Per- and Poly-Fluorinated Alkyl Substances Chemical Action Plan (PFAS CAP) – 2019 Updates

New Fate and Transport Chapter

In 2017, the Washington State departments of Ecology and Health shared draft PFAS CAP chapters with external parties for review and comment. Comments received are available <u>online</u>. This document is either an update of a 2017 draft or a new 'chapter.' Ecology and Health are sharing chapters with interested parties prior to the <u>April 2019 PFAS CAP webinar</u> (*previously planned for March*). Updates will be discussed during the April webinar. We expect to publish the entire Draft PFAS CAP around June 2019 followed by a 60-day comment period.

In April 2019, Ecology and Health will host a PFAS CAP webinar (*date not yet set*) to:

- Briefly review activities underway: firefighting foam, food packaging, drinking water.
- Review updated/new chapters comments will be accepted on the updated chapters. Responses will be provided after the 2019 public comment period (summer 2019).
- Discuss preliminary recommendations requesting comments and suggestions from interested parties due a week after the webinar.
- Submit comments <u>online</u>.

Quick summary of PFAS CAP efforts:

- PFAS CAP Advisory Committee and interested parties met in 2016, 2017 and 2018.
- September 2017 Draft PFAS CAP chapters posted:

Intro/Scope	Environment
Biosolids	Health
Chemistry	Regulations
Ecological Toxicology	Uses/Sources

- March of 2018, Ecology and Health published the Interim PFAS CAP.
- The 2019 updated PFAS CAP "chapters" to be posted (in the order we expect to post on the PFAS CAP website):

Biosolids	Analytical methods (new)
Ecological Toxicology	Chemistry
Environment	Fate and Transport (new)
Regulations	Economic analysis (new)
Uses/Sources	Preliminary
Health	Recommendations (new)

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This document is posted on the PFAS CAP Website https://www.ezview.wa.gov/?alias=1962&pageid=37105

Appendix #: Fate and Transport

Abstract

This chapter explores the chemical transformation and fate of per- and polyfluorinated alkyl substances (PFAS) released to the environment.

Key Points Include:

Transformation

- All PFAS are either perfluoroalyl acids (PFAAs) or PFAA precursors
- It is believed that all PFAA precursors will transform to PFAAs with a timeframe of hours to hundreds of years
- Precursor hazard and exposure should be considered when evaluating PFAS risk
- PFAS polymer will likely serve as a continued source of PFAS emission

Fate

- PFAS can be released as a solid, liquid, or gas
- Gas phase transport can cause PFAS contamination long distances from emission source
- With the exception of polymers, most PFAS are water soluble and can be transported by water movement
- Adsorption to carbon compounds in soil and sediments can slow PFAS transport by groundwater and surface water
- "Short-chain" PFAS are more mobile, less bioaccumulative, and equally persistent as "long-chain" versions
- Landfill waste and biosolids from composting and wastewater treatment plants (WWTPs) will serve as a continued sources of PFAS emissions into the environment
- Chemical transformation of precursor compounds may change preferential partitioning into transport media and rate of transport
- PFAS can bio-accumulate in plants and animals, and bio-magnify in higher organisms in the food chain

1.0 Introduction

With thousands of different per- and polyfluorinated alkyl substances (PFAS) currently on the market, their environmental fate and transport, which describes the chemical transformation and geographic distribution of compounds after release to the environment, can vary greatly. PFAS can exist in many different forms (vapor, water, solid) and will partition (group with separate media) differently depending on the type of compound. Rate of PFAS chemical transformation can also vary quite dramatically depending on the chemical in question, the phase, and the environment where it is located. Some compounds have a half-life as low as hours in the environment, while others do not transform naturally. In this chapter, we will start by reviewing PFAS transformation, and then proceed to transport and, finally, partitioning of PFAS.

2.0 Transformation

More than 4730 PFAS have been registered in the Chemical Abstract Service, with many of these compounds likely containing other unintentional PFAS as impurities^{1,2}. All of these PFAS are either a type of PFAS called perfluoroalkyl acids (PFAAs) or substances that eventually transform into PFAAs (precursors). PFAAs have not been shown to degrade or transform under natural conditions^{3,4}.

