Reply to 'Comment on egusphere-2025-2861' by Tim Wallington

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Replies are given in blue.

Changes to manuscript are highlighted in green.

Henne et al. report the results of a comprehensive set of measurements of trifluoroacetate (TFA) in surface waters in Switzerland. There is substantial research interest in the sources, concentrations, and effects of trifluoroacetate in the environment. This paper is an important contribution to better understanding the levels, sources, and trends of trifluoroacetate in the environment. We have the following comments for the authors to consider.

We would like to thank the authors for their insightful comments and have adopted most of the suggestions as outlined below.

First, the United Nations Environmental Effects Assessment Panel of which some of us are members has assessed that the risks to human and ecosystem health from trifluoroacetate formed as a degradation product of ODS replacements are currently *de minimis* (Neale et al., 2025). For balance in the introduction where the toxicological effects are discussed the authors may wish to mention the assessment of the UNEP panel and note the need for further work to reconcile the divergent assessments in the literature.

We added a reference to the report/publication of the UNEP Assessment panel and repeat their main conclusion in the introduction.

"The UNEP Environmental Effects Assessment Panel reviewed the risks of TFA to ecosystems and human health and conclude that at current TFA concentration levels the risk to humans is de minimis *(Neale2025 et al., 2025)".*

Second, there are new measurements published by the German UBA (Umweltbundesamt) of trifluoroacetate in samples from the Atlantic Ocean collected from surface waters (n = 33) and from seven distinct depth profiles (n = 41) in 2022–23. Using these data, Neale et al. estimated that the mass of TFA measured in the oceans in the late 1990s and early 2000s, assuming even distribution of 200 ng L^{-1}, was about 500–1000 times higher than the estimated total anthropogenic TFA input to the environment (including Montreal Protocol gases, pesticides, pharmaceuticals, and industrial uses) over the period 1930–1999. The evidence for the contribution of one or more natural source(s) of TFA to the marine environment is relevant and should be mentioned.

We would like to thank the reviewers for their comment and acknowledge that we did not mention the UBA report so far because it is only available in German (besides the summary). We also don't think that the few samples for the deeper ocean are sufficient to estimate global mean ocean concentrations of 200 ng L^{-1}. More and representative observations in all major ocean basins would be necessary to arrive at this conclusion. Moreover, samples presented by Frank et al. (1996) were taken in 1995 near to the coast. Therefore, the latter TFA ocean concentrations rather overestimate the deep sea/open ocean TFA concentration, as wastewater (e.g. Nödler et al., 2014) and other inputs (e.g. groundwater exfiltration with impact from agriculture) may increase the coastal concentration of micropollutants in seawater. In the end, there is no consensus on the possibility of a natural TFA source in the oceans and we had acknowledged this by citing the study by

Lindley (2023), on the one hand, and the arguments of Joudan et al. (2021) on the other hand. Nevertheless, we added the results from the UBA report to the introduction, but without the conclusion that mean TFA concentrations in the ocean are at 200 ng L^{-1}, which the UBA authors also did not suggest but rather speculated on mechanisms that would bring TFA down towards the deeper ocean on shorter time scales (*Atlantic Meridional Overturning Circulation*, *Dense Shelf Water Cascading, sedimentation of particles and dead organisms*).

"Earlier studies have speculated about the existence of natural sources of TFA (i.e., deep-sea vents Scott et al., 2005). More recently (2022/2023), TFA concentrations of ocean samples down to a depth of 4590 m in the North Atlantic were estimated in the range of 237 to 294 ng L^{-1}, with slight decreases with depth and higher TFA concentrations at the ocean surface, 260 – 306 ng L^{-1} (UBA, 2024). A comparison with earlier observations is hindered by questions of measurement quality and validity."

Third, using the flux of trifluoroacetate (TFA) measured at several locations on the Rhine River in the Netherlands (2017-2023), an average flux into the Rhine basin of ca 0.5 kg TFA km^{-2} yr^{-1} can be estimated (Neale et al., 2025). This is of a similar magnitude to that estimated in Switzerland by Henne et al. There was no discernable trend in the flux of TFA in 2017-2023 suggesting either that degradation of HFO-1234yf was not a major contributor to TFA in the Rhine basin for 2017–2023, or that its increasing contribution was masked by compensating decreases in contributions from other sources. A discussion of how their findings compare with those of Neale et al. (2025) would be a useful addition.

