

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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The manuscript by Shivendra G. Tewari presents a study of the atmospheric degradation of HFO-1234ze(E) and hydrological fate of one of its degradation products, the environmentally persistent trifluoroacetic acid (TFA). The study is specific for the emissions of HFO-1234ze(E), used as a propellant in metered-dose inhalers, and does not discuss emissions of other use cases. Although, the applied atmospheric and hydrological modelling appear appropriate in the first place, there is very little information on validation of the model results in terms of discussion of previous simulations and observations. In addition, the focus on three selected watersheds for the hydrological part of the paper seems very arbitrary and not suited to provide global worst-case scenarios. Hence, the main conclusion of the study, that the use of HFO-1234ze(E) for inhalers will not pose a risk for TFA in drinking water, may not be valid everywhere on the globe and should be revisited. Although, the manuscript is well-structured and written and only a few additional clarifications are required in this respect, addressing the main concerns may require major revisions of the manuscript before publication.

Response: We thank the Reviewer for their feedback. In the revised manuscript, we have addressed all their concerns. Below, we provide our point-by-point responses to each issue raised.

Major comments

Generalisation of results: Although, it is explicitly said that results are derived for three selected watersheds, the final sentence of the abstract and the final paragraph of the conclusions seems to imply that the use of HFO-1234ze(E) in inhalers does to pose a threat globally. The selection of these watersheds is very arbitrary (L227/228). "prominent" and "large population" seem to be the only criteria. However, for all three continents one can very easily come up with watersheds that have a larger population. Figure 4 shows that there are also word regions where we expect larger TFA deposition. However, in the end it is not the deposition flux but the rainwater concentration that will determine surface water concentrations. Hence, I would have expected that a selection of watersheds would focus on those for which largest TFA concentrations in precipitation are predicted. Previous studies have shown that TFA concentrations will be enhanced in more arid regions and, hence, a look at river systems in such areas would be more helpful than considering the 3 current watersheds, from which we cannot conclude that TFA levels will stay within the safety margins globally.

Response:

In this study, our objective was to investigate TFA levels in surface waters within three representative watersheds. The Rhine watershed in Europe was selected primarily because it offers a rich body of TFA-related literature, enabling comparative analysis and contextualization of our findings. The US was selected because it has the highest pMDI sales/usage globally. For the third watershed, India was chosen as it represents the third-largest pMDI market globally—after the US and UK. Since our study already included a European watershed (the Rhine), we opted for India instead of the UK to maximize geographical diversity.

Within the US, several watersheds were considered, but the Hudson one was selected for its proximity to New York City, which has the country's highest population density and, thus, presumably, has the highest pMDI usage, i.e., propellant emissions. The selection of the Cauvery watershed in India was guided by the availability of watershed modelling parameters and the fact that it represents a source of drinking water to a very large population centre, i.e., Bengaluru. In the revised manuscript, we have elaborated on this selection rationale to provide greater transparency.

We appreciate the Reviewer's observation regarding the interplay between atmospheric TFA mass and precipitation volume in determining surface water concentrations. Our choice of watersheds prioritized regions with high pMDI emissions, which should reasonably correspond to areas of higher atmospheric TFA mass. While we acknowledge that arid regions may experience higher surface water concentrations due to lower precipitation volumes and increased relevance of dry deposition—an aspect illustrated in Figure 4, which shows more significant dry deposition in such areas—pMDI sales and propellant emissions are comparatively lower in these arid regions. Note that even though arid regions may experience higher TFA rainwater concentrations, the net TFA deposition in these regions will be lower due to limited precipitation (Vet et al., 2014). Given the scope and resource constraints of the present study, it was not feasible to include a fourth watershed focused on an arid environment for detailed fate-and-transport analysis.

Isolated view on the TFA budget: There is one more danger in the presentation of isolated results of TFA from a single precursor and use case. Obviously, it is the sum of contributions from all precursors that determines environmental TFA levels. If ten studies like the current for specific use cases all come to the conclusion that individually there is no problem, the sum may still present an environmental problem. It is mentioned that compared to current levels of TFA in precipitation in Germany, TFA from degradation of HFO-1234ze(E) in pMDIs would add less than 1 %. Again, this may not be true globally. I would suggest to put the current use case more into the perspective of the global TFA budget (as much as this is known, for example see Madronich et al. 2023).

