PFAS
Chemistry and Concerns

PFAS Action Team Meeting
Rachel Carsen Building, Harrisburg, PA
November 30, 2018

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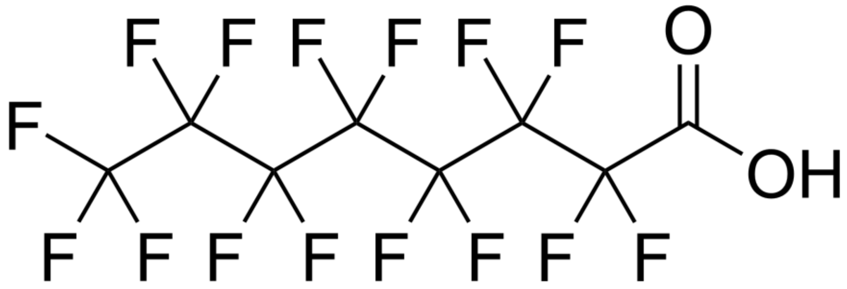
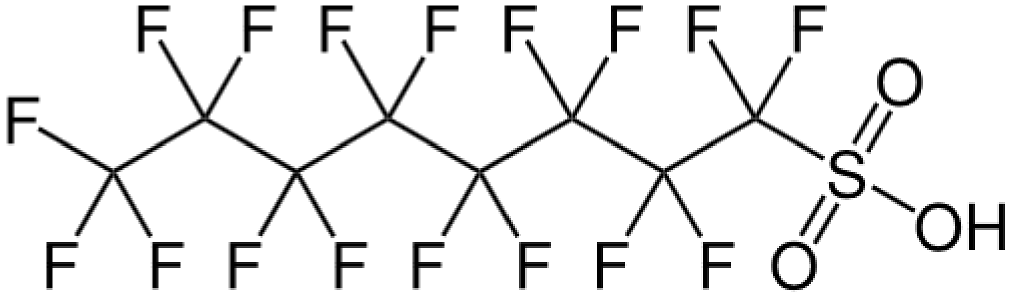
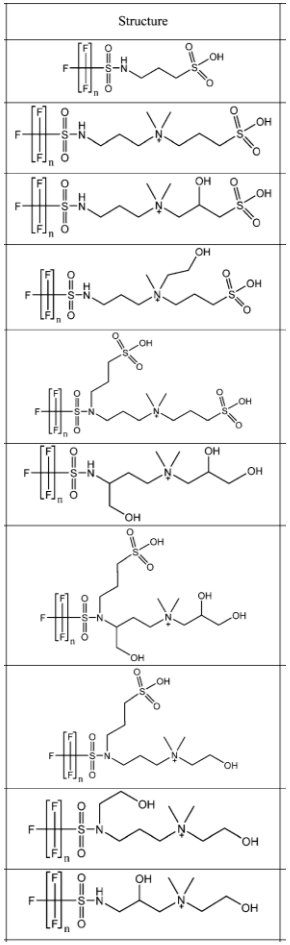


PFOA Perfluorooctanoic acid

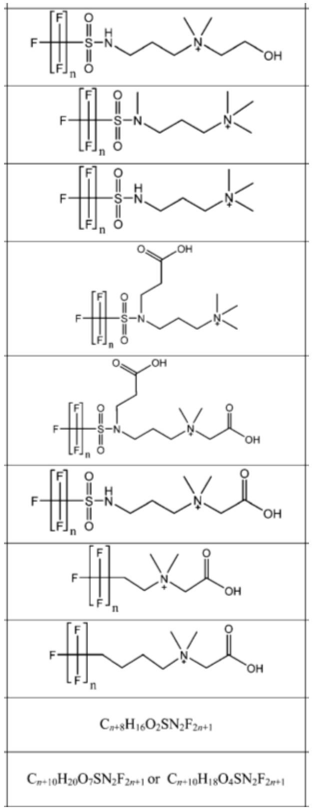


PFOS Perfluorooctanesulfonic acid

These are just two of more than 50 classes of Polyfluoroalkyl substances (PFAS) that have been used as **A**queous **F**ilm **F**orming **F**oams (AFFF)

