



Quantitative Characterization of Individual PFAS in Environmental Matrices – An Account of Different Methods and Lists

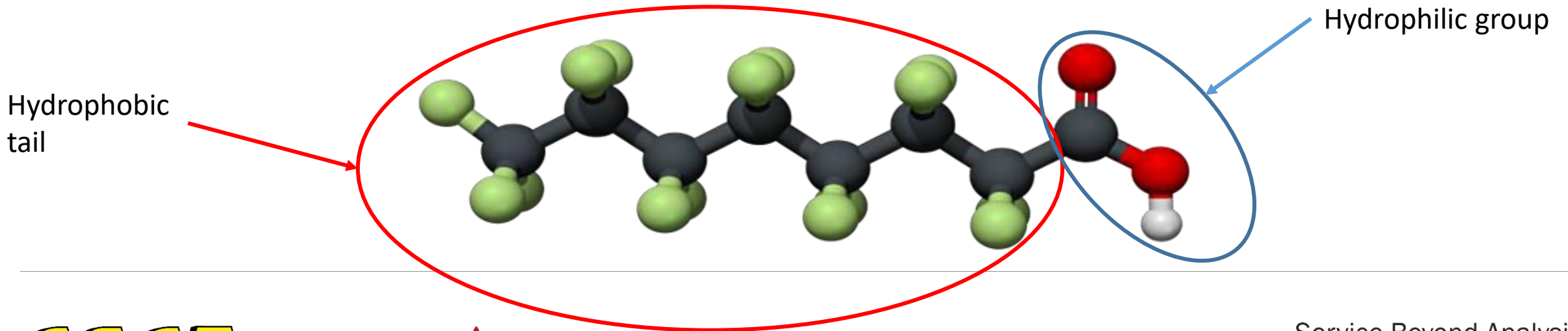
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Content

