Tissue talk: challenges and considerations when designing PFAS measurement in fish and wildlife tissue

Anna Ruth Robuck, PhD

Improving the Understanding and Coordination of Science Activities in the Chesapeake Watershed

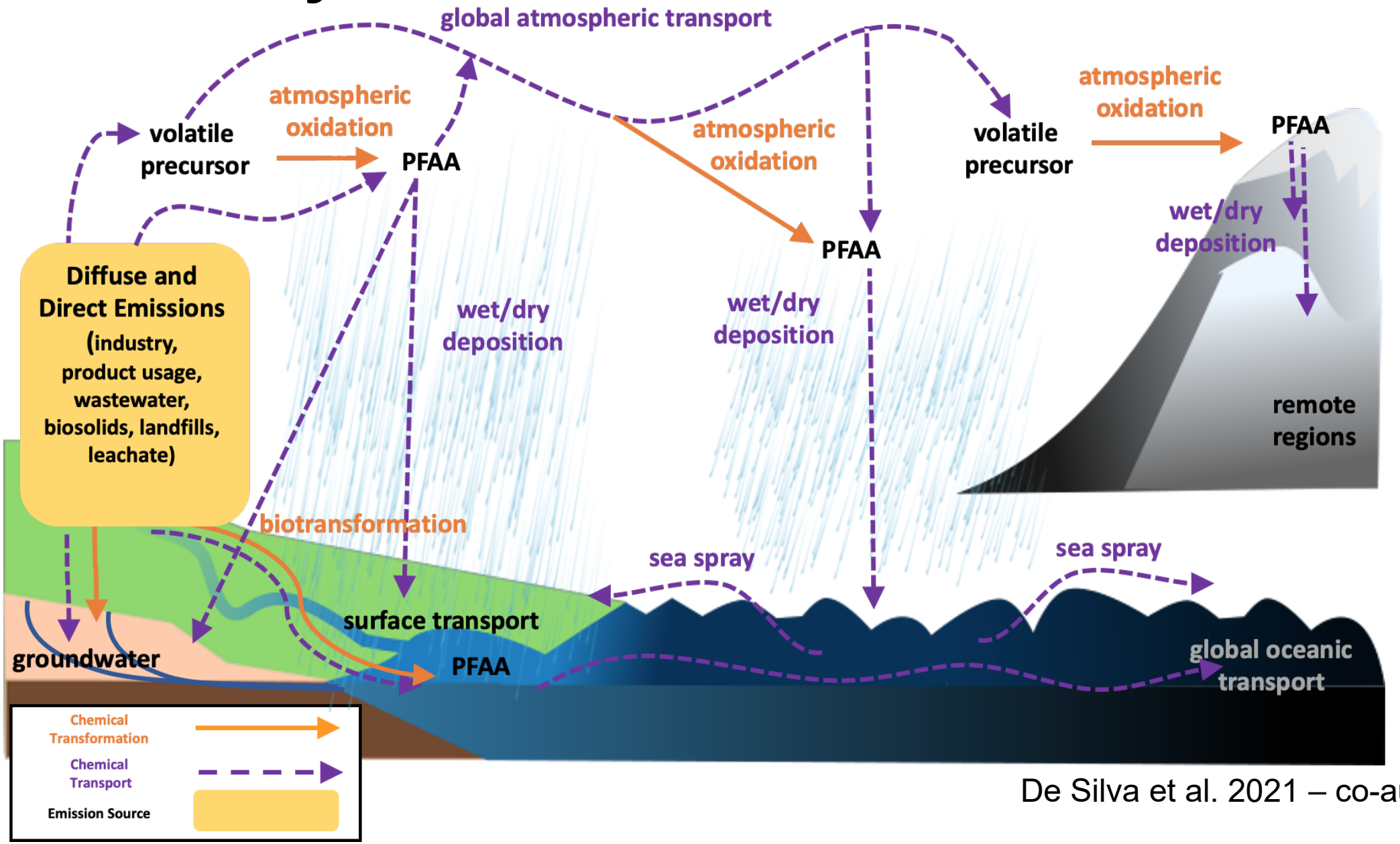
18 May 2022

Image taken under NOAA Fisheries permit #14245

Overview

- What tissues should be evaluated?
- What species should be included in monitoring?
- What compounds are of interest/importance?
- What analysis/preparation methods are used for tissue?

Aquatic ecosystems are the final sink for most PFAS



De Silva et al. 2021 – co-author work

Tissue monitoring is vital because water patterns ≠ tissue patterns

Removed – a figure of unpublished data. Figure showed that compound distribution in water does not match the compound distribution observed in fish muscle or liver.

