

FLORIDA STATEWIDE PFAS PILOT STUDY AT DRYCLEANING SITES

Sponsored By:



Florida Department of Environmental Protection
Waste Site Cleanup Program
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ABSTRACT

The Florida Department of Environmental Protection Division of Waste Management recognizes the public health concerns related to the occurrence of Per and Polyfluoroalkyl Substances (PFAS) in the environment. As a means to evaluate the relationship of the occurrence of PFAS at drycleaning facilities within the state-administered Drycleaning Solvent Cleanup Program, a Pilot Study was commissioned to conduct background research, field investigations of environmental media, and analysis of waste stream components for PFAS related to drycleaning facilities. The Study, completed over the course of 26 months, found PFAS to be present in soil and groundwater above Provisional Cleanup Target Levels at 10 of the 15 pilot study sites. The drycleaners appeared to be the source of PFAS. Data indicates the PFAS likely originates from the leaching of PFAS from fabrics during the drycleaning and/or wet laundering activities. This White Paper summarizes the scientific research, investigative techniques, interpretations of results, and lessons learned from the Study.

INTRODUCTION

PFAS

Per- and Polyfluoroalkyl Substances (PFAS) are a group of more than 4,700 individual synthetic compounds that have been manufactured and used in a variety of consumer and industrial products since the 1940s (ITRC, 2020). The most common or notable uses for PFAS have been for fire-fighting foams, and protectants that improve water, grease, and oil repellency, on paper/cardboard packaging products, nonstick coatings on cookware, textiles, waterproof clothing, leather products, electrical wire casing, fire- and chemical-resistant tubing, and plumbing thread seal tape. While no longer manufactured in the United States, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) were extensively manufactured and used for decades. The presence of PFAS in the environment only began to be studied in the early 2000s. These chemicals remain in the environment today due to their persistent chemical properties. In addition, PFOA and PFOS continue to be produced internationally and can be imported into the United States marketplace in consumer goods/products (ITRC, 2020).

Studies have suggested that the exposure to some PFAS in the environment can be harmful for human health, with a greater focus on the longer-chain perfluoroalkyl acids (PFAAs), sometimes referred to as “terminal PFAS”, including perfluoroalkyl carboxylic acids (PFCAs) such as PFOA and perfluoroalkane sulfonic acids (PFSAs) such as PFOS. Although there are thousands of other chemicals that fall into the PFAS group, most interest has been focused on PFOA and PFOS, given their ubiquitous presence in the environment and availability of extensive toxicity studies.

In 2016, the US Environmental Protection Agency (EPA) issued a Lifetime Health Advisory Level (HAL) for the two most detected PFAS (PFOA and PFOS) at a threshold limit of 70 nanograms per liter (ng/L) for those two substances (individually as well as in combination). In 2018, the Florida Department of Environmental Protection (FDEP) developed provisional groundwater cleanup target levels (PGCTLs) of 70 ng/L for PFOA, PFOS, and the sum of PFOA and PFOS, that are protective of sensitive life stages. Based on the PGCTL of 70 ng/L for PFOA and PFOS, the FDEP also developed groundwater-based leachability provisional soil cleanup target levels (SCTLs) for these two compounds, along with Direct Exposure SCTLs for residential and commercial/industrial land uses. Information, sources, and threshold limits of PFAS continue to be studied by the US EPA (EPA 2020) and various other agencies (ITRC, 2020), due to the extent of their environmental impacts being still novel amongst the regulatory community.

Study Objectives

As part of the committed efforts to protect the groundwater resources of the state and the public health and safety of its residents, the Division of Waste Management (DWM) of the FDEP began investigations to assess potential sources and associated environmental impacts related to PFAS at known or suspected sites, including Department of Defense (DOD) facilities, fire training facilities, and state funded waste cleanup sites. Although PFAS are not typically known to be used by the drycleaning industry, the FDEP Drycleaning Solvent Cleanup Program (DSCP) initiated a pilot study to investigate the potential presence of PFAS at DSCP facilities. The objectives of this study were to:

- Determine whether PFAS impacts may be present at drycleaning sites,
- Evaluate whether PFAS impacts are attributable to drycleaning operations or to an offsite source, and;
- Understand the environmental behavior of PFAS and its impacts at drycleaning facilities.

INVESTIGATION APPROACHES AND METHODOLOGY

Literature Review

PFAS-based agents are commonly used, among other functions, for the surface treatment of clothing fabrics and other textiles to make the materials water and stain resistant. "Side-chain-fluorinated polymers" can be formed by impregnating a mixture of reactive PFAS to the surface of the fabrics (Holmquist, et al. 2016). Clothing and other textiles can also contain a variety of non-polymeric PFAS, consisting of trace residues of raw materials, intermediates or metabolites from the production of impregnating agents and impregnated clothes or through formation by the decomposition of the impregnating agents in the textiles.

A variety of PFAS have been detected in textiles and clothing. PFAS could be released from PFAS-impregnated clothing through cleaning (wet/dry) of the textiles. Theoretically, drycleaning solvent is anticipated to enhance PFAS release rates from clothes, with limited studies having shown that PFAS were released in greywater or drycleaning site effluent (Clara, et al. 2008, Lassen, et al. 2015). Although PFAS have been incorporated in many surfactant/solvent production processes, no studies are available regarding their presence in chlorinated solvents. A study by the US EPA (EPA, 2009) revealed that PFCAs are present in 116 articles of commerce, including commercial carpet care products, household fabric-care liquids and foams, and impregnated apparel. In addition to PFAS use in fabrics, PFAS may be used as ingredients of cleaning agents. To date, no studies have been reported regarding PFAS presence and release mechanisms from drycleaning processing and facilities.

It should be noted that potential release rates of PFAS from drycleaning operations would depend on the type and age of laundered clothes and the operational practices of the facility. PFAS releases to the environment would be expected to closely mimic that of chlorinated solvents in drycleaning practices (i.e., waste material spills, mop water discharges, separator water discharges, etc.). Upon release, PFAS may remain in the unsaturated zone where high organic carbon content in the matrix exists and subsequently migrates into the saturated zone from precipitation events. Because of their persistence and mobility PFOS/PFOA may travel as far as trichloroethene under the same conditions without degradation based upon reported organic carbon and mineral partitioning coefficient values. PFAS in the saturated zone may have relatively larger groundwater plumes than volatile organic halogens (VOHs) when considering much lower health based cleanup target levels. In addition, some PFAS may be precursors and slowly transition to "terminal PFAS" of PFCAs and PFSAs in the environment. For example, perfluoralkane sulfon-amides and fluorotelomer sulfonic acids in textiles released into the environment can be converted to PFOA and PFOS.

Currently available information does not indicate that PFAS are a known constituent of raw drycleaning solvents, but instead could be attributable to other drycleaning facility functions such as spot treatment solutions, wet laundry, solvent releases following contact with PFAS-containing fabrics, or post-drycleaning fabric treatments.

Description of Study Sites and Initial Screening

In June 2019, the FDEP pilot project was initiated at a subset of eligible DSCP sites to determine whether PFAS are a constituent of concern that may be present. The initial screening included groundwater sample collection from two existing monitoring wells at fifteen pre-selected DSCP facilities throughout the state. The pilot facilities were selected by FDEP and represented sites with known VOH groundwater quality impacts (at varying concentrations) and located throughout the state of Florida (**Figure 1**). Accordingly, the sites exhibit a range of geology, hydrogeology, and surrounding land uses. Furthermore, the sites represented both active and non-active drycleaning facilities, with varying VOH

remediation technologies employed. The two sampling locations at each site were determined based upon the known presence of VOHs and likely VOH release source areas.

The initial screening results indicated the presence of PFAS in groundwater above laboratory practical quantitation limits (PQLs) at fourteen of the fifteen sites, and concentrations above the PGCTLs for PFOA, PFOS, or the sum of PFOA and PFOS in nine of the fifteen sites. The PFOA concentrations reported during the initial screening ranged from below detection limits up to 98 ng/L, while PFOS concentrations ranged from below detection limits up to 120 ng/L. A tenth site (Dryclean World) initially exhibited concentrations below the PGCTLs but greater than one half of the PGCTL. This site later exhibited exceedances of the applicable PGTLs during supplemental sampling. The initial screening sites are illustrated on **Figure 1**:

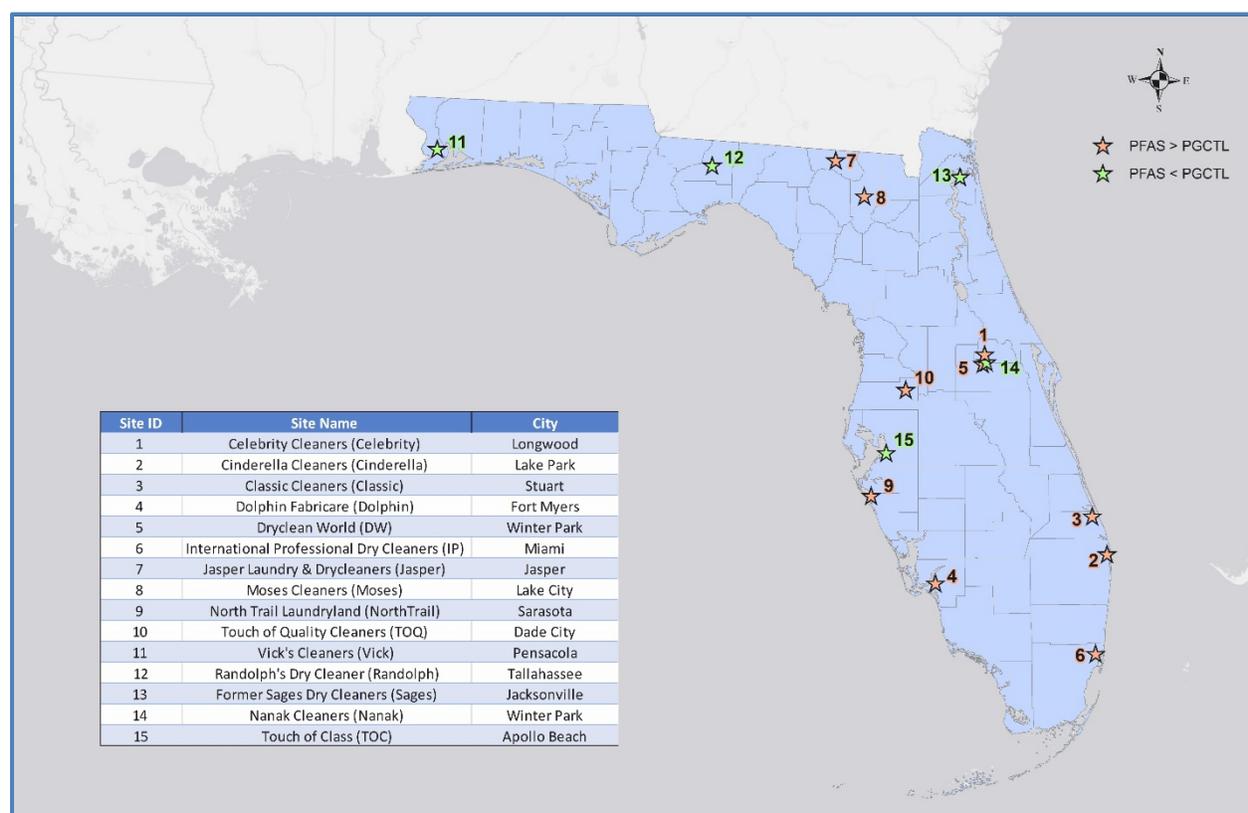


Figure 1. Site Location Map

Site Review and Work Plan

Based upon the results of the initial screening event of the Pilot Study, expanded PFAS investigation activities were conducted at ten (10) sites to further evaluate the extent of PFAS presence to determine whether PFAS are attributable to drycleaning operations, or from offsite sources. The expanded PFAS investigation activities included further evaluations of the site surroundings, site histories, and each site's representative geology and hydrogeology, to facilitate a sampling plan for further investigation activities. A summary of the operational histories of these ten sites is provided in **Table 1**.

Table 1. Summary of Ten Pilot Study Sites

Site ID	Site Name	Years of Active Operations	Solvents Used	PCE Release Mechanism	Remedial History
1	Celebrity Cleaners (Celebrity)	Prior to 1988 - 2020	PCE	Drycleaning Machine Septic Drainfield	SVE ISCO Bioremediation
2	Cinderella Cleaners (Cinderella)	1963 - Current	PCE	Drycleaning Machine	SVE Bioremediation
3	Classic Cleaners (Classic)	1992 - 2017	PCE & Petro-based	Drycleaning Machine	SVE
4	Dolphin Fabricare (Dolphin)	1987 - Current	PCE & Petro-based (Exxon F2000)	Drycleaning Machine	SVE Pump & Treat
5	Dryclean World (DW)	1986 - Current	PCE & Petro-Based (HC Boost™)	Drycleaning Machine Septic Drainfield	Excavation SVE ISCO
6	International Professional Dry Cleaners (IP)	Prior to 1979 - Current	PCE	Drycleaning Machine Rear door area	Ozone Sparging SVE Pump & Treat
7	Jasper Laundry & Drycleaners (Jasper)	Prior to 1946 - 2013	Stoddard Solvent & PCE	Drycleaning Machine Filter Powder Dumping	None
8	Moses Cleaners (Moses)	1968 - Current	PCE	Drycleaning Machine Rear door & Dumpster areas Sanitary Sewer Leaks	AS/SVE Pump & Treat at nearby petroleum site
9	North Trail Laundryland (NorthTrail)	1959 – 1994 (DC) 1994 – Current (Laundromat)	PCE	Possible Drycleaning Machine & Exterior Dumping	None
10	Touch of Quality Cleaners (TOQ)	1989 - Current	PCE & Petro-based (Sensene™)	Drycleaning Machine Possible Sanitary Sewer Leaks	Zero-Valent Iron Injection & pH Adjustment

Sample locations from soil and groundwater included locations near drycleaning machines, near sanitary sewer lines, former drainfield areas, and hydraulically upgradient monitoring wells in order to understand PFAS release mechanisms and subsurface impacts. A questionnaire was also developed to obtain information from current drycleaner operators about former and current operational practices. Samples from raw materials and/or waste stream processes were collected for evaluation of PFAS occurrence during current operations. Based on a typical drycleaning process layout (**Figure 2**), waste stream samples were collected from available locations at most study sites.

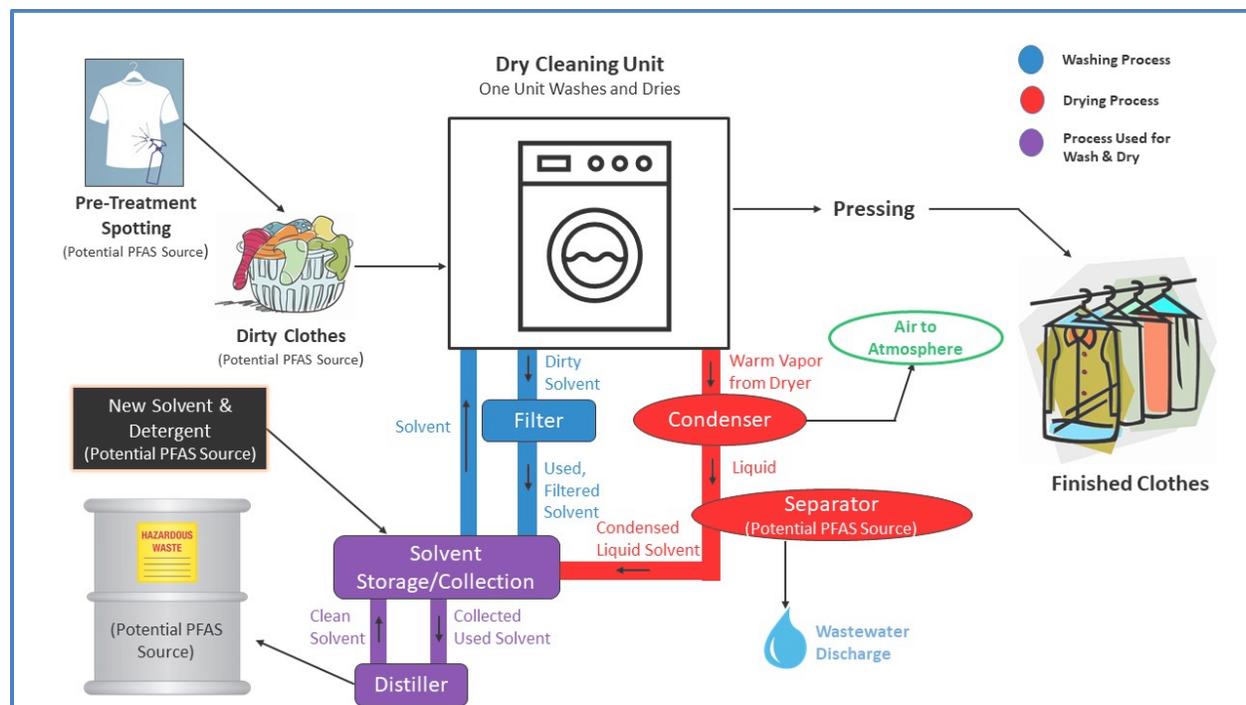


Figure 2. Diagram of the Typical Drycleaning Process and PFAS Sampling Locations

Sample Collection and Analysis

The field investigation activities were performed between June 2019 and August 2021. Quality assurance (QA) and Quality Control (QC) measures included the use of specific field sampling guidelines intended to minimize the potential for sample cross-contamination, along with the incorporation of field/laboratory blanks, and duplicates. All groundwater, soil, and waste stream samples were collected in accordance with the FDEP Field Sampling Standard Operating Procedures (SOPs), including the FDEP's PFAS sampling SOP (FDEP, 2019) and HSW's PFAS Sampling Guidelines (HSW, 2019). Specifically, to reduce the chance of inadvertent PFAS contamination of samples, HSW sampling personnel avoided using PFAS-containing items during the sampling process, such as items commonly used in sampling processes that may contain PFAS include polytetrafluoroethylene (PTFE, also known as Teflon). HSW field personnel avoided using other items which are commonly recognized as potentially containing PFAS such as aluminum foil, post-it notes, waterproof field books, chemical ice packs (e.g., blue ice), and certain decontamination soaps. In addition, field personnel avoided the use of PFAS-containing products such as cosmetics, moisturizers, insect repellent, sunscreen, and hand creams. Nitrile gloves were used during all sample collection activities, including equipment set-up, sample collection, and sealing of containers.

