Sampling Groundwater for PFAS: Materials Considerations, Field Protocols and Equipment Options

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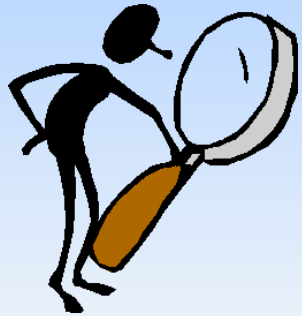
Sampling Groundwater for PFAS – Addressing the challenges

- Sampling for PFAS contamination poses challenges very different from sampling for “point source” contaminants such as fuels & solvents – potential PFAS sources are widespread throughout industrial and consumer products
- PFAS has been detected in surface water and groundwater, wastewater and landfill leachate
- Regulatory MCLs for drinking water and groundwater currently as low as 2 ng/L (ppt), and analytical detection limits are sub-ppt levels

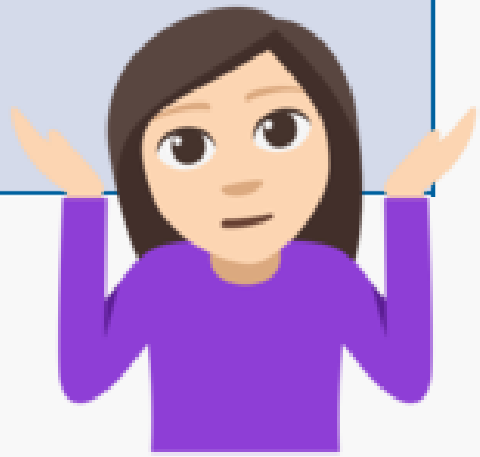


Sampling Groundwater for PFAS – Addressing the challenges

- There is concern that sampling for PFAS using equipment made from fluoropolymers (Teflon®, PTFE, etc.) could result in sample contamination
- Regulatory guidance documents and industry fact sheets generally recommend avoiding the use of all fluoropolymers
- This abundance of caution approach is based on limited available published research and the potential that even tested materials may contain PFAS
  - *What do we know about fluoropolymer chemistry?*
  - *Could some fluoropolymers be used without causing PFAS sample contamination?*
  - *Are alternate materials readily available to replace fluoropolymers?*

Table 5.2. General Sampling Equipment and Field Supplies

Avoid Use	Approved Alternatives
General Sampling Equipment	
Standard decontamination water or municipal water	Water from a known source that has been analyzed for PFAS and has been determined to be acceptable for the specific sampling program
Decon 90™ detergent	Alconox™ and Liquinox™ are the only detergents approved for decontamination (EDQW 2016)
Glass or Teflon™-lined sampling bottles and lids	Polypropylene or high-density polyethylene (HDPE) sample bottles with an unlined polypropylene HDPE screw cap
Fluoropolymer tubing, valves, and other parts in pumps	HDPE and silicon materials (EDQW 2016)
Teflon™ tubing, bailers, tape, and plumbing paste	HDPE and silicon materials or disposable equipment
Pumps, packers, transducers, tubing, liners, valves, and wiring with polytetrafluorethylene or ethylene tetrafluoroethylene	Alternative materials



From NGWA, Groundwater and PFAS: State of Knowledge and Practice, March 2018

Michigan Department of Environmental Quality

October 2018

MDEQ PFAS Sampling Quick Reference Field Guide[1]

All Items Used During Sampling Event

● Prohibited
• Items or materials that contain fluoropolymers such as ○ Polytetrafluoroethylene (PTFE), that includes the trademarks Teflon® and Hostaflon® ○ Polyvinylidene fluoride (PVDF), that includes the trademark Kynar® ○ Polycholotrifluoroethylene (PCTFE), that includes the trademark Neoflon ® ○ Ethylene-tetrafluoro-ethylene (ETFE), that includes the trademark Tefzel® ○ Fluorinated ethylene propylene (FEP), that includes the trademarks Teflon® FEP and Hostaflon® FEP • Items or materials that contain any other fluoropolymer

Pumps, Tubing, and Sampling Equipment

● Prohibited	■ Allowable	▲ Needs Screening[2]
• Items or materials containing any fluoropolymer (potential items include tubing, valves, or pipe thread seal tape)	• High-density polyethylene (HDPE) • Low-density polyethylene (LDPE) tubing • Polypropylene • Silicone • Stainless-steel • Any items used to secure sampling bottles made from: ○ Natural rubber ○ Nylon (cable ties) ○ Uncoated metal springs ○ Polyethylene	• Any items or materials that will come into direct contact with the sample that have **not** been verified to be PFAS-free ○ Do not assume that any sampling items or materials are PFAS-free based on composition alone

