



Trifluoroacetate mobilization by subsurface stormflow: the role of soil layer connectivity and prior flushing history

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Abstract. Trifluoroacetate (TFA) is an environmentally persistent degradation product of fluorinated compounds that is ubiquitously deposited through precipitation. While TFA retention in vegetation and organic soil has been documented, the hydrological processes governing its mobilization and export to surface waters remain poorly understood. Here we test whether TFA export depends on the hydrological activation of near-surface soil compartments and thus carries a legacy signal in comparison to classical chemical tracers. For this purpose, we used high-resolution sampling of subsurface stormflow (SSF) at a trenched forest hillslope in the Black Forest, Germany, combined with multi-tracer analysis of normalised tracer trajectories and qualitative event-water inference during rainfall events with contrasting antecedent conditions. We also investigated TFA pools in organic-rich topsoil and litter.

Freshly fallen autumn litter showed the highest TFA concentrations of all sampled compartments (up to 1862 $\mu\text{g kg}^{-1}$), with concentrations declining from old litter to mineral soil. TFA concentrations in SSF (median 1.96–2.06 $\mu\text{g L}^{-1}$) substantially exceeded open-field precipitation inputs (0.22 $\mu\text{g L}^{-1}$), with episodic peaks of up to 3.82 $\mu\text{g L}^{-1}$ during events following dry antecedent conditions.

The prior flushing state of the soil profile emerged as the primary control on TFA export via SSF. TFA, together with potassium and nitrate, departed from the shared dilution behavior of the other major ions only when the profile was unflushed, with recently flushed events showing little deviation. This flushing-state-dependent divergence reflects TFA's near-surface source in litter and topsoil: mobilized TFA is carried down through the profile by rapid, macropore-dominated vertical percolation and diverted laterally into the SSF flow path once the wetting front establishes hydrological connectivity at that depth. Event magnitude and duration determined how deep, and for how long, this connectivity was sustained, producing either a single brief TFA spike or a sustained, multi-peak signal depending on event size. This event-scale variability was damped, though not absent, in streamflow, consistent with spatial integration across the catchment and dilution by TFA-depleted deep groundwater. These findings provide first insights into the processes that govern TFA mobilization in forested headwaters and call for further research on TFA behavior in the unsaturated zone.



1 Introduction

Trifluoroacetate (TFA) is an environmentally persistent degradation product of fluorinated precursor substances, e.g. refrigerants, plant protection products (PPP) or pharmaceuticals. Ongoing emissions of precursors have resulted in ubiquitous atmospheric TFA deposition through precipitation (Franklin, 1993; Jordan and Frank, 1999; Freeling et al., 2020), while the expanding use of fluorinated PPPs adds a terrestrial diffuse source in agricultural areas (Scheurer et al., 2017; Bhat et al., 2022). Once released into the environment, TFA is highly mobile and essentially non-degradable under environmental conditions (Boutonnet et al., 1999), and concentrations are rising across environmental compartments including surface water and groundwater (Liang et al., 2023; Albers and Sültenfuss, 2024; Freeling and Björnsdotter, 2023). The persistence and continuous input of TFA raise growing concerns about long-term, irreversible accumulation, particularly considering that natural remediation pathways are absent (Garavagno et al., 2024; Arp et al., 2024). In agricultural areas, TFA, combined with other tracers, could be used to identify different surface water types and groundwater of different ages (Lange et al., 2025). However, field and laboratory evidence points to relevant retention in vegetation and organic matter, particularly in forests. Freeling et al. (2022) documented increasing TFA concentrations in leaves and needles of multiple tree species over three decades, and elevated soil TFA concentrations have been reported by Li et al. (2010). Earlier field studies in forested and wetland catchments estimated that plants may retain 5–35 % and soils 10–60 % of atmospherically deposited TFA over half-year observation periods, with considerably higher retention in wetlands than in forests (Berger et al., 1997; Likens et al., 1997). These findings suggest that litter, vegetation, and organic soil horizons may represent important TFA reservoirs in forest catchments, yet the hydrological conditions under which stored TFA is remobilized and exported to streams remain poorly understood.

At the catchment scale, Frenzel et al. (2026) analyzed a two-year dataset of weekly TFA concentrations across multiple compartments within the Dreisam catchment (Black Forest, Germany), including precipitation, nested stream gauges, and a hillslope spring. By correlating TFA dynamics with environmental tracers and building upon local knowledge of runoff generation processes, subsurface stormflow (SSF) was identified as the most likely pathway for mobilization and export of TFA from hillslope soils. However, weekly grab sampling could not resolve the event-scale dynamics that governed this process. Moreover, the terrestrial compartments involved, the degree to which SSF depletes TFA storage, and the role of different flow pathways within the hillslope remained unexplained.

In general, SSF entails the rapid lateral, near-surface, underground movement of water during and shortly after rainfall events, and can be the dominant runoff generation mechanism in forested headwater catchments (Bachmair and Weiler, 2014). Its occurrence and magnitude are governed by antecedent soil moisture, event magnitude (Thoenes et al., 2026), and the presence of low-permeability layers that impede vertical drainage and promote lateral connectivity across the slope (Hopp and McDonnell, 2009). Often, the chemical composition of SSF is characteristic of flow pathways. Water slowly moving through the soil matrix acquires a typical chemical signature through prolonged contact with soil minerals and organic matter, while water routed rapidly through preferential flow pathways like macropores retains a composition closer to that of precipitation (Tsuboyama et al., 1994; Weiler and McDonnell, 2006). In most cases, antecedent wetness governs the relative contributions



of these two flow modes, and thereby shapes both the volume and the chemical characteristics of SSF exported during events (Kienzler and Naef, 2008; Pyschik et al., 2025).

