Where does TFA come from?

Isotope signature as an assessment method for contamination cases involving trifluoroacetic acid (TFA) and short-chain PFAS in drinking water and groundwater

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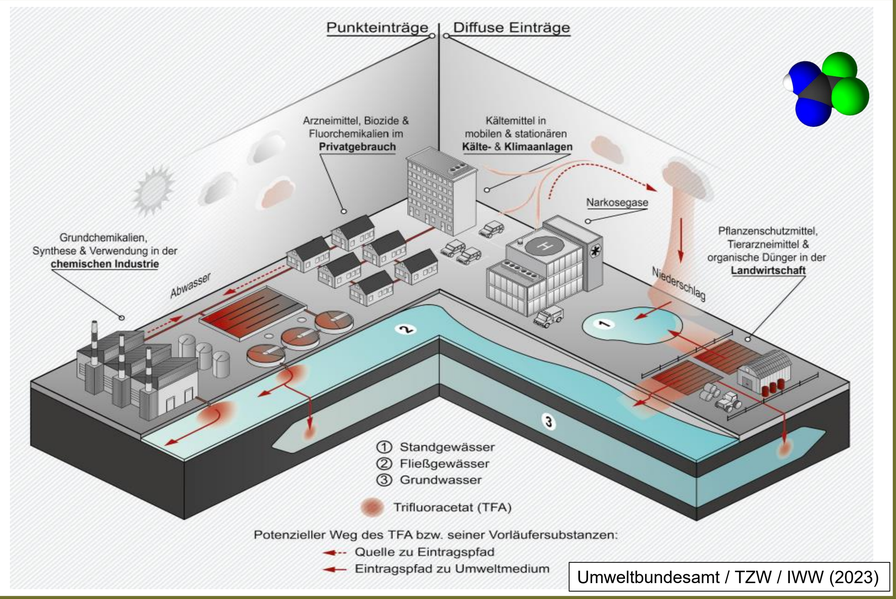
MOTIVATION - "A Substance Without a Sender"

- Shortest-chain perfluorinated carboxylic acid
- Most abundant PFAS in aquatic environments
- Highly water-soluble, mobile, and practically not retained during soil passage
- TFA reaches groundwater and drinking water almost unhindered.
- Biological or chemical degradation pathways are hardly known
- TFA is considered highly persistent and accumulates irreversibly.
- Not removed by conventional drinking water treatment methods (activated carbon, oxidation)

TFA has a variety of parallel input pathways:

- Atmosphere: photochemical degradation of fluorinated refrigerants and CFC replacements (e.g., HFO-1234yf)
- Degradation of trifluoromethyl-containing pesticides and pharmaceutical active ingredients
- Industrial discharge and municipal wastewater treatment plants
- Possibly geogenic sources (discussed, not confirmed)



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$\delta^{13}C$ (C_xF_{2x+1} group) - signature of the perfluorinated part

For the position-specific analysis, TFA is cleaved Via its silver salt with iodine; this produces trifluoroiodomethane (CF_3I), whose $\delta^{13}C$ directly gives the signature of the C_xF_{2x+1} group:

C_xF_{2x+1}-$COOAg + I_2 \rightarrow C_xF_{2x1}I + CO_2 + AgI$

$\delta^{13}C$-CF_3-group (I_2-Method)

$\delta^{13}C$=-60,3±0,6 ‰$_{VPDB}$ (GC-IRMS)

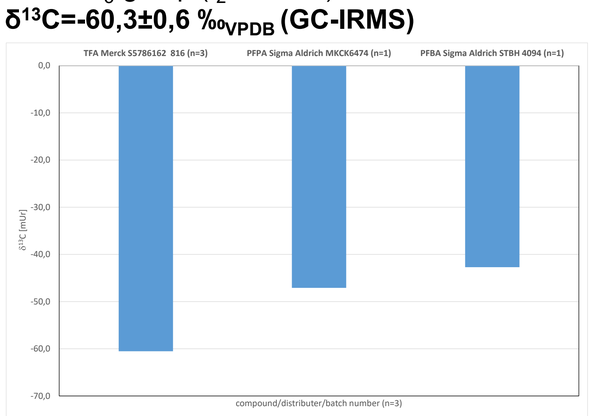
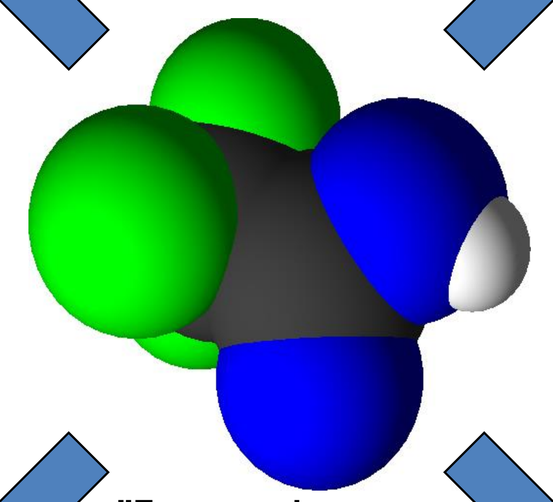


Figure 1: $\delta^{13}C$ (CxF2x+1) values of different PFAA from various suppliers

