

Geochemical and Hydrologic Factors Controlling Subsurface Transport of Poly- and Perfluoroalkyl Substances, Cape Cod, Massachusetts

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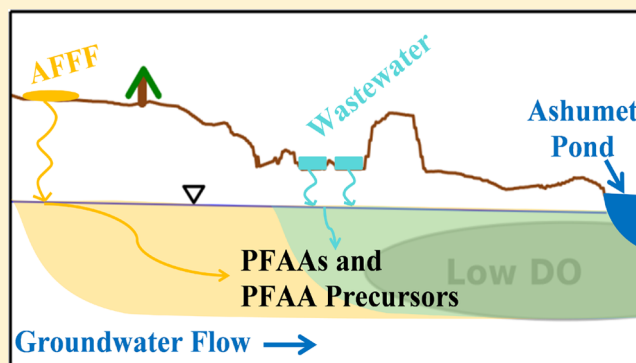
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Supporting Information

ABSTRACT: Growing evidence that certain poly- and perfluoroalkyl substances (PFASs) are associated with negative human health effects prompted the U.S. Environmental Protection Agency to issue lifetime drinking water health advisories for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) in 2016. Given that groundwater is a major source of drinking water, the main objective of this work was to investigate geochemical and hydrological processes governing the subsurface transport of PFASs at a former fire training area (FTA) on Cape Cod, Massachusetts, where PFAS-containing aqueous film-forming foams were used historically. A total of 148 groundwater samples and 4 sediment cores were collected along a 1200-m-long down-gradient transect originating near the FTA and analyzed for PFAS content. The results indicate that unsaturated zones at the FTA and at hydraulically downgradient former domestic wastewater effluent infiltration beds both act as continuous PFAS sources to the groundwater despite 18 and 20 years of inactivity, respectively. Historically different PFAS sources are evident from contrasting PFAS composition near the water table below the FTA and wastewater-infiltration beds. Results from total oxidizable precursor assays conducted using groundwater samples collected throughout the plume suggest that some perfluoroalkyl acid precursors at this site are transporting with perfluoroalkyl acids.



INTRODUCTION

Poly- and perfluoroalkyl substances (PFASs) are common contaminants in the aquatic environment because of their widespread use in consumer and industrial applications, such as protective coatings, and as a major component in aqueous film-forming foams (AFFFs).^{1–4} PFASs have been associated with cancer, immune dysfunction in children, obesity, and thyroid disease, among other adverse health outcomes.^{5–8} Given that groundwater is a major source of drinking water and constitutes approximately 22% of total water use in the United States,⁹ there is an urgent need to understand the subsurface fate and transport of PFASs.

Groundwater, soil, and surface water contamination from use of AFFFs during fire-related emergencies and fire-training activities has caused increasing concern for groundwater quality because AFFFs are a highly concentrated PFAS point

source.^{3,10} Fire training areas (FTAs) are potential sources of long-term PFAS influx to the unsaturated zone and groundwater, particularly where hydrocarbon fires were repeatedly extinguished with AFFFs over unlined soil. Studies conducted at several sites impacted by use of AFFFs report groundwater concentrations of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA, also known as perfluorooctanoate in the anionic form) above the U.S. Environmental Protection Agency (EPA) lifetime drinking water health advisory level of 70 ng L⁻¹ for the combined concentration of PFOS and PFOA, with some sites reaching up to 5 orders of

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magnitude above this limit.^{11–18} Other PFASs do not presently have EPA health advisories.

AFFF formulations are complex mixtures that generally contain 1–5% w/w PFASs,¹⁰ and are diluted with water before use such that the final solution contains 1–6% v/v of the initial formulation. In 2004, the U.S. inventory of AFFFs was estimated to be 3.75×10^7 kg.¹⁹ Major users include the military (29%), commercial aviation (16%), fire departments (14%), and the petrochemical industry (39%).¹⁹ Polyfluoroalkyl substances, often a major constituent of AFFFs and other products, can transform into perfluoroalkyl acids (PFAAs), which are extremely recalcitrant to further transformation.^{20–26} PFAAs include both perfluorinated sulfonates and carboxylates.

Another significant source of PFASs to the aquatic environment is their use in consumer products and discharge from wastewater treatment plants (WWTPs).^{27–29} PFASs are typically not removed through the treatment process, and some PFAAs have been shown to increase in concentration during treatment as a result of PFAA precursor (from now on referred to as precursor) transformation.^{27–29}

The main objective of this study was to provide information on the factors affecting subsurface mobility of PFASs and the potential for precursor transformation at a site with groundwater contamination from both FTA and WWTP sources. High resolution spatial data at sites contaminated with PFASs are currently lacking and there is limited knowledge of the complex processes controlling PFAS subsurface fate and transport. To address this gap, groundwater samples were collected from wells located along a 1200-m-long transect oriented in the direction of the regional groundwater flow on western Cape Cod, MA. The upgradient wells are located around a former FTA, and 580–690 m downgradient along the flow path is a former WWTP where secondarily treated domestic wastewater effluent was disposed of into infiltration beds. Concentrations of PFASs were measured in groundwater samples collected from wells located at various depths and distances from the FTA to characterize subsurface distributions in a shallow, unconfined sand and gravel aquifer. Sediment cores were collected adjacent to selected groundwater sampling locations and analyzed for PFASs to determine in situ sediment/water distribution coefficient (K_d) values. In addition, total oxidizable precursor assays were conducted in the laboratory on selected groundwater samples to determine the presence of precursor compounds and the potential for transformation to PFAAs. The results of this study provide a unique data set on a complex groundwater contamination plume originating from multiple sources.

