

PFAS – What we know?

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23 August 2016

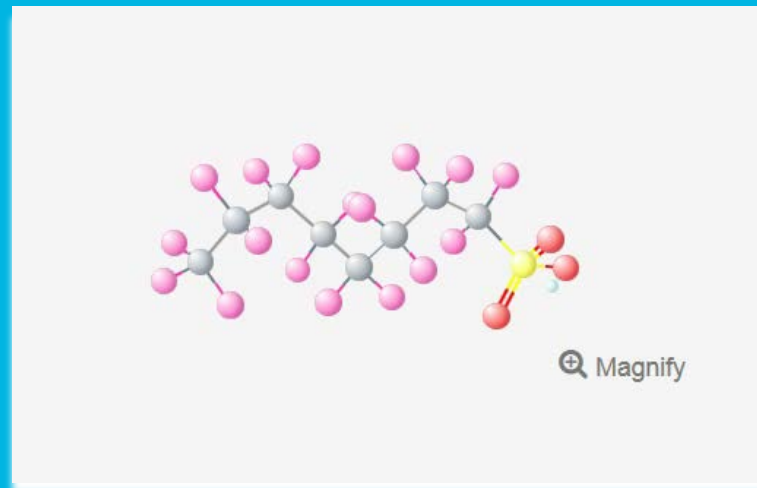
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PFAS Investigations amongst Uncertainty

- PFAS chemistry
- PFAS environmental fate and transport
- Analytical detection and quantitation
- Ever changing guidelines
- Remediation Options?

Chemistry 101...

- Essentially class of synthetic fluorinated organic compounds with C–F bond
- Diverse range of PFAS = confusion
- Strong C-F bonding
- Persistent and resistant to degradation



1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonic acid ...What the...?

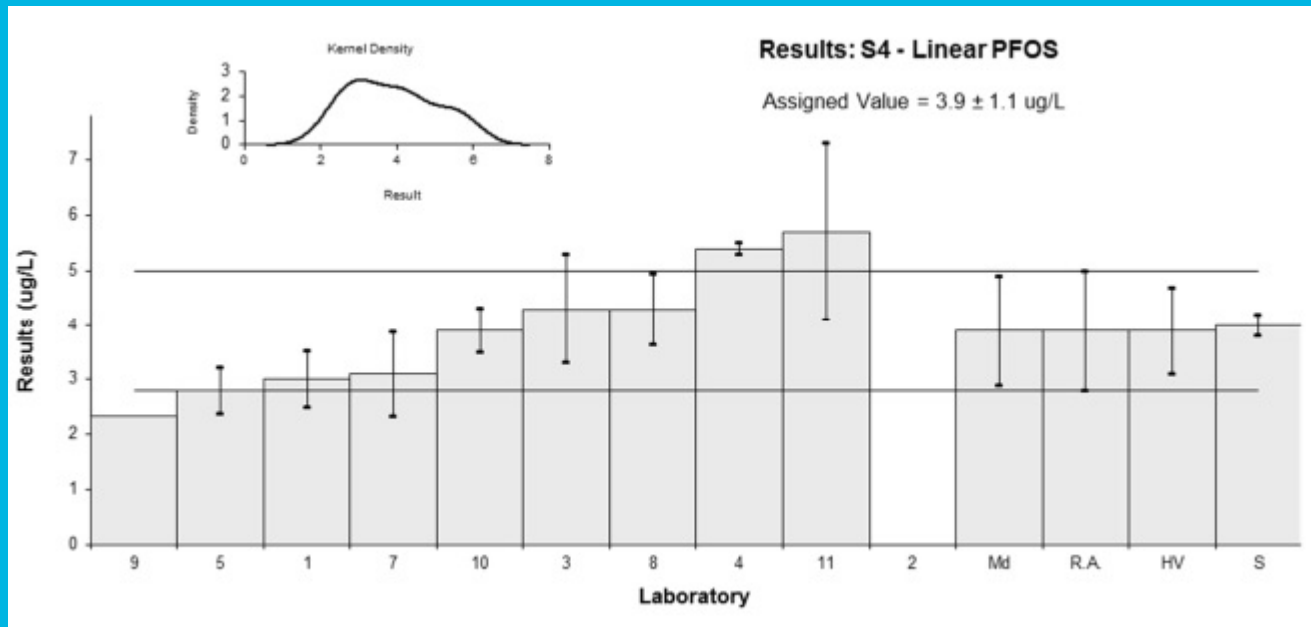
- Perfluorinated (PFC) – completely fluorinated, $\text{F}-(\text{CF}_2)_n-\text{R}$
- Polyfluorinated – partially fluorinated, $\text{F}(\text{CF}_2)_n-(\text{CH}_2)_m-\text{R}$
- X:Y fluorotelomer, the X = number of fully fluorinated carbon atoms, Y = number of non-fluorinated carbon atoms.
- AFFF – Aqueous film forming foam (surfactant)

