

[Interactive
Comment](#)

Interactive comment on “X-ray fluorescence mapping of mercury on suspended mineral particles and diatoms in a contaminated freshwater system” by B. Gu et al.

B. Gu et al.

gub1@ornl.gov

Received and published: 30 July 2014

Author's Responses to Referee 1 Comments: 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

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

[Discussion Paper](#)



what the authors intended to show.

Response: We thank Reviewer's helpful comments. However, we point out that this work was focused on the localization, rather than "speciation", of mercury on suspended particles. Our main conclusion was that "mercury is heterogeneously distributed among phytoplankton (e.g., diatoms) and mineral particles that are rich in iron oxides and natural organic matter (NOM)". In discussion, we hypothesized (or speculated) that Hg association with NOM-minerals was due to the formation of Hg–NOM-Fe-oxide ternary complexes based on the fact that NOM strongly sorb onto Fe and Al oxide surfaces via carboxyl or hydroxyl functional groups, whereas Hg(II) can form strong complexes with NOM via sulfhydryl and other functional groups (many references cited). Therefore, NOM acted as a bridging agent between Hg and iron oxides by forming Hg–NOM-oxide complexes, and our limited data in fact support this argument (i.e., XRF showed strong correlations between Hg and Fe, and FTIR and elemental mapping clearly indicate NOM coatings on mineral particles).

We note again here that we are simply interpreting our results (as discussion). It is the hypothesis based on the literature review and our limited data, and it was never stated as "fact" but as possible explanations. Nonetheless we reworded these sentences and removed any ambiguous words related to Hg speciation in the revised manuscript. Therefore, we believe that additional data are unnecessary since our work is not focused on the speciation or mechanisms of Hg binding and transport per se.

1) 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.

Response: As stated above (also see abstract and introduction), the primary objective of this work is to apply the X-ray fluorescence (XRF) microprobe to directly visualize and quantify the spatial localization of Hg and its correlations with other elements of in-

BGD

11, C3899–C3906, 2014

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



terest on suspended particles. Rigorous surface complexation and speciation modeling is beyond the scope of this work. We have carefully reviewed our revised manuscript and removed any ambiguous words related to Hg speciation.

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.

Response: We made this statement more general to include both sulfhydryl and other functional groups in the revised manuscript. We also cited many references showing the strong binding between Hg and sulfhydryl functional groups and a reference on determining sulfhydryl functional groups on NOM.

3) Correlation between Hg and sulfide in the RSM is not tested quantitatively. The importance of sulfhydryl binding is thus difficult to assess.

Response: See above responses.

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.

Response: Again see above responses. We also point out that the existence of S-groups within NOM has been demonstrated spectroscopically in many previous studies (Gu et al., 2011; Nagy et al., 2011; Skyllberg et al., 2006) and also in recent studies using fluorescent labeling techniques (Joe-Wong et al., 2012; Rao et al., 2014). These references are cited in the revised manuscript.

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.

Response: We agree and changed this sentence accordingly. Our intent was to say

C3901

BGD

11, C3899–C3906, 2014

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



that suspended particles have a large capacity to sorb Hg, leaving a small portion of Hg in the solution phase.

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.

Response: We revised this statement. Please also see above responses.

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?

Response: These sentences were removed in the revised manuscript. As stated in the introduction, particle-bound Hg comprises up to 90

p. 7525, Materials and Methods. The authors present original approach to characterize different size fraction of RSM using 0.2 and 3.0 μm 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 μm ...

Response: Justifications are provided in the revised manuscript. The size fraction between 0.2 and 3 μm consisted of mostly mineral particles, and diatoms existed mostly in the size fraction $>3 \mu\text{m}$ (along with some large mineral particles or aggregates). We also note that this study was not intended to do a detailed characterization of different size fractions of the particles.

p.7526, L 9: “of 617 $\mu\text{g g}^{-1}$, which is XX times higher than the non - contaminated sample”

Response: Corrections were made accordingly.

C3902

BGD

11, C3899–C3906, 2014

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



p. 7526, L 18 - 25: The depth of X-ray probe should be provided. This is important to assess the minimal detectable concentration.

Response: The X-ray penetration depth was considerably greater than the sample thickness ($\gg 100 \mu\text{m}$).

L 27-29: Is it possible to provide a table with a detection range?

Response: Table 1 shows the average concentration of each element. The ranges of detection limits of this technique are now provided in the revised manuscript.

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

Response: See above. Under given operating conditions, the estimated detection limits are about 10^{-4} ug/cm^2 for Hg, 10^{-4} to 10^{-3} ug/cm^2 for Mn, Fe, Ni, and Zn, and 2 ug/cm^2 for Si, P, and Cl. In the revised manuscript, we cited additional references (Ortega et al., 2004; Twining et al., 2003) and pointed out that the detection limit of this technique depends on 1) incident energy used to probe the sample, 2) the atomic number of the element of interest (the heavier element gives lower LOD), and 3) the sample matrix (Ortega et al., 2004; Twining et al., 2003).

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

Response: These data were presented as a bar graph in Figure 1c. It would be redundant to provide these data again 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% 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?