Response: We thank the Reviewer for highlighting this concern and indeed it is important to consider all possible precursors of TFA in the environment and that was the reason for comparing existing TFA surface water concentration in Rhine (Germany), which presumably encompass all sources of TFA, with our estimates of surface water TFA due to pMDI-usage based propellant in that region. It is indeed possible that relative contribution of propellant-based TFA in surface water would be different in different regions; therefore, comparison with global TFA budget is the best possible alternative. As per Madronich et al 2023, HFC-134a and HFO-1234yf are the two main sources of TFA in the environment. Their combined annual production rate of TFA is $0.04 - 0.06 \text{ Tg yr}^{-1}$. Considering our estimates of annual pMDI-associated HFO-1234ze(E) emissions and theoretical TFA yield, the global total TFA deposition due to future pMDI usage would be $\sim 0.0002 \text{ Tg yr}^{-1}$, i.e., 4.736×0.04 , which suggests that propellant emissions based TFA production represents less than 0.5% of the annual global TFA in the environment estimated by Madronich et al. 2023. In the revised manuscript, we have added this new information as well.

Emission scenario: It is assumed that future emissions from pMDIs will follow the same global usage as taken from current pMDI sales (L271). Figure 3 reveals that some world regions are underrepresented with this assumption. Especially emissions in densely populated China seem to be unrealistically low. Is this because sales data from China is potentially incomplete? Even if it is complete, would one not expect that access to pMDIs will increase in China in the future? In general, it would be better to work with projected consumption numbers then with present day values. Since Southeast Asia also seems to be an area of intense TFA deposition (Figure 4b), realistic Chinese emissions seem to be critical for a fair assessment of future TFA levels in this region. Furthermore, instead of using NO as a proxy for the spatial distribution of HFO emissions, it seems more appropriate to use population density directly. NO distributions may be skewed by individual point sources like power plants.

Response: We thank the Reviewer for this prudent observation. Note that the lower propellant emissions in China is because the IQVIA pMDI sales data for that region is only available from Hospitals. With the revised manuscript, we have provided our estimates of monthly propellant emission rates for the top 51 countries as supplement data; therein, we have annotated that lower emissions in China are due to lack of data availability.

We agree that there are limitations to this study, such as assuming pMDI sales do not increase over time. Without hard evidence, it is difficult to predict what world regions will see the most increase in pMDI sales. Moreover, we cannot predict weather patterns for the next thirty years which should also affect TFA formation and deposition globally. Therefore, for relative simplicity, we used region-specific annual TFA deposition flux for calculating net accumulation of TFA in surface water, soil, and sediment over time. In the revised manuscript, we have addressed this limitation under a new “Limitations of the Study” section.

As specified in the manuscript, the NO emissions used as a spatial proxy for HFO-1234ze(E) emissions are only from the residential and commercial sectors of the CEDS inventory. This was done intentionally, as these sectors are representative of population density and human activity and are therefore more likely to correlate with pMDI usage. Emissions from unrelated sources—such as biogenic, aircraft, or maritime—were not included in this proxy.

Minor comment

Section 2.1-2.3: There are several questions concerning the setup of GEOS-Chem that need clarification. What is the name/version of the utilised chemistry scheme? How many compounds are treated? How are the NMVOC emissions mapped onto model species? Are there any validation results of GEOS-Chem for the classical air pollutants (O₃, NO_x, ...)? Done as part of this study or published elsewhere for the same setup of the model. These would be helpful to understand if simulated OH levels and, hence, HFO reaction rates are realistic.

Response: We used GEOS-Chem version 14.2.2 with the standard full-chemistry simulation, as described in lines 75–76 of the submitted manuscript and referenced accordingly. This version includes 324 chemical species, which comprises the standard species set plus 15 additional species added for HFO chemistry in this study.

Non-methane volatile organic compound (NMVOC) emissions are pre-specified in the emission inventories (e.g., HTAP, RETRO, EDGAR, NEI) used in GEOS-Chem. That is, emissions are mapped directly to individual model species (e.g., ISOP, ACET, ALK4) at the point of input. There is no in-model speciation of total NMVOC; instead, species are defined based on inventory-provided breakdowns.

