The paper studies the retention and transport of Trifluoroacetate (TFA) in three catchments – two where atmospheric deposition is the only source and one with additional sources of agriculture and waste water treatment plants – and a spring in the southern Black Forest of Germany. The objectives of this paper include 1) investigating whether TFA retentions occurs within these catchments; 2) estimating TFA input through agricultural activities based on water flux measurements and their TFA concentrations; 3) identifying the primary pathways through which TFA reaches the stream; and 4) estimating evapotranspiration (ET) using TFA as a tracer. The paper uses the TFA concentration data in precipitation, stream water samples and groundwater and the fluxes of these water flows to calculate the mass balance of TFA at annual scale to examine whether TFA retention occurred in these catchments. They concluded that retention does not occur in catchments with only atmospheric deposition. Considering "non-retention" to hold for bigger downstream Dreisam catchment as well, the agricultural surplus there was back calculated from TFA mass balance. Based on the "non-retention" in upstream catchments, their evapotranspiration was estimated using TFA as tracer. The subsurface storm flow was identified as primary pathway for mobilizing TFA to streams by examining the temporal dynamics of TFA and their correlation with other solutes.

TFA, one of the Per- and Polyfluoroalkyl Substances (PFAS) or "forever chemicals", has been increasing concentrations across various environmental compartments, raising concerns about their potential ecological and health implications. This study on the retention and mobilization of PFA in agricultural and forest catchments provides valuable insights into catchment scale PFA dynamics and its potential as a tracer to hydrologists. The paper is well written and concise. It will be of interest to the wider audience of HESS. However, there is need to provide more justification for underlying assumptions, acknowledge limitations of a 2-year study and present the results and conclusions in more cautious language. I recommend publishing the manuscript following major revisions.

Major comments:

Introduction

The introduction is concise and frames the knowledge gap effectively. I appreciate how the research questions are laid out clearly. I would suggest stating in introduction that TFA is a PFAS (Per- and Polyfluoroalkyl Substances) as PFAS are more commonly known and may help attract broader interest.

Methods

Lines 94-96 suggest event water reaches stream mainly as overland flow, whereas lines 104-110 suggest event water flows mainly through subsurface flow pathways. Please clarify whether overland flow occurs substantially during storms in this catchment or if it occurs only in localized areas with most event water reaching stream through subsurface flow pathways.

The following sentences are vague with lack of logical flow from first sentence to second. Please edit them.

Line 105-107: "During discharge peaks, SSF contributed up to 50% of the streamflow in a catchment in the vicinity of the DRC (Bachmair and Weiler, 2014). Then, a network of pores interconnects to a system of hydrological flow paths that respond to precipitation according to its connectivity. Thus, SSF intensity depends both on soil moisture and event magnitude."

Since SSF refers to a flow rather than the flow pathways through which water moves, I suggest modifying the following sentence accordingly.

Line 107-109: “Although event water may travel rapidly through SSF, a considerable portion of the mobilized water consists of "old" water already present in the flow system”

Line 115: I suggest adding a brief sentence explaining that these precursors are “volatile fluorinated organic compounds" and are typically used as refrigerant to provide additional context to readers.

The following sentence is a bit dense. It might be better to split it into two sentences and make the meaning more explicit. Also, while it’s common to say that samples are enriched, it’s less usual to say concentrations are enriched—maybe using ‘concentrations are higher’ would sound more natural.”

Line 116-117: “Concentrations are typically enriched in samples from low precipitation volumes, necessitating precipitation volume weighting for representative input concentrations

Lines 121 onwards: Since WWTP are also terrestrial sources, I suggest replacing “terrestrial sources” with “agricultural activities”.

Lines 123-125-> I recommend introducing pesticides in the first sentence itself. For example, “Pesticides are fluorinated compounds that contain ….” can naturally lead into second sentence.

Line 137 -> Since ski wax is mentioned here, please clarify whether ski wax is an additional source for TFA in this catchment or can be disregarded.

Line 149 -> It seems like drinking water TFA level increased from 0.64 µg/l to 0.84 µg/l from November 2024 to April 2025, amounting to ~30% increase. 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?

Line 152 -> Table 4 is introduced before Table 1. Please number the tables in the order they are first mentioned in the manuscript.

Line 161-164 -> This sentence is quite long and complex. It can be either split or restructured to improve readability

Table 1 appears in the manuscript but not referenced in the main text. Please ensure all tables are referenced in the manuscript.

Lines 200 -> How large and frequent were these data gaps? Please provide a clear justification for using linear interpolation from weekly samples for gap filling a time series with a 15- or 10-minute resolution. Also, what was the source of discharge for Talbach? I suggest adding the years for which you have data for each of these catchments as well here.

Line 213-214 -> Over how many years was Mann-Kendall trend calculated? While change in storage is often neglected in long term water balance, this term cannot be neglected at annual scale. Please add a stronger justification as to why this term was ignored for annual water balance. Were the groundwater levels at the start and end of time period same perhaps?

Why was the water input into Zipfeldbel spring considered as precipitation occurring in nine pixels around the spring? The aquifer feeding it could be receiving water from a broader area which could even be located far away. Therefore, the input should include precipitation over the recharge area. Has the recharge zone for the aquifer been delineated?