METHODS

Site Description and Hydrologic Setting. The study was conducted on western Cape Cod, Massachusetts (Figures 1 and S1), at the U.S. Geological Survey (USGS) Cape Cod Toxic Substances Hydrology Research Site³⁰ located on Joint Base Cape Cod. At this site, a groundwater contaminant plume resulting from disposal of treated domestic wastewater has been the subject of long-term hydrogeology and biogeochemistry research.^{31–40} The FTA at Joint Base Cape Cod (FTA-1) was used from 1958 to 1985, and records indicate that jet fuel, chlorinated hydrocarbons, transformer oils, paint thinners, and gasoline were released at the site.⁴¹ Use of AFFFs at FTA-1 likely began in 1970 and continued until 1985, with one additional application in 1997.^{42,43} Thermal soil remediation targeting fuel constituents and chlorinated solvents was

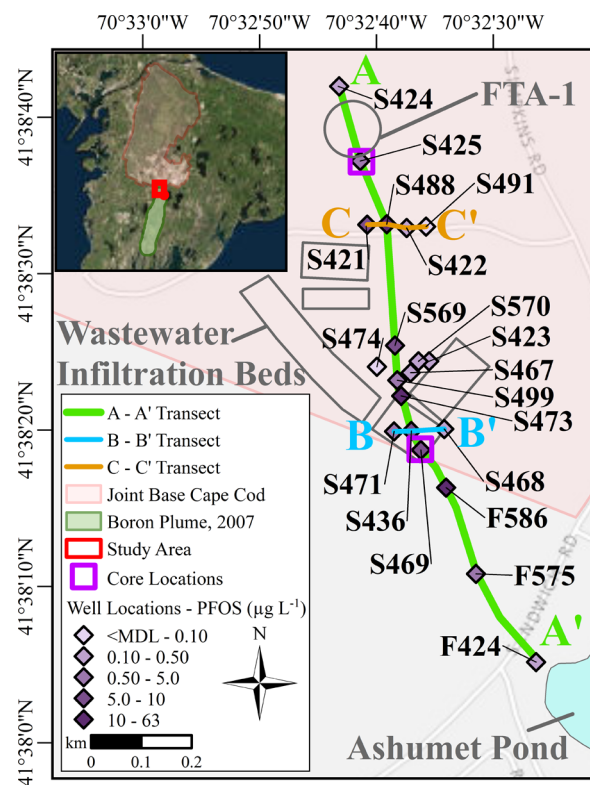


Figure 1. Locations and identifiers of groundwater monitoring sites (diamond symbols) sampled during 2015 at the Cape Cod study site. Symbol shading corresponds to the maximum PFOS concentration at each site because PFOS was often the highest PFAS concentration in groundwater samples. Nearly all locations were sampled at multiple depths. The boron plume indicates the extent of the wastewater plume.³⁴

undertaken at FTA-1 in 1997.⁴³ The soil was excavated to a maximum depth of 11 m below land surface (the water table is approximately 17 m below land surface) and heated to between 157 and 204 °C before being backfilled.⁴³ Because PFOA is thermally stable up to 300 °C, and perfluorinated sulfonates require even higher temperatures for thermolysis,^{44,45,46} the soil treatment was unlikely to have reduced concentrations of PFAAs. Some precursors may have been thermolyzed to form PFAAs.

FTA-1 is located 580 m upgradient of a WWTP, where domestic wastewater produced on the military base was treated from 1936 to 1995 and the effluent disposed of into the sand and gravel aquifer through infiltration beds (Figure 1).⁴⁷ Wastewater effluent disposal to the aquifer resulted in a large and chemically complex contaminant plume currently characterized by low dissolved oxygen (DO) concentrations and elevated concentrations of dissolved organic carbon (DOC), nitrate, phosphate, ammonium, boron, and organic micro-pollutants.^{35,36,39} Boron is used as an indicator for the wastewater plume location (Figure 1).³⁴

The glacial outwash sediments that comprise the unconfined aquifer at the study site consist of medium to coarse sand and gravel. Hydraulic properties measured during a large-scale tracer experiment at the site include a hydraulic conductivity of 110 m d^{-1} , porosity of 0.39, and average flow velocity of 0.42 m d^{-1} .^{48,49} Recharge to the aquifer from precipitation is 73 cm year^{-1} .⁵⁰ The water table altitude can fluctuate by $\sim 1 \text{ m year}^{-1}$

Table 1. Compound Names, Abbreviations, and Key Properties of Poly- and Perfluoroalkyl Substances and the Organic Carbon Normalized Sediment/Water Partition Coefficients (K_{oc}) Measured in This Study, as Well as Select K_{oc} Values from the Literature^a

compound name	abbrev.	mol formula	mol wt	pK_a ^{53,54}	av log K_{oc} (this study)	av log K_{oc} (lit., laboratory-based) ^{55–58} low–high range provided	av log K_{oc} (lit., field-based) ^{12,59,60} low–high range provided
perfluorinated carboxylates							
perfluorobutanoate	PFBA	C ₃ F ₇ COO [−]	213	0.4		1.72 ± 0.29–1.88 ± 0.11	2.17 ± 1.10
perfluoropentanoate	PFPeA	C ₄ F ₉ COO [−]	263	−0.1	2.17 ± 0.77	1.37 ± 0.46–1.71 ± 0.07	1.85 ± 0.70
perfluorohexanoate	PFHxA	C ₅ F ₁₁ COO [−]	313	−0.16	2.56 ± 0.17	1.31 ± 0.29–1.90 ± 0.04	1.91 ± 0.39–2.06 ± 0.67
perfluoroheptanoate	PFHpA	C ₆ F ₁₃ COO [−]	363	−0.19	2.76 ± 0.09	0.23 ± 0.92–1.63 ± 0.15	2.04 ± 0.48–2.19 ± 0.65
perfluorooctanoate	PFOA	C ₇ F ₁₅ COO [−]	413	−0.2	2.61 ± 0.69	−0.22 ± 1.26–2.4 ± 0.12	1.9 ± 0.1–2.31 ± 0.35
perfluorononanoate	PFNA	C ₈ F ₁₇ COO [−]	463	−0.21	2.82 ± 0.01	1.83 ± 0.43–2.39 ± 0.09	2.33 ± 0.31–2.4 ± 0.1
perfluorodecanoate	PFDA	C ₉ F ₁₉ COO [−]	513	−0.21	3.39 ± 0.02	2.59 ± 0.45–2.96 ± 0.15	3.17 ± 0.14–3.6 ± 0.1
perfluoroundecanoate	PFUnDA	C ₁₀ F ₂₁ COO [−]	563	−0.21	4.31 ± 0.08	3.30 ± 0.11–3.56	4.8 ± 0.2
perfluorododecanoate	PFDoDA	C ₁₁ F ₂₃ COO [−]	613	−0.21			
perfluorinated sulfonates							
perfluorobutane sulfonate	PFBS	C ₄ F ₉ SO ₃ [−]	299	0.14		−0.76 ± 0.58–1.79 ± 0.10	2.06 ± 0.77
perfluorohexane sulfonate	PFHxS	C ₆ F ₁₃ SO ₃ [−]	399	0.14	2.32 ± 0.15	0.66 ± 0.65–2.05 ± 0.08	2.28 ± 0.70–3.6 ± 0.1
perfluorooctane sulfonate	PFOS	C ₈ F ₁₇ SO ₃ [−]	499	0.14	3.37 ± 0.27	2.40 ± 0.46–3.7 ± 0.56	3.14 ± 0.66–3.8 ± 0.1
perfluorodecane sulfonate	PFDS	C ₁₀ F ₂₁ SO ₃ [−]	599	0.14	3.63	3.53 ± 0.12	
perfluoroalkyl sulfonamides							
perfluorooctane sulfonamide ^a	FOSA	C ₈ F ₁₇ SO ₂ NH ₂	499	6.52	4.86	4.1 ± 0.35	4.3 ± 0.2
fluorotelomer sulfonates ^b							
6:2 fluorotelomer sulfonate	6:2 FtS	C ₆ F ₁₃ CH ₂ CH ₂ SO ₃ [−]	427	0.36	2.62 ± 1.01		
8:2 fluorotelomer sulfonate	8:2 FtS	C ₈ F ₁₇ CH ₂ CH ₂ SO ₃ [−]	527		3.65 ± 0.54		

