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PFAS SAMPLING VARIABILITY

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2022 MSSC Annual Salinity Summit

February 24th

Strategy for Success

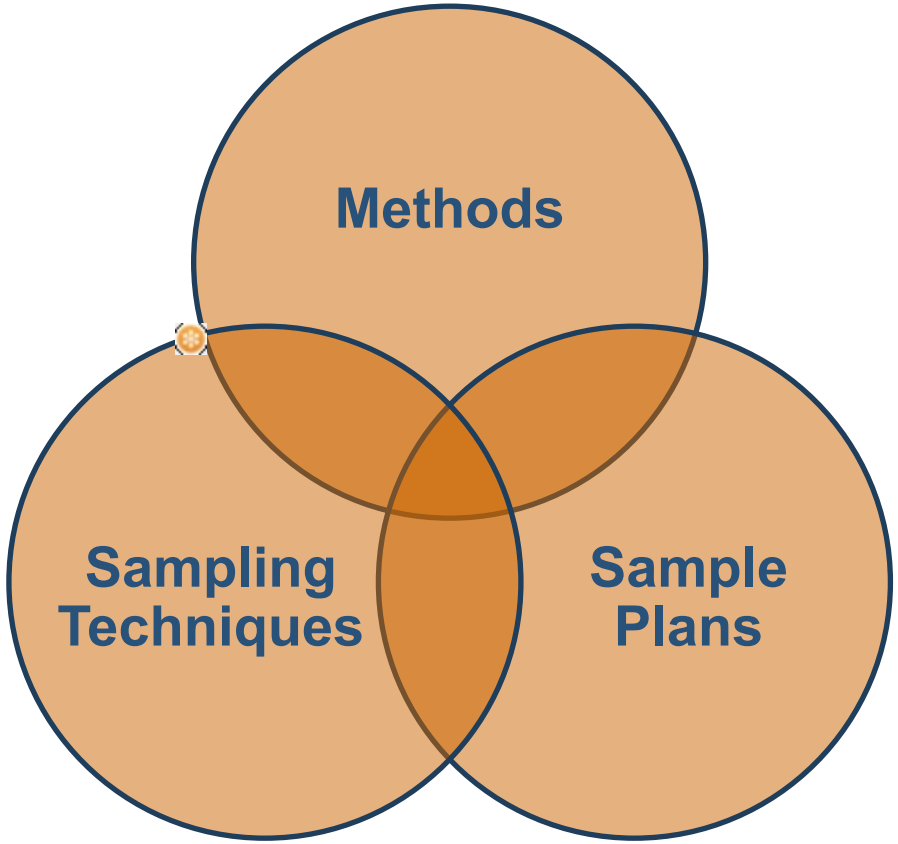


Selection of Sampling Techniques

And Analytical Methods

to Help Ensure

High Quality Data



Sampling



Sampling & Subsampling Strategies

- Sampling Precautions
- Field blanks
- Surface adsorption losses
- Treatment Process Sampling
- Sampling points

Sampling Instructions



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EPA 537/537.1 PFAS Sampling Instructions*

Sampling Clothing and Other Considerations

- Avoid wearing clothing or boots containing Gore-Tex or using materials containing Tyvek.
- Avoid using cosmetics, moisterizers, heavy fabric softeners on clothes the day of sampling.
- Sample PFAS first if your cooler contains other sample collection bottles! Other sample containers for other methods may have PFAS present.

Consideration of Supplies

- Do not use chemical ice packs.
- Felt-tip pens and permanent markers should not be used. Use regular ball point pens only.
- Avoid adhesive products like sticky notes.
- Avoid plastic clipboards, binders, hard covers, etc.
- Sampler must wash hands before wearing nitrile gloves in order to limit contamination during sampling.
- Only use the containers that have been provided by the laboratory.