Robuck unpublished data – no photos or sharing please ☺

Species selection must consider the unique physicochemical behavior of PFAS

- Amphiphilic
- Preferentially partition to protein, not fat
- **Many** unique chemistries, all PFAS

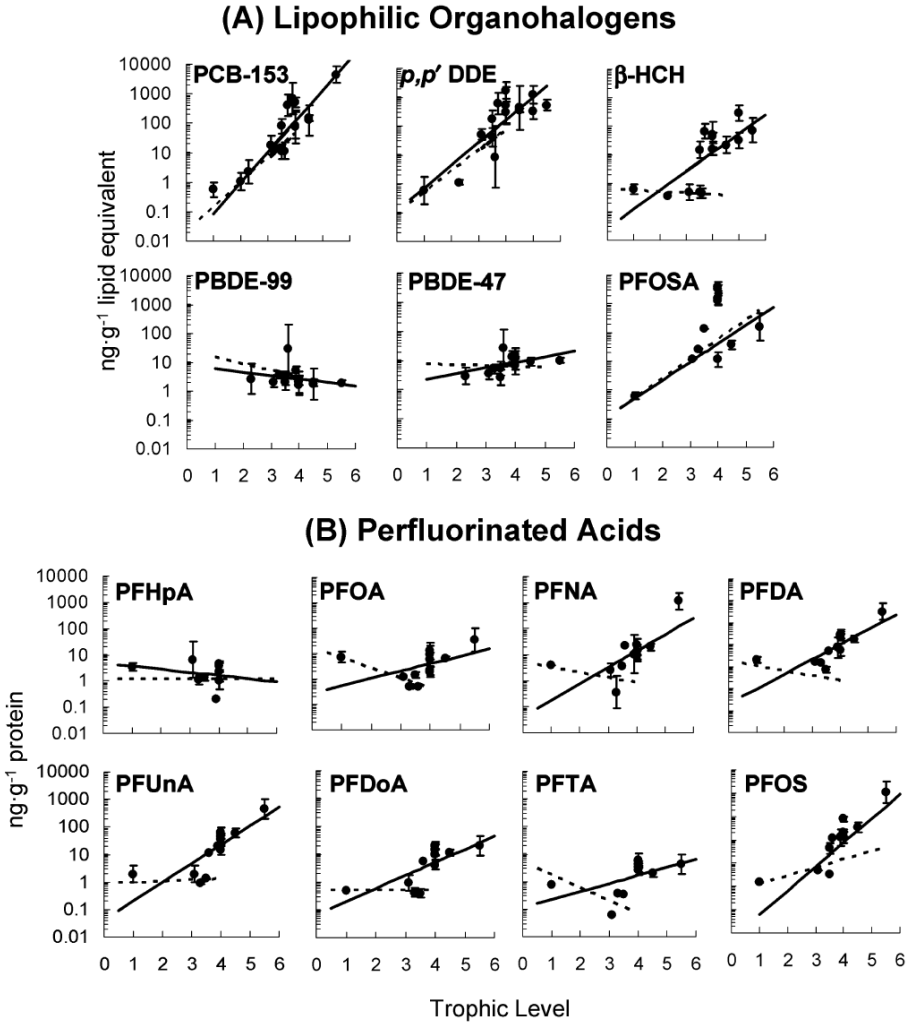


FIGURE 2. Chemical concentrations in organisms of the Arctic marine food web versus trophic level (TL) for (a) lipophilic organohalogens (ng·g^{-1} lipid equivalent) and (b) perfluorinated acids (ng·g^{-1} protein). Data are geometric means ± 1 SD. Data for E. Hudson Bay sculpin and polar bears are from references *4*, *7*, and *37*. Solid lines represent log-linear regression of C_B–TL relationship over the entire food web. Dashed line represents those regressions using only data for the piscivorous food web.

