Per- and Polyfluoroalkyl Substances (PFAS) in Agroecosystems

Water Conservation and Management Unit USDA-ARS, US ARID-LAND AGRICULTURAL RESEARCH CENTER

PFAS

Per- and polyfluoroalkyl substances

Large class of synthetic compounds widely used due to their:

water- and oil-repellent properties

resistance to heat and degradation

ability to strongly reduce surface tension

Polyfluoroalkyl Substances

Figure 1. Classification of PFASs major groups (Schiavone & Portesi, 2023).

Non-Polymers

Polymers

Side-chain Fluorinated Polymers

Fluoropolymers

Perfluoropolyethers

COMPOUND LIST

Names, Abbreviations, and CAS Registry Numbers for Target PFAS, Extracted Table 1. Internal Standards, and Non-extracted Internal Standards¹

¹ The target analyte names are for the acid and neutral forms of the analytes. See Table 2 for the names and Chemical Abstract Service Registry Numbers (CASRN) of the corresponding anion forms, where applicable.

NA = Not assigned a CAS Registry Number

* These analytes may not perform as well as others in some matrices (see Section 1.6): PFDS, PFDoS, and 11CLPF3OUdS in aqueous samples; PFDoS and 11CLPF3OUdS in biosolid samples; and PFDoS in tissue samples.

Perfluor Abbrevi **PFBA** PFPeA PFHxA PFHpA PFOA PFNA PFDA PFUnA PFDoA PFTrDA PFTeDA Perfluor PFBS PFPeS PFHxS PFHpS **PFOS PFNS** PFDS PFDoS

 47.14×4

January 2024

Method 1633

Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue **Samples by LC-MS/MS**

Table 2. Cross-reference of Abbreviations, Analyte Names, and CAS Registry Numbers for the Acid and Anion Forms of the Perfluoroalkyl Carboxylates and Perfluoroalkyl Sulfonates

CASRN = Chemical Abstracts Service Registry Number

Why "forever chemicals"?

The **high energy required to break the C-F bond** explains why PFAS are so persistent in the environment. They do not easily degrade through natural processes such as: hydrolysis, oxidation, or biodegradation.

The bond between (C-H) is much weaker in comparison. Energy required to break a C-H bond : ~436 kJ/mol. (less polarized and less resistant bond).

3. Strength of the C-F Bond:

Energy required to break a C-F bond ~563 kJ/mol. One of the highest bond energies for a single carbonelement bond.

A-B bond length, r (A)

4. Comparison with C-H Bond:

A diverse group of thousands of chemicals used in hundred of products.

PFAS can be found in water, soil, air, and food from industrial sites, wastewater treatment plants, and household products.

non-stick cookware

firefighting foam

food packaging

waterproof clothing

The PFAS backbone is constituted by single-bonded carbon atoms with fluorine atoms covalently bonded to the alkyl chain.

PubChem (2024).

PRESENCE IN ENVIRONMENTAL SAMPLES

Widespread contamination

Sources of contamination

PFASs have been detected in surface water, groundwater, sediments, soils, and the atmosphere.

Include industrial activities, landfills, sewage sludge application, and the use of products containing PFASs.

Due to their high persistence and mobility, PFASs can disperse widely in the environment, accumulating in both aquatic and terrestrial ecosystems.

Dispersion mechanisms:

Safe Drinking Water Act

Per- and Polyfluoroalkyl Substances (PFAS)

Final PFAS National Primary Drinking Water Regulation

- · Summary
- Supporting Materials
- o General Information
- o Communications Toolkit
- o Technical Information for States, Tribes and Water Systems
- o Español
- Regulatory Information and Supporting Documents
- Webinars
- · Background

CONTACT US

• Public water systems must monitor for these PFAS and have three years to complete initial monitoring (by 2027), followed

by ongoing compliance monitoring. Water systems must also provide the public with information on the levels of these PFAS in their drinking water beginning in 2027.

