Analytical Testing for Emerging Contaminants

November 2024

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Testing for Life

Definition

An “emerging contaminant” is a chemical or material that is characterised by a perceived, potential, or real threat to human health or the environment or a lack of published health standards.

A contaminant may also be “emerging” because a new source or a new pathway to humans has been discovered or a new detection method or treatment technology has been developed.

Emerging Contaminants

Metals

- Tungsten
- Lithium
- Strontium
- Manganese

Organics

- 1,4-Dioxane
- Perchlorate
- PFAS
- PPCPs

Particulates

- PM2.5 & PM10
- Microplastics
- Nanoplastics

Biological toxins

- Cyanotoxins
- Microcystin(s)
- Cylindrospermopsin
- Anatoxin(s)
- Saxitoxin(s)

Waterborne pathogens

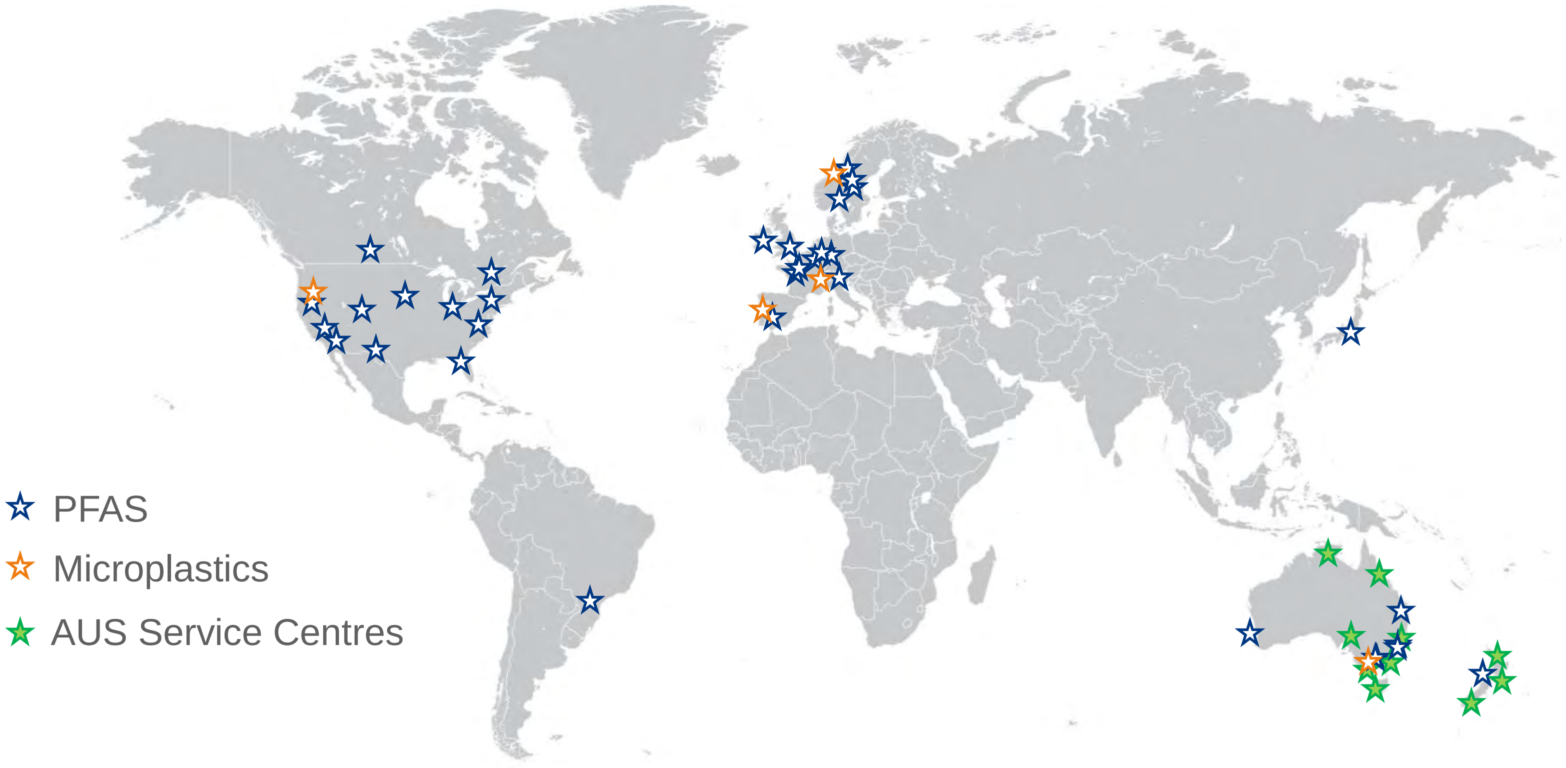
- *Naegleria fowleri* (brain-eating amoeba)
- *Legionella pneumophila*

Disinfection by-products (DBPs)

- Chlorate
- Formaldehyde
- NDMA

Antimicrobial resistance (AMR)

Eurofins Environment Testing Australia & Aotearoa NZ



PFAS Overview

PFAS Basics

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Example Uses

Semiconductor
Automotive
Aerospace
Pesticides

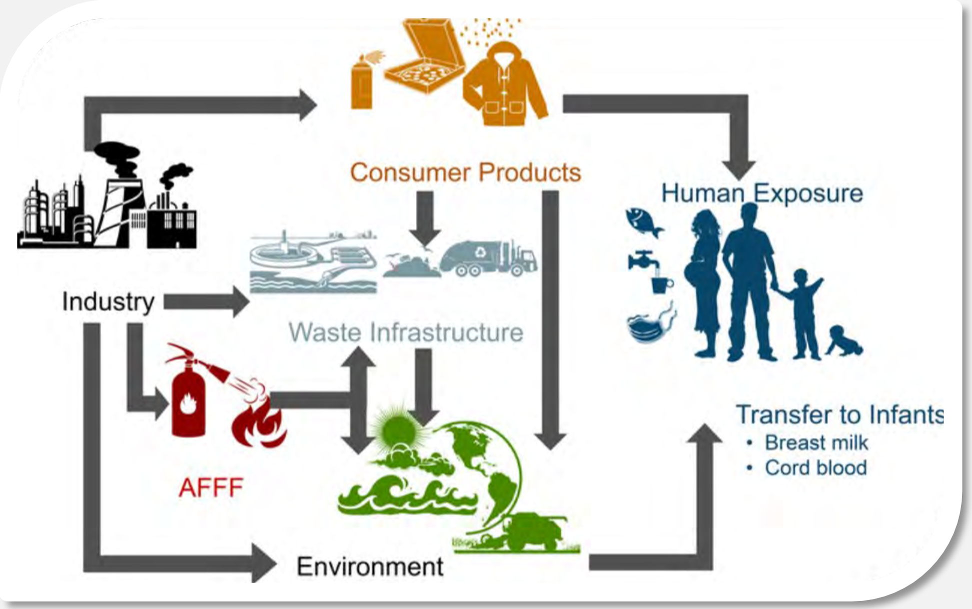
Paint
Chemicals
Personal Care/Cosmetics

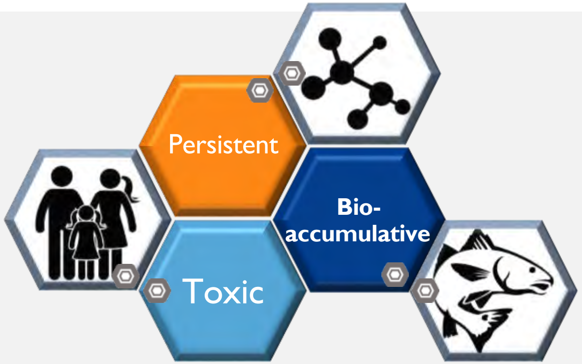
Textiles Carpet/Furniture
Paper/Packaging
Cookware
Lithium-ion batteries

Metal Finishing
Mining
Stone Cutting
Car Washes

Source: Sunderland et al. (2019)

How are we exposed to PFAS?





