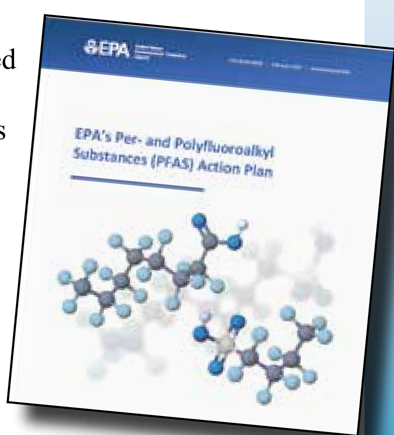
Updates on Per- and Polyfluoroalkyl Substances (PFAS)

We published an article in the April 2017 edition of the *Journal FES* addressing a group of contaminants of emerging concern (CECs), per- and poly-fluoroalkyl substances (PFAS), specifically Perfluorooctanoic Acid (PFOA) and Perfluorooctyl Sulfonate (PFOS).[1] This article provides an update on the scientific and regulatory actions over the last two years, focusing on site characterization and treatment.

Federal Actions

On May 22-23, 2018, the EPA convened a two-day National Leadership Summit on PFAS to discuss steps to address challenges with PFAS. On February 14, 2019, the EPA issued a PFAS Action Plan based on input from federal, state, and local leaders from across the country as well as public, community, and tribal engagement.[2]
The EPA PFAS Action Plan is the most comprehensive cross-agency plan to address an emerging chemical of concern ever undertaken by EPA. The Action Plan describes long- and short-term actions that the EPA is taking to address PFAS contamination, including:


EPA's Per- and Polyfluoroalkyl Substances (PFAS) Action Plan

The Florida Department of Environmental Protection (FDEP) has developed provisional Cleanup Target Levels for soil, irrigation water, and groundwater based upon their own methodologies in previously promulgated regulation.


Ziqi He, PhD, PE
HSW Engineering Inc

Derek Huston, PE
HSW Engineering Inc.

- establishing a maximum contaminant level (MCL) in drinking water for PFOA and PFOS;
- listing PFOA and PFOS as hazardous substances under CERCLA aka Superfund;
- drafting Interim Recommendations for Addressing Groundwater Contaminated with PFOA and PFOS;
- including additional PFAS chemicals in nationwide drinking water monitoring;
- developing new analytical methods and tools for PFAS chemicals;
- expanding knowledge of human health and ecological effects, exposure, and fate and transport; and
- identifying cost-effective treatment technologies.

State Actions

Some states have adopted the USEPA's Health Advisory Level (HAL) of 70 parts per trillion (ppt), while others have developed separate standards and guidance values. The states most heavily affected by PFAS contamination are revising their standards as new scientific information becomes available. For example, on April 3, 2019, the Minnesota Department of Health issued a new health-based advisory value of 15 ppt for PFOS to replace the previous value of 27 ppt set in 2017. Florida has not yet enacting a cleanup standard for PFOA and PFOS, but many states have (Tables 4.1 and 4.2 in the Interstate Technology Regulatory Council (ITRC) PFAS Fact Sheets).[3] The Florida Department of Environmental Protection (FDEP) has developed provisional Cleanup Target Levels for soil, irrigation water, and groundwater based upon their own methodologies in previously promulgated regulation.

In addition, several states have been actively involved in addressing PFAS contamination, primarily focusing on drinking water monitoring, suspected source investigation, and remediation. For example, in Florida, the FDEP has been coordinating with the Department of Defense (DOD) on investigating PFOS/PFOA impacts at statewide fire training facilities where usage or suspected usage of Aqueous Film Forming Foam (AFFF) has occurred.