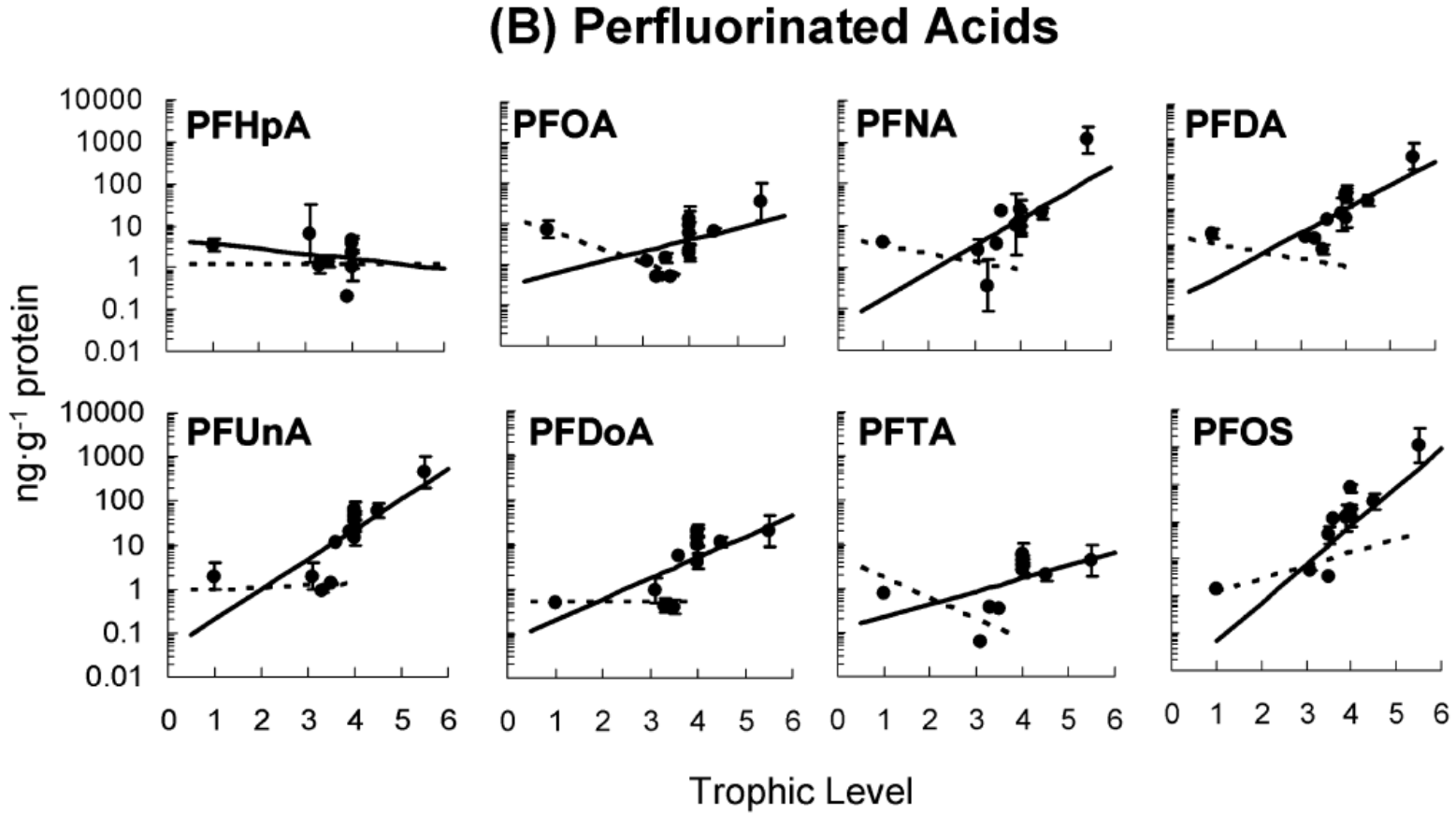
Perfluoroalkyl Contaminants in an Arctic Marine Food Web: Trophic Magnification and Wildlife Exposure

BARRY C. KELLY,† MICHAEL G. IKONOMOU,*,‡ JOEL D. BLAIR,† BLAIR SURRIDGE,§ DALE HOOVER,§ RICHARD GRACE,§ AND FRANK A. P. C. GOBAS†

School of Resource and Environmental Management, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6, Contaminant Sciences, Institute of Ocean Sciences, Fisheries and Oceans Canada (DFO), 9860 West Saanich Road, Sidney, British Columbia, Canada, V8L 4B2, AXYS Analytical Services Ltd, 2045 Mills Road, Sidney BC Canada, V8L 5X2