Samples were transferred into laboratory-supplied containers, stored at appropriate temperatures, and submitted to selected laboratories for analysis of PFAS compounds by EPA Method 537 (modified) and laboratory specific SOPs. The PFAS compounds analyzed included eleven PFCAs (C4 through C14 carbon-chain), seven PFSA (C4 through C10 carbon-chain), three perfluoroalkane sulfon-amides (N-Me perfluorooctanesulfonamide acid (MeFOSAA), N-Et perfluorooctanesulfonamide acid (EtFOSAA), perfluorooctane sulfonamide (PFOSA)), three fluorotelomer sulfonic acids (4:2 Fluorotelomer sulfonate (4:2 FTS), 6:2 Fluorotelomer sulfonate (6:2 FTS), 8:2 Fluorotelomer sulfonate (8:2 FTS)) and four replacement compounds in lieu of PFOS/PFOA (11Cl-PF3OUdS (F-53B Minor), 9Cl-PF3ONS (F-53B Major), ADONA, and HFPO-DA (GenX)). These PFAS are reportedly used as nonpolymer coatings or side-chain

polymers in textiles to provide oil- and water- repellent and stain release finishes (ITRC, 2020). In order to evaluate the correlation between PFAS and drycleaning solvents, VOHs were analyzed for select samples by EPA Method 8260. In addition, field parameters and groundwater elevations were measured to evaluate PFAS fate and transport in groundwater.

Some non-aqueous samples such as pure solvent samples and waste stream samples were prepared/processed by a laboratory-specific SOP prior to analysis. Specifically, a subsample of 15 mL for each solvent sample (like PCE) was concentrated to dryness through evaporation and reconstituted prior to analysis; and other cleaning products were diluted (e.g., 25 mL portion of sample diluted to 250 mL with PFAS-free water) prior to Liquid Chromatography and Tandem Mass Spectrometry (LC-MS/MS) analysis. Validation of the laboratory data was conducted upon receipt.

RESULTS AND DISCUSSION

Groundwater Results

Results from the initial June 2019 statewide sampling event indicated the presence of PFAS above laboratory practical quantitation limits (PQLs) at fourteen (14) of the fifteen (15) sites sampled. At nine sites, concentrations of PFOA, PFOS, or the sum of PFOA and PFOS exceeded the PGCTL of 70 ng/L. Following review of the data from the limited sampling project, expanded PFAS investigations were initiated at the nine sites exhibiting data above the PGCTLs, and an additional site was added based on subsequent sampling exhibiting PFAS above PGCTLs. The expanded investigations included the sampling of additional existing monitoring wells both onsite and offsite, with installation of additional monitoring wells conducted at select sites to assist in the investigations. A summary of the PFOA and PFOS concentrations in groundwater reported during the pilot project are summarized in **Table 2** below:

Table 2. Maximum Detected PFOA and PFOS Concentrations in Groundwater

Site Name	Maximum Detected Concentration (ng/L)*		Sample Description
	PFOS	PFOA	
Celebrity	716	113	Shallow/Former drainfield area onsite
Cinderella	1,520 (879)	111 (72.5)	Intermediate/Sidegradient well offsite
Classic	355	106	Shallow/downgradient well onsite
Dolphin	130	890	Infiltration gallery sample
DW	561 (25.3)	82 (11)	Shallow/Former drainfield area at rear of drycleaner (onsite)
IP	3,480 (1,980)	2,640 (1,180)	Shallow/Former drainfield area onsite
Jasper	2,000	758	Shallow/downgradient well offsite near rear of former drycleaner
Moses	139	50.9	Shallow/upgradient well offsite
NorthTrail	340	96	High PFOS in shallow upgradient well High PFOA in shallow downgradient well
TOQ	40.1	58.6	Shallow onsite well

* (#) Represents minimum temporal concentrations detected at the same well

The maximum groundwater PFOA concentration from all samples collected was 2,640 ng/L and the maximum PFOS concentration was 3,480 ng/L, reported from the same sample from a monitoring well located at International Professional Dry Cleaners (IP) in Miami. This sample was located near a former drainfield that was historically used for disposal of effluent from an onsite wastewater treatment system for the tenants of a shopping center. Although no historical operational data is available, the aeration and oxidation process of the wastewater treatment system would be expected to remove VOHs if any releases occurred into the historical system, but have limited effectiveness on PFAS. The second highest

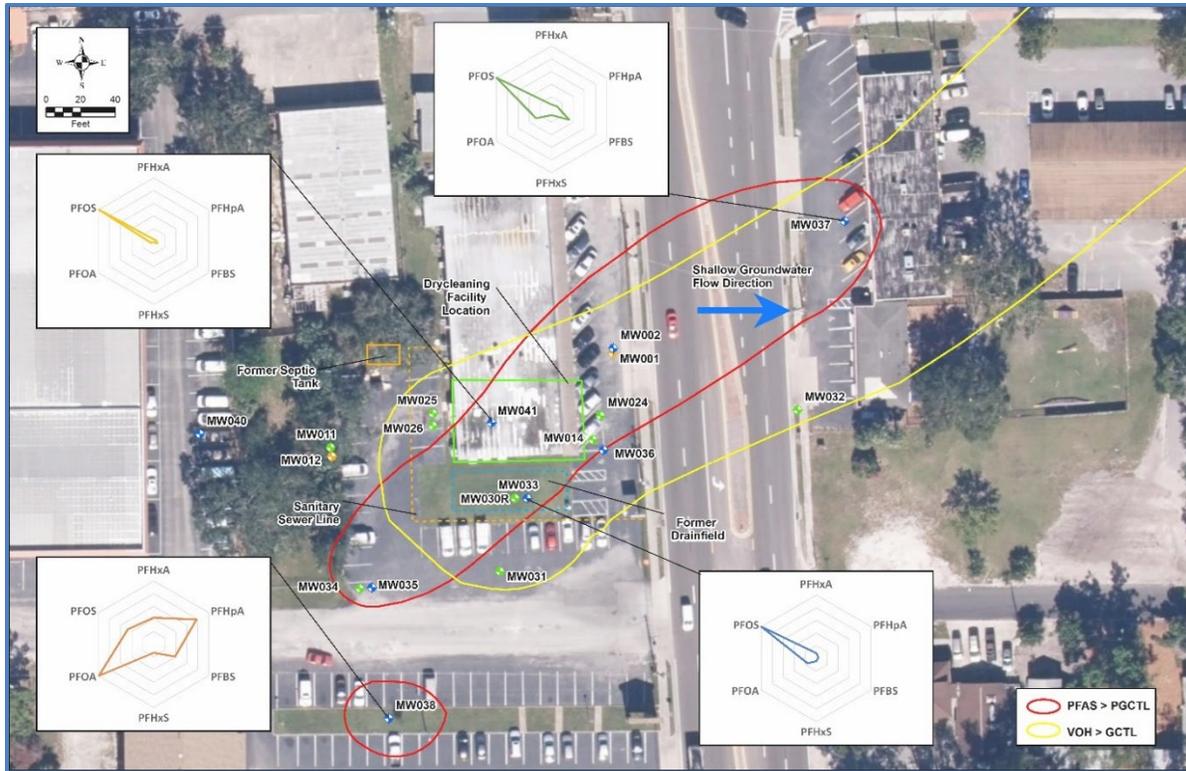
PFOS concentration of 2,000 ng/L of PFOS was measured in a monitoring well located at the Jasper site, near a location where drycleaning filter powder is known to have been disposed of, resulting in substantial PCE impacts. The maximum concentrations of PFOA/PFOS at the remaining sites ranged from approximately 50 ng/L to 900 ng/L.

Temporal fluctuations in PFAS concentrations were noted in some source wells, believed to be due to mass flux from the vadose zone source caused by rainfall infiltration and/or desorption when the groundwater table rose. For instance, at the Dryclean World (DW) site, PFOA and PFOS concentrations in groundwater in the source area with vadose zone soil impacts varied from below the PGCTL to several hundred ng/L, over the course of several quarterly sampling events.

