

What you should know about Per- and Polyfluoroalkyl substances (PFAS)

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Introduction

**You breathe PFAS
you drink PFAS
you eat PFAS
all day long
without knowing it**

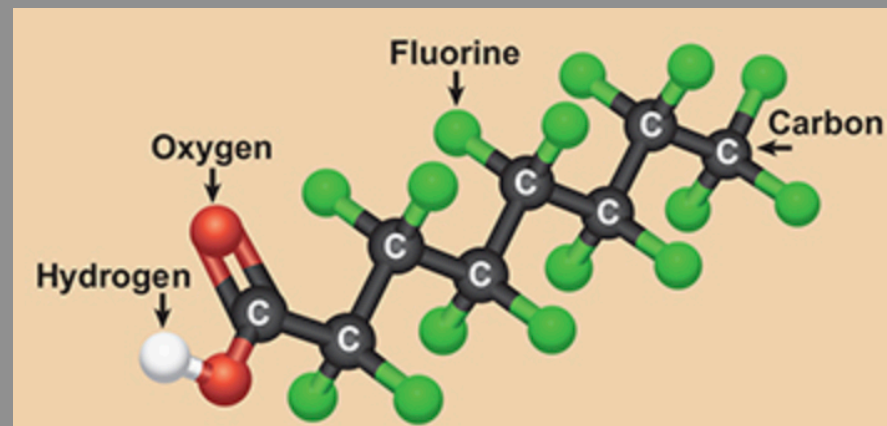
Outline

- Understanding PFAS
- Structure and nomenclature examples
- Major sources of PFAS in the environment
- Concentration limit values of PFAS
- Site investigation challenges
- Treatment technologies
- PFAS forensics in practice

Understanding PFAS

PFAS is the term for a family of highly fluorinated chemicals that have been used and manufactured since the 1940s in various industries around the world

It's hard to define them because they have different modes of action and means of transport, but they all have a carbon and fluorine atom backbone

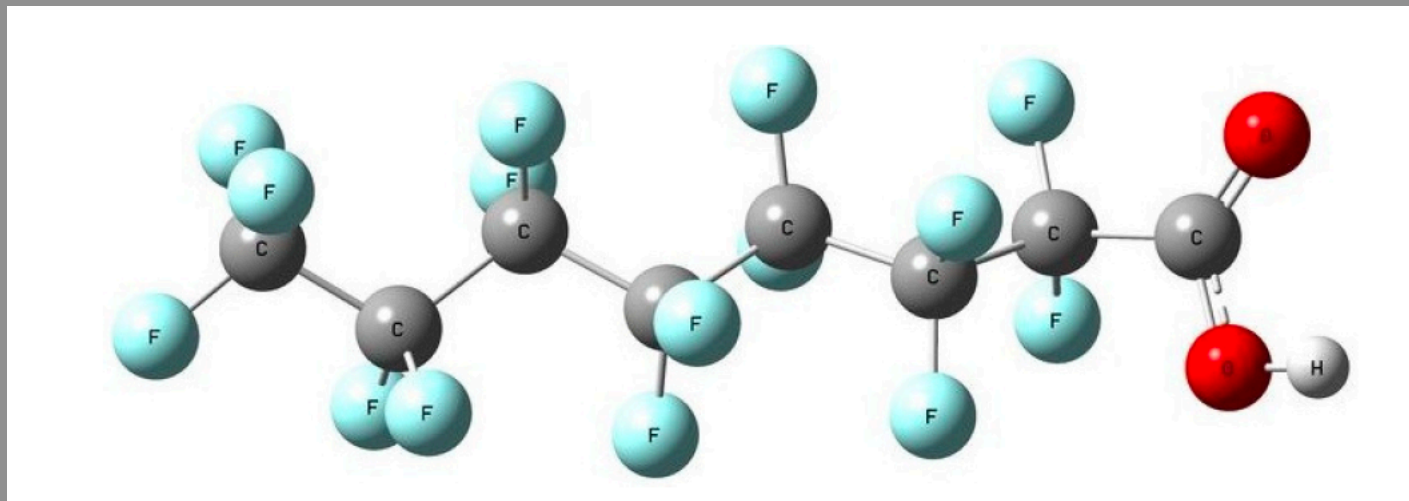


These synthetic compounds are designed to be resilient and can withstand extremely harsh environmental conditions

