EXECUTIVE SUMMARY

Evaluating the Importance of Precursor Transport and Transformation for Groundwater Contamination with PFAS

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Elsie M. Sunderland
Chad Vecitis
Harvard University

Rainer Lohmann, Ph.D.
University of Rhode Island

SERDP

SERDP Project ER18-1280

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ACRONYMS AND ABBREVIATIONS

AFCEC	Air Force Civil Engineering Center
AFFF	aqueous film-forming foam
ECF	electrochemical fluorination
EOF	extractable organofluorine
FASA	perfluoroalkyl sulfonamides
FHxSA	perfluorohexane sulfonamide
FT	fluorotelomerization
FTSA	fluorotelomer sulfonates
HRMS	High-resolution mass spectrometry
JBCC	Joint Base Cape Cod
K_{ai}	Air-water interface partition coefficient
K_d	sediment-water partition coefficient
MDL	method detection limit
PFAA	perfluoroalkyl acid
PFAS	per- and poly fluoroalkyl substances
PFBS	perfluorobutane sulfonate
PFCA	perfluoroalkyl carboxylates
PFHxS	perfluorohexane sulfonate
PFHxSAm	perfluorohexane sulfonamido propyl amine
PFHxSAmS	perfluorohexane sulfonamido propyl quaternary amine
PFOA	perfluorooctanoate
PFSA	perfluoroalkyl sulfonates
TOP	total oxidizable precursor assay
TOP+BI	total oxidizable precursor assay interpreted using Bayesian inference
USGS	United States Geological Survey

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1.0 INTRODUCTION

The project team investigated how perfluoroalkyl acid (PFAA) precursor transport and biotransformation are affected by varying geochemical conditions in groundwater environments. The work was conducted at the Joint Base Cape Cod (JBCC) site and surrounding areas that historically received per- and polyfluoroalkyl substances (PFAS) inputs from aqueous film-forming foams (AFFF) used during fire training exercises. The JBCC fire training area sits atop an unconfined aquifer with soils that consist of medium to coarse grain sand and gravel, with extremely low organic carbon (<0.1%), anion exchange capacity, and silt/clay content. The project team leveraged from decades of U.S. Geological Survey (USGS) research for this project and their detailed understanding of subsurface hydrology of this area.

2.0 OBJECTIVES

The overarching objective of this project was to better understand factors affecting the mobility and accumulation of PFAS in groundwater, and included four specific objectives:

1. Characterize the mobility of PFAA precursors in groundwater environments using column experiments.
2. Assess factors affecting biotransformation of PFAA precursors and quantify the potential rates of these reactions in natural environments using biotransformation experiments.
3. Formalize understanding of PFAA precursor chemistry in groundwater environments using a model to quantify the mobility of these compounds.
4. Develop and validate a new tool (passive sampler) for measuring time-weighted average concentrations of PFAS.

3.0 TECHNICAL APPROACH

The project team focused research on the PFAS most frequently detected at the JBCC field site. The relative abundance of electrochemical fluorination (ECF)-derived precursors in groundwater from JBCC suggested that the use of 3M products constituted approximately 80% of total AFFF use at the site. This result was based on results of the total oxidizable precursor assay interpreted using Bayesian inference (TOP+BI) in groundwater from JBCC immediately below the former fire training area. 3M AFFF contained a propriety mixture (Confidential Business Information under the Toxic Substances Control Act) of 850–900 mM fluorine as PFAS that was approximately 50% precursors, mainly sulfonamido compounds with 4 and 6 perfluorinated carbons (Barzen-Hansen et al., 2017; Ruyle et al., 2021a).

Since a main driver of PFAS retardation in groundwater is partitioning and sorption to solids, the project team used column experiments to determine site-specific sediment-water partition coefficients (K_d). Sediment on Cape Cod, which is primarily quartz and feldspar, has a net negative charge in the range of reported groundwater pH. Partitioning to organic carbon is less important at JBCC compared to other AFFF-impacted sites, and ionic interactions with charged sites on sediment surfaces (electrostatic attraction/repulsion) and other ionic co-solvents (ion exchange, divalent cation bridging) likely play a larger role in sorption.