- Industrial Discharges
- Application of AFFF
- Waste Infrastructure
- Land Application of Biosolids
- Ambient and Indoor Air
- Indoor Dust
- Consumer Goods

Source: Sunderland et al. (2019)

PFAS Family - Nomenclature

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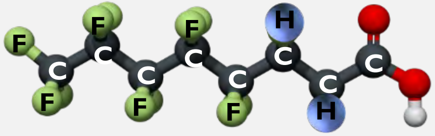
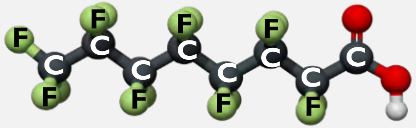
PFAS
Per- and Polyfluoroalkyl Substances

- **Polymers**
- **Non-Polymer**
  Per- and Polyfluorinated
  - **PFAAs**
    Perfluoroalkyl Acids
    - **PFSAs**
      Perfluoroalkylsulfonic acids
      - **PFOS**
    - **PFCAs**
      Perfluoroalkylcarboxylic acids
      - **PFOA**

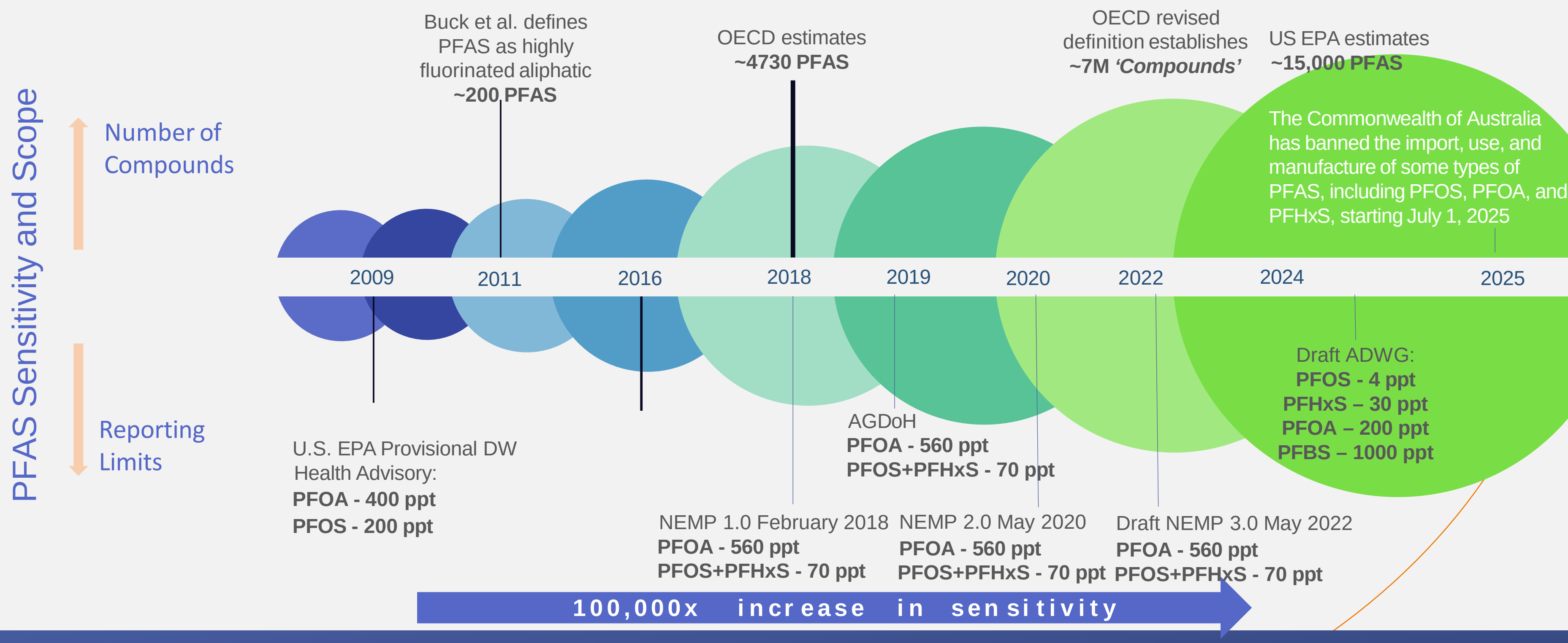
Completely & Incompletely Fluorinated



Completely Fluorinated



Defining PFAS: Evolution of the Science



Source – PubChem Classification Browser (nih.gov)

Analytical Methods

ANALYTICAL METHODS

Analysing for PFAS

There are some options!

Individual PFAS

Targeted PFAS by LC-MS/MS or GC-MS/MS

EPA 537.1

EPA 533

EPA 1633

Up to 100+ non-polymer PFAS compounds

Fluorine

Total or Organic Fluorine by CIC

“CIC-TOF”

EPA 1621

Total Fluorine (inorganic + organic)
Extractable Organic Fluorine (EOF)
Adsorbable Organic Fluorine (AOF)
(may include polymers)

Precursors

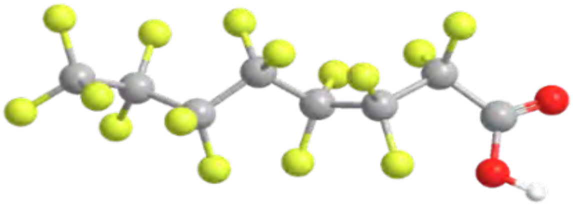
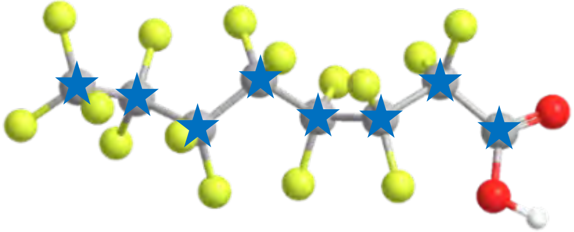
Total Oxidisable Precursors by LC/MS/MS

“TOP Assay”

Unknown PFAA precursors

Isotope Dilution

ISOTOPE DILUTION

	Native	$^{13}C_8$ labeled
	PFOS	PFOS
		
RT	7.59	7.59
Parent Ion	498.9	507.1
Quantification	498.9 → 79.9	507.1 → 79.9
Confirmation	498.9 → 98.9	507.1 → 98.9

★ = ^{13}C

EPA 1633

- Surface water, wastewater, groundwater, landfill leachate, soil, sediment, biosolids, and fish and shellfish tissue
- Targeted Analysis of 40 PFAS
- Multi-laboratory Validated method
- Aqueous – WAX SPE, carbon
- Solid–solvent extraction, WAX SPE, carbon
- LC-MS/MS utilising Isotope Dilution

EPA 1633 – Analyte List

Target Analyte	Target Analyte	Target Analyte	Target Analyte
PFBA	PFBS	PFOSA	PFMPA
PFPeA	PFPeS	NMeFOSA	PFMBA
PFHxA	PFHxS	NEtFOSA	NFDHA
PFHpA	PFHpS	NMeFOSAA	9Cl-PF3ONS
PFOA	PFOS	NEtFOSAA	11Cl-PF3OUdS
PFNA	PFNS	NMeFOSE	PFEESA
PFDA	PFDS	NEtFOSE	3:3 FTCA
PFUnA	PFDoS	HFPO-DA	5:3 FTCA
PFDoA	4:2 FTSA	ADONA	7:3 FTCA
PFTrDA	6:2 FTSA		
PFTeDA	8:2 FTSA		

ANALYTICAL METHODS

Identifying "Unknown Unknowns"!