Regarding model evaluation, GEOS-Chem has been extensively validated in previous studies for classical air pollutants such as O₃, NO_x, CO, and related species. Some key references include:

- Hu et al. (2017): Evaluated the global ozone budget and tropospheric chemistry in v10-01 using satellite (OMI), aircraft (IAGOS), and ozonesonde data.
<https://doi.org/10.1016/j.atmosenv.2017.08.036>
- Wang et al. (2022): Assessed ozone trends and radiative impacts using v13.3.1 with multiple long-term observational datasets (IAGOS, ozonesondes).
<https://doi.org/10.5194/acp-22-13753-2022>
- Lin et al. (2024): Compared GEOS-Chem v14.1.1 with CAM-Chem in CESM2, focusing on oxidant chemistry.
<https://doi.org/10.5194/acp-24-8607-2024>
- David et al. (2019): Evaluated tropospheric ozone over the Indian subcontinent using v10-01.
<https://doi.org/10.1016/j.atmosenv.2019.117039>

Additionally, the GEOS-Chem team conducts comprehensive benchmark comparisons for each major model version to ensure scientific consistency and detect any significant changes in model behaviour. These

benchmarks track changes in model outputs such as ozone, NO_x, CO, and VOCs across versions to ensure internal consistency, but they are not designed as full evaluations against observations. For example, a benchmark was performed for version 14.2.0, but not for minor updates such as 14.2.1, 14.2.2, or 14.2.3, which typically involve bug fixes or minor code changes. Benchmark results for version 14.2.0 are available at: https://wiki.seas.harvard.edu/geos-chem/index.php/GEOS-Chem_14.2.0

Separate evaluation studies—many published—compare GEOS-Chem outputs against surface, aircraft, and satellite observations, providing confidence that key aspects of the model's chemistry and transport are scientifically robust.

L153f: How valid is the use of absorption cross sections of CH₃C(O)CHO for CF₃C(O)C(O)F? Can this be corroborated from similarities from any known cross sections for other similar molecules?

Response: Thank you for raising this important point regarding the choice of absorption cross sections for CF₃C(O)C(O)F. As direct experimental data for the absorption cross section of CF₃C(O)C(O)F are currently unavailable, we followed established precedents in the photochemical literature—specifically the approach outlined by Jenkin et al (2019). In such cases, it is common practice to use cross sections from structurally analogous compounds as surrogates.

CH₃C(O)CHO was selected as a substitute based on its analogous carbonyl functionality and overall structural similarity to CF₃C(O)C(O)F, particularly in terms of the presence of conjugated carbonyl groups that strongly influence UV absorption behaviour. The selection is further supported by the fact that photolysis in these compounds typically occurs via the n→π* transition in the carbonyl group, for which absorption cross sections have demonstrated comparable spectral features among simple and perfluorinated aldehydes and ketones; see, for example, Orlando and Tyndall (2012). While small differences can arise due to the electronic effects of fluorination, the absence of directly measured data justifies the use of this pragmatic surrogate.

We acknowledge that acquiring measured cross sections for CF₃C(O)C(O)F would improve accuracy and recommend this as a focus for future work. In the meantime, our choice is in line with methods used in previous atmospheric modelling studies for compounds lacking explicit spectroscopic data.

Figure1 and section 2.3: The figure seems to indicate an alternative path for trifluoroacetic aldehyde (TFAA) to TFA through hydration. This path is not discussed in the text. Is this based on the diol mechanism suggested by Franco et al. (2021) for other aldehydes? Please comment if it was included in the chemistry scheme and if it showed any relevance.

Response: The reviewer is correct that the dotted path from TFAA to TFA in Figure 1 represents the in-cloud hydration of TFAA. To clarify, TFAA hydration and TFAA diol formation refer to the same process: when trifluoroacetic aldehyde (CF₃CHO) reacts with water, it forms the corresponding geminal (1,1-) diol, CF₃CH(OH)₂. This hydrated intermediate may then partition back to the gas phase, where it is thought to react with OH radicals, potentially contributing to TFA formation. The possible involvement of gem-diol formation for TFAA in atmospheric waters, as discussed in Franco et al. (2021), remains a proposed mechanism; to our knowledge, no direct experimental evidence yet confirms TFA formation proceeding specifically through this hydrated intermediate. Critical information is still lacking, such as reliable values for the Henry's Law coefficient of TFAA, hydration/dehydration kinetics in the aqueous phase, the rate coefficient for the OH + CF₃CH(OH)₂ reaction, and the gas-phase dehydration kinetics of the diol. Recognizing its potential importance, we are currently conducting experiments to better understand the fate and reactivity of the TFAA hydrate. A note to this effect has also been added to the Figure 1 caption in the revised manuscript.

