EGUSPHERE-2025-2882 Reply to Report #1

Comments are copied in plain text.

Replies are blue.

Changes to the manuscript are in green.

Response to RC1: 'Did you test that it did not leach or adsorb TFA?'
The revised text (Line 143-149) states that 'We blank tested the PE material to exclude any contamination. Because of the strong hydrophily of the TFA molecule, we did not consider sorption to the hydrophobic PE'. This can rule out contamination, but it does not demonstrate negligible loss due to sorption/adsorption. And the statement that TFA will not sorb to PE because it is hydrophilic is an assumption and should be presented as such unless supported by data or a specific reference. I think it will be good to clarify explicitly that sorption was assumed negligible and provide a supporting citation if available.

We agree and admit that we cannot present literature supporting the hypothesis that our precipitation setup does not adsorb TFA. We framed more carefully:

Lines 143-147:

We collected weekly streamflow samples from the river at a fixed position with turbulent flow. On the same day, we retrieved precipitation samples: rainwater was stored in a tank located below the funnel, which was emptied after sampling. The tank, funnel, and connecting tube (0.82 m) were composed of polyethylene (PE). We blank-tested the PE material to exclude any contamination. Because TFA is a small, negatively charged ion, we assumed sorption to the precipitation sampling setup to be negligible.

Response to RC2: 'This hints at seasonality in aquifer concentrations. Was this seasonality considered when calculating mass flux of TFA? In other words, was the groundwater discharge weighted with a "constant" groundwater TFA concentration or seasonal values of groundwater TFA concentration?'
The revised text (Appendix H, Lines 683–685) states that 'The mean TFA groundwater concentration error was set to 30% because measurements in the Freiburg drinking water supply indicated seasonal variability, with the same magnitude'. While this acknowledges variability, it does not actually account for seasonality in the groundwater mass-flux calculation. Please state explicitly whether groundwater TFA concentration was treated as constant in the groundwater export term and where this enters the load calculation.

The groundwater value was once measured as the mean of 8 deep wells. We treated the value as constant. As the reviewer mentioned, the 30% error accounts for variability. We rephrased to highlight the constant groundwater value in the main manuscript.

Line 253:

… c_{GW} (µg L^{-1}) is the mean groundwater TFA concentration of eight deep wells, which we assumed to be constant (Eq. 6).

Response to RC2: ‘There is a TFA surplus in Dreisam catchment which you attribute to manures. However, could this surplus be from legacy storage of TFA from previous years? Given that 2023 was dry year, the TFA from previous years could have been retained in catchment and subsequently be mobilized in the wet year, 2024.’
The revised text (Line 433-439) states that ‘The absence of an export deficit during the preceding dry year contradicts the assumption that the TFA export surplus in 2024 originated from the previous year. Since the surplus might stem from PPP use, discussing potential legacy storage is warranted’. This explanation is not logically compelling. A dry year can still export measurable TFA while simultaneously increasing subsurface storage because reduced hydrologic connectivity can limit flushing. Moreover, PPP-related inputs could contribute in 2023 without producing a clear annual surplus if low discharge and limited connectivity reduce catchment-scale export. Legacy effects may also operate on multi-year timescales and can involve multiple pools (stored dissolved TFA and/or persistent PPP residues/intermediates that generate TFA with delayed kinetics). Accordingly, please soften the inference that 2023 observations rule out legacy contributions and explicitly acknowledge that the elevated export in 2024 could reflect a combination of hydrologic flushing of previously stored dissolved TFA, and delayed formation and mobilization of TFA from persistent PPP residues and degradation intermediates. Finally, without direct measurements of PPP residues/precursors (or application records), statements such as “supported by our data” appear too strong; “consistent with our observations” would be more appropriate.

