Safety in Technology and Chemistry

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Finding the most suitable PFASs sum parameter method

A Comparison of AOF vs. EOF and CIC vs. HR-CS-GFMAS

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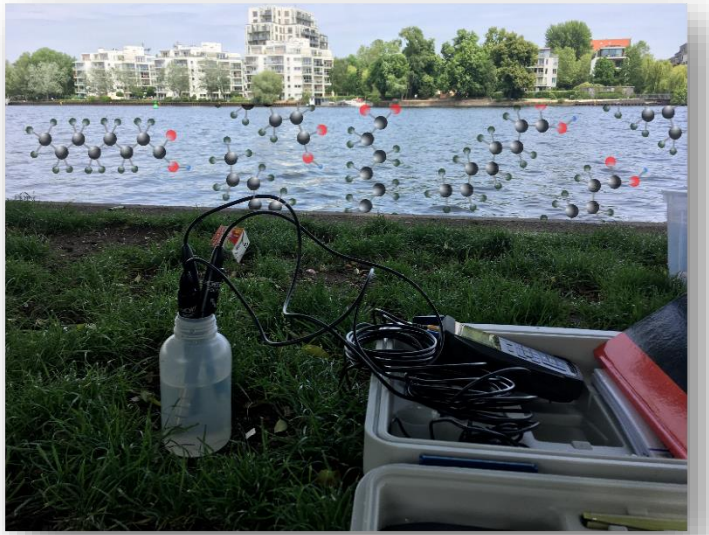
Motivation

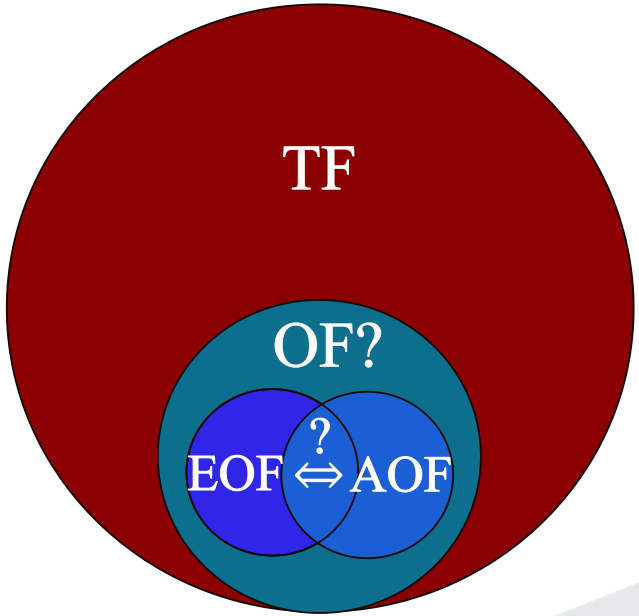
- Diverse entry routes of PFASs complicate monitoring
- PFASs regulatory of target compounds is circumvented by substitutes

- To reduce surface water contamination a detection method is needed which:
  - Reveals PFASs hot spots
  - Includes unknown substitutes
  - Provides robust results with low detection limits
  - Is easy to handle



Concept of PFASs Sum Parameter Methods

- Target analytical approaches limited to up to 53 substances
- Therefore sum parameter approaches use fluorine specific detection methods
  - PFASs must be separated from inorganic fluoride
  - Converted into detectable species
- Two separation techniques are common:
  - Adsorption of organically bound fluorine (OF) on activated carbon → AOF
  - Extraction of OF using SPE/solvents → EOF



Concept of PFASs Sum Parameter Methods

- Conversion and detection either by combustion ion chromatography (CIC) or graphite furnace-molecular absorption spectrometry (GFMAS)
- CIC: Combustion of sample
  → quantitative conversion of fluorine species into HF and adsorption in trapping solution
  → quantification via IC using conductivity detection

881 compact IC pro system (Metrohm GmbH & Co. KG, Filderstadt, Germany)

