Reviewer 1 comments

Atmospheric and Watershed Modelling of Trifluoroacetic Acid from Oxidation of HFO-1234ze(E) Released by Prospective Pressurized Metered-Dose Inhaler Use by Shivendra G. Tewari et al. MS Preprint egusphere-2025-1031 This paper is a resubmission of "Atmospheric and watershed modelling of HFO1234ze(E) emissions from prospective pressurized metered-dose inhalers usage" after public peer review on egusphere. The revised paper shows significant improvements to the original and takes on board many of the reviewers comments. Due to the content of the paper being scientifically valuable as not many studies have been published on pressurised metered dose inhaler emissions, and the improvements made, the paper merits publication in ACP after the minor corrections outlined below.

General comments: The addition of the final section on limitations of the study, into the production of trifluoroacetic acid (TFA) from the atmospheric oxidation of HFO-1234ze(E), outlines clearly the limitations that help to contextualise the results within the wider scientific landscape. The inclusion of the additional atmospheric oxidations routes, notably the ozonolysis of HFO-1234ze(E) and the photolysis of trifluroacetylealdehyde (TFAA) to produce HFC-23 (CF3H) greatly improves the paper, despite these routes having little impact on the overall results of the paper. The addition of this information helps to contextualise the results and mechanisms being reported. For completeness, it would be beneficial to outline what the "several other TFAA degradation pathways have been suggested in the literature" (lines 72-73 of the revised manuscript) are. This inclusion isn't imperative as it does not relate to the production of TFA; however, it demonstrates that the authors are aware of the full routes and contextualises the oxidative pathways. The inclusion of the author derived HFO emissions based on the sales data is a welcome inclusion in the supplementary information. It is acknowledged that the inclusion of the sales data is potentially commercially sensitive, despite the data being country aggregates for all producers of pMDIs. The method used to derive these emissions is explained within section 2.2, so there is suffice information on the provenance of the data.

Response: We thank the Reviewer for their feedback. In the revised manuscript, we have specified the additional TFAA degradation pathways. Below, we address each comment point-by-point:

Specific comments: Whilst I understand why the Dutch drinking water threshold for TFA is cited on line 26 to contextualise the Rhine values, especially as the mouth of the Rhine is in the Netherlands, it isn't clear to me why the values for the Cauvery are compared to this threshold.

Response: Thank you for this pertinent observation. We agree that the Cauvery values cannot be directly compared to Dutch drinking water threshold. Therefore, in the revised manuscript, we now only compare the Dutch drinking water thresholds for TFA with the Rhine watershed value due to the river's mouth being in the Netherlands. We have now removed the direct comparison of this specific threshold with Cauvery results from the Abstract, since an appropriate guideline is missing for this region.

Some of the naming of references in the text seem to be incorrect and might be caused due to the use of a reference management software. These should be checked and corrected. Examples of erroneous naming in citations include: line 38 "(Organization, 2022)" instead of World

Meteorological Organization, line 42 “(Union, 2024)” instead of Official Journal of the European Union.

Response: We appreciate you highlighting these inconsistencies in our reference citations. We have reviewed the manuscript thoroughly and corrected all instances of improper naming—including the specific examples you provided—to ensure accurate and formal citations in accordance with the journal’s guidelines.

The authors have addressed a previous comment by the reviewers on the inclusion of ozonolysis as an atmospheric oxidative pathway for HFO-1234ze(E). They have rightfully acknowledged the temperature dependence of the ozonolysis reactions, which are not included in the McGillen et al (2023) paper (lines 47 – 54 of the revised manuscript). Moreso than the temperature dependence, one would expect OH-initiated chemistry to dominate over ozonolysis due to the reaction rates. An acknowledgement of this limitation in the production in HFC-23 from HFO-1234ze(E) would be beneficial to show why the authors have not looked into the production of HFC-23 in this paper.

Response: We concur with your assessment regarding the dominance of OH-initiated chemistry over ozonolysis for HFO-1234ze(E) degradation due to differences in reaction rates. We have added an explicit acknowledgment in the revised manuscript (within lines 47–57) further clarifying that formation of HFC-23 via the ozonolysis pathway represents a minor contribution relative to OH-driven removal and other loss pathways. This explanation helps to underscore why ozonolysis, though acknowledged, is not a primary focus of our quantitative analysis given its comparatively lower significance.

There is no description of how the modelled deposition data from GEOS-CHEM is superimposed onto the basin boundaries used for the watershed modelling. It would be good to include the information that was provided as a response to one of the reviewers on this topic in section 2.4

Response: We thank the reviewer for their feedback. This detail was presented in Section 3.2; for completeness, we have also added details of the methodology used for superimposing the atmospheric deposition data onto the watershed boundaries in Section 2.4 (Lines 245-251).

Technical comments:

Line 56: add in “known” between 15,000 and chemicals to read “… PFAS are a group of nearly 15,000 known chemicals…”.

Response: The suggested edit has been incorporated. Line 60 of the revised manuscript now reads: "…PFAS are a group of nearly 15,000 known chemicals…".

