-2013-supplement.pdf.

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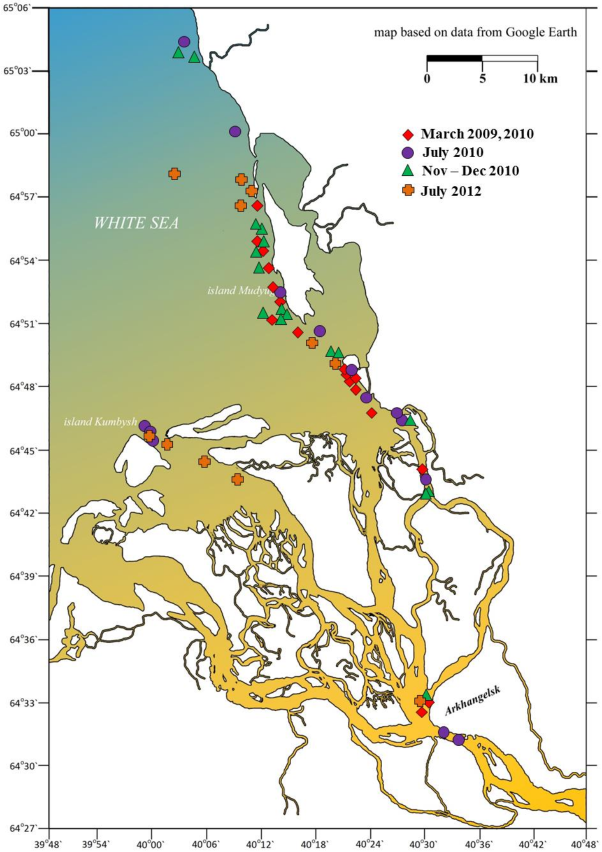

Fig. 1. Schematic map of sampling sites during different seasons. Diamonds, March 2010, 2009; Circles, July 2010, 2012; Triangles, November–December 2011.

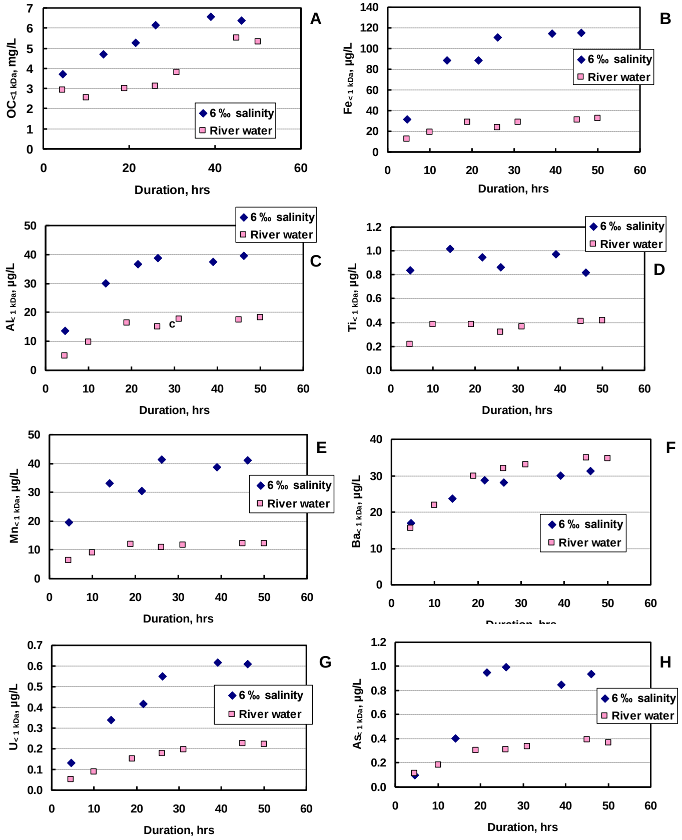

Fig. 2. Concentration of LMW$_{<1\,\mathrm{kDa}}$ dialysable fraction as a fucntion of exposure time in freshwter and estuarine water experiments. In January 2010. Note significantly higher concentrations in estuarine zone, consistent with the increase of LMW fraction seawards (see Sects. 3.3 and 4.2 below).

