Reply to 'Comment on egusphere-2025-2861' by Anonymous Referee #2

Comments are copied in plain text.

Replies are given in blue.

Changes to manuscript are highlighted in green.

The authors present a comprehensive assessment of TFA concentrations recorded in precipitation and surface waters in Switzerland 2021-2023. They compare these measurements with those taken from archived water samples and demonstrate significant increases in TFA concentrations in recent years. They also conduct a number of modelling studies to determine TFA deposition from the atmosphere and determine that this cannot be the sole driver of the observed TFA increases. They propose terrestrial inputs from PPP and veterinary pharmaceuticals as a more significant contributor to TFA contamination in surface waters. They also suggest an atmospheric TFA source that predates the introduction of known precursors (though it seems they are suggesting a further anthropogenic source, in which case this should be made clearer in the abstract).

The report is generally well written and presents an important study into TFA contamination at a national level. However, there a few areas that need further discussion or that have been omitted.

Firstly, there should be full justification of the veracity of the archived water samples as these form a major basis for many of the conclusions drawn.

Archived water samples were analysed for stable water isotopes signature and stored accordingly to prevent contamination from the atmosphere during storage (amber glass bottles with screw lock and rubber septa, in the dark, at 12-14°C room temperature). Repeated isotope analysis after more than 20 years of storage revealed no signs of contamination in the water isotopes. Contamination by other compounds is without compromising the water isotopic signature is extremely unlikely. We rephrased the paragraph as follows:

"Archived samples were stored in amber glass bottles capped with screw tops and inserted septa at temperatures of 12 to 14 °C (Schotterer et al., 2010) under predominantly dark conditions in a cellar. Storage conditions were checked for long-term stability of stable water isotope consistency by redetermination of stable isotopes using Cavity Ring Down Spectrometry after decades of storage (Leuenberger and Ranjan, 2021) in comparison to previous conventional determination by mass spectrometry on these samples right after sampling as part of the IAEA GNIP programme (International Atomic Energy Agency, 2025)."

Secondly, the relationship between CF_3CHO and TFA formation has been omitted from this study. Given the recent literature on the potential impacts of CF_3CHO on TFA concentrations and the uncertainty it introduces to TFA yields etc. it should at least be discussed and could go some way to closing the gap seen between the modelled deposition and the measurements.

We would like to thank the referee for this comment. We have included a brief discussion of the degradation of CF3CHO and how recent studies may change the best estimate of TFA yields in our discussion of the gap between observed and simulated deposition rates.

Furthermore, the relative importance of the degradation pathways of the intermediate CF3CHO (trifluoroacetaldehyde), formed during degradation of some HFCs (e.g., HFC-143a, 236fa, 245fa, 365mfc) and HFOs (e.g.,

HFO-1234ze(E), HFO-1336mzz(Z), HCFO-1233zd(E)) may differ from what was assumed in the yields used here (see Table 2 and 3). Three main degradation paths exist for CF3CHO: reaction with OH, photolysis, and hydrolysis. TFA yields from the OH reaction are small, whereas hydrolysis leads mostly to TFA and no TFA is formed in the photolysis path. However, the latter gained recent attention due to the potential of forming HFC-23 (a very stable compound with a large GWP). Hence, lifetimes of CF3CHO lifetimes were recently re-evaluated (Baumann et al., 2025; Sulbaek Andersen et al., 2023; Nielsen et al., 2025). The updated results suggest that previously used TFA yields may be too small and that yields will strongly vary across the troposphere. Even with larger yields the degradation of HFCs along this path may not add considerable amounts to TFA deposition (compare Table 2). However, increased TFA yields from the degradation of HFOs (other than 1234yf) could likely explain gaps between observed and simulated TFA deposition rates.

More generally, tables and figures could be better placed throughout the manuscript (i.e. near the text the references them) and more accessible for those with colour-blindness (though I appreciate this is difficult to achieve with figures such as those presented here).

We admit that the placement of figures and tables was not optimal in the submitted manuscript. However, this should be dealt with at the time of typesetting. All figures have been re-visited in terms of readability and accessibility for color-blindness and should now meet the suggestions by Copernicus.

Specific comments:

Line 7: unnecessary '-'

Removed.