We would like to thank the authors for pointing us to the TFA measurements at the lower Rhine in the Netherlands as published in the RIWA annual reports (Dutch only). However, we feel that the assessment of these concentration measurements in Neale et al. (2025) over-simplifies the complexities of the TFA budget in the large Rhine basin as it does not consider other hydrological pathways other than river run-off (e.g., groundwater formation, water extraction for irrigation) and lateral TFA fluxes. Scheurer et al. (2017) had analyzed TFA fluxes in the Rhine catchment and identified massive industrial releases in the river Neckar draining into the Rhine, but also concluded that there were additional industrial or waste water sources required to maintain and even increase TFA concentrations further downstream. Very similar to the TFA observations in the Netherlands, they reported TFA concentrations of 1.3 ug L^{-1} at the Rhine in Düsseldorf (close to the Dutch boarder). Following the publication by Scheurer et al. some attention was given to abate the TFA sources in Germany and it is very likely that the absence of a trend in TFA concentrations in the Rhine at Lobith (Netherlands) is due to a combination of decreasing industrial releases and increasing atmospheric inputs. However, without detailed hydrological modelling for the Rhine basin it seems impossible to better quantify these inputs. We re-evaluated the data mentioned by Neale et al. (2025) for the Rhine River water measurements at Lobith. For the years 2021-2023 (as in our study) we estimate an average TFA load of 79 Mg yr^{-1}, based on monthly TFA concentrations and water flow data. This compares to 93 Mg yr^{-1} in Neale et al., who applied a single average TFA and flow to derive the load. Please note that month-to-month variability in the loads is large and depends considerably on water levels. This variability also complicates the robust estimation of a trend. If we make the same assumption as in Neale et al. that the TFA load of the Rhine can be equated to the total TFA input through atmospheric deposition in the Rhine catchment (185'000 km^2), we arrive at an average deposition flux of 0.43 kg km^{-2} yr^{-1}, 0.5 kg km^{-2} yr^{-1} in Neale et al. This compares to a simulated average deposition flux of 0.46 kg km^{-2} yr^{-1} in the Rhine catchment directly taken from our model runs. Hence, the conclusion that atmospheric inputs dominate the TFA budget of the Rhine might be drawn. However, the average simulated TFA rainwater concentration for the same area was only 0.43 ug L^{-1}, compared to 1.2 ug L^{-1} in the Rhine at Lobith. This concentration enhancement still points towards additional sources and the need for more detailed hydrological modelling, which is beyond the scope of this study. Neale et al. (2025) used the discussion of the TFA concentrations at Lobith to dispute rising atmospheric TFA inputs. Given the results of our current analysis, which use a much more direct way to quantify atmospheric TFA inputs (i.e., archived precipitation samples), there can be no doubt about increased inputs after the market introduction of HFOs (compare Fig. 10, which uses a logarithmic scale). Furthermore, Freeling et al., (2020) reported observed TFA wet deposition rates of around 0.2 kg km^{-2} yr^{-1} for 3 sites in the Rhine catchment (see ES, SU, WK in their Table 2) and for the year 2018. Compared to our recent observations and simulations, this is in line with a strong increase in deposition in recent years. Hence, we don't think the discussion of the larger Rhine catchment and the connected uncertainties mentioned above, would add to our current manuscript. Nevertheless, we added the observation of Scheurer et al. (2017) for the Rhine in Basel to Fig. 11 and added the following general discussion of TFA in the Rhine.

" Since 2000 concentrations rose exponentially (Fig. 11, note logarithmic y-axis). In 2017, Scheurer et al. (2017) reported TFA concentrations in the Rhine in Basel of 0.4 µg L^{-1}, in line with the long-term increase and current (2021-2023) levels of 0.65 µg L^{-1} (Tab. 1). Further downstream (Scheurer et al., 2017) observed strongly enhanced TFA concentrations in the Rhine (up to 1.3 µg L^{-1}) and traced these to industrial sources and WWTP discharges. In the Netherlands, TFA is monitored by RIWA at several locations along the Rhine. Annually reported concentrations have largely remained above 1 µg L^{-1} since 2017, although peak concentrations (as expected from industrial discharges) have decreased in recent years (Fig. 1.18 in RIWA-Rijn, 2024)."

Fourth, it should be possible to propagate the error bars for the relevant parameters for both the precursor measurements and the TFA measurements/modelling results. This would allow for better comparison of the contributions to TFA accounted for and the “unaccounted” remainder. On the same note, greater clarity on how the TFA deposition fluxes from the individual precursors were calculated would be beneficial for the reader, for example which molar yield of TFA from HFO-1233ze was used for the calculations. This combined information would be informative and most interesting. Possibly, it could hint at additional atmospheric sources of TFA or lacking/incorrect understanding of the atmospheric oxidation chemistry involved.

