An Equipment Manufacturer's Perspective on Regulatory Guidance and Ambiguity on PFAS in Groundwater Sampling

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Why do we use Teflon®?

- Groundwater sampling equipment, including pumps, bailers, tubing and other components, 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 matrix components (well, okay, PFAS, but no VOCs, SVOCs, etc.)
  - 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)*

What about PFAS? Addressing the materials issues

- There is concern that sampling for PFAS using sampling equipment manufactured from fluoropolymers (e.g., Teflon, PTFE, ETFE, FEP) could result in sample contamination
- Recommendations or requirements in regulatory guidance documents, SOPs and “fact sheets” from industry organizations to avoid the use of all fluoropolymers have been based on an abundance of caution, and research continues to determine which materials can be safely used
- Manufacturers of sampling equipment and components such as plastic tubing are challenged with finding alternate materials that can meet performance requirements while meeting needs for both PFAS sampling and other organic compounds

Some examples…

RESEARCH ARTICLE

WILEY

Evaluating PFAS cross contamination issues

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Abstract

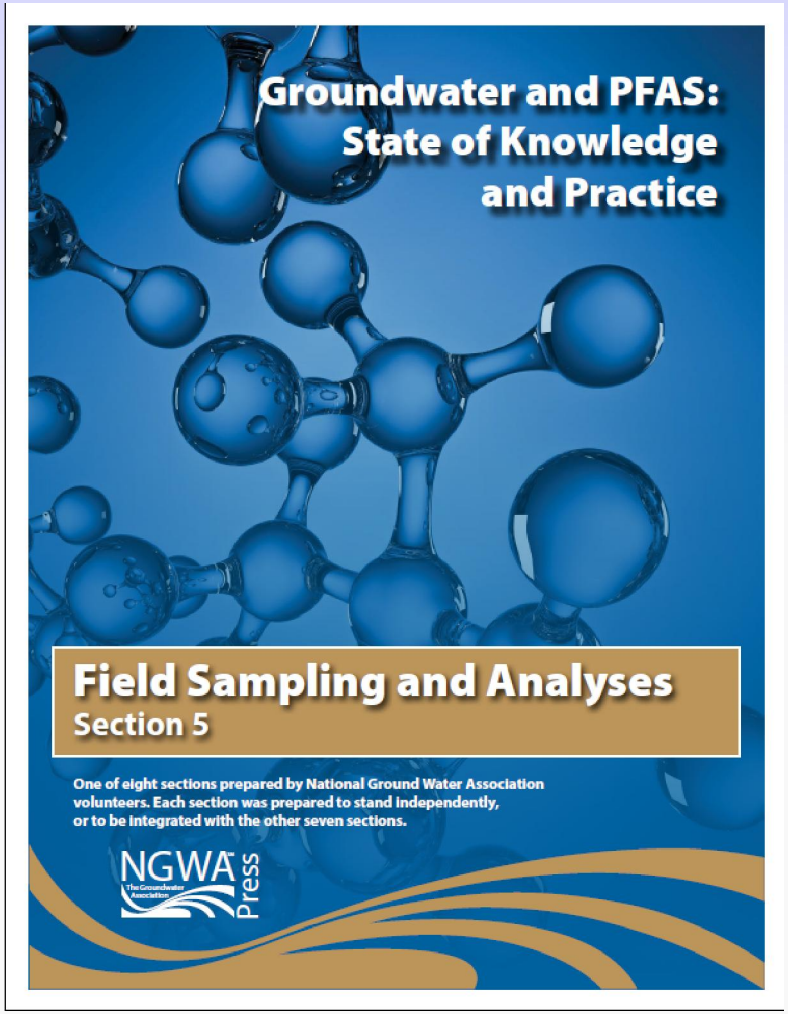
Avoiding cross contamination from per- and polyfluoroalkyl substances (PFAS) that may occur during sampling of environmental media is the key to ensure reliable analytical results during a PFAS sampling program. Due to the ubiquitous nature of PFAS in commonly used sampling materials and personal protective equipment, mitigating the risk of cross contamination is a challenge that requires a conservative approach when planning and executing a PFAS sampling program. This article describes a conservative approach to PFAS sampling and includes a case study that evaluated three insect repellent products to determine their suitability for use during PFAS investigation. The three products were verified to be PFAS-free for the 17 PFAS included in the analysis and, therefore, these products are suitable for use during PFAS sampling activities without concern for cross contamination.

