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INVESTIGATIVE SOIL AND WATER ANALYSIS AT AN OUTSTANDING LARGE-SCALE CONTAMINATED SITE: HOW NOVEL APPROACHES CAN HELP TO SOLVE THE PFAS PUZZLE

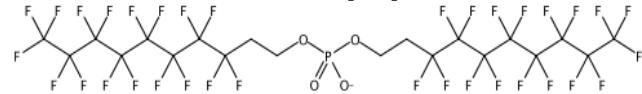
Frank Thomas Lange

Total PFAS burden? In source and sink

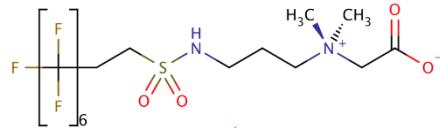
Known/unknown

PFAA precursors (polyfluorinated)

fluorochemicals in paper-fibre biosolids



fluorosurfactants in AFFFs



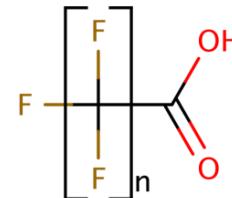
A small campfire illustration featuring three logs arranged in a triangular shape, with a bright orange flame at the base. The fire sits on a green, textured base.

Degradation processes

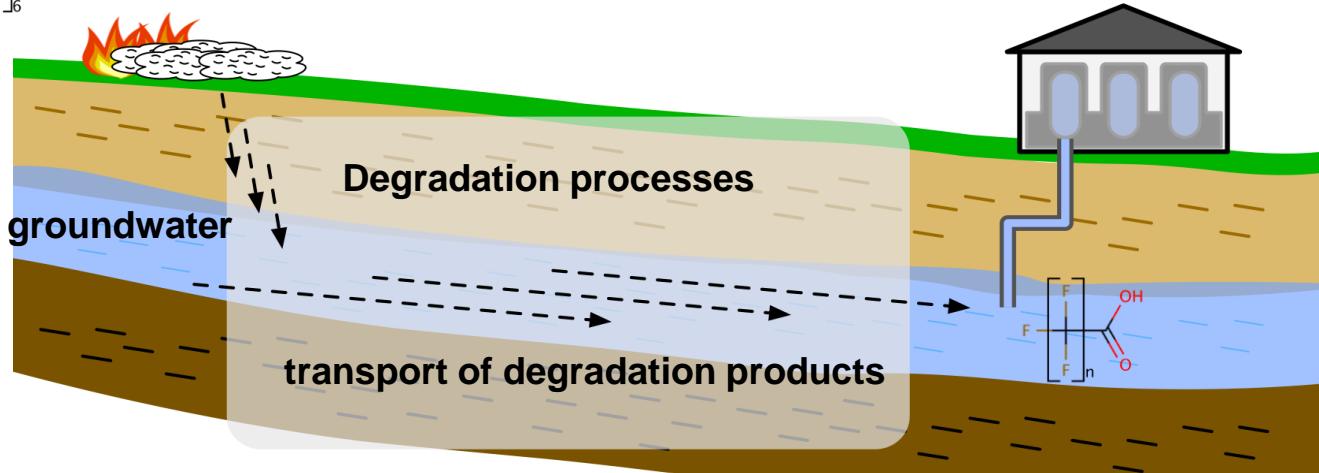
groundwater

transport of degradation products

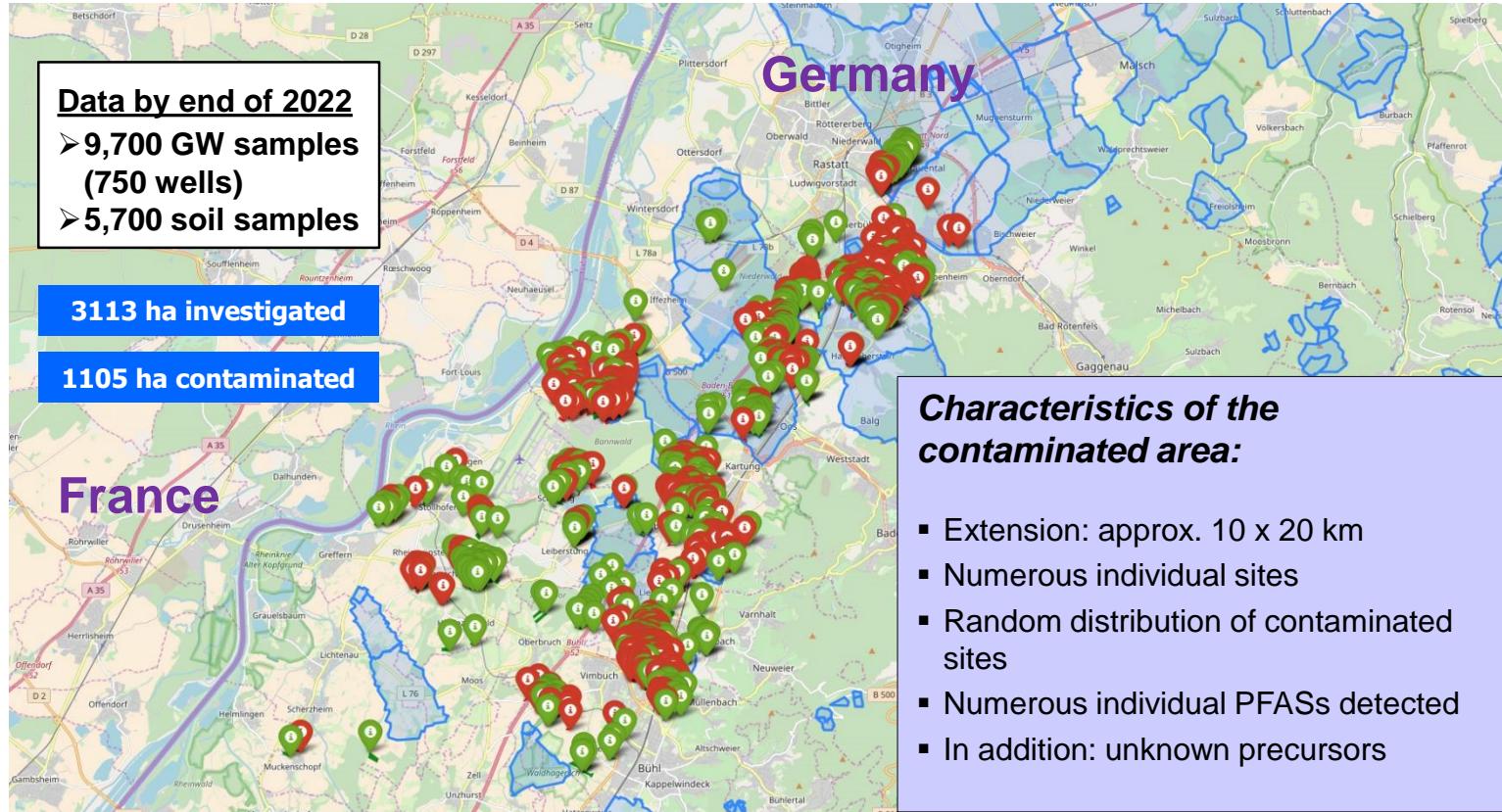
PFAAs as terminal degradation products (perfluorinated)



