Authors' response to anonymous reviewer 1

We would like to thank the anonymous reviewer for taking the time to review our manuscript and for the kind words. Please find below our answers to the reviewers' comments. This is organized as follows: The original comments are written in blue text and our responses are given in black. Changes to the manuscript are written in red text. All line numbers (outside the reviewers' original comments) correspond to line numbers in the revised manuscript (and with "Show Markup" turned off).

Bases on the diurnal variations in GEM and a mixing model, the authors suggest a binary mixing of boundary air and free tropospheric air and reemission of Hg from vegetated surfaces are the dominant factors controlling the diurnal GEM variation. Exchange of Hg between atmosphere and vegetations are currently a popular topic, which, however, appears unable to explain the observations solely. As predicted in the manuscript, a daytime emission fluxes of from 8-22 ng m-2 h-1 from vegetated surfaces is needed to explain the difference between the observations and binary mixing diagram. However, many previous studies observed Hg depositions over foliage, and the occasional emission events during daytime generally showed mean reemission fluxes less than 0.3 ng m-2 h1 (based on leaf areas and would not exceed 2 ng m-2 h-1 even through a multiplication of LAI). Therefore, there should be additional daytime emissions around the sampling sites, such as daytime anthropogenic emissions in downslope residential areas, Hg emissions from soils as well as reemissions of Hg from seawater (the authors assume a constant GEM level for marine boundary layer air mass). I wish the authors to discuss the effects of these sources on the diurnal GEM variations.

These are valid points. It is true that reported mean daytime GEM reemission is usually of significantly lower magnitude. That said, as an example, we would like to draw attention to Figure.2 in Obrist et al., 2021[1] (*see footnote*). For several months of their observations, the 75th percentile of the daytime hourly GEM flux was well above 20 ng/m2/h, suggesting that daytime emission of that magnitude might be not particularly rare (although it must be acknowledged here that direct flux measurements tend to be relatively "noisy"), even though the average is typically lower. We hypothesize that such daytime reemission might occur more regularly in tropical mountain environments, partly because of significantly stronger solar radiation than at midlatitudes, higher reactive mercury deposition at night due to katabatic winds, different plant physiology, etc.

It is also important to highlight that the derived flux should be interpreted as a whole-ecosystem flux, i.e. it includes all layers of vegetation and soil. We tried to express this with the wording "vegetated surfaces" instead of "vegetation", but we acknowledge that this wording alone was imprecise and somewhat misleading. We thus added at strategic locations the clarification that "vegetated surfaces" is defined as vegetation + soil.

Line 34 (in the abstract):
Added clarification: vegetated surfaces (i.e. vegetation + soil)

Line 596 to 597 (when the photo-reemission hypothesis is introduced):
Added clarification: vegetated surfaces (i.e. vegetation + soil),

Lines 690 to 691 (in the conclusions):
Added clarification: vegetated surfaces (i.e. vegetation + soil)

[1] Obrist, D., Roy, E. M., Harrison, J. L., Kwong, C. F., Munger, J. W., Moosmüller, H., Romero, C. D., Sun, S., Zhou, J., and Commane, R.: Previously unaccounted atmospheric mercury deposition in a midlatitude deciduous forest, Proc Natl Acad Sci USA, 118, e2105477118, https://doi.org/10.1073/pnas.2105477118, 2021.

We also slightly adapted the graphical abstract so that one "reemission arrow" clearly strikes bare soil.

We also added a short discussion about the possible influences of soil emissions, and why we do not specifically address anthropogenic emissions, between lines 618 and 622 (right after reporting the flux).

> Added: It should be noted that our flux estimate corresponds to the full ecosystem, i.e. the sum of vegetation and soil fluxes, with their relative contributions being unknown. In addition, our estimate assumes that GEM concentrations at Maïdo are not strongly affected by anthropogenic emissions downslope, similar to what has been reported for CO and CO2 (mean anthropogenic contribution at noon < 7 ppbv and < 0.2 ppm, respectively; Callewaert et al., 2022).

