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RESEARCH ARTICLE

Quantitative Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Selective South Bay Water Bodies

Aryanka V. Rekhi

Pioneer High School, 1290 Blossom Hill Road, San Jose, CA 95118, USA; aryankarekhi08@gmail.com
Mentor: Haiqiang Yu

ABSTRACT: Per- and polyfluoroalkyl substances (PFAS) are persistent environmental pollutants, often termed "forever chemicals," known to cause adverse environmental and human health effects. In the San Francisco Bay Area, local surface water bodies and groundwater aquifers serve as critical water supplies, making the monitoring of PFAS concentrations essential for public health protection. While most existing water quality data have predominantly focused on groundwater and aquifers, a detailed quantitative analysis of surface water reservoirs is equally important. Proactive reservoir monitoring provides early detection of contamination before pollutants infiltrate groundwater, where cleanup and remediation are significantly more complex and costly. This study employs targeted quantitative liquid chromatography–tandem mass spectroscopy (LC-MS/MS) of surface waters to analyze a chemical signature dominated by short-chain PFAS compounds, with distributions varying significantly across different water sources. Through advanced analytical chemistry techniques, we present a quantitative assessment of PFAS and related contaminants in selected surface water bodies within the South Bay Area. Furthermore, we correlate these findings with the acceptable concentration limits proposed by environmental regulatory agencies. Ultimately, this research provides actionable, quantitative data to assist local authorities in mitigating PFAS-related contamination in the South Bay Area.

KEYWORDS: Chemistry, Liquid Chromatography, Mass Spectroscopy, Experimental Quantification of Trace PFAS and Related Contaminants, Water Bodies around the San Francisco Bay Area.

Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group of persistent, and forever chemicals, and these compounds have a wide range of commercial product applications including industrial polymers, stain repellents, surfactants, waterproofing products, packaging, and aqueous film-forming foams used for firefighting They are known as "forever chemicals" because they do not break down in the environment.[1] PFAS are often found in river/lake water near industrial manufacturing sites, due to their excellent water solubility and chemical stability posing risks to the ecosystem. They can also accumulate in the human body over time, leading to adverse human health effects, especially related to the liver and immune system.

The Bay Area/Silicon Valley is the center of technology and innovation, particularly in software, hardware, and semiconductors. Additionally, it is also a major hub for various other industries such as medical device manufacturing, biotechnology, and life sciences. Industrial discharge has been reported to contribute to the release of PFAS compounds, which could contaminate the nearby water bodies.[2] The South Bay is geographically different from the Central and North Bay Area and has limited tidal flushing. This can increase the residence time of contaminants, and SFEI shows elevated PFAS concentrations linked to the region because of manufacturing, industrial, municipal, and fire training sites. Because a major portion of the local water supply comes from surface water bodies and groundwater, it is very critical to understand and determine the level of PFAS-related compounds in these water bodies and understand the overall extent of PFAS exposure in the ecosystem. We conducted a quantitative analysis of various South Bay reservoirs to reveal elevated total PFAS concentrations and the distribution of these contaminants, aiming to study a direct correlation with their proximity to urban and industrial point sources.

This study is significant because much of the available water quality data in the Bay Area has historically focused on groundwater and aquifer contamination.[3] The long-chain PFAS compounds (containing eight or more carbon atoms) are highly hydrophobic (water-repelling), causing them to partition out of the water system and absorb into the sediments. Conversely, the short-chain compounds are highly water-soluble and are highly mobile in aquatic environments.

Although the surface water in these reservoirs may not be directly suitable for drinking, it is more vulnerable to PFAS contamination than well water.[4] Furthermore, these reservoirs remain interconnected components of the broader water supply system; monitoring them is critical because they serve as early indicators of contaminants before they migrate into the groundwater supply, where remediation efforts become significantly difficult and costly. Therefore, we hypothesized that a targeted quantitative LC-MS/MS analysis of surface water would reveal a chemical signature dominated by short-chain PFAS compounds, and their distribution would vary significantly across different water sources.