n = 3, PFBA
n = 4, PFPeA
n = 5, PFHxA
n = 6, PFHpA



PFASs in the Rastatt/Baden-Baden area



Source: Rainer Söhlmann, Landratsamt Rastatt

Analytical challenge: measuring “PFAS Total”

- Driver for PFAS Total is the sheer number of possible PFASs
- **4.730 CAS registry numbers for PFASs** (OECD, 2018)
- Estimated <3% measurable by quantitative target analyses due to
 - Missing knowledge on chemical structures
(confidential information of companies)
 - Missing reference compounds (native and isotopically labelled)
 - Missing analytical protocols
- Strategy: (i) Extension of target list, and (ii) sum parameters

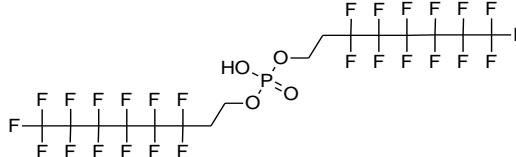
The challenge: fibre residues on agricultural land



Grease-proofing
agents for food-
contact materials

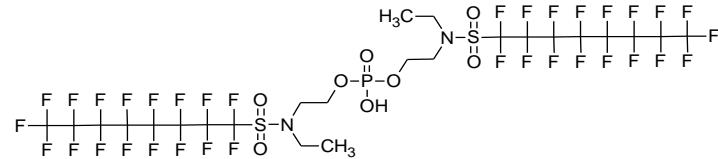


Polyfluorinated phosphate esters
(PAP: mono-, di-, and triPAP)



Final degradation products:
Perfluoroalkyl carboxylic acids (PFCAs)

bis[2-(*N*-ethyl perfluorooctane-1-sulfonamido)ethyl] phosphoric acid ester,
(diSAMPAP): until 2002



Final degradation product:
Perfluorooctane sulfonic acid (PFOS)