A total of 17 PFAS were chosen for analysis in column experiments because they were the only compounds detected above method detection limit (MDL = 2.5–40 ng/L) in the groundwater from the fire training area: these included the perfluoroalkyl carboxylates (PFCA) with three through seven perfluorinated carbons (C3–C7), the C4–C8 perfluoroalkyl sulfonates (PFSA), the 6:2 and 8:2 fluorotelomer sulfonates (FTSA), and the C4, C6, and C8 perfluoroalkyl sulfonamides (FASA). Sediment and groundwater were collected from the site to perform the column experiments. The hydrodynamics of the columns were tested using bromide as a conservative tracer.

The project team conducted biotransformation experiments on the most abundant precursors in 3M AFFF with available commercial standards. The most common precursor structures in 3M AFFF are C6 perfluoroalkyl sulfonamido compounds that are expected to biodegrade into perfluorohexane sulfonate (PFHxS). Two commercially available analytical standards exist for precursors in this class (perfluorohexane sulfonamido propyl amine [PFHxSAm] and perfluorohexane sulfonamido propyl quaternary amine [PFHxSAmS]) as well as one additional standard for a suspected intermediate metabolite (perfluorohexane sulfonamide [FHxSA]). The project team incubated water and sediment slurries representative of the groundwater/surface water boundary from the JBCC field site fortified with diluted concentrations of individual precursor spikes or 3M AFFF and subsampled at defined intervals. Experiments were performed in triplicate and abiotic controls were included in each experiment.

The project team analyzed archived groundwater samples (*n*=191 samples) from the plume originating from the JBCC fire training area collected between 2002 and 2021. PFAS concentrations showed substantial variability in the downstream plume, and determined that additional sampling would be needed to fully define the plume position and extent of the contamination. The project team therefore refined the spatial domain of the modeling to focus on PFAS transport and transformation in the immediate vicinity of the fire training area, where abundant data for the well immediately below the fire training area were available from archival USGS samples and data reported by the Air Force Civil Engineering Center (AFCEC) and the National Institute of Standards and Technology.

PFAS precursors released to the environment may undergo abiotic or biotic transformation and eventually form PFAA as terminal products. Precursors that originate from the ECF process have a fully fluorinated backbone in their chemical structure, while those manufactured by the fluorotelomerization (FT) process are not fully fluorinated (Buck et al., 2011). Targeted mass spectrometry methods only capture a small fraction of the PFAS used in commerce and released to the environment (Yeung and Mabury, 2016; Koch et al., 2019). It is challenging to detect most precursors using targeted methods because many analytical standards are not commercially available. High-resolution mass spectrometry (HRMS) can be used to confirm the presence of specific precursors and assign probable structures to unknown PFAS. However, these results are not quantitative and are difficult to interpret when diverse precursors are present at low concentrations, which is often the case with AFFF-impacted systems. Semi-quantification of PFAS from HRMS measurements has been used to estimate the concentrations of analytes that lack matched analytical standards, but uncertainties are not quantifiable and could span an order of magnitude or more (Nickerson et al., 2020; Charbonnet et al., 2021).

To address some of the challenges associated with PFAS precursor detection, the project team developed a statistical method for interpreting results from the TOP assay, which groups precursors by their perfluorinated carbon chain length and manufacturing origin (ECF or FT) using Bayesian inference (TOP+BI) (https://github.com/SunderlandLab/oxidizable-pfas-precursor-inference; Ruyle et al., 2021a). The TOP assay transforms oxidizable precursors to PFCA with known perfluorinated carbon chain lengths that are detectable at trace levels using targeted mass spectrometry analysis. The TOP+BI method is preferred over analytically detected changes in PFCA concentrations (only TOP) because it explicitly accounts for analytical uncertainties, incomplete recoveries, and variability in product yields following precursor degradation. This toolbox can quantify all PFAS originating from legacy ECF AFFF produced by 3M (validated using extractable organofluorine [EOF] measurements) and was applied in this study to samples collected from immediately below the fire training area for more than a decade.