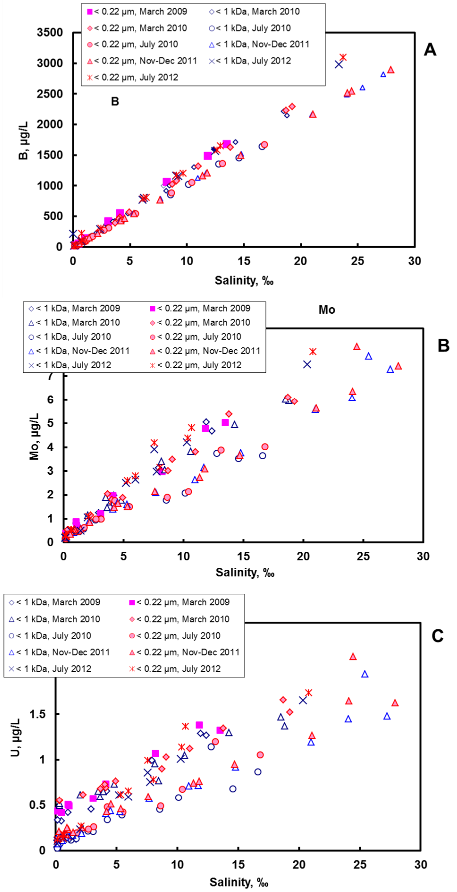

Fig. 3. Boron **(A)**, molybdenum **(B)** and uranium **(C)** concentrations in the estuary.

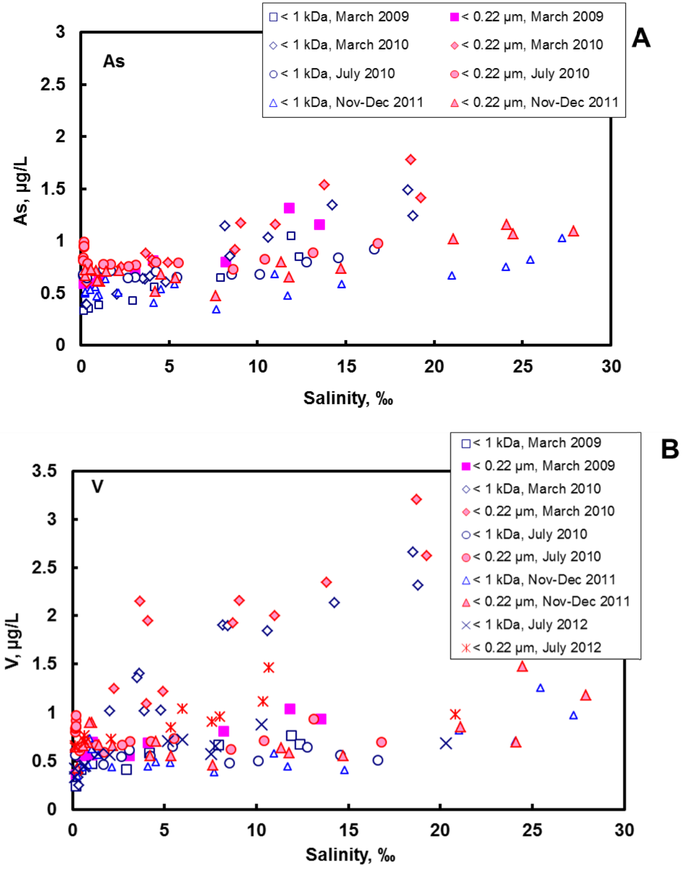

Fig. 4. Arsenic **(A)** and vanadium **(B)** concentrations in the estuary.

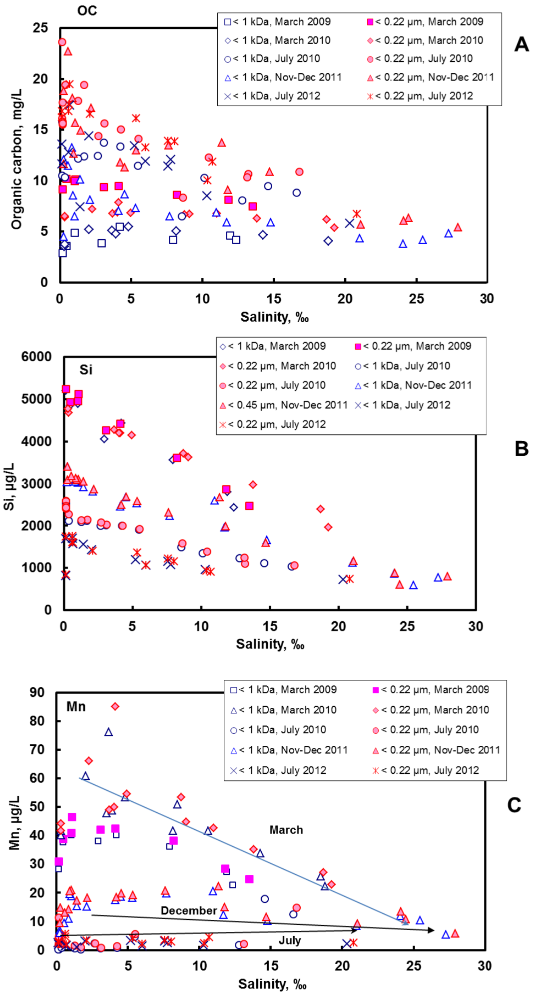

Fig. 5. Organic carbon **(A)**, Si **(B)** and Mn **(C)** concentrations as a function of salinity.

