University of North Carolina Asheville
Journal of Undergraduate Research
Asheville, North Carolina
May 2022

Analysis and Quantification of Per- and Polyfluoroalkyl Substances in Western North Carolina Surface Waters

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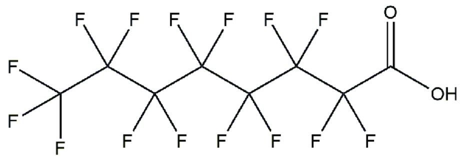
Abstract

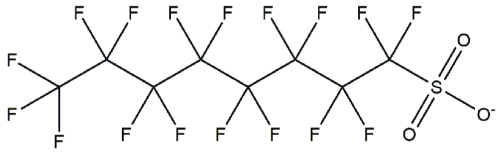
Per- and polyfluoroalkyl substances (PFAS) are an anthropogenic class of compounds used in a wide variety of consumer products. These compounds do not biodegrade, and the CDC's last national exposure report found that 98% of people in the US have PFAS in their blood. The CDC's monitoring of PFAS compounds, including legacy, compounds PFOA, and PFOS, over the past 40 years shows persistent and ubiquitous exposure to PFAS among the population in the US with implied adverse health effects including kidney and testicular cancers, reduced response to vaccines, and hyperthyroidism. After 2006, novel PFAS derivatives were synthesized, and officials worry this new generation of PFAS derivatives has similar toxicological profiles to the banned compounds because of their similar chemical properties. The goal of this study is to understand the prevalence, measure, and associate PFAS within Western North Carolina (WNC) surface waters with possible sources. This study utilizes EPA Method 533, including weak anion exchange (WAX), liquid chromatography-tandem mass spectrometry (LC-MS/MS), and an adapted solid-phase extraction (SPE) protocol to determine the prevalence of 26 PFAS compounds. The 64 sample sites included locations recommended by the Southern Environmental Law Center (SELC), in the vicinity of relevant industries, and indicated by previous literature across the greater Buncombe County area within western North Carolina. We detected the presence of 20 different PFAS. Of the 64 sites, only five had an individual PFAS concentration higher than 70 ppt WNC surface waters. ΣPFAS concentrations ranged from 0.5 – 1903 ppt, and 11 of the 64 sites had ΣPFAS levels of 70 ppt. These data show that sites associated with the firefighting stations, the Asheville Regional Airport, and the Pidgeon River downstream from Canton had the highest levels of PFAS. Further analysis of WNC surface water is required to have a full understanding of the presence of PFAS in Buncombe County and influence local legislation on PFAS regulations in surface waters.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a class of compounds similar to hydrocarbons but with the C-H bonds entirely or partially fluorinated. The C-F bonds are strong and subsequently are very resistant to natural, chemical, and thermal degradation. PFAS have been determined to have an approximate half-life of about 4 years in humans[1]. Due to this strong C-F bond, PFAS compounds persist within the environment and bioaccumulate within wildlife and humans. PFAS has many consumer and industrial uses as PFAS compounds are being used in plastics, non-stick cookware, waterproofing materials like Teflon, stains, and varnishes used for upholstery, aqueous film-forming foams (AFFFs), paper production, and chromium and plastic plating. Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), often referred to as legacy compounds, were the two primary PFAS used by the chemical industry until 2006 when under EPA guidelines were voluntarily phased out[2].



Perfluorooctanoic acid (PFOA)



Perfluorooctane sulfonate (PFOS)

Figure 1: Chemical structures for PFOA and PFOS

PFAS has been found in 98% of Americans' blood and the CDC's most recent national exposure report states that the average level of PFOA in the blood of Americans is 1.56 µg/L and 4.72 µg/L for PFOS[3,4]. Human exposure to PFOA can result in high cholesterol, increased liver enzymes, decreased response to vaccines, thyroid disorders, and testicular and kidney cancers[5,6]. With the phasing out of PFOA and PFOS, the chemical industry has derivatized the legacy compounds by making shorter-chain, longer-chain, ester, and fluorotelomer sulfonic acids (FTS) PFAS. These novel PFAS compounds have the same chemical properties and fill the same industrial purposes as the legacy PFAS, but with much less toxicological data for humans. Officials worry about the possible health effects of these novel compounds due to their similarities to the legacy compounds.