Because they contain carbon–fluorine bonds, which are among the strongest bonds found in nature, PFAS resist breakdown by the typical forces of degradation like enzymes in organisms and bacteria in the environment

The unique physiochemical properties of PFAS impart characteristics like repellency to oil, grease and water, as well temperature resistance and friction reduction

They can therefore help make non-stick products that repel many substances and resist stains



Approximately 5000 of these synthetic compounds have been created and used in commercial products, and roughly 500 - 600 are estimated to be in active use

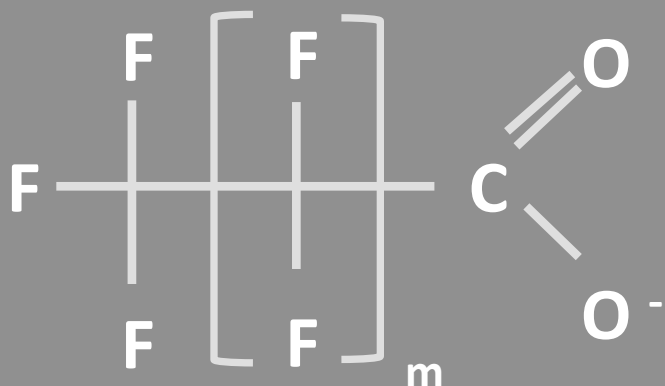
The scientific community, however, has good knowledge about only a few of them

The two that have been most thoroughly researched and are best understood are PFOA and PFOS

Structure and nomenclature examples

Per = fully fluorinated alkyl tail (No hydrogen)

Perfluoroalkyl carboxylates (PFCAs)

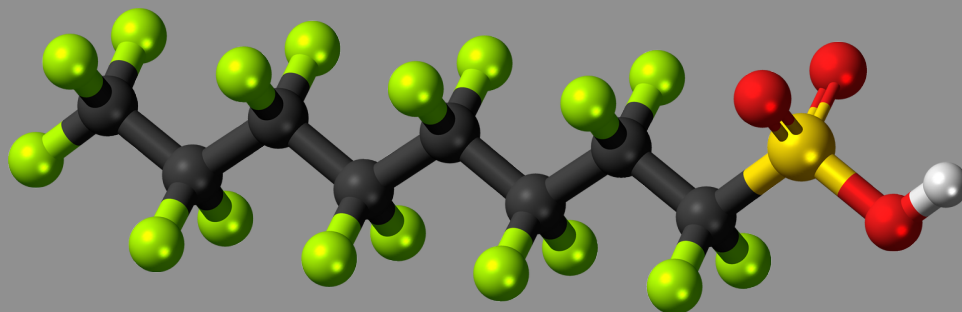


Examples :

$m = 2 \Rightarrow$ PFBA

$m = 4 \Rightarrow$ PFHxA

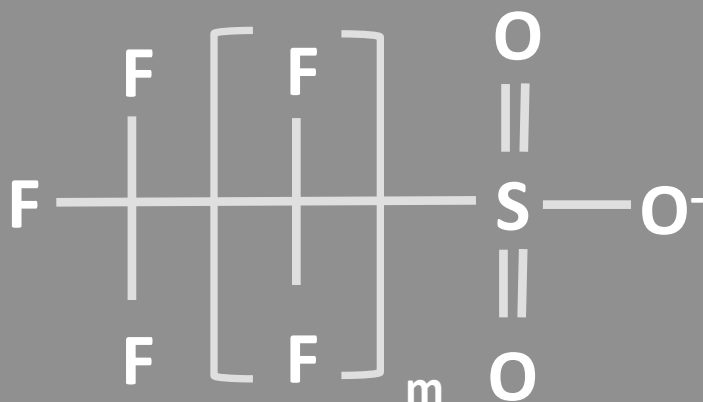
$m = 6 \Rightarrow$ PFOA



PFOA (**Per**fluorooctanoic acid)

