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

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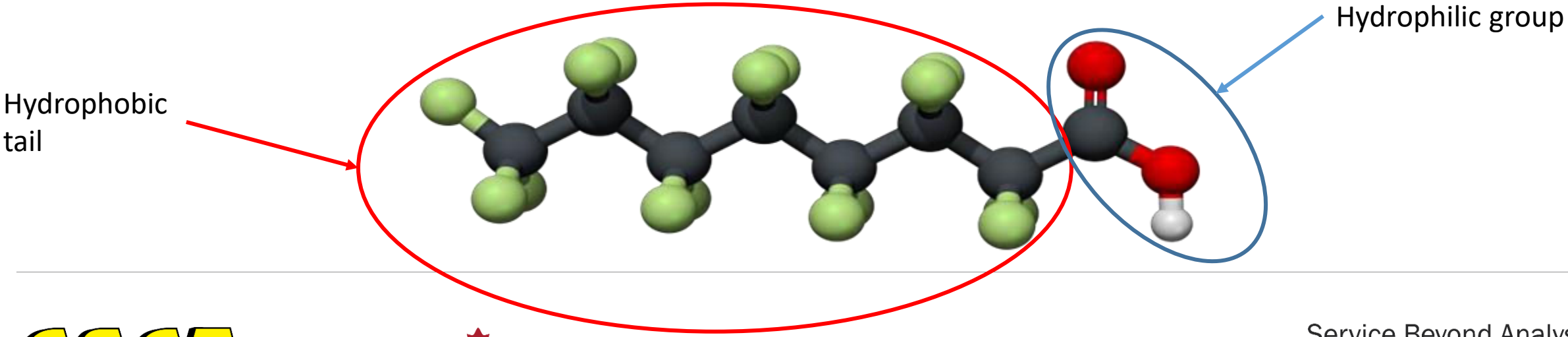
Content

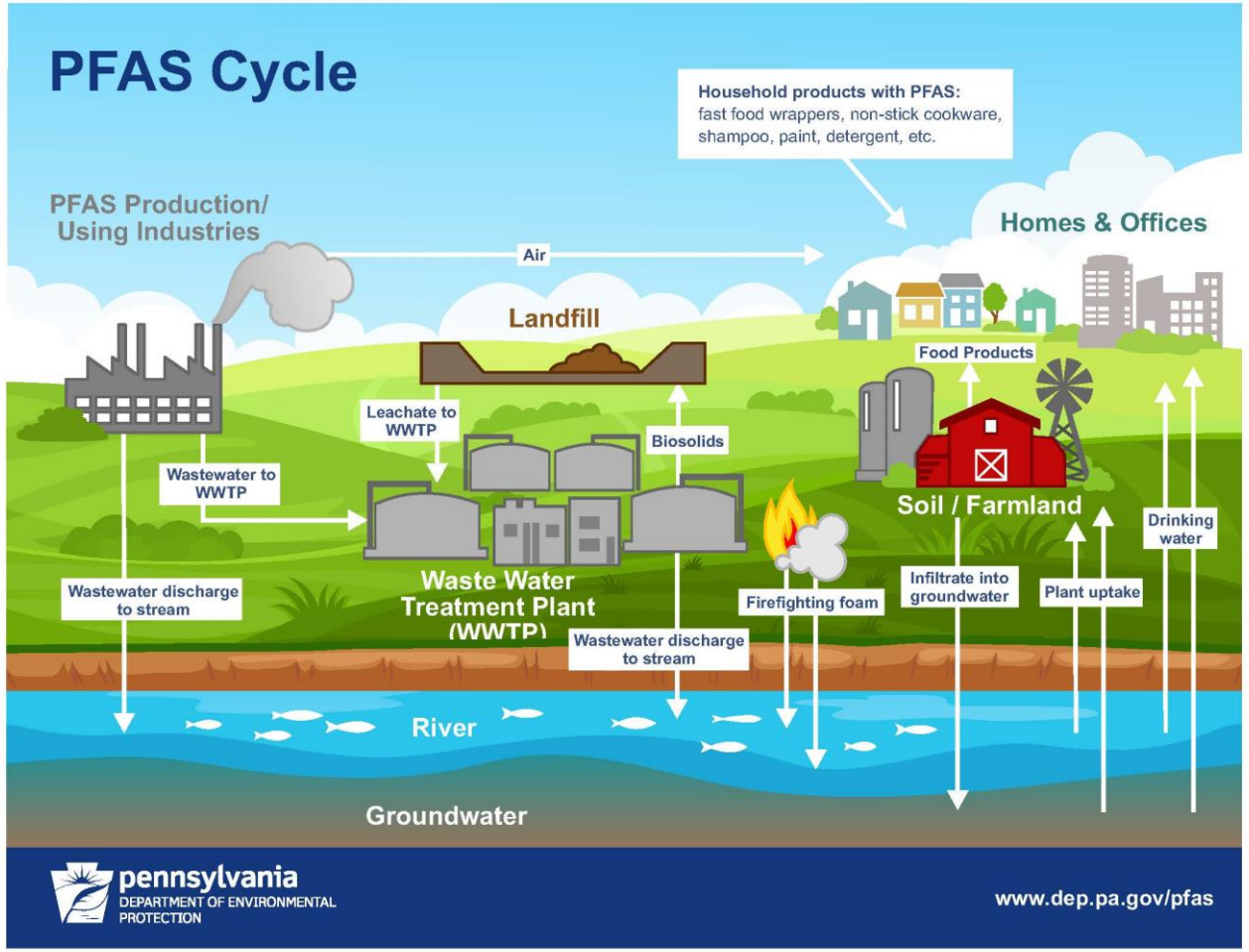
- PFAS chemistry
- Fate and Transport of PFAS
- Analytical Challenges
- PFAS methods and lists
- Quantitative analysis of PFAS
  - PFAS sampling
  - Sample preparation
  - Data Acquisition and Quantification
- Method selection