GOAL & APPROACH

TFA Merck S5786162 816



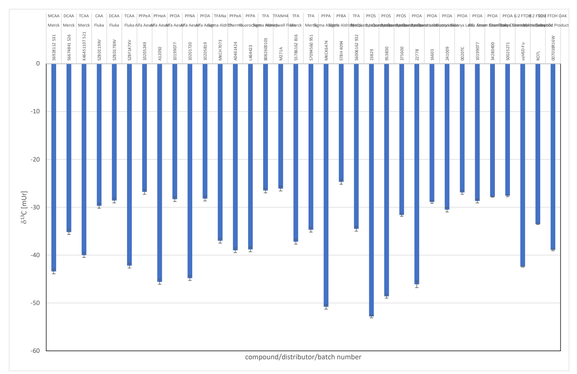
"Four numbers from a molecule"

$\delta^{13}C$ (bulk) - overall carbon signature of the molecule

- TFA occurs in water as a non-volatile anion, not directly accessible for gas chromatography
- Conversion of TFA for GC analysis via Precipitation as Na-TFA followed by evaporation
- Conversion to free TFA using concentrated sulfuric acid
  - Thermal purging, cryogenic trapping, and introduction onto GC column via CIS
  - Oxidation to CO_2 (NiO/CuO/Pt) and isotope-ratio measurement by IRMS (m/z 45/44)

$\delta^{13}C$=-37,2±0,5 ‰$_{PDB}$ (GC-and EA-IRMS)

Figure 2: $\delta^{13}C$-(bulk) values of different PFAA from different supplyers



$\delta^{13}C$ (COOH group)-position-specific

Calculated: $\delta^{13}C\text{-}COOH = 2*\delta^{13}C\text{-}TFA - \delta^{13}C\text{-}CF_3$

$\delta^{13}C$=-14,1±1,6 ‰$_{VPDB}$ (calculated from $\delta^{13}C$-CF_3-group and $\delta^{13}C_{bulk}$)

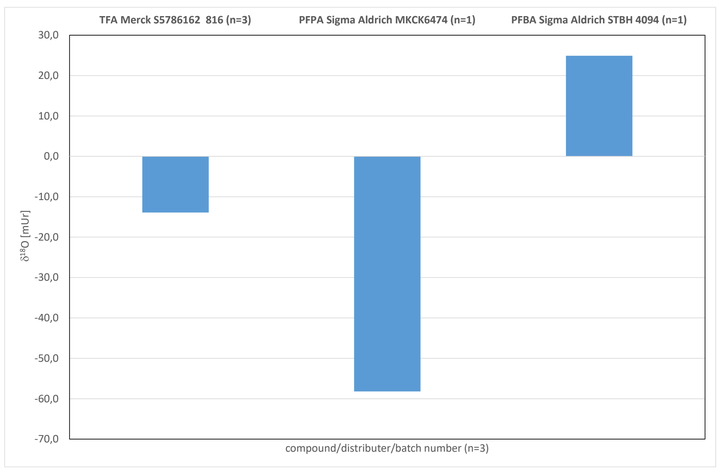


Figure 3: $\delta^{13}C$-COOH values of different PFAA from various suppliers

$\delta^{18}O$ (COOH group) - oxygen signature of the carboxyl group

- Release of the carboxyl group as CO_2 by decarboxylation at 1000 °C
- Analysis of the free acid or PFAEt synthesized from PFAAg and EtI
- Current $\delta^{18}O$ measurement by EA-IRMS (m/z 46/44)

$\delta^{18}O$=+2,7±1,0 ‰$_{VSMOW}$ (measured EA-Py-IRMS)

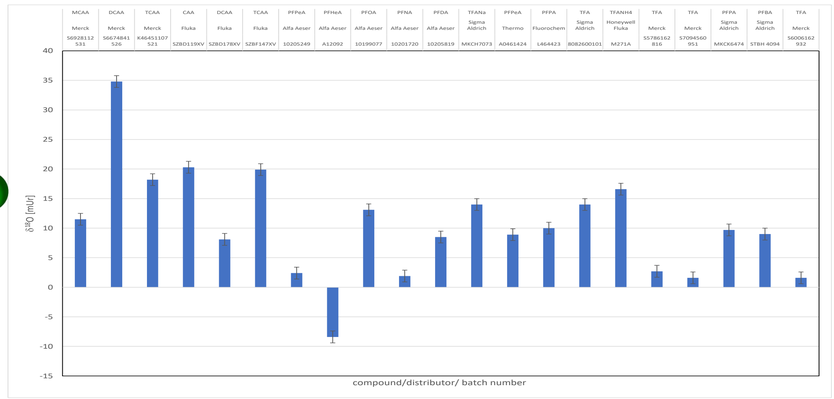


Figure 4: $\delta^{18}O$-COOH values of different PFAA from various supplyers

Outlook

- Increase sensitivity to 0.1 µg/L through a new, enlarged purge-and-trap unit to bring the entire sample onto the GC column.
- Further development and validation of position-specific ^{13}C and ^{18}O methods, including investigation of fractionation effects, especially for ^{18}O if there is an exchange with water
- Creation of an evaluation database from environmental, transformation, and standard samples as a basis for source attribution.
- Enrichment procedures for short-chain PFAS.

Summary

- TFA is ubiquitous and highly persistent.
- There are numerous entry pathways (basic chemical, metabolite of biocides, pesticides and pharmaceuticals, breakdown product of refrigerants, possibly geogenic formation).
- There are no limit values for TFA, only guideline values; differentiation of entries has not been possible so far.
- Isotope analyses can explain formation pathways (Wacker-Höchst process from C_2 compounds, Monsanto process from C_1 compounds via $CH_3OH + CO$) and thus entry routes.
- There is a wide range of $\delta^{13}C$ and $\delta^{18}O$ values depending on the production.
- The main analytical challenges are: low concentrations, the aggressiveness of TFA, and interfering substances like chloride.

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