^aSee referenced work for details. The poly- and perfluoroalkyl substances are reported in anionic form (except for perfluorooctane sulfonamide). K_{oc} values from this study are calculated from measured K_d values and fraction of organic carbon (f_{oc}) values (see Table S2), and may be uncertain based on the difficulty in quantifying low total organic carbon values (<0.0003). ^bPerfluorooctane sulfonamide and the fluorotelomer sulfonates are specific perfluoroalkyl acid precursor compounds analyzed for this study.

depending on precipitation⁴⁹ and is about 17 and 6.5 m below land surface at FTA-1 and the infiltration beds, respectively.

Groundwater and Aquifer Sediment Sampling. Groundwater samples (Figures 1 and S1) were collected according to USGS field protocols⁵¹ during 2014 and 2015 from a network of monitoring-well clusters, multilevel samplers, and continuous multichannel tubing wells (herein, all sampling types are referred to as wells). Sediment cores were collected at S425 (one 1-m core) and at S469 (three 1-m cores) using a piston-type coring device (see Methods section of SI).

A total of 148 groundwater samples were collected during June and December 2014 (19 samples), May–July 2015 (118 samples), and November 2015 (11 samples) from 25 well locations. Note that most well locations (Figure 1) have multiple depths associated with each site.⁵² The 1200-m-long A–A' longitudinal transect (Figure 1) includes 11 well locations (81 sampling points) along the direction of groundwater flow. There are 9 additional well locations (37 sampling points) located transverse to the A–A' transect (Figure 1), including the B–B' and C–C' transects (Figure S2). During June 2014, 5 additional well locations were sampled that are located at greater downgradient distances than the A–A' transect (Figure S1). Unless otherwise noted, the discussion and statistics focus on the major sampling in May–July 2015 to minimize any temporal variability. All distances within the A–A' transect are given along the direction of groundwater flow relative to the estimated center of FTA-1

based on site maps.⁴¹ The transect passes through the infiltration beds and ends near Ashumet Pond (Figure 1). Ancillary water quality analyses³⁷ were conducted and include specific conductance, pH, temperature, DO, phosphate, nitrate, and DOC.⁵²

Analytical Materials. Native and isotopically labeled PFAS standards were purchased from Wellington Laboratories (Guelph, Canada). The PFAS compound names, abbreviations, and key properties are listed in Table 1. Details on the analytical internal standards are listed in Table S1. A Barnstead NANOpure Infinity (Lake Balboa, CA) water system provided deionized water (DI) with a resistivity of >18 MΩ cm^{−1}. Other materials are described in the SI.

Sample Analysis. Samples were analyzed for PFASs with liquid chromatography-tandem mass spectrometry (LC-MS/MS) using modifications of previously described methods (see SI).^{12,21} All groundwater samples, laboratory DI water blanks, and calibration curve points were prepared in a 50:50 water/methanol solution with internal standards. Samples were analyzed with an Agilent (Santa Clara, CA) 6460 triple quadrupole LC-MS/MS in negative ion mode using an Agilent Poroshell 120 EC-C18 column with mobile phases of 2 mM ammonium acetate in water and 2 mM ammonium acetate in methanol. Duplicate measurements of ~30% of the samples produced good sample reproducibility (<20% relative standard deviation on average) for 6:2 FtS and PFAAs with a chain length of C₉ or less. 8:2 FtS and FOSA had relative standard

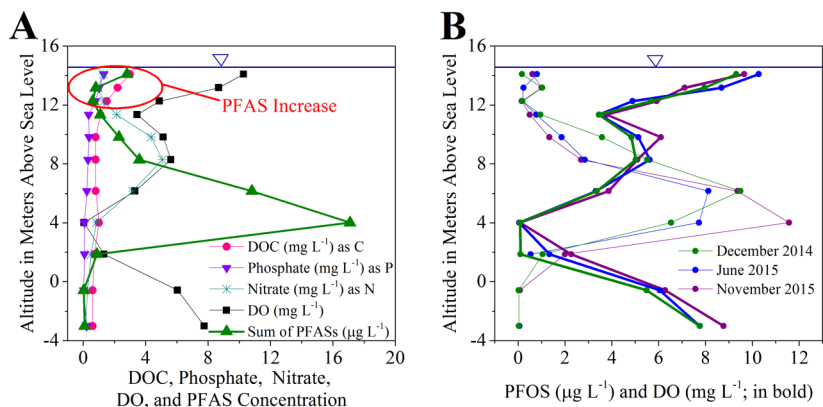


Figure 2. Vertical profiles at well S469 located in the wastewater infiltration beds showing (A) geochemical conditions and distribution of the sum of poly- and perfluoroalkyl substances (PFASs) in June 2015 and (B) time series profiles for dissolved oxygen (DO) and perfluorooctane sulfonate (PFOS). In June 2015, PFOS is on average 46% of the total molar concentration of the sum of measured PFASs at well S469. Inverted triangles show the position of the water table.