Much is known about what PFAS compounds, and their approximate levels, are present within the Cape Fear River and the surrounding areas due to the notoriety of the DuPont and Chemours chemical plants in Fayetteville, North Carolina on the Cape Fear River watershed[7]. In the Cape Fear River 31.2 ng/L of PFOS, 43.4 ng/L of PFOA and 400 ppt GenX was found[8,9]. Recent studies found total concentrations of PFAS in the Truckee River to be 441.7 ng/L and 2234.3 ng/L in Las Vegas Wash water[10]. However, less is known about PFAS's presence exists in Western North Carolina (WNC) surface waters. There has been some data collection within WNC however, including a set of unpublished data from Dr. Detlef Knappe from North Carolina State University. Unfortunately, the data collected by Dr. Knappe only accounts for a small fraction of potential sites within WNC.

This research aims to increase our understanding of the prevalence of PFAS, and at what levels PFAS compounds are present, within WNC. Through analysis and quantification of PFAS in 74 groundwater samples within the greater Buncombe County area, we hope to fill the void in the knowledge of PFAS in WNC and identify any possible major sources of contamination within the region.

2. Methodology

2.1 LC-MS/MS Method

Previous literature has established liquid chromatography (LC) tandem triple quad mass spectrometry (MS) in multi reaction monitoring (MRM) to be the gold standard for the analysis and quantification of PFAS. Liquid chromatography-tandem mass spectrometry (LC-MS/MS) along with weak ion exchange (WAX) solid-phase extraction (SPE) is used for analysis and quantification of PFAS based on EPA Method 533, and Agilent methodologies[11–13]. MRM will allow for the analysis of multiple PFAS analytes at the same time. Liquid chromatography will allow for the separation of these compounds based on polarity and subsequently provide a better resolution when the compounds are detected by the MS. A triple quadrupole mass spectrometer allows for higher selectivity and resolution by using fragmentation. With PFAS being used in many plastics, some of which are commonly found within laboratories, and because of PFAS's high affinity to sticking to the glass, high-density polyethylene (HDPE) plasticware will be used whenever possible to limit background contamination and potential losses. Using HDPE and minimizing sample contact with glass allows for higher mass spectrometer sensitivity. A delay column was also installed before the analytical LC column so that if there is PFAS contamination present within solvents or the plastic tubing within the LC, these PFAS compounds will be affected by the delay column and elute later not affecting quantification[8].

The analysis of PFAS compounds was done using a Shimadzu LCMS-840 triple quadrupole liquid chromatograph-mass spectrometer (LC-MS/MS) with electrospray ionization in negative ion mode, a C18 liquid chromatography (2 x 50 mm, 3.0 µm) column, and a solvent system of A: 20 mM ammonium acetate and B: Methanol was utilized with the following gradient program across the 35-minute analysis time (Table 1)

Time (min)	% A (20 mM $NH_4C_2H_3O_2$)	% B (MeOH)
0	95	5
0.5	95	5
3	60	40
16	20	80
18	20	80
20	5	95
22	5	95
25	95	5
35	95	5

Table 1: Liquid chromatography solvent system program

3. Water Sampling protocol

Samples were taken using 1 L HDPE bottles previously rinsed with 10 mL of methanol and then allowed to dry before samples were taken. Samples (1 L) samples were taken in the field with 5 mL of 35% nitric acid being added to all samples to stop the growth of any living organisms. Every batch of samples included a field blank comprised of 1 L of deionized water and a spiked blank comprised of 500 mL of deionized water at 0.5 ppb PFAS internal standard and 5 mL of 35% nitric acid. This is to account for any PFAS inherently present within the bottles that can leech out during sampling. The use of a Van Dorn sampler was utilized to allow for the sampling of waterways that are hard to reach or difficult to sample. If in a specific set of samples, the Van Dorn sampler was used, and a Van Dorn blank was made by filling the sampler with 1 L of water and filling a bottle with that water. This allows for the determination of possible persistent PFAS compounds in the Van Dorn sampler. All field blanks and spiked blanks were brought into the field for a day of sampling to allow for all samples to be under the same conditions. Field blank and spike blank samples allow for the comparison of field samples by removing background contamination. Samples were stored on ice while in the field and then stored in a refrigerator until sample processing. Samples were extracted within 2 weeks of initial sampling to ensure no degradation of PFAS analytes occurred. During field sampling, pH, conductivity, and temperature data were collected at each sampling site. The turbidity of each sample was also collected for comparison between storm event samples and non-storm event samples.

