

Peer Review File

Manuscript Title:

Mercury stable isotopes constrain atmospheric sources to the Ocean

Editorial Notes: Redactions – Third Party Material

Parts of this Peer Review File have been redacted as indicated to remove third-party material.

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Ref #1

A,B &E. This interesting paper uses the newly developing data on seawater Hg isotope composition to re-examine Hg cycling between the atmosphere and ocean. The authors point out that this very important component of global Hg cycles is not very well constrained, and they are right about that. There is sparse but fairly consistent data from a fair amount of the world's ocean and then the exchange estimates are made by applying gas-exchange models. These models certainly do have uncertainty associated with them but do a reasonably good job of describing the cycling of other species (like CO₂). This presents presents a radically different view, however, of that Hg cycling and in a way that is hard for me to wrap my head around. For example:

1) The new data say the evasion rate from the ocean is about 8x lower than the model they compare to (btw, the model they compare to is perhaps not the state-of-the-science...Outridge et al. 2018 may be closer to the mark, but they are close). While the models are uncertain, a factor of 8x inaccuracy seems hard to imagine. So, if true, the isotope data suggest that the field data are wildly wrong. To be sure the data are not high resolution, and wintertime in high/middle latitudes is especially missing and a time of year when saturation levels are their lowest, but this is still hard to accept.

2) The new isotope data suggests the ocean is a net sink not just for total Hg, but for Hg₀, which is a species we know to be supersaturated in most places for most of the year. So, even if the gas-exchange models do not work well for Hg for some reason, saturation alone seems to discourage the view of large net invasion of Hg₀.

So, one must ask: Is the conventional data and the modeling that goes with it wrong, or are the isotopes? To be sure the conventional data is lacking in coverage and isotopes are used by geochemists to solve that kind of problem in other systems...but this is a very new measurement with few data, and the conventional data is fairly consistent and much more plentiful. I'm a reviewer, so I will argue that the isotope data are either wrong or mis-interpreted. Doesn't mean the authors are wrong and I am right but I leave the authors to make the case that the conventional data are wrong.

The first argument against the results presented in the paper is the absolute values, which I as noted above, depicted a much more sluggish air-sea exchange than the conventional data. The new isotope data actually provide no guidance here, and the authors rely entirely on one paper to calculate their estimates for Hg(II) fluxes in (actually only a wet Hg(II) deposition number which they scale up using some common estimates of the ratio of wet to dry deposition of Hg(II)) and then their own isotope data to add on Hg₀ invasion. So, the absolute value is entirely based on the wet Hg(II) flux in from one paper. These data, and many others, have been used by others to arrive at the higher values they contrast themselves with...so, there's nothing intellectually new here, it's just a matter which data you include or exclude in getting that wet Hg(II) flux in. I looked quickly at that paper again (Sprovieri et al., 2017) and had a few questions about the approach they used, but also would not have arrived at the very low 1.6 micrograms/m²/y

estimate from these same data that the authors here did. Since this part of the current story is really out of realm of these new isotope data to help judge, it feels inappropriate to include it in this paper...or at least so centrally (could be mentioned in the text, but a figure that dramatically contrasts their results to others is an oversell of the isotope data). So, I recommend cutting Figure 4. If the authors want a summarizing cartoon, they could do so without the values of the fluxes emphasized, but instead focusing on the relative sizes of the fluxes they estimate compared to those of others.

Now, to the real meat of the paper, the $\Delta^{200}\text{Hg}$ data. Even Hg isotope mass-independent fractionation (or $\Delta^{200}\text{Hg}$) is thought to have only one source, namely photochemistry in the upper atmosphere and no in-water processing can give rise to it. Because their seawater values (and additional kinds of samples that should derive from the seawater values like particles and sediment) lie in between Hg(II) in rain and Hg0 in the gas-phase, they infer that the Hg in seawater must be a combination of Hg0 and Hg(II) inputs. But as noted above, the ocean is very supersaturated with Hg0, so net fluxes of Hg0 into the ocean are just not supported by field data. Regardless of the absolute magnitudes of the fluxes, this must be true.

So, how can you get a $\Delta^{200}\text{Hg}$ value that's not the same as Hg(II) in rain if there is no further even MIF? Let's perform a thought experiment: if there was no oxidation of Hg in the atmosphere and no removal from the ocean other than evasion, then the $\Delta^{200}\text{Hg}$ of the surface water and the air should look identical. This would be a situation of saturation in surface water and no net flux but could be supported by a substantial bi-directional flux. So, an alternative interpretation of their data is that to the extent that seawater does not appear to be identical to Hg0 in the air, means that Hg(II) provides all the net flux into the ocean. The distance away from the $\Delta^{200}\text{Hg}$ of Hg0 in the air then provides an estimate for the relative sizes of the net Hg(II) flux to a Hg0 recycling flux. So, I can't support publication until the authors have at least considered alternative explanations that are more consistent with our field observations of supersaturation.

C. Data and methodology seem fine.

D. Their apportioning of source strengths didn't come with stats. This should be incorporated in their modeling.

F. Consider alternative modeling as discussed above...and others perhaps.

G. Fine

H. Good...minor points below.

Line 115, the citations for "23, 23, 25" I think is supposed to be "23-25".

Figure 3. Part of the captions states "The atmospheric sources are shown in red for Hg0 and blue for Hg(II) in rainfall, the dashed line represents the median and the shaded are the interquartile range." This confused me...as there are dashed lines but no shading. Is the second part of the sentence about the box-whisker plots? If yes, then there's a misstatement since the median line is solid. If it's about the Hg0 and Hg(II) data in the air, then there's no shading.

Ref #2

This paper by Jiskra et al reports on new Hg stable isotope measurements in various types of samples from the Mediterranean Sea and Atlantic Ocean. It also compiles Hg stable isotope data from the literature on the Pacific Ocean and on atmospheric measurements from other studies at several locations around the globe. The paper synthesizes and interprets this data and in so doing claims to overturn a longstanding paradigm about the proportion of the various chemical species of Hg that enter the oceans from the atmosphere. The seawater purge-and-trap method used here seems to be robust and this is one of the first studies I have seen that utilizes 10^{12} Ohm resistors on the mass spectrometer amplifiers to measure the minor isotopes of Hg, which is an interesting advance in methods.

The conclusions claimed in this paper are quite novel and would overturn long-standing views of

the relative importance of Hg(0) versus Hg(II) in Hg transfer between the atmosphere and oceans. However, I don't believe that the data are adequate to support these conclusions and as such I do not find this paper appropriate for publication in Nature.

The main point of the paper is that the $\Delta 200\text{Hg}$ value of total and particulate Hg in the oceans can be used to calculate the ratio of the amounts of Hg(II) versus Hg(0) that enter the ocean on an annual basis. The authors base their conclusions on comparison of median values of $\Delta 200\text{Hg}$ for Hg(II) and Hg(0) in the atmosphere and then extrapolation between them for THg and pHg. However, there are a few major problems with this practice.

Most importantly, the analytical uncertainty is too high given the size of the natural isotopic signal. When comparing analytical uncertainties it is important to consider the Hg concentration of solutions that were run on the mass spectrometer for Hg isotope ratios. Eight process replicate seawater THg samples were run with Hg at 1.6 ng/g, which is much higher than any of the seawater THg or pHg isotope measurement run solution concentrations of offshore samples used to support the conclusions.

The offshore seawater THg analyses were performed using run-solutions with Hg content of only 0.25 ng/g, which evidence from Table S4 suggests is below the level at which isotope results can be obtained with high enough precision. One of the samples does not have a reported value for $\Delta 201$ despite having been measured twice. Seven of the 16 samples have paired $\Delta 199\text{Hg}$ and $\Delta 201\text{Hg}$ values of opposite sign, which is likely an analytical artifact. Thirteen of the samples have 2SD of within-mass-spec-session replicate measurements larger than assigned analytical uncertainty from ETH Fluka; in some cases resulting in analytical uncertainty that exceeds 0.4 ‰. Results from the eight NIST3133 procedural standards are highly variable, especially those from the four measured at 0.25 ng/g. Although each procedural standard was measured twice, average δ and Δ values that should all be close to 0 range from -0.21 to +0.28 ‰.

The apparent quality of the particle isotope results, which were all measured using run solutions with Hg at 0.5 ng/g, is not much better. Sixteen of the 25 samples have 2SD of within-mass-spec-session replicate measurements larger than assigned analytical uncertainty from ETH Fluka and NIST1632d; in a number of cases resulting in analytical uncertainty that exceeds ± 0.2 ‰, and in the most extreme case is larger than ± 0.9 ‰.

The error bars plotted for $\Delta 200\text{Hg}$ on Figure 2 are ± 0.10 ‰, but, based on the discussion above, they should be at least ± 0.20 ‰. The difference between the median values for $\Delta 200\text{Hg}$ in Hg(0) and Hg(II) endmembers is, however, only 0.21 ‰. The range of values for Hg(0) and pHg is almost completely overlapping, and the SD of each group overlaps. Finally, it is worth pointing out that the samples that were measured and included in this plot were collected where the logistics of various cruises and sampling campaigns allowed, and were therefore understandably opportunistic, rather than being spatially representative of each sample type. Thus, the range of isotope values may be more representative than the median value when comparing sample groups.

The authors have done no statistical tests on their data beyond calculating the mean and quartile of collections of data and so I am left skeptical of the paper's conclusions. And to make matters worse the supplementary, extended and data tables are unclear, poorly formatted and incomplete—making it challenging for readers to explore the data themselves.

The conclusions of this study as written hang, in large part, on the visual interpretation of Figures 2 and 3. The text also refers to $\Delta 200\text{Hg}$ data in Figure 4, but I think that was an error and that Figure 4 was changed at some point. My visual inspection tells me that the nearly complete overlap between Hg(0) and pHg and the large scatter in each of the four sample types, makes it impossible to perform the mixing calculations that are proposed on the paper. Similarly, Figure 3 is very misleading in that the endmember Hg(0) and Hg(II) values are depicted by the vertical

dashed red and blue lines. Only the median values are shown--yet the range of values dwarfs the values shown as box and whiskers.

In conclusion, I don't think the data are depicted clearly enough nor do I think the data are of high enough precision to support the conclusions of the paper.

Ref #3

This is an interesting study using stable Hg isotope measurements of total Hg in waters of the Atlantic and Mediterranean to infer the relative contributions of atmospheric deposition of Hg(II) and net Hg(0) oceanic uptake. Many aspects of the Hg biogeochemical cycling remain poorly constrained and this study attempts to constrain one element regarding net deposition to the oceans. Isotopes can be a powerful tool to investigate this question. The authors' results show that atmospheric Hg(II) deposition accounts for 41% of the deposition to the ocean and Hg(0) uptake accounts for 59%. This is in contrast with global models which predict a much larger contribution from Hg(II) deposition.

The manuscript is generally well written and the results are interesting. The two main concerns I have regard 1) the lack of discussion of how the dynamic cycling of Hg in the marine boundary layer and surface ocean might affect the isotopic signature of Hg and its interpretation; and 2) the large leaps that the authors make from their measurements at very specific locations to the generalization for the entire atmosphere-ocean interactions and the lack of assessment of error ranges (the authors tend to give single numbers which don't reflect the true uncertainties, 41%, 1000 Tg/yr, etc...). I elaborate on these two issues below.

The marine boundary layer displays a very dynamic chemical cycling of Hg due to the local formation of Hg(II) promoted by Br released from sea-salt aerosols. This Hg(II) will deposit to the surface ocean where it might undergo reduction back to Hg(0) and escape to the atmosphere. How would this cycling affect the isotopic signature of marine tHg and pHg in the samples? This cycling might also affect the isotopic signature of the rainfall samples. Is there any reason to believe that rainfall samples collected at continental locations would have the same isotopic signature as samples collected at marine locations. (Are any of the rainfall samples listed in Table S1 from marine locations?)

Line 125. The authors refer to a new study (submitted) showing that gaseous atmospheric Hg(II) have the same $\Delta^{200}\text{Hg}$ as Hg(II) in wet deposition. This study seems that have been done at one high altitude location in the Pyrenees Mountains. The authors do not provide any justification as to why measurements at this single location can be generalized to the marine boundary layer. The local chemistry and origin of Hg(II) at that location might be very different than over the marine boundary layer, where sea salt aerosol can provide a large source of Br and oxidize Hg(0) locally.

Line 130. "We therefore suggest that the median NH rainfall $\Delta^{200}\text{Hg}$ of 0.17permil is a reasonable estimate..." I might be missing something, but I do not see the connection between this sentence and the previous sentences in this paragraph. At the beginning of the paragraph the authors mention 0.16 permil observed in NH Hg(II) wet deposition. How to the authors go from 0.17 to 0.16 permil? Or is it a typo?

Inferring the global Hg(II) wet deposition flux to the ocean from 6 coastal monitoring sites is a very big stretch given the high variability of precipitation over the oceans (Line 147). It is equivalent to assessing the total rainfall to the oceans from the measurement of precipitation at these 6 sites. Why would that be a valid approach? Are these sites representative? How can the authors assess that? The authors then scale up that number to include dry deposition, using a 60%/40% split between wet/dry deposition from a global model. This is from the same global model that the authors suggest is overestimating oceanic deposition of Hg(II) by a factor of 4.6. Why would the authors trust the 60/40% split from that model? Overall, I find that there are too

many assumptions made along the way to have much confidence on the 1000 Mg y⁻¹ the authors infer from the 6 sites and global model estimates of dry vs wet deposition. One way to assess whether the 6 sites are representative would be to sample wet deposition from that same global model at the location of these sites and see whether applying the same assumptions (taking the median and scaling by the surface area of the ocean + 40%/60% split in dry/wet deposition) give the same results as the actual calculated Hg(II) deposition flux over the oceans.

The authors come up with a single estimate (1350 Mg y⁻¹) for net Hg(0) deposition to the Oceans based on the 41% number from their mixing model. The range of uncertainty given for that number is 32-65%. I suggest that the authors use that range and derive the range of estimates for net Hg(0) deposition to the oceans and include the ranges in both the abstract and Figure 4.

