Update on Emerging Contaminants

SC SWANA MEETING
Pauley's Island, SC
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Introduction

<u>Contact information</u>

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Discussion Topics

- 1,4-Dioxane
  - Overview
  - Landfills
  - Analytical Methods

- PFAS
  - Overview
  - DWM Projects
  - Leachate and Landfills
  - Sampling Considerations

1,4-Dioxane Overview

- Used as a solvent for cellulose formulations, resins, oils, waxes and other organic substances. It is also used in wood pulping, textile processing, degreasing, lacquers, paints, varnishes and stains; and in paint and varnish removers.

- Typically found at some solvent release sites and sites with 1,1,1-Trichloroethane contamination.

- Can be found in consumer products: detergents, shampoos, deodorants and cosmetics

- Relatively resistant to biodegradation in soil and water
  - Moves rapidly from soil to groundwater
  - Migrates rapidly in groundwater ahead of other contaminants

- Considered an emerging contaminant

- EPA 1,4-Dioxane Technical Fact Sheet
  - https://www.epa.gov/fedfac/technical-fact-sheet-14-dioxane

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1,4-Dioxane and Landfills

- 1,4-Dioxane
  - NC 2L Groundwater Standard = 3 ug/l
  - NC Surface Water Protective Value = 0.35 ug/l
    - Water supply, Class WS I – V
  - NC Surface Water Protective Value = 80 ug/l
    - Aquatic Life and Secondary Recreation, Class C and SC

- Remediation and Treatment Technologies
  - Very Mobile - Low absorption potential and miscibility
  - Standard Air Stripping or Granular Activated Carbon systems do not remove 1,4-Dioxane from water
  - Effective treatments include UV or Ozone, Advanced Oxidation

- Analytical method SW 846 Method 8260/8270 SIM (Select Ion Monitoring) is recommended

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1,4-Dioxane and Landfills

- May 29, 2018 Memo: All landfills must analyze for 1,4-Dioxane in both groundwater and surface water samples as of July 1, 2018

- Current Summary Groundwater Detections:
  - Currently 30 sites with 1,4-Dioxane groundwater exceedances
  - Concentrations range from 4 ug/L to 1,100 ug/l
  - Present at all landfill types (lined and unlined MSW, C&D and Industrial)
  - 20+ groundwater reports still under review
  - Several facilities yet to sample for 1,4-Dioxane or used inappropriate laboratory analytical method.

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1,4-Dioxane Analytical Methods and Detection Limits

- The discontinued use of the Solid Waste Section Limits (SWSLs) was also included in the May 29, 2018 Memo
- SWSLs were developed in 2006
  - Ensure that low level analytical data was consistently being reported
- Advanced technologies have rendered most of the SWSLs outdated, and the need to maintain them is not warranted.
- Facilities should choose EPA approved analytical methods with sufficient sensitivity to quantify the presence of a constituent at or below applicable standards.
- Facilities should continuously and clearly communicate with their associated laboratory on a regular basis prior to each sampling event.

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1,4-Dioxane Analytical Methods and Detection Limits

Volatile Organic Compounds	SW 846 Method 8260
1,4-Dioxane	SW 846 Method 8260 SIM SW 846 Method 8270 SIM
Semi-Volatile Organic Compounds	SW 846 Method 8270
Metals, Pesticides, PCBs, Dioxins, Cyanide, Formaldehyde, and any other constituents not covered by above methods	SW 846 Methods, USEPA methods, or method published in Standard Methods for the Examination of Water and Wastewater having the lowest detection limits or having detection limits below applicable standards

- The analytical methods should be the most recent versions. For SW- 846 Methods, the latest edition of SW-846, including any subsequent updates which have been incorporated into the edition, must be used. Sampling must be planned so that required holding times for analytical methods are met.
- Select Ion Monitoring (SIM) is recommended when analyzing for 1,4-Dioxane to achieve applicable detection limits. SIM may be useful for other VOCs/SVOC constituents.
- SW-846 Method 1610 does not have detection limits below the 15A NCAC 2L standards for all of the hazardous substance list metals.
- The Section considers “J” flag values valid and relevant in the decision making process. From now on, all “J” flag values should be reported

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What are PFAS?

- Per- and polyfluoroalkyl substances (PFAS) are a group of manmade chemicals that have been in use since the 1940s.

- There are many PFAS chemicals, including the chemicals perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and GenX chemicals (HFPO dimer acid and its potassium salt).

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PFAS and Industry

PFAS[1]	Development Time Period							
	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s
PTFE	Invented	Non-Stick Coatings			Waterproof Fabrics			
PFOS		Initial Production	Stain & Water Resistant Products	Firefighting foam				U.S. Reduction of PFOS, PFOA, PFNA (and other select PFAS[2])
PFOA		Initial Production		Protective Coatings				
PFNA					Initial Production	Architectural Resins		
Fluoro-telomers					Initial Production	Firefighting Foams		Predominant form of firefighting foam
Dominant Process[3]		Electrochemical Fluorination (ECF)						Fluoro-telomerization (shorter chain ECF)
Pre-Invention of Chemistry /			Initial Chemical Synthesis / Production			Commercial Products Introduced and Used		

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PFAS and Industry

- Textiles and Leather-Factory – Consumer-applied coating to repel water, oil and stains. Applications include protective clothing and outerwear, umbrellas, tents, sails, architectural materials, carpets, and upholstery.