Line 8: Where does the 60-70% come from? From the other % range seems like it should be 52-71%?

We admit that the given ranges were not explained well due to the brevity of the abstract. The values give the range across the precipitation sites on the Swiss Plateau. The lowest (highest) ranges of the individual contributions don't have to add up to the overall ranges, since the sites with the lowest contribution from HFOs does not necessarily have the lowest contribution from long-lived compounds. However, we rephrased the sentence, clarifying what the ranges represent and giving the mean across the sites in addition.

"Simulated atmospheric degradation of known TFA precursors accounted for 63 (58-70) % of the observed deposition (48 (41-54) % hydrofluoroolefins and 15 (12-18) % long-lived fluorinated gases; mean and range across sites) for sites on the Swiss Plateau."

Line 11: Presumably this value refers to total atmospheric deposition (wet + dry?)

Inputs from PPP and veterinary pharmaceuticals do not enter through the atmosphere but through degradation in the soils. We rephrased to make this more obvious. For the case that the comment referred to L9, we also added '(wet and dry)' in front of deposition.

"In Switzerland, atmospheric (wet+dry) deposition amounted to 24.5+/- 9.6 Mg yr^{-1}, whereas TFA terrestrial inputs from the degradation of plant protection products (PPP) and veterinary pharmaceuticals in soils, estimated from the literature, ranged from 3.9 to 13.2 Mg yr^{-1}, depending on the assumption on degradation efficiency. TFA inputs from the degradation of PPP dominated 2-3 times over atmospheric deposition in Swiss croplands."

Line 14: 1990s instead of 1990ies (also occurs …)

Replaced everywhere.

Line 24: There are some reports that suggest TFA may bioaccumulate in plant material

This was expressed in the following sentence that referred to the accumulation in leaf material and plant extracts, most likely due to water transpiration, while icons (trifluoroacetate) remain in the plant. We rephrased somewhat to improve the link between both sentences.

" *Although TFA does not generally bioaccumulate, elevated TFA concentrations were, however, observed in leaf material and plant extracts (references)*".

Line 39: 'As a consequence' as opposed to 'In consequence', 'potential risk' as opposed to 'risk'

We would like to thank the referee for these suggestions and adopted them.

Line 56: () within ()

This was fixed in the revised manuscript.

Line 117: Is the conducted test sufficient to prove the veracity of the archived samples?

See major comment above.

Line 169: Error of 10% for the emissions estimates – please justify this number?

The 10 % uncertainty estimate for the average hemispheric deposition rate is fully based on the uncertainty estimate of the global emissions of long-lived compounds. These uncertainties were estimated as part of the global inverse modelling calculations with the 12-box model and incorporate uncertainty due to atmospheric observations, the transport model and OH lifetime (see Henne et al., 2025 and Rigby et al., 2008). We slightly rephrased the paragraph for clarification.

"*The uncertainty on the estimated average hemispheric deposition rate will mainly be driven by the uncertainty of the emissions. The latter was estimated as part of the 12-box model simulations and, as an a posteriori estimate of a Bayesian inversion, includes contributions from the observational uncertainty and transport model uncertainty. Furthermore, uncertainties of the OH lifetime are considered. For details on the 12-box model please refer to Henne et al. (2025) and Rigby et al. (2008).*"

Line 197: You should justify why the model was run for 60 days, as from a trajectory viewpoint it seems far too long to give a reliable distribution

Please note that trajectories in FLEXPART should be seen from a stochastical point of view. Although, an individual trajectory cannot be expected to give a very good representation of an air mass transport after 60 days, FLEXPART represents air masses by a multitude of model particles which undergo both, transport by the mean wind as well as turbulent and convective transport simulated as a stochastic process. Here, we repre-

sent HFO-1234yf emissions from Europe within an individual month with 10 million released model particles. On average, this corresponds to approximately 5 model particles released per day from grid cells that contain any HFO emissions (at a spatial resolution of 0.1° x 0.1°). However, the number of released particles is kept proportional to the mass emissions in each grid cell, meaning that considerably more model particles are released in areas with high emissions. We agree that the number of model particles may is still too small to interpret simulated concentrations and deposition rates on a sub-daily scale, but the good agreement of simulated and observed HFO-1234yf at daily resolution (Figures 5 and A4), indicates that the approach is robust on this time scale. We modified some of the model description in order to emphasize the stochastical approach.

