Sampling for Per- and Polyfluoroalkyl Substances (PFAS) by the Groundwater Ambient Monitoring and Assessment Priority Basin Project

What are Per- and Polyfluoroalkyl Substances (PFAS)?

Per- and polyfluoroalkyl substances (PFAS) are a family of more than 4,700 human-made chemicals that have been used in hundreds of products worldwide for decades (National Institute of Environmental Health Sciences, 2020). Some of the most well-known PFAS are surfactants with a water-soluble (hydrophilic) functional group side and a water-insoluble (hydrophobic) side consisting of carbon atoms bonded to fluorine atoms (Buck and others, 2011). The carbon–fluorine bond is the strongest covalent bond in organic chemistry (Huang and Jaffé, 2019) and imparts chemical properties that help PFAS repel oil and water, reduce friction, and resist breakdown. These properties make PFAS useful for industrial applications (such as metal-plating) and for many consumer products such as carpeting, clothing, upholstery, nonstick cookware, food wrappers, and foams used to fight fuel fires. The same properties that make PFAS useful in these products also make them persistent in the environment. For this reason, they are sometimes called the “forever chemicals.”

PFAS are released into the environment from a number of sources, including PFAS manufacturing plants, industries using PFAS, landfills (that receive PFAS-containing consumer products, food waste, and so on), wastewater treatment facilities, septic systems, and places where PFAS-containing foams were used such as at airports and military fire-training areas. PFOA (perfluorooctanoate), PFOS (perfluorooctanesulfonate), and other long-chain PFAS substances have been phased out from emissions and from products in the United States under the Environmental Protection Agency’s PFOA Stewardship program (U.S. Environmental Protection Agency, 2006). Once PFAS are in the environment, they can affect groundwater and surface waters used as sources of drinking water. The removal of PFAS from drinking-water sources poses challenges unlike those of other groundwater contaminants due to their persistence and unique chemical properties (Newell and others, 2020).

PFAS have been detected in most environmental matrices including soil, precipitation, surface water, groundwater, biota, and in 97 percent of human blood samples (Lewis and others, 2015). Health risks associated with exposure to some PFAS include elevated cholesterol, thyroid disorders, decreased vaccination response, and decreased birth weight (Danish Environmental Protection Agency, 2015). The California State Water Resources Control Board Division of Drinking Water (SWRCB-DDW) has established notification and response levels as health-based benchmarks for three PFAS (California State Water Resources Control Board, 2021b): perfluorooctanoate (PFOA), perfluorooctanesulfonate (PFOS), and perfluorobutanesulfonate (PFBS). If a chemical concentration is greater than its notification level in drinking water, the SWRCB-DDW recommends that the utility inform its customers about health concerns associated with the chemical (California State Water Resources Control Board, 2021a). If the concentration is greater than the response level, the SWRCB-DDW recommends that the water source be taken out of service. Notification levels for PFOA, PFOS, and PFBS are 5.1, 6.5, and 500 nanograms per liter (ng/L), respectively; response levels are 10, 40, and 5,000 ng/L, respectively.

GAMA-PBP and PFAS

The Groundwater Ambient Monitoring and Assessment Priority Basin Project (GAMA-PBP) began in 2004 as a collaboration between the U.S. Geological Survey (USGS) and the California State Water Resources Control Board (SWRCB) to provide a representative assessment of the quality of groundwater used for public and domestic supply (U.S. Geological Survey, 2013). In 2019, the GAMA-PBP added PFAS to the large list of chemicals analyzed in samples to assess the geographical distribution of PFAS in groundwater used for drinking water across all land-use settings. GAMA-PBP samples were analyzed by SGS Laboratory in Orlando, Florida, for 24 PFAS compounds that have a long history of use and are among the most commonly detected PFAS analytes in groundwater. In 2020, four more PFAS “replacement” compounds were added to the GAMA-PBP analyte list (table 1). Replacement PFAS are compounds that have been designed and synthesized to be less toxic than conventional PFAS compounds, but studies have not yet determined whether they are significantly less harmful either to the environment or to human health (Hopkins and others, 2018).
Preliminary PFAS Findings by the GAMA-PBP

From May 2019 to September 2020, the GAMA-PBP collected PFAS samples from 107 public-supply wells and 104 domestic wells Statewide (fig. 1). Results for GAMA-PBP PFAS sampling are available in a data release (Kent, 2021). At least one PFAS was detected in 49 of these 211 samples (23 percent). Total concentrations of PFAS in these samples ranged from 1 to almost 16 ng/L (fig. 1). PFAS were detected more frequently (fig. 2), and generally at greater concentrations (fig. 3), in samples from public-supply wells (detection frequency 36 percent) than in samples from domestic wells (detection frequency 11 percent).

Of the 28 individual PFAS analytes, 14 were detected in at least one GAMA-PBP sample at concentrations ranging from 1 to almost 16 ng/L (fig. 3). In general, the same PFAS compounds were detected (fig. 2) and generally at greater concentrations (fig. 3), in samples from public-supply wells (detection frequency 36 percent) than in samples from domestic wells (detection frequency 11 percent).

The following table provides a list of the 28 PFAS analytes included in the GAMA-PBP study.