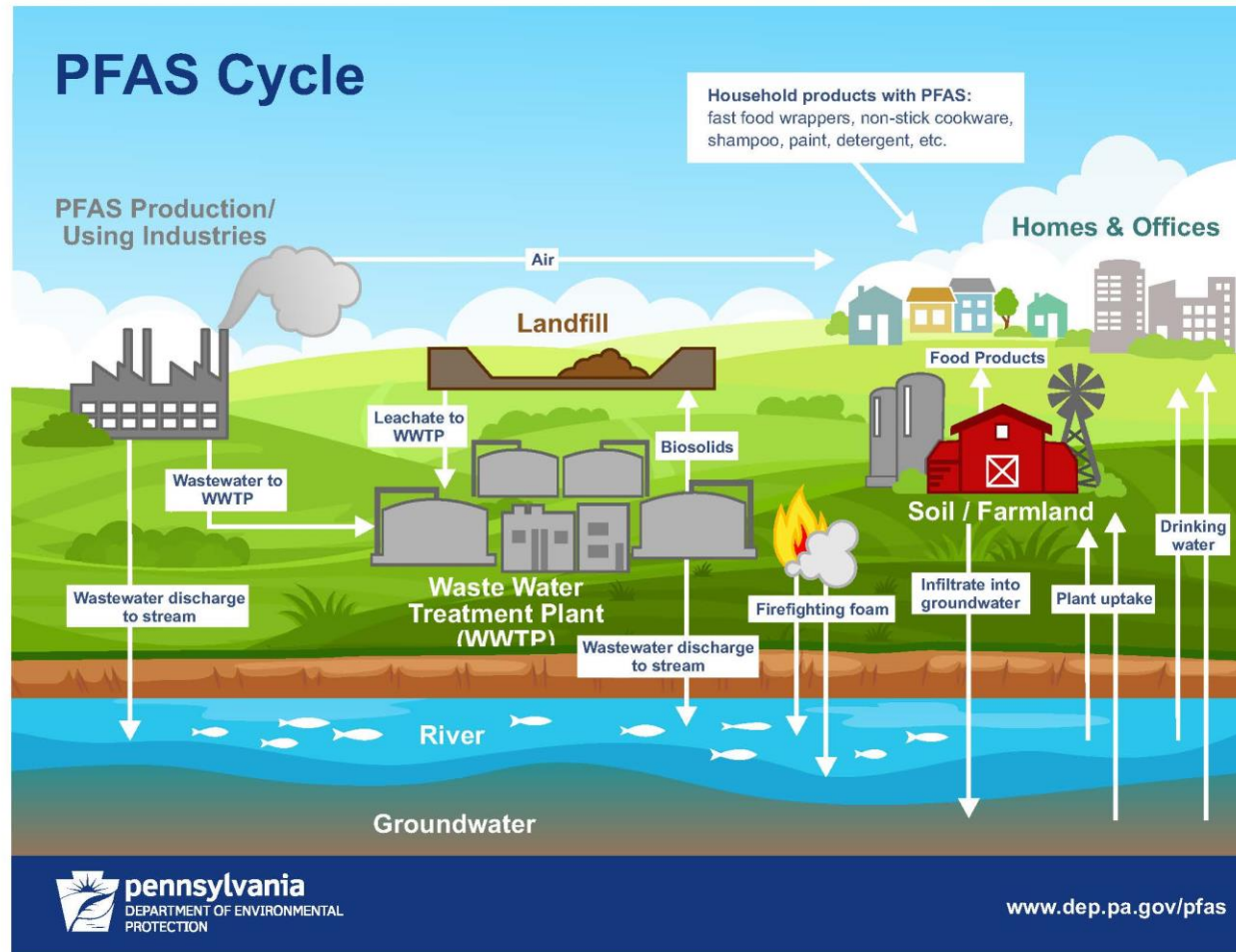
- PFAS chemistry
- Fate and Transport of PFAS
- Analytical Challenges
- PFAS methods and lists
- Quantitative analysis of PFAS
 - PFAS sampling
 - Sample preparation
 - Data Acquisition and Quantification
- Method selection

