

Biogeosciences Discuss., referee comment RC2
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Comment on bg-2020-466

Brett Poulin (Referee)

Referee 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-RC2>, 2021

Summary

The study titled "Mercury mobility, colloid formation and methylation in a polluted fluvisol as affected by manure application and flooding draining cycle" aims to identify the release dynamics of Hg in two soils under two conditions (with and without manure) over two flooding periods. Two soils were characterized and incubated in laboratory microcosms with synthetic rainwater and with/without manure over two flooding cycles. Pore water was documented at numerous points over the two flooding periods, and measured for total Hg, metals, anions, cations, DOC, and pH and Eh. Colloids were collected at 3 time points during each of the 2 flooding periods, and AF4 measurements determine the size distribution and some elemental composition (Hg, Cu, Fe, Mn, carbon). Methylmercury was quantified in the soil a 4 time points between $t=0$ and $t=final$ conditions.

Overall, the study documents some nice results from the incubation experiment that test the effects of soil properties and manure addition. The study design and methods are well done, and I agree with the majority of the conclusions. However, my main comments are about the presentation of the work and ways to improve the clarity in presentation. I have itemized general comments and specific comments that should be addressed by the authors before considering this work for publication. The authors are encouraged to edit the manuscript thoroughly for editorial clarity. I did not identify all the sentences and statements that were unclear, but have listed some editorial comments in the Specific Comments section below.

General Comments:

- The importance of sulfate reduction should be revisited in this paper, as inorganic sulfide will scavenge pore water Hg(II) and result in authigenic formation of β -HgS. There is very little to no discussion of the decrease in sulfate concentrations in the microcosms, which indicates sulfate reduction and is a key biogeochemical transformation that can result in Hg partitioning back to the soils. Figure S7 in the SI shows very high levels of sulfate at the start of the experiments (150-1000 mg/L) and drastic decreases in concentration with flooding time.
- For the presentation of the Microcosm results, and figure presentation, I recommend the authors (1) use the redox ladder to guide the initial presentation, (2) consider discussing the Hg release dynamics in terms of "stages" or periods of time describing trends in the concentrations, and (3) detail the release dynamics of the other metals separately. Regarding item 1 of the redox active elements, in Lines 247-255, there is no mention of Fe or sulfate and all pertinent constituents (nitrate, Mn, Fe, sulfate) should be presented together in a single figure (at present, the reader has to look to the SI and main text figures). The observation that reductive dissolution of Fe wasn't observed in Flooding period 1 is still a result that needed to be stated, and there is no mention of the decrease in sulfate from \sim 1000mg/L to 500 mg/L in flooding period 1 of the HMLC incubations. Regarding item #2 of the Hg release dynamics, on Lines 274-278, you may consider revising to describe the release dynamics in 'stages'. "Concentrations of Hg were low between X-X days (phase 1), increased to a maximum at 4 days (phase 2), and decreased between 4 and 14 days (Phase 3)." These same 'stages' could be references when describing the colloidal data. Regarding the third item on other metal contaminants, the study presents data on diverse metals (Cu, and all metals in Figure S8), but Cu is the only metal discussed. The authors need to discuss the data they present in all figures, otherwise it is unclear why those data are presented in the first place. I commend the authors for a nice study and recognize that presenting the various non-metal metal data is challenging.
- Have the authors considered including an analysis that estimates if the thiol content of the DOM was exceeded in their experiments, to contrast with the soil analysis (Lines 339-345)? The strong binding site capacity of DOM has been quantified to be \sim 5 nmol/mg DOM (<https://pubs.acs.org/doi/10.1021/es025699i>). They can assume DOC is 50% of the DOM, and compare the strong binding site capacity of the DOM to the total Hg concentration $< 0.02 \mu\text{m}$. Further, they could estimate how the addition of manure changed the Hg binding state (saturated vs unsaturated) in both the soil and pore water.
- As a reader, it will improve clarity if you spell out the various soils and treatments. I had to go back repeatedly to the methods to remind myself what the various acronyms meant ("HMLC"). This is important because of the two soils and two treatments (control vs manure).

Main Text Specific Comments:

Line 28 – consider deleting "again".

Line 30 – consider "formation and aggregation" of ...

Line 46-47 – There is “cinnabar” in the environment, but in the form of mineral deposits or associated with mercury mining activities. In the vast majority of environments, mercuric sulfide is present as authigenic nanoparticulate metacinnabar (β -HgS nano).

Line 59 – consider deleting “e.g.”.

Line 62-63 – consider expanding to include the microbial process. At present, it reads awkward because Hofacker 2013 and 2015 are referenced but it is somewhat unclear what the 2015 study contributed.

Line 66 – The first reports of DOM facilitating the dissolution of HgS were by <https://pubs.acs.org/doi/10.1021/es9804058>. This study should be cited.

Line 66-68; here you reference “altering the reaction kinetics of HgS(s) formation”, in which case you should cite Ravichandran et al., 1999 and Deonaraine and Hsu-Kim, 2009.

Line 72-74; Ligand exchange is important, but in the vast majority of systems there is an excess of strong thiols binding sites in the DOM for all the Hg(II). This was first documented by <https://pubs.acs.org/doi/10.1021/es025699i> and should be integrated into this sentence.