In this study, we collected water samples from several rivers/lakes around the SF Bay Area and used LC-MS/MS to identify 12 different types of PFAS compounds. These 12 PFAS compounds are well studied, widely used in the industry, and

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heavily regulated by the EPA, the Environmental Protection Agency,[5] and the California Water Resources Control Board.[6] Currently, the EPA does not have a single enforceable standard for all rivers and lakes, but has established enforceable drinking water standards, called MCLs Maximum Contaminant Levels,[7] for 5 specific PFAS chemicals. For drinking water, PFOA and PFOS have an MCL of 4.0 ppt (parts per trillion), while PFNA and PFHxS have an MCL of 10.0 ppt, and for PFHxA, the EPA does not currently have a finalized federal MCL. For protecting aquatic life, the EPA has established non-enforceable benchmark values for PFOA and PFOS, which are 4.0 ppt for PFOA and 8.0 ppt for PFOS.

LC-MS/MS is widely used for PFAS analysis due to its high sensitivity and selectivity at trace concentration levels.[8,9] Given the low detection limits required for PFAS in water, precautions were taken to reduce system-derived contamination, including the use of a trap column and large-volume injections to ensure reliable quantification. Due to the low detection limit requirements (parts per trillion) of PFAS in water, there have been a lot of analytical challenges due to potential contamination from lab equipment and reagents. In this study, we used a trap column after the LC pump to prevent potential contamination from the system and large-volume injection to achieve the targeted sensitivity needed for the PFAS quantification.

Methods

Thousands of different PFAS exist, are used in countless products, and are now present in the environment. Table 1 lists the most prominent PFAS compounds along with their associated information.

Table 1: Detailed list of PFAS compounds. This table summarizes the 14 per- and polyfluoroalkyl compounds to be analyzed, spanning C4 to C14 chain lengths with molecular weights from 214.03 to 714.11 g/mol.

Compound Code	Full Name	MW g/mole	Formula	CAS
PFPeA	Perfluoropentanoic acid	263.9	$C_5HF_9O_2$	2706-90-3
PFHxA	Perfluorohexanoic acid	314.1	$C_6HF_{11}O_2$	307-24-4
PFHpA	Perfluoroheptanoic acid	364.1	C7HF13O2	375-85-9
PFNA	Perfluorononanoic acid	464.1	$C_9HF_{17}O_2$	375-95-1
PFDA	Perfluorodecanoic acid	514.1	$C_{10}HF_{19}O_2$	335-76-2
PFUnDA	Perfluoroundecanoic acid	564.1	C11HF21O2	2058-94-8
PFDoDA	Perfluorododecanoic acid	614.1	C12HF23O2	307-55-1
PFBS	Perfluorobutane sulfonic acid	300.1	$C_4HF_9O_3S$	375-73-5
PFOS	Perfluorooctane sulfonic acid	500.1	C8HF17O3S	1763-23-1
PFOA	Perfluorooctanoic acid	414.1	$C_8HF_{15}O_2$	335-67-1
PFTA	Perfluorotetradecanoic acid	714.1	$C_{14}HF_{27}O_2$	376-06-7
PFTrDA	Perfluorotridecanoic acid	664.1	$F_3C(CF_2)_{11}CO_2H$	72629-94-8
PFHxS	Perfluorohexane sulfonic acid potassium salt	438.2	$C_6F_{13}KO_3S$	3871-99-6
PFBA	Perfluorobutanoic acid	214.0	$C_4HF_7O_2$	375-22-4

Methanol (LC-MS/MS Grade, Fisher Scientific, Lot number: 222630), Water (LC-MS/MS grade, Fisher Scientific, Lot number: 242945), Trap Column (Thermo Scientific BDS Hyersil Gold (50x2.1 mm, 5 µ, Lot number: 21524), Analytical Column (Thermo Scientific Hypersil Gold 100x2.1 mm, 1.9 µ, Lot number: 21565) and LC vials (Catalog number: 03452223, Lot number: TSKM4D176GF). All the standards with a specific concentration were diluted with LC-MS/MS-grade water.