PFAS Chemistry

- Perfluorinated: all carbons are saturated with fluorine
- Polyfluorinated: not all carbons are saturated with fluorine
- Water and stain repellent
- Surfactant
- Chemical and temperature resistant



PFAS in the Environment



Analytical Challenges

Diverse chemicals

Sub-classes of PFASs	Examples of Individual compounds*	Number of peer-reviewed articles since 2002**	
perfluoroalkyl acids (PFAAs)	PFCA _s (C _n F _{2n+1} -COOH)	PFBA (n=4)	928
		PFPeA (n=5)	698
		PFHxA (n=6)	1081
		PFnHA (n=7)	1186
	PFSA _s (C _n F _{2n+1} -SO ₃ H)	PFDA (n=8)	4056
		PFNA (n=9)	1496
		PFDA (n=10)	1407
	PFPA _s (C _n F _{2n+1} -PO ₃ H ₂)	PFUnA (n=11)	1069
		PFDoA (n=12)	1016
	PFPIA _s (C _n F _{2n+1} -PO ₂ H-C _m F _{2m+1} -R)	PFTrA (n=13)	426
PFTeA (n=14)		587	
PFECAs & PFESAs (C _n F _{2n+1} -O-C _m F _{2m+1} -R)	PFBS (n=4)	654	
	PFHxS (n=6)	1081	
PFAS _s (C _n F _{2n+1} -R)	PFOS (n=8)	PFOS (n=8)	3507
		PFDS (n=10)	340
	PFAS _s (C _n F _{2n+1} -R)	PFBA (n=4)	3
		PFHxPA (n=6)	33
	PFPIAs (C _n F _{2n+1} -PO ₂ H-C _m F _{2m+1} -R)	PFOPA (n=8)	31
		PFDPA (n=10)	35
	PFECAs & PFESAs (C _n F _{2n+1} -O-C _m F _{2m+1} -R)	C ₄ /C ₄ PFPA (n=4)	4
		C ₆ /C ₆ PFPA (n=6)	12
	PFAS _s (C _n F _{2n+1} -R)	C ₈ /C ₈ PFPA (n=8)	12
		C ₆ /C ₈ PFPA (n=6, m=8)	8
PFAS _s (C _n F _{2n+1} -R)	ADONA (C ₄ F ₉ -O-C ₆ F ₁₃ -O-CHFCF ₂ -COOH)	4	
	GenX (C ₂ F ₄ -CFECF ₂ -COOH)	26	
PFAS _s (C _n F _{2n+1} -R)	EEA (C ₂ F ₄ -O-C ₆ F ₁₃ -O-CF ₂ -COOH)	6	
	F-538 (C ₄ F ₉ -O-C ₆ F ₁₃ -O-C ₆ F ₁₃ -SO ₃ H)	14	
PFAS _s (C _n F _{2n+1} -R)	MeFBSA (n=4, R=N(CH ₃) ₃)	25	
	MeFOSA (n=8, R=N(CH ₃) ₃)	134	
PFAS _s (C _n F _{2n+1} -R)	EtFBSA (n=8, R=N(CH ₃) ₃)	7	
	EtFOSA (n=8, R=N(CH ₃) ₃)	259	
PFAS _s (C _n F _{2n+1} -R)	MeFBSA (n=4, R=N(CH ₃) ₂ CH ₂ OH)	24	
	MeFOSA (n=8, R=N(CH ₃) ₂ CH ₂ OH)	116	
PFAS _s (C _n F _{2n+1} -R)	EtFBSA (n=4, R=N(CH ₃) ₂ CH ₂ OH)	4	
	EtFOSA (n=8, R=N(CH ₃) ₂ CH ₂ OH)	146	
PFAS _s (C _n F _{2n+1} -R)	SAmPAP (C ₄ F ₉ -SO ₂ -N(CH ₃) ₂ -C ₆ H ₄ -O-PO ₂ H)	8	
	100s of others	8	
PFAS _s precursors	4:2 FTOH (n=4, R=OH)	106	
	6:2 FTOH (n=6, R=OH)	375	
PFAS _s precursors	8:3 FTOH (n=8, R=OH)	412	
	10:2 FTOH (n=10, R=OH)	165	
PFAS _s precursors	12:2 FTOH (n=12, R=OH)	42	
	6:2 diPAP (C ₆ F ₁₃ CH ₂ OH)-PO ₂ H]	23	
PFAS _s precursors	8:2 diPAP (C ₈ F ₁₇ CH ₂ OH)-PO ₂ H]	25	
	100s of others	25	
PFAS _s precursors	polytetrafluoroethylene (PTFE)		
	polyvinylidene fluoride (PVDF)		
PFAS _s precursors	fluorinated ethylene propylene (FEP)		
	perfluoroalkoxy polymer (PFA)		
others	perfluoropolyethers (PFPEs)		

Image: Wang et al., 2017.

Ubiquitous nature



Image: Pennsylvania PFAS Action Team Report, 2019.