From MDEQ General PFAS Sampling Guidance, October 2018
https://www.michigan.gov/documents/pfasresponse/General_PFAS_Sampling_Guidance_634597_7.pdf

Per- and Polyfluoroalkyl Substances (PFAS) Sampling Guidelines for Non-Drinking Water

CALIFORNIA STATE WATER QUALITY CONTROL BOARD

DIVISION OF WATER QUALITY

SWRCB PFAS Website: https://www.waterboards.ca.gov/pfas/
DDW PFAS Website: https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/PFOA_PFOS.html

September 2020

3.1 Sampling Equipment

Sampling equipment used for PFAS sampling must be made from acceptable materials, which include high-density polyethylene (HDPE), polypropylene, silicone, stainless steel, nylon, polyvinyl chloride (PVC), acetate, and cotton. Sampling equipment that contain PFAS-based (fluoropolymers) parts that would be in direct contact with the sample or sampling environment are prohibited. These fluoropolymers include, but are not limited to:

- Polytetrafluoroethylene (PTFE), including the trademark Teflon® and Hostaflon®, which can be in ball check-valves on certain bailers, lining of some hoses and tubing, wiring, certain kinds of gears, lubricant, and some objects that require the sliding action of parts.
- Polyvinylidene fluoride (PVDF), including the trademark Kynar®, which can be in tubing, films/coatings on aluminum, galvanized or aluminized steel, wire insulators, and lithium-ion batteries.
- Polychlorotrifluoroethylene (PCTFE), including the trademark Neoflon®, which can be in many valves, seals, gaskets, and food packaging.
- Ethylene-tetrafluoro-ethylene (ETFE), including the trademark Tefzel®, which can be in many wire and cable insulation and covers, films for roofing and siding, liners in pipes, and some cable tie wraps.
- Fluorinated ethylene propylene (FEP), including the trademarks Teflon® FEP and Hostaflon® FEP, and may also include Neoflon®, which can be in wire and cable insulation and covers, pipe linings, and some labware.

Equipment that contain PFAS-coated parts (e.g. Teflon-coated parts) can be used if the PFAS-coated part is internal to the equipment and is not in direct contact with the external environment or the sample. Sampling equipment that have parts made of low-density polyethylene (LDPE) should be avoided if the part comes in direct contact with the sample. However, if it is absolutely necessary, equipment that have parts made of LDPE may be used if an equipment blank has confirmed it to be PFAS-free.

From Per- and Polyfluoroalkyl Substances (PFAS) Sampling Guidelines, CALIFORNIA STATE WATER QUALITY CONTROL BOARD, Sept 2020. https://www.waterboards.ca.gov/water_issues/programs/pfas/

Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS)

3.1 Equipment and Supplies

Many materials used in the course of environmental investigation can potentially contain PFAS. Further, as there are limited peer-reviewed studies (Denly et al. 2019) on the potential for cross-contamination from commonly used sampling materials, most of these guidance documents default to a conservative approach in implementing measures and controls for prevention of cross-contamination (for example, washing cotton shirts with no fabric softener prior to use in the field). Obtain and review all Safety Data Sheets (SDSs) before considering materials for use during PFAS sampling. Materials that may come into contact with samples and therefore could potentially introduce bias include, but are not limited to:

- polytetrafluoroethylene (PTFE)
- waterproof coatings containing PFAS
- fluorinated ethylene-propylene (FEP)
- ethylene tetrafluoroethylene (ETFE)
- low-density polyethylene (LDPE)
- polyvinylidene fluoride (PVDF)
- pipe thread compounds and tape.

