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Interactive comment on "A model of mercury cycling and isotopic fractionation in the ocean" *by* David E. Archer and Joel D. Blum

Anonymous Referee #2

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Archer and Blum present model simulations for marine Hg speciation and isotopes using the fast, coarse resolution Hamocc model. The prospect in doing so is exciting, and commendable, but as I read through the MS the long list of model limitations (no real air-sea exchange, forced steady state, no upwelling etc.), the total lack of discussion of Hg speciation observations, and the handful of relevant Hg isotope observations. . . .it all leaves me wondering how useful this MS will be to the community. The MS reads like a special issue rush job; did J Blum even read the final draft? Hg isotope notation is often incorrect; Hg isotope phrasing is awkward if not incorrect; units are lacking throughout; numerous statements are unreferenced; in fact most of the relevant marine Hg literature and paradigms are not discussed. We don't even know who or what generates dimethyl-Hg; so it's fine to speculate on this, but it needs to be properly

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[Discussion paper]

argumented or other scientists risk considering all assumptions for truths. Despite all that, I enjoyed reading the sensitivity analysis and the insights on how transformation and isotope fractionation processes balance out. With all its shortcomings, this study will stimulate others and help the field move forward.

Detailed comments: P1, L11. Write . . .atmospheric Hg deposition rate. . .' P1, L12. "Hg particle transport has only a relatively small impact on anthropogenic Hg uptake" Suggest . . ..Hg uptake by biota. . .. Also, this conclusion seems to contradict the previous phrase that states that Hg particle transport is essential to reproduce the nutrient type marine Hg profile. P1, L13 check . . .for long after. . .. (instead of longer) P1, L16. Final phrase of abstract is not informative. Try to write on what we can learn from the Hg isotope model version. P1, L21. "only heavy metal known to magnify its toxicity by bio-accumulating" Seems like a strange expression; not sure toxicity can be magnified. Suggest to revise.. P1, L27. Suggest to also cite Lamborg et al., 2014 Nature, who used a different method to assess the same enrichment. P1, L29. Hg is a soft acid, but not a soft atom. Revise. P2, L4. Suggest to add Obrist et al., 2017 Nature reference to the permafrost statement. P2, L18 Opening phrase of Hg isotope section: "Stable isotopes provide a powerful tool for determining the origins ((Kwon et al., 2014;Li et al., 2014;Sherman et al., 2015;Sherman et al., 2013;Balogh et al., 2015;Demers et al., 2015;Donovan et al., 2014) and transformations (Kwon et al., 2013;Kwon et al., 2014) of Hg in the natural environment."

Might it be that other groups than the Blum group also published interesting papers on Hg isotopes?

P2, L25-32 The NVE and even-MIF statements need proper referencing: Schauble 2007, GCA; Estrade 2009 GCA, Zheng and Hintelmann 2010 JPChem etc..

P2, L31 "Even-MIF has only been observed in atmospheric samples"

Even-MIF has also been observed in reservoirs that receive atmospheric deposition, including organic soils (Zheng et al., GBC 2016) and coastal sea water (Strok et al.,

2015, CRG)

P3, L17 Marine Hg(0) is not metallic, because it is a mono-atomic dissolved gas.

P3, L18. "The rates of the dark reactions are correlated to each other and to the overall rate of metabolic activity in the (Semeniuk and Dastoor, 2017) model and ours, with the scaling factors as shown in Figure 1."

Suggest to start the phrase with 'We assume…'. Figure 1 caption mentions rate constants; here the text mentions scaling factors. This is unclear; add units for rate constants (1/h, 1/s ?) to caption and text.

P3, L28. "The rates of gas evasion of Hg(0) and DMHg are taken to be proportional to the concentrations of the species, on the assumption that atmospheric concentrations are negligible. The Hg system in the surface ocean is driven by deposition influx of Hg(2+), which is applied at a uniform rate around the world."

Maybe mention that in Hamocc the atmosphere is a boundary condition, which is the reason for these assumption I suppose. That said, these assumption are known to be incorrect.

Section 2.2.1 Please provide units for all parameters discussed: Hg, POC concentrations, rate constants, scavenging constants, sinking velocity, rainfall Hg deposition etc..