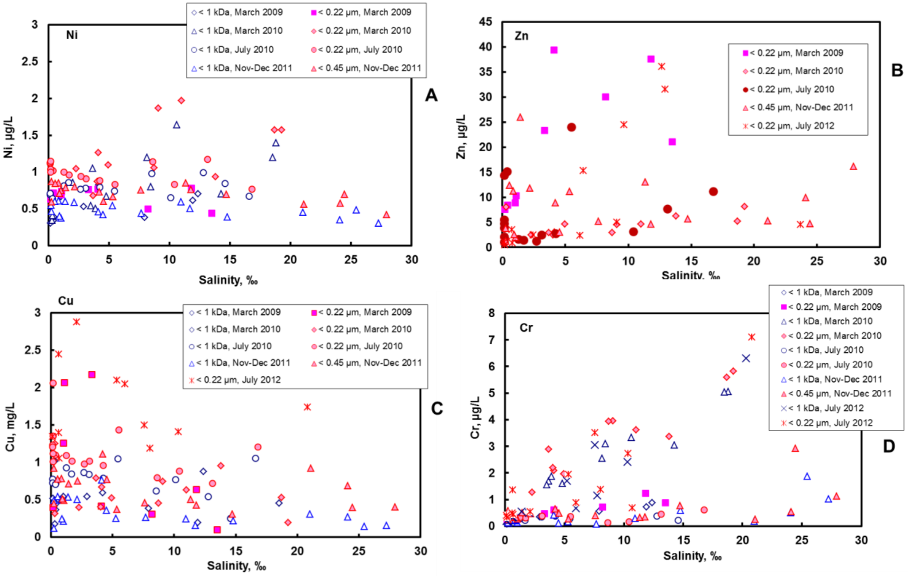

Fig. 6. Ni **(A)**, Zn **(B)**, Cu **(C)** and Cr **(D)** concentrations as a function of salinity.

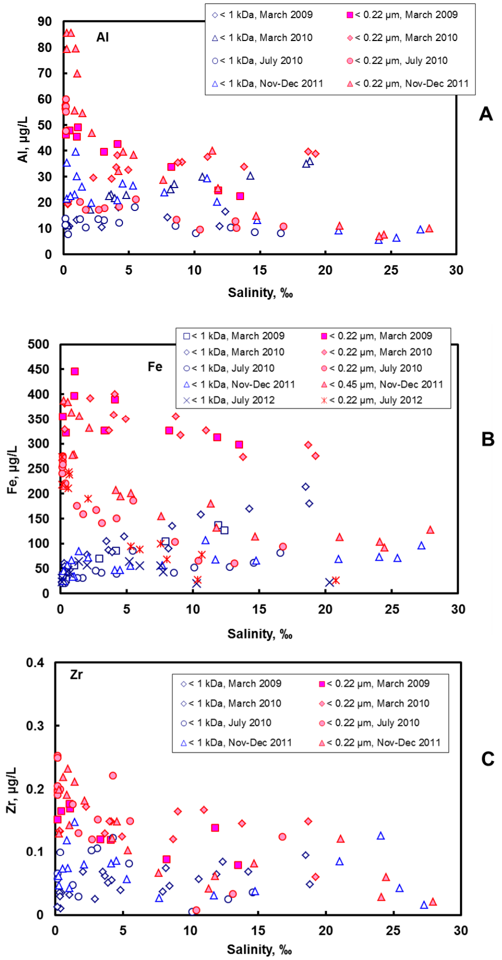

Fig. 7. Al **(A)**, Fe **(B)** and Zr **(C)** concentration as a function of salinity in the estuary.

