CFPUA RESOURCE PAPER
8/3/2023

OVERVIEW OF PERFLUOROPROPANOIC ACID (PFPrA)

Description

Perfluoropropanoic acid (PFPrA) is an ultra-short-chain PFAS, which is defined as having three or fewer carbon atoms.

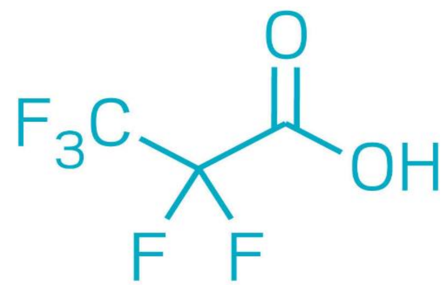

Figure 1 The chemical structure of one PFPrA.

Per- and polyfluoroalkyl substances (PFAS) are a class of several thousand synthetic chemicals used widely in consumer and industrial products because of their stainproof, greaseproof, waterproof, non-stick and other properties.[1] A member of the perfluoroalkyl carboxylic acid subclass of PFAS[2], the molecular formula for PFPrA is C_2F_5COOH or $C_3HF_5O_2$, as shown in *Figure 1*. PFPrA is referenced under multiple names and identifiers, including pentafluoropropionic acid, perfluoropropionic acid, PPF Acid, and CAS registry number 422-64-0.[3] The safety data sheet for PFPrA indicates that in sufficient quantities it is corrosive, an irritant, and its label is to include the signal word "danger."[4]

Sources

PFPrA is manufactured for use in various products. It is also a product of longer-chain PFAS decomposition and a byproduct of manufacturing.

Chemical manufacturers such as Fisher Scientific define PFPrA as "an efficient catalyst for the preparation of dibenzo[a,j] xanthenes by a condensation reaction of beta-naphthol with aryl aldehydes."[5] Xanthenes have a wide range of biological and pharmaceutical uses, including agricultural disinfectant, anti-inflammatory, antiviral, photodynamic therapy, dyes, laser technology, and fluorescent to view biomolecules.[6] In the research literature, the various sources of PFPrA in the environment are still debated. It is widely agreed that PFPrA is a "breakdown product", i.e., a result of chemical and physical processes that can degrade longer chain PFAS into PFPrA .[1 7 8] Studies have detected PFPrA in rainwater, drinking water, source water, and even in ice cores [9]. This has been linked by researchers to the switch from ozone-depleting CFCs to replacement refrigerants such as hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs) and hydrofluoroolefins (HFOs) which break down to PFPrA and other ultra-short-chain PFAS[9].

It is a known byproduct of the PFAS manufacturing process in the Cape Fear River. It is referenced in compliance reports issued by Chemours under the Consent Order signed on February 26, 2019.[10] PFPrA (PPF Acid) was also included in a table labeled as "Classification of Table 3+ PFAS" in an appendix to a Corrective Action Plan submitted by Chemours on December 31, 2019.[11] This plan states: "The PFAS that originate from the Site are referred to as Table 3+ PFAS." Because of the well documented contamination at the Fayetteville Works site, it is clearly evident the PFPrA contamination in the lower Cape Fear is sourced from Chemours/DuPont manufacturing activities of the last 40 years.

Prevalence in Drinking Water

Research conducted in the United States and in other countries has detected PFPrA in drinking water and other media.

Laboratory testing methods cannot identify, isolate, and measure all of the thousands of known PFAS compounds in various media, including water. Work is ongoing to expand this field of knowledge.

PFPrA is not among the 29 PFAS compounds captured by the U.S. Environmental Protection Agency's (EPA) approved PFAS testing procedures (Methods 533 and 537.1).

The National Resource Defense Council (NRDC) conducted a pilot study across 16 states. This study used advanced PFAS testing or "modified methods" (MM 533 & 537.1) from contract laboratory Eurofins that can detect 70 different types of PFAS compounds.[7]

This study found that PFPrA was the most frequently occurring compound in drinking water systems, detected in 24 of 30 samples.[7] It was also the PFAS compound reported at the highest concentrations in 15 of 30 samples.

If the NRDC study proves to be an accurate representation of the extent of PFPrA contamination nationwide, it suggests that ongoing monitoring at drinking water utilities under the fifth unregulated contaminate monitoring rule (UCMR 5) will likely underreport the prevalence of PFAS in drinking water due to the absence of such a prevalent PFAS.

Testing

While tests are available to detect PFPrA, no approved methodology exists, and challenges have been observed with testing accuracy and repeatability.