Author Rebuttals to Initial Comments:

Referees' comments:

Dear reviewers, thank you for your time and efforts in commenting and questioning our study and manuscript; there was clearly room for improvement.

Referee #1 (Remarks to the Author):

A,B &E. This interesting paper uses the newly developing data on seawater Hg isotope composition to re-examine Hg cycling between the atmosphere and ocean. The authors point out that this very important component of global Hg cycles is not very well constrained, and they are right about that. There is sparse but fairly consistent data from a fair amount of the world's ocean and then the exchange estimates are made by applying gas-exchange models. These models certainly do have uncertainty associated with them but do a reasonably good job of describing the cycling of other species (like CO₂). This presents a radically different view, however, of that Hg cycling and in a way that is hard for me to wrap my head around. For example:

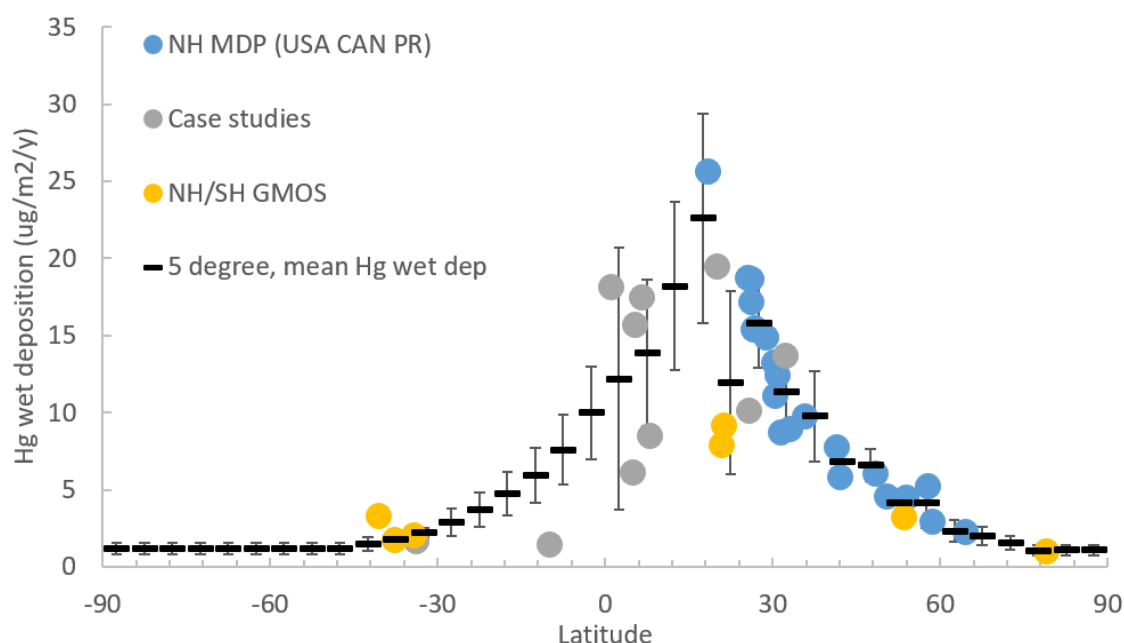
Thank you for your in-depth review and many constructive comments; it is very satisfying to be able to have such detailed discussion via the review process. We offer much discussion below, but would like to put upfront that we have removed Figure 4 from the main text, and have overhauled the Hg wet deposition budget by including more (all) relevant observational data (from n=278 we go to n=12,812); you were correct that our wet dep budget was erroneous, and the correct numbers are key to a more realistic discussion of Hg air-sea exchange.

1) The new data say the evasion rate from the ocean is about 8x lower than the model they compare to (btw, the model they compare to is perhaps not the state-of-the-science...Outridge et al. 2018 may be closer to the mark, but they are close). While the models are uncertain, a factor of 8x inaccuracy seems hard to imagine. So, if true, the isotope data suggest that the field data are wildly wrong. To be sure the data are not high resolution, and wintertime in high/middle latitudes is especially missing and a time of year when saturation levels are their lowest, but this is still hard to accept.

Regarding choice of model for comparison: indeed it would have been more satisfactory to compare to a model ensemble, but the few model intercomparisons published focus only on the two strongest observational constraints: atmospheric Hg(0) concentrations and terrestrial Hg wet deposition, either globally (Bieser et al., 2017; Travníkov et al.,

2017) or in polar environments (Angot et al., 2016), but not on air-sea exchange. We have chosen to compare to (Horowitz et al., 2017), because this study uses the state of the art GEOS-Chem/MITgcm coupled 3D ocean-atmosphere model. It is the only study providing gross Hg(0) air-sea exchange fluxes, i.e. Hg(0) invasion (ocean uptake) and marine Hg(0) evasion to air. The (Outridge et al., 2018) UNEP GMA budget is based on a similar coupled-ocean atmosphere model, from an earlier publication by (Zhang et al., 2014) with close results indeed. Finally, Outridge'18 (or the GMA) does not specify the gross Hg(0) invasion or gross Hg(0) evasion flux, only the net flux, and is therefore less useful for comparison here.

Based on your comments below, in the revised MS, we revisit global rainfall data at coastal sites by including MDN, GMOS and case studies. We now find an observational budget (2561 Mg/y wet deposition over Oceans instead of 600 Mg/y; and 4268 Mg/y total HgII deposition) in line with the Horowitz'17 4600 Mg/y budget and with other models. This makes sense, because Hg cycling models are generally fitted to the same data we review here. We initially chose the Sprovieri'17 database because it was global, but it turned out to be biased by low Hg deposition at high latitude southern hemisphere sites. The new marine Hg(II) deposition flux of 4268 Mg/y has important implications for our budget discussion (see below); it has also paved the way to provide a full analysis of the latitudinal Hg(II) deposition, Hg(0) invasion, and marine Hg isotope gradients (coastal Hg wet deposition shown in new Figure S5 here below)



New Figure S5

2) The new isotope data suggests the ocean is a net sink not just for total Hg, but for Hg0, which is a species we know to be supersaturated in most places for most of the year. So, even if the gas-exchange models do not work well for Hg for some reason, saturation alone seems to discourage the view of large net invasion of Hg0.

So, one must ask: Is the conventional data and the modeling that goes with it wrong, or are the isotopes? To be sure the conventional data is lacking in coverage and isotopes are used by geochemists to solve that kind of problem in other systems...but this is a very new

measurement with few data, and the conventional data is fairly consistent and much more plentiful. I'm a reviewer, so I will argue that the isotope data are either wrong or misinterpreted. Doesn't mean the authors are wrong and I am right but I leave the authors to make the case that the conventional data are wrong.

This is an excellent summary of the issue! In our defense, yes we produce few THg and pHg isotope data, but we back it up with more abundant open ocean sediment and pelagic biota data, which ultimately are supplied with surface ocean Hg. So we consider that we present sufficient data (n=317 in the first version, and n=787 in the revised MS) to support our suggestion of important marine Hg(0) uptake. Secondly, we acknowledge the difficulty in making the sea water THg isotope measurements, and overall it has taken us 10 years to make it happen. We made a point in this MS to provide all method details, and abundant QA/QC data. We show that our methods and data are reproducible, and we demonstrate this with repeat measurements. So it turns out we were wrong, but not on the isotope data; we were wrong on the rainfall budget.

The first argument against the results presented in the paper is the absolute values, which I as noted above, depicted a much more sluggish air-sea exchange than the conventional data. The new isotope data actually provide no guidance here, and the authors rely entirely on one paper to calculate their estimates for Hg(II) fluxes in (actually only a wet Hg(II) deposition number which they scale up using some common estimates of the ratio of wet to dry deposition of Hg(II)) and then their own isotope data to add on Hg₀ invasion. So, the absolute value is entirely based on the wet Hg(II) flux in from one paper.

That is correct; the paper (Sprovieri et al., 2017) is a comprehensive global compilation of coastal (and continental) rainfall Hg data from GMOS (global mercury observation system). The median coastal rainfall Hg flux of 1.6 ug/m²/y is correct, but it is unfortunately biased by mid-latitude southern hemisphere observations. In the revised MS we complete the Sprovieri data set with data from MDN (Mercury Deposition Network, <http://nadp.slh.wisc.edu/mdn/>) and case-studies. We now examine and find a significant latitudinal trend in Hg wet deposition in both hemispheres, centered on the ITCZ (Figure S5, above, and new SI Table S6 with full data). The subtropical maximum in wet deposition is well known from MDN sites in Florida and now known to be related to convecting clouds scavenging Hg(II) in the middle and upper troposphere (Holmes et al., 2009). The subtropical maximum is also visible at Asian coastal sites and Hawaii. By using this comprehensive dataset, and latitudinal trends, we now obtain a revised marine Hg wet deposition budget of 2561 Mg/y. This means that model estimated marine Hg(II) dry deposition is 1707 Mg/y (40% of total Hg(II) deposition), and total Hg(II) deposition itself is 2561+1707=4268 Mg/y, which is identical within error (30%) to model Hg(II) deposition of 4600 Mg/y in (Horowitz et al., 2017; Outridge et al., 2018).

These data, and many others, have been used by others to arrive at the higher values they contrast themselves with...so, there's nothing intellectually new here, it's just a matter which data you include or exclude in getting that wet Hg(II) flux in.

Our revised budget now concurs with previous estimates.

I looked quickly at that paper again (Sprovieri et al., 2017) and had a few questions about the approach they used, but also would not have arrived at the very low 1.6 micrograms/m²/y

estimate from these same data that the authors here did. Since this part of the current story is really out of realm of these new isotope data to help judge, it feels inappropriate to include it in this paper...or at least so centrally (could be mentioned in the text, but a figure that dramatically contrasts their results to others is an oversell of the isotope data). So, I recommend cutting Figure 4. If the authors want a summarizing cartoon, they could do so without the values of the fluxes emphasized, but instead focusing on the relative sizes of the fluxes they estimate compared to those of others.

We have removed Figure 4 from the MS and replaced it with the latitudinal analysis of Hg(II) deposition, Hg(0) invasion and marine $\Delta^{200}\text{Hg}$ (new Figure 4).

Now, to the real meat of the paper, the $\Delta^{200}\text{Hg}$ data. Even Hg isotope mass-independent fractionation (or $\Delta^{200}\text{Hg}$) is thought to have only one source, namely photochemistry in the upper atmosphere and no in-water processing can give rise to it. Because their seawater values (and additional kinds of samples that should derive from the seawater values like particles and sediment) lie in between Hg(II) in rain and Hg(0) in the gas-phase, they infer that the Hg in seawater must be a combination of Hg(0) and Hg(II) inputs. But as noted above, the ocean is very supersaturated with Hg(0), so net fluxes of Hg(0) into the ocean are just not supported by field data. Regardless of the absolute magnitudes of the fluxes, this must be true.

We agree on supersaturation and on large marine Hg(0) emission. With a corrected, observation-based Hg(II) deposition flux that agrees with models (4600 Mg/y) we can now refocus the discussion on the nature of air-sea exchange, and the model gross Hg(0) invasion (1700 Mg/y) and gross evasion (also 4600 Mg/y) fluxes. What is key, is the bi-directional nature of air-sea gas exchange: even at equilibrium, when no net Hg(0) evasion occurs, large invasion and evasion fluxes occur, but at equal rates. Similarly, even during typically supersaturated dissolved Hg(0) conditions, a substantial Hg(0) invasion flux continues to take place. Horowitz et al (2017) quantify exactly these simultaneously occurring gross Hg(0) invasion and evasion fluxes (1700 and 4600 Mg/y) by separating the flux equation:

$$F_{\text{net}} = k(C_w - C_a/H)$$

into the respective evasion and invasion parts:

$$F_{\text{inv}} = k \times C_a/H$$

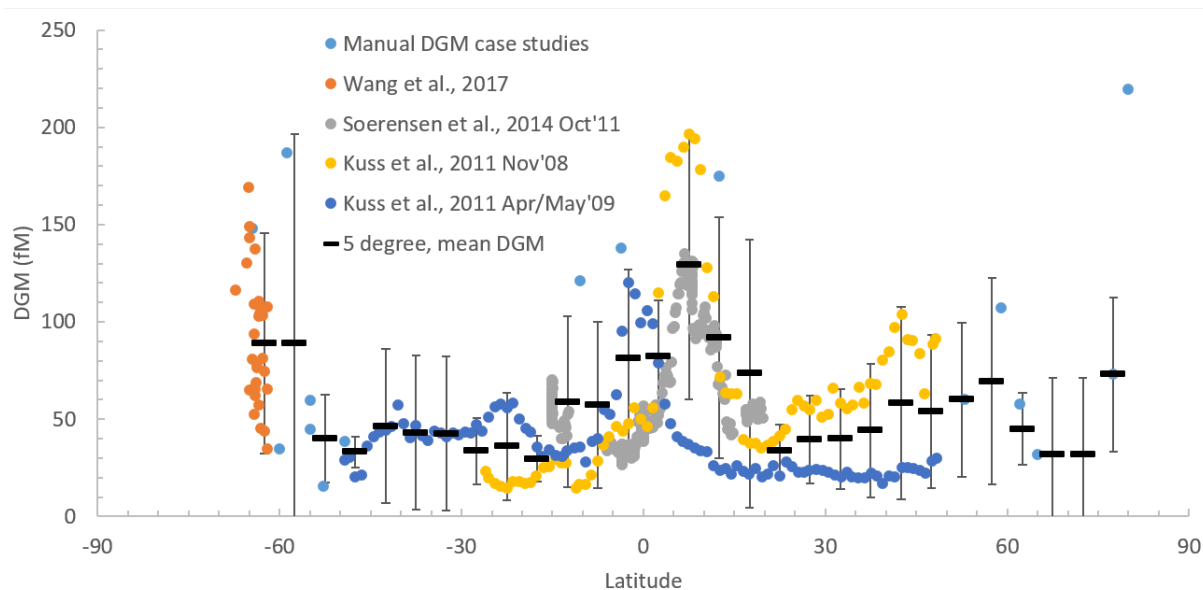
$$F_{\text{ev}} = k \times C_w$$

where C_w is the Hg(0) concentration in water (ng/m³ water), C_a the Hg(0) concentration in air (ng/m³ air), k is the gas exchange velocity for Hg(0) (Nightingale et al., 2000), and K is the dimensionless Henry's law constant (Andersson et al., 2008).