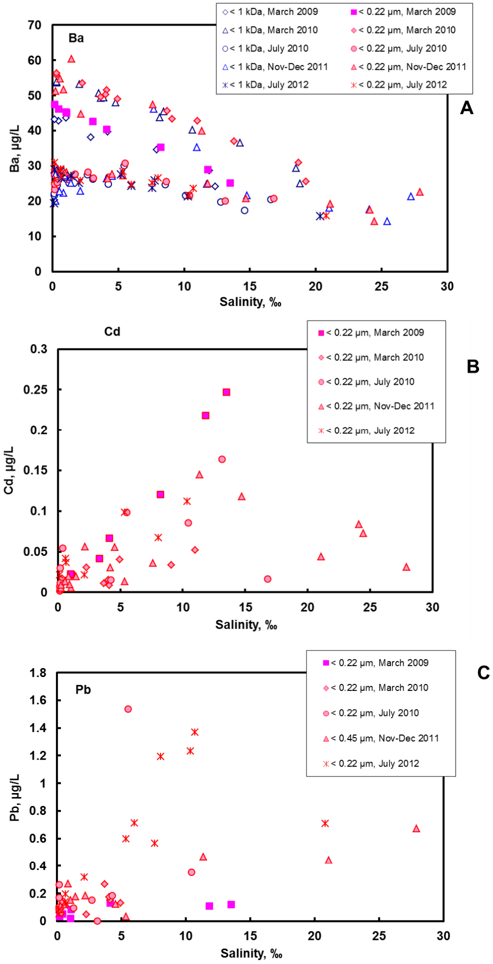

Fig. 8. Ba **(A)**, Cd **(B)** and Pb **(C)** concentration as a function of salinity in the estuary.

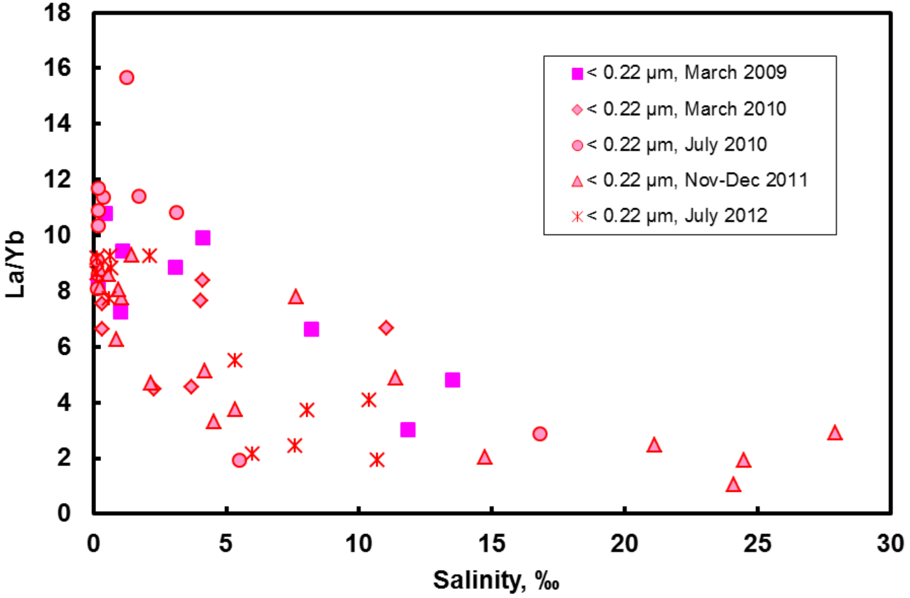

Fig. 9. Plot of La/Yb 0.22 µm fraction concentration ratio as a function of salinity during different seasons in the Severnaya Dvina estuary.

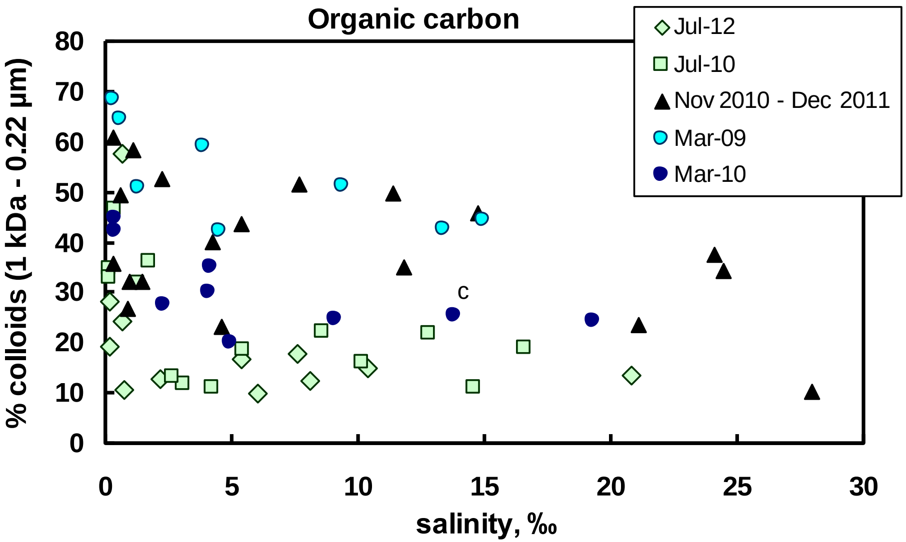

Fig. 10. Relative proportion of colloidal organic carbon as a function of salinity during different seasons in the Severnaya Dvina estuary.