This paper aims to investigate the behavior of TFA during SSF in a trenched forest hillslope in the Black Forest. We hypothesize that TFA preferentially accumulates in organic-rich surface compartments such as litter and topsoil, rather than in the underlying mineral soil, and that this near-surface pool acts as a legacy source for TFA export: TFA accumulated during periods without hydrological activation is mobilized once a sufficiently large event connects the near-surface compartments to SSF. Then vertical percolation carries the mobilized TFA down through the profile until it is intercepted by the lateral SSF flow path at increasing depth. This presumes that, between events, vertical percolation is reduced in the near-surface soil compartment to promote continuous TFA accumulation. We test this hypothesis by comparing TFA with traditional tracers like Cl^- and Si, whose storage is less preferential across slope profiles. Using event-scale, 2-hour sampling and multi-tracer concentration trajectories, we address the following research questions:

1. Which compartments act as TFA pools that can hydrologically be activated by SSF?
2. To what extent does hillslope TFA export deviate from other tracers?
3. How do antecedent conditions and event dynamics control the timing and magnitude of TFA export via SSF?

2 Study Site and Methods

2.1 Study Site

The study was conducted in the Eberbach headwater catchment on the western edge of the Black Forest, Au, Germany, at 340–585 m a.s.l., with a mean annual precipitation of 970 mm and a mean annual temperature of 11°C; rainfall is dominated by intense convective storms in summer and prolonged, lower-intensity events in winter (Bachmair and Weiler, 2014). Soils are periglacial drift-derived sandy loam Cambisols, stratified into a compact, low-permeability basal layer that promotes lateral flow and a finer-textured, more permeable upper layer. The site is described in detail in Pyschik et al. (2025); only information directly relevant to this study is repeated here. A map of the trench, well, and soil moisture profile locations is provided in Thoenes et al. (2026). We focused on trench 3, a trenched forest hillslope excavated to the weathered bedrock on a steep, convergent, south-facing slope (trench width 11.0 m, total depth 1.2–2.1 m; Thoenes et al. 2026) under mixed forest dominated by hornbeam (*Carpinus betulus*) and fir (*Abies alba*). SSF was collected separately from two outlets: a top outlet draining the soil from the surface down to the base of the coarser upper layer (approximately 0.4–0.6 m depth) and a bottom outlet draining the remainder of the profile down to the trench base (1.2–2.1 m depth), with continuous discharge measurements at both. We refer to these as the top and bottom SSF fractions throughout. A single vertical profile of soil moisture sensors (Truebner SMT100) provided one sensor at each of the depths 10, 30, 60, 100, 140, and 200 cm, and three shallow groundwater wells were located approximately 3 m upslope, providing continuous information on subsurface hydrological conditions. A meteorological station recording precipitation volume is located approximately 500 m from the trench on an adjacent meadow. At the studied



Table 1. Summary of sampled SSF events. Event A comprised two rainfall pulses, A1 and A2 (Sect. 2.2).

Event	Start	Precip. [mm]	Dry days	Flushing state (season)	Peak Bottom SSF [L s ⁻¹]	Peak streamflow [L s ⁻¹]
A	20 Aug 2025	69	15	Unflushed (warm)	0.958	>170
B	21 Sep 2025	56	6	Flushed (warm)	0.955	>170
C	28 Jan 2026	16	20	Unflushed (cold)	0.056	20.9
D	13 Mar 2026	15	2	Flushed (cold)	0.147	29.9

For Event A, only 4 water samples from the top SSF outlet were recovered due to an autosampler malfunction. For Event B, water samples from the top outlet were collected but discharge data are unavailable due to a failure of the tipping-bucket flow gauge at that outlet. Peak streamflow values of >170 L s⁻¹ (Events A and B) are truncated: above this discharge the flow-measurement profile overflows and stage no longer correlates with discharge. Dry days refer to consecutive days without significant precipitation (>0.1 mm h⁻¹) prior to event onset.

trench, SSF delivery can reach up to 2.5 L min⁻¹ m⁻² of trench area following 63 mm of precipitation over 10 days (Pyschik et al., 2025), substantially exceeding matrix infiltration rates once an event begins.

2.2 Study Events

90 Four SSF events were sampled between August 2025 and March 2026, hereafter referred to as Events A, B, C, and D (Table 1). Precipitation volumes during Events A and B were markedly higher than during Events C and D, producing correspondingly higher peak SSF discharges. Soil moisture profiles in the days preceding each event indicated different flushing histories (Fig. 1): Events A and C showed no wetting response during their respective 15- and 20-day dry periods, whereas Events B and D were preceded by transient soil moisture pulses propagating across the soil layers 6 and 2 days before event onset, respectively. Soil moisture at 140 and 200 cm depth remained near-saturated throughout most of the study period, consistent with proximity to the permanent groundwater zone; the 140 cm sensor transiently desaturated during Event A, marking a brief excursion of the saturated-zone boundary rather than an unflushed, hydrologically inactive layer. Accordingly, Events A and C are regarded as unflushed, the soil profile not having been hydrologically activated by SSF for an extended period, while Events B and D are regarded as recently flushed. The two unflushed events span the warm (A) and cold (C) season, as do the two flushed events (B and D), so the four events form a season × flushing-state matrix. Event magnitude is, however, confounded with season in this matrix: the warm-season events had substantially larger precipitation totals than the cold-season events. The within-season pairs (A vs. B; C vs. D), by contrast, had comparable magnitude and provide the cleanest isolation of the flushing-state effect.

2.3 Water Sampling

105 SSF from the top and bottom outlets, as well as streamflow at the catchment outlet, were sampled using ISCO Teledyne autosamplers equipped with polyethylene (PE) bottles (500 or 1000 mL). Autosamplers were started 2–6 hours before predicted rainfall onset, based on weather forecast, to ensure pre-event samples were available to normalise event tracer trajectories