Per = fully fluorinated alkyl tail (No hydrogen)

Perfluoroalkyl sulfonates (PFSA's)



Examples:

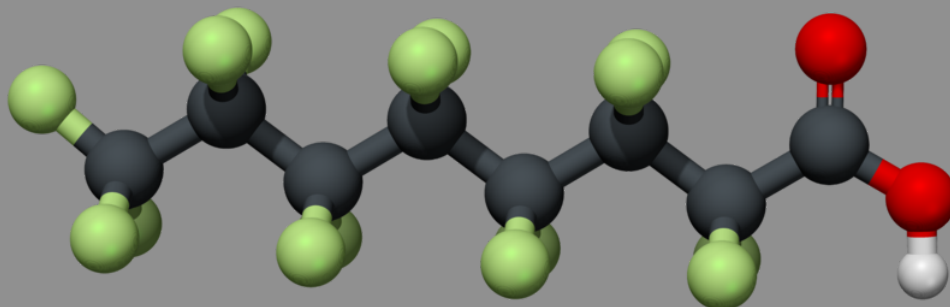
$m = 3 \Rightarrow$ PFBS

$m = 5 \Rightarrow$ PFHxS

$m = 7 \Rightarrow$ PFOS



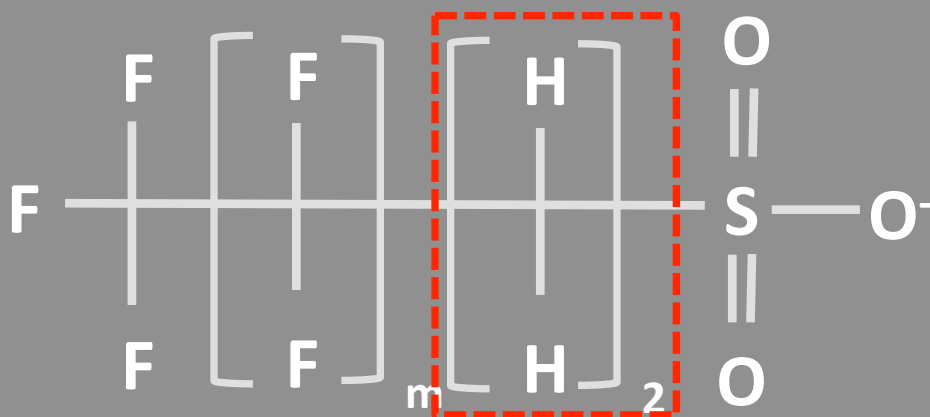
Soluble and
persistent



PFOS (**Per**fluorooctane
sulfonate)

Poly = partially fluorinated alkyl tail

Polyfluoroalkyl substances: Fluorotelomer sulfonates



Examples:

$m = 5 \Rightarrow 6:2 \text{ FtS}$

$m = 7 \Rightarrow 8:2 \text{ FtS}$



Biodegradable

General nomenclature

PFX_Y



Functional group:

A = Acid, S = Sulfonate and CH = Alcohol

Carbon chain length:

O = Octa (8) and Hx = Hexa (6)

PF: Perfluoroalkyl

FT: Fluorotelomer

Major sources of PFAS in the environment

Major sources of PFAS in the environment

1. Production and manufacturing facilities

- ✓ Textile and leather (coatings to repel water, oil and stains)
- ✓ Paper products (surface coatings to repel grease and moisture). Non-food and food-contact materials
- ✓ Metal plating and etching (corrosion prevention, wetting agent...)