"A common trend in many PFAS sampling documents is to completely prohibit the use or even the presence of suspected items on a project site undergoing PFAS sampling."

"A conservative PFAS sampling guidance should include testing procedures to evaluate whether a material suspected of containing PFAS presents a risk of cross contamination."

Some examples, continued

"The materials of construction…. should be free from polytetrafluorethylene (PTFE) or ethylene tetrafluoroethylene (ETFE) to the maximum extent practicable.



From NGWA, March 2018

Per- and Polyfluoroalkyl Substances (PFAS) Sampling Guidelines

CALIFORNIA STATE WATER QUALITY CONTROL BOARD

DIVISION OF WATER QUALITY

Water Boards

March 20, 2019

3.1 SAMPLING EQUIPMENT

The actual list of PFAS-containing materials potentially encountered onsite will change based on the specific sampled media and site-specific sampling conditions. Allowable materials include high-density polyethylene (HDPE), polypropylene, silicone, stainless steel, nylon, PVC, acetate, and cotton. Do not use any equipment that contains any known fluoropolymers including, but not limited to:

- Polytetrafluoroethylene (PTFE), including the trademark Teflon® and Hostaflon®, which can be found in many items, including but not limited to ball check-valves on certain bailers, the lining of some hoses and tubing, some 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 found in many items, including but not limited to tubing, films/coatings on aluminum, galvanized or aluminized steel, wire insulators, and lithium-ion batteries.
- Polychlorotrifluoroethylene (PCTFE), including the trademark Neoflon®, which can be found in many items, including but not limited to valves, seals, gaskets, and food packaging.
- Ethylene-tetrafluoro-ethylene (ETFE), including the trademark Tefzel®, which can be found in many items, including but not limited to 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 found in many items, including but not limited to wire and cable insulation and covers, pipe linings, and some labware.
- Low density polyethylene (LDPE) should not be used for any items that will come into direct contact with the sample media. LDPE can be found in many items, including but not limited to containers and bottles, plastic bags, and tubing.

From Per- and Polyfluoroalkyl Substances (PFAS) Sampling Guidelines, CALIFORNIA STATE WATER QUALITY CONTROL BOARD, March 2019. https://www.waterboards.ca.gov/water_issues/programs/pfas/

What are my options?

- Examples of alternate materials offered in guidance documents all have some limitations:
  - HDPE isn't as strong and flexible as PTFE and FEP – cycle life testing on HDPE bladders showed 1,500 – 3,000 cycles to failure, equal to 1-2 years of use for dedicated pumps (PTFE = 200K cycles, 100-200 years use)
  - Polypropylene is rather inflexible and tends to take a set when used for materials such as tubing, making it difficult to impossible uncoil, especially in cold weather
  - Silicone rubber is flexible but has a high capacity for sorption of organics
  - Vinyl (Tygon or flexible polyvinyl chloride) is made flexible through the use of phthalate plasticizers that will leach into samples, also absorbs organics
  - Alternatives to Viton (FKM), such as nitrile rubber, often leach other organic compounds - QED testing of nitrile showed up to 10,000 µg/l carbon disulfide

Is there actually PFAS in my Teflon?

