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Interactive comment on “Transformation of organic carbon, trace element, and organo-mineral colloids in the mixing zone of the largest European Arctic river” by O. S. Pokrovsky et al.

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The reviewer correctly pointed out that an important finding of the study is that the concentration of LMW (<1 kDa) organic carbon and many trace elements increase with increasing salinity in the estuary. He/she further requires proving that this is not a method artefact. According to this reviewer, if the passage of LMW organic complexes through the membrane is influenced by electric double-layer (EDL) repulsion from the membrane, this repulsion should decrease with increasing salinity, which could increase the fraction of LMW organic complexes passing the membrane. This is very good point. Testing possible artifacts of dialysis procedure is discussed in previous papers

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of our group referenced in the present manuscript (Pokrovsky et al., 2005, 2011, 2012a; Vasyukova et al., 2010, 2012; Shirokova et al., 2013). The majority of these works were performed in the freshwater zone, within 1 ‰ of salinity. Concerning the increase of the electrostatic effects with the increase of salinity, we expect that this effect would be first visible for trace metals present in the form of negatively or positively charged ions (Mo, Rb, Cs. . .) most susceptible to electrostatic interactions. However, the concentrations of these elements in LMW(<1 kDa) fraction are not at all affected by salinity (see Table ESM-1, Fig. 3B, 15). As an approximation of neutral species similar to OC, one can consider Si and B those LMW< 1 kDa fractions also remain constant throughout the salinity profile (Fig. 2A, 4 B). Therefore, electrostatic repulsion is unlikely to control the distribution of LMW fraction between the external and internal solutions during dialysis. In case of EDL repulsion of organic and organo-mineral colloids, one would also expect similar to all components “artificial” increase of LMW fraction at higher salinities. Yet, this increase is observed mostly for Fe and it is much less visible for OC or other organically-bound trace elements (compare Figs. 4A, 6B, 6C). Another important argument against artifacts of EDL repulsion is the physical properties of the EDL around organic surfaces and organo-mineral colloids. Mineral and colloidal particles in seawater are often covered by carboxylate groups (Hunter, 1980), presumably similar to those of microorganisms. According to available electrophoretic measurements of algae and bacteria, the main decrease in electrophoretic mobilities due to EDL contraction occurs at ionic strengths between 0.001 and 0.1 M. This range of electrolyte concentration corresponds to 0.1 - 3-5 ‰. However, it can be seen from results presented in this study that the most important increase of LMW fraction occurs between 5 and 25 ‰ salinity (cf. Fig. 6 B). In this range, the contraction of the EDL is much smaller and thus the electrostatic effects should be much less than those at the beginning of estuarine mixing. Another line of evidences against dialysis artifacts is that, unlike ultrafiltration or DGT, dialysis is fully equilibrium processes, since steady-state distribution is achieved within 1-2 days (see Fig. ESM-1). As such, what we measure after steady-state concentration attainment (Fig. ESM-1) is an equilibrium distribution

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of dissolved or colloidal component between two compartments. The influence of electrostatic repulsion in this case will be much smaller than that for irreversible filtration or DGT. Note also that the adsorption of dissolved organic carbon and trace metals onto dialysis membrane itself is negligible as shown in our previous works. And finally, the LMW<1 kDa fraction is considered as an approximation of cell wall pores that control the passage of ions inside the cells. Since polysaccharidic nature of cell surfaces and cellulose dialysis membrane are similar, we think the conventional separation of truly dissolved and colloidal fractions performed in the present work can be used for evaluation the degree of biological availability of OC and related metals. In response to this comment, we added a big deal of discussion on possible dialysis artifacts in the Electronic Supporting Information ESM-1.

2. The reviewer correctly pointed out that it can be seen from Fig. 5a and Fig. 7b that the total dissolved concentrations of organic carbon and Fe also decrease more rapidly in July than in March. He/she suggested that the river contained a higher concentration of aquatic organic biopolymers in July than in March, enhancing the aggregation of colloids in July, and recommended pertinent paper (Wilkinson et al., 1997).

We thank the reviewer for providing us this useful supplementary explanation and we added it in the revised text (section 4.2). In addition, we would like to note that, in the freshwater temperate settings, the increase of LMW carbohydrates during summer time occurs (Wilkinson et al., 1997). Besides, bacterial consumption of DOC is known to increase with temperature increase in the estuary (Raymond and Bauer, 2000). Altogether, the increase of LMW production by photo- and bio-destruction of large-size allochthonous DOC, by the phytoplankton activity, and the increased input of the organics from the freshwater endmember, as suggested by reviewer, can be responsible for observed difference in LMW between July and March. We added pertinent explanations in the revised text.

We agree and corrected the minor remarks of this reviewer: p. 1719, L 9; p.1723, L11;

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We properly referenced the figures when discussing the results as suggested. We added a plot of Rb in Fig. 3 (now Fig. 2)

We fully agree with the remark of the reviewer that Cr show a mid-salinity maximum similar to Ni and this could be linked to the presence of Cr(III) complexed with humic substances, as well as desorption from the suspended material. We revised the text and provided a pertinent reference (Schroeder and Lee, 1975).

Page 1724, line 6: “Replacement” is not a suitable term to use, since both Fe-rich colloids and organic complexes are present in the river water, but the colloids are removed from the water at a higher rate by salinity-induced aggregation. We fully agree with this remark and revised the text accordingly. We would like to point out however, that, in addition to the preservation of “original” riverine organic complexes in the estuary, there is an appearance of LMW organic ligands forming strong complexes with HREE.

Page 1727, line 2: Please explain why the enrichment of the LMW-fraction with increasing salinity is not a method artefact. Can you be sure that the permeability of the dialysis membrane is not affected by the ionic strength (see my general comments)? Please see our response to the first (general) comment of this reviewer. We added a big deal of discussion on possible dialysis artifacts in the Electronic Supporting Information

Fig. 17: Organic carbon is shown in November-December and March, but not in July. The missing plot is given below and provided in Figure 16 of the manuscript was revised.

We corrected all technical comments noted by this reviewer: p. 1728, p. 1729 Fig. 18 (now Fig. 17): We revised the colors of this figure as recommended by the reviewer.

Interactive comment on Ocean Sci. Discuss., 10, 1707, 2013.

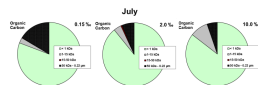
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