- Paper Products – Surface coatings to repel grease and moisture. Uses include non-food paper packaging (for example: cardboard, carbonless forms, masking papers) and food-contact materials (for example: pizza boxes, fast food wrappers, microwave popcorn bags, baking papers, pet food bags)

- Metal Plating and Etching – Corrosion prevention, mechanical wear reduction, aesthetic enhancement, surfactant, wetting agent/fume suppressant for chrome, copper, nickel and tin electroplating, and post-plating cleaner.

- Wire Manufacturing – Coating and insulation.

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PFAS and Industry

- Industrial Surfactants, Resins, Molds, Plastics – Manufacture of plastics and fluoropolymers, rubber and compression mold release coatings; plumbing fluxing agents; fluoroplastic coatings, composite resins and flame retardant for polycarbonate.

- Semiconductor Industry – Photoresists, top anti-reflective coatings, bottom anti-reflective coatings, and etchants, with other uses including surfactants, wetting agents and photo-acid generation.
- Aqueous Film Forming Foams – Class B Flourine-containing fire-fighting foams

*Certain PFAS chemicals, including PFOA and PFOS, are no longer manufactured in United States but are still produced internationally and can be imported as consumer goods such as carpet, leather, textiles, paper and packaging, coatings, rubber and plastics.

**PFAS History and Use Slides: ITRC, History and Use of PFAS, November 2017*
https://pfas-1.itrcweb.org/wp-content/uploads/2017/11/pfas_fact_sheet_history_and_use__11_13_17.pdf

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PFAS in North Carolina: Brief History

- 2016 – DEQ Department of Defense Coordination at Aqueous Film Forming Foam (AFFF) sites

- 2017 – GenX in North Carolina's Cape Fear River
  - Multi-agency response (DWM, DWR, DAQ, DHHS)

- 2018 – Active discussion on potential PFAS sources (military bases, fire training facilities, electro platers, landfills, etc.)

- 2019 – PFAS symposiums and seminars

PFAS and DWM

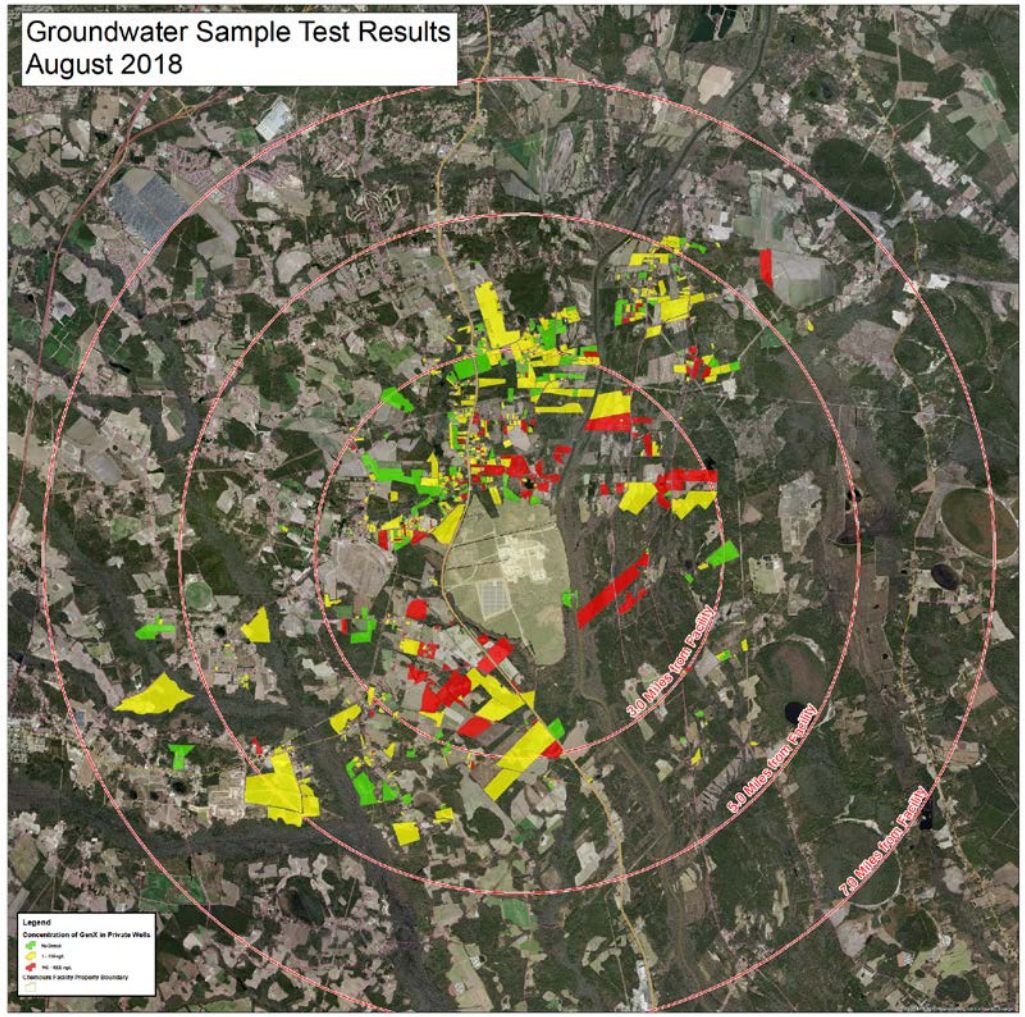
- Hazardous Waste Section
  - Chemours
  - Environmental monitoring/assessment at fire training facility

- Superfund Section
  - Historical operations at airplane hangar – groundwater, surface water and WSWs (~42) investigated
  - DOD facility – groundwater and WSWs (~258) investigated

- UST Section
  - Two separate Ethanol spill incidents – soil, groundwater and WSW being investigated

