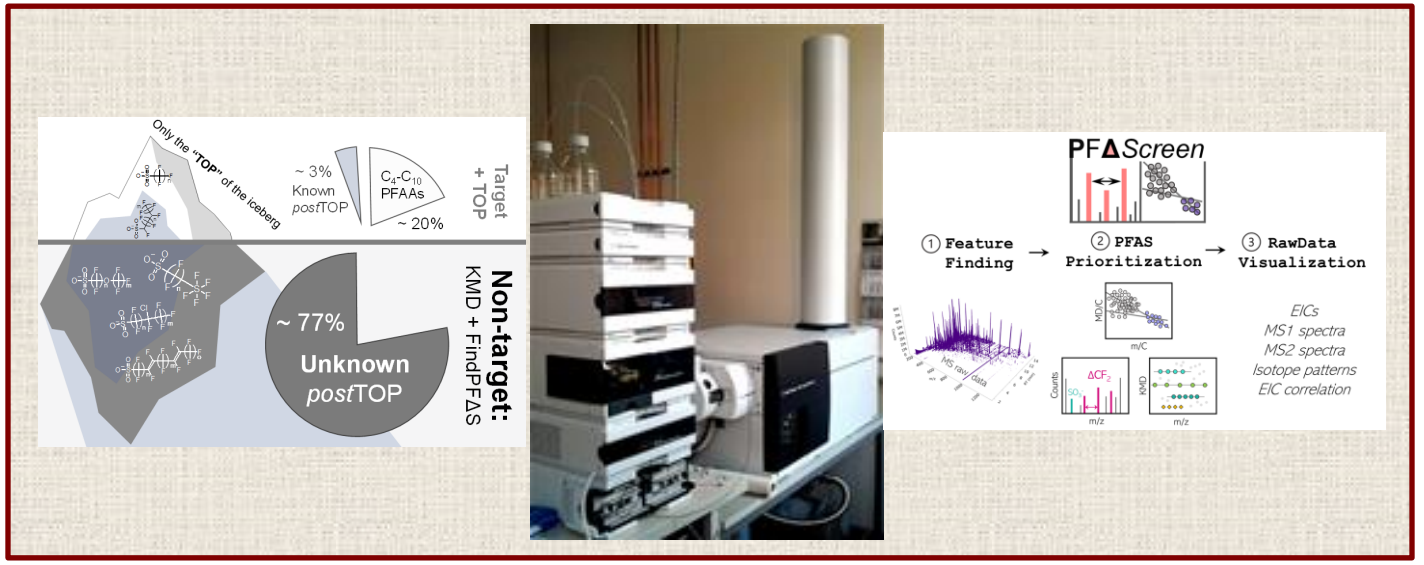
Brauchen wir LC-HRMS-Screening für PFAS-kontaminierte Standorte? –

Möglichkeiten und Grenzen am Beispiel von 3 Standorten

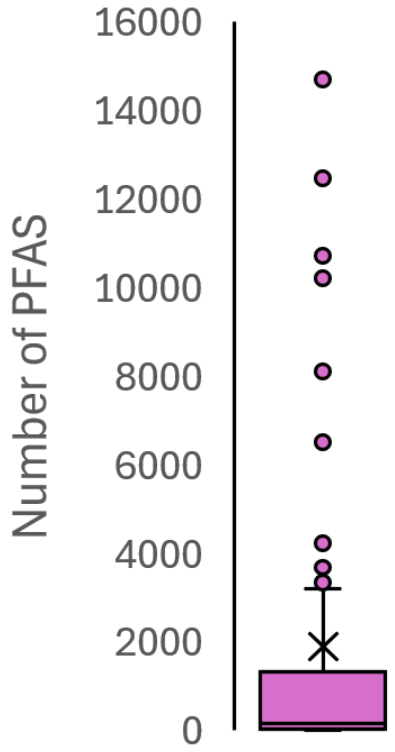
Christian Zwiener



Umweltanalytik, Universität Tübingen

PFAS?

How many?



Target: ~20…

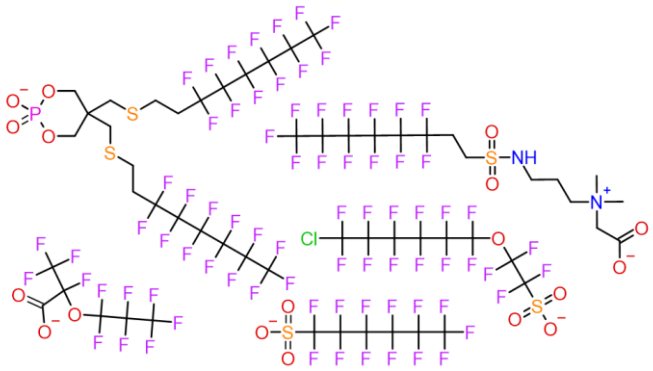
Standards: ~100…?

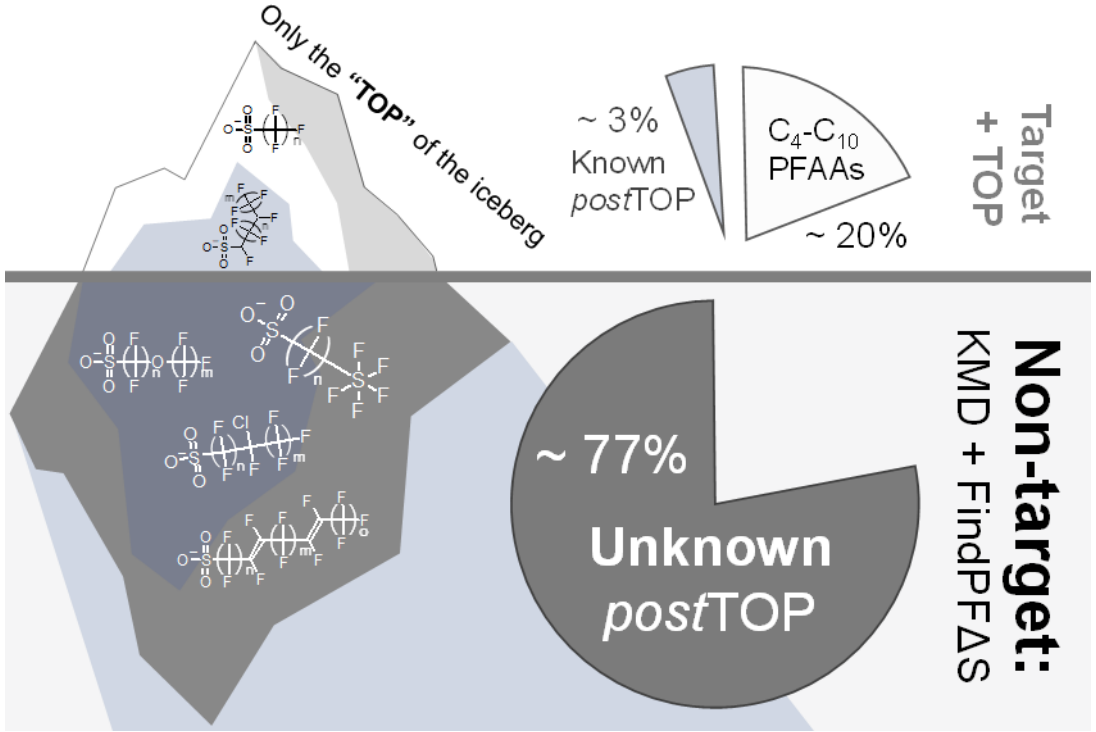
Suspect lists in PubChem

Total: 7 Million OECD PFAS…?

What are the challenges?

- PFAS or their TPs are persistent
  - Mobile or bioaccumulative
- ~ 60 reference standards vs. 10000 PFAS
  - Many yet unknown PFAS occur in the environment!

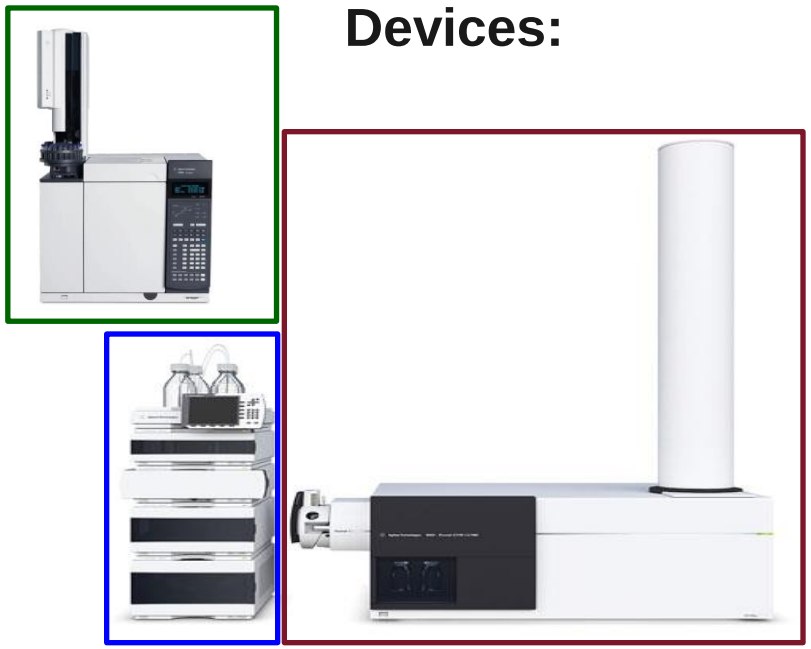




- **New analytical approaches for PFAS and TPs**
- **Nontarget screening by HRMS**
  - data prioritization
  - identification

