The direct total oxidizable precursor (dTOP) assay as a tool to detect unknown PFAS in German rivers

SETAC Europe May 18, 2022

Bernd Göckener[1]

Annette Fliedner[1]

Heinz Rüdel[1]

Mark Bücking[1]

Alexander Badry[2]

Jan Koschorreck[2]

[1] Fraunhofer Institute for Molecular Biology and Applied Ecology IME

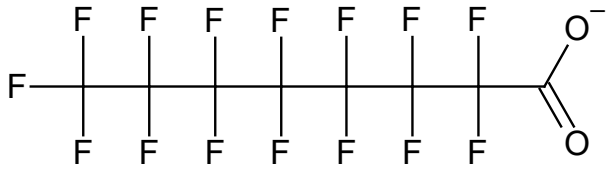
[2] German Environment Agency (Umweltbundesamt)

Fraunhofer IME

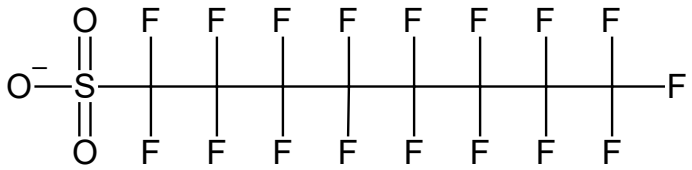
Umwelt Bundesamt

Introduction

- „Classical“ legacy PFAS: perfluorocarboxylic and -sulfonic acids



PFOA



PFOS

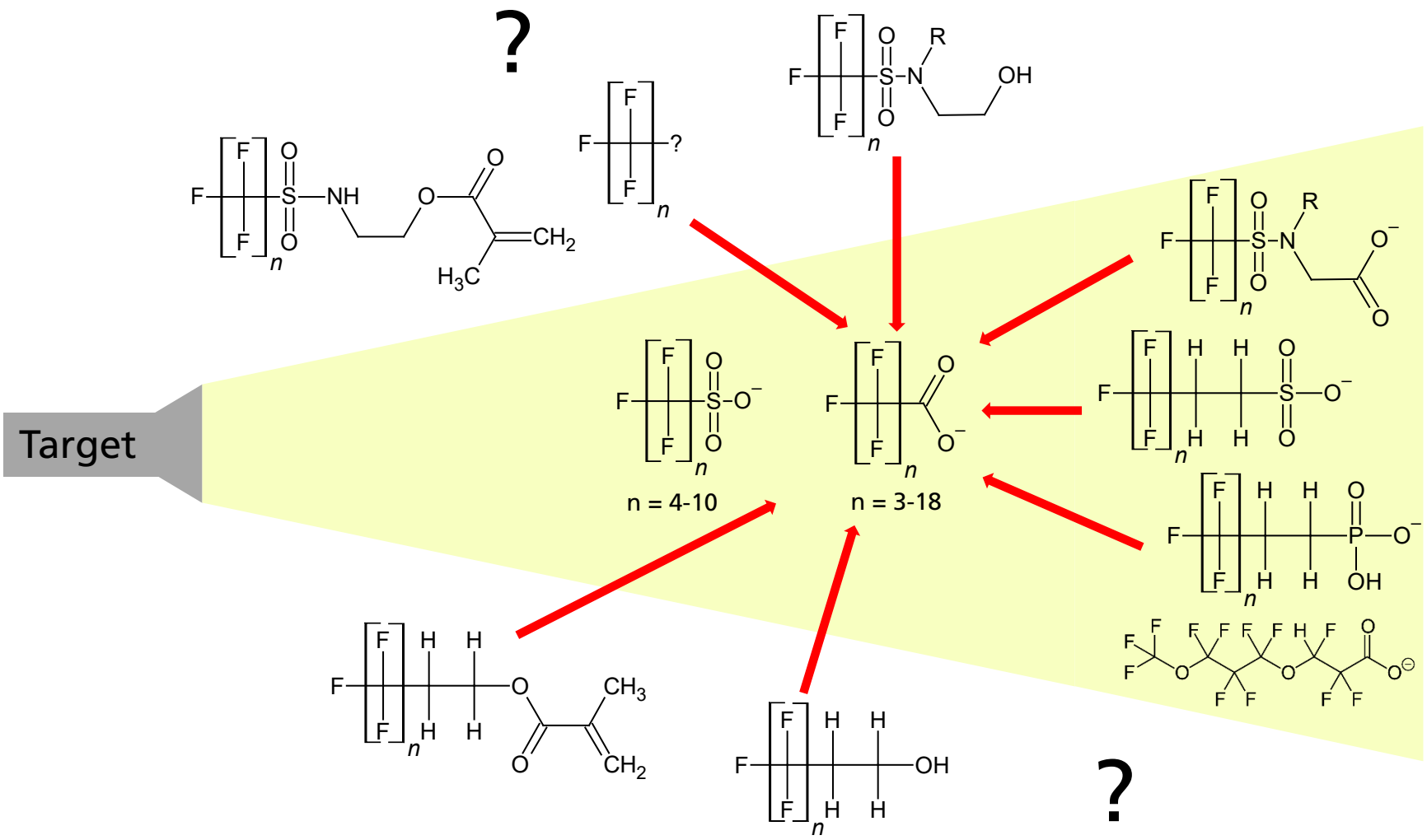
- OECD (2021): PFASs are defined as fluorinated substances that contain **at least one fully fluorinated methyl or methylene carbon atom** […]

