Division of Science, Research and Environmental Health

Research Project Summary

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Identification of Perfluorinated Carboxylic Acids (PFCAs) in the Metedeconk River Watershed

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Abstract

In a 2009 statewide study of perfluoroalkyl compound (PFC) occurrence in public water supplies conducted by NJDEP, the concentration of the PFC compound perfluorooctanoic acid (PFOA) was higher in a drinking water intake along the South Branch Metedeconk River in Ocean County than in the other raw surface water sources tested. The Brick Township Municipal Utilities Authority (BTMUA), which relies on the Metedeconk River as its primary source of water supply, subsequently initiated a PFC source track down study in collaboration with the NJDEP Division of Science, Research, and Environmental Health. The data collected from a series of sampling events show that low levels of various PFCs are present in the study area and likely originate from a number of sources. However, BTMUA documented a localized area of high-level PFC contamination along the South Branch Metedeconk River in Lakewood Township. A groundwater contamination plume emanating from an industrial park on the south side of the river is suspected to be the principle source of PFCs observed in the Metedeconk River and the BTMUA intake samples. Groundwater PFOA levels were found to be as high as 70,000 ng/L in this area. While various PFCs were detected in water samples throughout the study area, and particularly in groundwater samples, PFOA is the primary contaminant of concern with respect to South Branch Metedeconk River water quality and the BTMUA water supply.

Introduction

Perfluoroalkyl compounds (PFCs) are a family of persistent emerging contaminants with widespread environmental occurrence in a variety of media, including aquatic systems (Ahrens 2011, Ferrey et al. 2012, Post et al. 2013). They have unique properties that make them useful in a wide range of products and industrial applications (Lindstrom et al. 2011, Post et al. 2012). PFCs are soluble in water, which aids their ability to disperse in the environment (Eschauzier et al. 2012, NJDEP 2014).

PFCs are currently unregulated contaminants in drinking water. The U.S. Environmental Protection Agency (USEPA) has developed a Public Health Advisory of 0.4 micrograms per liter (µg/L) (400 nanograms per liter (ng/L)) for short-term (defined by USEPA IRIS as up to 30 days) exposure to perfluorooctanoic acid (PFOA), one of the most common PFC compounds found in the environment (USEPA 2009). The New Jersey Department of Environmental Protection (NJDEP) has also issued health-based drinking water guidance level of 0.04 ug/L (40 ng/L). NJDEP's guidance is intended to protect from chronic (lifetime) exposure, normally defined as 70 years, consistent with other New Jersey drinking water guidance values, drinking water standards, and ground water standards (Post et al. 2009).

