PFAS Sampling & Analysis Training

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Introduction & Background

- Requirements to test residuals for numerous contaminants and now PFAS
- Sampling programs and sampling plans
- NEIWPCC has developed a sampling guidance to address concerns (regulator, operators, & public) http://neiwpcc.org/our-programs/wastewater/residuals/biosolids-sampling-guide/
- NEBRA has developed a sampling guidance specifically for PFAS sampling based on the NEIWPCC sampling guide

What is a sampling plan and why is it necessary?

- Sampling program vs. sampling plan
- “Sampling plan is a blueprint for how a sampling program will be executed.”
- First step in implementing a sampling program
- Ensures representative samples and data
- Ensures the goals of the sampling program are meet

Special Considerations for PFAS

PFAS – per- and polyfluoroalkyl substances

- Large diverse chemical group
- Ubiquitous in commerce and therefore the environment

Regulation/requirements pertaining to PFAS are changing rapidly

- PFOA (perfluorooctanoic acid) and PFOS (perfluorooctane sulfonic acid) are the two compounds of primary concern at this time
- PFOA and PFOS are the two compounds for which health advisories, drinking water standards, or soil screening standards have commonly been set
- States and the Federal government may require testing for additional PFAS, and are just starting to set standards
- Most states have not set standards for PFAS in residuals (Maine is an exception)

Special Considerations (continued)

- **No approved PFAS analytical method for residuals, soil, wastewater**
- EPA Method 537 is approved **only** for drinking water
- A Modified 537 is used for other matrices
- Potential bias of results:
  - Low results from adherence of analytes to containers
  - High results from contaminants introduced both during sampling and the lab
- Numerous potential sources of extraneous contamination are a significant concern

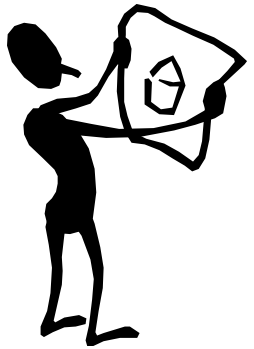
Bottom Line!

If you are going to sample for PFAS,

YOU NEED A Sampling Plan!

Elements of a Sampling Plan

- Goals
- Facility description
- Data quality objectives
- Sampling point selection and description
- Sample collection procedures
- Sample handling procedures
- Evaluation of completeness
- Record-keeping and reporting procedures



Sampling Plan Goals

- What is the goal of the facility sampling program?
- Representative samples vs. real goal
- Can have varied goals
- Goal(s) will dictate other elements of sampling plan
- Goal statement doesn't need to be long or complex

Example of Goal Statement

An example of a goal statement is:

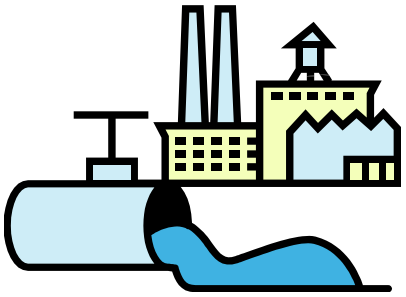
"The goal of our sludge sampling program, as detailed in this sludge sampling plan, is to demonstrate compliance with state and federal biosolids regulations."