"As a Lagrangian particle dispersion model, FLEXPART does not forecast concentrations in a spatially-fixed grid, but along a multitude of trajectories of the flow field assuming a Markov process to describe turbulent transport. Trajectories were calculated for air parcels released at the model's surface and representing a given amount of emitted HFO-1234yf (see below). Individual air parcels were tracked for 60 days in the atmosphere undergoing mean transport and turbulent and convective dispersion. The chemical composition of these air parcels was simulated according to the above description. Gridded concentrations and deposition rates were then obtained by sampling all air parcels within a given grid cell or column and during a respective averaging interval."

Line 241: What is the timescale of hydrolysis of TFF to TFA?

In the model this happens instantaneously with a model time step of 600 seconds as soon as cloud water is present. This was already mentioned on line 187, but we now added the values of time step to clarify. This model time step is much longer than the time for complete hydrolysis of TFF with a hydrolysis rate of 150 s^{-1} (George et al., 1994). The revised text reads:

"The hydrolysis of TFF to TFA was considered to be complete within a single model time step of 600 seconds (compared to a hydrolysis rate of 150 s^{-1} George et al., 1994), too short for the current model scale to allow for quantitative sensitivity tests and to assess it as a source of uncertainty."

Line 247: Why did you use The Henry's Law constant of HNO_3 when there are reported values for TFA? There is uncertainty in the TFA value that may mean it diverges from the HNO_3 value. Given the importance of this parameter in wet deposition and the importance of this loss to the atmospheric fate of TFA, the uncertainty of this would be a useful thing to explore. Regardless, the value used should be given in the text with ref

We agree that the uncertainty associated with the wet deposition grants further exploration. We already mention that with the revised deposition scheme in the latest FLEXPART release (version 11, Bakels et al., 2024) additional studies should be carried out. In addition, and given the large Henry's Law constants involved, meaning that most TFA will go into the aqueous phase, it is probably not these constants themselves that introduce uncertainty in wet deposition, but rather simulated cloud water content and precipitation rates (the latter determining below cloud scavenging in the current parameterization in FLEXPART as already discussed in the manuscript). We used Henry's Law constant for HNO_3, since this was done in several previous studies. The employed value of the effective Henry's Law constant of $1x10^{14}$ M atm^{-1} goes back to the value published for HNO_3 in the original publication of FLEXPART's wet deposition scheme (Wesely, 1989), which was calculated with near-neutral pH. The effective Henry's Law constant for TFA at near-neutral pH is considerably smaller ($2.7x10^{10}$ M atm^{-1}, based on H=8900 M atm^{-1} and pKa=0.52 for TFA; Burkholder et al., 2015). Currently, FLEXPART does only employ a Henry's Law constant that is constant and does not vary with tem-

perature or pH of cloud droplets. We added this information in the manuscript and emphasized this source of uncertainty and its improved treatment in future studies.

"Both processes are represented in FLEXPART, assuming that TFA behaves like nitric acid (employing a constant effective Henry's Law constant of $1 \cdot 10^{14}$ M atm^{-1}, Wesely, 1989; Stohl et al., 2005), which corresponds to the vast majority of TFA residing in the liquid phase and, hence, fast washout through in-cloud wet scavenging. FLEXPART treats in-cloud and below-cloud scavenging of gases separately, with the latter only depending on precipitation rates."

"The latest version of FLEXPART (v11, Bakels et al., 2024) features an improved description of atmospheric deposition and future simulations should benefit from this update and should also consider a more specific and temperature dependent Henry's law constant for TFA."

Line 255-275: There should be mention of recent publications relating to CF_3CHO that dispute TFA yields, specifically the 4-60% value for HFO-1336mzzZ, and introduce extra uncertainty that hasn't been accounted for in this study as it stands

This relates back to the major comment above. We now reflect on the role of CF3CHO degradation pathways in the discussion. We also emphasize that a re-evaluation will be especially important for the HFOs (other than HFO-1234yf) as their contribution may thus be similar to that of HFO-1234yf.