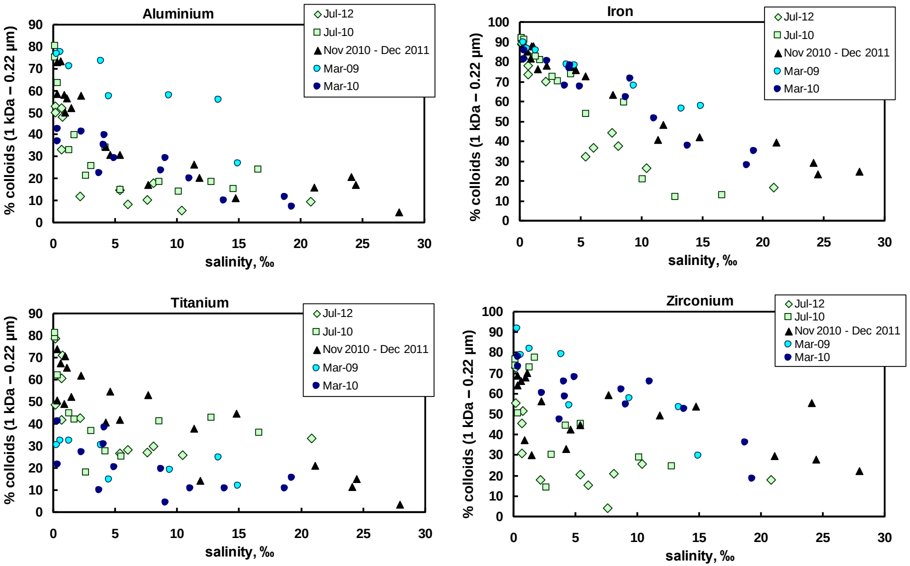

Fig. 11. Proportion of colloidal Al, Fe, Ti and Zr as a function of salinity during different seasons in the Severnaya Dvina estuary.

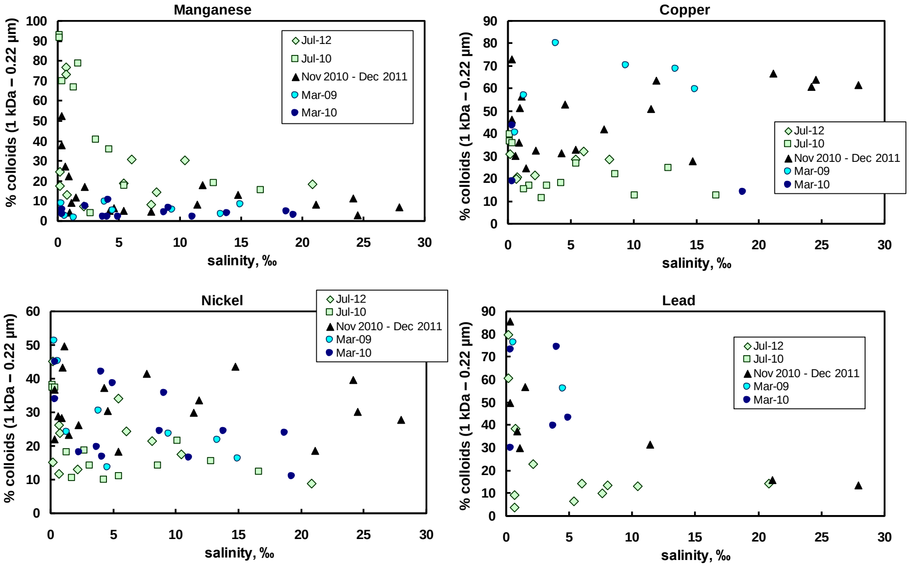

Fig. 12. Proportion of colloidal Mn, Cu, Ni and Pb as a function of salinity during different seasons in the Severnaya Dvina estuary.