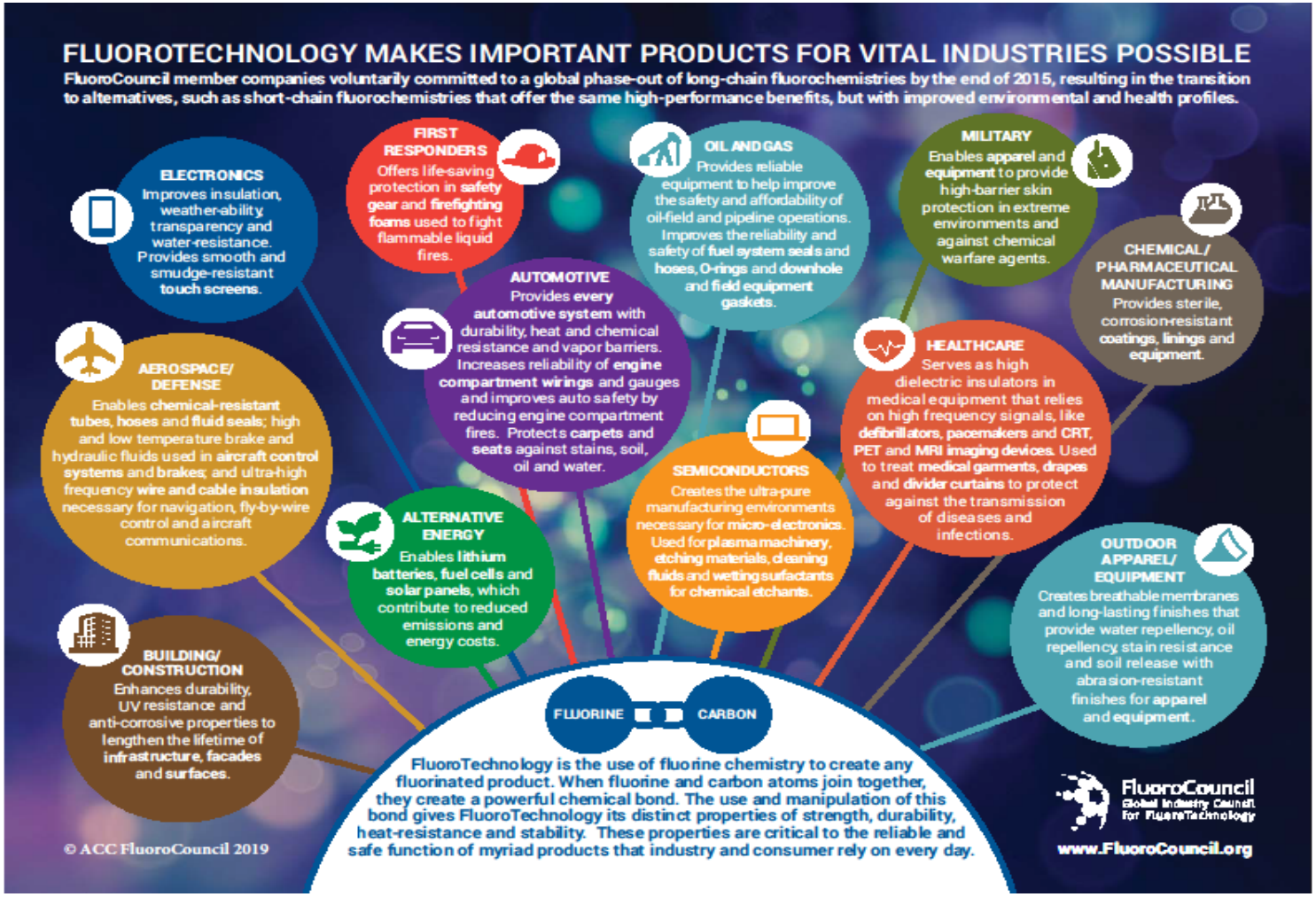
For PFAS:

"The goal of our sludge sampling program, as detailed in this sludge sampling plan, is to comply with NHDES requirements for testing of PFAS in biosolids."

Facility Description

- Sampling plans should include a thorough description of the generating facility
- Sludge handling and treatment are particularly important
- Should include a description of anything that might impact sludge quality
- Description of industrial pretreatment is important **(Do you have any PFAS producers or users?)**
- Schematic diagrams are efficient and helpful

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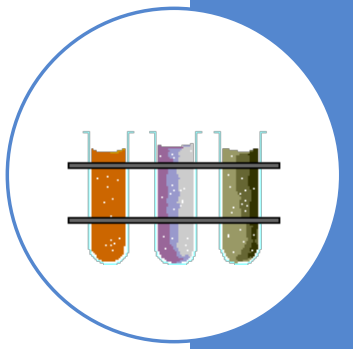
Data Quality Objectives

- Primary planning phase of sampling plan
- Determine required data and define minimum quality standards
- Defining data quality objectives can be the basis for an RFP for lab services
- Required analytes
- Required analytical methods
- QA/QC procedures
- Sample types, frequency, and size
- Cost of sampling and analysis

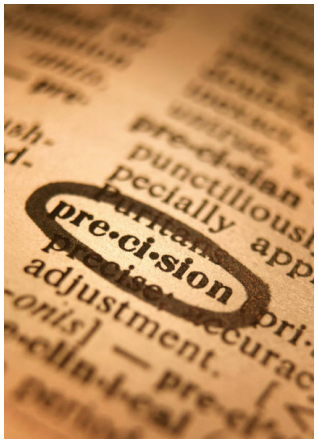
Required Analytes and Analytical Methods