The stability of PFAAs is due to the strength of the high energy carbon-fluorine bond (531.5 kJ/mol¹)⁵ and the shielding effect of the carbon backbone conformation⁶. Precursor compounds, which will eventually turn into PFAAs, have additional moieties added on to the carbon-fluorine chain where other substances and organisms can attack and degrade them. After this process, all that is remaining is the carbon-fluorine backbone and a headgroup: a PFAA. Thus, most scientists consider PFAAs "dead-end" chemicals because they will not undergo further transformation in the natural environment, and will most likely exist longer than humans can observe.

There has been one controversial study^{7,8} showing slight degradation of PFAAs under extreme natural conditions. There has also been successful decomposition of PFAAs in the lab using experimental techniques^{9–11} such as fungal treatment¹² and high temperature reaction with persulfate¹³. However, current research suggests that all PFAS ever produced will eventually transform into a PFAA and never degrade under common conditions in our environment.

The timeframe for the transformation from precursor to PFAA depends on the compound and the conditions. Half-lives are not known or studied for most precursors, with some calculated values ranging from hours to more than a thousand years ^{14–16}(Figure 1). With the vast number of potential starting materials and environments, the exact mechanism and changes that occur for each precursor is unknown. However, scientists have studied many changes in the laboratory, and are starting to characterize transformations in the field.

¹ kj/mol = kilojoule per mole – unit of energy per amount of material

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Figure 1. A: Illustration of precursor transformation leading to PFAAs.B: Examples of precursor aerobic biotransformation to PFAAs with half-lives^{17–19}.

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3.0 Abiotic Transformation

Abiotic transformation (transformation without living organisms) can form both perfluorosulfonic acids (PFSAs) and perfluoro-carboxylic acids (PFCAs)-the main two types of PFAAs, from a wide range of precursors. For example, reaction with hydroxyl radicals gives N-methyl perfluorobutane sulfonamidoethanol (NMeFBSE) a half-life of two days, and creates both sulfonic and carboxylic acid byproducts²⁰. Additionally, fluorotelomer alcohol (FTOH) compounds have been found to transform in the atmosphere through reactions with chlorine and hydroxyl radicals to form PFCAs^{21,22}. N-ethyl perflurobutanesulfonamide (NEtFBSA) can transform into PFCAs through a similar mechanism in the atmosphere, with a lifetime in air of 20-50 days²³.

3.1 Biotic Aerobic Transformation

Researchers have demonstrated aerobic biotransformation (transformation by organisms with access to oxygen) of PFAA precursors several times, and this type of modification is probably the most prevalent form of PFAS chemical transformation. Several studies have been performed with focus on transformation that may occur at wastewater treatment plants (WWTPs) or aqueous film forming foam (AFFF)-impacted sites²⁴. Laboratory studies have shown degradation of FTOHs into PFCAs. In addition, N-ethyl perfluorooctane sulfanamido ethanol (N-EtFOSE) is biodegraded into perfluorooctane sulfonate (PFOS) with a half-life of 0.7-44 days^{18,25-27} and perfluorooctaneamido quaternary ammonium salt (PFOAAmS) transforms into perfluorooctanoic acid (PFOA) with a half-life of 142 days¹⁷. Perfluoroacylphosphates (POPs) have also been shown to biodegrade into FTOHs and eventually to PFCAs²⁸. All precursors tested have shown the ability to be aerobically bio-transformed to PFAAs, with most perfluoralkane sulfonyl fluoride (PASF)-based substances eventually being bio-transformed into PFCAs²⁹.

3.2 Biotic Anaerobic Transformation

Anaerobic biotransformation (transformation by organisms without oxygen) has been studied much less than aerobic biotransformation. Most evidence suggests that it is slower and transformation into final PFAA forms is less complete. For instance, some PFAA precursors have been shown to remain stable for long periods of time under anaerobic conditions^{30–32}, with most fluorotelomer sulfonates (FTSAs) remaining more stable than FTOHs³³. However, in general, anaerobic studies have had similar results to aerobic studies, with PFAAs not biodegrading and other compounds eventually leading to PFAAs.

3.3 Consequences of Chemical Transformation

Because of the transformation processes outlined above, even though production of PFOS was phased out in 2002 and production of PFOA was phased out in 2015, levels of PFAAs have continued to increase in wildlife^{14,34}. Manufacturers continue to make precursor compounds, which will change into PFOS, PFOA, and other PFAAs once released to the environment. Tracking changes in environmental levels of all PFAS is difficult because there are a large number of precursors, and it is only practical to test for a small fraction in each experiment. Most precursors require advanced analytical methods to detect. These are expensive, available in only a few labs around the world, and often cannot accurately measure quantities of compounds.