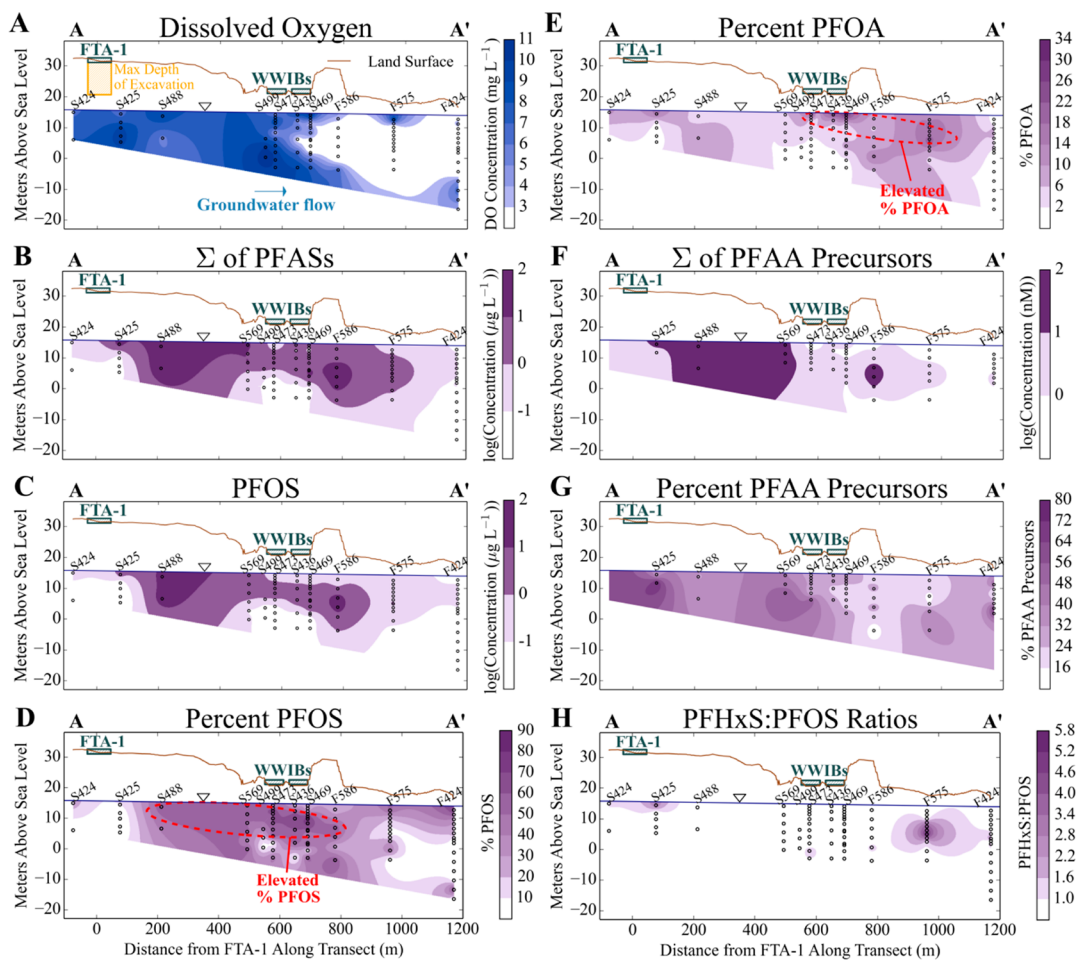


Figure 3. Vertical sections along longitudinal transect A–A' showing (A) dissolved oxygen concentrations (max = 11 mg L⁻¹), (B) the sum of poly- and perfluoroalkyl substance (PFAS) concentrations listed in Table 1 (max = 95 μg L⁻¹), (C) perfluorooctane sulfonate (PFOS) concentrations (max = 63 μg L⁻¹), (D) PFOS molar percentage of total measured PFASs (max = 82%), (E) perfluorooctanoate (PFOA) molar percentage of total measured PFASs (max = 32%), (F) the molar sum of perfluoroalkyl acid (PFAA) precursors as determined by the total oxidizable precursor assay (max = 78 nM), (G) precursor molar percentage of total PFASs (the sum of precursors and measured perfluoroalkyl acids pre-oxidation) (max = 78%), and (H) the perfluorohexane sulfonate (PFHxS):PFOS ratios (max = 5.8). [Circles indicate sampling sites. Inverted triangles indicate the water table. FTA-1 refers to the fire training area and WWIBs refers to wastewater infiltration beds. Box beneath FTA-1 in panel (A) shows maximum depth of soil excavated and thermally treated in 1997. Vertical exaggeration is 10× for all vertical sections. The lower boundary of the colored areas is the line connecting the maximum sampled depths, and the upper boundary is set at the water table.]