Environ. Sci. Technol. **2009,** *43,* 4037–4043

Air-breathing organisms are particularly vulnerable to bioaccumulation



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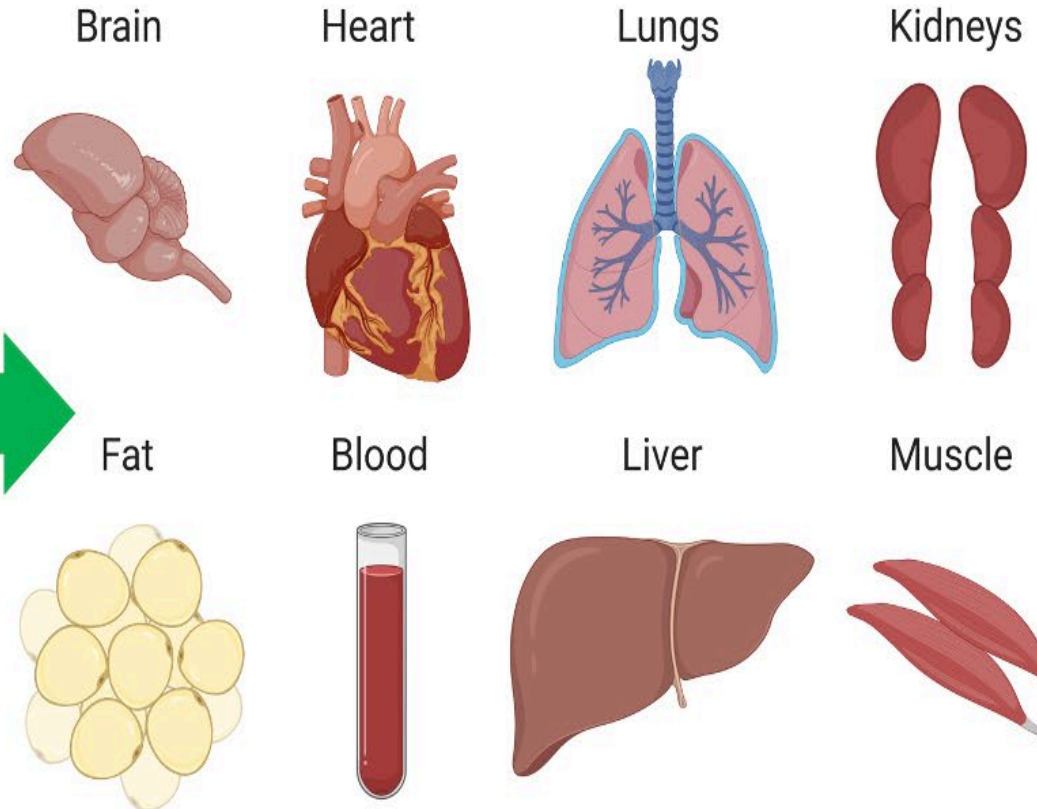
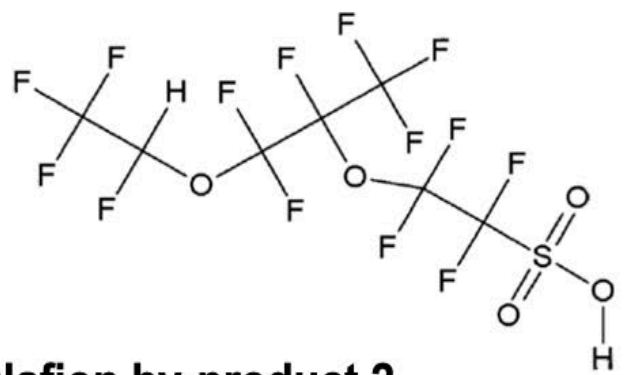
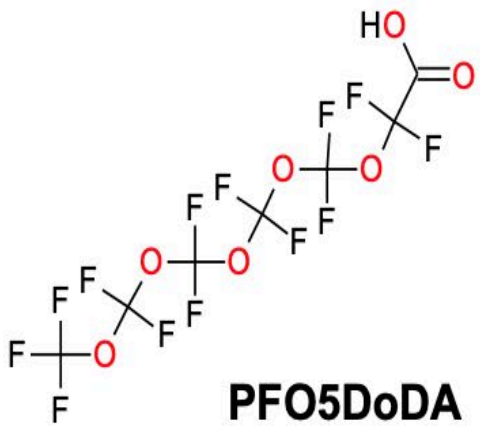
See also: Pendland et al. 2020, ES&T