Line 274: Typo 'emissions'

Fixed.

Line 280: Are the samples below the estimated quantification limit considered in the average? How can you quantify a value below the limit of quantification? What is the limit of detection? How is the limit of quantification derived?

Few samples below LOQ are present in the presented TFA dataset (97 of 1570 samples). These were estimated as 0.04 ng L^{-1} and were considered as such in any aggregation/averaging. The LOQ was estimated in Scheurer et al. (2017) following DIN 32645 (DIN, 2008) by equidistant calibration. No level of detection was defined in their study. We slightly revised our statement pointing to the original publication of the analytical method.

"All water samples were filled in PE centrifuge vials prepared at FOEN, RüS or Eawag and shipped to the DVGW-Technologiezentrum Wasser (German Water Centre) in Karlsruhe, Germany, where they were analysed by ion exchange liquid chromatography (LC) coupled to electrospray tandem mass spectrometry (MS-MS) with a limit of quantification (LOQ) determined as 50 ng L^{-1} (Scheurer et al., 2017). Any values reported below the LOQ (97 of a total of 1570 samples) were given as 0.04 ng L^{-1} and were treated as such in any averaging"

Line 281: Is this 0.58 ± 0.58 correct?

Yes.

Line 283-303: Are you using T-dependent rate constants for HFO+OH? Some of the HFOs you are considering have a negative relationship between k and T

Yes. The temperature dependency was considered for the explicitly treated HFO-1234yf. For the smaller contributors (HFO-1234ze(E), HFO-1336mee(Z), and HCFO-1233zd(E)) no explicit simulations were done and, hence, their potentially opposite lifetime dependency on temperature was not considered. To clarify, we added the utilized rate constants for HFO-1234yf to the text:

"HFO-1234yf degradation due to reaction with OH and Cl is described following the scheme and rate constants (k_{OH} = $1.26 \cdot 10^{-12} exp(-35/T)$ $cm^3 molec^{-1} s^{-1}$ and k_{Cl} = $7.03 \cdot 10^{-11}$ $cm^3 molec^{-1} s^{-1}$) suggested by Hurley et al. (2008). "

Line 311: Could deposition not also be a driver of load seasonality (in addition to discharge seasonality)?

Yes, this is what we wanted to express with these two sentences. Although, we don't directly see the seasonality in rainwater concentrations reflected in the river concentrations, we see the same seasonality in the loads. Hence, additional run-off (meltwater and groundwater) dilute the precipitation concentration signal. We slightly rephrased to clarify our intention:

"However, seasonality of TFA loads (concentration multiplied by flow rate) with a summertime peak was observed at S-Chanf and Diepoldsau, where there are no greater lakes in the catchment upstream and we can expect little delay between the concentration maximum in precipitation and that in river discharge (Fig. 3b). The latter seasonality of loads is clearly related to the discharge seasonality at these sites, with greater discharge in the summer, partly from snow and glacier melt, offsetting the concentration signal."

Line 327-329: 'underlines' and 'underlining' should be replaced with 'supports' and 'reinforcing'

We would like to thank the referee for these suggestions, which we adopted accordingly.

Line 330-334: Does this evidence not serve as an argument against pre known-precursor TFA?

The glacial ice dates from 1892 to 1978. The absence of TFA (i.e., concentrations below LOQ) in these samples underlines that there were no major atmospheric precursors contributing to TFA deposition before 1978. However, about a decade later TFA can be quantified at least in summer-time precipitation samples. The precipitation weighted mean TFA from the archived precipitation samples collected in 1986/87 was not much higher than the LOQ, 0.08 ug L-1 (N=25), for which nine samples were below the LOQ (see section 3.4). Hence, we can conclude that the unknown pre-cursor gained importance in the 1980ies but at a relatively slow rate. We added this information in the discussion of the unknown precursor in section 3.5.1.

Furthermore, and as described above, glacial ice dating back to 1978 did not contain TFA above the LOQ, which would imply an earliest possible onset and slow growth of a significant contribution of an atmospheric precursor to TFA deposition in the Swiss Alps at the beginning of the 1980s.

Line 343: 'No significant TFA gradients with depths were detected in the other lakes' so concentrations at depth were the same as the surface? Were the values elevated?

