

Biogeosciences Discuss., author comment AC1
<https://doi.org/10.5194/bg-2022-170-AC1>, 2022
© Author(s) 2022. This work is distributed under
the Creative Commons Attribution 4.0 License.

Reply on RC1

Laura Balzer et al.

Author comment on "Role of formation and decay of seston organic matter in the fate of methylmercury within the water column of a eutrophic lake" by Laura Balzer et al.,
Biogeosciences Discuss., <https://doi.org/10.5194/bg-2022-170-AC1>, 2022

We would like to thank reviewer 1 for the detailed comments and suggestions to improve the quality of our work.

The paper aims to assess the role of seston in the production of methylmercury in a eutrophic lake. The paper is based on water, seston, trap and sediment sampling at seven dates between April and November 2019.

The paper is well written and structured, methods thoroughly described, and results generally well presented. In general, I like this paper, but I find that there are weaknesses in the design of the research and then over-interpretation of some results. MeHg has not been measured in the dissolved phase, then there is no clear picture of the overall situation. Based on partition coefficients, and on the concentration of seston in water column, it appears that usually most the MeHg in the raw water column is in the dissolved (or colloidal phase) (see Gallorini and Loizeau 2022, Chemosphere).

We thank the reviewer for this positive assessment.

We are aware that analyses of MeHg in the dissolved phase would have been useful. However, our paper is focused on seston and specifically the fate of MeHg during decay of algae derived organic matter. Our intend was not to resolve the entire biogeochemical Hg/MeHg cycle in this lake. We further believe, that the situation is different in eutrophic lakes compared to oligotrophic lakes (such as lake Geneva in Gallorini and Loizeau 2022) regarding the partition of MeHg between the dissolved and the solid phase as there is so much more organic matter present during algae blooms that the dissolved phase is of minor importance here. Previous studies have shown, that dissolved Hg is depleted after algae blooms due to water phase Hg scavenging by sinking seston (Schütze et al, 2021).

The authors rule out the possibility of diffusion of MeHg from the sediment, without clear evidence, as there is no measurement of seston and MeHg in the water column below RTZ. They invoke "that mixing is minor during times of high productivity (line 265)", however diffusion seems to occur and shown by the Mn profiles. The "pronounced" maximum concentration at the RTZ that is at the base of the all discussion and interpretation is not so evident. In line 250 it reads "During periods in which the RTZ was clearly defined, MeHg concentrations in seston showed a pronounced maximum at the RTZ that did not occur in April,

when no RTZ was observed (Fig. 3).” The pronounced maximum is clear only in Aug. 19.

The reason why there is no data from below the RTZ in some of the profiles is that there was not enough suspended matter below the RTZ which could be sampled with our method (25 µm net several 2 hours pumping) (see L254). From our data in the solid phase, we assumed that MeHg diffusion from the sediment is unlikely, but we agree with the reviewer that we cannot rule this out. We have now added the depth profiles of DOC from the different sampling days. MeHg released from bottom sediments is most likely bound to DOM as chloride concentrations in lakes are too low to be competitive. The DOC profiles clearly indicate that DOC release from the sediment occurs as indicated by the highest DOC concentrations found in the deepest water samples and it is likely that MeHg released from decaying organic matter in the uppermost sediment layers is bound to DOM and distributed in the water column during lake mixing. However, DOC profiles do not show diffusion gradients during the summer months when the algae blooms occur and concentrations were even higher in the upper water layers indicating DOC release from decomposing algae organic matter which suggests rather MeHg formation in the water phase (labile algae derived DOM supports microbial MeHg formation in the water phase (Bravo et al...)) than uptake of MeHg released from the sediment although both is possible. We will revise the manuscript accordingly.

Some discussed variations are very small and probably within uncertainties (e.g. C/N ratio). But the authors do not give uncertainty of the measurements, so it is impossible to evaluate the relevance of the variations.

We will add uncertainties of the measurements, which, however, cannot explain the observed variations and trends in the data. We will also tone the interpretation of the relatively small variations of C/N ratios in the upper water layers down and will focus on the changes in the RTZ.

Detailed remarks

L25 “The methylation of inorganic divalent forms of Hg(Hg(II)) to toxic MeHg is carried out...”. The sentence implies that Hg(II) is not toxic, which is not the case.

We agree. Will be changed accordingly.

L 29 “ being influenced by temporal and spatial variabilities”. It is not clear to which processes these variabilities refer.

We refer to the variability in redox-conditions. Will be revised

L 32 all these references on marine environment (19) are too much. Better to select the most relevant for your purpose.

Will be changed accordingly.

L50 About MeHg formation in lake snow, see Gallorini and Loizeau 2022, Chemosphere.

Reference will be added

L84 As a pump and tubing have been used to sample water and seston, how potential contaminations (mainly for dissolved THg in water) have been evaluated?

Pump and tubing has been cleaned (acid washed) thoroughly. Blanks will be added.

L89 text reads "PE Falcon tubes for." The end of the sentence is missing.

Will be corrected

L94 text reads "but in most cases covered the upper 4 m". However most figures indicate that the lower sample is at 5 m depth. Moreover, it is not clear why samples below 5 m were not collected.

Will be changed to 5 m. We were not able to gain sufficient material for solid phase analyses during 2 h sampling/ pumping as the amount of suspended matter below 5 m was, in most cases, very low. Longer pumping was not possible due to overheating of the pumps etc.

L97 Is electrical conductivity corrected for temperature? Explain how it and other parameters were measured? From CTD or on the boat?

Water parameters have been measured on the boat and are corrected for temperature.