Response: This is a great suggestion, and we modified this part of the discussion and added the following statement: “This result is similar to the adsorption of such metal ions as Zn^{2+} , which is predominately sorbed onto diatom membranes, rather than on Si frustule (Gelabert et al., 2007). This result also explains the co-localization of Hg and Zn since both of them are soft metals.”

However, we note that we cannot directly compare our XRF results (Table 1) with those determined by ICP-MS in literature. This is because ICP-MS gives the bulk concentration in $\mu\text{g/g}$ solids, whereas XRF measures the “localized” concentration within a given surface area (in $\mu\text{g/cm}^2$). As our results demonstrate, mercury is heterogeneously distributed among phytoplankton (e.g., diatoms) and mineral particles, and the concentration varies widely among these particles.

p. 7529, L 16: Total Hg shown in Fig. 1d does not necessarily imply “inorganic only”.
Response: We determined MeHg (one of the major known organo-mercuric compounds), which comprised $< 0.01\text{L20-23}$: What are the “mineral particulates” noted by the authors – sulfides, oxides, carbonates? Presumably these are not silicates...

Response: Revised; here iron oxides may be the major component.

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

Response: We clarified this sentence in the revised manuscript as “Strong association between NOM and naturally-occurring Fe- or Mn-oxyhydroxides is commonly observed in water”.

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

Response: Yes, the cited references by Skjellberg et al. 2006 and Nagy et al. 2011 (and many others) detected S-bands in NOM using spectroscopic techniques, as stated earlier. We did not perform these analyses in this study because the technique requires a relatively high NOM concentration.

C3904

BGD

11, C3899–C3906, 2014

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



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

Response: Please also see our response to the general comments. We revised and clarified this part of the discussion. We disagree that these statements are purely hypothetical. They are based on the fact (with many references cited in text) that NOM strongly sorb onto Fe and Al oxide surfaces via carboxyl or hydroxyl functional groups, whereas Hg(II) can form strong complexes with NOM via sulfhydryl or other functional groups. Therefore, NOM can act as a bridging agent between Hg and iron oxides, and our data (FTIR and elemental mapping) support this argument.

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

Response: We revised and clarified this part of the discussion. Please also see our responses above regarding surface complexation and speciation.

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.

Response: As suggested, we deleted these sentences and provided the method detection limits in the revised manuscript (in Materials and Methods). Please also see our responses above. Again, surface complexation modeling of Hg binding to various components of the RMS is a significant undertaking and beyond the scope of this work. Our main objective is to demonstrate the ability to use XRF technique to directly visualize and quantify the spatial localization of Hg on suspended particles.

Figure 1 is invisible in black and white mode.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Response: We re-plotted Figure 1.

Cited References: Brooks, S. C. and Southworth, G. R.: History of mercury use and environmental contamination at the Oak Ridge Y-12 Plant, *Environ Pollut*, 159, 219-228, 2011. Gelabert, A., Pokrovsky, O. S., Schott, J., Boudou, A., and Feurtet-Mazel, A.: Cadmium and lead interaction with diatom surfaces: A combined thermodynamic and kinetic approach, *Geochim. Cosmochim. Acta*, 71, 3698-3716, 2007. Gu, B., Bian, Y., Miller, C. L., Dong, W., Jiang, X., and Liang, L.: Mercury reduction and complexation by natural organic matter in anoxic environments, *Proc. Natl. Acad. Sci. USA*, 108, 1479-1483, 2011. Joe-Wong, C., Shoenfelt, E., Hauser, E. J., Crompton, N., and Myneni, S. C. B.: Estimation of reactive thiol concentrations in dissolved organic matter and bacterial cell membranes in aquatic systems, *Environ. Sci. Technol.*, 46, 9854-9861, 2012. Nagy, K. L., Manceau, A., Gasper, J. D., Ryan, J. N., and Aiken, G. R.: Metallothionein-like multinuclear clusters of mercury(II) and sulfur in peat, *Environ. Sci. Technol.*, 45, 7298-7306, 2011. Ortega, R., Bohic, S., Tucoulou, R., Somogyi, A., and Deves, G.: Microchemical element imaging of yeast and human cells using synchrotron X-ray microprobe with Kirkpatrick-Baez optics, *Analytical Chemistry*, 76, 309-314, 2004. Rao, B., Simpson, C., Lin, H., Liang, L., and Gu, B.: Determination of thiol functional groups on bacteria and natural organic matter in environmental systems, *Talanta*, 119, 240-247, 2014. Skylberg, U., Bloom, P. R., Qian, J., Lin, C. M., and Bleam, W. F.: Complexation of mercury(II) in soil organic matter: EXAFS evidence for linear two-coordination with reduced sulfur groups, *Environ. Sci. Technol.*, 40, 4174-4180, 2006. Twining, B. S., Baines, S. B., Fisher, N. S., Maser, J., Vogt, S., Jacobsen, C., Tovar-Sanchez, A., and Sanudo-Wilhelmy, S. A.: Quantifying trace elements in individual aquatic protist cells with a synchrotron X-ray fluorescence microprobe, *Analytical Chemistry*, 75, 3806-3816, 2003.

Interactive comment on Biogeosciences Discuss., 11, 7521, 2014.

BGD

11, C3899–C3906, 2014

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