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

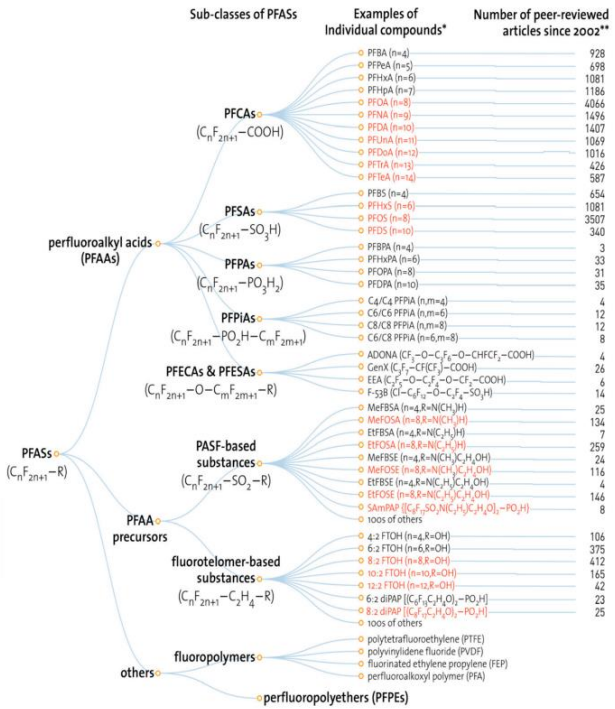
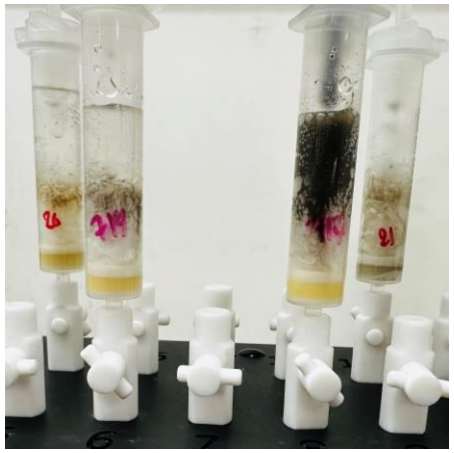


Image: Wang et al., 2017.