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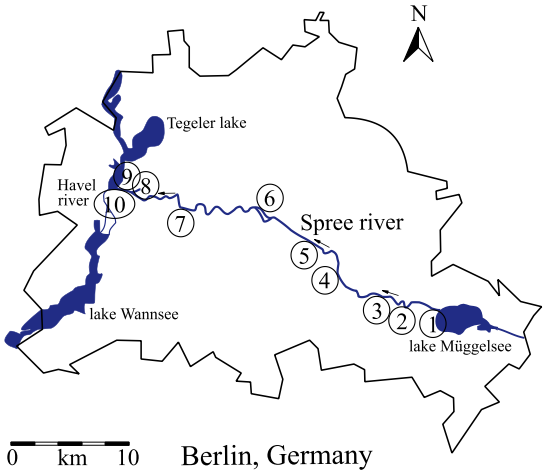
- GFMAS: atomization of sample in graphite furnace;
  → formation of diatomic molecule with molecule forming agent (e.g. Ga)
  → detection of characteristic molecular absorption wavelength (λ_{GaF}=211.2488 nm)

881 compact IC pro system (Metrohm GmbH & Co. KG, Filderstadt, Germany)

contrAA 800 HR-CS-GFMAS system (Analytik Jena AG, Jena, Germany)

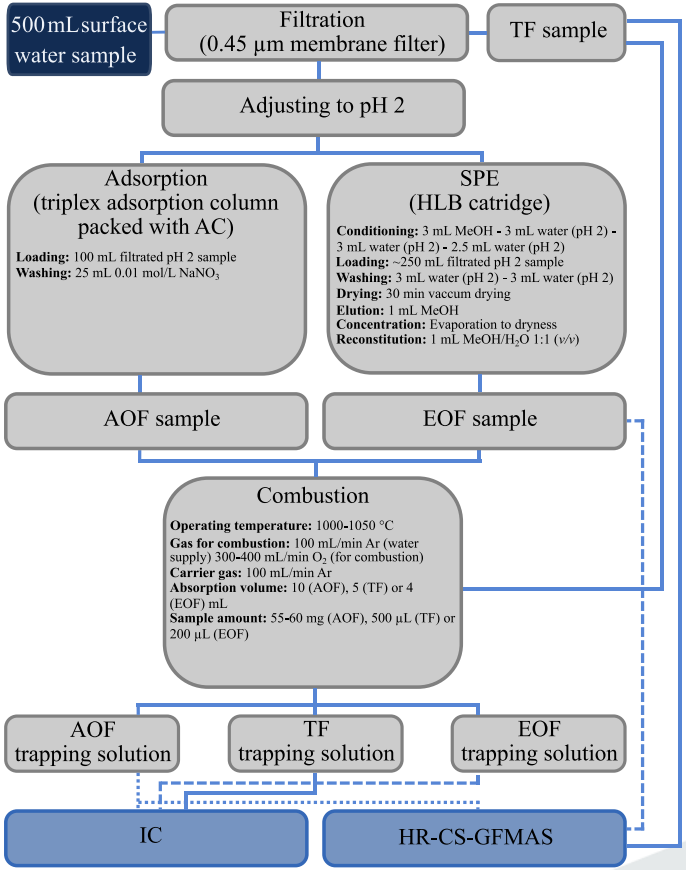
Sampling Campaign of Comparison Study

- 10 sampling locations along the river Spree (Berlin, Germany)
  - No known polluted sites
  - Surfaces water samples of 20-30 cm depth
    1.5-2 m distance to riverbank