- „PFAS“ comprise thousands of different substances, e.g.:
  - Stable replacement chemicals
  - Precursor substances that can or may degrade to the legacy PFAS by biotic and abiotic processes

Umwelt Bundesamt

Fraunhofer IME

The Challenge



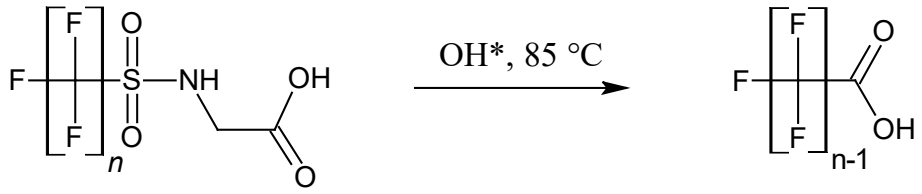
TOP-Assay

- Total Oxidizable Precursor (TOP) Assay: Houtz and Sedlak 2012/2013

$$S_2O_8^{2-} \xrightarrow{85\ °C} 2\ SO_4^{-*}$$

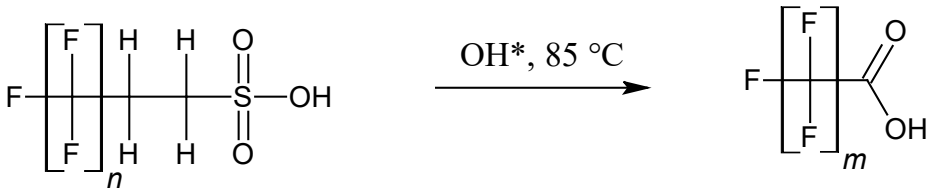
$$SO_4^{-*} + OH^- \longrightarrow SO_4^{2-} + OH^*$$

- Oxidation of PFCA and PFSA precursors to PFCA of corresponding chain lengths:



sulfonamido acetic acids (FASAA)

PFCA



fluorotelomer sulfonic acids (FtS)

