

Final response

Reply on RC1 (F. Slemr)

First, we would like to express our sincere gratitude to Dr. Franz Slemr, one of the true doyens of the field, for taking the time to provide a thoughtful and constructive feedback on the manuscript.

Responses to general comments

1. "Because of the length of the review, a table of contents at the beginning would improve the orientation for readers looking for a specific topic".

The only possible obstacle is getting the editor to consent to include a TOC.

2. "The ever-increasing complexity of mercury behaviour in the atmosphere seems at times to obscure the fact that it is a subject, as other trace gases, to general constraints imposed by atmospheric circulation...."

To address this criticism, we have decided to rewrite, modify, and rearrange large portions of Section 3.2 (until L206 in the original manuscript) as follows:

3. 2 Stability of atmospheric Hg⁰

Hg⁰ represents the primary form of atmospheric mercury in both the troposphere and stratosphere. Considering the spatial variability of Hg⁰ concentrations ¹, which depart from a uniform vertical distribution throughout the atmosphere (Slemr et al., 2018), a singular global atmospheric lifetime is not appropriate. A more pertinent measure is the effective lifetime of Hg⁰, expressed on an annual basis and as a function of its horizontal and vertical location within the atmosphere. The observed disparity in tropospheric Hg⁰ concentrations between the Northern and Southern Hemispheres of a factor ~1.41 (Tang et al., 2025), despite anthropogenic emissions in the Northern Hemisphere being about 2.5 times greater than those in the Southern Hemisphere (Streets et al., 2019; Sonke et al., 2023), implies that Hg⁰ has a relatively short effective lifetime in comparison to the inter-hemispheric air mass exchange time of approximately 1.3 years (Geller et al., 1997). As Hg⁰ crosses the intertropical convergence zone, it undergoes convective uplift, enabling its transport into the stratosphere. Historically, troposphere-to-stratosphere Hg⁰ transport was regarded as limited (100 - 176 Mg yr⁻¹) (Lyman and Jaffe, 2012; Horowitz et al., 2017). Nevertheless, recent modeling suggests the stratosphere is critical for the biogeochemical Hg cycling, acting as the primary pathway for Hg⁰ exchange between hemispheres, explaining the minor inter-hemispheric gradient (Saiz-Lopez et al., 2025). As posited by models developed by (Shah et al., 2021) and (Saiz-Lopez et al., 2025), approximately 17% of the aggregate atmospheric Hg load is situated within the stratosphere, whereas a previous study reported 12% (Horowitz et al., 2017). Given the stratosphere's mass (9.06 x 10¹⁷ kg) constitutes approximately 18% of the total atmospheric air mass (5.13 x 10¹⁸ kg) (Warneck and Williams, 2012), one might infer that the fraction of mercury present in the stratosphere is comparable to the proportion of stratospheric air relative to the entire atmosphere. However, this scaling is not supported by empirical data. Aerial measurements of Hg in the troposphere and lower stratosphere show a steep Hg gradient around and above the tropopause with lower Hg mixing ratios in the upper atmospheric layers (Radke et al., 2007; Talbot et al., 2007; Slemr et al., 2018) linked to a larger contribution of oxidized Hg species partitioned to aerosols (Murphy et al., 1998) from the gas phase.

Regarding the tropospheric Hg budget, there is relative consensus that the Hg load is close to 4 Gg ((Saiz-Lopez et al., 2020); 3.9 ± 1.0,(Saiz-Lopez et al., 2025); 3.8,(Zhang et al., 2023b); 4.0,(Shah et al., 2021); 3.9, (Horowitz et al., 2017), with some exceptions suggesting closer to 5 - 6 Gg (Holmes et al., 2010; Zhang et al., 2025), and that anthropogenic emissions, excluding biomass burning, are about 2.2 – 2.6 Gg yr⁻¹ (Horowitz et al., 2017; Shah et al., 2021; Zhang et al., 2023b; Geyman et al., 2024; Saiz-Lopez et al., 2025), with significant reductions across developed countries of the Northern Hemisphere observed in the near term (Custódio et al., 2022; Feinberg et al., 2024). Aircraft-based observations

¹ There is a widespread practice in the Hg research community to report Hg⁰ air concentrations in ng m⁻³ referenced to one atmosphere (101.325 kPa) and 0 °C (STP). By that, the unit represents a mixing ratio not an absolute (mass) concentration.

reveal a comparatively consistent mixing ratio of Hg^0 within the troposphere below the tropopause, encompassing the planetary boundary layer in regions characterized by low primary emissions (Banic et al., 2003; Talbot et al., 2007; Swartzendruber et al., 2008; Weigelt et al., 2016b; Bieser et al., 2017). This uniformity supports the adoption of a steady-state procedure (Seinfeld and Pandis, 2006), where the inverse of the Hg^0 lifetime ($\tau_{\text{troposphere}}$) is approximated by the sum of its loss rates:

$$1/\tau_{\text{troposphere}} = 1/\tau_{\text{rxn}} + 1/\tau_{\text{ocean}} + 1/\tau_{\text{land}} + 1/\tau_{\text{wash}} + 1/\tau_{\text{stratosphere}} \quad (1)$$

where the indices rxn, ocean, land, wash, and stratosphere are used to represent net oxidation, oceanic uptake, assimilation in the land ecosystems, processes that lead to wet deposition and net transfer to the tropopause/stratosphere, respectively. As will be discussed subsequently, all of the terms in equation 1 are subject to significant uncertainties. However, as is the case with many other trace gases, the chemical lifetime (τ_{rxn}) undoubtedly plays a controlling role in determining the effective lifetime of Hg^0 . Representing net oxidation, τ_{rxn} encompasses the duration of the initial two-step oxidation to molecular forms and the subsequent red-ox cycling of the photo-labile fraction of these molecules in the gas phase and aerosols prior to deposition. According to the latest redox schemes (Shah et al., 2021; Castro Pelaez et al., 2022; Saiz-Lopez et al., 2025), the extent of bi-directional Hg mass flux by atmospheric chemical conversion (oxidation and reduction, 10.4 - 13.0 vs. 6.0 - 6.9 Gg yr⁻¹, respectively) appears to be much larger than previously assumed (e.g., 8.0 vs. 3.7 Gg yr⁻¹, (Holmes et al., 2010)), which also holds for the bidirectional fluxes (emission and depositional uptake) that occur in the gas exchange of Hg^0 between the atmosphere and the land and ocean. Aggregate atmospheric emissions and dry deposition have been approximated at 7.4 - 11.2 and 2.9 - 6.8 Gg Hg^0 yr⁻¹, respectively (Horowitz et al., 2017; Shah et al., 2021; Sonke et al., 2023; Zhang et al., 2023b), following a tendency of researchers towards augmenting the role of re-emission of legacy Hg from the oceans (3.7 - 7.2 Gg Hg^0 yr⁻¹) and gross biospheric assimilation from the atmosphere (1.2 - 3.2 Gg Hg^0 yr⁻¹) (Horowitz et al., 2017; Yuan et al., 2019; Obrist et al., 2021; Zhou and Obrist, 2021; Feinberg et al., 2022; Wang et al., 2022; Szponar et al., 2025), respectively. For transferring Hg^0 from the oceans into the atmosphere, the mass transfer rate is usually parameterized using wind speed dependencies that have been tested for CO₂ emissions. However, recent evidence (Osterwalder et al., 2021) suggests that Hg^0 , which is less soluble than CO₂, behaves similarly to O₂ and N₂, where the impact of bubble-mediated transfer is greater. As a result, ocean emissions have an increased role in the global Hg budget, accounting for approximately 60% of total Hg emissions to the atmosphere due to a wind speed dependence with a cubic power exponent instead of quadratic in model simulations (Zhang et al., 2023b). The greater gross emissions from seawater must be balanced by gross deposition of Hg^0 , which is, within uncertainties, of comparable magnitude to that of Hg^{II} deposition over oceans (Jiskra et al., 2021) and much higher than previously assumed (Soerensen et al., 2010). Global net exchange of Hg^0 from the oceans was estimated at 0.8 - 4.0 Gg Hg^0 yr⁻¹ (Lamborg et al., 2002; Strode et al., 2007; Selin et al., 2008; Holmes et al., 2010; Chen et al., 2014; Horowitz et al., 2017; Shah et al., 2021) and the fraction of Hg^0 emissions resulting from Hg^{II} reduction in surface waters at an upper limit of 2.25 ± 0.89 Gg Hg^0 yr⁻¹ (Tang et al., 2025). In summary, the latter terms in Equation 1 correspond to lifetimes, the spans of which are all conservatively estimated to exceed one year. However, their inverses referring to Eq. 1, when summed, can shorten $\tau_{\text{troposphere}}$ by tens of percent beyond what the tropospheric chemical lifetime of Hg^0 (τ_{rxn}) dictates, taking into account the inherent uncertainties. Currently, Hg^0 is estimated to have a $\tau_{\text{troposphere}}$ of between 3.8 to 7 months (Shah et al., 2016; Horowitz et al., 2017; Saiz-Lopez et al., 2020; Shah et al., 2021; Saiz-Lopez et al., 2025) and an average atmospheric lifetime (troposphere + stratosphere) of 8.2 months (Saiz-Lopez et al., 2025).

The sources of atmospheric Hg^{II} are twofold: primary Hg^{II} emissions from anthropogenic sources and atmospheric Hg^0 oxidation. The proportion of Hg^{II} compared to Hg^0 in anthropogenic emissions and the troposphere is not well-defined. One estimate suggests 74% of cumulative anthropogenic Hg emissions to air have been Hg^0 (Streets et al., 2017). Currently, East Asia has the largest emissions worldwide (Streets et al., 2019); however, there is compelling evidence that the magnitude of total Hg air emissions in this region has already peaked (Zhang et al., 2023a) and is declining in recent years (Wu et al., 2023; Feinberg et al., 2024). Nevertheless, a shift in the contributions of distinct source categories, with cement production emerging as the predominant source since 2009 in China (Wu et al., 2016), suggests an augmentation in the proportion of Hg^{II} within Hg emissions (Zhang et al., 2016; Wang et al., 2024). Hg speciation profiles from anthropogenic sources may vary significantly across regions; for example, in continental Europe, Hg^{II} contribution from coal-fired power plants may represent less than 25% (Weigelt et al., 2016a) while in the tropics, artisanal and small-scale

gold mining represent a substantial yet largely unconstrained source of atmospheric Hg^0 (Obrist et al., 2018). On average across the globe, contemporary global models employ a 60 to 65 % Hg^0 speciation in current anthropogenic emissions to the atmosphere (Horowitz et al., 2017; Shah et al., 2021; Zhang et al., 2023b). There are significant differences in the accounting of the tropospheric pool of Hg^0 (~3.3 - 4.8 Gg), separated from Hg^{II} (0.1 - 1.0 Gg), within the above-mentioned constrained budgets for the total tropospheric Hg load in contemporary models. Having estimated the atmospheric load of Hg^{II} up to 20 km at ~0.36 Gg based on a synthesis of RM measurements at different heights in the atmosphere (Saiz-Lopez et al., 2020), a later contribution (Saiz-Lopez et al., 2025) involving stratospheric transport and chemistry deployed a much larger tropospheric Hg^{II} pool (0.51 Gg) associated with downward transport (0.35 Gg yr^{-1}) of mostly photostable Hg^{II} from the stratosphere (Hg^{II} pool of ~0.2 Gg). Corresponding amount of (wet and dry) Hg^{II} deposited on Earth's surface is $6.92 \pm 1.70 \text{ Gg yr}^{-1}$, outside the previously estimated range of $4.8 - 6.8 \text{ Gg yr}^{-1}$ Hg^{II} (Strode et al., 2007; Zhang et al., 2019; Feinberg et al., 2022; Sonke et al., 2023). The effective $\tau_{\text{troposphere}}$ of Hg^{II} is a few weeks (Horowitz et al., 2017), while Hg^{I} species are intermediates (lifetimes $\ll 1 \text{ s}$) in the $\text{Hg}^0/\text{Hg}^{\text{II}}$ redox cycle and their tropospheric mass is negligible (Shah et al., 2021).

L206 → L235 (end): uncut text

Responses to specific comments

3. “In lines 199-200 the authors report that “Hg in the stratosphere is estimated to account for about 20% of the total atmospheric Hg mass...”. No reference is given for this statement, the references at the end of the sentence relate to exchange flux between stratosphere and troposphere. This statement cannot be true.”

We have not previously reflected further on the referenced figure of 20% derived from Shah et al. (2021). It is noteworthy that a comparable figure of $17 \pm 4\%$ is given in the study by Saiz-Lopes et al. (2025). We acknowledge the reviewer's skepticism and have made a substantial revision to address this concern, as outlined in **L183** through **L191** above.

4. “In the paragraphs, L193 - 215 and 216 - 235, different lifetimes are presented and compared: the tropospheric, the chemical, the stratospheric, the lower stratospheric against surface deposition, the mid- and upper-stratospheric, and the mean atmospheric ones. This discussion needs a common denominator...”

We agree with the reviewer on this comment and have made the following adjustments:

The term atmospheric lifetime is presented (**L173 – L175**), the conditions to justify a global tropospheric lifetime (**L197 – L199**), the equation with explanatory notes (**L200 – L205**), the importance of the chemical lifetime (**L206-L210**), the final presentation of the Hg^0 lifetime (**L230 – L235**), something about the effective lifetime for Hg^{I} and Hg^{II} (**L256 – L258**).

5. “The definition inconsistencies in these paragraphs can be illustrated e.g. by the statement (lines 203-204) that “Based on correlations of Hg^0 with N_2O in the stratosphere within 4 km above the thermal tropopause, Slemr et al. (2018) provided a lifetime estimate of $74 \pm 27 \text{ yr}$ while Lyman and Jaffe (2012) inferred a relatively short lifetime for Hg^0 in intercepted descending air with stratospheric origin”. Stratospheric lifetime estimated by Slemr et al. (2018) has been derived from hundreds of CARIBIC measurements and is consistent with the definition of Seinfeld and Pandis (1998). “A relatively short Hg^0 lifetime in the stratosphere of $<1\text{yr}$ ” mentioned by Lyman and Jaffe (2012) seems to be the local chemical one which cannot be compared to the lifetime according to the definition of Seinfeld and Pandis (1998).”

We recognize that our review must be critical enough not to allow these references to stand next to each other without comment, and that the range of measurement data between the references is abysmal. We break out L200 - L206 and move parts of this paragraph to **L188 – L190** and to Section 5.1.5, which deals with the lower stratosphere. We now suggest reading from the middle of L713 to the end of the section:

...(Fig. 8a,b). The prediction of these model calculations, that Hg^0 converts to long-lived (photostable) oxidized

forms and thus leads to a higher RM/TAM ratio, is supported by hundreds of profile measurements made with an Airbus 340-600 passenger aircraft in intercontinental traffic as an upper troposphere-lowermost stratosphere observatory (Slemr et al., 2018). In addition to frequently observed higher RM/Hg⁰ ratios, a steep decrease of the Hg⁰ mixing ratio occurs when crossing the tropopause. In the stratosphere, this ratio drops to 0.25 - 0.7 ng m⁻³ (STP), measured up to an altitude of 4 km (Slemr et al., 2018). The results of both studies above show a more than tenfold increase in Hg⁰ lifetime in the lower stratosphere compared to the troposphere. The chemical lifetime of Hg⁰ increases and approaches 10 years the higher you go in the lower stratosphere bounded by the ozone layer. (Saiz-Lopes et al. 2025).

Responses to minor comments

Line 58: Perhaps a reference Jiskra et al. (2018) should be added here.

This reference has been added.

Line 65: What do you mean with "reductionist"?

Try to give an explanation based on breaking the problem down into smaller and smaller units. We have chosen to delete the word from the sentence, as it is still clear that understanding is sought down to the molecular level.

Line 71: "compilation" is perhaps a better word than "tabulation".

Rephrasing applied.

Line 102: Why "filtered"? The AAS method will measure elemental mercury even with some aerosols as long as there is enough light coming through. LIDAR technique shows that aerosol poses no problem. In fact, back scattering on aerosol is the basis of the LIDAR techniques.

Correct. We delete the word.

Line 113: Awkward wording – "Since gold does not trap only Hg⁰ but..." would be perhaps better.

We have adapted it.

Line 121: "...the risk of artifact formation of Hg^{II} by co-sampling GOM with PBM..." – I think that no new Hg^{II} is being formed but Hg^{II} from GOM and PBM is being co-measured, later called RM.

We have deleted "artifact formation of Hg^{II} by", so the sentence now reads:

"The automated KCl denuder method, with its variable efficiency, can thus lead to serious underestimation of GOM, while the refluxing mist chamber method, which is an alternative, carries the risk of co-sampling GOM with PBM (Gustin et al., 2021)".

Line 153-154: Awkward wording: "... is not recommended because it cannot be applied in multi-stage atmospheric pressure systems..." perhaps better.

We have adapted it.

Line 155: "...of ambient GOM species..." may be perhaps better.

We have adapted it.

Line 290: "Hinshelwood" instead of "Hinselwood".

We have adapted it.

Table 1, caption: "are" instead "is"

We have adapted it.

Table 3: In reactions G24 and G25 appears BrHg^{II}O* - where does it come from? Is the oxidation stage of Hg

consistently described? Please check the consistency of all chemical formulas, in the tables and in the text.

We have removed the oxidation numbers completely from Table 3 (i.e. for **G24** & **G25**), but in our opinion they are still warranted occasionally in the text for accessibility to a less advanced reader.

Line 453: "...determined by Donohue..."

We have deleted "absolutely".

Line 466: Please define what RR studies are? If that means "reaction rate" it could be replaced "kinetics studies". Or omit it altogether – the type of studies is given by the context.

The acronym RR has been introduced in L452.

Line 538: decreases with decreasing temperature?

It should read "decreasing with increasing temperature".

Line 542: "and" instead "och"

Mistake corrected.

Line 574: "they" – Dibble et al or Castro Pelaez et al?

