PFAS Status Report

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Town of Merrimack NH
Pretreatment Manager
January 23, 2018

Overview

- Brief Merrimack PFAS History
- Summary of Regulatory Compliance requirements.
- Overview of current EPA method
- Overview of ASTM methods
- The need for standardized tests
- Impact on Regulatory Compliance
- Summary and Conclusion

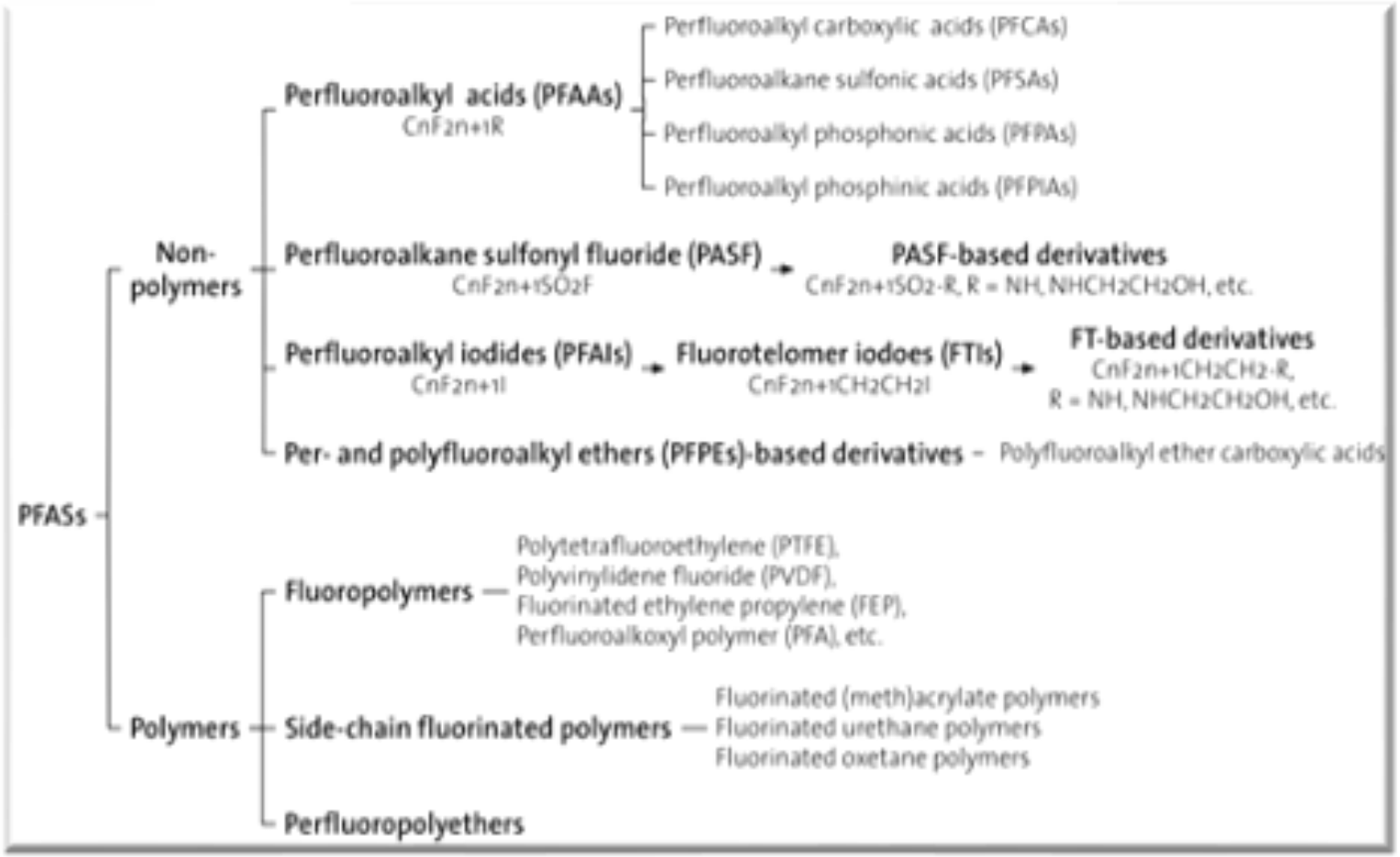
Uses of PFAS

- Food contact surfaces such as cookware[1], pizza boxes, fast food wrappers, popcorn bags, etc.
- Polishes, waxes and paints
- Stain repellants for carpets, clothing, upholstered furniture, etc.
- Cleaning products
- Dust suppression for chrome plating
- Electronics manufacturing
- Oil and mining for enhanced recovery
- Performance chemicals such as hydraulic fluid, fuel additives, etc.