Ubiquitous nature

Image: Pennsylvania PFAS Action Team Report, 2019.

Matrix effects



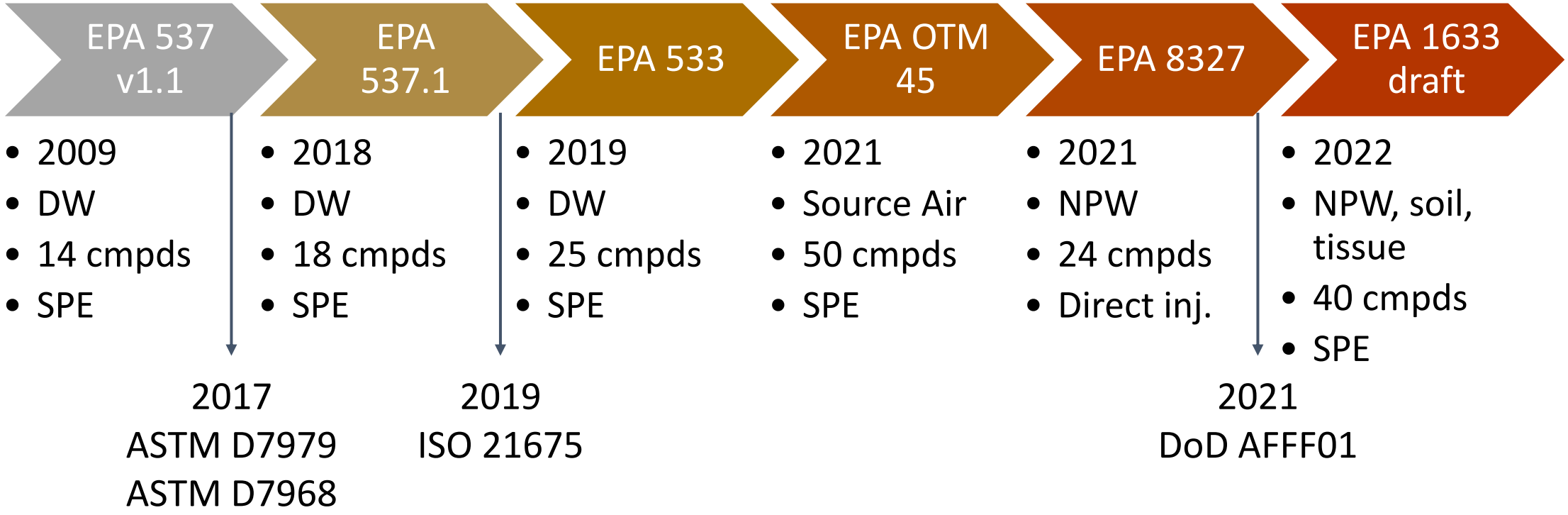
Lack of analytical standards

NEW STANDARD

PFAS Methods Timeline

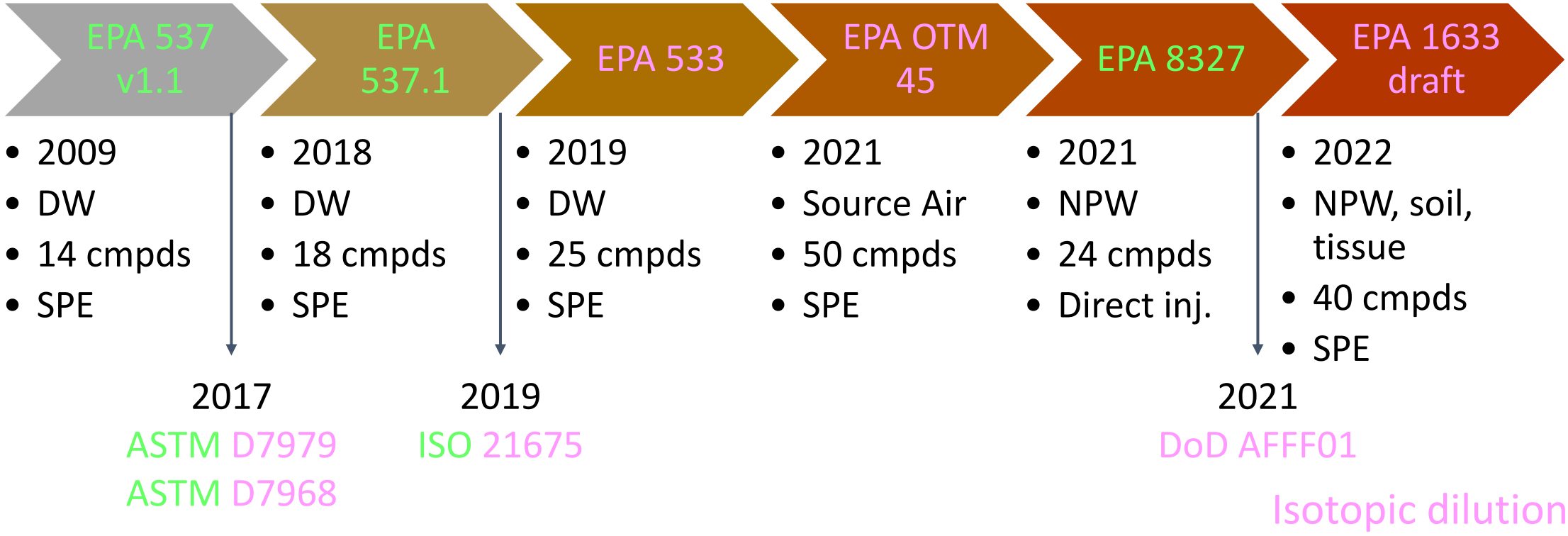
EPA 537 v1.1	EPA 537.1	EPA 533	EPA OTM 45	EPA 8327	EPA 1633 draft
• 2009 • DW • 14 cmpds • SPE	• 2018 • DW • 18 cmpds • SPE	• 2019 • DW • 25 cmpds • SPE	• 2021 • Source Air • 50 cmpds • SPE	• 2021 • NPW • 24 cmpds • Direct inj.	• 2022 • NPW, soil, tissue • 40 cmpds • SPE