"they" has been substituted by "Castro Pelaez et al. (2022)".

Lines 714-715: But above the O₃ maximum in the stratosphere the reactions of excited Hg atom become important? See section 5.1.6. Perhaps the Section 5.1.5 should be merged with 5.1.6 to avoid misunderstanding.

We made an error in using "above" instead of "below" in reference to the ozone layer. Paragraphs L713 - L715 have been completely rewritten. The new wording of the paragraph can be found above under the heading **Responses to specific comments**. In addition, the titles of Sections 5.1.5 and 5.1.6 have been changed to "**Chemical transformation of Hg in the lower stratosphere**" and "**Chemical transformation of Hg in the upper stratosphere**", respectively.

Line 765: "Hg(³P)" – Hg(³P₁) or Hg(³P₀) or both?

In order not to exclude the one from the other, we have added "states" after Hg(³P).

Line 983: "bis-sulphite complex is thermally stable" perhaps better.

"is not thermally unstable" has been changed to "is thermally stable".

Sections 6 and 7: Interaction of HgCl₂ with H₂SO₄ droplets would be interesting because they constitute the major aerosol particles in the stratospheric Junge layer. Are any data available? Any comment on this? Here or in the Section 9?

In reference to the response to RC2, the chapter "Gas to nucleation" has been renamed "Can mercury species nucleate in the atmosphere?" and its introduction has undergone complete revision. On line 694, the following statement appears: "Interestingly, Hg^{II} is empirically correlated with bromine and iodine in these particles of organic-sulfate type and has the highest relative concentrations in the stratosphere near the tropopause (Murphy et al., 2006)." Therefore, there is empirical evidence that Hg^{II} is trapped in heavier halogen-doped organics-sulfuric acid/sulfate-type particles in the stratosphere, but it is "only rarely observed in the relatively pure sulfuric acid particles characteristic of the main stratospheric aerosol layer."

Line 1215: "Brunauer-Emmett-Teller" instead of "BET" perhaps better for non-specialists.

"Brunauer-Emmett-Teller" has been adopted.

Line 1239: "aerosolized"?

Changed to "aerosols"

Lines 2110 - 2111: Reliable measurement of Hg^0 in wet deposition? Perhaps “...despite generally reliable measurements of Hg^0 in air and Hg^{II} in wet deposition.” would be less ambiguous. These measurements may not be sufficient for verifying model studies in detail but they provide constraints with which the model results have to comply.

The sentence now reads: “... mean that the basis for verifying *models in detail* is insufficient, despite reliable measurements of Hg^0 in air and Hg^{II} in wet deposition”.

References: The titles of the papers are sometimes written with capital letters, sometimes without. Please homogenize.

References have been homogenized, meaning that words are not now capitalized.

References

- Banic, C. M., Beauchamp, S. T., Tordon, R. J., Schroeder, W. H., Steffen, A., Anlauf, K. A., and Wong, H. K. T.: Vertical distribution of gaseous elemental mercury in Canada, *Journal of Geophysical Research-Atmospheres*, 108, art. no.-4264, 2003.
- Bieser, J., Slemr, F., Ambrose, J., Brenninkmeijer, C., Brooks, S., Dastoor, A., DeSimone, F., Ebinghaus, R., Gencarelli, C. N., Geyer, B., Gratz, L. E., Hedgecock, I. M., Jaffe, D., Kelley, P., Lin, C. J., Jaegle, L., Matthias, V., Ryjkov, A., Selin, N. E., Song, S. J., Travníkov, O., Weigelt, A., Luke, W., Ren, X. R., Zahn, A., Yang, X., Zhu, Y., and Pirrone, N.: Multi-model study of mercury dispersion in the atmosphere: vertical and interhemispheric distribution of mercury species, *Atmospheric Chemistry and Physics*, 17, 6925-6955, 10.5194/acp-17-6925-2017, 2017.
- Castro Pelaez, P., Kellö, V., Cernusak, I., and Dibble, T.: Together, Not Separately, OH and O_3 Oxidize $\text{Hg}(0)$ to $\text{Hg}(II)$ in the Atmosphere, *The Journal of Physical Chemistry A*, 126, 10.1021/acs.jpca.2c04364, 2022.
- Chen, L., Wang, H. H., Liu, J. F., Tong, Y. D., Ou, L. B., Zhang, W., Hu, D., Chen, C., and Wang, X. J.: Intercontinental transport and deposition patterns of atmospheric mercury from anthropogenic emissions, *Atmospheric Chemistry & Physics*, 14, 10163-10176, 10.5194/acp-14-10163-2014, 2014.
- Custódio, D., Pfaffhuber, K. A., Spain, T. G., Pankratov, F. F., Strigunova, I., Molepo, K., Skov, H., Bieser, J., and Ebinghaus, R.: Odds and ends of atmospheric mercury in Europe and over the North Atlantic Ocean: temporal trends of 25 years of measurements, *Atmospheric Chemistry and Physics*, 22, 3827-3840, 10.5194/acp-22-3827-2022, 2022.
- Feinberg, A., Dlamini, T., Jiskra, M., Shah, V., and Selin, N. E.: Evaluating atmospheric mercury (Hg) uptake by vegetation in a chemistry-transport model, *Environmental Science: Processes & Impacts*, 24, 1303-1318, 10.1039/D2EM00032F, 2022.
- Feinberg, A., Selin, N. E., Braban, C. F., Chang, K.-L., Custodio, D., Jaffe, D. A., Kyllonen, K., Landis, M. S., Leeson, S. R., Luke, W., Molepo, K. M., Murovec, M., Mastromonaco, M. G. N., Pfaffhuber, K. A., Ruediger, J., Sheu, G.-R., and St. Louis, V. L.: Unexpected anthropogenic emission decreases explain recent atmospheric mercury concentration declines, *Proceedings of the National Academy of Sciences of the United States of America*, 121, 10.1073/pnas.2401950121, 2024.
- Geyman, B. M., Streets, D. G., Thackray, C. P., Olson, C. L., Schaefer, K., and Sunderland, E. M.: Projecting Global Mercury Emissions and Deposition Under the Shared Socioeconomic Pathways, *Earth's Future*, 12, e2023EF004231, <https://doi.org/10.1029/2023EF004231>, 2024.
- 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 Chemistry and Physics*, 10, 12037-12057, 2010.
- Horowitz, H. M., Jacob, D. J., Zhang, Y. X., 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 Chemistry and Physics*, 17, 6353-6371, 10.5194/acp-17-6353-2017, 2017.
- Jiskra, M., Heimbürger-Boavida, L.-E., Desgranges, M.-M., Petrova, M. V., Dufour, A., Ferreira-Araujo, B., Masbou, J., Chmieleff, J., Thyssen, M., Point, D., and Sonke, J. E.: Mercury stable isotopes constrain atmospheric sources to the ocean, *Nature*, 597, 678-682, 10.1038/s41586-021-03859-8, 2021.
- Lamborg, C. H., Fitzgerald, W. F., O'Donnell, J., and Torgersen, T.: A non-steady-state compartmental model of global-scale mercury biogeochemistry with interhemispheric atmospheric gradients, *Geochimica Et Cosmochimica Acta*, 66, 1105-1118, 2002.
- Lyman, S. and Jaffe, D.: Formation and fate of oxidized mercury in the upper troposphere and lower stratosphere, *Nature Geoscience*, 5, 114 - 117, 2012.
- Murphy, D. M., Thomson, D. S., and Mahoney, M. J.: In situ measurements of organics, meteoritic material, mercury, and other elements in aerosols at 5 to 19 kilometers, *Science*, 282, 1664-1669, 1998.

Obrist, D., Kirk, J. L., Zhang, L., Sunderland, E. M., Jiskra, M., and Selin, N. E.: A review of global environmental mercury processes in response to human and natural perturbations: Changes of emissions, climate, and land use, *Ambio*, 47, 116-140, 10.1007/s13280-017-1004-9, 2018.

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, *Proceedings of the National Academy of Sciences*, 118, e2105477118, 10.1073/pnas.2105477118, 2021.

Osterwalder, S., Nerentorp, M., Zhu, W., Jiskra, M., Nilsson, E., Nilsson, M. B., Rutgersson, A., Soerensen, A. L., Sommar, J., Wallin, M. B., Wängberg, I., and Bishop, K.: Critical Observations of Gaseous Elemental Mercury Air-Sea Exchange, *Global Biogeochemical Cycles*, 35, e2020GB006742, <https://doi.org/10.1029/2020GB006742>, 2021.

Radke, L. F., Friedli, H. R., and Heikes, B. G.: Atmospheric mercury over the NE Pacific during spring 2002: Gradients, residence time, upper troposphere lower stratosphere loss, and long-range transport, *Journal of Geophysical Research-Atmospheres*, 112, 10.1029/2005jd005828, 2007.

Saiz-Lopez, A., Travníkov, O., Sonke, J. E., Thackray, C. P., Jacob, D. J., Carmona-Garcia, J., Frances-Monerris, A., Roca-Sanjuan, D., Acuna, A. U., Davalos, J. Z., Cuevas, C. A., Jiskra, M., Wang, F., Bieser, J., Plane, J. M. C., and Francisco, J. S.: Photochemistry of oxidized Hg(I) and Hg(II) species suggests missing mercury oxidation in the troposphere, *Proceedings of the National Academy of Sciences of the United States of America*, 117, 30949-30956, 2020.

Saiz-Lopez, A., Cuevas, C. A., Acuña, A. U., Añel, J. A., Mahajan, A. S., de la Torre, L., Feng, W., Dávalos, J. Z., Roca-Sanjuán, D., Kinnison, D. E., Carmona-García, J., Fernandez, R. P., Li, Q., Sonke, J. E., Feinberg, A., Martín, J. C. G., Villamayor, J., Zhang, P., Zhang, Y., Blaszczak-Boxe, C. S., Travníkov, O., Wang, F., Bieser, J., Francisco, J. S., and Plane, J. M. C.: Role of the stratosphere in the global mercury cycle, *Science Advances*, 11, eads1459, doi:10.1126/sciadv.ads1459, 2025.

Seinfeld, J. H. and Pandis, S. N.: *Atmospheric chemistry and physics: from air pollution to climate change*, Book, Whole, Wiley, Hoboken, N.J.2006.

Selin, N. E., Jacob, D. J., Yantosca, R. M., Strode, S., Jaegle, L., and Sunderland, E. M.: Global 3-D land-ocean-atmosphere model for mercury: Present-day versus preindustrial cycles and anthropogenic enrichment factors for deposition, *Global Biogeochemical Cycles*, 22, 10.1029/2007gb003040, 2008.

Shah, V., Jacob, D., Thackray, C., Wang, X., Sunderland, E., Dibble, T., Saiz-Lopez, A., Cernusak, I., Kellö, V., Castro, P., Wu, R., and Wang, C.: Improved Mechanistic Model of the Atmospheric Redox Chemistry of Mercury, *Environmental Science & Technology*, 55, 14445 - 14456, 2021.

Shah, V., Jaeglé, L., Gratz, L. E., Ambrose, J. L., Jaffe, D. A., Selin, N. E., Song, S., Campos, T. L., Flocke, F. M., Reeves, M., Stechman, D., Stell, M., Festa, J., Stutz, J., Weinheimer, A. J., Knapp, D. J., Montzka, D. D., Tyndall, G. S., Apel, E. C., Hornbrook, R. S., Hills, A. J., Riemer, D. D., Blake, N. J., Cantrell, C. A., and Mauldin, R. L.: Origin of oxidized mercury in the summertime free troposphere over the southeastern US, *Atmospheric Chemistry and Physics*, 16, 1511-1530, 10.5194/acp-16-1511-2016, 2016.

Slemr, F., Weigelt, A., Ebinghaus, R., Bieser, J., Brenninkmeijer, C. A. M., Rauthe-Schoch, A., Hermann, M., Martinsson, B. G., van Velthoven, P., Bonisch, H., Neumaier, M., Zahn, A., and Ziereis, H.: Mercury distribution in the upper troposphere and lowermost stratosphere according to measurements by the IAGOS-CARIBIC observatory: 2014-2016, *Atmospheric Chemistry and Physics*, 18, 12329-12343, 2018.

Soerensen, A. L., Sunderland, E. M., Holmes, C. D., Jacob, D. J., Yantosca, R. M., Skov, H., Christensen, J. H., Strode, S. A., and Mason, R. P.: An Improved Global Model for Air-Sea Exchange of Mercury: High Concentrations over the North Atlantic, *Environmental Science & Technology*, 44, 8574-8580, 10.1021/es102032g, 2010.

Sonke, J. E., Angot, H., Zhang, Y., Poulain, A., Björn, E., and Schartup, A.: Global change effects on biogeochemical mercury cycling, *Ambio*, 52, 853-876, 10.1007/s13280-023-01855-y, 2023.

Streets, D. G., Horowitz, H. M., Lu, Z., Levin, L., Thackray, C. P., and Sunderland, E. M.: Global and regional trends in mercury emissions and concentrations, 2010–2015, *Atmospheric Environment*, 201, 417-427, <https://doi.org/10.1016/j.atmosenv.2018.12.031>, 2019.

Streets, D. G., Horowitz, H. M., Jacob, D. J., Lu, Z., Levin, L., ter Schure, A. F. H., and Sunderland, E. M.: Total Mercury Released to the Environment by Human Activities, *Environmental Science & Technology*, 51, 5969-5977, 10.1021/acs.est.7b00451, 2017.

Strode, S. A., Jaegle, L., Selin, N. E., Jacob, D. J., Park, R. J., Yantosca, R. M., Mason, R. P., and Slemr, F.: Air-sea exchange in the global mercury cycle, *Global Biogeochemical Cycles*, 21, 10.1029/2006gb002766, 2007.

Swartzendruber, P. C., Chand, D., Jaffe, D. A., Smith, J., Reidmiller, D., Gratz, L., Keeler, J., Strode, S., Jaegle, L., and Talbot, R.:

Vertical distribution of mercury, CO, ozone, and aerosol scattering coefficient in the Pacific Northwest during the spring 2006 INTEX-B campaign, *Journal of Geophysical Research-Atmospheres*, 113, -, ArtID10305, 10.1029/2007jd009579, 2008.

Szponar, N., Vega, C. M., Gerson, J., McLagan, D. S., Pillaca, M., Delgado, S., Lee, D., Rahman, N., Fernandez, L. E., Bernhardt, E. S., Kiefer, A. M., Mitchell, C. P. J., Wania, F., and Bergquist, B. A.: Tracing Atmospheric Mercury from Artisanal and Small-Scale Gold Mining, *Environmental Science & Technology*, 10.1021/acs.est.4c10521, 2025.

Talbot, R., Mao, H., Scheuer, E., Dibb, J., and Avery, M.: Total depletion of Hg degrees in the upper troposphere-lower stratosphere, *Geophysical Research Letters*, 34, 5, L23804, 10.1029/2007gl031366, 2007.

Tang, K., Song, Z., Fu, X., Zhang, Y., Zhang, H., Sun, Y., Zhang, H., Wu, X., Deng, Q., Zhang, L., Suratman, S., Seng, T. H., and Feng, X.: An Interhemispheric Difference in Atmospheric Gaseous Elemental Mercury Isotopes Reveals a New Insight in Oceanic Mercury Emissions, *Journal of Geophysical Research-Atmospheres*, 130, 10.1029/2024jd042178, 2025.

Wang, B., Yuan, W., Wang, X., Li, K., Lin, C.-J., Li, P., Lu, Z., Feng, X., and Sommar, J.: Canopy-Level Flux and Vertical Gradients of Hg0 Stable Isotopes in Remote Evergreen Broadleaf Forest Show Year-Around Net Hg0 Deposition, *Environmental Science & Technology*, 56, 5950-5959, 10.1021/acs.est.2c00778, 2022.

Wang, C., Yang, S. C., Li, R. L., Yan, J. Y., Hu, Y. X., Lai, C. Y., Li, Z. G., Li, P., Zhang, L. M., and Feng, X. B.: Atmospheric Mercury Concentrations and Isotopic Compositions Impacted by Typical Anthropogenic Mercury Emissions Sources, *Environmental Science & Technology*, 58, 16855-16866, 10.1021/acs.est.4c07649, 2024.

Warneck, P. and Williams, J.: *The atmospheric chemist's companion: numerical data for use in the atmospheric sciences*, Book, Whole, Springer Netherlands, New York, 10.1007/978-94-007-2275-0, 2012.

Weigelt, A., Slemr, F., Ebinghaus, R., Pirrone, N., Bieser, J., Bodewadt, J., Esposito, G., and van Velthoven, P. F. J.: Mercury emissions of a coal-fired power plant in Germany, *Atmospheric Chemistry and Physics*, 16, 13653-13668, 10.5194/acp-16-13653-2016, 2016a.

Weigelt, A., Ebinghaus, R., Pirrone, N., Bieser, J., Bodewadt, J., Esposito, G., Slemr, F., van Velthoven, P. F. J., Zahn, A., and Ziereis, H.: Tropospheric mercury vertical profiles between 500 and 10,000 m in central Europe, *Atmospheric Chemistry and Physics*, 16, 4135-4146, DOI 10.5194/acp-16-4135-2016, 2016b.

Wu, Q., Wang, S., Li, G., Liang, S., Lin, C.-J., Wang, Y., Cai, S., Liu, K., and Hao, J.: Temporal Trend and Spatial Distribution of Speciated Atmospheric Mercury Emissions in China During 1978–2014, *Environmental Science & Technology*, 50, 13428-13435, 10.1021/acs.est.6b04308, 2016.

Wu, X., Fu, X. W., Zhang, H., Tang, K. H., Wang, X., Zhang, H., Deng, Q. W., Zhang, L. M., Liu, K. Y., Wu, Q. R., Wang, S. X., and Feng, X. B.: Changes in Atmospheric Gaseous Elemental Mercury Concentrations and Isotopic Compositions at Mt. Changbai During 2015-2021 and Mt. Ailao During 2017-2021 in China, *Journal of Geophysical Research-Atmospheres*, 128, 10.1029/2022jd037749, 2023.