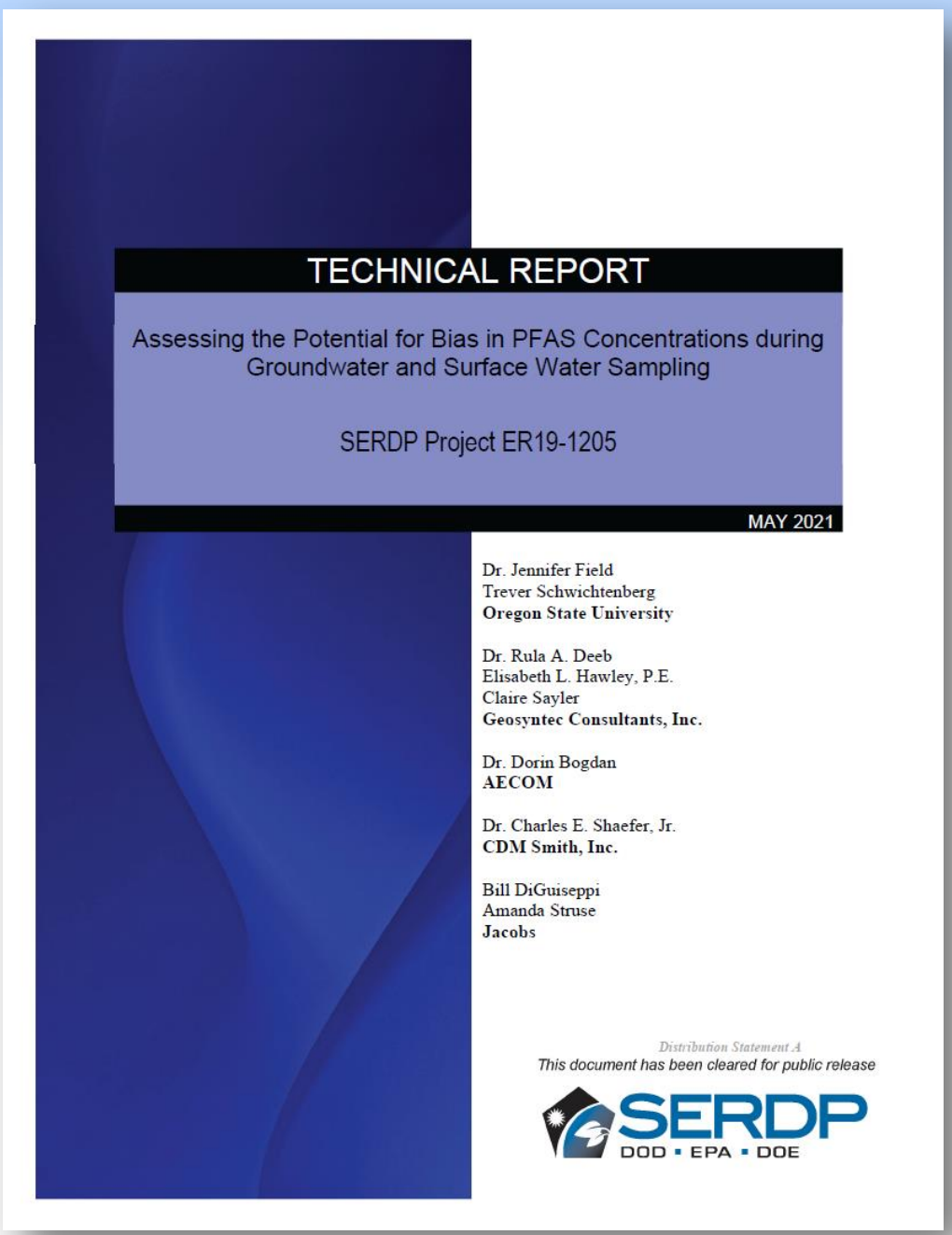
3.6.1 Groundwater

The most inert material (for example, stainless steel, silicone, and HDPE), with respect to known or anticipated contaminants in wells should be used whenever possible. Dedicated sampling equipment installed in existing wells prior to investigation should be thoroughly checked to ensure that the equipment is PFAS-free. For long-term investigations, samples may be collected in duplicate with and without existing dedicated equipment. If PFAS analyses show that the equipment does not affect results, the equipment may be kept and used long term. This determination depends on project-specific requirements, however, and should only be used by a project team with full disclosure to all stakeholders.

From ITRC, April 2020

PFAS Sampling Guidance - Summary

- Much of the early regulatory guidance and industry fact sheets borrowed recommendations on acceptable and prohibited materials & supplies from a February 2016 Western Australia guidance (updated in January 2017)
  - *Those recommendations were taken from a unpublished consultants report with no references or data presented to support them*
- Subsequent guidance places greater emphasis on published results of materials testing studies and encourages users to test their own sampling systems, equipment and supplies to determine acceptable options
- However, current guidance doesn't address whether a plausible pathway exists for materials to affect PFAS concentrations in samples (SERDP, 2021)
- Some PFAS sampling guidance includes general sampling procedures that advocate for high-rate pumping, well volume purging or evacuation, bailers and inertial lift pumps, and well bottom sounding at each sampling event – all actions that are **not recommended** for obtaining high quality samples with low turbidity for accurate PFAS sample results and risk assessment



A recent SERDP-funded research report (May 2021) provides an excellent summary of PFAS sampling guidance documents, published and unpublished research on materials testing and field blank detections and new information on the potential for stratification of PFAS in groundwater and surface water.