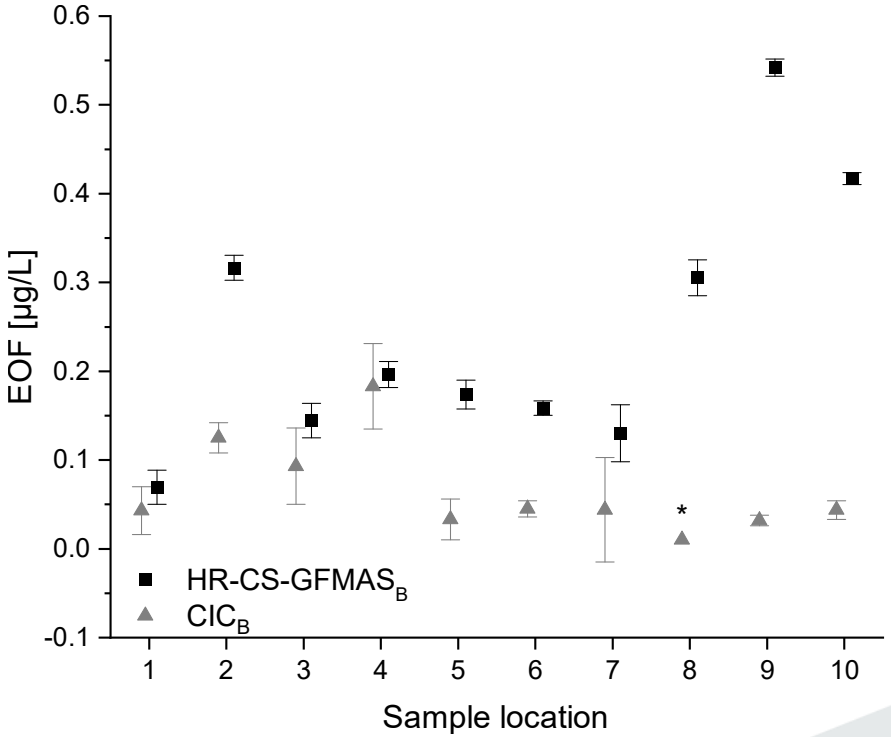
Methods

Both sum parameters were determined for each sample using both instrumental set ups



Results & Discussion (1) – EOF

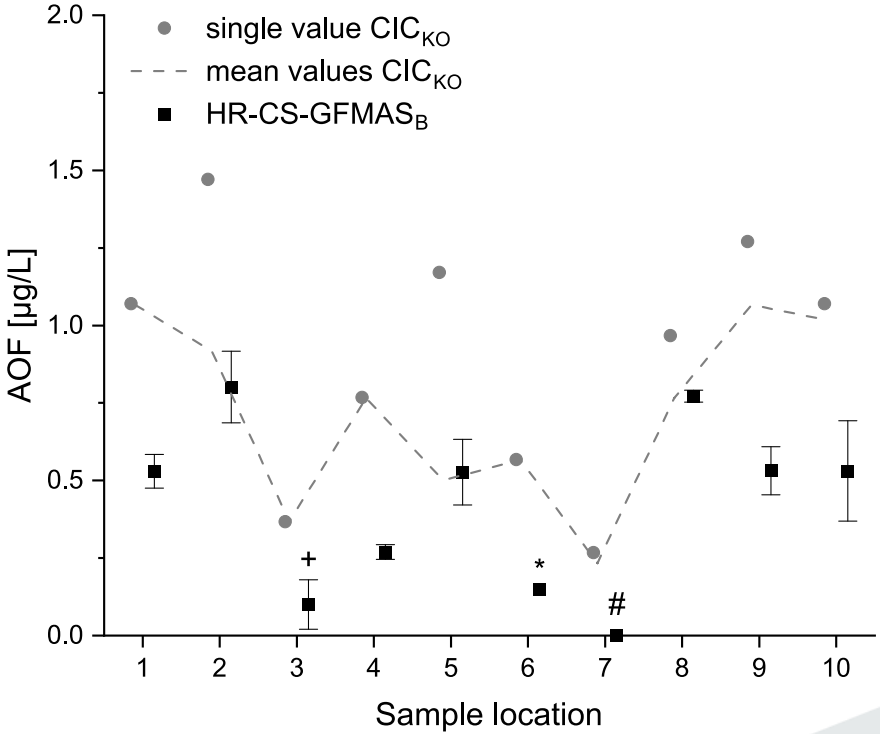
- After SPE extraction aliquots of methodical triplicates were measured using both instrumental set ups
- Shown are EOF concentrations related to the original sample volume
- Error bars based on SD