Zweigle et al. ES&T 57 (2023) 6647-55

Nontarget Screening



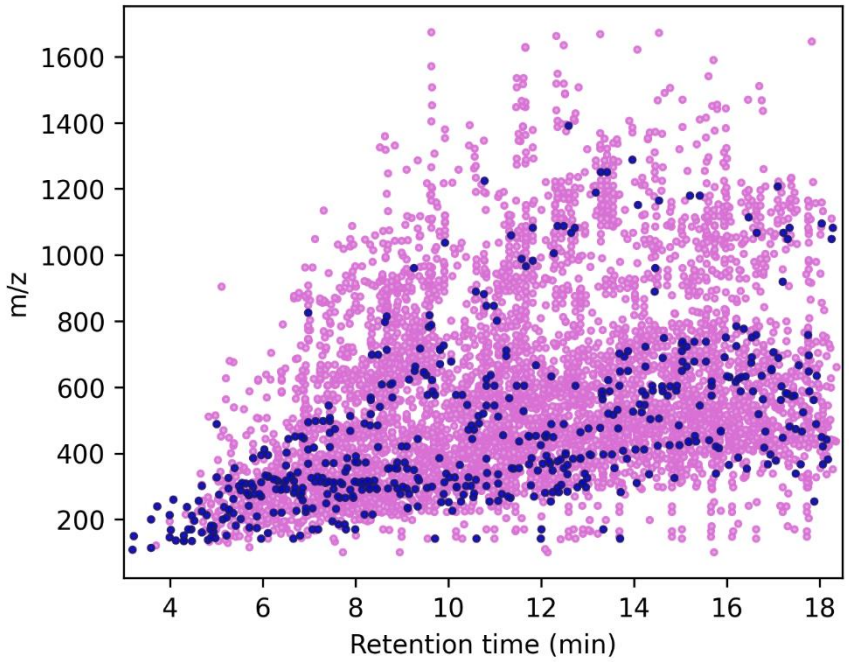
Devices:

Liquid chromatography (Agilent 1260 Infinity System)

Gas chromatography (Agilent 7890B)

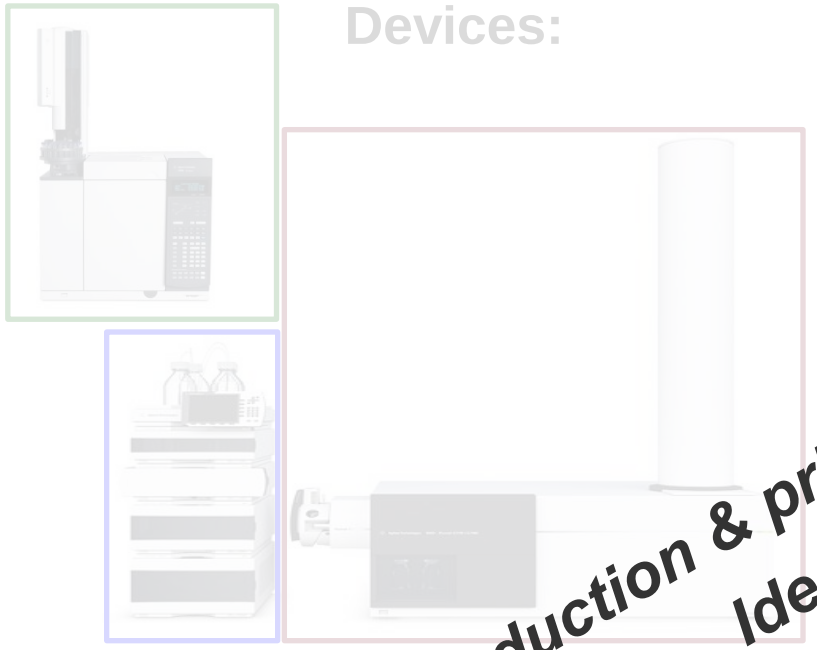
High-resolution mass spectrometry
6550 iFunnel Q-TOF (Agilent Technologies)

LC-HRMS data: 5743 features



- **Electrospray-ionization** (ESI)
- **Atmos. press. chem. ionization** (APCI)
- **DDA or DIA of MS/MS for** a defined mass range (e.g. 100-1000 Da)

Nontarget Screening



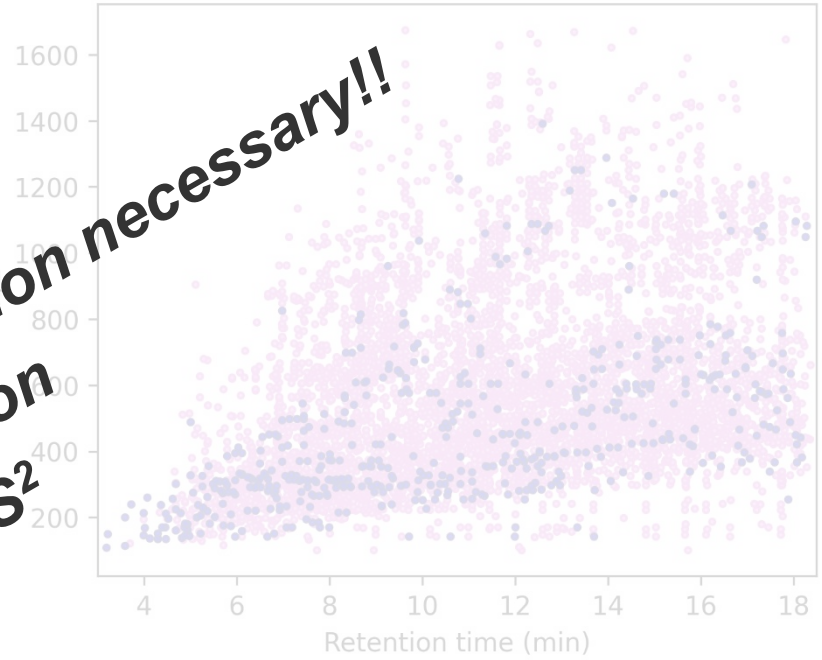
Devices:

Liquid chromatography (Agilent 1260 Infinity System)

Gas chromatography (Agilent 7890B)

High-resolution mass spectrometry
6550 iFunnel Q-TOF (Agilent Technologies)

LC-HRMS data: 5743 features



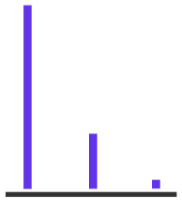
Data reduction & prioritization necessary!!
Identification
MS^1 /MS^2

- **Electrospray-ionization** (ESI)
- **Atmos. press. chem. ionization** (APCI)
- **DDA or DIA of MS/MS for** a defined mass range (e.g. 100-1000 Da)

MD/C – m/C approach

„Typical“ molecule:

$C_{27}H_{43}NO_2$
413.3294 Da
m/C ≈ 15



PFAS:

$C_8HF_{15}O_2$
413.9737 Da
m/C ≈ 52!

5743 → 345 features
Data reduction ≈ 95%

Analytical and Bioanalytical Chemistry
https://doi.org/10.1007/s00216-023-04601-1

PAPER IN FOREFRONT

Efficient PFAS prioritization in non-target HRMS data: systematic evaluation of the novel MD/C-m/C approach

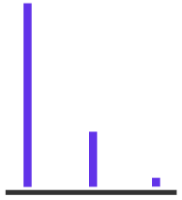
Jonathan Zweigle[1] · Boris Bugsel[1] · Christian Zwiener[1]

Kaufmann et al. (2022) *J. AOAC Int.* 105: 1280-1287.