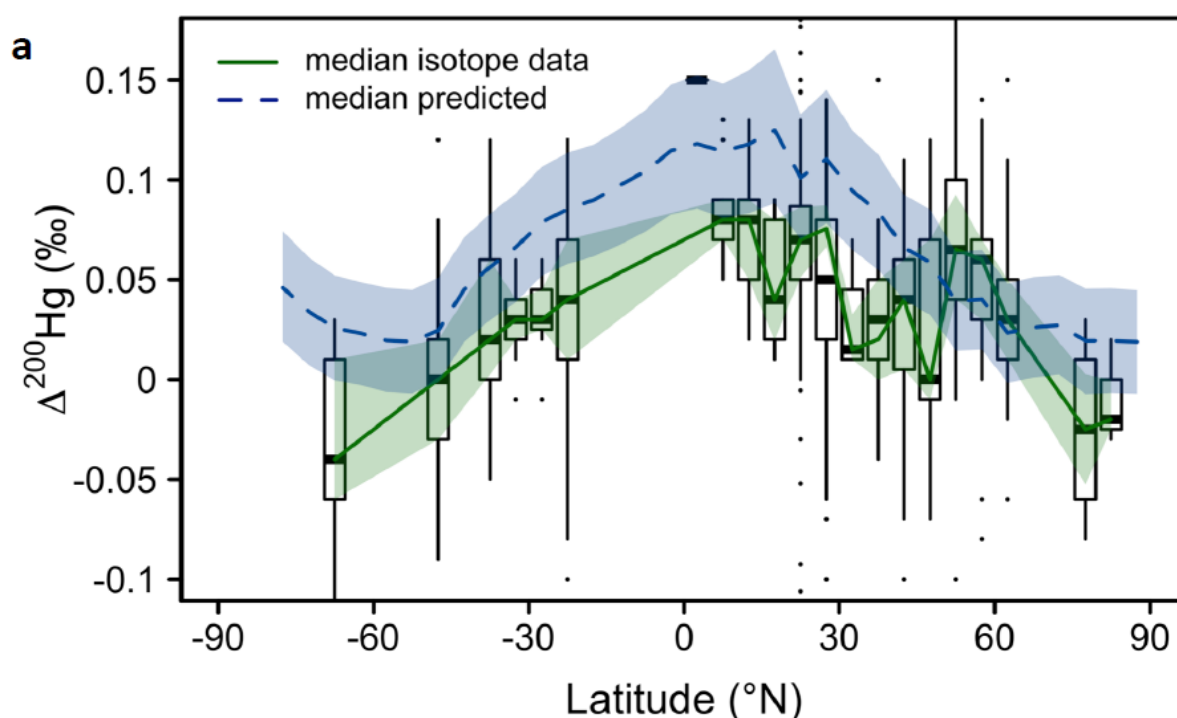
With this knowledge at hand, we have re-examined the marine DGM and air-sea exchange literature; in particular the latitudinal cruise transects (Kuss et al., 2011; Soerensen et al., 2014) but also shorter campaigns (new Figure S6 shown below). In the revised MS, we determine a latitudinal consensus DGM transect, and use Copernicus mean wind speed and SST (temperature) products to estimate the global gross Hg(0) invasion (=uptake) and evasion fluxes, and find 1950 and 4840 Mg/y (Table S7). These

large, observation-based, gross flux estimates agree with modeled gross fluxes of 1700 and 4600 Mg/y.

We then expand (from $n=347$ to $n=787$ data points, mostly biological) our marine $\Delta 200\text{Hg}$ analysis to also include latitudinal variability. This uncovers a fascinating trend showing higher $\Delta 200\text{Hg}$ in the sub-tropics and lower $\Delta 200\text{Hg}$ at high latitudes (new Figure 4, shown here below). We recognize this is fully coherent with the latitudinal Hg(II) deposition observations, and Hg(0) invasion distribution (driven by wind). However, it keeps pointing towards our main finding: the observed marine $\Delta 200\text{Hg}$ distribution is shifted to a dominant Hg(0) source, and not Hg(II) . Figure 4a below illustrates this by comparing model predicted $\Delta 200\text{Hg}$ with observed $\Delta 200\text{Hg}$. We provide a detailed discussion of these trends in the SI, and in the main text we conclude that marine $\Delta 200\text{Hg}$ observations are not compatible with current Hg cycling models. We propose that most likely the marine Hg(II) deposition budget (Figure S5, above) is overestimated, because the mainly coastal Hg wet deposition observations (Figure S5 above) are potentially biased by regional continental Hg emission sources. Alternatively we mention that the Hg(0) gas exchange parameterization could be the culprit, as it is uncalibrated, and potentially ignores chemistry effects in the diffusive microlayer. Nevertheless, the higher Hg(0) invasion (higher gas exchange velocity, K_w) needed to explain marine $\Delta 200\text{Hg}$ would also increase evasion, and the ocean would become a net Hg source rather than a net Hg sink. Such a scenario is more unlikely, but not impossible and would require a dedicated 3D modeling study.



New Figure S6



New Figure 4a

So, how can you get a $\Delta^{200}\text{Hg}$ value that's not the same as Hg(II) in rain if there is no further even MIF? Let's perform a thought experiment: if there was no oxidation of Hg in the atmosphere and no removal from the ocean other than evasion, then the $\Delta^{200}\text{Hg}$ of the surface water and the air should look identical.

OK so far (note that without oxidation, there would be no $\Delta^{200}\text{Hg}$ anywhere!)

This would be a situation of saturation in surface water and no net flux but could be supported by a substantial bi-directional flux.

OK, no net flux suggests Hg(0) dissolution = Hg(0) evasion; in fact air and ocean are in equilibrium, and the invasion flux equals evasion.

So, an alternative interpretation of their data is that to the extent that seawater does not appear to be identical to Hg(0) in the air, means that Hg(II) provides all the net flux into the ocean.

Sorry this is unclear; our logic is that of mass balance in a binary isotope mixing system, i.e. 2-end members. There are three key notions to this logic on which we elaborate in much more detail in the revised MS:

- Hg in the marine samples set we compile is mainly derived from the two atmospheric Hg(0) and Hg(II) sources, and not from hydrothermal inputs or rivers. We provide arguments that this is likely so.**
- Hg(II) deposition is the sum of Hg(II) dry deposition and Hg(II) wet deposition. Abundant isotope data exist for wet deposition but less so for Hg(II) dry deposition; in the revised MS we expand our preliminary free tropospheric Hg(II) data at Pic du Midi (Fu et al., 2020) with marine boundary layer (MBL) aerosol data from (Rolison et al., 2012; Washburn et al., 2020; Yu et al., 2020), and MBL Hg(0) data by (Demers et al., 2015; Fu et al., 2018; Rolison et al., 2012). Importantly, the MBL aerosol and Hg(0) $\Delta^{200}\text{Hg}$ data are not very different from the Hg(0) and Hg(II) end-members we use thus far: for Hg(0) , MBL and PBL (planetary boundary layer) and FT (free troposphere) $\Delta^{200}\text{Hg}$ are the same, -0.06‰ . For Hg(II) , rainfall Hg(II) and aerosol+gaseous Hg(II) (in MBL and FT) are slightly different, -0.16‰ , and -0.12‰ respectively. We use these data to discuss and set aside an important**

scenario, i.e. the possibility that Hg(II) deposition in the MBL inherits a low (i.e. - 0.06‰) $\Delta^{200}\text{Hg}$ from Hg(0) in the MBL. Apparently this is not the case. In our latitudinal analysis we vary the Hg(II) end-member $\Delta^{200}\text{Hg}$ composition according to the approximate proportions of Hg(II) wet deposition and Hg(II) dry deposition as a function of latitude.

3. The link between aqueous Hg redox transformation rates and the gross or net nature of the deposition fluxes in the $\Delta^{200}\text{Hg}$ mass balance. The current consensus in Hg cycling models is that marine aqueous Hg reduction and oxidation rates are fast (Semeniuk and Dastoor, 2017; Soerensen et al., 2010; Zhang et al., 2014), leading to global surface ocean oxidation and reduction fluxes of $2.6 \times 10^6 \text{ Mg y}^{-1}$ (see budget in (Sun et al., 2019)), which are large compared to deposition and evasion. This implies that the contrasting $\Delta^{200}\text{Hg}$ signatures of gross Hg(0) invasion (-0.06 ‰) and gross Hg(II) deposition (+0.14 ‰) will be rapidly homogenized in the surface ocean before Hg(0) is partially re-emitted to the atmosphere. The $\Delta^{200}\text{Hg}$ derived 1:2 Hg(II):Hg(0) deposition ratio then represents the gross deposition ratio, which we compared to the Hg cycling model 3:1 gross deposition ratio throughout the MS. We contacted Hannah Horowitz on 24/9/2020 to double check one more time if the model Hg(0) emission and invasion fluxes of 4600 and 1700 Mg/y in the Horowitz'17 paper are gross fluxes. She confirmed.

In the revised MS we added two paragraphs on items 2 and 3 above, and we developed a paragraph in the SI on the bi-directional nature of Hg(0) air-sea exchange, and the latitudinal distribution of deposition, invasion, evasion and marine $\Delta^{200}\text{Hg}$.

The distance away from the $\Delta^{200}\text{Hg}$ of Hg(0) in the air then provides an estimate for the relative sizes of the net Hg(II) flux to a Hg(0) recycling flux.

Sorry, unclear; How to define 'Hg(0) recycling flux'? Define as Hg(0) invasion - Hg(0) evasion? Or, the net Hg emission flux (Hg(II)dep+Hg(0)invasion – Hg(0) evasion)?

Note that above and in the revised discussion we address the gross vs net nature of the $\Delta^{200}\text{Hg}$ mass balance; fast oxidation and reduction in surface sea water, both on the order of 10^6 Mg/y , suggest that marine $\Delta^{200}\text{Hg}$ reflect the gross input fluxes (10^3 Mg/y). We explain in the discussion that rapid oxidation and reduction homogenizes the $\Delta^{200}\text{Hg}$ composition of gross Hg(0) and Hg(II) inputs in the surface ocean, before re-emission takes place.

So, I can't support publication until the authors have at least considered alternative explanations that are more consistent with our field observations of supersaturation.

C. Data and methodology seem fine.

D. Their apportioning of source strengths didn't come with stats. This should be incorporated in their modeling.

Expanded uncertainty estimates are now added by using a Monte Carlo method that propagates uncertainty on all parameters involved in the $\Delta^{200}\text{Hg}$ mass balance. And extensive SI Table S7 is included with uncertainty on all observed and calculated parameters.

F. Consider alternative modeling as discussed above...and others perhaps.

G. Fine

H. Good...minor points below.

Line 115, the citations for "23, 23, 25" I think is supposed to be "23-25".

Corrected

Figure 3. Part of the captions states “The atmospheric sources are shown in red for Hg⁰ and blue for Hg(II) in rainfall, the dashed line represents the median and the shaded are the interquartile range.” This confused me...as there are dashed lines but no shading. Is the second part of the sentence about the box-whisker plots? If yes, then there’s a misstatement since the median line is solid. If it’s about the Hg⁰ and Hg(II) data in the air, then there’s no shading.

We apologize; in the pdf conversion process the shaded interquartile range got lost, and was no longer visible in the Figure. We have fixed this.

Referee #2 (Remarks to the Author):

This paper by Jiskra et al reports on new Hg stable isotope measurements in various types of samples from the Mediterranean Sea and Atlantic Ocean. It also compiles Hg stable isotope data from the literature on the Pacific Ocean and on atmospheric measurements from other studies at several locations around the globe. The paper synthesizes and interprets this data and in so doing claims to overturn a longstanding paradigm about the proportion of the various chemical species of Hg that enter the oceans from the atmosphere. The seawater purge-and-trap method used here seems to be robust and this is one of the first studies I have seen that utilizes 10¹² Ohm resistors on the mass spectrometer amplifiers to measure the minor isotopes of Hg, which is an interesting advance in methods.

The conclusions claimed in this paper are quite novel and would overturn long-standing views of the relative importance of Hg(0) versus Hg(II) in Hg transfer between the atmosphere and oceans. However, I don’t believe that the data are adequate to support these conclusions and as such I do not find this paper appropriate for publication in Nature.

The main point of the paper is that the $\Delta^{200}\text{Hg}$ value of total and particulate Hg in the oceans can be used to calculate the ratio of the amounts of Hg(II) versus Hg(0) that enter the ocean on an annual basis. The authors base their conclusions on comparison of median values of $\Delta^{200}\text{Hg}$ for Hg(II) and Hg(0) in the atmosphere and then extrapolation between them for THg and pHg. However, there are a few major problems with this practice.

Most importantly, the analytical uncertainty is too high given the size of the natural isotopic signal.

We thank the reviewer for her/his critical assessment of our work; below we clarify concepts and observations on uncertainty in our dataset. While we remain confident in the higher than usual uncertainty (due to low concentrations analyzed), the issues raised by the reviewer have led us to thoroughly revisit rules on reporting, and we have made two small corrections (outlier omissions) to the new tHg and pHg data. In addition, we have expanded the marine pelagic $\Delta^{200}\text{Hg}$ dataset with more biological data from recent papers, and we now discuss the latitudinal distribution of n=787 marine $\Delta^{200}\text{Hg}$ data points, the majority of which were analyzed at high concentrations.