Yuan, W., Sommar, J., Lin, C.-J., Wang, X., Li, K., Liu, Y., Zhang, H., Lu, Z., Wu, C., and Feng, X.: Stable Isotope Evidence Shows Re-emission of Elemental Mercury Vapor Occurring after Reductive Loss from Foliage, *Environmental Science & Technology*, 53, 651-660, 10.1021/acs.est.8b04865, 2019.

Zhang, L., Wang, S., Wu, Q., Wang, F., Lin, C. J., Zhang, L., Hui, M., Yang, M., Su, H., and Hao, J.: Mercury transformation and speciation in flue gases from anthropogenic emission sources: a critical review, *Atmospheric Chemistry & Physics*, 16, 2417-2433, 10.5194/acp-16-2417-2016, 2016.

Zhang, Y., Horowitz, H., Wang, J., Xie, Z., Kuss, J., and Soerensen, A. L.: A Coupled Global Atmosphere-Ocean Model for Air-Sea Exchange of Mercury: Insights into Wet Deposition and Atmospheric Redox Chemistry, *Environmental Science & Technology*, 10.1021/acs.est.8b06205, 2019.

Zhang, Y., Zhang, L., Cao, S., Liu, X., Jin, J., and Zhao, Y.: Improved Anthropogenic Mercury Emission Inventories for China from 1980 to 2020: Toward More Accurate Effectiveness Evaluation for the Minamata Convention, *Environmental Science & Technology*, 57, 8660-8670, 10.1021/acs.est.3c01065, 2023a.

Zhang, Y., Xu, Z., Han, G., Chu, Z., Zhou, Q., Chen, Q., Wu, G., Shi, G., Wang, X., and Chen, L.: Improved Mechanistic Modeling on Reproducing Particle-Bound Mercury in the Marine Atmosphere, *Environmental Science & Technology*, 59, 2611-2622, 10.1021/acs.est.4c09481, 2025.

Zhang, Y. X., Zhang, P., Song, Z. C., Huang, S. J., Yuan, T. F., Wu, P. P., Shah, V. R., Liu, M. D., Chen, L., Wang, X. J., Zhou, J., and Agnan, Y.: An updated global mercury budget from a coupled atmosphere-land-ocean model: 40% more re-emissions buffer the effect of primary emission reductions, *One Earth*, 6, 316-325, 10.1016/j.oneear.2023.02.004, 2023b.

Zhou, J. and Obrist, D.: Global Mercury Assimilation by Vegetation, *Environmental Science & Technology*, 55, 14245-14257, 10.1021/acs.est.1c03530, 2021.

Reply to RC2 (anonymous)

Responses to general comments

"It will be beneficial if the authors shape this manuscript more as a critical review".

The point was made by both reviewers to be more critical in selecting the references that can be considered well-founded and to provide a base line for comparison, so to speak, commented or uncommented. In the response to RC1 under point 3, we have removed one of the references. Here, we have deleted L461 - L464 and removed the corresponding reference (L2268 - L2270). To be critical, it is perhaps questionable to include relative rate experiments, especially those performed on dirty systems, but for the OH reaction (**Rxn G3**), which has only been studied in absolute terms, leading to an upper limit on the rate constant, it seems justified. The two RR experiments are well re-analyzed and converge to the rate coefficient reported in Table 3, which comes from high-level quantum chemical calculations. Otherwise, Table 3 contains only experimental data determined in an absolute way (exceptions are **Rxn G75 & G76**).

"Hence, it would be beneficial for the reader to know which work provides more accurate data by design".

To remedy the problem, we have revised section 4.7 L392: "Table 3 summarizes the gas-phase reactions with the rate coefficients *considered most accurate* and the corresponding reaction enthalpies".

"There are a number of other places where the authors might have indicated the confidence degree associated with different presented data. I understand that this is not always an easy task."

We have reviewed the kinetic data presented and have double-checked that the data presented in Tables 3 and 4 are accompanied by confidence intervals, where these are available in the reference literature. Altogether, about a dozen adjustments were made.

"Regarding the increased stability of HgO at lower temperatures in the stratosphere. I suggest adding "at lower temperatures and pressures", as this reaction is collision activated. I should note that according to my estimate, the lifetime is still about 1 ms at 250 K and 0.1 atm, which is very short, making this species irrelevant."

We follow the reviewer's suggestion and make changes starting in line 640:

"Taken together, this information suggests that gas phase HgO in the troposphere is highly unstable. Although the decay slows down at lower temperatures and pressures as the reaction is collisionally activated, the thermal lifetime is still only about 1 ms at 250 K and 0.1 atm".

"The Gas to nucleation" subtitle is awkward and the message of this subsection is unclear. Do you imply that mercury oxidation products have a sufficiently low vapor pressure and sufficiently high concentration to nucleate new particles or contribute to their growth in the atmosphere? I highly doubt this proposition."

We thank the reviewer for this constructive remark. We agree and have made a throughout revision as follows:

Can mercury species nucleate in the atmosphere?

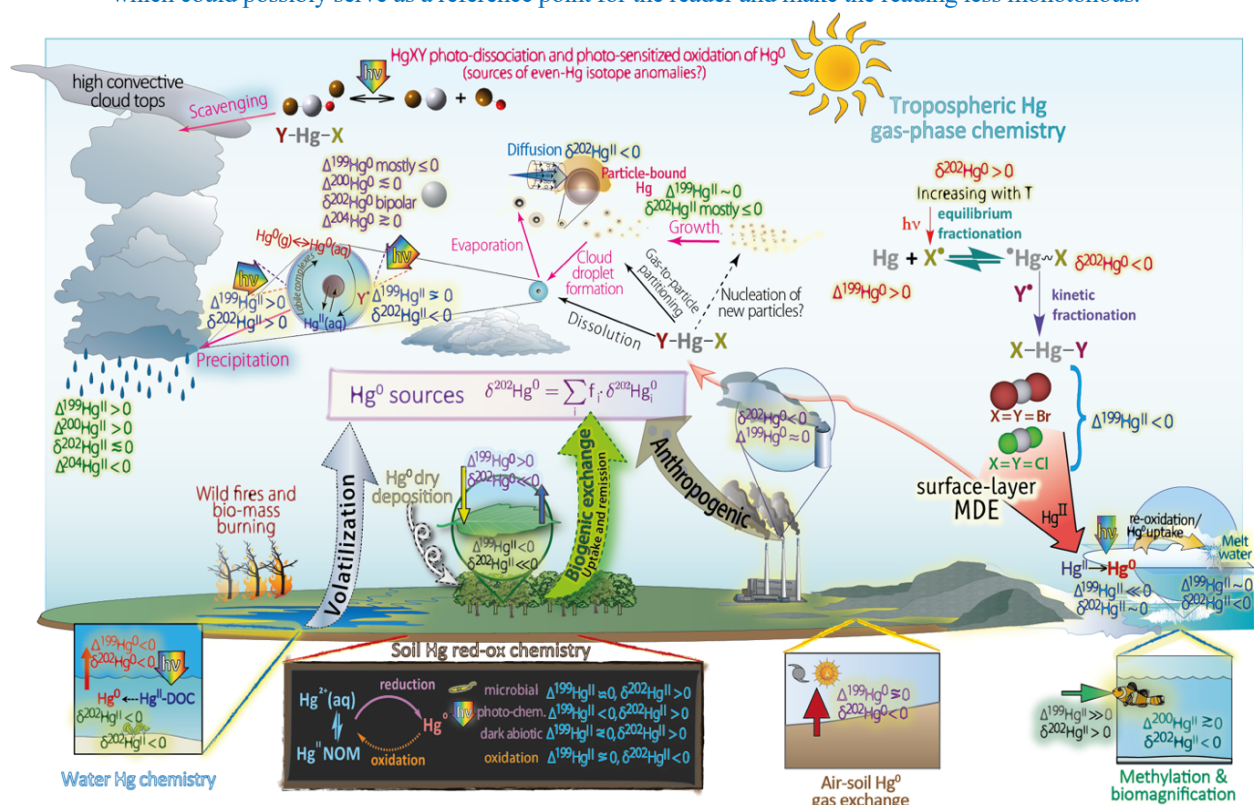
While Hg⁰ vapor has been observed to nucleate homogeneously in laboratory experiments conducted under high pressures (Martens et al., 1987), neither Hg⁰ atoms nor GOM species, which are molecular rather than ionic entities, have a vapor pressure that is sufficiently low and a concentration that is sufficiently high in the atmosphere to nucleate new particles by simple condensation (Murphy et al., 1998). However, the concerted action with a foreign gas phase precursor (perhaps amines, highly oxygenated organics, sulfuric, nitric, and iodic acid, etc., as candidates, (Lehtipalo et al., 2025; He et al., 2021)) or, classically, heterogeneous condensation on pre-existing nuclei of subcritical or critical size may result in the transfer of GOM species to aerosols (Ariya et al., 2015). Measurements of individual aerosol particles have shown that a significant portion of the aerosols

present in the lowest kilometers of the stratosphere contain small yet measurable amounts of Hg^{II} . Interestingly, Hg^{II} is empirically correlated with bromine and iodine in these particles of organic-sulfate type and has the highest relative concentrations in the stratosphere near the tropopause, but that Hg^{II} is only rarely observed in the relatively pure sulfuric acid particles characteristic of the main stratospheric aerosol layer (Junge Layer) (Murphy et al., 2006). While bromine and iodine aerosols are also observed throughout the troposphere, no Hg can be detected in these, indicating that the Hg^{II} products can evaporate rapidly into GOM species (Murphy et al., 2014). Both Br and I, with the oceans as the primary sources, are injected into the stratosphere, where they account for most of the ozone depletion caused by halogens (Koenig et al., 2020). It is challenging to determine whether there is a causal mechanistic relationship and, if so, what it is that can explain the observed correlation between aerosol Hg, Br, and I. Nevertheless, there is a plethora of clues that can be utilized to assemble a coherent narrative. Firstly, the combination of Br^{\cdot} (Rxn G14a) and O_3 (Rxn G22) constitutes a significant oxidation pathway for Hg^0 to Hg^{II} . However, as mentioned above, there is no firm evidence that this reaction pathway is relevant when I^{\cdot} is a substitute for Br^{\cdot} . Secondly, the gas phase system $\text{I}^{\cdot} + \text{O}_3 + \text{H}_2\text{O}$ has been identified as a substantial precursor of particle nucleation (as iodine oxoacids) and growth that possess a considerable significance within marine (Sipilä et al., 2016) and stratospheric (Koenig et al., 2020) environments. Thirdly, condensed phase Br^- and I^- act as robust complexing ligands (Table 1) for GOM partitioned to the aerosol, thereby impeding its re-cycling back to the gas phase. Presumably, the fundamentals are similar for a particle formation event observed in the context of the polar spring partial AMDE in the East Antarctic pack ice by Humphries et al. (2015), where the formation of 3 nm particles lags behind the phase of gaseous Hg^0 loss in the air mass.

L712 (old L690) → old L707 (end): uncut text

Chapter 8 on isotope effects makes this review stand apart from other atmospheric mercury reviews. It has a very large amount of important information, but I found this chapter difficult to read...

We have prepared an illustration of the biogeochemical cycle of isotopic mercury focusing on the atmosphere, which could possibly serve as a reference point for the reader and make the reading less monotonous.



At a minimum, I urge the authors to add a table that summarizes the different parameters (both deltas, beta, alpha, etc.) along with their definitions, meaning, and usage.

We have prepared a list of the symbols and acronyms used in this paper along with their explanations (See Appendix below).

Perhaps, it would be beneficial for one of the co-authors with an intermediate knowledge of isotope fractionation (who is not an expert), to read this chapter and edit it a bit to make it more digestible for the readers who are less familiar with the isotope field, e.g., by making sure that every time a value of a parameter is mentioned, the meaning of this value is fully interpreted.

We revised the chapter to improve its readability. We corrected sloppy mistakes and ensured that terms were explained the first time they appeared in the text. We also included these terms in the separate list of symbols and acronyms (See Appendix below).

1007 & -8, 1011 & -12, 1056, 1099, 1765, and Caption **Table 5**: "NOM" replaced by "DOM"

1351: Rewritten: "Natural processes, including redox reactions, complexation, sorption, precipitation, dissolution, evaporation, diffusion, and biological processes, can alter the isotopic composition, i.e., causing stable isotope fractionation".

1361: New symbols in equation 12

$$\delta^{xxx}\text{Hg} = 1000 \cdot \left[\left(\frac{^{xxx}\text{Hg}}{^{198}\text{Hg}} \right)_{\text{sample}} / \left(\frac{^{xxx}\text{Hg}}{^{198}\text{Hg}} \right)_{\text{NIST3133}} - 1 \right]$$

1362: Re-shuffled: "...per mill (‰). $\delta^{202}\text{Hg}$ expresses the total mass dependent fraction (TMDF, containing contributions from conventional mass-dependent fractionation, hereafter, MDF and nuclear field shift, NFS see **Section 8. 1**), while the isotope anomalies caused by mass-independent fractionation, MIF are expressed by capital delta, Δ is defined as the difference between the measured δ -value and that predicted from the measured $\delta^{202}\text{Hg}$ value and the scale factor for kinetic MDF ($\beta_{\text{KIE-MDF}}^{xxx}$, see **Section 8. 1**) and is approximated for δ -values < 10‰ according to:

$$\Delta^{xxx}\text{Hg} = \delta^{xxx}\text{Hg} - \beta_{\text{KIE-MDF}}^{xxx} \cdot \delta^{202}\text{Hg} \quad (13)$$

which is expressed numerically for each relevant Hg isotope:

Inserted L1442-L1443. The fractionation between two compounds A and B (assume that A is a product of a reaction and B is the remaining reactant.) is expressed with the fractionation factor, α , which is defined as the ratio of the isotope ratios in the compounds:

$$\alpha_{\text{A-B}}^{xxx} = R_{\text{A}}^{xxx/198} / R_{\text{B}}^{xxx/198} = \frac{1000 + (\delta^{xxx}\text{Hg})_{\text{A}}}{1000 + (\delta^{xxx}\text{Hg})_{\text{B}}} \quad (14)$$

The last term is obtained by substituting Eq. 12 into the first term of Eq. 14.

Inserted L1365 followed by old Eq. 14 (now Eq. 15) and L1366 (... than 10‰).

Substitute Eq. 13 into Eq. 15 and obtain:

$$\epsilon_{\text{A-B}}^{xxx} \cong \{(\Delta^{xxx}\text{Hg})_{\text{A}} - (\Delta^{xxx}\text{Hg})_{\text{B}}\} + \beta_{\text{KIE-MDF}}^{xxx} \cdot [(\delta^{xxx}\text{Hg})_{\text{A}} - (\delta^{xxx}\text{Hg})_{\text{B}}] \quad (16)$$

Equation 16 expresses total fractionation during the process $\text{A} \rightarrow \text{B}$, with the first term representing the MIF enrichment factor and the second term representing the total mass-dependent enrichment factor. Thus, the enrichment factor for MIF is written as a capital epsilon:

$$\epsilon_{\text{A-B}}^{xxx} = \{(\Delta^{xxx}\text{Hg})_{\text{A}} - (\Delta^{xxx}\text{Hg})_{\text{B}}\} = \epsilon_{\text{A-B}}^{xxx} - \beta_{\text{KIE-MDF}}^{xxx} \cdot \epsilon_{\text{A-B}}^{202} \quad (17)$$

Inserted L1366 "Many kinetics..." Numbering on mathematical equations updated (15') → (18) etc.

1373: Inserted "... normal kinetic isotope effect, **KIE**)..."

1381: Rewritten: "Heavier isotopes are preferentially concentrated in compounds with the highest force constant, where the element is most rigidly bound and has greater potential energy. Conversely, compounds enriched in lighter isotopes have weaker bonds and require less energy to break, so they preferentially enter chemical reactions and are enriched in the product (Criss, 1999). Combining kinetic and equilibrium MDF makes it possible to achieve a limit of approximately 10‰ fractionation (Sun et al., 2022)".

1386: Rewritten and shortened: "...the expected MDF relationships. The nuclear field shift (NFS, Rosenthal and Breit, 1932) is the interaction of nuclear volume on electrons (NVE, Schauble, 2007). It is highly relevant for very heavy metals, including Hg, Tl, Pb, and U. NFS is a shift in the ground electronic energy of an atom or molecule due to differences in nuclear size and shape between isotopes. The shift caused by an odd (neutron number) nucleus scales non-linearly between those of the even isotopes of the next higher and lower atomic mass. The odd isotope *electronic energy* level is shifted towards the next lower even nucleus (odd-even staggering). Due to its smaller size and greater surface charge density, the electronic energy of a light isotope is lower than that of a heavier isotope. The amount of shift is a product of two factors: the electron density at the nucleus and the charge, size, and shape of the nucleus and the change in the latter two between isotopes. Hg 6s-orbitals electrons significantly overlap with the nucleus, whereas 5p-, 5d-, and 4f-orbitals do not, although f-electrons in inner shells have a smaller screening effect on 6s-valence electrons (Bigeleisen and Wolfsberg, 1957). The lowest energy of a system occurs when the heavier isotopes of Hg are enriched in the chemical species with the fewest s-electrons in the bonding or valence orbital. The largest shifts, therefore, occur when the number of Hg 6s electrons is greatly reduced by the formation of an ionic bond (to an electronegative element), while a covalent bond has less influence. Examples of Hg species in the former category are chloro- or aqua-complexes with high coordination numbers (e.g., $[\text{Hg}(\text{H}_2\text{O})_6]^{2+}$), while the latter includes soft ligands with typical linear bi-coordination (e.g., $\text{Hg}(\text{SH})_2$ and $(\text{CH}_3)_2\text{Hg}$)..."