MD/C – m/C approach

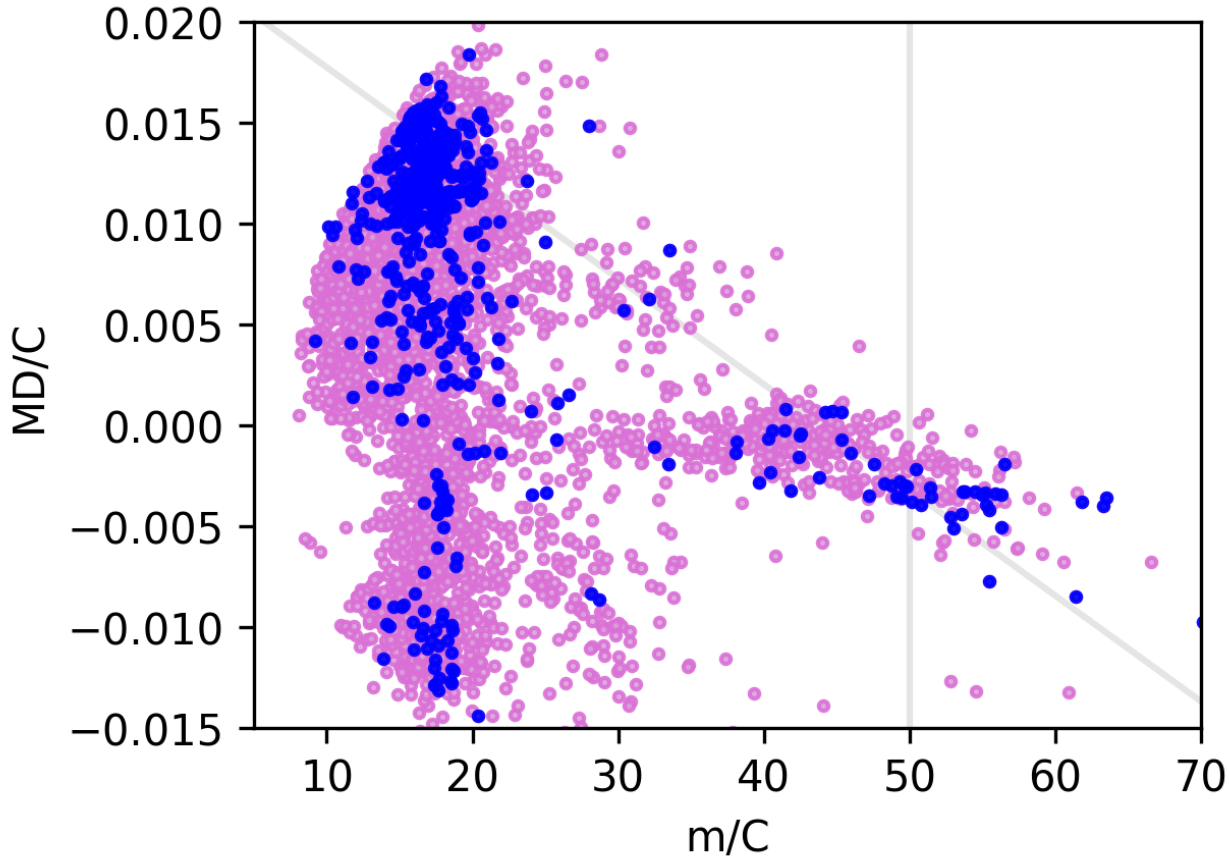
„Typical“ molecule:

$C_{27}H_{43}NO_2$
413.3294 Da
m/C ≈ 15

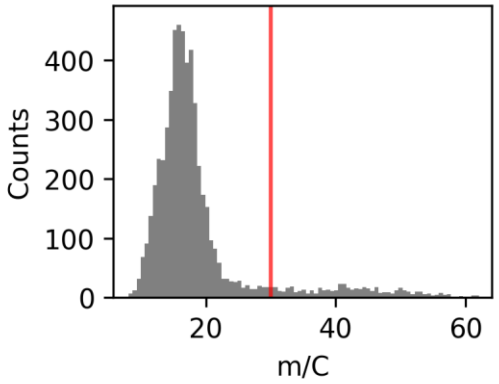


PFAS:

$C_8HF_{15}O_2$
413.9737 Da
m/C ≈ 52!



5743 → 345 features
Data reduction ≈ 95%



Analytical and Bioanalytical Chemistry
https://doi.org/10.1007/s00216-023-04601-1

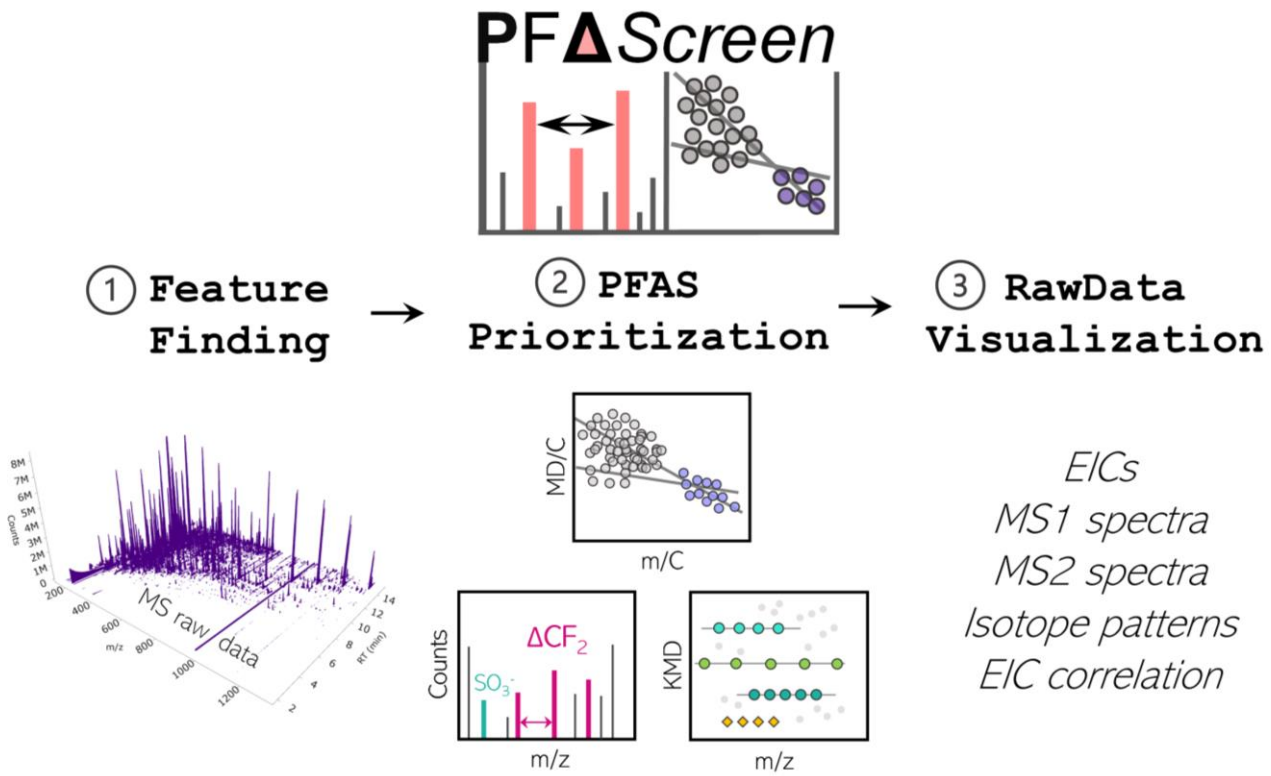
PAPER IN FOREFRONT

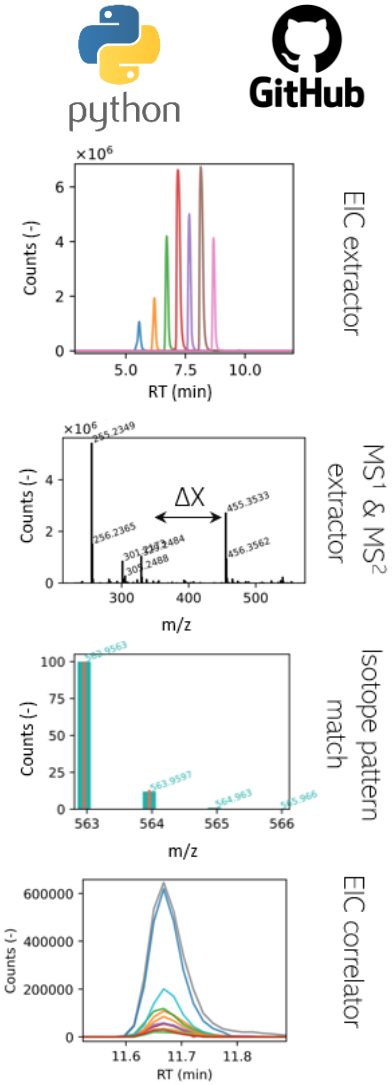
Efficient PFAS prioritization in non-target HRMS data: systematic evaluation of the novel MD/C-m/C approach

Jonathan Zweigle[1] · Boris Bugsel[1] · Christian Zwiener[1]

Kaufmann et al. (2022) *J. AOAC Int.* 105: 1280-1287.

PFΔScreen – new Open-Source Tool





- Easy to use! (GUI)
- No programming required!
- Vendor independent!