Section 2.4: Does the model take evapotranspiration in the watershed into account? Should it be considered in warmer climates.

Response: We can confirm that the model does account for evapotranspiration, with region-specific values applied in our simulations for each of the three studied watersheds. These values are detailed in the Supplementary Information. We agree that incorporating more spatially refined values would be particularly valuable for studies in warmer climates where evapotranspiration plays a critical role. This will be an important focus for future work, aiming to improve the resolution and accuracy of our simulations.

Figure 4 and Table 3: Earlier model studies on HFO degradation and TFA deposition all came to the conclusion that wet deposition dominates over dry deposition. This was the case for HFO-1234yf, where the formation of TFA should be fast (e.g., Luecken et al., 2010; Henne et al., 2012; Wang et al., 2018), but also for HFO-1233zd(E) (Sulbaek Andersen et al., 2018) for which TFA formation also proceeds through TFAA. Please comment, why and how this could be different in the present case. This also questions the statement made on line 298 concerning 'akin' deposition fluxes as in (Sulbaek Andersen et al., 2018), which then seems oversimplified.

Response: While earlier studies (e.g., Luecken et al., 2010; Henne et al., 2012; Wang et al., 2018; Sulbaek Andersen et al., 2018) concluded that wet deposition dominates TFA removal, our results suggest that dry deposition may play a more significant role under specific tropical and subtropical conditions. This difference likely stems from the chemical formation pathway (via TFAA) and regional meteorology that affects deposition processes.

1. Enhanced tropical photochemistry

In the tropics, intense solar radiation and high temperatures accelerate:

- $\text{CF}_3\text{C}(\text{O})\text{O}_2$ formation via OH oxidation of CF_3CHO :



- TFA production through the reaction $\text{CF}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2 \rightarrow \text{CF}_3\text{C}(\text{O})\text{OH} + \text{O}_3$, driven by elevated HO_2 concentrations.

These reactions lead to elevated TFA levels in the lower troposphere.

2. Suppressed wet deposition efficiency

Despite frequent rainfall, tropical meteorological conditions reduce the effectiveness of wet scavenging:

- Shallow convection: Rain is often produced by clouds that are limited in vertical extent and do not efficiently mix with near-surface air, where much of the TFA resides.
- High evaporation rates: In hot, humid conditions, raindrops can evaporate before reaching the ground, re-releasing dissolved TFA back into the atmosphere.
- Short cloud processing times: Warm, fast-evolving clouds allow little time for gases like TFA to dissolve into droplets, reducing uptake efficiency.

3. Favourable conditions for dry deposition

With wet removal suppressed and chemical degradation slow, more TFA remains near the surface. In subtropical regions (descending branches of the Hadley cell), conditions such as low rainfall, dry soils, and sparse vegetation promote efficient dry deposition, making it the dominant sink in these areas.

In summary, our study highlights that, under specific tropical and subtropical conditions, dry deposition can rival or exceed wet deposition as a removal pathway for TFA, a finding not emphasized in previous work. In the revised manuscript, we have briefly discussed this distinction.

Figure 4: In order to assess the global impact of TFA deposition, it would be beneficial to add another figure that shows average rainwater concentrations of TFA. Since these are usually strongly enhanced during the summer months, I would suggest to show these with three panels: overall average, summer average, winter average. Derived concentrations could be used in the discussion against currently observed TFA in precipitation (see below).

Response: Thank you very much for the helpful suggestion. Because summer and winter months vary across the globe in response, we have added a new Figure 8 in the manuscript showing overall average and a supplement figure (Fig. S14) presenting monthly modelled mean TFA rainwater concentrations, calculated as the ratio of monthly modelled wet deposition flux to monthly precipitation, which is taken from MERRA-2 reanalysis that is an assimilated product. To address your further point, we now compare our average modelled rainwater concentrations with values reported in the scientific literature for corresponding continents:

Figure 8 reveals that, across all continents, model-predicted TFA rainwater concentrations are substantially lower than those typically reported in the literature. Specifically, our modelled values range from about 0.005 to 0.040 $\mu\text{g/L}$ (5–40 ng/L) globally, with most regions—including North America, Europe, and Asia—falling at the lower end of this range. In contrast, literature values compiled from large-scale precipitation sampling report TFA concentrations that are often several times higher. For example, measured concentrations in North America frequently fall between 10 and 340 ng/L (Solomon et al., 2016), in Europe (including Germany) medians range from 69 to 350 ng/L (Freeling et al., 2020), and in Asia (China and Japan) values as high as 60–550 ng/L have been reported (Wang et al., 2014; Yamanaka et al., 2012). Note that even though arid regions, such as North Africa and the Middle East, have higher TFA rainwater concentrations, the net TFA deposition in these regions will be lower due to low precipitation (Vet et al., 2014). We have provided these comparisons in the revised manuscript (Figure 8).

