

How is Groundwater Quality Affected by Per- and Polyfluoroalkyl Substances (PFAS)?

White Paper Prepared by the Texas Groundwater Protection Committee (TGPC)
Groundwater Issues (GWI) Subcommittee

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Executive Summary

There are thousands of per- and polyfluoroalkyl substances (PFAS) in the environment. PFAS have been used for decades in industrial applications and consumer products, such as non-stick surfaces for cooking implements and food packaging. They may impact groundwater quality as they leach into the ground. This occurs not only at former PFAS production facilities and landfills, but also at military and firefighter training facilities. The presence of PFAS in groundwater can lead to potential health concerns. PFAS can build up in human tissues and it can take a long time to be eliminated from the body. Studies suggest that sufficiently high exposure to some PFAS may negatively affect the health of adults and children, including pregnant women and their fetuses. These chemical substances have been associated with low birth weight, decreased immune response, and other health issues. The health-based guidance for some PFAS from federal agencies and individual states is included in this report.

Acronym List

3M	Minnesota Mining and Manufacturing Company
AFFF	aqueous film-forming fire-fighting foam
ATSDR	Agency for Toxic Substances and Disease Registry
CASRN	Chemical Abstracts Service Registry Number
CDC	Centers for Disease Control
DOD	Department of Defense
ECF	electrochemical fluorination
EPA	Environmental Protection Agency
FDA	Food and Drug Administration
FR	Federal Register
ITRC	Interstate Technology & Regulatory Council
kg	kilogram
m ³	cubic meter
MCL	Maximum Contaminant Level
mg	milligram
MRL	Minimal Risk Level
NaDONA	Sodium Dodecafluoro-3H-4,8-dioxanonanoate
ng/L	nanograms per liter
PCL	Protective Concentration Levels
PFAA	Perfluoroalkyl acid
PFAS	Perfluoroalkyl substances and polyfluoroalkyl substances
PFBA	Perfluorobutanoate (Perfluorobutanoic acid)
PFBS	Perfluorobutane sulfonate (Perfluorobutane sulfonic acid)
PFC	Perfluoro compounds
PFCA	Perfluorinated carboxylic acid
PFDA/PFDeA	Perfluorodecanoic acid
PFDoA	Perfluorododecanoic acid
PFDS	Perfluorodecane sulfonate
PFHpA	Perfluoroheptanoic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexane sulfonate (Perfluorohexane sulfonic acid)
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoate (Perfluorooctanoic acid)
PFOS	Perfluorooctanoic sulfonate (Perfluorooctane sulfonic acid)
PFOSA	Perfluorooctane sulfonamide
PFPeA	Perfluoropentanoic acid
PFProPrA	Perfluoro-2-propoxypropanoic acid
PFSA	Perfluorinated alkylsulfonic acid
PFTeDA	Perfluorotetradecanoic acid
PFTTrDA	Perfluorotridecanoic acid
PFUnA	Perfluoroundecanoic acid

PHA	Public Health Advisory
ppt	parts per trillion
PTFE	Polytetrafluoroethylene
PWS	Public Water System
RCRA	Resource Conservation and Recovery Act
RfC	Reference concentration
RfD	Reference dose
SDWA	Safe Drinking Water Act
TCEQ	Texas Commission on Environmental Quality
Tox	Toxicological
UCMR3	Unregulated Contaminant Monitoring Rule 3
U.S.	United States of America