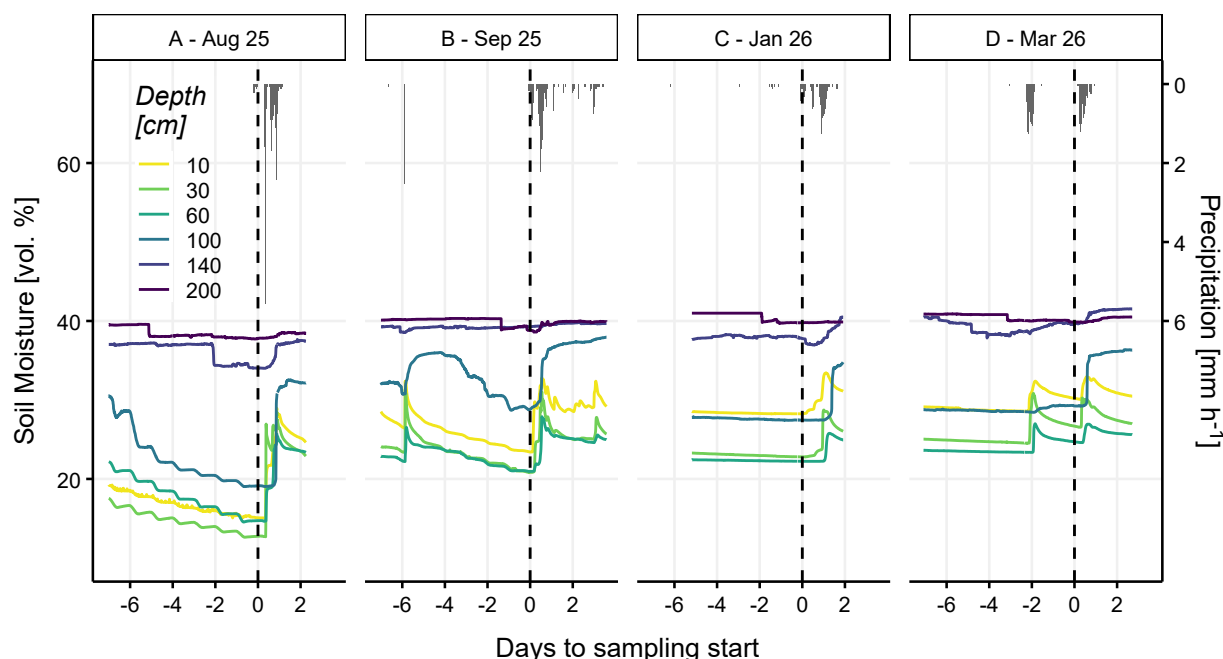


Figure 1. Soil moisture profiles and precipitation at events A–D in the days preceding each event. Events A and C were unflushed (preceded by 15 and 20 dry days respectively), with low soil moisture across all depths. The start of a sampling interval is indicated by the vertical dashed lines. Events B and D were recently flushed, having received rainfall that produced transient wetting responses across the 10–100 cm layers, evident as wetting pulses across these layers in the days before the event rather than as elevated absolute moisture at onset.

against. Samples were collected at 2-hour intervals throughout the events. Surface runoff was sampled using a 5 L container buried flush with the ground surface approximately 5 m from the trench, alongside a footpath that channeled overland flow into the container during events. Since this footpath is compacted and largely free of litter cover, the collected runoff may not fully represent overland flow generated on the undisturbed hillslope. Before each event, three shallow groundwater samples were collected manually from the wells located upslope of the trench. Two deep groundwater samples were obtained from an 18 m deep well approximately 200 m upslope of the trench. Precipitation was sampled using PE canisters, PP funnels fitted with a fly net to exclude debris, and a ping-pong ball for evaporative protection. Five rainfall collectors were placed within the forest and two on the adjacent meadow, distinguishing throughfall and open-field precipitation inputs. All sampling equipment, was blank-tested prior to operation to confirm the absence of TFA contamination.



2.4 Biological and Soil Sampling

Biological and soil samples were collected within a 30 m radius of trench 3 on three occasions: early September 2025 ($n = 10$ samples across all species and compartments), November 2025 (freshly fallen autumn litter and leaves only), and mid-March 2026 ($n = 8$ samples across all species and compartments). Leaf and needle samples were collected from seven species: Douglas fir (*Pseudotsuga menziesii*), silver fir (*Abies alba*), robinia (*Robinia pseudoacacia*), red beech (*Fagus sylvatica*), hornbeam (*Carpinus betulus*), sessile oak (*Quercus petraea*), and holly (*Ilex aquifolium*), each as a mixed sample from five sampling positions. Litter and mineral soil were collected by hand digging as mixed samples from five positions, distinguished by depth and colour: upper-soil samples were taken from a visually darker, organic-enriched layer directly beneath the litter, selecting positions where this layer was visibly present, and lower-soil samples from approximately 15–20 cm depth, from the underlying, uniformly coloured mineral soil corresponding to the Cambisol matrix. The darker upper layer was not present at every location within the 30 m sampling radius, so this distinction reflects a field colour/depth criterion rather than a formal pedogenic horizon description. Both sampled depths are near-surface; no soil samples were collected at the greater depths relevant to the bottom SSF fraction. Biological and soil samples were collected into brand-new 50 mL polypropylene (PP) vials, which were blank-tested prior to use to confirm the absence of TFA contamination. All biological samples were dried at 60 °C for 24 hours prior to extraction.

2.5 Chemical Analysis

TFA in biological and soil samples was extracted following the method of Freeling et al. (2022), downscaled for practicability (liquid-to-dry-mass ratio of 7.5:1 per extraction step, using 0.75 mL of solution on 0.1 g of dried sample, vs. 6.4:1 and 1.6 mL on 0.25 g in the original method): the sample was extracted with a 50:50 methanol:MilliQ water solution containing 1 % formic acid (Thermo Scientific), using 2 mL Eppendorf tubes, and the procedure was repeated twice per sample. Freeling et al. (2022) reported limits of quantification of $18 \mu\text{g kg}^{-1}$ dry weight (dw) for deciduous and $30 \mu\text{g kg}^{-1}$ dw for coniferous leaves and needles.

Water samples were analyzed for major ions (Ca^{2+} , Mg^{2+} , K^{+} , Na^{+} , Cl^{-} , SO_4^{2-} , NO_3^{-}), silica (Si), electrical conductivity, and TFA. Ion chromatography and TFA quantification were performed according to the methods described in Frenzel et al. (2026), with the exception that water was sampled into 2 mL Eppendorf tubes rather than 50 mL centrifuge tubes to save storage space. TFA quantification achieved a mean relative standard deviation of 1.9 % across duplicate measurements, a mean absolute percent error of 8 % against in-house standards, and a limit of quantification of $0.08 \mu\text{g L}^{-1}$ (Frenzel et al., 2026). Silica was determined by photometry analog to the procedure described in Pyschik et al. (2025) with a LOQ of 0.045 mg L^{-1} .