The project team developed a 4-box geochemical model to represent the temporal evolution of precursors and changes in reservoirs of the terminal PFAS in soils and groundwater at the former fire training area over time. The model includes individual compartments for precursors and terminal compounds in soil and groundwater. It was forced by inputs from AFFF-use, constrained by known dates of use and measurements of PFAS in soil cores at the fire training area, and in groundwater over time. The project team used uniform prior probability distributions to characterize plausible uncertainty of AFFF use (PFAS loading), precursor biodegradation rates, and retardation due to partitioning to solids and retention at the air-water interface, using data obtained from the literature (Weber et al., 2017; Guo et al., 2020) and column experiments as part of this study. Advection rates through soil and groundwater were based on hydrological information from USGS. The project team then optimized the simulation using Bayesian inference (PFAS loading, biodegradation rate, and retardation) to reproduce measured concentrations by selecting parameter values within their uncertainty ranges that result in the smallest differences between modeled and observed soil and groundwater concentrations. Specifically, the project team sampled from the data-optimized distribution of parameters using Markov Chain Monte Carlo simulations with the same sampler and hyperparameters that were used to infer oxidizable precursor concentrations from the TOP assay (see Ruyle et al., 2020a). The project team calculated site-specific K_d and air-water interface partition coefficients (K_{ai}) from inferred retardation factors using the equations derived in Brusseau et al. (2018).

A novel tube passive sampler was developed using microporous polyethylene tubes filled with Oasis hydrophilic lipophilic balance sorbent. Samplers were deployed in the lab and field and tested under different flow conditions, environments, and in the presence of biofouling. In the lab, triplicate tube passive samplers were deployed at four different flow rates (0, 10, 20, and 60 cm s^{-1}) and two different temperatures (15°C and 25°C). Passive samplers were deployed in the Schaefer field for 14-28 days at three locations, including AFFF-impacted groundwater (JBCC) and a river downstream of the former fire training area on JBCC, and a river downstream of a historical textile mill in Westerly, RI (Pawcatuck). Uptake of nine PFAA was compared under experimental tank deployments, field deployments on Cape Cod, MA, and to a numerical model for integrative passive sampling from the literature (Schaefer et al, 2019; Vrana et al., 2005) that was customized to predict sampling rates (mL day^{-1}) from the physicochemical properties of PFAS and the passive sampler design.

4.0 RESULTS AND DISCUSSION

Results of column experiments showed site-specific log K_d values for PFAS in Cape Cod, MA sediment ranged from -1.7 to 0.6. Each additional perfluorinated carbon was associated with a 0.72 ± 0.05 increase in log K_d averaged across all PFAS classes. For the same number of perfluorinated carbons, sorption also depended on the functional group and followed the order PFCA < PFSA < FTSA < FASA. Lab-derived K_d values agreed with field-derived K_d reported by Weber et al. (2017) within an order of magnitude. A spike in aqueous-phase concentration due to desorption was observed for the anionic PFAS with log K_d values > -1 during elution with PFAS-free groundwater with much lower Ca^{2+} concentrations. This likely reflects an important role for divalent cation bridging on sorption in these low organic carbon sediments. Carboxylates exhibit greater complexation than sulfonates to divalent cations such as Ca^{2+} and Fe^{2+} due to their lesser degree of hydration (Groenendijk et al., 2021). The project team hypothesize that cation bridging could explain field data from a nearby kettle lake that showed substantially greater sorption of PFCA compared to PFSA in infiltrating groundwater under reducing conditions, which produce divalent Fe^{2+} and Mn^{2+} (Tokranov et al., 2021).

