TECHNICAL BRIEF

A Quick Review of Best Practices for Sampling and Analysis of Per- and Polyfluoroalkyl Substances

OVERVIEW

This technical brief offers a quick review of the best practices for sampling and analysis of per- and polyfluoroalkyl substances (PFAS) in environmental media. It condenses advice published in EPRI's 2022 report, Best Practices for Sampling and Analysis of Per- and Polyfluoroalkyl Substances (3002025843). Readers of the brief will find background information about PFAS and their occurrence in the environment, the development of regulations culminating in current standards and guidance, best practices for sampling and analysis, and health and safety precautions that prevent workplace exposure. For a complete discussion of these issues, along with references and detailed tables, the reader is directed to the original report (EPRI 2022).

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are synthetic organic compounds that exhibit strong bonds between fluorine (F) and carbon (C) atoms. They form a large class of a few thousand to tens of thousands or more chemicals currently present in the environment, depending on the definition of PFAS used.

PFAS have been manufactured for more than 60 years and used in a variety of industries as fire-fighting foams, lubricants, surfactants, and water and oil/grease repellents in applications ranging from food packaging to fabrics, carpets, construction materials, cleaning products, and more. Their formulations and unique ability to repel water and oil make them persistent, potentially hazardous, bioaccumulative, and ubiquitous environmental contaminants across a wide range of media including soil, surface water, groundwater, wastewater, and biota (e.g., fish).

PFAS standards and guidance values are typically very stringent, in the parts-per-trillion (ppt) range. Environmental professionals face the challenging task of quantifying trace concentrations of PFAS over widespread areas and differing conditions while avoiding sample cross contamination of these ubiquitous chemicals. Achieving reliable results therefore requires careful attention and implementation of sampling and analysis best practices. This is becoming more important given increasing requirements for monitoring under state and federal NPDES discharge permits.

PFAS OCCURENCE IN THE ENVIRONMENT

The chemical structure of an organic compound governs its behavior in various environmental media. PFAS are highly fluorinated, synthetic organic compounds in which fluorine (F) atoms attach to alkyl chains of carbon (C) and hydrogen (H) atoms, forming the "tail group" of the compound (ITRC 2023). This arrangement creates one of the strongest bonds in organic chemistry, the F-C bond which resists degradation in the environment (ITRC 2023).

Figure 1 illustrates the chemical structure of perfluorooctanoic acid (PFOA), a PFAS with a carboxylic acid “head group” (-C(+O)–OH) attached to an F-C tail group (NCBI 2024). The head group dissolves in water, supporting the use (since discontinued) of PFOA as an industrial surfactant to reduce surface tension in chemical processing. But the tail group does not dissolve; it is water-repellant and likely to sorb to organic matter in soils and sediments. PFAS with this chemical structure may partition to two different environmental media at interfaces (ITRC 2023, NCBI 2024).

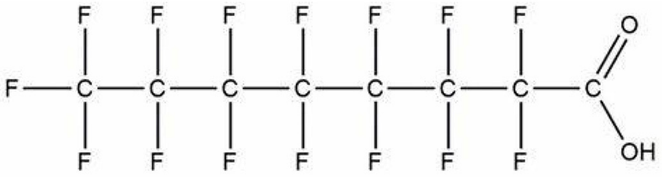

Figure 1. *Perfluorooctonoic Acid (PFOA) (NCBI 2024)*

Because they have been widely used, PFAS may be present in diverse environmental media, including drinking water, surface water, groundwater, wastewater, stormwater, landfill leachate, solid waste, biosolids, and soil, as well as biota (e.g., fish). PFAS that repel water sorb to organic matter in soils and sediments. Others partition at interfaces between media—air/water, soil/water, or non-aqueous phase liquid (NAPL)/water. Wherever they reside, PFAS persist in the environment. They are extremely stable, do not break down under typical environmental conditions, and can be formed in the environment from PFAS precursor chemicals. The PFAS water cycle, shown in Figure 2, traces the environmental pathways PFAS may take to reach drinking water supplies and other environmental media.