L99 The exposure time of the sediment trap (141 days) is very long, and then the material experience early diagenesis if no preservative was added. Then it is not clear why this sample was collected.

The idea of the sediment-trap approach was to get an idea what the integrated material looks like after a period of some months of decomposition and if/how it differs from bottom sediments.

L162 change "the" to "then"

Will be changed

L182 and following. It should be better stressed how the author link parameters to productivity. For instance, L188 text reads "Chlorophyll a concentrations were 2.5 to 2.8 8 µg, indicative of low phytoplankton productivity." Chl a is not a measurement of the productivity, as other factors may change the Chl a concentrations (for instance grazing). Chl a may be a direct proxy of algal biomass, not productivity.

We agree, will be changed

L202 the profile of Fe in May is strange, as Fe(III) is essentially insoluble. So what is the "dissolved" species found in the upper layer in May? Then what happened in August 19, Fe dropped from > 500 to 100 ug/L and increase again > 500 in September.

We did not analyse dissolved Fe-species, but we assume that the small amount of dissolved Fe found in the upper water layers is organically bound Fe, probably release during algae matter decay or from zooplankton. DOM-Fe is soluble under oxic conditions. The appearance of dissolved (reduced) Fe changes in the deep water layers between August 12, 19 and Sep.02 are most likely due to a change in redox zonation caused by more or less amount of suspended organic matter and differences in productivity/amount of algae biomass produced. Note, that pH is higher on Aug.12 = higher productivity compared to August 19. Similar, pH and Chl a at Sept 02 is higher (higher productivity) than on Aug. 19.

L203 text reads "After mixing in November, the Mn and Fe concentrations were uniformly low". From Fig 1, Mn isn't low in November, with values much higher than in surface waters measured the other months.

We agree, although the message is clear that there is no more redox zonation. Text will be changed.

L207 C/N ratio compare organic carbon to organic nitrogen in samples. Is all C in the sample from organic matter? For instance, the sediment trap results indicate C concentration of ~9%, that is 18 to max 30% of the sediment is organic matter. What is the composition of the remaining 70% of the sediment? Does it contain C as carbonates? This point should be clarified.

Will be clarified. The remaining material in the traps is mineral matter. There is no carbonate formation in the lake. In addition, samples have been decarbonated prior to carbon analysis. In addition, in the deep layers where the sediment trap was installed the lower pH will cause dissolution of calcite.

L213 The decrease of C/N ratio explained by mineralization is not obvious. A reference is needed here, as usually it is the reverse that is observed as mentioned the given reference Meyers and Lallier Vergès 1999. Moreover, is the decomposition the only processes, what about selected grazing or change in composition of the seston (phyto vs. zooplankton) to explain the C/N variation?

We agree with the reviewer that changes in C/N ratio above the RTZ are probably too small to undoubtedly indicate organic matter decomposition. We also agree, that some of the small changes seen here could have been caused by the occurrence of zooplankton. We will therefore restrict the interpretation of C/N ratios as a measure for organic matter decomposition to the values within or below the RTZ.

L260 text reads "This would explain the continuous increase in MeHg concentrations with depth..." What is the explanation? The absence of microniches does not explain the formation of MeHg at depth, where O₂ saturation is still > 20%. Diffusion from sediments?

This sentence is indeed not clear and will be clarified. We believe that the increase in MeHg concentrations with depth in April is mainly caused by mass loss due to progressive organic matter decomposition (comparable to what has been described by Gallorini et al, 2022) although we cannot exclude MeHg formation by Mn reducing bacteria.

L294 Mass loss is the only explanation of the THg increase with depth. However, C concentration decrease by max a factor 3.9, whereas THg increase is a factor 26. Then the mass loss cannot account totally for the increase in THg concentration.

We are not sure if we understand this comment correctly. THg and C do not necessarily have to increase by the same extent because C (and other elements) is lost during mineralisation, but Hg is not. An additional explanation might be that some Hg released to the water phase during organic matter decomposition is scavenged by sinking seston as it has been observed in marine studies.

L314 text reads "The sulphide produced may form insoluble complexes with Hg (Shanks and Reeder, 1993; Bianchi et al., 2018), such as Hg sulphides (HgS), meaning that Hg becomes less available for methylation" It is not so clear that the presence of S decreases the bioavailability of Hg. Barrouilhet et al 2022 ESPR show that methylation potential increases with S concentration before to

decrease at high S concentration.

Our data indicates that there is no sulfate reduction and thus formation of sulphide. The increase in S concentration in seston is thus rather due to mass loss during organic matter decomposition. This was an assumption which we could not prove in the frame of this study (only based on the increase of S concentration). The amount of material gained was too small to do Hg-thermo-desorption analyses or similar. The study of Barrouilhet et al 2022 is quite different from what we did and we could hardly say if their findings do apply here.

L318 text reads "Thus, THg and MeHg fluxes to the sediment are largely determined by changes in OM composition and mass loss during decomposition." While these processes may change the MeHg fluxes, it is not clear why these processes change the flux of THg: i) if the authors are correct, the increase in THg concentration is due to mass loss in OM, then the quantity of THg remain the same, so the flux, and transformation of THg to MeHg will not change the flux of THg as MeHg is included in THg.

We agree, will be revised

L341 MeHg concentrations in the sediments are not sufficient to assess fluxes from sediments to interstitial water to overlying water.

We agree, statement will be toned down

L354 "Water column MeHg formation and degradation in eutrophic lakes appears to be intense and occurs rapidly and at rates similar to what we observed within the bottom sediments" This statement is not supported by the data/discussion. No rate has been determined neither in the seston nor in sediments.

We agree will be changed or removed

Fig 1. The scales do not cover the entire range of the results.

Will be adapted