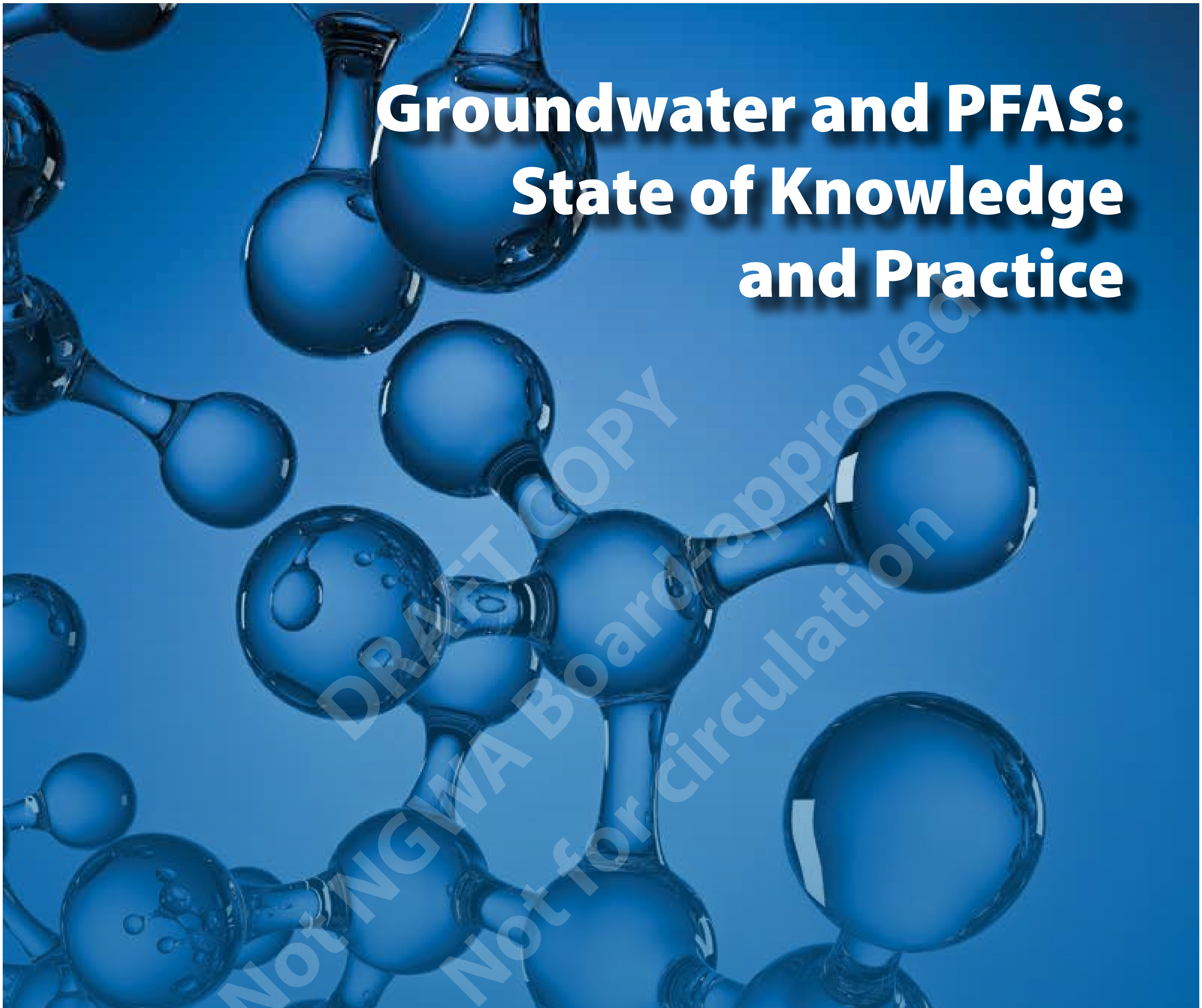
Groundwater and PFAS: State of Knowledge and Practice



Overview

Section 1

One of eight sections prepared by National Ground Water Association volunteers. Each section was prepared to stand independently, or to be integrated with the other seven sections.

