EGUSPHERE-2025-2882, reply on RC3

Comments are copied in plain text.

Replies are blue.

Changes to the manuscript are in green.

This study presents a valuable and comprehensive investigation into the atmospheric and terrestrial pathways, retention, and export of trifluoroacetate (TFA) at the catchment scale. The two-year dataset and multi-compartment sampling approach (precipitation, streamflow, springs, WWTPs) provide an important basis for understanding TFA dynamics. The manuscript is generally well written and organized; however, several methodological clarifications and interpretations should be addressed before publication.

We thank the reviewer for the time and effort that was put into the comments. We address the comments regarding methodology and other sections of our manuscript in the following answers.

Line 160–165:

Please clarify the rationale for choosing this separation column for TFA analysis. What are its advantages compared with other commonly used columns for PFAS analysis, such as the Hypersil Gold C18 column?

PFAS carry a hydrophobic fluorinated carbon chain, which would make them prone to binding to a C18-column. In the special case of the ultra-short chain TFA, this lipophilicity is reduced to a minimum (chain length is equal to one), and the negative charge on the organic acid group dominates the binding properties of the molecules to solid phases. Therefore, we use the AS17-C, which is optimized for separating anionic substances.

We changed the sentence accordingly:

The injection volume was set to 50 µl, with separation performed on an IonPac AS17-C column (2 × 250 mm) and an IonPac AG17-C guard column (2 × 50 mm) (both from Thermo Fisher Scientific, Waltham, USA), which is optimized for separating small anionic molecules like TFA.

Line 165–170:

The role of 50 mM ammonium hydrogen carbonate in pure water as mobile phase A should be clarified. If the separation column is hydrophilic, the use of methanol as mobile phase B may not be ideal. Please confirm the column chemistry and justify the chosen mobile phase composition.

We confirm the use of a 50 mM ammonium hydrogen carbonate buffer and methanol. The combination of methanol and buffer is intended to modulate the polarity of the mobile phase to achieve divided loading and unloading of the column. Starting conditions with 20% buffer were sufficiently polar to carry TFA on the column from the aquatic samples. Increasing the buffer to 50% was enough to re-eluate all TFA from the column. We therefore chose this composition. We want to mention that the initial work on finding these gradients was performed by Scheurer et al. (2017).

We added a sentence for clarification:

… and all samples were analyzed using the following gradient: 20% of eluent *A* (0-1 min), 20-50% *A* (1-10 min), 50-20% *A* (11-16 min). This gradient was sufficient for efficient binding and elution of TFA.

Line 175–176:

You mention Mill-Q blank samples as procedural blanks. Were these blanks also used to assess potential TFA contamination from the LC–MS system (e.g., tubing, fittings, internal components)? Please describe any specific cleaning or pre-conditioning procedures used to minimize TFA background signals from the instrument.

The main way to ensure the absence of contamination from the LCMS was by measuring MQ samples before starting a batch. This usually took 1-3 samples until the background levels were stable below 20 ng/L, which we considered as negligible. We added the following sentence to account for the comment:

To prevent contamination from the LC-MS system, we measured MQ-blanks until the background levels were below 20 ng L^{-1} before each batch.

Line 190–195:

It is mentioned that the same separation and guard columns used for LC–MS analysis were also used for IC analysis of major anions and cations. Does this imply that the IC system could potentially be used for TFA determination as well? If so, was this tested or verified?

Columns for IC have a wider diameter (4 instead of 2 mm), but the column material is the same. Berger et al. (1997) measured TFA with IC during their spiking experiments, but LOD for IC with a conductivity reading was about 0.06 mg/L, which is about one to two orders of magnitude above environmental TFA concentrations. Hence, TFA measurement with IC is possible, but not for environmental concentrations.

Additionally, please clarify whether “supplier” refers to the supplier of the IC instrument or of the columns. Did you determine quantification limits for each ion using your own calibration curves under actual operating conditions, which might be more accurate than supplier-provided values?

The actual *LOQ* values are below the supplier-defined ones, but they differ for the different ions. We followed the reviewer's suggestion and included them in the text:

Actual LOQ values, calculated analog to the TFA LOQ, were below the supplier-defined ones (Na^+ 0.83, K^+ 0.18, Mg^{2+} 0.026, Ca^{2+} 0.15, Cl^- 0.66, NO_3^- 0.126, SO_4^{2-} 0.188, all mg L^{-1}).

Actually, the suppliers for the column and the IC are the same. To avoid confusion, we specified this in the text as suggested by the reviewer:

Thermo Fisher Scientific reported a precision of 5% and an LOQ of 1 mg L^{-1} for the IC system.

Line 275–276:

Please elaborate on the factors leading to the highest TFA levels in the Dreisam River during the 2023–2024 winter.

We changed this section due to another reviewer’s comment:

Despite low TFA levels in precipitation, high TFA levels were observed in the Dreisam River during winter.

We now elaborate on this in the discussion section.

We argue that elevated TFA concentrations in the main catchment were caused by the use of PPP on the arable land at the valley floor: The Dreisam exhibited higher …

Figure 2:

Does the gray shading in panels (a–c) represent dry and wet conditions? Please specify this in the figure caption.

We apologize for the unclear phrasing and have changed the captions as the reviewer suggested:

Grey areas, showing changes from dry to wet conditions, are highlighted in Figure 3.

Line 303–304:

Based on the correlation data in Table 2, it seems that TFA showed positive correlations with all tracers except nitrate. Please confirm and revise accordingly.