- Not all fluoropolymers will leach PFAS into groundwater samples
- The only way to be certain that sampling equipment is PFAS-free is through material testing and analysis
- QED testing has shown that PTFE pump bladders and seals and FEP tubing have tested to be free of PFAS based on the lowest available laboratory reporting limits
- Manufacturers of sampling equipment and components such as plastic tubing are challenged with finding alternate PFAS-free materials that can meet engineering performance requirements while also meeting sampling program needs for other organic compounds such as fuels and solvents (VOCs and SVOCs) without sample bias or contamination
- Portable and dedicated sampling pumps and passive sampling systems are available that are entirely PFAS-free and Teflon-free

Some early research studies of common commercial and consumer products show PTFE thread tape and "pipe dope" as likely sources of PFAS

Table 6-1. Comparison of source strengths for total amount of PFCA (TPFCA) in a hypothetical, "typical" American home [a]

Group ID	Article category	TPFCA in article	Article quantity [b]	TPFCA in home (mg)
A	Pre-treated carpeting [c]	48.4 ng/cm^2	150 m^2	72.6
B	Commercial carpet-care liquids	12000 ng/g	6 kg [d]	71.8
C	Household carpet/fabric-care liquids and foams	953 ng/g	1 kg	0.95
D	Treated apparel	198 ng/g	2 kg	0.40
E	Treated home textile and upholstery	336 ng/g	5 kg	1.68
F	Treated non-woven medical garments	795 ng/g	0 kg	0
G	Treated floor waxes and stone/tile/wood sealants	2430 ng/g	1 kg	2.42
H	Treated food contact paper	3100 ng/g	0.01 kg	0.03
I	Membranes for apparel	124 ng/g	1 kg	0.12
J	Thread seal tapes and pastes	603 ng/g	0.02 kg	0.01
K	Non-stick cookware	0.028 ng/cm^2	1 m^2	0.0003
L	Dental floss and plaque removers	31.3 ng/g	0.005 kg	0.0002
M	Miscellaneous	69.5 ng/g	0	0

[a] The average, single-family home size in the U.S. in 2004 was 2330 ft^2 (http://www.nahb.org/). [b] The quantities of articles are rough estimates. [c] Assuming 70% of floor area is carpet; conversion factors for total PFCA are given in supporting information. [d] For one application; dilution factor is considered.

From Perfluorocarboxylic Acid Content in 116 Articles of Commerce, EPA/600/R-09/033, March 2009

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
- Flexible elastomeric tubing, such as silicone, is required at pump head but can be attached to other non-fluoropolymer tubing materials such as HDPE & LDPE
- While peristaltic pumps are often cited as less accurate for gas sensitive parameters (e.g., VOCs, metals), PFAS are not volatile and quite stable in water, so no sample bias is expected

Battery-powered peristaltic pump

AC-powered peristaltic pump

Electric Submersible Pumps

- Fit into 2-inch (50mm) well casings
- Sampling depths up to 275 feet (84m) for AC-voltage pumps and 50 – 200 feet (15m - 60m) for DC-voltage pumps
- Greater depths for DC pumps using drop tube inlet where water depth <150'
- May not work where guidance or GWSAP for PFAS sampling prohibit use of Teflon (fluoropolymers) - many electric pumps have PTFE motor seals, PTFE wear parts and ETFE-coated motor cable
- 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 testing of ETFE tubing detected PFBA at 750 ng/L