- Solid Waste Section
  - New Hanover County Landfill sampling event

PFAS and DWM – Chemours



- Well Sampling Results in Chemours area,
- Approximate distances from facility boundary:
- Northeast – 5.5 miles
- West – 3 miles
- Southwest – 5 miles
- East – 3.5 miles

- GenX: NC provisional health goal = 140 ppt
- >140 ppt
- 0 - 140 ppt
- Non detect

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PFAS and DWM – Chemours

Combined Phase I, II, III , IV (partial) Private Well PFAS Data, also Includes Robeson Co. and DEQ-collected Data

Private Well Water GenX Summary	
Distance from Chemours' border	Up to 5.5 miles
Well Collection Dates	9/6/2017 – 12/20/2018
Number of Addresses Sampled	837
Number of Exceedances of the GenX Provisional Health Goal	173
Number of Non-detected GenX Analysis	223
Number of GenX Detections Less than the Health Goal	441
Maximum Detection	4000 ng/L

The NC DHHS Provisional Drinking Water Health Goal for GenX is 140 ng/L (July 2017)

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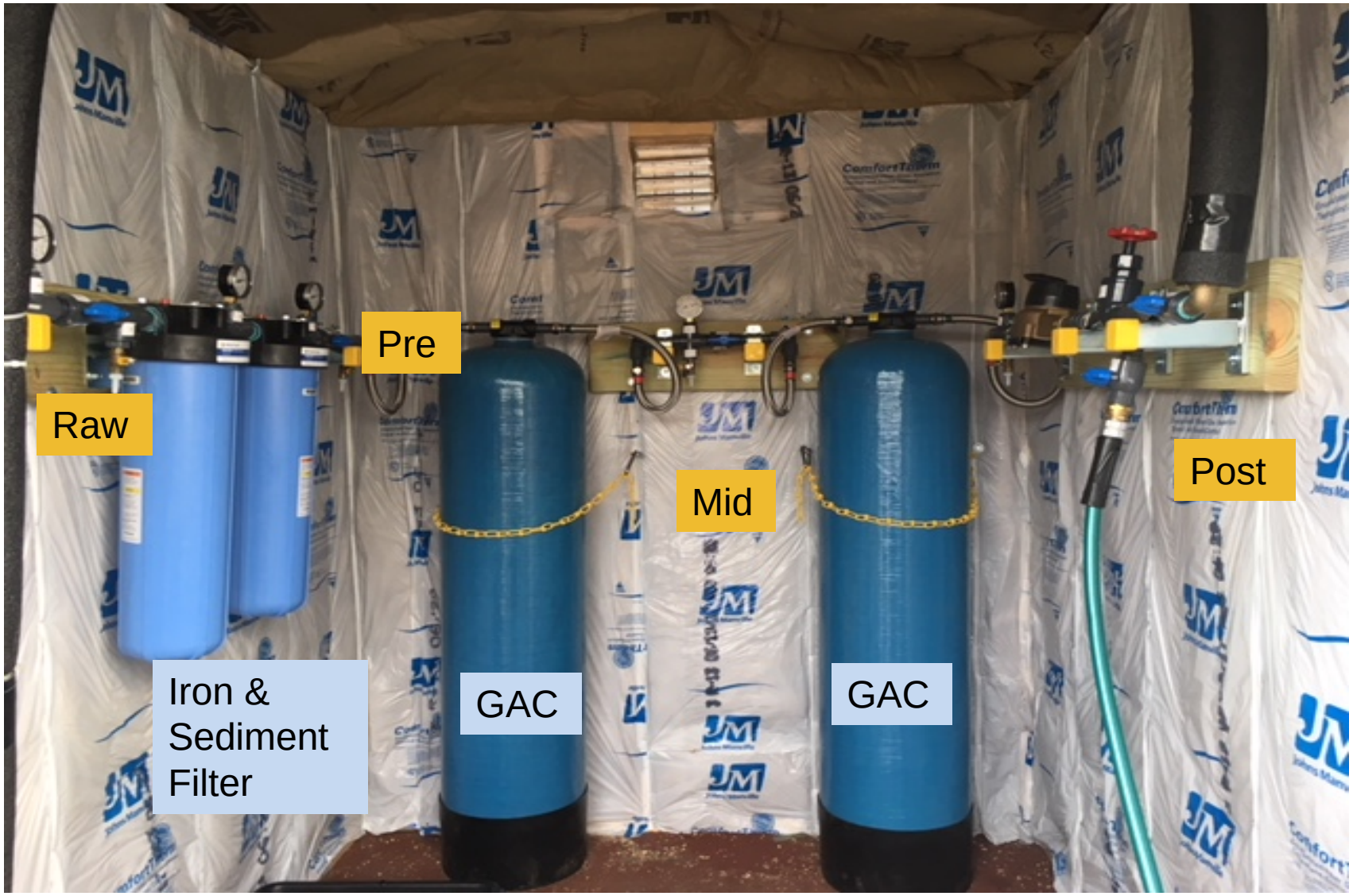
PFAS and DWM – Chemours



