

Interactive comment on “Effect of permafrost thawing on the organic carbon and trace element colloidal speciation and microbial activity in thermokarst lakes of Western Siberia” by O. S. Pokrovsky et al.

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General comments:

I think this is a very interesting article, as it specifically addresses the role of lake processes in the export of organic carbon and trace metals from the thawing permafrost in the Arctic. I have not seen many articles discussing this specific subject before, although lake processes may be very important for the DOC and trace metal-export from the Arctic. This is therefore a study of great importance. A very large dataset

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is presented, with DOC and trace metal-concentrations in a number of size fractions, from a large number of lakes. The scientific quality of the paper is therefore excellent. The presentation quality is good, but I have some comments and suggestions on the discussion. I recommend this article for publication in Biogeosciences, after a minor revision.

Specific comments:

Page 9, Fig. 4: Why is < 1 kDa OC referred to as “potentially bioavailable”? On the contrary, the bioavailability of OC is usually considered to decrease with decreasing size (see the following references: Amon, R.M.W., Benner, R. (1996) *Limnol. Oceanogr.* 41(1), 41-51.; Amon, R.M.W., Benner, R. (1996) *Geochim. Cosmochim. Acta.*, 60(10), 1783-1792; Benner, R., Benitez-Nelson, B., Kaiser, K., Amon, R.M.W. (2004), *Geophys. Res. Lett.* 31, L05305, doi:10.1029/2003BL019251; Guo, L., Macdonald, W. (2006), *Glob. Biogeochem. Cycles*, 20, GB20011, doi: 10.1029/2005GB002593). The logarithmic scale of the y-axis in Fig. 4 is a bit confusing, and it should probably be clarified in the figure caption that the scale is logarithmic.

Page 9, Line 21-24: Coagulation and flocculation of organic matter cannot explain the observed changes in size distribution of OC presented in Fig. 5. Going from U1 to U11, there is an absolute increase in OC-concentration in the total $5 \mu\text{m}$ filtered water, while the $< 0.45 \mu\text{m}$ and < 10 kDa fractions are constant and the < 3.5 kDa and < 1 kDa fractions decrease only slightly. This shows that there is a dramatic increase in $0.45\text{-}5 \mu\text{m}$ organic matter at this stage of lake development, which cannot be explained by flocculation of smaller organic matter. If phytoplankton production increases at this stage of lake development, I think that the most likely explanation to this increase in $0.45\text{-}5 \mu\text{m}$ organic matter is the degradation of large plankton cells, which produces cell fragments in this size range. Exopolymeric substances from phytoplankton and bacteria may also be a major constituent (see references: Chin, W.-C, Orellana, M. V., Verdugo, P. (1998), *Nature* 391, 568-572; Wilkinson, K.J., Juz-Roland, A., Buffle, J. (1997), *Limnol. Oceanogr.*, 48(2), 1714-1724). Going from U11 (un-drained lake) to

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U13 (drained lake), the most striking change is the dramatic decrease in the 0.45-5 μm fraction, which is accompanied by an increase in the 10 kDa-0.45 μm fraction, while < 10 kDa organic matter decrease in concentration. I would think that the development from an un-drained lake to a drained lake could result in a number of changes that could alter the size distribution of organic matter (e.g. increased input of terrestrial organic matter from surface runoff, decreased phytoplankton production etc). However, flocculation of organic matter is not likely to be an important factor, since small (< 3.5 kDa) organic macromolecules generally do not flocculate.

Page 10, Line 1-2: In addition to these factors, perhaps the smaller size of OC in the larger and mature lakes can be a result of a relatively lower input of soil and peat-derived organic matter to these lakes, as a result of a larger water-body in relation to the length of the shoreline? The average residence time of the allochthonous organic macromolecules in these lakes is therefore longer, and they have been exposed to degradation by bacterioplankton for a longer time, and are therefore smaller in size than in the smaller lakes (see references Amon, R.M.W., Benner, R. (1996) *Limnol. Oceanogr.* 41(1), 41-51.; Amon, R.M.W., Benner, R. (1996) *Geochim. Cosmochim. Acta.*, 60(10), 1783-1792).

Page 10, Line 6-12: The bioavailability of natural organic matter is usually considered to decrease with decreasing size. If the organic matter is mainly allochthonous and soil-derived, the results in Fig. 7 are surprising, as the < 1 kDa fraction is expected to be the more refractory component, left after bacterial consumption. If there is a significant contribution of small OM from phytoplankton, this could however explain a higher bioavailability < 1 kDa OM, since the phytoplankton OM would be fresher.

Page 11, Line 2: "elements present in the form of neutral molecules". Please check if this is correct. Are Si, Ge, Sb and As really present as neutral molecules in these waters?

Page 12, Lines 16-21: Higher proportions of < 1 kDa Cu and Cd in the mature lakes

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can also be explained by that the allochthonous soil-derived organic matter is smaller in size in these lakes (shown in Fig. 6) as a result of longer heterotrophic degradation. Fulvic acid just a few nm in size (see reference: Lead, J. R., Wilkinson, K. J., Balnois, E., Cutak, B. J., Larive, C. K., Assemi, S., Beckett, R. (2000), *Environ. Sci. Technol.*, 34, 3508-3513) and it is not surprising if a large fraction of soil-derived organic matter is found in the < 1 kDa fraction. Cu, Cd and Pb were the only elements that correlated with DOC. Therefore, the finding that only Cu and Cd increase in proportion in the < 1 kDa fraction, while most other elements show the opposite behavior, can be explained by that Cu and Cd are not influenced by the coagulation of colloidal Fe and Al oxyhydroxides.

Page 12, Lines 25-28: Decrease in the percentage of < 1 kDa Fe, or decrease in the 'Fe-solubility' with increasing pH is a known phenomenon. It is caused by the increase in the kinetics of Fe-oxyhydroxide formation with increasing pH. The concentration of organic matter has a major influence, since organic acids both lower the pH, and stabilize Fe in the < 1 kDa fraction as small organic complexes. Is there any correlation between OC-concentration and proportion of Fe in the < 1 kDa fraction?

Page 13, Lines 1-3: I would expect the proportion of small sized Fe to decrease with increasing hydroxyl ion-concentration, as Fe-hydroxide is the first step in the formation of Fe-oxyhydroxide particles. This is also what was observed, as < 1 kDa Fe decreased with increasing pH.

Page 15, Line 9-11: This process, i.e. coagulation of colloidal Fe and Al linked to the consumption of organic matter by bacterioplankton, may also explain the inverse relationship between pH and percentage Fe in the < 1 kDa fraction (described on page 12, lines 25-28), as decreased concentration of organic acids may lead to a higher pH. In addition, it is shown in Fig. 5 that the concentration of 0.45-5 μm organic matter could increase when going from thermokarst lake to ecosystem stabilization (U1 to U11). This increase in particulate organic matter, which may be explained by biopolymers and other organic matter from phytoplankton, could contribute to the coagulation of

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colloidal Fe and Al (see references: Wilkinson, K.J., Juz-Roland, A., Buffle, J. (1997), *Limnol. Oceanogr.*, 48(2), 1714-1724.; Perret, D., Gaillard, J.-P., Dominik, J., Atteia, O. (2000), *Environ. Sci. Technol.*, 34, 3540-3546).

Technical corrections:

Page 9, Line 21: U-12 is not shown in Fig. 5, only U-11 and U-13.

Page 9, Line 28: allochthonous, I assume this should be autochthonous.

Interactive comment on *Biogeosciences Discuss.*, 7, 8041, 2010.

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