Degradation of fluorotelomer alcohol-based PFASs

Precursor: 6:2 diPAP

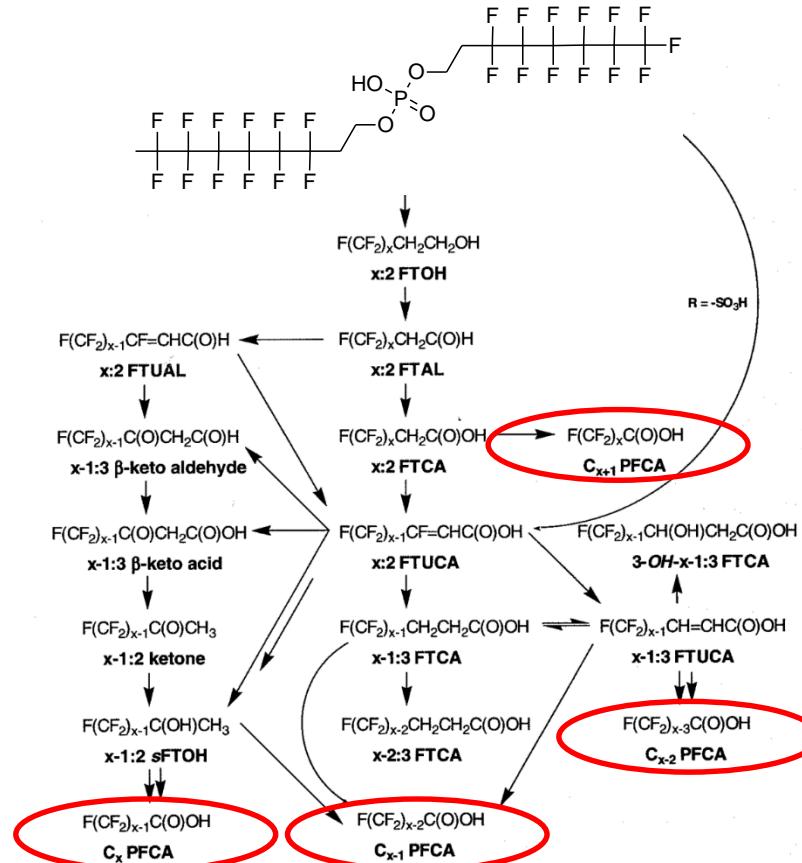
Persistent
terminal products

C_{x+1} PFCA

C_x PFCA

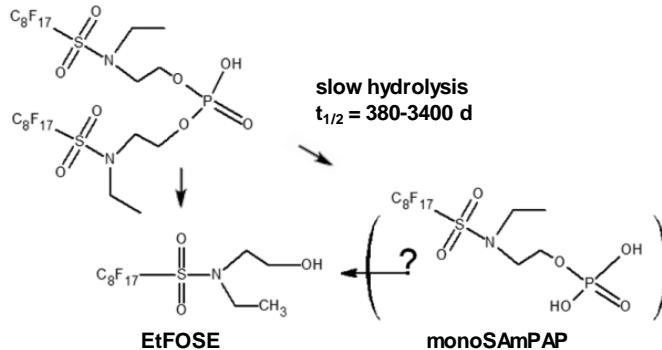
C_{x-1} PFCA

C_{x-2} PFCA

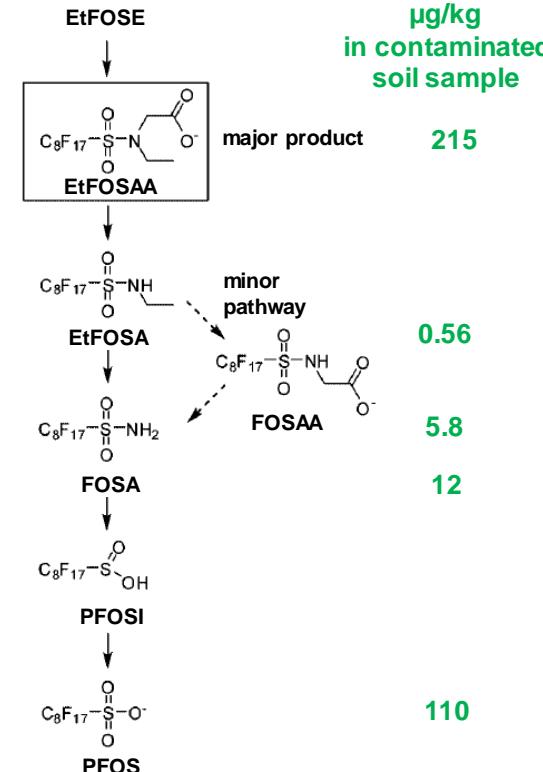


Aerobic degradation of EtFOSE-based PFASs

Precursor: diSAMPAP



compound	1. order rate constant (in d^{-1})	half-life (in d)
EtFOSE	0.99 ± 0.08	0.71 ± 0.05
EtFOSAA	0.093 ± 0.012	7.5 ± 1.0
FOSAA	0.41 ± 0.15	1.89 ± 0.79
FOSA	0.075 ± 0.003	9.2 ± 0.3
EtFOSA	0.92^a	0.75^a
PFOSI	0.95 ± 0.07	0.73 ± 0.054



Benskin, J.P.: Environ. Sci. Technol. 47(3):1381-1389 (2013)

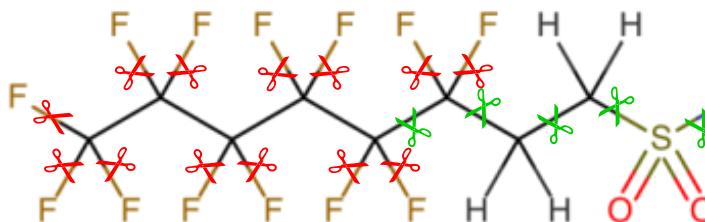
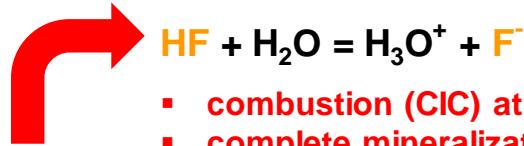
Rhoads, K.R. et al.: Environ. Sci. Technol. 42(8):2873-2878 (2008)

stable

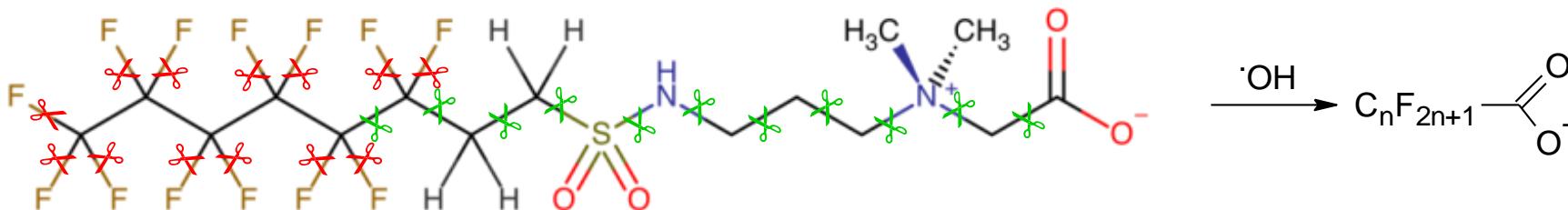
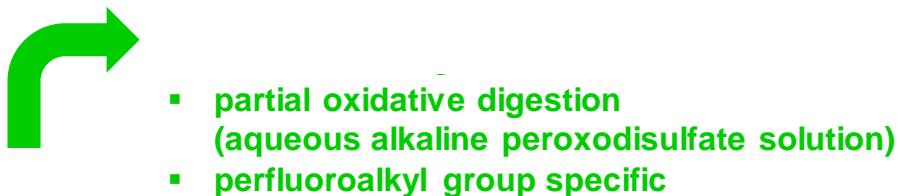
terminal product

Surrogate parameters for organofluorine/PFASs

extractable organically bound fluorine (EOF)



Total oxidizable precursor (TOP) assay



^{19}F -NMR

- Non-destructive
- Perfluoroalkyl group-specific

EOF(soil): principle of sample preparation



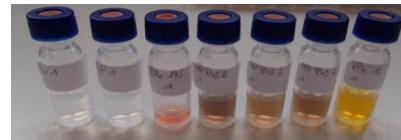
LS extraction
ultrasonic extraction: MeOH at neutral pH

Extraction closely related
to DIN 38414-14:2011-08
(PFAS analysis from soil)