Before Sampling

- Read all lab specific instructions before sampling.
- Plan to have samples collected just prior to the pick-up time of your overight carrier to limit potential on-site environmental contamination.
- If your sampling point has a faucet with an aerator, remove prior to collection of the samples.

Sampling Steps

- ***Caution: bottles may contain chemical preservatives. Avoid skin contact.***
- Wash hands and put on Nitrile gloves (provided). They must be worn during the sampling.
- Find the PFAS bottles in your Cooler: 2 - 250 mL (SB) or 2 - 275 mL (MON) plastic bottles pre-preserved with 1.25g Trizma.
- Flush the cold water sampling line approximately 15 minutes immediately prior to sampling. Slow the water stream before collection.
- Remove cap, fill the sample bottle to the neck, replace cap and tighten. Allow a small amount of head space for mixing the sample with preservative. Do not overfill. Do not flush away the preservative.
- Do not touch inside of the cap or around the edge of the bottle.
- Cap and invert at least 5 times to mix sample with preservative.
- Indicate sampling date, time and site on both the bottle labels and the enclosed Chain of Custody. Information on the Chain of Custody and labels must match and be complete.

PFAS Field Blank *

- Open bottle and pour field blank water (provided) into the empty bottle labeled Field Blank.

Shipping Instructions

- Place wet ice, samples and Chain of Custody into the shipping container and return to the laboratory immediately after collection. Sample bottles may be hand delivered or sent by overnight carrier. The laboratory must be notified prior to shipment of samples for Saturday delivery.
- Samples must arrive at the laboratory within 48 hours of sampling at or less than 10°C, and greater than 0°C (not frozen).
- Maximum holding time is 14 days from time of collection.
- Try to collect only on a Monday, Tuesday or Wednesday and ship no later than Thursday of each week. Try to NOT collect samples on Friday, Saturday or Sunday unless special arrangements have been made for the receipt of samples at the laboratory within 48 hours of collection.

Please contact Eurofins Eaton Analytical at one of the locations below or visit www.eurofinsus.com/environment-testing/testing-services/pfas-analysis for more information.

* There may be altered or additional practices required by individual states or regulatory programs. We recommend www.epa.gov/pfas or refer to your state or regulatory agency for specific guidance.

Eurofins Eaton Analytical

Monrovia Laboratory
750 Royal Oaks Drive, #100
Monrovia, CA 91016
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South Bend Laboratory
110 South Hill Street
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574-233-4777

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Sampling Precautions



Sampling Clothing and Other Considerations

- Avoid wearing clothing or boots containing Gore-Tex or using materials containing Tyvek.
- Avoid using cosmetics, moisturizers, heavy fabric softeners on clothes the day of sampling.
- Sample PFAS first if your cooler contains other sample collection bottles! Other sample containers for other methods may have PFAS present.

PFAS Free Sampling Supplies



Are my containers and supplies are PFAS free?





Including a blank sample is always a good practice.

Field Blanks

Surface Adsorption Issues



What is my sample concentration level?

Long-chain PFAS concentrations can become lower due to surface adsorption during storage.

The correct sample concentration should be the measured concentration.

Surface Adsorption Issues



How much PFAS can be lost on HDPE bottle surfaces?