AC-voltage pump, control box and generator

DC-voltage pump and control box

ETFE Tubing, 24 hour minimum soak test

Perfluorinated Sulfonic Acids and Perfluorinated Carboxylic Acids by HPLC/MS

Analysis Method: PFC/537M
Prep Method: EPA 3535A

Analyte Name	Result	MRL	Dil.	Date Analyzed	Date Extracted	Q
HFPO-DA	ND U	6.3	1	09/24/16 09:07	8/26/16	
Perfluorobutanoic Acid	750	10	1	09/29/16 12:39	9/29/16	*
Perfluoropentanoic Acid	ND U	6.3	1	09/24/16 09:07	8/26/16	
Perfluorobutane Sulfonate	ND U	6.3	1	09/24/16 09:07	8/26/16	
Perfluorohexanoic Acid	ND U	6.3	1	09/24/16 09:07	8/26/16	
Perfluoroheptanoic Acid	ND U	6.3	1	09/24/16 09:07	8/26/16	
Perfluorohexane Sulfonate	ND U	6.3	1	09/24/16 09:07	8/26/16	
Perfluorooctanoic Acid	ND U	2.5	1	09/24/16 09:07	8/26/16	
Perfluorononanoic Acid	ND U	6.3	1	09/24/16 09:07	8/26/16	
Perfluorooctane Sulfonate	ND U	6.3	1	09/24/16 09:07	8/26/16	
Perfluorodecanoic Acid	ND U	6.3	1	09/24/16 09:07	8/26/16	
Perfluoroundecanoic Acid	ND U	6.3	1	09/24/16 09:07	8/26/16	
Perfluorodecane Sulfonate	ND U	5.0	1	09/29/16 12:39	9/29/16	*
Perfluorododecanoic Acid	ND U	6.3	1	09/24/16 09:07	8/26/16	
Perfluorooctylsulfonamide	ND U	5.0	1	09/29/16 12:39	9/29/16	*
Perfluoro-n-tridecanoic acid	ND U	6.3	1	09/24/16 09:07	8/26/16	
Perfluoro-n-tetradecanoic acid	ND U	5.0	1	09/29/16 12:39	9/29/16	*
Perfluoroheptane sulfonate	ND U	6.3	1	09/24/16 09:07	8/26/16	
N-ethylperfluoro-1-octanesulfonamide	ND U	5.0	1	09/29/16 12:39	9/29/16	*
N-methylperfluoro-1-octanesulfonamide	ND U	6.3	1	09/24/16 09:07	8/26/16	
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	ND U	6.3	1	09/24/16 09:07	8/26/16	
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	ND U	6.3	1	09/24/16 09:07	8/26/16	
6:2 Fluorotelomer sulfonate	ND U	6.3	1	09/24/16 09:07	8/26/16	
8:2 Fluorotelomer sulfonate	ND U	6.3	1	09/24/16 09:07	8/26/16	