Group	Class	Chemical Name	Abbreviation	Chemical Structure
Perfluorinated compounds (PFC)	Perfluoroalkyl Sulfonic Acids (PFSA)	Perfluorobutane sulfonic acid	PFBS	$F(CF_2)_4SO_3H$
		Perfluoropentane sulfonic acid	PFPeS	$F(CF_2)_5SO_3H$
		Perfluorohexane sulfonic acid	PFHxS	$F(CF_2)_6SO_3H$
		Perfluoroheptane sulfonic acid	PFHpS	$F(CF_2)_7SO_3H$
		Perfluorooctanesulfonic acid	PFOS	$F(CF_2)_8SO_3H$
		Perfluorodecane sulfonic acid	PFDS	$F(CF_2)_{10}SO_3H$
	Perfluoroalkyl Carboxylic Acids (PFCA)	Perfluorobutanoic acid	PFBA	$F(CF_2)_3COOH$
		Perfluoropentanoic acid	PFPeA	$F(CF_2)_4COOH$
		Perfluorohexanoic acid	PFHxA	$F(CF_2)_5COOH$
		Perfluoroheptanoic acid	PFHpA	$F(CF_2)_6COOH$
		Perfluorooctanoic acid	PFOA	$F(CF_2)_7COOH$
		Perfluorononanoic acid	PFNA	$F(CF_2)_8COOH$
		Perfluorodecanoic acid	PFDA	$F(CF_2)_9COOH$
		Perfluoroundecanoic acid	PFUnDA	$F(CF_2)_{10}COOH$
		Perfluorododecanoic acid	PFDoDA	$F(CF_2)_{11}COOH$
		Perfluorotridecanoic acid	PFTTrDA	$F(CF_2)_{12}COOH$
		Perfluorotetradecanoic acid	PFTeDA	$F(CF_2)_{13}COOH$
Polyfluorinated compounds	Polyfluoroalkyl sulfonamides (FSA)	Perfluorooctane sulfonamide	PFOSA	$F(CF_2)_8SO_2NH_2$
		N-ethyl perfluorooctanesulfonamido acetic acid	N-Et-FOSAA	$F(CF_2)_8SO_2N(C_2H_5)CH_2CO_2H$
		N-methyl perfluorooctanesulfonamido acetic acid	N-Me-FOSAA	$F(CF_2)_8SO_2N(CH_3)CH_2CO_2H$
		N-ethyl perfluorooctane sulfonamide	N-Et-FOSA	$F(CF_2)_8SO_2N(C_2H_5)H$
		N-ethyl perfluorooctane sulfonamidoethanol	N-Et-FOSE	$F(CF_2)_8SO_2N(C_2H_5)C_2H_4OH$
		N-methyl perfluorooctane sulfonamide	N-Me-FOSA	$F(CF_2)_8SO_2N(CH_3)H$
		N-methyl perfluorooctane sulfonamidoethanol	N-Me-FOSE	$F(CF_2)_8SO_2N(CH_3)C_2H_4OH$
	Fluorotelomer Sulfonic Acids (FTS)	4:2 Fluorotelomer sulfonic acid	4:2 FTS	$F(CF_2)_4(CH_2CH_2)SO_3H$
		6:2 Fluorotelomer sulfonic acid	6:2 FTS	$F(CF_2)_6(CH_2CH_2)SO_3H$
		8:2 Fluorotelomer sulfonic acid	8:2 FTS	$F(CF_2)_8(CH_2CH_2)SO_3H$
		10:2 Fluorotelomer sulfonic acid	10:2 FTS	$F(CF_2)_{10}(CH_2CH_2)SO_3H$

Evolving Analytical Detection

- Commercial analysis began c.2008
- Direct injection methods – 0.01 ppb
- Now with pre-concentration methods – 0.0003 to 0.002 ppb
- Systematic differences in results for real world samples reported by different labs.