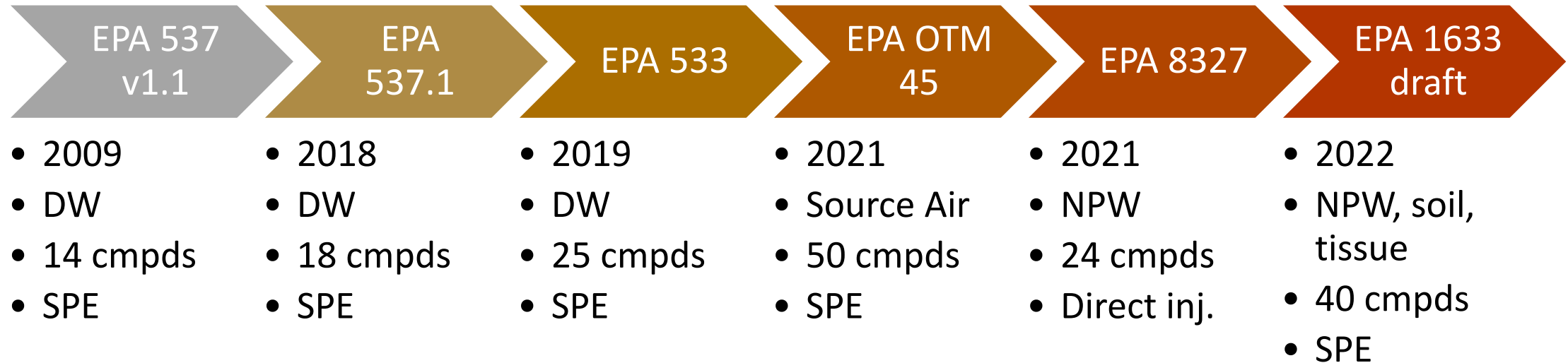
Matrix effects



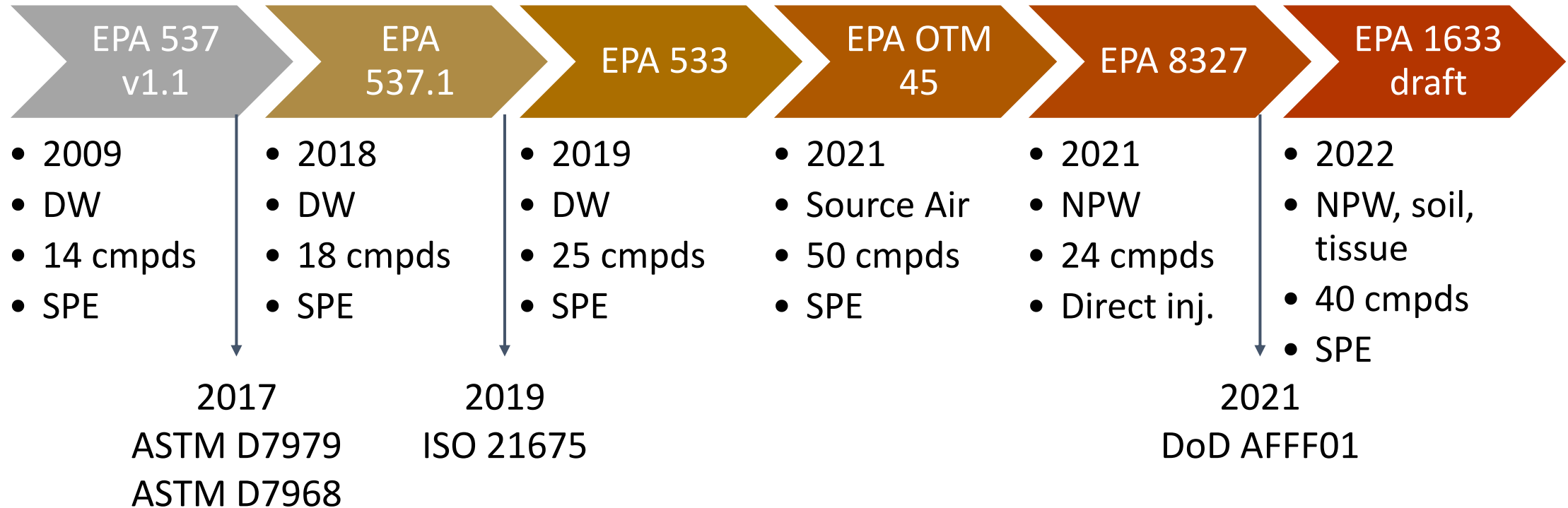
Lack of analytical standards



PFAS Methods Timeline

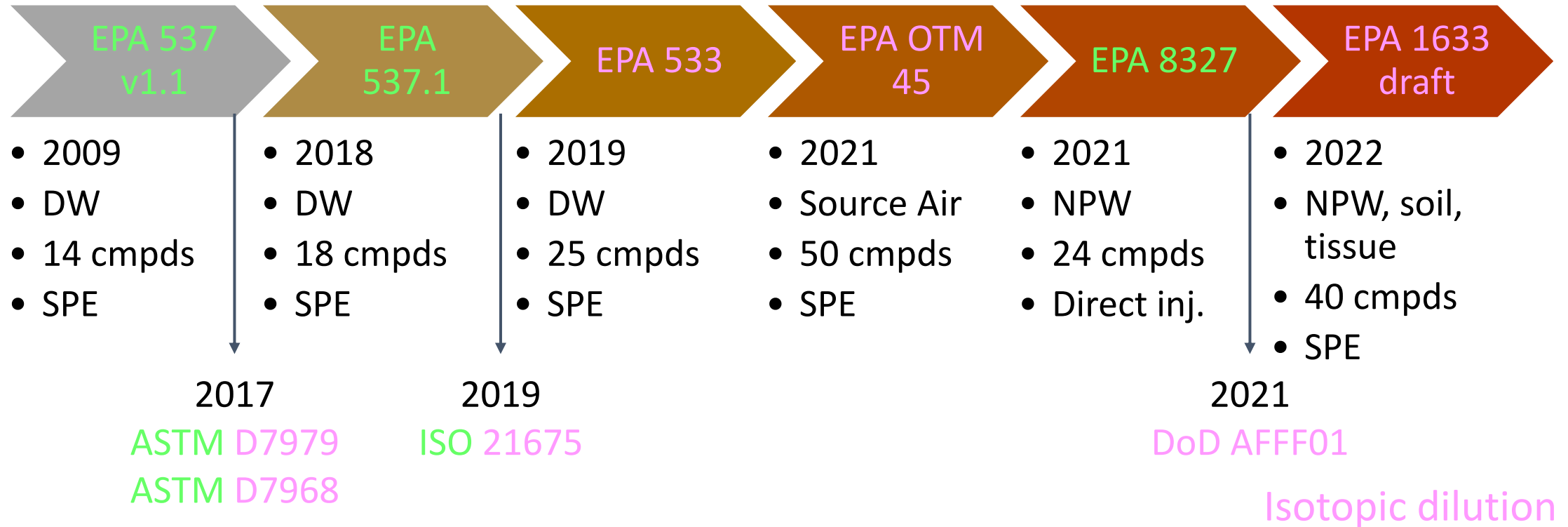


PFAS Methods Timeline