NGWA℠ The Groundwater Association Press

Overview

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a unique class of emerging drinking water contaminants that have shown widespread occurrence in groundwater and surface water resources, and due to their toxicological characteristics are increasingly the focus of environmental protection agencies worldwide.

For example, the U.S. Environmental Protection Agency (USEPA) recently set drinking water health advisories for perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) at 0.07 micrograms per liter (μg/L). These new parts-per-trillion (ppt) health advisory levels are orders-of-magnitude lower than regulatory levels for most groundwater contaminants and were practically unheard of during conventional hydrogeologic investigations and remediation programs performed since the 1980s. Moreover, PFAS include *thousands* of individual chemical compounds, each with at least one carbon-fluorine (C-F) bond and most of which are soluble in groundwater. The C-F bond has been called the strongest atomic bond in nature and imparts unique characteristics to PFAS that make them useful to society in a wide variety of applications. But the unique C-F chemistry of PFAS also creates significant challenges in water treatment and remediation.

Additionally, the fate, transport, and chemical transformations of most PFAS in the environment are still unknown and areas of active scientific research. The combination of these factors creates a need for a technical guidance document.

The National Ground Water Association (NGWA) is publishing this PFAS guidance document to assist members and other groundwater professionals who may be tasked with investigating the transport pathways and extent of PFAS in groundwater and surface water, assessing potential risks to receptors, or designing and constructing engineering controls to manage subsurface PFAS contamination. The main purpose of this document is to summarize the current state of knowledge and practice regarding PFAS fate, transport, remediation, and treatment, recognizing that knowledge in this field is advancing. This document also aims to summarize current technologies, methods, and field procedures being used to characterize sites and test remediation and treatment technologies.

This document is organized as follows. It was written so each section could stand alone from the others, if desired:

- Section 1 introduces the problem and summarizes the key takeaways.
- Section 2 provides a glossary of key PFAS-related terminology.
- Section 3 summarizes the chemistry and known human health and ecological impacts of PFAS.
- Section 4 discusses PFAS fate and transport in the environment.
- Section 5 discusses PFAS-specific field sampling technologies, methods, and procedures.
- Section 6 discusses the legal and regulatory status of PFAS in the United States.
- Section 7 discusses PFAS risk communication challenges and solutions.
- Section 8 discusses PFAS remediation and treatment options.

OVERVIEW OF SECTIONS

Section 3: Human and Ecological Impacts

Section 3 describes physical and chemical properties of PFAS that are relevant to investigating and understanding human and ecological impacts, and summarizes the current state of knowledge regarding human exposure, exposure of ecological receptors, and the toxicokinetics and toxicological effects of PFAS. Key findings are summarized as follows:

- Biomonitoring studies have estimated more than 95% of the United States population has been exposed to PFAS and have measurable concentrations in their blood. However, PFAS concentrations in humans have demonstrably decreased since the discontinuation of production of these chemicals in 2002.
- Human exposure to PFAS can occur through ingestion, direct contact, inhalation, and occupational exposure.
- The greatest portion of chronic human intake is likely from the ingestion of contaminated foods and drinking water. Small children experience higher exposure due to hand-to-mouth transfer of chemicals from treated carpets and indoor dust.
- Because of the unique properties of many PFAS, they do not preferentially partition to lipids, but instead tend to bind to proteins. In humans, the highest PFAS concentrations have been detected in serum and liver, and to a lesser extent the kidney and other organs.
- The Stockholm Convention Persistent Organic Pollutants Review Committees for PFOS and PFOA considered the weight of evidence sufficient to support conclusions that both PFOS and PFOA are bioaccumulative.
- PFAS have been detected in the tissues of invertebrates, fish, birds, and mammals around the globe. Of all the PFAS monitored, PFOS is the most frequently detected PFAS, it has generally been measured at the highest concentrations, and it is the dominant PFAS found in all species and locations around the world.
- PFOA and PFOS have been linked to a multiplicity of adverse effects, including hepatic toxicity, reproductive and developmental toxicity, suppression of the immune system, and cancer. The data for PFNA, PFHxS, and PFBS are much more limited, but suggest that these compounds also affect the liver.