Line 59: There are some PFAS compounds that take tens of decades to decompose. It might be better to show this rather than stating “many years”. Line 65: Add in “known” between 2,000 and chemicals to read “… presently, there are nearly 2,000 known chemicals that have…”.

Response: We have addressed both points. In the revised manuscript, "many years to decompose" has been revised to "tens of decades to decompose, e.g., perfluorooctanoic acid" to more accurately reflect the persistence of some PFAS compounds (Lines 61-62). The word "known" has been added, so the sentence now states: "…presently, there are nearly 2,000 known chemicals that have…" (Line 69 of the revised manuscript).

Line 107: Subtitle “Anthropogenic, Natural, and HFO-1234ze(E) emissions” does not make sense. Suggest altering to “Anthropogenic and Natural Trace gas, and HFO1234ze(E) emissions”.

Response: We appreciate the suggestion for a more precise subtitle. The subtitle on line 111 of the revised manuscript has been updated to "Anthropogenic and Natural Trace gas, and HFO-1234ze(E) emissions" as recommended.

Lines 109 – 111: Try to avoid using double parentheses, better to list species as “… reactive gases (sulfur dioxide, SO2; nitrogen oxides, NOx; ammonia, NH3; …”. Table 1 footnotes: Adsorption spelt incorrectly on line 3 of the footnotes. Additionally, units of L/kg need to be changes to L kg-1 .

Response: We have reviewed and corrected these formatting and textual issues. In the revised manuscript, lines 113-115, the double parentheses have been restructured to the suggested format for listing reactive gases. In Table 1, the spelling of "Adsorption" on line 3 of the footnotes has been corrected, and the units "L/kg" have been uniformly updated to "L kg^{-1}".

Line 309, replace “Gg/yr (or kiltons/year)” with Gg yr-1 (or kilotonnes yr -1). Figure 3 units are not consistent with the rest of the paper – shown as kg/m2 • yr instead of kg m-2 yr -1 .

Response: Thank you for pointing out these unit inconsistencies. On line 319 of the revised manuscript, "Gg/yr (or kiltons/year)" has been replaced with "Gg yr^{-1} (or kilotonnes yr^{-1})". Additionally, the units in Figure 3 have been standardized to "kg m^{-2} yr^{-1}" for consistency with the rest of the manuscript.

Line 484: Remove “i.e. 4.736 x 0.04 x 10-3 ” as this does not add any extra information to the paper than the preceding value.

Response: We agree that the explicit numerical breakdown was redundant. The phrase "i.e. 4.736 x 0.04 x 10^{-3}" has been removed from line 494 of the revised manuscript, enhancing conciseness without loss of information.

Line 493 – 494: It would be pertinent to reference the limitations of this study, or at least the following section, on the results.

Response: We thank the Reviewer for their feedback. In the revised manuscript (Lines 503-505; Lines 519-526), we have signposted the reader to “Limitations of the Study” in the final paragraph of the “Conclusions.”

Lines 506 – 510: Again, these results are based on the limitations of the study that should be acknowledged (or at least signed posted to the section on limitations) rather than stating something outright as it is misleading.

Response: We have addressed this by revising the statements on lines 519-526. These results are now explicitly framed within the context of the study's limitations, with direct acknowledgment and a clear signpost to the dedicated limitations section. This ensures that the conclusions are presented accurately and are not misleading.

Supplemental data: Units in the table need to be changes to Gg month-1. Additionally, the number of significant figures need to be thought about here. Captions are needed for the two plots below

the table that show propellant emissions released per month in the UK and Brazil, as well as month names.

Response: Thank you for the feedback on the supplemental data. We have implemented the unit change and added captions for the two plots beneath the emissions table. We have carefully reviewed and adjusted the number of significant figures across the supplementary tables to four digits, which were necessary to capture seasonal emission variations for all countries.

Reviewer 2 comments

This is my second assessment of the manuscript now entitled: "Atmospheric and Watershed Modelling of Trifluoroacetic Acid from Oxidation of HFO-1234ze(E) Released by Prospective Pressurized Metered-Dose Inhaler ". Although I appreciate how the authors have reacted to several of my concerns and improved the manuscript in many ways that are in line with my suggestions, I feel that my two major concerns are still not sufficiently acknowledged. Especially for the first one I don't see how the tendency of the conclusions ("no risk") can be upheld with the limited study areas.