We see the point that nitrate only correlates minimally with TFA in precipitation. We changed the section as the reviewer suggested:

In rainfall, TFA exhibited statistically significant positive correlations with all tracers except nitrate, showing the strongest associations with potassium and stable water isotopes.

Line 306:

The sentence “The same was true for the negative correlation with deuterium excess” is ambiguous. Please rephrase for clarity (e.g., “Similarly, TFA exhibited a negative correlation with deuterium excess”).

We changed the sentence as the reviewer suggested.

A significant negative correlation was found for rain volume and deuterium excess (D-excess).

Line 364–365:

You state that “Potassium negatively correlated with TFA; however, concentrations were below LOQ and could not be reliably interpreted.” How was the correlation established if potassium concentrations were not quantifiable? Please clarify or reconsider this statement.

The reviewer’s observation is correct; this indeed sounds confusing. Anyhow, potassium could be quantified despite the concentration being below the supplier-defined LOQ. We now used the LOQ we found for our IC-system, and most K^+ values were above this threshold, so we added an interpretation for potassium to the draft.

Potassium negatively correlated with TFA. Potassium in the spring water mainly stems from the weathering of silicate minerals in the soil or at the soil/rock interface. Therefore, low concentrations might indicate old water from deep aquifers, depleted of TFA. However, we advocate for care when interpreting the potassium-TFA correlation, because changes in potassium and TFA concentrations were minor and for potassium within the uncertainty range of the measurement (5%) (see Fig. F3).

Line 366–367:

Given that the spring pH is around 6, the previously cited finding that “TFA sorption to soils decreased with increasing pH up to pH 5” (Richey et al., 1997) may not adequately explain the observed behavior at the Zipfeldobel spring. Please discuss this limitation.

As the reviewer suggested, the findings on TFA sorption being dependent on pH do not apply to the spring because its pH is above 6. We reworded the paragraph:

Furthermore, p*H* showed a negative correlation with TFA. Prior findings indicated that TFA sorption to soils decreased with increasing p*H*. The increased sorption potential was observed up to p*H* 5 for soils with organic content smaller than 10% (Richey et al. 1997). The springs’ primary flow path lies at the bedrock soil interface in the hillslope, where organic content is low. However, the spring's p*H* levels were above 6. Consequently, sorption and desorption are unlikely to be the driving processes explaining the correlation between TFA and p*H* at the Zipfeldobel spring.

Line 428–430:

Considering TFA’s high mobility, the lack of significant retention in water bodies contrasts with reported TFA retention in plants and soils (Likens et al., 1997; Berger et al., 1997). Please elaborate on possible mechanisms or environmental conditions explaining this discrepancy.

There might be a misunderstanding. We think that TFA-retention from Likens and Berger et al. was primarily caused by their short sampling time. The mechanism that was missed was a delayed release of TFA from plants and soils.

We made it clear that the following sentences refer to the differences between the historical studies and the findings of our study. We rephrased the section:

…retention in plants and soils (Likens et al. 1997; Berger et al. 1997). Potentially, differences compared to our findings originate from the study design of both historic field experiments: Labeling with roughly a 1000-fold of today's annual background flux might have led to higher TFA uptake, and a sampling duration of less than one year might have missed the delayed release of previously taken up TFA. With up to 1 mg kg^{-1} dry weight (Freeling et al. 2022), leaves and needles might build up a substantial organic TFA pool. The decomposition of organic matter might release TFA from soils during wet conditions, aligning with the observation from the previous chapter (correlation with nitrate and discharge due to SSF through the soil zone). Both 1997-studies did not capture the wet winter following labeling in summer, and therefore might have missed delayed TFA export, resulting in higher retention values.

Line 430:

The sentence “Potentially, differences originate from the study design of both field experiments” should include more detail on what specific design differences (e.g., sampling frequency, soil types, hydrological setting) might explain the divergent results.

We added the fact, that both labelling studies form 1997 took place during summer and did not capture the winter export from litter TFA.

Please also see the comment above.

Line 447–449:

Please provide references supporting the statement that patterns/concentrations “were attributed to the distribution of TFA precursor molecules in the atmosphere.”

The reviewer is right: little is known about small-scale variability of TFA in precipitation. We rephrased more carefully to show that this is speculative.

Furthermore, heterogeneities in the precipitation input might cause TFA export excess. Elevated concentrations in precipitation in the vicinity of cities (Wang et al. 2014; Freeling et al. 2020) might be attributed to the distribution of TFA precursor molecules in the atmosphere. Whether those observations hold on a meso-catchment scale remains unclear. The lower part of the DRC is located downwind of the city of Freiburg. Therefore, elevated precipitation concentration in the Dreisam valley might be possible. Consequently, the spatial variation of input concentrations near Freiburg might explain some differences in the agricultural excess TFA amounts.

Line 380 vs. Line 470:

You stated that “our hypothesis of a temporal TFA storage, most likely associated with organic soil, seems valid,” yet later conclude that “We identified the organic soil zone as a primary TFA storage.” Since the data suggest only temporary accumulation, the latter conclusion may overstate the findings. Please rephrase to maintain consistency and avoid overinterpretation.

We took the comment of the reviewer into account and rephrased more carefully:

The study suggests that the organic soil zone exhibits temporary TFA storage, and SSF may be the process by which TFA is transported from soils to the river.

Line 475:

You compare TFA loads from farming activities with values reported for precursor PPP degradation in Joerss et al. (2024). If those values were derived from a different catchment, the comparison may not be meaningful. Please clarify whether the data are directly comparable.

The quantification of agricultural TFA excess and the corresponding sections were removed from the draft following another reviewer's suggestion.