- Public water systems have five years (by 2029) to implement solutions that reduce these PFAS if monitoring shows that drinking water levels exceed these MCLs.
- · Beginning in five years (2029), public water systems that have **PFAS in drinking water which** violates one or more of these MCLs must take action to reduce levels of these PFAS in their drinking water and must provide **notification** to the public of the violation.

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journal homepage: www.elsevier.com/locate/yrtph

Table 1

Safe doses of PFOA and PFOS from international authorities.

^a Factor is not needed since PODs are based on serum concentrations. ^b The use of a 3 is the US EPA default position (U.S. Environmental Protection Agency EPA, 2014); the IPCS (2005) default is 2.5.

Many government agencies and expert groups have estimated a dose-rate of perfluorooctanoate (PFOA) that would protect human health. Most of these evaluations are based on the same studies (whether of humans, laboratory animals, or both), and all note various uncertainties in our existing knowledge. Nonetheless, the values of these various, estimated, safe-doses vary widely, with some being more than 100,000 fold different. This sort of discrepancy invites scrutiny and explanation. Otherwise what is the lay public to make of this disparity?

Range of the perfluorooctanoate (PFOA) safe dose for human health: An international collaboration

Lyle D. Burgoon^a, Harvey J. Clewell^b, Tony Cox^c, Wolfgang Dekant^{d, 1}, Linda D. Dell^b, James A. Deyo^c, Michael L. Dourson^{f,*}, Bernard K. Gadagbui^f, Philip Goodrum^g, Laura C. Green^h, K. Vijayavel¹, Travis R. Kline^j, Tamara House-Knight^{k, 1}, Michael I. Luster¹, Therese Manning^m, Paul Nathanailⁿ, Frank Pagone^o, Katie Richardson^p, Tiago Severo-Peixe^q, Anurag Sharma^r, James S. Smith⁸, Nitin Verma^t, Jackie Wright^m

ince of average group from Zhang et al. (2013, Table 2) by a iang et al. (2013, Table 2).

ning steady state.

ent endpoints in different populations to derive an RfD.

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Discussion

Alison L. Ling

Estimated scale of costs to remove PFAS from the environment at current emission rates

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Using estimated emission rates of 20,000 to 100,000 metric tonnes per year of PFAAs and precursors and applying estimated unit costs of 0.9 million to 67 million USD per kg PFAA removed and destroyed, cost to achieve steady-state global PFAA stocks would be between 20 and 7000 trillion USD per year. This range brackets the estimated global GDP of 106 trillion USD (International Monetary Fund, 2023). This order-ofmagnitude cost estimate is subject to significant, compounding uncertainties, including those associated with variations in treatment efficacy, characteristics and concentrations of specific PFAA, which PFAA are reported, and site-specific constraints that cannot be captured in a broad survey. However, the estimated scale of costs (tens to thousands of trillions of USD per year) provides a useful benchmark highlighting the impracticality of relying on environmental remediation alone to control global stocks of PFAAs in the environment.

4.1. Theoretical cost estimate for steady-state global PFAAs

Method 1633 Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS

- Clean all equipment prior and after each use cleaning solvents used include ❑ Water ❑ Methanol ❑ methanolic ammonium hydroxide
-
-
-
-

-
- Do not use PTFE-lined caps on sample containers.

Prior to use, baked glassware must be solvent rinsed and then air dried \Box methanolic ammonium hydroxide (1%) ❑ Toluene ❑ methanol

Liquid samples

❑Waters ❑Sludges \Box similar materials < 50 mg solids Solid samples

❑Soils ❑sediments ❑biosolids ❑contain more than 50 mg solids

Aliquots

❑Disposable polypropylene collection tubes

➢Sample bottle, HDPE ➢with linerless HDPE or polypropylene caps

➢Sample bottle or jar ➢wide-mouth, HDPE ➢with linerless HDPE or polypropylene caps

❑To mix soil cores and to store samples for other analysis, polyethylene sealed bags were used.