Our study focuses on the water samples collected from different water bodies in the SF Bay Area. Table 2 lists the names of lakes/rivers and the sources of water samples. Most of these water reservoirs are man-made, or significant portions of their watershed are altered by man-made features. Based on our understanding, Vasona Lake/ Reservoir is managed by Valley Water, and it is a source that feeds the drinking water system after treatment. Almaden Reservoir is one of the Santa Clara Valley Water District's 10 reservoirs and supplies water to drinking water plants from groundwater recharge. Calero Reservoir captures runoff and provides water directly to drinking water plants. The others are recreation, flood control, or groundwater recharge.

Table 2: Name and location of reservoirs (water sample sources) chosen for this study. Nine water bodies were selected across the SF Bay Area to capture a gradient of urban, recreational, and drinking-water supply reservoirs.

Sample Source	Location
Vasona Lake (57 acres)	Los Gatos, CA
Lake Cunningham (50 acres)	East San Jose, CA
Lake Elizabeth (83 acres)	Fremont, CA
Guadalupe Creek (10 miles)	Almaden San Jose, CA
Cottonwood Lake (~13 acres)	San Jose, CA
Sandy Wool Lake (~14 acres)	Milpitas, CA
Almaden Reservoir (62 acres_	South San Jose, CA
Calero Reservoir (349 acres)	Almaden valley CA
Lake Almaden (32 acres)	South San Jose, CA

According to existing literature, various inorganic pollutants, including heavy metals and Biotoxins, may exist in these reservoirs; however, our study is solely focused on the PFAS compounds. We collected the water samples in properly labeled, clean glass bottles; all the water samples were centrifuged, and the supernatants were transferred to a 1.5 mL LC autosampler vial.

A Vanquish UHPLC system equipped with a special PFAS Kit, including a solvent filter and solvent tubing, and coupled with a TSQ Altis Plus (Thermo Fisher Scientific, San Jose, California) and a heated electrospray ion source (HESI), was used to acquire SRM (Selected Reaction Monitoring) mass spectra in negative mode. The HESI source parameters were set with an ion spray voltage of 2.8 kV (negative ionization mode); sheath gas flow rate of 40 arbitrary units, and auxiliary gas flow rate of 10 arbitrary units; the temperatures of the vaporizer and capillary were both kept at 325 ˚C. Table 3 lists the detailed SRM methods for targeted compounds.

Table 3: Detailed SRM method parameters for targeted compounds. Chromatographic separation was performed on a Thermo Hypersil Gold C18 column with a BDS Hypersil Gold trap column at 0.25 mL/min using water (mobile phase A) and methanol with 10 mM ammonium acetate and 0.1% acetic acid (mobile phase B). The gradient was 0-30% B (0-1 min), 30-45% B (1-6 min), 45-80% B (6-13 min), 80-95% B (13-14 min), and 95% B hold (14-18 min), followed by a 7 min equilibrium. The injection volume was 10 µL.

Compound	Retention Time (min)	RT Window (min)	Precursor (m/z)	Product (m/z)	Collision Energy (V)	RF Lens (V)	Min Dwell Time (ms)
PFBA	4.84	4	212.98	168.97	9	30	73.05
PFPeA	7.58	4	262.98	219.04	9	31	48.38

PFBS	8.26	4	298.94	79.96	34	116	28.52
	8.26	4	298.94	98.95	29	116	28.52
PFHxA	10.17	4	312.97	63.19	15.46	39	15.28
	10.17	4	312.97	119.04	18.76	39	15.28
	10.17	4	312.97	268.97	9	39	15.2
PFHpA	11.79	4	362.97	119.05	19.52	43	11.12
	11.79	4	362.97	168.97	15.53	43	11.12
	11.79	4	362.97	319.04	9	43	11.12
PFHxS	11.92	4	398.93	79.95	39	135	11.12
	11.92	4	398.93	98.95	35	135	11.12
PFOA	12.93	4	412.96	169	16.1	49	10.63
	12.93	4	412.96	219	14.55	49	10.63
	12.93	4	412.96	369.04	9	49	10.63
PFNA	13.82	4	462.96	169	17.51	52	10.63
	13.82	4	462.96	219.01	15.23	52	10.63
	13.82	4	462.96	418.97	9	52	10.63
PFOS	13.85	4	498.93	79.96	47	159	10.63
	13.85	4	498.93	98.95	40	159	10.63
	13.85	4	498.93	129.95	20	159	10.63
	13.85	4	498.93	168.98	20	159	10.63
PFDA	14.56	4	512.96	219.01	16.14	56	10.63
	14.56	4	512.96	269.04	15.8	56	10.63
	14.56	4	512.96	469.04	9	56	10.63
PFUnDA	15.16	4	562.95	219	17.32	62	10.63
	15.16	4	562.95	269.03	16.94	62	10.63
	15.16	4	562.95	518.97	9	62	10.63
PFDoDA	15.62	4	612.95	169.03	23.69	67	10.63
	15.62	4	612.95	319.04	17.54	67	10.63
	15.62	4	612.95	569	9	67	10.63
PFTrDA	15.9	4	662.95	168.97	25.16	71	10.63
	15.9	4	662.95	369.07	17.85	71	10.63
	15.9	4	662.95	619.04	9	71	10.63
PFTeDA	16.1	4	712.94	319.05	19.86	74	10.63
	16.1	4	712.94	369.04	18.87	74	10.63
	16.1	4	712.94	668.97	9	74	10.63

