

Interactive comment on “Dynamic mercury methylation and demethylation in oligotrophic marine water” by Kathleen M. Munson et al.

Anonymous Referee #1

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Manuscript “Dynamic mercury methylation and demethylation in oligotrophic marine water” by Munson et al. presents information that the mercury research community has been waiting for. This study addresses Hg transformations that occur in seawater. Specifically, this study is addressing these transformations in nutrient depleted waters in Equatorial Pacific Ocean and the research took place during Metzyme cruise in 2011. The incubation experiments used seawater collected from depths that were autotrophic organisms were most abundant i.e. chlorophyll maximum, and from depths where oxygen was most rapidly consumed mostly due to intensified organic matter remineralization. I commend author’s choice of their experimental plan as autotrophic as well as heterotroph driven processes have been hypothesized as strongly coupled with MeHg in the ocean. Other elements of Hg cycling have been also shown to be

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coupled with biological processes. Analytical work has been designed carefully. Most important details are included and the readers should be able to imagine how the study was conducted and how analyses were conducted with some exceptions, which I will list in my specific comments. Munson et al. have conducted incubation by triplicating bottle, this has not been done that way and so it is great to be able to see the error bars on data representing specific time points. One can notice that error bars are not non-negligible further reinforcing the importance of replication in bottle incubations – I commend Munson et al. for following such procedure. To understand differences between formation of MeHg (Note: as authors have done, I am combining into this category any organic Hg form that would be detected as monomethylmercury or MMHg) and degradation of MMHg Munson et al. have computed potential reaction rates as done in some previous studies. Authors refer to the Lehnher et al. articles in reference to their calculations of k_d , the demethylation rate however surprising little detail is provided for a reader to fully understand how the rates presented in the Munson et al. study have been calculated. This description needs to be improved and authors need to present which time points were included in rate calculation. It is becoming even more complicated for the calculated for k_d as authors seem to use two approaches to calculate them i.e. 1). based on a spike of isotopically labeled MM198Hg and 2). based on degradation of “newly formed” [from a spike of 202Hg(II)] MMe202Hg during the time course incubation experiment. I find that dedicating more attention to proper description of this component is critical as all the Hg related results depend on these calculations. One other note I want to make in relation to the reporting of the “potential methylation rates” is that authors well realize that the these estimated rates are very likely inaccurate. The uncertainties associated with the reported rates are merely due to differences in detected MMHg between replicate bottles, while other factors might influence the results too, they are just not considered here. At this point there is such limited body of work on this subject and my feeling is that methods to accurately and confidently provide rates of Hg transformations are not fully worked out – this work is not straightforward and as authors mention the other publications reported on “rates”

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that were determined based on somewhat different procedures. I would urge the authors to caution readers, especially those from the modeling community, to consider that even though called “potential rates” might be misrepresenting the actual rates. More research using water incubations with Hg stable isotopes must be published and the community needs to work out “common practices” in this type of research. Still, all this caution and hesitation to take the “rates” values seriously, I believe that the data set generated in this study is impressive, novel and deserves publication. Surely, this study pushes the field forward. However, there are some items that must be addressed before this manuscript turns into a publication. This study provides time series with good replication – you could do statistics to compare curves – why wasn’t this done? I don’t have many comments for the “Introduction”, I think that authors have provided a solid background. However while authors notify the reader in the last paragraph of this section, they were aiming “to gain insight into the mechanisms of Hg methylation in the ocean”. Sure they have provided some insight. My criticism is that the study isn’t presenting clear hypotheses that authors were testing for. It is clear that hypotheses were posed but authors have forgotten to include them into this manuscript. I am a strong believer in hypothesis driven research, especially in experimental research type. Statement of goal and hypotheses would help structure the discussion of results which is at the moment following the different kinds of experiments there went on during that cruise – 3.1 Unamended samples, 3.2 Amended samples etc. – these titles are not very exciting. I already know about all these experiments because I read through the materials and methods – I would advise to think of a title that is more informative i.e. provides a clue about the main message/finding/phenomenon that experimentation provided supporting evidence for. I don’t see why this article has to be split up in the current fashion. Again, if you had hypotheses then these could be used for a structure of discussion and the flow would be largely improved. I would recommend that authors consider changing. It is a great study, my recommendation is to help making it even greater (of course that is in my opinion)!