Sources and Site Characterization

Major Sources and Releases

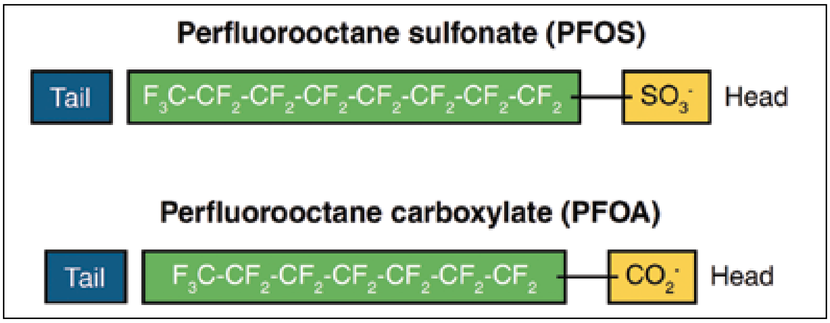
Major sources of PFAS releases into the environment include:

- Industrial facilities that produce PFAS or use PFAS chemicals (e.g., including metal plating, surfactant and fluorotelomer production, semiconductor, paper products and packaging, textiles and leather, wire coating, and building construction materials).
- AFFF use or release (e.g., fire stations, airports, fire/emergency response sites, fire training sites, companies who install or maintain AFFF systems);
- Waste management facilities (e.g., landfills, wastewater treatment plants, and areas of biosolids production and application).

PFAS environmental release mechanisms associated with industrial facilities include air emissions, spills, and disposal of manufacturing wastes and wastewater. Potential impacts to air, soil, surface water, stormwater, and groundwater are present not only at release areas but potentially over the surrounding area.

continued on next page

PFAS environmental release mechanisms associated with industrial facilities include air emissions, spills, and disposal of manufacturing wastes and wastewater.



PFAS investigations should consider the type of sources, site layout, history of use, fate and transport, and possible distribution of PFAS due to prior remedial activities.

Fate and Transport

Understanding relevant fate and transport processes for PFAS is critical in predicting migration, persistence, and the potential for exposure. Critical properties for PFAS fate and transport are the chain length (i.e., hydrophobic fluoroalkyl tail) and the type of functional group (e.g., hydrophilic anionic head group). Site conditions affecting fate and transport are soil surface charge, organic carbon content, anion exchange capacity, and the presence of co-contaminants. The partitioning behavior of PFAS to soil tends to primarily associate with the organic carbon fraction of soil and soil surface charge dependent on pH conditions (e.g., PFAS sorption and organic carbon content are typically positively correlated, whereas PFAS sorption and pH are negatively correlated). Due to their low volatilization property, PFAS may remain in the unsaturated zone where high organic carbon concentrations exists. In environments with low to moderate mitigating properties, large groundwater plumes (e.g., miles from sources) can result from the persistence and mobility of PFAS (e.g., based on Koc values, PFOS/PFOA can travel as fast as trichloroethene but without degradation) in the saturated zone.

Comparison between PFOA/PFOS and Compounds with Well-Known Fate and Transport Properties

Property	PFOA	PFOS	Benzene	TCE
Solubility (mg/L)	9,500	680	2,000	1,100
K_{OC} (L/kg)	114	371	59	166
Vapor Pressure (mm Hg)	0.525	0.002	87	23
Henry's Law Constant (unitless)	Not Measurable (Estimated at $5x10^{-5}$)	Not Measurable (Estimated at $5x10^{-5}$)	0.23	0.42

Data source: EPI Suite, FDEP 62-777, and EPA Technical Fact Sheet – PFOS and PFOA (Nov. 2017)

Furthermore, PFAS have a low potential for biological and chemical degradation. Biotic and abiotic degradation of many polyfluoroalkyl substances can result in the formation of end products, perfluoroalkyl carboxylic acids (PFCAs) such as PFOA and perfluoroalkane sulfonic acids (PFSAs) such as PFOS. These transformable substances are referred to as "precursors" and may play a role as continuing sources for decades.

Development of Site Investigation Plan

PFAS investigations should consider the type of sources, site layout, history of use, fate and transport, and possible distribution of PFAS due to prior remedial activities. A solid conceptual site model (CSM) is key to conducting a successful assessment, with the following considerations to collect sufficient data to understand PFAS fate and transport.

- PFAS can migrate through air from industrial sources multiple miles away;
- Secondary sources such as irrigation wells, infiltration galleries, or application of biosolids in farming and agricultural lands may be significant sources of PFAS;
- PFAS precursors, unmeasured chemicals that can be transformed into PFAS, should be considered prior to remediation, and
- Geochemical parameters should also be considered during the investigation including cations, anions, naturally occurring radiological materials, total organic carbon, total dissolved solids, fouling parameters (e.g., iron, manganese, hardness), as well as other organic compounds in groundwater.