Additionally, there are very few validated methods endorsed by governmental bodies, so much of the testing done uses experimental techniques. With different methods used by different researchers, comparing results from different studies can be poorly reliable.

PFAA dead-end chemicals are the most prevalent and the most persistent type of PFAS, so they have been studied the most. However, the fact that several precursors have measurable levels in both surface waters^{35,36} and wildlife³⁷ shows that it is not only PFAAs that have to be considered when evaluating impact and risk, since exposure to precursors can be significant. A study in the Baltic Sea found PFAAs and precursors in most aquatic organisms, but concluded that PFAA levels were not necessarily correlated with precursor intake³⁸. This suggests that it is important to evaluate exposure to precursors and PFAAs separately when considering risk.

In another example of precursor exposure, North Atlantic pilot whales do not contain the enzyme to convert perfluorooctanesulfonamide (PFOSA) to PFOS like most animals do, so when they adsorb PFOSA, they are exposed to its effects for much longer than other species¹⁴. Scientists will need to consider the rate of a chemical's transformation to PFAA in addition to the chemical hazards of itself and the PFAA dead-end to get the full picture of risks involved with use and emission.

The PFAS released to the environment from products and manufacturing operations transform over time into a variety of chemical transformation products. The lifetimes and toxicity of these individual transformation products and the final dead-end degradates all contribute to a still uncertain environmental impact.

4.0 Polymers

Polymers are a special class of PFAS to consider when looking at transformation and hazard. It is not only the polymer compound to consider, but also how the polymer backbone may degrade, and what unreacted monomers and catalysts may be present. There is evidence that bacteria or light can degrade some fluorotelomer based PFAS polymers. This would release soluble monomer or other PFAS fragments to the environment with a half-life of decades to two centuries^{16,39–42}. However, this finding is still unsettled, due to alternate reports using different methods, which show a half-life of approximately 15,000 years for fluorotelomer-based acrylate polymers ^{43,44}.

The finding of a half-life of thousands of years contrasts with degradation times for similarly structured monomers, which have half-lives of days to years. Intact fluoropolymers are generally agreed to be inert and not bioavailable or bioaccumulative, suggesting minimal health impact⁴⁵. If PFAS polymers, which are often used as oil- and water-resistant treatment for consumer products, degrade, then they could be an potential source of PFAS emissions for decades or centuries if not properly disposed and contained in landfills⁴⁶. One study suggests that degradation of polymers could increase PFAS loading to the environment by 4-8 times in coming years³⁹.

In addition to polymer degradation as a source of PFAS, the production of PFAS polymer requires the use of monomers and processing aids. These may be a source of PFAS emissions into the environment. In the past, PFOA was used as a processing aid in fluoropolymer manufacture^{47,48}. Manufacturers have since switched to chemicals thought of as safer, such as or

Ammonium 4,8-dioxa-3H-perfluorononanoate (ADONA) and Hexafluoropropylene oxide (HFPO) dimer acid (GenX)⁴⁹. Although these substitutes are not used in the final polymer, they have been detected numerous times worldwide, including in drinking water in North Carolina and the Netherlands^{35,36,50}.

5.0 Emission Sources

PFAS can be released into the environment either in the air (stack emissions), water (manufacturing discharge or AFFF application), or as a solid (solid waste from manufacturing or disposal of consumer goods). Properties of an individual PFAS compound will affect its solubility in water, adsorption to soil, or ability to exist as a gas. These attributes will affect the rate of transport. Chemical changes caused by environmental exposure further complicate the rate of transport. An emitted compound may initially have more affinity for one type of media, but as time passes, it may change and be more likely to exist in another (Figure 2).



KEY () Atmospheric Deposition () Diffusion/Dispersion/Advection () Infiltration () Transformation of precursors (abiotic/biotic)

Figure 2. Conceptual site model for industrial site (*Source: Adapted from L. Trozzolo, TRC, used with permission*)

5.1 Air

When released to the air, such as through stack emissions, PFAS can be either in the gaseous phase as a vapor, or as an aerosol in small particles. Most PFAS are not very volatile, but those that are (mostly FTOHs) may also vaporize into a gas after emission as a liquid or solid. Anionic forms of PFAS, such as PFCAs at low pH, are more likely to be adsorbed to particulates in the air⁵¹. Once in the air, PFAS can travel large distances before deposition. Deposition occurs via settling of particulates or by transformation of vapor into a non-volatile compound. Deposition can occur either by dry deposition (particles landing by themselves) or by wet deposition (precipitation contributing to deposition)⁵².