When comparing analytical uncertainties it is important to consider the Hg concentration of solutions that were run on the mass spectrometer for Hg isotope ratios. Eight process replicate seawater THg samples were run with Hg at 1.6 ng/g, which is much higher than any

of the seawater THg or pHg isotope measurement run solution concentrations of offshore samples used to support the conclusions.

The process replicate seawater tHg samples from the coastal Endoume site were indeed run at 1.6 ng/L. They are however not included in the ‘open sea water’ $\Delta^{200}\text{Hg}$ mass balance that supports the conclusions, because they are coastal. This is visible in the ‘n=12’ information for MedSea tHg in Table S2 that summarizes $\Delta^{200}\text{Hg}$ mass balance results: n=16 refers to the 4 Atlantic and 12 MedSea open sea water samples. Other NIST3133 process standards were run at 0.25 ng/g (Table S4, corresponding to typical open sea waters of 1 pM (0.2 ng/L), and similar to our samples) with good results.

The offshore seawater THg analyses were performed using run-solutions with Hg content of only 0.25 ng/g, which evidence from Table S4 suggests is below the level at which isotope results can be obtained with high enough precision.

‘Enough precision’ is a relative term, and it is of importance only with respect to the scientific question one attempts to answer, and with respect to instrumental signal/noise ratio. Our analytical QA/QC shows reproducibility of standards, samples, blanks that is ‘imprecise’ to the reviewer, but satisfactory for the low levels that we analyze, and for the $\Delta^{200}\text{Hg}$ mass balance we try to resolve.

Regarding instrumental MC-ICPMS limits, we briefly review key concepts here to advocate why 0.25 ng/g solution analysis is possible:

1. The first limitation concerns instrumental sensitivity, detector signal to noise ratio, and counting statistics: As indicated in the methods, for a 0.25 ng/g Hg samples solution we obtain 180 mV on the 202Hg isotope, 140mV on 200Hg, 102 mV on 199Hg, and 61mV on 198Hg. Below 100mV, signal detection on Faraday Cups suffers from dark noise; our use of a 10^{12} Ohm amplifier on 198Hg lowers dark noise, and increases signal to noise ratio by a factor of 3, providing access to low mV signals (Koornneef et al., 2013).
2. The theoretical limit of precision of the 202/198Hg ratio and d202/198Hg delta value follows Poisson counting statistics, where the standard deviation of a single isotope beam, for ex. 202Hg beam = $\sqrt{n}$, and where n is the number of 202Hg ions hitting the Faraday Cup. A 1mV signal corresponds to 62,500 Hg⁺ ions hitting the Faraday cup each second. During a 2*6 minute duplicate sample analysis (720 sec), about $8.1 \cdot 10^9$ 202Hg ions hit the Faraday Cup, with an uncertainty of $9.0 \cdot 10^4$ counts. Doing the same for all isotopes, expressing ratio and deltas, and propagating uncertainties gives a theoretical internal 2SD precision limit of $\pm 0.044 \text{ ‰}$ on d202Hg, and 0.07‰ on the $\Delta^{200}\text{Hg}$ of a 0.25 ng/g pre-concentrated sea water sample (corresponding to 20L of 1pM sea water=4ng Hg). Our open sea water data in Table S4 shows external 2SD reproducibility of $\pm 0.20 \text{ ‰}$ on d202Hg, and 0.14‰ on the $\Delta^{200}\text{Hg}$ of a 0.25 ng/g ETH-Fluka standard, and mean sample replication (n=2) of $\pm 0.30 \text{ ‰}$ on d202Hg, and 0.14‰ on the $\Delta^{200}\text{Hg}$ of a 0.25 ng/g sea water sample. Observed sample uncertainties are therefore 2 to 7 times worse than the theoretical instrument’s limit, due to the numerous contributions of sample preparation and sample introduction uncertainties before mass spectrometric detection. Such contributions are naturally higher for mass dependent fractionation (MDF, d202Hg) than for mass independent fractionation (MIF, $\Delta^{200}\text{Hg}$) signatures, because instrumental MDF can take place during mass bias, but no Hg MIF takes place inside a mass spectrometer.

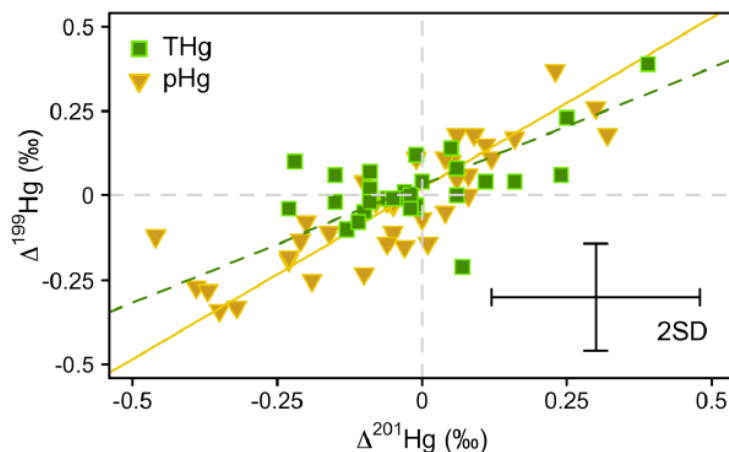
We understand that because sea water has $\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$ and $\Delta^{200}\text{Hg}$ signatures all close to 0 ‰, our raw data gives the impression that we are analyzing just noise. We have applied the same method (i.e. 0.25 ng/g samples) to the analysis of atmospheric reactive Hg(II) samples on cation exchange membranes. The results for those samples show significantly non-zero $\Delta^{199}\text{Hg}$ down to -3‰, coherent with previously observed snow Hg photoreduction (Sherman et al., 2010). For what it's worth, it gives us additional confidence in the low-level Hg isotope analysis we carry out with the new 10^{12} Ohm amplifier.

One of the samples does not have a reported value for $\Delta^{201}\text{Hg}$ despite having been measured twice.

Correct, the $\Delta^{201}\text{Hg}$ for this sample had unsatisfactory replication: two values were measured of +0.17‰ and -0.17‰, with a mean of 0.00 ± 0.48 ‰ (2SD).

Seven of the 16 samples have paired $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$ values of opposite sign, which is likely an analytical artifact.

Correct, but not an artifact, and illustrated in Figure S2 below:



The 2SD error bars illustrate that despite opposite $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$ signs in some samples (upper left quadrant, green tHg symbols), these data are not lying significantly off the expected slope 1.0 line through or near the origin. Similarly the THg slope and intercept (mentioned in the caption; SI line reflect this uncertainty: York regression for tHg: $\Delta^{199}\text{Hg} = 0.79(\pm 0.29) \times \Delta^{201}\text{Hg} + (0.03 \pm 0.04)$, ($\pm$ se), MSWD = 0.2). Therefore, while the data is less precise than what readers are used to from the Hg isotope literature, the results are geochemically coherent with observed MIF phenomena such as a slope of 1.0. A last comment is that the intercept of slope 1.0 data regressions does not necessarily have to go through the origin (0,0); in Masbou et al., (2018) we discuss this phenomena for marine biota in our own and in JD Blum's datasets which have 0.10 to 0.26‰ $\Delta^{199}\text{Hg}$ intercepts. Such intercepts imply that naturally, some of the marine MIF data lies in the upper left quadrant, and displays opposite $\Delta^{201}\text{Hg}$ and $\Delta^{199}\text{Hg}$. Cyclical isotope fractionation is one of the likely causes of this phenomena.

Thirteen of the samples have 2SD of within-mass-spec-session replicate measurements larger than assigned analytical uncertainty from ETH Fluka; in some cases resulting in analytical uncertainty that exceeds 0.4‰.

Correct; sample 2SD is generally always equal to or larger than ETH-Fluka 2SD because the latter is a pure inorganic Hg standard in nitric acid, and samples suffer from potential matrix carry over during the processing. We therefore follow the rule

that if sample 2SD is lower than ETH-Fluka 2SD during mass spec sessions, than this should be considered fortuitous. In that case the sample gets attributed the ETH-Fluka 2SD (Revised MS, Methods lines 372-374). Therefore in our Tables, one will never find a sample 2SD lower than the external reproducibility on ETH-Fluka (or UM-Almaden) 2SD. In doing so we follow the 'Chemical Geology' standards for publishing isotope ratios (Goldstein et al., 2003):

“In the usual case that the internal measurement errors of samples are smaller than the 2SD external reproducibility of the standard, then the 2SD external reproducibility, rather than the sample measurement error, represents the estimate of sample error.”

Results from the eight NIST3133 procedural standards are highly variable, especially those from the four measured at 0.25 ng/g. Although each procedural standard was measured twice, average δ and Δ values that should all be close to 0 range from -0.21 to +0.28‰.

All our NIST procedural standards have delta values that are not significantly different from 0, as expected, and within the stated uncertainty. The stated uncertainty, 0.23‰ on $\delta^{202}\text{Hg}$, 0.16‰ on $\Delta^{199}\text{Hg}$, 0.14‰ on $\Delta^{200}\text{Hg}$, 0.18‰ on $\Delta^{201}\text{Hg}$, is of course slightly more elevated for a sea water sample analyzed at 0.25 ng/g, than for more common analyses (soil, rain, biota etc) performed at 1.0 ng/g (in fact it is $\text{SQRT}(1/0.25)=2$ times less precise).

The apparent quality of the particle isotope results, which were all measured using run solutions with Hg at 0.5 ng/g, is not much better. Sixteen of the 25 samples have 2SD of within-mass-spec-session replicate measurements larger than assigned analytical uncertainty from ETH Fluka and NIST1632d; in a number of cases resulting in analytical uncertainty that exceeds $\pm 0.2\text{‰}$, and in the most extreme case is larger than $\pm 0.9\text{‰}$.

Same answer as above; sample 2SD is always equal to or higher than ETH-Fluka or NIST1632d (Methods lines 372-374). The extreme case of sample 'ICC-pHg-K1-100m' which indeed has a $\delta^{202}\text{Hg}$ of $-0.24\text{‰} \pm 0.93\text{‰}$ merits omission as an outlier due to non-reproducibility of the two replicate analyses. We removed the sample in the revised MS.

The error bars plotted for $\Delta^{200}\text{Hg}$ on Figure 2 are $\pm 0.10 \text{‰}$, but, based on the discussion above, they should be at least $\pm 0.20\text{‰}$.

In Figure 2, typical 2SD error on $\Delta^{200}\text{Hg}$ shown is 0.12‰; based on Table S4 they should be at least 0.14‰ for tHg and 0.07‰ for pHg. The procedural standards for pHg, which the reviewer refers to above, have 2SD of 0.07‰ on ETH-Fluka and 0.04‰ on NIST1632d for the particular mass spec session. We erroneously reported 1SD uncertainties for ETH-Fluka in Table S4; these are now corrected to 2SD, e.g. 0.07‰ on $\Delta^{200}\text{Hg}$ instead of 0.04‰. It is unclear to us why according to the reviewer 'they should be at least 0.20‰'. We report uncertainties of a duplicate pHg isotope measurement, which is at least 0.07‰ (i.e. that of ETH-Fluka), and sometimes larger, but never 0.20‰.

The difference between the median values for $\Delta^{200}\text{Hg}$ in Hg(0) and Hg(II) endmembers is, however, only 0.21‰. The range of values for Hg(0) and pHg is almost completely overlapping, and the SD of each group overlaps.

In Table S1 (SI pdf) we report the following median and interquartile range (IQR) for the Hg(0) and Hg(II) endmembers (the data are non-normally distributed):

Hg(II) rainfall: median 0.17 (IQR, 0.11 to 0.22, n=106)

Hg(0):median -0.05 (IQR, -0.08 to -0.03, n=220)

Therefore while the range of 0.21‰ variation between the endmembers is indeed relatively small, the differences are significant. In addition, all seawater tHg and pHg samples, including published Pacific Ocean pHg²⁹, show $\Delta^{200}\text{Hg}$ values statistically larger than atmospheric Hg(0) (one-sided t.test, $p<0.001$) and lower than Hg(II) end-members (one-sided t.test, $p<0.001$)(Figure 2 & Figure 4A). We added statistics to the revised MS on lines 134-136.

Finally, it is worth pointing out that the samples that were measured and included in this plot were collected where the logistics of various cruises and sampling campaigns allowed, and were therefore understandably opportunistic, rather than being spatially representative of each sample type. Thus, the range of isotope values may be more representative than the median value when comparing sample groups.

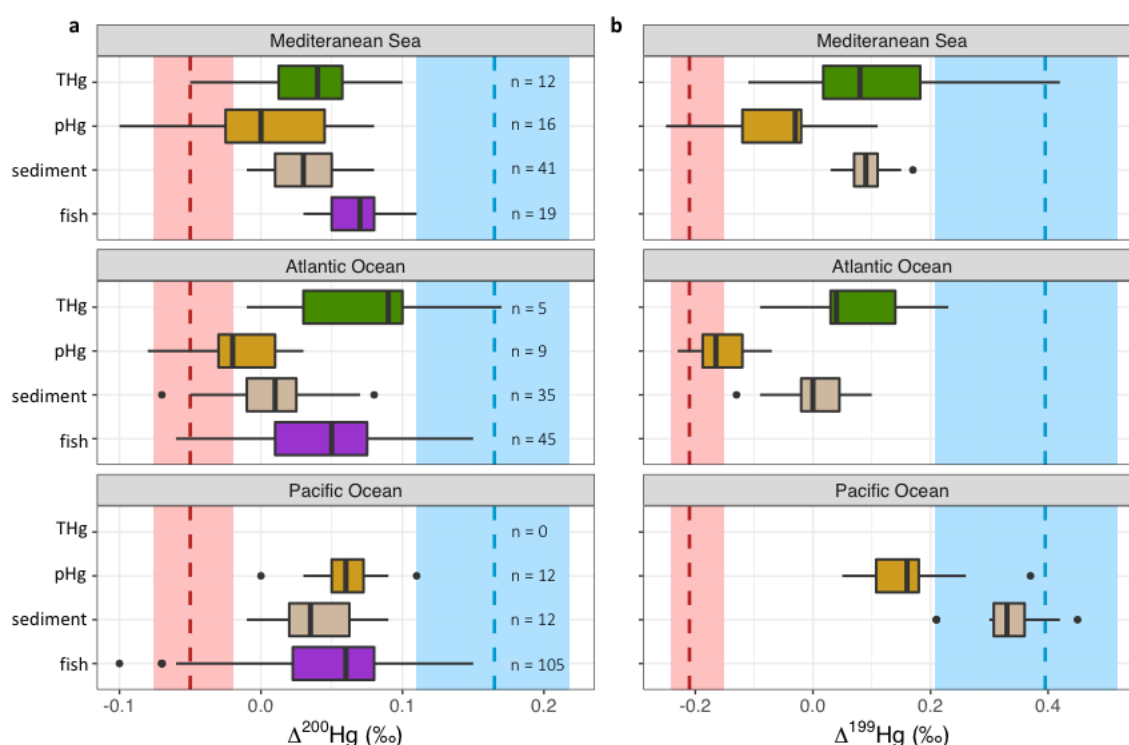
The authors have done no statistical tests on their data beyond calculating the mean and quartile of collections of data and so I am left skeptical of the paper's conclusions. And to make matters worse the supplementary, extended and data tables are unclear, poorly formatted and incomplete—making it challenging for readers to explore the data themselves.