Non-Targeted PFAS analysis using LC-QToF-MS or GC-QToF-MS

Per- and Polyfluoroalkyl Substances – Non-Targeted Analysis Interlaboratory Study Final Report

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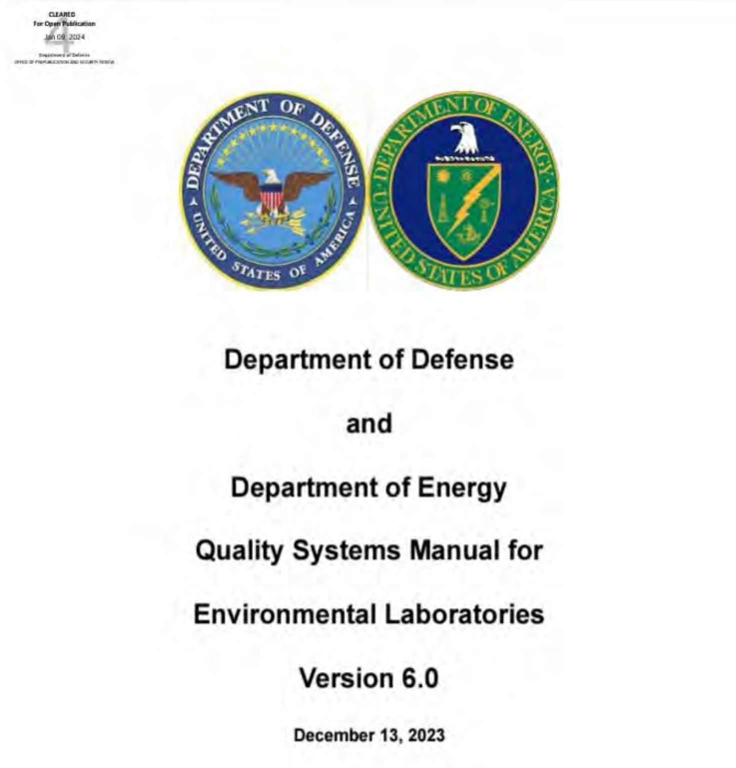
https://doi.org/10.6028/NIST.IR.8544

NIST NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY U.S. DEPARTMENT OF COMMERCE

Data Reporting

Data Deliverables

- Excel Tables
- Level II data packages (PDF)
- Level IV validation packages (PDF)
- Electronic Data Deliverables
    - ESdat, EQuIS, csv etc.


CLEARED
For Open Publication
Jan 09, 2024

Department of Defense and Department of Energy Quality Systems Manual for Environmental Laboratories

Version 6.0

December 13, 2023

Data Deliverables

DoD Environmental Data Quality Workgroup Fact Sheet
Subject: QSM Version 6.0 Accreditation/Implementation
Guidance Update July 21, 2024

Bottom Line Up Front:

All ELAP Laboratories must be accredited to QSM 6.0 by June 30, 2026. While the EDQW does not believe that data defensibility is significantly impacted by the changes from QSM 5.4 to 6.0, there are many changes which simplify requirements, streamline processes, and provide better consistency with other accreditation standards and underlying method requirements for analysis. The EDQW recommends laboratories compare the requirements of QSM 5.4 and 6.0 to determine the benefits of moving to QSM 6.0 during the laboratory's routine accreditation cycle or earlier.

Data Deliverables

Client Sample ID			[illegible]
Sample Matrix			Water
Eurofins Sample No.			B24-Oc0081531
Date Sampled			Oct 30, 2024
Test/Reference	LOR	Unit	
Perfluoroalkyl carboxylic acids (PFCAs) - Ultra Trace			
Perfluorobutanoic acid (PFBA)[N11]	0.005	ug/L	12
Perfluorodecanoic acid (PFDA)[N11]	0.001	ug/L	0.029
Perfluorododecanoic acid (PFDoDA)[N11]	0.001	ug/L	< 0.001
Perfluoroheptanoic acid (PFHpA)[N11]	0.001	ug/L	[N09]17
Perfluorohexanoic acid (PFHxA)[N11]	0.001	ug/L	[N09]56
Perfluorononanoic acid (PFNA)[N11]	0.001	ug/L	[N09]1.4
Perfluorooctanoic acid (PFOA)[N11]	0.001	ug/L	[N09]23
Perfluoropentanoic acid (PFPeA)[N11]	0.001	ug/L	33
Perfluorotetradecanoic acid (PFTeDA)[N11]	0.001	ug/L	< 0.001
Perfluorotridecanoic acid (PFTrDA)[N15]	0.001	ug/L	< 0.001
Perfluoroundecanoic acid (PFUnDA)[N11]	0.001	ug/L	0.001

13C4-PFBA (surr.)	1	%	89
13C5-PFPeA (surr.)	1	%	102
13C5-PFHxA (surr.)	1	%	91
13C4-PFHpA (surr.)	1	%	88
13C8-PFOA (surr.)	1	%	139
13C5-PFNA (surr.)	1	%	90
13C6-PFDA (surr.)	1	%	60
13C2-PFUnDA (surr.)	1	%	57
13C2-PFDoDA (surr.)	1	%	60
13C2-PFTeDA (surr.)	1	%	55

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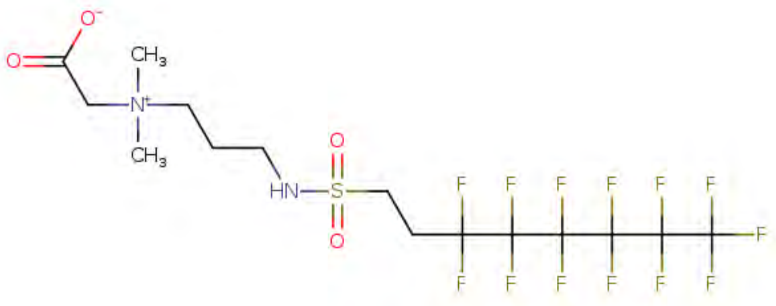
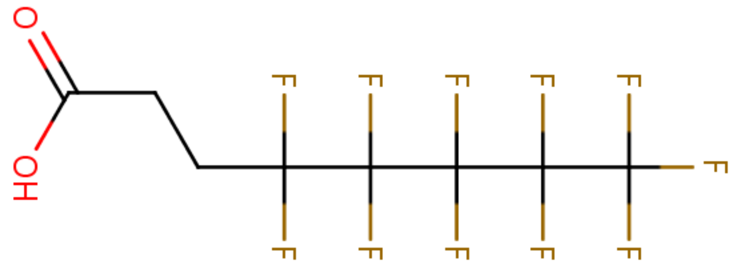
Data Deliverables

PFASs Summations			
Sum (PFHxS + PFOS)*	0.001	ug/L	480
Sum of US EPA PFAS (PFOS + PFOA)*	0.001	ug/L	333
Sum of enHealth PFAS (PFHxS + PFOS + PFOA)*	0.001	ug/L	503
Sum of WA DWER PFAS (n=10)*	0.005	ug/L	644.91
Sum of PFASs (n=30)*	0.005	ug/L	696.108
Per- and Polyfluoroalkyl Substances (PFAS) - 8 additional compounds			
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS)	0.005	ug/L	[G01]< 0.5
3:3 Fluorotelomercarboxylic acid (3:3 FTCA)	0.005	ug/L	0.71
4.8-dioxa-3H-perfluorononanoic acid (ADONA)	0.005	ug/L	[G01]< 0.5
5:3 Fluorotelomer carboxylic acid (5:3 FTCA)	0.005	ug/L	14
6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB)	0.005	ug/L	0.012
9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (9Cl-PF3ONS)	0.005	ug/L	[G01]< 1
Hexafluoropropylene oxide dimer acid (HFPO-DA)(GenX)	0.005	ug/L	< 0.005
Perfluoroethylcyclohexane sulfonate (PFECHS)	0.005	ug/L	[G01]< 0.5





How do PFAS get into biosolids?

PFAS load from cosmetics at WWTPs?!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News

EnviroNote

EnviroNote 1136 - April 2024

PFAS in Cosmetics

What are PFAS and why are they used in Cosmetics?