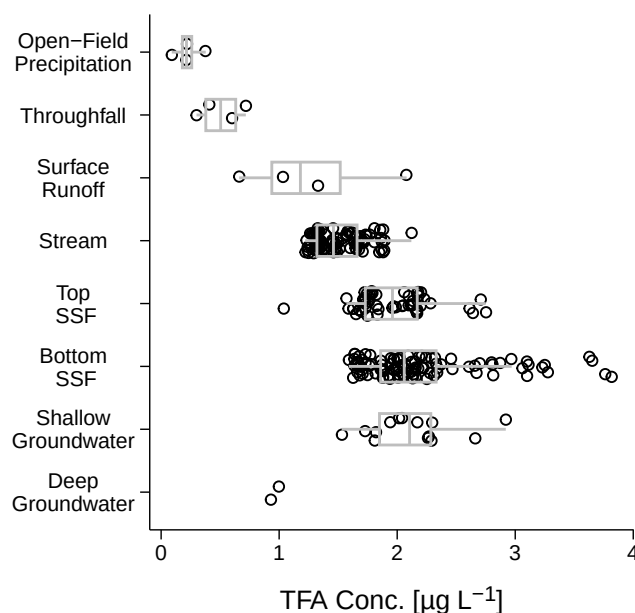


Figure 2. TFA concentrations in all sampled water compartments. Boxes show the interquartile range with median indicated; whiskers extend to 1.5 times the interquartile range; individual points show all observations. Note the systematic increase from open-field precipitation through throughfall, surface runoff, streamflow, and SSF to shallow groundwater, with deep groundwater showing lower concentrations than SSF.

145 3 Results

3.1 TFA Concentrations Across Water Compartments

TFA concentrations varied systematically across sampled water compartments (Fig. 2). Open-field precipitation showed the lowest median concentrations ($0.22 \mu\text{g L}^{-1}$), while throughfall was notably higher ($0.50 \mu\text{g L}^{-1}$). Surface runoff showed a further increase (median $1.18 \mu\text{g L}^{-1}$). Streamflow concentrations were higher still (median $1.46 \mu\text{g L}^{-1}$), while both SSF outlets clustered at substantially elevated levels: $1.96 \mu\text{g L}^{-1}$ for the top fraction and $2.06 \mu\text{g L}^{-1}$ for the bottom fraction. The bottom SSF fraction also exhibited the widest concentration range of all sampled water compartments, with individual samples reaching up to $3.82 \mu\text{g L}^{-1}$, indicating episodic mobilization of highly concentrated TFA. The top SSF fraction showed a somewhat lower maximum of $2.75 \mu\text{g L}^{-1}$. Shallow groundwater concentrations were broadly similar to SSF (median $2.11 \mu\text{g L}^{-1}$, $n = 3$ samples per event). Deep groundwater was markedly lower (mean $0.96 \mu\text{g L}^{-1}$, based on $n = 2$ samples), close to surface runoff and well below SSF and streamflow values.

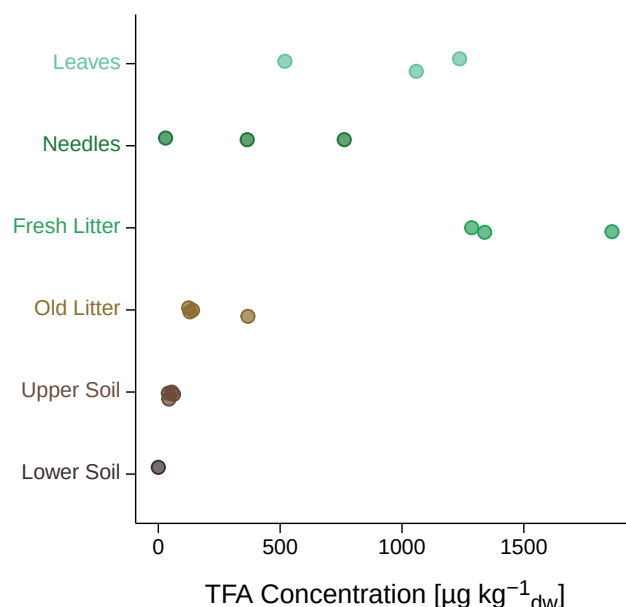


Figure 3. TFA concentrations in biological and soil samples.

3.2 TFA in Biological and Soil Samples

TFA concentrations in biological and soil samples spanned more than three orders of magnitude across compartments (Fig. 3). Freshly fallen autumn litter, sampled in November 2025, following a full growing season of TFA accumulation in the canopy, showed the highest concentrations of all compartments, ranging from 1287 to 1862 $\mu\text{g kg}^{-1}$. Leaves sampled in September 2025 ranged from 518 to 1236 $\mu\text{g kg}^{-1}$ and needles from 364 to 763 $\mu\text{g kg}^{-1}$, with leaves generally showing higher values than needles. In March 2026, needles showed considerably lower concentrations (31 $\mu\text{g kg}^{-1}$), while leaves remained elevated (1060 $\mu\text{g kg}^{-1}$). Old litter concentrations were substantially lower than freshly fallen litter, ranging from 124 to 142 $\mu\text{g kg}^{-1}$ in September and 369 $\mu\text{g kg}^{-1}$ in March. Upper soil concentrations were low and relatively consistent across sampling dates, ranging from 40 to 62 $\mu\text{g kg}^{-1}$. Lower soil showed the lowest concentrations of all sampled compartments, at approximately 1 $\mu\text{g kg}^{-1}$, well below the method's quantification limit (Sect. 2.4) and should be treated as indicative only. This pattern indicates a strong vertical decline in TFA from the canopy and freshly fallen litter layer down through the soil profile, and suggests that soil does not appear to be a major TFA source compared to leaves and litter (see Sect. 4.1).