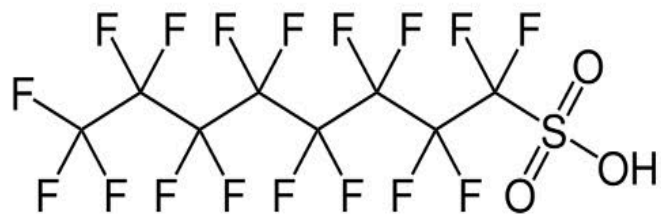




Nafion by-product 2

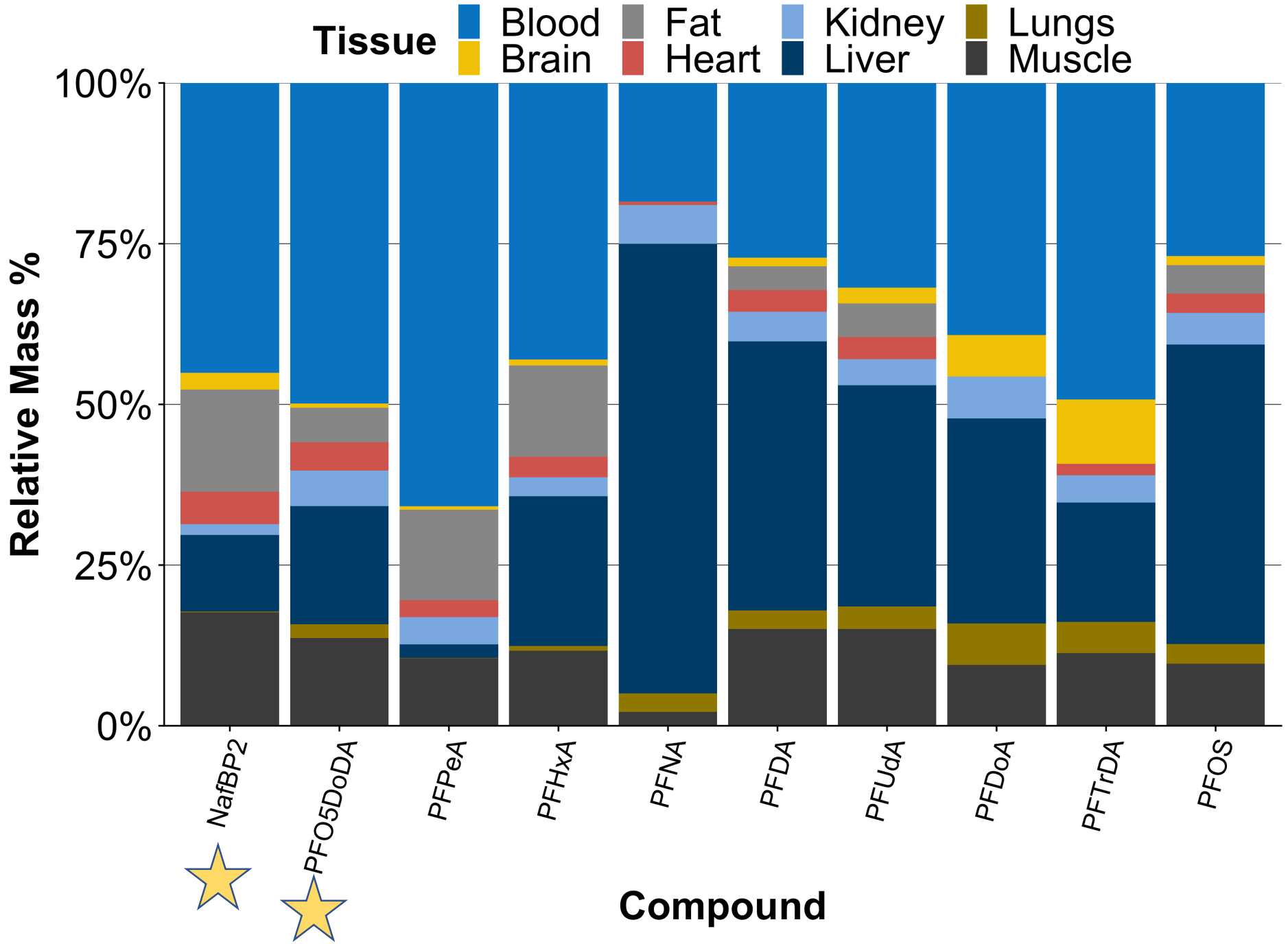


PFO5DoDA



PFOS

Robuck et al. 2020, ES&T Letters



Fat = largest compartment

Blood = 2nd largest volume

Liver = highest concentrations

Robuck et al. 2020, ES&T Letters

Some considerations for species/tissue selection

Species selection:

1. Reassess species used for POPs, e.g. SCCWRP EC monitoring plan
2. Migratory status of species
3. Compartment of interest/importance: benthic vs pelagic
4. Respiratory matrix
5. Impacts of salinity on bioaccumulation (e.g. mussels)
6. Commercial importance
7. Food web length/complexity

Tissue selection:

1. Ease/ethics of access: invasive/lethal vs opportunistic vs catch and release
2. Intent of data use: Source tracking? Ecological integrity? Human health?

But overall…*some data is better than nothing and can inform future refinement of monitoring*…

Tissue remains a continued analytical challenge

- Few validated methods exist for tissue
  - USA: EPA draft method 1633 for 40 compounds
  - EU: HBM4EU
- ILS established two NIST references for fish fillet in 2012
- SERDP/DOD rely on performance reporting given lack of standardized methods
- In literature, we see:
  - Solvent extraction with Oasis cartridge clean-up (WAX or HLB),
  - Ion-pairing extraction using MTBE (IPE),
  - Protein precipitation with or without dispersive carbon clean-up

What compounds?