P6, L1-5 Plz provide units of Kd.

P6, L10. Mention explicitly what the sedimentation flux of Semeniuk 2017 was….to help put Figure 5 in context. It would also be helpful to have now what the observed (or accepted estimate) flux is (see remarks below).

Figure 4 and caption. What are the colors?

Figure 2,4,5 and associated main text. It would be useful if benchmark observations were shown and discussed.

For ex. the Hg literature over the past two decades states a marine global sedimentation flux of 1 Mmol/y (ex. Mason et al., 2012 review), which in Fig5 corresponds to a sinking velocity of 800 m/day, and not the 400 m/day that is preferred by the authors.

Another example from Figure 2. The simulated oligotrophic atlantic has surface enrichment in THg by 5pM. Observations in the same area (Bowman et al. 2014) show surface depletion at 0.5 pM.

P8, L7. "By construction in the model, and apparently to a large extent in the real ocean, the reactions that produce and consume MMHg in the dark are biologically mediated and selfbalancing, resulting in a nearly uniform proportion of MMHg of total Hg in the deep ocean."

This is very well phrased. . ..it just needs some references to observations.

P8, L15 "The top panel shows the relative change in MMHg concentration at 250 meters water depth from enhancing MMHg production in low-oxygen waters (increasing by a factor of 1+exp(-O2/50 micromolar))."

This is an interesting scenario, but what does the 1=exp. . .parameterization of MMHg reduction correspond to? Where does it come from?

P9, L15. Clarify 'that deposition period' (avoid pronouns)

Figure 10 caption and y-axis need units. A top and bottom panel are discussed in the main text but not Figure.

P9, L28. "A guiding principle in understanding these results is that in the steady state the isotopic degassing flux, a combination of Hg(0) and DMHg degassing fluxes, has to balance isotopically the input by Hg(2+) rain, which is 0.4‰ in d202 and 0.05‰ in ïĄĎ199."

The Hg isotope notation is incorrect here. . ...did J Blum actually read the paper ïĄŁ The d202Hg and D199Hg numbers for rain are not referenced, and are also

incorrect….they are possibly switched: D199Hg should be 0.4 per mil…. Shouldn't the Hg flux to sediment also figure in the isotope balance?

P10, L4. "When configured in this way, the Hg cycle was unable to fractionate MMHg without Hg(2+) following along, because of this reaction. The isotopic composition 5 of total Hg throughout the entire ocean picked up this fractionation signature.

This way….this signature….makes it all very unclear. I cannot follow this section.

P10, L9. "This pathway is consistent with the photochemical mechanism for Hg reaction, which involves accepting an electron to form an intermediary Hg(1)."

This needs referencing; what is 'an intermediary Hg(1)'?

Figure 11 caption. Panels J, K, L are not described.

P10, L17. The Hg evasion fractionation factor needs references. Authors reports "Because DMHg is not returned to the Hg pool as quickly in the model as Hg(0), the isotopic deviation in DMHg does not pass to the other pools, which remain near 0 ‰."

Where does evading DMHg go in the model, since there is no atmosphere? In my mind it is not a matter of 'not passing to other pools; rather surface Ocean DMHg is low, therefore the evasion flux is low, and the ensuing isotope imprint of DMHg degassing remains near 0. But I may be wrong..

P10, L22. "Fractionating the reduction step from Hg(2+) to Hg(0) (Figure 11d) has only a slight impact on the isotopic signatures of any of the species, because there is more Hg(0) produced from MMHg than from Hg(2+)."

More Hg(0) produced from MMHg than from Hg(2+) seems odd; I now see in Figure 1 that indeed Hg(2) photoreduction is curiously small. Current thinking (see for ex. Soerensen et al., ES&T 2010), and current marine models have massive, balancing photo-oxidation and photo-reduction fluxes. Why is the photoreduction so small in this model? How to justify this?

C5

Section 3.3.2 The authors need to explain what literature their various fractionation factors are based on.

P11, L3. "while fractionation in MMHg reduction results in Hg(2+) that is isotopically light"

Unclear because the Hg valence in MMHg is also 2.....so this can't be reduction.....but just demethylation

Figure caption 14. What are a,b,c,d?

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