Please note that we did not specifically address marine reemissions in the above discussion, as this was already covered in lines 560 to 562. In our simple models, marine influences are not represented through marine surface fluxes, but through a defined MBL concentration. This allows us to omit the complicated Hg chemistry in the MBL, by assuming that the interplay of oceanic surface fluxes and redox chemistry within the MBL leads to more or less constant MBL concentrations. Low diurnal variability in MBL concentrations (amplitude < 0.04 ng/m3) is supported by observations from Amsterdam Island and Cape Point (see figure below, please note: This figure was not included in the main text or supplementary material).

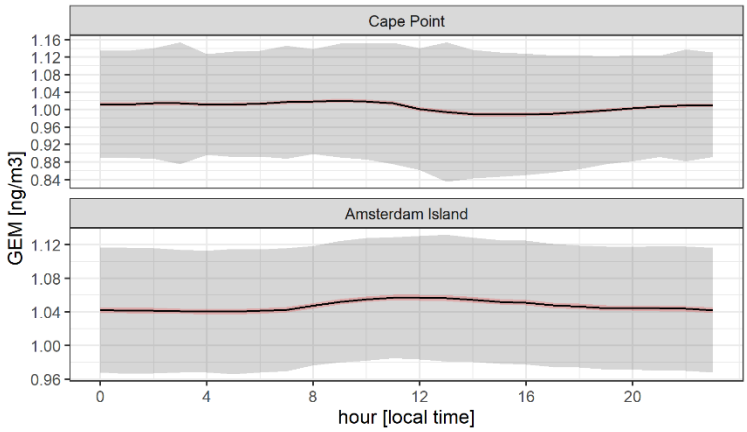

Figure: Diurnal GEM variation for Cape Point and Amsterdam Island. Black line: Mean. Grey shaded area: Mean +- standard deviation. Red shaded area: Mean +- 2 standard error (standard deviation/ sqrt(n)).*

Finally, when discussing the flux and putting it into context, we now draw attention on high soil Hg concentrations at Maido observatory and their possible role:

> Added (lines 631 to 636): It is well-reported that daytime emissions from terrestrial surfaces correlate with soil Hg concentrations and solar radiation (Agnan et al., 2016). Soil Hg concentrations on Réunion Island are high (median: 0.16 mg kg-1; range: 0.03-0.81 mg kg-1; Dœlsch et al., 2006) compared to European and other tropical topsoils (median ~0.02 and ~0.06 mg kg-1, respectively; Panagos et al., 2021; Lim et al., 2020). This, alongside the strong

incident solar radiation around Maïdo (see Fig.5), might explain the large daytime emission flux found here.

Section 3.2.1: The authors attribute the seasonal trend to the transformation of GEM to RM in free troposphere. This is not a big issue but seems to neglect other mechanisms such as seasonal variations in the long range transport of anthropogenic and/or biomass burning emissions. In Figure 3, the seasonal variations in GEM levels resemble those of CO and CH4 levels. This may indicate the long range transport of emissions should be also important, in addition to atmospheric oxidations. I would suggest to analyze the relationship between air mass transport pathways and seasonal GEM levels to see whether anthropogenic and/or biomass emission would also affect the seasonal changes.

We would like to point out that we do not unequivocally attribute the seasonal trend to GEM redox reactions, although we think that the redox seasonality might be an important (and maybe the dominant) driver. As stated in lines 389 – 392, it is likely that biomass burning affects the GEM seasonality as well, but most likely only in the biomass burning season (biomass burning could not explain why LFT GEM rises after January, for example). As for air mass transport, it is true that it might (and probably does to a certain degree) affect the GEM seasonality. We agree that this should be mentioned.

While the transport pathways to Maido as we estimated with flexpart-arome did not vary strongly during the year of observation (see supplementary Sect. S1, Fig.S1), these results correspond admittingly only to the mesoscale (a few hundred km around Maido) and not to the synoptic scale and long-range transport. We thus added an analysis of the synoptic-scale transport to Maido in the supplementary information. Briefly: We computed the synoptic-scale transport to Maido with the help of HYSPLIT (10-day back trajectories) and summarized the results in the new supplementary Fig. S2. Synoptic-scale transport appears relatively similar for the different seasons, with the exception of some northerly equator-crossing air masses between December and March (DJFM). It appears unlikely though that the lower LFT GEM concentrations in DJFM (~0.66 ng/m3) are linked to these northerly air masses, considering the interhemispheric gradient of Hg. We also added this reasoning to the discussion.