Zweigle et al. Anal. Bioanal. Chem. (2024) 416: 349 - 362

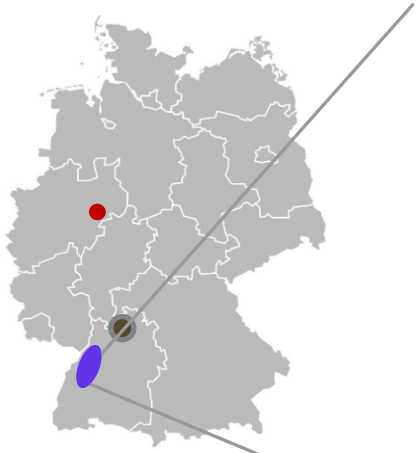
NTS applications: Contaminate soils

1) Paper samples (FTMAPs & FTSAs)

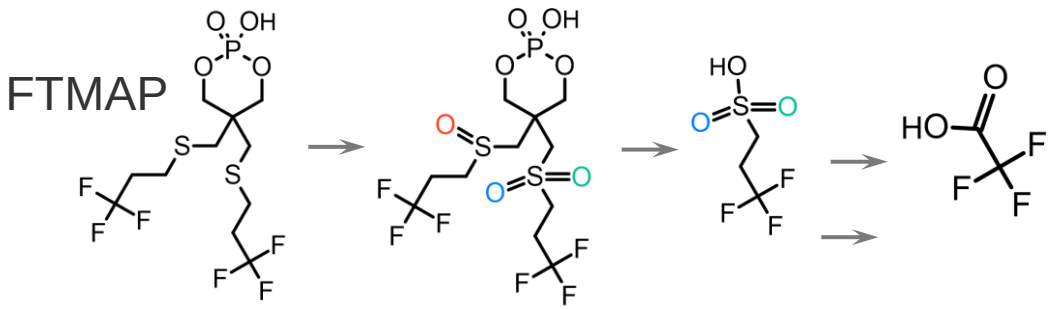
2) Paper samples (diPAPs)

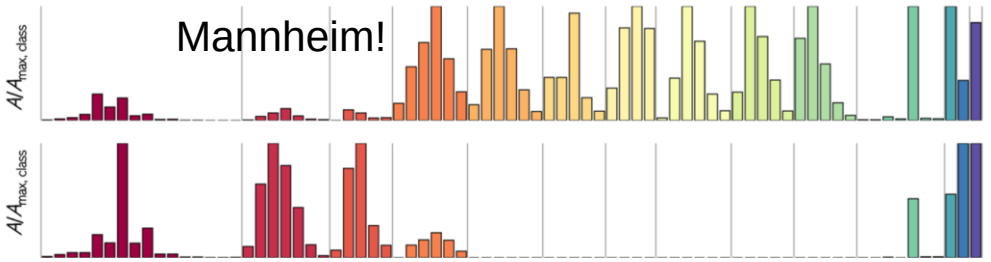
3) Soil samples (diPAPs, diSAmPAPs + TPs)

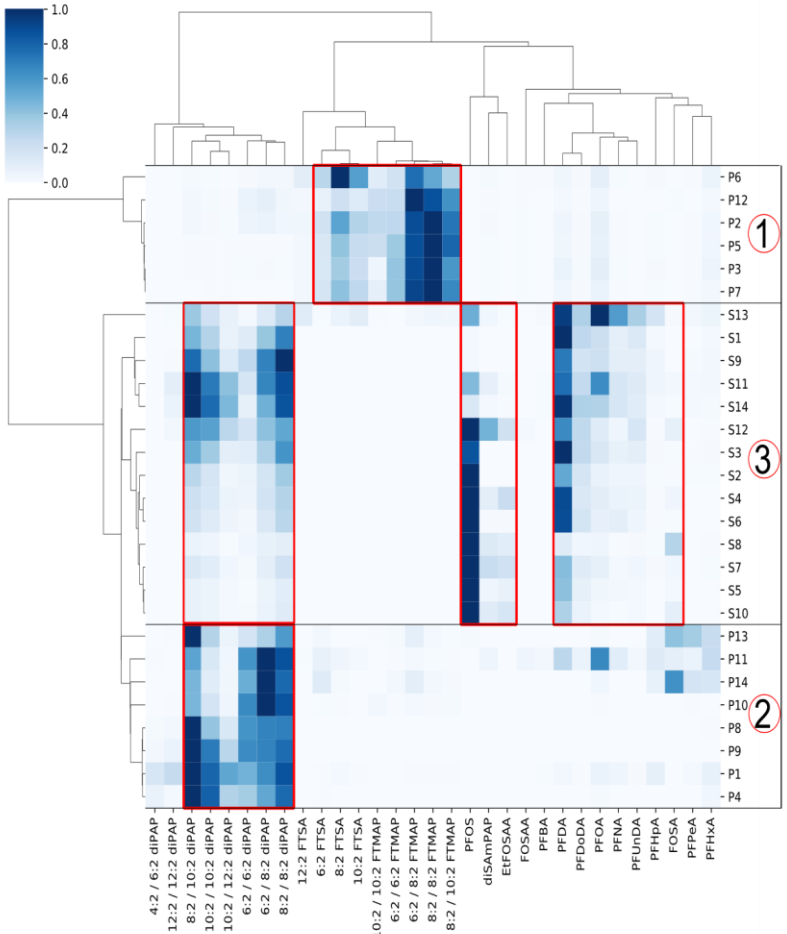
Bugsel et al. ABC 414 (2022) 1217-25



Rastatt + Mannheim
> 1000 ha
Paper sludge



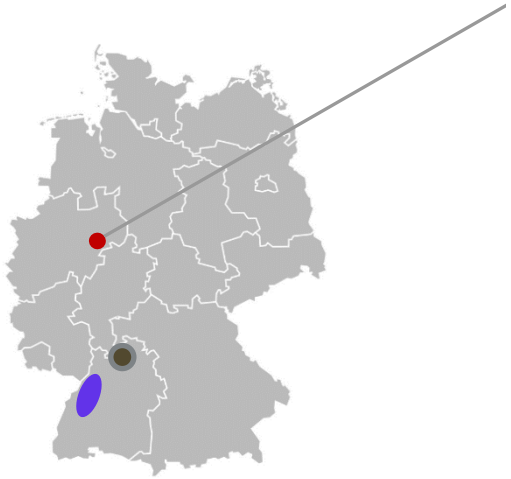


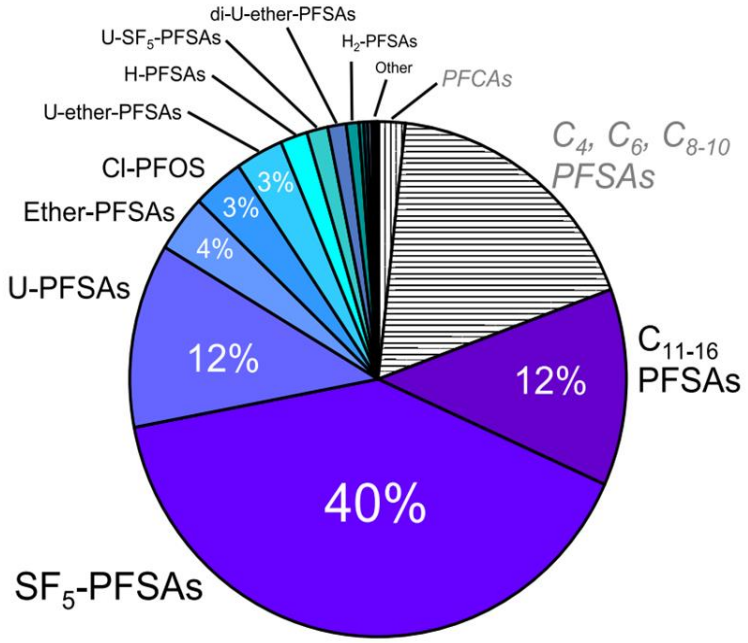


Bugsel & Zwiener ABC 412 (2020) 4797-4805; Zweigle et al. ABC 416 (2024) 349-362

NTS applications: Contaminate soils

Brilon-Scharfenberg
~10 ha
Waste?



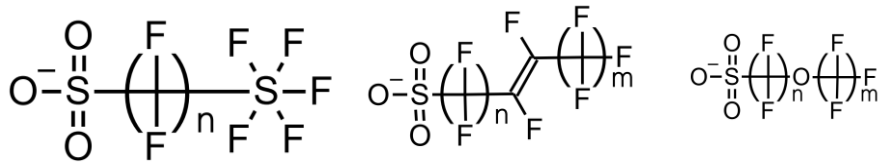


Environmental Science & Technology
pubs.acs.org/est
Article

PFAS-Contaminated Soil Site in Germany: Nontarget Screening before and after Direct TOP Assay by Kendrick Mass Defect and FindPFΔS

Jonathan Zweigle,[‖] Boris Bugsel,[‖] Klaus Röhler, Alexander Arthur Haluska, and Christian Zwiener*

Cite This: https://doi.org/10.1021/acs.est.2c07969
Read Online



- 77% „new“ PFAS on this site
- 70 „new“ PFAS from 10 further PFAS classes
- Perfluorinated PFAS are dominating
  - Pentafluorosulfanyl-PFAS (C7-C11)
  - PFSA and U-PFSAs (C8-C16)
- TOP assay & target analysis captured only < 25%