Short-range air transport causes PFAS distribution to be much more extensive than just waterbased transport, which is the focus of most concerns from manufacturing plants and regulators. Air-based transport can cause contamination of soil, groundwater, and surface water that otherwise would not be anticipated from merely looking at water flow. Long-range air transport is responsible for the wide distribution of PFAS across the globe, as shown by their occurrence vast distances from all manufacturing sites, including both the Arctic and Antarctic. In addition, sea spray may help re-aerosolize PFAS that have been deposited in oceans^{53,54}, contributing to further air-based transport.

5.2 Water

Most PFAS manufacturing processes involve aqueous solutions, which are often a mixture of compounds. Environmental release may be from a dilution by a large amount of water during manufacturing. Firefighting using AFFF represents a large source of release of water-based PFAS mixtures into the environment due to mixing of the compounds with water to form foam. Most PFAS transport easily through groundwater and surface water due to their high solubility. Dispersion, diffusion, and advection will all affect the movement of PFAS in water, but generally, the compounds will follow the water flow. It is estimated that the oceans are the main final sink for PFAS⁵⁵.

One important process that affects PFAS transportation and can complicate water transport is adsorption to organic compounds. Most PFAS have a fluorinated carbon "tail", which is both hydrophobic and lipophobic, and a polar headgroup, which is hydrophilic. Depending on the types of tail and headgroup, properties of the compound will change. This means that different PFAS can have significantly different attraction to both water and soil. Hydrophobic, lipophobic, and electrostatic interactions will all influence the affinity for different phases. Due to the differences in the chemical and physical properties between the head and the tail, PFAS will often localize at phase interfaces, such as soil/water and water/air boundaries^{56,57}.

Individual PFAS will adsorb to organic carbon in soil to varying degrees using hydrophobic interactions or electrostatic interactions with minerals⁵⁸. Scientist have mostly studied this interaction in PFAAs, which are relatively soluble in water over a wide range of pH. Because of this solubility, they move easily through water flow, either in groundwater, surface water, or through leaching. However, water transport can be slowed by association with organic carbon in soil^{56,58}.

PFSAs tend to adsorb more strongly to soil than PFCAs do^{56,58} and thus are less mobile. Longer carbon chain lengths are also generally associated with increased adsorption relative to shorter chains.⁵⁶. This indicates that a partitioning may occur during wastewater treatment. Shorter chains tend to leave in the effluent and longer chained compounds are more likely to stay in the solid fraction.

Adsorption of PFAS to soil increases as the soil's total organic carbon percentage increases. Soil type and its organic carbon content directly affects the leaching rate (or retention time) of PFAS when spilled on the ground such as during firefighting or training with AFFF. In addition, the chemical constituents of the flammable materials onto which AFFF is applied may influence transport of PFAS through soil and groundwater. Spills into coarse, poorly aggregated soils (such as drainage ditches) will likely leach PFAS faster compared to soil with good structure and high organic carbon.

The retention time of PFAS in soil is dependent upon numerous site specific variables though there is evidence that desorption is often incomplete⁵⁹. Soil contaminated with PFAS may

remain as a low volume source of contamination for ground and surface water for a long time, complicating hazard assessment.

5.3 Solids

Solid phase PFAS contaminants will serve as potential future sources for emission. Solid phase PFAS are disposed in solid waste landfills or recycled in compost facilities⁶⁰. Farmers often use compost as well as solid phase biosolids from WWTPs as amendments for agricultural soils. In the US, solid sewage sludge from WWTPs not used as biosolids is landfill disposed or incinerated.

Due to the high solubility of most PFAS, compounds are susceptible to leaching from landfills and contaminated soils when exposed to water^{60–62}. Leachate from PFAS contaminated landfills is estimated to contain around 600 kg per year of PFAS in the US⁶². Sources include products such as carpets and clothing, and leachate PFAS include PFOS, PFOA, perfluorohexane sulfonate (PFHxS), and many PFAA precursors^{61,63}. In Washington, landfill leachate is collected, tested, and either treated or discharged to a WWTP.