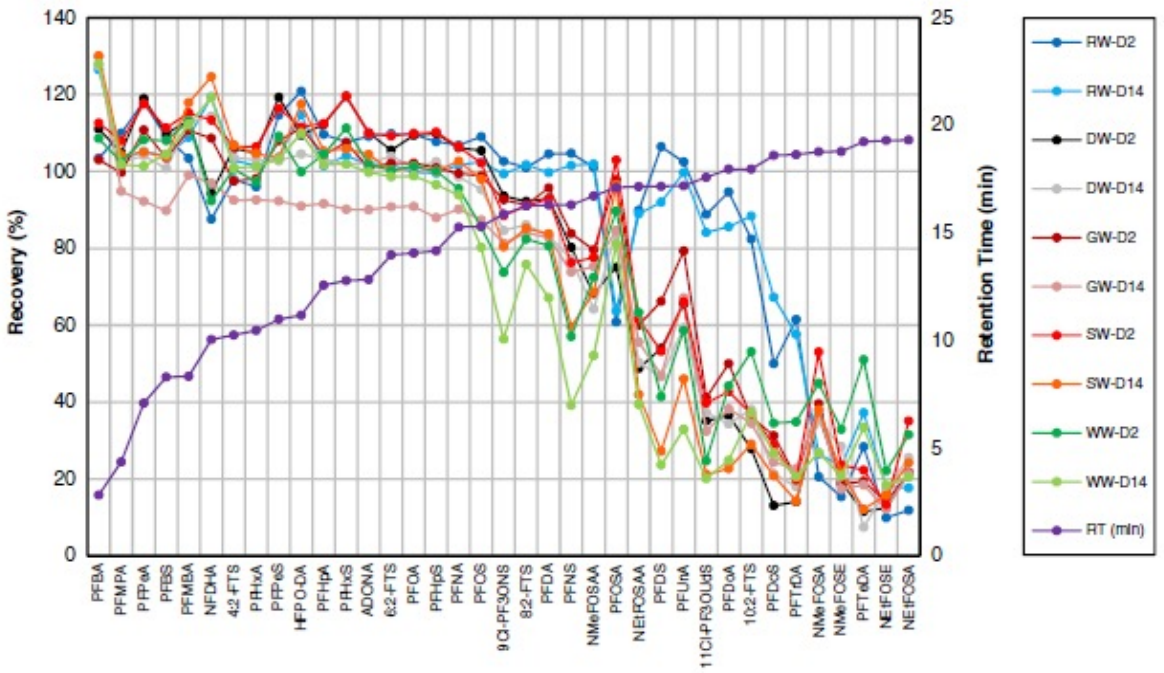
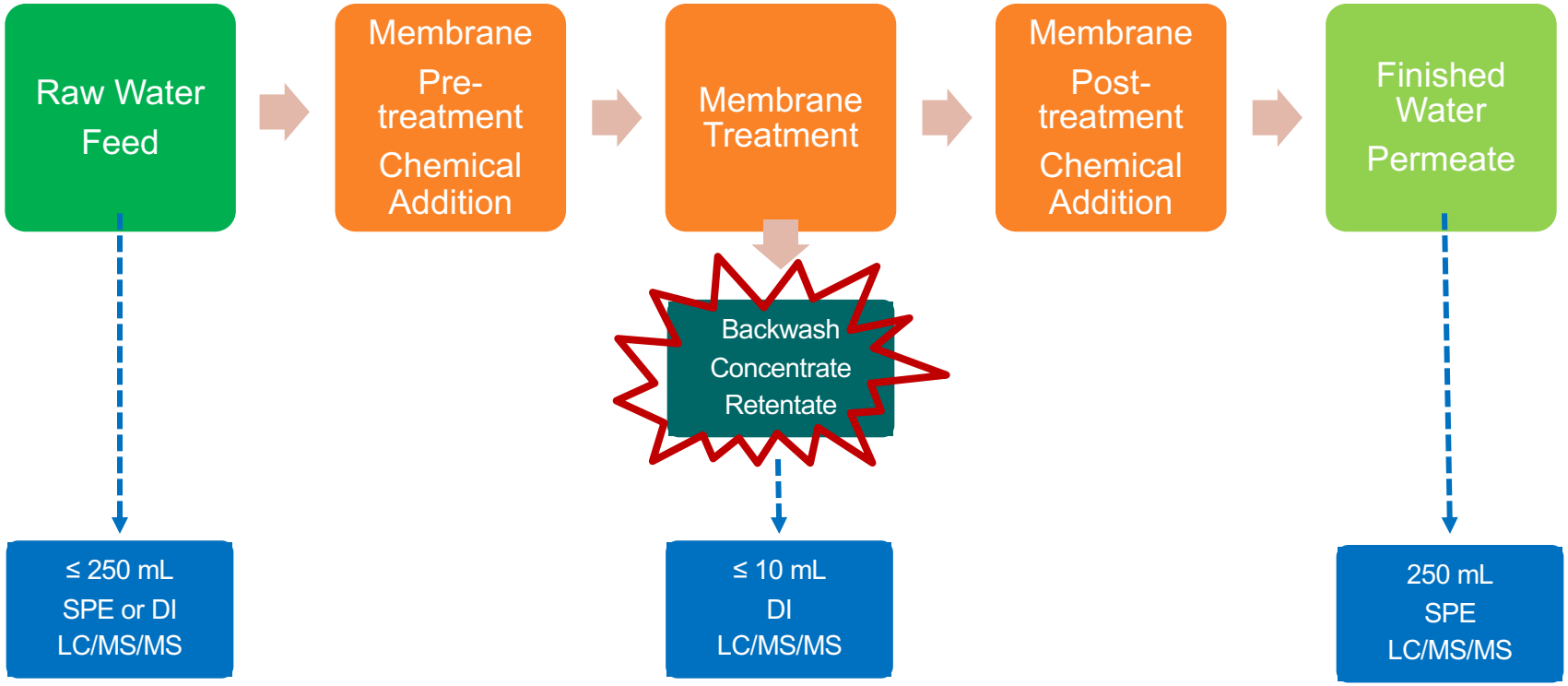