Section 3.1: What was the total global TFA deposition flux? How does it compare to the HFO emissions and what can be concluded in terms of TFA yields for this compound?

Response: We thank the Reviewer for raising this important point. The primary goal of this manuscript was to evaluate TFA concentrations in surface water, soil, and sediment resulting from prospective pMDI usage and the associated release of HFO-1234ze(E) emissions into the atmosphere. While our model provides estimates of total global TFA deposition flux, calculating precise TFA yields—even with a single environmental precursor—requires rigorous integration of emission inventories, atmospheric processes, and chemical pathways. This level of quantitative analysis, directly linking emissions to deposition, was beyond the scope and objectives of this study.

Recognizing the importance of this issue, we note that our group is actively pursuing dedicated research to determine global TFA yields with the necessary precision. To maintain the clarity and integrity of our current work and ongoing studies, we have therefore not included a direct comparison of propellant emissions with TFA deposition fluxes. These critical aspects will be addressed in forthcoming publications.

Figure 5 and L325f: To me it remains unclear how the conclusions can be reached from what is presented in the figure. Is it only the spatial correlation between the two quantities? But then TFA concentrations will strongly depend on the removal not just the production pathway. Furthermore, how does the correlation look for other intermediates? This requires additional explanation.

Response: We thank the Reviewer for highlighting this important point and appreciate the opportunity to elaborate. To directly address the concern: while it is generally true that the steady-state concentration of any atmospheric species is governed by both its production and removal, in the case of gas-phase TFA, our analysis reveals a distinct scenario.

The key detail is that gas-phase TFA is removed from the atmosphere almost exclusively through a single OH-driven, temperature-independent oxidation process (Reaction 67 in Table S1). The rate of this removal pathway is significantly lower—by about an order of magnitude—than the rates of the major TFA formation reactions, including the OH-dependent reaction that forms TFA. As a result, the atmospheric burden and spatial patterns of gas-phase TFA are primarily determined by spatial patterns of chemical species that form TFA, rather than remove it. [Note that any OH-dependent changes in the removal rates of TFA would be negated by the corresponding OH-dependent reaction that forms TFA.]

We demonstrate this by showing that the spatial distribution of TFA closely matches that of the ratio $([\text{HO}_2] \times [\text{CF}_3\text{C}(\text{O})\text{O}_2])/[\text{OH}]$, which includes species that form and remove TFA in the atmosphere. The numerator reflects the major formation processes, while the denominator includes the OH species responsible for both TFA formation and removal. Thus, the observed spatial correlation in the figure is not simply a reflection of two unrelated quantities but encapsulates the dominant chemistry controlling TFA's presence in the atmosphere.

We derived this spatial correlation of the ratio by performing a detailed analysis of the chemical reactions that form and remove TFA from the atmosphere. With the supplement of the revised manuscript, we now provide the entire process which shows atmospheric concentration of other crucial intermediates. This new section (Section S2) demonstrates that the spatial patterns observed for TFA are distinct and are not mirrored by other intermediate species in the same way. This further supports our mechanistic interpretation.

We have clarified these points in the revised manuscript, making explicit how the data and analysis support our conclusions regarding TFA's atmospheric behaviour.

Figure 6: The plot reveals another potential shortcoming in the assessment of maximal TFA concentrations. The global chemistry simulations were performed at relatively coarse resolution. However, precipitation and hence TFA deposition often varies at much smaller scales as can be covered by the global chemistry model. As a consequence actual TFA inputs into individual watersheds may largely differ from the grid cell average of GEOS-Chem. Please add a note of caution and discuss the possible implications.

Response: We thank the Reviewer for raising this concern. The $2^\circ \times 2.5^\circ$ resolution of the TFA deposition data does not fully capture granularity, specifically in smaller subbasins, but this resolution is necessary considering the global scale of the modeling and is typical of such modeling. In the revised manuscript, we have added the limitations of using such a resolution in the new “Limitations of the Study” section.