Response: We thank the Reviewer for the feedback. Below, we address each comment point-by-point:

1) Generalisation of results. Again, it is concluded form the analysis of three watersheds that the TFA production from HFO-1234ze(E) emitted by pMDIs and following deposition "is minimal and does not present a risk to human health or the environment" (L33f). There is a new constraint in the same sentence ("for the regions assessed"), which is a valuable addition, but to the reader the regions assessed may still appear as being representative for maximum loads. In my view, this is not at all justified by the selection of the three watersheds. In their reply the authors claim that the watersheds were chosen because of "high pMDI emissions, which should reasonably correspond to areas of higher atmospheric TFA mass". This is a curious statement as the authors provide TFA deposition maps that clearly show that transport of HFO-1234ze(E) leads to deposition patterns that are very much different from emission patterns (compare Figures 3 and 4). I am also repeating my statement that it is also rainwater concentration rather than only deposition, which should be looked at, to assess areas with maximum impact. More TFA throughput does not mean larger concentrations. From Figures 4 and new Figure 8 I would then rather select river basins in the American Southwest as well as in Spain for the analysis instead of two only moderately affected basins (Rhine and Hudson). Although, the text does not explicitly make a universal claim anymore, the tendency is still to justify the use of HFO in pMDIs globally and, in my view, the analysed watersheds are simply not the ones one should be looking at for a worst-case scenario. At the very least section 5 and the abstract need to reflect the limitation of the obtained results in terms of global representativeness in a much clearer way before the article can get published.

Response: We appreciate the reviewer's emphasis on representativeness and on distinguishing emissions, deposition, and concentrations. We have revised Section 4 (Lines 519-526), Section 5 (Lines 556-564) and the title to state explicitly that our conclusions apply only to the regions and scenarios assessed, and that extension to other sectors will require additional work. We acknowledge that deposition patterns differ from emissions because transport and scavenging govern wet and dry fluxes (cf. Figs. 3–4). We also agree that concentrations depend on hydrologic dilution as well as deposition: arid regions can exhibit higher rainwater concentrations for a given atmospheric burden, yet their annual wet-deposited mass is generally lower due to limited precipitation (Vet et al., 2014).

Consistent with this, Figure 4a shows relatively higher dry deposition in parts of the American Southwest, whereas wet deposition is higher along the U.S. East Coast (Fig. 4b), reflecting greater scavenging efficiency and regional emissions (e.g., Hudson watershed). Note that, compared with

dry deposition— which tends to settle on surfaces and reach waterways indirectly via wash-off/runoff—wet deposition delivers TFA directly via rain/snow to rivers and, therefore, to surface waters. Moreover, comparing TFA rainwater concentrations between eastern and western U.S. regions (Fig. 8), we do not find a substantial difference, suggesting broadly comparable atmospheric burdens across these coasts. Wet deposition of TFA to the adjacent East Coast Ocean (Fig. 4b) is substantially higher than along the West Coast, reflecting stronger precipitation scavenging and regional transport patterns. While total pMDI use is higher in populous Eastern corridors (including the New York metropolitan area), precipitation and synoptic meteorology are the primary determinants of wet deposition.

We agree that observations in one region need not translate to others. However, based on our modelled fields, we do not find evidence that surface-water concentrations in candidate West-coast basins would be an order of magnitude higher than in the Hudson. To demonstrate the limited scope of our results, we have (i) strengthened the signposting in Section 4 (lines 521–526) regarding representativeness and study limitations; (ii) focused the abstract's quantitative comparison on the Rhine watershed, relating results to the conservative Netherlands drinking-water thresholds (as per Reviewer 1's feedback) to illustrate how our conclusions are tied to specific regions rather than global worst-case conditions; and (iii) revised the manuscript title to include "in Three Major River Basins," thereby clarifying the scope of the results.

2) Isolated view on a single use case. The authors have taken my concern up in the sense that they now compare TFA resulting from pMDI usage to TFA produced from other compounds/processes. However, the general concern that a study for an individual compound and use case concludes that there is no environmental threat, to me, is still misleading. Yes, we are not talking about the main contributor here compared to the HFOs used in refrigeration, but several small use cases will still add up and lead to an overload. I see that this is more of a philosophical question, but it should be made clear that the conclusions drawn are really isolated for the presented use case. As such I would encourage adding at least one sentence in section 5 and the abstract that reflects on this isolated view and accommodates the concerns of rising TFA levels from various usages as a whole.

Response: We agree that our assessment is intentionally limited to the pMDI use case and should not be interpreted as a statement about cumulative TFA from all sources. Our objective was to evaluate the implications of prospective HFO-1234ze(E) use in pMDIs, given its development as a replacement propellant. To make this scope explicit, we have revised Section 5 (lines 556–564) to state that a cross-sector, cumulative assessment (e.g., refrigeration/air-conditioning and other applications) is an important avenue for future work and that our conclusions apply only to the regions and scenarios analysed. We have also ensured that the title clearly restricts the scope, rather than expanding the abstract. In addition, as suggested by Reviewer 1, we underscore the specificity of our approach by reporting results for the Rhine watershed and comparing them with Netherlands drinking-water thresholds since the mouth of the Rhine river is in Netherlands.

References

Vet, R., Artz, R. S., Carou, S., Shaw, M., Ro, C.-U., Aas, W., Baker, A., Bowersox, V. C., Dentener, F., and Galy-Lacaux, C.: A global assessment of precipitation chemistry and deposition of sulfur, nitrogen, sea salt, base cations, organic acids, acidity and pH, and phosphorus, Atmospheric Environment, 93, 3-100, 2014.