Review of the manuscript « X-ray fluorescence mapping of mercury.. » submitted by Gu et al. to Biogeosciences Discussion

This paper addresses important and poorly investigated question – the localization (speciation) of mercury in river suspended matter, linked to highly contaminated river systems.

The authors used state of the art method to localize Hg in particles sampled in a contaminated freshwater system and they concluded on the mechanisms of Hg binding and transport in the environment. While the methods are adequate, their interpretation and major authors' conclusions are not fully supported by the data. I am not sure that simple arrangement of the discussion will help here and collection of new data is necessary to demonstrate what the authors intended to show.

- To assess Hg speciation adsorbed onto mineral and organic particles, rigorous surface complexation modeling using available constants is necessary. Without such a modeling, only quantitative – and not really novel – picture of Hg interaction with RSM can be drawn.
- 2) According to the authors, sulfhydryl is the main surface binding group for Hg. Therefore, S⁻ group concentration in dissolved and suspended river water fractions should be assessed.
- 3) Correlation between Hg and sulfide in the RSM is not tested quantitatively. The importance of sulfhydryl binding is thus difficult to assess.
- 4) If, according to the authors, the NOM-coated Fe-oxyhydroxide minerals provide a sink for Hg via formation of Hg-sulfhydryl complexes, then the existence of such S- groups within the NOM should be demonstrated spectroscopically and their concentration should be measured via conventional techniques.

Specific comments

p.7522, L 12: localized sorption cannot be a sink for Hg in rivers; rather, RSM is an important carrier of Hg in the riverwater providing Hg transport from the land to the ocean. The sink would be in sediments; the RSM is a carrier agent

p.7523, L25-30: Hg association with POM and Al, Fe oxyhydroxide in lakes and rivers cannot be a hypothesis – this is a well-known fact. A hypothesis which is later discussed in the text is Hg main binding to sulfhydryl groups of OM coating oxy(hydr)oxide, yet this has to be better demonstrated. The link to phytoplankton uptake and localization is unclear.

p. 7524, L 20-23: It is awkward to present the most important quantitative result in the Introduction.

The Introduction still gives the impression of research having mainly local interest presenting project report on highly contaminated sites. How efficient would be the extrapolation of obtained results to other river systems?

p. 7525, Materials and Methods. The authors present original approach to characterize different size fraction of RSM using 0.2 and 3.0 μ m filters. However, the methodological aspects should be better elaborated: the choice of these specific filters should be justified. There are other useful commercial filters of 5, 8, 10, 20 μ m...

p.7526, L 9: "of 617 μ g g⁻¹, which is XX times higher than the non-contaminated sample"

p. 7526, L 18-25: The depth of X-ray probe should be provided. This is important to assess the minimal detectable concentration. L 27-29: Is it possible to provide a table with a detection range?

p. 7527, L1-13: What is the detection limit by this method? At which lowest concentration the elements are still detectable?

p. 7528, L7-10: It will be useful to present the results of ICP MS analysis of these elements, at least in the Appendix.

p. 7529. The association of Hg with biomass rather than with Si frustule is consistent with results on other metals: For example, in case of Zn, not more than 10% of surface-bound metal is associated with diatom frustules, and the rest is in within the organic matrix of the cell wall (Gelabert et al., 2007, GCA). This is especially important in view of co-localization of Hg and Zn, observed in this study.

The data provided in Table 1 are based on XRF technique. It is worth giving there the average values with uncertainty and compare these results with ICP-MS data, but also with world average RSM composition (Viers et al., STOTEN, 2009, doi: 10.1016/j.scitotenv.2008.09.053). What is the typical Hg concentration in other rivers RSM?

p. 7529, L 16: Total Hg shown in Fig. 1d does not necessarily imply "inorganic only". L20-23: What are the "mineral particulates" noted by the authors – sulfides, oxides, carbonates? Presumably these are not silicates...

p. 7530, L 4: Are these oxy(hydr)oxides located in the RSM or in the colloidal fraction?

p. 7530, L 25: Do the authors detect S- bands using the spectroscopic techniques?

p. 7530, L 23-27: The statements given here are highly hypothetical and not really proven by the data available in this study

p. 7531, L 1-5: This text is repetitive to what is stated above. The Surface Complexation Approach is necessary.

Conclusions, L 11: We encounter this important information, on the limitation of authors' technique, only at the conclusion section. Detection limits should be carefully discussed at the beginning and analysis of certified samples should be presented.

Surface complexation modeling of Hg binding to various components of the RMS, based on available literature data should be executed and results compared to what the authors observe

Figure 1 is invisible in black and white mode.