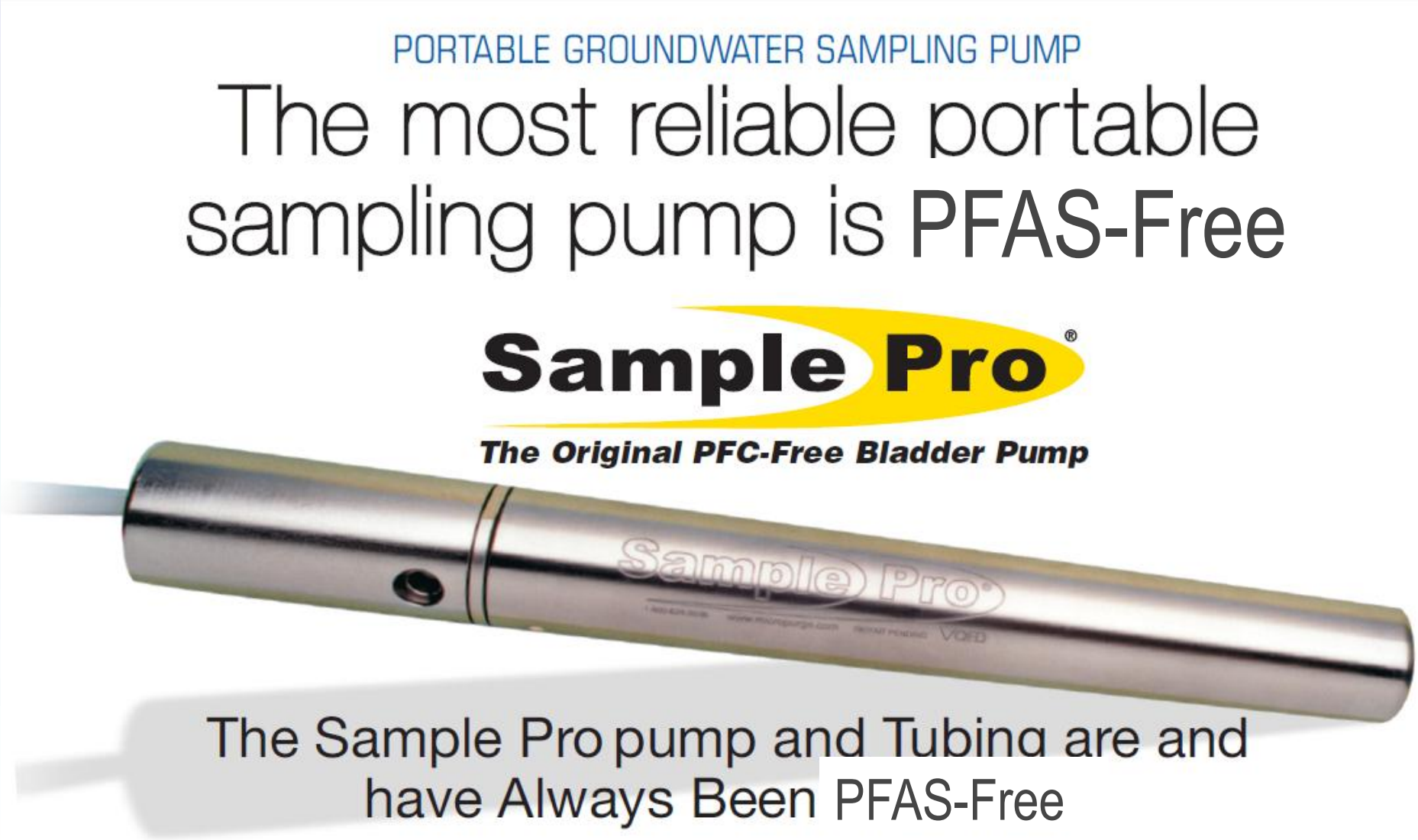
Air-Powered Bladder Pumps

- Designs are available to fit well as small as 0.5” well casing and multilevel tubing wells
- 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 – BUT – dedicated pumps historically use PTFE bladders, which can’t be used under some sampling plans
- Portable and dedicated pumps are available with HDPE & LDPE bladders, but these often don’t have the long bladder life typical of PTFE bladders and are designed to be replaced frequently, which defeats the purpose of a dedicated system

Dedicated Bladder Pumps

Portable Bladder Pumps

QED Sample Pro® PFAS-Free/Teflon-free Portable Bladder Pump Sampling Systems



WELL WIZARD®

Zero™ and Clear™

- Well Wizard Zero models are constructed entirely from non-fluoropolymer plastics that have been tested and certified to be PFAS-free
- Well Wizard Clear models will use the same components but retain the PTFE bladder for very low level organic testing - also tested PFAS-free
- QED's industry-first HDPE twin bonded tubing meets all PFAS sampling program requirements and has been tested for PFAS, VOCs and SVOCs
- Models available to sample to 600 feet depth (300 PSI pressure) and can sample to nearly unlimited depths using drop tube inlet systems
- **Available November – December 2019**