Per- and polyfluoroalkyl substances (PFAS) are a diverse group of human-made chemicals used in a wide range of consumer and industrial products. These compounds contain fluorinated carbon chains and are known for their persistence in the environment, earning them the nickname "forever chemicals" and are broadly classified as both polymers and non-polymers. While most interest has been in firefighting foams, certain PFAS are intentionally added as ingredients in cosmetic products. They are used in cosmetics in the following ways:

1. Conditioning and Smoothing: PFAS are used in cosmetics to condition and smooth the skin, giving it a shiny appearance.
2. Consistency and Texture: They also affect product consistency and texture, contributing to the overall feel and application of cosmetic items.

Common PFAS used as ingredients in cosmetics include:

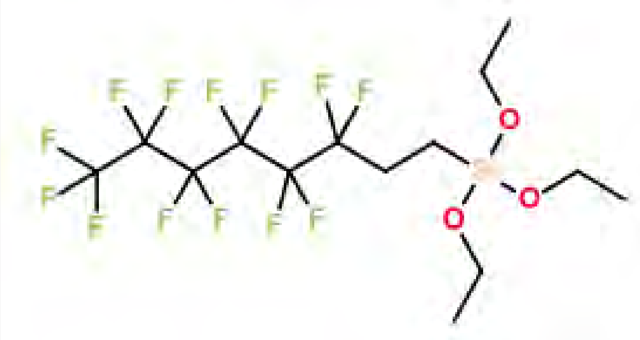
- PTFE (polytetrafluoroethylene)
- Perfluorooctyl triethoxysilane
- Perfluorononyl dimethicone
- Perfluorodecalin
- Perfluorohexane

It's important to note that not all PFAS found in cosmetics can be readily measured due to their specific chemical composition. Research on the presence and potential health risks of PFAS in cosmetics is still limited. While some studies have detected PFAS in cosmetics, more research is needed to understand their toxicological profiles, skin absorption levels, and potential health risks. The FDA continues to monitor the literature for toxicity studies and dermal absorption information related to PFAS in cosmetics.

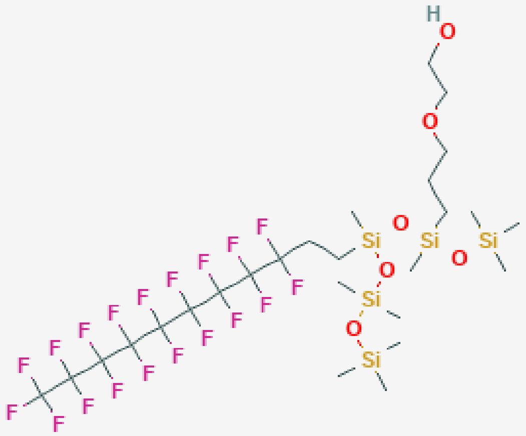
The presence of per- and polyfluoroalkyl substances (PFAS) in cosmetics raises important concerns that cover the following:

1. Undisclosed PFAS: Laboratory analyses have detected PFAS in cosmetic products, but many of these compounds are not explicitly disclosed in the listed ingredients. This lack of transparency makes it challenging for consumers to make informed choices about the products they use.
2. Direct Contact with Skin, Eyes, and Mouth: Cosmetics are applied directly to the skin, eyes, and mouth. As a result, any PFAS present in these products can potentially be absorbed or ingested by users. This direct contact increases the risk of exposure.
3. Enhanced Absorption and Ingestion: Enhanced absorption occurs when PFAS molecules penetrate the skin barrier more effectively due to their unique properties. Similarly, ingestion can occur if users accidentally ingest cosmetic products containing PFAS.
4. Characterisation and Toxicological Studies: To mitigate exposure, it is crucial to conduct thorough characterisation and toxicological studies on PFAS compounds present in cosmetic formulations. These studies help identify specific PFAS, assess their toxicity, and determine safe exposure levels.

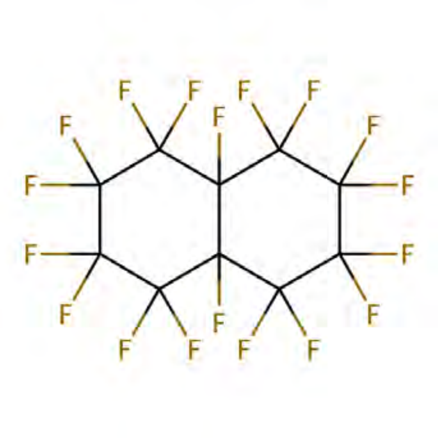
PFAS load from cosmetics at WWTPs?!



Perfluorooctyl triethoxysilane



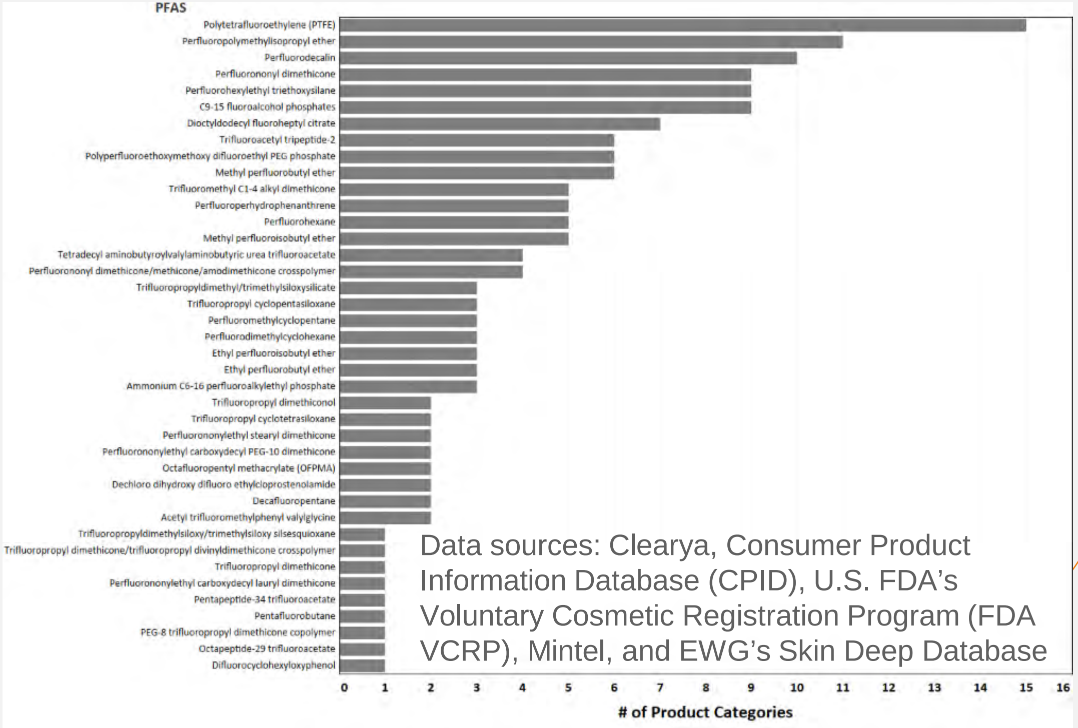
Perfluorononylethyl PEG-8 Dimethicone



Perfluorodecalin

PFAS load from cosmetics at WWTPs?!