Adsorption
Weak anion exchanger

Clean-up
for F⁻ removal
0,01% NH₄OH in MeOH

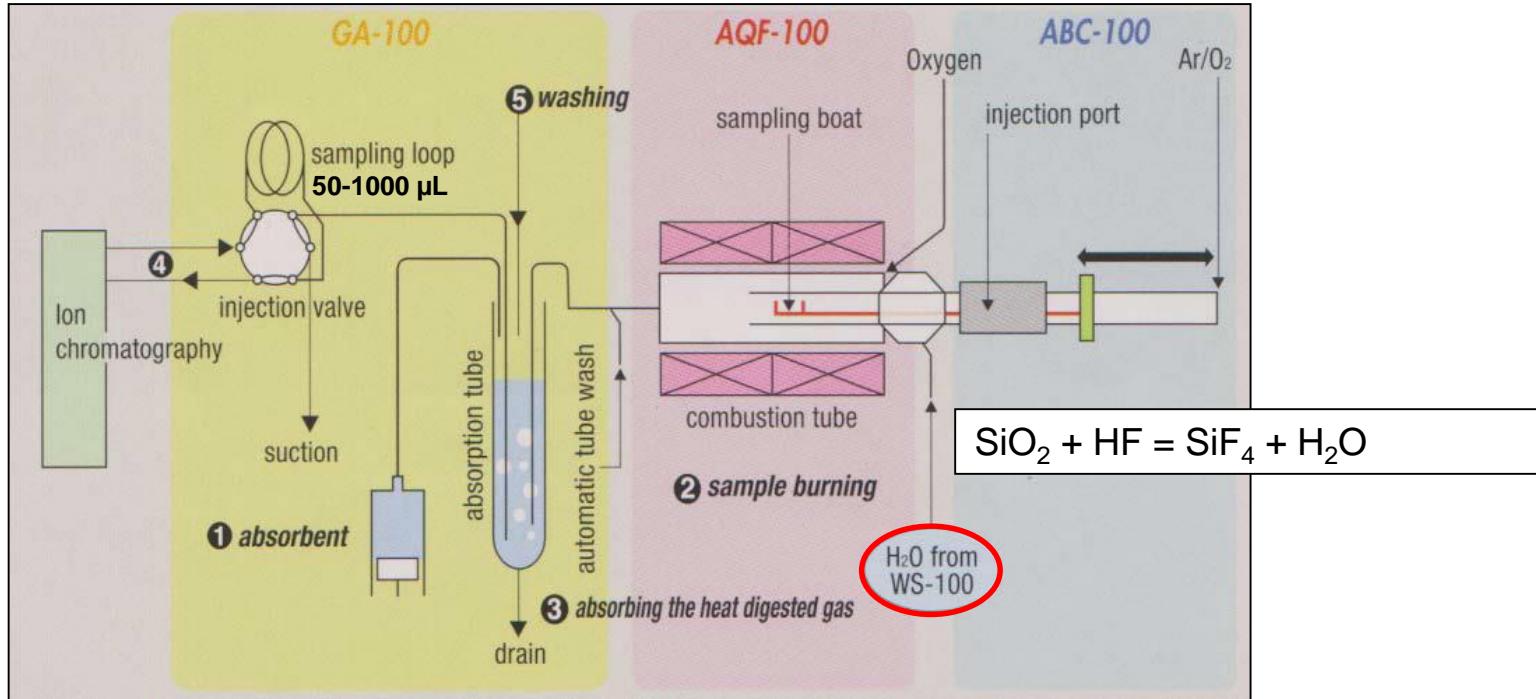
Elution
e.g. with MeOH,
0,1% NH₄OH in MeOH



Combustion-Ion Chromatography (CIC)

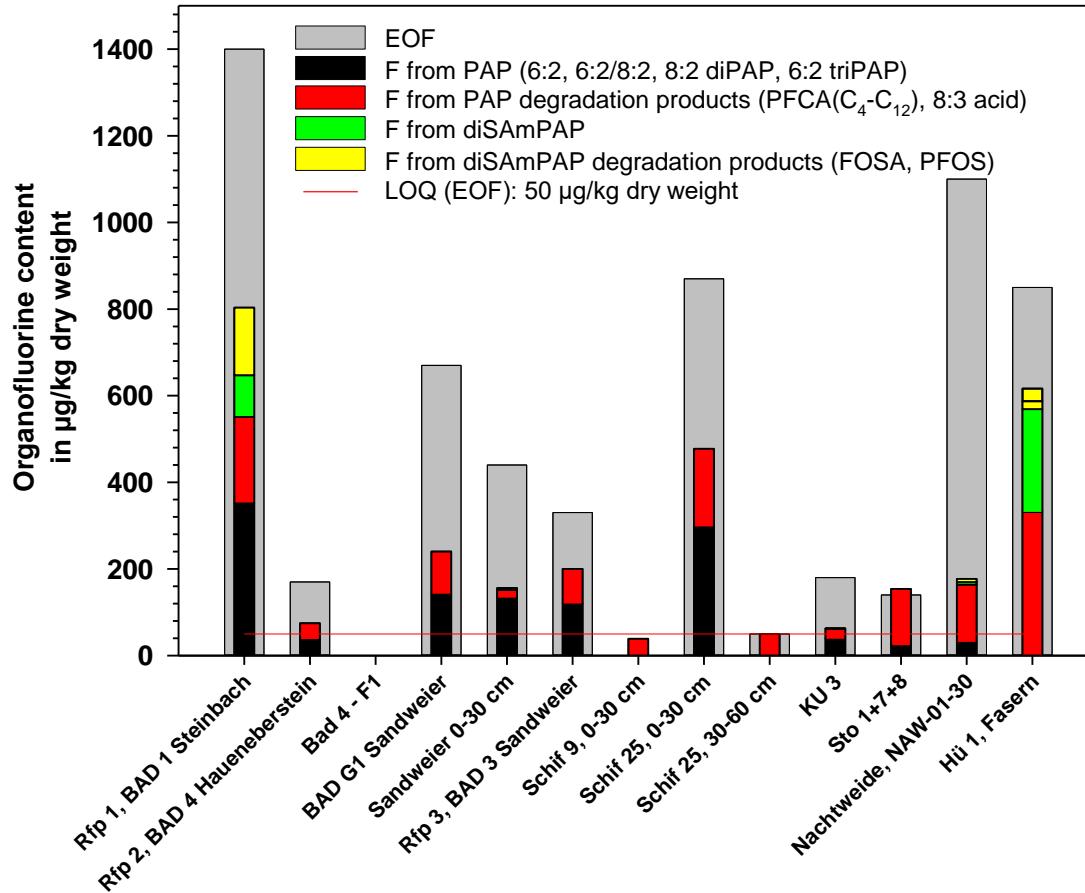
Sacher et al. (2019)
<https://pudi.lubw.de/detailseite/-/publication/64684>

Combustion ion chromatography (CIC)



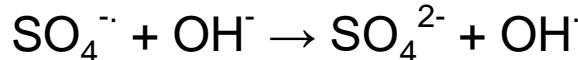
- (1) Combustion of solids or liquids with addition of water (hydrolysis)
- (2) Absorption of combustion gases (HF, CO₂ etc.) in neutral or alkaline adsorbent
- (3) (Large volume) injection of the absorption solution into IC
- (4) IC analysis of fluoride

Contaminated soils - organofluorine balance



Total Oxidizable Precursor (TOP) assay

OH[·] radical mediated oxidative digestion

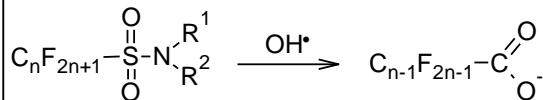


Original protocol for weakly contaminated water samples

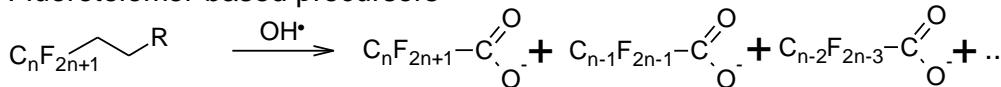
Houtz & Sedlak 2012, ES&T 46, 9342-9349

Numerous existing in-house protocols!