Zweigle et al. ES&T 57 (2023) 6647-55

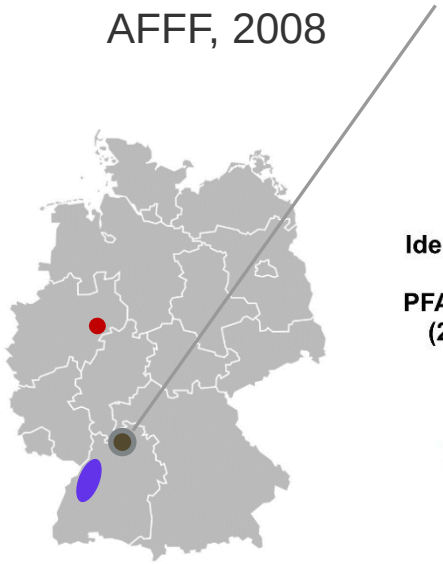
NTS applications: Contaminate soils

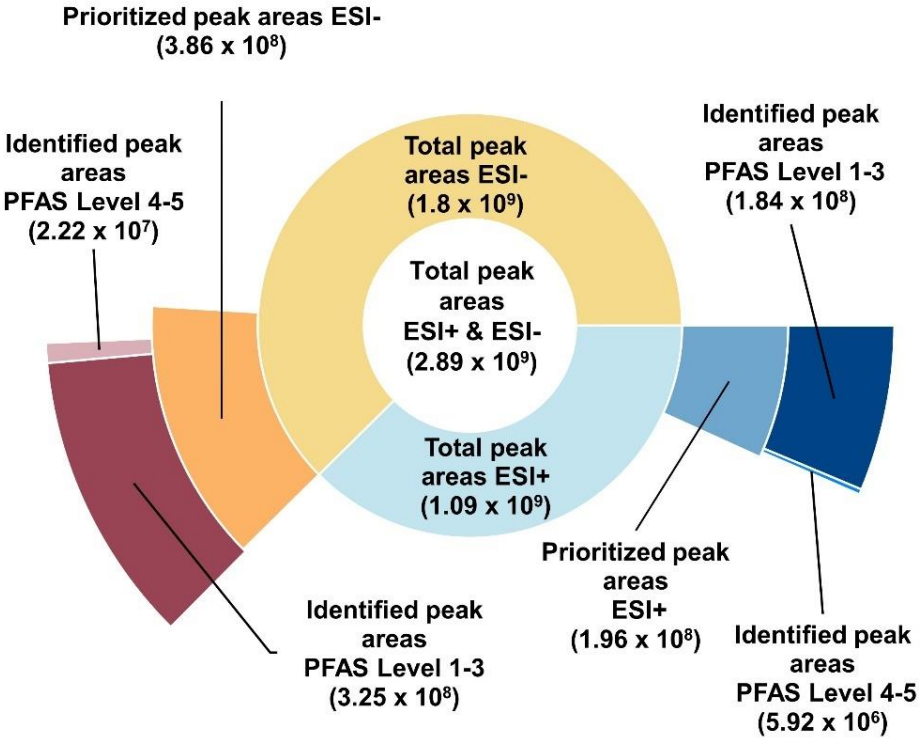
Known contaminants: Capstone B, 6:2/8:2 FTS, PFOSA, PFAAs (8 PFCA, 5 PFSA)

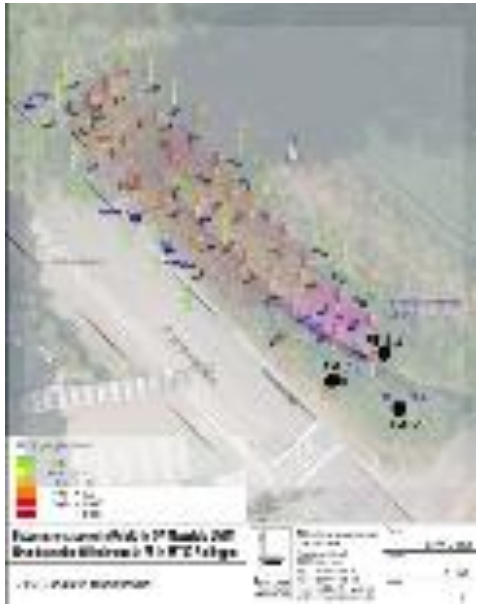
PF∆*Screen*: **124 PFAS** from 42 compound classes

