Biogeosciences Discussions

Biogeosciences Discuss., referee comment RC1
https://doi.org/10.5194/bg-2020-466-RC1, 2021

Comment on bg-2020-466

Jan G. Wiederhold (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-RC1, 2021

Review of manuscript bg-2020-466 (submitted to Biogeosciences)

Title: Mercury mobility, colloid formation and methylation in a polluted fluvisol as affected by manure application and flooding-draining cycle.

Authors: Lorenz Gfeller, Andrea Weber, Isabelle Worms, Vera I. Slaveykova, Adrien Mestrot

Reviewer: Jan G. Wiederhold (German Federal Institute of Hydrology, BfG)

This manuscript reports the results of laboratory experiments in which two Hg-contaminated soil samples were incubated with and without addition of manure for six weeks over a controlled flooding-draining-flooding cycle. Soil solution samples were collected repeatedly during the experiments through open-pore suction cups, followed by measurements of colloidal and dissolved Hg, methyl-Hg and many other parameters using a variety of analytical techniques. The topic of the study is suitable for Biogeosciences and the results are novel and relevant for the large research community interested in mercury biogeochemistry.

The experiments were well-designed, the methods are described and validated in great detail, and the quality of the analytical data is high. The interesting results are presented and discussed in a detailed manner and supported by nice figures and tables (only with slightly too small font sizes for my taste in some cases). Some of the main findings include the association of Hg with Mn during the mobilization into soil solution after flooding, the lower Hg mobility in the manure-treated soils, a detailed characterization of Hg-bearing colloidal particles, the relatively large differences between the first and the second flooding period, and the inference that Hg methylation was limited by microbial activity/uptake rather than bioavailable Hg during the experiments. I congratulate the authors to their very interesting study and I recommend that the manuscript should be published in Biogeosciences after moderate revisions considering the following comments and suggestions.

My only general comment refers to the direct comparison of the results with previous related studies and therewith a more concise identification of the new insights generated by this study and their implications for Hg biogeochemistry in contaminated floodplains. I acknowledge that the authors present a thorough literature review in the introduction (a few additional recent studies are listed below), but the later parts of the discussion and conclusion sections could maybe still be improved by highlighting the similarities and differences of the new results with previous studies investigating contaminated soils from other field sites. Despite the detailed soil characterization and previous work at the site, the main binding form(s) of Hg in the soils at the studied contaminated site still remains somewhat unclear, making a direct transfer of the results to other contaminated legacy sites more difficult. Anyway, this is just an appeal to try carving out the specific new findings of the study and their implications to a larger extent than what is already done in the well-prepared manuscript. I look forward to seeing the final product in print.

l12: I would use “ecosystems” instead of “eco-systems”.

l19: I am not sure whether the term “control soils” is helpful in this context. The same two soils were used in all experiments, once with manure addition and once without manure addition. The experiments without manure addition could be denoted as control experiments to assess the effect of the manure addition, but the soils are not “control soils” in my opinion.

l21: I don´t think that you were able to monitor "methylation of Hg in the soil solution". You measured MeHg levels in the soil solution, but it´s not clear that the methylation process also took place in the soil solution.

l22: "lower" instead of "lowest"?

l25-26: What do you mean by "proportional increase"? Do you refer to a higher fraction of colloidal Hg relative to total Hg in the manure vs. the non-manure experiments? Do the percent values indicate relative or absolute values? Maybe "higher relative" instead of "proportional"? Please rephrase to clarify.

l27: "Net Hg methylation" is not the same as "MeHg/Hg", but it could be maybe described as "increase of MeHg/Hg relative to the initial condition" if no absolute MeHg values can be compared.

l47: Hg is not "found as FeS" but can be associated with this mineral phase. HgS could be both cinnabar or metacinnabar.

l55: The term "immediate decrease" is not really clear in my view. A release of Hg into soil solution first causes a concentration increase. Maybe "relatively rapid" instead of

“immediate”?

l62: Here and throughout the manuscript: If a publication is cited with the author name in the text, then the year should be in brackets (here: “(2013)”.

l72: I understand that Hg(II) binding to thiol-rich NOM is thermodynamically favored but I am not sure about the term “larger”. Do you refer to molecular mass/size and can you give a reference to support this statement?

l89: “has” instead of “had”

l96: The charge of sulfate is “2-“.

l102: Weber et al. (2009) did not study Hg. Some additional Hg studies on temperate floodplain soils include for example Wallschläger et al. (1998, doi: 10.2134/jeq1998.00472425002700050009x) and Lazareva et al. (2019, doi: 10.1007/s12665-019-8253-9).

l104: You may also refer here to the recent studies on Hg dynamics in similar experimental systems with biochar additions (e.g., Beckers et al., 2019, doi:

10.1016/j.scitotenv.2019.03.401 and 10.1016/j.envint.2019.03.040; Wang et al. 2020, doi: 10.1016/j.envpol.2020.115396 and 2021, doi: 10.1016/j.chemosphere.2020.127794). Concerning similar experimental studies on other types of Hg-contaminated material, the recent studies by Zhu et al. (2018, doi: 10.1016/j.gca.2017.09.045) and Eckley et al. (2021, doi: 10.1016/j.envpol.2020.116369) could be of interest as well.