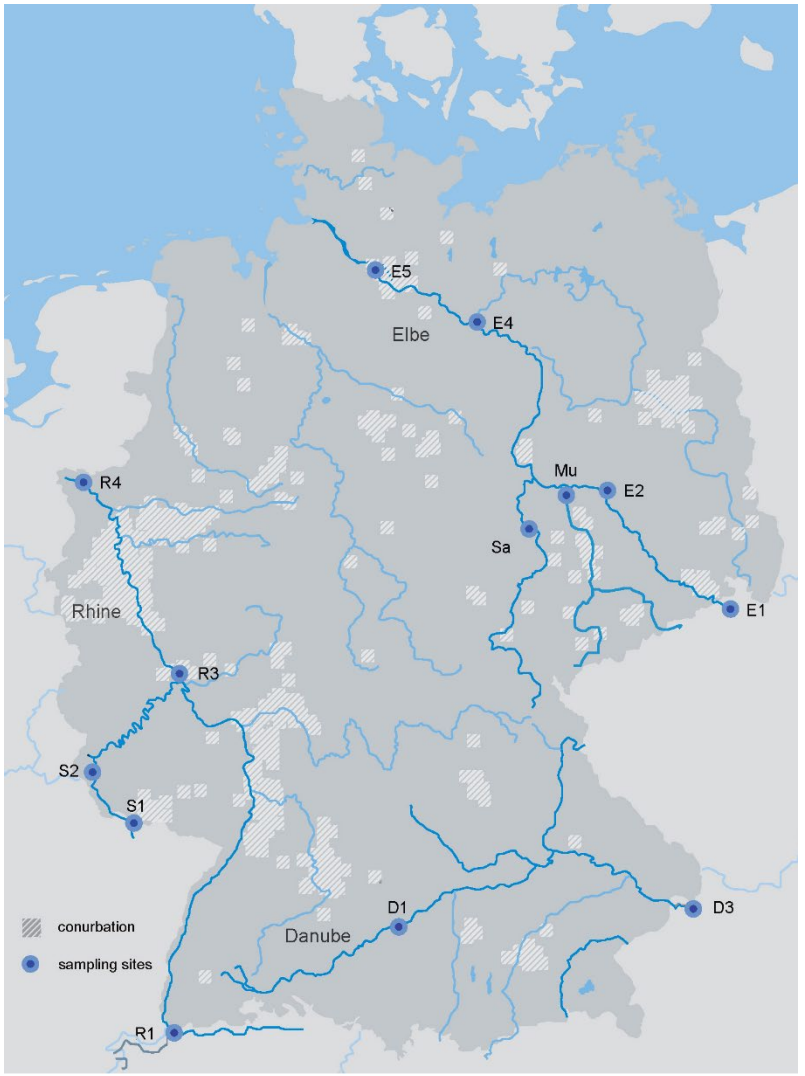
PFCAs
m= n-2; n-1; n-3

dTOP-Assay

- Limitation of the original method:
  - Solid or complex samples have to be extracted prior to oxidation
    - Potential loss of non-extracted precursors
    - Co-extraction of organic matrix compounds might impede a total oxidation
- Fraunhofer approach: direct TOP Assay (dTOP)
  - Very small amount of sample (ca. 100 – 250 mg) is completly digested with high amounts of oxidation agent
    - No extraction, no extraction losses
    - Organic matrix components are fully oxidized
    - More comprehensive overview on the total PFAS burden possible
    - LOQs: quite high (1.0 – 2.5 µg/kg)

Samples

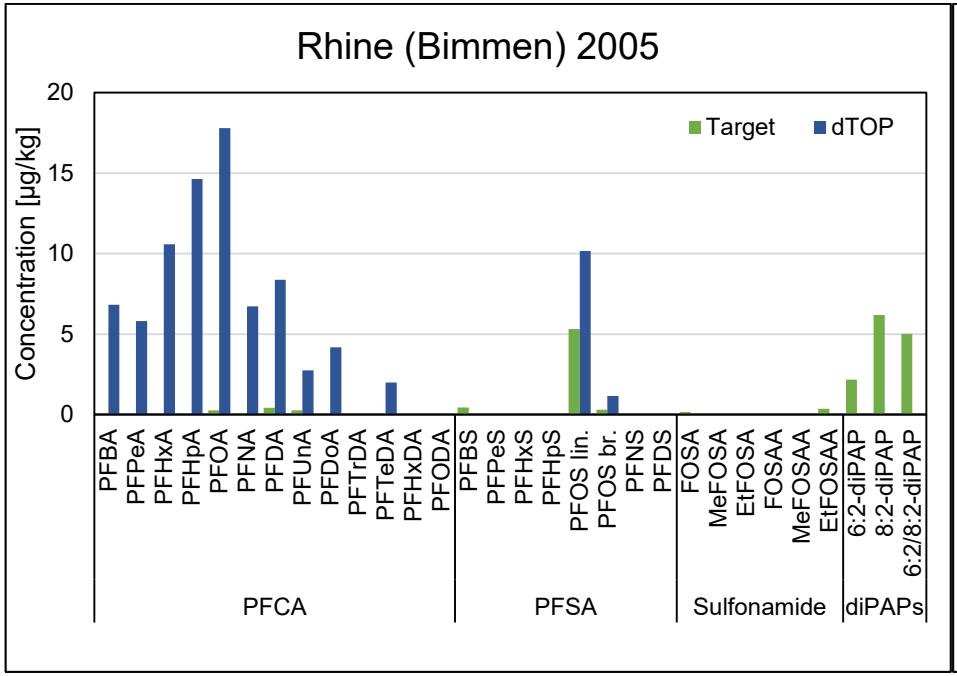
- Analysis of annual composite samples of suspended particulate matter (SPM) from 2005 – 2019 for the major German river systems
- All samples obtained from the German Environmental Specimen Bank