1406 & 7: Deleted: "regular"

1453: Correction: **Table 7**

1460: Deleted: "conventional"

1465 "MDF" changed to "TMDF"

1484: Rewritten: "Studies examining the vertical distribution of mercury (Hg^0) concentrations from near the ground to above the canopy in different forest types reveal clear gradients averaging 10% (Wang et al., 2022) and 20% (Fu et al., 2016b) of ambient Hg^0 , respectively".

1491: Rewritten: "In a subtropical, perennial forest in southwestern China, where there is little seasonal variation in the photosynthetic activity of vegetation, the existing seasonal variation in $\delta^{202}\text{Hg}^0$ (with an amplitude of 0.4 ‰) can be attributed to the influence of long-range anthropogenic emissions, which primarily occur during the warmer seasons. However, over the last five to seven years, the air concentrations of Hg^0 have fallen significantly in the two mentioned forest reserves due to decreasing regional anthropogenic emissions, as evidenced by the median value of $\delta^{202}\text{Hg}^0$ shifting from 0.42 to 0.46‰ and from 0.17 to 0.57‰".

1497: Rewritten: "Coastal measurements in the Gulf of Mexico show that the marine-influenced air isotopically represents background air modified by Hg^0 emitted from the sea after being formed in surface water by photoreduction (Demers et al., 2015)".

1499 Deleted "(MBL)"

1504: Rewritten: "The generally negative signature of $\Delta^{199}\text{Hg}^0$ in the background air indicates that Hg^0 has been added to the pool subsequent to Hg^{II} photoreduction (of the variant that induces (+)MgIE in the reactant and complements it by depleting the product Hg^0 isotopically for odd isotopes) in oceans and aerosols."

1508: Shortened: "An analysis of gas exchange in a subtropical beech forest revealed bidirectional fluxes of Hg^0 , with uptake partially balanced by reemission of previously metabolized Hg^{II} . Photo reduction recirculates Hg^0 , contradicting a retro flux of deposited Hg^0 at the leaf surface (data...."

1514: Rewritten: "A mass balance based on isotope measurements indicates that, compared to the uptake of Hg^0 from the air, re-emission from the beech foliage gradually increases from emergence to senescence, accounting for an average of 30% (Yuan et al., 2019b). Observations from a temperate deciduous forest revealed 0.06–0.09 ‰ higher $\Delta^{199}\text{Hg}^0$ values during the growing season than in winter, suggesting that foliar Hg^0 efflux contributes to atmospheric enrichment of odd Hg isotopes (Fu et al., 2019a)."

1518: Rewritten: "The large spread of odd-MIF shown by Hg^0 in polar air (Araujo et al., 2022; Yu et al., 2021; Sherman et al., 2010, Fig. 13a) is due to the portion of the collected data that includes Hg^0 depletion events in the spring and Hg^0 enhancement during the summer, when reemissions of Hg^0 occur from the cryosphere."

1521: Corrected: "With respect to $\Delta^{199}\text{Hg}$, a dichotomy between the polar and temperate data is striking for both Hg^0 and Hg^{II} (RM), in that montane oxidized Hg is enriched in a limited range (0.14 to 0.77‰) while the polar *one* is depleted in a greater range (−2.15 to −0.18‰), with a complementary relationship existing for Hg^0 (−0.31 to −0.16‰ versus −0.22 to 1.32‰)."

1524: Revised: "This relationship could be caused by surface layer airborne Hg **being** strongly influenced by the oxidation of Hg^0 to Hg^{II} , **which is** controlled by halogen atoms during AMDEs, processes characterized by $E^{199}\text{Hg}$ of −0.37‰ and −0.23‰ for Cl^\bullet -initiated and Br^\bullet -initiated oxidation, **respectively** (Table 7, Sun et al., 2016)."

1527: Rewritten: "However, this interpretation is not corroborated by the measured $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ ratio of nearly unity in airborne Hg, which is more typically indicative of Hg^{II} photo-reduction (−MgIE) occurring in snow. It has been proposed that this process also operates in aerosols of the boundary layer, with Hg^0 reemissions providing such a strong positive imprint that the entire boundary layer of the Hg^0 pool becomes enriched in odd isotopes."

1531: Inserted: "...using CEM (**cf. Section 3.1**)..."

1566: Rewritten: "A strong anticorrelation between $\Delta^{199}\text{Hg}^{\text{II}}(\text{p})$ (up to ~1.2‰, but initially at near-zero) and the concentration of particle-bound Hg, rationalized as caused by photo-produced Hg^0 loss from the aerosol, was observed in samples from these stations, with the major potential source area identified as northeastern China and the regions along the lower reaches of the Yangtze River to its mouth (Fu et al., 2019b)."

1580: Rewritten: "The Antarctic coast has shown uniquely high positive $\delta^{202}\text{Hg}^{\text{II}}(\text{p})$ values (up to ~3‰ and anticorrelated with $\Delta^{199}\text{Hg}^{\text{II}}(\text{p})$) in air masses transported by katabatic winds from the continental shelf, where oxidation of Hg^0 persists during summer..."

1610: Inserted: "... consistent with **precipitation** observations in the..."

1641 Caption Fig. 12: "MDF" changed to "TMDF"

Caption Table 7 Inserted: "... factors ($\epsilon^{202}\text{Hg}$, $E^{199}\text{Hg}$) determined..."

Table 7: reads "detected" should read "0.06‰"

1687: Corrected: **Rxn G72**

1699: "dissolved organic matter" replaced by "DOM".

1703: Deleted: conventional

1732: "The figure" changed to "Fig. 16".

1738: Corrected: Stowe and Knight **Jr.**

1755: Revised: "Another example of the impact of pH/complexation on the evolution of MgIE can be seen in the UVC photodegradation of MMHg⁺ in acidic and alkaline (adjusted with NH₃) solutions. In the former, (+)MgIE is significant, but in the latter, it is very limited."

1759: Inserted: "As **seen** in..."

1762: Rewritten: "To better interpret odd-MIF signatures and systematically elaborate the roles of reaction parameters (pH, presence of O₂, light wavelength, etc., Rose et al., 2015) in excited state kinetic isotope effects, experimental research is needed."

1766: Rewritten: "Zhang and Hintelmann (2009) observed an E199Hg optimum ($\geq 5\%$) in anoxic photo-experiments with the DOM fraction from Dorset Lake, Ontario. This optimum is associated with a ligation mode in which all S-bonding functional groups are saturated by Hg²⁺ cations, increasing the proportion of Hg-O bonds and the ratio of bright triplets to bright singlets, thus making the MgIE increasingly positive."

Table 8: All occurrences of "NVE" have been replaced by "NFS". The entry "0.24 \pm 0.01" under the reference to Schwab et al. (2023) is in the wrong column and should be moved one column to the left.

Footnote 40: Mistake corrected

1807: New entry: **"8.4.2 Oxidation"**

To the extent that isotopic effects in the aqueous phase Hg⁰ oxidation have been studied in the laboratory, it has been observed that oxidized Hg becomes isotopically heavier than the reactant. The observed fractionation does not conform to the Rayleigh model, but it is consistent with EIE in a closed system. Consequently, the isotope ratio of the product(s) linearly approaches that of the reactant at the beginning of the reaction. An example of atmospherically relevant oxidation is the rapid reaction with •OH (**Rxn W2**, generated by photolysis of NO₃⁻) with $\epsilon^{202}\text{Hg} = 1.20 \pm 0.14 \text{ ‰}$ (Stathopoulos, 2014). Experiments with thiol-substituted carboxylic acids in the dark produced similar fractionation results (see Table 8, **Rxn W7**). Additionally, the NFS produced a small odd-MIF signal that consistently acts in the opposite direction of the mass-dependent fractionation (Zheng et al., 2019). The reason for observing EIE despite the continuous oxidation of Hg⁰ without any indication of reversibility in the form of back reactions has been attributed to a rapid exchange of Hg isotopes between the remaining Hg⁰ and the formed Hg^{II} complexes (Wang et al., 2020). There is currently debate surrounding the mechanism by which this exchange occurs (Wang et al., 2020; Zheng et al., 2019; Wang et al., 2021). In the presence of humic acid, the oxidation of dissolved Hg⁰ exhibits two kinetic regimes where the EIE is not fully established in the initial regime (Zheng et al., 2019). KIE-MDF during dark reduction in the presence of DOM and EIE-MDF during dark oxidation caused by humic acid give rise to fractionation in the same direction and magnitude, so it can be difficult to unmask the controlling redox process from isotopic measurements."

1810, 1827 & 1871: "NVE" replaced by "NFS".

1824: "MDF" changed to "TMDF"

1833: Revised into "... this time, positive..."

1839: Correction: "Section 3.2"

1847: Clarifying addition: "In the following, we express absolute deposition with negative values and vice versa for emission throughout."

1850: Inserted: "Isotope-based modeling by binary (**example in Eq. 25**) and... ", "MDF" changed to "TMDF"

1862: Inserted: "The isotope mixing formula is used to determine the proportions of different isotope sources in a mixture, which in its simplest form is:

$$\begin{aligned}(\delta^{\text{xxx}}\text{Hg})_{\text{mix}} &= f_1 \cdot (\delta^{\text{xxx}}\text{Hg})_1 + f_2 \cdot (\delta^{\text{xxx}}\text{Hg})_2 \\ f_1 + f_2 &= 1\end{aligned}\quad (25)$$

1885 & 1903: "MDF" changed to "TMDF"

1929: (aq) deleted.

1939: Correction: "Section 3.2"

1947: "MDF" changed to "TMDF"

2016: "Regression of the Alaskan DFC experiment $\Delta^{199}\text{Hg}$ plotted against $\delta^{202}\text{Hg}$ data (-3.44 ± 0.70)."

2037: "(DGM)" deleted.

2038: "MDF" changed to "TMDF"

2047: Correction: " ... photodegradation **have been suggested** (Chen et al., 2016)"

Chapter 9 on future perspectives is a hit-and-miss. I suggest that the authors rethink the structure and contents of this chapter. It must summarize the achievements, identify the remaining challenges and gaps, propose future work, and when possible, suggest ways of addressing the challenges. Having a concluding sentence or brief paragraph would be nice, too.

We've revised and expanded the chapter, and we hope that we've been able to address the criticisms that were raised.

This examination of the advancements made in our comprehension of the mercury cycle in the troposphere and stratosphere reveals iterative interactions among three distinct branches of atmospheric chemistry (modeling, field measurements, and laboratory measurements). Particularly, advances in computational chemistry have made seminal contributions to our understanding of gas-phase $\text{Hg}^{\text{(I,II)}}$ molecules in terms of their geometries, energies, UV-VIS spectra, and reaction kinetics. The treatment of strong relativistic effects, which largely determine the chemistry of Hg-containing species, is crucial for accurate results. Ab initio thermochemical calculations for atmospheric Hg species are performed at a higher level of theory, which incorporates core-valence electron correlation and coupled-cluster methods. This approach yields a significantly improved accuracy of $\leq 4 \text{ kJ mol}^{-1}$, in accordance with high-quality experimental data. However, significant uncertainties in the estimates of binding strength, thermal and photolytic stability of $^*\text{Hg}^{\text{I}}$ (**Section 5.1.2**) remain, limiting the ability to assess the occurrence and significance of iodine-induced Hg^0 oxidation in the troposphere and lower stratosphere, as has been suggested from atmospheric observations (Murphy et al., 2006; Lee et al., 2024).

Compared to ab initio thermodynamics, the calculation of ab initio kinetics is a much more challenging task, for which Transition State Theory (TST) and RRKM theory are often used for barrier and non-barrier bimolecular reactions, respectively. More flexible methods (e.g., variational TST) are now applied to optimize the position of the transition state (TS) by varying it along the reaction coordinate to minimize the free activation energy, which more accurately estimate the rate compared to that of traditional TST which

assumes a single, fixed TS that irreversibly leads to products. The calculation of TS energies is more challenging than the calculation of energies of relative minima (metastable species) due to the involvement of extended bonds where the electronic wave function is less dominated by a single electronic configuration. Obtaining a correct barrier energy is crucial to calculating reliable rate constants, since an bias of ~4 kJ/mol in the barrier height can lead to an error of almost an order of magnitude in the resulting rate constant (Ariya and Peterson, 2005; Ariya et al., 2009).

For gas-phase reactions (Section 5.1), calculated rate constants have been presented and compared with those where there are experimentally determined ones in the laboratory. The level of agreement varies from relatively good ($\leq 30\%$ as **Rxn G1 - G3**) to inconsistent (**Rxn G20a,b & G22**). Due to the complex shape of their potential energy surfaces, the rates of assumed key reactions such as **Rxn G27, G45, and G63** are inherently difficult to constrain theoretically (Section 5.1.4) and thus require empirical verification, preferably using PLP-LIF or similar techniques. A direct reaction between water vapor and $\text{YHg}^{\text{II}}\text{O}^{\bullet}$ has recently been proposed for $\text{Y} = \text{OH}$ (**Rxn G60**, Saiz-Lopez et al., 2022). If this reaction is realized with the given rate expression in models, it will result in the conversion of essentially all $\text{HOHg}^{\text{II}}\text{O}^{\bullet}$ to the completely stable $\text{Hg}(\text{OH})_2$ in the tropics. This type of reaction also requires empirical verification and should be given priority in laboratory experiments.

Absolute determination of rate constants experimentally with pulsed laser-assisted methods (reaction time typically < 0.1 ms) such as PLP-LIF is more easily facilitated when secondary reactions are negligible and therefore do not contribute to the measured values. In general, absolute determination is conducted by obtaining pseudo-first order conditions, whereby the more stable reactant is present in a density exceeding tenfold that of the other reactant. However, for Hg, this method is viable only for studies that are conducted at elevated temperatures (typically $\geq 100^\circ\text{C}$). At atmospheric temperatures, the relatively low vapor pressure of Hg^0 (in comparison to, for instance, DMHg) precludes the possibility of such experiments. Despite the challenges for Hg^0 , a flow PLP-LIF system has many advantages, including the ability to measure the rate coefficient over a wide range of temperatures and pressures and to test the effect of a change in bath gas (third body). Nevertheless, to exploit these advantages, alternative methods have been used in which the Hg species is not in excess, but in which the excess is $\text{X} = \text{Cl}$ and Br when the reaction $\text{Hg} + \text{X}^{\bullet} + \text{M}$ is studied, while it is instead $\text{Y} = \text{O}_3$, NO_2 , NO , and O_2 when the interaction between $^{\bullet}\text{Hg}^{\text{I}}\text{Br}$ and Y is studied. In the study of the former reaction type, X^{\bullet} is present in excess, but its concentration decreases over time due to the rapid three-body recombination of the species into X_2 and M . This results in additional Hg^0 exponential decay. To achieve a fit to the observed Hg^0 time profiles, rate coefficients must be obtained through numerical integration. This requires monitoring both the X^{\bullet} and Hg^0 time profiles using LIF, with the absolute concentration of X atoms known with precision. The measurements of the rate coefficients for the $\text{Hg} + \text{X}^{\bullet} + \text{M}$ reaction experimentally by Donohoue et al. are in accordance with the findings of the theoretical computational studies.

The study of the conversion of $^{\bullet}\text{Hg}^{\text{I}}\text{Br}$ by bimolecular elimination reduction (**Rxn G18 & G20b**; Wu et al., 2020; Wu et al., 2022), addition (oxidation assisted by M [**Rxn G20a**]; Wu et al., 2020), or abstraction (**Rxn G22**, Gómez Martín et al., 2022) is constrained by the capacity to generate sufficiently high densities of $^{\bullet}\text{Hg}^{\text{I}}\text{Br}$ through the gas-phase photolysis of HgBr_2 in the deep UV. Because the vapor pressure of HgBr_2 is low (less than one-tenth that of Hg^0), it is necessary to keep the HgBr_2 source at least 30°C and the flow tube reactor at least 10°C higher to prevent vapor condensation. A higher temperature increases the thermal dissociation of $^{\bullet}\text{Hg}^{\text{I}}\text{Br}$, and therefore, a large excess of Y is required for the $^{\bullet}\text{Hg}^{\text{I}}\text{Br} + \text{Y}$ reaction to dominate the conversion of $^{\bullet}\text{Hg}^{\text{I}}\text{Br}$. In the context of laboratory experiments necessitating deep UV irradiation, it is essential to consider that oxygen atoms are formed through the partial photolysis of O_3 and NO_2 , thereby enabling $\text{O}(^3\text{P})$ to react with $^{\bullet}\text{Hg}^{\text{I}}\text{Br}$ ($\text{O} + \text{HgBr}^{\bullet} \rightarrow \text{Hg} + \text{BrO}^{\bullet}$, **Rxn G23**). The experiments to study the reactions of $^{\bullet}\text{Hg}^{\text{I}}\text{Br}$ with NO_2 and O_3 will inevitably result in the observation of a partially reversible oxidation process. This is due to the occurrence of secondary chemistry, including the reactions **G14, G23,**

G24, and **G29**, which take place concurrently with the title reactions **G20** and **G22**. Furthermore, to elucidate the influence of secondary chemistry on the observed $^1\text{Hg}^{\text{I}}\text{Br}$ disappearance, a comprehensive series of experiments must be conducted, with pressure, temperature, $[^1\text{Hg}^{\text{I}}\text{Br}]$, $[\text{Y}]$, and $[\text{O}]$ as variables. This necessitates numerical modeling to isolate the individual rate constants. While the laboratory study of $^1\text{Hg}^{\text{I}}\text{Br} + \text{O}_3$ gives an experimental rate constant for the reaction **G22** that is in good agreement with computational predictions (Castro Pelaez et al., 2022), experimental kinetic data for $^1\text{Hg}^{\text{I}}\text{Br} + \text{NO}_2$ (**Rxn 20**), which must be decoupled in termolecular oxidation (**Rxn 20a**) and reduction (**Rxn 20b**), respectively, indicate that computational methods give overestimated rate constants for both channels (Wu et al., 2020). Later experimental investigations found that **Rxn 20** cannot fully account for observations, but that significant losses of $^1\text{Hg}^{\text{I}}\text{Br}$ must occur via side reactions, probably involving **Rxn G23**, which was unexplored at the time. These intractable shortcomings present a challenge to validate a majority of the proposed reaction steps by computational quantum chemistry in the atmospheric Hg redox cycle, including $\text{YHg}^{\text{II}}\text{O}^\bullet$ chemistry, through experimental means. As requested by theoretical chemists (Edirappulige et al., 2023) and modelers (Shah et al., 2021), better rate constants are needed for the $\text{YHgO}^\bullet + \text{CH}_4$ and $\text{YHgO}^\bullet + \text{CO}$ reactions, especially for $\text{Y} = \text{Br}$ and OH , to better assess the atmospheric fate of YHgO^\bullet , i.e., whether YHgO^\bullet will be mainly reduced or form closed-shell Hg^{II} compounds under different atmospheric conditions. As a workaround in the absence of experimentally determined rate constants, (Khiri et al., 2020) have proposed efforts to perform molecular dynamics simulations using computationally more sophisticated variational TST with multidimensional tunneling.