Cosmetics sold in California during a one-year period contain 650 to 56,000 kg PFAS, including 330 to 20,000 kg fluorinated side chains



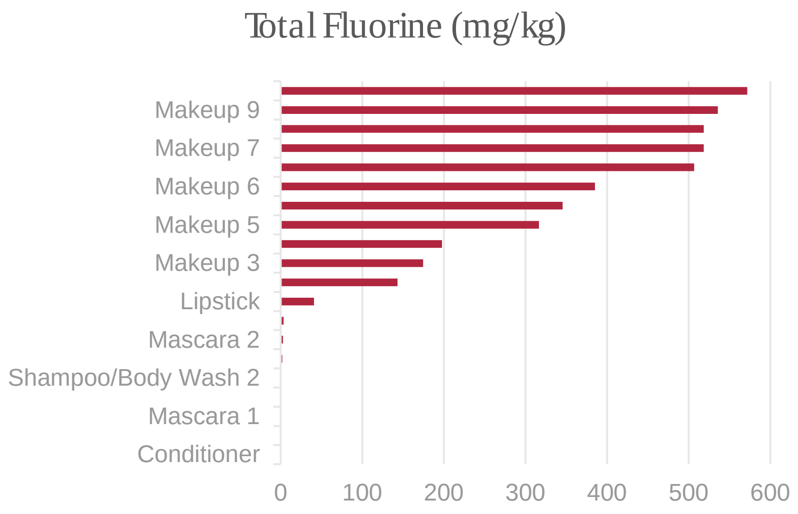
Data sources: Clearya, Consumer Product Information Database (CPID), U.S. FDA's Voluntary Cosmetic Registration Program (FDA VCRP), Mintel, and EWG's Skin Deep Database

The Total Mass of Per- and Polyfluoroalkyl Substances (PFASs) in California Cosmetics
Simona A. Bălan, Thomas A. Bruton, Kyle Harris, Logan Hayes, Christopher P. Leonetti, Vivek C. Mathrani, Abigail E. Noble, and Diana S. C. Phelps
Environmental Science & Technology 2024 58 (27), 12101-12112
DOI: 10.1021/acs.est.3c06539

PFAS load from cosmetics at WWTPs?!

Total Organic Fluorine or Total Fluorine **Combustion Ion Chromatography**

PFAS load from cosmetics at WWTPs?!



- 20 different Cosmetic Products tested for TF
  - Blush
  - Conditioner
  - Cream
  - Lipstick
  - Makeup
  - Mascara
  - Shampoo/Body Wash
- TF concentration range: **0 - 572 mg F/kg**
- **Mascara 3** contained **>500 mg F/kg** was isolated to be tested further

THE UNIVERSITY OF AUCKLAND NEW ZEALAND

PFAS load from compostable products at WWTPs?!

*Not actual products pictured to preserve anonymity of brands

PFAS load from compostable products at WWTPs?!

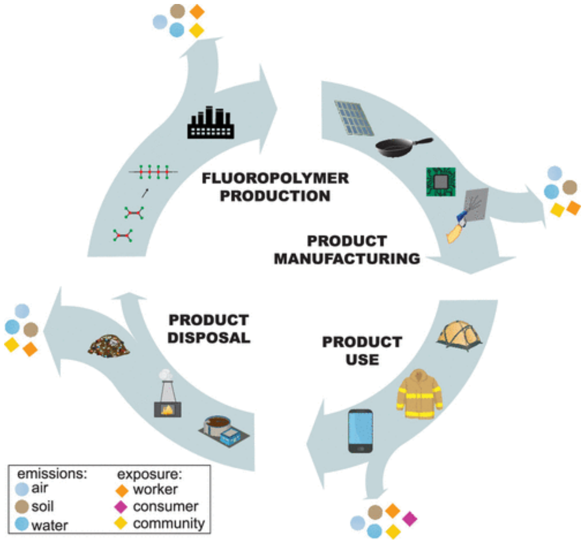
Item	TF (mg/kg)
Aqueous-coated Paper Cup	**6.2**
PLA Cold Cup	< 5
PLA-lined Paper Cup	**29**
Compostable Tea Bag	**15**
Bin Liner	< 5
Flat Brown Paper Bag	**14**
Newspaper	< 5
Cardboard Pizza Box	**15**
Wooden Cutlery	< 5
Unlined Fibre Tray (Sugarcane)	**810**

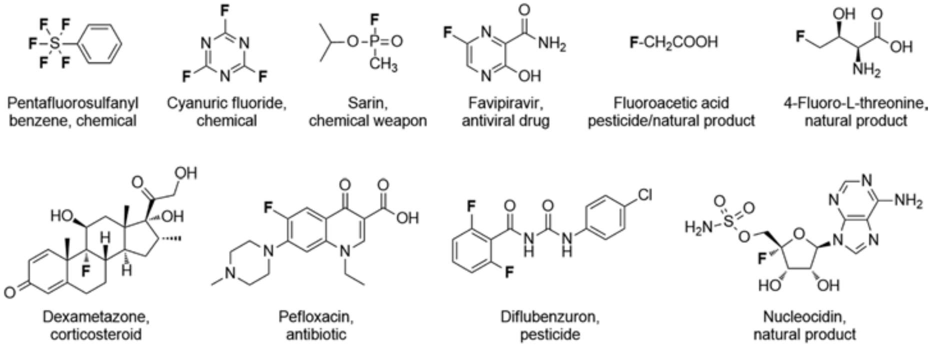
LC-MS/MS screening hits	% Peak area relative to largest peak (Linear PFOA)
PFPrA	23.44
PFBA	9.76
PFPeA	3.12
PFHxA	33.91
PFHpA	4.47
6:2 FTUCA	37.53
6:2 FTCA	1.05
Br_PFOA	**10.99**
PFOA	**100**
5:3 FTCA	0.31
6:2 FTOH	0.55

6:2 FTOH and its breakdown products 6:2 FTCA, 6:2 FTUCA, 5:3 FTCA, PFHxA, PFPeA, PFBA, and PFPrA are likely coming from the breakdown of a fluoropolymer and will be where the bulk of the PFAS may be hiding

PFOA is a concern (~100 µg/kg).

PFAS load from compostable products at WWTPs?!





Source: *Environ. Sci. Technol. 2020, 54, 20, 12820–12828*

Microplastics Overview

Environment Testing

Emerging Contaminants - Microplastics

Microplastics are increasingly recognised as one of the most pervasive environmental pollutants of modern times. These small plastic particles, which are less than 5 mm in size, pose significant threats to ecosystems, wildlife, and potentially human health.

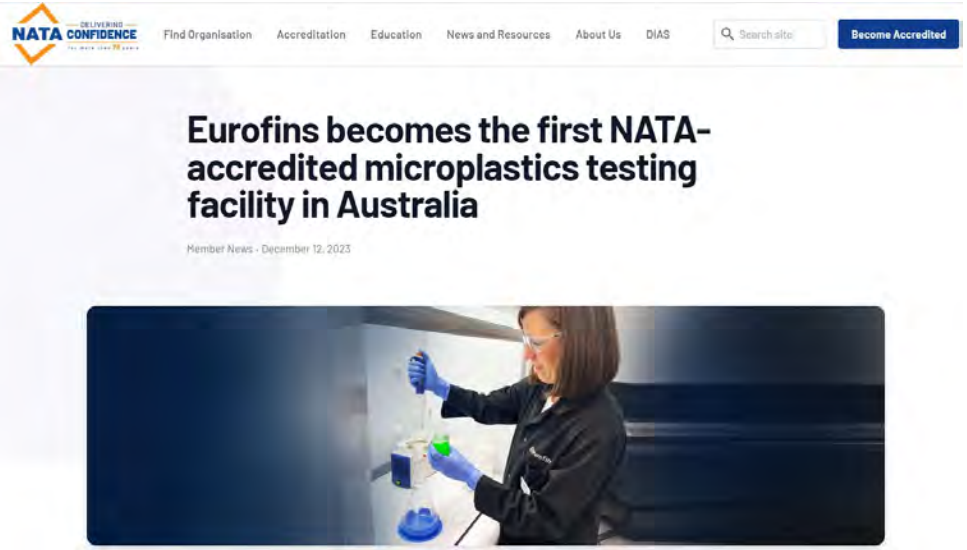
What Are Microplastics?