QED

Passive and No-Purge Samplers

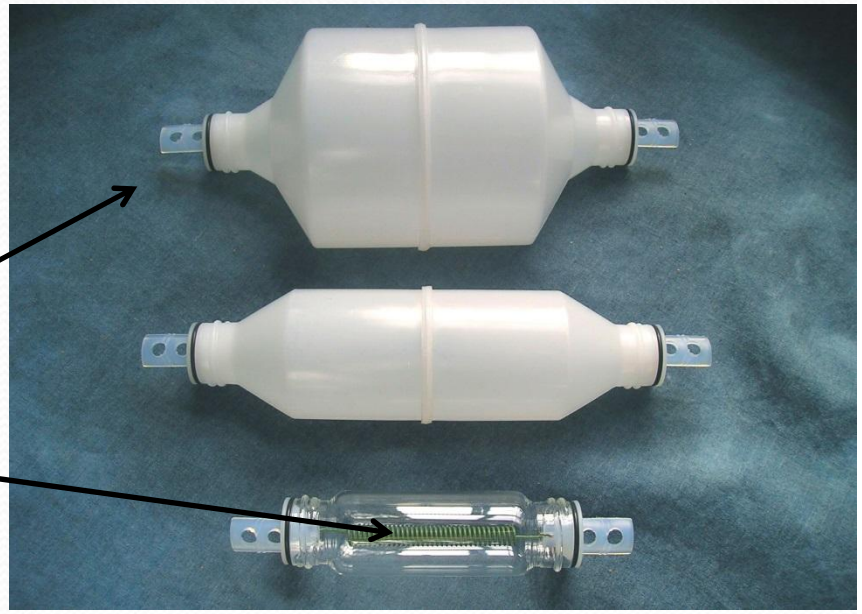
- Much simpler to design without any fluoropolymers - few to no moving parts
- Polyethylene Diffusion Bag (PDB) won't work for PFAS – will not equilibrate
- Whole water samplers can work if sample volume requirements are met
- Some available without any fluoropolymers, but testing is still recommended to ensure that no PFAS can leach from materials used

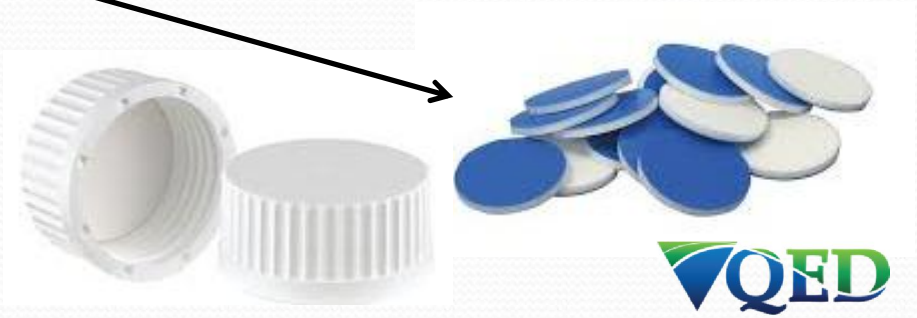
PDB Sampler

Snap Sampler®

SNAP SAMPLER Zero™

- All components tested for PFAS
- Molded acetal “snap caps” with EPDM O-ring seals
- Passivated stainless steel center springs
- Distinctive white HDPE liner bottle caps for 125 mL and 350 mL poly bottles and white/blue septa caps for 40 mL VOA vials sealed in separate packaging
- **Available November - December 2019**





Sampling Equipment Recommendations

- Follow a common sense approach to the use of any materials and supplies – look for studies on PFAS content in materials and, when in doubt, either test your system or eliminate suspect materials
- For new dedicated pump systems, portable pump systems and passive samplers, equipment blank testing can determine if they're PFAS-free, or obtain certification from the manufacturer that the equipment and tubing has been tested and is PFAS-free
- For existing dedicated sampling systems, test in place for absence or presence of PFAS in samples before replacing any components
  - Where results are ND in all wells, systems can be used (unless GWSAP or regulatory restrictions on existing materials exist)
  - Where PFAS is detected in some or all wells, those wells can be sampled again using a known PFAS-free system to determine if source is the sampling system or if PFAS existing in the water
  - When a sampling system shows PFAS, look for sources such as PTFE thread tape, gaskets or seals that could be eliminated or replaced with alternate materials

Questions?

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