We agree with the reviewer. We acknowledge that TFA might stem from different pools (previously wet-deposited TFA or PPP precursors) and legacy effects apply on long time scales, and the sampling period of two years might be too small to catch that. We rephrased more carefully:

Lines 434-439:

The increased export observed in 2024 was particularly pronounced in the DRC compared to the Talbach, Brugga, and Zipfeldobel catchments. ~~The absence of an export deficit during the preceding dry year contradicts the assumption that the TFA export surplus in 2024 originated from the previous year.~~ The surplus might stem from previous year’s wet deposition or PPP use. PPP applications have been shown to leave residues in soils. Moreover, prolonged transformation times in soils, dependent on moisture conditions, have been reported for PPPs such as flufenacet, a compound that degrades into TFA. Thus, the hypothesis that fluorinated PPPs accumulate in soils and create a potential legacy storage of TFA is consistent with our observations. Moreover, contributions from previous years’ wet deposition might also add to TFA export.

EGUSPHERE-2025-2882 Reply to Report #2

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The description of sample storage is unclear (Lines 151-155). Do you mean the samples used for TFA analysis were stored in dark at room temperature for 4 months? Please specify the temperature range considered as “room temperature” here. I suggest substantiating the claim that TFA concentrations do not change even after storing at room temperature for 4 months with relevant literature, as the number of reanalyzed samples (n=3) is very small.

We agree that the number of reanalyzed samples is relatively small. However, we might have understated the amount of measurement, since in total we did 22 measurements over one year on the three samples. Reanalyzed environmental TFA samples stored in a basement for over 3 decades at temperatures ranging from 12 to 14°C and found plausible TFA values, many of them below the LOQ of 0.05 µg/L, indicating the storage does not significantly increase TFA concentrations (Henne et al. 2025). As for decreasing concentrations, TFA does not undergo degradation under the present storage conditions. Since standards prepared in the same vials also used for sampling still measure at the same concentrations as they did a month ago, we did not consider sorption to the vials as an issue. We integrated this into the manuscript to strengthen the hypothesis of stable TFA concentrations under the present storage conditions.

Lines 151-155:

The same number of TFA samples was collected in parallel in 50 ml polypropylene centrifuge tubes (Greiner, Kremsmünster, Austria) for subsequent analysis. Samples were stored in the dark and at room temperature (15-20°C) for up to four months. Numerous reanalyses of three samples over one year (n = 22) suggest that TFA concentrations remained stable during storage, which is also supported by the reanalysis of samples stored over several decades in current literature (Henne et al. 2025).

Since the section “3.5 TFA mass balance and agricultural TFA excess” has been removed, I suggest editing the introduction accordingly. Lines 47-51 give the impression that paper will refine or improve agricultural TFA excess estimates.

We thank the reviewer for this helpful comment. We agree that, after the removal of section 3.5, the introduction should not suggest that the present study refines or improves estimates of agricultural TFA excess. We have therefore revised lines 47-51:

Line 46-51:

Thus, we identify a general lack of comprehensive field studies concerning the accumulation, retention, and transport of atmospherically deposited TFA at the catchment scale. This gap extends to terrestrial TFA input from agriculture, since recent meta-analyses relied on sales data, estimated application masses, and hypothetical transformation rates to derive potential TFA contributions from PPPs for European countries and the contiguous USA (German Environment Agency 2023; Joerss et al. 2024). Although TFA formation from some PPP has been proven in theory, it remains unknown if agricultural TFA plays a notable role in a catchment’s TFA balance.

Line 60-61:

Third, we compared the TFA balance in the main catchment with mixed land use to the agricultural-free sub-catchments, acquiring insights into a potential impact of agriculture on the TFA balance.

In the following lines quoted from the conclusion, please specify that this estimation is reliable only

for headwater catchments without agricultural influence in DRC catchment. You might also consider using “catchment” rather than “case”:
“Our results showed that ET could be estimated from just two years of weekly TFA concentrations in the DRC case.”

Lines 534-535:

Our results showed that *ET* could be estimated from just two years of weekly TFA concentrations in areas of the DRC devoid of intensive agriculture.

References

Henne, Stephan; Storck, Florian R.; Wöhrnschimmel, Henry; Leuenberger, Markus; Vollmer, Martin K.; Reimann, Stefan (2025): Trifluoroacetate (TFA) in precipitation and surface waters in Switzerland: trends, source attribution, and budget. In: *Atmos. Chem. Phys.* 25 (23), S. 18157–18186. DOI: 10.5194/acp-25-18157-2025.