FIGURE 5 Recoveries of per- and polyfluoroalkyl substances fortified into 8-oz high-density polyethylene sample bottles at 400 ng/L and stored at refrigeration temperature (1–6 °C). DW, drinking water; GW, groundwater; RW, reagent water; SW, surface water; WW, wastewater

Treatment Process Sampling



Membrane Treatment



Subsampling may not be a good idea unless it is done properly.

Analytical Methods



Methods and method attributes

- Solid phase extraction / direct injection methods
- Branched vs. linear PFAS
- Isotope dilution
- Method Reporting Limits

Solid Phase Extraction (SPE) Methods

SPE-LC/MS/MS
250 mL sample to 1 mL extract

- **EPA 537/537.1 – RP-SPE, Internal Standards**
  14/18 analytes, potable water
- **EPA 533 – WAX-SPE, Isotope Dilution**
  25 analytes, potable water
- **Draft CWA EPA 1633 – WAX-SPE, Isotope Dilution**
  ~ 40 analytes, non-potable water
- **DoD/DoE QSM 5.3 – WAX-SPE, Isotope Dilution**
  ~ 25 analytes, non-potable water

Direct Injection (DI) Methods



DI-LC/MS/MS
1:1 Sample:MeOH

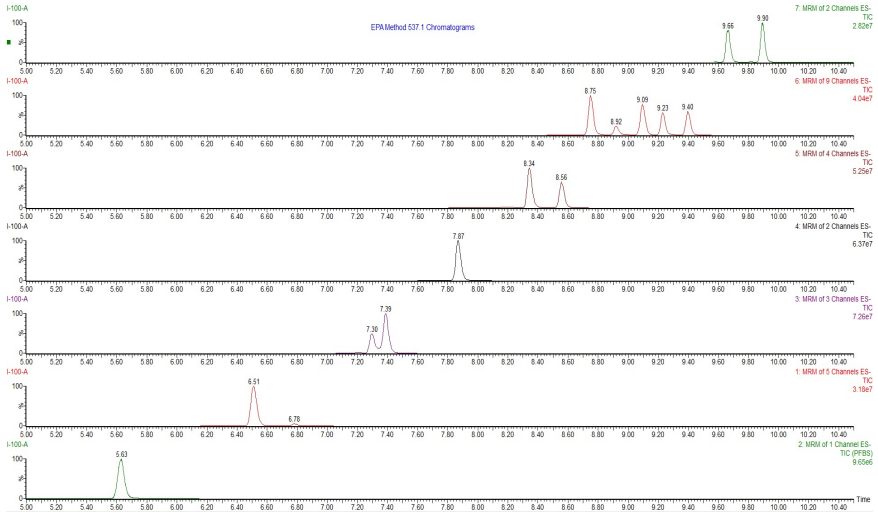
- **SW 846 EPA 8327 – External Standard Calibration**
  24 analytes, non-potable water
- **ASTM D7979-17 – External Standard Calibration**
  14+7 analytes, non-potable water