L340: There seems to be another important simplification for the hydrological modelling which needs to be addressed. It is well known that TFA inputs from the atmosphere have a strong seasonal cycle in midlatitudes (both observed and simulated rainwater concentrations show this). In order to assess maximum concentrations in the watersheds it therefore seems very important to consider the seasonality in the inputs and see how this variability propagates through different strata.

Response: We appreciate the Reviewer's comment regarding the pronounced seasonal cycle in atmospheric TFA deposition, as also reflected in Figures S3 and S4, which present the temporal and spatial variability in deposition fluxes. For this study, our primary goal was to estimate long-term (30-year) cumulative TFA accumulation in surface water, soil, and sediment. To provide a first-order estimate suitable for this timescale, we assumed no inter-annual variability in annual TFA deposition, using the mean annual deposition rates as input to the surface fate and transport modelling. This approach was necessitated both by the scope of available deposition data and the absence of multi-decade, high-resolution model simulations, as well as by the uncertainty in how deposition seasonality itself might change over such an extended period.

We acknowledge that this simplification may underestimate short-term or peak TFA concentrations in particular strata resulting from seasonal maxima in deposition. We have revised the relevant section in the manuscript to clarify this point and to guide interpretation of the results:

“Assuming no inter-annual variability in the annual TFA deposition fluxes (Table 3), we estimated net TFA accumulations in the surface water, soil, and sediment of the three watersheds over a 30-year period. While TFA deposition varies seasonally, the focus here is on the accumulation of TFA over the 30-year period. Also, it is unknown how the seasonality itself would vary over the 30-year period. So the surface fate and transport modeling was based on the mean annual deposition flux.”

We trust this revision clarifies the rationale for our modelling approach and its limitations.

L353f and L362: Both statements seem to suggest that a large fraction of TFA will accumulate in the soil. To me it is not clear on which time scales you are discussing this. In steady state (which apparently is reached quickly), input from the atmosphere should be equal to outflow to the ocean. Or is what you call deep soil a open boundary for the model as well? Furthermore, this strong flux to soil seems to contradict the statement in the footnote of Table 1: " Adsorption/desorption tests results show that TFA is poorly adsorbed to the soil and is considered as a mobile organic compound in the majority of soils investigated." Please clarify.

Response: We appreciate your helpful comment. To clarify, TFA is considered highly mobile in soil due to its low octanol-water partition coefficient (K_{ow}), which indicates a strong preference for remaining in the aqueous phase rather than adsorbing to soil organic matter. Adsorption/desorption tests of TFA confirm that TFA is poorly retained by most soils, consistent with its classification as a mobile organic compound. Because of this high mobility, TFA does not accumulate in the soil over long timescales. Rather, it tends to leach downward from surface soil into subsurface layers and potentially into groundwater. The apparent accumulation in "soil" discussed in our manuscript refers to transient retention in the soil column before leaching, rather than long-term storage. In this context, "deep soil" serves as a transitional boundary in the mass balance model rather than an open system boundary or final sink. Importantly, our model does not explicitly simulate transport through the full vadose zone or groundwater systems. Instead, the mass flux from surface soil to deeper compartments is estimated through mass balance. Our primary focus is on the surface water compartment and the timescale on which TFA reaches steady state in surface waters. We have revised the text to clarify this in the discussion of mass allocation analysis to avoid confusion regarding the contradiction with TFA's known mobility in soil.

L378: For the Rhine catchment a more direct comparison between simulated atmospheric inputs and measured TFA in precipitation could be done (see Freeling et al., 2020).

Response: We thank the Reviewer for highlighting the opportunity to compare our simulated atmospheric TFA inputs with observed precipitation data, specifically those published by Freeling et al. (2020). We acknowledge that Freeling et al. provides an important dataset for TFA concentrations in precipitation (rain and snow) in the Rhine catchment, which is highly relevant for validating atmospheric deposition models. However, a validation

using observed rainwater TFA concentrations from Freeling et al 2020 would not be appropriate here because we are simulating TFA formation due to prospective pMDI usage only. Also, the focus of our study is on quantifying TFA concentrations in surface waters, rather than simulating or directly analysing atmospheric deposition fluxes or precipitation concentrations. Consequently, our direct modelling outputs, i.e., surface water, are not comparable to the precipitation measurements reported in Freeling et al. (2020) but rather to direct measurements from Sturm et al. (2023), which specifically reports TFA concentrations in Rhine surface waters. For completeness, in the revised manuscript, we have now calculated global TFA rainwater concentrations (Figure 8 and Section S3) and performed qualitative comparison of those results with that from Freeling et al. 2020 and other relevant TFA rainwater concentrations globally.