PFAS Methods Timeline

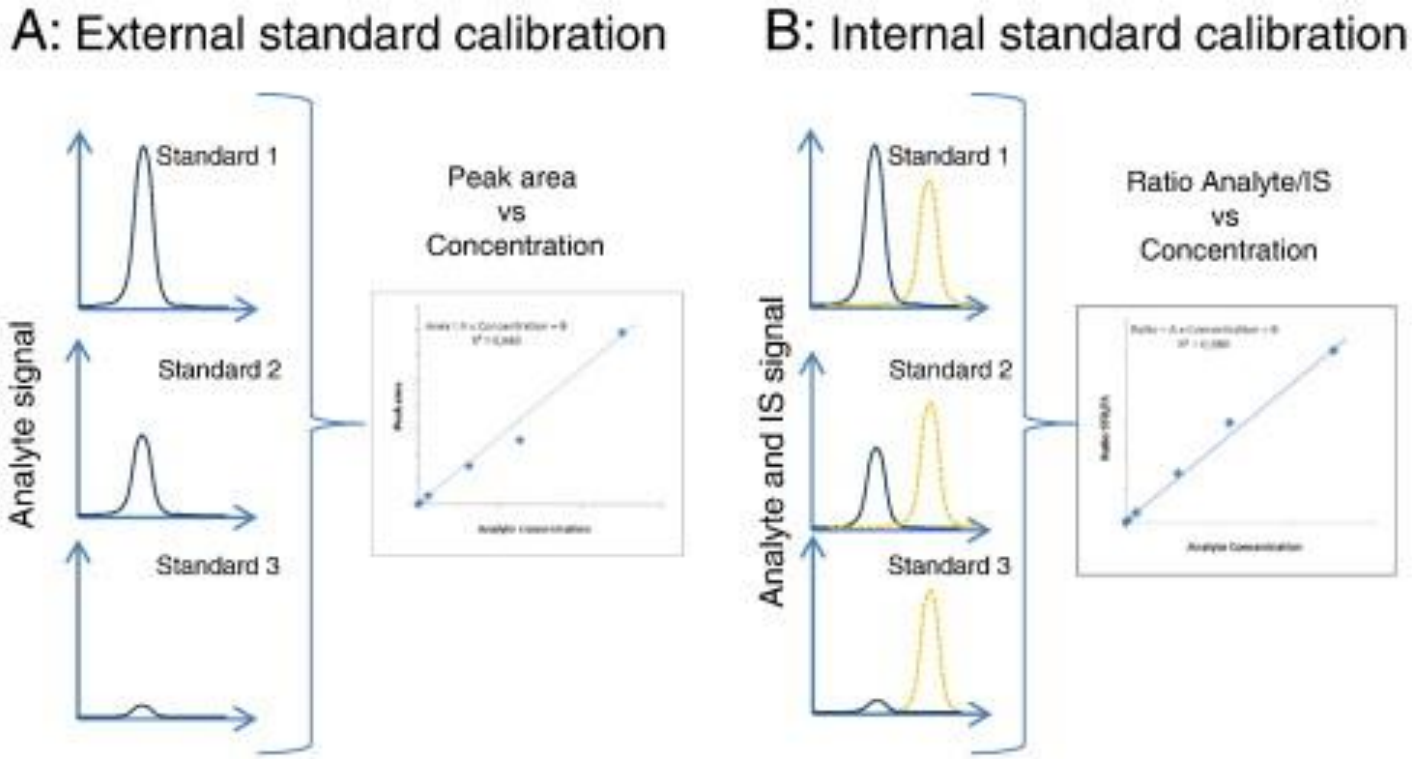


PFAS Methods Timeline

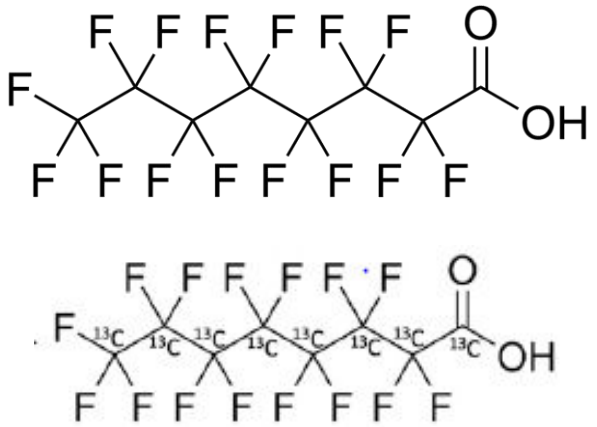
Internal/external standard



Quantification schemes

