Response to:

Comment on bg-2020-466 – Jan Wiederhold

Referee Comment:

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.

Author Response:

We thank the referee very much for this positive review of our study. We acknowledge the need for comparison to similar studies and appreciate the suggestions made by the referee. With your valuable input, we were able to discuss our results more thoroughly.

Referee Comment:

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

Author Response:

Changed to “ecosystems”.

Referee Comment:

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.

Author Response:

We agree that the use of “control soils” can be misleading.

Changed L19 “control soils” to “soils” and removed the term “control” throughout the manuscript.

Referee Comment:

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.

Author Response:

Changed accordingly.

Referee Comment:

l22: “lower” instead of “lowest”?

Author Response:

Changed to lower.

Referee Comment:

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.

Author Response:

We agree with the reviewer’s comments: and changed accordingly to “a relative increase of colloidal DOM-Hg...”

Referee Comment:

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.

Author Response:

We agree that “Net Hg methylation” can be misleading. In the new version we used the term “net MeHg production” when talking about changes in absolute MeHg concentrations. As these changes are the results of both methylation and demethylation processes in soil.

Referee Comment:

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

Author Response:

Changed from “found as” to “associated with”.

Referee Comment:

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”?

Author Response:

We agree with the reviewer’s comment. The term “immediate” describes the closed possible sequential time relationship. “relatively rapid”/ “relatively fast” is a more suitable term to use for the described phenomenon.

Changed to: “relatively rapid”.

Referee Comment:

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)”.

Author Response:

Agreed: Changed throughout the manuscript according to the format of BG. Here: Hofacker et al. (2013).

Referee Comment:

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?

Author Response:

This is correct. Here we intent to refer to high molecular weight hydrophobic NOM which was show to have a high density of strong binding sites (thiols).

We changed this accordingly.

Referee Comment:

l89: “has” instead of “had”

Author Response:

changed to “has”

Referee Comment:

l96: The charge of sulfate is “2-“.

Author Response:

Changed to ”SO_4^{2-}“

Referee Comment:

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).

Author Response:

Corrected the misassignment of the reference used earlier in the text.

Removed “Weber et al. (2009)” added “Lazareva et al. (2019)”

Referee Comment:

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.

Author Response:

We appreciate the input the most recent literature and added a selection to this list to introduction and discussion.

Eckley et al. 2021, doi: 10.1016/j.envpol.2020.116369

Beckers et al., 2019, doi: 10.1016/j.scitotenv.2019.03.401

Wang et al. 2020, doi: 10.1016/j.envpol.2020.115396

Wang et al. 2021, doi:10.1016/j.chemosphere.2020.127794

Referee Comment:

l106: “studies” or “researchers” but not “researches”

Author Response:

Changed: “researches” to “researchers”

Referee Comment:

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.

Author Response:

We added our working hypotheses, “Based on the presented state of knowledge, we hypothesize that the manure addition would accelerate the release of Hg by accelerated reductive dissolution of Mn-oxyhydroxides and eventually change the complexation of Hg in the system towards Hg-NOM complexes.”

Referee Comment:

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”.

Author Response:

We acknowledge that in the scope of this study the expression “waste water releases” might be more precise.

Changed: “emissions” to “waste water releases”

To date, the pollution history is still not fully understood at this specific legacy site. Emissions of Hg(0) in the area can not be ruled out.

Referee Comment:

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).

Author Response:

This is true. We referred to acetaldehyde because is still produced and was the main process applied during the time of highest Hg emissions (1960-1970s).

For completeness and clarity: removed “acetaldehyde producing” – added: “...chemical plant upstream historically using Hg in different processes (chlor-alkali electrolysis, acetaldehyde- and vinyl chloride production)”

Referee Comment:

l137: through

Author Response:

changed “though” to “through”

Referee Comment:

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

Author Response:

We changed “pollution” to “Hg level”

Referee Comment:

l147: add “and” after “soil”

Author Response:

For clarification we remove “soil” completely. Other possibility would be “soil’s pore space”.

“soil and pore space” may be misleading.