Many of the proposed key gas-phase Hg species lack experimental characterization (such as spectral proofs). The main method for studying such gas-phase molecules has been spectroscopy after preparation by matrix isolation, which has so far been used to study the products of photochemical reactions of excited Hg atoms with e.g. O_3 (Butler et al., 1979), O_2 (Andrews et al., 2023), H_2 (Wang and Andrews, 2005b), H_2O (Wang and Andrews, 2005a), F_2 (Wang et al., 2007), and OF_2 (Andrews et al., 2012) in a matrix host of solid Ar and Ne at a cold (typically 4 - 7 K) surface. Section 5.1.4 has already described some of the isolated molecules of interest to us, namely $\text{Hg}(\text{OH})_2$ (Wang and Andrews, 2005a) and the fluorine analog of $\text{YHg}^{\text{II}}\text{O}^\bullet$ (Andrews et al., 2012). Other studies involve mercury halide molecules (Loewenschuss et al., 1969) and their adducts (Tevault et al., 1977). The reaction mechanism for the formation of $\text{Hg}(\text{OH})_2$ tentatively involves insertion as a first step: $\text{Hg}(^3\text{P}) + \text{O}_2 + \text{H}_2 \rightarrow (\text{OHgO})^* + \text{H}_2 \rightarrow \text{HOHgOH}$, where $\text{OHgO} (^3\Sigma_g^-)$ is implicitly indicated as a reactive intermediate (c.f., **Rxn G12**, although, unlike the analogous complexes for the other Group 12 metals, OZnO and OCdO , it has yet not been identified by IR spectra (Chertihin and Andrews, 1997)). Apart from MS experiments of laser desorption ionization and time-of-flight type with solid HgO as the source and detection of $(\text{HgO})_x$ clusters in the gas phase (Jayasekharan and Sahoo, 2014), there is one early (Butler et al., 1979) and one recent (Andrews et al., 2023) matrix study of the products of the $\text{Hg}(^3\text{P}) + \text{O}_2$ system, where both $^{16}\text{O}_2$ and $^{18}\text{O}_2$ were used as reagents. The former experiments required co-deposition of Hg with 0.5 to 5% O_3 in excess of Ar under deep UV photolysis for oxidation to occur, while the latter experiments used laser ablated Hg atoms energetic enough to form oxygen atoms when deposited in a cryogenic matrix doped with 0.3% $^{16}\text{O}_2$ or $^{18}\text{O}_2$, which react upon annealing to form O_3 and a series of HgO_x species ($x = 1$ to 3). The observed fundamental harmonic vibrational frequencies in different cryogenic matrices for the simple oxide $\text{Hg}-\text{O}$ are in the range (500 - 600 cm^{-1}) predicted by high-level calculations (Shepler and Peterson, 2003; Peterson et al., 2007) indicates a weakly ionic molecule. This is also true for HgO_2 and HgO_3 , which are of the superoxide (Hg^+O_2^-) and ozonide (Hg^+O_3^-) character, respectively (Andrews et al., 2023). It should be noted that the study did not isolate the linear mercury dioxide, OHgO , and evidence for this species remains weak. Nevertheless, this species is included as a metastable adduct in **Rxn G12** scheme, the key reaction for Hg^0 turnover in the stratosphere, whose complex potential energy surface forms the basis of ab initio kinetic calculations. In these calculations, (Saiz-Lopez et al., 2022) assumes the energy of the $\text{Hg}-\text{O}$ bond to be 27.3 kJ mol^{-1} , which is significantly higher than the most recently published high-level calculation

values (Peterson et al., 2007; Cremer et al., 2008). Increased activity and innovation in the area of advanced experimental studies characterizing key species and reactions are needed to verify models of atmospheric Hg chemistry that currently appear overly reliant on computational chemistry. The innovation could be, for example, finding a laboratory method to capture the temporal behavior of HgO (perhaps generated by the spin-allowed $\text{Hg}(^1\text{S}) + \text{O}(^1\text{D})$ reaction or by reacting DMHg with $\text{O}(^3\text{P})$) in the presence of gas-phase co-reactants (with reference to **Rxn G73 & G74**), performing a detailed study of **Rxn G12**, or finding a synthetic route to matrix-isolate species such as BrHgO^\bullet from laser-ablated Hg atoms.

Current limitations and challenges to accurately measuring speciated atmospheric mercury (Gustin et al., 2024; **Section 3.1**) mean that the basis for verifying models in detail is insufficient, despite reliable measurements of Hg^0 in air and Hg^{II} in wet deposition. Nevertheless, there are models developed by including in the reference material KCl-denuder based Hg^{II} measurements (Shah et al., 2021; Fu et al., 2024), which are known to suffer from low bias, and others (Saiz-Lopez et al., 2020; Saiz-Lopez et al., 2025) that seem to stick strictly to RM data for validation or include KCl-denuder based Hg^{II} measurements corrected according to (Maruszczak et al., 2017), which has the consequence that the evaluation is qualitative (Shah et al., 2021), consistently fails to simulate the magnitude of recurring episodes of highly oxidized mercury originating in the free troposphere (underestimation by up to several hundred percent, (Elgiar et al., 2025; Gustin et al., 2023)). In **Section 3.2**, we have highlighted the discrepancies that exist in the view of the atmospheric budget and the fluxes into and out of it. In particular, new model results on the importance of the stratosphere are inconsistent with existing empirical data and require further elaboration, as does the stratospheric chemistry discussed above. Recent observations have shown that there are abundant anthropogenic emissions of reactive halogens (e.g., Br_2 and BrCl) over continental, densely populated areas of South and East Asia that also have high Hg emissions. This is now beginning to be modeled as a key component of the regional atmospheric Hg redox cycle (Fu et al., 2024), but more field measurements are needed for confirmation.

The difficulties of accurately determining the speciation of Hg^{II} in atmospheric water through equilibrium modelling, and thus identifying the pool of reducible complexes, have been elaborated (**Section 4.3**). Additionally, the potential for simulating the gas-particle distribution of atmospherically oxidized Hg has been explored (**Section 7.1.1**). Stable isotope data have been analyzed to constrain the Hg redox chemistry in the atmosphere (Song et al., 2024; Zhen et al., 2024), but there are profound knowledge gaps that require state-of-the-art theoretical and experimental investigations. **Section 8.2** describes the isotopic composition of atmospheric samples, a pool generally consisting of filtered air divided into PBM and gaseous mercury ($\sim\text{Hg}^0$), and precipitation samples, including those of cloud and fog water. The isotope measurements on RM, which are now also performed, are briefly presented here (Fu et al., 2021). With a measuring line consisting of a CEM ($\text{Hg}^{\text{II}}(\text{g})$), a filter ($\text{Hg}^{\text{II}}(\text{p})$) and a trap consisting of halogen-impregnated activated carbon (Hg^0) in series, the analysis shows that the three groups are clearly isotopically separated from each other and that the resulting samples can thus provide further insights into atmospheric processes (X. Fu, pers. comm). The discovery, made over a decade ago, that atmospheric samples contain a significant level of the even-mass-number isotope MIF with seasonal and geospatial variations has been a source of both benefit and puzzlement for scientists (**Section 8.2.3 & -4**). As the even Hg MIF variation is limited to samples from a few localities so far (compare **Figs. 13 & 14**), $\Delta^{200}\text{Hg}$ & $\Delta^{204}\text{Hg}$ in the environment is considered a conservative tracer due to its generally narrow range, and values of $\Delta^{200}\text{Hg}$ & $\Delta^{204}\text{Hg}$ on the land surface and in water confine the relative contribution of Hg^0 to Hg^{II} exchange process with the atmosphere. Nevertheless, the underlying chemical processes that give rise to the anomalous MIF and the atmospheric conditions that facilitate its occurrence remain to be elucidated in greater detail. In addition to laboratory-based investigations, future field experiments that report on the vertical profiles of isotopic Hg^0 and Hg^{II} in the atmosphere may prove invaluable in further constraining the sources of even-MIF.

Responses to minor comments

L24: Consider replacing “impact” with “threat”

Replaced.

L47: Consider replacing “However, it” with “Although this route was discarded, ozone”

Replaced.

L48: Replace “more unstable” with “less stable”

Replaced.

L59-63: Sort out by year, and possibly cluster by major focus of each review.

General (biogeochemical cycle (Lindqvist and Rodhe, 1985; Lindqvist et al., 1991; Schroeder and Munthe, 1998; Selin, 2009; Lyman et al., 2020), *observations* (Slemr et al., 2003; Sprovieri et al., 2010; Dommergue et al., 2010; Fu et al., 2015; Steffen et al., 2015; Mao et al., 2016; Zhang et al., 2019; Custódio et al., 2022; Bencardino et al., 2024), *isotopic observational data* (Kwon et al., 2020; Liu et al., 2024), *atmospheric measurement techniques* (Pandey et al., 2011; Huang et al., 2014; Gustin et al., 2015; Davis and Lu, 2024; Gustin et al., 2024), *emissions (anthropogenic)* (Carpi, 1997; Zhang et al., 2016; Cheng et al., 2023), *natural volcanism* (Edwards et al., 2021), *physical removal and air-surface exchange* (Zhang et al., 2009; Sommar et al., 2013; Zhu et al., 2016; Agnan et al., 2016; Cooke et al., 2020; Sommar et al., 2020; Zhou et al., 2021; Liu et al., 2024) with emphasis on *global change* (Obrist et al., 2018; Sonke et al., 2023), *polar atmospheric surface layer mercury depletion events* (Steffen et al., 2008), *chemical conversion in the atmosphere* (Schroeder et al., 1991; Lin and Pehkonen, 1999; Lin et al., 2011; Si and Ariya, 2018), *aqueous homogeneous and heterogeneous photoredox chemistry* (Zhang, 2006; Si et al., 2022), *multi-phase atmospheric chemistry* (Ariya et al., 2015), *assessment of critical atmospheric chemical processes using state-of-the-art experimental and computational chemistry methods* (Ariya and Peterson, 2005; Ariya et al., 2008; Hynes et al., 2009), *receptor-* (Cheng et al., 2015) *and global models* (Lin et al., 2006; Lin et al., 2007; Subir et al., 2011, 2012; Amos et al., 2015; Travníkov et al., 2017).

L87: “as the electron approaches” – the electron on which orbit?

We have rewritten the sentence, which now follows as:

The electronic configuration of the mercury atom has filled f- and d-orbitals with a high density of 6s-valence electrons near the nucleus ($[\text{Xe}]4f^{14}5d^{10}6s^2$), which is related to a relativistic radial contraction of *all* s- and p-shells as the inner electrons approach a significant fraction of the speed of light (which for an Hg 1s electron is 58%, implying a radial shrinkage of 23%).

L240: Replace “at which it occurs” with “at which the reaction occurs”

Replaced.

Ibid: “The rate of a reaction is determined by 240 the interaction between kinetics, a rate process, and thermodynamics that describes the energetics of the process” – This sentence is very imprecise. “kinetics” of what? For instance, for a gas phase reaction the rate depends on the number of collisions between the reactants and thermodynamics of their interactions (the change in entropy and enthalpy upon passing through the transition state).

We thank the reviewer for this valuable comment and have amended the paragraph to read:

... Elementary processes involve a transition between two atomic or molecular states separated by a potential energy barrier representing the activation energy. The rate of a gas-phase reaction depends on the number of collisions between the reactants and the thermodynamics of their interactions (i.e., the change in entropy, ΔS , and enthalpy, ΔH , upon passing through the transition state), whereas for the rate of a reaction in aqueous solution there are a number of additional factors that can influence the rate, such as solvation, ionic strength, pH, and diffusion rates.

L290: I believe that instead of Pankow, 2007 the reference should be to Mao, et al 2021.

We thank the reviewer for pointing this out. Corrected.

L303: “These positive potentials indicate”

Corrected.

L356-357: Replace M with Hg in chemicals formulas, as you focus solely on one metal – mercury – in this review

Corrected.

L370: Replace “it is mainly in hexavalent form” with “the sulfur it is mainly present in hexavalent form”

Replaced.

L371-373: “Whose presence in AOM is not universal”, “which is not relevant in this context”,

Replaced.

“questionable to apply speciation by geochemical equilibrium modeling”. The meaning is not clear. Why is it questionable? In which context? For what specific reason?

The term geochemical, which includes both the solid Earth and the atmosphere, causes confusion. We have revised the sentence to use the more specific term geospheric:

"Therefore, the application of speciation by equilibrium modeling based on a geospheric basis to assess the interaction between atmospheric DOM and Hg^{II} , as in some studies, is questionable".

L377: Replace “speciation is controlled” with “speciation is represented”

Replaced.

L380: What does “It” refer to?

We feel that the sentence structure and referencing here is substandard and have made the following change:

"In this regard, Yang et al. used complexation with fulvic acids under conditions of binding to predominantly O-donors (1:2 complexes with $\log\beta = 5.6$, Haitzer et al., 2002) as a surrogate for Hg^{II} -AOM interaction, which, when applied, was found to dominate overall Hg^{II} speciation of rural and urban rainwater samples in France (Yang et al., 2019)."

L385: What do you mean by “less constrained”?

We have again failed to formulate ourselves well and decided to rearrange the sentence.

"In conclusion, until the complexation of Hg^{II} with AOM is well understood, there is considerable uncertainty regarding the partitioning of aquatic Hg^{II} between stable and reduction labile complexes in the photic atmosphere."

Table 1: Elemental mercury is shown as a ligand in the first row. Does it indeed complex with Hg^{2+} ? Is it just complexation or a redox reaction?

The line concerns the reverse of the equilibrium introduced on L349, in which Hg^{2+} and Hg^0 comproportionate into Hg_2^{2+} .

L401: Clarify what you mean by “in the electronic ground state of atmospheric importance”. Perhaps “in the electronic ground state” would be sufficient.

We agree and have adjusted accordingly.

Table 2: Are photolysis rates calculated using the global annual average photon flux? There is an extra O₂ among the products in Reactions G22b and G22c.

The calculations are indeed based on this flux. This information has been included in the caption of Table 3. **Rxn G22** is actually without branching. The last two entries (**Rxn G22b & c**) are completely wrong and the products listed are derived from **Rxn G25a & b**. We have corrected this gross error.

L542: “och”?

‘och’ is Swedish for ‘and’. This embarrassing error has been corrected.

L559: Replace “obsolete” with a more appropriate word

We have replaced “obsolete” with “infeasible” in a sentence that now reads:

“..., was considered infeasible by theoretical calculations due to steric hindrance.”

L580: Clarify what you mean by “speciated”

We have replaced “speciated Hg” with “GOM” in a sentence that now reads:

“Field observations of GOM in urban air may suggest...”

L584-586: Simplify the sentence, e.g., “HgX can neither abstract hydrogen atoms from volatile organic compounds nor add to double bonds”.

“Finally, it should be noted that the reactivity of •Hg^IX towards volatile hydrocarbons is rather low, as •Hg^IX does not abstract a hydrogen atom from an alkane (e.g., from CH₄) nor does it significantly add to a double bond of an alkene (e.g., to CH₂=CH₂).”

L889: Rewrite, e.g., “Although atmospheric generally more stable than Hg(I) species, Hg(II) species are still labile and the atmospheric pool”

Rewritten

L592: “indicated”

Corrected.

L596: I suggest to clarify that BrHgY are molecules while XHgO are radicals, e.g., “Mixed compounds such as BrHg^{II}Y molecules (Y = ONO, OOH, OH, OCl, OBr etc.) and XHg^IO• radicals (X = Br, OH)”

OK! Revised.

L607: “computer-assisted theoretical calculations” – be more specific

We have changed from “computer-assisted theoretical calculations” to “computer-aided calculations based on 2D potential energy surfaces”

L609: Did you mean that “Photolysis of BrHgONO forms NO and BrHgO”?

Yes, corrected!

L614: What do tilde means in O~O~H?

Tilde indicates that the bond is unstable. We have adjusted (sic) “•Hg^IBr + O~O~H (2%)” to “•Hg^IBr + O~O~H (≤3%)”, thus including both of the •Hg^IBr + O + •OH (2%) and •Hg^IBr + •OOH (≤1%) product channels.

L636: Consider revising “The enthalpy of thermal decay of HgO is weakly endothermic”, as for diatomic molecules thermal dissociation is always endothermic. Did you mean “only weakly endothermic”?

We are grateful for this comment, and have revised the sentence to read ad notam.

L646: “marginal” – did you mean “scarce”?

Yes, corrected!