Table 2: List of PFAS being analyzed with name and associated precursor and product mass per charges

Name of PFAS Compound	m/z
PFBA	212.85>168.95
PFPeA	262.85>219.05
PFBS	298.85>79.90
4:2 FTS	327.00>306.95
PFPHxA	312.85>268.95
PFPeS	349.00>79.95
PFHxS	398.95>79.95
PFHpA	363.00>318.95
6:2 FTS	427.05>407.00
PFOA	413.00>369.00
PFHpS	448.95>79.95
PFOS	498.95>79.95
PFNA	463.00>418.95
8:2 FTS	526.85>506.95
FOSA	498.00>77.80
N-MeFOSAA	570.05>418.90
PFNS	548.90>79.90
PFDA	513.10>469.00
N-Et-FOSAA	583.85>419.00
PFDoA	612.80>568.90
PFUdA	562.80>518.95
PFDS	598.90>79.95
PFTrA	663.05>618.95
PFTeDA	713.00>668.85
PFHxS	398.95>79.95
PFOS	498.95>79.95

3.1 Selection of Sample Sites

Sample sites were chosen based on the Southern Environmental Law Center (SELC) recommendations, and sites that have businesses or industries that use PFAS compounds near waterways and other water sources. The Swannanoa River, French Broad River, Pigeon River, Bee Tree Creek, Hominy Creek, Lake Julian, Bent Creek, and Beaver Lake were sampled. The Pigeon River was sampled at the outflow from Evergreen Packaging in Canton, NC, and three seeps associated with a historic landfill in Canton, NC. Airport and the associated sites on the French Broad River around the airport and sites of interest like Westfeldt Park were studied to see if the usage of PFAS-containing products is present at the Asheville Airport. The analysis of PFAS containing AFFFs is being monitored by sampling at fire stations and other sites where the practice and usage of AFFFs are common.

