

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

### **Anonymous Referee #1**

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A really interesting paper that describes modeling efforts to describe oceanic Hg cycling, making use of recent data as well as isotopes. There have been a couple of these in recent years, each using different models and emphasizing different aspects of data as important constraints. This is the first to incorporate isotopic data, which is still very sparse, but has the potential to provide unique boundary conditions that might be very powerful.

The overall approach is sound and the experiments conducted with the model were appropriate and interesting. However, I take issue with some of the formulations and the source functions used to drive the model. I don't have specific fixes to recommend, but I think there's enough data pointing in other directions that I was disappointed the authors didn't game out other scenarios. The authors argued that the engine behind their

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experiments, the HAMOCC model of the late Ernst Maier-Reimer and colleagues, is fast and coarse enough to make it particularly useful for trying all sorts of scenarios...so this added to my disappointment.

The authors used a particularly low particle partition coefficient ( $K_d$ )...even lower than that used by other modelers and whose values were recently suggested to be too low to begin with. As the authors very briefly suggest, this must imply that their supplement of particles onto HAMOCC is not quite right, but then leave that point. In order to get the percent of particulate Hg right, and using a very low  $K_d$  value, their model must be drastically overestimating the amount of particulate matter in the ocean. Perhaps this is a situation of “two wrongs making a right” but the authors should have spent more time examining and explaining this situation and whether it creates downstream problems.

• Formulation criticisms...not necessarily to be changed, but perhaps to be discussed: 1) In Figure 1 and in the text, the authors argue that they will mostly adopt the reaction scheme developed by Semeniuk and Dastoor. They later make some changes (loss of demethylation to Hg(II)) to reconcile isotopic trends. That modification flies in the face of data, both spiking experiment results (Monperrus, Lehnherr, Perrot) and distributional data. This last point is perhaps best illustrated by noting that in Figure 1, using the relative reaction rate constants listed would imply steady state (in the dark) MeHg/Hg(II) ratios of 0.2 (which are too high compared to real data); Hg<sup>0</sup>/Hg(II) ratios of 0.01 (too low); DMHg/Hg(II) ratios of 0.3 (too high). So, while I appreciate the difficulty of developing a reaction scheme, the authors seem to have adopted an approach (from S&D) that probably was not quite right to begin with and felt compelled to modify it to reconcile with isotopic data. I would have liked to have seen them play with the reaction scheme in various ways to see if they could get it to fit real data both in terms of totals, species and isotopes. This feels like a missed opportunity. 2) The total amount of Hg in the ocean seems much too high in the Present Day scenarios (e.g., Figure 2). Both the Atl and Pac profiles have maxima that are just not seen in the ocean. Deep waters are close to right, but surface waters are much too high, and the subsurface

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max is also too high by perhaps a factor of two or more. This is probably the result of using the Streets emissions, which some are arguing does not represent how much Hg is actually moving around the planet (probably a lot is sequestered in soils). But, the authors do not comment on this inconsistency.

• Minor points In several locations, in-text citations are inconsistent in format. Sometimes single name for a multi-author article, sometimes not.

Page 1 Line 11, perhaps use “a” instead of “an” in front of “Hg,” since someone reading the text would say “a mercury maximum” instead of “an ‘h’ ‘g’ maximum.”

Line 21, “it is the only heavy metal known to magnify its toxicity by bio-accumulating up the food chain...” not true...most heavy metals undergo some level of bio-accumulation, and bio-magnification (the latter is the term I think the authors mean to use). It may be the most dramatic example, but it’s not the only example.

Line 25, the references cited for the various pollution sources of Hg are mostly derivative references...Streets 2017 is probably all that’s needed there.

Line 27, citing Streets for the factor of 3-5 increase is not accurate. They do not make a claim about that in that particular paper. That team also mostly favors a much larger degree of perturbation, as exemplified in Amos 2013, with even larger values implied with the enhanced emissions suggested by Horowitz and in the Streets reference.

Page 2 Line 18, extra left parenthesis before “Kwon”

Line 20, “six at high abundance (<10%)”...change “<” to “>”.

Line 32, after all that info in the previous few sentences about isotopes, a reference is probably needed...Blum of some sort?

Page 3 Line 2, hyphen missing in “Maierreimer”

Line 16, extra left parenthesis before “but”. Also, the authors say that they will describe differences in their model compared to Semeniuk and Dastoor in the Results section.