SPE Methods – Drinking Water



Solid Phase Extraction LC/MS/MS Methods

NOTE USE OF ISOTOPES



Method	EPA 537.1	EPA 533
250 mL sample	14 days Trizma pH 6 – 8 ≤6°C	28 days ammonium acetate pH 6 – 8 ≤6°C
1 mL extract	28 days 96% MeOH/water Room Temp.	28 days 80% MeOH/water Room Temp.
IS / IPS	Internal standards	Isotope performance standards
SS / IDA	Surrogate standards	Isotope dilution analogues
Calibration	Internal standard calibration	Isotope dilution calibration

Branched and Linear PFAS



PFAS Isomers

Isomer	Name	Structure	Percent Composition by ^{19}F-NMR
1	Potassium perfluoro-1-octanesulfonate	$CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2SO_3^-K^+$	78.8
2	Potassium 1-trifluoromethylperfluoroheptanesulfonate**	$CF_3CF_2CF_2CF_2CF_2CF_2CF(CF_3)SO_3^-K^+$	1.2
3	Potassium 2-trifluoromethylperfluoroheptanesulfonate	$CF_3CF_2CF_2CF_2CF_2CF(CF_3)CF_2SO_3^-K^+$	0.6
4	Potassium 3-trifluoromethylperfluoroheptanesulfonate	$CF_3CF_2CF_2CF_2CF(CF_3)CF_2CF_2SO_3^-K^+$	1.9
5	Potassium 4-trifluoromethylperfluoroheptanesulfonate	$CF_3CF_2CF_2CF(CF_3)CF_2CF_2CF_2SO_3^-K^+$	2.2
6	Potassium 5-trifluoromethylperfluoroheptanesulfonate	$CF_3CF_2CF(CF_3)CF_2CF_2CF_2CF_2SO_3^-K^+$	4.5
7	Potassium 6-trifluoromethylperfluoroheptanesulfonate	$CF_3CF(CF_3)CF_2CF_2CF_2CF_2CF_2SO_3^-K^+$	10.0
8	Potassium 5,5-di(trifluoromethyl)perfluorohexanesulfonate	$CF_3CF(CF_3)CF_2CF_2CF_2CF_2SO_3^-K^+$	0.2
9	Potassium 4,4-di(trifluoromethyl)perfluorohexanesulfonate	$CF_3CF_2C(CF_3)CF_2CF_2CF_2SO_3^-K^+$	0.03
10	Potassium 4,5-di(trifluoromethyl)perfluorohexanesulfonate	$CF_3CF(CF_3)CF_2CF_2CF_2CF_2SO_3^-K^+$	0.4
11	Potassium 3,5-di(trifluoromethyl)perfluorohexanesulfonate	$CF_3CF(CF_3)CF_2CF(CF_3)CF_2CF_2SO_3^-K^+$	0.07

Linear PFOS

Branched PFOS

- Isomers have the same molecular formula and but differ in “shape or structure”
- Different industrial processes produce linear over branched isomers
- Mixed usage of formulas has resulted in blends in the environment

Only including the linear isomer will bias the results low.