ENVIRONMENTAL Science & Technology
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Feature

Widening the Lens on PFASs: Direct Human Exposure to Perfluoroalkyl Acid Precursors (pre-PFAAs)

Carrie A. McDonough,* Wenting Li, Heather N. Bischel, Amila O. De Silva, and Jamie C. DeWitt

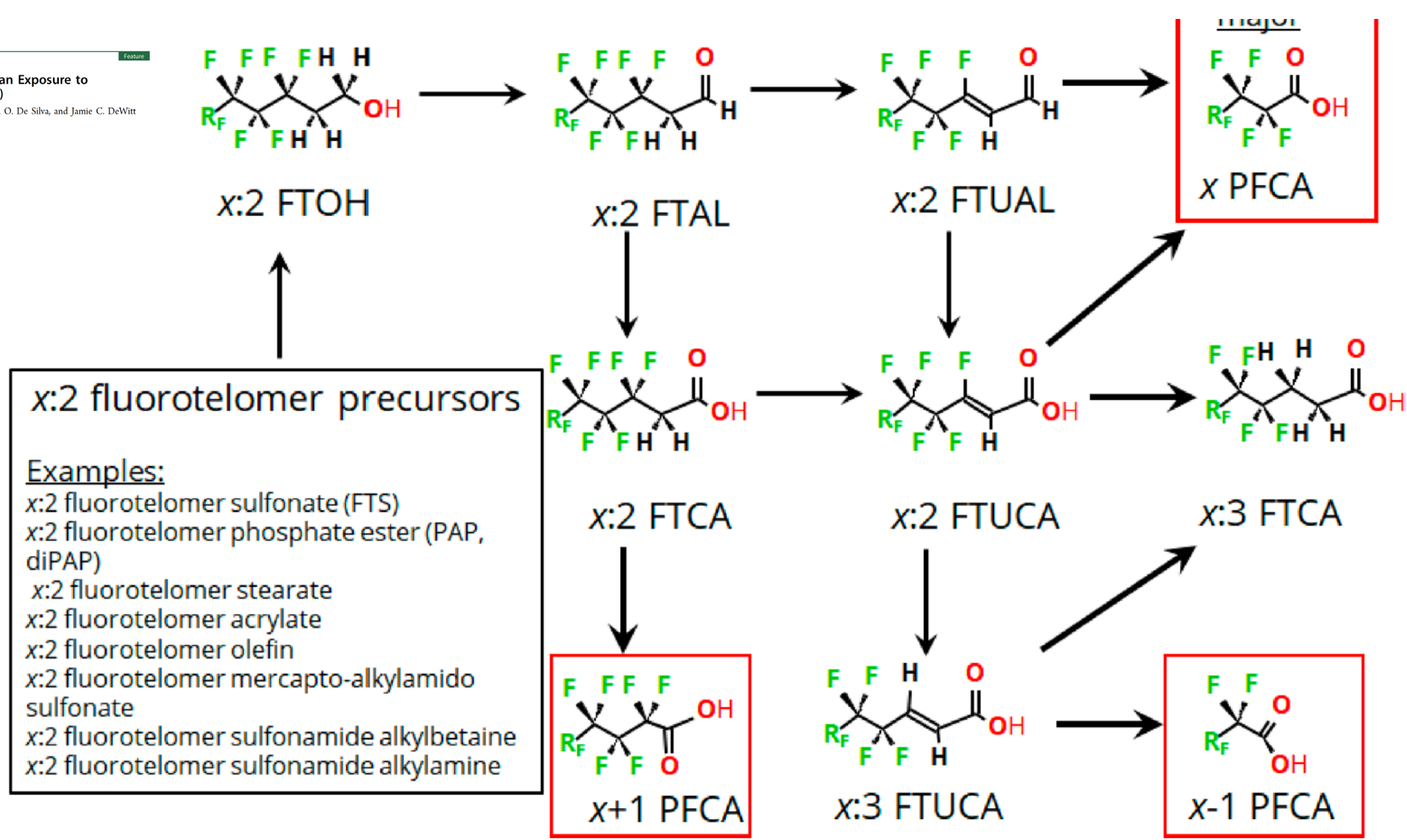

Figure 2. Generalized biotransformation pathway for a diverse suite of *x*:2 fluorotelomer precursors producing PFCAs with *x* carbons as major product and minor pathways yielding PFCAs with *x*:1 and *x*−1 carbons. Also shown is formation of *x*:3 fluorotelomer carboxylate (FTCA) which is known to be a stable final product. R_F = fluorinated aliphatic moiety.

Some considerations for compound/analysis selection

Compound selection:

1. PFAAs = most data, highest priority for regulation, terminal endpoints of many precursors, ability to measure quantitatively in targeted analysis
2. PFAAs are tip of the iceberg, e.g. precursors, polyethers, chlorinated, etc.