Pilot Testing

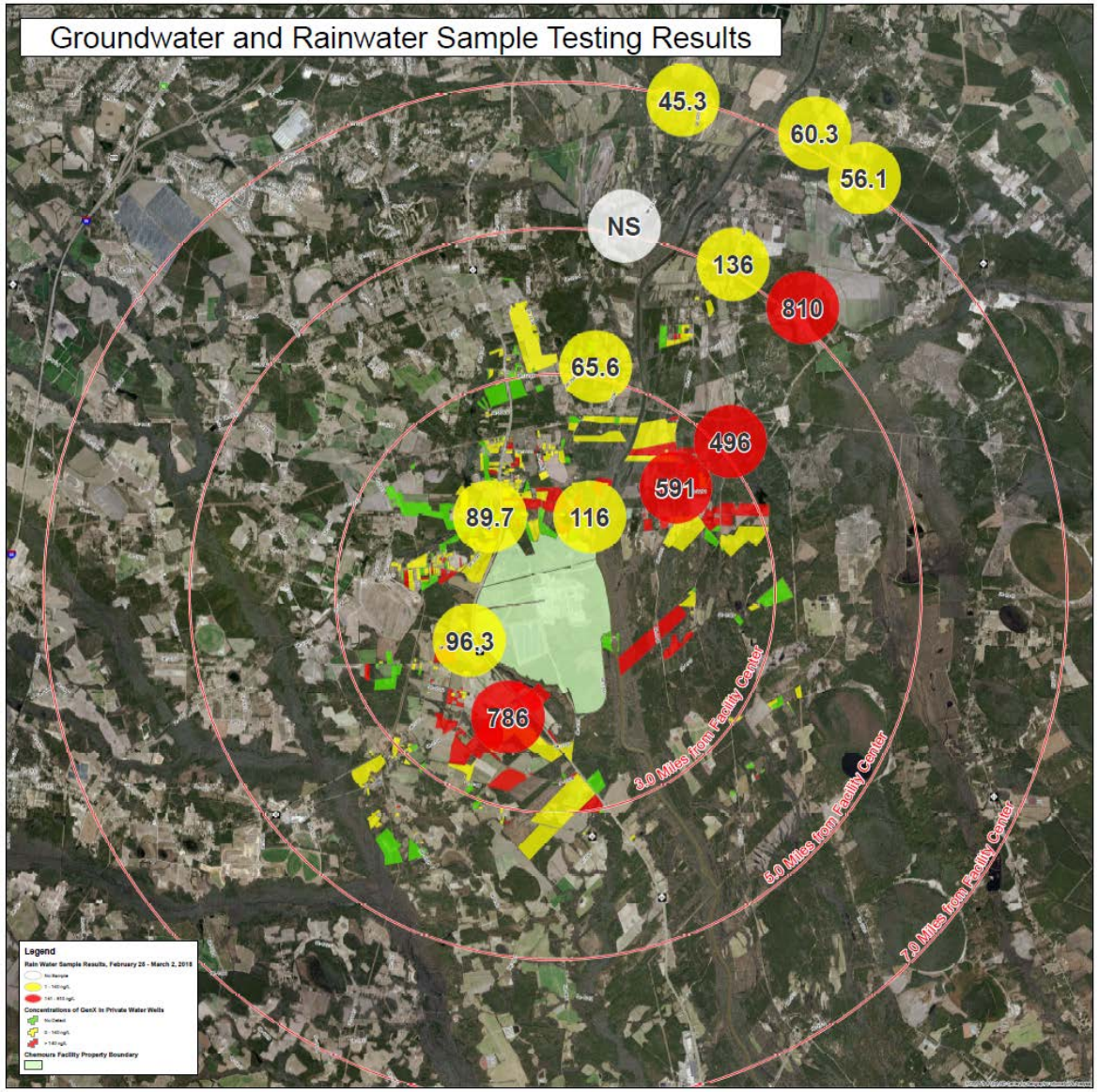
6 Locations

GenX in untreated water = 159 - 1,910 ng/L

Water usage = 450 to 2,500 gallons/week

Analyzing for GenX and 32 other PFAS compounds

PFAS and DWM – Chemours



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PFAS and DAQ – Chemours

Rainwater Sampling Updates

DEQ's Division of Air Quality purchased and installed 5 automatic samplers around the Chemours facility

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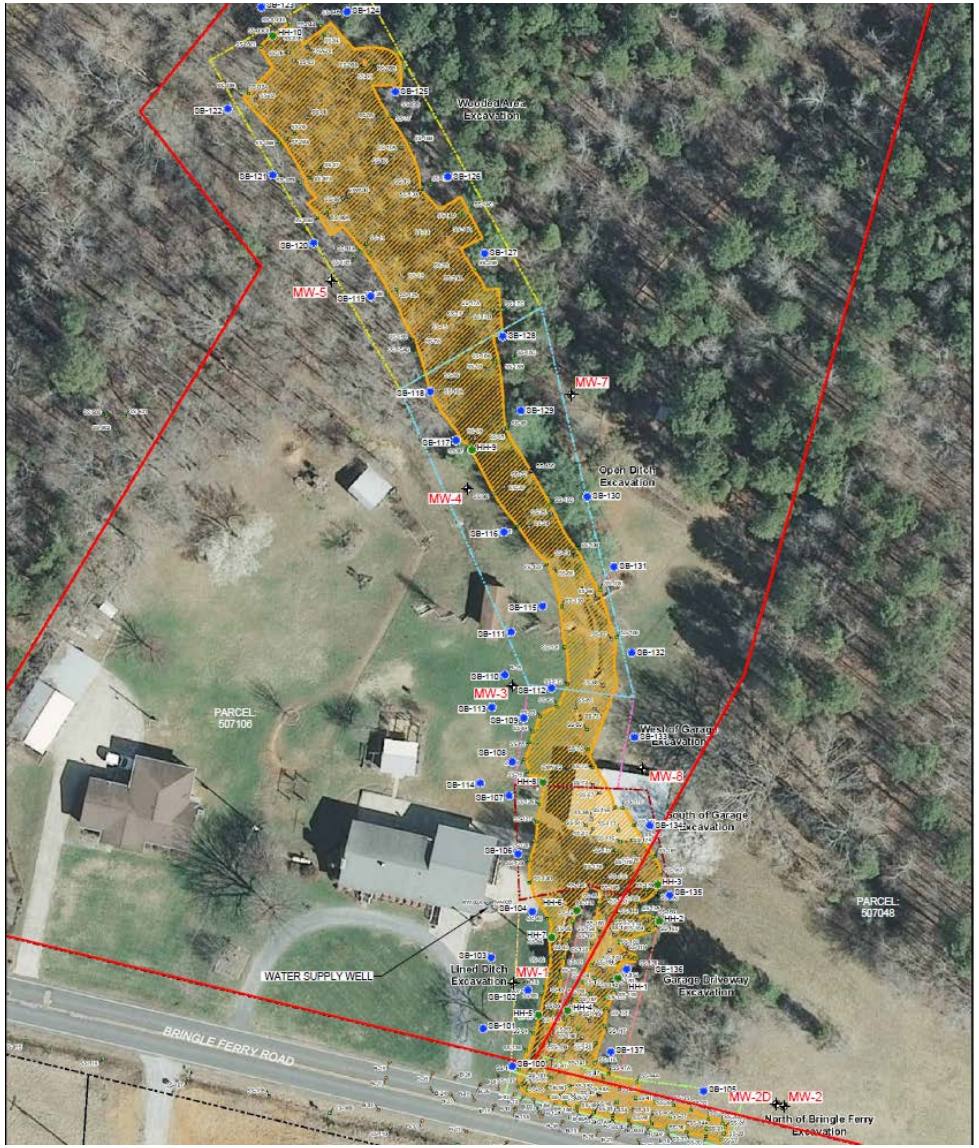
PFAS and DAQ – Chemours