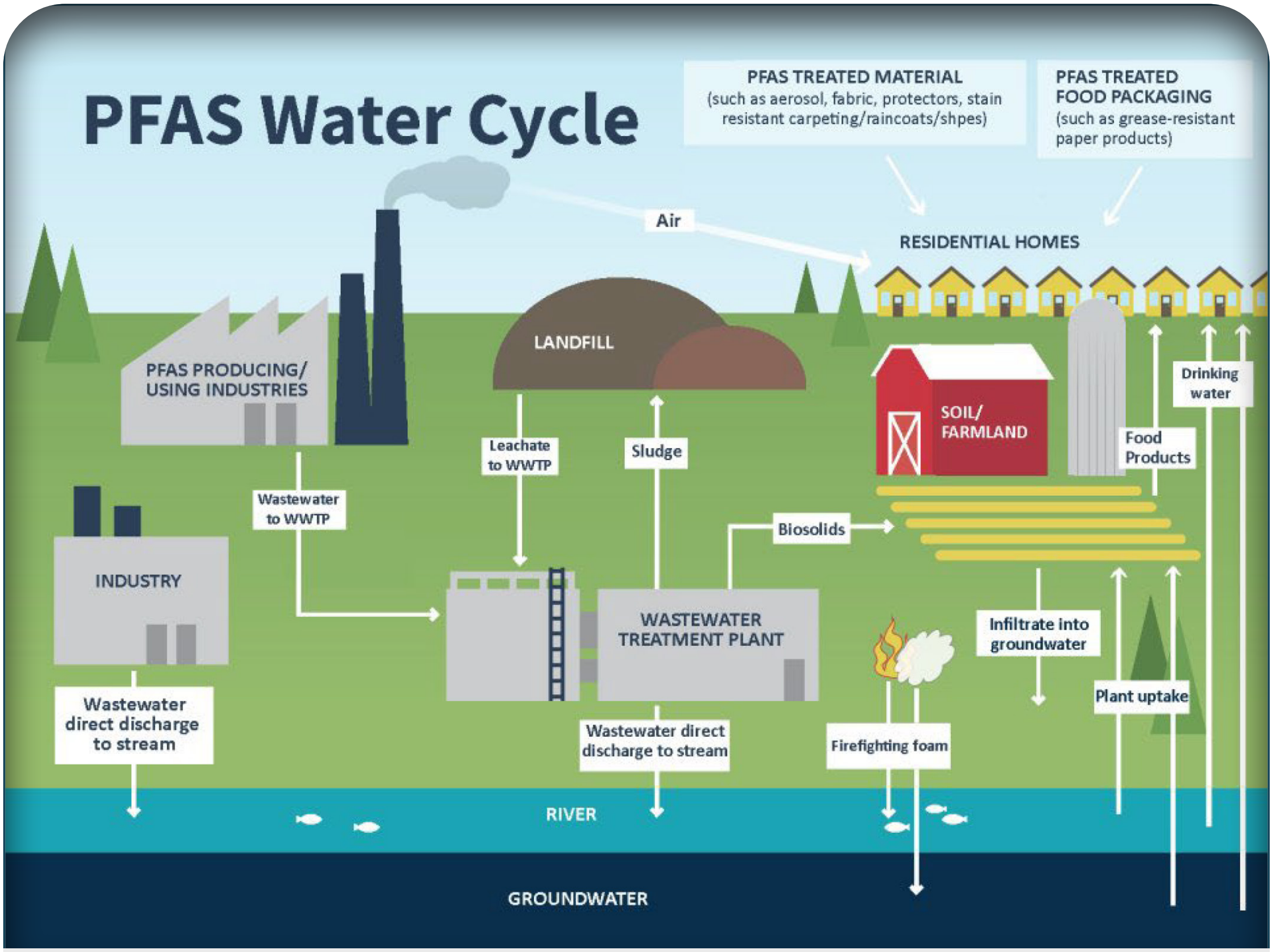

Figure 2. *PFAS Water Cycle (EPA 2024a)*

STANDARDS AND GUIDANCE

Since the first guidance established by West Virginia in 2002—150,000 nanograms per liter (ng/L) for PFOA—standards and guidance values have steadily become more stringent (Figure 3). Health advisory (HA) values released by EPA in 2022 for four PFAS compounds range from 0.004 ng/L (ppt) for PFOA (interim) to 2000 ppt for PFBS (final).