To reiterate, PFPrA is currently not measured under EPA-approved methods 533 or 537.1 and is not included on the UCMR 5 list of contaminants for nationwide monitoring. All other analytical methods, including the one used by CFPUA's contract laboratory, are considered experimental or unvalidated, with various levels of confidence among members of the scientific community. There seems to be, however, general agreement that the modified methods (MM 533 & 537.1) used by certain contract laboratories are valid and adequate for Chemours Consent Order compliance monitoring.

As early as 2019, Chemours had included PFPrA (PPF Acid) in monitoring results, but later correspondence with State officials led to the removal of PFPrA from Table 3+PFAS monitoring. On May 18, 2022, correspondence from Chemours to NCDEQ indicated the development of new analytical methods that could be used for PFPrA.[12] It is unclear at this time whether Chemours has resumed monitoring for PFPrA as part of its Consent Order compliance.

GEL laboratories performs PFAS analysis for both CFPUA and NCDEQ. GEL has undergone extensive laboratory verification and onsite audits by NCDEQ and the U.S. Department of Defense (DOD). GEL uses an internally developed modification of EPA Method 537.1 that incorporates isotope dilution. Methods incorporating isotope dilution are generally considered the most accurate at lower detection levels for all PFAS, including short- and ultra-short-chain compounds. Nevertheless, as this method is not certified and its development is still evolving, there are periodic issues with quality assurance and quality control (QA/QC), as well as potential variations in results between laboratories.

Toxicity

More studies are needed to assess the spectrum of potential health risks. There is low confidence in recently published findings, which have been modified at least once.

On July 7, the EPA Office of Research and Development (ORD) published a human health toxicity value for PFPrA with a calculated non-cancer chronic reference dose (RfD) of 0.0001 mg/kg per day.[13] This value was revised as of August 1, 2023, to a calculated non-cancer chronic reference dose (RfD) of 0.0005 mg/kg per day. A chronic RfD is defined as "an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure of the human population to a substance that is likely to be without an appreciable risk of deleterious effects during a lifetime," according to EPA.[14] An RfD is one input often used to establish non-regulatory advisories (HALs or PHGs) and regulatory limits (MCLs) for contaminants.

Limited available health hazard and dose-response relevant evidence prompted EPA to have "low confidence" in its RfD for PFPrA. As a result, there is a "high level of uncertainty in the derived RfD" according to the study.[9] In animal studies, the compound was associated with altered liver function. No clear associations were established with health conditions such as thyroid, hormone, and fertility conditions. PFPrA was not tested for carcinogenicity.

There is not enough information at this time to confidently project a future PFPrA Health Advisory Level (HAL), Preliminary Health Goal (PHG) or Maximum Contaminant Limit (MCL).

We do know that the final chronic RfD for GenX of 0.000003 milligrams per kilogram body weight per day (mg/kg bw-day)[15] is two orders of magnitude lower than that of PFPrA, suggesting a much higher potential threshold for future HALs or PHGs for PFPrA. The HAL and proposed MCL for GenX is 10 ppt, and two orders of magnitude would suggest a PRPrA HAL or MCL of more than 1,000 ppt. These assumptions are only speculation at this time.

On July 31, 2023, CFPUA staff spoke with NCDEQ environmental toxicology staff familiar with PFAS and the evolving issue of PFPrA. NCDEQ staff are still evaluating the new EPA publication. As of July 31, 2023, PFPrA was not identified as a compound of concern on either EPA's PFAS Strategic Roadmap or NCDEQ's Action Strategy for PFAS, indicating the evolving understanding of the regulatory community regarding this contaminant.

Environmental Impact

Research shows that, like other per- and polyfluoroalkyl substances, PFPrA can travel from water to plants, leading to bioaccumulation in animals.

As mentioned previously, PFPrA is an asserted product of the degradation of other chemicals. Experiments with a substitution for PFOS in wheat plants have been shown to break down into PFPrA and other PFAS compounds. The existence of these compounds in the wheat plant also seemed to have had an adverse effect on the plant's health.[16] Additionally, experiments on the interaction of gaseous PFPrA resulted in the creation of new particles when exposed to other common atmospheric molecules.[17]

Relevance to CFPUA

PFPrA has been detected in the Monterey Heights, Sweeney, and Richardson water systems, in both raw water sources and in finished water samples, in varying low concentrations.

Cape Fear Public Utility Authority's (CFPUA) practice has been to add new PFAS compounds to its regular testing framework as academic and commercial laboratories develop analytical methods to test and provide repeatable results for new compounds. As noted previously, these methods are experimental and not certified.