Introduction

Per- and polyfluoroalkyl substances (PFAS) have been used in industrial applications and consumer products for decades and they represent a large number of chemical substances with various physical and chemical properties. This family of chemical substances can exist as gases, liquids, surfactants, and solid material high-molecular weight polymers. Two primary production methods for PFAS include electrochemical fluorination (ECF), the process of transferring an F⁻ ion to other substances, and telomerization, which inserts fragments of one molecule (a taxogen) into the tail of another (a telomer) to create a longer molecule. PFAS can be divided into two primary categories: non-polymer and polymeric [1]. Non-polymer PFAS are the most commonly detected and they are further classified as perfluorinated or polyfluorinated substances. Polymeric PFAS are formed by combining various smaller identical molecules in a repetitious manner, and these may pose limited risk for immediate human health because they can be excreted from the body faster [2, 3]. Aside from these classifications, PFAS are also described as long-chain and short-chain with the long-chain PFAS reportedly posing a greater potential threat to human health and the environment because they have a greater tendency to bioconcentrate and/or bioaccumulate. However, it is important to note that generalizations regarding PFAS behavior based solely on chain length should be avoided. Short-chain and long-chain PFAS are relatively persistent, and the health effects of short-chain PFAS are not well understood [2, 4].

The United States (U.S.) Environmental Protection Agency (EPA) classifies PFAS as emerging contaminants, which means that they are characterized as a perceived, potential, or real threat to human health or the environment. As some PFAS are bioaccumulative, they build up in the body over time and they are slow to be eliminated[4]. Individuals may have varying levels of exposure to PFAS, depending on how long a person has been exposed and other personal factors, such as age.

The impact of PFAS on pregnant women and the developing fetus is of special concern, as they may be vulnerable to these bioaccumulative chemicals during fetal development. Maternal exposure to some PFAS has the potential to affect the developing fetus, as some PFAS have been shown to cross the placental barrier [5]. In cohort studies, higher levels of PFAS in cord blood or maternal serum samples have been associated with low birth weight, [6], increased lower respiratory system infections and common colds [7], and decreased immune response in young children [6].

The Agency for Toxic Substances and Disease Registry (ATSDR) states that in adults, PFAS have been associated with higher cholesterol levels [8-10], interfering with the body's natural hormone levels [11], and affecting metabolism [12, 13]. The presence of high levels of PFAS in the body and their potential effects on health is an area of emerging concern. The potential long-term health effects of PFAS in humans will need to continue to be studied.

The production of PFAS started in the 1940s with perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). In the early 1960s, the U.S. Food and Drug Administration (FDA) approved polytetrafluoroethylene (PTFE) Teflon® brand cookware and five years later its use in food packaging. In 2000, the Minnesota Mining and Manufacturing Company (3M) was the primary producer of PFOS but the company phased it out after safety concerns were raised. In 2006, the U.S. EPA and eight major manufacturing companies initiated the PFOA Stewardship Program. However, other PFAS are still manufactured within the U.S. and globally [2, 14].

PFAS are chemicals with unique properties that require innovative remediation technologies. Currently, one of the only full-scale treatments in water is sorption using carbon, or mineral media such as clay. Performance and operating costs depend on concentrations and type of PFAS, and general water quality parameters. The most common water treatment method for PFAS is granular activated carbon. It has been proven to reduce concentrations of select PFAS; however, usage capacities, breakthrough times, and change-out frequency make it a high-maintenance option. Additional technologies are being developed and tested, but more research is needed [2].

Sources in Groundwater

Sources of PFAS include fire training/response activities, industrial sites, landfills, and wastewater treatment plant/treated sewage sludge. Appendix A shows some of the observed PFAS concentrations in groundwater. PFAS are used in non-stick coatings, textiles, paper products, some firefighting foams, and many other products. A general population study of Europe and North America estimated that the greatest source of chronic exposure to PFOS and PFOA results from ingestion of contaminated food, including drinking water [15]. According to the U.S. EPA [16], PFAS found in drinking water is typically localized and associated with a specific facility (e.g., manufacturer, landfill, wastewater treatment plant, or firefighter training facility).

