Atmospheric and watershed modelling of HFO-1234ze(E) emissions from prospective pressurized metered-dose inhalers usage by Shivendra G. Tewari et al.
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This paper investigates the production of trifluoroacetic acid (TFA) from the atmospheric oxidation of a latest generation hydrofluoroolefin (HFO), HFO-1234ze(E), that is being used as a replacement for previous generation propellants in pressurised metered-dose inhalers (pMDI). The paper also investigates the subsequent TFA deposition within three separate river drainage basins, produced from the atmospheric oxidation of HFO-1234ze(E). The paper uses well-tested methods and models but I have several concerns (outlined below) with regards to the oxidation pathways, data used and conclusions made. The paper is interesting and scientifically valuable as not many studies have been done on pMDI emissions; therefore, once the following issues have been addressed, the paper merits publication in ACP.

General comments

Based on the title of the paper, I would expect to see more information on other atmospheric oxidation routes of HFO-1234ze(E). Despite OH being the most probable oxidation pathway for this HFO due to the reaction rate, ozonolysis has been shown as a viable oxidation pathway to ultimately produce trifluoromethane (HFC-23; CHF_3) with yields of 3.11 ± 0.05% (https://doi.org/10.1073/pnas.2312714120) despite the lower reaction rates. As pMDI emissions are likely to occur in the lower troposphere, un regionally polluted areas with high ozone, ozonolysis will play a role in the oxidation of HFC-1234ze(E). The authors allude to another oxidation process, i.e. photolysis, of trifluoroacetyl aldehyde (TFAA) that does not produce TFA; however, it does produce HFC-23. Considering the main focus of this paper is the atmospheric breakdown of HFO-1234ze(E), these mechanisms that produce other trace gases should be outlined at least in the introduction, irrespective of if the focus is only on TFA production.

The study uses nitric oxide (NO) emission estimates as a proxy for the spatial distribution of HFO-1234ze(E), which are then scaled based on the monthly pMDI sales from the top 51 countries to calculate total emissions per month per country. A significant limitation of this methodology does not account for biogenic NO emissions (i.e. partial denitrification), aircraft or ship emissions, which would not be associated with pMDI usage. Rather than using NO as a proxy, a priori information of population density or nighttime light could be used to better resolve emissions distributions. Furthermore, the full inclusion of information used to estimate emissions of HFO-1234ze(E) from the use of pMDI should be included. Currently no sales data are included in the paper or supplement, making it impossible for the reader to recreate the results given in the paper. Additionally, the limitation of only using sales data from one pharmaceutical company reduces the representativeness of the results. It would be better to use total global sales of pMDIs instead. If the latter has been used, it was not made clear within the paper.

The conclusion that even if HFO-1234ze(E) was the only propellant used in pMDIs, the continuous emission to the atmosphere would have negligible effects on surface water and soil TFA concentrations is misleading. Albeit that the results from this study might indicate that this is the case, they are based on a single emission rate of HFO-1234ze(E) that does not vary over time and on sales data from one single pharmaceutical company. Considering the total number of asthma and COPD diagnoses continue to increase globally (https://doi.org/10.1586/17476348.2016.1114417), a time varying emission estimate would be more representative, as well as using global sales data.

Specific comments

Lines 1-2: As previously outlined in the general comments, the title is not representative of the true focus of the paper and is too broad. Greater specificity is needed so that a reader truly knows what the paper is about. A suggested title, based on the current scope, is “Atmospheric and watershed modelling of trifluoroacetic acid from the oxidation of HFO-1234ze(E) from pressurized metered-dose inhaler usage”.

Lines 13 – 15: Halogenated hydrocabons with a ‘—CF_3’ moiety also have the possibility to produce HFC-23. Despite this not being within the scope of the paper, this pathway should at least be acknowledged.

Despite the ACP house style specifically stating that units must be written exponentially (i.e. Gg yr^{-1}), the authors have not done this throughout the paper.

Lines 20 - 22: The authors assume that the model-predicted TFA deposition rates, which are higher in tropical regions than northern-temperate regions despite higher sales of pMDI in the latter region, is based on photolysis of TFAA being the dominant process; however, this assumption does not seem to take into account atmospheric transport and the lifetime of HFO-1234ze(E). Moreover, this could be a function of the spatial distribution estimation using NO emissions (see General comments). Have the authors looked into a sensitivity analysis to verify if the photolysis reaction of TFAA is dominant in northern-temperate zones?

Watershed is a contentious word within hydrology as it can have different meanings depending on readers nationality (c.f. river drainage basin as a unit, line that separates neighbouring drainage basins, a time of day in broadcasting). To avoid confusion and increase readership beyond that of North America, it would be good to either change the word to a less contentious naming or have a definition of what is meant by watershed.

Lines 26 – 28: It might be that pMDI usage-based HFO-1234ze(E) emissions only do not pose a risk to human health based on the results and data used in this study but they contribute to other sources. It would be good to acknowledge that the culmination in other sources and growth in pMDI usage might change this, as well as contextualising with the limitations of the paper.

Lines 38 – 40: As the scope of the paper is global, it would be good to include other non-USA regulations on the phase out of HFCs too, i.e. European F-gas regulation.

Line 80 – 81: Why were emissions calculate at 30-minute time steps as this must have made the running of the model computationally expensive? As the anthropogenic and biogenic emission estimates outlined in section 2.2 that are used in the model have a temporal resolution of one month, why was the 30-minute time step chosen?