[1] PFOA has been phased out, however there is little evidence that the chemicals that have replaced PFOA are much safer.

PFAS – Gets Complicated Fast

(Not going here in this webinar)



Source: Lawrence B. Zintek, Danielle Kleinmaier, Dennis J. Wesolowski, Solidea Bonina# and Carolyn Acheson* US EPA Region 5 Chicago Regional Laboratory (CRL) #Pegasus Technical Services, Inc. *US EPA ORD/NRMRL, Cincinnati, OH.

Merrimack History

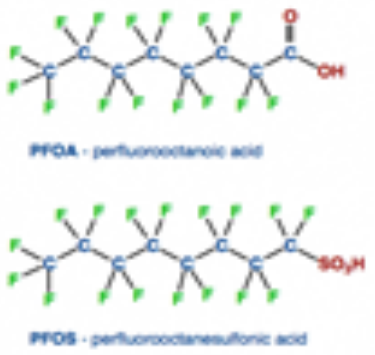
- PFOA is a fluorinated organic synthetic acid used to produce fluoropolymers.
  - manufacturing of non-stick, waterproof and grease-proof materials such as coating clothing, cookware, carpets, furniture, food wrappers and more.
  - DuPont used to use PFOA to make Teflon coatings but eventually phased it out.
- The New Hampshire Department of Environmental Services (DES) announced in May 2016 that they were working with the Merrimack Village District Water System (MVDWS) and Saint-Gobain Performance Plastics to investigate the potential presence of perfluorochemicals (PFCs) in drinking water in Merrimack.

Merrimack History (cont.)

- Since May 2016:
  - EPA drinking water Health Advisories for PFOA and PFOS lowered to 70 parts per trillion (ppt) for both compounds.
  - NHDES adopted the HA as a groundwater quality standard.
  - NHDES investigated Saint Gobain and surrounding communities.
  - Require Drinking water treatment (MVD).
  - NHDES announces Saint-Gobain Performance Plastics Agrees to Fund Design Study to Extend Manchester Water Works service to Bedford Residents – October 2017.
  - CA has listed PFOA & PFOS under Prop. 65.
- NHDES Samples WWTP's in NH.
- NHDES samples composite.
- NH legislature proposed bill to institute lower limits for PFOA and PFOS.
- NH legislature proposes bill to introduce MCL for PFOA,PFOS, and two other PFAS compounds.
- Vermont Health Advisory limit for PFOA and PFOS is 20 parts per trillion.
- NJDEP Commissioner Bob Martin announced that the DEP would accept the Drinking Water Quality Institute recommended health-based maximum contaminant level of 14 parts per trillion (ng/L).

Brief PFAS Background

- PFOA
- PFOS



PFOA/PFOS Drinking Water Health Advisory- 70 ng/L Combined

- 6:2 FTS

- PFOSA (FOSA)

- N-EtFOSAA

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Health Advisories

- Health Advisories identify the concentration of a contaminant in drinking water at which harmful health effects are not expected to occur if a person consumes the water over a certain timeframe.
- Health Advisory levels are not a federal standard that can be legally enforced and could change as new information becomes available.

US EPA Cross-Agency Coordination of PFAS Activities

Robert J. Kavlock, PhD

Assistant Administrator (Acting)

US EPA Office of Research and Development

- *ERIS Board-EPA Joint Meeting*
- *July 12, 2017*

Current PFAS Activities: OW

- **Published Drinking Water Health Advisories (HA) in 2016 for PFOA and PFOS**
  - HAs are non-regulatory information for federal, state and local officials to consider when addressing drinking water contamination.
  - Identified 0.07 µg/L (70 parts per trillion) as the HA level for PFOA and PFOS combined and provided information about treatment and monitoring.
- **Evaluating PFOA and PFOS for regulatory determination under the Safe Drinking Water Act (SDWA)**
  - PFOA and PFOS are on the fourth Contaminant Candidate List (CCL 4) published in November 2016. EPA's Office of Water is assessing PFOA and PFOS against the three SDWA regulatory determination criteria:
    - *May have an adverse effect on the health of persons*
    - *Is known to occur or there is a substantial likelihood that it will occur in public water systems with a frequency and at levels of public health concern*
    - *In the sole judgment of the Administrator, regulating the contaminant presents a meaningful opportunity for health risk reductions for persons served by public water systems*
  - EPA must decide whether or not to regulate at least five CCL4 contaminants by January 2021.
  - Preliminary regulatory determinations for public comment expected in 2019 (to enable final regulatory determinations by January 2021).