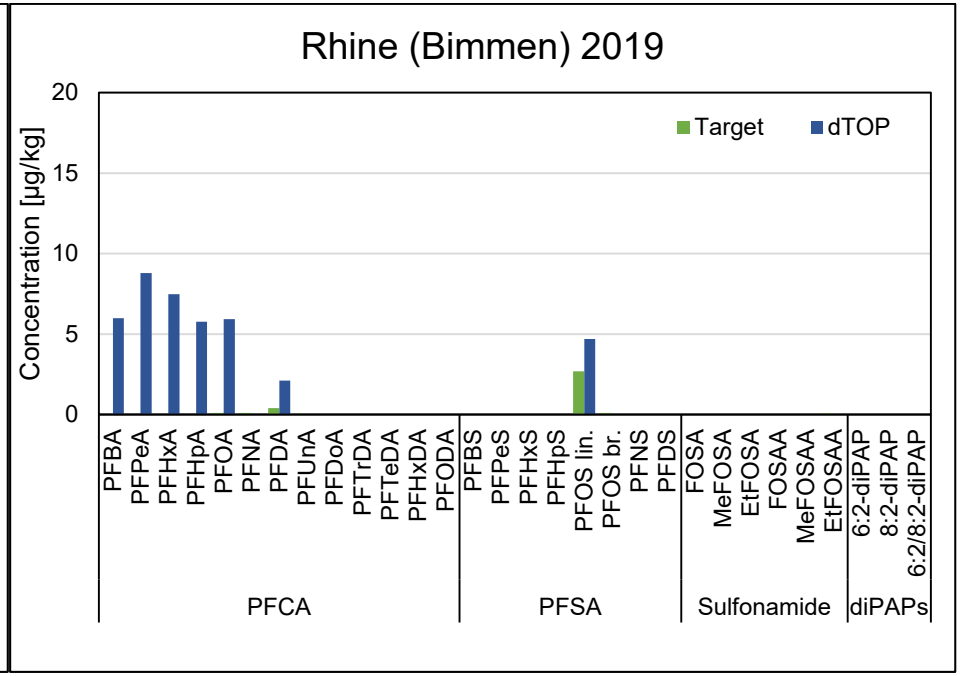


Umwelt Bundesamt

Fraunhofer IME

Results (Rhine)



