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Out from the shadows – Lifting the veil on ultrashort per- and polyfluoroalkyl substances (USC-PFAS) – analysis, occurrence, remediation, and emerging regulations

Ultrashort chain per- and polyfluoroalkyl substances (USC-PFAS), defined as those with three or fewer carbon atoms, are characterised by their significant mobility within the environment, high water solubility, and low affinity for organic matter. These properties contribute to their widespread presence in environmental waters and wastewaters, as well as drinking waters. The environmental concerns associated with USC-PFAS include their persistence, potential for groundwater contamination, and challenges in remediation due to their resistance to conventional treatment methods.

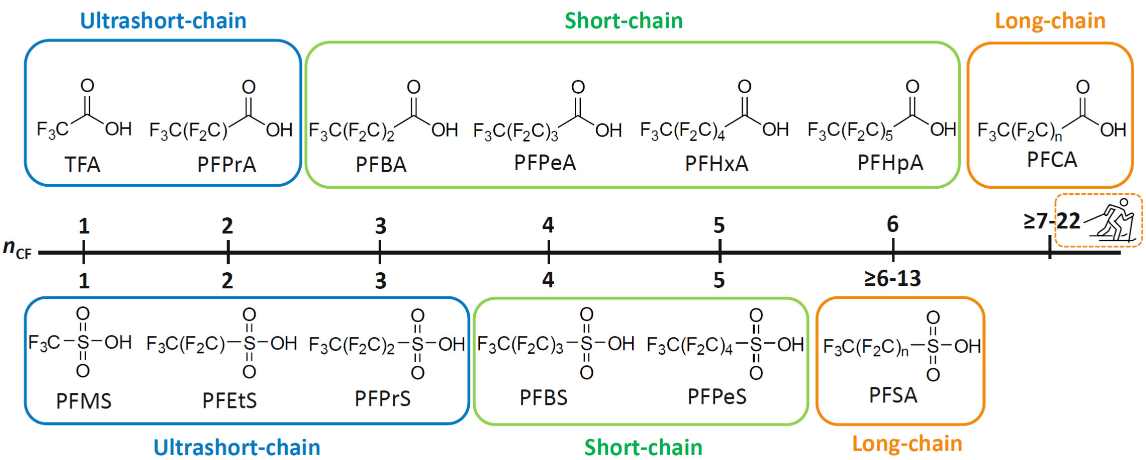


Figure 1: PFSA and PFCA categorization based on carbon chain length – ultrashort-chain, short-chain and long-chain. (Image provided courtesy of Phenomenex and SCIEX).

Occurrence, uses and sources

Ultrashort chain PFAS have been poorly characterised compared with their longer chain counterparts, and understanding of their intended and unintended transformation processes is limited. Sources of USC-PFAS include degradation of precursor compounds, atmospheric degradation of hydrofluorocarbons and hydrochlorofluorocarbons used as refrigerants, and intentional direct use in products like batteries. They are also byproducts from historical electrochemical fluorination (ECF) manufacture of longer chain PFAS. USC-PFAS are also found in urban and industrial waste, as well as aqueous film-forming foams (AFFFs) used in firefighting.