Isotope Dilution



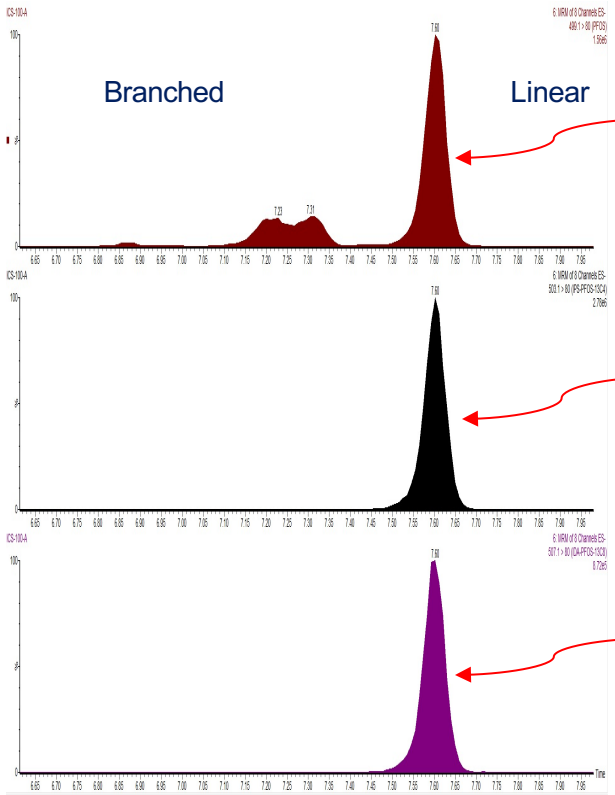
Why Use Isotope Dilution Analysis?

Isotope dilution analogues (IDA) have same retention time as target PFAS.

Data are corrected for interferences using IDA.

Adds confidence to data.

Mitigates false negatives and false positives.



PFAS Method Reporting Limits (MRL)



MRLs 2 to 20 ng/L (PPT)

One part per trillion
is the equivalent of
one grain of sand
in an
Olympic-size swimming pool.