We regret that the SI format is unclear; we have on purpose provided an SI in xls format so that reviewers and readers can explore the data with ease, not having to convert Word Tables.

We acknowledge that we did not do an expanded uncertainty analysis on the $\Delta^{200}\text{Hg}$ binary mixing model; this is now included in the revised MS using a Monte Carlo approach.

The conclusions of this study as written hang, in large part, on the visual interpretation of Figures 2 and 3. The text also refers to $\Delta^{200}\text{Hg}$ data in Figure 4, but I think that was an error and that Figure 4 was changed at some point. My visual inspection tells me that the nearly complete overlap between Hg(0) and pHg and the large scatter in each of the four sample types, makes it impossible to perform the mixing calculations that are proposed on the paper. Similarly, Figure 3 is very misleading in that the endmember Hg(0) and Hg(II) values are depicted by the vertical dashed red and blue lines. Only the median values are shown--yet the range of values dwarfs the values shown as box and whiskers.

We apologize that in Figure 3 end-member D200 values were only visible as a median line; during the pdf generation the shaded uncertainty range (IQR), referred to in the caption, got lost. The original Figure is shown below, and the revised Figure 3 in the MS file, with 2x more data points (n=787). Figure 3 clearly shows that most marine sample types (tHg, pHg, sediments and biota) are exhibiting D200Hg values lower than the 1st quartile of the reported atmospheric Hg(II) endmember, and higher than the 3rd quartile of the Hg(0) end-member.



In conclusion, I don't think the data are depicted clearly enough nor do I think the data are of high enough precision to support the conclusions of the paper.

We clarify end-member uncertainties in the revised Figure 3, and we add an expanded uncertainty analysis to the $\Delta^{200}\text{Hg}$ binary mixing model, and the latitudinal air sea exchange Hg flux derivations.

Referee #3 (Remarks to the Author):

This is an interesting study using stable Hg isotope measurements of total Hg in waters of the Atlantic and Mediterranean to infer the relative contributions of atmospheric deposition of Hg(II) and net Hg(0) oceanic uptake. Many aspects of the Hg biogeochemical cycling remain poorly constrained and this study attempts to constrain one element regarding net deposition to the oceans. Isotopes can be a powerful tool to investigate this question. The authors' results show that atmospheric Hg(II) deposition accounts for 41% of the deposition to the ocean and Hg(0) uptake accounts for 59%. This is in contrast with global models which predict a much larger contribution from Hg(II) deposition.

The manuscript is generally well written and the results are interesting. The two main concerns I have regard 1) the lack of discussion of how the dynamic cycling of Hg in the marine boundary layer and surface ocean might affect the isotopic signature of Hg and its interpretation; and 2) the large leaps that the authors make from their measurements at very specific locations to the generalization for the entire atmosphere-ocean interactions and the lack of assessment of error ranges (the authors tend to give single numbers which don't reflect the true uncertainties, 41%, 1000 Tg/yr, etc...). I elaborate on these two issues below.

The marine boundary layer displays a very dynamic chemical cycling of Hg due to the local formation of Hg(II) promoted by Br released from sea-salt aerosols. This Hg(II) will deposit

to the surface ocean where it might undergo reduction back to Hg(0) and escape to the atmosphere. How would this cycling affect the isotopic signature of marine tHg and pHg in the samples? This cycling might also affect the isotopic signature of the rainfall samples. Is there any reason to believe that rainfall samples collected at continental locations would have the same isotopic signature as samples collected at marine locations. (Are any of the rainfall samples listed in Table S1 from marine locations?)

Good questions; Of the 106 remote rainfall samples we included in our Hg(II) end-member a large number are from coastal locations in Hawaii, California, Florida, and the Pic du Midi, which receives Atlantic Ocean air masses and moisture (Fu et al., 2020; Motta et al., 2019; Sherman et al., 2010, 2012; Washburn et al., 2019).

In the revised version we also review Hg(0) and aerosol Hg isotope data in the marine boundary layer (MBL), and expanded the paragraph on this (L122-132):

“Modern, northern hemispheric Hg(II) wet deposition is characterized by a positive $\Delta^{200}\text{Hg}$ of 0.17 ‰ (0.11 ‰ to 0.22 ‰, median and IQR), $n = 106$, for background sites with Hg concentrations $< 25 \text{ ng L}^{-1}$; Table S1). We also need to consider the $\Delta^{200}\text{Hg}$ of Hg(II) dry deposition, suggested to represent 40% of total atmospheric Hg(II) deposition to oceans³⁹. Aerosol and fog water Hg(II) observations in the marine boundary layer (MBL) and free tropospheric gaseous Hg(II) in Atlantic air masses also have positive but slightly lower $\Delta^{200}\text{Hg}$ of 0.10 ‰ (0.07 ‰ to 0.1 ‰; median, IQR, $n = 66$)^{40–42}. For end-member mixing calculations we estimated the $\Delta^{200}\text{Hg}$ of combined wet and dry Hg(II) deposition to vary between 0.13 ‰ and 0.15 ‰ with latitude (Figure S9). Atmospheric Hg(0), the largest Hg pool in the atmosphere, exhibits negative $\Delta^{200}\text{Hg}$ of -0.05 ‰ (-0.08 ‰ to -0.03 ‰; median, IQR, $n = 220$, for continental background samples with Hg(0) concentrations $< 2 \text{ ng m}^{-3}$; Table S1). MBL Hg(0) observed at coastal sites and during cruises shows an identical $\Delta^{200}\text{Hg}$ of -0.06 ‰ (-0.08 ‰ to -0.02 ‰, median and IQR, $n = 80$, two-sided t.test, $p = 0.96$)^{40,43,44}.”

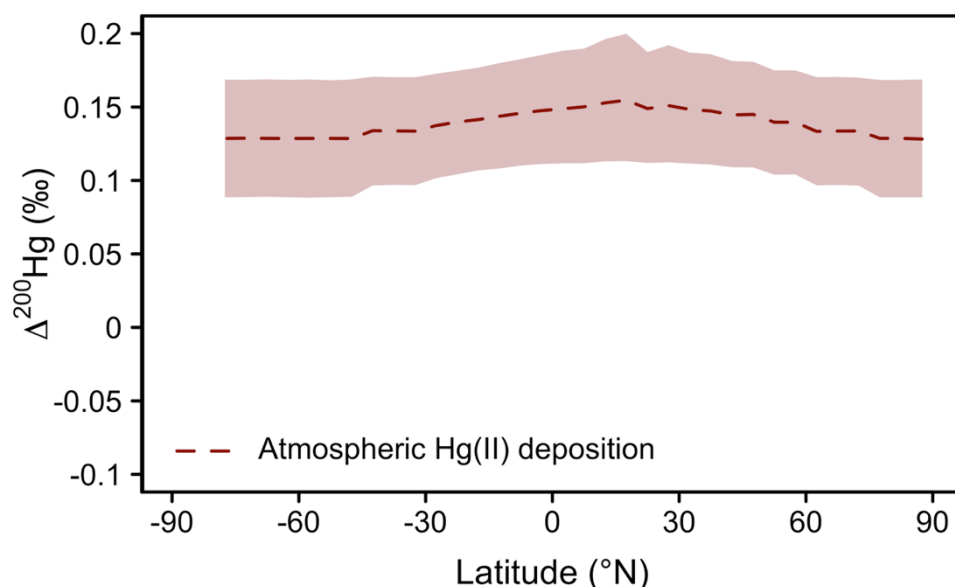
Note that we thus revise the Hg(II) end-member to include MBL aerosol data.

Line 125. The authors refer to a new study (submitted) showing that gaseous atmospheric Hg(II) have the same $\Delta^{200}\text{Hg}$ as Hg(II) in wet deposition. This study seems that have been done at one high altitude location in the Pyrene Mountains. The authors do not provide any justification as to why measurements at this single location can be generalized to the marine boundary layer. The local chemistry and origin of Hg(II) at that location might be very different than over the marine boundary layer, where sea salt aerosol can provide a large source of Br and oxidize Hg(0) locally.

Good point again; answers are mostly given at the previous point. The Pic du Midi location is indeed not representative of the MBL, but its gaseous Hg(II) dynamics and rainfall does represent free tropospheric Hg(II) formed over the Atlantic Ocean (Fu et al., 2016, 2020), and supplying the Atlantic MBL and surface waters with Hg(II).

Line 130. “We therefore suggest that the median NH rainfall $\Delta^{200}\text{Hg}$ of 0.17permil is a reasonable estimate...” I might be missing something, but I do not see the connection between this sentence and the previous sentences in this paragraph. At the beginning of the paragraph the authors mention 0.16 permil observed in NH Hg(II) wet deposition. How to the authors go from 0.17 to 0.16 permil? Or is it a typo?

Sorry this is indeed confusing; the reason was that 0.16‰ is the rainfall mean, and 0.17‰ the median. In the revised MS we include new MBL aerosol and fog water data, and define separate Hg(II) wet deposition and Hg(II) dry deposition end-members of 0.17 and 0.10‰. Note that in the new latitudinal analysis we then vary the total Hg(II) end-member composition as a function of latitude between 0.13 and 0.15‰ (Figure S9 below); this does not affect the main conclusions.



New Figure S9

Inferring the global Hg(II) wet deposition flux to the ocean from 6 coastal monitoring sites is a very big stretch given the high variability of precipitation over the oceans (Line 147). It is equivalent to assessing the total rainfall to the oceans from the measurement of precipitation at these 6 sites. Why would that be a valid approach? Are these sites representative? How can the authors assess that?

Agreed, this is not as much data as one would like to see and we took time to review wet deposition observations from MDP and case studies to revise this estimate (see new Figure S5 above, Table S6 for data); for clarity, at each GMOS site, multi-annual single event rainfall was monitored and the total amount of single rainfall events analyzed by GMOS is 278. In the revised MS we now cover a total number of 12,812 single rainfall events at coastal and island sites, and show a significant latitudinal gradient that we use to revise global Hg(II) wet deposition to Oceans to 2561 Mg/y, and global total Hg(II) deposition to 4268 Mg/y, in agreement with Hg cycling model estimates of 4600 Mg/y (see discussion with reviewer 1).

The authors then scale up that number to include dry deposition, using a 60%/40% split between wet/dry deposition from a global model. This is from the same global model that the authors suggest is overestimating oceanic deposition of Hg(II) by a factor of 4.6. Why would the authors trust the 60/40% split from that model?

Please note that in the revised version of the manuscript our Hg(II) wet deposition estimate aligns with the modeled estimate. Concerning the wet Hg(II) deposition to dry

Hg(II) deposition split, we agree that that is somewhat unsatisfactory, but we have little choice here. We must use a global estimate of the Hg(II) dry deposition flux and account for it in a global air-sea exchange budget. Contrary to Hg wet deposition observations, there is no robust global observational data on Hg(II) dry deposition. Therefore we use the model estimate. Fortunately, the model estimate of the Hg(II) wet : dry deposition ratio depends on atmospheric chemical and physical factors (aerosol partitioning of gaseous Hg(II), cloud scavenging of Hg(II) forms, meteorology) that are mostly independent of air-sea Hg exchange.

Overall, I find that there are too many assumptions made along the way to have much confidence on the 1000 Mg y⁻¹ the authors infer from the 6 sites and global model estimates of dry vs wet deposition. One way to assess whether the 6 sites are representative would be to sample wet deposition from that same global model at the location of these sites and see whether applying the same assumptions (taking the median and scaling by the surface area of the ocean + 40%/60% split in dry/wet deposition) give the same results as the actual calculated Hg(II) deposition flux over the oceans.

Mea culpa; in the revised MS we correct the Hg(II) wet deposition flux, and expand the discussion to include a full latitudinal analysis of Hg(II) deposition, Hg(0) invasion and evasion, and latitudinal marine D200 distribution.

The authors come up with a single estimate (1350 Mg y⁻¹) for net Hg(0) deposition to the Oceans based on the 41% number from their mixing model. The range of uncertainty given for that number is 32-65%. I suggest that the authors use that range and derive the range of estimates for net Hg(0) deposition to the oceans and include the ranges in both the abstract and Figure 4.

We apologize for not having provided a full uncertainty analysis. In the revised MS, we use a Monte Carlo method to propagate uncertainties for the $\Delta^{200}\text{Hg}$ mass balance, and for the flux calculations.