L647: Rephrase “computational calculations”

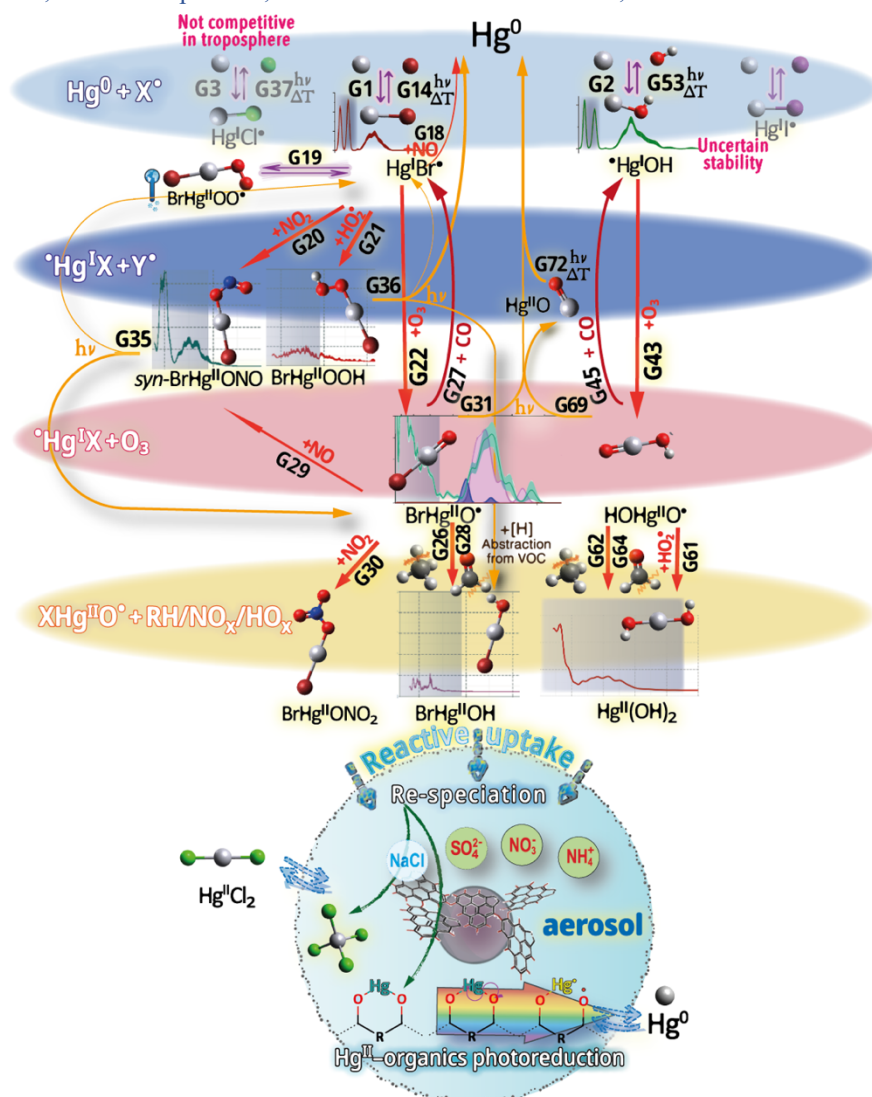
This sentence has been rephrased as well as expanded.

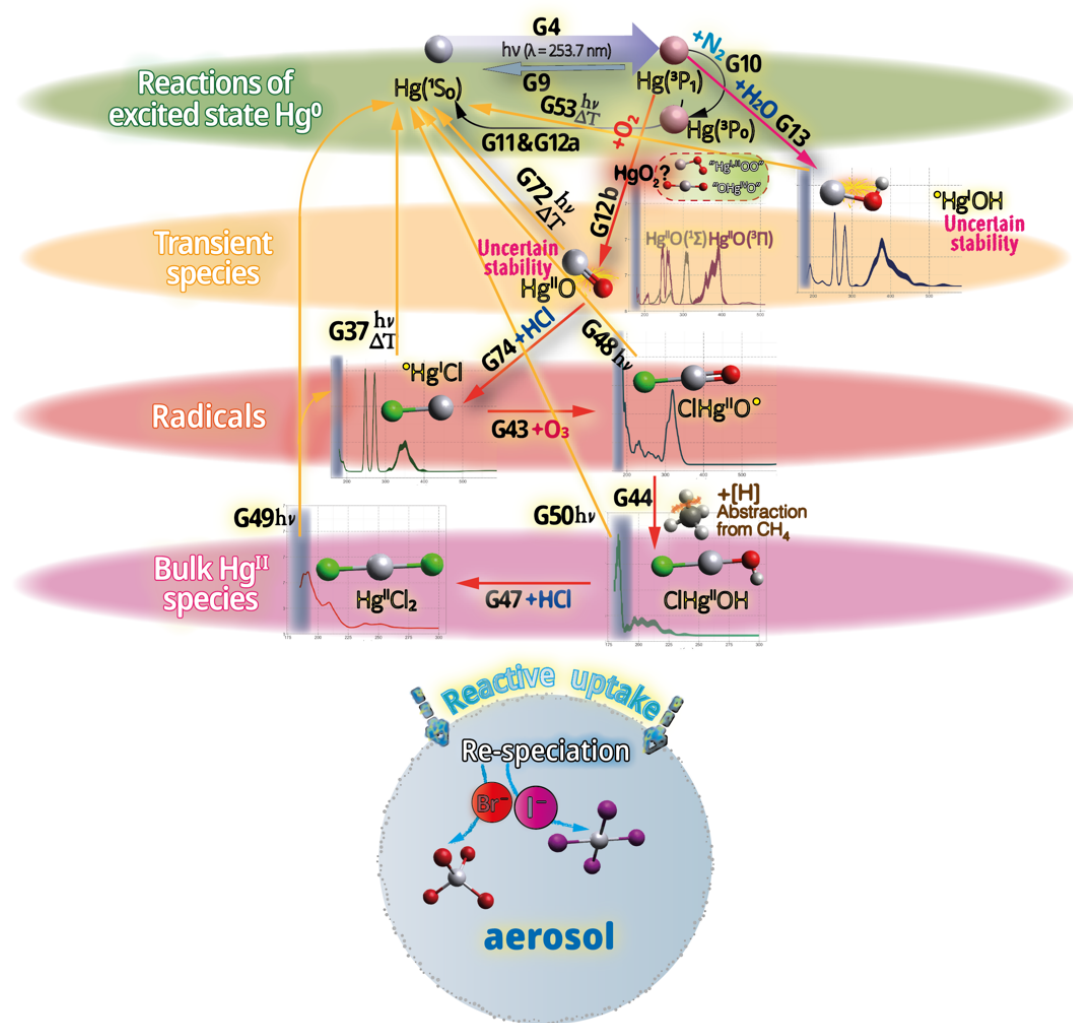
“Initially, the focus of computer simulations was on the bromine analog and its reactions. Later, the scope was expanded to include the thermochemistry for the hydroxyl and chlorine analogs, which will be recapitulated below.”

Figure 6: add a citation to the source of this figure.

Added to the caption: Adopted from Sun et al. (2016).

Figure 7: It looks pretty but highly overloaded and messy, making it hard to read. Consider removing molecular structures, keeping only the formulas. Spectra look aesthetically nice, but also complicate the figure. Aim at striking a balance between prettiness and legibility. The same applies to several following figures. In this figure caption, I would not put NO_2 , BrO and OH as abundant radicals, as their concentrations are vastly different.





Revised figures 7 and 9 are attached above. Part of the caption to the former figure has been reworded as follows:

“... but also by radicals (in descending order of abundance) such as $\text{NO}_2 > \text{HO}_2 > \text{BrO} \approx \text{OH}$ etc. It should be noted that NO cannot efficiently oxidize...”

L739: “elemental oxygen”

We agree with this and change from "molecular" to "elemental".

L760: Instead of asterisk provide the specific state of O_2

The state $\text{O}_2(^3\Sigma_u^+)$ has been inserted in Rxn 5 & 6.

L775: “less energetic than the reactants” – awkward, consider revising.

Revised to “lower in energy...”

L789: Is it the excited HgO ?

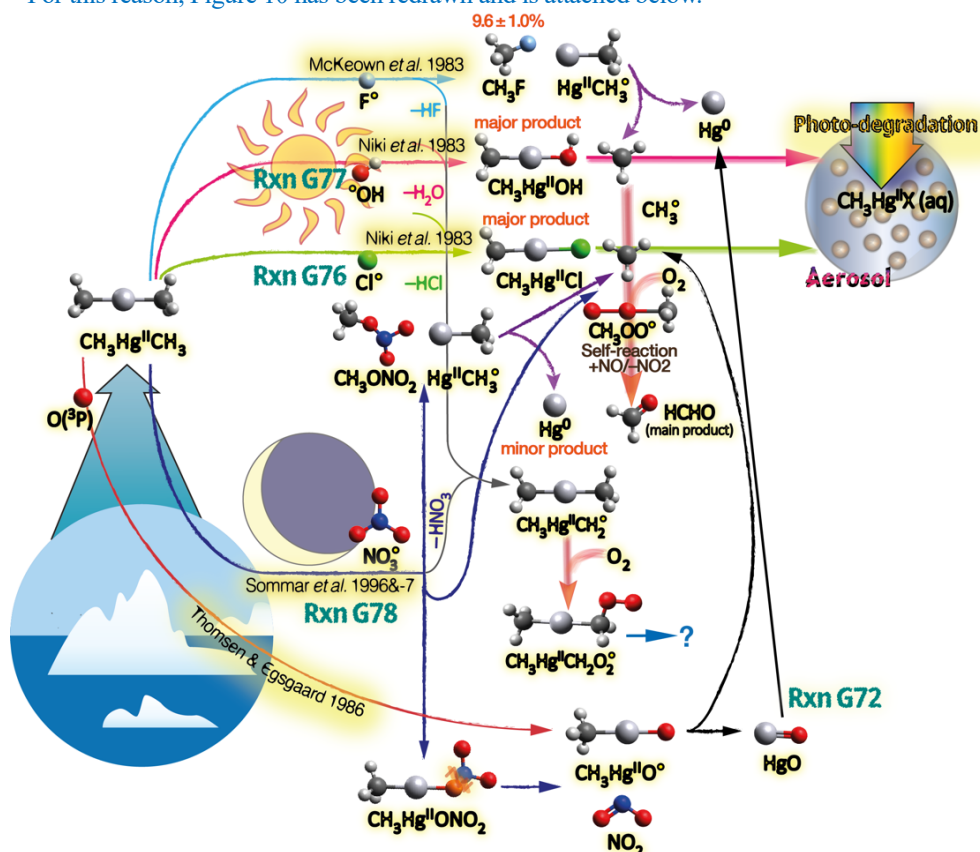
$\text{HgO}(^3\Pi)$ is the ground state.

L819: “automatically measured” is confusing. Is “automatically” important here?

No, we delete “automatically”.

Figure 10: The pathway resulting in polymerization of HgO is inconsistent with its extremely short lifetime and extremely low concentration under typical atmospheric conditions, even in the stratosphere.

It was premature and incorrect to indicate that the clustering of HgO would have some atmospheric significance. For this reason, Figure 10 has been redrawn and is attached below.



L861: I highly doubt that the MMHg^+ cation can be volatilized. Did you mean a species with its counter-anion, e.g., MMHgCl ?

" MMHg^+ species" refers to the series of chemical compounds containing MMHg^+ group. For clarification, we have added "(e.g., MMHgCl)" to the sentence.

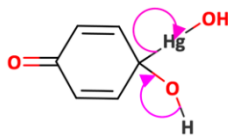
Table 4: W17 appears to show a wrong reaction mechanism

As stated in footnote 32, the actual reductant is provisionally determined to be a hydroxylated reduced form that emerges as a consequence of solution irradiation, rather than AQDS. The reaction formula provided is of a schematic nature rather than being exhaustive.

L1025: Is this a dark reaction? What do you mean by "divergent"? Divergent in what sense?

No, the reaction is totally photolytic. We've changed "strongly divergent" to "much larger".

Rxn10: flip the second structure horizontally



L1130-1131: This sentence is bizarre. Clarify why that literature is irrelevant to the atmosphere.

We have clarified with the following revised text:

Despite a wealth of studies addressing the multiphase chemical or physical transformation of Hg under processes such as those under simulated post-combustion conditions, which undoubtedly pertain to the interaction with certain environmental surfaces, the findings offer limited insight into the surface and heterogeneous atmospheric Hg chemistry. The subsequent chapter will address the studies that have been identified as contributing meaningfully to the advancement of understanding in this domain.

L1181: Define “FF”

The term "FF" (fast flow) has been previously defined (line 281). Would you consider this to be sufficient?

L1229: “its freezing point” – water freezing point?

No, revised into “the freezing point of the metal”.

L1240: As written, this contradicts the information given in the previous paragraph (L1235) that adsorption reduces the energy required for photoreduction. Consider rephrasing.

The reviewer's comment eludes us here. We don't understand what is contradictory or wrong.

L1251: A second order rate constant is given for a photolytic process. Why? Is this reaction limited by the rate of the complex formation? Does it depend on light intensity and wavelength? Please clarify.

According to the reference, it is evident that all experiments were conducted under conditions of a total irradiance of 99 W m^{-2} , within the wavelength range of 300 to 420 nm. This indicates that the experiments were performed without any variation in either wavelength or intensity. The variables of interest included pH, chemical composition (with the exception of the 60 nM Hg^{II} doping, which was constant), and temperature. The complexity of evaluating the pseudo-first order rate constant (k') in the disappearance of Hg^{II} prompted the study to employ the mean values of k' scaling linearly with [org] and to present the result in the form of an apparent bimolecular rate constant. In light of the study's remarkably scattered data, our revision is as follows:

“... the release of Hg^0 , which was most rapid in the presence of benzophenone at high pH.”

L1273: Replace “means” with “tweezer”

Replaced.

L1363: “Parenthesized”?

“The prevailing practice of expressing isotope ratios relative to the lightest stable isotope for each element is not applicable to Hg due to the rarity of ^{196}Hg (0.15% occurrence)”.

L1204 and L1407: Consider sticking to a single term (NFS vs NVF).

We stick to NFS and made 19 changes accordingly.

L1581: “Antarctica are interpreted”

where it says “interpreted as originating” it should just say “originate”

Appendix

List of symbols and acronyms

Symbol	Quantity	Unit etc.
α	mass accommodation coefficient	dimensionless
$\alpha^{xxx/198}$	fractionation factor of the Hg isotope with mass number xxx (relative to 198)	
α_{A-B}	$\equiv \alpha^{xxx/198}_{A-B}$, isotope fractionation factor between any two parts (chemicals, phases etc.) of a system	
β^{xxx}	$\equiv \beta^{xxx/198}$, scaling factor for an isotope effect acting on the Hg isotope with mass number xxx.	
β_{NFS}	$\equiv \beta^{xxx/198}_{NFS}$, scaling factor for NFS acting on the Hg isotope with mass number xxx.	
$\beta_{EIE-MDF}$	$\equiv \beta^{xxx/198}_{EIE-MDF}$, scaling factor for equilibrium MDF acting on the Hg isotope with mass number xxx.	
$\beta_{KIE-MDF}$	$\equiv \beta^{xxx/198}_{EIE-MDF}$, scaling factor for kinetic MDF acting on the Hg isotope with mass number xxx.	
β_{qr}	cumulative stability coefficient for a complex of the type $\{\text{HgL}_q(\text{OH})_r\}^{(2-r)+}$	miscellaneous
γ	uptake coefficient (probability)	dimensionless
γ_{net}^0	initial net uptake coefficient (probability)	
$\gamma_{\text{net}}^\infty$	steady-state net uptake coefficient (probability)	
$\delta^{xxx}\text{Hg}$	δ -notation for the ^{xxx}Hg isotope composition in a sample relative to that of the NIST3133 standard.	dimensionless (‰)
$\delta^{202}\text{Hg}$	δ -notation to describe total mass-dependent fractionation	
δ_A, δ_B	δ -notation for an isotope in reservoir A and B, respectively	
δ_0	$\equiv (\delta^{xxx}\text{Hg})_0$, initial $\delta^{xxx}\text{Hg}$ of a process	
$\Delta^{xxx}\text{Hg}$	Δ -notation, deviation from mass dependence ($\delta^{202}\text{Hg}$) of the Hg isotope with mass number xxx.	
$\epsilon^{xxx}\text{Hg}$	enrichment factor for an Hg isotope with mass number xxx.	
ϵ_{A-B}	enrichment factor for an isotope between two reservoirs A and B.	dimensionless
$E^{xxx}\text{Hg}$	enrichment factor for an Hg isotope of mass number xxx for the mass-independent part of a process.	
Γ_g	conductance (= 1/resistance) of diffusion of a gas to the surface in a resistance model of gas-droplet interaction.	
Γ_{rxn}	conductance (= 1/resistance) of reaction in the liquid phase in a resistance model of gas-droplet interaction.	dimensionless
Γ_{sol}	conductance (= 1/resistance) of solubility and diffusion in the liquid phase in a resistance model of gas-droplet interaction.	
λ	wavelength of light	nm
σ	absorption cross section	$\text{cm}^2 \text{ molecule}^{-1}$
τ	atmospheric lifetime	s
\bar{v}_X	mean thermal velocity of a gas X	m s^{-1}
ϕ	photolysis quantum yield	dimensionless
c	$\equiv c^{\text{Hg}^0}, c^{\text{Hg}^0}_{\text{index}}$, gas-phase mass concentration normalized to standard temperature (0 °C) and pressure (101.325 kPa).	ng m^{-3}
a	parameter for T dependence of K_{gp}	dimensionless
b	parameter for T dependence of K_{gp}	
D_g	gas-phase diffusion coefficient	$\text{m}^2 \text{ s}^{-1}$
D_l	liquid-phase diffusion coefficient	$\text{m}^2 \text{ s}^{-1}$
E^0	standard electrode potential	V
E	electrode potential	
E_a	activation energy	J mol^{-1}
f	fraction (isotope mixing)	dimensionless