- Typical sampling equipment did not contaminate samples based on equipment blank results
- PFAS in groundwater columns tested after three months showed no depth stratification
- Authors concluded that many PFAS sampling restrictions in current guidance are not science based, but are based on precaution

https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Risk-Assessment/ER19-1205

Why have we used Teflon® for sampling?

Water sampling equipment and sample container caps & lids have historically been manufactured using Teflon* and other fluoropolymers due to its many advantageous properties:

- Chemically inert
- Non-reactive
- Highly resistant to sorption and leaching of common groundwater contaminants
- No leachable VOCs, SVOCs
- Very low gas permeability
- Very high temperature resistance
- Very high working pressures (tubing, bladders, seals)
- Extremely good flex properties for moving parts (e.g., bladders, seals)

**Teflon® is a registered trademark of the Chemours company (formerly DuPont) and refers to a range of fluoropolymers, the best known of which is polytetrafluoroethylene (PTFE)*

Is all Teflon bad for PFAS sampling? What materials should I use if I can't use Teflon?

- Polymer chemistry information and materials testing show that not all fluoropolymers are manufactured using PFAS and many common fluoropolymers do not leach PFAS into water samples, even with long-term exposure (e.g., dedicated systems)
- However, most regulatory guidance documents state that no fluoropolymer materials can be used, and recommendations for alternative materials in those documents vary widely
- Manufacturers of sampling equipment and components such as plastic tubing are challenged with finding alternate PFAS-free materials that can:
  - meet engineering performance requirements
  - meet sampling program needs for other organic compounds such as fuels and solvents (VOCs and SVOCs) without sample bias or contamination

Are the recommended alternatives good options?

Examples of alternate materials offered in guidance documents all have some limitations:

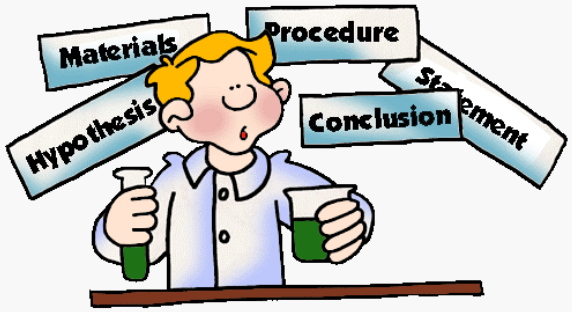
- Polyethylene bladders aren't as flexible and durable as PTFE, so cycle life is much shorter – dedicated pumps would last only 1-2 years before bladder replacement is needed vs 10-30 years with PTFE
- Polypropylene tubing is not very flexible and tends to take a set when coiled, making it difficult to use, especially in cold weather
- Silicone rubber is very flexible but has a high capacity for sorption of organics, making it less desirable for low-level VOC & SVOC sampling
- Vinyl (Tygon®, flexible PVC) also readily absorbs organics and contains phthalate plasticizers that can leach into samples causing false positives
- Elastomers such as nitrile rubber often leach other organic compounds - QED testing of nitrile rubber showed up to 10,000 µg/l carbon disulfide

QED Materials Testing Program

Beginning in 2016, QED has been testing a wide range of materials commonly used in groundwater sampling and remediation equipment to identify sources of PFAS and determine suitable alternatives

Materials that have been tested to date:

- Bladders – PTFE & TFE (Teflon®), HDPE and LDPE (polyethylene) and proprietary fluorine-free flexible plastic (used in QED Well Wizard® ZERO bladder pumps)
- Tubing – FEP (Teflon & Teflon-lined), ETFE (Tefzel®), HDPE and LDPE
- O-rings and seals – FKM (Viton®), EPDM, nitrile rubber (NBR,Buna-N)
- Check balls & poppet valves – TFE and acetal (Delrin®)
- Pump & passive sampler components – Polypropylene, PVC, PVDF (Kynar®), acetal (Delrin)
- Sealants & lubricants – Loctite®, Vibratite®, Gasoila®, Molykote®, PTFE thread tape



**Well Wizard is a registered trademark of Q.E.D. Environmental Systems, Inc.; other trademarks shown above are registered to other companies, including DuPont, Chemours, Arkema Chemical, Henkel IP & Holding GmbH LLC, Federal Process Corp*

QED Materials Testing Procedures & Results

Testing procedures are soak tests in PFAS-free water

- Minimum soak time is 24 hours, some samples shipped to lab are 48-72+ hours
- Blank water samples are always collected, even when using lab-supplied PFAS-free water
- Test conditions are far more stringent that typical equipment blank tests
- All components are also tested for VOCs (Method 8260) and SVOCs (Method 8270)
- Results are reported based on lowest available laboratory reporting limits (RL)