Analytical Methods

- Only PFOS, PFOA and PFBS have vetted toxicity values at this time. Therefore, for initial investigations these would be the primary PFAS contaminants of concern.
  - Drinking Water: EPA Method 537 Version 1.1
  - Media other than drinking water: Each contract lab has their own method (most loosely based on EPA 537) since a standard HW method does not exist
- ORD, Region 5 and others are developing methods for PFAS precursors and PFAS in non-DW matrices (surface waters, groundwater, wastewater, biosolids, soils, sediments, etc).
- OLEM, OW, ORD, and Regional Labs currently conducting a multi-lab validation effort to establish an EPA method(s) for non-DW media.
- ORD and others are developing methods to identify unknown PFAS in environmental samples due to transformations, degradation, new formulations, etc.

Chris Impellitteri - EPA Update – January 2018

Non Drinking Water Samples (ground, surface, waste waters):

- Direct injection method for 24 analytes - start a 10 lab external validation at the beginning of February and have results back by the end of March for statistical analysis. This method is based on an EPA Region 5 SOP.
- Isotope dilution method (same 24 analytes). A draft SW846 Method is currently circulating w/in EPA for internal review. This method had a lot of input from DoD/Navy.
  - The basis of the method is an EPA-ORD SOP out of Dr. Mark Strynar's lab in NC.
  - After internal review of the current draft, one EPA lab will test/validate the method, address any issues, redraft, and go straight to an external validation.

Chris Impellitteri - EPA Update – January 2018 (cont.)

Solids (soils, sediments, biosolids/sludge)

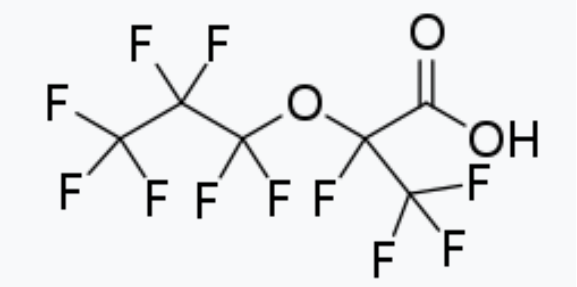
- Begin drafting SW846 Method in March after the water validation studies are going. Based on an EPA-ORD SOP (with DoD input as well).

GenX, ADONA (and other PFECAs) in water

- Drinking Water. EPA-ORD and the Office of Water are currently developing a method for perfluoroalkyl ether carboxylic acids (PFECAs) in DW (emphasis right now on GenX, ADONA).
  - The chromatography and MS conditions are such that we probably will not be able to add an addendum or update Method 537; it will likely be a separate method.
  - The testing and validation requirements for DW methods are much more rigorous (relative to SW846) and there will probably not be a draft for public review until early 2019. However, an interim draft may be issued prior to that depending on the method efficacy based on preliminary data.

Chris Impellitteri - EPA Update – January 2018 (cont.)

- Non-DW. EPA Regions 3 and 4 have been applying the direct injection method to the analysis of GenX.