f_R	fraction of reactant remaining	
F	Faraday constant	96485 C mol^{-1}
F_c	form factor describing the transition region of a gas-phase reaction, typically ~ 0.7	dimensionless
$F(\lambda)$	photon flux	$\text{photons cm}^2 \text{ s}^{-1}$
ΔG_R	Gibbs free energy of reaction	J mol^{-1}
ΔG^0	standard Gibbs free energy	
ΔH_f	enthalpy of formation	
ΔH_R	enthalpy of reaction	
ΔH_{ads}^0	standard enthalpy of adsorption	
J_X	net flux of the gas X into the condensed phase	$\text{mol m}^{-2} \text{ s}^{-1}$
$k, k(T)$	rate coefficient	miscellaneous
k_0	$\equiv k_0^T$, low-pressure limit gas-phase rate coefficient	$\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$
k_∞	$\equiv k_\infty^T$, high-pressure limit gas-phase rate coefficient	$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
k_f	forward rate coefficient	miscellaneous
k_r	reverse rate coefficient	
k_{H}^{cc}	Henry's law coefficient	dimensionless
k_{H}^{cp}	Henry's law coefficient	$\text{mol L}^{-1} \text{ atm}^{-1}$
k_{ads}	adsorption rate coefficient	miscellaneous
k_{des}	desorption rate coefficient	
k_{het}	heterogeneous rate coefficient	
k_{obs}	effective first-order rate constant	s^{-1}
k_{gas}	bimolecular rate coefficient of the gas phase part of a partially heterogeneous reaction	$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
k_{surf}	surface bimolecular rate coefficient (normalized by reactor surface-volume ratio)	$\text{cm}^4 \text{ molecule}^{-1} \text{ s}^{-1}$
K_a	acid constant ($\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$)	mol L^{-1}
K_{gp}	coefficient for absorptive partitioning of GOM onto existing aerosol	$\text{m}^3 \mu\text{g}^{-1}$
K_q	stepwise stability coefficient for a $\text{HgL}_{q-1} + \text{L} \rightleftharpoons \text{HgL}_q$ type equilibrium	L mol^{-1}
$[M]$	third body concentration	molecule cm^{-3}
m	empirically fitted exponent	dimensionless
m_{xxx}	mass of the isotope $^{\text{xxx}}\text{Hg}$	amu
n	number of electrons transferred in a red-ox reaction	mol
$\Delta N / \Delta \log r$	particle number concentration in the size range $\Delta \log r$ (log-normal distributed polydisperse aerosol)	m^{-3}
pK	$-\log K$	dimensionless
pK_a	$-\log(K_a)$	
PM	particulate matter	$\mu\text{g m}^{-3}$
r	radius (droplet or tubular reactor)	m
$\langle r_{\text{xxx}}^2 \rangle$	mean-square nuclear charge radius	fm^2
R	gas constant	$8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
$R^{\text{xxx}/198}$	ratio of isotope xxx to isotope 198	dimensionless
ΔS_{ads}^0	enthropy of adsorption	$\text{J mol}^{-1} \text{ K}^{-1}$
T	absolute temperature	K
V	volume	m^3
$[X]_{\text{g},\infty}$	background (bulk) gas-phase concentration of species X	mol m^{-3}
$[X]_{\text{surf}}$	$[X]_{\text{g}}$ at the surface of a droplet	
$[X]_{\text{g}}$	gas-phase concentration of species X	
$[X]_{\text{p}}$	particle-phase concentration of species X	

Acronym	Plain text
AAS	atomic absorption spectroscopy
AMDE	atmospheric mercury depletion event
AOM	atmospheric organic matter
AQ	anthraquinone
CFPP	coal-fired power plant
CI-MS	chemical ionization mass spectrometry
CV-AFS	cold vapor atomic fluorescence spectroscopy
DFC	dynamic flux chamber
DMHg	dimethylmercury
DOM	dissolved organic matter
EIE	equilibrium isotope effect
EIE-MDF	equilibrium MDF
even-MIF	mass-independent fractionation of even Hg isotope (^{200}Hg , ^{204}Hg)
FEP	polymeric fluorinated ethylene propylene
FF	fast flow reactor, chemical reactor designed for rapid mixing and reaction of gases or liquids
FF-ID-CI-MS	fast flow ion-drift chemical ionization mass spectrometry
FT-IR	Fourier Transform Infrared
GOM	$\equiv \text{Hg}^{\text{II}}(\text{g})$, gaseous oxidized mercury
HMDE	hanging mercury drop electrode
HFC	hyperfine coupling
KIE	kinetic isotope effect
KIE-MDF	kinetic MDF
LIDAR	light detection and ranging
LMCT	ligand to metal charge transfer
LMWO	low molecular weight organics
LOD	limit of detection
MDF	mass-dependent fractionation
MgIE	magnetic isotope effect (acting on ^{199}Hg , ^{201}Hg)
MIF	mass-independent fractionation
MMHg^+	species containing a methyl mercuric cation and an unspecified counter-anion.
m/m	mass-to-mass ratio
M/M	mol-to-mol (stoichiometric) ratio
MRB	metal-reducing bacteria
MS	mass spectroscopy
NFS	nuclear field shift, synonym for NVE
NVE	nuclear volume effect, synonym for NFS
odd-MIF	mass-independent fractionation of odd Hg isotope (^{199}Hg , ^{201}Hg)
PBM	$\equiv \text{Hg}^{\text{II}}(\text{p})$, particle-bound mercury
PLP-LIF	pulsed laser photolysis-laser induced fluorescence
PM	particulate matter, synonym for TSP
$\text{PM}_{2.5}$	particulate matter $\leq 2.5 \mu\text{m}$
PM_{10}	particulate matter $\leq 10 \mu\text{m}$
POA	primary organic aerosol
PTR-MS	proton transfer reaction mass spectroscopy
RH	relative humidity (% of absolute humidity)

RKKM	Rice-Ramsperger-Kassel-Markus (theory)
RM	reactive mercury (GOM + PBM)
RR	determination of rate constant by a relative rate method, opposite to an absolute determination
Rxn	abbreviation for reaction, representing a chemical reaction
SOA	secondary organic aerosols
STP	standard temperature and pressure (one atmosphere (101.325 kPa) and 0 °C)
TAM	total atmospheric mercury (Hg^0 + GOM + PBM)
TGM	total gaseous mercury (Hg^0 + GOM), in practice not quantitative for GOM
TSP	total suspended particles, all particle sizes suspended in the air
TS	transition state
TST	transition state theory
UV-A	ultraviolet A, 315 – 400 nm
UV-B	ultraviolet B, 280 – 315 nm
UV-C	ultraviolet C, 100 – 280 nm, also called deep UV
UV-VIS	ultraviolet (A + B) + visible light (400 – 700 nm)

References

- Agnan, Y., Le Dantec, T., Moore, C. W., Edwards, G. C., and Obrist, D.: New constraints on terrestrial surface-atmosphere fluxes of gaseous elemental mercury using a global database, *Environmental Science & Technology*, 50, 507 - 520, 10.1021/acs.est.5b04013, 2016.
- Amos, H. M., Sonke, J. E., Obrist, D., Robins, N., Hagan, N., Horowitz, H. M., Mason, R. P., Witt, M., Hedgecock, I. M., Corbitt, E. S., and Sunderland, E. M.: Observational and Modeling Constraints on Global Anthropogenic Enrichment of Mercury, *Environmental Science & Technology*, 49, 4036-4047, 10.1021/es5058665, 2015.
- Andrews, L., Wang, X., Gong, Y., Schloeder, T., Riedel, S., and Franger, M. J.: Spectroscopic observation of a group 12 oxyfluoride: A matrix-isolation and quantum-chemical investigation of mercury oxyfluorides, *Angewandte Chemie-International Edition*, 51, 8235-8238, 10.1002/anie.201204331, 2012.
- Andrews, L. S., Tsegaw, Y. A., Cho, H.-G., and Riedel, S.: Observation and characterization of the Hg-O diatomic molecule: A matrix-isolation and quantum-chemical investigation, *Chemistry – A European Journal*, 29, e202202740, <https://doi.org/10.1002/chem.202202740>, 2023.
- Ariya, P. and Peterson, K. A.: Chemical transformation of gaseous elemental mercury in the atmosphere, in: *Dynamics of Mercury Pollution on Regional and Global Scales: Atmospheric Processes and Human Exposures Around the World*, edited by: Pirrone, N., and Mahaffey, K. R., Springer, 261-294, 2005.
- Ariya, P. A., Skov, H., Grage, M. M. L., and Goodsite, M. E.: Gaseous elemental mercury in the ambient atmosphere: Review of the application of theoretical calculations and experimental studies for determination of reaction coefficients and mechanisms with halogens and other reactants, in: *Advances in Quantum Chemistry: Applications of Theoretical Methods to Atmospheric Science*, edited by: Sabin, J. R., and Brandas, E. J., Academic Press, 43-55, 10.1016/s0065-3276(07)00204-3, 2008.
- Ariya, P. A., Amyot, M., Dastoor, A., Deeds, D., Feinberg, A., Kos, G., Poulain, A., Ryjkov, A., Semeniuk, K., Subir, M., and Toyota, K.: Mercury Physicochemical and Biogeochemical Transformation in the Atmosphere and at Atmospheric Interfaces: A Review and Future Directions, *Chemical Reviews*, 10.1021/cr500667e, 2015.
- Bencardino, M., D'Amore, F., Angot, H., Angiuli, L., Bertrand, Y., Cairns, W., Diéguez, M. C., Dommergue, A., Ebinghaus, R., Esposito, G., Komínková, K., Labuschagne, C., Mannarino, V., Martin, L., Martino, M., Neves, L. M., Mashyanov, N., Magand, O., Nelson, P., Norstrom, C., Read, K., Sholupov, S., Skov, H., Tassone, A., Vítková, G., Cinnirella, S., Sprovieri, F., and Pirrone, N.: Patterns and trends of atmospheric mercury in the GMOS network: Insights based on a decade of measurements, *Environmental Pollution*, 363, 125104, <https://doi.org/10.1016/j.envpol.2024.125104>, 2024.

Butler, R., Katz, S., Snelson, A., and Stephens, J. B.: Identification of HgO_x species by matrix-isolation spectroscopy, *Journal of Physical Chemistry*, 83, 2578-2580, 1979.

Carpi, A.: Mercury from combustion sources: A review of the chemical species emitted and their transport in the atmosphere, *Water Air and Soil Pollution*, 98, 241-254, 1997.

Cheng, I., Xu, X., and Zhang, L.: Overview of receptor-based source apportionment studies for speciated atmospheric mercury, *Atmospheric Chemistry and Physics*, 15, 7877-7895, 10.5194/acp-15-7877-2015, 2015.

Cheng, Y. C., Watari, T., Seccatore, J., Nakajima, K., Nansai, K., and Takaoka, M.: A review of gold production, mercury consumption, and emission in artisanal and small-scale gold mining (ASGM), *Resources Policy*, 81, 3370-3370, 10.1016/j.resourpol.2023.103370, 2023.

Chertihin, G. V. and Andrews, L.: Reactions of laser-ablated Zn and Cd atoms with O_2 : Infrared spectra of ZnO, OZnO , CdO, and OCdO in solid argon, *Journal of Chemical Physics*, 106, 3457-3465, 10.1063/1.473441, 1997.

Cooke, C. A., Martínez-Cortizas, A., Bindler, R., and Gustin, M. S.: Environmental archives of atmospheric Hg deposition - A review, *Science of the Total Environment*, 709, 10.1016/j.scitotenv.2019.134800, 2020.

Custódio, D., Pfaffhuber, K. A., Spain, T. G., Pankratov, F. F., Strigunova, I., Molepo, K., Skov, H., Bieser, J., and Ebinghaus, R.: Odds and ends of atmospheric mercury in Europe and over the North Atlantic Ocean: temporal trends of 25 years of measurements, *Atmospheric Chemistry and Physics*, 22, 3827-3840, 10.5194/acp-22-3827-2022, 2022.

Davis, M. and Lu, J. L.: Calibration Sources for Gaseous Oxidized Mercury: A Review of Source Design, Performance, and Operational Parameters, *Critical Reviews in Analytical Chemistry*, 54, 1748-1757, 10.1080/10408347.2022.2131373, 2024.

Dommergue, A., Sprovieri, F., Pirrone, N., Ebinghaus, R., Brooks, S., Courteaud, J., and Ferrari, C. P.: Overview of mercury measurements in the Antarctic troposphere, *Atmospheric Chemistry and Physics*, 10, 3309-3319, 2010.

Edirappulige, D. T. H., Kirby, I. J., Beckett, C. K., and Dibble, T. S.: Atmospheric chemistry of $\text{HOHg}^{\text{II}}\text{O}^\bullet$ mimics that of a hydroxyl radical, *Journal of Physical Chemistry A*, 10.1021/acs.jpca.3c04159, 2023.

Edwards, B. A., Kushner, D. S., Outridge, P. M., and Wang, F.: Fifty years of volcanic mercury emission research: Knowledge gaps and future directions, *The Science of the total environment*, 757, 143800-143800, 10.1016/j.scitotenv.2020.143800, 2021.

Elgiar, T. R., Gratz, L., Hallar, A. G., Volkamer, R., and Lyman, S. N.: Underestimation of atmospheric oxidized mercury at a mountaintop site by the GEOS-Chem chemical transport model, *EGUsphere*, 2025, 1-23, 10.5194/egusphere-2025-977, 2025.

Fu, X., Jiskra, M., Yang, X., Maruszczak, N., Enrico, M., Chmieleff, J., Heimbürger-Boavida, L.-E., Gheusi, F., and Sonke, J. E.: Mass-Independent Fractionation of Even and Odd Mercury Isotopes during Atmospheric Mercury Redox Reactions, *Environmental Science & Technology*, 55, 10164-10174, 2021.

Fu, X. Personal communication

Fu, X., Sun, X., Travníkov, O., Li, Q., Qin, C., Cuevas, C. A., Fernandez, R. P., Mahajan, A. S., Wang, S., Wang, T., and Saiz-Lopez, A.: Anthropogenic short-lived halogens increase human exposure to mercury contamination due to enhanced mercury oxidation over continents, *Proceedings of the National Academy of Sciences*, 121, e2315058121, doi:10.1073/pnas.2315058121, 2024.

Fu, X. W., Zhang, H., Yu, B., Wang, X., Lin, C.-J., and Feng, X. B.: Observations of atmospheric mercury in China: a critical review, *Atmospheric Chemistry & Physics*, 15, 9455-9476, <https://doi.org/10.5194/acp-15-9455-2015>, 2015.

Gustin, M. S., Amos, H. M., Huang, J., Miller, M. B., and Heidecorn, K.: Measuring and modeling mercury in the atmosphere: A critical review, *Atmospheric Chemistry and Physics*, 15, 5697 - 5713, 2015.

Gustin, M. S., Dunham-Cheatham, S. M., Allen, N., Choma, N., Johnson, W., Lopez, S., Russell, A., Mei, E. R., Magand, O., Dommergue, A., and Elgiar, T.: Observations of the chemistry and concentrations of reactive Hg at locations with different ambient air chemistry, *Science of the Total Environment*, 904, ARTN 166184, 10.1016/j.scitotenv.2023.166184, 2023.

Gustin, M. S., Dunham-Cheatham, S. M., Lyman, S., Horvat, M., Gay, D. A., Gacnik, J., Gratz, L., Kempkes, G., Khalizov, A., Lin, C.-J., Lindberg, S. E., Lown, L., Martin, L., Mason, R. P., Macsween, K., Nair, S. V., Nguyen, L. S. P., O'Neil, T., Sommar, J., Zhang, L.,

Weiss-Penzias, P., and Zivkovic, I.: Measurement of atmospheric mercury: Current limitations and suggestions for paths forward, *Environmental Science & Technology*, 58, 12853-12864, 10.1021/acs.est.4c06011, 2024.

He, X.-C., Tham, Y. J., Dada, L., Wang, M., Finkenzeller, H., Stolzenburg, D., Iyer, S., Simon, M., Kürten, A., Shen, J., Rörup, B., Rissanen, M., Schobesberger, S., Baalbaki, R., Wang, D. S., Koenig, T. K., Jokinen, T., Sarnela, N., Beck, L. J., Almeida, J., Amanatidis, S., Amorim, A., Ataei, F., Baccarini, A., Bertozzi, B., Bianchi, F., Brilke, S., Caudillo, L., Chen, D., Chiu, R., Chu, B., Dias, A., Ding, A., Dommen, J., Duplissy, J., El Haddad, I., Gonzalez Carracedo, L., Granzin, M., Hansel, A., Heinritzi, M., Hofbauer, V., Junninen, H., Kangasluoma, J., Kempainen, D., Kim, C., Kong, W., Krechmer, J. E., Kvashin, A., Laitinen, T., Lamkaddam, H., Lee, C. P., Lehtipalo, K., Leiminger, M., Li, Z., Makhmutov, V., Manninen, H. E., Marie, G., Marten, R., Mathot, S., Mauldin, R. L., Mentler, B., Möhler, O., Müller, T., Nie, W., Onnela, A., Petäjä, T., Pfeifer, J., Philippov, M., Ranjithkumar, A., Saiz-Lopez, A., Salma, I., Scholz, W., Schuchmann, S., Schulze, B., Steiner, G., Stozhkov, Y., Tauber, C., Tomé, A., Thakur, R. C., Väisänen, O., Vazquez-Pufleau, M., Wagner, A. C., Wang, Y., Weber, S. K., Winkler, P. M., Wu, Y., Xiao, M., Yan, C., Ye, Q., Ylisirniö, A., Zauner-Wieczorek, M., Zha, Q., Zhou, P., Flagan, R. C., Curtius, J., Baltensperger, U., Kulmala, M., Kerminen, V.-M., Kurtén, T., Donahue, N. M., Volkamer, R., Kirkby, J., Worsnop, D. R., and Sipilä, M.: Role of iodine oxoacids in atmospheric aerosol nucleation, *Science*, 371, 589-595, 10.1126/science.abe0298, 2021.

Huang, J., Lyman, S. N., Hartman, J. S., and Gustin, M. S.: A review of passive sampling systems for ambient air mercury measurements, *Environmental Sciences: Processes and Impacts*, 16, 374-392, 2014.