Major sources of PFAS in the environment

1. Production and manufacturing facilities (Cont.)

- ✓ Wire manufacturing
- ✓ Industrial surfactants, resins, molds, plastics
(Manufacture of plastics and fluoropolymers, rubber and compression mold release coatings)
- ✓ Semiconductor industry

Major sources of PFAS in the environment

2. Fluorine-containing firefighting foams

Firefighting foams are a complex mixture of both known and unidentified PFAS of differing molecular structures present in varying proportions

Foams were produced to meet firefighting specifications, rather than formulated to contain a specified mixture of PFAS

These types of firefighting foams have been in use since the 1960s

Major sources of PFAS in the environment

3. Waste disposal

Disposal of wastes generated during primary PFAS production and secondary manufacturing using PFAS can be sources of PFAS environmental contamination

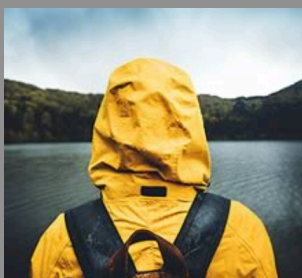
Other sources of PFAS in the environment

4. Use of commercial and consumer products

PFAS are widely used in consumer products and household applications, with a diverse mixture of PFAS found in daily use in varying concentrations

Other sources of PFAS in the environment

4. Use of commercial and consumer products



Outdoor clothing



Outdoor equipment



Stain resistant clothing



Stain resistant furniture
& furnishings



Grease proof take-away
packaging



Non-stick cookware



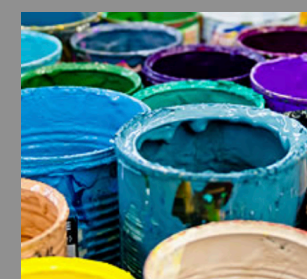
Baking paper & baking
cases



Ski & snowboard wax



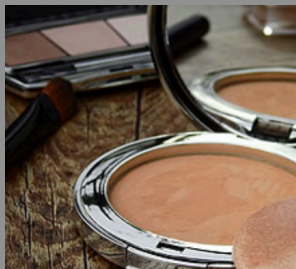
Bike oil



Paints adhesives &
sealants

Other sources of PFAS in the environment

4. Use of commercial and consumer products



Cosmetics



Cleaning products

...

Concentration limit values of PFAS

Concentration limit values of PFAS

Modern, commercially available analytical techniques identify only up to 25-30 individual PFAS compounds

PFAS	Units	LQ	Groundwater			Drinking water							
			Germany (Quotient)	Switzerland	Texas	Germany	Switzerland	Sweden	Denmark	Italy	USA	New Jersey	Australia
PFBA	µg/l	0,01	C/10	700	71	10			0,1	7			
PFBS	µg/l	0,015	C/6	700	34	6		0,09	0,1	3			
PFPeA	µg/l	0,01		100	0,093	3		0,09	0,1	3			
PFPeS	µg/l	0,015											
PFHxA	µg/l	0,01	C/6	40	0,093	6		0,09	0,1	1			
PFHxS	µg/l	0,015	C/0,1	0,7	0,093	0,1	0,3	0,09	0,1				0,07
PFHpA	µg/l	0,01		9	0,06	0,3		0,09	0,1				
PFHpS	µg/l	0,01				0,3							
PFOA	µg/l	0,01	C/0,1	4	0,29	0,1	0,5	0,09	0,1	0,5	0,07	0,014	0,06
PFOS	µg/l	0,01	C/0,1	0,7	0,06	0,1	0,3	0,09	0,1	0,3	0,07	0,013	0,07
PFOSA	µg/l	0,01			0,29	0,1			0,1				
PFNA	µg/l	0,01	C/0,06		0,29	0,06			0,1			0,013	
PFDA	µg/l	0,01			0,37	0,1			0,1				
PFDS	µg/l	0,01			0,29								
PFUnA	µg/l	0,01			0,29								
PFDoA	µg/l	0,01			0,29								
PFTTrA	µg/l	0,01											
PFTA	µg/l	0,01											
7 PFC			$\Sigma(C/Seuil) < 1$										