All data acquisition and analysis were conducted by Xcalibur 4.5 and TraceFinder 5.1. Samples were separated on a Thermo Hypersil Gold C18 column, and the mobile phase consisted of water (mobile phase A) and 10 mM ammonium acetate, 0.1% acetic acid in MeOH (mobile phase B: 0.078 g ammonium acetate and 1 mL acetic acid were added into 1000 mL methanol). The gradient is from 0% B to 30% B in 0–1 min, from 30% B to 45% B in 1-6 min, from 45% B to 80% B in 6-13 min, from 80% to 95% in 13-14 min and hold at 95% B for 4 min for a total of 18 min run with the flow rate of 0.25 mL/min. The system was equilibrated with 95% A for 7 min before the next injection. The sample injection volume for water samples and standard samples from the lakes is 10 µL. A trap column was used right after the LC pump and before the autosampler to prevent system contamination and increase sensitivity.

Results and Discussion

To evaluate chromatographic separation and detection of PFOA, PFOS, PFNA, PFHxS, and PFHxA, and the suitability of the method, the chromatograms of five PFAS standards at 4 ng/L made in LC-MS/MS grade water were measured and are shown in Figure 1.

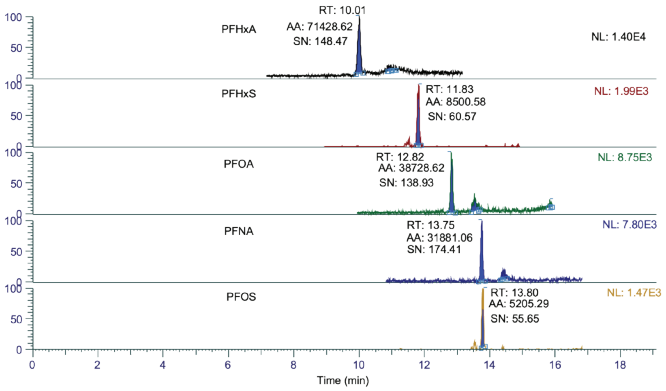

Figure 1: Representative LC-MS/MS chromatogram of PFHxA, PFHxS, PFOA, PFNA, and PFOS spiked at 4 ng/L in LC-MS/MS grade water. Peak retention time (RT), integrated peak area (AA), and signal-to-noise (S/N) were used to assess chromatographic performance and detection sensitivity. All five target compounds show baseline chromatographic separation with retention times between 10 and 15 minutes. Signal-to-noise (S/N) ratios for all analytes exceeded 55 at 4 ng/L, demonstrating method sensitivity well above the typical S/N = 10 quantification threshold and suitability for low-level environmental monitoring.