Supplementary material Sect.S1, changed wording: "regional" to "mesoscale" (for FLEXPART-based results).

Supplementary material, added text and figure (S2) below to Sect.S1 (Please note that this insertion changes the numbering of other supplementary figures in the revised manuscript):

> We characterized synoptic scale transport with the help of HYSPLIT ("Hybrid Single-Particle Lagrangian Integrated Trajectory"; Stein et al., 2015) back trajectories and using GDAS1 ("Global Data Assimilation System" with 1° x 1° resolution) as meteorological input. Between 2017.08.01 and 2018.08.01, back trajectories were launched hourly from coordinates of Maïdo (21.0792°S, 55.38°E) and a starting altitude of 2200 masl (~40 m above Maïdo). Trajectories were followed 10 days back in time.

The computed 10-day trajectories reveal that even though transport to Maïdo was dominated by easterlies in the mesoscale (**Error! Reference source not found.**), most of these air masses appear to originate west of Maïdo in the synoptic scale, i.e. they took a turn before arrival at Maïdo. Only a few back-trajectories originated as far east as the Australian West Coast, while some trajectories extend far westwards, even to South America and beyond (Figure S1a). Easterlies were mostly of low elevation and often boundary-layer influenced, while westerlies were of significantly higher elevation (Figure S1b). In the synoptic scale, the air mass origin for Maïdo was predominantly extratropical, especially for westerly air masses. Synoptic scale transport pathways appear similar for all seasons, with some exceptions for the wet season (Dec. 2017 – Mar. 2018), during which long-range westerlies were less influential and some air masses originated significantly north of Maïdo, reaching even into the Northern Hemisphere.

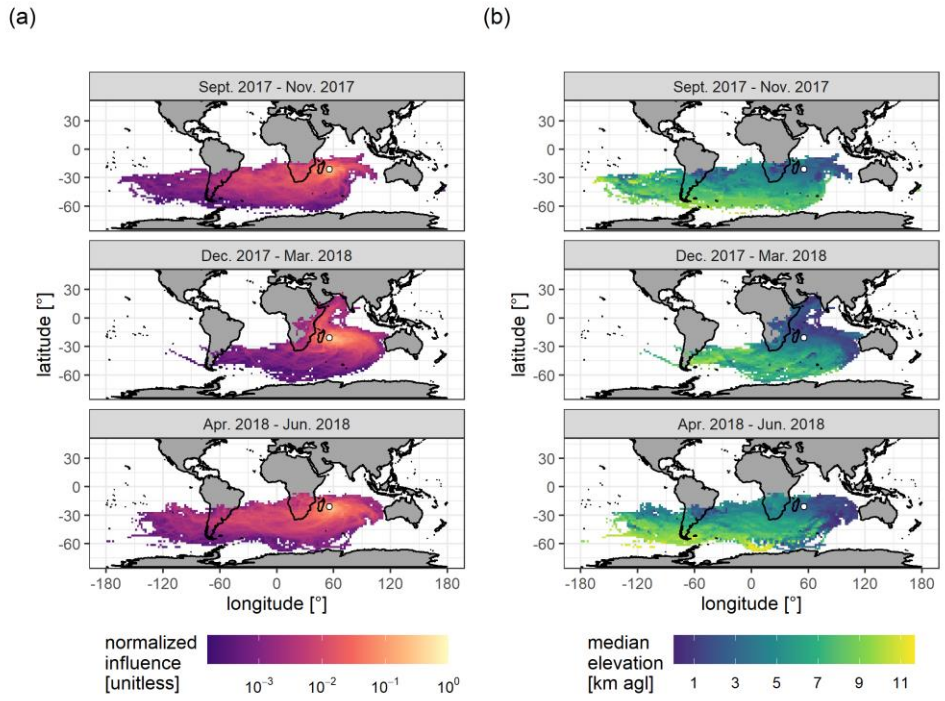

Figure S1. Seasonality of synoptic scale transport to Maïdo (white dot), as characterized by 10-day HYSPLIT back trajectories.

a) Estimated influence of source regions. The colour scale is normalized so that "1" corresponds to the most influential cell, i.e. the cell with the maximum number of trajectory endpoints falling within. Cells influenced by less than 5 individual back trajectories are not shown.

b) Median elevation of air masses upon passage over source regions.