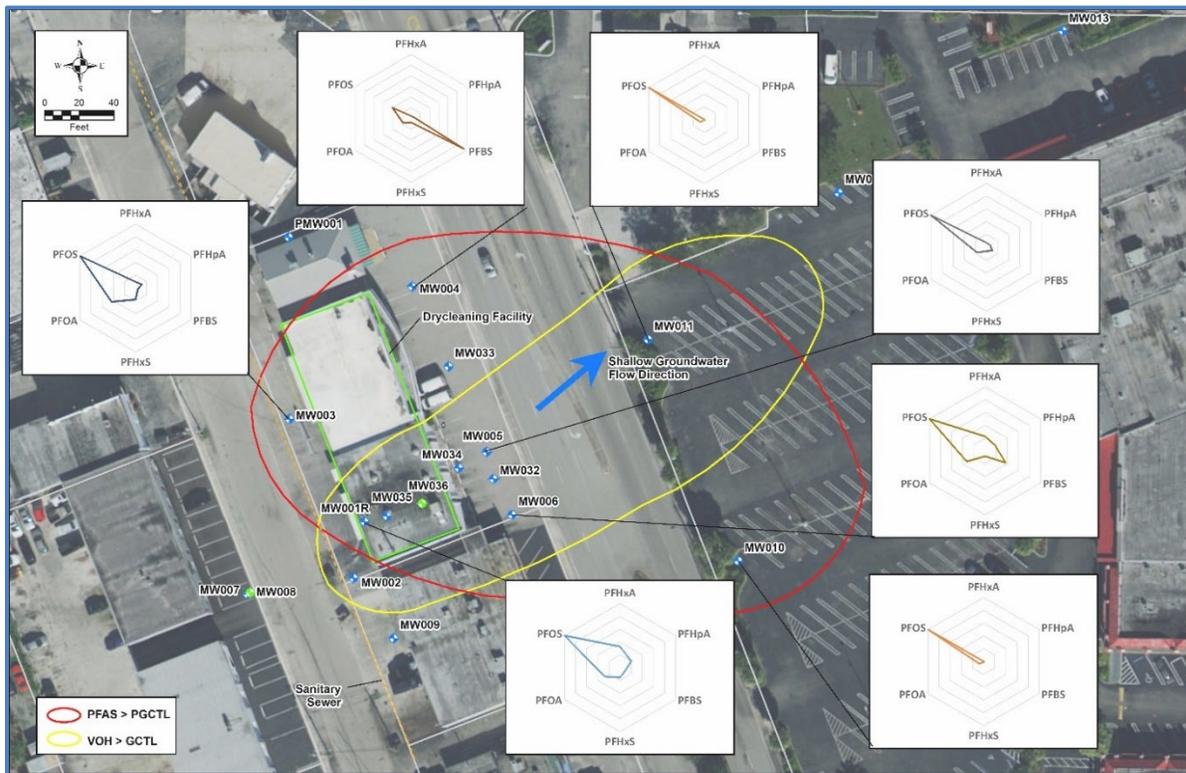
Evaluations of the PFAS data, as compared to applicable drycleaning-solvent related constituent (PCE and metabolic breakdown products) concentrations, generally did not exhibit strong positive correlations in concentrations, with some exceptions (i.e., Jasper, Moses). This circumstance is believed to be due to differences in the fate and transport between PFAS and PCE. PCE may have undergone faster natural degradation through abiotic and biological processes in the subsurface, whereas PFOA/PFOS are not anticipated to undergo natural attenuation other than physical processes (e.g., sorption/desorption, and dilution). Another potential factor affecting the poor correlation between PFAS and PCE concentrations is previous remedial activities (i.e., in-situ chemical oxidation, soil vapor extraction, and enhanced anaerobic bioremediation) which are known to remove PCE but have limited effects upon PFAS compounds.

Excluding chemical and biological degradation, due to relatively higher hydrophobic characteristics (i.e., higher retardation factors), PFAS molecules have a tendency to migrate slower than PCE and its breakdown products in saturated zones. PFOA/PFOS were rarely detected at intermediate or deep zones where PCE and its breakdown products were present, supporting the relatively slower migration for PFOA/PFOS than PCE. In addition, other sources of PFAS from upgradient or nearby locations may have contributed to PFAS in groundwater. Specifically, PFOA/PFOS were detected at elevated concentrations at hydraulically upgradient locations at the North Trail Laundryland, the Moses Cleaners, and the Celebrity Cleaners sites.

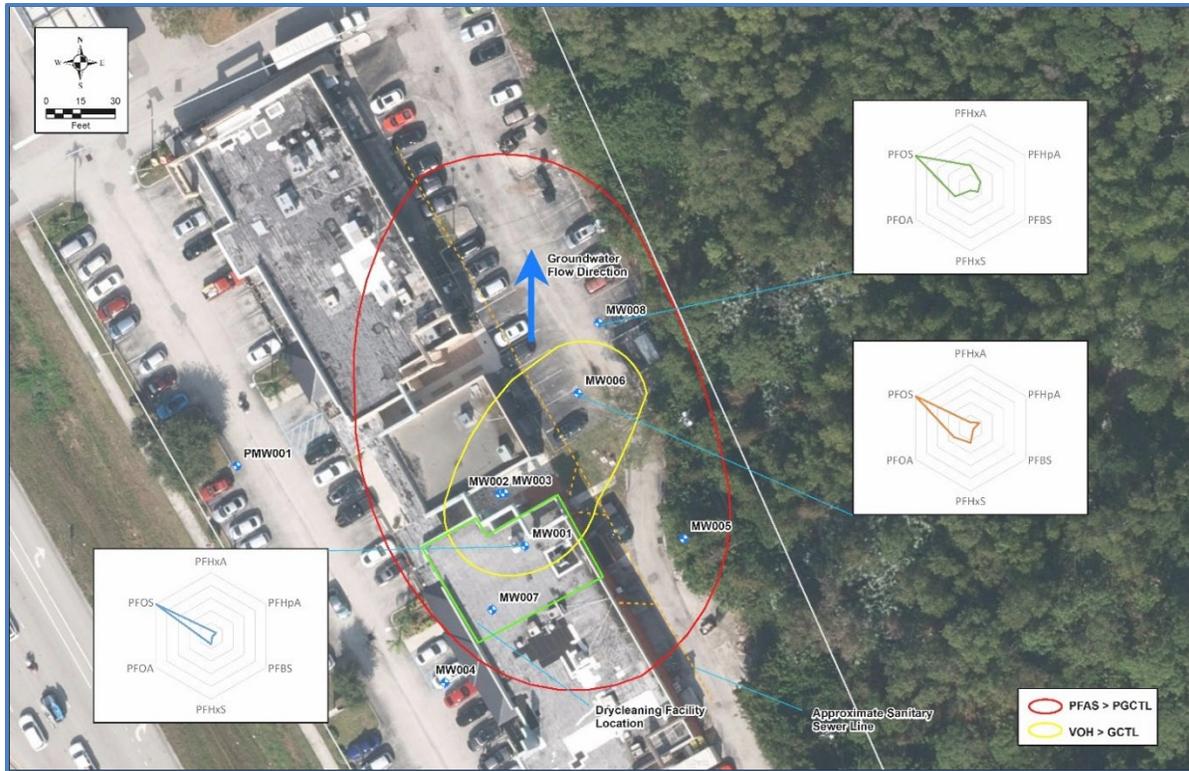
Although upgradient or regional urban background PFAS may be present at some sites (e.g., Celebrity, Dolphin, Moses, North Trail), a PFOA/PFOS plume is generally co-present with chlorinated solvents in the vicinity of the subject drycleaning sites (**Figure 3**), supporting that elevated PFOA/PFOS are associated with the drycleaning sites. The lateral extent of PFOA/PFOS impacts above their PGCTL are mostly limited to the shallow groundwater in the vicinity of the drycleaning facilities. Radial diagrams of detected PFAS were used to illustrate spatial trends for individual PFAS constituents (inserts of six-PFAS radial diagrams are shown for key wells on each site plume map below). Different PFAS distribution patterns at hydraulically upgradient offsite monitoring wells from onsite or hydraulically downgradient wells provided evidence of upgradient offsite PFAS sources in addition to the drycleaning facilities, such as MW038 at Celebrity (Figure 3. a), PMW002 at Dolphin (Figure 3. d), MW041 at Moses (Figure 3. h), and MW021 at North Trail (Figure 3. i). In addition, the six-PFAS radial diagrams indicate variations in PFAS-distribution patterns between locations near drycleaning facility and locations hydraulically downgradient at most of the sites, indicating that distribution patterns change along the fate and transport based on retardation factors for the six PFAS compounds (relative migration rates $PFHxA > PFHpA > PFOA > PFBS > PFHxS > PFOS$ based upon their reported Koc values (ITRC, 2020)). Theoretically, relatively more PFCAs than PFSAs are expected along a transport pathway, which were observed at most of the sites; however, there are exceptions such as the Cinderella site (**Figure 3.b**), where relatively dominant PFOS was noted at downgradient locations. The relatively more dominating PFOS at downgradient wells is likely due to offsite sources or earlier PFOS-dominating releases.