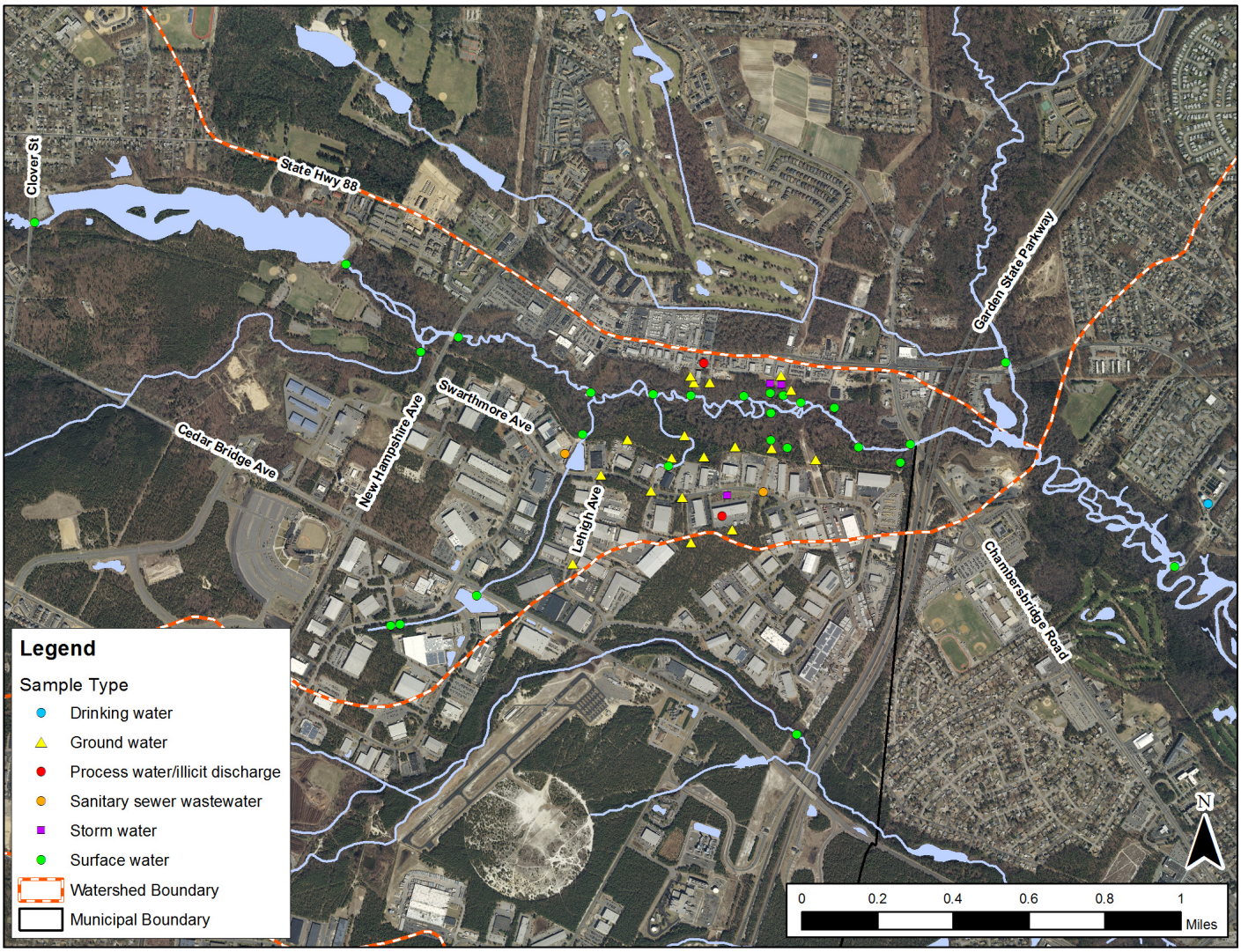
In 2009, NJDEP conducted a statewide PFC occurrence study of the drinking water sources for thirty-one community water systems throughout the state (NJDEP 2014). This study served as a supplement to an earlier 2006 study that focused primarily on targeted areas in the state where PFC occurrence might be expected to be present (NJDEP 2007, NJDEP 2009, Post et al. 2013). In the 2009 study, the PFOA concentration in the sample from the South Branch Metedeconk River was higher than in any other surface water source tested in the survey. The Metedeconk River is the primary water source for the Brick Township Municipal Utilities Authority (BTMUA).

In December 2010, BTMUA sampled and quantified the range of PFC concentrations along the Metedeconk River in an effort to identify potential PFOA source locations. Through this testing, BTMUA confirmed findings from the 2006 and 2009 studies. PFOA concentrations as high as 150 ng/L were detected in the river, and the location of a potential PFOA source area roughly 3 square mile (mi^2) in Lakewood Township, Ocean County was identified. Following the 2010 assessment, BTMUA developed the study reported here in collaboration with and funded by the

Table 1. Dates and descriptions of samples collected over the course of eight sampling events between September 2011 and July 2014.

Sampling Event	Date	Types of Water Samples Collected
1	9/20/2011	Surface water
2	12/13/2011	Surface water, stormwater infrastructure, process water/illicit discharge
3	2/15/2012	Surface water, stormwater infrastructure
4A	7/25/2012	Surface water, stormwater infrastructure
4B	8/27/2012	Stormwater runoff, sanitary sewer collection system
4C	9/20/2012	Surface water (high river flow)
5	12/18/2012	Surface water, stormwater runoff, potable well
6	6/13/2013	Equipment blank/decon water (pre-screen), lab reagent water
7	8/13/2013 – 8/16/2013	Surface water, groundwater, process water/illicit discharge
8	6/30/2014 – 7/1/2014	Surface water, groundwater

Figure 1—Sampling Locations from Sampling Event 1 through Sample Event 8



NJDEP Division of Science, Research, and Environmental Health to further identify the source of the PFC contamination.

Methods

Beginning in September 2011, a systematic water quality sampling program was coupled with information-gathering activities to develop a detailed understanding of the occurrence of PFCs in the study area.