Lines 66-70 and 430-431; the authors need to cite primary literature that document how DOM controls the nanocrystalline structure of β -HgS particles, which is a key property influencing the bioavailability of mercury under sulfidic conditions. Two papers that should be considered due to conditions that closely represent natural conditions include <https://pubs.acs.org/doi/abs/10.1021/es201837h> and <https://pubs.acs.org/doi/10.1021/acs.est.7b02687>.

Line 88; the authors may consider also looking at a recent paper on OM amendments to mine tailings. <https://www.sciencedirect.com/science/article/pii/S0269749120370585>

Line 92-93; The authors are encouraged to revise this sentence, as it could be improved to highlight the various environments where methylation is prominent (riparian zones, saturated soils etc) because of the redox conditions.

Lines 108-2213; somewhere in this paragraph it should be mentioned that “microcosm experiments” were carried out.

Line 112 – revised to “0.02 and 10 μm ” or an equivalent term. At present, “0.02/10 μm ” is a fraction and doesn’t make sense to me.

Line 132: First, this sub-header should read “Microcosm Experiments”. It is confusing to call them “incubations” when later you refer to them as microcosms – please be consistent and in all instances state “microcosms”. Second, in a section below you detail the “Incubation experiment blanks” but those are not detailed in this section, and they should be.

Line 135-136 – revised to “After the initial incubation period soils were used in the flooding and draining experiments, which were conducted in 1 L borosilicate glass aspirator bottles (Fig. S2).” It would appear Fig. S2 should be called out.

Line 137- revise to “Microcosm experiments were performed in experimental triplicate...”

Line 141-142; revise “were” to “was”; rainwater is singular.

Line 146; I presume you mean “remove any remaining air bubbles...”

Lines 192-195; consider revising to “At each sampling time, sample splits were preserved without further filtration (<10 μm) and filtered at 0.02 μm (add filter details). Additionally, at 2, 5 and 9 days an additional sample split was filtered at 0.45 μm for colloid characterization.” What was the filter type for the 0.45 μm filter?

Line 102 – DOC should be reported in units of mg/L, for consistency with incubation results.

Line 206 – revise to “filtered” fractions. And, it is not common to use “suffix” to describe a subscript, which is what is presented for each term.

Line 231 – revise to “0.5% HCl and 1.0% HNO₃”.

Line 249 and 275 – consider revision to “NO₃⁻ depletion” or “exhausted”.

Line 260262; this sentence doesn't make sense and needs revision.

Line 261 – when describing concentrations in the text, the same units should be used as presented in the figure. Figure 2 presents Mn in units of mg/L.

Line 270 – The reader probably won't remember the "cornfield soil" is the HMLC soils. See my comment above to just spell out the soil type. Consider revising "throughout the experiment" to "over both flooding periods".

Figure 4 caption; it is entirely unclear what is meant by "Details on the deconvolution procedure are provided in the supplement".

Figure 4 – should the y-axis label for the top panel indicate "particulate" and should state "total Hg".

Section 3.2 – Consider finding locations in this section to emphasize that you're looking at time points across the two flooding events. Visually, the size proportion of Hg species data look interesting as they show trends in the first flooding period and little change after that.

Section 3.3; the sub-header title should specify this is for the 'soil'.

Line 329-330; I don't agree with this conclusion regarding the association of Hg to particulate Mn. In looking at Figure 2, the relative proportion of particulate Mn and Hg decreases with flooding time, but their overall concentration is still low. It is more likely that Hg is released from the soil. The decomposition (and solubilization) of OC in the soils can also release Hg. The pore water DOC concentration is reflecting both release and utilization of DOC, so may not necessarily capture the role of DOC on the Hg mobilization due to carbon mineralization.

Lines 346-349 – can you discount the possibility that soil heterogeneity could have contributed to the observed variability?

Lines 367-368 – the pore water data strongly support that sulfate reduction is occurring, which show drastic decreases in the concentration of sulfate with increased flooding time. In microcosms of this nature, several biogeochemical processes are occurring simultaneously and the Eh of the system isn't sufficient to assess if sulfate reduction is or is not occurring. My assessment is that it is more likely that sulfate reduction resulted in

the re-association of porewater Hg with soils, compared to the NOM complexation.

Line 378 – Poulin et al 2016 shows distinct Hg(0) formation in contaminated soil incubations, and should be cited here.

Lines 380 – one would need citations for the sentence on abiotic vs biotic reduction.

Lines 436-438 – one interpretation is that the soils had been subject to period soil flooding that contributed to mercury methylation.

Lines 444-445; could the higher microbial activity be the result of addition of labile carbon? The author should consider highlighting here the diversity of microbial communities that can methylate Hg, as is provided in the Introduction. Sulfate reducing bacteria, metal reducing bacteria, and fermenters are possible contributors to mercury methylation.

Figure 2 – the y-axis labels are very hard to read, and would be nearly impossible to read in print form. Consider re-working the figures as I suggest above, where all terminal electron acceptor processes and DOC are included in a single figure, then all Hg measurements, then all other trace metals.

SI Specific Comments:

Line 7 – this figure should be revised to state “total Hg” when total Hg is measured. This needs to be fixed in all cases in text and figures, in the main text and SI.