Reilingen

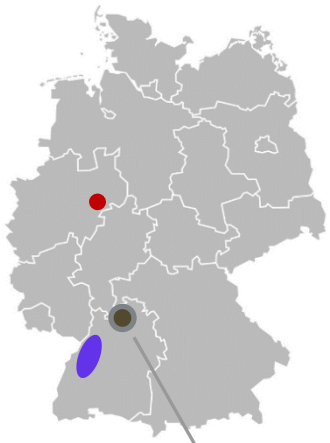
AFFF, 2008







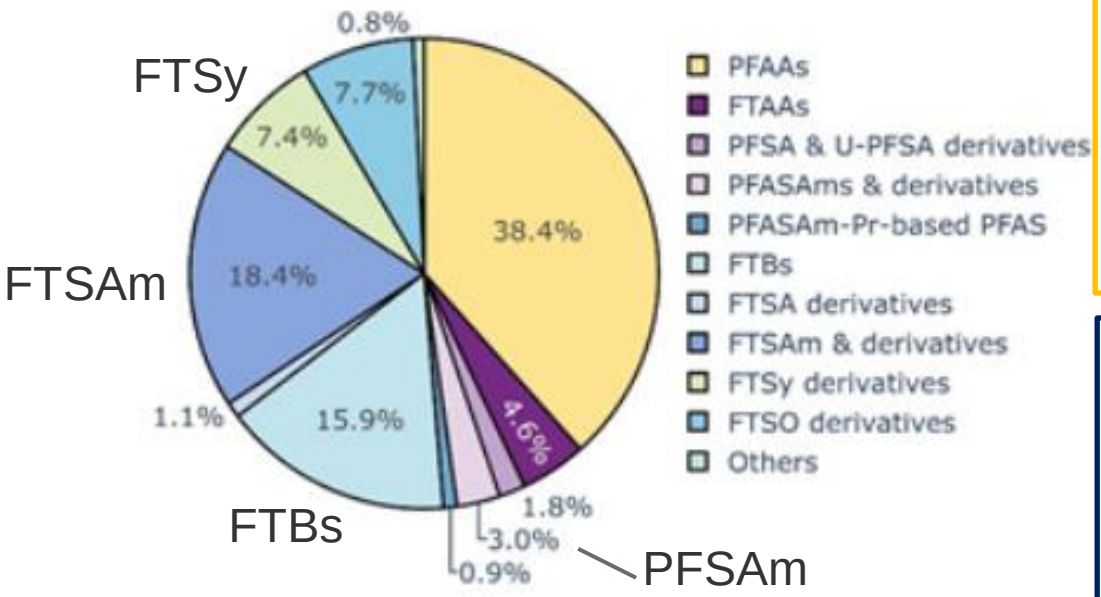
NTS applications: Contaminate soils

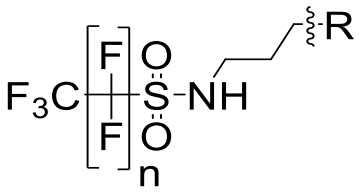


Reilingen

AFFF, 2008

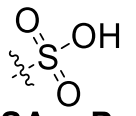
FTSO





PFSAm-

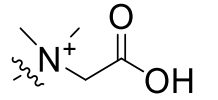
PFASAm-PrSA

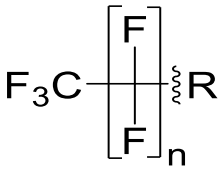


PFASAm-Pr-DiMeAm

PFASAm-Pr-TriMeAm

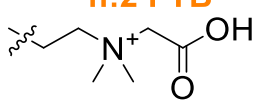
PFASAm-Pr-B



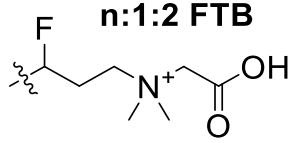


FTB-

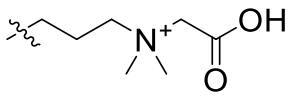
n:2 FTB



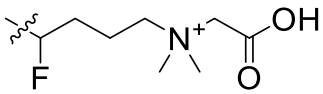
n:1:2 FTB



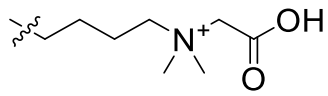
n:3 FTB

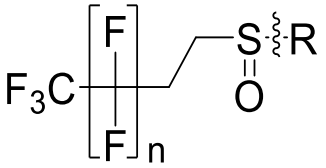


n:1:3 FTB



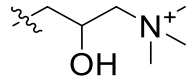
n:4 FTB



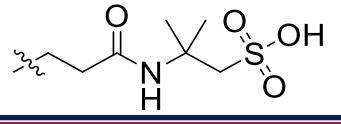


FTSO-

n:2 FTSO-(2)OHPr-TriMeAms



n:2 FTSO-Pr-Ad-(5,5)DiMeEtSAs

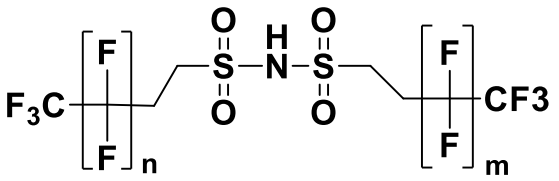


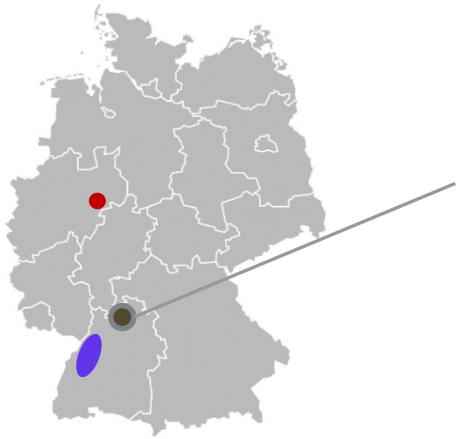
Reilingen Site – PFAS screening

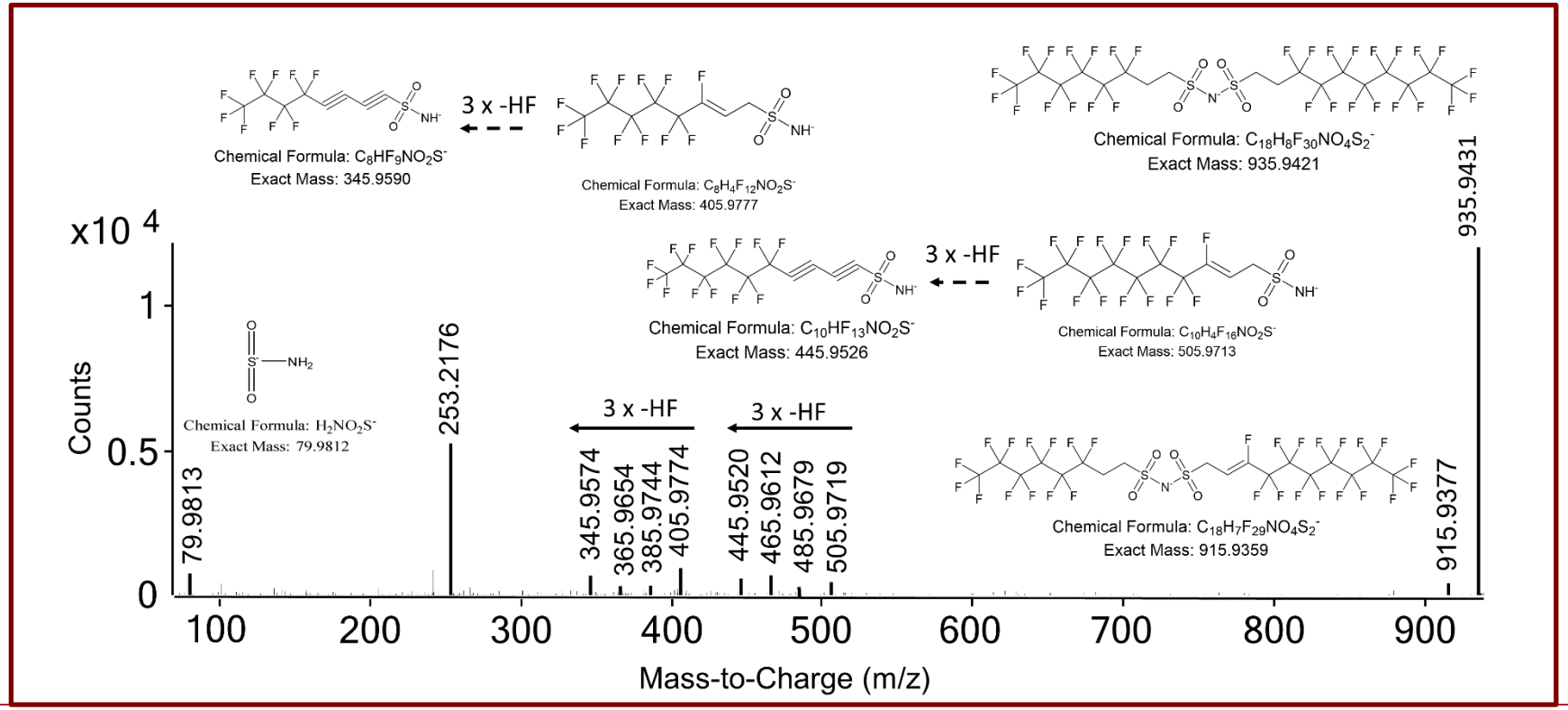
New identified PFAS in soil samples

- n:2/m:2 FTSAm-dimer
- Diagnostic MS^2 fragments
  and mass fragment differences (HF loss)

n:2/m:2 FTSAm dimer
(n = 6 / m = 6, 8)





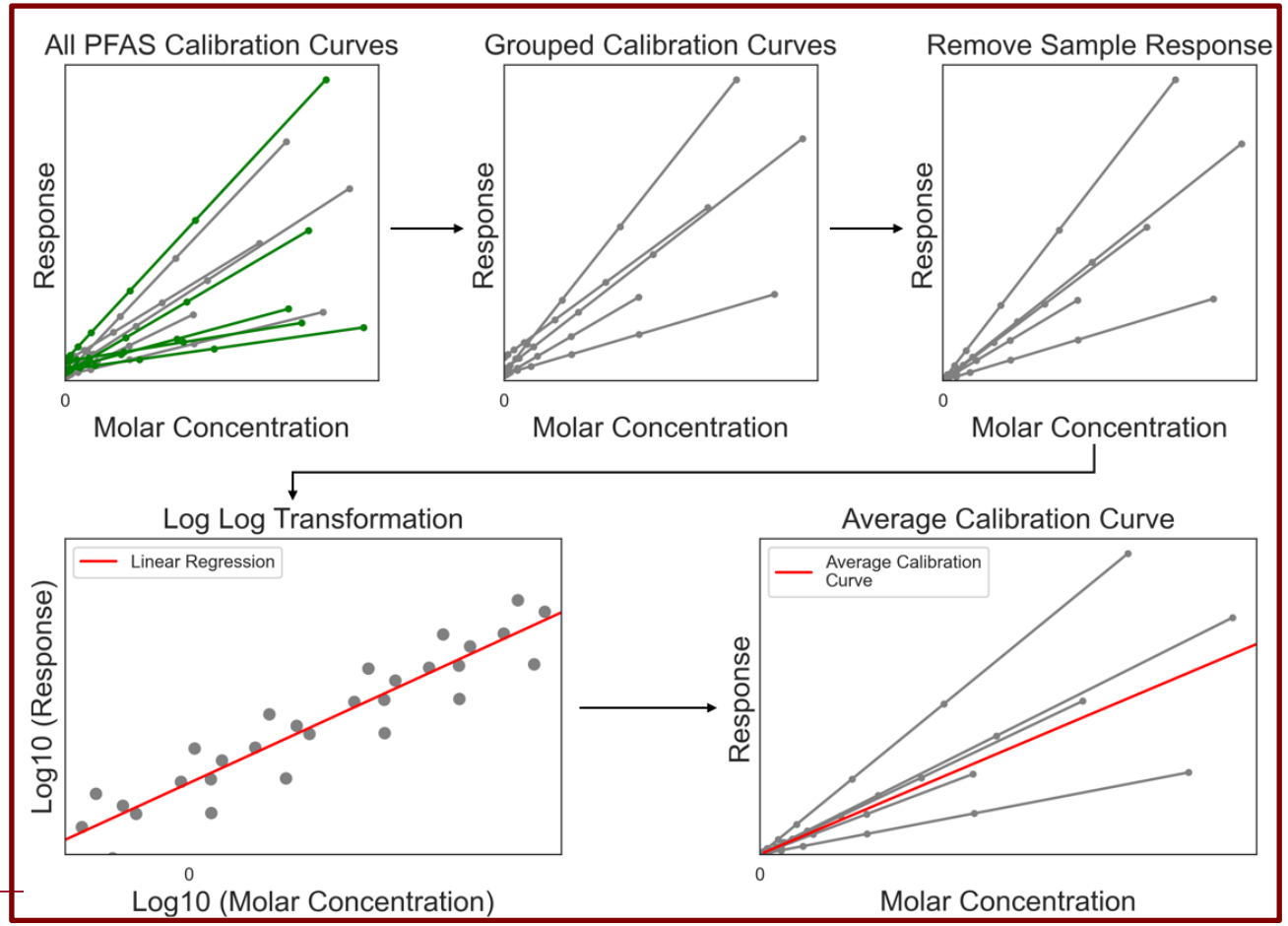


Reilingen Site – Semiquantification

- PF∆*Screen*: **124 PFAS** detected
  only **28 PFAS** covered by analytical standards → quantification
  96 PFAS → semiquantification