**Table 1.** Per-and polyfluoroalkyl substances (PFAS) analyzed in samples collected by the Groundwater Ambient Monitoring and Assessment Priority Basin Project (GAMA-PBP).

| Per- or polyfluoroalkyl substance | Abbreviation | Detected in GAMA samples? |
|-----------------------------------|--------------|---------------------------|
| Perfluorobutanoate                 | PFBA         | yes                       |
| Perfluorobutanesulfonate           | PFBS         | yes                       |
| Perfluoropentanoate                | PFFeA        | yes                       |
| Perfluoropentanesulfonate          | PFFeS        | yes                       |
| Perfluorohexanoate                 | PFHxA        | yes                       |
| Perfluorohexanesulfonate           | PFHxS        | yes                       |
| Perfluoroheptanoate                | PFHpA        | yes                       |
| Perfluoroheptanesulfonate          | PFHpS        | yes                       |
| Perfluorooctanoate                 | PFOA         | yes                       |
| Perfluorooctanesulfonate           | PFOS         | yes                       |
| Perfluorononanoate                 | PFNA         | yes                       |
| Perfluorononanesulfonate           | PFNS         | no                        |
| Perfluorodecanoate                 | PFDA         | yes                       |
| Perfluorodecanesulfonate           | PFDS         | no                        |
| Perfluoroundecanoate               | PFUnA        | no                        |
| Perfluorododecanoate               | PFDoA        | no                        |
| Perfluorotridecanoate              | PFTrDA       | no                        |
| Perfluorotetradecanoate            | PFTeDA       | no                        |
| Perfluorooctanesulfonamide         | FOSA         | no                        |
| N-Ethylperfluorooctanesulfonamido-acetate | N-EtFOSAA     | no                        |
| N-Methylperfluorooctanesulfonamido-acetate | N-MeFOSAA     | no                        |
| 4:2 Fluorotelomersulfonate         | 4:2 FtS       | no                        |
| 6:2 Fluorotelomersulfonate         | 6:2 FtS       | no                        |
| 8:2 Fluorotelomersulfonate         | 8:2 FtS       | yes                       |
| Perfluoro-2-propoxypropanoate      | HFPO-DA*     | no                        |
| 4,8-Dioxo-3H-perfluorononanoate    | ADONA*       | no                        |
| 9-Chlorohexadecafluoro-3-oxanonane-1-sulfonate | F-53B Major* | no                        |
| 11-Chloroicosafluoro-3-oxaundecane-1-sulfonate | F-53B Minor* | no                        |

*Replacement compound added to list of analytes in 2020.
were detected in samples from public-supply wells and from domestic wells. Perfluorohexanesulfonate (PFHxS), detected in 17 percent of all samples, was the most frequently detected PFAS in the GAMA-PBP study (fig. 2). PFOA and PFOS were each detected in 13 percent of GAMA-PBP samples. PFOA, PFOS, and PFBS are the only three PFAS with health-based thresholds in California, and PFOA and PFOS are the most extensively used and researched PFAS. Concentrations exceeded the State notification levels for PFOA (5.1 ng/L) and PFOS (6.5 ng/L) in six and seven samples, respectively (fig. 3). The concentration of PFOA in one sample from a public-supply well exceeded the State response level of 10 ng/L (fig. 3). Perfluorobutanesulfonate (PFBS) and perfluohexanoate (PFHxA) were each detected in 10 percent of samples. PFBS concentrations in GAMA-PBP samples did not exceed the notification level of 500 ng/L. The other nine PFAS were detected in less than 10 percent of samples.

The GAMA-PBP detected PFAS less frequently and at lower concentrations than a PFAS assessment completed by the California State Water Resources Control Board Division of Drinking Water (SWRCB-DDW). During quarterly sampling between April 2019 and March 2020, the SWRCB-DDW sampled more than 1,100 public-supply wells from one to four times, detecting at least one PFAS in about half of the wells (California State Water Resources Control Board, 2021b). The SWRCB-DDW study used several different laboratories that had varying analytical capabilities. Figure 2 shows detection frequencies for all detected PFAS and for samples with concentrations above and below the SWRCB-DDW required target reporting limit of 5 ng/L, which was used to facilitate comparison among programs, well types, and compounds without bias caused by differing analytical sensitivities (California State Water Resources Control Board, 2021b). Most of the SWRCB-DDW PFAS detections exceeded the required target reporting limit of 5 ng/L (median about 8.0 ng/L). In contrast, most GAMA-PBP detections did not exceed the required target reporting limit of 5 ng/L (median about 2.5 ng/L).

Wells sampled in the SWRCB-DDW assessment were selected for monitoring because they are considered “hot spots” near known PFAS sources (such as landfills and airports) or near other wells with previous detections of PFOA or PFOS. In contrast, the GAMA-PBP selects sampling sites in a spatially distributed manner to provide an unbiased assessment of groundwater quality in California. Therefore, PFAS are detected less frequently and at lower concentrations by the GAMA-PBP. Preliminary results from the GAMA-PBP representative-sampling strategy indicate that groundwater from most wells used for public and domestic supply in California does not have PFAS at concentrations above the detection limits for this study (0.83–4.2 ng/L).

**Ongoing PFAS Sampling by the GAMA-PBP**

This fact sheet presents preliminary results of PFAS sampling of public-supply and domestic wells by the GAMA-PBP between May 2019 and September 2020. GAMA-PBP sampling is ongoing and includes re-sampling a network of public-supply and domestic wells to monitor temporal variability (“trends” networks) and denser sampling of domestic wells in selected areas to assess the quality of groundwater resources used for domestic supply. Between October 2020 and September 2021, the GAMA-PBP plans to collect samples from 130 public supply wells and about 120 domestic wells. By April 2024, GAMA-PBP plans to complete PFAS sampling for all of the public-supply trends networks, for five domestic trends networks, and for several more domestic well assessment areas (fig. 4). Because wells sampled by the GAMA-PBP are selected to be representative of ambient groundwater rather than targeted to investigate known or suspected contamination by PFAS, the GAMA-PBP dataset can provide information on the extent of PFAS in resources used for drinking-water supplies. In addition, GAMA-PBP sampling includes analysis of a broad suite of water-quality constituents and geochemical tracers and collection of ancillary data, and future work includes evaluation of processes that may be controlling the types and concentrations of PFAS in groundwater.
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