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Reviewer Reports on the First Revision:

Ref #1

This a resubmission, so I won't go through steps A-H explicitly. The authors have made some substantial changes, all to the good, and I think the manuscript is much improved. In their response, which initially completely confused me, they seemed to be saying what I thought was my position: that there is net evasion of Hg⁰. Their initial draft, however, contained language like this from the abstract: "We use an isotope mass balance to estimate that sea water tHg can be explained by the mixing of 41% atmospheric Hg(II) deposition and 59% Hg(0) uptake," which I read as net input is comprised of roughly equal parts Hg(II) and Hg⁰...but that is apparently not their position (or at least, not any more). Thus, I think my confusion came from them not making clear that they were talking about net Hg(II) inputs and GROSS Hg⁰ inputs, with an even larger gross Hg⁰ output. Thus, I think all of my remaining issues can be solved by them be extremely explicit about what kind of terms they are talking about. For example, one should not put net and gross flux terms in the same sentence as they have in the abstract and elsewhere without qualifying language because it will lead to confusion for folks like me. I think they should talk about these terms as they have in the response, which is inputs of Hg(II) and unbalanced recycling of Hg⁰, which moves the isotope values in the water towards that of Hg⁰ in the air in accordance with the relative size of the net Hg(II) input and the gross Hg⁰ input (what I called a recycling flux in my first review).

With this clarifying language, I think the manuscript is ready and will certainly be an important paper in the mercury biogeochemistry community.

Ref #2

After reading the revised manuscript and the three reviews, and responses to reviewers from the authors, my recommendation is to reject this paper. In their 20 page rebuttal document the authors have done a reasonable job of responding in a rational way to the many criticisms and inconsistencies pointed out by the reviewers. But the machinations that they had to do through emphasize that this does not belong as a short-format letter to *Nature*. Instead it belongs in a full-length, specialist journal where all of the caveats can be discussed and vetted in detail. I think that the conclusions of this paper could be right—or due to things we don't yet understand about even-

mass MIF—they could be wrong.

I am, in particular, apprehensive about the effects of Hg(0) supersaturation and how this is resolved. The authors seem too fluid in terms of changing their model and the data sets they are considering, to make them compatible with their interpretation of the Hg isotope data. I don't find convincing enough arguments to believe the small and poorly understood D200Hg signal (with small signal to noise ratio) over the conventional Hg flux modeling. The Hg modeling has too many adjustable parameters and it seems the authors are manipulating them fluidly to reach a single answer, when there might be alternate interpretations.

Ref #3

The authors have made substantial revisions to the original manuscript as their initial assumptions to construct a global estimate of marine mercury deposition based on a small sample of observations was flawed. Their more complete approach in the new version of the manuscript seems more valid. The basic finding remains the same: the isotope mass balance suggests that deposition to the global oceans due a 42%/58% split between atmospheric Hg(II) deposition and Hg(0) uptake. This is contrast with one estimate from one model, which is 73%/27%.

While the manuscript is much improved, I still have a number of concerns that I list below.

1) It took me a while to understand what the 'reference' model is. The way it is first mentioned is in parenthesis in line 160. Emphasizing the underlying assumptions in this model would help. Similarly the figure legend should explain what this model is. I remain puzzled by the choice of the authors to use a mixture of observations (for Hg(II) wet deposition and Hg(0) deposition) and results from the GEOS-Chem model (for the fraction if dry vs wet deposition of Hg(II)). How does the assumption of using the GEOS-Chem model for the Hg(II) dry deposition affect their results? What do other studies suggest for this fraction? What if it varied with latitude? The default assumption is that dry deposition of Hg(II) is uniform with latitude. Is that what GEOS-Chem predicts? An alternative approach would be to use GEOS-Chem as their reference model.

2) The bottom 2 panels of Figure 4 are not quite clear to me. How were the green lines obtained?

3) Throughout the text the authors choose one model (GEOS-Chem in its latest published version by Horowitz et al.) to compare their estimate of the relative contributions between Hg(II) deposition (4600 Mg yr⁻¹) and Hg(0) deposition (1700 Mg yr⁻¹). This lends to the impression that this is the only estimate out there. The manuscript would benefit from having a more complete description of the range of deposition estimates from different mercury models that are available.

Author Rebuttals to First Revision:

[We would like to thank the reviewers for their additional time and effort in providing new comments. We provide detailed feedback below and new edits to the 2nd revised MS.](#)

Referees' comments:

Referee #1 (Remarks to the Author):

This a resubmission, so I won't go through steps A-H explicitly. The authors have made some substantial changes, all to the good, and I think the manuscript is much improved. In their response, which initially completely confused me, they seemed to be saying what I thought was my position: that there is net evasion of Hg0. Their initial draft, however, contained language like this from the

abstract: "We use an isotope mass balance to estimate that sea water tHg can be explained by the mixing of 41% atmospheric Hg(II) deposition and 59% Hg(0) uptake," which I read as net input is comprised of roughly equal parts Hg(II) and Hg(0)...but that is apparently not their position (or at least, not any more). Thus, I think my confusion came from them not making clear that they were talking about net Hg(II) inputs and GROSS Hg(0) inputs, with an even larger gross Hg(0) output. Thus, I think all of my remaining issues can be solved by them be extremely explicit about what kind of terms they are

talking about. For example, one should not put net and gross flux terms in the same sentence as they have in the abstract and elsewhere without qualifying language because it will lead to confusion for folks like me. I think they should talk about these terms as they have in the response, which is inputs of Hg(II) and unbalanced recycling of Hg(0), which moves the isotope values in the water towards that of Hg(0) in the air in accordance with the relative size of the net Hg(II) input and the gross Hg(0) input (what I called a recycling flux in my first review).

With this clarifying language, I think the manuscript is ready and will certainly be an important paper in the mercury biogeochemistry community.

We fully agree on clarifying language regarding net and gross terms. We have amended the 2nd revised MS with explicit 'gross' adjectives for clarification. We have added 6 lines at the beginning of the discussion (L115-121, below, bold text) explaining that air-sea Hg(0) exchange is bi-directional, and that even during net Hg(0) emission, Hg(0) invasion remains an important flux. Finally, we added a schematic Figure 1 illustrating the various gross and net Hg deposition and emission fluxes, and the main Hg isotope-based flux results.

L115-121: "We use $\Delta^{200}\text{Hg}$ to quantify the combined contribution of gross Hg(II) wet and dry deposition, and gross Hg(0) invasion to marine tHg and pHg (Methods, Eq. 3). **It is important to clarify that Hg(0) gas exchange is bi-directional (Figure 1), i.e. at any time atmospheric Hg(0) dissolves into the surface microlayer (invasion), and dissolved aqueous Hg(0) evades to the atmosphere. Although generally surface oceans are supersaturated in Hg(0), and gross Hg(0) evasion exceeds gross invasion, the gross Hg(0) invasion flux is substantial and an important contributor to marine Hg (Figure 1). The Hg(II) dry and wet deposition flux is per definition a gross flux. Hg(II) deposition, after reduction to Hg(0) in ocean waters, does however contribute to the large Hg(0) emission flux. We exclude other Hg sources such as hydrothermal or river inputs.**"

new Figure 1:

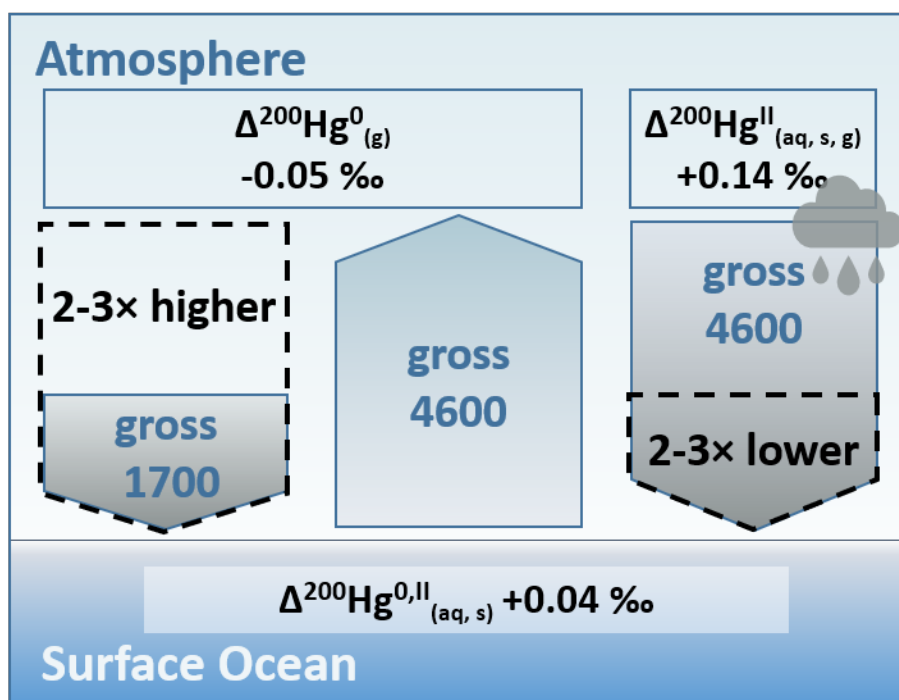


Figure 1. Summary of marine Hg(II) deposition and Hg(0) air-sea exchange fluxes. Gross fluxes (solid arrows, Mg y^{-1}) are based on published 3D model estimates³. Hg(0) exchange is bi-directional, meaning that despite surface ocean Hg(0) supersaturation and large Hg(0) evasion, Hg(0) invasion is substantial. Marine $\Delta^{200}\text{Hg}$ signatures of 0.04‰ indicate a relatively more important contribution of the atmospheric Hg(0) end-member to marine Hg than current 3D models suggest. This indicates that either 3D model Hg(II) deposition is overestimated or that Hg(0) invasion is underestimated (black dotted arrows, indicating 2-3x lower or 2-3x higher fluxes, required to fit $\Delta^{200}\text{Hg}$ data).

Referee #2 (Remarks to the Author):

After reading the revised manuscript and the three reviews, and responses to reviewers from the authors, my recommendation is to reject this paper. In their 20 page rebuttal document the authors have done a reasonable job of responding in a rational way to the many criticisms and inconsistencies pointed out by the reviewers. But the machinations that they had to do through emphasize that this does not belong as a short-format letter to Nature. Instead it belongs in a full-length, specialist journal where all of the caveats can be discussed and vetted in detail. I think that the conclusions of this paper could be right—or due to things we don't yet understand about even-mass MIF—they could be wrong.

I am, in particular, apprehensive about the effects of Hg(0) supersaturation and how this is resolved. The authors seem too fluid in terms of changing their model and the data sets they are considering, to make them compatible with their interpretation of the Hg isotope data. I don't find convincing enough arguments to believe the small and poorly understood D200Hg signal (with small signal to noise ratio) over the conventional Hg flux modeling. The Hg modeling has too many adjustable parameters and it seems the authors are manipulating them fluidly to reach a single answer, when

there might be alternate interpretations.

We understand the criticism, and we would not work towards publication if we would not be convinced that our interpretation stands up to detailed scrutiny. We have taken much time in the Fall of 2020 to expand our interpretation with the latitudinal Hg isotope and air-sea exchange analysis. These show that the HgII deposition, Hg0 invasion/evasion and observed D200 trends are 'geochemically consistent', which is a prerequisite used by many respectful colleagues in the geosciences.

First, the sea water D200Hg trends are internally consistent with the biota and sediment Hg stable isotope signatures discussed in our manuscript. The D200 mixing between atmospheric Hg0 and Hg(II) is consistent with D199Hg measurements of tHg, pHg and sediments as shown in Figure 4b (note that for biota which accumulate methyl-Hg, the D199Hg of the source signatures is masked by magnetic isotope effects during marine photo-demethylation of methyl-Hg). For 339 out of 791 samples the D204Hg signature has been measured and the latitudinal trends are inverse to the D200Hg latitudinal trend and therefore also consistent with our interpretation.

Secondly, the D200Hg trends are externally consistent with unpublished data. We have the luxury of working on two large unpublished Hg isotope datasets that are fully consistent with the D200 trends discussed here: one on a global tuna fish database (n>300) that shows identical latitudinal D200 distribution, and another dataset on southern hemisphere rainfall HgII and atmospheric Hg0 D200, which mirrors the abundant northern hemisphere data we use here to define D200 end-members.

Finally, we see no other convenient means, than by Hg isotopes, to constrain atmospheric Hg delivery pathways to the Ocean. Our findings will allow modelers to remove a major source of uncertainty in global models. Future detailed Hg isotope mapping of ocean sub-basins will allow refining the budgets and dynamics.

Referee #3 (Remarks to the Author):

The authors have made substantial revisions to the original manuscript as their initial assumptions to construct a global estimate of marine mercury deposition based on a small sample of observations was flawed. Their more complete approach in the new version of the manuscript seems more valid. The basic finding remains the same: the isotope mass balance suggests that deposition to the global oceans due a 42%/58% split between atmospheric Hg(II) deposition and Hg(0) uptake. This is contrast with one estimate from one model, which is 73%/27%.

While the manuscript is much improved, I still have a number of concerns that I list below.

1) It took me a while to understand what the 'reference' model is. The way it is first mentioned is in parenthesis in line 160. Emphasizing the underlying assumptions in this model would help. Similarly the figure legend should explain what this model is.

We clarified phrasing in the discussion, moving the term 'reference model' up in the text and explicitly calling it 'zonal reference model': "We therefore examined current best knowledge on the

latitudinal variation of Hg(0) invasion vs Hg(II) deposition by a full latitudinal analysis of marine $\Delta^{200}\text{Hg}$, rainfall Hg(II) flux, atmospheric and dissolved gaseous Hg(0) concentrations, and climatology observations as a function of latitude (indicated by zonal 'reference model' here and in SI text, Tables S5, S6, S7)."

We added the following text to Figure 5 legend to clarify the meaning of zonal 'reference model':
"Zonal 'Reference model' refers to the combination of zonal model and observation derived fluxes; i.e. 1) the gas-exchange model which assimilates atmospheric and dissolved Hg(0) observations, 2) 3D model global Hg(II) dry deposition, and 3) Hg(II) wet deposition observations (see SI text, Figures S5-S8)."

