Ocean Sci. Discuss., 10, C810–C814, 2014
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Ocean Science
Discussions
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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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Received and published: 18 January 2014

This reviewer suggested changing the title to "Fate of colloids during estuarine mixing in the Arctic" and we agree with this proposition.

The reviewer proposed to reduce the text following his/her specific comments as given below and we followed this recommendation.

The reviewer stated that "It is very difficult to read fig 4-fig 8," and he/she proposed to connect the symbols with lines to follow each sampling occasion. We tried out best to improve the visibility of these quite complex figures. Unfortunately, adding the connecting lines is not suitable for these figures. Such lines complicate the reading of the symbols and mask the physical reality. Adding trend lines for all elements as for Mn (Fig. 5 C) also unjustified because the concentration – salinity dependence is quite complex and vary from one season to another. In response to this comment, we would like to stress that these figures: 1) are essential for presenting the novelty of our observations (LMW< 1 kDa and conventional 0.22 μm fractions as a function of salinity) 2) comprise the majority of most essential trace elements belonging to different chemical groups having distinct physico-chemical properties 3) then presented in color, allow clear distinguishing between LMW (blue) and 0.22 μm (red) fractions which does not require the connecting lines As such we have not significantly modified these figures but we have increased their size and reorganized the discussion via proper referencing of each figure as requested by both reviewers.

The reviewer correctly stated that “the spring flood is the major event (usually 50-70 % of the yearly discharge) but the authors have no measurements during this period.” Therefore the reviewer proposed to discuss the problems with the lack of spring flood data and present the implications for any of the conclusions. We are aware of the importance of the spring flood as stated in the last paragraph of section 4.3. 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 μm) fraction compared to winter and summer baseflow and a factor of 2 to 3 higher concentration of 0.22 μm 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 LMW< 1 kDa fraction may be as following: photodestruction > heterotrophic mineralization > exometabolites production. From the other hand, due to significantly higher discharge in spring, the water residence time

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in the estuary becomes shorter and thus the time necessary for colloidal coagulation might be insufficient to produce the non-conservative behavior of insoluble elements. Thus, Fe-rich HMW colloids may travel further seaward, north of the Mud'yug Island (Fig. 1) due to significantly higher freshwater zone influence. We added a pertinent discussion in the section 4.2 of revised text in response to this comment.

Specific comments of 2nd reviewer

Line 22 page 1709 As a general scheme, delete. Done.

Line 11 page 1710 rephrase. We revised as following: "The majority studies of the arctic estuaries were carried out during summer baseflow periods"

Line 19 page 1711 hydrological year (is this correct to say?) Corrected to : "systematic studies over several seasons…".

Line 5 page 1712 remove line 5-7 P. Done

Page 1712, 1713 1714, 1715, 1716: The authors can remove much of this text. It is possible to use references to explain the methods. We only partially agree with this comment. The present manuscript reports the analysis of trace metals conducted using several complementary techniques, and analysis of some metals in the estuarine zone is not trivial. However, to save the space and facilitate the reading, we moved the text from pages 1712 -1716 to the Electronic Supplementary Material (ESM-1).

Line 14- 22 page 1718 Is this text necessary? In the first half of this text, we alerted the reader on the possibility of the same element being present simultaneously in several groups. This is important for scientific rigor. The second half of this paragraph describes the behavior of rarer earth elements, important tracers in the oceanography and hydrology. Analyzing La/Yb ratio as a function of salinity nicely illustrates the fractionation of light versus heavy REEs and as such essential for the content of this work and for the following discussion.

Line 4 page 1720 DOC is not a colloid, change to OC. Done.

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Line 8 page 1723 ::amount of oxyanions? There are several elements present as oxyanions in the water but in the colloidal phase? We corrected as following: “This drop can be linked to the coagulation of the majority of HMW50 kDa – 0.22μm Fe colloids at the beginning of the mixing zone, because the proportion of colloidal form in total dissolved concentration of As and V achieve 20-25% (Fig. 15)”

Line 8 page 1725 The text on line 8 to 15 can be removed. Start with The Mn concentration. We do not agree to remove the discussion of estuarine behavior of Mn. Testing various hypotheses and presenting possible explanations for Mn concentration – salinity profile are essential for discussion of scientific results. Note that the anoxic groundwater discharge is very important factor of Mn concentration enrichment in boreal surface waters and as such it deserves very careful consideration.

Line 24 page 1725 to line 17 page 1726. I think this paragraph can be removed. The reviewer suggests removing the discussion on the geochemical behavior of Cd and Pb in the estuary. Without considering possible mechanisms controlling the interaction of this element with surrounding components, one cannot explain the observed maxima of their concentrations at the intermediate salinities, also common in other estuaries. Analyzing this possibility for the Arctic estuary is essential for interpretation of our results. We have not modified the text in response to this comment.

Line 20-22 page 1726 Can be removed. We agree and have done so in the revised version.

Page 1730 The whole section 4.3 can be condensed and rewritten. We fully agree. In the revised section we shortened the original text of this section more than a half and greatly reorganized the discussion. For convenience we present the revised section below

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 LMW< 1 kDa fraction in the seaward direction highlighted for the first time in this work may have significant

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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...) 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 often exhibit isotopic signatures drastically different from those of conventionally dissolved < 0.22 μm 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 57Fe relative to the <0.22 μm 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 of various metals relative to what might be predicted from the flux of the < 0.22 μm fraction. Upon the climate warming, the on-going increase in the LMW metal organic and complex and OC concentration occurring in the surface waters on land (cf., Shirokova et al., 2013; Pokrovsky et al., 2013) will be further accentuated in the estuaries because this LMW pool not only passes through the mixing zone without coagulation. This phenomenon might influence the following: i) the primary productivity of the coastal zone leading to CO2 drawdown from the atmosphere and ii) heterotrophic respiration of the allochthonous DOC accompanied by CO2 release to 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 μm) is observed during summer across the entire the salinity zone. 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 LMW< 1 kDa fraction.

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