Summary of testing results

- PTFE and TFE bladders, LDPE bladders and proprietary ZERO bladders = all ND
- PTFE and Delrin acetal check balls and poppets = all ND
- HDPE, FEP and FEP-lined HDPE tubing = all ND
- PVC, Delrin acetal, and polypropylene components = all ND
- EPDM O-rings & seals, Loctite, Vibratite, Molykote lubricant = all ND
- Other materials had mixed results – some Viton O-rings and one PVDF material passed while others showed low to very high 6:2 FTS detections, PTFE tape PFOA at 39 ng/L

Selecting the right equipment for your PFAS sampling program

- PFAS are generally not affected by changes in pressure, temperature and air exposure possible with common sampling equipment
- However, the sampling device selected needs to minimize sample alteration for other analytes (e.g., VOCs, heavy metals), so the most sensitive sampling parameter should dictate equipment selection
- A sampling device that doesn't elevate turbidity in samples is important, as PFAS can adhere to solids present in the water
- PFAS samples should not be filtered – from the ITRC Fact Sheet, Section 11.1 on Sampling*:

  "Sample filtration is not recommended for sample with high particulate content because retention of PFAS onto filters has been noted."

  "Do not filter the sample, as filtration may be a source for contamination (Ahrens L 2009; Arp and Goss 2009) or PFAS may be adsorbed to the filter."

*https://pfas-1.itrcweb.org/11-sampling-and-analytical-methods/#11_1

Bailers

- Fit into any well diameter, including small diameter direct-push wells and multi-level systems
- Bailers are available in a wide variety of acceptable materials for PFAS sampling, including HDPE, polypropylene, and PVC
- Materials questions should always extend to the bailer cord or cable - when in doubt, test before choosing
- For PFAS sampling, the biggest issue is the inability to control sample turbidity – purging the well often results in greatly elevated turbidity and can vary widely from one sampling event to the next

Peristaltic Pumps

- Fits any well diameter, including small direct-push wells and multi-level systems
- Suction lift limited to 20 - 26 (6 – 8m) feet water depth, including drawdown
- Elastomeric tubing, such as silicone rubber, is required at the pump head and is acceptable for PFAS sampling
- HDPE & LDPE tubing can be connected to the elastomeric tubing for sampling wells, surface water, tanks, etc.
- Peristaltic pumps are often cited as less accurate for gas sensitive parameters (e.g., VOCs, metals); while most PFAS are not volatile and quite stable in water, no data is available on potential PFAS bias due to suction imparted on samples

Battery-powered peristaltic pump

AC-powered peristaltic pump

Electric Submersible Pumps

- Fit into 2” (50mm) well casings
- Sample to depths up to 275 feet, depending on design and power supply
- Greater sampling depths possible for designs the allow drop tube inlets
- Many electric pumps have PTFE motor seals, PTFE wear parts and ETFE-coated motor cable, and some use PTFE grease on seals and O-rings
- Testing for PFAS in Grundfos Redi-Flo2 (DiGuiseppi, et al., 2014) showed PFBA detection >100 ng/L – most likely source is ETFE (Tefzel®) wire insulation.
- QED soak testing of ETFE detected PFBA at 750 ng/L

AC-voltage pump, control box and generator

DC-voltage pump and control box

Air-Powered Bladder Pumps

- Fit into well as small as 0.5” (25mm) well casing and multilevel sampling systems
- Sampling depths to 1,000’ (300 m) lift, even greater depths with drop tube inlets
- Wide range of material choices (PVC, stainless steel, poly) to match contaminant chemistry and background water quality
- Portable designs are available with disposable HDPE & LDPE bladders
- Dedicated bladder pumps historically use PTFE bladders, which may not be acceptable for some PFAS sampling
- Dedicated designs that use HDPE & LDPE bladders may require frequent replacement
- Newer fluorine-free/PFAS-free dedicated pump bladders have longer life of 20+ years

Dedicated Bladder Pumps

Portable Bladder Pumps

Passive and No-Purge Samplers

- Fit into wells down to 1” (25mm), most have unlimited depth capability
- Many are available without fluoropolymers & certified as PFAS-free
- Dedicated passive samplers work for PFAS and all other organic & inorganic analytes, with sample volume up to 1.5L in 2” wells, 2.25L in 4” wells
- Polyethylene diffusion bag (PDB) **won’t work for PFAS** – will not equilibrate
- Dual membrane passive diffusion bag samples (DMPDB) have been evaluated for PFAS sampling, but no published data are available to confirm field efficacy