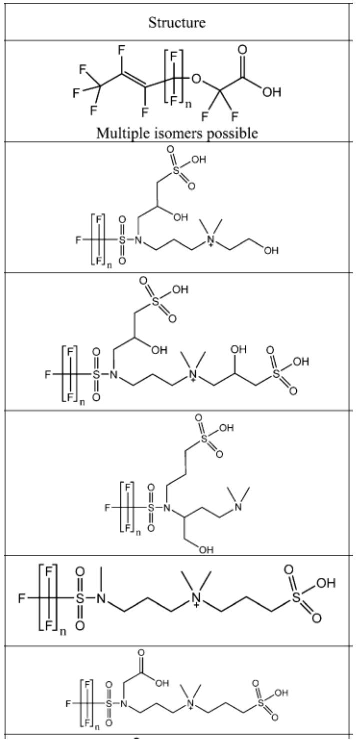


Structure



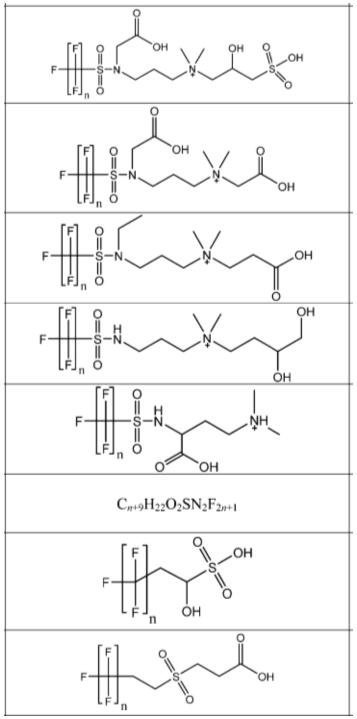
$C_{n+8}H_{16}O_2SN_2F_{2n+1}$

$C_{n+10}H_{20}O_7SN_2F_{2n+1}$ or $C_{n+10}H_{18}O_4SN_2F_{2n+1}$

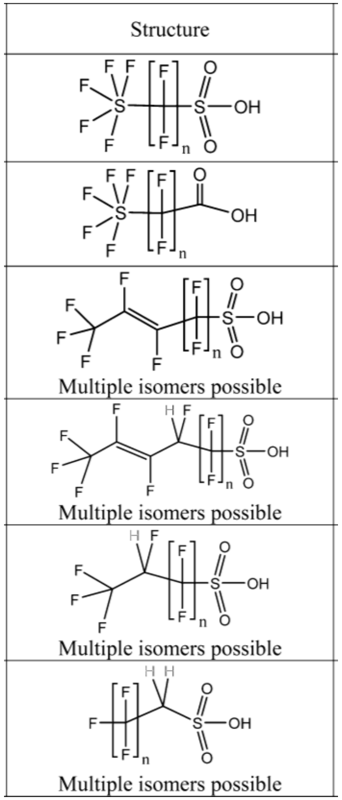


Structure

Multiple isomers possible



$C_{n+9}H_{22}O_2SN_2F_{2n+1}$



Structure

Multiple isomers possible

Multiple isomers possible

Multiple isomers possible

Multiple isomers possible

Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater

Krista A. Barzen-Hanson, et al, *Environmental Science & Technology*, 2017, 51, 2047-2057

https://cswab.org/wp-content/uploads/2018/07/Firefighting-Foams-AFFF-Fluorotelomers-Persistent-Barzen-Hanson-2017.pdf

- Within each class of PFAS AFFF there can be members from 4 to 14 carbons
- Within member of a class of PFAS with the same number of carbons, there are a number of branched isomers
- There are well over 50 chemical classes of PFAS
- There are tens of thousands of different PFAS that can be found in drinking water
- Currently just looking at the sum of the concentration of linear PFOA and linear PFOS and comparing the sum to a HAL of 70 ppt does a poor job of assessing the health impacts caused by the cryptic PFAS