We added the following discussion to the main text (lines 392 to 399):

Seasonal variation in transport pathways and long-range transport of anthropogenic emissions could conceivably impact Maïdo LFT GEM seasonality. While long-range transport pathways were very similar for SON (Sept. – Nov. 2017) and AMJ (Apr. – Jun. 2018), some differences could be seen in DJFM (Dec. 2017 – Mar. 2018), during which a fraction of northerly air masses even originated north of the equator (within the last 10 days before arrival at Maïdo; see supplementary Sect.1). However, given that Hg concentrations tend to be significantly higher in the NH than in the SH (Horowitz et al., 2017; Shah et al., 2021), it appears unlikely that the low LFT GEM concentrations in DJFM are linked to these northerly air masses.

Furthermore, to mitigate the weight put on GEM photochemistry and to acknowledge that modelled seasonality does not depend solely on chemistry (but also on biomass burning, transport, etc.), we made a small change in wording in the conclusions (line 674):

Before: Significant **photochemistry-driven** Hg seasonality reported in modeling studies
After: Significant and **photochemistry-dependent** Hg seasonality reported in modeling studies

The authors used abbreviations at many places, such as "BB" in line 385 and "H'17" in figure 4, and this makes it difficult to understand the meanings in these discussions. Please consider to use full or standard name.

We replaced "BB" with "biomass burning" in all instances and replaced H'17 and S'21 in figure 4 with the more standard Horowitz et al. (2017) and Shah et al. (2021), respectively. We also shortened the caption of figure 4 (as some of the information was moved into the legend).

Line 114: would any Hg emissions from the dormant volcano, and would it have an impact on the observations.

This is an interesting question. Generally, it can be said that air masses do not often pass directly over the volcanic area of Piton de la Fournaise before arrival at Maido, so whatever (direct) influence from the volcano is likely of sporadic nature. That said, we do know of at least one isolated event where GEM levels were clearly influenced by a volcanic plume. However, manifested not as a GEM enhancement, but as a GEM depletion! We are currently working on the analysis of this isolated GEM depletion event, which will be subject to another publication. In any case, the direct influence of gas emission from Piton de la Fournaise on the summary statistics presented here appears to be insignificant.

Line 167-168: I am not sure whether the PFA material could isolate the UV radiations. Please consider to delete

Our wording was misleading. We did not want to state that the PFA itself blocks the UV radiation, but that the PFA line was additionally sheltered from UV light (by use of another material). We adapted the wording to make this distinction clear.

Changed to (now lines 167 to 168):

> The ¼'' unheated PFA sampling line was protected from UV radiation with a white opaque tube (polyvinyl chloride) to avoid photochemical reactions inside the line.

Line 175: is the flow rate of 1.3 L min-1 under standard conditions or a volumetric flow rate?

This is the flow rate under standard conditions (STP). We added this information.

Line 196-198: the digestion method is different from that used in Marusczak et al., 2017 (20% inverse aqua regia). Have any laboratory test being done to verify such a diluted digestion would digest the RM efficiently?

Probably yes in the past. Normally both 20% acid and 2.5% acid can be considered as very acidic, corresponding to approximately to 3 N and 0.4 N acid (pH = 0.4 for the latter). At that low pH all Hg is efficiently stripped from the cation exchange surface on the membrane. In Osterwalder et al. we intercompared 2.5% inverse aqua regia with the slightly weaker 1% HCl digestion used by Mae Gustin's group, with very good, similar results. Gustin's group has done extensive method validation of the membranes we all use, including Hg loading onto membranes and desorption efficiency, with good results (Dunham-Cheatham et al., 2020)[2].

Line 200: Marusczak et al., 2016 should be 2017

Corrected. Thanks for noticing.

Line 209-211: it is better to present the purpose for the measurements of VOCs, which should be related to the objectives of GEM or RM studies.