Referee Comment:

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

Author Response:

Changed numbers accordingly.

Referee Comment:

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

Author Response:

Changed: “Quartz, Albite, Orthoclase, Illite/Muskovite, Calcite.” to “quartz, albite, orthoclase, illite/muskovite, calcite.”

Referee Comment:

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?

Author Response:

Roughly, 4-6 % of the added water volume are sampled at each time point (30- 45ml). We added the information about the volume of water sampled in section 2.5 Soil solution sampling and analyses and added the sum of sampled porewater with respect to time in a supplement figure. We attached this figure at the end of this document.

Indeed, we think that sequential sampling from the bottom of a soil/water column may result in a relation between the sampling points. We now also further highlight this in the paragraph "Experimental Limitations". It is hard to evaluate if a correction of the data is reasonable.

Referee Comment:

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

Author Response:

Changed: molarity to concentration (w/v). "Incubation experiment blanks were below 4.75 mg L-1 and 22.4 µg L-1 for DOC and TNb, respectively."

Referee Comment:

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

Author Response:

Changed: "Mercury dynamics (mobilization and sequestration)." To "Soil solution chemistry and Hg dynamics."

Referee Comment:

l251: I assume 1SD of the triplicate experiments?

Author Response:

For clarification we added: "Uncertainties of soil solution parameters are display as 1SD of the triplicate incubation experiments throughout the manuscript." In section 2.5: Soil solution sampling and analyses.

Referee Comment:

l288: delete “but”?

Author Response:

We assume you refer to l280.

Change: Replaced “but” with “and” and added “ the release” after “after”.

Referee Comment:

l342: “suggests” instead of “suggest, “

Author Response:

Changed: “suggests” instead of “suggest, “

Referee Comment:

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.

Author Response:

Unfortunately, we could not find any literature on the competition between functional carboxyl-sites, Mn- and Fe-oxide surfaces. We acknowledge that input and would like to express the need of further research in the area.

Referee Comment:

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

Author Response:

Change: We chose the versions “sulphide and sulphate” and changed accordingly.

Referee Comment:

l386: Add “of “ after “formation”

Author Response:

Change: Added “of “ after “formation”

Referee Comment:

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

Author Response:

We added:

"...However, the released Hg-pool is relatively small compared the HgT levels of the soil. We estimate that about 12.8 ± 4.2 µg kg-1 Hg (0.02 % of HgT_{soil}) was evacuated by sampling during the experiment."

Referee Comment:

l439: words/values are missing after "up to"

Author Response:

Added the maximum value observed for MeHg in soil after the first flooding period.

44.81 µg kg-1

Referee Comment:

l455: delete "A"

Author Response:

Change: Accepted

Referee Comment:

l470: from

Author Response:

Change: Accepted

Referee Comment:

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.

Author Response:

Thank you for this suggestion. We further discussed the effect of the concentration gradient and the soil solution sampling influenced the element concentrations in the remaining soil solution in this section. We referred to the high relative amount of soil solution (4-6 %) sampled at each time point resulting in a change of water levels.

Referee Comment:

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.

Author Response:

In Switzerland commercially used NPK fertilizers contain Potassium in the form of KCl and K2SO4. Fertilizers may contain up to 100% of the Potassium in the form of KCl. Please refer to https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=&cad=rja&uact=8&ved=2ahUKEwibnPvqxrLvAhWLwAIHHROlDh8QFjAEegQIDhAD&url=http%3A%2F%2Fwww.landisense-oberland.ch%2Fmedia%2F0494af6b-2751-4de9-876a-3147f1180733%2FPQLbcw%2FMedien%2520LANDI%2520Sense%2520Oberland%2FTeaser%2FD%25C3%25BCngersortiment%25202020.pdf&usg=AOvVaw00mIyoQoWZGrMndpatdBS5

a recent fertilizer catalogue.

As we show in Fig. S6 and S7 both K and Cl are in the range of 0.8 g/L and 0.5 g/L in soil solution at the beginning of the incubation. The ionic strength of this solution is close to brackish waters and surprisingly high. We assume that K and Cl concentrations would have decreased upon the next rain events in the area, given that K and Cl are conservative elements which are highly soluble and marginally interact with high specific surface minerals. This points towards a proximate fertilization of the soils in the area.