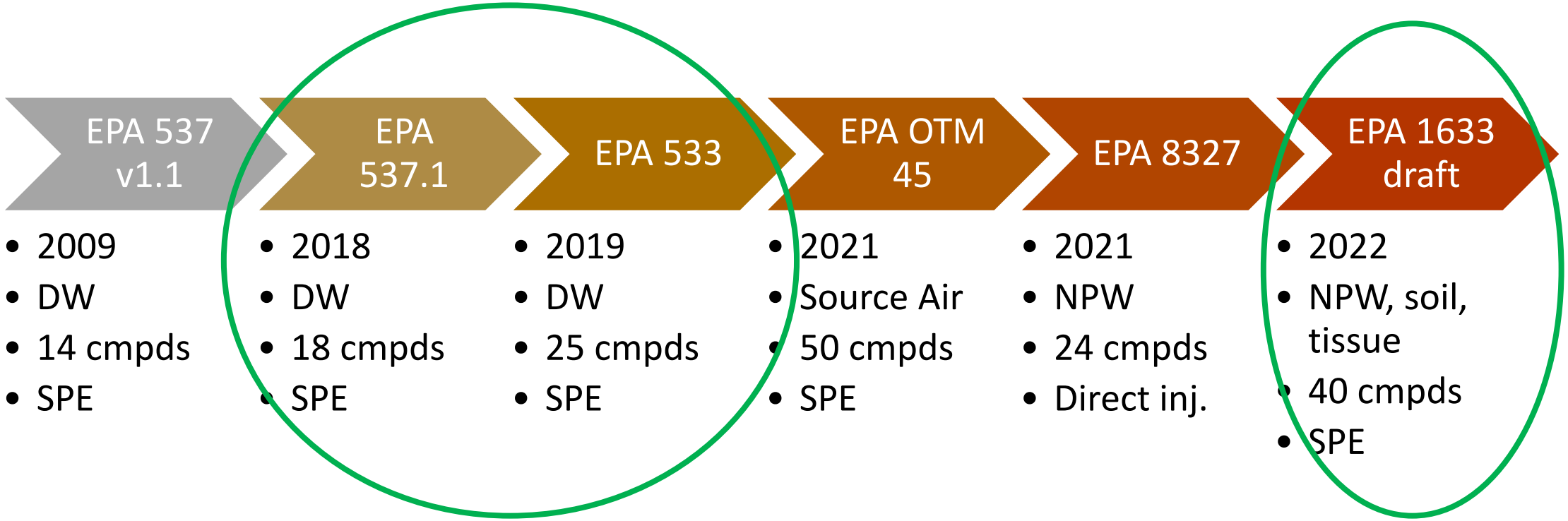


Isotope dilution



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_4Ac	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