Beneath, I will list my more specific comments: Materials and methods Line 86 – should

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it be “Hg species” or “Hg form”? - consider throughout the manuscript. Line 112 – “ $\frac{1}{2}$ ” would be nicer if spelled out, I think. (- > this is also in line 259) Line 114 – Instead just “T0” perhaps it would read nicer if an additional description appear near e.g. T0 = time of the initial sampling or something like that. Line 116 – How about “Equator” instead of “0°” ? Line 117 – I am not sure why the incubation was set at the highest temperature setting? Please explain in text. Line 118 – Provide final concentration of sulfuric acid in seawater. Line 123 – Apropos “generally low” – This give a feeling as if kinetics of DMHg degradation and even MMHg degradation in different seawaters were well established but the first one was measure in only one study thus far! Please revise this text. Lines 126-127 – Make it clear that this is an assumption – reword appropriately. Line 131 - Provide more information about your Matlab script - is it freely available? Who has written the code etc. Line 136 – present your assumption about the amount of MM198Hg spike used as an internal standard. Line 139 - You highlight the “potential rates” but you have also assumed the linear reaction, which is a far cry from what we see in your data. Again, clarity to how the rates were determined would be beneficial. Line 146 – Do you mean that the recoveries were comparable? – This sentence is not clear to me. Line 148 – Do you decide to use the term “apparent” or “potential”? Decide to choose one. I actually think that “apparent” is a more appropriate. You would need to check throughout the manuscript. I think these rates are apparent based on specific experimental design and should be treated with a grain of salt.

Line 151-154 - This paragraph needs to be improved and more information is required as I already noted in my general comments.

Results and Discussion

First paragraph reads like “material and methods”

Line 162 – Yay for triplicates!

Line 165 - What exactly is the 1st order here? Fig. 1 doesn’t show rates. Again, maybe I am unsure because you have not really specified how the potential rates were

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calculated. If the publisher does not limit figures then why not include all the data – show results from all incubations?

Line 175 - You mean reactivation of dormant cells? Sessile doesn't seem right in this context.

Line 177 - This sentence feel unfinished. Could you put a coma there and finish it off with something similar to this "therefore decreasing the likelihood of microbe-mediated Hg methylation".

Lines 182- 183 - You say: "...enhanced methylation in filtered water may dominate in Pacific water" but this is too general. Please be sure that this statement is only relevant to your study region.

Line 223 – Remove extra period.

Lines 237-244 - This paragraph is not coherent. The topic sentence is talking about the importance of demethylation but this is not developed any further. In the topic sentence specify differences in what.

Line 253 - If Fig. S3 is so important and it seems that authors use it to support their claims then why not include it into the main text? Also, this figure could use O2 information interpolated on top of the OCRR values.

Line 258 – *in situ* should be in italics

Line 266 - it should be "filtered particulate matter" as it was no longer in suspension.

Line 271 - This comment is for the caption in Fig. S2 – please change wording. For example: Concentration of Hg(II) as calculated by balancing measured dissolved Hg forms i.e. THg, MeHg, Hg(0) based on equation 1 in the main text.

Equation 1 – where is the MeHg diss. From? Why isn't it presented here? Also, where are the other measured values from?

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For the paragraph beginning at Line 270 - I think that the discussion here is poor and should be expanded. There have been studies discussing the issue of availability whether bioavailability or chemical availability/reactivity.

Line 280 – Wording here is awkward – please revise

Line 282 – Again, please revise wording "additive additions" ??? That doesn't sound right.

Line 292 - Isn't C succinate? If so I would just provide that name and remind the reader that it was a generic source of carbon.

Line 296 - What exactly do you mean by "dynamic methylation" – it sounds scientific but it delivers no meaning. Please consider changing it. You can simply describe the pattern of how and when things changed, just the way you did it in the second sentence.

Line 317 – But the release of Hg(II) during the two processes i.e. sinking and remineralization are connected because enhanced microbial processes are associated with sinking particles that when nearer to surface are more organic matter rich.

Lines 330 - till conclusions – great discussion on the shortcomings of spiking. Ligands need to be addressed in future research.

Line – 360 – this is the first I read about any effort to identify genes from Metzyme- this comes out of nowhere. The whole issue of genes here is completely unexpected – I don't see how this fits as a conclusion to this particular paper. I recommend rethinking the conclusion.

Fig. 3 – I would get rid of all the lines – they blur the figure, which already contains a lot of symbols. Perhaps you can consider splitting these two panels into more small panels? - it would show patterns more easily and then you can keep lines connecting data for specific time points. Scale on y-axis in a) is too large. I would increase resolution of the x-axis.

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