*: determined concentration below instrumental LOQ

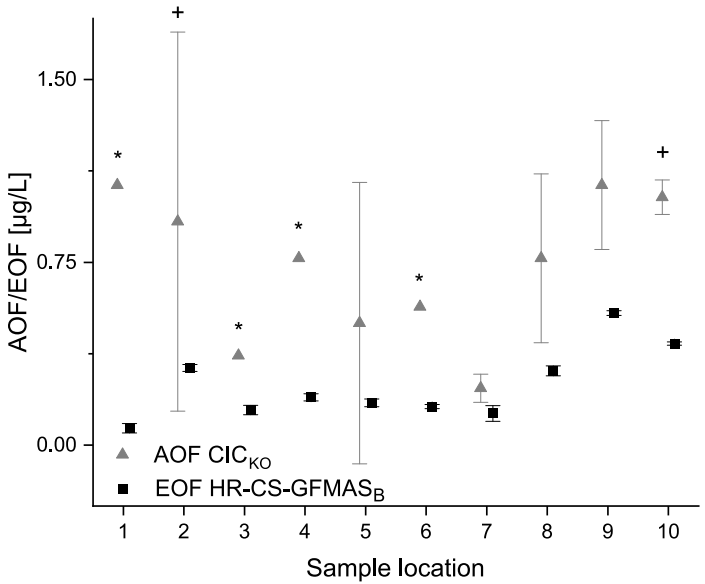
Results & Discussion (2) – AOF

- After combustion aliquots of one set of trapping solutions were measured using both instrumental set ups
- Shown are AOF concentrations related to the original sample volume
- Error bars for GFMAS based on SD of instrumental triplicates



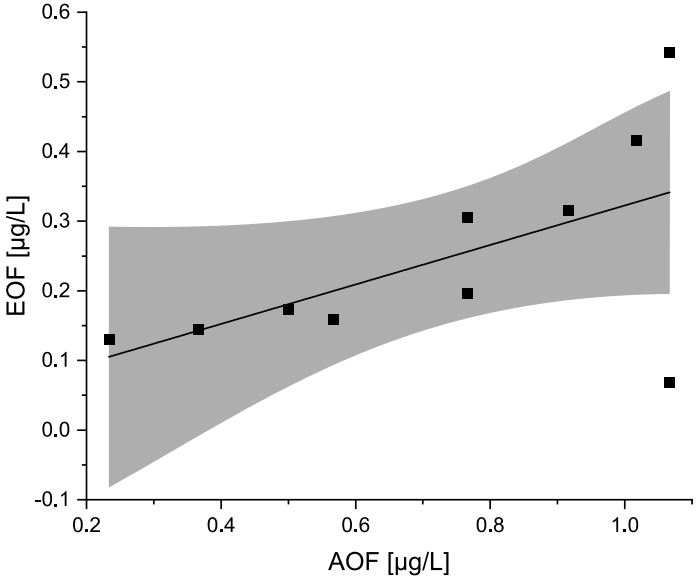
determined concentration below instrumental LOQ
for +: one; *: two; # all three measurements

Results & Discussion (3) – Comparison



- EOF determined via HR-CS-GFMAS; AOF determined via CIC
- error bars refer to SD (n=3)

determined concentration below instrumental LOQ
for +: one; *: two measurements



- EOF values plotted against AOF values of the same sampling location
- Scatter plot reveals systematically lower EOF (factor ~0.25)

Conclusion

HR-CS-GFMAS vs. CIC

- both powerful devices in fluorine trace analysis
- HR-CS-GFMAS analysis is faster, more sensitive, and more precise
- CIC loses enrichment due to high volume of trapping solution => lower sensitivity
- Lower instrumental LOQs were determined for HR-CS-GFMAS (2.7 µg/L vs. 10 µg/L)

=> HR-CS-GFMAS is beneficial compared to CIC to determine OF

AOF vs. EOF

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AOF vs. EOF

- AOF seems to represent a higher proportion of the OF => more sensitive
- EOF values scattered less and blank values were negligible => more precise
- High fluoride backgrounds in AC => low reproducibility/higher SD

=> Both parameter methods showed similar trends over the sampling locations and were able to reveal concentrations in < 1ppb

But: further optimization for more accurate determination of OF is needed

Thanks...

Funding

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„Untersuchung des Vorkommens von PFAS (Per- und polyfluorierte Alkylverbindungen) in Abfallströmen“

Cooperation

Division 4.3 - BAM
Department G2 - Aquatic Chemistry, Federal Institute of Hydrology (BfG)

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References

Gehrenkemper L & Simon F et al. Anal. Bioanal. Chem. 2021. DOI: 10.1007/s00216-020-03010-y.