Analysis selection:

1. Performance needs
2. Targeted analysis: most widely used, easy to set up/contract, misses any PFAS not included in method, many matrix issues
3. TOP = immature for biological tissues (IMHO), good screening tool
4. NTA = time-consuming, requires specialized skillset/instrumentation, provides very rich dataset
5. CIC = detection limit issues, requires specialized skillset/instrumentation, good bulk evaluation tool, very powerful paired with NTA or targeted analyses

Different methods vary in their extraction of different classes of PFAS

Analytical and Bioanalytical Chemistry (2021) 413:865–876
https://doi.org/10.1007/s00216-020-03041-5

RESEARCH PAPER

Comparison of extraction methods for per- and polyfluoroalkyl substances (PFAS) in human serum and placenta samples—insights into extractable organic fluorine (EOF)

Andreas-Marius Kaiser[1,2] · Rudolf Aro[3] · Anna Kärrman[3] · Stefan Weiss[1] · Christina Hartmann[1] · Maria Uhl[1] · Martin Forsthuber[2,4] · Claudia Gundacker[2] · Leo W. Y. Yeung[3]

See also: Jahnke and Berger 2009, Valsecchi et al. 2013, Nilsson et al. 2021

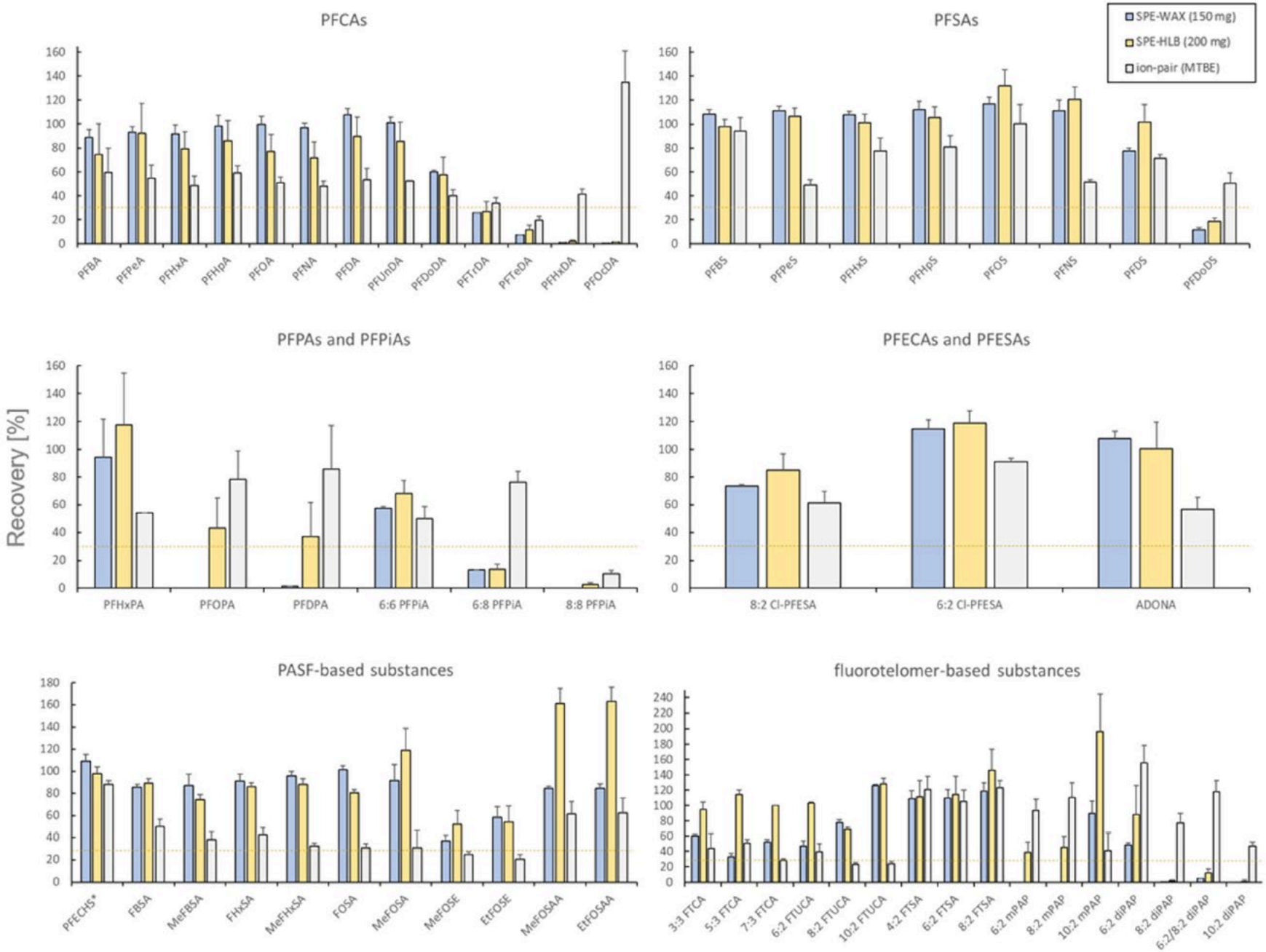

Fig. 2 The recoveries in % are based on the comparison of the sample peak area with the calibration standard peak area. For all substances and methods $n = 3$, except for PFUnDA, PFOcDA, PFNS, PFECHS, MeFOSE, EtFOSE, PFHxPA, 6:8 PFPiA, 8:8 PFPiA, and 6:2 Cl-PFESA for the ion-pair method which were $n = 2$

Materials and lab technique also impact performance

Environmental Science
Water Research & Technology

