Assessment of Total PFAS Risk

This Fact Sheet is an accompaniment to the HIDOH Technical Memorandum *Interim Soil and Water Environmental Action Levels (EALs) for Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs)* and the HIDOH PFAS webpage (HIDOH 2024a,b). The Fact Sheet summarizes a method to calculate the cumulative health risk posed by exposure to different groupings of PFAS compounds. The approach is intended to be used by environmental professionals familiar with the collection of samples and basic methods used to quantify the health risk posed by exposure to contaminants in environmental media.

What are PFASs?

Per- and polyfluoroalkyl substances (PFASs) are manmade chemicals used in many industries since the 1940s to make things waterproof, non-stick, and stain resistant. Examples of materials that may contain PFASs include firefighting foam, carpet, furniture, waterproof clothing, and certain types of food packaging. Similar compounds are also found in influent, effluent and biosolids associated with municipal and industrial wastewater treatment plants as well as leachate from landfills. These chemicals are often described as “forever chemicals” because they do not breakdown over time and can build up in the environment and our bodies. Additional information can be found on the Hawai´i Department of Health PFAS webpage (HIDOH 2024).

	Ultrashort / Short / Long — Terminal Endpoint Compound	Abbreviation	# Carbons
Sulfonates	Perfluoro butane sulfonate	$PFBS^-$	4
	Perfluoro pentane sulfonate	$PFPeS^-$	5
	Perfluoro hexane sulfonate	$PFHxS^-$	6
	Perfluoro heptane sulfonate	$PFHpS^-$	7
	Perfluoro octane sulfonate	$PFOS^-$	8
	Perfluoro decane sulfonate	$PFDS^-$	10
Carboxylates	Perfluoro ethanoate (TFA)	$PFEtA^-$	2
	Perfluoro propanoate	$PFPrA^-$	3
	Perfluoro butanoate	$PFBA^-$	4
	Perfluoro pentanoate	$PFPeA^-$	5
	Perfluoro hexanoate	$PFHxA^-$	6
	Perfluoro heptanoate	$PFHpA^-$	7
	Perfluoro octanoate	$PFOA^-$	8
	Perfluoro nonanoate	$PFNA^-$	9
	Perfluoro decanoate	$PFDA^-$	10
	Perfluoro undecanoate	$PFUnDA^-$	11
	Perfluoro dodecanoate	$PFDoDA^-$	12
	Perfluoro tridecanoate	$PFTrDA^-$	13
	Perfluoro tetradecanoate	$PFTeDA^-$	14
Other	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy) propanoate	$HFPO\text{-}DA^-$	11

Figure 1. Terminal PFAS compounds. HFPO- DA considered “terminal” due to recalcitrance to breakdown in the environment.

PFASs are named in part based on the number of carbons in the compound. Long-chain compounds are generally more toxic than shorter chain compounds. Toxicological studies have demonstrated that exposure to even low levels of PFASs over many years in food, water and other media can pose health risks. Health risk is assessed in terms of a short list of “Terminal PFASs” (Figure 1). These compounds have been extensively studied and are believed to pose the greatest health risk. The compounds might be originally present in contaminated soil, water or food or they might be generated by the breakdown of more complex, “precursor” PFASs compounds after being ingested.

What are Environmental Action Levels?

The Technical Memorandum accompanying this Fact Sheet presents “Environmental Action Levels (EALs)” for soil, water and, for volatile PFAS, indoor air and vapors that can accumulate underground at PFAS spill areas (HIDOH 2024a). Action levels are provided for each of the Terminal PFASs noted in Figure 1 plus a short list of more complex, “precursor” PFASs. The EALs reflect concentrations of PFASs in soil and drinking water and air that are not expected to pose a significant health risk to young children or adults even after many years of exposure. Exceeding an action level does not necessarily indicate an imminent health risk, but it does indicate that additional evaluation is warranted.