3.3 TFA Deviation from the Shared Dilution Pattern

Normalised to their pre-event concentrations, Cl^- and Si, together with Ca^{2+} , Mg^{2+} , Na^+ , SO_4^{2-} , and electrical conductivity, followed a common dilution signal in the bottom SSF as event water entered the profile (Fig. 4). TFA, K^+ , and NO_3^- departed from this shared pattern, but not uniformly. In the unflushed Event A, TFA concentrations rose above this baseline as the wetting

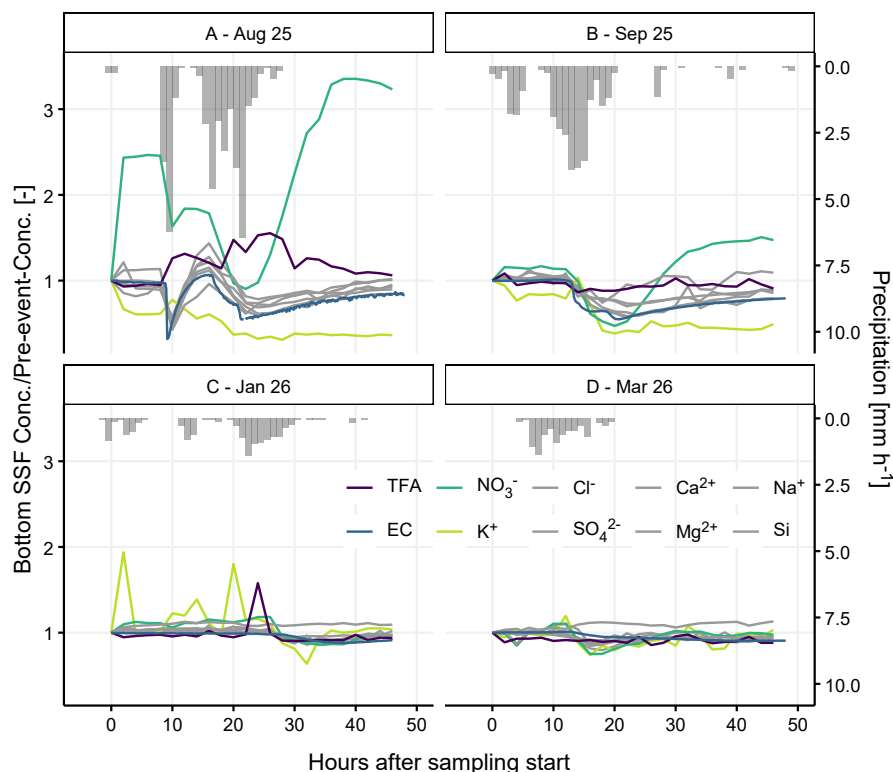


Figure 4. Tracer concentrations in the bottom SSF normalised to their pre-event values, over time (hours after sampling start) for Events A–D. Cl^- and Si, the further ions Ca^{2+} , Mg^{2+} , Na^+ and SO_4^{2-} , and electrical conductivity (EC) all follow a common dilution pattern as event water enters the profile, whereas TFA, K^+ and NO_3^- depart from this shared behavior.

front progressed through previously dry soil layers, most clearly during the two rainfall pulses A1 and A2, while nitrate was diluted alongside the coherently behaving group before rebounding later in the event, indicating that TFA and nitrate diverge from the shared dilution pattern in solute-specific, not shared, ways. In the recently flushed Event B, TFA tracked this group far more closely throughout, consistent with a depleted reservoir. Events C and D followed the same qualitative pattern as their respective unflushed and flushed counterparts. This was evident by a single TFA peak in SSF and streamflow ($2.02 \rightarrow 3.25 \mu\text{g L}^{-1}$ and $1.30 \rightarrow 2.12 \mu\text{g L}^{-1}$) at the event onset. In general, streamflow showed the same tracer divergence pattern, differing only slightly from the SSF signal (Fig. A1 in the Supplement).

3.4 Co-dynamics of SSF and Soil Layer Activation

The temporal evolution of TFA concentrations in both SSF depth intervals closely corresponded with soil moisture dynamics at different depths (Fig. 5). During Event A, TFA in the bottom SSF rose sharply when sensors in shallow soil layers (10–60 cm depth) rapidly responded after a dry period of 15 days. This TFA peak tracked the activation of a previously unflushed TFA

