

Biogeosciences Discuss., community comment CC1
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Comment on bg-2020-466

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Community comment on "Mercury mobility, colloid formation and methylation in a polluted Fluvisol as affected by manure application and flooding–draining cycle" by Lorenz Gfeller et al., Biogeosciences Discuss., <https://doi.org/10.5194/bg-2020-466-CC1>, 2021

Very interesting data set on Hg-colloids and Hg methylation during flooding events! Agree with R1 comment on highlighting the novel and unexpected results in this study. Be careful though with overstating your conclusions, particularly with respect to HgS(s) formation (does the redox data support sulphate reduction/sulphide production?) and microbial activity (not measured)

Detailed comments:

Line 69: Consider citing

Zhang, T., et al. (2012). "Methylation of mercury by bacteria exposed to dissolved, nanoparticulate, and microparticulate mercuric sulfides." *Environ. Sci. Technol.* **46**: 6950-6958.

Line 80: Consider citing

Gilmour, C. C., et al. (1992). "Sulfate stimulation of mercury methylation in freshwater sediments." *Environ. Sci. Technol.* **26**: 2281-2287.

Compeau, G. and R. Bartha (1985). "Sulfate reducing bacteria: principal methylators of Hg in anoxic estuarine sediments." *Appl. Environ. Microbiol.* **50**: 498-502.

Kerin, E. J., et al. (2006). "Mercury methylation by dissimilatory iron-reducing bacteria." *Applied and Environmental Microbiology* **72**(12): 7919-7921.

Section 2.2: Was there a control for the manure only? AF4, Hg and MeHg data might be interesting for comparison.

Line 144: Could you clarify what one application of the manure was?

Line 241: There is a correction which can be made for the Fe contribution to SUVA. See Poulin, B., et al. (2014). "Effects of iron on optical properties of dissolved organic matter." *Environ. Sci. Technol.* **48**: 10098-10106.

Line 242: What exactly do you mean by "associated"? Which wavelengths were run for the humic-like fluorophores? Why was FLD run – what does it provide in addition to SUVA?

Line 320: Why do you think this fraction consists of HgS colloids?

Line 322: Consider including values here.

Line 340: Red-S and Hg concentrations should be expressed in mol/g. Also, Hg can complex with other functional groups such as O-containing functional groups in OM. How does this fit into the competition scenario between OM and Mn oxides?

Is it possible considering the pH and pzc of Mn oxides that Hg can adsorb to the surface?

Are there any other studies which have reported Hg- Mn interactions?

Line 357: Have you considered that OM can directly reduce Mn oxides or act as an electron shuttle?

Line 367: There are many minerals which form black precipitates. Is there geochemical modeling data or XRD data to support this? Does the redox data support sulphide production?

Line 368: Is there a reference for the formation of sulphide minerals in meso- and micro-pores?

Line 386: Does the redox data support sulphide production?

Line 406-408: This is very interesting. How do you think this relates to the decrease in Hg-0.02 um after 4 days for HMLC+MNR?

Line 404: Complexation is driven by thermodynamics and not necessarily by ligand concentration. Geochem modeling might help support this statement on chloride complexation.

Line 415: What is the fraction of the total Hg in the "small pool"?

Line 425: Does the redox data support sulphide production?

Line 442: What were the concentrations of bioavailable Hg?

Line 444-445: We don't know the Hg species that are bioavailable. Consider the following papers and the influence of thiols on Hg bioavailability (source: manure)

Graham, A. M., et al. (2013). "Effect of dissolved organic matter source and character on microbial Hg methylation in Hg-S-DOM solutions." *Environ. Sci. Technol.* **47**: 5746-5754.

Graham, A. M., et al. (2012). "Dissolved organic matter enhances microbial mercury methylation under sulfidic conditions." *Environ. Sci. Technol.* **46**: 2715-2723.

Conclusion: Any thoughts on land use as a factor in Hg methylation and Hg mobilization?

Figure 3: Is there Fe data?

Figure 4: Consider revising the legend labels to be more descriptive of the different fractions. There is overlap between the 6-25, 6-450 and 30-450 nm size fractions, which makes interpreting the Hg proportion data difficult (sum to 100%).

Table 3: Be careful with de/methylation. What you are quantifying is a decrease in net methylation and not necessarily demethylation processes.