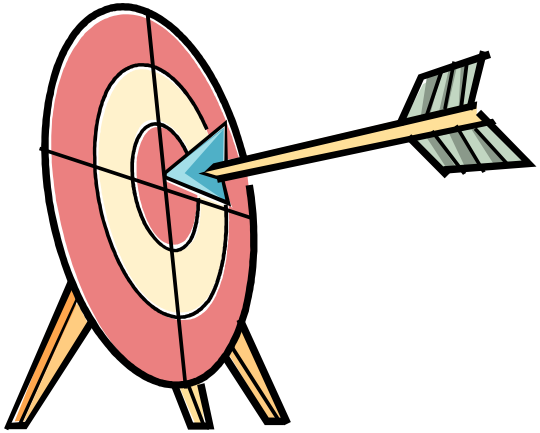
- Two important questions:
  - What chemicals do I test for?
  - What testing methods are required?
- The answers are typically found in state and federal regulations, but PFAS is an exception
- **As state agencies have begun to require testing or residuals for PFAS, they specify the compounds required to be tested and sometimes certain requirements for analytical protocols**
- Appendices C-1 and C-2 of the NEBRA guide provides assistance, but requirements are rapidly changing
- State agencies are the final authority and should be consulted regarding required analytes and analytical methods



Quality Assurance (QA) vs. Quality Control (QC)

- Quality Assurance (QA) equates with process control where quality standards (for accuracy and precision) are set and a plan for monitoring adherence is devised.
- Quality Control (QC) are the tools used to determine if quality standards are meet.
- **QA/QC associated with PFAS analysis includes terms such as isotope dilution, isotopically-labeled surrogates, surrogate recoveries**





Accuracy and Precision

- “Accuracy” is an evaluation of how close the observed value is to the “true value”
- “Precision” is an evaluation of the agreement between repeated measurements

Example of QA/QC and Accuracy/ Precision

Precision – the relative deviation between duplicates should be less than 10% (QA), duplicate sample results are 100 mg/kg and 91 mg/kg

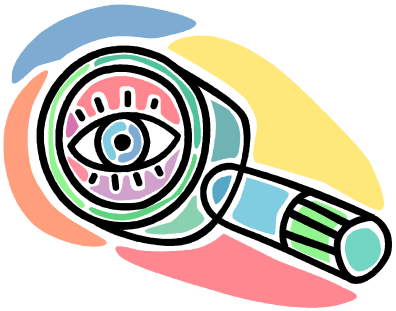
- ((100-91)/100) x100 = 9% (QC)

Accuracy – spike recovery should be between 80% and 120% (QA), the initial sample results was 100 mg/kg and a spike of 10 mg/kg was added. The spiked sample result was 108 mg/kg

- (108/(100+10)) x100 = 98% recovery (QC)

Detection Limits

- Detection limits should be less than any existing regulatory limit.
- Check applicable regulations for required minimum detection limits (MDL)
- Labs use different names for detection limits (MDL, RDL, PQL)
- **Check with applicable state agency for required detection limits, especially for PFAS testing**



Good/Bad News!

- The Good News - Most methods published by EPA and Standard Methods specify QA/QC
- Important for operators to have some familiarity with QA/QC requirements
  - Be good consumers of lab services
  - Ensure that QA/QC supports analytical results
- **The Bad News – Since EPA Method 537 is not approved for residuals, the QA/QC established in the method is not applicable**

Analytical Method and Data Quality

- **Poor** laboratory practice even when coupled with flawless sampling technique can result in poor data quality
- Most private environmental labs analyzing non-drinking water samples are using a “modified” version of EPA Method 537
- Without the constraints of an approved method, labs are free to modify Method 537 in any manner deemed expedient
- Inappropriate modifications and a lack of method standardization can result in poor data quality:
  - Accuracy
  - Precision
  - Comparability