Samples were taken both at surface and lake bottom, as indicated in Table 1. Both for Lake Zurich and Lake Geneva no significant concentration difference were observed. We rephrased to clarify our statement:

" No significant TFA differences between lake surface and lake bottom were observed in the Lake Zurich and Lake Geneva (Table 1)."

Line 383: Replace ‘the latter’ with ‘this’

Done.

Line 391: ‘large HFO emissions in the Po Valley’ ? Are these emissions simulated in the model at an appropriate resolution to be able to make this claim?

Emissions are provided to the model at a resolution of 0.1° x 0.1° (see section 2.3.2 and Figure A2). At this resolution the emission maximum in the Po Valley is well resolved. No changes to the text seemed required.

Line 400: ‘compared with’ instead of ‘compared to’

Done.

Line 409: Remove ‘as well’ and replace with also earlier in the sentence

Done.

Line 415: It also suggests that if these unknown sources exist, they are likely to be anthropogenic

We agree with this conclusion and have added it to the sentence.

"The explained fraction was considerably smaller for two sites in more urban/suburban environments (Bern, Basel-Binnigen), which may indicate additional anthropogenic primary sources of TFA to the atmosphere."

Line 426: What is the estimated combined uncertainty of the simulated TFA deposition? It should be reported here along with the specific contributions of the TFA yield vs the precursor emissions

The estimated combined uncertainty of the simulated TFA deposition was given in Figure A5. This was not very clear and has now been added to the sentence and an average uncertainty is now given for the Swiss Plateau sites as well.

The estimated combined uncertainty of the simulated TFA deposition, accounting for uncertainty in TFA yields and precursor emissions, was about 66 % for the precipitation sites on the Swiss Plateau (compare Fig. A5) and cannot fully explain the unaccounted fraction of TFA in the observations.

Line 430-431: This sentence ‘faster (slower) … increased (decrease)’ is not worded clearly.

We rephrased to:

"A 10 % faster OH degradation resulted in an increase of TFA deposition in the Swiss domain of 4 %. Vice-versa, a 10 % slower OH degradation decreased deposition by 4 %."

Line 448: ‘which is in the range smaller 0.3%’ does not make sense and there is also an unclosed ‘(‘

The threshold of 0.3 % was given as an upper limit for individual compounds, whereas the example for the most important HFC yields a smaller contribution. We rephrased as follows:

"However, since hemispheric background mole fractions determine the TFA deposition, the domestic fraction should be similar to the Swiss contribution to global emissions of these compounds, which is smaller 0.3 % for

the long-lived compounds considered. In the case of HFC-134a, Swiss emission of 410 Mg yr^{-1} (Swiss Federal Office for the Environment, 2024b) in 2022 can be contrasted by global emissions of 250 Gg yr^{-1} (Henne et al., 2025), hence, a Swiss contribution of 0.16 %."

Line 451: 'For non-atmospheric sources of TFA'

Done.

Line 484: Need an 'is' between 'discharge' and 'below'

Done.

Line 489: This should be more specific e.g. 'PPPs may be a more relevant source of TFA to environmental aqueous phases (i.e rivers and lakes) in Switzerland'

We would like to thank the referee for this suggestion and rephrased it accordingly.

" *These results indicate that over Swiss cropland PPPs may be the more relevant source of TFA to environmental aqueous phases (i.e., rivers, lakes and groundwater).* "

Line 494: Remove () from reported flux to be consistent

Done.

Line 503: Missing '('

Done.

Line 511: TFA in rainwater in Bayreuth?

Yes, in rainwater. The information was added to the text.

Line 514-518: Clarify that you're talking about TFA concentration in rainwater and in archived plant material

This paragraph reviewed earlier TFA in rainwater concentrations reported in the literature and compared them to the archived rainwater samples as analyzed for this study. There was no mention of archived plant material. Hence, no changes were made to the text.

Line 528: Was 2019 when HFO use started to increase exponentially? If yes, I would explicitly make this link

Yes, HFO emissions increased strongly after 2019 as indicated in Figure A1. The growth was more linear than exponential, but since we did not use the latter term for the increase in TFA in precipitation either, the link between TFA in precipitation and HFO emissions remains fairly obvious and was added to the sentence.