In January 2022, CFPUA gained access to testing capabilities for several newly isolated compounds (including PFPrA) from its contract laboratory (Enthalpy). Because of several ongoing laboratory issues including questionable accuracy of the results for PFPrA, CFPUA switched to Gel laboratories in June 2022. Accuracy for PFPrA analysis was an issue within a few months of making this change and was not resolved until April 2023. Accuracy of data for PFPrA from samples prior to this date is questionable.

PFPrA has been detected in the Sweeney and Richardson water systems, in both raw water sources and in finished water samples, in varying concentrations. PFPrA has also been detected in water produced by the Monterey Heights groundwater system.

The Richardson Water Treatment Plant (WTP) is a reverse osmosis (RO) facility, and the Sweeney WTP is a conventional sedimentation-flocculation design with ozonation, biological filters, new deep bed granular activated carbon (GAC) filters and ultraviolet (UV) disinfection.

Interestingly, testing at both facilities also indicated a disparity in paired raw water and finished water samples, with finished water samples frequently having higher PFPrA results than raw water samples taken at the same time.

PFPrA data from both Enthalpy and GEL labs are displayed below in Figures 2 and 3. It should be noted that between January 2022 and March 2023, some samples were flagged by the contract labs for quality assurance and quality control (QA/QC) errors. The method blanks used in the testing procedure were contaminated with and/or had an interference with PFPrA.

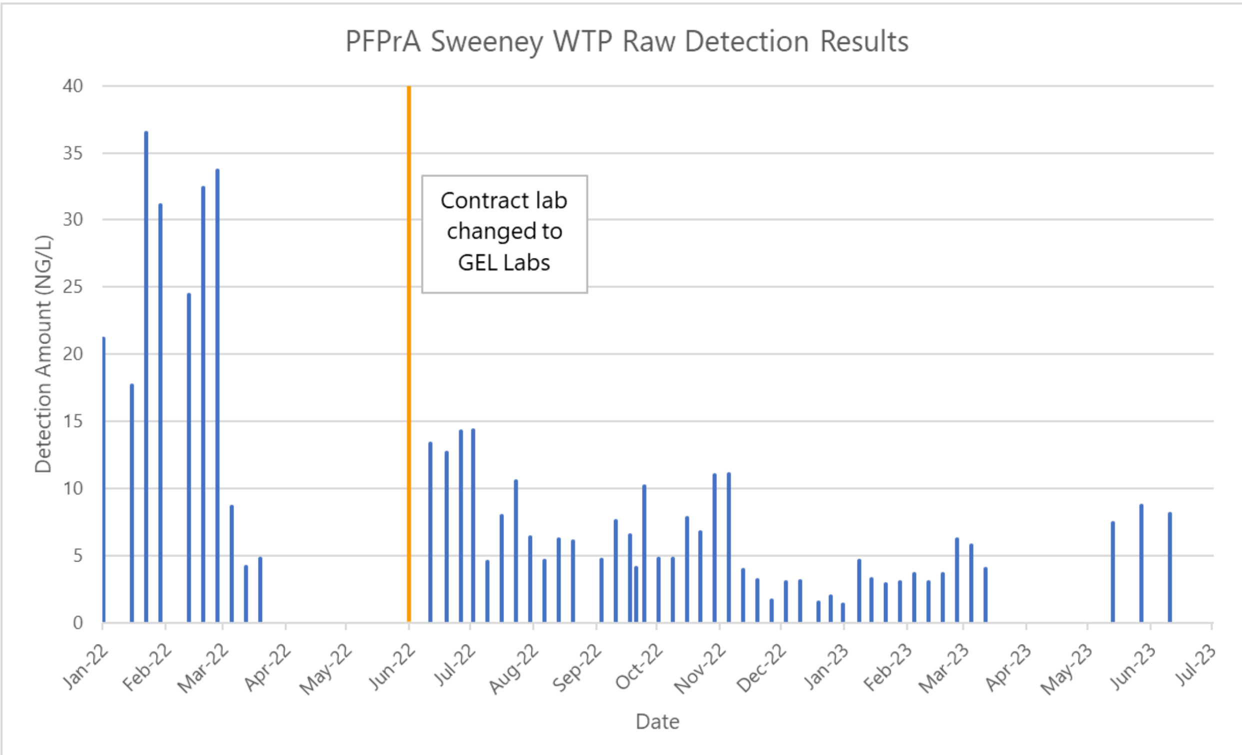

Figure 2. Detected levels of PFPrA in Sweeney raw water samples collected from January 2022 to present