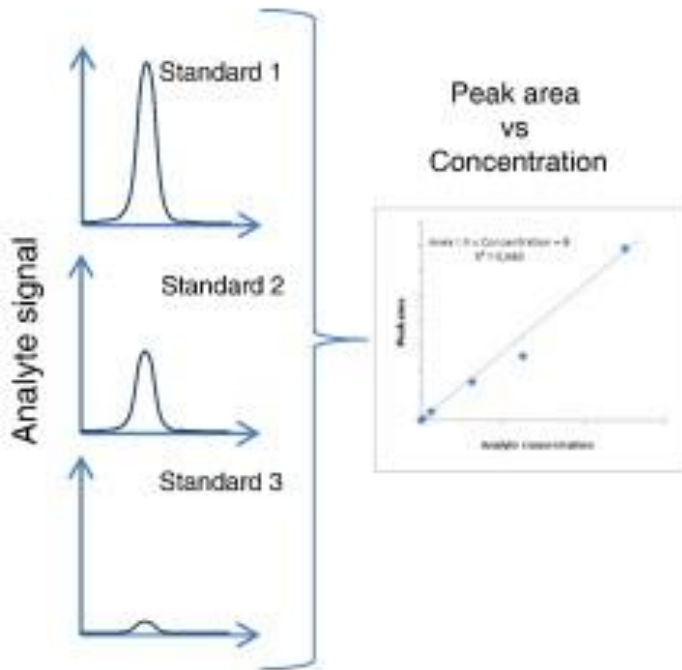
PFAS Methods Timeline

Internal/external standard

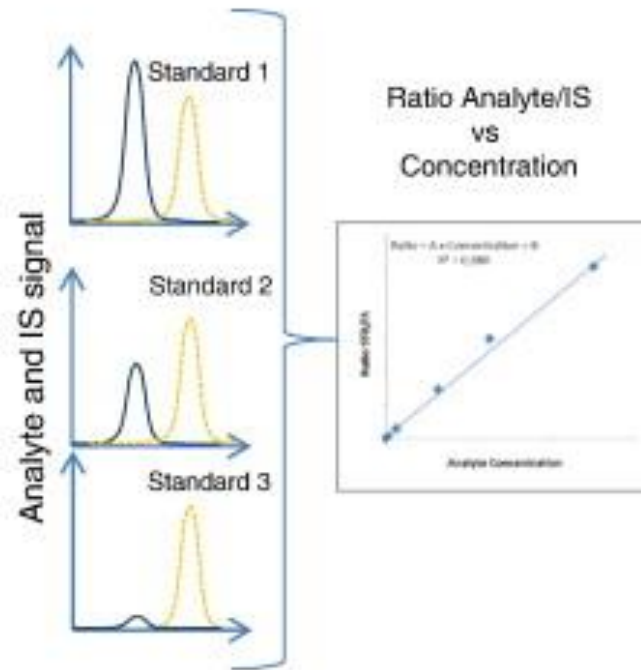


Quantification schemes

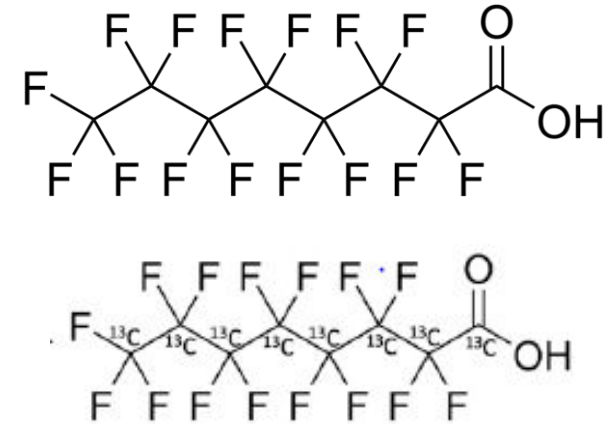