PFTrDA	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
9Cl-PF3ONS	x	x	x
11Cl-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.

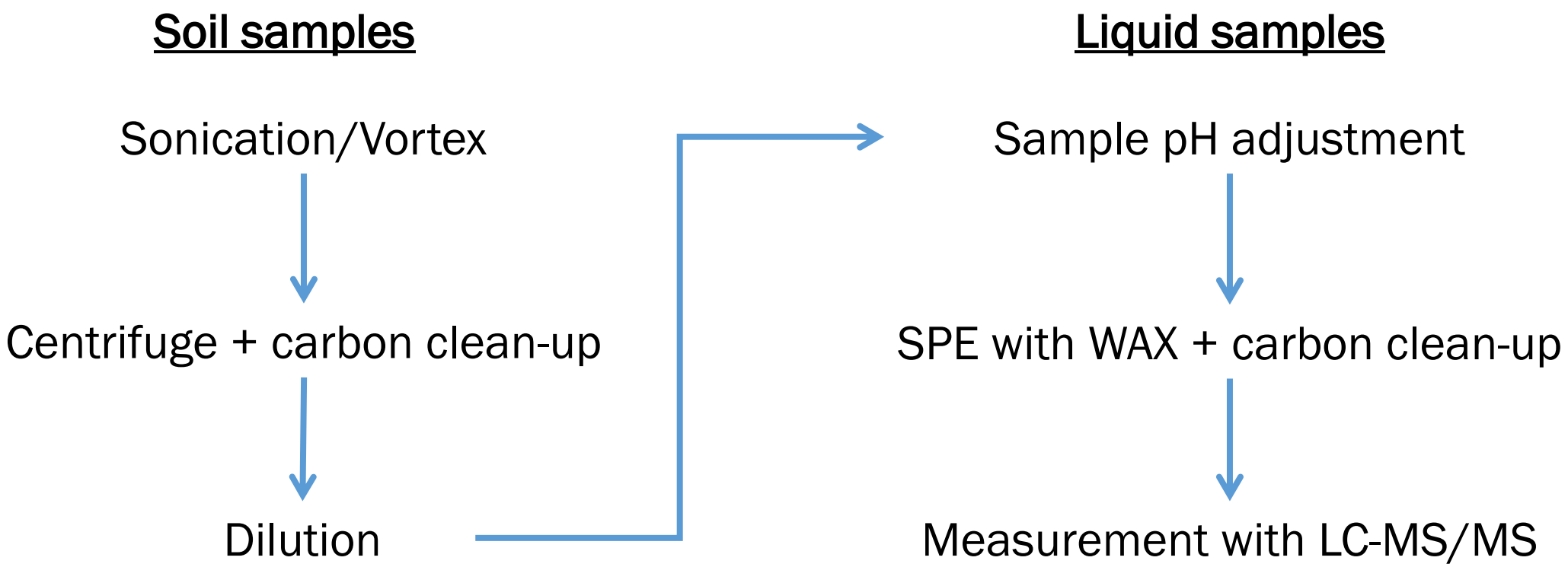
What About Air?