Lines 95 – 112: How come the method for HFO-1234ze(E) emissions calculations are not outlined in this section? It would be a pertinent location to include it to help any reader find the necessary information to run GEOS-Chem to verify your results. It would also allow the authors to give more information on the sales data used (c.f. one company vs. global sales values) and how this was scaled. Currently very little information is given on how these emissions are calculated and this is crucial information to be able to replicate the results.

Lines 132 - 134: The exclusion of O_2 and H_2O from GEOS-Chem reactions is significant limitation in the study as atmospheric mole fractions of these vary spatially and temporally and will have an impact on the different reactions associated with the oxidation of HFO-1234ze(E). For example, O_2 is required in the $CF_3CH(OH)CHF(O^\bullet)$ pathway to produce TFAA (see figure 5 in Behringer et al., 2021).

Lines 226 – 229: What was the rationale for choosing the southern Indian drainage basin? India is an Article 5 party under the Montreal Protocol and its Amendments; therefore, it has a delayed phase-down of HFCs compared to non-article 5 countries (i.e. western countries such as USA or Europe). As such, the use of HFCs in pMDI would be expected to continue on longer in India than the USA or Europe.

Lines 232 – 235: How do you account for the granularity in GEOS-Chem spatial resolution and the resultant TFA deposition rates (model resolution of 2° x 2.5°) on the deposition rates put into the drainage basin model?

Lines 256 – 268: How does the model account for infiltration and percolation rates across the river drainage basins, as these will vary spatially based on soil and bedrock types.

Lines 271 – 281: The results and discussion section should not be where the method of distributing HFO-1234ze(E) emissions from pMDI usage I located. Instead, it should be included in section 2.2. Furthermore, the monthly pMDI sales data used within the paper should be included, either in figure or tabulated form, so that readers of the paper can use the data along with other methods outlined in the paper to verify the results presented in the paper.

Lines 287 – 291: Considering that NO is used as a proxy and often total emissions of this gas do not vary significantly temporally, would one not expect to see the same in the HFO-1234ze(E) emissions considering NO is used as an emissions proxy? Furthermore, based on your methodology, I don't believe you can current definitively state that there are sustained demand of pMDIs in the respiratory disease community without temporal variations.

Lines 301 – 302: How does TFA deposition flux vary seasonally? It would be good to describe it here in the main text, despite not requiring the figures in the main text.

Lines 302 – 206: See Specific Comment for Lines 20 – 22, regarding transport of TFA and the subsequent dry deposition.

Lines 334 – 336: The description of the model and compartmentalisation should be included in the methods section.

Figure 6: The GEOS-Chem gridded TFA deposition over the selected river drainage basins often bridge both the drainage basin and the surrounding area. How are these deposition rates accounted for in the sections where the gridded deposition has both regions contained within it?

Lines 340 – 343: Why are the authors assuming the TFA deposition fluxes do not change temporally? Does Fig. S3 and S4 not show that these do vary both temporally and spatially for dry and wet deposition, respectively.

Lines 404 – 414: I find these three points hard to read and believe that they should be rewritten. Additionally, I find the language used to be quite emotive and political. Rather than pushing an agenda, results should be presented scientifically and then contextualised, but taking the assumptions and limitations of the study into account.

Lines 416 – 420: As for the previous point, this whole paragraph is pushing an agenda, whereas it would be better to outline that these results are from sales figures from a single pharmaceutical company and that emissions of HFO-1234ze(E) are not limited to this one source or company. Instead, it contributes to total emissions.

Technical corrections

Line 13: HFO is not defined prior to its first use.

Line 16: What is environmental TFA? Suggest removing “environmental” as it is unnecessary.

Line 36: Please use a more up-to-date GWP_{100} value for HFC-134a. The Annex to the WMO Scientific Assessment of Ozone Depletion 2022 has a more recent value of 1,470.

Line 41: HFO-1234ze(E) wasn’t purely developed by the pharmaceutical industry as a propellant and is currently being used as a refrigerant and foam blowing agent. Emissions are already observed globally by the AGAGE network (see https://doi.org/10.1021/es505123x). Please reword this sentence.

Lines 49 – 52: As far as I am aware, the PFAS regulation was passed in the EU and should be coming into law soon. Please update this sentence to reflect this.

Lines 62 – 65: Please outline the other TFAA degradation pathays that have been suggested in the literature. From the literature cited, it looks like the authors are mostly suggesting the photolysis of TFAA to produce HFC-23 but it is not entirely clear. There are pathways of TFAA oxidation through hydrolysis that can produce TFA – see Figure 8 in Berhringer et al (2021; https://www.umweltbundesamt.de/sites/default/files/medien/5750/publikationen/2021-05-06_texte_73-2021_persistent_degradation_products.pdf) for more information.

Line 65 – 66: The assertion that no prior work has explored TFA production from HFO-1234ze(E) is slightly misleading. The authors have produced a similar study using a box-model with chemical degradation mechanisms included (see https://doi.org/10.3389/fenvs.2023.1297920).

Lines 75 – 81: Please include that GEOS-Chem is a Eularian model.

Line 119: If stating the authors name in the text, it does not then need to be included in the citation in parenthesis – "… in GEOS-Chem by Mao et al. (2010) for the …". See the ACP house style for more information (https://www.atmospheric-chemistry-and-physics.net/submission.html#references)

Lines 139 - 140: This sentence is not complete.
Line 375: Replace "Alphine" with "Alpine".

Line 389: state what the GWP_{100} For HFO-1234ze(E) is.

Fig. S6: Correlation values are usually stated as an R value in statistics, whereas p-values are the statistical significance of each test. Both should be reported.