Dedicated Passive Sampler

No-Purge Sampler

PDB & DMPDB Samplers

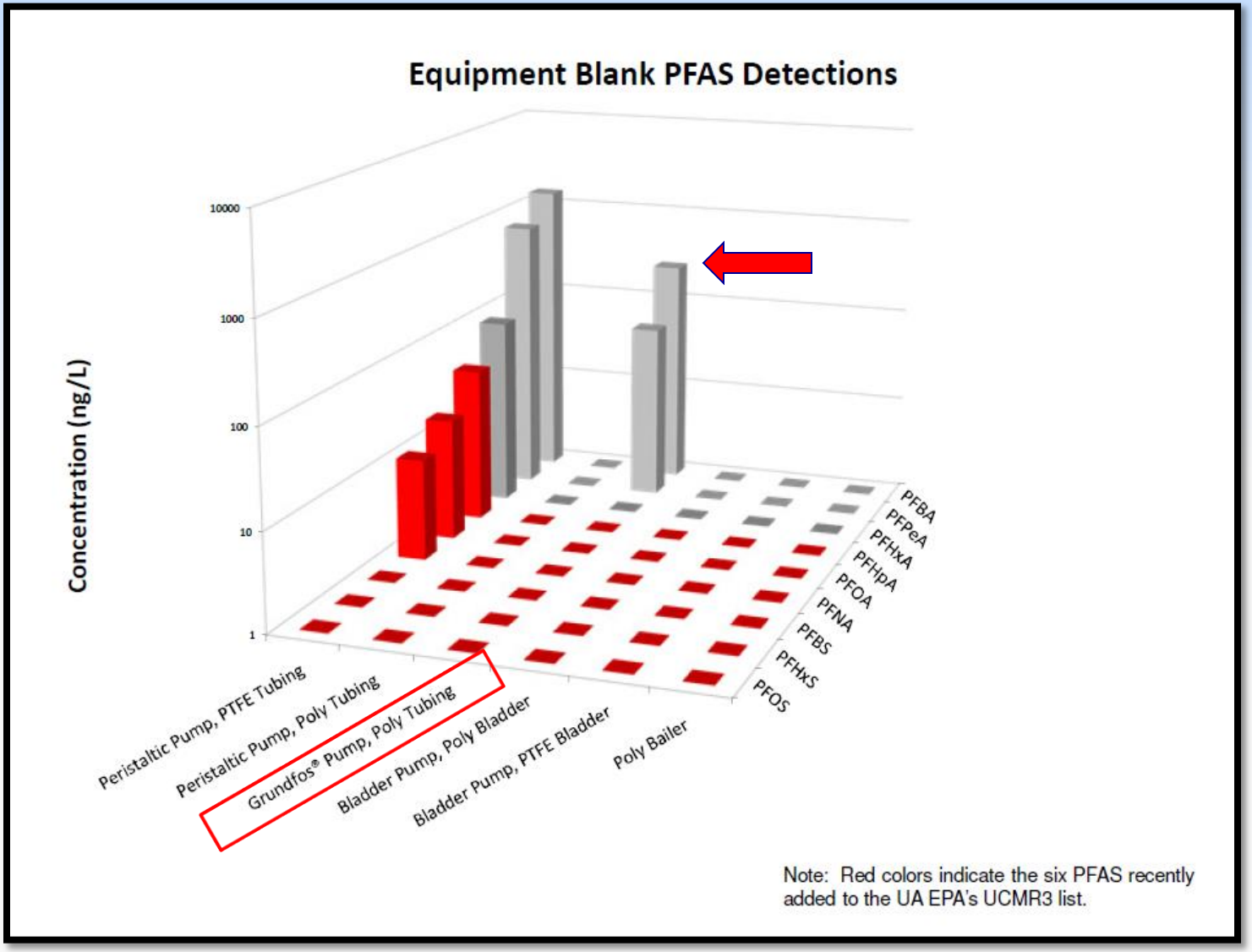
Sampling Equipment Recommendations

- Follow a common sense approach to selection of materials and supplies:
  - look at published research on PFAS content in common sampling materials
  - soak test existing equipment for compatibility with PFAS sampling requirements
  - never assume that the same type of material from different sources is PFAS-free
- Look for certification from manufacturers that all equipment, including tubing and support lines, has been tested and is PFAS-free, or use **equipment blank samples** to determine if they're PFAS-free
- For existing dedicated sampling systems, test in place for PFAS in samples before replacing any components
  - Where results are ND in all wells, systems can be used unless restrictions on existing materials apply
  - Where PFAS is detected in some or all wells, sample again using a known PFAS-free system to determine if source is the sampling system or if PFAS is present in the groundwater
  - If the sampling system is identified as the source of PFAS, look at component materials for obvious sources such as PTFE thread tape, ETFE wire insulation, TFE-based lubricants

What about decontamination of field equipment for PFAS sampling?