Underreporting the concentrations of PFAS

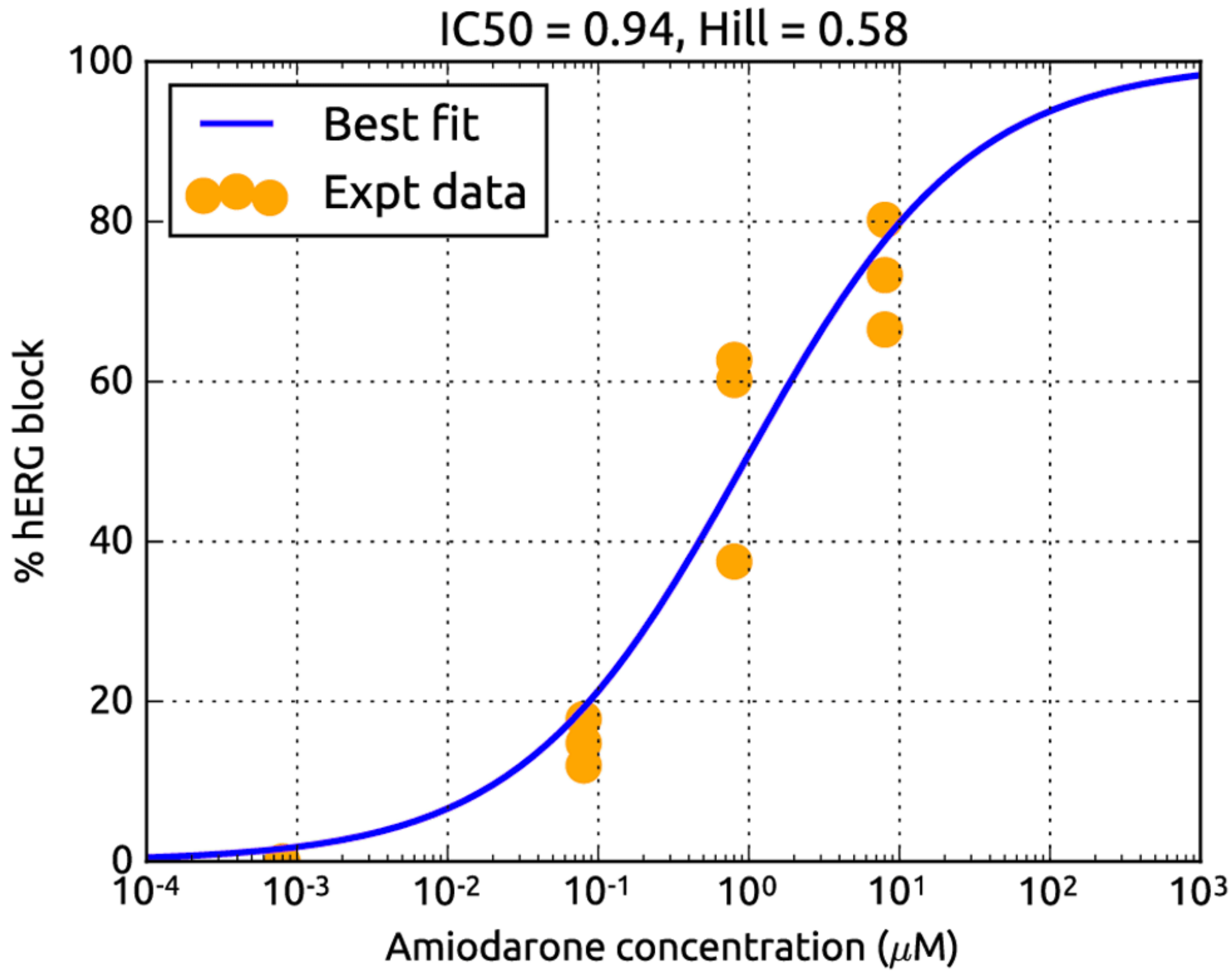
- Not accurately quantifying branched chain PFAS isomers
  - Branched chain isomers have different LC/MS/MS response factors
  - Few branched standards are commercially available
- Shorter and longer homologs may not be quantified at all
- What protocols are there for identifying and quantifying cryptic PFAS?
- Proficiency tests have shown reasonable accuracy, but uniformly underreports the concentration of PFAS by 20%
- The TOP assay needs to be carried out at each contamination site to assess the impact of cryptic PFAS for situational management
  - Median increase of 67% in PFAS in water at waste water treatment plants; Erika F. Houtz and David L. Sedlak, *Environ. Sci. Technol.* 2012, **46**, 17, 9342-9349 https://pubs.acs.org/doi/10.1021/es302274g

The Precautionary Principle

The principle is used by policy makers to justify discretionary decisions in situations where there is the possibility of harm from making a certain decision when extensive scientific knowledge on the matter is lacking. The principle implies that there is a social responsibility to protect the public from exposure to harm, when scientific investigation has found a plausible risk. These protections can be relaxed only if further scientific findings emerge that provide sound evidence that no harm will result.

https://en.wikipedia.org/wiki/Precautionary_principle

Dose Response Curve



How are HAL Determined?

Recently NJ PFNA HAL was set at 14 ppt
A series of concentration corrections are made from an adverse biological endpoint

Uncertainty factors that were used:

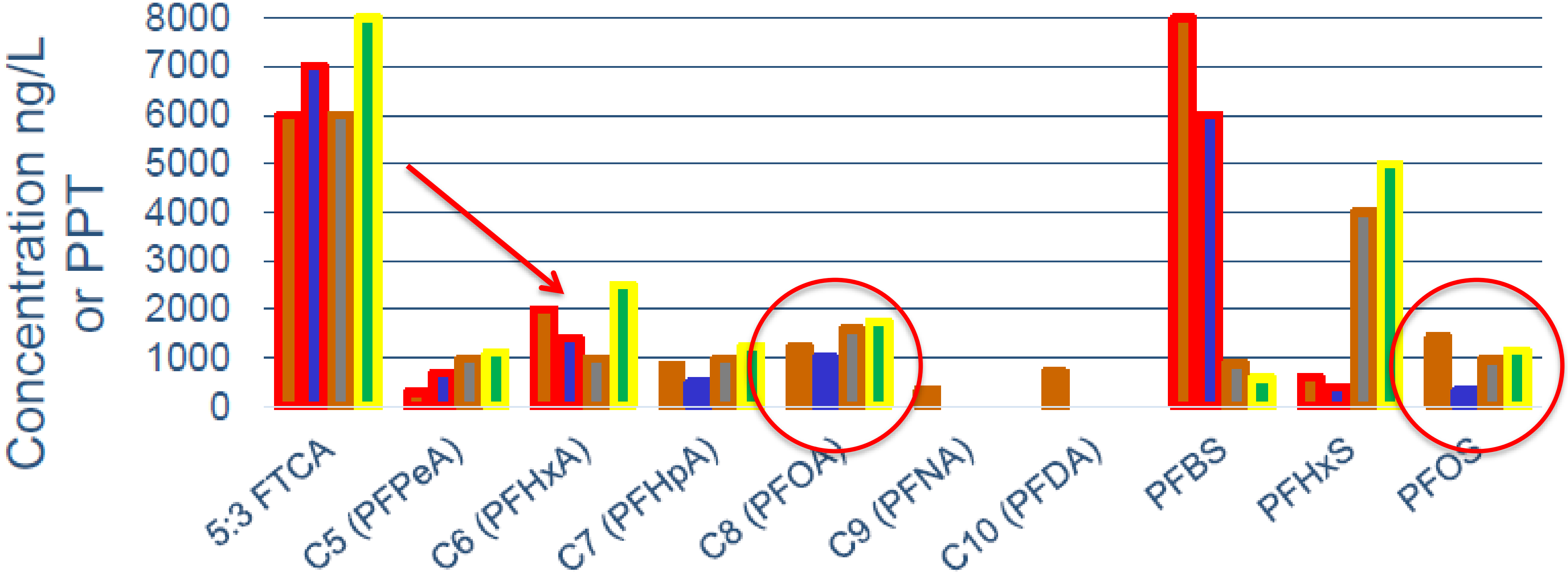
10	Intraspecies variability
3	Interspecies variability
10	To account for less than chronic study duration
3	Gaps in the toxicological database

This gives 10 X 3 X 10 X 3 = 900 times the health effect level for translation from a rodent to a human

With uncertainty factors of 1000 that are typical for PFAS, parsing out subtle differences from individual PFAS HAL may be an academic exercise

https://www.state.nj.us/dep/wms/bears/docs/pfna_fact_sheet.pdf

National Estimate of Polyfluoroalkyl Substance (PFAS) Release to U.S. Municipal Landfill Leachate



JR Lang, et al, *Environmental Science &Technology,* 2017, **51**(4), pages 2197-2205

State	Drinking Water Action	Compounds	Level (ppt)
Connecticut	Action Level	Sum of PFOA, PFOS, PFNA, PFHxS, & PFHpA	70
Massachusetts	Office of Research & Standards Guideline	Sum of PFOA, PFOS, PFNA, PFHxS, & PFHpA	70
Vermont	Groundwater Quality Enforcement Standards	Sum of PFOA, PFOS, PFNA, PFHxS, & PFHpA	20

HAL Proposal

Administratively set the HAL as the sum of all quantifiable PFAS to 70 ppt

Or

Minimally follow the lead of CT, MA, & VT and set the HAL as the sum of PFOA, PFOS, PFNA, PFHxS, & PFHpA

The End

Thank you for your attention

For a copy of the ppt send an email request to

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Back-up Slides

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https://www.forensicscienceeducation.org/about/forensic-fellows/
www.forensicscienceeducation.org
www.frfoundation.org

While at NMS labs I developed and validated an LC/MS/MS assay for PFAS in human serum/plasma:

http://www.nmslabs.com/tests/Perfluoroalkyl-Substances--PFAS---Serum-Plasma/3427SP

Perfluoroalkyl Substances (PFAS), Serum/Plasma Test (3427SP)

PFBA	Perfluorobutanesulfonic Acid	(as the linear isomer)
PFHpA	Perfluoroheptanoic Acid	(as the linear isomer)
PFHxA	Perfluorohexanesulfonic Acid	(as the linear isomer)
PFNA	Perfluorononanoic Acid	(as the linear isomer)
PFOS	Perfluorooctanesulfonic Acid	(as the linear isomer)
PFOA	Perfluorooctanoic Acid	(as the linear isomer)