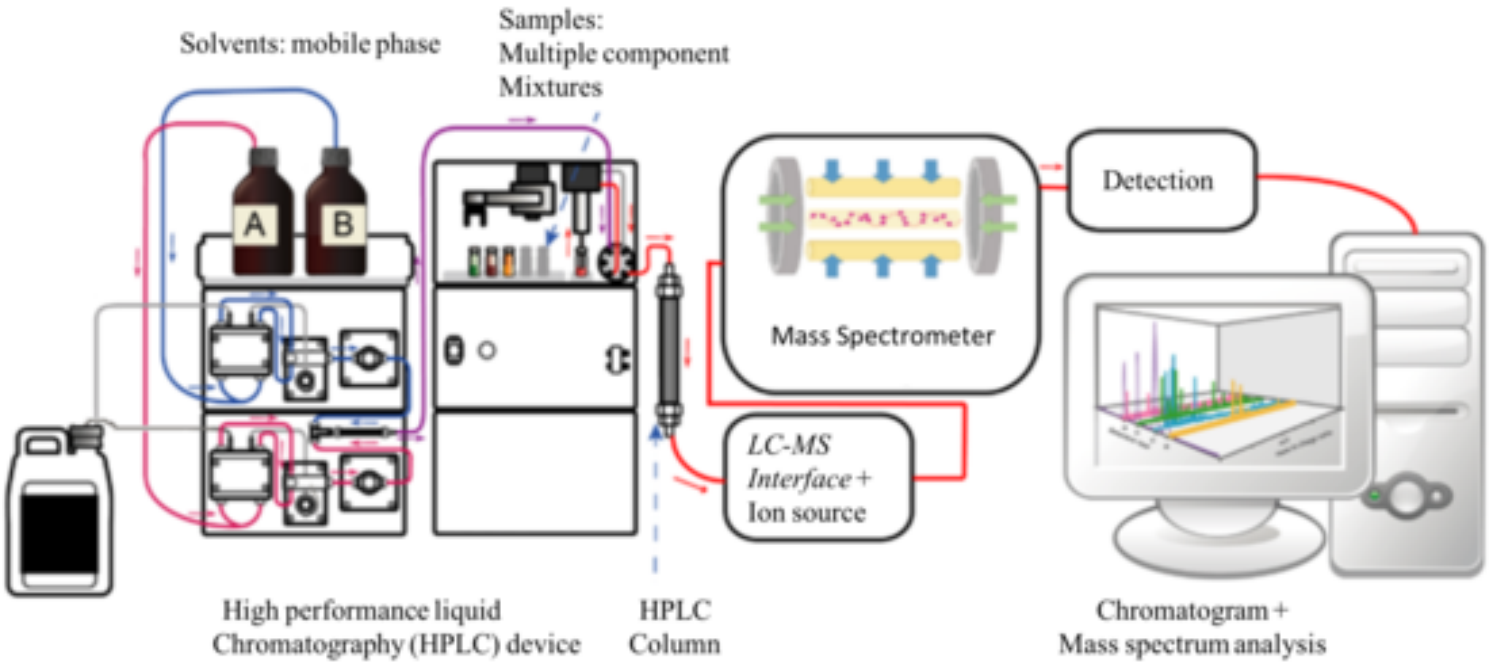
NEBRA Concerns Pertaining to PFAS Analyses

- **Contamination of samples from extraneous sources** – PFAS is ubiquitous in commerce and the environment. In addition, PFAS regulatory limits are being set at very low concentrations. Consequently, contamination of samples both during collection and in the laboratory can be a serious problem.
- **The addition of isotopically labelled surrogates after the extraction process** – Solids analysis requires an extraction step unnecessary for aqueous samples. If surrogates are added after the extraction process, extraction efficiency can not be evaluated, and adjustment of analytical results based on surrogate recoveries is inappropriate.
- **Excessive correction of analytical results of target compounds based on poor and/or highly variable recovery of isotopically-label surrogates** – The target analyte results are being adjusted based on extremely poor surrogate recoveries that do not meet data quality objectives typically established in approved analytical methodologies.
- **Excessively shorten run times and inadequate chromatographic separation** – Section 1.6, Method Reflexibility, of Method 537 (Nov. 2018 rev.) states that chromatograph conditions can be modified, but that analytes must be "adequately resolved chromatographically" to avoid a reduction in instrument sensitivity resulting from the elution of too many compounds within a retention time window.