Although the binding of Hg to NOM might be favorable, an addition in of KCl to this extend in NOM poor soil might still influence Hg speciation in the upper 10 cm of the soil column.

We did not consider conducting aqueous geochemical modelling of Hg species. Here, the characterization of the DOM is crucial to get a good picture. We did not further characterize DOM.

Referee Comment:

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.

Author Response:

Thank you for this suggestion. We reformulated the conclusions, specified the effects of manure addition (e.g. formation of meta cinnabar, accelerated Mn oxyhydroxide reduction) and compared our work with previous studies to emphasize the novelty of our study.

Referee Comment:

l489: suggests

Author Response:

Changed: “suggest” to “suggests”

Referee Comment:

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?

Author Response:

We refer to a soil reduction. Changed accordingly.

Referee Comment:

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

Author Response:

Change: “However, MeHg may subsequently either be removed from the soil by advective transport of dissolved MeHg in the soil column or be transformed by reductive demethylation.”

Referee Comment:

l492: add “of” after “changes”

Author Response:

Change: Accepted

Referee Comment:

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

Author Response:

Changed

Referee Comment:

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

Author Response:

Replaced “facilitated” by “stimulated”.

Referee Comment:

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.).

Author Response:

The novelty of our findings was better characterized in the discussion and the conclusions in order to differentiate this study from previous ones.

Referee Comment:

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)?

Author Response:

Added comparisons with biochar amendments (Eckley et al. 2021, doi: 10.1016/j.envpol.2020.116369, Beckers et al., 2019, doi: 10.1016/j.scitotenv.2019.03.401, Wang et al. 2021, doi:10.1016/j.chemosphere.2020.127794) and organic amendments (Li et al. 2019 doi:10.1016/j.chemosphere.2019.05.234, 2019.)

Referee Comment:

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

Author Response:

Change Accepted

Changed: “We emphasize the need of field trials integrating biogeochemical processes, hydrological transport and Hg soil-air exchange in order to establish Hg flux models to better understand in situ soil Hg mobility.”

Referee Comment:

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

Author Response:

Complete sentences.

Referee Comment:

l511: Stephane

Author Response:

Change: Accepted

Referee Comment:

l514: “advice” instead of “advises”

Author Response:

Change: Accepted

Referee Comment:

l582: Historische

Author Response:

Changed: Histoische to “Historische”

Referee Comment:

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

Author Response:

Agreed. Changed font size. Moved table to landscape turned table to landscape.

Referee Comment:

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.

Author Response:

We followed the suggestion of the referee and:

1.) Created a new figure in response to reviewer 2

2.) Removed the x-axis labelling except the lowest one.

3.) We added P-Fe and discussed it in the main text.

4.) Made sure that all “-1” were superscript.

Referee Comment:

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.

Author Response:

We followed the referee’s suggestion:

1.) Mentioned the display of Hg concentrations in ng L-1

Figure 4: y-axis caption “colloid”

Changed.

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

Changed.

Referee Comment:

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.

Author Response:

We followed the referee’s suggestion and:

Adjusted the lower limit of the y-axis to 0 and changed MeHg/Hg ratios to the more frequently used %

Referee Comment:

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

Author Response:

Agreed with referee’s suggestion.

Referee Comment:

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

Author Response:

This is correctly assumed by the referee.

Added: Uncertainties are given as 1σ standard deviation of triplicate experiments (method triplicates).

Referee Comment:

S3, l5: from

Author Response:

Change: Accepted

Referee Comment:

S3, l8: have

Author Response:

Change: Accepted

Referee Comment:

S3, l25: Merck

Author Response:

Change: Accepted

Referee Comment:

S3, l26: subscript “3”

Author Response:

Change: Accepted

Referee Comment:

S4, l25: define abbreviation DCM (dichloromethane)

Author Response:

Change: Accepted

Referee Comment:

S4, l29: add “to” after “transferred”

Author Response:

Change: Accepted

Referee Comment:

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.