Total Oxidative Precursor Assay (TOP), key references

Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff
Erika F. Houtz, and David Sedlak; *Environmental Science & Technology*, 46, 2012, 9342-9349
https://pubs.acs.org/doi/abs/10.1021/es302274g

Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil, Erika F. Houtz, et al, *Environmental Science & Technology*, 2013, 47, 8187-8195
https://pubs.acs.org/doi/abs/10.1021/es4018877

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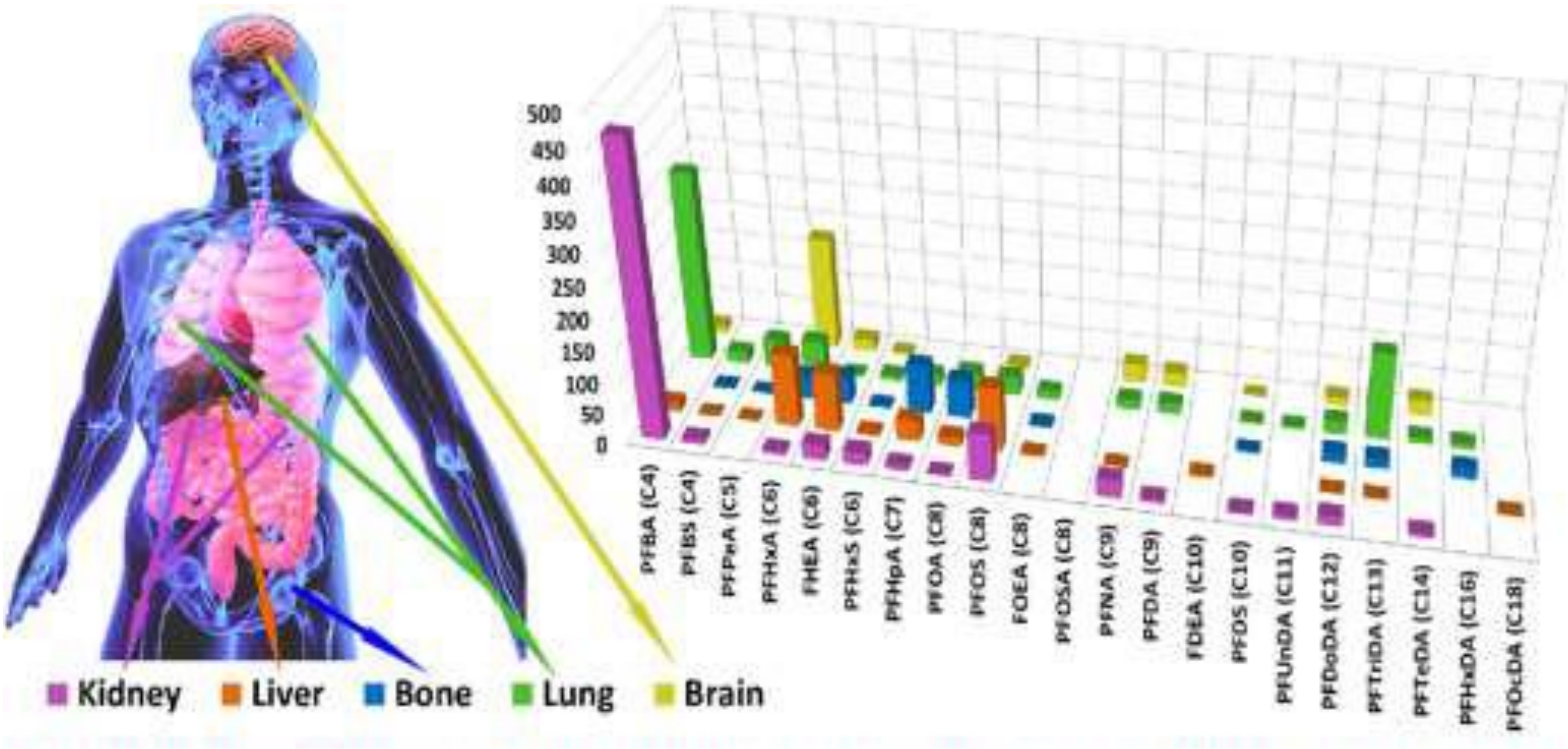


Francisca Pérez , et. al. , *Environment International*, Vol **59**, (2013), Pages 354-362

EPA ORD and the Office of Land and Emergency Management (OLEM) lead a cross-EPA workgroup on characterizing human health hazards

https://www.epa.gov/sites/production/files/2017-07/documents/pfas_kavlock_presentation.pdf