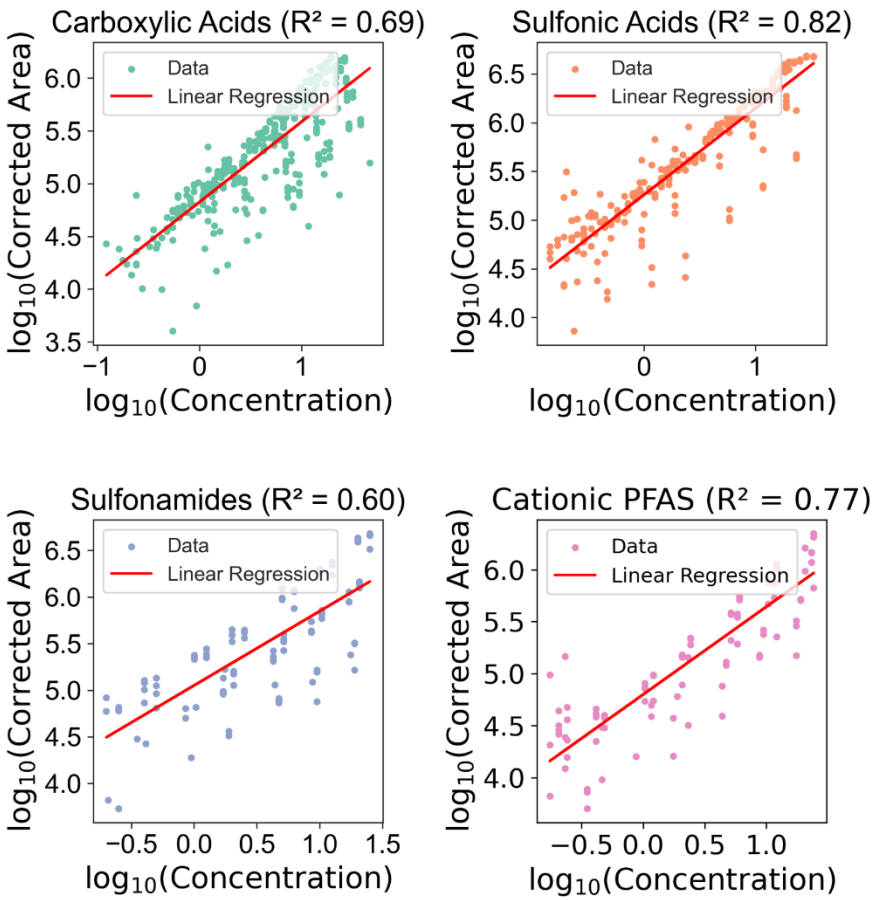
- Novel semiquantification approach

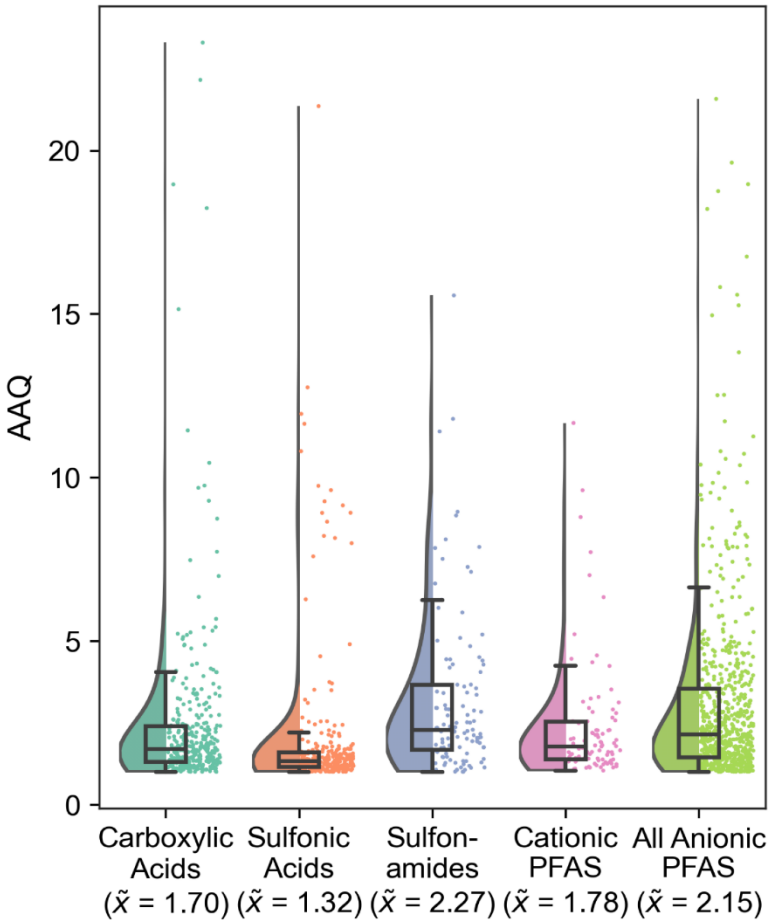
  - Matrix-matched calibration
  - Average calibration curves for specific functional groups
    - ➢ Carboxylic acids (20)
    - ➢ Sulfonic acids (12)
    - ➢ Sulfonamides (6)
    - ➢ Cationic/zwitterionic PFAS (5)



Cao et al. JASMS 34 (2023) 939-47

Reilingen Site – Semiquantification



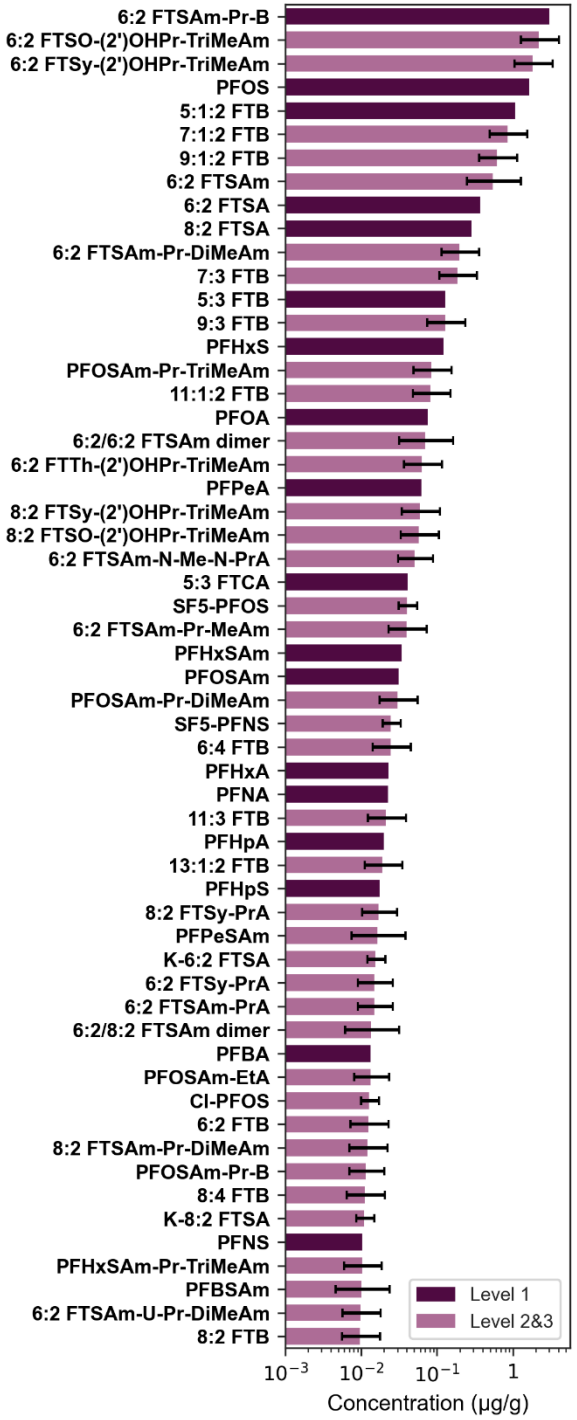


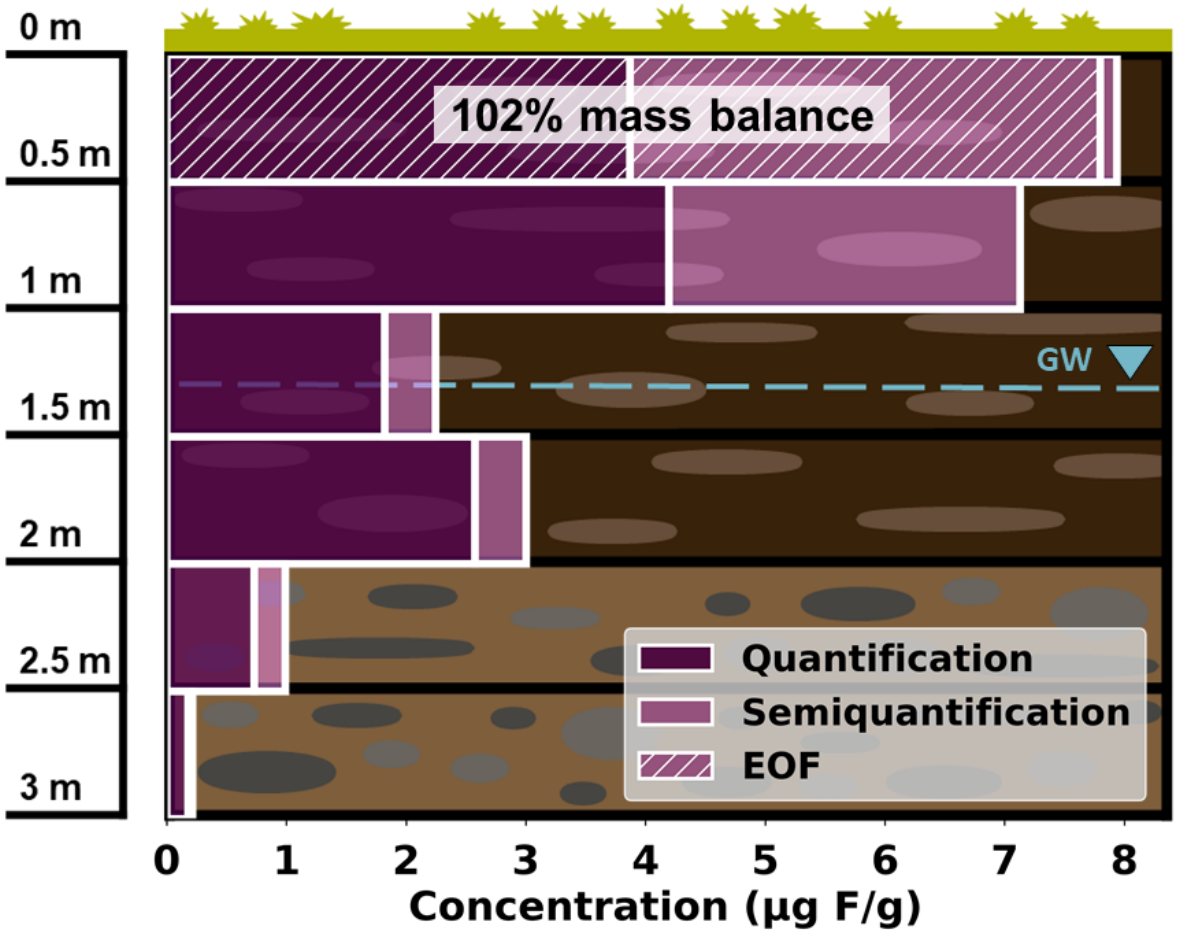
- 39 PFAS standards at 7 calibration levels
- 4 Matrix dilutions
- $\widetilde{AAQ}$: 1.32× - 2.27×
- Differentiation into ionization classes improves accuracy