Sampling and Analysis:

Eight sampling campaigns were undertaken to better define the PFOA source area (Table 1). A total of 172 water samples were analyzed during the course of the project. The majority of the samples were grab samples from groundwater and a three mile reach of the South Branch Metedeconk River. Other samples included drinking water, stormwater, sanitary sewer collection system wastewater, process water/suspected illicit discharges, and laboratory reagent water. A total of 35 quality assurance samples, which included trip, field, and equipment blanks, were collected during the study. Grab samples of BTMUA's Metedeconk River surface water intake and point of entry (POE) to the distribution system were tested during most sampling events.

Sampling locations were drawn from BTMUA's network of Metedeconk River watershed sampling sites. Additional localized sampling sites were incorporated to target specific locations in the investigation area. All sample sites were geo-located. A total of 53 unique locations were sampled (Figure 1). To avoid potential variability from increased pollutant loading from nonpoint source runoff or dilution during high river flows, surface water samples were collected under baseflow conditions except when stormwater sampling was the focus of the sampling event.

Samples were analyzed for the compounds shown in Table 2 by Eurofins Eaton Analytical, Inc., Monrovia, California.

In order to minimize the possibility of introducing PFC contamination prior to and during sampling, samplers avoided contact with PFC-containing items. Samplers wore PFC-free clothing and footwear and nitrile gloves during sampling. Sample containers were supplied by the contract laboratory. All non-consumable sampling equipment utilized in the study underwent a rigorous decontamination process following procedures drawn from a similar study (Bousenberry 2012).

Samples were collected in duplicate by BTMUA personnel and shipped to the analytical laboratory. Trip blank and field blank samples were analyzed with each batch of samples. Split samples were submitted to different referee laboratories on two occasions in order to evaluate the performance of the primary laboratory.

PFC analyses were conducted by Eurofins' using the Standard Operating Procedure (SOP) for "Determination of Perfluorinated Pollutants in Environmental Matrices by Online Solid-Phase Extraction coupled with High-Performance Liquid Chromatography/Mass Spectrometry in Tandem Analysis". The technology and the analytical protocols used by the Eurofins method for this project are equivalent to those of EPA method 537 (Shoemaker et al. 2013), and have been used in other NJDEP PFC occurrence studies (NJDEP 2014).

Information Gathering:

Information gathering activities focused on the compilation and review of available environmental PFC data sources and development of a Geographic Information System (GIS) database. A search of publicly available NJDEP databases was performed to identify commercial and industrial facilities that could be potential PFC sources. BTMUA's internal Source Water Protection Program files, which included documentation of upstream spill incidents and observations from routine surveys of the industrial park and automotive commercial corridor located within the study area, were also reviewed. A business inventory was completed for the easterly section of the study area where water quality testing showed high concentrations of PFCs. BTMUA inspected the storm water system for illicit discharges, dry-weather flows, and unusual stormwater characteristics. Results of the file searches and business inventory were incorporated into the GIS databases.

Table 2 – Perfluoroalkyl Compounds (PFC) analyzed, the class of compound, and the laboratory reporting limit of each compound.

Acronym	Analyte	PFC Class	Laboratory Reporting Limit (ng/L)
PFBA	Perfluorobutanoic acid	Perfluorocarboxylic acids (PFCAs)	10
PFPA	Perfluoropentanoic acid	Perfluorocarboxylic acids (PFCAs)	5
PFHxA	Perfluoro-n-hexanoic acid	Perfluorocarboxylic acids (PFCAs)	5
PFHpA	Perfluoro-n-heptanoic acid	Perfluorocarboxylic acids (PFCAs)	5
PFOA	Perfluorooctanoic acid	Perfluorocarboxylic acids (PFCAs)	5
PFNA	Perfluorononanoic acid	Perfluorocarboxylic acids (PFCAs)	5
PFDA	Perfluorodecanoic acid	Perfluorocarboxylic acids (PFCAs)	5
PFBS	Perfluorobutanesulfonic acid	Perfluorosulfonic acids (PFSAs)	5
PFHxS	Perfluorohexanesulfonic acid	Perfluorosulfonic acids (PFSAs)	5
PFOS	Perfluorooctanesulfonic acid	Perfluorosulfonic acids (PFSAs)	5

Results

Sampling Event 1 confirmed the results of BTMUA's December 2010 Metedeconk River watershed testing and reduced the PFC source area from 3 mi^2 to approximately 1 mi^2 along the South Branch Metedeconk River. PFOA was the primary PFC detected, with several samples showing a few other PFCs (PFPA, PFHxA, and PFHpA) at concentrations just above the laboratory reporting limits. Levels of PFOA ranged from below the detection limit to 130 ng/L. A minor PFOA source was also found emanating from a stormwater retention pond and tributary that transects the western portion of the Lakewood Industrial Park. However, based on flow and dilution, this source was considered a relatively insignificant contributor to the BTMUA intake PFOA concentration.