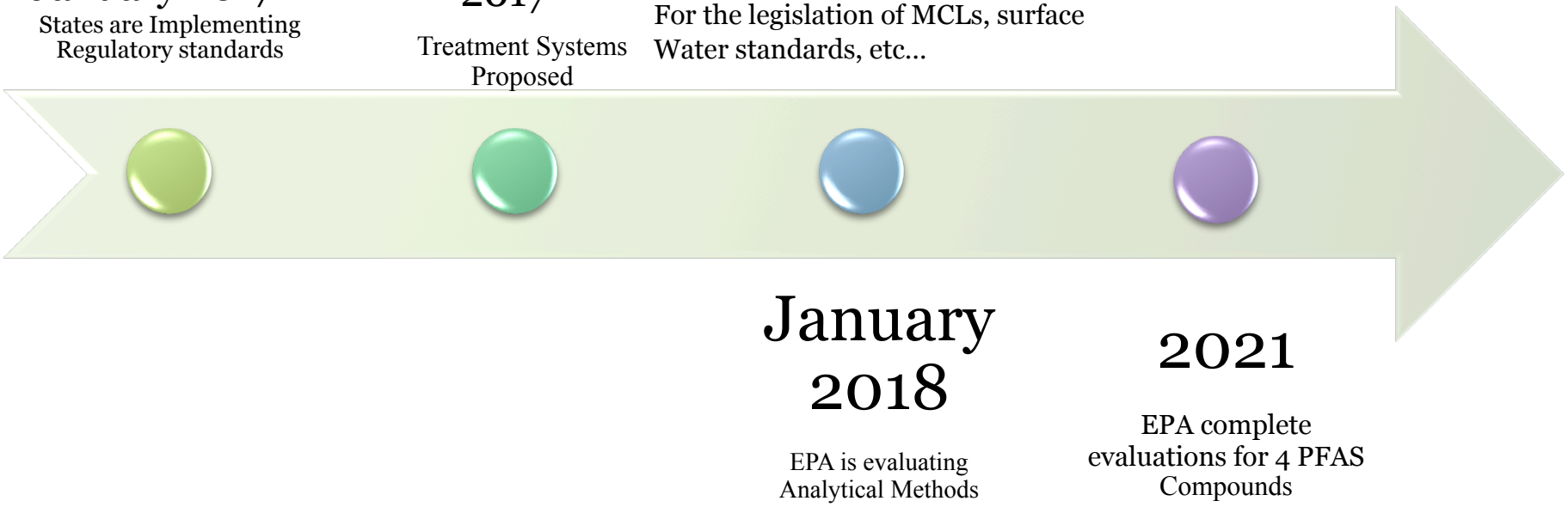


- EPA is aware of the interest/urgency in some areas of the country with PFECAs and will likely need to perform some validation of the methods in 1a and 1b above for PFECAs in the future, however, we will continue to focus on the 24 listed in the attachment for the external validation studies.

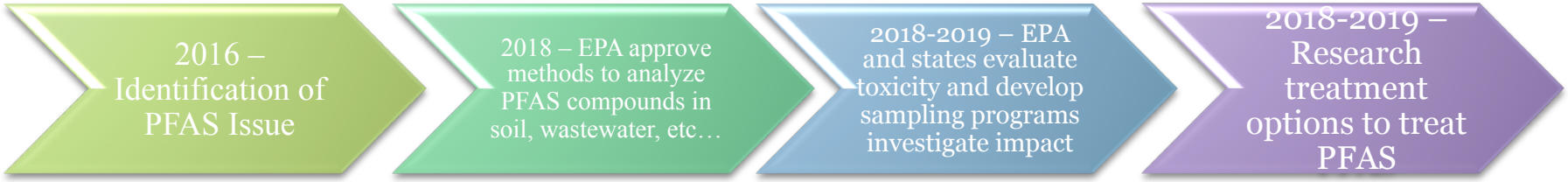
EPA PFAS Workgroup

- Purpose: Develop robust analytical methods and sampling protocols for solids and water other than drinking water.
- Workgroup Co-Leads: OLEM/OSRTI, Region 3, ORD/SSWR
- Program Offices
  - OLEM: OEM, OSRTI, and OCRC
  - OW: OS&T and OGWDW
  - ORD: NRMRL, NERL, NHEERL, and NCEA
  - NEIC, OCIR/RO, OPP/BEAD/ACB
- Regional Offices: 1, 2, 3, 4, 5, 6, 9, and 10

Timeline – A couple of Discrepancies



How is This?
We need time for science to catch up with the issue.



Regulation development begins after a comprehensive understanding of the problem (current, past, and future) has been completed.

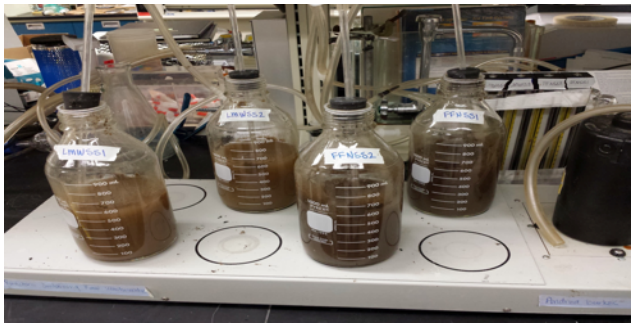
What are the Issues?