NEBRA Concerns Pertaining to PFAS Analyses
(continued)

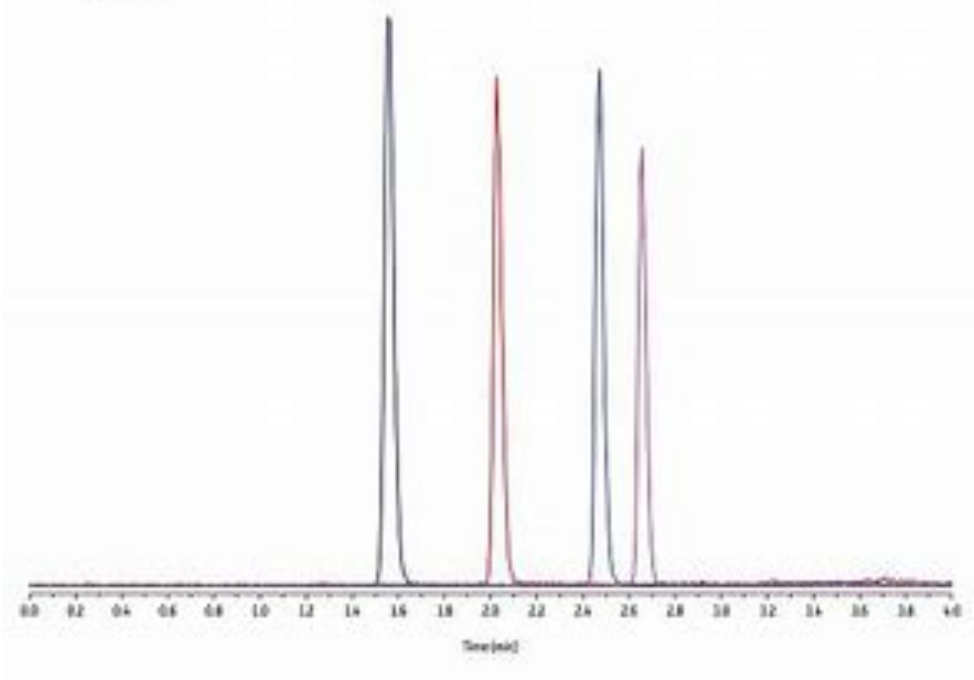
- **Processing of sample aliquots –** A low bias has been observed when aliquots of the entire sample collected are taken for sample processing and analysis. Target analytes can adhere to the inside of sample containers and be removed from the sample matrix.
- **Excessively large retention time windows:** Some of the retention time windows for analyte identification seem overly large and could lead to misidentification in a messy matrix.
- **Loss of short-chain PFAS during sample concentration:** It has been suggested that the process of concentrating samples to dryness using heat will volatilize the shortest-chain compounds, such as PFBS and PFBA.
- **Lack of pH adjustment for solids sample extraction** - ASTM D-7979, a method specifically developed for PFAS analysis in wastewater and wastewater solids, calls for the addition of ammonium hydroxide to sludge to attain reach a pH of 9. It is unclear whether this adjustment to alkaline pH is necessary to achieve the best extraction efficiency