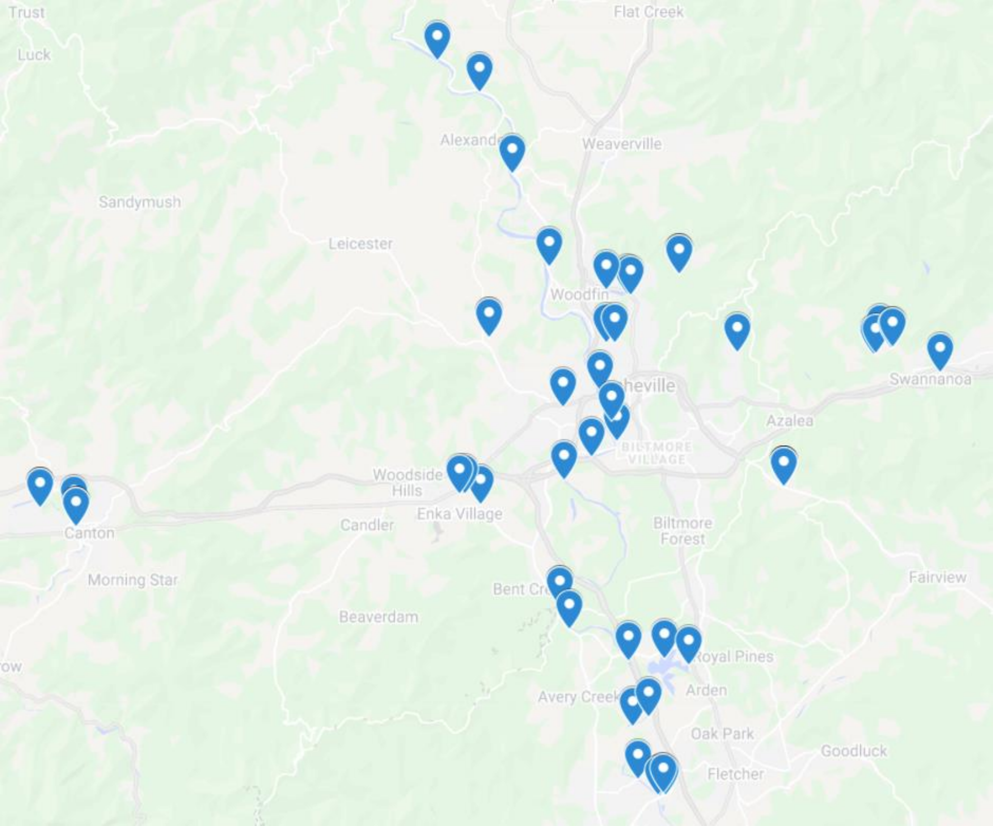


Figure 2: Map of sample sites

3.2 Solid Phase Extraction Method

The SPE method involves preconditioning of the column and sample, elution of sample, and then drying of sample for LC-MS/MS analysis. Before every extraction, all equipment is rinsed with methanol to rinse off any PFAS that may be present from previous runs to minimize contamination across samples.

First, an aliquot (250 mL) of the water sample was measured into polypropylene (PP) graduated cylinder. To the 250 mL water sample 2.5 mL of glacial acetic acid and 200 µL of 100 ppb internal PFAS standard were added. The sample was then filtered through a Buchner funnel with a glass fiber membrane filter into a PP vacuum flask. This is to remove any sediment or other particulate present in the sample that could damage the instrumentation. PFAS could be present in the particulate sediment within a sample, but for this study, our concerns are with the analysis of water, so keeping sediment is unnecessary. The vacuum manifold is set up with three 15 mL PP Falcon tubes for the preconditioning of the cartridge and elution of the sample. The manifold is set up between 10 – 15 mm Hg and never exceeds 15 mm Hg.

A solid-phase extraction (SPE) cartridge (Water Oasis Wax) was preconditioned by rinsing with 5 mL of 5% ammonium hydroxide in 60:40 acetonitrile and methanol solution. Then add 5 mL of deionized water and 6 mL of 1% acetic acid were added. A vacuum filter is set up to allow for prepared water samples to flow through the preconditioned SPE cartridge at approximately a 10 mL/min flow rate. After all the sample has been filtered through the SPE cartridge, the vacuum flask previously holding the sample and the barrel before the SPE cartridge is washed twice with 7.5 mL of DI water to ensure all samples pass through the SPE cartridge and any present PFAS is caught on the cartridge. The cartridge is returned to the manifold and the cartridge can dry in the manifold at a high vacuum (10-15 mm Hg) for 5 minutes. Finally, the SPE cartridge has 8 mL of 5% ammonium hydroxide in 60:40 acetonitrile and methanol solution introduced to the cartridge but does not allow for the ammonium hydroxide solution to soak in the manifold for 5 minutes. Then, the solution is eluted into a new clean 15 mL PP Falcon tube. The eluted sample is dried using a TurboVap at 55 °C and N_2 gas to blow the total sample volume to ~2.0 mL. If needed, the volume is adjusted to 2.0 mL by adding 96% LC/MS grade methanol. Samples are then labeled and put into PP HPLC vials for LC-MS/MS analysis.