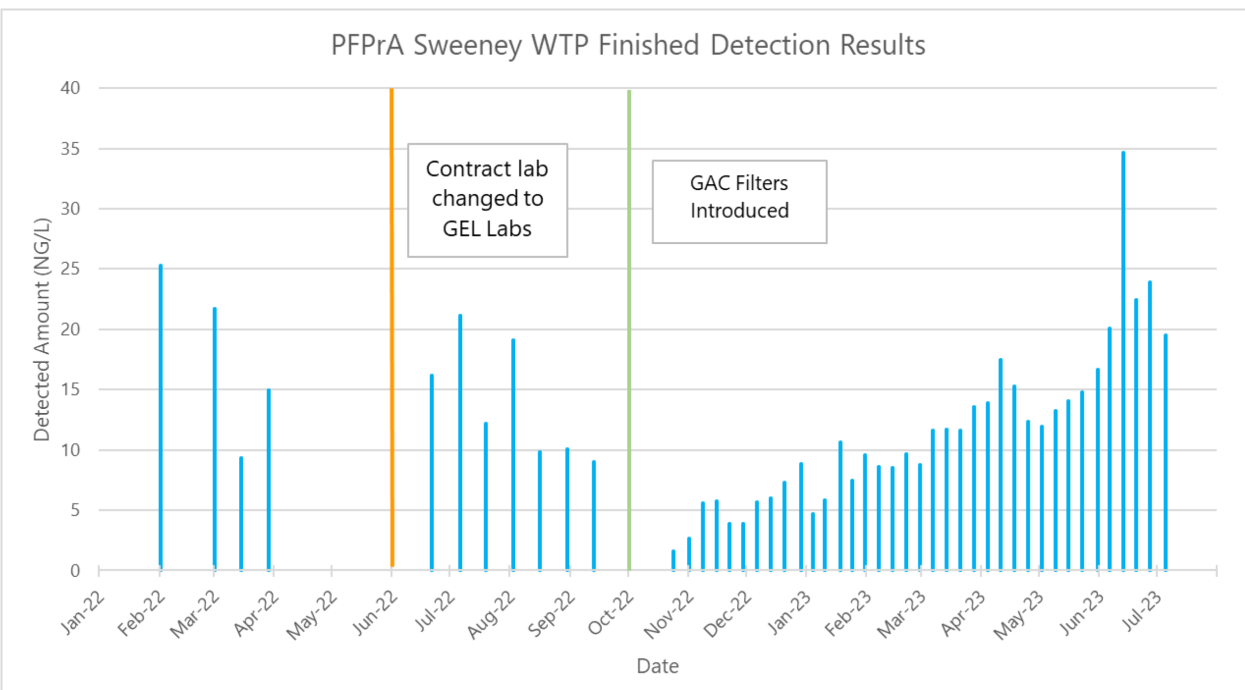

Figure 3. Detected levels of PFPrA in Sweeney Finished samples collected from January 2022 to present. The green line indicates when the GAC filters were introduced in October 2022.

CFPUA continues to monitor for PFPrA and to publish all results on our website. New deep bed GAC filters began operating at Sweeney on October 10, 2022. Following this, there was only one testing period of no detection (ND) for all tested compounds. Thereafter PFPrA was the only compound detected in finished water until December 29, 2022. As noted earlier, CFPUA staff have low confidence in PFPrA results prior to April 2023.

Testing at both treatment facilities also continues to display a disparity in raw water and finished water samples, with finished water samples often having higher PFPrA results than paired raw water samples.

At Sweeney, the disparity may be caused by desorption of PFPrA from the biologically active GAC filters and/or from the deep bed GAC filters themselves. For the Richardson facility, the disparity may be tied to the specific well or section of well fields used as source water to stabilize the permeate through post-membrane blending. More research at each facility is required.

Conclusions and Next Steps

- Available information is insufficient to draw conclusions regarding the impact of PFPrA on drinking water at a national, state, or local level.
- The best estimates by CFPUA staff suggest current finish water concentrations of PFPrA would be well below any future health advisory levels or maximum contamination limits, but this is only speculation.
- CFPUA staff will continue to monitor raw and finished water from Sweeney, Richardson, and Monterey Heights for PFPrA and will publish results on the CFPUA website following review by contract laboratories and CFPUA staff for laboratory QA/QC.
- CFPUA staff will engage NCDEQ to undertake an evaluation of PFPrA and seek its addition to the State's NCDEQ Action Strategy for PFAS, if necessary.
- CFPUA's Sweeney deep bed filter facility was designed with flexibility regarding treatment techniques and sorbents. This flexibility will be useful if different sorbents are required to treat PFPrA or other ultra-short chain PFAS in the future.
- CFPUA will work with academic partners such as the North Carolina Collaboratory, as well as with consultants and vendors, to evaluate treatment techniques for ultra-short-chain PFAS such as PFPrA.

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