SOUTHEASTERN WISCONSIN REGIONAL PLANNING COMMISSION
W239 N1812 ROCKWOOD DRIVE • PO BOX 1607 • WAUKESHA, WI 53187-1607 • TELEPHONE (262) 547-6721
FAX (262) 547-1103

Serving the Counties of: KENOSHA
MILWAUKEE
OZAUKEE
RACINE
WALWORTH
WASHINGTON
WAUKESHA

SEWRPC Staff Memorandum

PERFLUOROALKYL AND POLYFLUOROALKYL SUBSTANCES (PFAS)

August 25, 2022

INTRODUCTION

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a group of over 5,000 chemicals used in many industrial and consumer applications. PFAS are or have been used to produce water repellant and stain resistant fabrics and leather; grease and oil resistant coatings for paper; nonstick coatings for cookware; wire coatings and insulation; hydraulic fluids; industrial surfactants, resins, molds, and plastics; plated and etched metals; paints and polishes; semiconductors; photolithography; flame retardants; and fire-fighting foams. PFAS compounds are of concern because many are highly persistent in the environment, they accumulate in the tissue of organisms, and some have been linked to adverse health effects in humans and animals.

CHEMICAL PROPERTIES OF PFAS

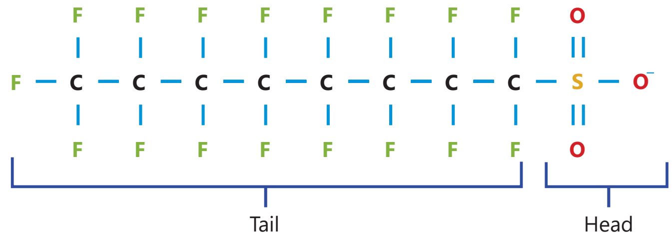
Figure 1 shows the structure of a typical PFAS molecule. These molecules consist of two parts: a tail consisting of a chain of two or more carbon atoms and a head consisting of a charged functional group. In the tails of perfluoroalkyl substances, fluorine atoms are attached to all the bonding sites on the carbon chain except for one site on the last carbon atom where the head is attached. The complete coverage of the tail by fluorine atoms makes perfluoroalkyl substances highly resistant to degradation. This is shown in Figure 2. In the tails of polyfluoroalkyl substances, at least one carbon atom in the chain has some other atom than fluorine bonded to it. The non-fluorine atom is typically, but not always, an oxygen or hydrogen atom. The presence of a non-fluorine atom along the tail creates a "weak point" in the carbon chain that is susceptible to degradation. The head of a PFAS molecule consists of a functional group that may contain one or more carbon atoms or sulfur atoms. While commonly-occurring functional groups include carboxylic acids (carboxylate), sulfonic acids (sulfonate), and sulfonamides, a wide range of functional groups may be found in different PFAS chemicals. The functional groups that serve as the head are typically acidic.

Depending on chemical conditions, PFAS molecules can exist in either anionic form in which a hydrogen atom has dissociated from the molecule's head or acidic form in which dissociation has not occurred. The physical properties of a PFAS molecule are highly dependent on which of these forms the molecule is in.

Reliable information on physical and chemical properties of PFAS compounds is scarce. This is a very large group of chemicals and only a few have been studied. Some of the available information consists of modeling results rather than measured properties. In addition, much of the available information comes from examination of compounds that are in the acidic form. In general, PFAS compounds occur in this form only under highly acidic environmental conditions in which the pH is less than 3.0 standard units. This is much more acidic than conditions that are normally found in the natural environment. For these reasons, the following general discussion of the properties of PFAS compounds should be read critically. Because this is such a large group of chemicals, not all the properties discussed below are universal to all PFAS compounds.

While each PFAS chemical has its own set of properties, some generalizations can be made. While many PFAS are solids at room temperature, some are liquids, and a few are gases. PFAS chemicals with longer tails tend to be solid. While there are exceptions, PFAS are generally less likely to evaporate than many other groundwater contaminants. PFAS chemicals also show high stability when heated. While some decomposition occurs at temperatures above about 750°F, complete degradation of perfluoroalkyl substances requires temperatures above 1,830°F. Perfluoroalkyl substances are highly chemically stable and show low chemical reactivity. The strength of the carbon-fluorine chemical bond and the shielding of the carbon chain by fluorine atoms make perfluoroalkyl substances resistant to many chemical degradation processes. The high stability of these substances means that they will persist in the environment. For this reason, they are sometimes called "forever chemicals." Polyfluoralkyl substances tend to be less stable than perfluoroalkyl substances; however, they tend to degrade into perfluoroalkyl substances. Many PFAS chemicals are strong acids and will dissociate completely at pH 7.0, which is neutral pH and near the pH of many natural waters.