We did propagate the uncertainties of the components of our calculations of TFA deposition at the individual observations sites wherever this was possible. This result was given as Figure A5 and briefly discussed in section 3.2. However, no complete description of the uncertainty calculation was given, and we now provide this information along with the Figure in the appendix. Other sources of uncertainty that cannot be quantified as easily (all model related elements like transport, reaction and deposition rates, representativeness of simulations are discussed qualitatively in the text. The following text on the uncertainty calculation was added to the appendix:

"The uncertainty of simulated TFA deposition rates for both long-lived and short-lived compounds was assessed as follows. For long-lived compounds we consider two sources of quantifiable uncertainty: simulated loss rates and TFA yields. The uncertainty of the former is taken from the a posteriori uncertainty estimate of global emissions for individual compound as estimated with the 12-box model. This estimate contains the uncertainty of the atmospheric observations propagated through the inverse modelling step and an additional lifetime uncertainty (see Rigby et al., 2008). For most compounds the by far larger uncertainty originates from the TFA yields. We assume that the values given in Table 2 represent the 95 % confidence range of the yields. We use Gaussian error propagation to combine both sources of uncertainty and sum over all long-lived compounds, where we assume fully uncorrelated uncertainty between yields and emissions and full correlated uncertainties for the yields

between compounds, since many of these come from uncertainties of yields from intermediate compounds. Similarly, we combine the uncertainty estimate on European emissions and yields for the additional HFO/HCFOs (Table3). Not formally quantified in this calculation are other sources of model uncertainty (transport, deposition rates) and representativeness, which are discussed qualitatively in the main text. The resulting uncertainty range for the relative contributions to observed deposition rates (Figure A5) represents the 95 % confidence range of this assessment."

Applied TFA yields for all HFCs and the direct impact on deposition rates are summarized in Table 2. For HFOs Table 3 contains the yields (range) and the European emission estimate. The last paragraph of section 2.3.2 discusses these numbers and where they were taken from. We feel that Table 2 and Table 3 already provide the information asked for (e.g., a yield of 2 – 30% for HCFO-1233zd(E).

Fifth, the statement in the conclusions "*Therefore, it is fundamental to continue efforts to abandon the use of fluorinated compounds, wherever possible, to avoid further, continued accumulation of TFA. Both industry and policy makers are called to increase their level of ambition*" is very generalized and simplistic. It fails to consider that not all fluorinated compounds degrade to produce TFA and that the stoichiometry is such that yields are not always molar. It also fails to recognize that the CF_3- group acts as a pseudo halogen that increases the efficacy of pharmaceuticals and pesticides to the direct and indirect benefits of humans and the environment. As discussed in Neale et al. (2025), TFA in the environment is present as salts that are highly water soluble and easily excreted. TFA-salts do not biomagnify in food webs and there are no known biochemicals or receptors that interact with TFA, although it is a moderately strong acid (pKa = 0.23), it is unreactive. There are wide margins of safety between current and predicted future concentrations in surface- and ground-waters levels of concern for human and environmental health. While continuous monitoring would be useful in quantifying future rates of change in concentrations, this should be focused on key matrices and should include measurements of systemic doses in the general population, such as those conducted in the NHANES program [1].

We agree with the reviewer insofar, that the reference to "fluorinated compounds" – while not irrelevant in terms of their effects on human health and the environment – is broader than the scope of our paper. We therefore adjusted the wording and refer now to "TFA and its precursors" instead. We do acknowledge the potential benefits of such compounds, why we formulated in our initial submission "wherever possible". We now provide further clarity on that point, referring to "abandoning all non-essential uses", instead.

We are aware that TFA does neither bioaccumulate nor biomagnify in food webs. However, as a persistent and mobile substance and with continuous emissions increasing environmental concentrations, it does accumulate in organisms. Together with its currently established classification as aquatic chronic 3 and its postulated classification as toxic to reproduction (Category 1B) as well as very persistent and very mobile (vPvM), a thorough application of the precautionary principle is warranted. Also the margins of safety (which under the current classification and existent guideline values in drinking water are on the order of 10) are decreasing and will continue doing so, until the effect of future regulation becomes visible.

We acknowledge the recommendation to place a focus on measurements in the general population and insert the corresponding remark.

Therefore, it is fundamental to continue efforts to abandon all non-essential uses of TFA and its precursors, to avoid further, continued accumulation of TFA. Both industry and policy makers are called to increase their level of ambition. Also, continued continent-wide monitoring, including human biomonitoring, will be necessary to *surveil progress and to further improve both our understanding of TFA budgets and our ability to forecast future burdens by atmospheric simulations.*

References

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