The action levels focus on the protection of mothers and young children from long-term exposure to PFASs and associated noncancer-related health risks, such as effects to the liver and kidney. Potential cancer risks are also considered for some PFASs, but noncancer-related risks and the protection of mothers and young children takes precedence. Protection against noncancer health risks to these groups is believed to also be protective against cancer risks. Refer to the accompanying Technical Memorandum for additional information.

How are samples collected and tested for PFASs?

Samples of soil and water to be tested for PFASs should be collected in accordance with methods described in the HIDOH *Technical Guidance Manual* (TGM, HIDOH 2024). Samples of soil, sediment, biosolids and other particulate matter must be obtained using Decision Unit and Multi Increment® Sample (DU-MIS) investigation methods outlined in Sections 3 and 4 of the TGM. (Multi Increment® is registered trademark of EnviroStat, Inc.) Methods for the collection of representative samples of surface water and groundwater are discussed in Section 6 of the TGM.

Assessment of Total PFAS Risk requires up to three separate laboratory analyses – analysis prior to sample oxidation, analysis following sample oxidation and analysis for Total Organic Fluorine. The method used to oxidize a sample is referred to as “Total Oxidizable Precursors” or “TOPs.” Sample data based on TOPs processing are most useful for assessment of risk. Analysis of a sample prior to sample oxidation is primarily useful for forensics proposes and determination of the origin of the PFAS contamination.

The same method is used for both pre-TOPs and post-TOPs analysis. Some laboratories have developed equivalent or improved methods. Check with the laboratory prior to the collection of samples to determine which method is most appropriate for your needs.

What is “TOPs” analysis?

Complex, PFAS precursor compounds are broken down to Terminal PFAS compounds through a laboratory sample processing method referred to as “Total Oxidizable Precursors” or “TOPs” (Houtz and Sedlak 2012, Ateia 2023, Pelch 2023). The sample is heated with an oxidizing agent under alkaline conditions. Much like pruning branches from a tree to exposure the underlying trunk, this strips functional groups from complex, “precursor” PFAS compounds and generates a new set of Secondary Terminal PFASs compounds specific to the types of precursors originally present (Figure 2).

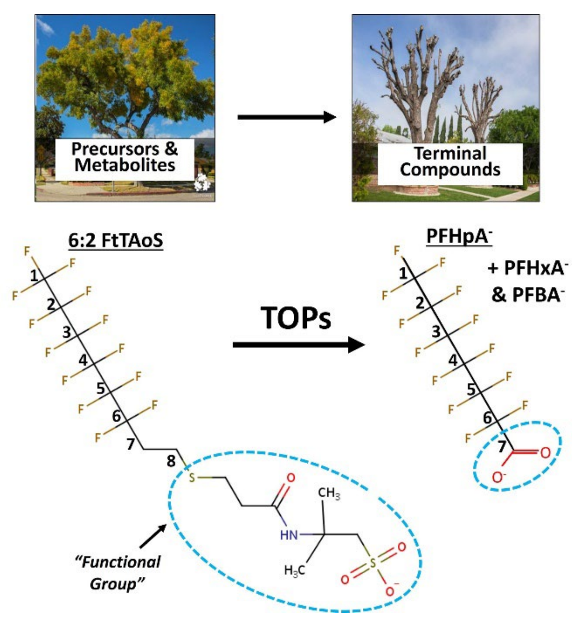

Figure 2. Oxidation of 6:2 FtTAoS to generate the Terminal Endpoint compound $PFHpA^-$.

An example is the oxidation of 6:2 fluorotelomer thioether amido sulfonic acid (6:2 FtTAoS), the primary PFAS compound in aqueous firefighting foam (AFFF). TOPs effectively clips off the large, functional group attached to 6:2 FtTAoS, leaving behind the Terminal PFAS compound perfluoroheptanoate ($PFHpA^-$). This simulates metabolism and breakdown of 6:2 FtTAoS in the body. For reasons that are not yet well understood, additional shorter-chain PFAS like pefluorohexanoate ($PFHxA^-$) and perfluorobutanoate ($PFBA^-$) can also be generated. Note that the anion forms of the compounds are typically found in nature.

How is the total health pisk posed by exposure to PFASs determined?