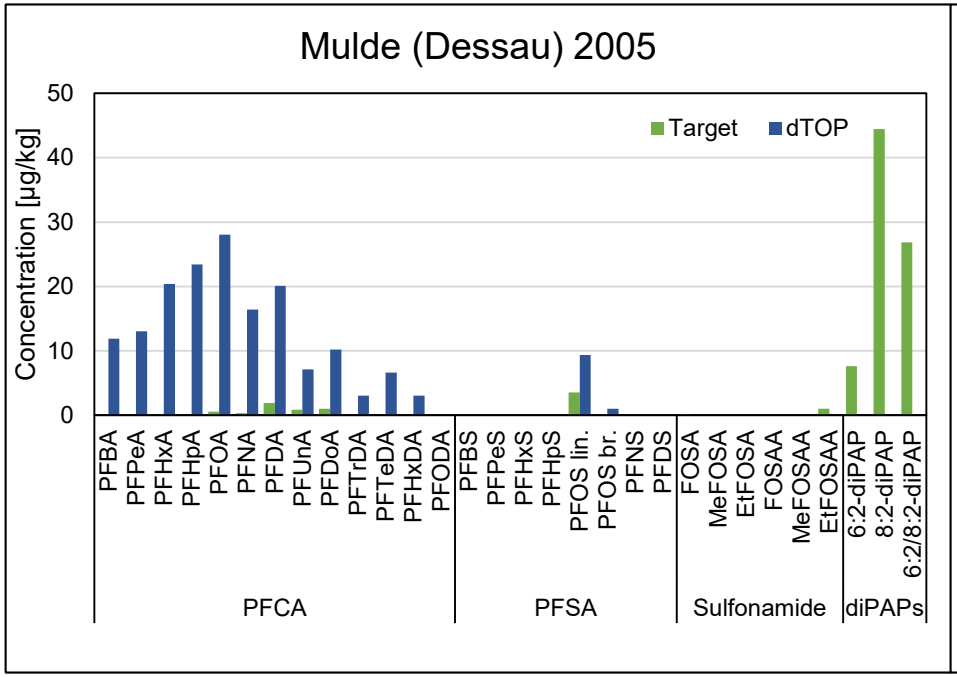


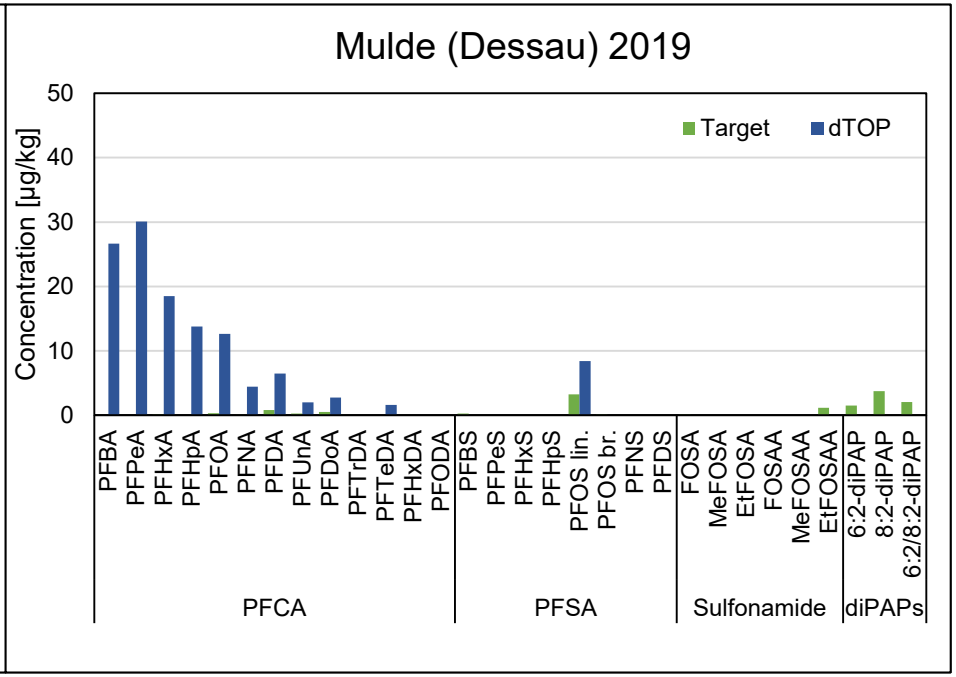
- dTOP analysis:
  - High amounts of precursors
  - 2005: broad chain length spectrum with PFOA (C8) dominating
  - 2019: smaller chain length spectrum with focus on short-chain PFCA

Umwelt Bundesamt

Fraunhofer IME

Results (Mulde)





- dTOP analysis:
  - High amounts of precursors, e.g. diPAP
  - 2005: broad PFCA spectrum (C4-C16)
  - 2019: focus on shorter-chain PFCA