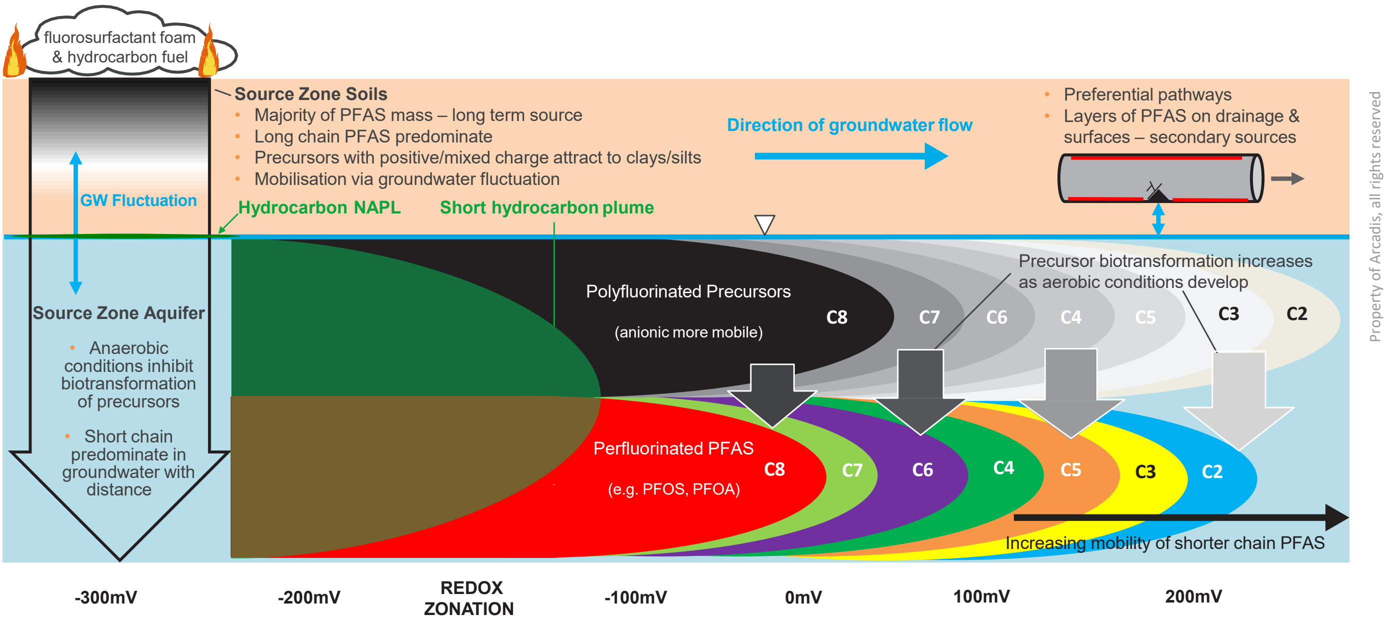


Figure 2: "Conceptual site model for PFASs from a fire training area source zone", from Managing Risks and Liabilities associated with Per- and Polyfluoroalkyl Substances (PFASs), CL:AIRE Technical Bulletin, Arcadis 2019. Used with permission.

Fate and transport

A recent survey of USC-PFAS in Australian environmental water samples (Gorji et al.) found ultrashort perfluorocarboxylic acids (USC-PFCAs) including PFPrA in wastewaters, surface waters and groundwaters. Ultrashort perfluorosulfonic acids (USC-PFSAs) were detected in wastewaters, surface waters, groundwaters, and drinking waters (to varying extents and specific to the PFSA compound identified), and hydrogen- substituted PFCAs (USC-H-PFCAs) were identified in surface water.

Carbon chain length plays a key role in determining the physicochemical characteristics of different PFAS chemicals. Long chain PFAS for instance are more hydrophobic, a property that has been leveraged by removal techniques using carbonaceous materials like granular activated carbon (GAC). By contrast, short and ultrashort chain PFAS are hydrophilic, with characteristically low pK_a values (i.e. more acidic), high water solubilities and decreased log K_{oc} values (i.e. less adsorptive to organic carbon). These attributes mean that USC-PFAS dissociate freely in aqueous environments and are less prone to sorption onto natural solids. The outcome is that USC-PFAS are highly mobile in the aquatic environment and can travel far from contamination source areas.

The global regulatory landscape

Awareness about the persistence and bioaccumulative nature of C8-C14 PFAS began to attract widespread concern near the turn of the millennium, and inclusion of PFOS, PFOA and PFHxS on the persistent organic pollutants (POPs) list of the Stockholm Convention soon ensued. Consequentially, manufacturers began adopting short and ultrashort chain alternatives.

However, with the change from C8 to C4 and shorter fluorinated carbon chains came the sacrifice to lower technical performance, and greater quantities were needed for equivalent performance. Hence, while it is generally accepted that short and ultrashort chain PFAS have lower toxicological profiles, environmental risks are not necessarily obviated since USC-PFAS presence, and continuous, cumulative, release suggests that adverse risks may lie ahead.