The peak identification, along with retention times, peak area, and signal-to-noise ratios information derived from the chromatogram in Figure 1, is listed in Table 4. All the analytes are well-separated and detected within the retention time window between 10 min and 15 min, and the peak signal/noise ratios are 55.65-148.47. The method achieved the necessary sensitivity to meet the reportable threshold for all 5 analytes. All the collected water samples were directly injected into the LC-MS/MS system with the targeted SRM method to conduct experimental quantitative screening of PFOA, PFOS, PFNA, PFHxS, and PFHxA across all water samples from different lakes and rivers. The raw data were processed and analyzed with TraceFinder software. We have used the peak area of a particular PFAS compound and compared it with the same compound with a known concentration in ultra-pure PFAS-free water. Before the water sample analysis, a mixture of PFAS standards was run with the same method, and the retention time data were summarized in Table 4. The screening of 14 PFAS compounds in water samples was conducted using the retention time of the individual PFAS compounds listed in Table 3. A peak from the raw data at a similar retention time to the standard mixture data indicated a positive hit. No peak from the raw data indicated a negative hit. The concentration determination of the positive hit was performed using direct comparison of the peak areas of unknown samples and standard samples.

Table 4: Peak Identification and peak parameters of PFHxA, PFHxS, PFOA, PFNA, and PFOS compounds. Target analytes were identified by comparing retention times with those of the standard reference mixture. Quantification was performed by direct comparison of peak areas between samples and corresponding external standards.

Peak No.	Compound Name	Retention Time (min)	Peak Area	Signal/Ratio
1	PFHxA	10.01	71428	148.47
2	PFHxS	11.83	8500	60.57
3	PFOA	12.82	38728	138
4	PFNA	13.75	31881	174
5	PFOS	13.80	5205	55.65

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The example chromatogram of water samples from Lake Cunningham is depicted in Figure 2. The chromatographic analysis indicated positive hits for PFHxA, PFHxS, and PFOA and negative hits for PFNA and PFOS, with no peaks at the expected retention time. The concentrations of PFHxA, PFHxS, and PFOA were determined based on the peak area. A detailed summary of PFAS occurrence across all nine reservoirs is listed in Table 5.

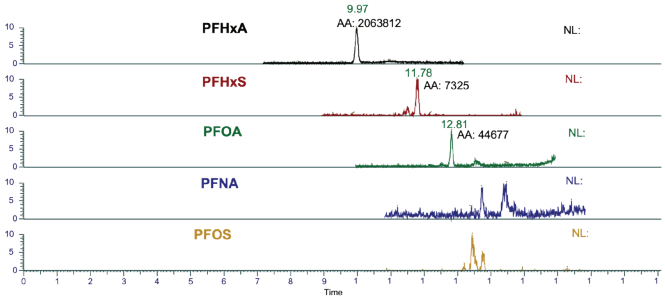

Figure 2: Chromatogram of water sample from Lake Cunningham. The chromatographic analysis revealed the presence of PFHxA, PFHxS, and PFOA, which were positively identified, whereas there were negative hits for PFNA and PFOS with no peaks at expected retention times. The concentrations of the detected analytes were determined based on integrated peak areas.

Table 5: Estimated concentration of different PFAS compounds in collected water samples measured across different collection trials within the same lake. Chromatographic analysis positively identified PFHxA, PFHxS, and PFOA, while PFNA and PFOS were not detected. PFHxA dominated the profile, indicating short-chain PFAS as major contributors at this site. Concentrations of identified analytes were quantified based on integrated peak areas. The estimated concentrations were determined based on the comparison between integrated peak areas from each water sample and the peak areas from the standards at 4.0, 10.0, 25.0, 50.0, and 100.0 ng/L. The method detection limit for all 5 standards is 4 ng/L.

	PFHxA (ng/L)	PFHxS (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFOS (ng/L)
Vasona Lake	4-10	< 4	< 4	< 4	< 4
Lake Cunningham	25 -50	< 4	4-10	< 4	< 4
Lake Elizabeth	25-50	< 4	< 4	< 4	< 4
Guadalupe Creek	25-50	< 4	< 4	< 4	< 4
Cottonwood Lake	25-50	< 4	<4	< 4	< 4
Sandy Wool Lake	50-100	< 4	< 4	< 4	< 4
Almaden Reservoir	25-50	< 4	< 4	< 4	< 4
Calero Reservoir	25-50	< 4	< 4	< 4	< 4
Lake Almaden	25-50	<4	<4	< 4	< 4

Detection Limit: 4 ng/L
(All values reported by values < 4 indicate concentrations below the method reporting limit of 4 ng/L)

Based on several city reports and government resources, Lake Cunningham is facing more ecological and water quality issues than merely PFAS contamination. However, our analysis indicates a higher level of PFOA in Lake Cunningham that may be linked to its location in a highly developed urban region in the surrounding hills, where stormwater runoff percolated through the underground gravel and flowed into Thompson Creek and Lake Cunningham. While it could be challenging to identify the exact source of PFOA, it is widely recognized that the common sources of PFOA within the water system may include firefighting foams, industrial waste, biosolids, and various consumer product industries. Poor circulation and flooding issues allow the contaminants to be trapped in the sediments for a long period of time.