Section 4: Fate and Transport

Section 4 discusses the environmental fate and transport of PFAS as a class of compounds, and compares their fate and transport characteristics to other classes of chemical compounds commonly found in groundwater such as hydrocarbons, chlorinated solvents, and polychlorinated biphenyls (PCBs). In addition, Section 4 discusses the environmental fate and transport of the six specific PFAS that USEPA identified in their Third Unregulated Contaminant Monitoring Rule (UCMR3), and focuses on PFOA and PFOS which are often associated with aqueous firefighting foams (AFFFs). Key findings are summarized as follows:

- There are multiple potential sources of PFAS to groundwater. Recognized sources of PFAS include (1) storage, transfer, and use of AFFF for firefighting and fire training; (2) disposal/land application of municipal biosolids; (3) discharge of effluent from municipal wastewater treatment systems; (4) release of landfill leachate; and (5) release from a variety of commercial and industrial sources. Some of these release mechanisms differ from typical leaks, drips, spills, and ruptures associated with many other contaminants, and may contribute to broader distribution in the environment and groundwater, rivaling migration via advective flow.
- PFAS molecules are miscible in water. They will readily exist in the aqueous phase and will not exist as separate non-aqueous phase liquids (NAPLs) in the subsurface. Therefore, migration of PFAS as pure-phase NAPLs is not expected at sites. However, some PFAS can dissolve into petroleum-based NAPL mixtures and be transported due to capillary phenomenon.
- PFAS molecules are stable and resistant to degradation. PFAS molecules are characterized by a chain (or "tail") comprised of interior carbon atoms bonded to exterior fluorine atoms. The carbon-fluorine bond is very strong and the exterior fluorine atoms form a protective "shell." These characteristics make PFAS molecules especially stable and particularly resistant to degradation by biological or chemical means. PFOS, a type of PFAS molecule, is a terminal degradation product, and may accumulate due to this process.

- The carbon-fluorine tail of PFAS molecules exhibits its hydrophobic and lipidphobic characteristics. PFAS also exhibit surfactant characteristics that enhance infiltration due to reduction in surface tension and potential for increased mobilization and solubility of separate phase liquid, especially in settings where AFFF and petroleum hydrocarbons are stored, handled, and used in proximity to one another (e.g., fighting petroleum hydrocarbon fires). Surfactant properties of the molecules complicate the interaction between PFAS and hydrophobic/hydrophilic substances.
- PFAS molecules are prone to sorption. When dissolved, PFAS molecules exhibit a negatively charged "head" end. Consequently, PFAS molecules are prone to sorption via electrostatic attraction to positively charged surfaces. PFAS also sorbs to organic carbon and oil. PFAS molecules exhibit relatively high Koc values compared to other common groundwater contaminants. However, Koc and degree of sorption is site-specific, contingent upon the sorptive medium (e.g., surface charge, mineralogy, and organic carbon content) and solution chemistry, especially ionic strength, pH, and Ca2+ activity.

Section 5: Field Sampling and Analysis

Section 5 discusses the collection and analysis of samples for PFAS. Emphasis is placed on water samples such as drinking water, groundwater, and surface water. Other media including soil, sediment, biota (e.g., fish tissue), and waste are not discussed. Field screening methods are briefly discussed to the extent commercially available in the U.S. Considerations for sampling equipment, sample containers, and collection methods are discussed. Key findings are summarized as follows:

- USEPA Method 537 Rev 1.1 (Method 537) is the only promulgated method for the analysis of PFAS. It is a liquid chromatography/tandem mass spectrometry (LC/MS/MS) method.
- There are currently no commercially available field screening methods that are capable of detecting PFAS at concentrations less than 50 parts per billion (ppb).
- Regulatory agencies are currently interested in PFAS at ppt levels. In conjunction, given the widespread use of PFAS in many consumer, commercial, and industrial products and processes, and very low concentrations to which PFAS are reported, it is critical that the sampling program consider as many sources of PFAS contamination as practicable. This includes the following:
  - Minimize cross contamination during a sampling event.
  - Laboratory-supplied water that has been determined to be PFAS-free should be used to prepare all FRBs and EBs.
  - The quality of the water used for any other purposes should be scrutinized, including public water supplies.
  - The materials of construction of all downhole and surface sampling and monitoring equipment—including pumps, packers, transducers, tubing, liners, valves, and wiring—be free from polytetrafluorethylene (PTFE) or ethylene tetrafluoroethylene (ETFE), to the maximum extent practicable.
  - A wide range of products commonly used in site investigations are known or suspected to contain PFAS.