Liquid Chromatograph/Dual Mass Spectrometer

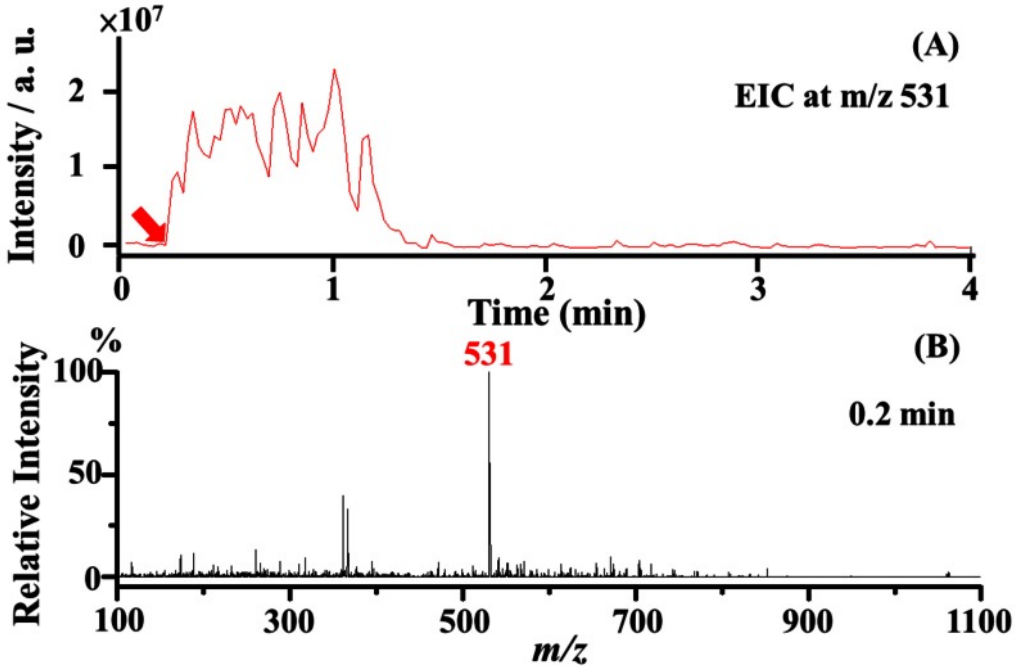


Total Ion Chromatogram

Peaks	t_R (min)	Conc. (ng/mL)	Precursor Ion	Product Ion
1. Perfluorobutanesulfonic acid (PFBS)	1.56	10	298.8	79.9
2. Hexafluoropropylene oxide-dimer acid (HFPO-DA/GenX)	2.02	10	328.9	284.9
3. Perfluorooctanoic acid (PFOA)	2.47	5	413.1	368.9
4. Perfluorooctanesulfonic acid (PFOS)	2.65	10	498.8	80.0



Extracted Ion Chromatogram and Ion Spectra



How Do I Find A Competent Lab for PFAS Analysis

- Look for guidance/recommendations
  - States sometimes provide lists of approved labs, specify methods, require specific analytical techniques, or mandate QA/QC
  - NEBRA, DOD, and other organizations provide similar guidance
- Before contracting with a lab, review its analytical methods and QA/QC procedures
  - SOP
  - Analytes
  - Calibration
  - QA/QC, isotope dilution
  - Recommended sampling procedures
  - Detection limits

How Do I Find A Competent Lab for PFAS Analysis (continued)

- Review the analytical reports
  - Request full QA/QC package (calibration curves, integration reports, chromatograms, etc.)
  - Read narratives for data qualification
  - Do various QC checks meet the labs internal limits (cal checks, surrogate recoveries, matrix spike, isotope recoveries, internal standards, lab blanks, etc.)
  - Review chromatograms
    - Retention time windows
    - Chromatographic separation and peak shape
    - Peak integration
    - Potential interferences
- If necessary, get help reviewing the data (lab, regulators, NEBRA, EPA) https://www.epa.gov/sites/production/files/2017-01/documents/national_functional_guidelines_for_organic_superfund_methods_data_review_013072017.pdf

Sample Size, Frequency, & Type

- Sample type: grab vs. composite
- Sampling frequency and size are related
- Larger samples tend to be more representative
  - Need minimum amount to perform analysis (250 mL, 2-5 grams)
  - Balance size with practical considerations
- How many grabs and how many samples (issues of size and frequency)?
- **Many methods and labs are recommending grab samples to prevent PFAS cross-contamination of residuals samples**

How Many Grabs and How Many Samples?

- Sampling frequency is specified in regulations or by regulatory mandate.
- Regulation don't specify the sample type or number of grab samples.
- Type and number of grabs based on variability of historical data
  - Standard deviation
  - Calculation in NEIWPCC guide

Selection of Sampling Points

- Proper sampling locations will allow the collection of representative samples that help meet the goals of the sampling program
- Type of Process: batch vs continuous
- Practical considerations
  - Accessibility
  - Safety
- Typical locations are after treatment (dewatering, PR, VAR,) when residuals are in the final product form

Sample Collection Procedures

- Equipment types
  - Liquid samplers (pitchers, cylinders, coliwasa)
  - Solids samplers (augers, thiefs, scoops, shovels)
- Equipment compatibility
  - No PTFE (teflon)
  - Stainless steel
  - HDPE and polypropylene
- Cleaning and preparation
- Sample containers (as provided by lab)

Sample Collection Procedures (continued)

- Facilities should develop SOPs to describe the actual procedure used in collecting a sample
- Preparing for sampling (checklists)
- Detailed description of sampling procedures
  - Equipment and procedure (type, size, timing)
  - Safety
  - Documentation (field records)
  - Sample labeling
  - Post-collection handling

Sample Handling Procedures

- Sample Preservation
  - Specified in method
  - Generally ice for solid samples (PFAS: Trizma, 0-6^{o}C)
- Hold times – specified in method (PFAS: 14 days, 28 days)
- Transportation to lab relative to hold times
- Chain-of-custody and custody seals to demonstrate sample integrity

Completeness Evaluation

- Is the sampling plan being implemented and is the goal of the sampling program being meet?
- Data evaluation (methods, MDLs, QA/QC, number and types of samples, reporting, billing)
- Review of sampling procedures
- Overall review and revision

Record-keeping and Reporting

- What records will be generated and kept?
  - Collection reports
  - Analytical results
  - Field QC
- How and when will these data be reported
  - Which compounds
  - Units
  - Reporting format
- Record retention
  - Which reports?
  - How long?
  - In what format?