In terms of regulatory context, PFOA is categorized by the International Agency for Research on Cancer (IARC) as Group 1, "carcinogenic to humans". This classification is based on sufficient evidence of carcinogenicity in animal studies and strong mechanistic evidence in humans, although there is limited evidence for renal cell carcinoma and testicular cancer.[10] Additionally, some epidemiological studies have reported associations with other cancer sites, such as thyroid, breast, and ovarian cancer; however, IARC has concluded that the current evidence on humans from these cancer sited insufficient.

Although the overall levels of PFAS material may fall within acceptable limits, localized areas of elevated concentration can still be present. A higher concentration of pollutants can significantly affect groundwater, as groundwater and surface water are inseparably linked components of the water cycle and facilitate the exchange of chemicals. The water on the surface could seep downwards, thereby replenishing the underlying aquifer, where the groundwater can stay longer for extended periods. Over time, this groundwater can cycle back into surface bodies such as streams and wells. The duration and concentration for which the water stays underground, along with the chemicals, can significantly alter the quality of the water. Consequently, the surface water has the potential to degrade the overall water quality of the ecosystem.

The presence of harmful substances in the environment underscores the critical need for effective management strategies to protect both the ecosystem and public health. In response, the authorities have implemented several measures, such as regulating stormwater and runoff, pollution prevention practices, reducing plastic materials, especially BPA-free, community training and involvement, and student education, such as Bio Site and Environmental Corps programs. The South Bay Water Department is also starting an ion exchange technology plant to eliminate PFAS and treat groundwater.[11] Alternative technologies, such as reverse osmosis and filtration, can effectively remove long-chain contaminants; however, increased awareness is needed to ensure the safety of surface water by restricting the source of contaminants into reservoirs and safeguarding waterways.

Conclusion

The results support the study's hypothesis that surface waters exhibit a chemical signature dominated by highly mobile, short-chain PFAS compounds (specifically PFHxA) rather than long-chain variants like PFOS. The elevated levels of PFOA in Lake Cunningham may be associated with urban stormwater runoff. While the overall levels of PFAS detected generally fall within acceptable regulatory limits, the study emphasizes the critical importance of continuous surface water monitoring. Because surface waters are interconnected with groundwater aquifers, these reservoirs serve as an essential early warning system for contamination before pollutants migrate into groundwater supplies, where remediation becomes substantially more complex and costly. The spatial analysis showed a clear link, indicating that PFAS levels drop as we move away

from urban locations. Locations within 1 km of busy developments or major highways had total PFAS concentrations that were 3.2 – 5.8 times greater than reference sites in less-developed areas. Recent studies have shown that concentration decreases by about 60% for every tenfold increase in distance from urban sources.[12] This quantitative relationship backs up the idea that stormwater runoff from hard surfaces is a significant way for PFAS to enter the environment and suggests that proximity to urban land use is a strong indicator of local PFAS levels.

These results are crucial for managing watersheds in areas that are becoming more urbanized. Additional studies could be conducted to provide a direct mechanism for stormwater runoff and to investigate the short-distance contamination gradient in high-density urban, suburban, and industrial areas compared to reference watersheds.

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Author

Aryanka V. Rekhi is currently a junior in high school located in San Jose, California. Alongside her core academic studies, she has been actively involved in diverse research projects focused on environmental chemistry, computational neuroscience, and the impact of GenAI in the academic environment. Her deep interest in medicine has driven her to explore various research opportunities. She is also pursuing a degree in classical dance, which she expects to complete by the summer of 2026. In her spare time, she enjoys volunteering and traveling to immerse herself in different cultures and experiences.

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