Site investigation challenges

Field preparation and planning:

Avoid cross-contamination and false positive results since PFAS are potentially present in variety of commonly-used materials

Sampling considerations

- ✓ Clothing
- ✓ Sampling equipment
- ✓ Food packaging
- ✓ Cosmetics, sunscreen, bug spray
- ✓ Personal protective equipment

Treatment technologies

Factors specifically challenging for PFAS remediation include:

- ✓ • Multiple ionic states
- ✓ • Variable isomers
- ✓ • Differing alkyl groups
- ✓ • Past remediation effects
- ✓ • Common co-contaminants

Treatment technologies

- ✓ Excavation and incineration is the primary approach for soils
- ✓ Adsorption onto granulated activated carbon (GAC) is the most widespread full-scale treatment method currently used for groundwater
- ✓ Other sorption and filtration processes
 - Membrane filtration
 - Ion exchange resins
 - Nano-filtration and reverse osmosis
- ✓ Need for destructive technologies

Treatment technologies

- ✓ In situ treatment
 - In situ injectable carbon-based systems
 - In situ chemical oxidation
- ✓ Other potential treatment technologies
 - Advance oxidation: ultraviolet radiation with hydrogen peroxide, or ozone and peroxide, or heat-activated persulfate
 - Electrocoagulation: an electrical current is applied to a solution along with a chemical coagulant to facilitate removal of PFAS

PFAS forensics in practice

Environmental forensic techniques

- ✓ Historical document review
- ✓ Chemical fingerprinting
 - Comprehensive chemical analysis
 - Homolog groups
 - Precursor compounds
 - Fluorotelomers
 - Branched vs. linear isomers
 - Chiral fingerprinting
- ✓ Multivariate statistics - Receptor models
- ✓ Other techniques?
 - Signature chemicals
 - Isotopic fingerprinting
 - Tree-ring fingerprinting

Manufacturing

Electrochemical fluorination (ECF)

- ✓ Licensed in 1945 by 3M => Commercial production started in 1951
- ✓ Since early 2000s, no longer used for PFOS, PFOA and C8-based AFFF

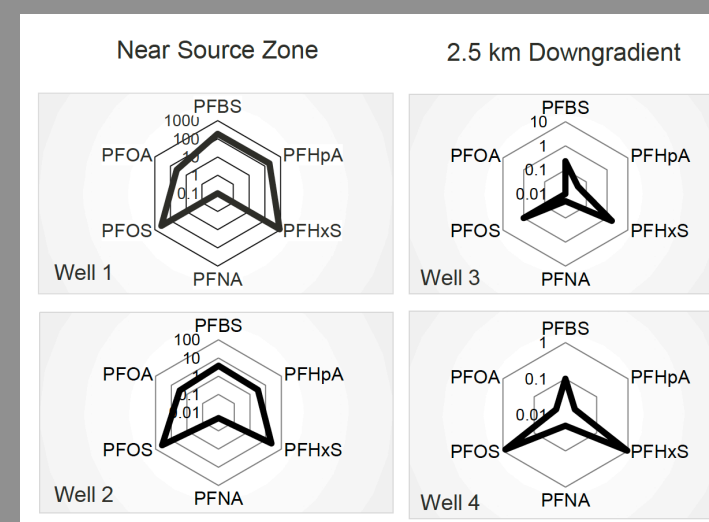
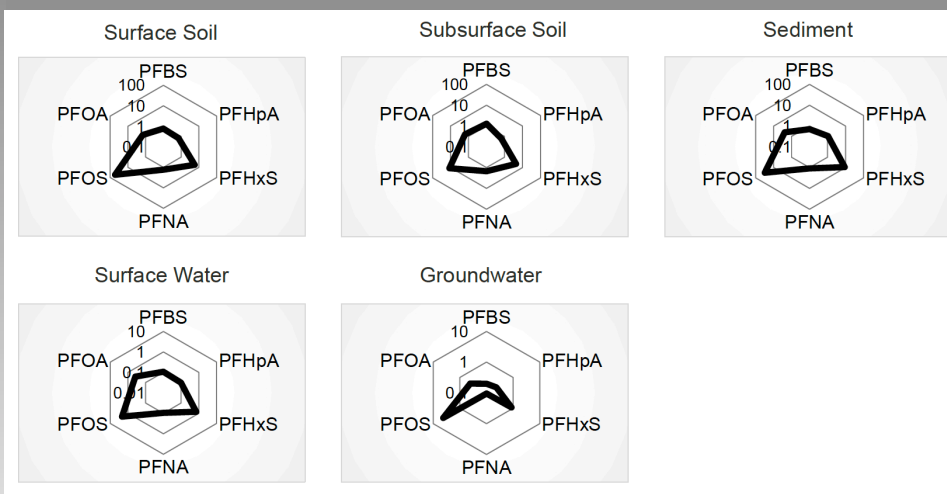
Telomerization