For the three C6 sulfonamido precursors included in this study (PFHxSAm, PFHxSAmS, FHxSA), the expected means of rate constants for microbial association exceeded sorption by at least a factor of 2x and ranged between -0.2 to -5.0 $days^{-1}$. At 29°C, the first order half-life of PFHxSAmS and PFHxSAm was less than half a day and approximately 5x faster than the bioassociation of FHxSA. Biotransformation of all three precursors was indicated by formation of PFHxS, the terminal product of microbial biotransformation of C6 sulfonamido precursors. Formation of PFHxS appeared to proceed at a constant rate throughout the experiment regardless of any changes in the concentrations of reactants (precursors). These results imply that the formation of PFHxS was not limited by the supply of precursors for biotransformation but rather by the microbial reactions catalyzing this transformation. Despite faster microbial association of the zwitterions compared to FHxSA, the rate limiting step for PFHxS production is the oxidation of the zwitterions to FHxSA rather than oxidation of FHxSA to PFHxS. This could explain why minimal accumulation of FHxSA was observed in the bioactive experiments. The relative stability of precursors against oxidation into PFAA in soils allows for their transport through the vadose zone into groundwater and downstream watersheds (Weber et al., 2017). Past work near the field sampling location for the groundwater/sediment slurries used in this study showed a distinct seasonality in precursor transport across the groundwater/surface water boundary immediately downgradient from the legacy AFFF plume (Ashumet Pond, MA) (Tokranov et al., 2021). Rapid removal (<36 hours) of up to 85% of PFHxS precursors was observed in field data during the summer months but not in the winter months. These field-observations are consistent with the large and rapid (<1 day) bioassociation of precursors observed experimentally in this study. The project team estimated based on modeling that biotransformation of all precursors into PFHxS would require more than a year. These results suggest that some of the precursors and/or intermediate metabolites associated with the immobile microbiome in the field would be released back into the aqueous phase during winter months when turnover of microbial biomass occurs, which is consistent with prior field observations (Tokranov et al., 2021).

In groundwater samples from below the JBCC fire training area, all EOF (101±7%) was accounted for by combining targeted PFAS measurements with the TOP assay interpreted using Bayesian inference. The C6 and C8 PFSA and the C7 PFCA were the predominant terminal PFAS, consistent with their composition in ECF AFFF (Ruyle et al. 2021a; Houtz et al. 2013).

High resolution mass spectrometry yielded unambiguous spectrum-structure matches for 15 precursors, 9/15 of which were C4 and C6 perfluoroalkyl sulfonamido compounds that had either been previously identified in 3M AFFF or were expected biodegradation intermediates. Large temporal variability but no clear temporal trends in PFAS concentrations were observed between 2007 and 2021. Temporal fluctuations for terminal PFAS with fewer precursors (perfluorooctanoic acid [PFOA]) and the most hydrophilic PFAS (perfluorobutane sulfonate [PFBS]) were significantly correlated with soil moisture ($p<0.05$), indicating saturation effectively flushes these PFAS through the vadose zone into groundwater. No correlation was observed for other PFAS, including all precursor classes, that have greater propensity for sorption and high surface-activity (high K_d and K_{ai}). Numerical modeling constrained by measurements suggested that soil contains a much larger reservoir of PFAS than groundwater (2–22-fold), and biodegradation of precursors (estimated half-life = 40 – 150 yr) is the greatest contributor (expected mean 56-98%) to 2021 concentrations of PFBS and PFHxS in groundwater below the former fire training area.

Results of passive sampler deployments showed that at 15 ℃, the measured sampling rates for perfluorohexanoic acid of 48-76 mL day^{-1} were in good agreement with the model predictions (51 mL day^{-1}) across 10-60 cm s^{-1} water flow speeds. PFHxS sampling rates at 15 ℃ were in similar agreement (11+/- 6 mL day^{-1} measured, 14 +/- 4 mL day^{-1} modeled) and displayed no discernible increase across variable water flows. Similar sampling rates were observed during field deployments, highlighting the general applicability of the sampler in environmental conditions. This research demonstrates that the polyethylene tube's sampling rates are predictable given a known temperature across a range of flow speeds, with no discernable impacts of biofouling.

5.0 IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS

This research highlights the potential role of divalent cation bridging at field-sites with low organic carbon, anion exchange, and silt/clay content for retarding PFAS transport. Biotransformation experiments show precursors are strongly bio-associated with the microbiome, but slowly transformed. Seasonal fluctuations in the microbiome may be an important factor dictating precursor transport in groundwater and at the groundwater/surface water boundary. The statistical inference procedure developed as part of this work differentiates the relative use of ECF versus FT AFFF in the environment (Ruyle et al. 2021b), which is particularly useful at military fire training areas where both types of products were often used but poor record-keeping prevented a priori knowledge of how much of each type of AFFF was used (Place and Field, 2012). Field data and modeling results suggested treatment of soil at AFFF impacted sites will most effectively prevent long-term groundwater contamination. A novel tube passive sampler design was developed as part of this study that can provide good time-integrated measurements of nine PFAA. This was important because large temporal variability in concentrations at the same groundwater wells were measured over time at JBCC.

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