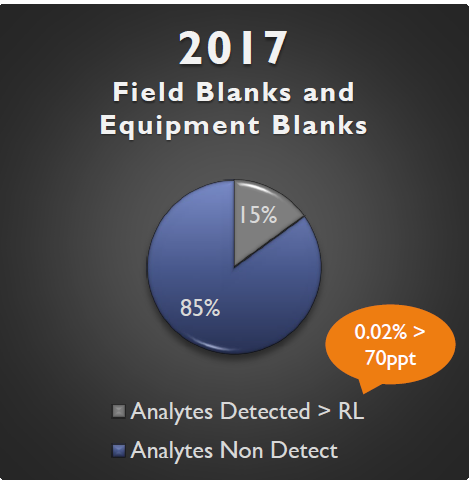
- Washing with laboratory-grade detergent solution (e.g., Liquinox®, Micro-90®, Contrad®, etc.) followed by water rinses is generally sufficient to remove PFAS from common field equipment
- Decontamination can require large quantities of PFAS-free water, but lab water can be costly and supplies limited
- Commercial or municipal water that has been tested for PFAS can be used for initial decon and rinse steps, followed by lab water final rinse
  - "PFAS-free water is defined as water that does not contain significant concentrations of any compound in a specific PFAS analyte list that is being analyzed at a project-defined level" e.g., < lab RL, 1/2 of PQL or other defined limit based on project data quality objectives (MDEQ, 2018 → ITRC, 2017)
- Equipment blanks require additional consideration:
  - Water that is certified as PFAS-free may NOT be free of all VOCs or SVOCs
  - Be sure to specific lab water that is free of all target analytes in your program
  - If using separate lab water for PFAS and VOC/SVOC blanks, collect PFAS first

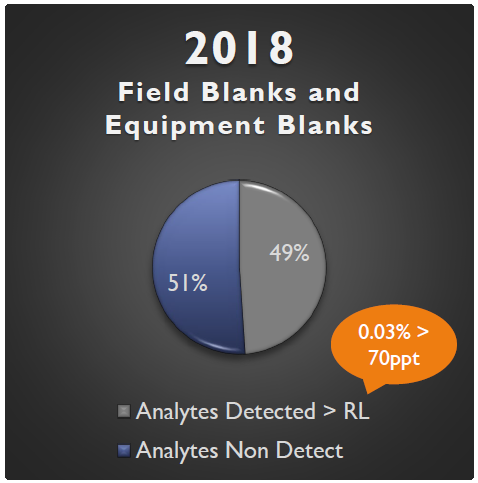
PFAS in equipment blank samples

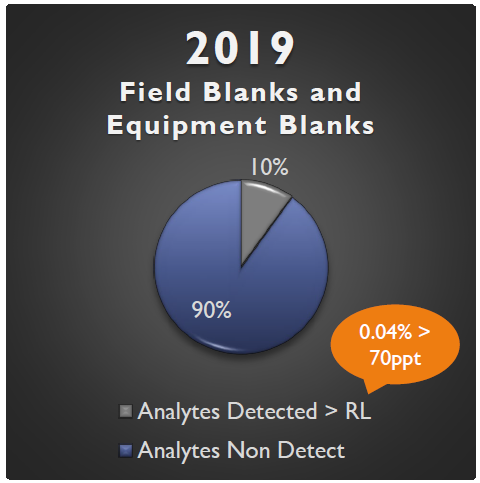


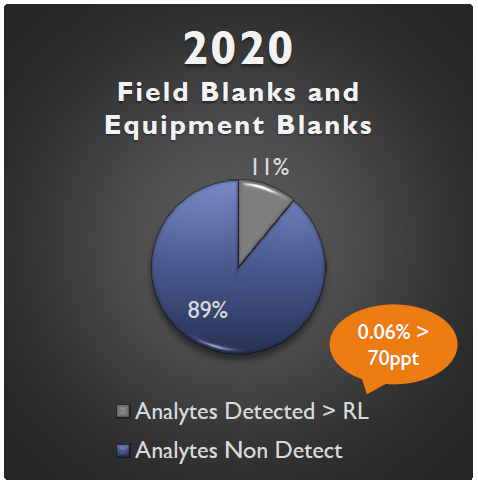
From "Groundwater Sampling Interference from Per- and Polyfluoroalkyl Substances in Sampling Equipment" Bill DiGuiseppi, Doug Winter, Travis Gwinn, Dr. Jennifer Field and Krista Barzen-Hanson. Battelle Conf. 2014