- Chemours will install and operate carbon absorbers to control a portion of the GenX emissions profile.
  - May 2018
  - About 40 percent reduction in GenX emissions facility-wide.

- Chemours will install and operate a Thermal Oxidizer by 2020
  - Expected 99.99 percent reduction of all PFAS emissions from those processes connected
  - 99 percent reduction in GenX emissions facility-wide

- Consent Order signed February 2019. Requires company to undertake many actions.

PFAS and DWM



Use of fire fighting foam in response to Ethanol spill

- Soil Excavation
- Soil Borings
- Groundwater Monitoring
- WSW Sampling

PFAS and DWM

- Marine Corps well sampling near MCOLF Atlantic
- Department of Defense (DOD) sampled 258 private wells within a one-mile radius of Marine Corps Outlying Landing Field Atlantic. The area lies over a broad continuous shallow aquifer. DOD sampled in all directions.
- Sampling results showed detections of PFOA/PFOS in 32 wells. Two wells exceeded the EPA health advisory of 70 ppt.
- DOD has provided whole-house filters to impacted residents.

Landfills and Leachate

- Want to be proactive as an industry
- EPA Action Plan for PFOA/PFAS (Feb. 14, 2019)
- Landfill leachate samples are being analyzed in other states for PFAS
- Landfill leachate work by EPA Office of Research and Development in Research Triangle Park
- Citizen questions about additional sources continue
- End game: continue to effectively manage North Carolina's waste while protecting public health and the environment

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Landfills and Leachate

- United States Landfill Study (Lang et al., 2017)
  – 95 samples from 18 landfills

- Results:
  1. 19 PFAS detected in >50% of samples
  2. PFOS: 3 to 200 ppt
  3. PFOA: 100 to 1,000 ppt
  4. Total PFAS: 2,000 to 29,000 ppt
  5. 5:3 FTCA (precursor) dominant in most leachates: 400 to 15,000 ppt

Landfills and Leachate

- Landfills are the ultimate repositories for PFAS-contaminated industrial waste, sewage sludge, waste from site mitigation and various PFAS-containing consumer products.

- Leachate treatment by wastewater treatment plants (WWTP) is common; however, standard WWTP technologies do little to reduce or remove PFAS.

- The Division of Waste Management has determined that the sampling of leachate for PFAS at Municipal Solid Waste Landfills is warranted.

Landfills and Leachate

- The Division of Waste Management is meeting collaboratively with the landfill industry to determine appropriate next steps.

- Next steps could include a sampling effort undertaken by DWM in coordination with landfill operators; coordination with the UNC Collaboratory (Dr. Mort Barlaz) on landfill leachate sampling; or coordination with industry on third-party sampling (following the Michigan model).

- Focus is on leachate at all lined MSW landfills
  - Raw Leachate/Leachate Endpoint (prior to WWTP, POTW, Surface Water)
  - Analyzing for PFOS and PFOA, GenX (where warranted) and full scan of PFAS compounds (site specific)

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New Hanover County Landfill Sampling Event

- New Hanover County Landfill Sampling Event
- Target analysis for 33 PFAS Compounds (in response to Cape Fear Public Utilities Authority sampling, NS&SS wastewater treatment plants)
- Samples collected at the following locations:

  1. Potable water supply well (all water uses); QA/QC matrix spike sample and a matrix spike duplicate sample (4 bottles); field blank
  2. Non-potable water supply well (used to fill water truck and one outdoor sink)
  3. Post reverse osmosis sample (effluent to river), plus duplicate
  4. Discharge pipe to aeration pond (raw leachate)
  5. River sample with DEQ's Division of Water Resources – Sampled plus field blank

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New Hanover County Landfill Sampling Event

New Hanover County Landfill Sampling Event

RAW Leachate Sampling Point

New Hanover County Landfill Sampling Event

Post Reverse Osmosis System Sample

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New Hanover County Landfill Sampling Event

Northeast Cape Fear River surface water sample

- Upstream of landfill discharge

RESULTS

- Two raw leachate samples were collected from raw leachate lagoon.
- Two effluent water samples were collected subsequent to leachate treatment via the reverse osmosis system.
- All samples were analyzed for 33 Perfluorinated Chemicals (PFCs).
- Total PFC concentrations from the two raw leachate samples ranged from 12,231 ppt to 13,792 ppt.
- No PFCs were detected in the effluent water after raw leachate was treated by the reverse osmosis system.