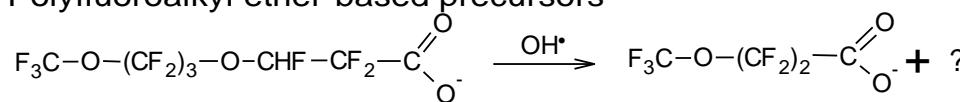
Perfluoroalkyl sulfonamide-based precursors



Fluorotelomer-based precursors



Polyfluoroalkyl ether-based precursors



Endpoints (most frequently):

C₄-C₁₄-PFCAs

Seldom: C₂- und C₃-PFCAs

Soil analysis: Janda et al., 2019

Environ. Sci.: Processes Impacts, 21, 1926

Dust analysis: Wang et al. 2022

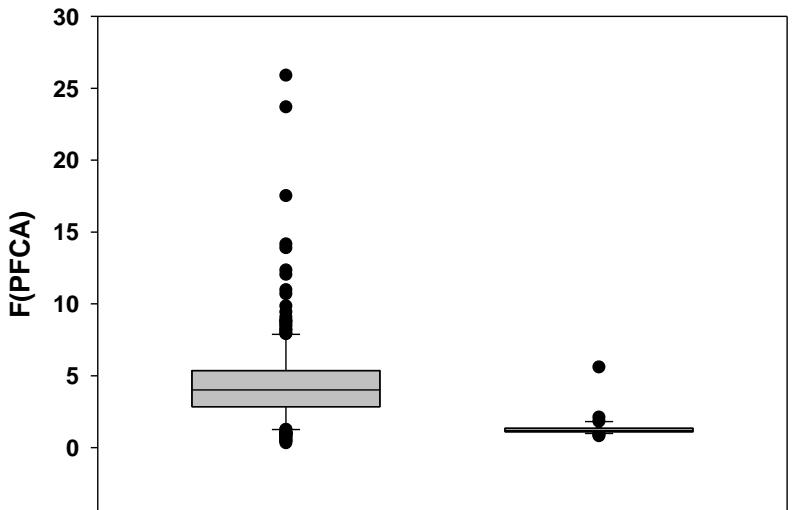
Environ. Sci. Technol. 56, 6036–6045



Photo: TZW/Marc Guckert

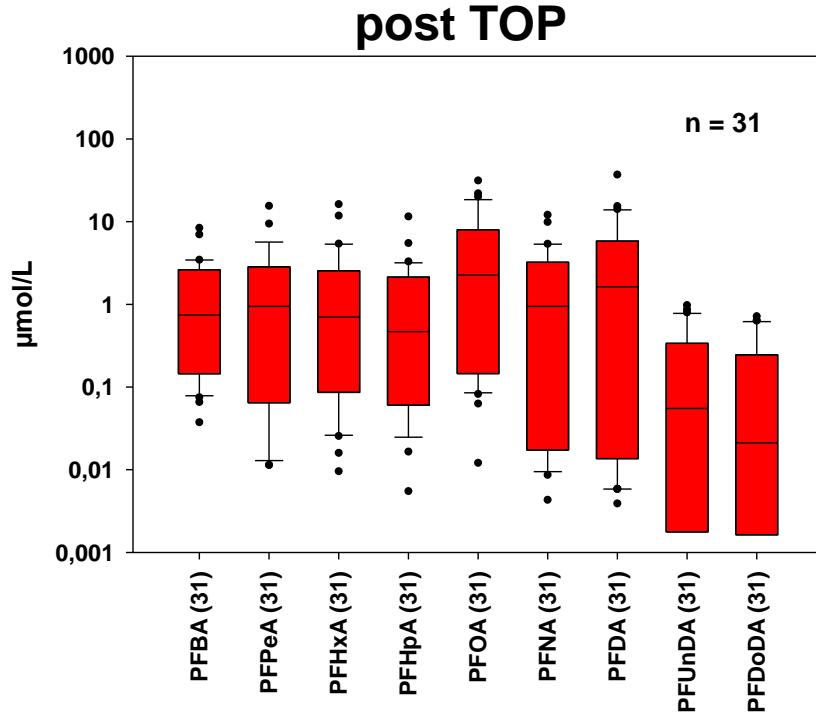
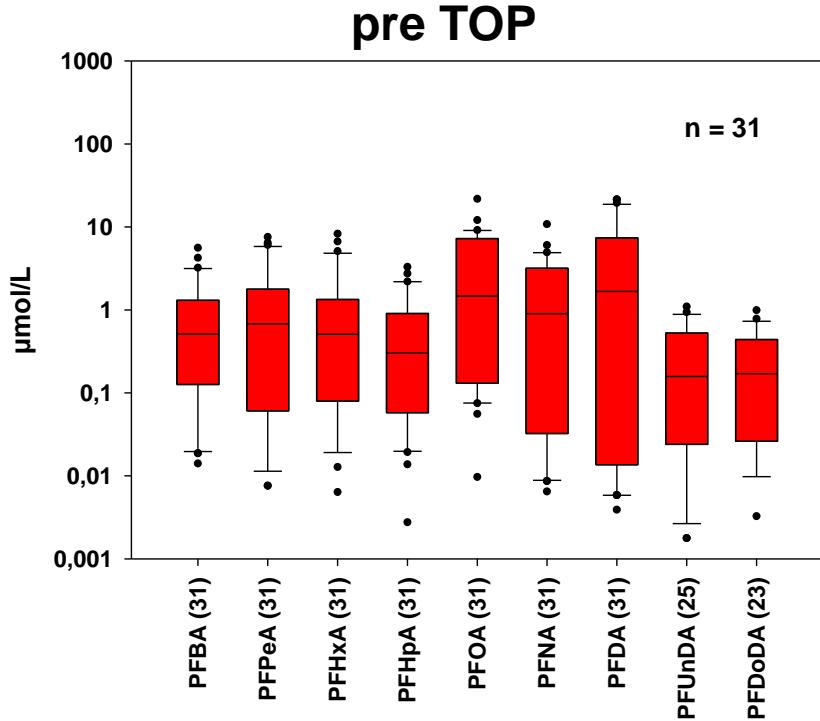
Comparison of molar PFCA increase during TOP assay oxidation

$$F(\text{PFCA}) = \sum \text{PFCA}_{\text{post}} / \sum \text{PFCA}_{\text{pre}}$$