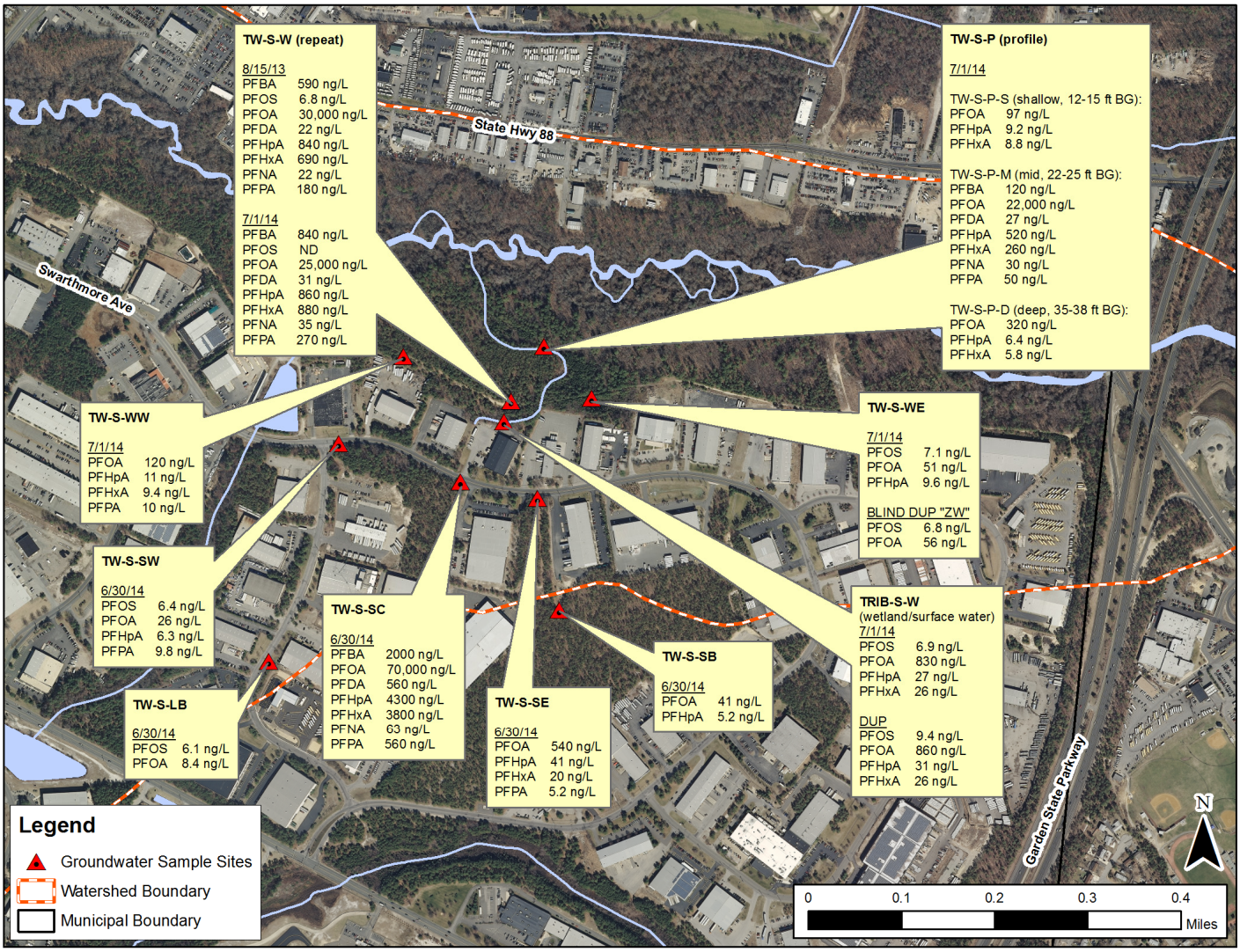
Sampling Event 2 further delineated the PFOA source area to an industrial park on the south side of the river and eliminated several commercial automobile sites and a car wash facility along the north side of the river as significant PFOA sources.