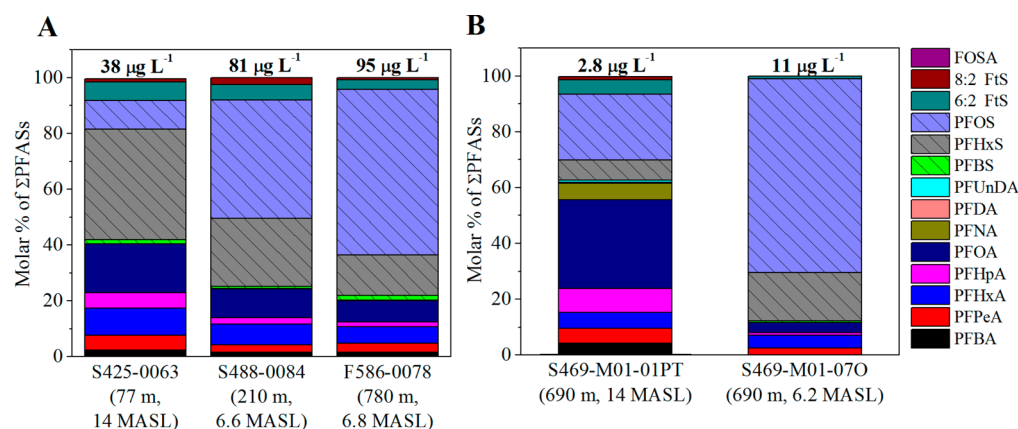


Figure 4. Molar percentages of individual poly- and perfluoroalkyl substances (PFASs) in groundwater collected (A) at well S425, located near FTA-1, and wells S488 and F586, located at 210 and 780 m downgradient from FTA-1, respectively, at the depths with the highest concentrations, and (B) at well S469, located 690 m downgradient from FTA-1 in the wastewater treatment plant infiltration beds, from just below the water table (14 m altitude) and from the deeper (6.2 m altitude) portions of the PFAS plume. [See Table 1 for explanation of abbreviations. Total PFAS concentration is shown at the top of each column, and distance from FTA-1 (m), followed by the altitude in meters above sea level (MASL) are shown in parentheses below each well name.]

deviations of 42% and 71% (FOSA concentration near method detection limit), respectively.

Total Oxidizable Precursor Assays. A slightly modified PFAS total oxidizable precursor assay developed by Houtz and Sedlak⁶¹ and Houtz et al.²¹ was employed here. For each of the 46 groundwater samples analyzed, 3 mL of a 120 mM potassium persulfate and 250 mM sodium hydroxide solution was added to 3 mL of groundwater sample in an 8 mL HDPE bottle and heated for 6 h at 85 °C in a circulating water bath.^{21,61} Samples were cooled, neutralized with hydrochloric acid,^{21,61} and stored at 4 °C until offline solid phase extraction (SPE) and LC-MS/MS analysis (see SI for experimental details and recoveries). Total oxidizable precursor experiments were duplicated for 30% of the samples. The relative standard deviation for duplicates was <15% on average for all PFAAs with C₉ or shorter chain lengths.

Partition Coefficient Experiments. Sediment cores were collected from the same depths as selected corresponding groundwater samples at the FTA-1 (near well S425) and infiltration bed (near well S469) sites to determine in situ K_d values. Subsamples of each sediment core were centrifuged at 4000 rpm for 20 min, and the pore water was removed for LC-MS/MS analysis. The sediment was dried, sieved to <2.36 mm, homogenized and extracted for PFAS content three times with 0.1% ammonium hydroxide in methanol (see SI for details).^{21,62} Sediment samples were analyzed for PFASs, organic carbon, and mineralogy as described in the SI (Tables S2 and S3).

RESULTS AND DISCUSSION

Spatial Analysis. Vertical profiles of water chemistry show variations with depth below the water table reflecting aquifer geochemical conditions and source zone influences. The full set of chemical results for all groundwater analysis are presented elsewhere.⁵² At well S469, which is located in one of the infiltration beds, concentrations of DOC and phosphate decreased rapidly with depth below the water table, the nitrate peak occurred at an altitude of 8 m, the DO minimum occurred at an altitude of 2–4 m, and total PFASs had a distinct peak at an altitude of 4 m (Figure 2A). The vertical relationships at S469 were stable over time, and the maximum PFOS

concentrations coincided with the DO minimum (Figure 2B). The low DO zone downgradient from S469 (Figure 3A) is a distinct characteristic of the wastewater plume from the infiltration beds, that developed from microbial activity during attenuation of the wastewater contaminants.^{35,63,64}

The A–A' longitudinal transect shows that the sum of PFASs (Figure 3B) forms a relatively shallow (<30 m below land surface) plume that originates beneath FTA-1, extends over 1200 m downgradient in the direction of groundwater flow, and passes beneath (and mixes with) the PFAS plume that originates at the infiltration beds. The sum of PFASs is referenced here primarily to describe the plume shape, while individual PFASs provide insight into sources, transport, and transformation. The width of the PFAS plume is relatively narrow as evidenced by the transverse B–B' and C–C' cross sections (Figures 1 and S2), but may widen downgradient from the infiltration beds. The maximum concentrations of PFOS (63 µg L⁻¹; Figure 3C) and sum of PFASs (95 µg L⁻¹; Figure 3B) were observed at F586 (780 m downgradient from FTA-1). The maximum PFOA (8.0 µg L⁻¹) and PFHxS (18 µg L⁻¹) concentrations occurred at S488 (210 m downgradient from FTA-1).⁵² The molar perfluorinated sulfonate:perfluorinated carboxylate ratios for the groundwater ranged from 0.3 to 14, with a median of 2.8. Except for FOSA, all PFASs are strong acids (Table 1) that are anionic at the groundwater pH (ranged from 4.7 to 6.3).^{53,54}

PFAS Sources. The distribution of PFASs in the groundwater immediately downgradient from FTA-1, particularly the elevated PFOS concentrations, along with the occurrence of branched isomers (Figure S3) confirms their origin from electrochemical fluorination–based AFFFs, as expected because of the history of electrochemical fluorination–based AFFF military usage.^{19,21,65} The detection of 6:2 FtS and 8:2 FtS in groundwater similarly indicates that fluorotelomer-based AFFFs also were used at this site,⁶⁵ although likely less frequently than electrochemical fluorination-based AFFFs, as evident from the observed prevalence of perfluorinated sulfonates and presence of branched isomers.

The FTA-1 and infiltration beds appear to be two distinct long-term PFAS contaminant sources to the aquifer as evidenced by elevated concentrations just below the water

table at both sites (Figures 2A and 3B). Further, the compositionally distinct PFAS signatures from these locations indicate two different sources. The composition of the shallow groundwater below FTA-1 (S425, 14 m altitude) is consistent with the characteristics of AFFF formulations and precursor transformation (Figure 4A). PFHxA and PFHxS, expected products of precursor transformation (since previously investigated AFFFs contained significant quantities of C₆ precursors),²¹ account for about 50% of the PFASs, and the remainder is primarily PFOA, PFOS, and 6:2 FtS. The deeper downgradient wells (S488 and F586 at 6.6 and 6.8 m altitude, respectively, Figure 4A) reflect an AFFF source based on the high sum of PFAS concentrations, with PFOS ranging from 42 to 59% of the molar sum of PFASs. The predominance of PFOS along the plume (Figure 3C and 3D), the known history of fire training with AFFF, and the clear outline of the PFOS plume emanating from the FTA (Figure 3C) indicate that the high PFAS concentrations (Figure 3B) result from the FTA-1 source.