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WWTP Coordination

- Establish communication with WWTP stakeholders
- PFAS management approach can be two-fold: treatment plant changes and industry pretreatment
- Sources of PFAS (other than landfills)
- Sampling Coordination
  - Plant volumes (MGD)
  - Influent, effluent, sludge
- Recommended leachate treatment standards?

WWTP Investigation- DWR

- Letter issued April 30, 2019 – POTW with Pre-treatment programs
- Requires 3 month of investigative sampling for 1,4-Dioxane and 21 analytes of poly compounds- Begin July 2019

- Develop a program to assess potential sources by industry
- Begin investigative monitoring
- Develop strategies for source control/reduction

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PFAS Sampling Considerations

- Solid Waste Section PFAS Sampling Team

- Planning Process (communication with landfill owner/operator and site survey)
  - Knowledge of the leachate collection and management system
  - Identify the sample collection point (designated sample valve, outfall location, manhole to vault or sump, etc.)
  - Determine equipment required (purge bucket, sampling dipper, HDPE sheeting, etc.)
  - Determine ultimate disposal (NDPES, WWTP, POTW)
  - Determine required Personal Protection Equipment; develop Health and Safety Plan.
  - Identify the date and time in which the sampling will occur

- Revise Solid Waste Section's sampling plan accordingly

PFAS Sampling Considerations

Resource: https://www.michigan.gov/pfasresponse/0,9038,7-365-86510_87154-469832--,00.html

Technical Guidance Documents

Fish Tissue PFAS Sampling Guidance (1/2019)

General PFAS Sampling Guidance (Revised 10/16/2018)

Groundwater PFAS Sampling Guidance (10/2018)

Residential Well PFAS Sampling Guidance (Revised 10/11/2018)

Soil PFAS Sampling Guidance (11/28/2018)

Surface Water PFAS Sampling Guidance (11/28/2018)

Wastewater PFAS Sampling Guidance (Revised 10/11/2018)

PFAS Sampling Quick Reference Field Guide (Revised 10/17/2018)

MDEQ PFAS Minimum Laboratory Analyte List

Residential Guidance Documents

Residential Well PFAS Sampling Guidance for Homeowners (10/2018)

Sampling and Lab Information (10//2018)

Michigan PFAS Action Response Team (MPART)

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PFAS Sampling Considerations

- EPA Action Plan (Feb. 14, 2019) – Moving forward with MCL process for PFOA and PFOS

- Perfluorooctanesulfonic acid (PFOS) and Perfluorooctanoic acid (PFOA)
  - EPA Health Advisory level of 70 parts per trillion (drinking water)
  - PFOA: NC IMAC of 2 ug/l (groundwater)
  - PFOS: PQL (groundwater)

- Perfluoro-2-propoxypropanoic acid (GenX)
  - North Carolina's Provisional Goal of 140 parts per trillion (drinking water)

- Quality Assurance / Quality Control is critical
  - Results in parts per trillion
  - 1 square inch in 250 square miles

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PFAS Sampling Considerations

- Cross-contamination can occur from:
  - Field clothing (Gore-Tex, fabric softeners)
  - Person care products (moisturizers, hand-creams, insect repellents, sunscreens)
  - Sampling equipment (Teflon)
  - Food packaging (candy wrappers, fast food wrappers, aluminum foils)
  - Decontamination equipment (need PFAS-free water; lab can supply)
  - Sample collect and handling (need powderless nitrile gloves)
  - Sample shipment (chemical (blue) ice packs → use regular ice)

DATA IS ONLY AS GOOD AS THE INTEGRITY OF THE SAMPLING.

QA/QC SHOULD BE A PRIORITY!

PFAS Sampling Considerations

- Prior to sampling obtain thorough knowledge of site.
  - Leachate collection system/treatment process
  - Sampling locations (WSW, surface water bodies, designated sampling ports)
  - Sampling equipment needed (sampling dipper/purge bucket)
  - Sample staging area
  - Finalize sampling plan for all media of concern (Health and Safety Plan as well)

- Prior to sampling have thorough discussion with lab.
  - # Bottles (duplicates, MS&MSD, field blanks, equipment blanks)
  - 5.0 g/L Trizma buffering reagent
  - Availability of PFAS-free water for decontamination if needed.
  - Analytical results wanted (33 PFAS Full Scan, 537-PFOA, PFOS, GenX)
  - Paperwork (sample and shipping labels, COC specifics)