Agreed. We added a short statement indicating why we use VOC observations and rephrased the paragraph

Changed to (lines 210 to 213):

> We make use of VOC observations to characterize the origin of sampled air masses and the extent to which they were impacted by surface influences. This data was generated in the framework of the OCTAVE project (http://octave.aeronomie.be; last accessed 25 May 2022), which aimed to better

[2] Dunham-Cheatham, S. M., Lyman, S., and Gustin, M. S.: Evaluation of sorption surface materials for reactive mercury compounds, Atmospheric Environment, 242, 117836, https://doi.org/10.1016/j.atmosenv.2020.117836, 2020.

understand the transport and role of VOCs in tropical regions (Verreyken et al., 2019, 2020, 2021; Rocco et al., 2020).

Line 300-304: the authors should make clear that previous studies were mainly conducted at low-altitude sites, and this would help to understand the difference in GEM levels between this and previous observations.

Agreed. We made additions to this phrase to qualitatively highlight the difference in altitudes (low-altitude, high-altitude, etc.), and also added the concrete site elevation for each mentioned site.

Modified lines 301-307 (additions in bold):

This is quite low in comparison to reported atmospheric Hg concentrations at **low-altitude** SH background sites such as Amsterdam Island in the southern Indian Ocean (**55 masl;** GEM mean: ~1.05 ng m-3; Angot et al., 2014; Slemr et al., 2015, 2020), Cape Point in South Africa (**230 masl;** ~1.0 ng m-3; Slemr et al., 2015, 2020) and Darwin in northern Australia (**25 masl**; ~0.95 ng m-3; Howard et al., 2017), but comparable to reported GEM concentrations from **the more elevated** Bariloche Argentina (**800 masl;** ~0.86 ng m-3, Diéguez et al., 2019) and the **high-altitude** Chacaltaya observatory in Bolivia (**5240 masl;** total gaseous mercury: ~0.89 ng m-3 during the ENSO-neutral year 2014-2015, Koenig et al., 2021).

Line 367: the arbitrary specific humidity values should be presented.

Agreed. We added a new supplementary section (now supplementary Sect. S3) containing this information. Please note that this insertion changes the numbering of other supplementary sections in the revised manuscript.

Supplementary material, added section and figure:

Sect.S3: ERA5 specific humidity threshold

We assigned to the lower free troposphere (LFT) nighttime air masses with a specific humidity lower than a seasonally variable threshold (see main text). To define this threshold, we used the monthly median of the nighttime (00:00 UTC, 04:00 local time) specific humidity from the ERA5 reanalysis (hourly data on pressure levels, between 2017.01.01 and 2018.12.31), at coordinates of Maïdo observatory (21.0792°S, 55.38°E) and 800 hPa. The resulting seasonality of the specific humidity threshold is shown in Figure S2.

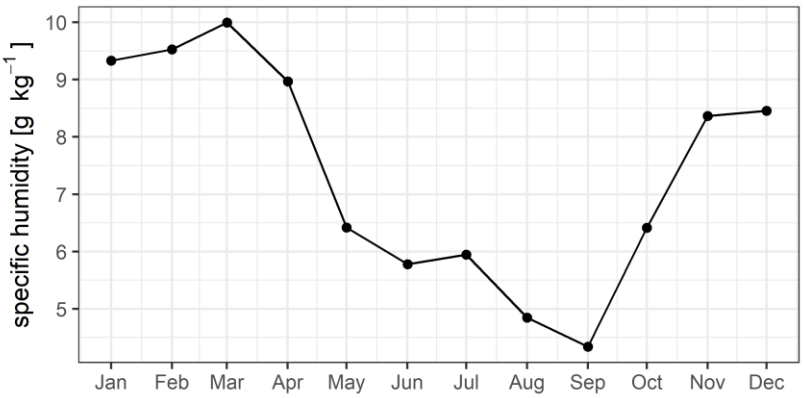

Figure S2. ERA5-based specific humidity threshold and its seasonality.

Line 587: are the reemissions solely referred as to vegetation foliage or forest ecosystems (including foliage and soils)?

We have no way of distinguishing between emissions from vegetation and soil with the used way of inverse modelling. Consequently, reemissions are whole-ecosystem fluxes, i.e. vegetation + soil (+ any other possible surface emission). We tried to express this with the wording "vegetated surfaces" (instead of "vegetation"), but see that this alone was clearly too imprecise. As already stated above, we made several additions in the text at strategic locations to clearly communicate this point.