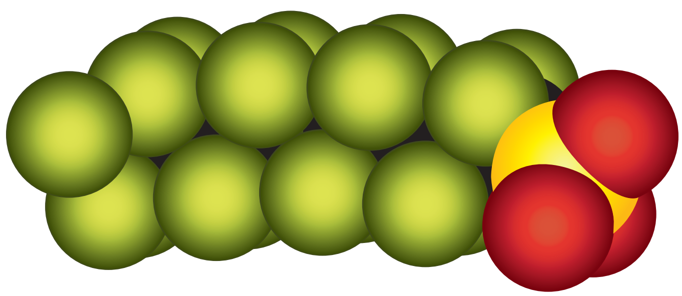
Figure 1
Skeletal Diagram of a PFOS Molecule in Anionic Form



Black C indicates a carbon atom, green F indicates a fluorine atom, yellow S indicates a sulfur atom, and red O indicates an oxygen atom.

Source: SEWRPC

Figure 2
Space Filling Model of a PFOS Molecule in Anionic Form



Fluorine atoms are shown in green, sulfur atoms are shown in yellow, and oxygen atoms are shown in red. Carbon atoms are hidden behind the fluorine atoms.

Source: Wikimedia Commons and SEWRPC

Only portions of most PFAS molecules are soluble in water. The heads are often hydrophilic, especially when the molecule is in the anionic form. This part of the molecule will dissolve in water. The tails are hydrophobic and do not dissolve in water. This difference between the two parts of the molecule means that PFAS molecules may sometimes straddle interfaces between aqueous and non-aqueous media. In addition, the tails may adsorb to soil or sediment particles containing organic carbon, with longer tail lengths being associated with a greater tendency to adsorb. Many PFAS compounds bind to proteins. Because their gross structure is similar to that of the phospholipids that make up cell membranes, some PFAS compounds may insert themselves into cell membranes of organisms.

PFAS compounds can bioaccumulate in organisms. The mechanisms through which this occurs are different from those that drive the bioaccumulation of other hydrophobic contaminants such as PCBs or legacy pesticides. The concentrations of PFAS compounds in organisms can be magnified as they are passed up the food chain, with highest tissue concentrations being found in top predators.

HEALTH EFFECTS OF PFAS

The health effects of most PFAS compounds have not been studied. Some of those that have been studied have been linked to adverse health conditions in humans. Studies conducted during and since the 1970s reported the presence of some PFAS in the blood of occupationally exposed workers. Similarly, studies conducted during and since the 1990s reported detections of PFAS chemicals in blood of the general human population. PFAS have been found in the blood of most people who have been examined due to their widespread use, their ability to bind to blood proteins, and their long half-lives in humans. Examples of PFAS half-lives in humans include 5.4 years for perfluorooctane sulfonic acid (PFOS), 8.0 years for perfluorooctanoic acid (PFOA), and 8.4 years for perfluorohexane sulfonic acid (PFHxS).

A major study on the effects of exposure to a single PFAS chemical was conducted by the C8 Science Panel. This panel consisted of three epidemiologists and was created by the West Virginia Circuit Court as part of the settlement to a class action lawsuit related to releases of PFOA, an eight-carbon PFAS, from a DuPont facility. The Panel collected and analyzed epidemiological data from exposed workers at the facility and members of the affected communities and reviewed the relevant scientific and medical literature to examine linkages between exposure to PFOA and human diseases. The Panel examined potential linkages of 72 diseases in 17 classes to PFOA exposure. They concluded that the data showed evidence of probable links for six diseases: high cholesterol, ulcerative colitis, thyroid disease, testicular cancer, kidney cancer, and pregnancy-induced hypertension.

