Diffuse sources of TFA: atmospheric and terrestrial inputs, retention and pathways at the catchment scale

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What is TFA?

- Trifluoroacetate (TFA) is an ultra-short-chain PFAS introduced into the environment by the degradation of precursors or direct emission from fluoro-chemistry:
  - Degradation of refrigerant gases leads to an ubiquitous atmospheric input.
  - Degradation of pesticides used in agriculture releases TFA.
  - Elevated TFA levels have been found in wastewater treatment outflow.
- Once released into the environment, TFA resists further degradation.
- Hence, environmental TFA levels are rising in parallel with the production of precursors. (Arp et al. 2024)

Our aim: Gain understanding of TFA sources, transport, and retention.

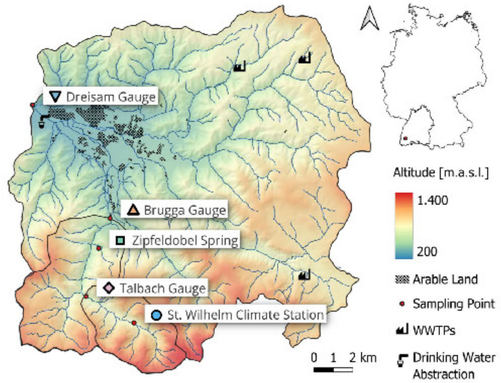
Methods and Study Area

Time Series and Correlation

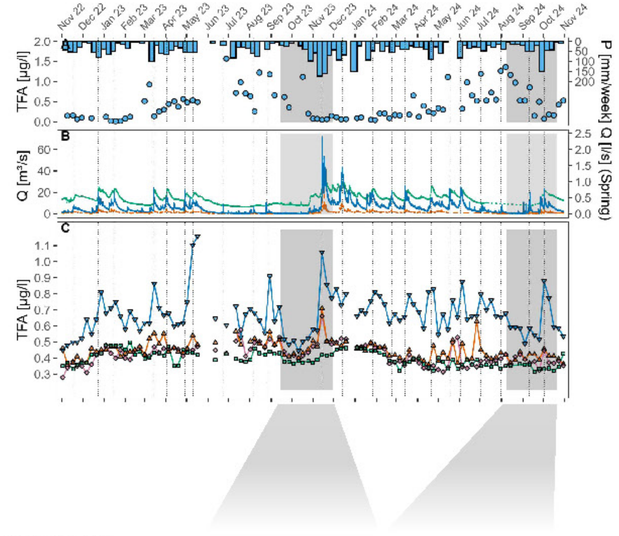
- Weekly sampling at 5 locations in the Dreisam catchment:
  - St. Wilhelm precipitation,
  - Zipfeldobel spring,
  - Dreisam, Brugga, and Talbach rivers.
- Analysis for:
  - TFA with HPLC-MS/MS
  - Major Ions with ion chromatography
  - Temperature, pH, and conductivity.
- Visual analysis of the TFA time series to identify major transport processes.
- Evaluation of TFA correlation with tracers to determine source areas.

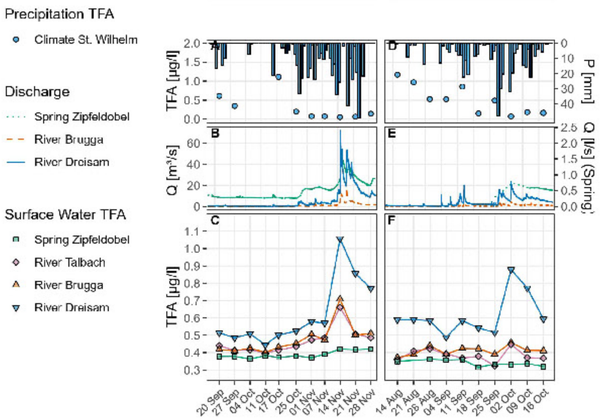
Water and TFA Mass Balance

- Sampling of point sources (wastewater treatment plants, WWTPs) and outputs (groundwater below Dreisam gauge, drinking water abstraction at Ebnet).
- Calculation of weighted mean TFA concentration for precipitation input (St. Wilhelm ●) and discharge output (Zipfeldobel ■, Talbach ◆, Brugga ▲, and Dreisam ▼).
- Establishing a water balance from HYRAS (Rauthe et al. 2013) precipitation input, recorded discharge data (LUBW, RP-Freiburg) and groundwater flow (Darcy-Approach) for 2023, 2024 and the 30-year average (10-year at Zipfeldobel).
- Combining TFA concentrations with water balance to obtain the mass balance for TFA, using the weighted mean TFA concentration of both years for the average year balance.