Section 6: Legal and Regulatory Issues

Section 6 focuses on the current status of PFAS regulation in the United States. It also discusses the potential liability for water systems and provides an overview of legal theories and case law. Statutory and regulatory authority are both at the state and federal levels and are summarized. Key findings include:

- There are multiple layers of laws and rules that govern PFAS in the environment. At the federal level, a number of laws may apply, including the Toxic Substances Control Act (TSCA) (related to the manufacture and use of PFAS); the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (related to remediation of contaminated sites); and the Safe Drinking Water Act (SDWA) (related to the presence of contaminants in drinking water). All have a role when PFAS are released into the environment.
- In addition, each state may have analogous standards that can be stricter than their federal counterparts. Currently, 12 U.S. states have their own regulatory standards for PFAS in water. Depending on the jurisdiction, the more stringent standard would apply.
- Different authorities in individual states, including regional water boards and environmental

protection agencies, may have drinking water and/or groundwater regulatory standards, health advisories, and/or guidance levels that govern PFAS in state waters.

Section 7: Risk Communication

Section 7 discusses methods for understanding the demographic and socioeconomic makeup of communities and effectively communicating scientifically valid perceptions of risk to all subpopulations. Key findings include:

- Risk communication is the process of informing stakeholders about health or environmental risks, risk assessment results, and proposed risk management strategies. Stakeholders can consist of any organization, group, or individual who takes an interest in a project and can influence project outcomes.
- The overall purpose of risk communication is to assist affected communities in understanding the process of risk assessment and management, to form scientifically valid perceptions of the likely hazards, and to participate in making decisions about how risk should be managed.
- Potential challenges of performing risk communication include:
  - Uncertainty/variability in regulatory cleanup criteria and policies
  - Misperception of proposed risk management strategies
  - Inability to provide effective risk communication to vulnerable subpopulations
  - Difficulty managing stakeholder expectations.
- Supporting materials to facilitate risk communication are publicly available from a wide range of public health and environmental agencies to assist professionals in communicating potential risks of PFAS exposures to affected parties.
- Development of a comprehensive stakeholder outreach strategy can address and help overcome distrust present between community members and decision-makers (such as regulatory authorities and responsible parties).
- Stakeholder engagement methods, vetted within the social science discipline, can be utilized to address the challenges presented above and facilitate meaningful risk communication.

Section 8: Remediation and Treatment

Section 8 was prepared to allow groundwater professionals with sufficient background and technical information to make informed decisions about treating groundwater impacted with PFAS. It identifies key information that groundwater professionals need to know to properly select, design, construct, implement, and maintain a remedial approach and how to vet a potential treatment technology from concept to full-scale field application. Key findings include:

- PFAS in groundwater present unique challenges with respect to treatment, specifically:
  - Some PFAS are very stable and do not readily degrade.
  - Some PFAS are not effectively treated by conventional remediation technologies or wastewater treatment plants.
  - Treatment of some PFAS may result in PFAS by-products that are more mobile, more toxic, and/or exhibit properties that make them less amenable to treatment.
- Remediation options are limited by the unique physicochemical properties of PFAS.
- Many remediation methods used to address hydrocarbon contamination, such as air stripping, air sparging, soil vapor extraction, and bioremediation, are ineffective at treating PFAS due to the low volatility of PFAS and their resistance to microbial degradation.
- Technologies currently being used for remediation of PFAS-contaminated sites include soil incineration, excavation to landfill, and groundwater extraction with PFAS sorption onto activated carbon or resins.
- The effectiveness of GAC for PFAS removal decreases with decreasing chain length of the PFAS.
- Other alternative remedial techniques include soil washing, soil solidification, and the use of in situ permeable reactive barriers or funnel and gate systems.
- Emerging water treatment technologies for PFAS such as photolysis, reductive decomposition, advanced oxidation, and sonolysis require high energy input per unit water volume and long residence times.