In April 2024, EPA issued the first federal drinking water standards for PFAS compounds (EPA 2024b). This legally enforceable standard limits drinking water levels of PFOA and PFOS (the compounds of most concern) to 4 ppt or less—the lowest level that can feasibly be measured – along with MCLs and Hazard Index MCLs for four other PFAS compounds. In addition, new final recommended federal water quality criteria for PFOA and PFOS and new water quality benchmarks for eight additional compounds were announced in October 2024.

BEST PRACTICES FOR PFAS SAMPLING

Extremely stringent standards and guidance values for PFAS make cross contamination of samples during collection a serious concern. This concern is amplified by the ubiquitous presence of the chemicals in:

- Materials and equipment used for environmental sampling (e.g., Teflon)
- Personal care products (such as sunscreen and insect repellent)
- Treated clothing (including Gore-Tex or other water- and chemical-resistant materials and coatings)
- Fabric softeners
- Other materials found at sampling sites, ranging from food wrappers to canopy tents

A PFAS sampling campaign begins with the development of a conceptual site model. This model considers the PFAS source, migration pathway, and potential receptors—which may be far from the source, given PFAS mobility. Sampling design should be based on this model.

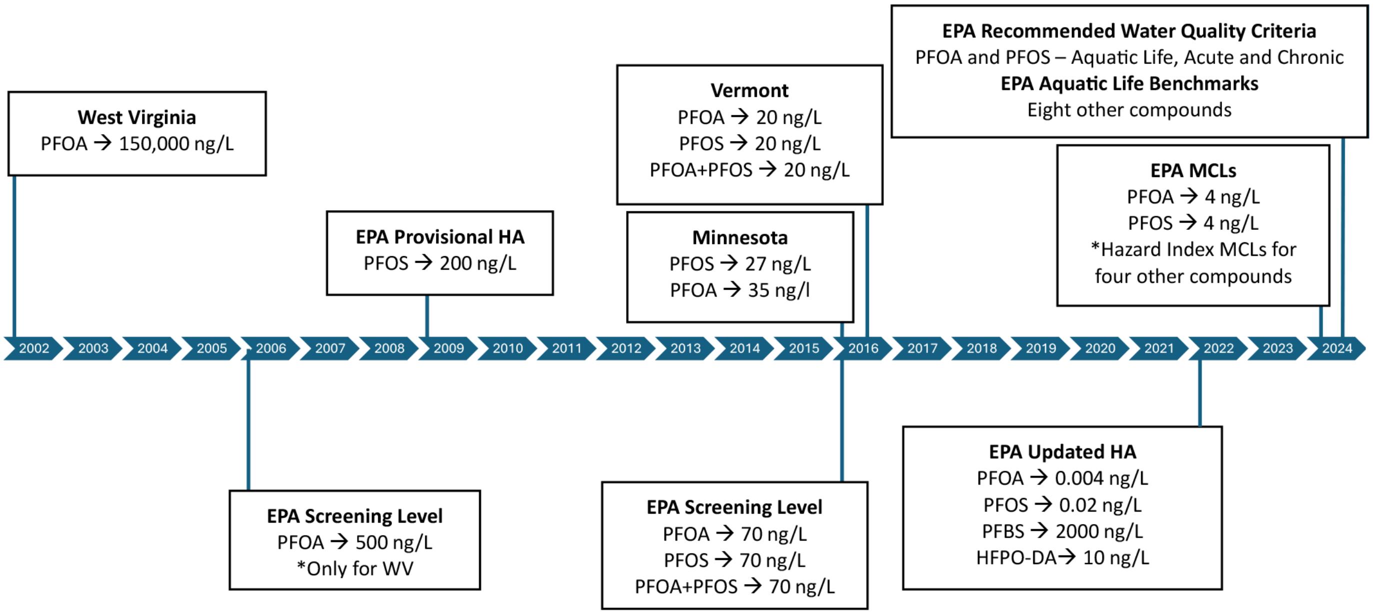

Figure 3. *PFAS Regulatory Timeline (updated from EPRI 2022).* ***Note:*** *confirm current MCLs/Criteria prior to implementing sampling plan.*

A vital partner in the sampling campaign is an analytical laboratory certified by the appropriate authority. Some states use the National Environmental Laboratory Accreditation Program (NELAP) and other have their own certification programs. Projects involving the Department of Defense (DOD) may require that the lab be approved by the DOD's stringent QA program. Laboratory personnel help plan and coordinate the sampling event by offering advice on appropriate analysis methods and providing suitable clean bottles (generally polypropylene or high-density polyethylene with unlined polypropylene caps). Glass containers should be avoided because PFAS can adsorb to glass surfaces.