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Wouldn't it be better to talk about that here in the Methods?

Line 20, “the rate constant for MMHg production from Hg(2+) is proportional to the rate of POC degradation...” This statement is not support by data...though it may be a reasonable place to start in terms of modeling. Some of this comes from Sunderland North Pacific data, but that trend is not universal, and really only speaks to steady MeHg concentrations, not the rate constants. If the sentence is meant to talk about how the methylation is set to be, then the sentence should be “is taken to be proportional to the rate of POC degradation...” and maybe add some caveats in there about “who really knows...” or something like that.

Line 21, “Other Hg transformation reactions are provoked by light, and only take place near the surface ocean...” This too is not supported by data. Furthermore, one of the other models out there by Zhang et al found that subsurface interconversion between Hg(II) and Hg(0) was key in getting the right Hg distributions in the ocean. Thus, this model is ignoring chemistry that other groups have already suggested happens and maybe critical to overall Hg cycling.

Line 29, “the rates of gas evasion...are taken to be proportional to the concentration of the species [should add “ocean concentrations,” here], on the assumption that atmospheric concentrations are negligible.” I understand what the authors are saying here, but the word “assumption” seems a little weird. We know that gas-exchange of Hg between ocean and air is under water-side control and that atmospheric concentrations are not so much negligible but constant, so that it can be easily folded into the flux calculations. There are large seasonal changes in surface Hg<sub>0</sub> concentrations, however, and mid- to high latitude waters in winter time are much closer to equilibrium with the atmosphere than during summer, so if the calculations are gradient based and are assuming concentration in the air is zero, then the model is currently overestimate evasion.

Line 29, “driven by deposition...uniform rate around the world.” This might be fine at

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this level of complexity, but it should be acknowledged that this is a clear distinction from reality. Deposition is known to have strong latitudinal gradients in concentration and in flux...larger fluxes at lower latitudes than at high latitudes.

Page 4 Line 10, “a factor of 3.96 scaling...” Not sure where this comes from...and wouldn't there be two values (one for 199 and one for 202)?

Line 16, the matrix could be set up more for the uninitiated...sentence leading into it is “the equations are...” but we see matrix instead of equations. Perhaps say explicitly what the equations are before rendering them in matrix notation...or skip the matrix notation altogether and show the equations (folks who know matrix notation would be able to turn the equations into your matrix without being shown it).

Matrix, no  $\text{km}^2$  or  $\text{kD}^2$ ? Demethylation to  $\text{Hg(II)}$  is probably the dominant demethylation pathway...as shown by spiking experiments. The  $\text{D}_2$  pathway is speculative...we don't actually know much about where D comes from or goes to. Much later in the text, the authors argue that the isotope patterns don't work if there's a  $\text{km}^2$  term. That argument should at least be alluded to here to avoid confusion. But, the larger problem is that we know that pathway exists and is pretty important. So, there must be some other thing going on to get the isotope patterns to work out right. There are other problems with the Semeniuk and Dastoor rate constants, apparently, but this pathway seems to need to be removed to make the isotopes work. Exploring this more deeply seems like huge missed opportunity of this paper, because we know this pathways exists...so what would the authors suggest is missing from the reaction scheme that would make the speciation and isotopes work out?

Line 20, strictly speaking, Hg does not “evaporate” from the ocean, it “evades.” Evaporation is liquid to gas conversion, not solute to gas.

Line 20, kb is not defined.

Page 5 Matrix, again, no  $\text{M}^2$  term.

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Line 23, HAMOCC is not capitalized.

Line 27, “sinking velocity...is much slower than the actual inferred...” This is backed up by geochemical data like that cited by Anderson. . .this sentence makes it sound like the references ignored the trap data and the discrepancy. Traps are biased to heavily undersample slow sinking material (there’s a large body of literature addressing this). The material collected in traps is perhaps representative of sinking material in general, but inferred rates are not necessarily representative.

Page 7 Line 6, “Motivated by reconstructed history...(Streets)...we subject our model to a 4.5x increase...” 4.5x is not really a Streets advocated value. He and his collaborators think it is much larger, perhaps 7x. Others think it is smaller, closer to 3x (Engstrom and others).