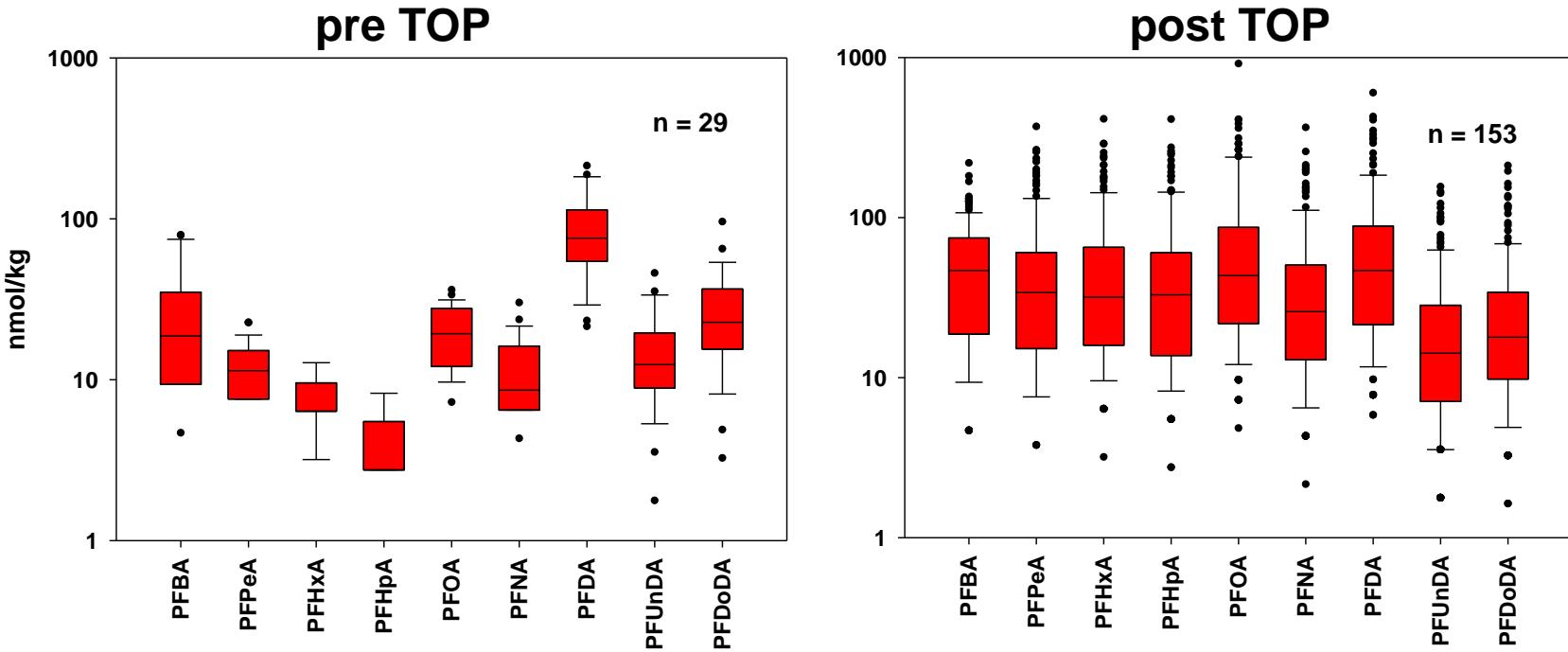
Lange et al.,
Mitt. Umweltchem. Ökotox.
4/2022, 134-138

Distribution of PFCA homologues in aqueous leachates (L/S = 2)



Low abundance of precursors, mainly leaching of PFCA as final (microbial) degradation products

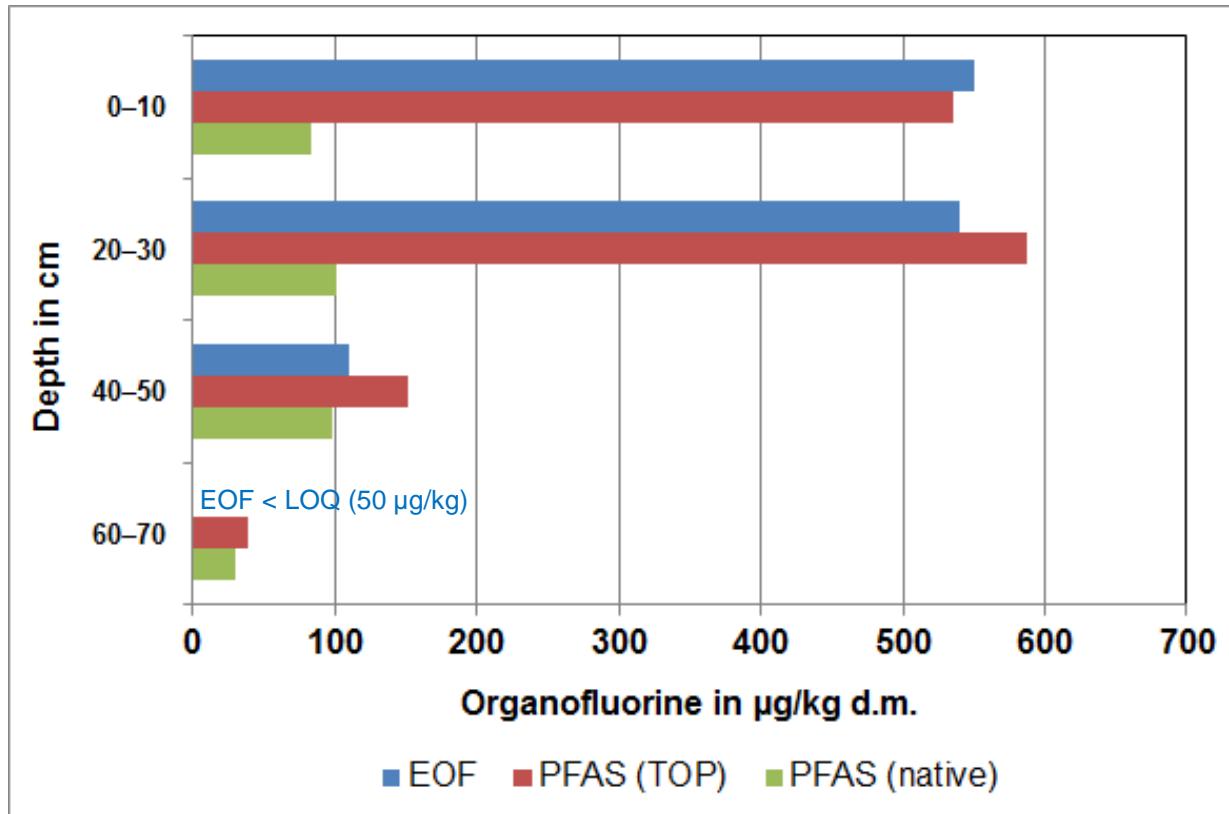
Distribution of PFCA homologues in methanolic soil extracts