- 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

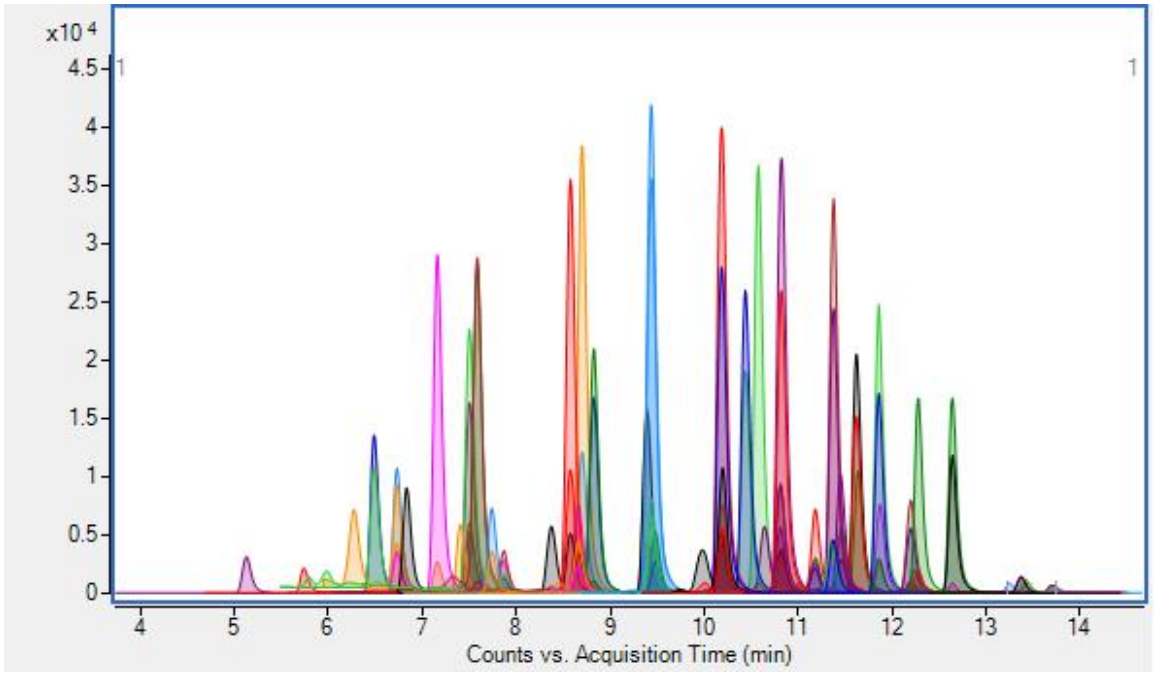
- Materials
  - HDPE, PP, silicone, stainless steel, nylon, acetate, and cotton.
  - Teflon-free bottle caps.
  - No coating in sampling equipment.
  - No glass, no LDPE.
- PCP and clothing
  - Waterproof clothing made with polyurethane, PVC, rubber or neoprene.
  - No Gore-Tex and similar water/stain-resistant 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



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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