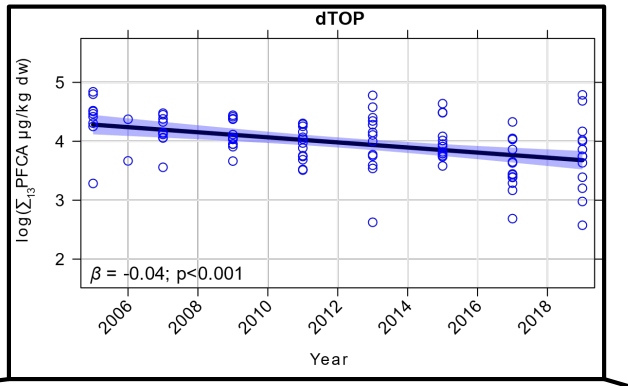
Umwelt Bundesamt

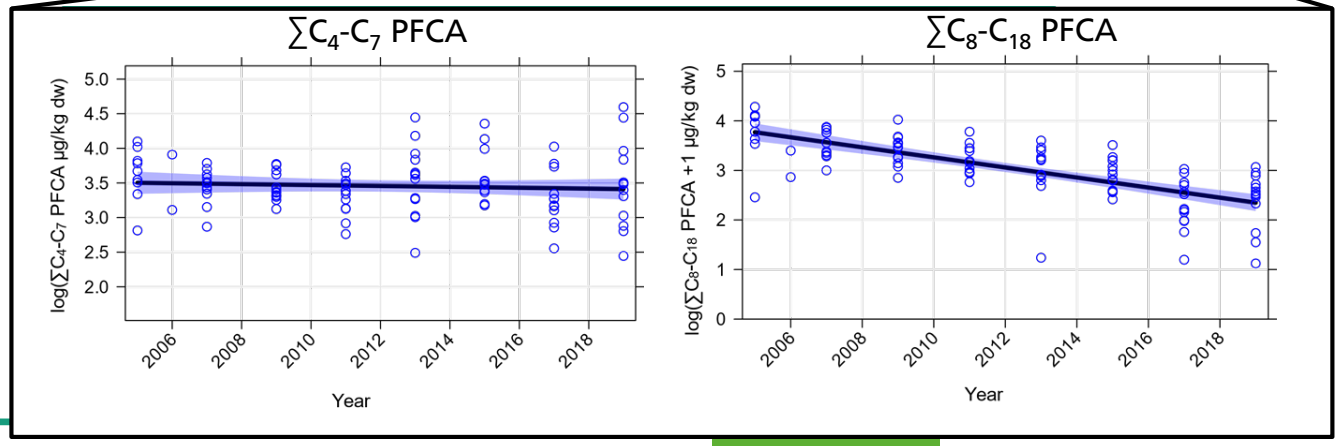
Fraunhofer IME

Temporal Trends

- Temporal trend analysis (combined for all sampling sites)

  - ➢ Declining trends mainly derived from precursors of long-chain PFCA
  - ➢ Increasing proportion of precursors of short-chain PFCA





Umwelt Bundesamt

Fraunhofer IME

Conclusions

- Ubiquitous distribution: PFAS found in SPM from every river
- Substantial differences in PFCA levels between target analysis and dTOP
  - Analysis of legacy PFAS overlooks a significant proportion of PFAS
  - Environmental PFAS burden is much higher than thought before
- Temporal trends
  - Declining trends for known PFAS; less pronounced for unknown PFAS
  - Shift to precursors of short-chain PFCA
- Next steps:
  - Analysis of samples from federal states: increased spatial resolution

The direct total oxidizable precursor (dTOP) assay as a tool to detect unknown PFAS in German rivers

Thank you very much for your attention!

Dr. Bernd Göckener

Fraunhofer IME

Auf dem Aberg 1 | 57392 Schmallenberg | Germany

Phone +49 (0) 2972 302-182

bernd.goeckener@ime.fraunhofer.de

www.ime.fraunhofer.de/en.html

Umwelt Bundesamt

Fraunhofer IME

dTOP-Assay

- Sample preparation

Oxidation (7 h, 85 °C) → Neutralization (pH 5-6) → SPE cleanup → UPLC-HRMS analysis

250 mg sample

+ 100 µL of IS solution

+ 200 mL oxidation solution

(200 mM $K_2S_2O_8$, 500 mM NaOH)

Houtz and Sedlak:

60 mM $K_2S_2O_8$, 125 mM NaOH

Umwelt Bundesamt

Fraunhofer IME

dTOP-Assay: conversion rates

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

pubs.acs.org/JAFC

Article

Transfer of Per- and Polyfluoroalkyl Substances (PFAS) from Feed into the Eggs of Laying Hens. Part 1: Analytical Results Including a Modified Total Oxidizable Precursor Assay

Bernd Göckener,* Maria Eichhorn, René Lämmer, Matthias Kotthoff, Janine Kowalczyk, Jorge Numata, Helmut Schafft, Monika Lahrssen-Wiederholt, and Mark Bücking