- ✓ Produces fluorotelomer sulfonates that can be found at AFFF sites
- ✓ Currently only for short-chain fluorotelomer-based products
- ✓ Produces mostly linear PFAS isomers with even-number of C atoms
- ✓ Since early 2000s, fluorotelomer-AFFF formulations (<C6) are predominant

Chemical fingerprinting

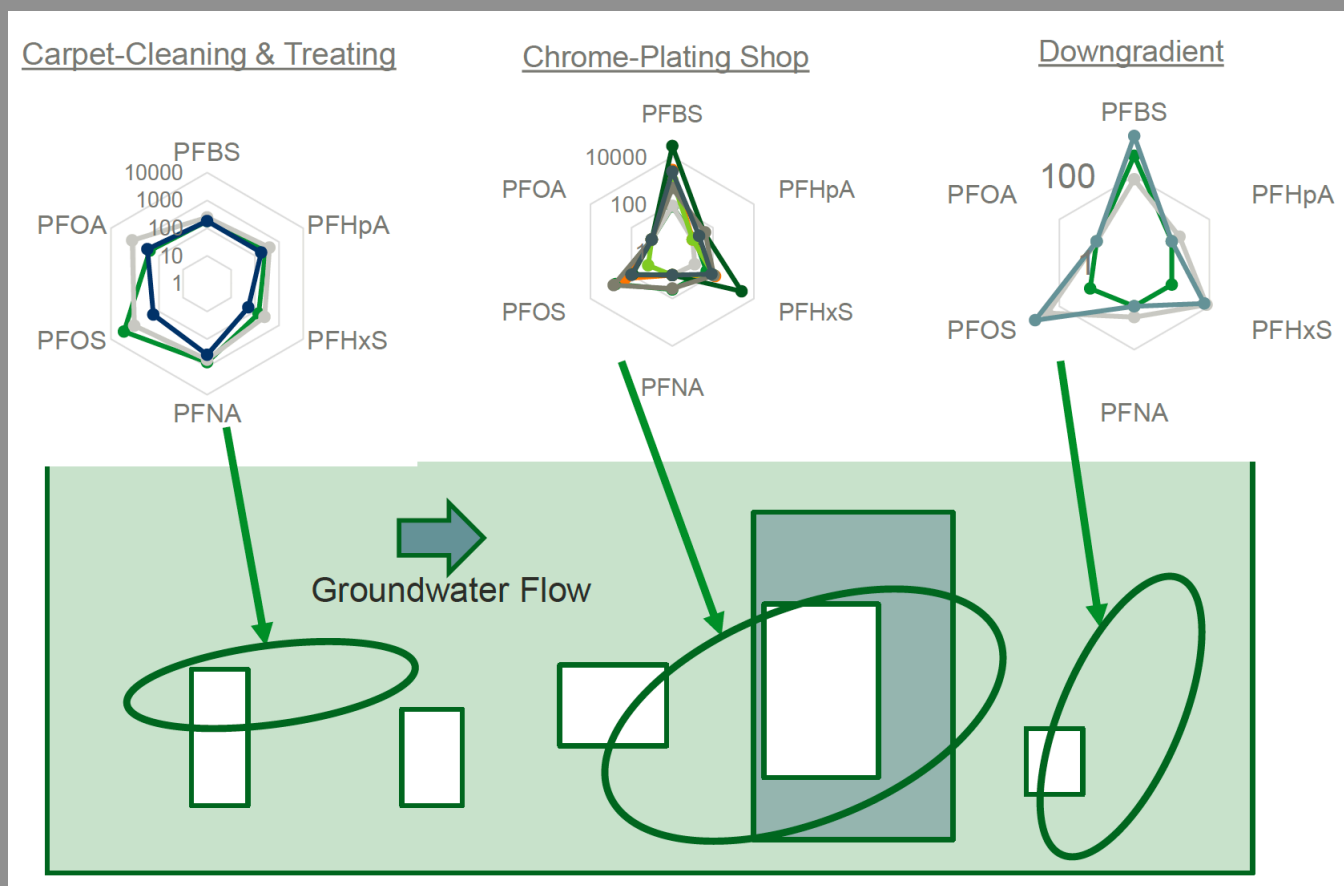
PFAS distribution

PFAS forensics in practice



Chemical fingerprinting

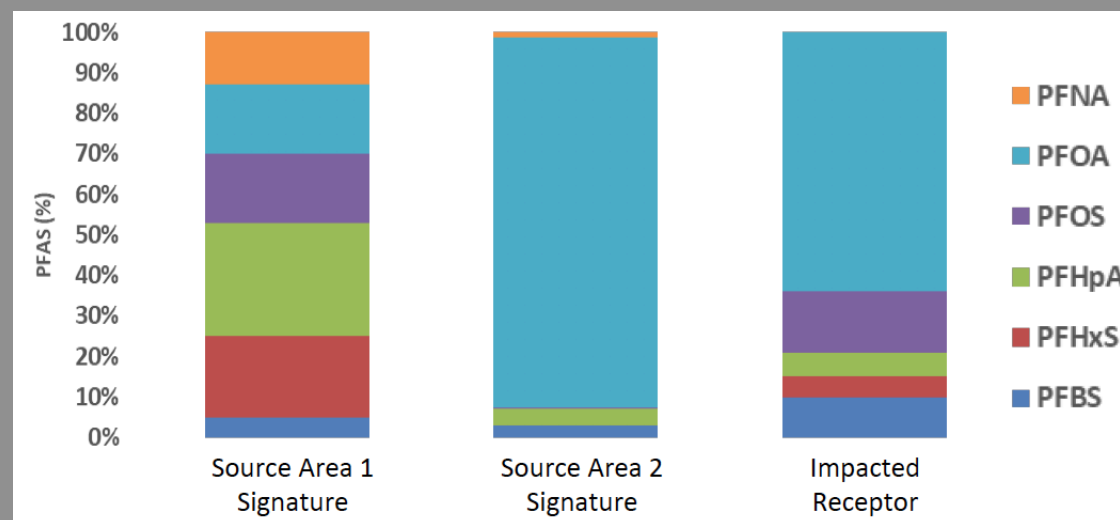
PFAS forensics in practice



Source: Hatton J, Di Guiseppi, B. 2018. PFAS Forensics. Presented at Battelle Conference on Chlorinated and Recalcitrant Compounds, 2018

Compounds ratio analysis

Compound ratios of perfluoroalkyl acids (PFAAs) and other PFAS compounds can be utilized to demonstrate unique signatures from different sources and provide evidence of multiple inputs to a receptor






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