Additional studies suggest that some PFAS may suppress the immune system. In 2016, the National Toxicology Program (NTP) of the U.S. Department of Health and Human Services conducted a systematic review of studies related to the effects of PFOA and PFOS on the immune system. Based on this review, the NTP concluded that PFOA is presumed to be a hazard to human immune systems based on its ability to suppress antibody response, reduce resistance to diseases, increase hypersensitivity-related outcomes, and increase the incidence of autoimmune diseases. The NTP also concluded that PFOS is presumed to be a hazard to human immune systems based on its ability to suppress antibody response, reduce disease resistance, and suppress natural white blood cells that detect and kill cells in the body that have been infected with viruses. More recent studies suggest that some PFAS compounds can reduce the effectiveness of vaccines in children by reducing antibody production.

Other studies suggest that exposure to certain levels of PFAS may lead to other health effects. These health effects include:

- Changes in liver enzymes
- Decreased fertility
- Increased risk of obesity
- Increased risk of prostate cancer
- Developmental effects in children, including accelerated puberty, bone variations, and behavioral changes
- Interference with hormones in the body
- Increased risk of thyroid disease

The health effects of PFAS compounds are an area of active research.

SOURCES OF PFAS TO THE ENVIRONMENT

There are four major sources that release PFAS to the environment: fire-fighting training and response sites, industrial facilities, wastewater treatment plants (WWTPs), and landfills. Other sources of PFAS exist and may be important locally in particular situations, but these are generally thought to make small contributions relative to the main four listed above. The major sources of PFAS to the environment are described in the following paragraphs.

PFAS are often released at fire-fighting training and response sites through the use of aqueous film-forming foams (AFFF) in firefighting (see Figure 3). AFFFs have been used to extinguish hydrocarbon fires at U.S. military installations, civilian airports, and other facilities since the 1960s. The exact composition of any specific AFFF product is highly variable and consists of a diverse mixture of PFAS chemicals, including both perfluorinated and polyfluorinated forms. This variable composition reflects the fact that they are typically formulated to fire-fighting specifications and not to chemical composition. AFFF applied during either firefighting, testing of equipment, or training may enter the environment by the following processes.

- Evaporate into the atmosphere and subsequently be deposited at locations away from the site of application
- Runoff to surface waterbodies leading to infiltration into groundwater or uptake by organisms
- Infiltrate into soils and subsequently into groundwater

Any of these processes may lead to dispersal of the PFAS contained in AFFF through the environment. In addition, these processes may lead to conversion of polyfluorinated PFAS chemicals into more persistent perfluorinated forms.

Figure 3
Firefighters Using Aqueous Film-Forming Foams

Use of fire-fighting foams containing PFAS can introduce these chemicals into the environment.

Source: Wikimedia Commons

Industrial sites may also release PFAS. Such sites include those manufacturing PFAS or PFAS-containing materials or products and those that use PFAS-containing materials as part of industrial processes. Some industrial uses of PFAS are listed in Table 1. Releases of PFAS into the environment from industrial sites may occur through wastewater discharges, stormwater discharges, emissions from smoke stacks, onsite and offsite disposal of wastes, and leaks or spills.

Wastewater treatment plants (WWTPs) may also release PFAS to the environment. Conventional primary and secondary wastewater treatment is not designed to degrade these chemicals. Concentrations of individual PFAS compounds may change during treatment as a result of conversion of polyfluorinated forms to perfluorinated forms. The composition of PFAS chemicals released by WWTPs depends on the types and composition of PFAS received by the WWTP, conversion of polyfluorinated forms to perfluorinated forms or intermediate compounds during treatment, and physical and chemical sorting of compounds between liquid and solid forms that occurs during treatment. PFAS may be released to the environment from WWTPs through discharge of effluent into receiving waters, leaks or unintended releases from surface impoundments, emission into the air, or disposal of biosolids. Applications of biosolids on agricultural lands can be a significant pathway into the environment as it can lead to PFAS ultimately entering surface waters, groundwater, and the food chain.