Sampling Event 3 focused on the industrial park and found a high PFOA concentration in a sample from a detention basin that collected observed discharge from a granite countertop manufacturer. Surface water samples were also collected from the river and tributaries. PFOA was the only PFC detected in Sampling Event 3.

Sampling Event 4 was carried out in three phases, designated Sampling Events 4A, 4B and 4C. Sampling Event 4A was designed to further delineate the PFC source area by sampling at closer intervals along the river, resampling of the outlet of retention basins and downgradient wetlands with known observed discharges, and sampling for PFCs along an unnamed tributary. Sites along the tributary were selected to capture suspected illicit discharges from granite manufacturing facilities. A surface water sample was also collected from Cedar Bridge Branch, a tributary that drains the southern portion of the industrial park, to determine whether PFC contamination was present in this separate drainage area. Test results showed consistent increases in PFOA concentrations between adjacent sample sites along the river with concentrations generally increasing downstream, from a west to east direction. It is notable that PFBS, PFPA, PFHxA, and PFOS were each detected in samples during this event.

Sampling Event 4B focused primarily on sanitary sewer wastewater and stormwater runoff. PFOA was detected

Figure 2—Groundwater Sampling Test Results from Sampling Event 8 in the Lakewood Industrial Park



at concentrations as high as 79 ng/L. Other PFCs detected included PFHxA, PFOS, PFBA, PFPA and PFHpA. Sample results indicated the presence of PFCs, but the source was unclear due to the mixed land uses in the sewer catchment area.

Sampling Event 4C consisted of a single surface water sample collected along the river during a period of higher river flow. PFOA was detected at 34 ng/L and was the only PFC detected in the sample. This value was considerably less than in the previous low-flow samples taken at the same site, suggesting that PFOA concentrations were diluted during higher river flows.

Sampling Event 5 focused on collection of samples from two potable wells owned by local businesses along State Highway 88 in order to determine whether shallow wells, located in close proximity to the South Branch Metedeconk River, showed detectable levels of PFCs. No PFCs were detected in either of the wells. Additional sampling took place at a detention basin and river sites. PFOA was the only PFC detected.

Sampling Event 6 involved the collection of additional river samples and pre- and post-filtration samples collected from BTMUA's laboratory deionized reagent water system for future groundwater sampling events. The pre-filter sample had a detectable PFOA concentration, but PFCs were not detected in the post-filter sample.

Sampling Event 7 involved collection of groundwater samples, continued monitoring of the surface water, and repeat testing of an observed discharge from a granite manufacturer where samples were taken at the point of release rather than a retention basin. Temporary well point sample sites were selected on the north and south sides of the river and sampled within five feet below the water table.

All groundwater samples, with the exception of a single background sample, showed the presence of at least one PFC compound. These results revealed the first indication of a source of contamination substantial enough to cause the level of PFCs being detected in the Metedeconk River. Specifically, the PFOA concentration was 30,000 ng/L in the westernmost sampling location on the south (industrial park) side of the river, well TW-S-W. (Figure 2). Numerous other PFCs were detected at high concentrations, including PFBA, PFPA, PFHxA, PFHpA, PFNA, PFDA and PFOS. As in the previous sampling events, the surface water samples showed that PFOA concentrations were significantly increased within a relatively short stretch of the river. When examined in the context of the groundwater test results, these data indicated that there was a strong likelihood that a PFC contamination plume was discharging to the river in this area.