Global regulations of USC-PFAS vary by region and are often included under broader PFAS regulations. For example, in the Americas, Europe, and Asia-Pacific (APAC) regions, there are specific guidelines and limits on total PFAS compounds for drinking water, environmental water, and wastewater. In Australia, regulations also cover these areas, with particular attention to the presence of USC-PFAS in aqueous film-forming foams (AFFFs) used in firefighting. Germany has introduced specific regulations for TFA in drinking water, to a level of 60 ug/L, but notes 10 µg/L should be the target threshold, while Denmark's limit is 9 µg/L, and the Dutch Institute for Public Health (RIVM) set a lower value of 2.2 µg/L.

Targeted analytical services are becoming more accessible

Testing for USC-PFAS compounds is challenging due to several factors. Analytical standards, especially isotopically labelled ones, are hard to find, which complicates the testing process. Background contamination and noise can interfere with the detection of these compounds, especially TFA and other USC-PFCAs. USC-PFSAs and the ether compound PFMOAA have lower ambient background concentrations and lower LOR values are more readily achievable. ALS has achieved a testing method that includes USC-PFAS compounds in environmental water matrices, to the LOR values summarised in table 1 – a more comprehensive compound information sheet is provided as an appendix to this EnviroMail.

Table 1 – ALS method EP230:

USC-PFAS Compounds and Limits of Reporting (LOR)	CAS No	LOR (µg/L)
Difluoroacetic acid (DFA)	381-73-7	1
Trifluoroacetic acid (TFA), Perfluoroethanoic acid (PFEtA)	76-05-1	1
Trifluoromethane sulfonic acid (TFMS), Perfluoromethane sulfonic acid (PFMeS)	1493-13-6	0.01
2,3,3,3-Tetrafluoropropanoic acid (2333-TFPA)	359-49-9	1
2,2,3,3-Tetrafluoropropanoic acid (2233-TFPA), Flupropanate	756-09-2	1
Perfluoroethane sulfonic acid (PFEtS)	354-88-1	0.01
Perfluoropropanoic acid (PFPrA)	422-64-0	1
Perfluoro-2-methoxyacetic acid (PFMOAA)	674-13-5	0.1
Perfluoropropane sulfonic acid (PFPrS)	423-41-6	0.01

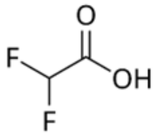
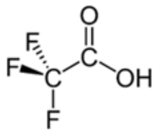
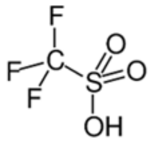
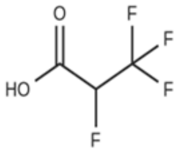
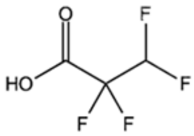
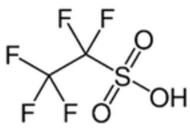
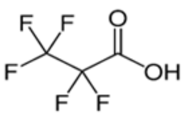
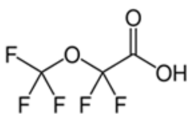
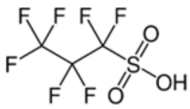
The HDPE sampling containers used for routine PFAS analyte suites are suitable for collecting samples for USC-PFAS. To request analysis for USC-PFAS, please include ALS code EP230 on analysis requisition documents. In the absence of well documented holding time criteria, ALS recommends a conservative holding time of 14-days after sample collection, although stability trials indicate that these analytes can be stable up to several months post sampling.

Get in touch with us

We would love to hear about how our services for this emerging class of PFAS might assist with your project needs, and we welcome feedback on how we might improve or expand our services to meet your needs. Don't hesitate to get in contact with your nearest ALS laboratory to discuss your PFAS testing requirements.