l106: "studies" or "researchers" but not "researches"

l110: Did you have an initial hypothesis on how the addition of manure would influence the system? If yes, it might be useful to present such a hypothesis here and then get back to it in the discussion/conclusion sections.

l118: Maybe better use the term "waste water releases" instead of "emissions" to clarify the pathway of the contamination. I think that many people primarily think about atmospheric pathways in the context of "emissions".

l118: The company did (and still does) not only produce acetaldehyde but also many other chemicals. Mercury was also used in several other processes including e.g., production of vinyl chloride and chlor-alkali electrolysis (see cited historical report by Glenz&Escher, 2011).

l137: through

l138: Maybe better “Hg level” instead of “pollution”. There could be also other pollutants present.

l147: add “and” after “soil”

l180: I think that it should be “Table 2” instead of “Table 1” here (change numbers if this is mentioned first).

l185: In my opinion, there is no need to capitalize mineral names.

l191: I suggest adding the information which relative fraction of the total solution phase was withdrawn via sampling during the experiments. Could the lower water level already have had an influence on the results for the later sampling points?

l202: DOC concentrations are later reported as mg/L, so I suggest using the same unit here for the blank value.

l246: This section does not only describe Hg dynamics but also many additional parameters.

l251: Here and in the following: I suggest clarifying early on in the manuscript what the indicated "+/-" values represent. I assume 1SD of the triplicate experiments?

l288: delete "but"?

l342: "suggests" instead of "suggest, "

l343: There could be also other relevant Hg(II) binding sites in NOM even if all the thiol groups are saturated. Is there any indication in the literature that Hg(II) binding to Mn oxide phases would be preferred relative to, for example, Hg(II) binding to carboxyl groups in NOM or binding to Fe oxide phases? Anyway, I certainly agree that your interesting data suggests that Mn oxides play an important role for Hg cycling in the studied system.

l368: The spelling of "sulfate/sulphate" and "sulfide/sulphide" should be consistent.

l386: Add "of " after "formation"

l415: Can you specify the approximate proportion of mobilized Hg relative to total soil Hg over the course of the experiment?

l439: words/values are missing after “up to”

l455: delete “A”

l470: from

l473: Please explain how the sampling could have influenced the element concentrations in the remaining soil solution. As written before, I suggest describing the water level changes in the microcosm during the experiment and its potential effects on the investigated parameters.

l477: Is chloride really an important component of inorganic fertilizers? I thought that most crop plants don´t like elevated chloride levels. And even though chloride forms could potentially form stable complexes with Hg(II) in soil solution, binding of Hg(II) to DOC (or generally NOM) is probably still dominant.

l481: I suggest that you try specifying the observed "distinct effect" of the manure addition. You could potentially come back here to initially defined hypotheses (see comment above) and conclude whether you have verified or falsified them. I could imagine that such an approach might be helpful in further highlighting the novelty of the findings compared with previous work. This is a carefully conducted and well-described experimental study, but I believe that it might be possible to identify more clearly which specific insights on Hg cycling in contaminated soils were generated and how these findings could be relevant to other field sites and future work.

l489: suggests

l489: Which changes in redox conditions do you refer to here? Higher/lower redox potential or do you mean that fluctuating redox conditions in general (irrespective of the direction) increase Hg methylation?

l490: Maybe better "is removed from the soil" instead of "declines from the soil"?

l492: add "of" after "changes"

l492: Wording: Are the "temporal changes" really limited by "microbial activity"? Or rather "controlled by the extent of microbial activity"?

l493: Maybe “stimulated” instead of “facilitated”?

l497: It´s nice if your findings are supported by earlier studies, but I suggest highlighting the novelty of your findings (e.g., important role of Mn redox dynamics? decreased mobility due to manure addition? etc.).

l498: How does this finding compare with other studies in which organic amendments were added to Hg contaminated soils (see e.g., references listed above)?

l499-500: In my view, the sentence on “more work is needed” is superfluous. This is always the case.

l510-514: Please make sure that each sentence contains a verb.

l511: Stephane

l514: “advice” instead of “advises”

l582: Historische

Figure 1: I suggest increasing the font size in the Table. This will be very small in a printed article.

Figure 2: This is a well-designed figure containing a lot of information. You could consider removing all the x-axes except the lowest one to make it a bit less busy. What about PFe (did you see a significant fraction of Fe colloids)? The “-1” in the y-axis caption of panel g should be superscript.

Figure 3: I suggest pointing out in the figure caption that Hg concentrations are shown here in ng/L instead of µg/L in Figure 2.

Figure 4: y-axis caption “colloid”

Figure 5: y-axis caption “Fluorescence”, legend “Composition” and “dissolved”

Figure 6: I suggest that all y-axis ranges should start at zero to avoid a wrong impression of relative changes between the treatments. For the MeHg/Hg ratio, I suggest that you consistently use either percent or permil throughout the manuscript text and in figures and tables.

Table 1: I suggest adding "Relative" before "Particulate" in the second last line.

Table 2: Please clarify the origin of the SD values (I assume based on triplicate experiments?).

S3, l5: from

S3, l8: have

S3, l25: Merck

S3, l26: subscript “3”

S4, l25: define abbreviation DCM (dichloromethane)

S4, l29: add “to” after “transferred”

S9: I suggest clarifying in the figure caption that not only the map but also the high-resolution Hg concentration data was taken from the DUS report.