Every element of the sampling design should be evaluated to ensure that sampling equipment does not itself contain traces of PFAS. Serious attention should be given to ensure that personal care products, food, clothing, personal protective equipment (PPE), waders, rainfall, thread tape on plumbing fixtures, etc. do not pose a risk of contaminating the samples. Likewise, personnel should wash their hands thoroughly and put on new, powderless nitrile gloves while they are within the sampling area. Less-impacted samples should be collected first and filters should not be used because they can absorb PFAS. Sample collectors may need to take additional quality-assurance (QA) precautions, depending on the media being sampled. For example, they should flush wells and, during surface water sampling, avoid collection of surface microlayers where PFAS can accumulate. Sample hold times range from 7–28 days, depending on analytical method, so all samples should be packed in ice and shipped as soon as possible.

Collection of duplicate and blank samples is part of the quality-assurance program. A minimum of one field duplicate should be collected for every 10 samples. Field reagent blanks, field blanks, ambient blanks, equipment rinsate blanks, and source water samples should be collected as appropriate.

BEST PRACTICES FOR PFAS ANALYSIS

When field samples arrive at the laboratory, analysts will need to take the same precautions as collectors by avoiding use of glassware, Teflon, and other materials containing PFAS. Soil samples should be cleaned of debris and homogenized. Aqueous samples should be prepared using the whole sample so that the sample bottle can be rinsed with solvent to collect any residual analyte that adheres to its walls. Aqueous samples containing suspended solids cannot be filtered but may be centrifuged and decanted so that bottles and solids can be rinsed for residual analyte. Samples containing NAPL, foam, or bulk PFAS should be specially flagged for the laboratory's attention, since they may require separate analysis or dilution.

Many different analytical methods are available (Table 1), depending on the matrix, compound of interest, and detection limit, with more under development. After ensuring that no permit or regulatory requirements dictate a particular method or analyte list, the sampling team can choose an optimal analytical method in consultation with their laboratory partners. Considering the stringent PFAS levels targeted for analysis and the challenge of avoiding contamination, it is recommended that all laboratory QA/QC reports be requested and reviewed. Whenever possible, it is recommended that raw data be requested along with the other laboratory deliverables. This will enable robust chemist review and comparison, since it is likely that a PFAS sampling program may involve different processing, analysis techniques, and quality standards over time. This will involve an additional cost.

Finally, as PFAS analysis remains in its infancy with new and evolving methods, environmental professionals should be aware that modified test methods are common among contract laboratories. Care should be taken to understand each contract laboratory's methods and any changes with time, noting that QA/Quality Control (QC) for modified methods may not align with the referenced method.

Additional methods for the analysis of total organic fluorine are available and may be useful as screening tools. Non-target analytical methods and forensic methods are also under development.