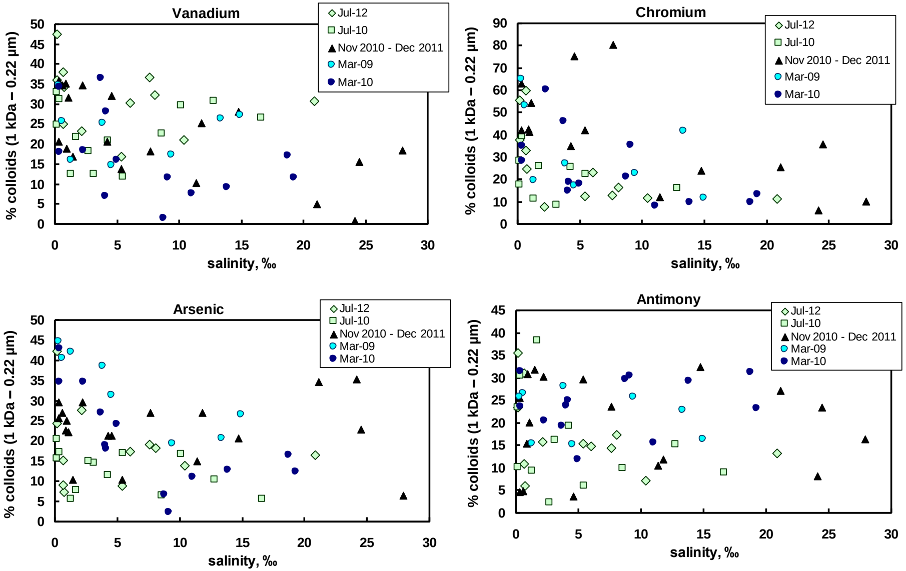

Fig. 13. Proportion of colloidal V, Cr, As and Sb as a function of salinity during different seasons in the Severnaya Dvina estuary.

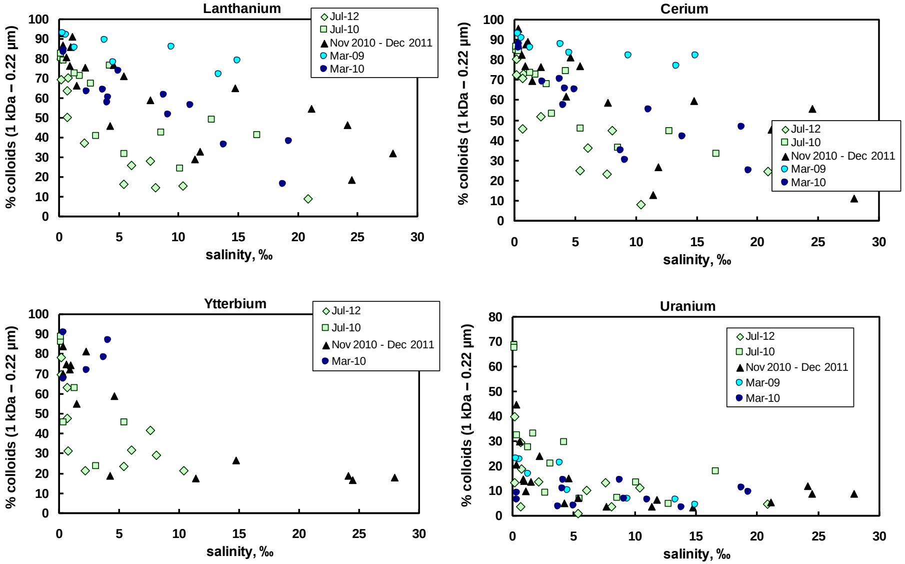

Fig. 14. Proportion of colloidal La, Ce, Yb, and U as a function of salinity during different seasons in the Severnaya Dvina estuary.

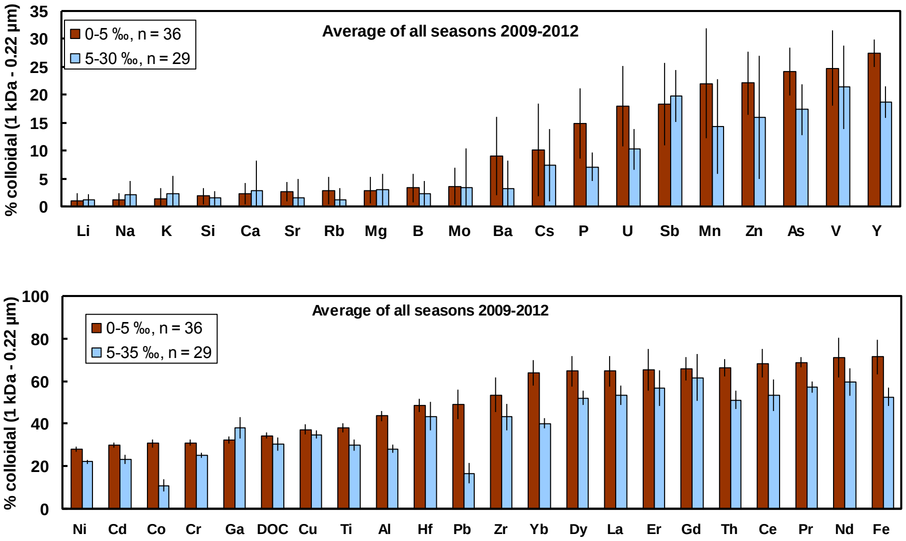

Fig. 15. A stack diagram of colloidal fractions of TE as an average of all seasons in low salinity and high salinity zones (dark and light columns, respectively).