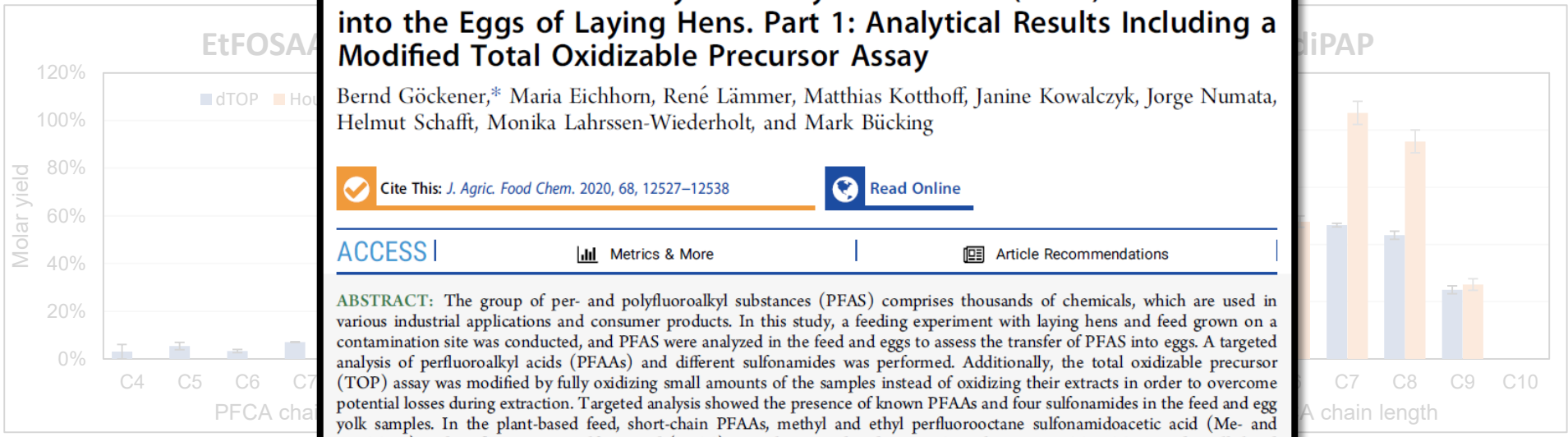
Cite This: *J. Agric. Food Chem.* 2020, 68, 12527–12538

Read Online

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: The group of per- and polyfluoroalkyl substances (PFAS) comprises thousands of chemicals, which are used in various industrial applications and consumer products. In this study, a feeding experiment with laying hens and feed grown on a contamination site was conducted, and PFAS were analyzed in the feed and eggs to assess the transfer of PFAS into eggs. A targeted analysis of perfluoroalkyl acids (PFAAs) and different sulfonamides was performed. Additionally, the total oxidizable precursor (TOP) assay was modified by fully oxidizing small amounts of the samples instead of oxidizing their extracts in order to overcome potential losses during extraction. Targeted analysis showed the presence of known PFAAs and four sulfonamides in the feed and egg yolk samples. In the plant-based feed, short-chain PFAAs, methyl and ethyl perfluorooctane sulfonamidoacetic acid (Me- and EtFOSAA), and perfluorooctane sulfonic acid (PFOS) were the most abundant PFAS. In the eggs, PFOS, FOSAA, and its alkylated homologues showed the highest concentrations. The TOP assay revealed the presence of substantial amounts of precursors with different chain lengths from C4 to C8. The highest relative increase of PFOA after oxidation was observed in egg yolk from the end of the exposure period (828%). The results of this study demonstrate the transfer of PFAAs and their precursors into hens' eggs and emphasize the contribution of (known and unidentified) precursors to the overall PFAS burden in edible products. The modified TOP assay approach was shown to be a powerful tool to better assess the total burden of samples with PFAS.

KEYWORDS: *PFAS, total oxidizable precursor assay, feeding study, biotransformation, PFOS precursors*



∑ 81,8 (of 10 … 200%)

- Comparab…
- reduced molar yields compared to the original method

Target analysis

- Sample preparation using MTBE and tetrabutylammonium as an ion pair reagent
- Analysis via UPLC-HRMS (Q Exactive Plus, Thermo Fisher)
- Analyte spectrum
  - 13 PFCA
  - 7 PFSA
  - 3 diPAP
  - 6 sulfonamides
  - 3 FTS
  - 8 replacements and “others”
    - ADONA, PFMOPrA, HFPO-DA (GenX), F-53B PFECHS, 7H-PFHpA
- LOQs between 0.05 und 0.5 µg/kg