Compound	acronym	CAS	537.1	533	L402	MRL
Perfluorobutanoic acid	PFBA	375-22-4		✓	✓	5
Perfluoropentanoic acid	PFPeA	2706-90-3		✓	✓	2
Perfluorohexanoic acid	PFHxA	307-24-4	✓	✓	✓	2
Perfluoroheptanoic acid	PFHpA	375-85-9	✓	✓	✓	2 (10)
Perfluorooctanoic acid	PFOA	335-67-1	✓	✓	✓	2 (20)
Perfluorononanoic acid	PFNA	375-95-1	✓	✓	✓	2 (20)
Perfluorodecanoic acid	PFDA	335-76-2	✓	✓	✓	2
Perfluoroundecanoic acid	PFUnA	2058-94-8	✓	✓	✓	2
Perfluorododecanoic acid	PFDoA	307-55-1	✓	✓	✓	2
Perfluorotridecanoic acid	PFTrDA	72629-94-8	✓		✓	2
Perfluorotetradecanoic acid	PFTeDA	376-06-7	✓		✓	2
Perfluorohexadecanoic acid	PFHxDA	67905-19-5			✓	2
Perfluorobutanesulfonic acid	PFBS	375-73-5	✓	✓	✓	2 (90)
Perfluoropenanesulfonic acid	PFPeS	2706-91-4		✓	✓	2
Perfluorohexanesulfonic acid	PFHxS	355-46-4	✓	✓	✓	2 (30)
Perfluoroheptanesulfonic acid	PFHpS	375-92-8		✓	✓	2
Perfluorooctanesulfonic acid	PFOS	1763-23-1	✓	✓	✓	2 (40)
Perfluorononanesulfonic acid	PFNS	68259-12-1			✓	2
Perfluorodecane sulfonic acid	PFDS	335-77-3			✓	2
Perfluorododecane sulfonic acid	PFDoS	NA			✓	2
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6	✓		✓	2
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9	✓		✓	2
Perfluorooctane sulfonamide	PFOSA	754-91-6			✓	2
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6		✓		20
Perfluoro (2-ethoxyethane) sulfonic acid	PFEESA	113507-82-7		✓		2
N-ethylperfluorooctane sulfonamidoethanol	NEtFOSE	1691-99-2			✓	2
N-methylperfluorooctanesulfonamidoethanol	NMeFOSE	24448-09-7			✓	2
N-ethylperfluorooctane sulfonamide	NEtFOSA	4151-50-2			✓	2
N-methylperfluorooctane sulfonamide	NMeFOSA	31506-32-8			✓	2
4:2 Fluorotelomer sulfonic acid	4:2 FTS	757124-22-4		✓	✓	2
6:2 Fluorotelomer sulfonic acid	6:2 FTS	27619-97-2		✓	✓	2
8:2 Fluorotelomer sulfonic acid	8:2 FTS	39108-34-4		✓	✓	2
10:2 Fluorotelomer sulfonic acid	10:2 FTS	120226-60-0			✓	2
Perfluoro-2-proxypropanoic acid	GenX (HFPO-DAfor 537.1)	13252-13-6	✓	✓	✓	1
Dodecafluoro-3H-4,8-dioxanonanoic acid	ADONA	958445-44-8	✓	✓	✓	2
		919005-14-4 (537.1)				
9-chlorohexadecafluoro-3-oxanonane-1 sulfonate	F-53B Major	73606-19-6	✓	✓	✓	2
	9Cl-PF3ONS (537.1)	756426-58-1 (537.1)				
11-chloroeicosafluoro-3-oxanonane-1-sulfonate	F-53B Minor	83329-89-9	✓	✓	✓	2
	11Cl-PF3OUdS (537.1)	63051-92-9 (537.1)				
Perfluoro-4-methoxybutanoic acid	PFMOBA	863090-89-5		✓	✓	5
Perfluoro-3-methoxypropanoic acid	PFMOPrA	377-73-1		✓	✓	5
Perfluoro-2-methoxyethoxyacetic acid	PFMOEOAA	151772-58-6			✓	5
Perfluoro-4-isopropoxybutanoic acid	PFIpOBA	80212-59-9			✓	5
Perfluoro-2-methoxyacetic acid	PFMOAA	674-13-5			✓	5
Perfluoro (3,5-dioxahexanoic) acid	PFO2HxA	39492-88-1			✓	5
Perfluoro (3,5,7-trioxaoctanoic) acid	PFO3OA	39492-89-2			✓	5
Perfluoro (3,5,7,9-tetraoxadecanoic)acid	PFO4DA	39492-90-5			✓	5
Nafion Byproduct 1	Nafion BP1	29311-67-9			✓	5
Nafion Byproduct 2	Nafion BP2	749836-20-2			✓	5
() MRL for UCMR3			18	25	45	

Conclusions



- **Sampling should use PFAS-free sample containers and supplies.**
  - It is a good practice to always collect a blank sample if applicable.
  - Isotope dilution methods are recommended to mitigate matrix interferences
- **EPA Methods 537.1 and 533 are effective for monitoring of PFAS in raw, finished and treatment process waters.**
  - Some laboratory proprietary methods are available for additional PFAS.
  - Subsampling is better to be avoided.
  - Quantitative subsampling with properly rinsing sample containers with methanol is critical to achieve reliable results.

Conclusions Cont'd



- **Adsorption losses of PFAS on surfaces in water feed tanks/bottles can be significant for calculating removal efficiency, depending on structures of selected target analytes.**
  - Adsorption losses of PFAS generally increase with the increase of PFAS chains longer than C8.
  - For fortified raw water, should consider to collect a sample to measure the feed concentrations.
- **Direct injection LC/MS/MS methods are applicable for backwash concentrate analysis.**
  - Isotope dilution analysis is highly recommended to compensate for matrix interferences.
  - Small sample volumes are ideal.

Thank you

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