The zonal 'reference model' therefore is a mix of GEOS-Chem output, GEOS-Chem parameterizations (used here along the latitude gradient), but also extrapolated atmospheric and marine Hg0 observations, and coastal HgII wet dep observations. It is perhaps true that we should have taken GEOS-Chem output to being with, but the genesis of the paper has simply not taken this route. Note that our latitudinal Hg0 invasion, evasion and HgII total deposition extrapolation reproduces GEOS-Chem output to within 13%.

I remain puzzled by the choice of the authors to use a mixture of observations (for Hg(II) wet deposition and Hg(0) deposition) and results from the GEOS-Chem model (for the fraction if dry vs wet deposition of Hg(II)). How does the assumption of using the GEOS-Chem model for the Hg(II) dry deposition affect their results? What do other studies suggest for this fraction? What if it varied with latitude? The default assumption is that dry deposition of Hg(II) is uniform with latitude. Is that what GEOS-Chem predicts? An alternative approach would be to use GEOS-Chem as their reference model.

Hg(II) wet deposition is based on real observations at coastal sites; Hg(II) dry deposition over oceans has not been observed, owing to the technical difficulties in doing so. Models like GEOS-Chem parameterize Hg(II) dry deposition to oceans, with an inverse latitudinal distribution compared to Hg(II) wet deposition, i.e. low Hg(II) dry deposition in the (sub-)tropics, and high Hg(II) dry deposition at mid and high latitudes. We consider that model tuning of an important global deposition flux such as Hg(II) dry deposition (i.e; 40% of 4600 Mg/y) is reasonable, because many indirect observational constraints come into play (global Hg0 concentration and HgII wet dep distribution). We consider however that there is no evidence for the modeled latitudinal Hg(II) dry deposition distribution. We there make a compromise; we set global Hg(II) dry deposition equal to the GEOS-Chem number, but we simply assume a flat latitudinal distribution.

Regarding the precise questions asked by the reviewer:

- This assumption (using GEOS-Chem HgII dry deposition) does not affect our main conclusion that total Hg(II) deposition to oceans is over-estimated. In fact, using the GEOS-Chem number is not really an assumption; it is the only model that provides a global HgII dry deposition estimate. This estimate is integral part of the current marine Hg deposition paradigm: 3:1 HgII:Hg0 deposition.
- Other global model studies use the same Hg(II) dry deposition parameterization (resistance-in-series scheme); four models were inter-compared by the GMOS group in (Travnikov et al., 2017), where 3 out of 4 models are show no bias in atmospheric Hg(II) concentrations (pasted Figure 6

below; note that these are not Hg(II) dry dep fluxes, but concentrations!). Unfortunately, that paper, nor the in-depth single model papers mention globally integrated Hg(II) dry deposition fluxes for comparison; since 3 out of 4 unbiased models use the same parameterizations for Hg(II) dry deposition, and the same observational global Hg₀, Hg(II) concentration and Hg(II) wet deposition constraints, they will likely be similar to GEOS-Chem. In our opinion the GEOS-Chem Hg community deserves much credit for systematically including budget figures and other details in their papers; it is the model with the largest user-base, always at the forefront, and therefore merits its use for comparison to Hg isotope constraints in our study.

- Yes GEOS-Chem Hg(II) dry deposition varies with latitude; this does not affect our final conclusions.

Redacted: Travnikov et al. <https://doi.org/10.5194/acp-17-5271-2017>, 2017.

2) The bottom 2 panels of Figure 4 are not quite clear to me. How were the green lines obtained?

This is explained for panel 4c (now 5c) in the SI text lines 255-257: “Using a fitting approach, minimizing the root mean square error (rmse) between observed and predicted $\Delta^{200}\text{Hg}$, we estimate that Hg(II) wet deposition would need to be approximately half (1252 Mg/y) the current estimate (2561 ± 768 , 1SD) to achieve a good fit (**Figure 5c, main text**).”

And for panel 4d in SI text lines 263-265: “We can also keep Hg(II) deposition constant, and increase ocean Hg(0) uptake by increasing the gas-transfer velocity, K_w in equations S1-S3, by a factor of 2.3 to achieve an optimum fit between observed and predicted $\Delta^{200}\text{Hg}$ (**Figure 5d, main text**).”

We added the text in bold to clarify. We also clarified the Figure 5 caption as indicated above, and we changed Figure 5c, d legend to ‘reference model’ in order to keep this homogeneous throughout Figure 5. Figure 5 caption was also modified as follows: “**The green $\Delta^{200}\text{Hg}$ -based curves in panels c) and d) represent the gross Hg(II) deposition and gross Hg(0) invasion needed to reconcile marine $\Delta^{200}\text{Hg}$ observations in panel a), i.e. either lower Hg(II) deposition, or higher ocean Hg(0) uptake (see SI text).**”

3) Throughout the text the authors choose one model (GEOS-Chem in its latest published version by Horowitz et al.) to compare their estimate of the relative contributions between Hg(II) deposition (4600 Mg yr⁻¹) and Hg(0) deposition (1700 Mg yr⁻¹). This lends to the impression that this is the only estimate out there. The manuscript would benefit from having a more complete description of the range of deposition estimates from different mercury models that are available.

Yes, we would prefer comparing our Hg isotope results to a model ensemble, but as indicated above, other models (GLEMOS, GEM-MACH-Hg, ECHMERIT) unfortunately do not provide global budgets (Travnikov et al., 2017; Semeniuk and Dastoor, 2017; Simone et al., 2016). The number of GEOS-Chem users is larger than the number of all other model users together, and different consecutive versions of GEOS-Chem, coupled for example to slab-oceans (Holmes et al., 2010), to the OFFTRACK gcm (Zhang et al., 2014), to MIT gcm (Horowitz et al., 2017) all conserve the same dominant Hg(II) over Hg₀ gross deposition pathway to oceans.

The idea that Hg wet deposition supplies global terrestrial and marine ecosystems with Hg is deeply rooted in the community. One may wonder why? Probably because it has been the easiest parameter to measure and monitor over the past decades. Hg isotopes help question such established ‘quasi-dogmatic’ ideas....a bit of fresh air if you will: both soil Hg and now ocean Hg have isotope signatures that resemble Hg⁰ much more than Hg^{II} (Demers et al., 2013; Zheng et al., 2016; Enrico et al., 2016; Zhou et al., 2021). It makes sense if you think about it: 95% of lower tropospheric Hg is in the form of Hg⁰. And at any place on Earth it rains only 3% of time on average. No wonder Hg⁰ interaction with land and sea is important.

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Demers, J. D., Blum, J. D., and Zak, D. R.: Mercury isotopes in a forested ecosystem: Implications for air-surface exchange dynamics and the global mercury cycle, *Glob. Biogeochem. Cycles*, 27, 222–238, <https://doi.org/10.1002/gbc.20021>, 2013.

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Holmes, C. D., Jacob, D. J., Corbitt, E. S., Mao, J., Yang, X., Talbot, R., and Slemr, F.: Global atmospheric model for mercury including oxidation by bromine atoms, *Atmospheric Chem. Phys.*, 10, 12037–12057, 2010.

Horowitz, H. M., Jacob, D. J., Zhang, Y., Dibble, T. S., Slemr, F., Amos, H. M., Schmidt, J. A., Corbitt, E. S., Marais, E. A., and Sunderland, E. M.: A new mechanism for atmospheric mercury redox chemistry: implications for the global mercury budget, *Atmospheric Chem. Phys.*, 17, 6353–6371, <https://doi.org/10.5194/acp-17-6353-2017>, 2017.

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Zhang, Y., Jaegle, L., Thompson, L., and Streets, D. G.: Six centuries of changing oceanic mercury, *Glob. Biogeochem. Cycles*, 28, 1251–1261, <https://doi.org/10.1002/2014GB004939>, 2014.

Zheng, W., Obrist, D., Weis, D., and Bergquist, B. A.: Mercury isotope compositions across North American forests, *Glob. Biogeochem. Cycles*, 30, 1475–1492, <https://doi.org/10.1002/2015GB005323>, 2016.

Zhou, J., Obrist, D., Dastoor, A., Jiskra, M., and Ryjkov, A.: Vegetation uptake of mercury and impacts on global cycling, *Nat. Rev. Earth Environ.*, <https://doi.org/10.1038/s43017-021-00146-y>, 2021.

Reviewer Reports on the Second Revision:

Ref #1

The authors added a lot of additional qualifying language, which I appreciate...and that almost does it for me.

But I'm still hung up on sentences like this one from the summary: "Our findings suggest that global atmospheric Hg(0) uptake by the oceans is equally important as Hg(II) deposition, which has implications for our understanding of atmospheric Hg." I think part of my problem with saying something like this is that "important" is vague. Important in what way? Setting the isotopic composition of surface seawater Hg? Yes, then I would agree. Important in setting the amount of Hg in the surface ocean (which is what the sentence seems to imply)? Then no, I don't agree. I return to the thought experiment I proposed in my first review: imagine no Hg(II) deposition...so only the Hg(0) exchange. The waters would reach equilibrium with the air and the isotopic composition looks just like air as well. But, the concentration would only be something like 25-50 femtomolar, rather than the 1000 femtomolar that's observed. Or, run the experiment the other way...if there were no air-sea exchange of Hg(0), the isotopes would look like rain and the concentration would be even higher than we observe. So, air-sea exchange lowers Hg in the ocean and simultaneously drives isotopes away from the rain value. The distance away from the rain value tells us the relative sizes of the rain flux in and the recycling flux associated with air-sea exchange. So, clarify "important" and avoid using words like "uptake" or "source" when talking about Hg(0).

If I understand correctly, the isotopes allow you to play this thought experiment out: if you grab an individual atom, and ask it "where did you come from, rain or gas?" the isotopic data suggest that half the atoms would say "gas" and half would say "rain." But if Hg(0) didn't oxidize to Hg(II) and vice versa, the answer would be about 1 would say "gas" and 40 would say "rain." So, another way to view the isotopic data is that it tells you about relative speeds of things like gas exchange and redox. Thus, it feels as if the authors fall back on wanting to talk in mass balance terms, but I think the bidirectionality of one of the processes makes that impossible.

Nature asked me to reflect on Reviewer #2's comments as well, and I'm guessing they are particularly interested in the issue of suitability for Nature. Reviewer #2 seems to argue that this information is just too complex for an adequate airing in a short, Nature-style manuscript. I think this is a good point, but I don't find the manuscript too hard to follow now in its present, Nature-style form. That being said, there's a lot in the supplemental material, so this might not have worked in the pre-digital days...thus, the paper really is much longer than 4 pages.

Ref #2

This is the third version of this paper that I am reviewing. I think that the authors have worked hard to satisfy criticisms and limitations of this paper and that it has been improved greatly. There are many complications and caveats in this story but the authors have highly packed a lot of information into the paper. It is my feeling that the paper could be publishable in its present form.

Ref #3

The authors have addressed my comments in their revised manuscript.

Author Rebuttals to Second Revision:

29th April 2021

Dear Dr Sonke

Your revised manuscript entitled "Mercury stable isotope composition of sea water suggests important gaseous elemental mercury uptake" has now been seen by the three original referees, whose comments are attached below. As you will see referee #2 and #3 have no further comments, but referee #1 suggests further clarifications that would need to be addressed. We will need to consider your response to these concerns in the form of a revised manuscript accompanied by a list to explain your revisions. You will also need to make some editorial changes to your paper so that it is as brief as possible and complies with our Guide to Authors (<https://www.nature.com/nature/for-authors>).

LENGTH: Your paper is with about 2900 words and five figures longer than our usual length limit of around 2000 words with four small display items. We have some flexibility and can allow the revised text with around 2600 words and four figures. We suggest that you submit figure 1 as an Extended Data item (please see below). Please also keep in mind that important technical details that are not central to the main message of the paper can be moved into the Methods section or, if necessary, a Supplementary Information section (see below).

[We moved Figure 1 to the Extended Data section.](#)

[We shortened phrasing left and right in the main text, and moved the 'particulate Hg isotope results' paragraph \(209 words\) to the Supporting Information. The revised manuscript has 2478 words \(including the Abstract of 214 words\) and is below the requested 2600 word limit. The methods section is now 2700 words, which is within the limited given below.](#)

TITLES: Titles cannot exceed 75 characters (including spaces); they must not contain punctuation and should reflect the main new finding if the paper. The current title is too long.

[We propose a new shorter title, following our rebuttal to R1 below:](#)

["Mercury stable isotopes constrain atmospheric deposition pathways to the Ocean"](#)

SUMMARY PARAGRAPH: All Nature papers begin with a fully referenced paragraph, typically no longer than 200 words, aimed at readers in other disciplines. This paragraph starts with a 2- to 3-sentence, basic introduction to the field; continues with a 1-sentence statement of the main findings starting 'Here we show' or an equivalent phrase; and finally, concludes with 2 to 3 sentences putting the main findings into general context so it is clear how the results described in the paper have moved the field forward. A downloadable, annotated example is available at <https://www.nature.com/nature/for-authors/formatting-guide>. In some cases it may be necessary to exceed this limit in order to explain complex material for readers in other fields – in such cases, summary paragraphs can be up to 230 words in length. The extra length, however, is for introduction and context, and not for additional technical information.

[Our abstract is 214 words long and follows Nature guidelines on style.](#)

MAIN TEXT: Further introductory material in the main text of the paper should not be necessary. Any discussion at the end of the paper should also be brief, and not repeat what is already written in the initial summary paragraph. Subheadings of up to 40 characters (including spaces) may be used to separate sections of the paper if this aids navigation.

We shortened two subheadings and added a third one

STATISTICS: Authors should ensure that any statistical analysis used is sound and that it conforms to the journal's guidelines (see <https://www.nature.com/nature/for-authors/formatting-guide> for guidance).