	Category	Draft Final PFAS List	Acronym	Carbon Number	Notes
1	Perfluoro carboxylic acids	Perfluorododecanoic acid	PFDoA	12	
2		Perfluoroundecanoic acid	PFUnA	11	
3		Perfluorodecanoic acid	PFDA	10	
4		Perfluorononanoic acid	PFNA	9	
5		Perfluorooctanoic acid	PFOA	8	HAL 70 ppt
6		Perfluoroheptanoic acid	PFHpA	7	
7		Perfluorohexanoic acid	PFHxA	6	
8		Perfluoropentanoic acid	PFPeA	5	
9		Perfluorobutyric acid	PFBA	4	
10	Perfluoro sulfonates	Perfluorodecanesulfonate	PFDS	10	
11		Perfluorononanesulfonate	PFNS	9	
12		Perfluorooctanesulfonate	PFOS	8	HAL 70 ppt
13		Perfluoroheptanesulfonate	PFHpS	7	
14		Perfluorohexanesulfonate	PFHxS	6	
15		Perfluoropentansulfonate	PFPeS	5	
16		Perfluorobutanesulfonate	PFBS	4	
17	Perfluoro sulfonamide	Perfluorooctanesulfonamide	PFOSA	8	
18	Fluorotelomer sulfonates	Fluorotelomer sulfonate 8:2	FtS 8:2	10	can metabolize to PFNA?
19		Fluorotelomer sulfonate 6:2	FtS 6:2	8	can metabolize to PFHpA?
20	Perfluoro sulfonamidoacetic acids	N-ethyl-N-((heptadecafluorooctyl)sulfonyl)glycine	NEtFOSAA	12	can metabolize to PFNA?
21		N-(Heptadecafluorooctylsulfonyl)-N-methylglycine	NMeFOSAA	11	can metabolize to PFHpA?
22	Fluorotelomer alcohols	Fluorotelomer alcohol 8:2	FtOH 8:2	10	can metabolize to PFOA?, but not by anaerobic biotransformation, more toxic than PFOA?
23		Fluorotelomer alcohol 6:2	FtOH 6:2	8	can metabolize to PFHxA?, but not by anaerobic biotransformation; more toxic than PFHxA?
24	Perfluoro ether carboxylic acids	Perfluoro(2-methyl-3-oxahexanoic) acid	GenX	6	
25		4,8-dioxa-3H-perfluorononanoic acid	ADONA	7	
26	Fluorotelomer phosphates	6:2 Fluorotelomer phosphate monoester	6:2 monoPAP		can metabolize to PFHpA?
27		6:2 Fluorotelomer phosphate diester	6:2 diPAP		can metabolize to PFHpA?
28		8:2 Fluorotelomer phosphate monoester	8:2 monoPAP		can metabolize to PFNA?
29		8:2 Fluorotelomer phosphate diester	8:2 diPAP		can metabolize to PFNA?
30		6:2/8:2 Fluorotelomer phosphate diester	6:2/8:2 diPAP		
31	Fluorotelomer carboxylic acid	5:3 Polyfluorinated acid	5:3 acid	8	can metabolize to PFHxA?

The Association of State Drinking Water Administrators (ASDWA)

https://www.asdwa.org/pfas/

PFAS Lab Testing Primer October 10, 2018 4
https://www.asdwa.org/wp-content/uploads/2018/10/ASDWA-PFAS-Lab-Testing-Primer-10-10-18-Final.pdf

The PFAS analyses described above may only quantify a fraction of the PFAS, PFAS precursors and/or total organic fluorine contamination that may be present when PFAS is detected in drinking water. Some water systems have worked with research laboratories to more fully quantify the potential for other highly fluorinated chemicals in drinking water. This work generally exceeds any regulatory guidance or requirements. More information on these testing methods can be found in this fact sheet prepared by the Interstate Technology Regulatory Council Fact sheet titled, "Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS)."
https://pfas-1.itrcweb.org/wp-content/uploads/2018/03/pfas_fact_sheet_site_characterization_3_15_18.pdf

Topic 4: What Reporting Limits Should Be Required?
Laboratory analytical methods with reporting limits (RL) of at least 2-4 nanograms per liter (ng/L) (ppt) should be utilized. Many commercial labs are achieving reporting limits of less than 1 ng/L ppt. Additional health studies are rapidly evolving and some states have determined that PFAS health advisory concentrations in drinking water should be based on the additive effect of PFAS compounds. Obtaining water quality results with low RL will improve the utility of the data in the event health guidance or standards are changed or that the state you are in develops health guidance or standards based on the additive effects of PFAS.