Absolute accuracy quotient (AAQ) $= \begin{cases} \frac{C_{semiquant}}{C_{quant}}, \text{ if } C_{semiquant} > C_{quant} \\ \frac{C_{quant}}{C_{semiquant}}, \text{ if } C_{quant} > C_{semiquant} \end{cases}$

Capitain, Schüssler et al. ES & T (revision submitted 02/2025)

Reilingen Site – Semiquantification





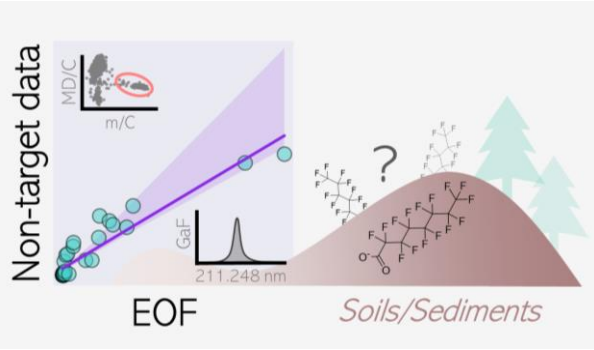
- 5 NT of 10 most abundant AFFF
- Precursors in topsoil (nontargets)
- qNTS ~ EOF
- PFAAs dominate in deeper soil

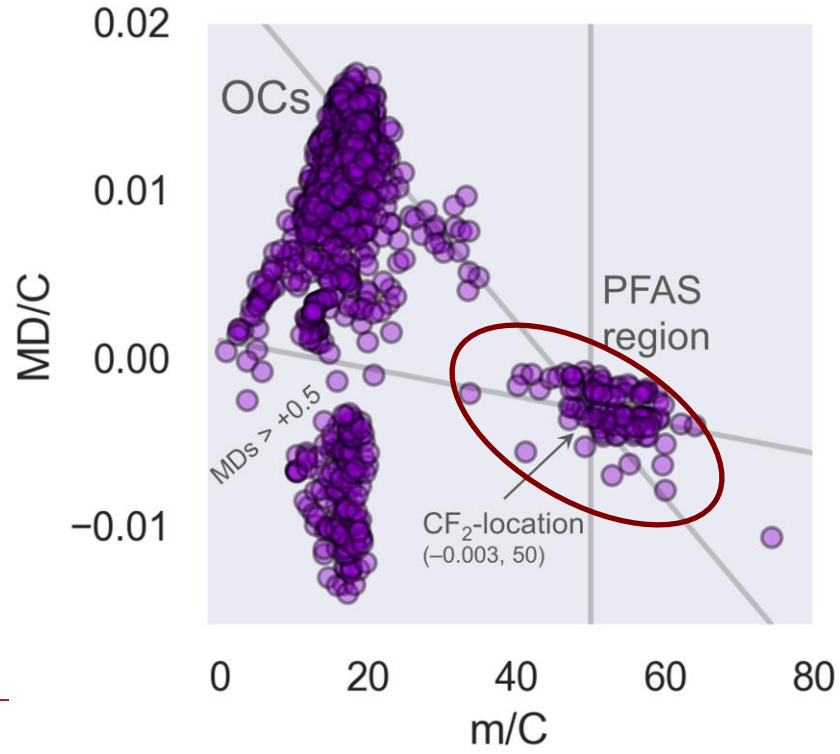
- AFFF concentration **doubled after semiquantification (7.86 → 15.19 µg/g**

EOF: C. Vogel, P. Leube, BAM, Berlin

Comprehensive PFAS analysis – EOF ~ NTS

- Correlation between **EOF and NTS features**
- **34 samples** from soils, sediments, ashes (D, F, LT)
- Prioritized NTS features (LC-HRMS)
- EOF (GaF molecular absorption, HR-CS-GFMAS)

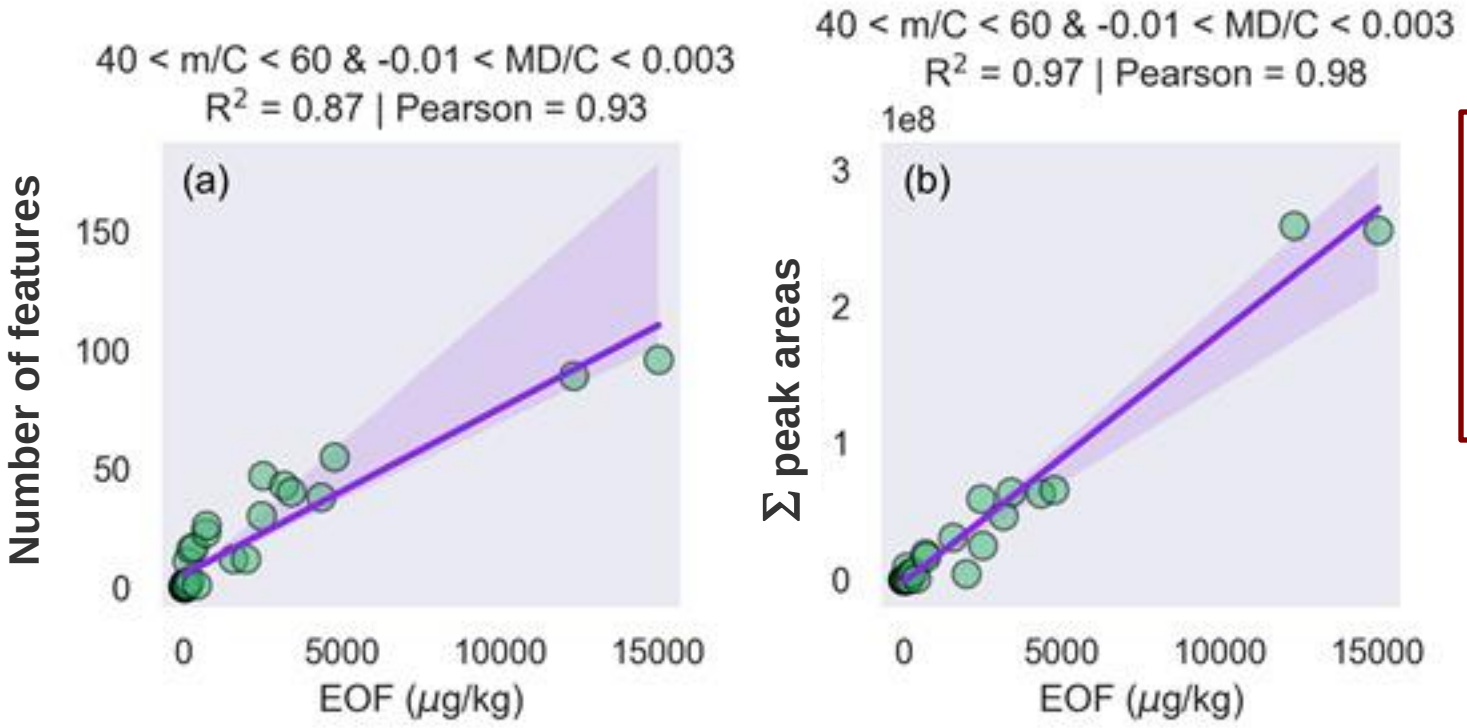




- EOF: < LOQ – 15030 µg/kg dry weight
- 202 – 5390 NTS features, in total 40431
- PFAS at m/C 40 – 60 → > 98% data reduction

Comprehensive PFAS analysis – EOF ~ NTS

- Strong correlations between EOF and prioritized features
  - number
  - sum of peak areas



- Highly fluorinated compounds contribute to EOF
- Semi-quantification of PFAS in NTS possible

Zweigle, Simon, Meermann, Zwiener (2024) Environ. Sci. Technol. Lett., DOI:10.1021/acs.estlett.4c00442

Conclusions

- Improved characterization of **PFAS contamination** necessary
- **Nontarget screening** using **PFΔScreen** (**MS1, MS2)**
- **Semi-quantification**
- **qNTS** provides crucial information for further remediation measures
- Well-coordinated and standardized methods needed for spezific PFAS and sum parameters

- **Project funding**
  EOFplus (L75 17012) BaWü Program
  FluorTech (BWPFC 19010) EA BaWü
- PFClean (BMBF 02WGW1665C)
- PFAWAS BaWü-Stiftung