Line 19, “a peculiarity....net sea surface fluxes of Hg are always balanced” Unclear to me why this was being brought up...do the authors think this isn’t the way nature is? I guess the word “peculiarity” here is confusing me.

Line 22-24, “because Hg concentrations in the top box...will underestimate the Hg surface concentrations...” Not sure I follow this. Why couldn’t upwelling terms be included in mass balance for surface Hg concentrations? This was just a choice made? Why that particular streamlining? Do the authors have a sense of how big a difference that might make?

Page 8 Line 11, too many parentheses around Schartup reference.

Line 12, “can be shut down by complexation with dissolved sulfide” this is not true. Especially see work of Heimburger and colleagues. . .methylation in euxinic water does happen. The trend/effect argued for here is seen in sediments, but is apparently not true in water. This is consistent with culture experiments that suggest Hg complexed with sulfide or thiols is fairly bioavailable (Schaefer, Hsu-Kim). Not sure why the sediment data are different. The Lamborg Black Sea data is apparently wrong on Hg

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speciation. Also, in the previous sentence, Chakraborty's data says the opposite, production is lower in low O<sub>2</sub> environments, as evidenced by %MMHg...a similar story to Sunderland's Pacific data. Low O<sub>2</sub> environments are not necessarily strong MeHg production locations on a specific rate basis...there's more MeHg there because there's more total Hg there. % MeHg is not always enhanced in low O<sub>2</sub> environments.

Line 21...title "particle sinking vs. the overturning circulation" Why is this section setup as a competition between these two forces? One doesn't steal Hg from the other...they both act to move Hg down into the interior, one is just isopycnal and the other is diapycnal.

Page 9 Line 2, "there are some regional variations in Hg, but they are not systematic, as compared to the clear Pac-Atl differences exhibited by nutrient-type elements..." Not true...the Lamborg 2014 paper specifically made the counter argument. The distribution of Hg is the nutrient like distribution with a transient anthropogenic signal superimposed.

Section 3.3, this first paragraph is written in a way that's a bit hard to follow. For example "some fractionation effect that we impose in the model pulls the isotopic composition of either Hg<sup>0</sup> or DMHg away from these values, and the other has to go the opposite way to compensate..." What is the "some fractionation effect"? And what is the "other" that "has to go the opposite way..." I think I know what they are talking about, but this is a bit to imprecisely written to be clear. Also, why can't particle sinking remove isotope signal from the surface as well? Wouldn't the isotope balance be between atmo inputs, and the combined effect of evasion and particle sinking (source vs all sinks)?

Page 10 Line 1, "D199" should be capital delta 199, I think. Also, "it has been observed that there is a large difference in the D199 values of MeHg vs Hg(II) in ocean surface water. Do we know the D199 of Hg(II) in ocean water? I guess fish could be used as a proxy for the D199 of MeHg in the water (is there really no MIF during uptake and biomag?), but do we have any data for the Hg(II) pool? I don't think the Blum 2013

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paper has any in it.

Line 2, too many parentheses.

Figure 2, would be nice to see a separate panel of Present/Preanth as a function of depth, to see how deep the anth signal goes.

Figure 4, what are the values of  $K_d$  for the lines other than the red one?

Figure 5, does “Total Hg” mean in the entire ocean? Is this the pre-anth ocean, or after some amount of human emissions? The value, between about 1.5 and 2.3 Gmoles is reasonable on the low end, but too high on the high end compared to data.

Figure 6 is mentioned only briefly, and it’s difficult to understand the point being made. Are we meant to expect a certain cross-over point? What is being tested in the figure?

Figure 7. Data don’t really support a plume of particularly high MeHg in the eastern equatorial Pacific...not remarked upon in the text.

Figure 8, unit is meant to be  $\text{pmole/L}$ . I realize changing the model will give big differences in the concentrations, but the No Advection scenario is so high that this probably is another reason to be suspicious of the Streets inventory.

Figure 9, similar to Figure 6, no real guidance is given on how to interpret these results, and no direct comparison to data is made either.

Figure 10, no unit on y axis.

Figures 11-15, Figure 11 is discussed in some length, but the others are not discussed extensively. This is disappointing as the incorporation of isotopic data is what is unique about this model. I realize data are scarce, but what would be extremely useful is if this model made some specific predictions about isotopic values of species or locations that could then be the target of measurements.

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