➤ *AFFF releases and Fire Training/Response Sites*

PFAS compounds produce a stable foam that can flow across liquid solvents which makes them highly desirable as a component of high performance “aqueous film-forming foam (AFFF).” The U.S. military, civilian airports, and other facilities used AFFF to extinguish hydrocarbon fires in training and emergency response at military bases, airports, oil refineries, and firefighting training facilities. These AFFF formulations are derived from ECF or the fluorotelomerization process, and both can lead to the production of highly diverse mixtures of PFAS. AFFF concentrate is mixed with water to create firefighting foams that are expelled through a nozzle by the gallons. AFFF are also used to suppress fires, fire training, and flammable vapor suppression at civilian airports, local fire departments, and military bases [17]. The U.S. Department of Defense (U.S. DOD) is currently evaluating groundwater contamination that has

resulted from the use of AFFF at these training and emergency response sites [18].

➤ *Industrial sites*

PFAS are used in various industries such as textiles & leather, paper products, metal plating & etching, wire manufacturing, industrial surfactants, and semiconductor industries [2]. These substances are applied as a coating to repel water, oil, and stains for food and non-food contact materials, metal plating, industrial surfactants, and semiconductors. Given widespread environmental PFAS contamination and phase-out of long-chain PFAS such as PFOS and PFOA, manufacturers are adopting the use of structurally similar short-chain PFAS [19-22]. However, further research is required to evaluate the safety and the efficiency of many of these replacement compounds.

➤ *Waste, Landfills, and Landfill Construction*

Discharge of PFAS occurs from disposal of landfill leachate and firefighting foam, as well as from wastewater treatment plants. Wastewater treatment plants are central offsite locations used to treat landfill leachate and industrial and municipal waste streams before effluent is discharged to surface water or reused for agricultural or industrial purposes. However, many wastewater treatment plants lack the technologies to sufficiently remove PFAS during the treatment process, which can then lead to a secondary source of PFAS release into the environment and cause PFAS to re-enter the water cycle. In addition to wastewater contamination, ambient air levels (1.5 to 15 times greater than reference sites) at wastewater treatment plants are also impacted by PFAS contamination [2, 23]. A large portion of domestic sludge or biosolids is not only applied to agricultural land, but it reportedly contains long- and short-chain PFAS [24-27]. Following land application of PFAS-impacted biosolids, PFAS may leach to groundwater, runoff to surface water, or be taken up by plants, soil organisms, and ultimately allow for these substances to enter the food chain [28-31]. Additional studies are needed to evaluate surface water and groundwater near agricultural fields impacted by PFAS-contaminated biosolids or treated sewage sludge [32].

Health-based guidance and other studies

As shown in [Table 1](#), various organizations have developed health-based values for PFAS substances. These values were derived from animal toxicological studies related to liver toxicity, developmental, reproductive, and carcinogenicity in both sexes using various animal models. In May 2011, the Texas Commission on Environmental Quality (TCEQ) derived chronic oral reference doses (RfDs) for sixteen perfluoroalkyl acids (PFAA) along with chronic inhalation reference concentrations (RfCs) for nine of them [3]. These toxicity factors are used to calculate risk-based values for soil, groundwater, sediment, and fish tissue. In May 2016, the U.S. EPA issued lifetime health advisories of 70 parts per trillion (ppt) for total PFOA and PFOS present in drinking water or 70 nanograms per liter (ng/L) for each individual substance [33]. In June 2018, the ATSDR

released updated Draft Toxicological Profiles (Tox Profiles) on PFAS for public comment which also included draft subchronic oral Minimal Risk Levels (MRLs) for four perfluoroalkyl compounds [34].

Data from the 2012-2016 Third Unregulated Contaminant Monitoring Rule (UCMR3) assessment for Public Water Systems (PWSs), 77 Federal Register (FR) 26072, included data for six PFAS [35]. The study monitored six PFAS, but hundreds of PFAS have been identified in environmental media, and thousands are or have been on the global market. The objective of this assessment was to guide U.S. EPA regulatory determinations based on the occurrence data for contaminants suspected to be present in drinking water but do not have health-based standards set under the Safe Drinking Water Act (SDWA). The UCMR3 study was conducted using PWSs that serve more than 10,000 people, as well as 800 representative PWSs serving 10,000 or fewer people [36]. No private drinking water wells were considered. PWSs included those sourced from both groundwater and surface water. U.S. EPA approved analytical methods and four equivalent consensus methods were used to monitor PWSs sampled within a 12-month period during 2013-2015. From this dataset, studies have estimated that as many as 6 million U.S. residents were exposed to drinking water in excess of the EPA lifetime health advisory at the time samples were collected, although no health advisory exceedances were found in Texas [17].