Collecting water

- \square sources that flow freely (e.g., effluents) are collected as grab samples.
- \Box if the purpose of the sampling is to characterize the PFAS content of the waterbody, samples should be collected from below the surface to avoid the enrichment in the surface layer .

■ Do not fill the bottle past the shoulder, to allow room for expansion during frozen storage

❑the nominal sample size is 500-mL.

- ❑Maintain all aqueous and solid samples protected from light and at or below 6 °C from the time of collection until shipped to the laboratory.
- ❑Once received by the laboratory, the samples may be stored at 0 - 6 ºC or at or below -20 ºC, until sample preparation

❑when sampling long distances cooler and ice are required to keep the samples always refrigerated.

❑once possible samples are transferred to freezers/fridges.

Field protocol

❑soil samples are collected using a plated soil probe. We use water from the area to wash it.

 \Box once clean the probe is thoroughly sprayed with methanol LC_MS grade

❑lastly the probe is thoroughly sprayed with water LC_MS grade.

❑All cleaning residues are kept.

■ Average collection time was 2.5 hours per

■ Clay loam soils took up to 4 hours

-
- location
-

❑Samples must be shipped with sufficient ice to maintain the sample temperature at or below 6 °C during transport for a period of at least 48 hours to allow for shipping delays.

Holding times

- ❑Aqueous samples may be held for up to 28 days when stored at or below 6 ºC, or 90 days when stored at or below -20 ºC and protected from the light.
- ❑Soil and sediment samples may be held for up to 90 days, if stored by the laboratory in the dark at either 0 - 6 ºC, or at below -20 ºC.
- ❑Biosolids samples may be held for up to 90 days, if stored by the laboratory in the dark at $0 - 6$ °C, but preferably at or below -20 ºC.
- ❑EPA recommends that samples be frozen if they need to be stored for more than a few days before extraction.
- issues have been observed with certain perfluorooctane sulfonamide ethanols and perfluorooctane sulfonamidoacetic acids after 7 days.
	- likely to elevate the observed concentrations of other PFAS compounds via the transformation of these precursors.

- soils and sediments may exhibit microbial growth when stored at 0 - 6 ºC.
	- samples may need to be extracted as soon as possible if NFDHA is an important analyte

Extra samples may be needed for other analysis

❑ Texture ❑ Nutrients ❑ Organic matter ❑ pH ❑ …

Sample Preparation and Extraction

Aqueous samples

- \blacksquare pH should be 6.5 \pm 0.5 adjust with 50% formic acid or ammonium hydroxide
- all parts of the SPE manifold must be cleaned between samples with methanolic ammonium hydroxide (1 %) and air dried prior to use
- sonication with methanolic ammonium hydroxide (1 %) may be used
- ❑ Homogenize the sample
- ❑ Pre-condition the cartridges
- \Box Do not allow the WAX SPE to go dry

■ Do not use any fluoropolymer articles or task wipes in these extraction procedures.

■ Use only HDPE or polypropylene wash bottles and centrifuge tubes.

maximum sample weight for sediment or soil is 5 g dry-weight maximum sample weight for biosolids is 0.5 g dry-weight

Soil samples

- \Box mix the sample 24 hs
	- □ determine water content in sample
	- ❑ weigh aliquot
	- ❑ add 0.3% methanolic ammonium hydroxide
	- ❑ vortex
	- ❑ shake for 30 minutes
	- ❑ centrifuge for 15 minutes
	- □ repeat the extraction steps 2 times
- ❑ concentrate the extract \Box add reagent water 5-7 hs

- ❑ SPE
- ❑ elution ❑ concentrate /reconstituted5-8 hs

3 hs

5-7 hs/ batch

❑ Biosolids ❑ Manure

❑ Aqueous Matrices

❑ soil

Eastern Region

❑ PFAS occurrence in aqueous matrices in North Carolina

❑PFAS occurrence in soil

COLLABORATIONS

Water Management and Conservation Research Unit