Table 1. *PFAS analytical method descriptions*

AMBIENT WATER					
METHOD	**MATRIX**	**DESCRIPTION**	**SAMPLE CONTAINER**	**HOLD TIME**	**PRESERVATION**
EPA Method 537.1	Treated drinking water	For analysis of 18 PFAS constituents, largely focusing on longer chain PFAS. A rigid method not allowing laboratory modification and utilizing internal standards.	• Polypropylene bottle with polypropylene screw cap • 250 mL • Two per sample recommended	• 14 d until extraction • 28 additional days until analysis	• 5 g/L Trizma added to bottles prior to sampling • Samples stored/shipped < 10°C
EPA Method 533	Treated drinking water	For analysis of 25 PFAS constituents, largely focused on shorter chain PFAS. A rigid method which uses isotopic dilution.	• Polypropylene bottle with polypropylene screw cap • 100 – 250 mL • Two per sample recommended	• 28 d until extraction • 28 additional days until analysis	• 1 g/L ammonium acetate added to bottles prior to sampling • Samples shipped < 10°C with ice remaining in the cooler if over 2 days in transit
EPA Method 1633	Surface water, groundwater	For analysis of 40 PFAS compounds. This new method is likely to become the regulatory standard featuring low reporting limits but requiring large sample volumes, solid phase extraction, and likely higher costs due to stringent QC requirements.	• High-density polyethylene (HDPE) bottle with linerless HPDE or polypropylene screw cap All Waters Other Than Landfill Leachate • One 500-mL aliquot (sample preparation) • Smaller container (% solid determination and screening purposes)	Stored at ≤ -20°C • 90 d until extraction Stored at 0 – 6°C • 28 d until extraction (FOSEs and FOSA As >8 days) Post-Extraction • 90 additional days until analysis (28 d for ether sulfanates, NFDHA ASAP)	• Samples stored/shipped at 0 – 6°C after collection • Samples must be received by the laboratory within 48 hours of collection • Samples are shielded from light
QSM Table B-15 (537 modified)	Surface water, groundwater	Flexible method based on Department of Defense's Quality Systems Manual (QSM) and useful for many matrices. The method uses isotopic dilution and solid phase extraction. Laboratory-dependent analyte list, but some labs can test for more than 50 analytes with low quantitation limits.	• HDPE or polypropylene bottles with screw caps • 125 – 250 mL • Two per sample recommended	• 14 – 28 d (lab dependent) to extraction • 28 additional days until analysis	• Lab dependent, typical conditions maintain 0 – 6°C from collection until receipt at laboratory
EPA SW-846 Method 3512, 8327 (Screening only)	Surface water, groundwater	An aqueous method using external standards for quantification and associated with low accuracy and precision. Suitable for screening but otherwise not recommended.	• HDPE or polypropylene bottles with screw caps	• Formal hold times are not established but those following EPA 537.1 (above) are recommended	• Samples must be preserved ≤ 6°C

Table 1 (continued). *PFAS analytical method descriptions*

AMBIENT WATER					
METHOD	**MATRIX**	**DESCRIPTION**	**SAMPLE CONTAINER**	**HOLD TIME**	**PRESERVATION**
ASTM D7979-20 (Not recommended)	Influent and effluent from water treatment	This method utilizes direct injection coupled with external standard quantification. The method can be problematic due to lack of homogenization, matrix interferences, and lack of concentration. Associated with high reporting limits. Not recommended.	• 5-mL polypropylene tube, at least two per sample	• Analysis within 28 d of collection	• Samples must be preserved ≤ 6°C
WASTEWATER					
EPA Method 1633	Wastewater	See discussion under ambient water for details.	• High-density polyethylene (HDPE) bottle with linerless HPDE or polypropylene screw cap All Waters Other Than Landfill Leachate • One 500-mL aliquot (sample preparation) • Smaller container (% solid determination and screening purposes) Landfill Leachate • Two 100 mL aliquots • (one sample preparation, the other for % solid determination and screening purposes)	Stored at ≤ -20°C • 90 d until extraction Stored at 0 - 6°C • 28 d until extraction (FOSEs and FOSA As >8 days) Post-Extraction • 90 additional days until analysis (28 d for ether sulfanates, NFDHA ASAP)	• Samples stored/ shipped at 0 – 6°C after collection • Samples must be received by the laboratory within 48 hours of collection • Samples are shielded from light
QSM Table B-15 (537 modified)	Wastewater	Although not explicitly defined in the QSM, the method can be used for wastewater. Matrices analyzed will be laboratory dependent. See discussion under ambient water for details.	• HDPE or polypropylene bottles with screw caps • 125 – 250 mL • Two per sample recommended	• 14 – 28 d (lab dependent) to extraction • 28 additional days until analysis	• Lab dependent, typical conditions maintain 0 – 6°C from collection until receipt at laboratory
ASTM D7979-20 (Not recommended)	Wastewater, water sludge	As discussed in the ambient water section, this method is not recommended.	• 5-mL polypropylene tube, at least two per sample	• Analysis within 28 d of collection	• Samples must be preserved ≤ 6°C