Pre TOP: dominance of fluorotelomer precursors of even chain lengths!

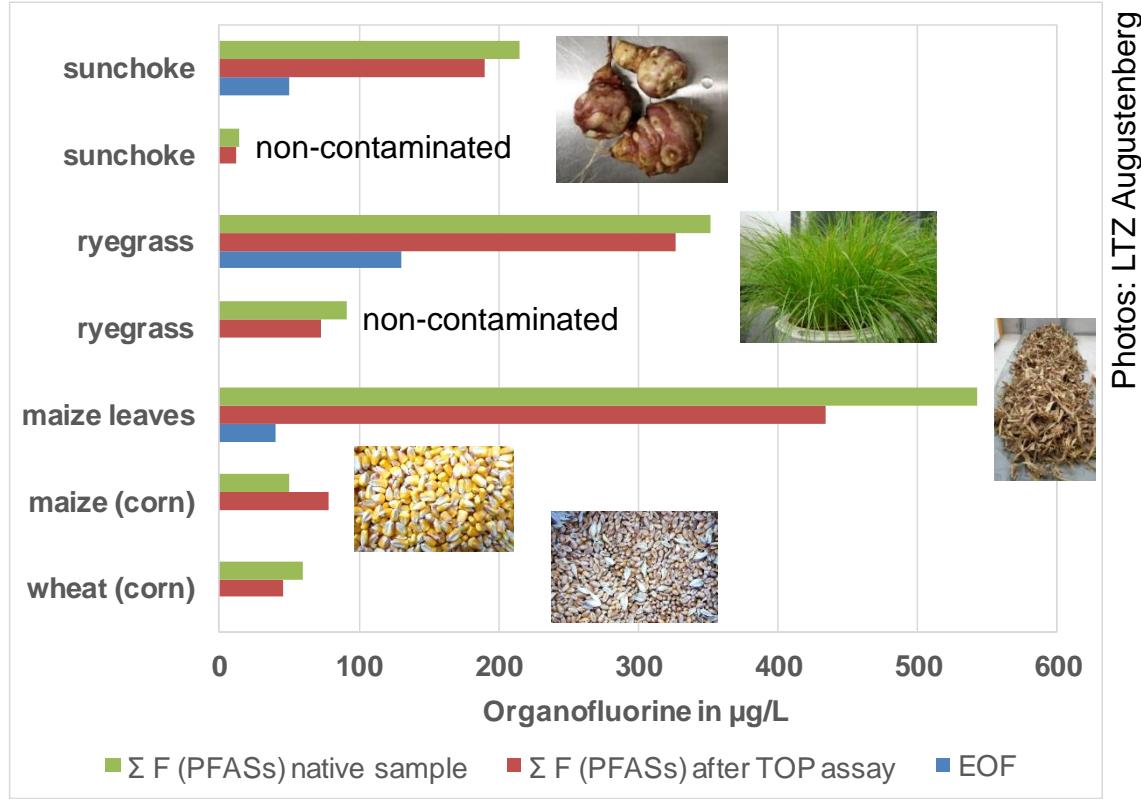
Comparison EOF/PFASs pre/post TOP in soil

Depth dependent organofluorine mass balance



Precursor located
in the upper layers,
i.e. in the plough
horizon!