Hynes, A. J., Donohoue, D. L., Goodsite, M. E., and Hedgecock, I. M.: Our current understanding of major chemical and physical processes affecting mercury dynamics in the atmosphere and at the air-water/terrestrial interfaces, in: *Mercury Fate and Transport in the Global Atmosphere - Emissions, Measurements and Models*, edited by: Mason, R. P., and Pirrone, N., Springer, 427 - 457, 2009.

Jayasekharan, T. and Sahoo, N. K.: Mercury mono oxide cluster ions $(\text{HgO})_n^+$ by laser desorption ionization time of flight mass spectrometry, *Journal of Mass Spectrometry*, 49, 248-250, 2014.

Khiri, D., Louis, F., Cernusak, I., and Dibble, T. S.: $\text{BrHgO}^+ + \text{CO}$: Analogue of OH plus CO and reduction path for Hg(II) in the atmosphere, *ACS Earth and Space Chemistry*, 4, 1777-1784, 2020.

Koenig, T. K., Baidar, S., Campuzano-Jost, P., Cuevas, C. A., Dix, B., Fernandez, R. P., Guo, H., Hall, S. R., Kinnison, D., Nault, B. A., Ullmann, K., Jimenez, J. L., Saiz-Lopez, A., and Volkamer, R.: Quantitative detection of iodine in the stratosphere, *Proceedings of the National Academy of Sciences*, 117, 1860-1866, doi:10.1073/pnas.1916828117, 2020.

Kwon, S. Y., Blum, J. D., Yin, R., Tsui, M. T.-K., Yang, Y. H., and Choi, J. W.: Mercury stable isotopes for monitoring the effectiveness of the Minamata Convention on Mercury, *Earth-Science Reviews*, 203, 103-111, 2020.

Lehtipalo, K., Nieminen, T., Schobesberger, S., Ehn, M., Kulmala, M., and Kerminen, V.-M.: How the understanding of atmospheric new particle formation has evolved along with the development of measurement and analysis methods, *Journal of Aerosol Science*, 184, 106494, <https://doi.org/10.1016/j.jaerosci.2024.106494>, 2025.

Lin, C.-J., Singhasuk, P., and Pehkonen, S. O.: Atmospheric Chemistry of Mercury, in: *Environmental Chemistry and Toxicology of Mercury*, edited by: Liu, G., Cai, Y., and O'Driscoll, N., John Wiley & Sons, Hoboken, New Jersey, 113 - 154, 2011.

Lin, C. J. and Pehkonen, S. O.: The chemistry of atmospheric mercury: a review, *Atmospheric Environment*, 33, 2067-2079, 1999.

Lin, C. J., Pongprueksa, P., Lindberg, S. E., Pehkonen, S. O., Byun, D., and Jang, C.: Scientific uncertainties in atmospheric mercury models I: Model science evaluation, *Atmospheric Environment*, 40, 2911-2928, 2006.

Lin, C. J., Pongprueksa, P., Russell Bullock Jr, O., Lindberg, S. E., Pehkonen, S. O., Jang, C., Braverman, T., and Ho, T. C.: Scientific uncertainties in atmospheric mercury models II: Sensitivity analysis in the CONUS domain, *Atmospheric Environment*, 41, 6544-6560, 2007.

Lindqvist, O. and Rodhe, H.: Atmospheric Mercury - a Review, *Tellus Series B-Chemical and Physical Meteorology*, 37, 136-159, 1985.

Lindqvist, O., Johansson, K., Aastrup, M., Andersson, A., Bringmark, L., Hovsenius, G., Håkanson, L., Iverfeldt, Å., Meili, M., and Timm, B.: Mercury in the Swedish Environment - Recent Research on Causes, Consequences and Corrective Methods, *Water Air and Soil Pollution*, 55, 1-261, 1991.

- Liu, Y., Liu, H., Guo, Y., Lu, D., Hou, X., Shi, J., Yin, Y., Cai, Y., and Jiang, G.: Atmospheric Hg(0) dry deposition over environmental surfaces: Insights from mercury isotope fractionation, *Eco-Environment & Health*, 10.1016/j.eehl.2024.04.009, 2024.
- Loewenschuss, A., Ron, A., and Schnepf, O.: Vibrational spectra of group IIB halides. II. The halides of cadmium and mercury, *Journal of Chemical Physics*, 50, 2502-2512, 10.1063/1.1671408, 1969.
- Lyman, S. N., Cheng, I., Gratz, L. E., Weiss-Penzias, P., and Zhang, L.: An updated review of atmospheric mercury, *Science of The Total Environment*, 707, 135575, 2020.
- Mao, H., Cheng, I., and Zhang, L.: Current understanding of the driving mechanisms for spatiotemporal variations of atmospheric speciated mercury: a review, *Atmospheric Chemistry & Physics*, 16, 12897-12924, 10.5194/acp-16-12897-2016, 2016.
- Maruszczak, N., Sonke, J. E., Fu, X., and Jiskra, M.: Tropospheric GOM at the Pic du Midi Observatory—Correcting bias in denuder based observations, *Environmental Science & Technology*, 51, 863-869, 10.1021/acs.est.6b04999, 2017.
- Martens, J., Uchtmann, H., and Hensel, F.: Homogeneous nucleation of mercury vapor, *The Journal of Physical Chemistry*, 91, 2489-2492, 10.1021/j100294a010, 1987.
- Murphy, D. M., Thomson, D. S., and Mahoney, M. J.: In situ measurements of organics, meteoritic material, mercury, and other elements in aerosols at 5 to 19 kilometers, *Science*, 282, 1664-1669, 1998.
- Murphy, D. M., Froyd, K. D., Schwarz, J. P., and Wilson, J. C.: Observations of the chemical composition of stratospheric aerosol particles, *Quarterly Journal of the Royal Meteorological Society*, 140, 1269-1278, 2014.
- Murphy, D. M., Hudson, P. K., Thomson, D. S., Sheridan, P. J., and Wilson, J. C.: Observations of mercury-containing aerosols, *Environmental Science & Technology*, 40, 3163-3167, 2006.
- Obrist, D., Kirk, J. L., Zhang, L., Sunderland, E. M., Jiskra, M., and Selin, N. E.: A review of global environmental mercury processes in response to human and natural perturbations: Changes of emissions, climate, and land use, *Ambio*, 47, 116-140, 10.1007/s13280-017-1004-9, 2018.
- Pandey, S. K., Kim, K. H., and Brown, R. J. C.: Measurement techniques for mercury species in ambient air, *TrAC - Trends in Analytical Chemistry*, 30, 899-917, 2011.
- Peterson, K. A., Shepler, B. C., and Singleton, J. M.: The group 12 metal chalcogenides: an accurate multireference configuration interaction and coupled cluster study, *Molecular Physics*, 105, 1139-1155, 2007.
- Saiz-Lopez, A., Acuña, A., Mahajan, A., Dávalos, J., Wuhu, F., Roca-Sanjuán, D., Carmona-García, J., Cuevas, C. A., Kinnison, D., Gomez Martin, J. C., Francisco, J., and Plane, J.: The Chemistry of mercury in the stratosphere, *Geophysical Research Letters*, 49, e2022GL097953, 10.1029/2022GL097953, 2022.
- Saiz-Lopez, A., Travnikov, O., Sonke, J. E., Thackray, C. P., Jacob, D. J., Carmona-Garcia, J., Frances-Monerris, A., Roca-Sanjuan, D., Acuna, A. U., Dávalos, J. Z., Cuevas, C. A., Jiskra, M., Wang, F., Bieser, J., Plane, J. M. C., and Francisco, J. S.: Photochemistry of oxidized Hg(I) and Hg(II) species suggests missing mercury oxidation in the troposphere, *Proceedings of the National Academy of Sciences of the United States of America*, 117, 30949-30956, 2020.
- Saiz-Lopez, A., Cuevas, C. A., Acuña, A. U., Añel, J. A., Mahajan, A. S., de la Torre, L., Feng, W., Dávalos, J. Z., Roca-Sanjuán, D., Kinnison, D. E., Carmona-García, J., Fernandez, R. P., Li, Q., Sonke, J. E., Feinberg, A., Martín, J. C. G., Villamayor, J., Zhang, P., Zhang, Y., Blaszcak-Boxe, C. S., Travnikov, O., Wang, F., Bieser, J., Francisco, J. S., and Plane, J. M. C.: Role of the stratosphere in the global mercury cycle, *Science Advances*, 11, eads1459, doi:10.1126/sciadv.ads1459, 2025.
- Schroeder, W. H. and Munthe, J.: Atmospheric mercury - An overview, *Atmospheric Environment*, 32, 809-822, 1998.
- Schroeder, W. H., Yarwood, G., and Niki, H.: Transformation Processes Involving Mercury Species in the Atmosphere - Results from a Literature Survey, *Water Air and Soil Pollution*, 56, 653-666, 1991.
- Selin, N. E.: Global Biogeochemical Cycling of Mercury: A Review, *Environment and Resources*, 10.1146/annurev.enviro.051308.084314, 2009.

Shah, V., Jacob, D., Thackray, C., Wang, X., Sunderland, E., Dibble, T., Saiz-Lopez, A., Cernusak, I., Kellö, V., Castro, P., Wu, R., and Wang, C.: Improved mechanistic model of the atmospheric redox chemistry of mercury, *Environmental Science & Technology*, 55, 14445 - 14456, 2021.

Shepler, B. C. and Peterson, K. A.: Mercury Monoxide: A Systematic investigation of its ground electronic state, *Journal of Physical Chemistry A*, 107, 1783-1787, 2003.

Si, L. and Ariya, P.: Recent Advances in Atmospheric Chemistry of Mercury, *Atmosphere*, 9, 76, 2018.

Si, L., Branfireun, B. A., and Fierro, J.: Chemical Oxidation and Reduction Pathways of Mercury Relevant to Natural Waters: A Review, *Water*, 14, 10.3390/w14121891, 2022.

Sipilä, M., Sarnela, N., Jokinen, T., Henschel, H., Junninen, H., Kontkanen, J., Richters, S., Kangasluoma, J., Franchin, A., Peräkylä, O., Rissanen, M. P., Ehn, M., Vehkamäki, H., Kurten, T., Berndt, T., Petäjä, T., Worsnop, D., Ceburnis, D., Kerminen, V.-M., Kulmala, M., and O'Dowd, C.: Molecular-scale evidence of aerosol particle formation via sequential addition of HIO₃, *Nature*, 537, 532-534, 10.1038/nature19314, 2016.

Slemr, F., Brunke, E. G., Ebinghaus, R., Temme, C., Munthe, J., Wängberg, I., Schroeder, W., Steffen, A., and Berg, T.: Worldwide trend of atmospheric mercury since 1977, *Geophysical Research Letters*, 30, 23-21, 2003.

Sommar, J., Osterwalder, S., and Zhu, W.: Recent advances in understanding and measurement of Hg in the environment: Surface-atmosphere exchange of gaseous elemental mercury (Hg⁰), *Science of The Total Environment*, 721, 137648, 10.1016/j.scitotenv.2020.137648, 2020.

Sommar, J., Zhu, W., Lin, C. J., and Feng, X.: Field approaches to measure Hg exchange between natural surfaces and the atmosphere - A review, *Critical Reviews in Environmental Science and Technology*, 43, 1657-1739, 2013.

Sonke, J. E., Angot, H., Zhang, Y., Poulain, A., Björn, E., and Schartup, A.: Global change effects on biogeochemical mercury cycling, *Ambio*, 52, 853-876, 10.1007/s13280-023-01855-y, 2023.

Sprovieri, F., Pirrone, N., Ebinghaus, R., Kock, H., and Dommergue, A.: A review of worldwide atmospheric mercury measurements, *Atmospheric Chemistry and Physics*, 10, 8245-8265, 2010.

Stathopoulos, D.: Fractionation of mercury isotopes in an aqueous environment: Chemical oxidation, M. Sc. Thesis, Faculty of Arts and Science, Trent University, Peterborough, Canada, 77 pp., 2014.

Steffen, A., Lehnher, I., Cole, A., Ariya, P., Dastoor, A., Durnford, D., Kirk, J., and Pilote, M.: Atmospheric mercury in the Canadian Arctic. Part I: A review of recent field measurements, *Science of the Total Environment*, 509, 3-15, 2015.

Steffen, A., Douglas, T. A., Amyot, M., Ariya, P. A., Aspmo, K., Berg, T., Bottenheim, J., Brooks, S., Cobbett, F., Dastoor, A., Dommergue, A., Ebinghaus, R., Ferrari, C. P., Gårdfeldt, K., Goodsite, M. E., Lean, D. R., Poulain, A. J., Scherz, C., Skov, H., Sommar, J., and Temme, C.: A synthesis of atmospheric mercury depletion event chemistry linking atmosphere, snow and water, *Atmospheric Chemistry and Physics*, 8, 1445-1482, 2008.

Subir, M., Ariya, P. A., and Dastoor, A. P.: A review of uncertainties in atmospheric modeling of mercury chemistry I. Uncertainties in existing kinetic parameters - Fundamental limitations and the importance of heterogeneous chemistry, *Atmospheric Environment*, 45, 5664-5676, 2011.

Tevault, D., Strommen, D. P., and Nakamoto, K.: Reactions of mercury halides with carbon monoxide, nitric oxide, molecular nitrogen, and unsaturated hydrocarbons in argon matrices, *Journal of the American Chemical Society*, 99, 2997-3003, 10.1021/ja00451a024, 1977.

Subir, M., Ariya, P. A., and Dastoor, A. P.: A review of the sources of uncertainties in atmospheric mercury modeling II. Mercury surface and heterogeneous chemistry - A missing link, *Atmospheric Environment*, 46, 1-10, Doi 10.1016/J.Atmosenv.2011.07.047, 2012.

Travnikov, O., Angot, H., Artaxo, P., Bencardino, M., Bieser, J., D'Amore, F., Dastoor, A., De Simone, F., Diéguez, M. D., Dommergue, A., Ebinghaus, R., Feng, X. B., Gencarelli, C. N., Hedgecock, I. M., Magand, O., Martin, L., Matthias, V., Mashyanov, N., Pirrone, N., Ramachandran, R., Read, K. A., Ryjkov, A., Selin, N. E., Sena, F., Song, S., Sprovieri, F., Wip, D., Wängberg, I., and Yang, X.: Multi-model study of mercury dispersion in the atmosphere: atmospheric processes and model evaluation, *Atmospheric Chemistry and Physics*, 17, 5271-5295, 10.5194/acp-17-5271-2017, 2017.

Wang, Q., Zhang, L., Liang, X., Yin, X., Zhang, Y., Zheng, W., Pierce, E. M., and Gu, B.: Rates and dynamics of mercury isotope exchange between dissolved elemental Hg(0) and Hg(II) bound to organic and inorganic ligands, *Environmental Science & Technology*, 54, 15534-15545, 10.1021/acs.est.0c06229, 2020.

Wang, Y. W., Bartov, G., Wang, T., Reinfeldt, J. R., Johnson, T. M., and Yee, N.: Rapid attainment of isotopic equilibrium after mercury reduction by ferrous iron minerals and isotopic exchange between Hg(II) and Hg(0), *ACS Earth and Space Chemistry*, 5, 1384-1394, 10.1021/acsearthspacechem.1c00026, 2021.

Wang, X. F. and Andrews, L.: Infrared spectrum of Hg(OH)₂ in solid neon and argon, *Inorganic Chemistry*, 44, 108-113, 2005a.

Wang, X. F. and Andrews, L.: Mercury dihydride forms a covalent molecular solid, *Physical Chemistry Chemical Physics*, 7, 750-759, 2005b.

Wang, X. F., Andrews, L., Riedel, S., and Kaupp, M.: Mercury is a transition metal: The first experimental evidence for HgF₄, *Angewandte Chemie-International Edition*, 46, 8371-8375, 10.1002/anie.200703710, 2007.

Zhang, H.: Photochemical redox reactions of mercury, in: *Structure and Bonding* 120, edited by: Atwood, D. A., *Structure and Bonding*, 120, Springer, Berlin Heidelberg, 37-79, 10.1007/430_015, 2006.

Zhang, H., Fu, X. W., Wang, X., and Feng, X. B.: Measurements and Distribution of Atmospheric Particulate-Bound Mercury: A Review, *Bulletin of Environmental Contamination and Toxicology*, 103, 48-54, 10.1007/s00128-019-02663-5, 2019.

Zhang, L., Wright, L. P., and Blanchard, P.: A review of current knowledge concerning dry deposition of atmospheric mercury, *Atmospheric Environment*, 43, 5853-5864, 2009.

Zhang, L., Wang, S., Wu, Q., Wang, F., Lin, C. J., Zhang, L., Hui, M., Yang, M., Su, H., and Hao, J.: Mercury transformation and speciation in flue gases from anthropogenic emission sources: a critical review, *Atmospheric Chemistry & Physics*, 16, 2417-2433, 10.5194/acp-16-2417-2016, 2016.

Zheng, W., Demers, J. D., Lu, X., Bergquist, B. A., Anbar, A. D., Blum, J. D., and Gu, B. H.: Mercury Stable Isotope Fractionation during Abiotic Dark Oxidation in the Presence of Thiols and Natural Organic Matter, *Environmental Science & Technology*, 53, 1853-1862, 10.1021/acs.est.8b05047, 2019.

Zhou, J., Obrist, D., Dastoor, A., Jiskra, M., and Ryjkov, A.: Vegetation uptake of mercury and impacts on global cycling, *Nature Reviews Earth & Environment*, 2, 269-284, 10.1038/s43017-021-00146-y, 2021.

Zhu, W., Lin, C. J., Wang, X., Sommar, J., Fu, X. W., and Feng, X. B.: Global observations and modeling of atmosphere-surface exchange of elemental mercury: a critical review, *Atmospheric Chemistry and Physics*, 16, 4451-4480, 10.5194/acp-16-4451-2016, 2016.