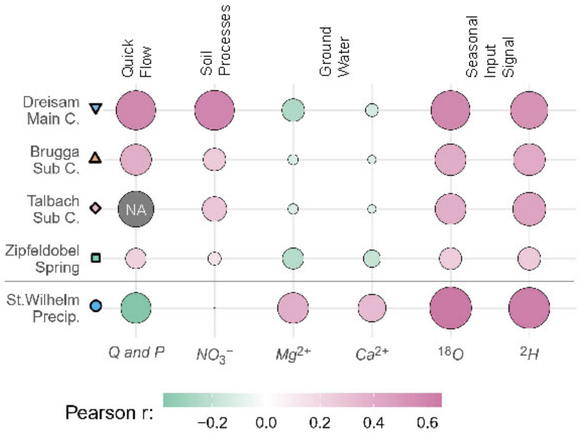


Dynamics

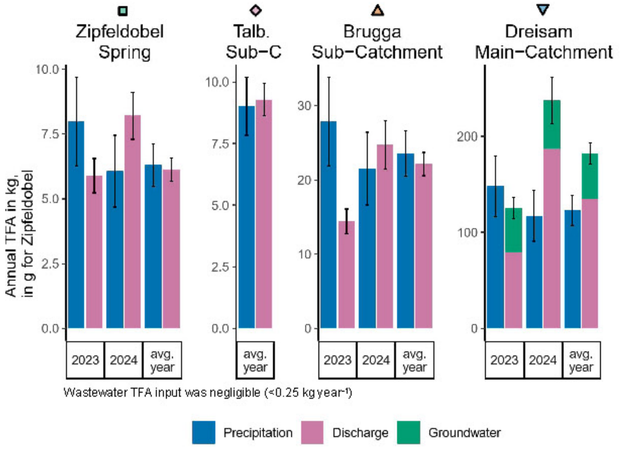




TFA Correlation with Tracers



Mass Balance



Sources, Storage and Transport

TFA is only stored temporarily ■▲◆

- Events in autumn 2023 and 2024 indicate that TFA is retained in both headwater catchments because streamflow-TFA peaked despite low precipitation concentrations.
- The mass balance suggests that TFA might be retained across years. Nevertheless, the TFA export matches the precipitation input for the average year in the subcatchments free of arable land.
- A correlation with nitrate suggests that retained TFA is stored in the soil zone.

The primary TFA transport process is SSF ■▲◆

- Correlation with discharge suggests that quick runoff components (mainly subsurface storm flow (SSF)) are the primary transport mechanism for TFA.
- The negative correlation with Ca^{2+} and Mg^{2+} implies the absence of groundwater influence.
- Wet conditions enhance SSF and TFA exports. Exports were higher in the wet year 2024 than in 2023.
- Low r-values indicate the absence of quick runoff components at the Zipfeldobel spring.

Agriculture is an additional source of TFA in the main catchment ▼

- Nitrate is additionally leached from agricultural soils, and precipitation is isotopically heavier in the lower parts of the catchment. Therefore, a stronger correlation at Dreisam compared to Talbach and Brugga indicates that water carrying high TFA loads stems from the agricultural valley.
- In the main catchment, we found an average-year TFA export excess of 11.4 ± 3.9 kg TFA per km² of arable land, twice as high as the literature (Joerss et al. 2024).

Estimating ET with TFA

- Lack of retention enables evapotranspiration *(ET)* calculation from the TFA concentration factor:

ET [mm] calculated from:	Brugga ▲	Talbach ◆	Zipfeldobel ■
Water Balance	644 ± 60	467 ± 72	300 ± 100
c_{TFA} and discharge	537 ± 241	521 ± 286	307 ± 214

- The approach is limited to areas with precipitation TFA input only and catchments with short transit times because TFA concentration in precipitation is rising.

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- Joerss, Hanna; Frei, Sven; Hafner, Klaus; Lee Lewis, Stefan; Hollender, Juliane; Lin, Xiaojing; Nödler, Karsten et al. (2024): Pesticides can be a substantial source of trifluoroacetate (TFA) to water resources. In: *Environmental International* 193, S. 109061. DOI: 10.1016/j.envint.2024.109061.
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