- Under the Clean Water Act - All methods must be promulgated at 40 CFR Part 136!
- Under RCRA - Methods are in the SW 846 Manual of Solid Waste. With a few exceptions – Guidance document (performance based)

Why not use EPA Method 537 for matrices other than Drinking Water?

Method 537 is a drinking water method!

- Not tested in other matrices
- Require Solid Phase Extraction
  - Won't work for all analytes of interest in one analysis
  - Pre-filter samples with particulates (bias low results)
- Limited number of surrogates to mimic the entire analyte mix
- Only one SRM transition
  - Makes quantitation difficult in dirtier matrices
  - Less confirmatory
- Blow down to dryness
  - Lose volatile PFAS



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What Do Environmental Labs Do?

- They run methods, not instruments!
- Methods are a prescription
- The method defines:
  - **MDL**
  - **Calibration range**
  - **QC acceptance criteria**
  - **Extraction**
  - **Instrument**

Source: William Lipps, Brahm Prakash - Shimadzu Scientific Instruments, Inc. Columbia MD - September 2017

Why is This Important

- All Labs are using the same method.
- All results can be compared.
- A third party (EPA) has established performance and acceptable QC requirements for the method.

Source: William Lipps, Brahm Prakash - Shimadzu Scientific Instruments, Inc. Columbia MD - September 2017

What Method 537 is:

- Solid Phase Extraction
- DRINKING WATER method
- Changes may not be made to sample collection and preservation (Sect. 8), the sample extraction steps (Sect. 11), or to the quality control requirements (Sect. 9).

EPA 537 Extraction procedure

Surrogate

10 ml/
Minute

4 ml
MeOH

Elute

EPA 537 Extraction procedure

Evaporate

1 ml 96% MeOH

Internal Standard

SHIMADZU

Method 537: Problems

- Variable, analyte dependent, recovery
- Must rinse sample bottle → must extract entire 250 ml
- Transfer sample like this

Method 537: Problems

- **Laboratory and field blank contamination:**
  - Many lab supplies and equipment can contain PFAS.

Non- Drinking Water PFAS

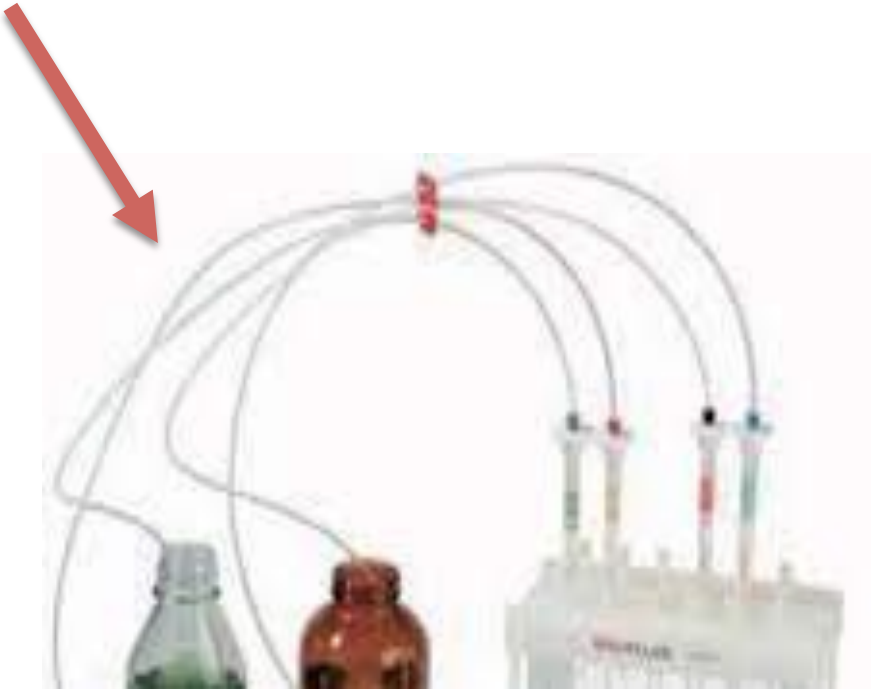

Wastewater and
wastewater
treatment

Land applied biosolids

SHIMADZU

Method 537 as written cannot be used for wastewater or soil. It is a prescription based Safe Drinking Water Act method.