Topic 5 : Technical Issues that Cause Variability in Testing Results Sample Results Prior to September 2016 May Be Under Reported
Many PFAS compounds can be present as a linear isomer or a branched isomer. When a compound can have the same chemical formula, but a different arrangement of atoms, it is considered an isomer. Initially, DuPont produced PFOA using telomerization processes that produced PFOA and other PFAS only in the linear isomer form. 3M later produced PFAS compounds using electrochemical processes that produced PFOA that contained linear and branched isomers at the ratio of 70%linear isomer to 30% branched isomer. [SEEPAGE538 https://www.atsdr.cdc.gov/toxprofiles/tp200-c5.pdf]

In September 2016, USEPA issued a technical advisory to laboratories utilizing Method 537 that the concentration of both the linear and branched isomers of PFOA need to be quantified and combined to determine the total PFOA concentration. Prior to the issuance of the technical advisory, USEPA Method 537 did not stipulate this requirement and some laboratories only reported PFOA in the linear isomer form, while other were reporting PFOA in the linear and branched isomer form. This means some PFOA results from analyses completed prior to September 2016 may be under reported by as much as 30%.

Expected Accuracy of Testing Results and Common Biases
In a recent proficiency testing program that included four commercial labs contracted by the New Hampshire Department of Environmental Services, USEPA established accuracy acceptance limits of 50% to 150% of the expected value meaning the expected accuracy of PFAS analyses using Method 537 or isotope dilution is +/- 50%.

The results of the proficiency testing programs determined:

Testing results for split samples sent to the laboratories were generally similar;
Testing results for split samples analyzed using Method 537 and isotope dilution were similar;
Results were generally accurate within 20% of the expected value but were almost always 20% under reported from the expected value; and
Occasional significant over or under reporting of PFAS concentrations occurred.

Existing PFAS analytical methods use an "extraction" process to isolate the PFAS in an aqueous sample so that it can be then measured by the instrument. This can be accomplished by using solvents to concentrate the compounds or an absorbent material to capture PFAS. Extraction methods are designed to minimize losses, but generally are not able to completely extract all PFAS that is in a water sample. Under reporting of PFAS results is likely associated with losses that occur during the analytical extraction process. Proficiency testing for other chemicals such as pesticides which rely on analytical methods that also use extraction processes show similar underreporting out comes.

Certified Standards Are Source of Variability
Laboratories purchase certified standards for PFAS analytes from different vendors.
Certified standards purchased from different sources have been shown to vary by as much as 20%.
PFAS standards that contain both branched and linear isomers of some PFAS compounds are not available.
Laboratories have to estimate the concentration of a PFAS compound in the branched form using the linear standard.