See the biosolids chapter for a more detailed discussion of biosolids application and risk assessment.

5.4 Wastewater Treatment

Studies show that conventional activated sludge treatment does not effectively remove most PFAS, though some specialized treatments can remove a large percentage of longer chained compounds^{64,65}. In fact, due to the transformation processes outlined above and the fact that most precursors are not tested for, researchers often found higher levels of PFAS in the effluent compared to the influent at WWTPs. This is especially true with PFAAs such as PFOS and PFOA.

6.0 Bioaccumulation

Unlike most other bio-accumulating compounds, PFAAs do not bind to lipids (fats), but instead bind to proteins⁶⁶. Because of this they are found mostly in the liver and $blood^{67}$, which complicates using measures such as K_{ow} (a chemical's characteristic octanol-water partition coefficient). Scientists often use K_{ow} to estimate bioaccumulation, but this oil/water separation factor is not applicable to how PFAS behave. This means it is hard to predict the bioaccumulation of compounds without experimental testing. In addition, half-lives for excretion vary greatly between species in animals, with serum elimination time of PFOS in humans being as much as 10-20x as long as in rodents and monkeys⁶⁸. Studies in one species are not as useful for informing about hazards in other organisms as with many other contaminants.

Due to the persistence and ability to transport large distances, animals do not need to be near sources of PFAS to show bioaccumulation. For example, numerous studies have shown elevated levels of PFAS in Scandinavian marine animals, although there is no production of PFAS in Scandinavia³⁴.

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Levels of PFSAs and PFCAs in organisms are consistently highest among PFAS, and chain lengths of 8 and above predominate^{14,69}. In fact, many studies have suggested that PFCAs and PFSAs with shorter than 7 and 6 fluorinated carbons respectively would not be considered bioaccumulative according to common regulatory criteria^{69,70}. However, some evidence exists that there could be exceptions to this. For example, the half-life of PFHxS (n=6) was found to be longer (8.5 years) than PFOS and PFOA (5.4 and 3.8 years respectively) in the human body⁷¹.

Additionally, due to the persistence of all PFAAs, including short chain PFAAs, exposure will continue regardless of accumulation because bioaccumulation is not required for sustained internal exposure⁷². For this reason the Norwegian and German environmental agencies have proposed adding a new designation to the REACH Substances of High Concern list-mobile (M) and very mobile (vM). This would allow short chain compounds, which do not categorize as persistent, bioaccumulative, and toxic (PBT) since they are not bioaccumulative, to still be added to the list as persistent, mobile, and toxic (PMT)⁷³. The theory is that PMT compounds would be an equivalent concern to PBT compounds, since they would also have sustained exposure.

See the chapters on ecological and human health for more information on bioaccumulation and its effects on risk assessment.

Some PFAS also have the ability to bio-magnify. In general, lesser levels of PFAS are observed in lower organisms with higher levels observed in animals higher on the food chain (seals, polar bears)^{74,75}. Plants have been shown to take up PFAS from the soil⁷⁶, an issue of concern since agricultural fields have the potential to be treated with PFAS contaminated biosolids from WWTPs. PFAS can accumulate in leaves, fruits, and roots, with levels correlating with water content of the plant⁷⁷.

7.0 References

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List of chemicals discussed

Acronym	Chemical Name
ADONA	Ammonium 4,8-dioxa-3H-perfluorononanoate
FTOH	fluorotelomer alcohol
FTSA	Fluorotelomer sulfonate
Gen X	Hexafluoropropylene oxide dimer acid
HFPO	Hexafluoropropylene oxide
NEtFBSA	N-ethyl perflurobutanesulfonamide
N-EtFOSE	N-ethyl perfluorooctane sulfanamido ethanol
NMeFBSE	N-methyl perfluorobutane sulfonamide ethanol
PASF	perfluoralkane sulfonyl fluoride
PFAA	perfluoroalkyl acid
PFAS	per- and poly-fluorinated alkyl substances
PFCA	perfluoro-carboxylic acid
PFHxS	perfluorohexane sulfonate
PFOA	perfluorooctanoic acid
PFOAAmS	perflurorooctaneamido quaternary ammonium salt
PFOS	perfluorooctane sulfonate
PFOSA	perfluorooctanesulfonamide
PFSA	perfluoro-sulfonic acid
POP	Perfluoroacylphosphate

These are the chemical acronyms and names used in this chapter.