There could be subsurface flows occurring within the aquifer feeding the spring. If such flows are present, they should be accounted for in the water balance. Please clarify whether the aquifer has known inflows or outflows or even other springs. If they are present but excluded, please provide a justification for neglecting them in the water balance.

What is the water transit time for the aquifer? What is the justification for considering the yearly change in storage term as zero? Possible reasons could be very long transit times, muti year stable groundwater levels or spring discharge, same groundwater level at the start and end of year, etc.

Line 260: Can you include the formula for calculating c_{dis} and c_{GW}? How is c_{QGW} different from c_{GW}?

Results

Line 276 -> It looks like the highest TFA levels in Dreisam river occur in May 2023. Also, it looks to me that precipitation was not that low during the winter. I suggest putting numbers to support these statements, since it is hard to judge them visually from the figure 2. Or perhaps the intention was to highlight the high levels of TFA in river despite low levels of TFA in precipitation during winter. In that case, please rephrase the sentence accordingly.

Line 306 -> Correlations for Deuterium excess is missing in Table 2.

Line 315-> If 2023 as dry year and 2024 as wet year, then water balance for years 2023 or 2024 separately wouldn't be close without a change in storage term.

Table 5 -> There is no equation 9 in the manuscript. Maybe it was accidently excluded.

While it is reasonable to make assumptions like the WWTP TFA levels remained constant over a year, I still suggest explicitly stating somewhere that the TFA levels were based on a single day measurement.

While groundwater TFA levels seem constant over two years, observations over longer period might reveal a trend. Considering that anthropogenic sources have bene increasing, most probably the groundwater TFA levels have also been increasing here. Please explicitly acknowledge this so that it doesn't give the impression that the groundwater TFA levels have stabilized.

Considering that groundwater TFA levels could have been seasonal, was this accounted for in calculating mass flux?

Discussion

The hypothesis on organic soil zone as temporal TFA storage which contributes to TFA pulses in streams during storm flows is interesting and insightful. This can be a good framework to explore TFA dynamics in other catchments as well.

While the short-term mass balance suggests limited TFA retention, I would caution that a two-year dataset may not be sufficient to conclusively rule out retention processes. Given the known

groundwater residence times in the Brugga catchment (ranging from a few to over ten years), some of the TFA currently reaching the stream could be originally from legacy sources, while recent TFA inputs may still be retained in subsurface. As such, I would suggest interpreting the apparent balance with some caution, and perhaps acknowledging the potential for longer-term storage and delayed transport within the system. I also suggest adding some discussion about systems with deep groundwater and long transit times where TFA might be retained more.

I appreciate the acknowledgement of potential uncertainties introduced by the use of data from a single precipitation sampling station as well as the spatial variability of TFA concentrations in precipitation.

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 ET estimates for each year from water balance as well as from TFA mass balance rely on the assumption of closed water balance for each year. Therefore, I suggest including direct ET measurements, if they are available, or summarizing results of previous studies that report ET ranges for these catchments to support that these are reasonable estimates.

TFA could be a valuable tool as tracer, especially considering that it is less expensive to measure than isotopes. Highlighting this could strengthen the case for its use as tracer.

Conclusion

Line 470 -> This is a strong statement. While the hypothesis that organic soil zone is the primary TFA storage, and SSF is the primary mechanism by which it reaches stream has high chances of being true, we need additional data like soil TFA profile or isotope tracer studies to support this. Therefore, I advise you to rephrase this into a more cautious statement and acknowledge the need for direct measurements.

In general, I suggest a more cautious wording of conclusions to reflect the limitations and assumptions of the study. That said, these assumptions and limitations do not reduce the value of your work.

Minor comments:

Line 54 -> "also" should be deleted.

Line 56-57 -> "we took weekly sample of precipitation at a weather station and stream water in three nested catchments and a hillslope spring.

Line 60 -> Consider changing to "headwaters, which are free of arable land."

Line 84 -> This sentence is not clear and grammatically doesn't make sense.

Line 86 -> Move inclinations to earlier: "with inclinations up to 62°"

Figure 1 -> Consider making the background of labels on figure transparent or removing them from figure, so that river network and catchment boundaries are visible.

Line 95-96 -> Since abbreviations “SOF” and “HOF” are not used even once after their introduction, please remove them

Line 121 -> For consistency, use “Fig. 1”

Line 122 -> Consider using “released from” instead for better flow

Line 128 -> The value of “n” does not add much meaning here and could be removed, unless you want to point out that the small number of samples makes this estimate uncertain. If so, it would be good to explicitly mention it.

Line 134 -> The full form of WWTP has already been introduced and therefore can be skipped here

Line 142 -> Did you probably mean “river”?

Line 167-170 -> Consider enclosing A and B – abbreviations for eluents – in brackets or quotes or put them in italics to avoid confusion

Line 175 -> remove brackets around Synek, 2008

Figure 2 -> Please correct the unit for Q in panel b. The green time series for spring looks like a solid line for most of the time except a short time period July-Oct 2024, when it is dotted line.

Line 279 -> Consider specifying the months you mean by “late summer”?

Line 372 -> “On” should be used instead of “At”.

Line 454 -> “Eq 9” is missing