PAPER

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Cite this: *Environ. Sci.: Water Res. Technol.*, 2019, 5, 1876

Towards the development of a standardized method for extraction and analysis of PFAS in biological tissues†

Adam D. Point,[a] Thomas M. Holsen,*[b] Sujan Fernando,[c] Philip K. Hopke *[d] and Bernard S. Crimmins[be]

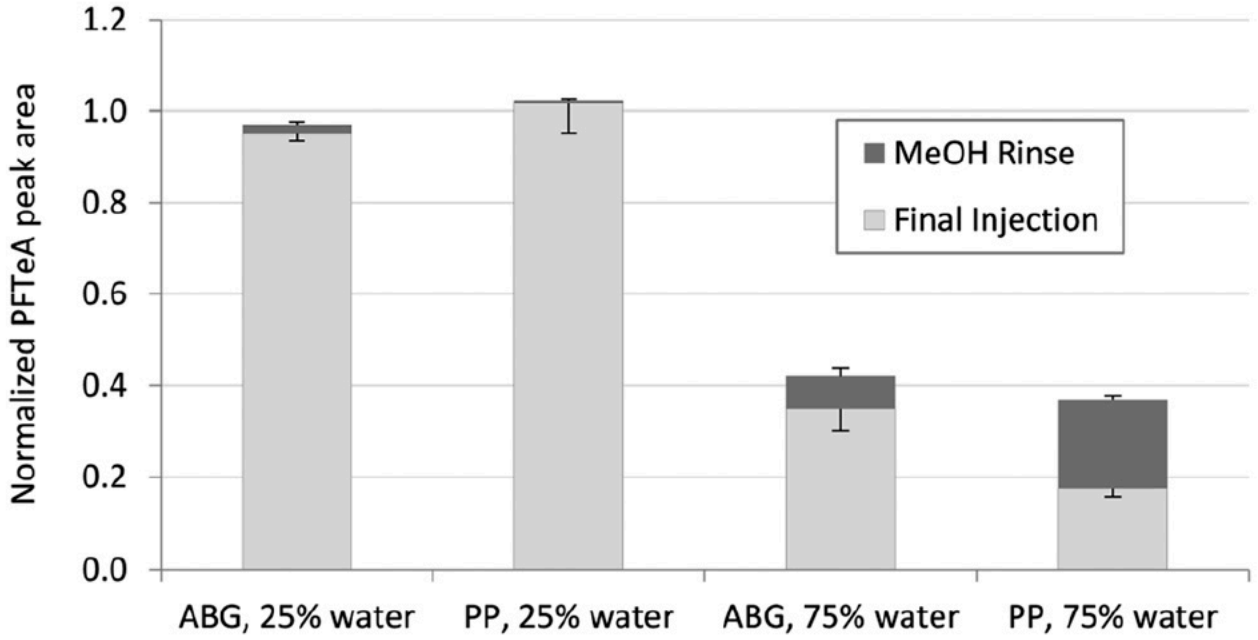

Fig. 3 Normalized mean (n = 3) PFTeA peak areas for both the final injection after sonication on day two and the methanol rinse for each vial material and solvent composition. For each vial type, plotted values are normalized to the mean of the first injections (day one) from the solutions containing 25% water. Error bars represent std. dev. Negative and positive error bars correspond to final injection and methanol rinse, respectively.

Some considerations for preparation selection

When selecting a method:

1. Analytical plans: LC-MS/MS? HRMS? GC? EOF or TOP?
2. Time: cartridge-based methods reduce sample throughput
3. Cost: variable cost of solvents, standards, consumables for each method
4. Expertise: skilled lab hands needed for all methods, some more than others
5. Accessibility: certain workflows require more equipment, reduces number of labs capable of analysis
6. Sustainability: more steps = more single-use plastics
7. Data interpretation: different methods = different data artifacts. What scale of data comparison meets monitoring needs?
8. Future needs: archival capacity, amount of tissue required

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