Landfills are a fourth source that can release PFAS to the environment. They constitute the ultimate repository for industrial waste, site-mitigation waste, sewage sludge, and consumer goods containing, treated with, or contaminated with PFAS. PFAS were manufactured, used, and disposed of for decades prior to the enactment of Federal and state waste disposal regulations. Consumer products containing PFAS have been landfilled since at least the 1950s. Examples of consumer products containing PFAS are shown in Table 2. Landfills constructed since the 1990s are required to have linings and leachate collections systems. Leachate from these newer landfills typically goes either to WWTPs or collection ponds. PFAS contained in leachate may enter the environment through these facilities. Failure of these leachate collection systems may also allow PFAS to enter the environment. Older landfills were not required to have linings or leachate collection systems. Wastes in these landfills are often in direct contact with soil and groundwater, which can allow PFAS to enter and disperse into the environment. Typically, landfills containing PFAS will release them at slow but relatively steady rates for decades following initial placement of PFAS-containing wastes.

REGULATION OF PFAS CHEMICALS

The State of Wisconsin and the Federal Government have developed some and are currently developing additional environmental regulations related to PFAS chemicals. These regulations include bans on certain uses of materials containing PFAS, development of water quality standards, rules on monitoring of drinking water contaminants, advisories on fish consumption, and rules related to hazardous waste.

Prohibitions on PFAS Use

In 2019, the Wisconsin Legislature passed Act 101, which prohibits the use of firefighting foams containing intentionally added PFAS except when used as part of an emergency firefighting or fire prevention action or when used for testing. The testing facility must have appropriate containment, treatment and disposal or storage measures to prevent discharge into the environment or into a storm or sanitary sewer. This law also prohibits using PFAS-containing foam for training purposes and requires fire departments to notify the WDNR immediately when such foams are discharged into the environment, used for emergency firefighting or fire prevention, or used for testing purposes. The WDNR has proposed permanent administrative rules implementing Act 101. A public hearing was held on November 4, 2021, to solicit comments on the proposed rule.

Table 1
Industrial Uses of PFAS

Industry	Uses
Textile and leather	Coatings to repel water, oils, stains
Paper products	Coatings to repel grease and moisture
Metal plating and etching	Corrosion prevention, wetting agent, mechanical wear reduction, surfactant
Wire manufacturing	Coatings and insulation
Industrial surfactants, resins, molds, and plastics	Production of plastics, rubber, plumbing fluxes, composites, flame retardants
Photolithograph and semiconductors	Photoresists, anti-reflective coatings, wetting agents, etchants

Source: SEWRPC

Table 2
Examples of Products Containing PFAS

Adhesives	Carpeting	Cleaning agents
Clothing	Cosmetics	Dental floss
Dyes	Hair conditioners	Herbicides
Hydraulic fluids	Inks	Non-stick cookware
Packaging	Paints	Paper
Pesticides	Polishes	Shampoos
Ski waxes	Sunscreen	Textiles
Toothpastes	Windshield wipers	

Source: SEWRPC

In 2006, the U.S. Environmental Protection Agency (USEPA) created the 2010/2015 PFOA Stewardship Program. As part of this program USEPA asked eight major companies in the PFAS industry to commit to a 95 percent reduction of both emissions of PFOA and precursor chemicals that can break down to form PFOA and levels of these chemicals in products by 2010. It also asked the companies to work toward eliminating these chemicals from emissions and products by 2015. To achieve these goals, most of the companies stopped manufacturing and importing PFOA and long-chain PFAS and substituted alternative chemicals in their products. A few companies left the PFAS industry and PFOA is no longer manufactured domestically. It is still produced internationally and may be imported into the U.S. in several products.

According to the USEPA's chemical data reporting efforts, PFOS is no longer manufactured in the United States. The last time PFOS manufacturing was reported to USEPA was in 2002.

In 2020, the U.S. Food and Drug Administration announced that manufacturers of certain PFAS compounds used for grease-proofing paper and paperboard used in food packaging had agreed to voluntarily phase out their sales of these chemicals as food contact substances over a three-year period beginning January 1, 2021. The manufacturers estimated that it will take it may take up to 18 months following completion of the phase out to exhaust existing stocks of paper and paperboard products containing PFAS substances from the market.

Water Quality Standards

Surface Water Quality Standards

Wisconsin's current surface water quality standards prohibit substances that are toxic or harmful to humans from being present in amounts that are found to be of public health significance or in amounts that are acutely harmful to animal, plant, or aquatic life. The State's water quality standards define levels of public health significance for two PFAS compounds. The level of public health significance for PFOS is eight nanograms per liter for all waters except those that cannot naturally support fish and do not have downstream waters that support fish. The level of public health significance for PFOA is 20 nanograms per liter for those waters classified as sources of public water supply and 95 nanograms per liter for all other surface waters.