Remediation

Most conventional remedial technologies used to address organic compounds, such as petroleum hydrocarbons and chlorinated solvents, are generally ineffective for treatment of PFAS. The Department of Defense is funding research for possible in-situ bioremediation, chemical and physical treatment technologies for PFOA/PFOS; however, ex-situ treatment is the only currently viable treatment method. Granular activated carbon (GAC) and anion exchange resin (AIX) are the most commonly used technologies for cost-effective water treatment of PFAS. Applications have been designed in lead-lag layouts using single or combined technologies. The table on the following page provides typical design parameters and pro and cos for GAC and AIX treatment for PFAS per our experience.

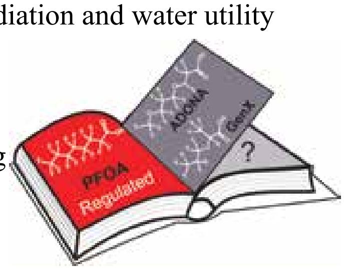
Although unit resin media is more expensive than GAC, overall capital cost for AIX is anticipated to be less because of the smaller footprint. The operating costs for both GAC and AIX depend on the media breakthrough time and changeouts, which

Parameter	GAC	AIX
Empty Bed Contact Time (min)	8 – 15	1.5 – 3
Typical Volumes	50,000 – 100,000	300,000 – 700,000
Est. Changeout (years)	0.5 – 2	2 – 4
Footprint	Larger/taller	Smaller/shorter
Limitation	Less effective for sort-chain PFAS; Organic co-contaminants compete sorption sites	More effective for sort-chain PFAS; Organic co-contaminants may foul media
Spent Media	Can be regenerated	Incinerated
Co-Contaminants	Removes other organics	Removes some organics
Material	Coal or coconut based GAC proven to be effective	Not all AIX proven to be effective

shall be determined during bench-scale and pilot scale study using site specific water matrix. For long-term treatment projects, selection of the treatment technologies and design shall consider the overall life cycle costs and environmental carbon footprint after the feasibility study.

What is Next?

The environmental remediation and water utility community of practitioners alike will undoubtedly be paying close attention to the science and policy supporting solutions for PFAS. For example, establishing MCLs for PFOS/PFOA, developing recommendations for groundwater cleanup levels at contaminated sites, or designating them as hazardous substances as well as finalizing toxicity values for other PFAS compounds (e.g., GenX, PFBS, PFBA, PFNA, etc.) will have significant potential to affect compliance obligations and costs, and enforcement actions for current and past manufacturers and users of PFAS.



References

1 He, Z. and D. E. Huston. *Contaminants of Emerging Concern – PFAS. Journal of the Florida Engineering Society*. April 2017, Volume 70 Number 8.

2 *US EPA's Per- and Polyfluoroalkyl Substances (PFAS) Action Plan*. February 2019.

3 ITRC. PFAS Fact Sheets. https://pfas-1.itrcweb.org/fact-sheets/

About the Authors;

Ziqi He, PhD, PE is a senior engineer at HSW Engineering Inc. with over 17 years of research and consulting experience in the area of fate and transport/transformation of hazardous materials and emerging contaminants, environmental forensics, vapor intrusion, risk assessment, geochemistry, and remedial system design and implementation/optimization. Dr. He has also been invited as a peer reviewer for frontier scientific journals and grant proposals, and is an active participant with the Interstate Technology & Regulatory Council (ITRC) PFAS team.

Derek Huston, PE is a senior engineer at HSW Engineering Inc. with 20 years of experience in assessment and remediation of environmental contamination. He has extensive experience in evaluation and selection of remedial action cleanup strategies for petroleum and chlorinated solvent sites, and is also experienced in assessment and remediation of emerging chemicals including 1,4-dioxane and PFAS. Mr. Huston is an active participant with the American Society for Testing and Materials (ASTM) PFAS team.