L407f: Why not discuss with the often quoted NOEC for the most sensitive freshwater algae, which is 120'000 ng/L? In addition, as TFA cannot be removed from drinking water at large scale, the discussion of an additional threshold much higher than the one suggested for drinking water seems a bit artificial.

Response: We thank the Reviewer for their thoughtful suggestions regarding the discussion of TFA concentration thresholds. In our manuscript, we used the German drinking water threshold of 10,000 ng/L as the most conservative regulatory guideline available at the time of our analysis. We acknowledge, however, that the Netherlands recently established a more stringent threshold for TFA in drinking water of 2,200 ng/L.

Regarding ecotoxicological relevance, we appreciate the Reviewer's point about the often quoted NOEC (No Observed Effect Concentration) for the most sensitive freshwater algae, which is 120,000 ng/L. We agree that including a comparison to this ecotoxicological benchmark provides important context for assessing potential ecological risks. In our study, the highest estimated TFA concentration in surface waters was ~19 ng/L. This value is orders of magnitude below both the German and Dutch drinking water thresholds, as well as the NOEC for sensitive freshwater algae.

We also agree that since TFA is highly persistent and not removable at large scale from drinking water, it is more appropriate to focus discussion on the most relevant and up-to-date regulatory limits, rather than any threshold substantially higher than the current drinking water guidelines. Following the reviewer's advice, we have revised the discussion to (i) include the recent Dutch drinking water threshold, (ii) compare our findings to the ecotoxicological NOEC for freshwater algae, and (iii) clarify that the concentrations we observed are well below all of these thresholds.

We have now revised the concluding relevant section to the following:

“Lastly, the model's predicted TFA levels can be effectively evaluated by comparison with several established reference values. The highest surface water TFA concentrations attributable to pMDI use are more than 500-fold lower than the German Environment Agency's conservative drinking water threshold of 10,000 ng L⁻¹ (Arp et al., 2024). Similarly, these modeled concentrations are greater than 100 times below the Netherlands' most recent drinking water guideline of 2,200 ng L⁻¹ (Arp et al., 2024), derived based on precautionary potency factors for PFAS. When placed in ecological context, the maximum TFA level estimated in surface water is also over 6,000 times below the frequently cited no-observed-effect concentration (NOEC) of 120,000 ng L⁻¹ for sensitive freshwater algae (Arp et al., 2024), indicating negligible risk to aquatic biota. For soils, predicted TFA loadings from pMDI emissions remain at least 90,000 times lower than the REACH long-term NOEC of 830,000 ng kg⁻¹ for plant health (Arp et al., 2024). Furthermore, given that the lowest TFA concentration empirically measured in Rhine surface water is 400 ng L⁻¹ (Sturm et al., 2023), prospective new emissions from pMDI use would represent less than 1% of the total TFA present in this major watershed (or catchment).

Taken together, these findings demonstrate that even if HFO-1234ze(E) were to become the sole medical propellant in future pMDIs of all manufacturers, its continual atmospheric release would result in only very low additional quantities of TFA in both surface water and soil—levels that are several orders of magnitude below thresholds for human health or ecological risk. The maximum TFA concentrations projected by this study remain much lower than all currently relevant drinking water, aquatic, and agro-environmental benchmarks. This demonstrates a substantial margin of safety, underscoring that, while TFA is environmentally persistent, its contribution from next-generation propellant use is expected to remain well within safe regulatory and ecotoxicological limits.”

We thank the reviewer for helping us improve the relevance and clarity of our discussion.

Technical comments

Citations in text: Luecken et al.(Luecken et al., 2010) should be Luecken et al. (2010). Applies to all references that should not include the author.

Response: This and other occurrences of incorrect formats of author name-based references have been corrected in the revised manuscript.

Andersen et al., 2018 and 2022: Should be Sulbaek Andersen et al., 2018. Sulbaek being part of the surname not the given name.

Response: We have corrected the incorrect format of references to the articles by Prof. Sulbaek-Andersen in the revised manuscript throughout.

Figure 6: The labels for the color scale of TFA deposition rates are too small and even with zooming in the pdf cannot be deciphered. Similarly for all other labels.

L375: "Alpine" instead of "Alphine".

Response: Corrected.

References

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