Brisbane	ALSEnviro.Brisbane@alsglobal.com
Sydney	ALSEnviro.Sydney@alsglobal.com
Melbourne	ALSEnviro.Melbourne@alsglobal.com
Perth	ALSEnviro.Perth@alsglobal.com
New Zealand	ALSEnviro.Hamilton@alsglobal.com

Appendix 1 – Ultrashort chain PFAS compounds information sheet

Compound name/s	Acronym	CAS No.	Structure	LOR (µg/L)	Industrial uses, occurrence in environmental compartments
Difluoroacetic acid	DFA	381-73-7		1	*Not strictly a PFAS by the OECD definition (no completely fluorinated carbon), but still a polyfluorinated compound under conventional chemical categorisation protocols A breakdown product of many pesticides, and known to be a metabolite of the pesticide flupyradifurone Many sources of DFA are still to be determined
Trifluoroacetic acid (aka Perfluoroethanoic acid)	TFA, (aka PFEtA)	76-05-1		1	Breakdown products of many pesticides Produced from atmospheric degradation of hydrofluorocarbons and hydrochlorofluorocarbons used as refrigerants Forms naturally from chemical reactions near sub-sea volcanic vents German Federal Agency prescribes a health guideline value = 60 µg/L but that 10 µg/L should be strived for Dutch Institute for Public Health and the Environment (RIVM 2023) set an indicative water value at 2.2 µg/L Denmark drinking water limit is 9 µg/L"
Trifluoromethane sulfonic acid (aka Perfluoromethane sulfonic acid)	TFMS, (aka PFMeS)	1493-13-6		0.01	Considered a superacid and is widely used as either a solvent or catalyst in organic compound synthesis Used in chemical production, electronics, lithium ion batteries Found predominantly in surface water (24% Gorji et al)
2,3,3,3-Tetrafluoropropanoic acid	2333-TFPA	359-49-9		1	Tetrafluoropropanoic acid (TFPA) structural isomers have been used as reagents in organic synthesis, particularly in the preparation of fluorinated compounds TFPA isomers have also been used in industrial refrigerant applications"
2,2,3,3-Tetrafluoropropanoic acid, (aka Flupropanate)	2233-TFPA	756-09-2		1	Used directly as a herbicide for controlling grasses, known as flupropanate Tetrafluoropropanoic acid (TFPA) structural isomers have been used as reagents in organic synthesis, particularly in the preparation of fluorinated compounds TFPA isomers have also been used in industrial refrigerant applications
Perfluoroethane sulfonic acid	PFEtS	354-88-1		0.01	Byproduct from ECF manufacture of longer chain PFSAs, found in urban and industrial waste, and AFFF formulations Wastewater influent and effluent detection in China - Influent: 1.4-17 ng/L, - Effluent: 0.08-11 ng/L Australia surface and groundwater detections at <1.8 – 75,000 ng/L Sweden groundwater and surface water detection at <1.8 – 1,700 ng/L Tap water detection in USA, Canada, Japan, China ~0.9 ng Groundwater contaminated with AFFF from fire training sites PFEtS have shown concentrations 11,000-75,000 ng/L
Perfluoroethane sulfonic acid	PFPrA	422-64-0		1	Found in rain and snow from Japan, USA, France (1.1-120 ng/L), wastewater influent and effluent from China (1-40 ng/L), drinking water detections in USA and NZ Wastewater and surface water detections in Canada, Japan, France, Sweden
Perfluoro-2-methoxyacetic acid	PFMOAA	674-13-5		0.1	PFMOAA and PFPrA have highlighted inadequate drinking water treatment. The use of granular activated carbon filters has shown that ultra-short PFAS are not retained and are being detected in treated drinking water. Detected at high concentrations (~10 µg/L) in drinking water in eastern North Carolina, USA Detected in human serum and breastmilk in China Rat models have shown a broad spectrum of maternal and neonatal effects
Perfluoropropane sulfonic acid	PFPrS	423-41-6		0.01	Wastewater influent and effluent from China (0.05-7.5 ng/L) Groundwater contaminated with AFFF from fire training sites PFPrS: 19-63,000 ng/L