We doublechecked and confirm all statistics are appropriate and commented in the Methods section

METHODS: At the end of the main text document (after the main figure legends), there should be a section entitled "Methods" (up to 3000 words), which provides a more detailed discussion of the additional methodological information that would allow other researchers to replicate the results (we define "Methods" quite broadly, so this is not limited to details of experimental protocols – supplementary discussion and analysis can also be included). The Methods section will not appear in the print version but will be fully copy-edited and appear online in the full-text HTML and PDF versions. The Methods section should be written as concisely as possible but should contain all elements necessary to allow interpretation and reproduction of the results. If there are additional references in the Methods section, their numbering should continue from the last reference in the main paper, and the list should follow the Methods section. If the methods require chemical structures, figures or tables, these should be supplied as Extended Data (see below). For mathematically complex methods, or methods that require an unusually large number of figures or tables (beyond what can be accommodated as Extended Data), the entire Methods section should instead be supplied as a separate Supplementary Information.

Methods are now 2700 words

REFERENCES: As a guideline, most papers should need no more than 30 references in the main text; up to 50 if essential; additional references can be cited in (and listed after) the Methods section, as detailed above.

We have 46 references with the main text and an additional 38 references with the Methods (10) and Extended Data Tables (28)); both are currently combined.

MAIN TEXT STATEMENTS: We require authors to provide a detailed Author Contribution statement immediately after the acknowledgements; the specific contributions of each author must be listed. It is also a condition of publication that authors include an Author Information statement indicating how to access information regarding reprints and permissions, stating whether or not there is a financial or non-financial competing interest, and naming the author to whom correspondence and requests for materials should be addressed. Please ensure that this section is included in the manuscript file after the Methods (but before the Extended Data legends) - it will not appear in the print version but will appear online in the full-text HTML and PDF versions. For details of "end note" style and an example see <https://www.nature.com/nature/for-authors/formatting-guide>.

Done

FIGURE LEGENDS: These should be listed sequentially after the references in the main text and not in the figures files. Each legend should begin with a brief title for the whole figure and continue with a short description of each panel and the symbols used. Any error bars in the figures must be defined (for example, s.d., s.e.m.) and the value of n indicated; see <https://www.nature.com/nature/for-authors/formatting-guide> for further explanation.

Done

DISPLAY ITEMS: We ask that you take stock of all the data that have been generated throughout the review process and ensure that only the data most central to the conclusions are presented in the main figures. Figures should be comprehensible to readers in other or related disciplines, and assist their understanding of the paper. We encourage authors who are describing complex processes to include a schematic of the main finding as part of the Extended Data to aid readers unfamiliar with the immediate discipline. Figures should be as small and simple as is compatible with clarity. All panels of a figure should be logically connected; each panel of a multipart figure should be sized so that the whole figure can be reduced by the same amount and reproduced on the printed page at the smallest size at which essential details are visible. For guidance, Nature's standard figure sizes are 89 mm (one column), 120 mm (one and a half columns), or exceptionally 183 mm (two columns) wide; the full depth of a Nature page is 247 mm. All panels of figures should be presented on a single page and assembled into a rectangular shape for publication; please indicate any essential alignments (parts horizontal, vertical, spacings of stereo pairs, etc.). Tables should be prepared using the Table menu in Microsoft Word.

Figures were reformatted

FIGURE FORMATTING: Lettering in all figures (labelling of axes and so on) should be in uniform, sans-serif font, in lower-case type, and large enough to permit substantial reduction for publication (minimum font size 5 pt). Separate parts of a figure are labelled a, b, etc. Units have a single space between the number and the unit, and follow SI nomenclature or the nomenclature common to a particular field. Thousands are separated by commas (1,000). Unusual units or abbreviations are defined in the legend. Scale bars rather than magnification factors should be used.

Done

IMAGE PRESENTATION: Authors should be aware that any image provided for publication, either in print or online (as Extended Data or Supplemental Information), may be subject to a quality control process to check for image integrity and manipulation. For a full discussion of our standards regarding how images should be prepared and presented, see www.nature.com/authors/editorial_policies/image.html.

OK, we foresee no issues

EXTENDED DATA: Nature is now integrating the supplemental figures and tables into the final version of most papers. Extended Data do not appear in the printed version of the paper but are included online within the full-text HTML and at the end of the online PDF. Extended Data are an integral part of the paper and only data that directly contribute to the main message should be presented. All Extended Data must be referred to in the main text, figure legends and/or Methods section, and their figure legends should be listed sequentially at the end of the main text, not in the

Extended Data files. Authors should assemble the Extended Data into a maximum of ten, A4 size, multi-panelled display items, submitted as individual JPEG, TIFF or EPS files. They must be provided at the same quality as figures for print, but there are important differences in their formatting. More specific instructions are provided in the Extended Data Formatting Guide

(http://s3-service-broker-live-19ea8b98-4d41-4cb4-be4c-d68f4963b7dd.s3.amazonaws.com/uploads/ckeditor/attachments/7823/3h_Extended_data.pdf).

We reorganized our SI file by moving nine items (7 Figures and 2 Tables) to the Extended Data section; we updated Figure and Table referencing in main text and SI.

SUPPLEMENTARY INFORMATION: Supplementary Information is online-only material published with the manuscript (<https://www.nature.com/nature/for-authors/supp-info>). For most papers, there should be no need for Supplementary Information beyond that already provided as Methods and Extended Data, the aim being to avoid unnecessary fragmentation of the paper online. Exceptions to this rule include large datasets that cannot be accommodated within Extended Data; video material; and more complex “Supplemental Methods” (and any associated references) that do not readily fit within the constraints of the Methods/Extended Data formats.

Please note that after the paper has been formally accepted you can only provide amended Supplementary Information files for critical changes to the scientific content, not for style. You should clearly explain what changes have been made if you do resupply any such files.

Revised and checked.

SOURCE DATA: To further increase transparency, we encourage authors to provide, in spreadsheet form, the data underlying the graphical representations used in the figures. This is in addition to our well-established data-deposition policy for specific types of experiments and large datasets. Readers of the online manuscript will be able to access the Source Data directly from the figure legend. Spreadsheets can only be submitted in .xls, .xlsx or .csv formats. One file per figure is permitted; thus, if there is a multi-panelled figure the Source Data for each panel should be clearly labeled in the csv/Excel file; alternatively the data for a figure can be included in multiple, clearly labeled sheets within an Excel file. File sizes of up to 30 MB are permitted; however, it is expected that the vast majority of Source Data files will be considerably smaller than this. When submitting these files with your manuscript, please select the file type “Source Data” and use the title field in the file description tab to indicate the figure to which the Source Data pertain.

Source data is now separately provided in xls format

Nature is committed to improving transparency in authorship. As part of our efforts in this direction, we are now requesting that all authors identified as ‘corresponding author’ create and link their Open Researcher and Contributor Identifier (ORCID) with their account on the Manuscript Tracking System prior to acceptance. ORCID helps the scientific community achieve unambiguous attribution of all scholarly contributions. You can create and link your ORCID from the home page of the Manuscript Tracking System by clicking on ‘Modify my Springer Nature account’ and following the instructions in the link below. Please also inform all co-authors that they can add their ORCIDs to their accounts and that they must do so prior to acceptance.

Referees' comments:

We thank R1 once more for this third round of comments that keep helping to clarify our main findings.

Referee #1 (Remarks to the Author):

The authors added a lot of additional qualifying language, which I appreciate...and that almost does it for me.

But I'm still hung up on sentences like this one from the summary: "Our findings suggest that global atmospheric Hg(0) uptake by the oceans is equally important as Hg(II) deposition, which has implications for our understanding of atmospheric Hg." I think part of my problem with saying something like this is that "important" is vague. Important in what way? Setting the isotopic composition of surface seawater Hg? Yes, then I would agree. Important in setting the amount of Hg in the surface ocean (which is what the sentence seems to imply)? Then no, I don't agree.

The wording issue ('important') directly relates to the quantitative science finding; Hg isotopes only constrain the relative HgII and Hg0 contributions, not the absolute. By 'important', we mean 'more important than previously thought' but based on the conversation with the reviewer we understand that there is some ambiguity in this wording. In the abstract we therefore replaced 'equally important' by 'equal' and get rid of the vagueness issue. We also propose an alternative title, again removing the word 'important':

"Mercury stable isotopes constrain atmospheric deposition pathways to the Ocean"

As we outline in the manuscript, current observations of Hg(II) deposition fluxes to oceans and bi-directional Hg(0) exchange are scarce. Mercury stable isotopes add a new constraint on atmospheric deposition pathways: the relative contribution of atmospheric Hg(II) and Hg(0) gross deposition. We show that there is a disagreement between state of the art models that deliver a 3:1 ratio; isotopes constrain a 1:1 ratio. We discuss the impact of this finding for ocean atmosphere fluxes in the final paragraph of our manuscript: "In order to fit observed marine $\Delta^{200}\text{Hg}$ variability, a 2-3x lower marine Hg(II) deposition or 2-3x higher ocean Hg(0) uptake flux would be required". We therefore emphasize that our findings have implications for global Hg cycling beyond setting the isotopic signature of seawater.

I return to the thought experiment I proposed in my first review: imagine no Hg(II) deposition...so only the Hg(0) exchange. The waters would reach equilibrium with the air and the isotopic composition looks just like air as well. But, the concentration would only be something like 25-50 femtomolar, rather than the 1000 femtomolar that's observed.

Well, aqueous photooxidation would still operate and move Hg(0) to the marine Hg(II) pools and thus total Hg concentrations in the Ocean would be larger than 25 to 50 femtomolar, which is based on the Henry's gas solubility constant only if we understand the reviewer correctly.

Or, run the experiment the other way...if there were no air-sea exchange of Hg(0), the isotopes would look like rain and the concentration would be even higher than we observe.

Such thought (or model scenarios) experiments are complicated; atmospheric chemists adhere to the following rule of thumb: 'global Hg emissions equal Hg deposition'. Otherwise we would see rapidly increasing or decreasing atmospheric Hg concentrations, which is not the case. Imagining absence of Hg₀ exchange, and only rainfall Hg^{II} supply would have to respect that rule of thumb, and would likely not affect surface ocean Hg concentrations. In our study we do not address impacts on marine Hg concentrations.

So, air-sea exchange lowers Hg in the ocean and simultaneously drives isotopes away from the rain value. The distance away from the rain value tells us the relative sizes of the rain flux in and the recycling flux associated with air-sea exchange. So, clarify "important" and avoid using words like "uptake" or "source" when talking about Hg(0).

We agree with the author that 'important' can be considered vague and removed the word from title, abstract and closing paragraph. 'uptake' and 'source' however are established terms in the scientific community and also used e.g. in context of CO₂ Ocean uptake. Since the previous round of revision we explain the concept of Hg(0) gross uptake in detail in the manuscript (L174 - 180).

If I understand correctly, the isotopes allow you to play this thought experiment out: if you grab an individual atom, and ask it "where did you come from, rain or gas?" the isotopic data suggest that half the atoms would say "gas" and half would say "rain." But if Hg(0) didn't oxidize to Hg(II) and vice versa, the answer would be about 1 would say "gas" and 40 would say "rain." So, another way to view the isotopic data is that it tells you about relative speeds of things like gas exchange and redox. Thus, it feels as if the authors fall back on wanting to talk in mass balance terms, but I think the bidirectionality of one of the processes makes that impossible.

That is correct: the isotope data constrain the relative rates (speeds) of the two main Hg deposition pathways, but not the absolute rates. We do discuss absolute rates (termed 'mass balance' by the reviewer) to provide some hint as to which of the model Hg₀ or Hg^{II} deposition rates is incorrect: most likely Hg^{II} deposition, but possibly Hg₀ deposition.

Nature asked me to reflect on Reviewer #2's comments as well, and I'm guessing they are particularly interested in the issue of suitability for Nature. Reviewer #2 seems to argue that this information is just too complex for an adequate airing in a short, Nature-style manuscript. I think this is a good point, but I don't find the manuscript too hard to follow now in its present, Nature-style form. That being said, there's a lot in the supplemental material, so this might not have worked in the pre-digital days...thus, the paper really is much longer than 4 pages.

Referee #2 (Remarks to the Author):

This is the third version of this paper that I am reviewing. I think that the authors have worked hard to satisfy criticisms and limitations of this paper and that it has been improved greatly. There are many complications and caveats in this story but the authors have highly packed a lot of information into the paper. It is my feeling that the paper could be publishable in its present form.

Referee #3 (Remarks to the Author):

The authors have addressed my comments in their revised manuscript.

Reviewer Reports on the Third Revision:

Ref #1

The authors have made some additional tweaks, and I'm newly concerned about the changed title, which features the word "deposition"...which their data really does not address (and which they acknowledge in the response...it's about relative rates of processes, not about absolute loadings) But by fellow reviewers seem ready to stop, so I will too. Congratulations on an important paper!

Ref #2

N/A

Ref #3

N/A

Author Rebuttals to Third Revision:

Referees' comments:

Referee #1 (Remarks to the Author):

The authors have made some additional tweaks, and I'm newly concerned about the changed title, which features the word "deposition"...which their data really does not address (and which they acknowledge in the response...it's about relative rates of processes, not about absolute loadings) But by fellow reviewers seem ready to stop, so I will too. Congratulations on an important paper!

We thank Referee 1 for her/his continued advice on improving our paper. Our current title (revision 3) is “Mercury stable isotopes constrain atmospheric deposition pathways to the Ocean”

The term ‘deposition’ goes together with ‘pathway’, since our Hg stable isotope approach assesses the relative importance of HgII deposition and Hg0 deposition pathways. These are different physicochemical pathways because Hg0 deposition refers to the exchange of a gas, and HgII deposition refers to a combination of wet and dry depositions of HgII forms. The title therefore refers to ‘deposition pathways’ and not ‘absolute deposition fluxes’, which the reviewer seems to refer to.

Our study, in our opinion, therefore addresses Hg deposition in general, and specific Hg deposition pathways in detail. We can propose to change the title to:

"Mercury stable isotopes constrain atmospheric sources to the ocean"

However, we consider both titles to be correct. We welcome editorial advice on the matter.