NEBRA PFAS Sampling Tips

- Keep potential contaminants out of sampling area (equipment, clothing, etc.)
- Use sample containers provided by the laboratory
- Appropriate equipment cleaning
- Wash hands and use nitrile gloves
- Only the sample should contact inside the sample container

NHDES PFAS Sampling Guidance

Category	Prohibited Items	Allowable Items
Pumps and Tubing	Teflon® and other fluoropolymer containing materials	High-density polyethylene (HDPE), low density polyethylene (LDPE), or silicone tubing, peristaltic pump or stainless steel submersible pump
Decontamination	Decon 90	Alconox® or Liquinox®, potable water followed by deionized rinse.
Sample Storage and Preservation	LDPE or glass bottles, PTFE-or Teflon®-lined caps, chemical ice packs	Laboratory-provided sample container -preferred; or, HDPE or polypropylene bottles, regular ice
Field Documentation	Waterproof/treated paper or field books, plastic clipboards, non-Sharpie® markers, Post-It® and other adhesive paper products	Plain Paper, metal clipboard, Sharpies®, pens
Clothing	Clothing or boots made of or with Gore-Tex™ or other synthetic water resistant and/or stain resistant materials, Tyvek® material	Synthetic or cotton material, previously laundered clothing (preferably previously washed greater than six times) without the use of fabric softeners
Personal Care Products (for day of sample collection)	Cosmetics, moisturizers, hand cream and other related products	Sunscreens: Alba Organics Natural Yes to Cucumbers Aubrey Organics Jason Natural Sun Block Kiss My Face Baby-safe sunscreens ('free' or 'natural) Insect Repellents: Jason Natural Quit Bugging Me Repel Lemon Eucalyptus Herbal Armor California Baby Natural Bug Spray BabyGanics Sunscreen and Insect Repellents: Avon Skin So Soft Bug Guard-SPF 30
Food and Beverage	Pre-packaged food, fast food wrappers or containers	Bottled water or hydration drinks

Equipment Preparation and Cleaning Procedure for PFAS Sampling

The following cleaning procedure should be used to clean all HPDE, polypropylene, stainless steel, or glass equipment used to collect samples for PFAS analysis. Because of the extremely low detection and reporting levels required for PFAS analysis, precaution should be taken to ensure cleaning materials (soap, tap water, deionized water, methanol) are not contaminated with PFAS prior to use. It may necessary to have cleaning materials analyzed (e.g. with a rinsate blank, see #7 below) to ensure thay are not contaminated.

- 1) Rinse equipment with warm tap water to remove most solids.
- 2) Using a brush and a low-phosphate lab detergent, scrub the equipment to remove all residues. Liquinox® or Luminox® are common lab detergents that can be used for this purpose.
- 3) After scrubbing, rinse the equipment three times with tap water.
- 4) The tap water rinse should be followed by rinsing three times with deionized water.
- 5) Finally, the equipment should be triple rinsed with methanol. The rinsate from this step should be collected for proper disposal.
- 6) After cleaning, allow the equipment to air-dry. Many cleaning protocols suggest covering or wrapping clean sampling equipment in aluminum foil. EPA Method 537 advises against this practice to avoid possible contamination of the equipment with PFAS. This caution is particularly important for water samples. To store, buckets, beakers and other container can be inverted in a clean dry location. Soil probes, trowels, augers and other sampling equipment should be covered or wrapped with clean, unused HDPE or polypropylene plastic sheeting.
- 7) Periodically and especially at the beginning of a sampling project, an equipment rinsate blanks should be collected. A rinsate blank is prepared by rinsing equipment previously cleaned using the method outlined above with deionized water and collecting the rinse water for analysis. Equipment rinsate blanks are particularly important when equipment is cleaned in the field between samples.

NEBRA Sampling Tips (continued)

- Seal each sample in a ziplock bag after collection
- Collect PFAS samples before other parameters and store in separate coolers
- Move from areas of low concentration to high concentration
- One person collects samples, the other performs other functions
- Utilized field QC (field blanks, trips blanks, equipment blanks) https://www.epa.gov/sites/production/files/2015-06/documents/blanks.pdf

QUESTIONS?

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