Microplastics are small plastic fragments that originate from various sources. There are two types:

- **Primary microplastics** are intentionally manufactured small plastics, such as microbeads found in personal care products like face scrubs, toothpaste, and cleansers. They are also used in industrial processes, such as abrasives in blasting techniques.
- **Secondary microplastics** result from the breakdown of larger plastic items, such as water bottles, plastic bags, and fishing nets. Environmental factors like sunlight, wind, and ocean currents degrade these plastics into smaller pieces over time.

These tiny plastic particles have been found in the air, water, and food consumed daily. Studies have even detected microplastics in human blood and organs, raising concerns about long-term health risks.

Emerging Contaminants - Microplastics

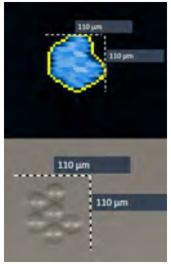


Particulates

- PM2.5 & PM10
- **Microplastics**
- Nanoplastics

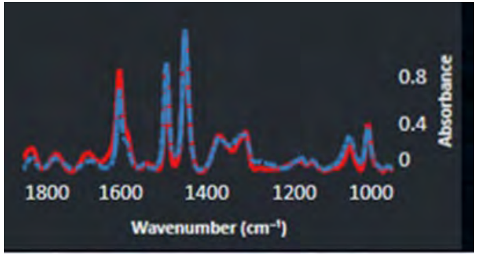
Laser Direct Infrared (LDIR) Imaging system

Imaging system: Particle enumeration and morphology



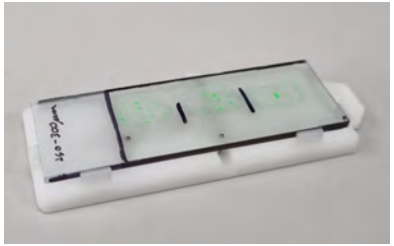
Information on:
- Number
- Size
- Morphology
- Colour

LDIR: Polymer identification



Library comparison – determination of polymer

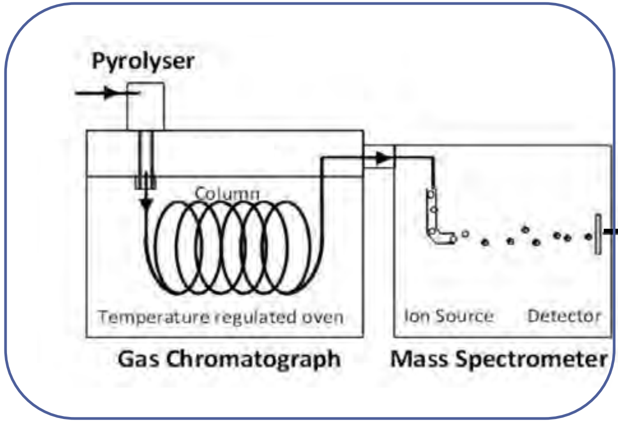
Information on:
- Type



Instrumentation

New

Pyrolysis – GC-MS/MS



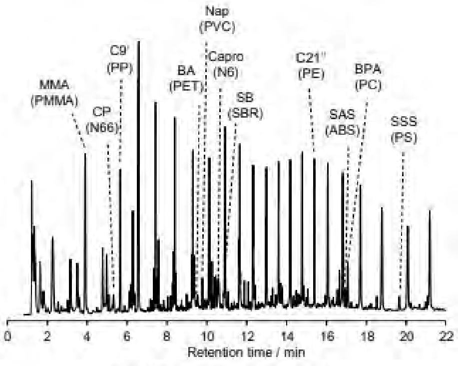


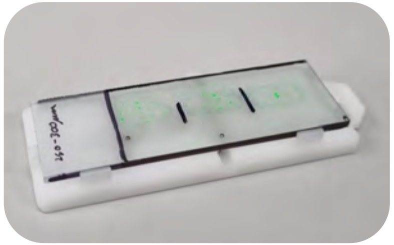
Fig. 2 Pyrogram of MPs-SiO2.

Information on:

- Type
- Concentration (µg/L, mg/kg)

Sample Preparation Methods

Cleanup → Concentration



ASTM INTERNATIONAL
Helping our world work better

CALIFORNIA
Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

ISO

Clean up - Removal of material that interferes with the microplastic analysis

Organic matter

Leaves, twigs, hair, cotton fibres, algae, proteins, fats, animals

Fenton's Reagent
(H_2O_2 + Fe(II))
NaOH, KOH
HCl
Enzymatic digestion

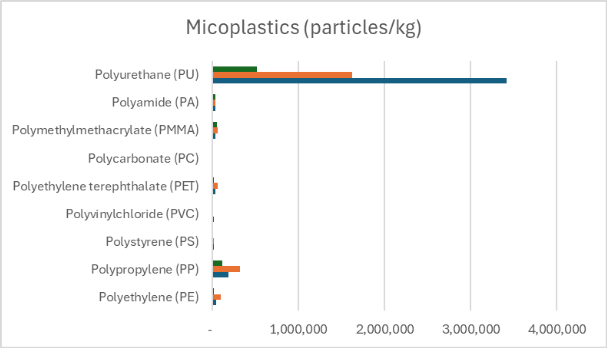
Veerasingam et al., 2016a

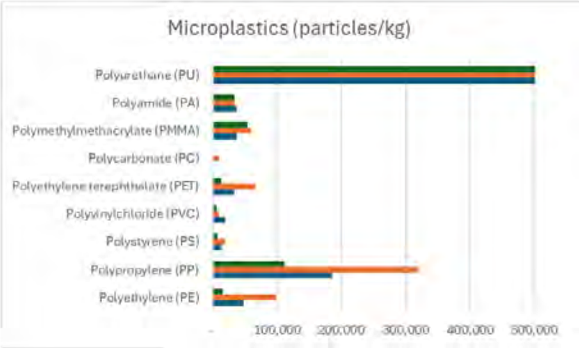
Inorganic matter

Sand, soil, shells, salt crystals, glass

Sieving
Filtration
Density separation

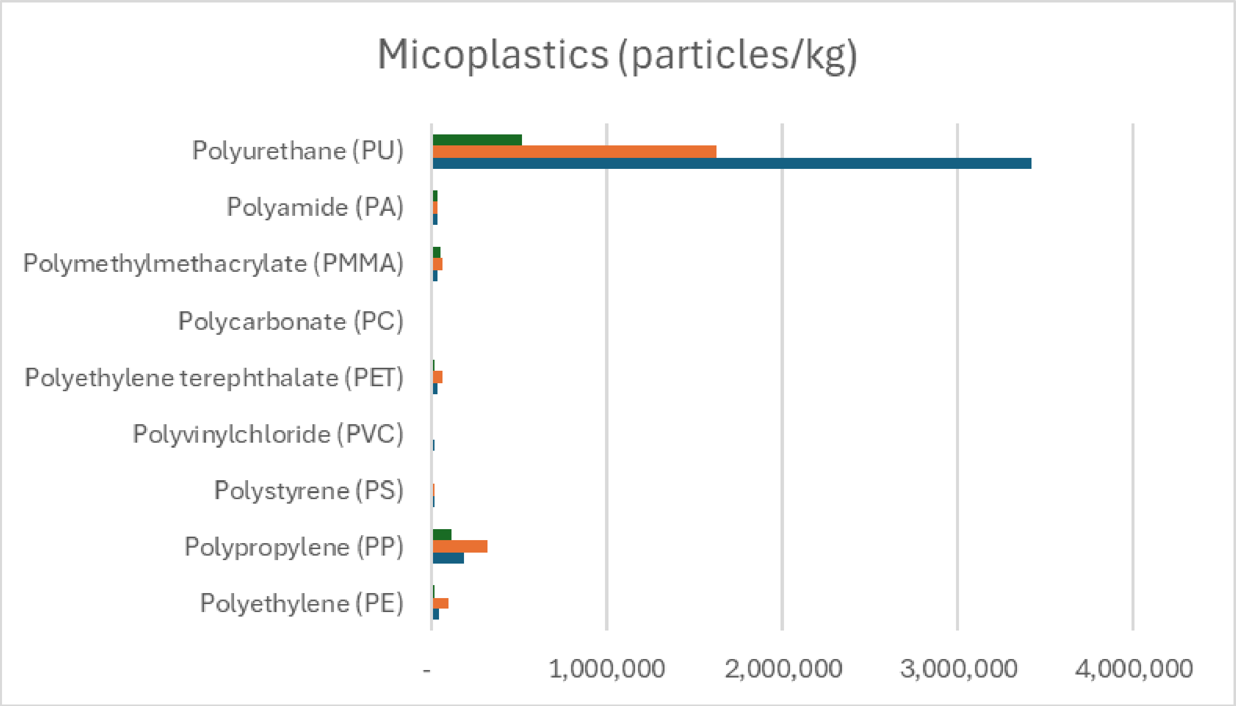
4 Trillion particles per tonne!!!