EOF/PFASs pre/post TOP in agricultural plants



Photos: LTZ Augstenberg

106

14

66

91

141

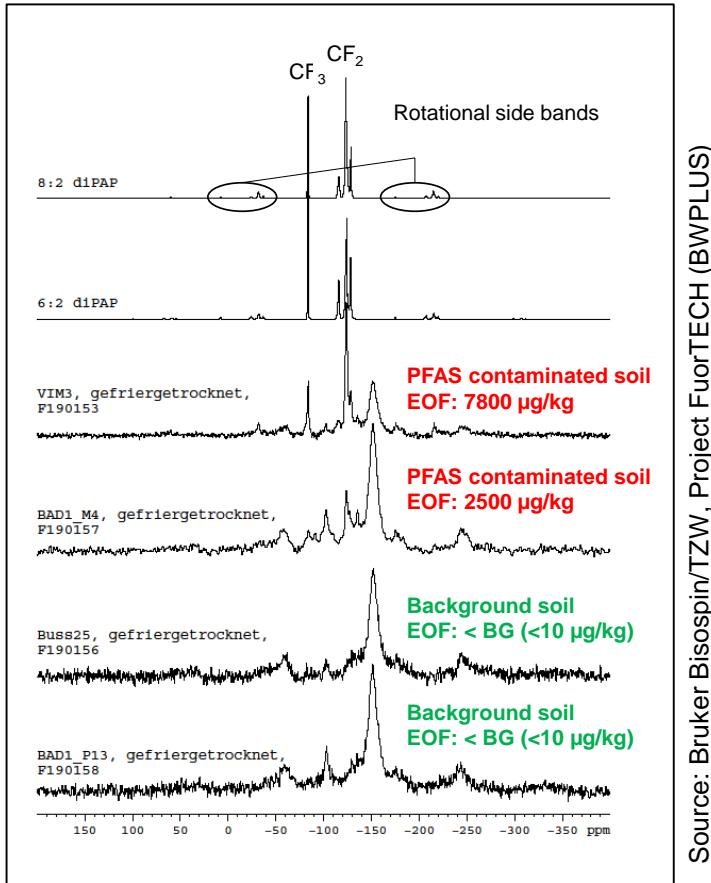
50

19

Organofluorine
(native sample)
from TFAA
in $\mu\text{g/kg d.m.}$

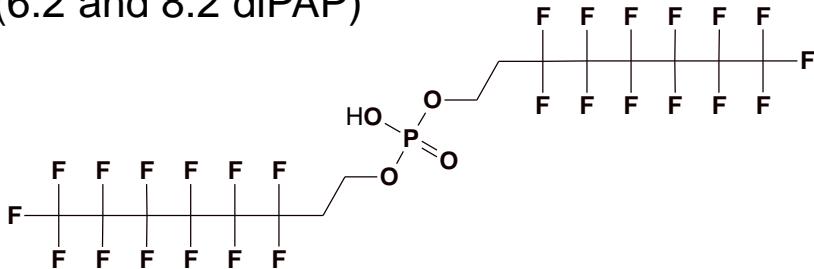
- **EOF discriminates ultra-short chain PFASs**
- **No significant transfer of precursors to plants!**

Perfluoroalkyl group-specific analysis: ^{19}F NMR

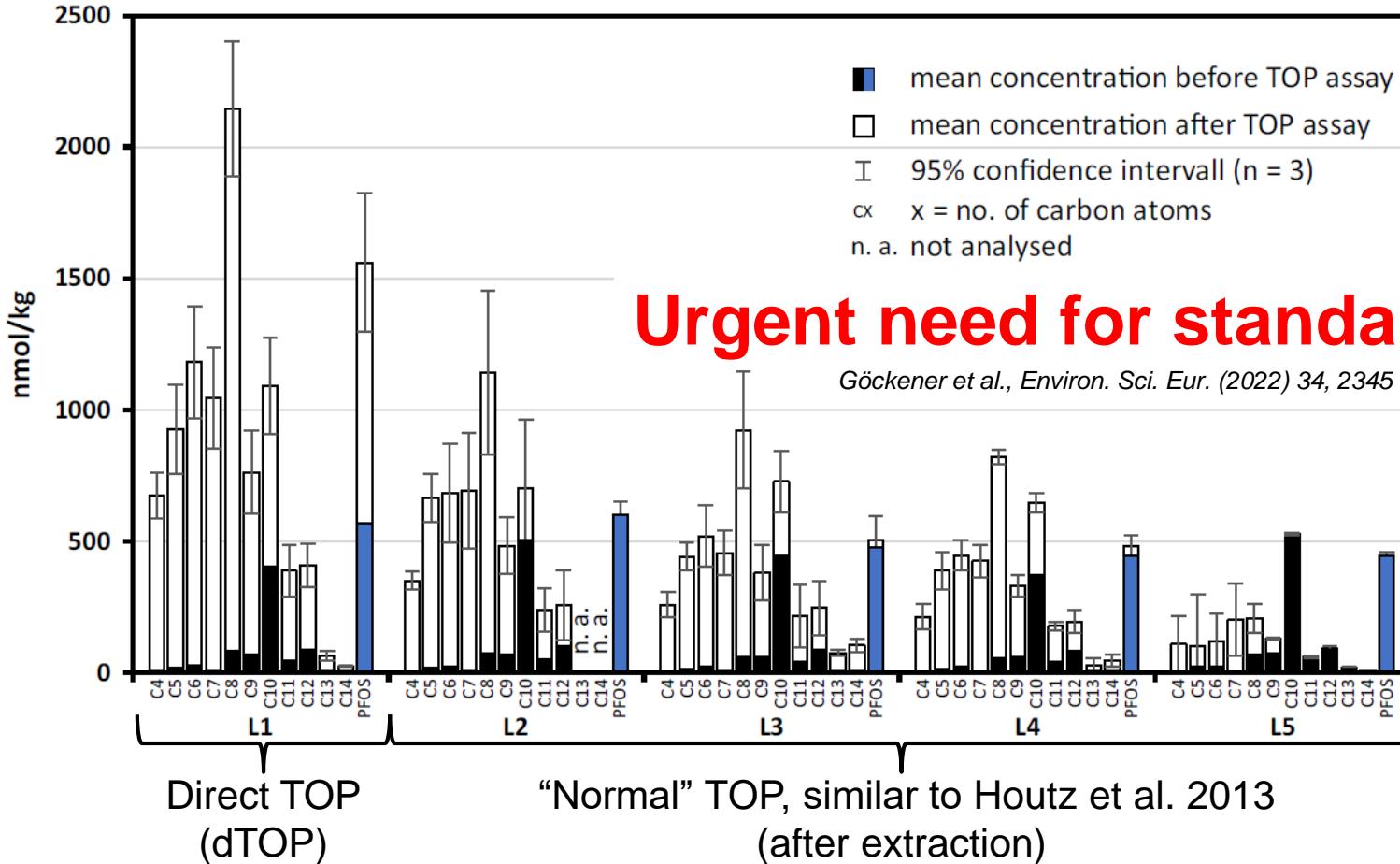


Source: Bruker Biospin/TZW, Project FuorTECH (BWPLUS)

- analysis of soil samples
(Rastatt/Baden-Baden area, SW Germany)
- ^{19}F solid-state NMR spectroscopy
(Magic Angle Spinning (MAS) technique)
- qualitative confirmation of the chemical shift of CF_2 and CF_3 groups by reference compounds
(6:2 and 8:2 diPAP)
- large fraction (>80%) of non-extractable residues



Direct TOP assay (dTOP) of soil



Acknowledgements

- Ministry for Environment, Climate, and Energy, Baden-Württemberg, program BWPLUS: projects L7515008, L7517011, BWPFC19007 (2015-2021)
 - LUBW: - PAP/SamPAP analytical projects (2016-2018)
- TOP assay study (2021-2022)
 - Regierungspräsidium Karlsruhe: investigation of soil profiles (2018)
 - Landratsamt Rastatt: Reiner Söhlmann

LANDKREIS
RASTATT
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Für eine lebenswerte Zukunft
- finally...** All former and present involved colleagues at TZW
- 



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