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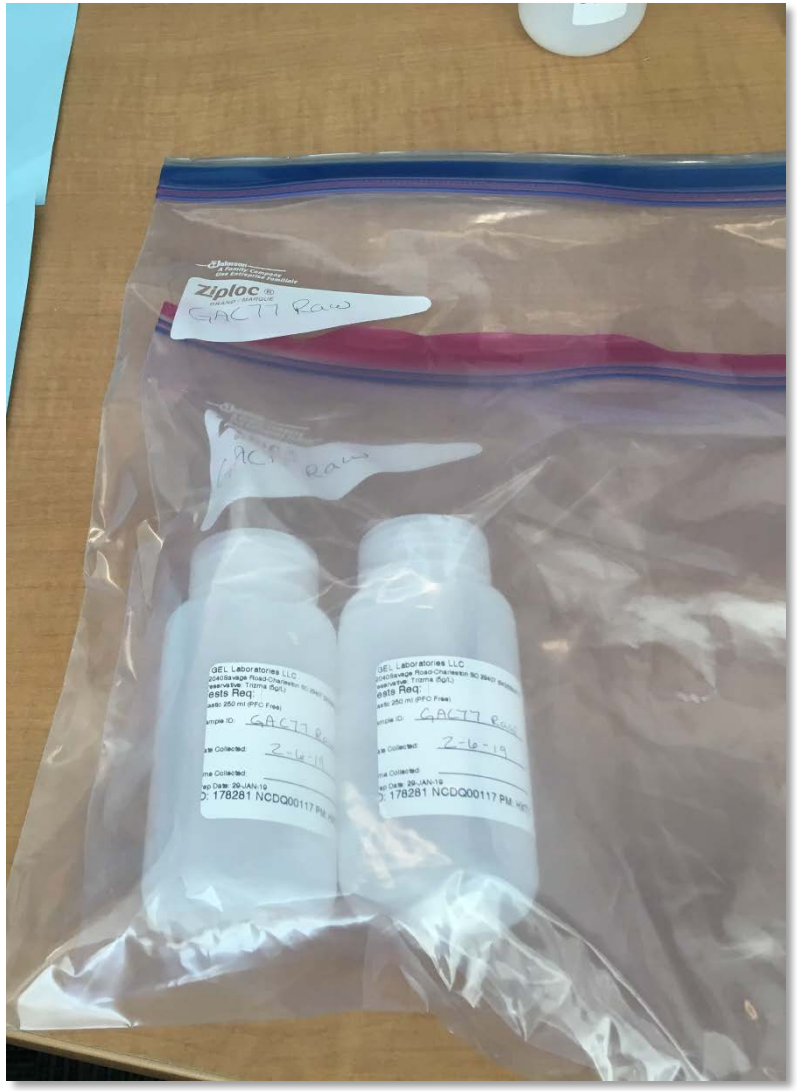
PFAS Sampling Considerations



Bottle Preparation

- Dedicated room for storage
- No sharpies, post-its, tapes, etc.
- Adhere to PFAS-free checklist (discussed later).
- Wear powderless nitrile gloves
- Label, double-bag, place in cooler
- Chain of custody

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PFAS Sampling Considerations

- Date: _____
- Site ID#: _____
- Weather (*temp./precipitation*):_____
- Site Name: _____
- ***Field Clothing and PPE:***
- ___No clothing or boots containing Gore-TexTM
- ___All safety boots made from polyurethane and PVC
- ___No materials containing Tyvek®
- ___Field crew has not used fabric softener on clothing
- ___Field crew has not used cosmetics, moisturizers, hand cream, or other related products this morning
- ___Field crew has not applied unauthorized sunscreen or insect repellant

Field Equipment:

- ___No Teflon® or LDPE containing materials onsite
- ___All sample materials made from stainless steel, HDPE, acetate, silicon, or polypropylene
- ___No waterproof field books on-site
- ___No plastic clipboards, binders, or spiral hard cover notebooks on-site
- ___No adhesives (Post-It Notes) on-site
- ___Coolers filled with regular ice only. No chemical (blue) ice packs in possession

Sample Containers:

- ___All sample containers made of HDPE or polypropylene
- ___Caps are unlined and made of HDPE or polypropylene

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PFAS Sampling Considerations

Wet Weather (as applicable):

- ___Wet weather gear made of polyurethane and PVC only

Equipment Decontamination:

- ___"PFC-free" water on-site for decontamination of sample equipment. No other water sources to be used.
- ___Alconox and Liquinox to be used as decontamination materials

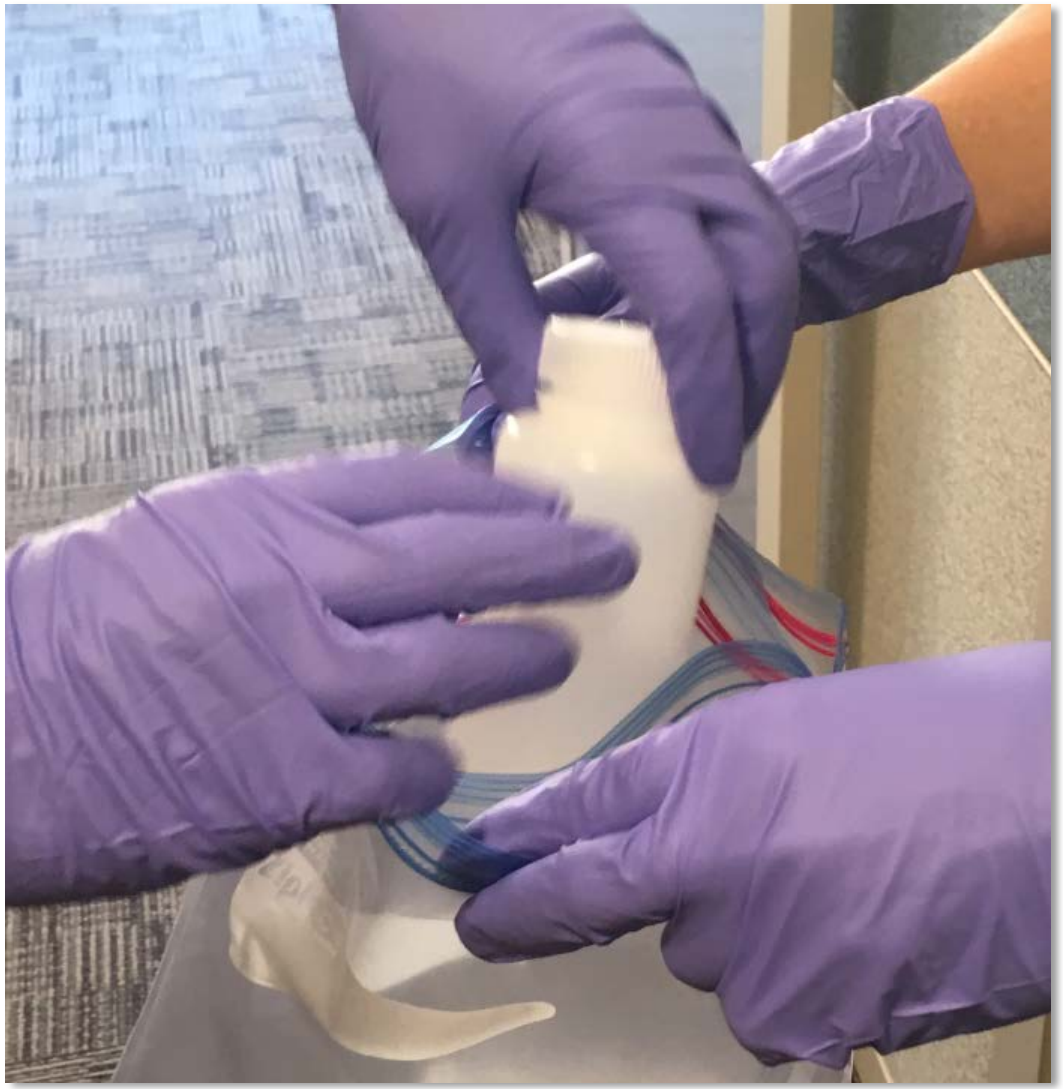
Food Considerations:

- ___No food or drink on-site with exception of bottled water and/or hydration drinks (i.e., Gatorade and Powerade) that is available for consumption only in the staging area. If any applicable boxes cannot be checked, the Field Lead shall describe the noncompliance issues below and work with field personnel to address noncompliance issues prior to commencement of that day's work. Corrective action shall include removal of noncompliance items from the site or removal of worker offsite until in compliance. Describe the noncompliance issues (include personnel not in compliance) and action/outcome of noncompliance:

_____

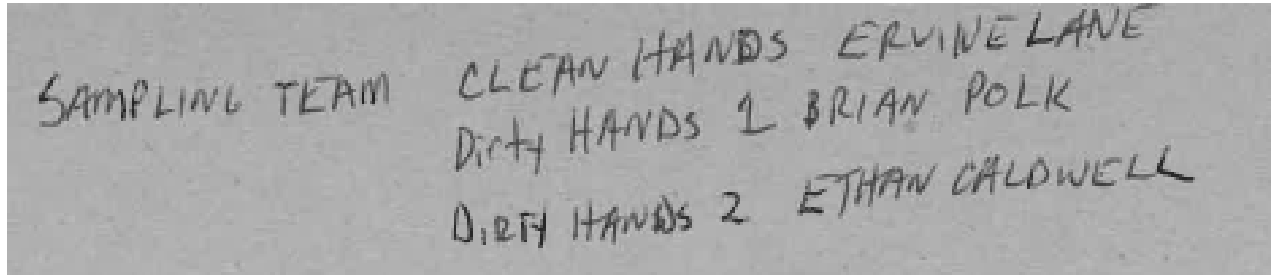
- Field Lead Name: _____
- Field Lead Signature: _____ Time: _____

PFAS Sampling Considerations



- Clean hands / dirty hands – similar to EPA method for sampling for trace metals (i.e., mercury)
- Clean hands:
  - Handle inner plastic bag
  - Handle sample bottle
  - Remove and replaces cap
- Dirty Hands:
  - Handle outer plastic bag
  - Handle all sampling equipment, valves, spigots, coolers, documentation, etc.

PFAS Sampling Considerations



QA/QC is critical when sampling for PFAS!

- Pipe sealant/thread tape
- Potable water well

PFAS and Treatment

- **Granular Activated Carbon (GAC)** – Chemicals like PFAS stick to the small pieces of carbon as the water passes through.

- **Powdered Activated Carbon (PAC)** – The carbon is powdered and is added to the water. The chemicals then stick to the powdered carbon as the water passes through.

- **Ion Exchange Resins** – Small beads (called resins) are made of hydrocarbons that work like magnets. The chemicals stick to the beads and are removed as the water passes through.

- **Nanofiltration and reverse osmosis** – A process where water is pushed through a membrane with small pores. The membrane acts like a wall that can stop chemicals and particles from passing into water.

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PFAS RESOURCES

Interstate Technology Regulatory Council (ITRC) – https://pfas-1.itrcweb.org/

- Series of Six Fact Sheets (Spanish Versions also available online)
    - Physical/Chemical Properties
    - Regulations and Advisories
    - History and Use
    - Environmental Fate and Transport
    - Site Characterization Tools
    - Remediation Technologies

PFAS RESOURCES

- EPA Resources on PFAS Basic PFAS Information
  - EPA Actions
  - Tools and Resources
  - https://www.epa.gov/pfas

- EPA Contaminated Site Clean-Up Information (CLU-IN)
  - Innovative treatment and site characterization technologies
  - https://clu-in.org/

- Michigan PFAS Action Response Team (MPART)
  - Useful Sampling Guidance Documents for different types of media
  - https://www.michigan.gov/pfasresponse/0,9038,7-365-86510_87154-469832--,00.html

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QUESTIONS?

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