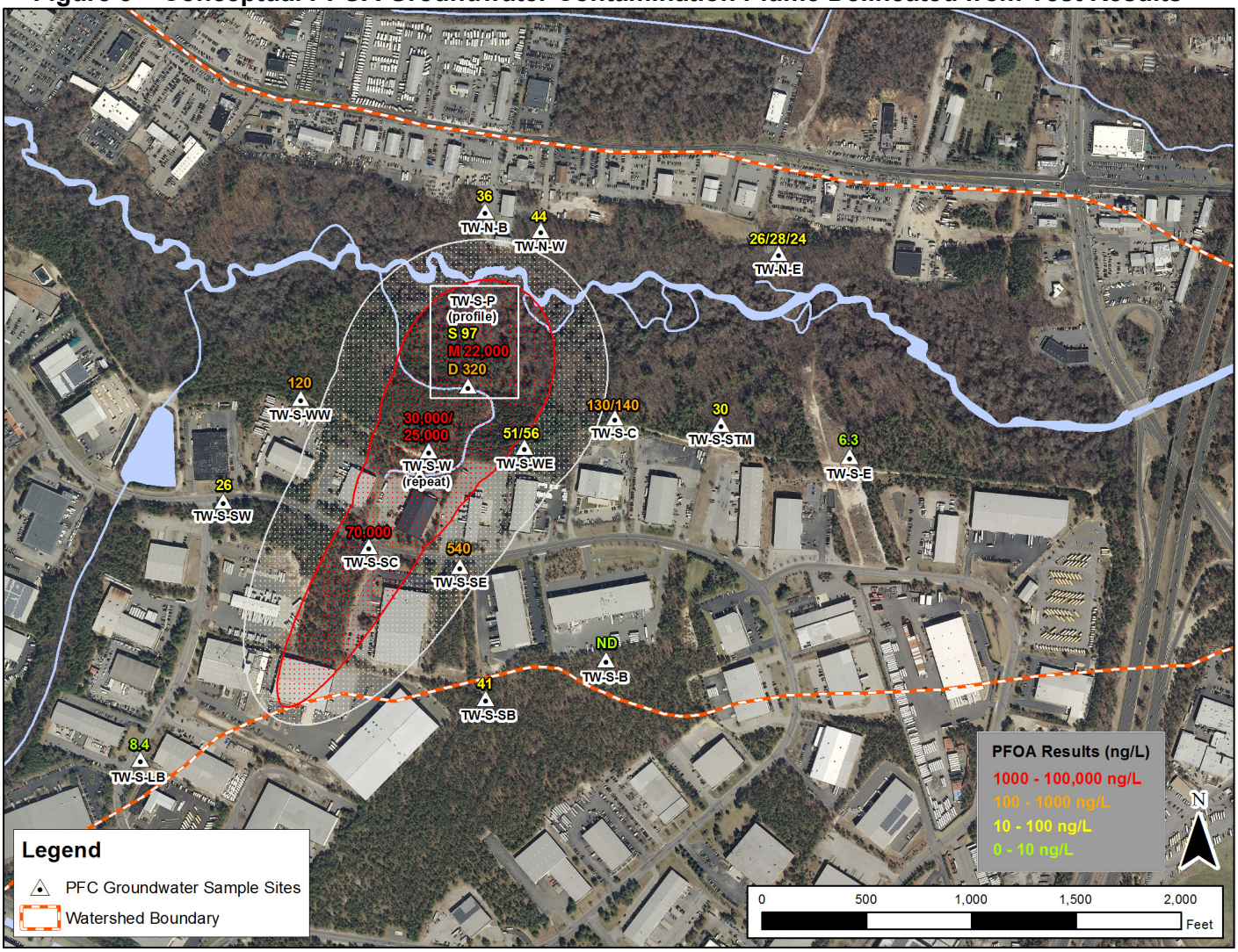
Sampling Event 8 focused primarily on groundwater sampling, but also included the collection of an additional sample from an intermittent stream/wetland area as well as continued monitoring of PFC concentrations in the river. Wells sampled during Event 7 were resampled to confirm previous results, and wells bracketing the east and west of these wells were added to characterize the extent of the plume. One well (TW-S-P), located between well TW-S-W and the Metedeconk River (Figure 2), was designated a "profile" site, where samples were collected from three separate screened intervals to provide information on the vertical migration of the PFC contaminants in the aquifer (Bousenberry 2013). Two background sites were also designated and sampled.

Well TW-S-SC, located along Swarthmore Avenue, showed significantly higher concentrations than the western (TW-S-W) site. PFOA was detected at 70,000 ng/L, with detections of other PFCs including PFBA (2,000 ng/L),

Table 3 – Summary of Test Results from Samples Collected within the PFC Study Area for Sampling Event 1 through Sampling Event 8. All quality assurance, duplicate, and finished drinking water samples were excluded from this summary. Refer to Table 2 for compound names.