https://www.publish.csiro.au/en/pdf/EN10145

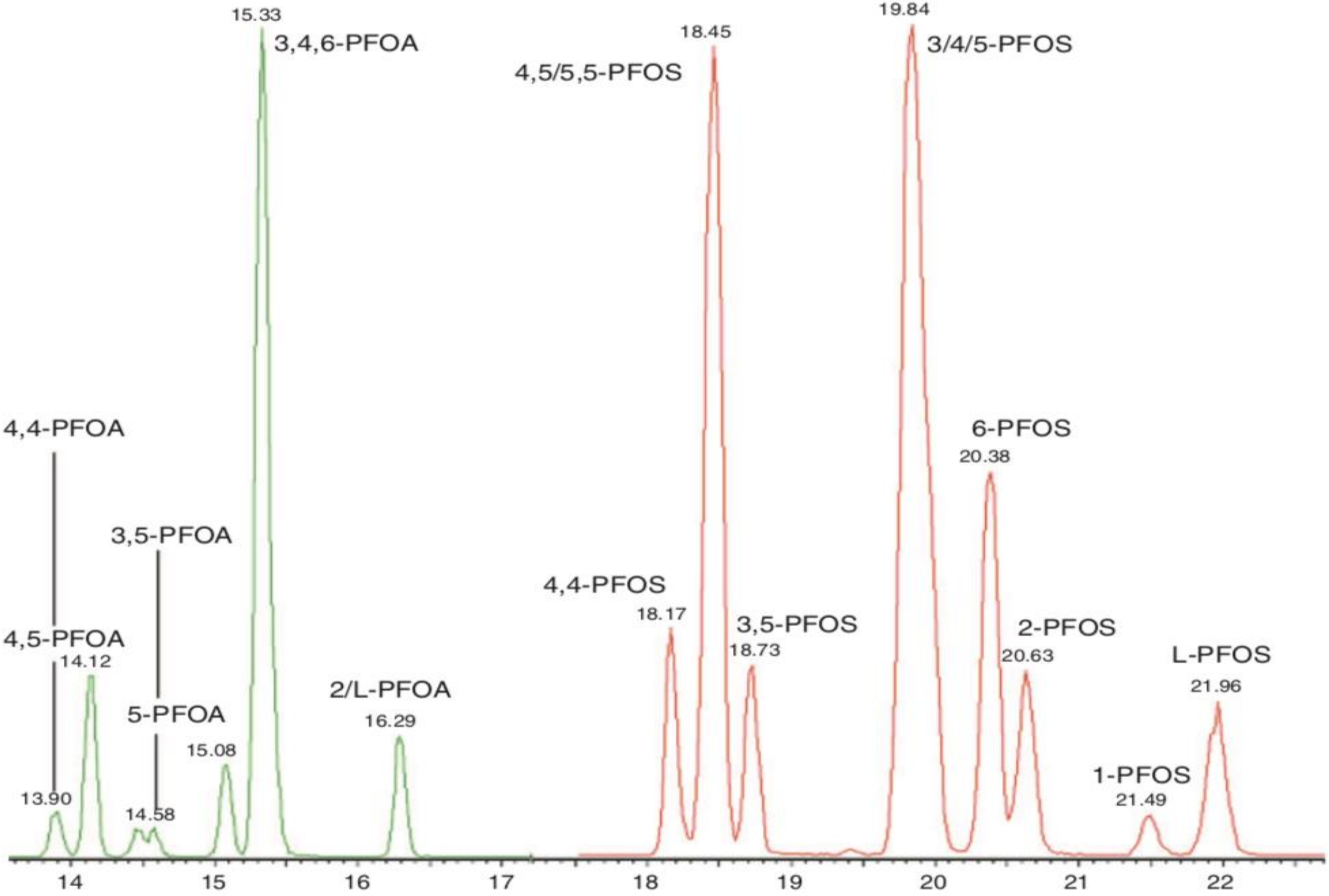
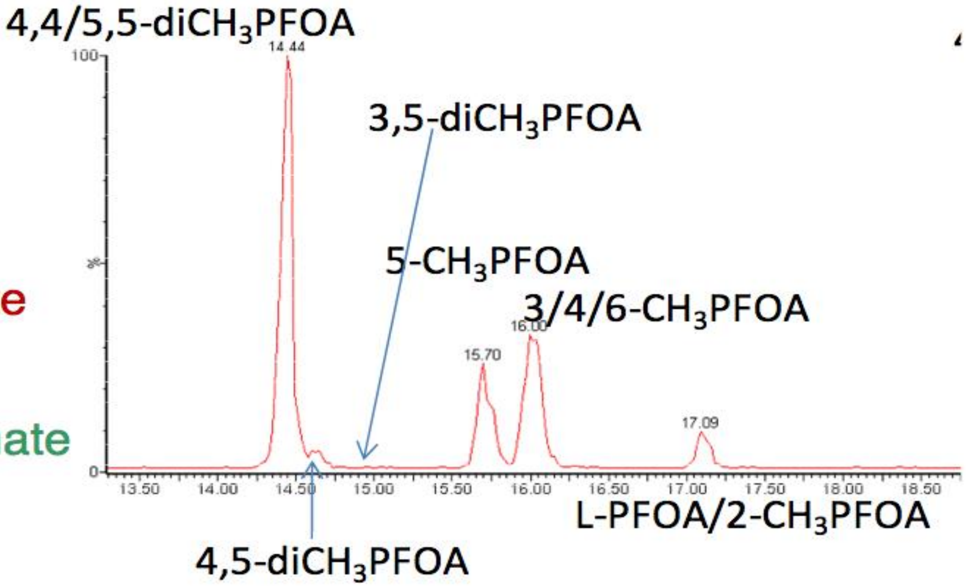


Fig. 1. Separation of PFOS and PFOA structural isomers on UPLC-MS/MS. Two MRM windows are overlapped, for PFOA, m/z 413 → 169, 413 → 369, and for PFOS m/z 499 → 80, 499 → 99.

https://www.dtsc.ca.gov/ECL/upload/ECL_Presentation_Perf-Compounds.pdf

Quantification using linear response



overestimate

underestimate

	4,4	5,5	4,5	3,5	5	3	4	6	2	Linear
413>369	<0.01	-	0.11	-	0.17	0.03	0.26	0.59	0.01	1
413>219	-	43	-	-	11	-	0.22	1	-	1
413>169	0.01	-	0.66	0.12	0.16	0.02	-	3.12	0.03	1