The PFAS composition of shallow groundwater beneath the infiltration beds (S469, 14 m altitude, Figure 4B) has a lower proportion of PFHxS and a higher proportion of PFOA than shallow groundwater from the same altitude beneath FTA-1 (S425). Concentrations of total PFASs at S469 were generally greatest at 4–6 m in altitude (from the influence of the upgradient FTA source) and decreased steadily upward before increasing just below the water table (Figure 2A), indicating the infiltration beds also are a continuing PFAS source, but with lower concentrations. Domestic wastewater is a well-known source of PFASs.^{27–29,66} Enrichment of PFOA and other PFAAs in the shallow groundwater beneath and downgradient from the infiltration beds (the percent PFOA is nearly twice that at FTA-1; Figure 4) indicates that the secondary treated wastewater had a different PFAS composition than the FTA-1 source. The influence of wastewater can be seen most clearly by the elevated proportions of PFOA in Figure 3E. PFOA is a major component of PFASs in wastewater (reaching 1050 ng L⁻¹ in one U.S. wastewater treatment plant) and has been shown to increase in concentration through the wastewater treatment process as a result of precursor transformation.^{27,28,66,67} PFNA concentrations also have been shown to increase during treatment as a result of precursor transformation.²⁸ Notably, PFNA concentrations were highest in the shallow sample from S469 at the infiltration beds (Figure 4B).

Formulations of AFFF previously measured by others had PFOS:PFOA ratios ranging from 49 to 110.²¹ The historical PFAS composition of the WWTP effluent is unknown, but the profile at S469 indicates that the composition of the shallow, lower concentration groundwater is consistent with a wastewater source and the composition of the deeper, higher concentration groundwater is consistent with an FTA source (Figures 2A and 4B). In the groundwater downgradient from the infiltration beds, the two PFAS sources combined and the high concentrations emanating from the FTA-1 overwhelm the lower wastewater concentrations. For example, the sampling location at F586 containing the maximum PFOS concentration at the field site (63 μg L⁻¹) also has 7.5% PFOA, greater than the median value of 4.5% PFOA (Figure 3C and 3E).

Because domestic wastewater disposal at the infiltration beds ceased in 1995,³⁵ the persistence of elevated PFAS concentrations near the water table suggests that they are sorbed to the unsaturated and saturated zone sediments beneath the infiltration beds and are slowly being desorbed and transported

to the groundwater. Precursors retained in the unsaturated zone also could be transforming into more mobile PFAAs, which then migrate to the saturated zone. Similar processes of sorption, desorption, and precursor transformation in the unsaturated zone and shallow saturated zone also are likely occurring at the FTA-1 source area. Overall, the unsaturated zones continue to be a source of PFASs to the groundwater after 18 years (FTA-1) and 20 years (infiltration beds) of inactivity.

Sorption and Advective Transport. Results from the field-determined in situ K_d values were normalized to the fraction of sediment organic carbon (f_{oc} ranged from 0.00013 to 0.0003), and the average $\log K_{oc}$ ($K_{oc} = K_d/f_{oc}$) values ranged from 2.2 to 4.9 L kg C⁻¹ (Tables 1 and S2, see SI for calculations). The PFAS K_{oc} results from this study are similar to other investigations where observed field-determined values are typically higher than laboratory-derived values. McGuire et al.¹² suggested that higher perfluorinated carboxylate $\log K_{oc}$ values may be due in part to carboxylate precursor breakdown during the sediment extraction process. The high K_{oc} values in this study suggest that other sorption mechanisms besides partitioning into sediment organic carbon are important for low organic carbon sediments. The aquifer mineralogy consists predominantly of quartz and feldspar with only trace amounts of metal oxides and clay minerals (Table S3).

Once PFOS is introduced into the groundwater beneath FTA-1, it is estimated to take 15 years to travel the 780 m distance to F586, where the highest PFOS concentrations were observed. This estimate is based on simple 1-D advective transport along the transect, a groundwater velocity of 0.42 m d⁻¹, and a PFOS K_d value of 0.45 L kg⁻¹ ($\log K_{oc} = 3.37$, $f_{oc} = \sim 0.00019$). On the basis of the estimated 15-year transport time to F586, the PFOS present at F586 in 2015 was introduced to the saturated zone around 2000. PFOS transport through the 17-m-thick unsaturated zone would have, therefore, taken between 3 and 30 years, given that AFFF use occurred between 1970 and 1997. PFOA, PFNA, and PFAAs with C₄–C₇ chain lengths are predicted to be transported farther than PFOS based on lower in situ K_{oc} and K_d values (Tables 1 and S2). However, the observed distribution of PFOA is similar to PFOS, possibly due to the in situ production of PFAAs from precursor transformation. The leading edge of the FTA-1 PFAS plume has likely been transported farther downgradient than the A–A' transect, as suggested by detection of PFOS in wells located up to ~4 km downgradient from FTA-1 (Figure S1).

Influence of Wastewater Disposal on Groundwater Geochemistry. Following the cessation of treated wastewater disposal at the infiltrations beds in 1995, the mobile components of the wastewater plume, such as boron, have been transported beyond the A–A' transect.³⁴ However, there is still a residual impact of wastewater disposal on the aquifer, clearly defined by the low DO zone downgradient from the infiltration beds (Figure 3A) more than 20 years after disposal ended. The highest PFOS concentration (Figure 3C) occurred in the zone with low DO concentrations.