Analyte	No. of Samples	No. of Detections	Percent Detections	Mean Detection (ng/L)	Median Detection (ng/L)	Min. Detection (ng/L)	Max. Detection (ng/L)
PFBA	96	9	9.4%	401.6	17	11	2,000
PFPA	96	39	40.6%	35	8.3	5.2	560
PFHxA	96	31	32.3%	190	9.4	5.1	3,800
PFHpA	96	22	22.9%	306.1	9.5	5.2	4,300
PFOA	96	92	95.8%	1,652.2	34.5	5.1	70,000
PFNA	96	7	7.3%	24	22	5.2	63
PFDA	96	4	4.2%	160	29	22	560
PFBS	96	4	4.2%	33.9	14.7	6.2	100
PFHxS	96	2	2.1%	9.3	9.3	5.5	13
PFOS	96	27	28.1%	11.6	6.8	5	50

Figure 3 – Conceptual PFOA Groundwater Contamination Plume Delineated from Test Results



PFPA (560 ng/L), PFHxA (3,800 ng/L), PFHpA (4,300 ng/L), PFNA (63 ng/L), and PFDA (560 ng/L) (Table 3). These test results represent the highest PFC concentrations detected in the study (Figure 2). The profile well (TW-S-P) samples were collected at depths of 12-15 feet, 22-25 feet, and 35-38 feet below grade. While all three samples contained high levels of PFOA and other detectable PFCs, concentrations were greatest at the middle depth where PFOA was detected at 22,000 ng/L. The remaining groundwater sample results showed significantly lower PFC concentrations and likely represent the outer boundaries of a contamination plume (Figures 2 and 3).

Results from the repeat sampling of temporary well point TW-S-W were consistent with those from Sampling Event 7. A split sample of TW-S-W was also sent to USEPA's National Exposure Research Laboratory in North Carolina with consistent results between both labs.

In general, these results indicate, with strong likelihood, that the source of contamination is on the south side of Swarthmore Avenue in the Lakewood Industrial Park, with the contamination directly impacting groundwater.

The contaminated groundwater is gradually migrating in a north-northeasterly direction towards, and ultimately discharging to, the South Branch Metedeconk River. A conceptual plume was delineated based upon the PFOA test results from Sampling Event 7 and Sampling Event 8 and is shown as Figure 3.

Table 3 summarizes the results from samples collected within the PFC source track down study area from Sampling Events 1 through 8, excluding all quality assurance, duplicate and finished drinking water samples.

Discussions and Conclusions

The primary PFC found in the BTMUA drinking water intake was PFOA, and PFOA was also the primary PFC found high in concentrations in the study samples. Various other PFCs were detected in water samples throughout the source track down study area and were most pronounced in the groundwater samples.

During the course of the study, numerous environmental records and databases were reviewed and field surveys were conducted to identify and document any indications

of dumping, negligent business practices, or poor housekeeping. Several suspected illicit discharges were identified, including process water from granite manufacturing facilities, recycled water from a commercial car wash, and vehicle wash water from the lots of large commercial auto dealerships. The information gathered offered few leads as to the PFC contamination source. Specific leads were either rejected based upon the sampling results or deemed insignificant given their magnitude relative to the observed PFC levels in the South Branch Metedeconk River.

The locations of groundwater samples with extremely high PFC concentrations were used to isolate the mostly likely PFC sources to the parcel level. The plume likely originates in the Lakewood Industrial Park, and a small location within this industrial park has been identified as a probable source. Based upon the assumption that groundwater in the area generally follows the surface topography and flows towards the River, the contamination source is most likely confined to one of three possible properties located in Lakewood Township on the south side of Swarthmore Avenue and east of Lehigh Avenue.

A facility located on these three properties manufactures industrial fabrics, composites, and elastomers, and uses or produces products that contain PFCs. In light of the groundwater sampling data, and in comparison to the other facilities in the area, this facility appears to be the most probable source and warrants further investigation. However, some other, as yet unknown source cannot be ruled out. In the event that groundwater flow assumptions are incorrect for this area, several other properties align with the groundwater plume area on the north side of Swarthmore Avenue. None of those properties appear to be manufactures or user of PFC compounds.

It is unclear how long PFCs have been contaminating the groundwater in this area. However, during Sampling Event 8, a split sample from one site was analyzed by USEPA's National Exposure Research Laboratory in North Carolina and evaluated for the presence of branched and linear PFCA isomers (Strynar and Lindstrom 2013). The presence of both linear and branched isomers and the presence of both even and odd numbered carbon chains suggest an older source of contamination (Benskin et al. 2012, Strynar 2014). The process that produced both branched and linear isomers and a relative mix of even and odd numbered carbon chains, known as electrochemical fluorination, was the dominant manufacturing process between the 1950s and 2002 and has since been phased out.

Upon completion of this study and receipt of the final report, the NJDEP Site Remediation and Waste Management Program has contacted the potential responsible party to take appropriate remedial actions.

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