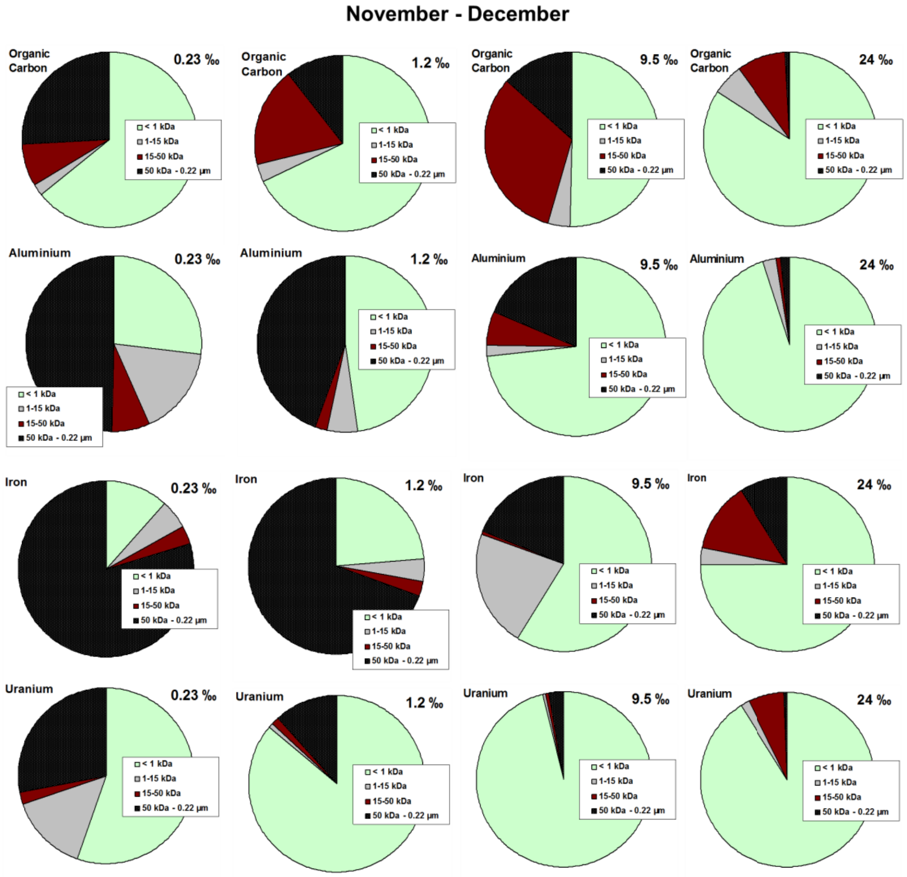

Fig. 16a. A diagram of relative fraction of colloidal material in the Severnaya Dvina River estuary during November–December ice formation period.

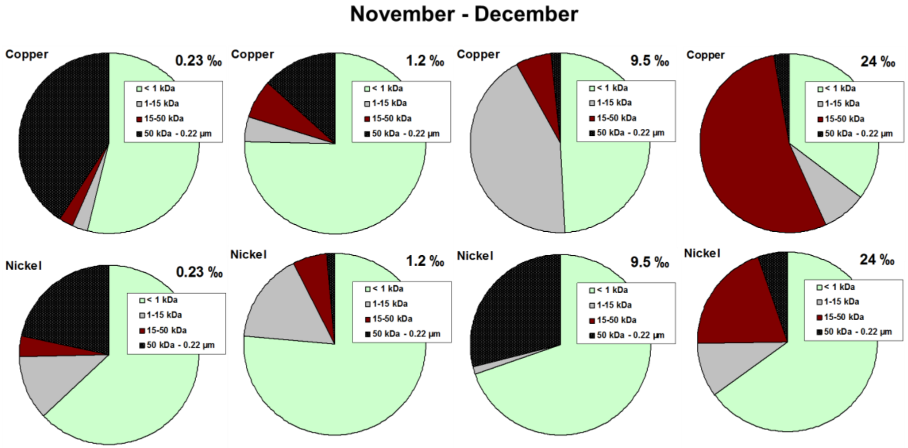

Fig. 16b. Continued.