The cumulative health effects posed by PFASs is assessed with respect to three groups of Terminal PFASs that could be present in a sample (Figures 3 & 4), defined for use in this guidance as: 1) "Primary Terminal PFASs," 2) "Secondary Terminal PFAS," and 3) "Excess Fluorine PFASs." Primary Terminal PFASs are compounds represent Terminal PFAS compounds originally present in the sample and reported prior to TOPs processing ("pre-TOPs"). Secondary Terminal PFASs are compounds generated by the breakdown of precursor compounds following TOPs processing. Any additional PFASs in a sample are identified by comparing the concentration of Total Organic Fluorine reported for the sample to the concentration of organic fluorine predicted by concentrations of Primary and Secondary Terminal PFASs. The difference is referred to as "Excess Fluorine." Detailed analysis of samples with excess fluorine typically identifies the associated compounds as "ultrashort" PFASs such as the two-carbon compound perfluoroethanoate ($PFEtA^-$, aka trifluoroacetate) and the three-carbon compound perfluoropropanoate ($PFPrA^-$).

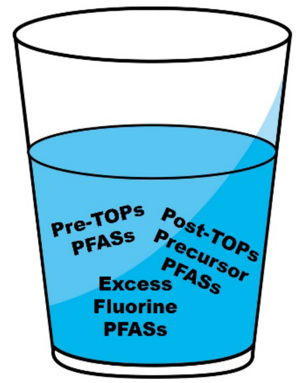

Figure 3. Three groups of PFASs potentially present in contaminated media.

Post-TOPs data are especially important for soil, biosolids and other particulate media, where significant concentrations of precursor compounds might be present. Total Organic Fluorine data tend to be more important for PFAS-contaminated water, where significant concentrations of ultrashort compounds have been identified in field studies.

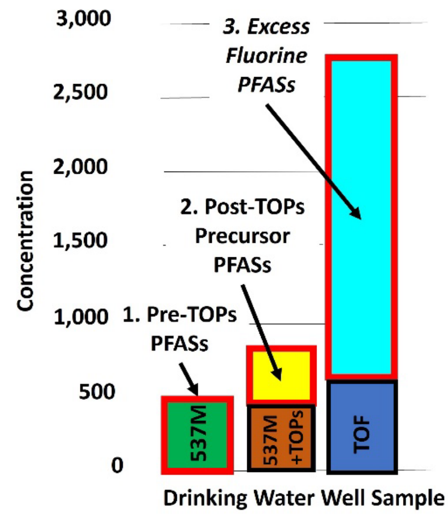

Figure 4. Three groups of PFAS-related compounds in contaminated media (Method 537M shown as an example).

Total PFAS Risk is calculated by dividing the concentration of each Primary Terminal PFAS and Secondary Terminal PFAS by the corresponding action level. The concentration of additional, Excess Fluorine PFASs is divided by the action level for the ultrashort compound $PFPrA^-$. The ratio of the reported concentration of a compound to the corresponding action level is referred to as the "Hazard Quotient (HQ)." The sum of the Hazard Quotients calculated for Primary and Secondary Terminal PFASs is referred to as a "Hazard Index (HI)." Adding the Hazard Indices for Primary Terminal PFASs and Secondary Terminal PFASs to the Hazard Quotient calculated for Excess Fluorine PFASs generates a cumulative Hazard Index for Total PFASs Risk as a whole:

Total PFAS Risk = Pre-TOPs HI + Post-TOPs Precursor HI + Excess Fluorine HQ.

A Hazard Index greater than "1" indicates a potential health concern that requires additional evaluation.

An Excel-based spreadsheet that accompanies this Fact Sheet and Technical Memorandum makes calculation of a Hazard Index easy. Use of the spreadsheet is strongly recommended.

Where can I get more information?

Detailed information on the methods used to assess PFAS health risk can be found in the HIDOH Technical Memorandum that accompanies this Fact Sheet (HIDOH 2024a). Additional information can be found in the references noted below and by searching for specific topics on the internet.

References:

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