- How do you extract 250 ml of wastewater or soil?
- Or transfer sample like this?



If Method 537 Rev 1.1 is Drinking Water Method Now what?

ASTM D7979 (waters & Sludges) and D7968 (soils)

- Original Methods
  - 21 Target analytes
  - 9 Surrogates (Isotopically labeled)
- Updated Methods (2017 Versions)
  - 31 Target Analytes and 14 Surrogates
    - Ten Additional Target Analytes added to Appendix with all MRM transitions, Tune parameters, recoveries in matrices …
    - Five Additional Surrogates (Isotopes) added to Appendix with all MRM transitions, Tune parameters, recoveries in matrices …

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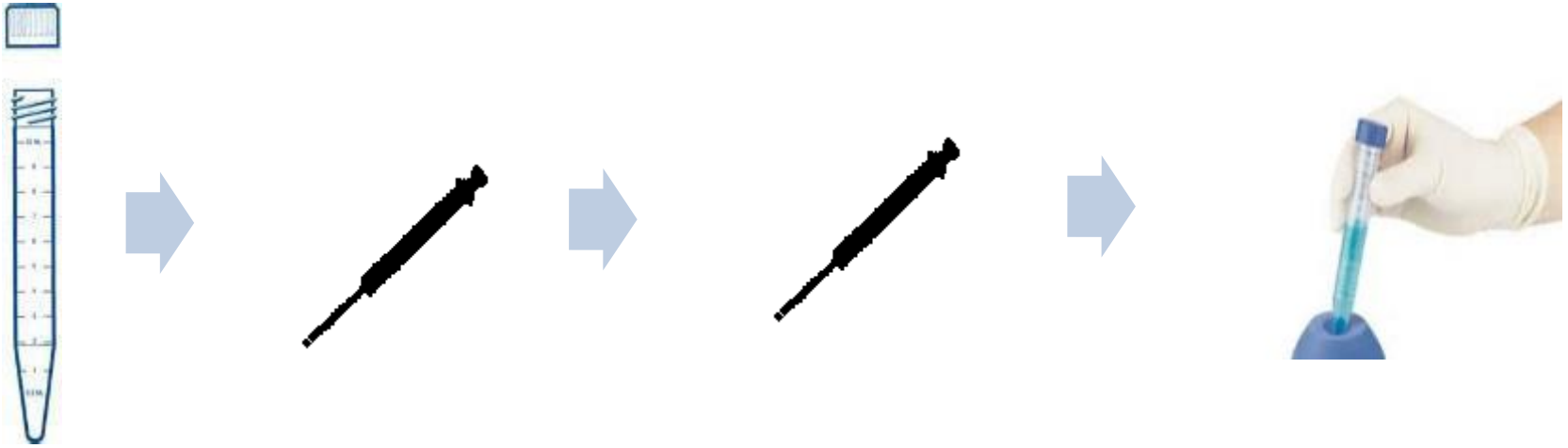
ASTM D7979 Extraction procedure



5 ml
Sample

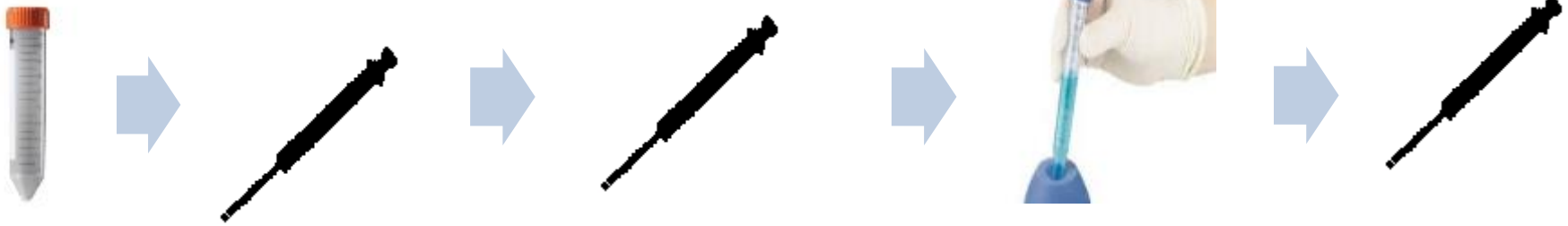
Surrogate

5 ml
MeOH

ASTM D7979 Extraction procedure

10 µL
Acetic Acid

ASTM D7968 Extraction procedure



2 g Sample Surrogate 10 ml (1+1) MeOH 20 µL NH_4OH

ASTM D7968 Extraction procedure

Tumble 1
hour

50 µL
Acetic Acid

Sampling and Analysis Issues

Contamination (Be cautious!)