3a. Celebrity Cleaners



3b. Cinderella Cleaners



3c. Classic Cleaners



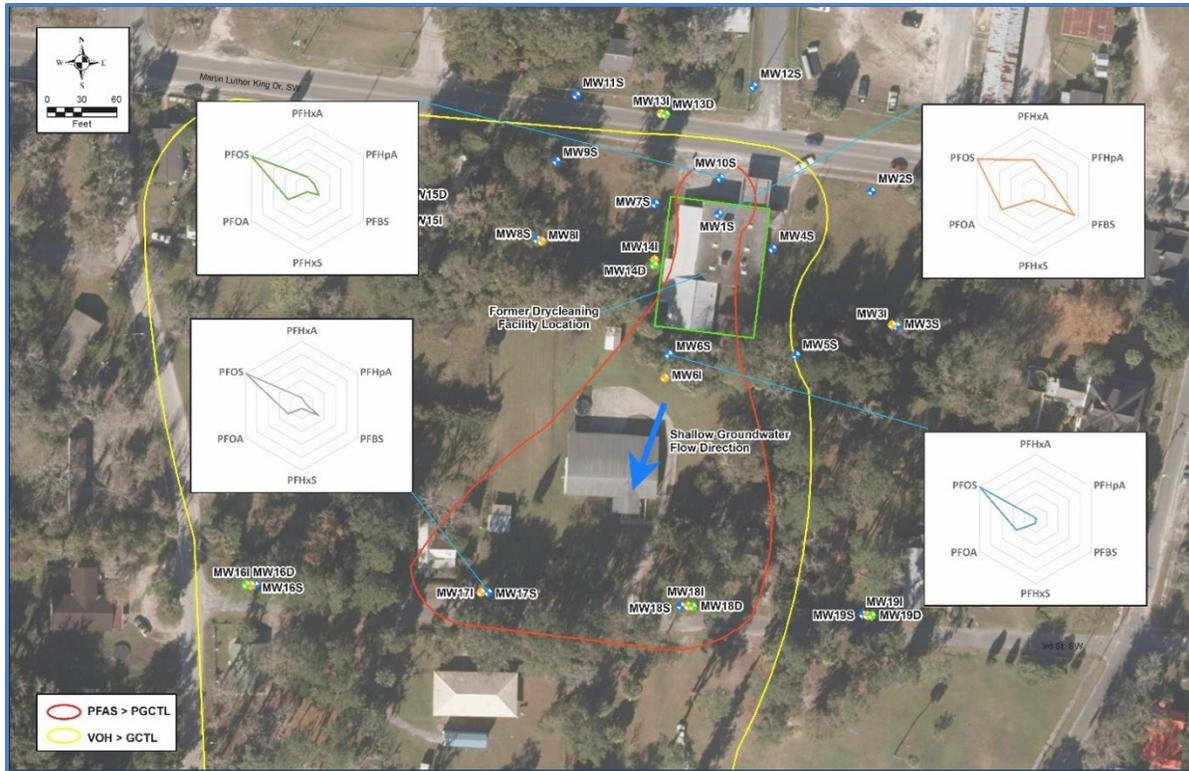
3d. Dolphin Fabricare



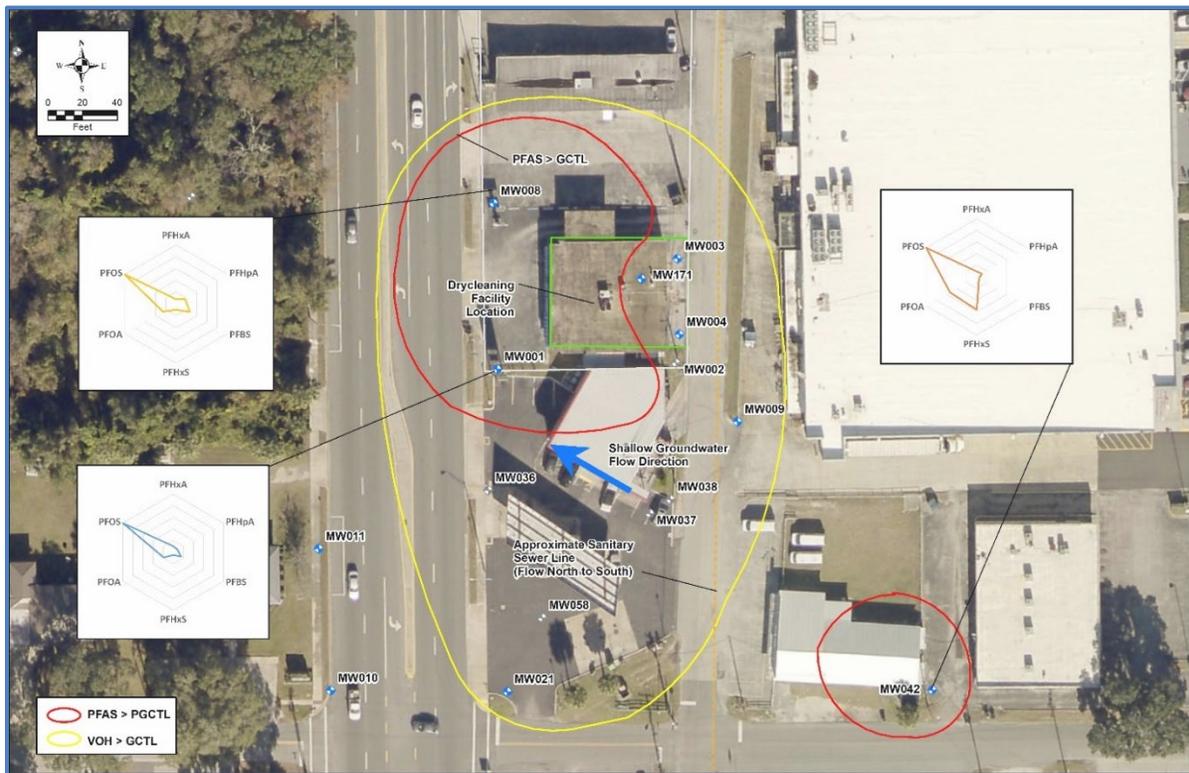
3e. Dryclean World



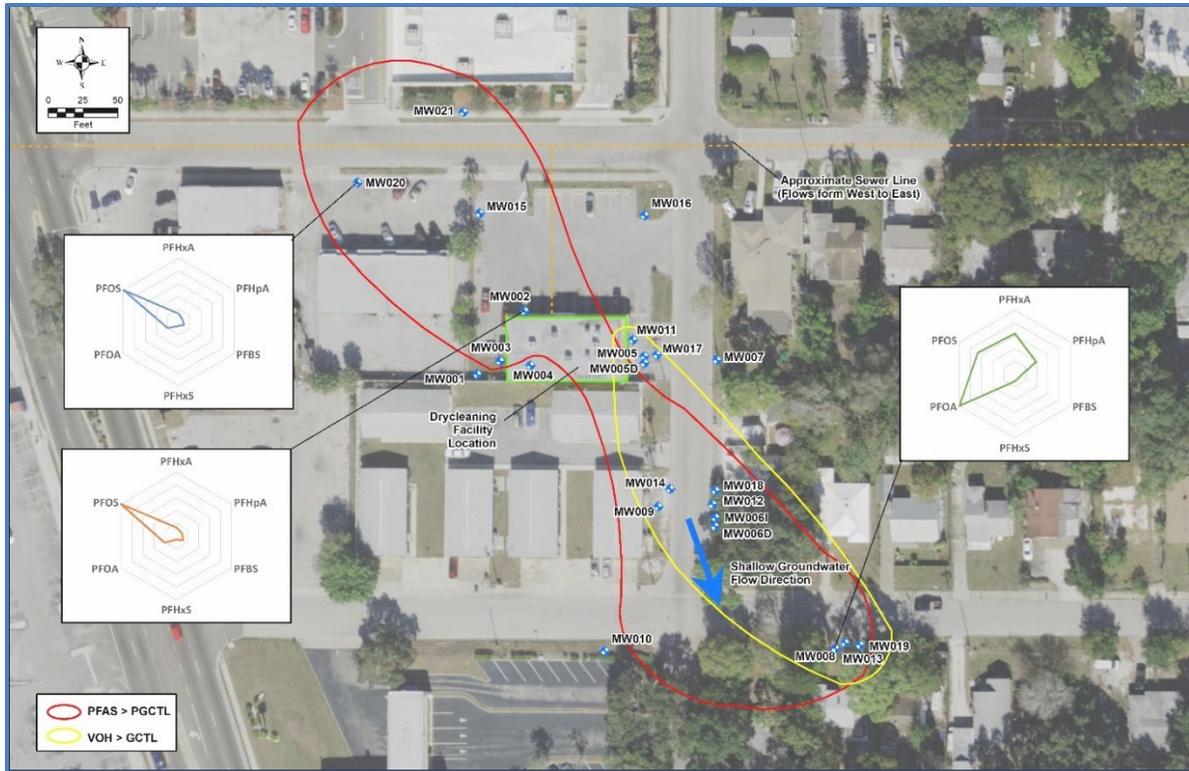
3f. International Professional Dry Cleaners



3g. Jasper Laundry and Dry Cleaners



3h. Moses Cleaners



3i. North Trail Laundryland



3j. Touch of Quality Dry Cleaners

Figure 3. PFOA/PFOS versus VOH Groundwater Plume at 10 Sites
 (inserts represent PFAS distribution at key wells across each site)

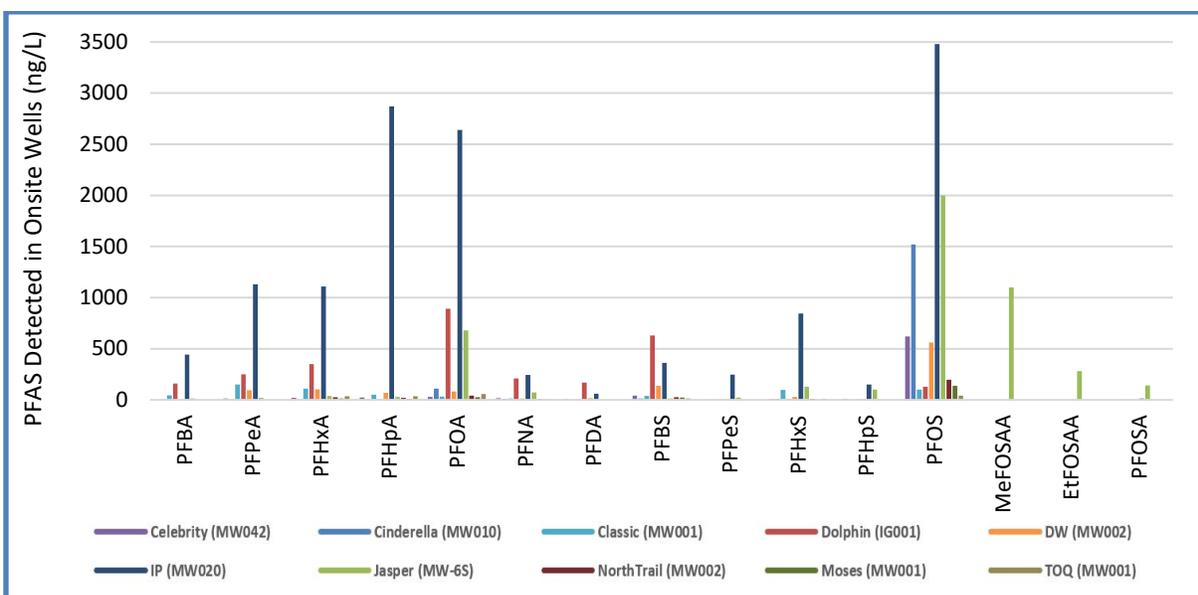


Figure 4. PFAS Detected at Onsite Monitoring Wells

In addition to prominently detected PFOA and PFOS, several other PFAS were detected in groundwater, primarily C4 through C10 carbon-chain PFCAs and C4 through C7 carbon-chain PFSA (Figure 4). PFOS precursors MeFOSAA, EtFOSAA and PFOSA were only detected in MW-6S at the Jasper site near the known filter powder disposal and PCE-release source area.