Author Response:

Change: Accepted

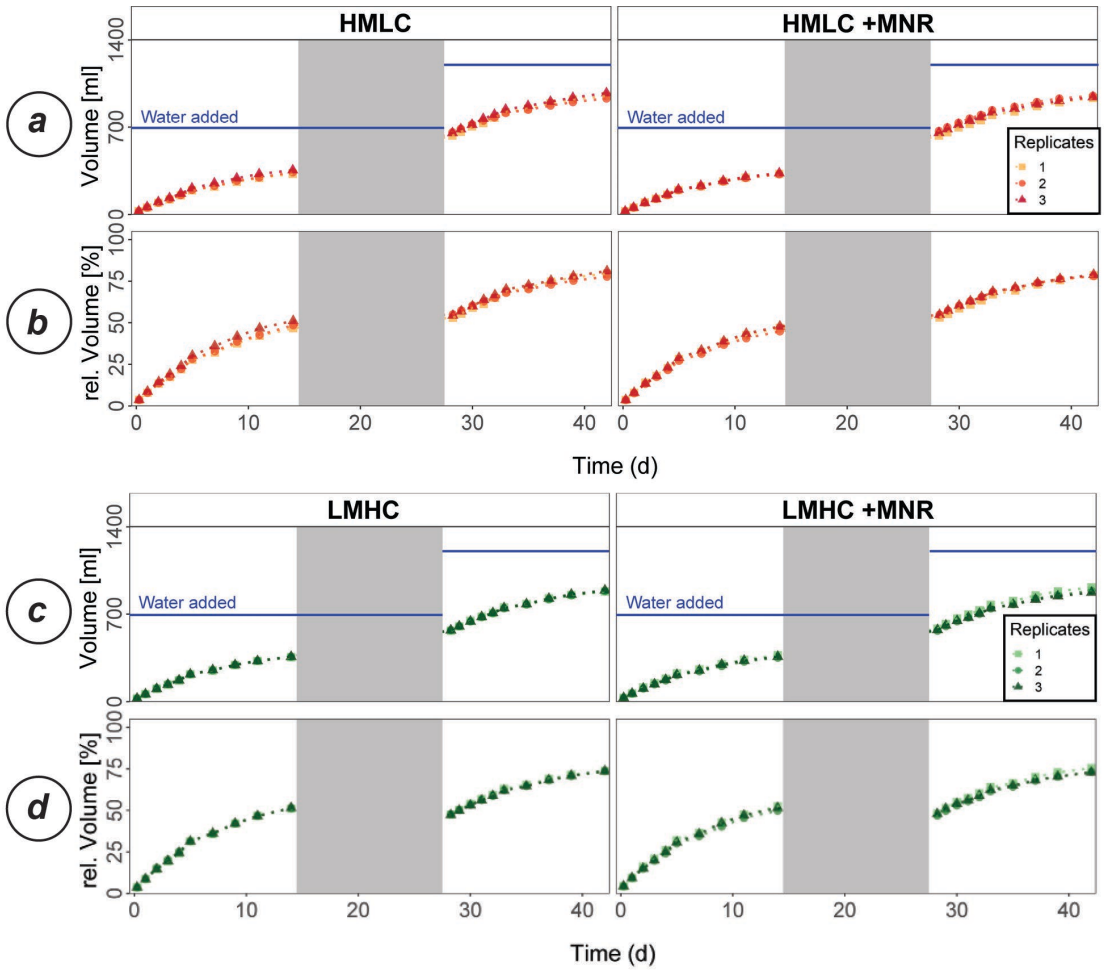

Figure S1 The evolution of sampled solution. a.) and c.) display the sum of sampled solution during the incubation experiment for the HMLC and LMHC soil respectively. b.) and d.) display the relative volume of previously sampled solution with respect to added artificial rainwater. Blue lines mark the sum of water added during the experiment. The gray area indicates the drained period. The three shades of green/orange distinguish the 3 replicate incubators.