In May 2022, USEPA released draft recommended surface water quality criteria for protecting aquatic organisms for PFOA and PFOS. These draft criteria are not regulations and do not constitute legally binding requirements, Instead, they provide guidance to states and tribes for developing and adopting water quality standards. States and tribes may adopt either the recommended criteria, the recommended criteria modified to reflect site-specific conditions, or criteria based on other scientifically defensible methods. Once adopted by the state, the criteria serve as the basis for issuing permits to control the discharge of pollutants and for assessing the impact of these PFAS compounds on surface waterbodies.

Table 3 shows the draft criteria for PFOA and PFOS. There are five criteria for each compound:

1. The **Criterion Maximum Concentration:** This criterion consists of a one-hour average concentration of the compound in the water column that is not to be exceeded more than once in three years, on average. It serves to protect aquatic organisms against toxic effects due to short-term acute exposure to the compound.

2. The **Criterion Continuous Concentration:** This criterion consists of a four-day average concentration of the compound in the water column that is not to be exceeded more than once in three years, on average. It serves to protect aquatic organisms against toxic effects due to long-term chronic exposure to the compound.

3. The **Invertebrate Whole-Body Concentration:** This criterion consists of an instantaneous average concentration of the compound throughout the bodies of aquatic invertebrates that is not to be exceeded more than once in 10 years, on average.

4. The **Fish Whole-Body Concentration:** This criterion consists of an instantaneous average concentration of the compound throughout the bodies of fish that is not to be exceeded more than once in 10 years, on average.

5. The **Fish Muscle Concentration:** This criterion consists of an instantaneous concentration of the compound in the muscle tissue of fish that is not to be exceeded more than once in 10 years, on average.

The invertebrate whole-body concentration, fish whole-body concentration, and fish muscle concentration criteria provide instantaneous measurements that reflect the accumulation of PFOA or PFOS over time in aquatic organisms at a given site.

In May and June 2022, the USEPA solicited comments from the public on the draft aquatic life surface water quality criteria for PFOA and PFOS. It is expected that USEPA will issue final criteria after it reviews and addresses any comments that it receives.

USEPA expects to issue human health criteria related to drinking water and fish consumption for some PFAS compounds in the fall of 2024. USEPA is also developing effluent limitation guidelines on levels of some PFAS compounds in wastewater that is discharged into surface waters and municipal wastewater treatment plants. These guidelines would inform state regulations on effluent limits required in discharge permits issued under the Federal Clean Water Act.

Groundwater Quality Standards

Wisconsin has not set groundwater quality standards for any PFAS chemicals.

Drinking Water Quality Standards

Wisconsin's drinking water quality standards set maximum contaminant limits for two PFAS chemicals. A maximum contaminant limit is the maximum permissible level of a contaminant that can be delivered in a public water supply system such as a municipal water utility. When a maximum contaminant level is exceeded, the utility, in consultation with the WDNR, must take actions to reduce the amount of the contaminant in the water it provides. Under the State's drinking water standards, the combined concentrations of PFOA and PFAS in drinking water are not to exceed 70 nanograms per liter. The WDNR is also currently developing drinking water maximum contaminant levels for an additional 16 PFAS compounds.

Under provisions of the Federal Safe Drinking Water Act (SDWA), USEPA issued an interim updated lifetime health advisory for four PFAS chemicals in drinking water in June 2022. This advisory replaced an earlier

Table 3
Draft Recommended Freshwater Aquatic Life Water Quality Criteria for PFOA and PFOS

Criteria Component	Criterion Maximum Concentration[a]	Criterion Continuous Concentration[b]	Invertebrate Whole-Body Concentration	Fish Whole-Body Concentration	Fish Muscle Concentration
PFOA Magnitude	49 mg/l[c]	0.094 mg/l[c]	1.11 mg/kg[d]	6.10 mg/kg[d]	0.125 mg/kg[d]
PFOS Magnitude	3.0 mg/l[c]	0.0084 mg/l[c]	0.937 mg/kg[d]	6.75 mg/kg[d]	2.91 mg/kg[d]
Duration	one-hour average	four-day average	Instantaneous	Instantaneous	Instantaneous
Frequency	Not to be exceeded more than once in three years, on average		Not to be exceeded more than once in 10 years, on average		