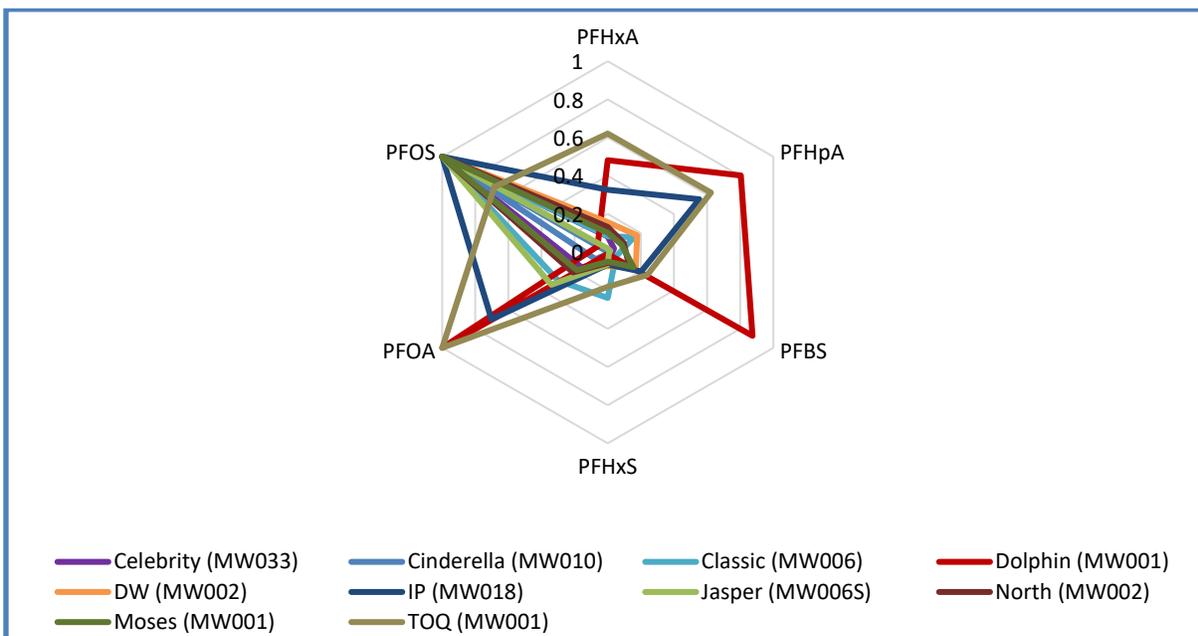


Figure 5. Normalized PFAS Radial Diagram at Onsite Wells with Highest Concentrations

Certain similar PFAS distribution patterns are not observed across the Pilot Study sites (Figure 5), due to lack of fabrics type/age and solvent release timeframe and locations, and other indistinguishable PFAS sources. However, a general similar pattern with relatively prominent PFOS was observed at most of the sites, with the exceptions of the Dolphin and TOQ sites, which had relatively higher abundance of PFOA, PFHxA, PFHpA and PFBS in comparison to PFOS. In addition, other PFAS compounds (PFHpA and PFOA) were detected at relatively higher concentration at the IP site. The relatively lower PFOS in Dolphin and

TOQ are likely effects of previous VOH remedial activities. For example, groundwater remediation using pump and treat with granular activated carbon was conducted at the Dolphin site and the treated groundwater was discharged into an infiltration galley. PFOS may have been removed more efficiently than other compounds due to its higher Koc value when compared to the other five PFAS. It is known that zero valent iron (ZVI) is effective in reducing concentrations of PCE and its breakdown daughter products, whereas limited studies are available regarding ZVI effectiveness on PFAS removal. A study by Arvaniti et al. (2015) indicates that ZVI has a higher removal efficiency for PFOS than PFOA, likely due to more surface adsorption on ZVI material. Therefore, the previous injection of ZVI as a remedy for VOHs at the TOQ site may have affected the PFAS distribution pattern. The former wastewater treatment system and discharge into the former drainfield at the IP site may have contributed more PFAS to the site.

Soil Results

Soil samples were collected for analysis to evaluate the potential presence of PFAS in soil that may contribute to groundwater quality impacts. The soil samples were collected from various locations based on the site review and work plan, while taking into consideration individual site logistics and constraints. These locations included near drycleaning machines, near sanitary sewer lines, former drainfield areas, and near monitoring wells exhibiting elevated concentrations of PFAS in groundwater in specific cases.

PFOA/PFOS concentrations in soil samples were reported at one to three orders of magnitude lower than the health based SCTLs for residential direct exposure (1,300 micrograms per kilogram ($\mu\text{g}/\text{kg}$)), however samples collected from several sites exhibited PFOA or PFOS concentrations near or above the Provisional Leachability based on Groundwater Criteria SCTLs (7 $\mu\text{g}/\text{kg}$ for PFOS and 2 $\mu\text{g}/\text{kg}$ for PFOA). Additional PFAS compounds, particularly C9 through C14 carbon-chain PFCAs, were detected above laboratory Method Detection Limits (MDLs) in some samples, however in most cases PFOS and/or PFOA were detected at higher concentrations or more frequently, with the exception of the Dolphin site, where FPDA, PFUnA, and PFDoA were detected at concentrations higher than PFOS, and the Jasper site, where MeFOSSA and EtFOSSA were detected at concentrations higher than PFOS. The soil sample results for PFOA and PFOS are summarized in **Table 3** below:

Table 3. Detected PFOA and PFOS Concentrations in Soil

Site Name	Maximum Detected Concentration ($\mu\text{g}/\text{kg}$)		Sample Description
	PFOS	PFOA	
Celebrity	5.6	0.25 I	PFOS at former drainfield area PFOA inside former facility building
Cinderella	1.2	0.25 U	Inside facility building
Classic	0.64	0.30 U	Outside rear of facility
Dolphin	2.3	1.5	Outside rear of facility
DW	61.2	3.3	Former drainfield area at rear of facility
IP	14.9	8.7	PFOS at former drainfield area PFOA at rear of drycleaner/former onsite wastewater treatment plant area
Jasper	121	24.8	Rear of former drycleaner
Moses	7	0.24 I	PFOS at offsite upgradient location PFOA inside facility building
NorthTrail	1.6	0.14 I	PFOS onsite near sanitary sewer line PFOA onsite outside building
TOQ	0.80	0.11 I	Onsite outside building

The Synthetic Precipitation Leaching Procedure (SPLP) was completed on select soil samples exceeding the default Provisional SCTLs for Leachability based on Groundwater Criteria, with the analytical results confirming leachate levels above the PGCTLs for PFOS, PFOA, and/or the sum of PFOS and PFOA. It is known that the default Provisional SCTLs are based on specific geotechnical values (fraction of organic carbon [Foc], for instance) and PFAS compound specific physical properties (organic carbon-water partition co-efficient, Koc) and that leaching of PFAS from soil to groundwater may occur at concentrations below the default SCTLs depending on site-specific conditions. The SPLP data exhibited PFOA/PFOS in soil at concentrations around their leachability-based Provisional SCTLs had potential to cause groundwater impacts.

As indicated in **Table 3**, the highest PFAS concentrations in soil were detected near former septic system drainfield areas at two sites (DW and IP) and outside the rear of the former drycleaner at the Jasper site (known historical filter powder dumping area). These elevated PFOA/PFOS concentrations in vadose zone soils are collocated with the highest PFAS groundwater impacts and generally with the historical VOH release areas at these sites (with exception of IP). Although PCE and its breakdown products are not present currently in these locations at DW and IP due to natural attenuation and/or active remediation activities, PFAS are still present in the vadose zone soil, resulting in continuing mass flux into groundwater dependent on infiltration and groundwater elevation changes. For example, PFOA and PFOS concentrations at the source well in the Dryclean World site varied by one order of magnitude, from 1 ng/L in June 2019 to 88 ng/L in October 2020 for PFOA and from 34 ng/L in June 2019 to 561 ng/L in October 2020 for PFOS, which was not surprising based upon the high SPLP results from the soil (highest concentrations reported at 113 ng/L for PFOA and 1,780 ng/L for PFOS).

Waste Stream Results

In addition to analysis of environmental media (soil and groundwater), samples of raw and waste materials from the drycleaning and wet laundry processes, where applicable and feasible based on the typical drycleaning process (**Figure 2**), were collected to further assist in the evaluation of the presence of PFAS associated with drycleaners. These types of samples were collected from active drycleaners, a recently abandoned drycleaner, and a former drycleaner now operating as a laundromat. Given the varying operational practices and layouts of the facilities, the types of samples collected varied, however where possible, samples were collected of or from:

- Solvents used in the drycleaning process;
- Sample(s) from the spotting agent(s) or detergent(s) used in the drycleaning or wet laundry process(es);
- Sample of potable water prior to the wet laundry process;
- Sample from spent solvent at the drain line of the drycleaning machine;
- Sample(s) from the hazardous waste storage containers (liquid, filtrate material, and unrecovered solvent);
- Sample from water collected after the condenser and separator process;
- Water and/or residue sample(s) from the discharge of the wet laundry process and/or at the sanitary sewer pipe, or nearby manhole;

A majority of the active drycleaners in the pilot study do not store raw solvents onsite. Rather, most drycleaners have solvent delivered and placed directly into the drycleaning machines for immediate use. One active drycleaner in the pilot project stored raw PCE-based solvent onsite and one active drycleaner had an alternative solvent (Sensene™) available for sample collection.