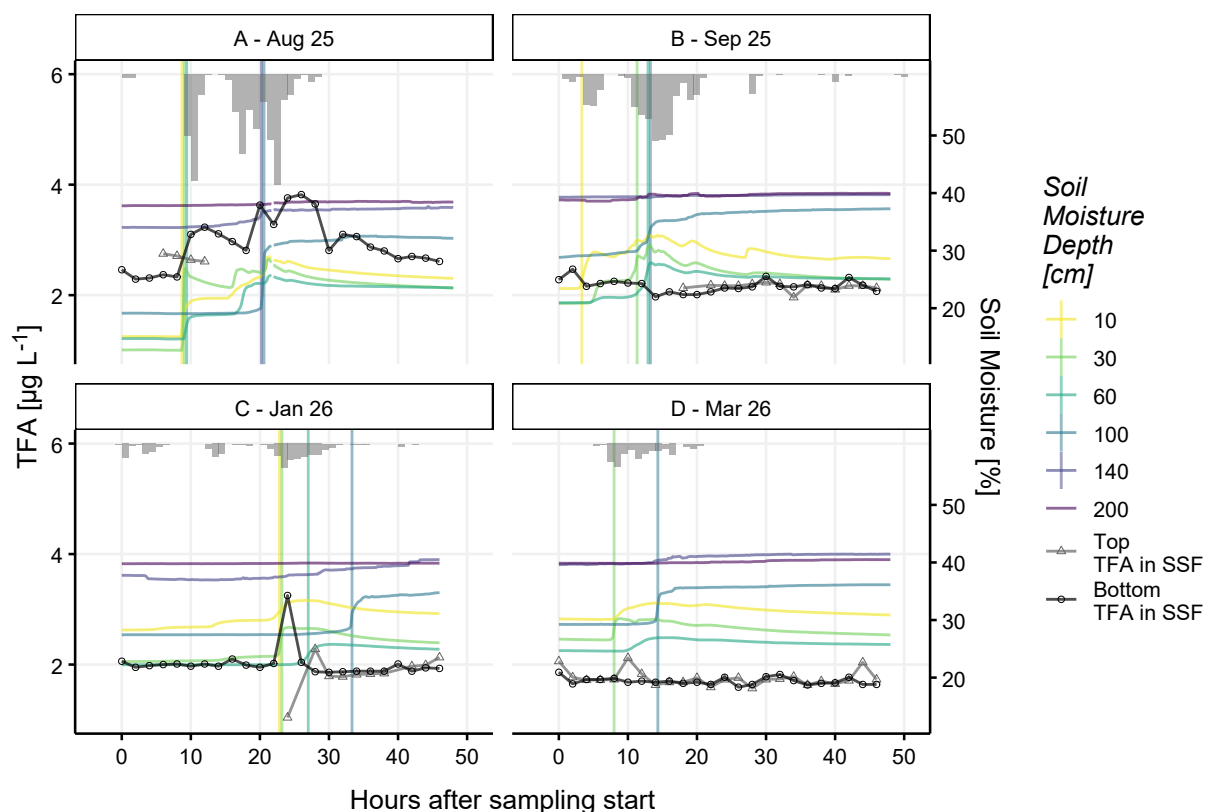


Figure 5. TFA concentrations in the bottom SSF (black circles, left axis) and soil moisture profiles at six depths (colored lines, right axis) over the course of each event. Vertical lines mark the onset of considerable wetting at each depth, i.e. the first time a given soil layer responds appreciably to the event.

pool. Secondary TFA maxima in both SSF fractions coincided with the wetting front reaching 100 cm and beyond. Due to an autosampler failure during Event A, only 4 water samples were available for the top SSF sampling spot, which precluded full interpretation of TFA dynamics. However, even across these 4 samples, the top SSF indicated initial dilution rather than a spike as observed in the bottom SSF fraction. During Event B, soils were already wet at all depths prior to the event; TFA in SSF only rose moderately. During Event C, the top SSF showed an initial dilution of TFA coinciding precisely with the spike in the bottom sampling spot, followed by its own TFA spike approximately 2 hours later. For Events B and D, the top SSF signal was broadly similar to that of the bottom fraction. Event D showed two small TFA spikes at approximately 10 and 46 hours after sampling start in the top fraction that were absent in the bottom SSF signal.



4 Discussion

4.1 TFA Source Hierarchy: From Canopy to Deep Groundwater

The systematic increase in median TFA concentrations from open-field precipitation ($0.22 \mu\text{g L}^{-1}$) to throughfall ($0.50 \mu\text{g L}^{-1}$) is consistent with canopy enrichment through dry deposition onto leaf and needle surfaces followed by washoff, evaporative concentration of intercepted precipitation, and leaching of TFA from leaf and needle tissue. Jordan and Frank (1999) reported a similar throughfall enrichment factor of approximately 2.6 in a conifer forest, attributing it to a combination of these processes. The atmospheric pathway likely reflects both wet and dry deposition, with Freeling et al. (2020) and Persaud et al. (2026) estimating roughly equal contributions of each. Fog deposition may add further TFA to the canopy, with Römpf et al. (2001) reporting fog TFA concentrations of up to $2 \mu\text{g L}^{-1}$ already in 2001, likely higher today given the continued increase in precursor emissions (Freeling et al., 2020). This apparent canopy enrichment does not necessarily imply a correspondingly large additional atmospheric TFA input at the catchment scale. If throughfall enrichment instead reflects TFA taken up by roots and translocated to, and subsequently leached from, leaves and needles, it represents internal recycling of TFA already present in the catchment rather than an additional external input. This would leave the open-field-precipitation-based catchment mass balance of Frenzel et al. (2026) for the neighbouring Dreisam catchment, including the Brugga and St. Wilhelmer Talbach sub-catchments, unaffected despite their high forest cover. Alternatively, if dry deposition is indeed enhanced under canopy, a correspondingly higher retention of TFA in forest biomass, litter, and soil could offset the additional input, again allowing the catchment-scale balance to close using open-field precipitation alone. The biological and soil samples identify the source compartments responsible for further concentration increase from throughfall to SSF and shallow groundwater (medians 1.96 – $2.11 \mu\text{g L}^{-1}$), consistent with the shallow wells sampling essentially the same water body as SSF, effectively its baseflow component, rather than a hydrologically distinct compartment (Pyschik et al., 2025). Living leaves and needles sampled in September 2025 already contained substantial TFA concentrations (364 – $1236 \mu\text{g kg}^{-1} \text{ dw}$), broadly consistent with the up to $\sim 1000 \mu\text{g kg}^{-1} \text{ dw}$ reported by Freeling et al. (2022) for archived leaves and needles from the German Environmental Specimen Bank, and the up to $767 \mu\text{g kg}^{-1} \text{ dw}$ found in poplar and maize leaves by Lan et al. (2020). TFA in freshly fallen autumn litter (1287 – $1862 \mu\text{g kg}^{-1} \text{ dw}$) exceeded concentrations in living leaves and needles of summer, suggesting continued accumulation over the growing season before fall of leaves. Old litter and upper soil showed progressively lower concentrations (124 – 369 and 40 – $62 \mu\text{g kg}^{-1} \text{ dw}$, respectively). This points to progressive leaching during decomposition and partial retention in organic soil horizons, as reported by Richey et al. (1997), who found that organic soils retained 20–60 % of added TFA while mineral soils only retained 0–15 %. Because TFA is preferentially retained by organic matter rather than by the mineral phase, the bulk dry-mass gradients reported are partly due to low organic matter contents in mineral soil. At a depth of 15–20 cm, TFA concentration was only approximately $1 \mu\text{g kg}^{-1}$, well below the method's quantification limit.