[a] *The Criterion Maximum Concentration is a criterion meant to protect freshwater organisms against toxic effects due to acute exposure.*

[b] *The Criterion Continuous Concentration is a criterion meant to protect freshwater organisms against toxic effects due to chronic exposure.*

[c] *Water column concentrations are measured as milligrams per liter (mg/l)*

[d] *Tissue concentrations are measured as milligrams per kilogram (mg/kg) on a wet weight basis.*

Source: U.S. Environmental Protection Agency

health advisory for PFOA and PFOS that was issued in 2016. It provides information on concentration thresholds intended to protect sensitive populations from health impacts and the concentrations given constitute nonenforceable levels to help drinking water suppliers address contaminants that lack drinking water standards. This advisory addresses four PFAS compounds. It recommends that:

- Drinking water concentrations of PFOA not exceed 0.004 nanograms per liter
- Drinking water concentrations of hexafluoropropylene oxide (HPFO) dimer acid and its ammonium salt (also known as GenX chemicals), which have been used as a replacement for PFOA in some applications, not exceed 10 nanograms per liter
- Drinking water concentrations of PFOS not exceed 0.02 nanograms per liter
- Drinking water concentrations of perfluorobutane sulfonic acid and potassium perfluorobutane sulfonate (PFBS), which have been used as a replacement for PFOS in some applications, not exceed 2 micrograms per liter

It is expected that the interim health advisory will provide information regarding safe levels of these compounds in drinking water until national primary drinking water regulations for PFAS take effect.

USEPA is currently developing national primary drinking water regulations for PFOA and PFOS. These rules are legally enforceable rules that apply to public water systems. States can set and enforce their own rules, if they are at least as stringent as the national regulations. USEPA expects to issue proposed regulations in the fall of 2022 and final regulations after considering comments from the public in fall of 2023.

Drinking Water Monitoring

The SDWA also requires that every five years USEPA issue a list of no more than 30 unregulated contaminants to be monitored by public water systems. The monitoring required under this provision of the SDWA can serve as a basis for developing drinking water regulations. In 2012, USEPA issued the third Unregulated Contaminant Monitoring Rule, which included monitoring of six PFAS compounds in drinking water systems including PFOA and PFOS. In late 2021, USEPA issued the fifth Unregulated Contaminant Monitoring Rule that requires monitoring of 29 PFAS compounds including the same six that were previously monitored. This monitoring will help USEPA understand how often these chemicals are found in drinking water systems and provide information needed to decide whether to design appropriate regulations.

Fish Consumption Advisories

The WDNR has issued fish consumption advisories related to PFAS chemicals. A consumption advisory is a recommendation that people avoid eating or limit the amount that they eat of certain species of fish

Table 4
General Fish Consumption Advisory for Wisconsin Inland Waters

Fish Species	Women Under 50 Years of Age, Children Under 15 Years of Age	Men, Women over 50 Years of Age
Bluegill, Crappie, Yellow Perch, Sunfish, Inland Trout, Bullheads	1 serving per week	Unrestricted
Walleye, Pike, Bass, Catfish, All other species not listed	1 serving per month	1 serving per week
Musky	Do not eat	1 serving per month

Note: The size of a serving depends on the weight of an individual. A serving consists of four ounces for a 75-pound person, eight ounces for a 150-pound person, or 12 ounces for a 225-pound person.

Source: Wisconsin Department of Natural Resources

caught from specific waterbodies or types of waterbodies due to chemical contamination of the fish. For all inland waters in Southeastern Wisconsin, the WDNR recommends that people follow the Statewide general consumption advisory which is shown in Table 4. The State has also issued more stringent consumption advisories for fish taken from some waterbodies. None of these waterbodies are located in Southeastern Wisconsin.

Hazardous Waste Rules

The USEPA is developing rules that would designate PFOA and PFOS as hazardous substances under the Federal Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund). Such a designation would require facilities that store or use these compounds to report releases that meet or exceed specified levels. The USEPA anticipates that it will issue a proposed rule in spring of 2022. They expect to issue a final rule in summer of 2023. The USEPA has also proposed conducting rulemaking to designate additional PFAS compounds as hazardous substances.