Table 4: PFOA/PFOS Concentrations from Samples Collected within Drycleaning Process

Site Name *	Detected Concentrations (ng/L)**		Sample Description
	PFOS	PFOA	
Celebrity	<15	<10	Raw Stain Remover
	<15	8.48	Raw Drycleaning Machine Cleaner
	--	--	Raw PCE Solvent not available
	<80	<80	PCE Inside Machine (after filter)
	2,901.2	1,621.1	PCE Waste (Machine Bottom)
	18,549.4	20,559.3	PCE Waste from Waste Drum
Cinderella	<80	<80	Raw Drycleaning Stain Remover
	--	--	Raw PCE Solvent not available
	11.34	31.56	Used PCE Inside Machine (after distiller)
	66.58	99.61	Used PCE Inside Machine (before distiller)
	13.87 (ng/g)	43.29 (ng/g)	PCE Waste from Waste Drum
Dolphin	<80	<80	Raw Drycleaning Machine Soap
	2,284.1	1,046.8	Raw Petro-based Solvent mixed w/Soap (prior to use)
	0.77	65.52	Drycleaning Machine Water Effluent
	121.9 (ng/g)	10.65 (ng/g)	Waste Contents from Waste Drum (Solid)
	16,597.6	2,812.4	Waste Contents from Waste Drum (Liquid)
DW	<80	<80	Raw Stain Remover
	<80	<80	Raw Drycleaning Detergent
	--	--	Raw Solvent (HC Boost™) not available
	<80	<80	Solvent Waste from Waste Drum
IP	<80	<80	Raw Stain Remover
	--	--	Raw PCE Solvent not available
	100.2	<80	Drycleaning Machine Separator Water
	97.7	<80	Spotting Machine Condensate Waste
	421.9	380.9	Used PCE Inside Machine
Moses	<16.67	<25	Raw PCE Solvent
	<16.67	<25	PCE Solvent at Separator
	56.83	641.68	Water Sample at Separator
	52.01	42.25	Spotting Machine Condensate Waste
	31.77	106.46	Used PCE Inside Machine
	9.52 (ng/g)	36.92 (ng/g)	PCE Waste from Waste Drum
TOQ	<80	<80	Raw Spotting Agent
	<80	<80	Raw Solvent (Sensene™)
	2.33 (ng/g)	4.37 (ng/g)	Filter Contents
	19,639.9	10,382.6	Spent Sensene™ Solvent from Waste Drum
	21,452.2	12,010.6	Spent Sensene™ Solvent from Waste Drum (Duplicate)

* No waste stream samples collected from inactive Classic and Jasper sites

**Certain samples analyzed as solid samples with analytical results provided in nanograms per gram (ng/g) (equal to micrograms per kilogram (µg/Kg))

Within the raw material and waste stream samples collected from the facilities themselves, elevated PFAS concentrations were detected primarily in the waste storage drums and from used solvent samples (both PCE and petroleum-based) collected from the discharge of the drycleaning machines, while influent water, raw solvents, detergents and soaps used during the drycleaning or wet laundry processes generally exhibited low or non-detect PFAS concentrations (Table 4 and Table 5). Compared to those in groundwater (Table 2), PFOA/PFOS concentrations in drycleaning waste streams were observed two to three orders of magnitude higher (Table 4). It should be noted that PFOA/PFOS were detected at low parts per trillion (ppt) levels in raw materials sampled, however, the solvent mixed with soap at the

Dolphin site exhibited PFOA/PFOS concentrations (1,046.8 and 2,284.1 ng/L, respectively) above their PGCTL of 70 ng/L.

In addition to PFOA/PFOS, several other PFAS were detected in the spent solvents at drycleaning facilities (**Figure 6**). PFHxA and PFOA precursors, 6:2 FTS and 8:2 FTS, were measured at similar or higher concentrations than PFHxA/PFOA (Celebrity and Dolphin sites), particularly 8:2 FTS at the Dolphin site. If this spent solvent is released to the subsurface, transformation of these precursors to PFOA over time may continue to contribute to PFOA concentrations in the groundwater. A very high concentration of C11 PFCA (PFUnA) was noted in the spent solvent at the Dolphin site, which represents an outlier to the other data sets. Low levels of MeFOSAA, EtFOSAA, PFOSA and GenX were detected above the method detection limits in the spent solvents at the Moses site (data not shown).

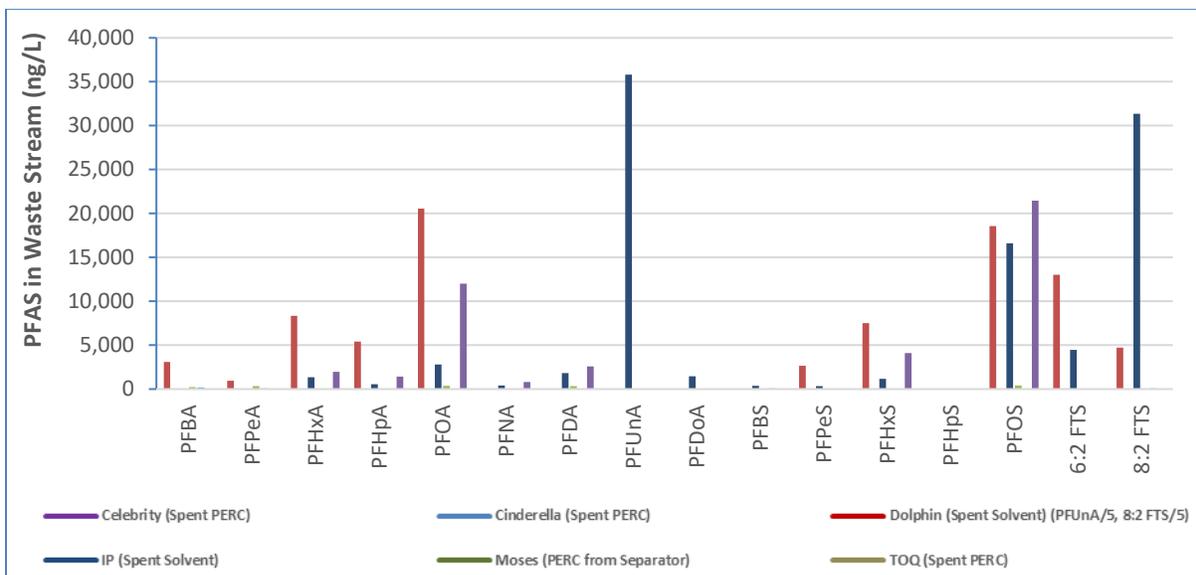


Figure 6. PFAS Detected in Waste Streams.

PFOA and PFOS were detected at low ppt levels in laundry influent waters, which represent the site tap water source. Slightly elevated PFOA/PFOS concentrations were observed in wet laundry effluent samples at the Dolphin site and the Moses site (**Table 5**). The concentrations at the Moses site were above the FDEP’s PGCTL of 70 ng/L for PFOA/PFOS. The levels of PFAS in wet laundry effluent water are similar to the values reported by previous reports (Lassen, et al. 2015).

Table 5: PFOA/PFOS Concentrations in Wet Laundry Samples

Site Name	Detected Concentrations (ng/L)		Sample Description
	PFOS	PFOA	
Celebrity	1.74	1.26	Influent Potable Water
Cinderella	<80	<80	Laundry Detergent
	1.12	1.04	Influent potable water
	2.8	2.1	Laundry discharge
Dolphin	<80	<80	Laundry Detergent
	3.22	0.88	Influent potable water
	14.88	8.4	Laundry discharge
IP	128	<80	Laundry Detergent
	21.2	6.2	Influent potable water
	24.6	<10	Laundry discharge
Moses	<2.06 (ng/g)	<2.06 (ng/g)	Laundry Detergent
	1.08	<1.21	Influent potable water
	279	103.16	Laundry discharge
DW	3.06	2.26	Influent Potable Water
TOQ	<80	<80	Influent potable water
	2.36	57.58	Laundry discharge

Raw Solvent Sampling

In addition to the environmental media sampling and drycleaning and wet laundry waste stream sampling, samples of various types of raw drycleaning solvents were obtained from solvent suppliers in Florida and analyzed for PFAS (**Table 6**). PFAS were not detected above the laboratory detection limits in any of the raw solvent samples analyzed, with the limited exceptions of a PFBS detection within one PCE sample and a PFBA detection within a sample of Intense solvent. PFBS was not detected in a subsequent analysis of PCE, and thus the detections of these analytes are deemed anomalous. Most notably, no PFOS or PFOA were reported above laboratory detection limits, indicating that drycleaning process is the primary contributor to the presence of PFAS in the spent solvents (**Table 4** and **Figure 6**).