Our upper soil (40 – $62 \mu\text{g kg}^{-1} \text{ dw}$) is a humus-rich organic layer and is not directly comparable to the soils sampled by Li et al. (2010) (93 – $188 \mu\text{g kg}^{-1} \text{ dw}$) or Scholl et al. (2025) (0.2 – $14 \mu\text{g kg}^{-1} \text{ dw}$), both of which are generic surficial mineral soils from urban, agricultural, and grassland land uses rather than an organic humus layer. Only our lower (mineral) soil is comparable in soil type, but its concentration ($\sim 1 \mu\text{g kg}^{-1} \text{ dw}$) is well below the method's quantification limit and



225 can therefore only be compared at the order-of-magnitude level: it falls within the range reported by Scholl et al. (2025) and considerably below that of Li et al. (2010). Together, this indicates that mineral soil does not appear to be a major TFA source compared to leaves and litter, consistent with subsurface flow paths acquiring most of their TFA load from the organic-rich litter and near-surface organic soil horizons before reaching the trench outlets, rather than from the mineral soil itself.

Streamflow (median $1.46 \mu\text{g L}^{-1}$) fell between SSF and deep groundwater concentrations, consistent with an anticipated
 230 mixture of SSF/shallow groundwater and deep groundwater (Pyschik et al., 2025). Deep groundwater (mean $0.96 \mu\text{g L}^{-1}$, based on $n = 2$ samples) showed notably lower TFA concentrations than SSF and shallow groundwater, yet remained elevated above open-field precipitation. One plausible explanation is that deep groundwater accumulated TFA during a longer recharge history than shallow SSF; this would make TFA an age tracer, consistent with findings by Lange et al. (2025) and Albers and Sültenfuss (2024). Since atmospheric TFA inputs have increased over recent decades with growing precursor emissions
 235 (Freeling et al., 2020; Freeling and Björnsdotter, 2023), older recharge would have been exposed to lower TFA inputs. Lower TFA in deep groundwater causing dilution during baseflow, was also visible in the neighboring Dreisam catchment during prolonged drought periods (Frenzel et al., 2026).

4.2 TFA's Deviation from Other Tracers: Extent and Mechanism

TFA, together with K^+ and NO_3^- , departs from the general dilution pattern in SSF defined by Cl^- , Si, Ca^{2+} , Mg^{2+} , Na^+ ,
 240 and SO_4^{2-} (Fig. 4). However, this deviation is neither uniform across solutes nor across events, but rather indicative of prior flushing state. In the unflushed Events A and C, TFA rose visibly above the shared dilution baseline once event water arrived, whereas in the recently flushed Events B and D, TFA matched the general water-quality pattern. The extent of TFA's departure from the dilution behaviour of other tracers therefore depended on the antecedent state of TFA accumulation in the soil profile.

This solute-specific pattern has a straightforward mechanistic explanation based on where these tracers reside in the soil
 245 profile. Cl^- , Si, and the other co-varying solutes are evenly distributed over depth and lack a concentrated, near-surface biogeochemical reservoir: if event water enters the soil profile, those tracers simply dilute and trace the mixing process itself. TFA, by contrast, accumulates preferentially in the organic-rich litter and topsoil compartments. When a previously unflushed soil layer is wetted during an event, percolating water may pick up a high TFA load, superimposing a source term onto the dilution signal that the other tracers do not carry. The deviation of TFA from the shared dilution pattern is then a visible signature of an
 250 additional, spatially concentrated source that is mobilized by a progressing wetting front.

The contrasting response of nitrate supports this as a solute-specific mobilisation effect rather than a generic flushing response shared by all reactive solutes. In the unflushed Event A, TFA and nitrate moved in opposite directions as event-water contributions rose, as indicated by declining Si: TFA increased, consistent with active mobilisation from the near-surface reservoir, while nitrate was simultaneously diluted. Only at a later stage did both solutes show similar dynamics, likely reflecting a
 255 similar source area (the organic topsoil) but different states of microbial nitrification, immobilisation, and dilution of nitrate in the soil profile. In the recently flushed Event B, by contrast, TFA more closely followed nitrate, and both behaved like the baseline of other tracers. Furthermore, our experimental design allowed a direct comparison of the TFA signal with the advance of the wetting front. During Event A, a first TFA peak in SSF resulted from the initial wetting of shallow soil layers (10–60 cm),



while a second, larger peak was mobilized when the wetting front extended down to 100 cm (Fig. 5). Our observations follow the general concept of threshold-controlled lateral connectivity on hillslopes (Tromp-van Meerveld and McDonnell, 2006): individual soil depth compartments were stepwise connected to the lateral SSF flow path as the wetting front proceeded, each becoming visible as a distinct TFA pulse in SSF.

This raises an apparent paradox: TFA accumulates almost exclusively in the litter and topsoil (Sect. 4.1), yet the second, larger TFA pulse originates at depths (≥ 100 cm) where our soil sampling found no comparable reservoir. We propose that water infiltrating through the TFA-rich topsoil picks up TFA and is carried downward via macropore flow, fast enough to reach these depths within the timescale of a single event, too fast for slow matrix percolation, and consistent with the macropore-dominated SSF dynamics reported for this site by Pyschik et al. (2025). As this vertically percolating water reaches each successive depth, the same threshold-controlled lateral connectivity described above diverts it into the SSF flow path, so the arrival of the wetting front at a given depth is what carries the TFA signal into SSF, rather than a locally stored, depth-specific TFA pool being released in place. This remains inferred rather than directly demonstrated, since we did not sample soil TFA at these depths.

4.3 Antecedent Conditions and Event Dynamics as Controls on TFA Export Timing and Magnitude

As shown above, flushing history controls the timing and duration of TFA export from our slope. Differences observed between the two unflushed events (A and C) allow additional insights. Although Event C followed a longer (20-day) dry period than Event A (15-day), it only produced a single TFA spike, compared to a sustained, multi-peak TFA response during Event A. This is because a much smaller precipitation input (16 vs. 69 mm) established only a brief, transient connection to the shallow TFA source layer. This suggests that the duration (and season) of dry periods may determine how much TFA is available for release, whereas event magnitude and duration determine the intensity of slope connectivity and thus of TFA export. Streamflow integrates SSF contributions from hillslopes at different flushing states across the catchment, and is diluted by deep, older groundwater carrying lower TFA concentrations. Hence, sharp, depth-sequential pulses visible from individual hillslopes are smoothed into a more gradual TFA signal at the catchment outlet (Fig. A1 in the Appendix). This event-scale variability has a direct implication for load estimation: events following extended dry periods export disproportionately more TFA than events occurring under recently flushed conditions. Hence, flow-weighted or low-frequency monitoring might over- or underestimate annual TFA loads, depending on the flushing state of the catchment at the time of sampling. Overall, these hillslope-scale, event-resolved observations provide process insights into the SSF-dominated TFA transport pathway inferred at the catchment scale for the neighbouring Dreisam River catchment by Frenzel et al. (2026).