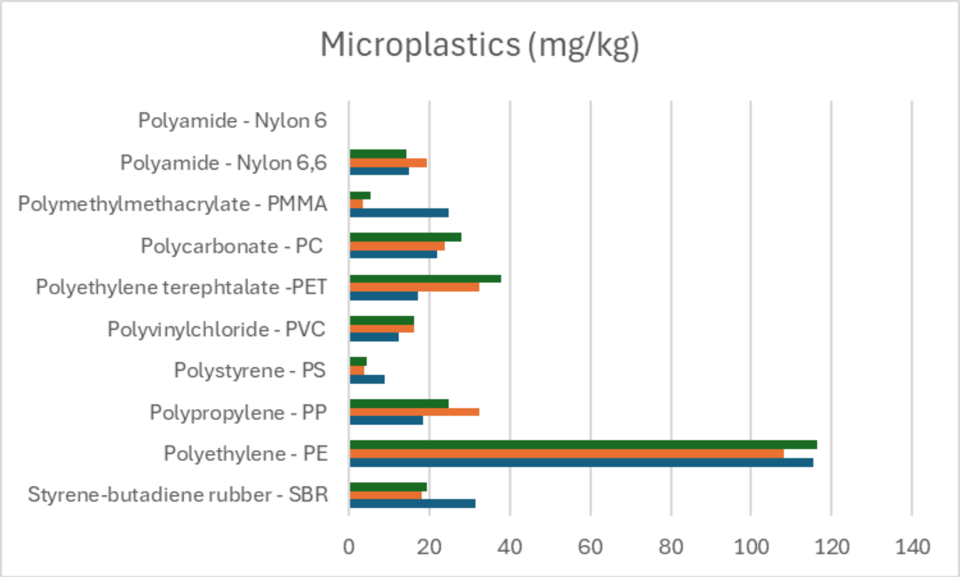


Biosolids - Microplastics

Biosolids - Microplastics



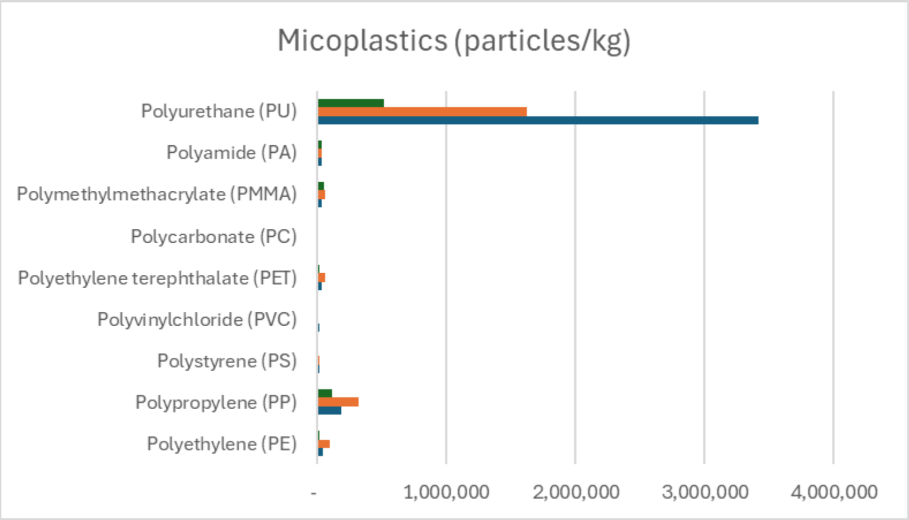
Biosolids - Microplastics

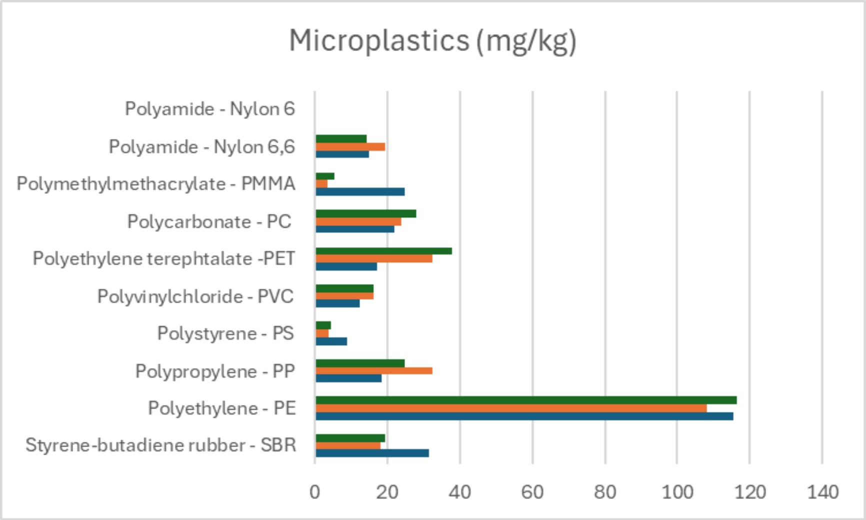


Emerging Contaminants - Microplastics

LDIR

Pyrolysis – GC-MS/MS



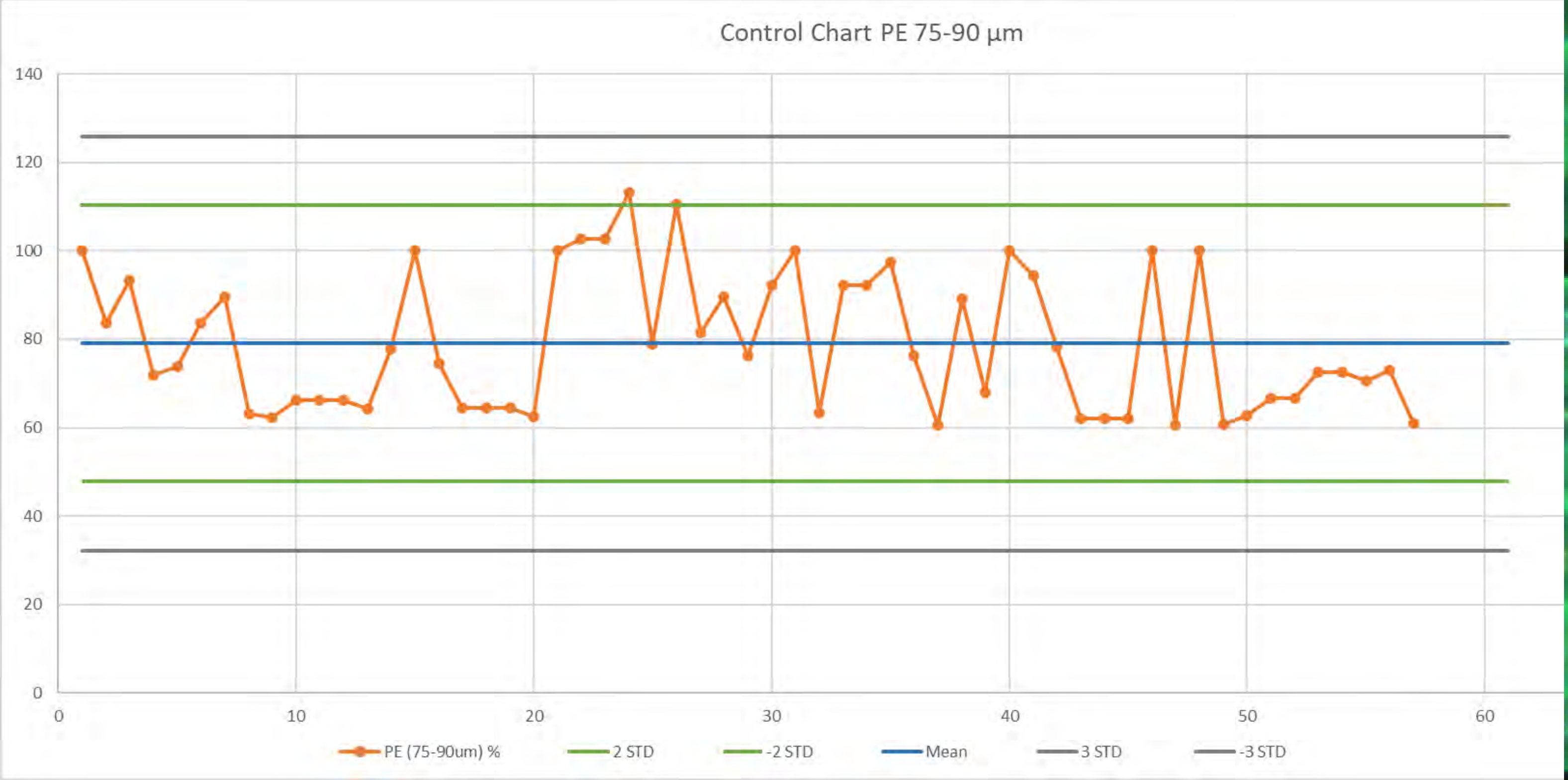


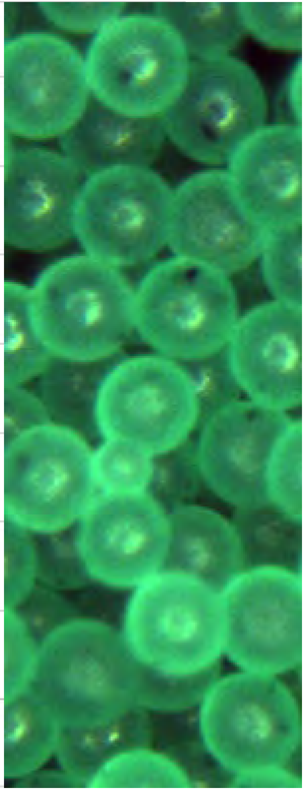
Interlaboratory/Proficiency Testing

Southern California Coastal Water Research Project (SCCWRP) 2021

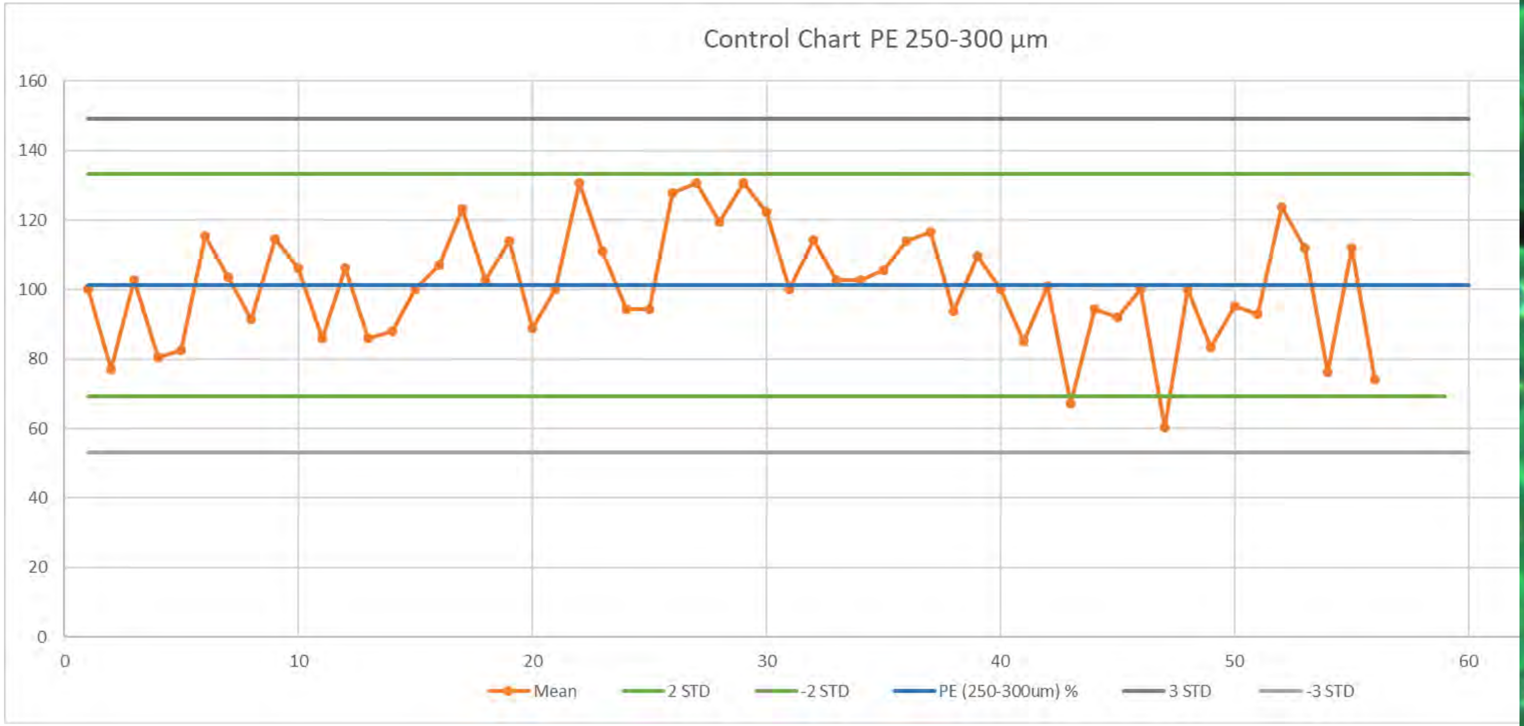
WEPAL-QUASIMEME/NORMAN Interlaboratory Study on the Analysis of Microplastics in Environmental Matrices Round 2024

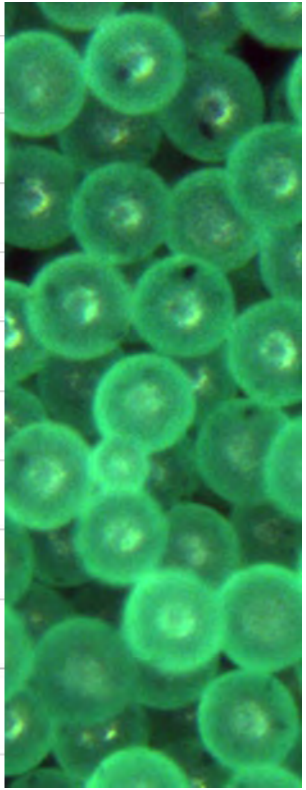
Green PE Microspheres 0.98g/mL 75µm-90µm





Green PE µpheres 0.98g/mL 250µm-3000µm





Summary

- Emerging contaminants represent a dynamic field of study, and ongoing research helps us better understand their behaviour, risks, and potential mitigation strategies
- Presently, most of these contaminants end up in biosolids.
- Advanced analytical techniques such as high-resolution mass spectrometry are being more widely used to help identify and quantify these unknown contaminants
- The ongoing research and attention to emerging contaminants are crucial for understanding their impact on the environment and human health

Thank you for your attention!