Table 1 (continued). *PFAS analytical method descriptions*

SOIL, SEDIMENT, AND OTHER SOLIDS (E.G. BIOSOLIDS, FISH TISSUE)					
METHOD	**MATRIX**	**DESCRIPTION**	**SAMPLE CONTAINER**	**HOLD TIME**	**PRESERVATION**
EPA Method 1633	Soil, sediment, other solids (e.g., biosolids, fish tissue)	See discussion under ambient water for details.	• Wide-mouth HDPE jar or bottle with linerless HDPE or polypropylene caps, fill no more than 3/4 full • Soil and sediment maximum amount used is 5.0 g dry weight • Biosolids maximum amount used is 0.5 g dry weight	<u>Stored at ≤ -20°C</u> • 90 d until extraction <u>Stored at 0 – 4°C</u> • 28 d until extraction (ASAP for NFDHA) <u>Post-Extraction</u> • 90 additional days until analysis (28 d for ether sulfanates, NFDHA ASAP)	• Samples stored/ shipped at 0 – 6°C after collection • Biosolids stored ≤-20°C • Samples are shielded from light
QSM Table B-15 (537 modified)	Soil, sediment, other solids (e.g., biosolids, fish tissue)	See discussion under ambient water for details. Matrices analyzed will be laboratory dependent.	• Typically HPDE or polypropylene containers with screw caps • 6 – 8 oz jars • Two per sample recommended	<u>Soil, Sediment, Biosolid</u> • Lab dependent (typically 14 – 28 d to extraction, additional 28 d to analysis) <u>Biota</u> • Lab dependent (typically up to 6 months if frozen to extraction, additional 28 d to analysis)	• Lab dependent, typical conditions maintain 0 – 6°C from collection until receipt at laboratory • Biota can be frozen upon arrival at laboratory.
ASTM D7968-17a (Not recommended)	Soil/sediment	This method resembles ASTM D7979-20 but is designed for soil/sediment analysis using solvent extraction. Not recommended.	• Polypropylene jar • Minimum 2 g for analysis • One per sample	• Analysis within 28 d of collection	• Shipped on ice

HEALTH AND SAFETY CONSIDERATIONS

The U.S. Centers for Disease Control and Prevention (CDC) have shown that certain PFAS may be linked to kidney and testicular cancer, liver damage, decreased fertility, increased asthma risk, and thyroid disease. Caution should be exercised when collecting and handling PFAS samples to prevent exposure via ingestion, inhalation, or dermal contact. Appropriate PPE may include boots, respirators, gloves, and chemical protective clothing such as aprons or coveralls. To minimize exposure, workers are allowed to wear PPEs containing trace amounts of PFAS as long as the practice is noted in the sampling logbook and the final analytical report. Although PFAS levels in the environment are generally not expected to cause adverse health effects, standard precautions still apply:

- Do not handle PFAS-containing media until all safety precautions are understood.
- Work in a well-ventilated area and always wear nitrile gloves.
- Do not breathe dust, fumes, gas, mist, vapors, or sprays containing PFAS.
- Wash skin thoroughly after handling potentially contaminated materials and wear a new pair of nitrile gloves when changing activities.
- Avoid PFAS contact during pregnancy and while nursing.

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TERMS

C	carbon
CDC	United States Centers for Disease Control and Prevention
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
EPA	United States Environmental Protection Agency
F	fluorine
H	hydrogen
HA	health advisory
HFPO-DA	hexafluoropropylene oxide dimer acid
MCL	maximum contaminant level
NAPL	non-aqueous phase liquid
NELAP	National Environmental Laboratory Accreditation Program
ng/L	nanograms per liter (or parts per trillion)
PFAS	per- and polyfluoroalkyl substances
PFBS	perfluorobutane sulfonate
PFOA	perfluorooctanoic acid
PFOS	perfluorooctanesulfonic acid
PPE	personal protective equipment
ppt	parts per trillion
QA/QC	quality assurance / quality control
QSM	Department of Defense Quality Systems Manual
RCRA	Resource Conservation and Recovery Act
WV	West Virginia
WWTP	wastewater treatment plant

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EPRI CONTACT

JEFF THOMAS, *Principal Technical Leader*
859.609.3651, jthomas@epri.com

For more information, contact:

EPRI Customer Assistance Center
800.313.3774 • askepri@epri.com

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EPRI
3420 Hillview Avenue, Palo Alto, California 94304-1338 USA • 650.855.2121 • www.epri.com

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