A: External standard calibration



B: Internal standard calibration

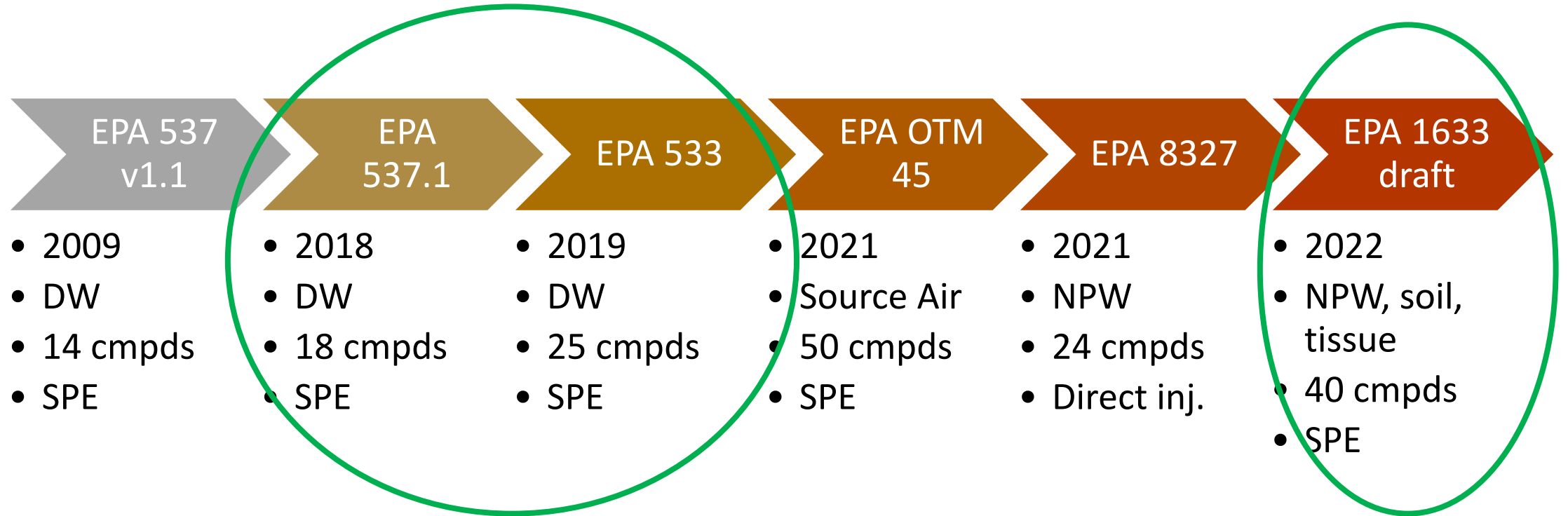


Isotope dilution



Behave the same way
Mitigate matrix effects
Reduces potential problems
Most accurate and precise