" *After 2019, the increase in TFA concentrations in precipitation accelerated reaching mean (all sites) concentrations of 0.643 µg L^{-1} in 2023 (PWM: 0.496 µg L^{-1}), which, qualitatively, is in line with a strong increase of HFO emissions in the same period (see Fig. A1).* "

Line 542: You should be specific as to what other sources you are suggesting (agricultural run-off? Natural sources?)

The remainder of the paragraph explains our suggestion that these emissions are from aluminum smelting. We added 'industrial' in this sentence to clarify the link with the following.

Line 548: Do these processes release fluorocarbons into the environment via wastewater etc only or is there a potential gaseous emission?

Both pathways are possible and the widespread fluorocarbon pollution on the grounds of the former aluminum smelter suggests considerable transport through the atmosphere. However, no quantitative knowledge of the importance of the pathways exists. The text was modified to acknowledge both possibilities.

Line 627: Also there's massive uncertainty in the yields?

We feel that the possibility of uncertainty in the yields was already addressed in the previous sentence and does not require repetition in this sentence, which points at the temporal and spatial variability of yields. No changes were made to the text.

Figure 2 & 3: Additional x-ticks representing the months or every 3 months would make these figures easier to interpret where variations are not exactly halfway through the year

Figures 2 and 3 were completely revised also to make them more suitable for color-blind readers. Instead of 3-monthly minor ticks, 6-monthly minor ticks were added and since the individual sites were more separated in the display, it should be much easier to follow the annual cycle.

Table 2 & 3: Should present the 3 yields used rather than the range, lifetime of '1' should be reported as '1.0' for consistency, last column in each needs () around units

The yields are now presented as mean (min – max). Values of 1 are now given with decimal point and all units are given in braces.

References

Bakels, L., Tatsii, D., Tipka, A., Thompson, R., Dütsch, M., Blaschek, M., Seibert, P., Baier, K., Bucci, S., Cassiani, M., Eckhardt, S., Zwaaftink, C. G., Henne, S., Kaufmann, P., Lechner, V., Maurer, C., Mulder, M. D., Pisso, I., Plach, A., Subramanian, R., Vojta, M., and Stohl, A.: FLEXPART version 11: improved accuracy, efficiency, and flexibility, Geosci Model Dev, 17, 7595-7627, doi: 10.5194/gmd-17-7595-2024, 2024.

Burkholder, J. B., Cox, R. A., and Ravishankara, A. R.: Atmospheric Degradation of Ozone Depleting Substances, Their Substitutes, and Related Species, Chemical Reviews, 115, 3704-3759, doi: 10.1021/cr5006759, 2015.

DIN, 2008. Chemical analysis - decision limit, detection limit and determination limit under repeatability conditions - terms, methods, evaluation. DIN 32645, 2008 - 2011.

George, C., Saison, J. Y., Ponche, J. L., and Mirabel, P.: Kinetics of Mass-Transfer of Carbonyl Fluoride, Trifluoroacetyl Fluoride, and Trifluoroacetyl Chloride at the Air/Water Interface, Journal of Physical Chemistry, 98, 10857-10862, doi: 10.1021/j100093a029, 1994.

Henne, S., Vollmer, M. K., Guillevic, M., Schlauri, P., and Reimann, S.: The Annual Kigali-Index (AKI): a climate change indicator in support of the hydrofluorocarbon phase-down of the Montreal Protocol, in preparation, 2025.

Rigby, M., Prinn, R. G., Fraser, P. J., Simmonds, P. G., Langenfelds, R. L., Huang, J., Cunnold, D. M., Steele, L. P., Krummel, P. B., Weiss, R. F., O'Doherty, S., Salameh, P. K., Wang, H. J., Harth, C. M., Mühle, J., and Porter, L. W.: Renewed growth of atmospheric methane, Geophys. Res. Lett., 35, L22805, doi: 10.1029/2008GL036037, 2008.

Wesely, M. L.: Parameterization of Surface Resistances to Gaseous Dry Deposition in Regional-Scale Numerical-Models, Atmos. Environ., 23, 1293-1304, doi: 10.1016/0004-6981(89)90153-4, 1989.