4. Results

Of the 26 tested PFAS compounds, 20 were detected across the 64 sampling sites. N-Ethyl perfluorooctanesulfonamidoacetic acid (N-Et FOSAA) was below the limit of detection of 1.4 ppt and PFDS was below the field blank level of 0.8 ppt. N-Et FOSAA and PFDA are long-chain PFAS and believed to be more nonpolar than the other compounds analyzed and might be sticking to the sediment present in surface waters. PFBA is not reported due to low recovery rates of spiked internal standards in the samples. This is likely due to how short-chained the molecule is, and possibly volatilizing during the extraction process, resulting in low recoveries of PFBA. The largest concentration of PFAS was found at sites associated with firefighting stations, the Asheville Regional Airport, and the historic landfills in Canton, With the highest individual concentration being 1000 ppt of PFOS found at Seep 2 in Canton. In all sites sampled, some concentration of PFAS was found with the ΣPFAS concentration for each site ranging from 0.5 – 1903 ppt. Eleven of the 64 sites were found to have ΣPFAS levels higher than the EPA's 70 ppt health advisory for water. Four were associated with firefighting stations, four were associated with historic landfills, two were associated with Asheville Regional Airport, and one was not directly associated with any specific source of pollution. While only 5 of the 64 sites had an individual PFAS concentration higher than the EPA's 70 ppt health advisory for an individual PFAS compound, most of the sampling sites had some level of PFOS or PFOA—showing and proving the longevity of these compounds and the widespread usage of products containing those legacy PFAS. PFHxA, which is associated with firefighting foams and is an early derivative of PFOA, was the most common analyte found in all sites except for three. PFPeA is used in nonstick food wrappers and other consumer products that are heat, stain, and water-resistant and is the second most common analyte and found in all sites except for five. A preliminary analyte correlation matrix was made to see if any correlations between analytes were found. The correlation matrix showed that there are correlations between analytes. Analytes within the same class are more likely to be found with shorter analytes of the same class. PFPeA, PFPHxA, PFHpA, PFNA, 8:2 FTS, and PFDA were all highly correlated together (>0.62). PFBS, PFPeS, and PFHxS were also highly correlated together (>0.89).

5. Discussion

Due to N-Et-FOSAA and PFDA's structure being a long non-polar structure we believe these compounds would stick to sediment allowing PFDA and N-Et FOSAA to stick to sediments and not be recovered during the extraction process, as sediment is not included in the extraction process. While EPA Method 533 has shown to be effective at collecting and analyzing medium-chain PFAS from this data set, Method 533 struggles to capture the 3 carbon chains and struggles greatly with carbon chains longer than 8. This may be due to the type of SPE cartridge being used as well as the way the cartridge is prepped. The pH and chemistry set up within the SPE cartridge may be designed to focus on the 4-8-long carbon chain PFAS compounds, as those are the most common among the legacy and early derivative compounds. A preliminary analyte correlation matrix was made to see if any correlations between analytes were found. The correlation between PFPeA, PFPHxA, PFHpA, PFNA, and PFDA is thought to be because they are all a part of the carboxylic acid forms of PFAS with the C5, C6, C7, C9, and C10 variations being present together. The absence of the C8 carboxylic acid PFAS PFOA could be due to PFOA being banned before the creation of the novel derivatives implying the PFAS contamination we found is due to newer AFFFs. These compounds along with 8:2 FTS which were all correlated together were found at higher levels at sampling sites associated with firefighting stations. The second group of compounds were found to be correlated together whereas PFBS, PFPeS, and PFHxS, the C4, C5, and C6 sulfonate PFAS compounds. Sampling sites that contained high levels of these analytes were associated with historic landfills.

6. Conclusion

WNC surface waters are contaminated with PFAS below and above the EPA's health advisory limit in water. Firefighting stations, historic landfills, and the Asheville Regional Airport had the highest levels of PFAS, with unique sets of compounds found in firefighting stations and historic landfills. Future research should seek to improve upon

EPA Method 533 to include longer chain PFAS (>C9) due to the current limitation of the methodologies, which excluded sediment. Other routes of future research could examine downstream contamination of a known pollutant, test AFFFs used by the Asheville Fire Department to confirm the sources of PFAS around firefighting stations, and further test around Asheville in both surface waters and sediments to fully understand the presence of PFAS within WNC.

7. Acknowledgments

The author wishes to express their appreciation to the Southern Environmental Law Center for funding for this project. Dr. Jeff Wilcox for his help with understanding waterways and lending equipment used to take field measurements. Dr. Dee Eggers for her help doing the statistical analysis of PFAS data. Steven Defiglia and Cassie Bailey for their help with the method development, analysis of samples, and field sampling.

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