Table 6: PFAS Concentrations from Raw Solvent Samples Obtained from Distributors

Solvent Type	PFOS (ng/L)	PFOA (ng/L)
Perchloroethylene	<156	<158
	<156*	<158*
Solvon K4	<156	<158
GreenEarth	<156	<158
Intense®	<156	<158
Exxon Mobil DF2000™	<156	<158
Solvon K4**	<156	<158
Exxon Mobil DF2000™**	<156	<158
Kwik Dri 66	<156	<158
HC Boost™	<156	<158
Sensene™	<156	<158

* Remaining sample volume from Sample 01 was reanalyzed and identified as Sample 01R

** Blind Duplicate

CONCLUSIONS AND IMPLICATIONS

Conclusions

Based on the findings from this pilot study, although urban background PFAS may provide some contribution to the PFAS concentrations reported in groundwater at several drycleaning sites, drycleaning and/or wet laundry activities are also contributing to elevated PFAS concentrations found in the vicinity of the pilot project facilities. The levels of PFAS exhibited in groundwater and soil at drycleaning facilities varied by one to two orders of magnitude, from low ppt levels to low parts per billion (ppb) levels. The median concentrations of PFAS detected at the pilot drycleaning facility sites are above typical urban anthropogenic background levels. Typical urban anthropogenic background levels are indicated on Figure 6-3 and Table 17-3 of the ITRC PFAS Technical and Regulatory Guidance Document and Fact Sheets.

Although strong positive correlations between PFAS and VOHs were not observed at the majority of the pilot sites, a PFOA/PFOS plume is generally co-present with chlorinated solvents in the vicinity of the facility, providing supporting evidence that elevated PFOA/PFOS are associated with the drycleaning sites. The highest PFOA/PFOS concentrations were often identified near drycleaning machines and site drainage locations, which were also identified as PCE sources areas, indicating that one potential release mechanism for PFAS is associated with drycleaning solvent waste releases. PFOA/PFOS were rarely detected at intermediate or deep zones where PCE and its breakdown products were present, supporting the relatively slower migration of PFOA/PFOS compared to PCE. Limited soil data also supports the presence of PFAS at known release areas. Concentrations of PFOA/PFOS detected in soil are below their Provisional Residential Direct Exposure SCTLs, but above their provisional leachability SCTL based on protection of groundwater quality at several sites.

PFOA and PFOS are not present above the laboratory method detection levels in the raw solvents themselves. Elevated PFAS concentrations are observed in wastes and discharges following drycleaning and wet laundry processes, indicating that PFAS are leaching from fabrics during the laundering or drycleaning processes. Waste materials from drycleaners generally contain high concentrations of PFAS, which along with their corresponding distribution in the environment, supports the hypothesis that the presence of PFAS at drycleaners is more likely attributed to releases following contact with PFAS-containing fabrics than a component of drycleaning solvents themselves.

A general pattern of PFAS composition or a correlation with drycleaning solvents was not observed due to uncertainties in the history of the facility operations and waste management practices, differences in fate and transport between solvents and PFAS, prior solvent remediation efforts, and offsite source contributions.

Lessons learned

Various lessons have been learned during the course of the pilot project, primarily including the following:

- The project findings reflect that the behavior and transport pathway of PFAS constituents in the environment are not necessarily the same as that of drycleaning solvent constituents. Sampling for PFAS at pre-determined high drycleaning solvent constituent locations may not be an appropriate approach to screen site PFAS impacts. As a matter of fact, only four wells out of the 30 initial screening wells exhibited the highest PFAS concentrations following the expanded PFAS investigations.

- Temporal variation in PFAS data is present, given the notable differences in concentrations across sampling events at some sites investigated over generally short intervals. It is not uncommon for PFAS concentrations in the same monitoring well to vary by several times over a different sampling period. Variations in hydrogeology and geochemistry can affect PFAS fate and transport in the subsurface.
- No consistent PFAS constituent composition and distribution patterns were observed across all sites, likely due to different PFAS release mechanisms and timeframes. Site-specific VOH remedial actions (SVE, ISCO, bioremediation, ZVI injection, etc.) may have played a role in altering the fate and transport of PFAS.
- The elevated long-carbon chain PFAS in waste streams are indicative that these compounds, particularly PFOA and PFOS, are still present in consumer products although manufacturing of these compounds has been phased out in the US since the last decade.
- PFAS may be present in laundry influent water at low ppt levels dependent on water sources and the effluent from conventional wet laundry can have elevated PFAS above the PGCTL of 70 ng/L for PFOA/PFOS leached from the laundry process.
- Cross-contamination during sample collection, transport, and laboratory analysis may occur considering the low regulatory levels for PFOA/PFOS and their ubiquitous presence in the environment. The field and laboratory QA/QC sample analytical results reported during the course of the pilot project were reviewed and the data was validated. Additionally, non-detects for 28 PFAS compounds were observed in groundwater plume boundary and deep monitoring wells at several sites. Thus, following the strict SOPs and sampling guidelines, cross-contamination was not noted during the pilot project.

Uncertainties/Future Study

Various uncertainties exist, including the precise timing and exact location(s) of PFAS release(s), current and historical types of PFAS used in fabrics, the degree of outside influences and/or additional sources upon the reported PFAS concentrations in environmental media, and how prior or current drycleaning-solvent constituent remediation efforts have or may affect the distribution or remediation of PFAS impacts. Although site histories and current/historical operational practices were studied through review of available historical documents and through questionnaires completed during waste stream sampling implementation, the precise practices of historical operators are difficult to determine. Several specific uncertainties and recommendations are provided below for consideration.

- Questionnaire survey results from current operators indicate that spent solvent volumes were typically less than raw solvent volumes used, though questionnaire results were relatively inconclusive. Example questions and responses from the questionnaires included:
 - In response to the question of how many gallons of solvent are used per month (or per quarter), the responses ranged from 1 to 5 gallons per month. However, in response to how many gallons of spent solvent are disposed of per month (or per quarter), the responses ranged from approximately 0.5 to 9 gallons per month.
 - Responses regarding how separator water was disposed of included containerizing for offsite disposal, onsite recycling, and evaporation.
 - All operators surveyed noted that stain resistance or water repellency treatment is not currently offered and has not previously been offered.

- No facilities surveyed currently use septic tanks for disposal of wet laundry wash water, with sanitary sewer disposal utilized at all locations.
- Solvent loss through emission to the air is one environmental pathway at drycleaning facilities. PFAS mixed with the solvent may be deposited to the land surface after the solvent evaporates in the air. The air pathway was not evaluated in this pilot study due to the lack of validated sampling methods for PFAS in ambient air samples.
- Up to 28 PFAS compounds were analyzed in this study, but there are many additional PFAS compounds that are not detected as discrete compounds by existing commercially available analytical methods. For example, it is generally recognized that fluorotelomer alcohols (e.g., 8:2 FTOH) are found in the highest concentrations in impregnating agents for textiles (Lassen, et al. 2015), but this group of FTOHs are not analyzed by current commercially available analytical methods. FTOHs can be transformed to PFCAs such as PFOA in the environment. Total oxidizable precursor (TOP) assay analysis can be used to evaluate the potential of precursors for PFCAs and PFASs.
- Relatively higher method detection limits reported for waste stream samples due to the matrix effects and non-detects in the raw materials do not necessarily indicate that PFAS are not present in the raw detergents or solvents used at the drycleaning sites. However, the presence of PFAS at these MDL levels would not be anticipated to contribute to elevated groundwater concentrations.
- Although groundwater was monitored at selected wells for two or more sampling events, duplicates or triplicates of samples or verifications by multi-laboratory analyses were not conducted in this study. Thus, the reported PFAS values may vary by certain degrees. Any anomalous outliers for one or more PFAS compound concentrations would have affected the PFAS distribution pattern analyses.
- Remedial activity effects on PFAS were qualitatively discussed as part of this pilot study; however, monitoring of PFAS changes in concentrations and distribution patterns during future remediation could provide information to further understand PFAS fate and transport.

REFERENCE

- Arvaniti, O.S., Y. Hwang, H.R. Andersen, A.S. Stasinakis, N.S. Thomaidis, and M. Aloupi. (2015). Reductive Degradation of Perfluorinated Compounds in Water using Mg-aminoclay coated Nanoscale Zero Valent Iron. *Chemical Engineering Journal*, 262:133-139.
- Clara, M.C., C. Scheffknecht, S. Scharf, S. Weiss and O. Gans. (2008). Emission of Perfluorinated Alkylated Substances (PFAS) from Point Sources – Identification of Relevant Branches. *Water Science & Technology*. 58 (1), 59-66.
- Florida Department of Environmental Protection (FDEP). (2019). DEP-SOP-Draft, PFAS Sampling. September.
- Holmquist, H., Schellenberger, S., van der Veen, I., G.M. Peters, P.E.G. Leonards, and I.T. Cousins (2016). Properties, performance and associated hazard of state-of-the-art durable water repellent (DWR) chemistry for textile finishing. *Environmental International*. 91, 251-264.
- HSW Engineering, Inc. (2019). PFAS Sampling Guidelines.
- Interstate Technology Regulatory Council – ITRC (2020). Per- and Polyfluoroalkyl Substances (PFAS). September 2020. <https://pfas-1.itrcweb.org/>
- Lassen, C., J. Kjøholt, S. H. Mikkelsen, M. Warming, A. A. Jensen, R. Bossi, and I. B. Nielsen. 2015. Polyfluoroalkyl Substances (PFASs) in Textiles for Children - Survey of Chemical Substances in Consumer Products. No. 136. Danish Environmental Protection Agency, Copenhagen, Denmark.
- United States Environmental Protection Agency – US EPA (2009). Perfluorocarboxylic Acid Content in 116 Articles of Commerce. EPA/600/R-09/033. March 2009.
- United States Environmental Protection Agency – US EPA (2020). EPA's Actions to Address PFAS. <https://www.epa.gov/pfas/epa-actions-address-pfas> (accessed in November 2020)