5 Conclusions

On a trenched forest hillslope in the Black Forest, Germany, TFA concentrations increased from open-field precipitation to throughfall, probably through canopy dry deposition, evaporative concentration, and leaf leaching. Biological and soil samples were most enriched in freshly fallen autumn litter (up to $1862 \mu\text{g kg}^{-1} \text{ dw}$), followed by old litter and organic soil horizons.



290 Mineral soil had the lowest TFA content, not exceeding the quantification limit of the analytical method. Hence, litter and topsoil organics were found to be the primary TFA pools.

During events, TFA deviated from the common dilution pattern of other major ions in SSF when the soil profile was unflushed, i.e. the event occurred after an extended dry period. Under recently flushed conditions, TFA was in line with other tracers. This solute-specific, flushing-state-dependent divergence is indicative of the near-surface source of TFA in the litter
295 and topsoil, filled over time; other tracers lack such a reservoir and are simply diluted by event water.

Depth-sequential connectivity of soil compartments governed the magnitude and duration of TFA export during events, whereas the duration and season of a preceding dry period was responsible for how much TFA had accumulated in the near-surface reservoir for release. A short, small event only produced a single, brief TFA spike, whereas a large, long event created a sustained, multi-peak TFA signal, as soil moisture sensors showed the wetting front reaching and activating deeper layers. In
300 streamflow, the response of individual hillslopes was damped by spatial integration across the catchment and by dilution with TFA-depleted deep groundwater.

Thus, events following extended dry periods disproportionately export more TFA than recently flushed events. This means that accurate load estimation requires event-scale, high-frequency sampling rather than flow-weighted or low-frequency averages, consistent with the SSF-dominated TFA transport pathway inferred at the catchment scale for the neighbouring Dreisam
305 River catchment by Frenzel et al. (2026). Overall, forested hillslopes with substantial litter and organic topsoil should be regarded as episodic TFA pools for receiving streams.

Code availability. Analysis scripts are available from the corresponding author upon request.

Data availability. Data will be made available upon publication.

Author contributions. I.F. designed the study, conducted field sampling, performed TFA analysis of water and biological samples, analyzed
310 the data, and wrote the manuscript. T.S. contributed to field sampling and data collection as part of his Master's thesis within this project. B.K. contributed to field sampling and laboratory work. B.H. facilitated and conducted ion chromatography and cavity ring-down spectrometry isotope measurements. M.M. provided access to the LC-MS/MS system for TFA measurements, co-supervised the study, and reviewed the manuscript. J.P. reviewed the manuscript. J.L. conceived and supervised the study and contributed to manuscript writing. All authors reviewed and approved the final manuscript.

315 *Competing interests.* The authors declare that they have no conflict of interest.



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320 We declare that Claude (Anthropic) was used to assist in revising manuscript wording and in editing the accompanying analysis scripts; all changes were reviewed and approved by the authors.

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Appendix A: Streamflow Tracer Dynamics

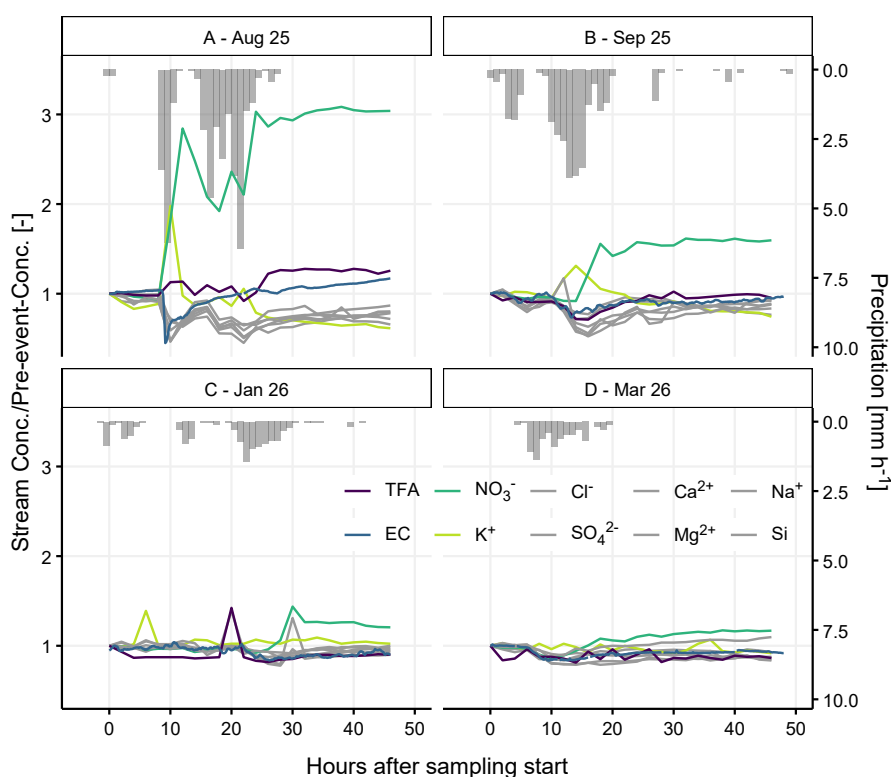


Figure A1. Tracer concentrations in streamflow normalised to their pre-event values, over time (hours after sampling start) for Events A–D. As in the bottom SSF (Fig. 4), Cl^- and Si, the further ions Ca^{2+} , Mg^{2+} , Na^+ and SO_4^{2-} , and electrical conductivity (EC) follow a common dilution pattern, while TFA, K^+ and NO_3^- depart from this shared behavior. The pattern differs only slightly from the SSF signal, consistent with streamflow representing a spatially integrated mixture of SSF from across the hillslope.