PFAS Methods Timeline



EPA method comparison

EPA 537.1	EPA 533	EPA 1633
Drinking water	Drinking water	All matrices other than drinking water
Cl ₂ quencher: Trizma	Cl ₂ quencher: NH ₄ Ac	No preservative
18 compounds	25 compounds	40 compounds
SPE SDVB	SPE WAX	SPE WAX
Hold Time: 14 days	Hold Time: 28 days	Hold Time: 28 days
Internal Standard	Isotope dilution	Isotope dilution
No clean up	No clean up	Carbon clean up
No recovery correction	Surrogate recovery correction	Surrogate recovery correction
Branched + linear isomers	Branched + linear isomers	Branched + linear isomers

Parameter comparison

Parameter	Method 537.1	Method 533	Method 1633
PFBA		X	X
PFPeA		X	X
PFHxA	X	X	X
PFHpA	X	X	X
PFOA	X	X	X
PFNA	X	X	X
PFDA	X	X	X
PFUnA	X	X	X
PFDoA	X	X	X
PFTTrDA	X		X
PFTeDA	X		X
PFBS	X	X	X
PFPeS		X	X
PFHxS	X	X	X
PFHpS		X	X
PFOS	X	X	X
PFNS			X
PFDS			X
PFDoS			X
PFOSA			X

Parameter	Method 537.1	Method 533	Method 1633
N-MeFOSAA	X		X
N-EtFOSAA	X		X
ADONA	X	X	X
HFPO-DA	X	X	X
9CI-PF3ONS	X	X	X
11CI-PF3OUdS	X	X	X
4:2-FTS		X	X
6:2-FTS		X	X
8:2-FTS		X	X
NFDHA		X	X
PFEESA		X	X
PFMBA		X	X
PFMPA		X	X
NMeFOSA			X
NEtFOSA			X
N-MeFOSE			X
N-EtFOSE			X
3:3 FTCA			X
5:3 FTCA			X
7:3 FTCA			X

EPA 1633

- Becoming an industry standard.
- A good selection of isotopically labeled analogues for surrogate recovery correction.
- The most extensive list of compounds so far.
- Applicable to all matrices.
- Carbon cleanup to increase accuracy of results for problematic samples.
- 500 mL sample volume.

What About Air?

- OTM-45 (Source)
 - Air train with XAD2 and LC-MS/MS with isotope dilution.
 - Not endorsed/approved by EPA.
 - A draft EPA method for PFAS in air by fall of 2022.
- Modified TO-13A (Ambient air)
 - PUF/ XAD2 cartridge and in-house LC-MS/MS method with isotope dilution.
 - Sample preparation: Methanol extraction (in-house method).
- Modified TO-17 (Vapour)
 - Thermal desorption tube and in-house GC-MS/MS method.

Quantitative Analysis – Sampling

- Materials
 - HDPE, PP, silicone, stainless steel, nylon, acetate, and cotton.
 - Teflon-free bottle caps.
 - No coating in sampling equipment.
 - No glass, no LDPE.
- PCP and clothing
 - Waterproof clothing made with polyurethane, PVC, rubber or neoprene.
 - No Gore-Tex and similar water/stain-resistant treated clothing.
 - Powderless nitrile gloves.
 - Sunscreens and insect repellents may contain PFAS.
 - No cosmetics, moisturizers, fragrances, and creams.
- QC samples
 - Travel blank, field blank, equipment rinse blank, field duplicate.