Various states have adopted the U.S. EPA lifetime health advisory for PFOA and PFOS or they have selected the same health-based values [2]. Meanwhile, Vermont, Minnesota, and New Jersey have developed health-based values generated from their own analysis of the available scientific data. Michigan is currently the only state that regulates certain PFAS in surface water, and Minnesota has established enforceable discharge limits for specific waterbodies. New Jersey adopted an interim Ground Water Quality Standard for perfluorononanoic acid (PFNA), and its drinking water advisory body has recommended proposed Maximum Contaminant Levels (MCLs) for PFOA and PFNA [2].

The primary aim of this white paper is to provide an overview of perfluoroalkyl and polyfluoroalkyl substances (PFAS) detected in the environment, specifically groundwater. Sources of PFAS include landfills, wastewater treatment plants, fire training and industrial sites. PFAS are a potential health concern due to the negative impacts they might have on humans. The U.S. EPA, ATSDR, and TCEQ have derived health-protective levels, RfDs/MRLs, and/or RfCs. In addition, several other states have developed their own values for this group of contaminants. There are thousands of PFAS and more research is needed to better inform the development of health-based standards.

Table 1. Health-based Guidance from ATSDR [34], U.S. EPA [16], and TCEQ [3]. Note that the ATSDR public comment period closed on August 20, 2018.

Poly-and perfluoroalkyl substances	Acronym	ATSDR	EPA	TCEQ	
Name		Intermediate oral MRLs (mg/kg/day)	Lifetime drinking water health advisory (ppt)	oral RfD (mg/kg-day)	inhalation RfC (mg/m³)
Perfluorobutyric acid	PFBA	-	-	2.90E-03	1.00E-02
Perfluorobutane sulfonate (Perfluorobutane sulfonic acid)	PFBuS	-	-	1.40E-03	4.90E-03
Perfluoropentanoic acid	PFPeA	-	-	3.80E-06	-
Perfluorohexane sulfonate (Perfluorohexane sulfonic acid)	PFHxS	2.00E-05	-	3.80E-06	1.30E-05
Perfluorohexanoic acid	PFHxA	-	-	3.80E-06	-
Perfluoroheptanoic acid	PFHpA	-	-	2.30E-05	-
Perfluorooctane sulfonic acid + Perfluorooctanoate	PFOA+PFOS	-	70	-	-
Perfluorooctanoic sulfonate (Perfluorooctane sulfonic acid)	PFOS	2.00E-06	-	2.30E-05	8.10E-05
Perfluorooctanoic acid (Perfluorooctanoate)	PFOA	3.00E-06	-	1.20E-05	4.10E-06
Perfluorooctane sulfonamide	PFOSA	-	-	1.20E-05	4.10E-06
Perfluorononanoic acid	PFNA	3.00E-06	-	1.20E-05	2.80E-05
Perfluorodecanoic acid	PFDeA	-	-	1.50E-05	5.30E-05
Perfluorodecane sulfonate	PFDS	-	-	1.20E-05	-
Perfluoroundecanoic acid	PFUA	-	-	1.20E-05	-
Perfluorododecanoic acid	PFDoA	-	-	1.20E-05	4.20E-05
Perfluorotridecanoic acid	PFTTrDA	-	-	1.20E-05	-
Perfluorotetradecanoic acid	PFTeDA	-	-	1.20E-05	-

ppt: parts per trillion

MRL: minimal risk levels

RfD: reference dose

RfC: reference concentration

ATSDR: Agency for toxic substances and disease registry

EPA: Environmental Protection agency

TCEQ: Texas Commission on Environmental Quality

Recommendations

TGPC GWI Subcommittee members include, but are not limited to:

- Texas Commission of Environmental Quality (TCEQ);
- Texas Water Development Board (TWDB);
- Railroad Commission of Texas (RRC);
- Texas Department of State Health Services (DSHS);
- Texas Department of Agriculture (TDA);
- Texas State Soil and Water Conservation Board (TSSWCB);
- Texas Alliance of Groundwater Districts (TAGD);
- Texas A&M AgriLife Research (AgriLife Research);
- Bureau of Economic Geology of The University of Texas at Austin (UTBEG);
- Texas Department of Licensing and Regulation (TDLR);
- Texas Parks and Wildlife Department (TPWD);
- Texas Tech University (TTU);
- Texas A&M AgriLife Extension Service (AgriLife Extension); and,
- United States Geological Survey (USGS).

The primary goals of the TGPC GWI Subcommittee are to:

- Facilitate interagency communication for assessment programs addressing groundwater contamination;
- Coordinate and assist member agencies with monitoring programs for:
 - Ambient groundwater conditions;
 - Pesticides; and,
 - Emerging contaminants or constituents of concern;
- Review published data reports and evaluate data independent of reports to assist in the determination of the effectiveness of existing regulatory programs;
- Review published data reports and evaluate data independent of reports for potential contaminants not addressed by existing regulatory programs; and,
- Develop recommendations for consideration by the TGPC to address potential groundwater contamination identified through monitoring and data review.

The TGPC GWI Subcommittee recommends:

- Continuing studies aimed at evaluating the extent of groundwater contamination with PFAS across Texas in order to reduce harm and appropriately treat the affected water sources;
- A future focus of groundwater testing in those areas where firefighting training using AFFF was known to have occurred;
- Evaluating treatment options for water containing PFAS;
- Testing of groundwater based on the U.S. EPA lifetime health advisory for PFAS; and,
- Adopting state-wide standards and appropriate treatment measures if elevated levels of PFAS are found.

The above recommendations represent the opinion of the TGPC GWI Subcommittee and do not necessarily reflect the views and policies of each participating organization.

For more information about this white paper, please contact the TGPC (<https://tgpc.texas.gov/contact-us/>).

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Appendix A

Observed PFAS concentrations in groundwater.

Location	Information	Concentrations (µg/L)
Various – New Jersey [37]	One or more PFAS detected in 19 of 21 untreated groundwater samples from drinking water treatment plants across the state; PFOA was detected in 7 and PFOS was detected in 5 of the 21 samples.	<ul style="list-style-type: none"> • PFOA: 0.009 – 0.057 • PFOS: 0.005 – 0.012
AFFF release sites other than fire training areas [38]	<p>Tested 149 groundwater samples; most commonly detected PFAAs: PFHxS (95%); PFHxA (94%), PFOA (90%), PFPeA (88%), PFBA and PFHpA (85%), PFOS (84%).</p> <p>The frequency of detections for PFSAs in groundwater was generally higher than those of PFCAs which has been attributed to the use of specific AFFF formulations.</p>	<p>Median (Maximum):</p> <ul style="list-style-type: none"> • PFHxS: 0.87 (290) • PFHxA: 0.82 (120) • PFOS: 4.22 (4,300) • PFOA: 0.405 (250) • PFPeA: 0.53 (66) • PFBA: 0.18 (64) • PFHpA: 0.235 (75)
Fire Training/Fire Response [39-41]	Studies at U.S. military installations and other AFFF release areas have documented relatively high detection frequencies of PFAAs in underlying groundwater.	<p>Maximum:</p> <ul style="list-style-type: none"> • PFOA: 6,570 • PFOS: 2,300

Table reproduced with permission from Interstate Technology & Regulatory Council (ITRC) PFAS Environmental Fate and Transport Fact Sheet [2].