Lines 595 to 597 (upon first mention of the hypothesis, changes are in bold):

> Considering all this, we propose the hypothesis that Maïdo GEM diurnal variation is, in addition to mixing between LFT and MBL air, driven by net daytime photo re-emission of GEM from the island's vegetated surfaces **(i.e. vegetation + soil)**, especially from the **vegetated mountain slopes** close to the observatory.

Line 34 (in the abstract):

Added clarification: vegetated surfaces (i.e. vegetation + soil)

Lines 690 to 691 (in the conclusions):

Added clarification: vegetated surfaces (i.e. vegetation + soil)

We also added the following clarification right after reporting the flux (lines 618 to 619):

> It should be noted that our flux estimate corresponds to the full ecosystem, i.e. the sum of vegetation and soil fluxes, with their relative contributions being unknown.

Finally, we specifically mention high soil Hg concentrations at Maido and their possible role (lines 631 to 636):

> It is well-reported that daytime emissions from terrestrial surfaces correlate with soil Hg concentrations and solar radiation (Agnan et al., 2016). Soil Hg concentrations on Réunion Island are high (median: 0.16 mg kg-1; range: 0.03-0.81 mg kg-1; Dœlsch et al., 2006) compared to European and other tropical topsoils (median ~0.02 and ~0.06 mg kg-1, respectively; Panagos et al., 2021;

Lim et al., 2020). This, alongside the strong incident solar radiation around Maïdo (see Fig.5), might explain the large daytime emission flux found here.

Line 610-612: these two studies were conducted over meadow in temperate zone, and other observations on the exchange flux over tropical and subtropic forest or soils might be better to support the hypothesis.

We agree that it would be beneficial to compare to other tropical or subtropical forests or soils in mountain environments. Unfortunately, to our knowledge there are no other studies (which also differentiate between daytime and nighttime fluxes) in environments that are in all aspects comparable to Reunion Island (i.e. mountain, tropical, background conditions). That said, in the revised manuscript we attempted to draw as good as possible parallels to other flux studies in other environments, and we aimed to clearly transmit the point that environments are not 100% comparable. With this goal in mind we rephrased and extended the section where we put our flux into context (see below):

Section modified (lines 623 to 638):

To our knowledge, no previous studies have derived differentiated day- and nighttime GEM fluxes for mostly pristine tropical mountain forests or shrublands comparable to those on Réunion Island. Observed daytime Hg emission fluxes from background sites in other terrestrial environments (i.e. predominantly low-altitude and extra-tropical) were generally below ~ 3.5 ng m-2 h-1 (median ~ 0.8 ng m-2 h-1), significantly lower than found here (Agnan et al., 2016). Mean daytime fluxes of up to ~6 ng m-2 h-1 (depending on the season) have been reported for temperate mountain meadows in the US (Converse et al., 2010) and Tibet (Sun et al., 2020). Daytime fluxes above ~10 ng m-2 h-1, similar to what we derived here, were observed in some tropical environments, e.g. for an open field soil in Amazonia (Almeida et al., 2009), and a naturally preserved but anthropogenically influenced (TGM > 5 ng m-3) forest soil (soil Hg: ~0.13 mg_Hg kg_soil-1) in tropical China (Fu et al., 2012). It is well-reported that daytime emissions from terrestrial surfaces correlate with soil Hg concentrations and solar radiation (Agnan et al., 2016). Soil Hg concentrations on Réunion Island are high (median: 0.16 mg kg-1; range: 0.03-0.81 mg kg-1; Dœlsch et al., 2006) compared to European and other tropical topsoils (median ~0.02 and ~0.06 mg kg-1, respectively; Panagos et al., 2021; Lim et al., 2020). This, alongside the strong incident solar radiation around Maïdo (see Fig.5), might explain the large daytime emission flux found here. In any case, given that studies in directly comparable environments are scarce, it is not yet possible to say whether a large daytime emission flux is specific to mountain forests and shrublands on Réunion Island, or characteristic of tropical mountain environments in general.