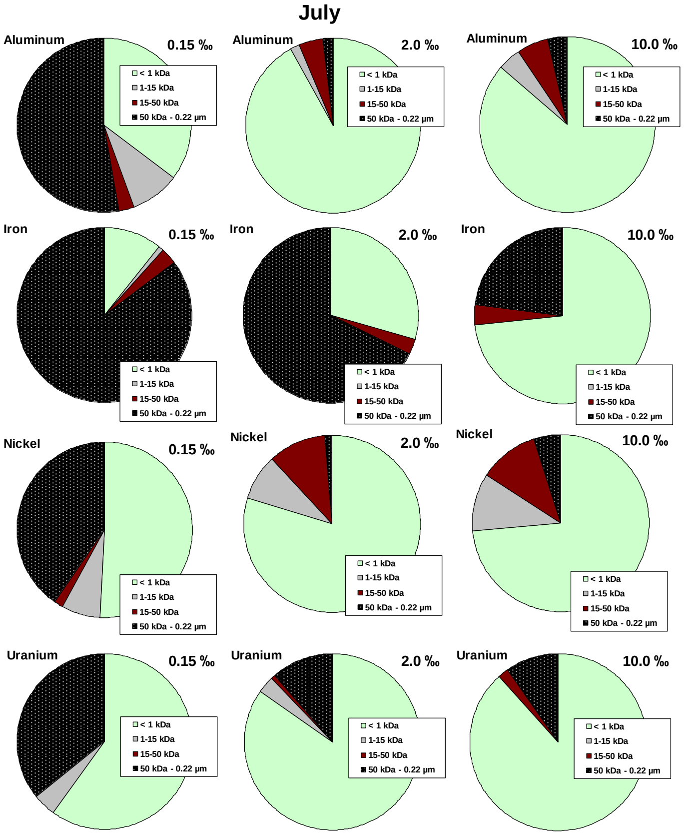

Fig. 17. A diagram of relative fraction of colloidal material in the Severnaya Dvina River estuary during July.

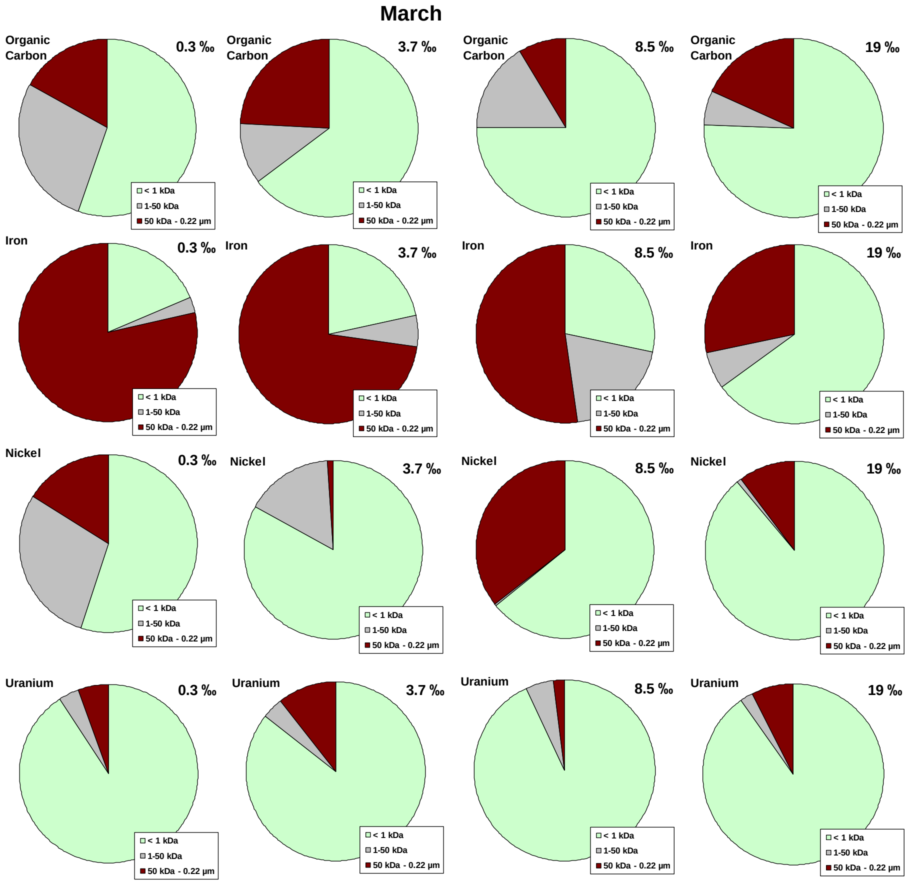

Fig. 18. A diagram of relative fraction of colloidal material in the Severnaya Dvina River estuary during March (winter baseflow).

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