Historical hydrologic loading of the treated wastewater to the aquifer is estimated to have been between 380 and 5700 m³ d⁻¹ between 1936 and 1995.⁶⁸ Specific conductance of the effluent ranged from 340 to 520 μS cm⁻¹ and DOC concentrations ranged from 6.4 to 19 mg L⁻¹.^{35,47} Continuous monitoring of groundwater quality at S469 since the end of wastewater disposal in 1995 has shown slowly decreasing DOC concentrations that continue to persist (3.0 mg L⁻¹ during

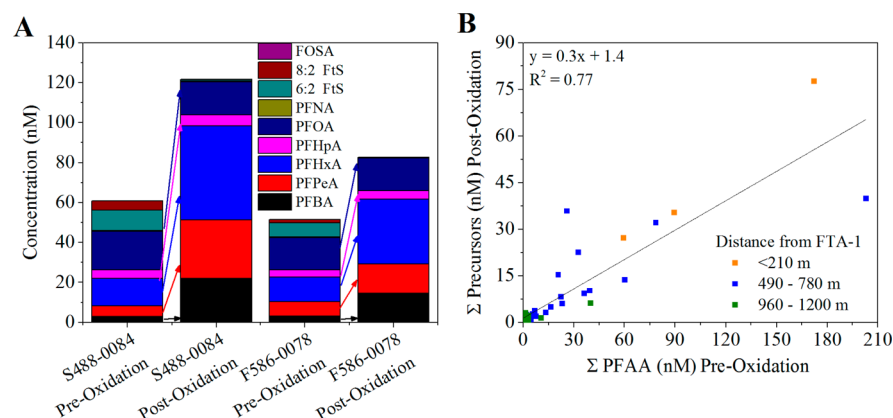


Figure 5. Results from the total oxidizable precursor assay conducted on selected groundwater samples. (A) Concentrations of poly- and perfluoroalkyl substances in groundwater samples from wells S488-0084 and F586-0078 pre- and post-oxidation and (B) linear relationship between the groundwater sample molar sum of perfluoroalkyl acid (PFAA) concentrations pre-oxidation and the molar sum of precursors post-oxidation ($n = 46$). [FTA-1 is the fire training area. Compound abbreviations can be found in Table 1.]

June 2015 sampling, Figure S4A) above background levels because of desorption of organic carbon from the aquifer sediments.^{35,63} Specific conductance also has remained elevated ($183 \mu\text{S cm}^{-1}$ at S469 during June 2015 sampling), and DO concentrations remain low because of persistent biogeochemical oxygen demand (Figures 2 and 3A).³⁵

The persistent wastewater-related geochemical conditions encountered by the FTA-1 PFAS plume as it passed through the residual wastewater plume include elevated concentrations of dissolved ions and sediment organic carbon, both factors that can influence PFAS transport.^{55,56,69} Groundwater beneath the infiltration beds remained oxic to suboxic during the period of wastewater disposal because of the introduction of oxygenated treated wastewater.^{63,64} The oxygenated conditions resulted in stability of iron and manganese oxide grain coatings on the aquifer sediments.^{63,64,70} The increased sediment organic carbon and ionic interactions resulting from wastewater loading may have enhanced PFAS sorption beneath the infiltration beds through both hydrophobic and electrostatic interactions. The higher K_{oc} values for PFOS indicate greater sorption to the sediments than PFOA and shorter chain length PFAAs.

The PFASs that were sorbed to the aquifer sediments under wastewater disposal conditions were potentially remobilized following cessation of disposal, owing to (1) reduction in dissolved ion concentrations, (2) desorption of sediment organic carbon, and (3) reductive dissolution of positively charged iron and manganese oxide grain coatings following the onset of anoxic conditions beneath the infiltration beds.^{35,64,70} Electrostatic interactions with dissolved iron(II) may promote transport of PFOS.⁷¹ The slow desorption of sediment organic carbon beneath the infiltration beds releases DOC and other hydrophobically sorbed contaminants, including PFASs, while a reduction in dissolved ion concentrations may increase the repulsion between the negatively charged quartz and feldspar aquifer sediments (Table S3)³¹ and anionic PFASs. A combination of factors likely led to the elevated PFOS concentrations at F586, although elevated concentrations of shorter-chain length PFAAs, such as PFBS at well F586 (Figure S4B), also suggest remobilization.⁷²

Total Oxidizable Precursor Assays. The total oxidizable precursor assay can be employed to estimate total PFAA precursor concentrations by oxidizing polyfluorinated compounds into perfluorinated carboxylates and measuring the

increase in molar carboxylate concentrations.^{21,61} A sulfonamide precursor with C_n ($n =$ the number of carbons in the chain) is expected to transform into a C_n perfluorinated carboxylate upon oxidation.²¹ A range of C_4 to C_{n+1} perfluorinated carboxylates are expected to form from oxidation of fluorotelomer precursors.²¹ Following oxidation of selected groundwater samples, PFBA concentrations increased by a factor of 5.0 ± 3.0 , PFPeA increased by a factor of 2.9 ± 1.3 , PFHxA increased by a factor of 3.7 ± 2.2 , PFHpA increased by a factor of 1.5 ± 0.4 , PFOA increased by a factor of 1.6 ± 2.2 , and PFNA increased by a factor of 1.2 ± 0.3 (Figure 5A).

The 6:2 FtS precursor is primarily transformed into PFBA, PFPeA, and PFHxA during oxidation, while 8:2 FtS is primarily transformed into PFPeA, PFHxA, PFHpA, and PFOA.^{21,61} If all of the fluorotelomers measured in the samples were oxidized into the expected PFAAs, 6:2 FtS would account for $9.9 \pm 9.3\%$ of the PFBA, PFPeA, and PFHxA increase and 8:2 FtS would account for $9.1 \pm 10\%$ of the PFPeA, PFHxA, PFHpA, and PFOA increase. FOSA is expected to transform into PFOA,²¹ although pre-oxidation concentrations were so low ($\leq 164 \text{ ng/L}$) that it produced negligible quantities. The additional post-oxidation increase in PFAAs is due to transformation of polyfluorinated compounds that were not quantified here.

Post-oxidation, PFBA, PFPeA, and PFHxA contributed $25 \pm 8.5\%$, $22 \pm 9.9\%$, and $44 \pm 17\%$ of the total molar carboxylate increase, respectively, consistent with other studies,²¹ and the substantial increase in PFHxA indicates that C_6 precursors were dominant in the original samples. Relatively small increases in PFHpA and PFOA indicate low abundance of C_7 and C_8 precursors. Increases in molar perfluorinated carboxylate concentrations following oxidation provide an estimate of total molar precursor concentrations,²¹ which comprised $31 \pm 15\%$ of the total PFASs at the Cape Cod site, within the range of what has been previously reported (23% for groundwater, 33–63% for wastewater).^{21,73} This suggests that the thermal soil remediation at FTA-1 either did not break down the precursors, or a substantial mass of precursors had passed through the unsaturated zone prior to remediation.