Analytical Method

Soil samples

Sonication/Vortex



Centrifuge + carbon clean-up



Dilution

Liquid samples

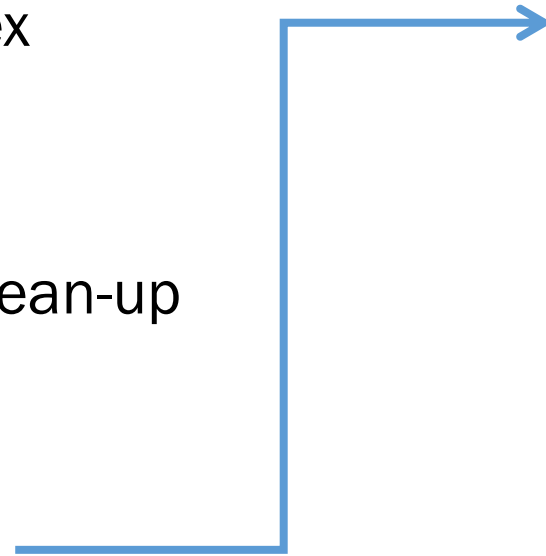
Sample pH adjustment



SPE with WAX + carbon clean-up



Measurement with LC-MS/MS



Quantitative Analysis – LC-MS/MS

- Importance

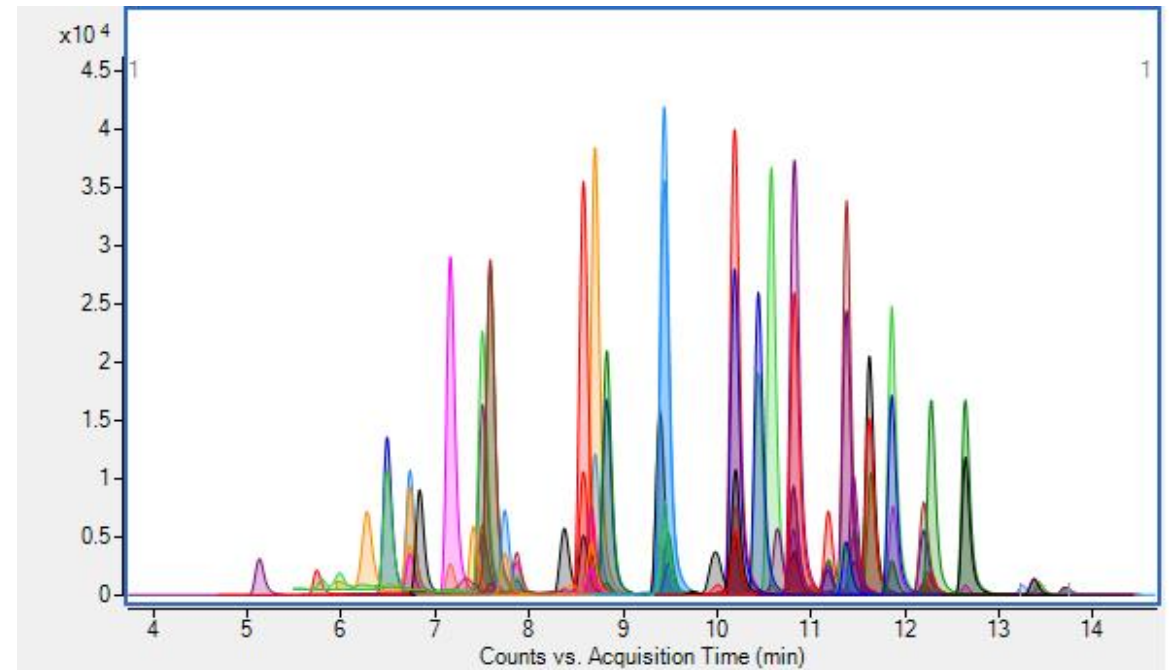
- Gold standard to derive definitive and sensitive information on PFAS.
- Selective and sensitive.
- Fast and reliable.
- Versatile.

- Where it can be used

- Regulatory compliance.
- Remediation and treatment studies.
- Monitoring surveys and risk assessment.

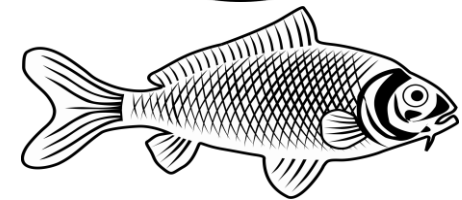
- Methods

- EPA 1633 for non-potable water/soil/tissue.
- EPA 533 for drinking water.
- Upcoming air methods.



Method Selection

- Data being used for:
 - Compliance -> Regulatory framework
 - Due diligence -> Risk management
 - Litigation -> Legal cases
 - Remediation -> Efficacy of the process
- Matrix:
 - Drinking water
 - Wastewater
 - Surface water/groundwater
 - Landfill leachate
 - Soil
 - Air
 - Biota/Tissue





Questions?

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