Evolving Analytical Detection



Evolving Analytical Detection

- Internal standardisation to correct for matrix effects/normalising recoveries on extraction had no correcting effect on the numbers reported
- Different standards used for instrument calibration was the issue
- Using linear PFAS as a standard likely to overestimate real samples containing both linear and branched PFAS isomers

Evolving Analytical Detection

- Analytical methods have out-paced toxicological studies
- Widespread detection of PFAS in the absence of health information may cause public alarm
- Total Organofluorine - Combustion Ion Chromatography (TOF-CIC),
- Total Oxidisable Precursor (TOP) analysis

PFAS Fate and Transport

- PFC highly stable, soluble and very mobile, very low adsorption affinity, resists biological and chemical degradation → persistent in the environment
- Fluorinated tail not known to degrade in nature
- Some PFAS bioaccumulate (e.g. PFOS and PFOA) – not lipids, more so in blood, liver, kidney, spleen

PFAS Fate and Transport

- Polyfluorinated compounds partially degrade to perfluorinated end-point compounds (perfluoroalkyl carboxylic acids (PFCA) and perfluoroalkyl sulfonic acids (PFSA))
- Half-life (unknown?) – PFOA, 2 to 235 yrs
- Generally shorter chain PFAS have shorter half-lives

Guidelines

- Still evolving
- 'Limits' to current PFAS science
- Lower guideline values, expanded analyte list,
- Human health – now derived from blood serum levels
- Impacting public perception (?)

Interim Guidelines

Exposure Scenario	PFOS	PFOA	6:2 FTS	8:2 FTS	Source
Water (µg/L)					
Drinking water	0.5	5	-	-	enHealth (2016)
Drinking water	0.070 (PFOS + PFOA)		5	0.4	USEPA (2009) USEPA (2016) Jarman <i>et al.</i> 2014
Recreational	5	50	-	-	enHealth (2016)
Ecological Freshwater Slightly – moderately disturbed systems (95% species protection) ³	0.13	220	-	-	Draft ANZECC (In: Government of Western Australia 2016)
Ecological (toxicity effect on aquatic organisms)	6.66	2900	-	2900	Qi <i>et al.</i> 2011 Giesy <i>et al.</i> 2010
Soil (mg/kg)					
Human Health (residential)	4	-	-	-	Government of Western Australia (2016)
Human Health (Industrial/Commercial)	100	-	-	-	Government of Western Australia (2016)
Human Health Interim Screening Levels (residential, direct contact)	6	16	60	16	USEPA (2009). Jarman <i>et al.</i> 2014
Human Health Interim Screening Levels (industrial, direct contact)	90	240	900	240	GHD (2015)
Ecological Interim Screening Levels (EISLs) for 95% species protection, terrestrial)	0.373	3.73	-	3.73	UKEA (2009)
EISLs (residential land use, 80% species protection, low reliability, terrestrial)	0.91				UKEA (2009)
EISLs (commercial/industrial land use, 60% species protection, low reliability, terrestrial)	4.71				UKEA (2009)

Site Investigation Method

- Assess if there is potential broad-based contamination problem
- Assess potential for precursors to transform to end-point PFAS
- Assess target and quantify individual PFAS
- Human health and environmental risk assessment
- Targeted toxicology studies

Remediation Options

- Still evolving
- High solubility of short-chain PFAS make treatment difficult
- Limited options for treatment of soil/groundwater (thermal, GAC, solidification)
- No in-situ treatment really available (ScisoR?)
- Management, containment and control (?)

Thank You

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