Precursors are cotransporting with the main FTA-1 derived PFAS plume (Figure 3F) and show a similar spatial distribution as PFOS (Figure 3C). There is a linear correlation between the sum of molar PFAA concentrations pre-oxidation and the calculated sum of molar precursor concentrations post-

oxidation from the different sampling locations (Figure 5B). This trend does not vary substantially with distance from FTA-1, and precursors exceed 50% of the total PFAS concentration at the farthest downgradient well (Figure 3G). Precursors have been suggested to be less mobile than PFAA, although data on this topic are limited and many precursors have yet to be identified.^{12,74} The results indicate that at least some precursor sorption coefficients for the low-carbon Cape Cod aquifer sediments are similar to PFAS sorption coefficients reported in this study (Table 1). Some precursors may be less mobile and retained in the unsaturated zone. A previous study on anaerobic biotransformation of 6:2 and 8:2 fluorotelomer alcohols in digester sludge (methanogenic conditions) reported low levels of PFAAs produced (≤ 0.4 mol % for PFHxA and PFOA) over the 181-day experiment.²⁴ If precursor transformation rates decrease under anaerobic conditions, then precursors would be expected to persist during transport in the low DO conditions associated with the wastewater plume downgradient from FTA-1. Overall, the finding of cotransport of PFAA precursors at this field site has implications for water resources, as precursors can increase the total PFAA mass over time through transformation.

The PFHxS:PFOS ratio can be related to the degree of precursor transformation,^{12,21} and electrochemical fluorination-based AFFF formulations from 1988 to 2001 were shown to have ratios between 0.08 and 0.14.²¹ The PFHxS:PFOS ratio observed in groundwater near the water table at FTA-1 (S425) was 3.1 (Figure 3H), and increased to 5.8 at F575 (960 m downgradient from FTA-1). Well F575 had minimal percentages of precursors (Figure 3G) and elevated PFHxS:PFOS ratios in the same location, suggesting different sources or that precursor transformation contributed to the PFHxS concentrations. Well F424 had PFHxS:PFOS ratios up to 3.8 (Figure 3H) and up to 68% precursors (Figure 3G), which suggests preferential transport of PFHxS relative to PFOS, and mobile precursors (perhaps intermediates).

Differential Transport: Chain Length and Head Group Effects. The relative mobility of PFASs can be assessed considering (1) the estimation of PFAS-specific retardation factors that are dependent on the sediment characteristics and geochemical conditions, (2) the estimation of precursor retardation factors, and (3) potential biotransformation of precursors into PFAAs.^{22,23,25,75,76} Negligible DO in groundwater downgradient from the infiltration beds may impede current precursor transformation rates, resulting in transport without the confounding factor of in situ production. The spatially dependent percentages of each PFAA relative to total PFASs measured suggests that differential transport is occurring, as illustrated by comparing the PFOS distribution (Figure 3D) with those of shorter chain PFAAs (Figure S5). Aside from the shallow samples beneath the infiltration beds, the highest percentages of PFOA along the transect (21%) were observed 960 m downgradient from FTA-1, although this is likely a result of wastewater inputs. The proportions of PFHxS were greatest in the groundwater near FTA-1 (S425) and at the deeper altitudes along the transect (Figure S5A). High percentages of PFHpA (12%), PFHxA (20%), and PFPeA (25%) were detected at lower altitudes and farther downgradient at F575 and F424 (Figure S5B–D). These results indicate that shorter chain length PFAAs are more mobile than PFOS both vertically and horizontally. The highest percentages of PFOS (82%) were near the infiltration beds (Figure 3D) between 580 and 690 m from FTA-1, indicating that PFOS has

not traveled as far compared to shorter chain length PFAAs ($\log K_{oc} = 2.17\text{--}2.76$), reflecting its relatively high $\log K_{oc}$ value (3.37). These results contrast with those of McGuire et al.¹² who reported no evidence of differential transport, potentially owing to in situ biotransformation of precursors. At the Cape Cod site, anoxic conditions may have allowed for the observation of differential transport through the elimination or reduction of in situ PFAA production from precursors. While the observed spatial distributions are likely due to a combination of factors including multiple sources, complex hydrological history, differential transport, and precursor transformation, the differences between percentages of PFOS and PFPeA, PFHxA, PFHpA, and PFHxS suggest differential transport is a primary factor determining spatial distributions.

Conceptual Site Model and Environmental Implications. The higher concentration PFAS plume emanating from FTA-1 comingles with the lower concentration PFAS plume emanating from the infiltration beds 580 m downgradient from FTA-1. The unsaturated zones at FTA-1 and the infiltration beds are continuing sources of PFASs to the aquifer decades after source removal. This finding suggests that the unsaturated zones beneath fire training areas and wastewater infiltration beds at other sites can act as long-term PFAS sources to groundwater over several decades. Furthermore, the shallow groundwaters beneath the two unsaturated zones at this field site are compositionally distinct. The unique profiles observed here may help with source identification in cases where the point source is not known. Another significant component of the conceptual site model is the finding that some precursors are quite mobile at this field site. Therefore, monitoring of precursors downgradient from point sources is essential to accurately predict future PFAA concentrations. Finally, there is evidence of differential transport dependent on chain length and headgroup, which has not been shown previously at field sites.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b05573.

Groundwater and aquifer sediment sampling, analytical materials, sample analysis, LC-MS/MS conditions, total oxidizable precursor assay, sediment organic carbon and mineralogy, partitioning experiments, advective transport calculations, LC-MS/MS parameters, K_{oc} and TOC results, mineralogy results, groundwater total oxidizable precursor assay results, results for PFOS analysis of groundwater samples collected from the Cape Cod well network during 2014, sum of all PFASs in transverse cross sections, example chromatogram of branched and linear isomers, DOC and PFBS concentrations within the A–A' transect, molar percentages of PFHxS, PFPeA, PFHxA, and PFHpA (PDF)

📄 Related Articles

Data release see: <https://doi.org/10.5066/F7Z899KT>.

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