- Teflon® Containing Materials
- Waterproof Field Books
- Plastic Clipboards, binders, or spiral hard cover books
- Post-it Notes
- Chemical (blue) ice packs
- Coated Tyvek®
- Glass Pipettes-PFAS contaminated- PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA

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Contamination (Be cautious!)

- Many types of water resistant, waterproof, or stain-treated clothing, clothing containing Gore-Tex™
- LDPE containers
- Decon 90
- Water from an on-site well
- Aluminum Foil
- Methanol

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Sample Collection

- Collect a 5.0 mL sample, grab would be best, in a graduated 15 mL polypropylene BD Falcon tube in the field so that the whole sample is processed in the lab (NO ALIQUOTING).
- In order to have accurate volumes, the weight of the 15 mL polypropylene BD Falcon tube may be taken before and after sampling in order to get an exact volume. The density of water is assumed to be 1.0 g/mL unless the exact density of the water sample is known, then that conversion should be used.

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Holding time/Sample Requirements

- 28 Days
- Required to collect a separate sample for each QC Sample (Co-located). Collecting in one container in the field and transferring to other containers may lead to low biased results.
- Have to prepare and use the entire sample.
- Take a couple extra samples in case re-extract required.

Review Data Generated by Other Methods

- Previously Published methods on PFCs
  - EPA Method 537, ASTM D7979 or D7968, Journal?
  - Are they really following the methods they cite?
    - Using the entire sample?
    - Many sample manipulations involved?
    - Pre-filter?
    - Complicated Sample Preparation?
    - Batch QC-Surrogates, duplicates, matrix spikes, reporting limit checks?
    - Ongoing Method Performance in Real Matrices?
    - Quantitation?
  - SRM or MRM, Ion Ratios?
  - Are they getting poor recoveries of their isotopes and correcting the data using isotope dilution?
  - Isotope dilution- are they diluting samples- diluting out isotope, adding more isotopes after dilution? Not isotope dilution anymore.
  - Equilibration time of the isotopes in the sample?
  - Are the isotopes at a similar concentration as their reporting range?

Source: Lawrence B. Zintek, Danielle Kleinmaier, Dennis J. Wesolowski, Solidea Bonina# and Carolyn Acheson

In Summary – EPA's Ongoing work

- Multi-lab validating methods
  - Internal EPA (now)
  - External
- Plan is to place in SW-846
- Updated ASTM D7979 (waters/sludges, not drinking water!) and D7968 (soils). www.astm.org

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WATER & ENVIRONMENTAL TECHNOLOGY CENTER

TEMPLE UNIVERSITY, 1947 N 12TH STREET, PHILADELPHIA, PA 19122

WET Center PFAS Capabilities & Ongoing Research

The research team led by Dr. Rominder Suri (rsuri@temple.edu) at the WET Center is conducting several projects dealing with PFAS analysis, water purification technologies, fate and toxicity effects.

- ***Removal of per-and polyfluorinated substances (PFAS) contaminants using ion-exchange and polymeric resin;***
- ***Regenerable Polymer Coated Sand adsorbent for the Removal of PFAS, VOCs and Chromium from Water;***
- ***Degradation of PFAS Using Advanced Oxidation Processes; &***
- ***In vivo and In vitro Toxicity Assessment of PFAS***.

Impact on Regulatory Compliance

- States are rushing to implement standards for PFOA/PFOS and other compounds without a promulgated method.
- Toxicological evaluations have not been completed for the myriad of other compounds in the PFAS family.
- Universities just are beginning the removal technology evaluation.
- Still need to understand the fate and transport of these compounds in wastewater.

Next Steps

- Talk to your legislators and regulators and ask for a science based approach to this problem.
- Science based evaluations.
- Life cycle analysis of products which currently have these compounds in consumer products.

Hang on... We must be doing something wrong...
How does the saying go again?