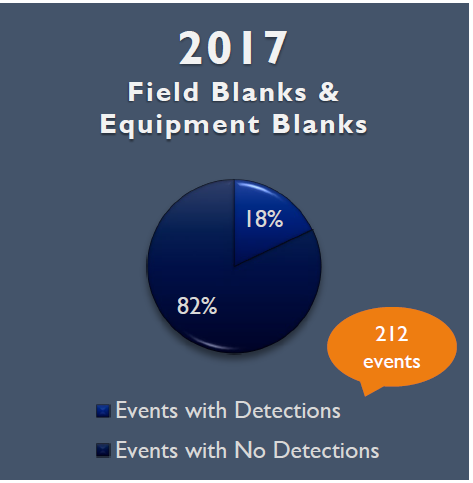
Field QC Associated with Potable and Non-Potable Water

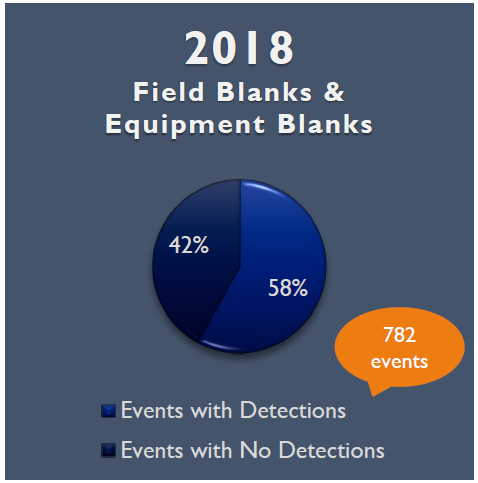


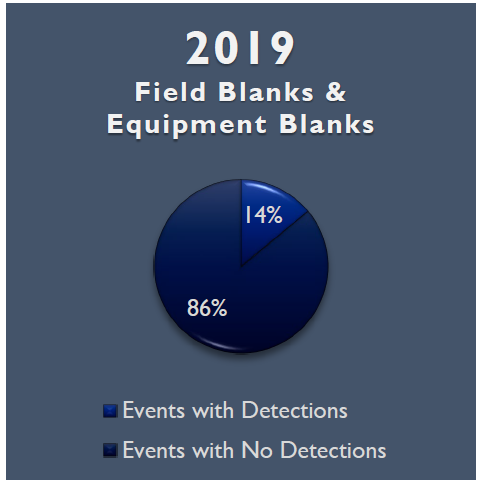


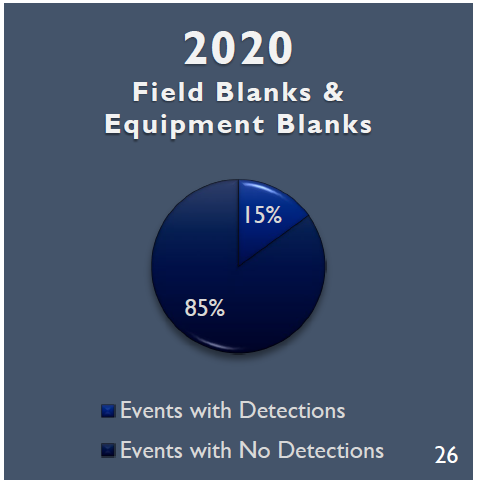












From “PFAS: Sample Collection, State of the Science” Webinar, Taryn McKnight
Eurofins Environment Testing America, March 2022
https://www.eurofinsus.com/environment-testing/resources/webinars/

PFAS in Sampling Systems - Summary

- Concern over fluoropolymers in sampling equipment and supplies led to regulatory and industry guidance to avoid using ANY fluoropolymers and even some non-fluoropolymers out of an abundance of caution, but this position overstates the risk and limits options for sampling equipment
- Latest studies have demonstrated that not all fluoropolymers will leach PFAS into water samples and not all field supplies and materials are sources of PFAS that will contaminate samples, and additional research is underway to provide a clear path for regulators and users
- Field testing can demonstrate if those systems can reliably produce accurate samples and determine if different equipment is needed to meet program requirements and avoid PFAS sample contamination
- The ONLY way to be certain that sampling equipment is PFAS-free is through material testing and analysis – this requires advance planning to get results prior to sampling and adds some cost, but is ALWAYS less expensive than making a mistake!

Referenced papers and documents

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"Groundwater Sampling Interference from Per- and Polyfluoroalkyl Substances in Sampling Equipment"
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Questions?

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