Title:	Contaminant threats to groundwater-supplied ecosystem services in the Farmington River watershed
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Summary

Per- and polyfluoroalkyl substances (PFAS) contamination of water resources and aquatic habitats is a global concern due to the widespread use and loading of PFAS compounds to the environment. In Connecticut (CT), PFAS pollution has become one of the most pressing environmental health concerns after a series of short-term and high-volume releases from an airport spill and fire in the Farmington River watershed in 2019. This study set out to characterize patterns of PFAS in groundwater discharges to stream surface waters of the Farmington River watershed. Between 2020-2022, we sampled waters in 24 streams distributed throughout the watershed and characterized these samples for 14 individual PFAS compound concentrations as well as their mixtures.

We detected 7/14 of the analyzed compounds in our groundwater discharge and surface waters samples (PFBS, PFHxA, PFHpA, PFHxS, PFOA, PFOS, PFNA). Average site-specific individual compound concentrations ranged from below detection limit (BDL) to 0.181 ng mL^{-1} and average sum concentrations of the seven detected compounds per site and sample type ranged from BDL to 0.24 ng mL^{-1}. Five percent of our samples (n = 10/186) exceeded the U.S. EPA and CT's Department of Public Health (CT DPH) health advisory levels for drinking water. Three specific PFAS compounds (PFHxA, PFOA, and PFOS) were most commonly detected in our analysis and they were detected together at 45% of our study sites (n = 11/24). Our results also indicated that PFAS concentrations and mixtures in groundwater discharges vary spatially among samples collected within a given stream as well as between sampling events at specific sampling locations. These results point to the need for sampling strategies that are designed to capture spatial and temporal variation to best characterize exposure scenarios for resident aquatic biota.

Introduction

Groundwater (GW) discharges (GWDs) to streams and rivers are primarily perceived as beneficial suppliers of ecosystem services in groundwater-dependent stream ecosystems. GWDs supply purified freshwater and fundamental nutrients and generate surface (base) flow during seasonal low flow and drought conditions (Cantonati et al. 2020; Cluer and Thorne 2014; Kløve et al. 2011). Surface water (SW) ecosystems and ecosystem services rely both extensively and substantially on GW contributions, with recent work indicating that 40% of U.S. streams have substantial GW contributions(Hare et al. 2021) and GW may supply as much as 40% of all U.S. streamflow (Alley, Reilly, and Franke 1999). GWDs to SW also sustain the diversity of ecological communities by creating dynamic habitat and refugia for aquatic fauna. In the context of ecosystem services, the growing body of evidence that GW discharges can also serve as point sources of contaminant loading indicates that groundwater-dependent stream ecosystems are compromised where discharge zones are connected to land surface contaminant sources (Cantonati et al. 2020; Mor et al. 2006; Tesoriero et al. 2013).

Surface land use practices (Kanno, Vokoun, and Letcher 2014) and insufficient waste-stream storage (Briggs, Lane, et al. 2018) facilitate percolation of contaminated water into shallow and deeper aquifers (i.e., recharge) with the potential to impair GW quality at sub-basin to regional watershed scales. Recharged contaminants stored in aquifers and carried along GW flow paths can cause widespread contamination of freshwater and marine receiving waters (Briggs et al. 2018; McKnight et al. 2015; Roy and Bickerton 2012; Walter, D.A., McCobb, T.D., and Fienen, M.N. 2019). GW flow path lengths and storage durations can also contribute to substantial temporal lags between the time of aquifer loading and subsequent GW discharge to SW (Hamilton 2012). Short-term spills of emerging contaminants have been shown to load shallow floodplain groundwater, causing contaminants to bleed back slowly to surface water over a period of years via preferential groundwater discharge zones, several km downstream of the original spill site (Cozzarelli et al. 2020). Provided that (a) GW contaminant burdens exceed those of associated SW systems, (b) that most of the GW contamination in the U. S .is in shallow aquifers with direct connections to SW habitats via GW discharges, and (c) GW contaminant loading potential is highest during baseflow conditions which are increasing in importance with climate-induced stream stress (Lookingbill et al. 2009; Winter et al. 1999), improved understanding and predictive capacity of where GWDs represent major and/or chronic conduits of SW pollution is required for accurate tracking of GW contaminant control points and informing both GW and SW quality management.

This study evaluated concentrations and mixture compositions of per- and polyfluoroalkyl substances (PFAS) in GWDs in the Farmington River watershed, a 5th order river network with mixed forested, agricultural, and urban land uses in Connecticut (CT). PFAS pollution has become one of the most pressing environmental health concerns in CT after a series of short-term/high-volume releases from an airport spill and fire in 2019 (Hladky 2019; The Dangers of PFAS n.d.). The distribution of both active and closed landfills within the watershed are a probable, additional source of long-term/low-volume PFAS releases to local aquifers and subsequently to surface water resources and habitats. This proposed study built on previous GW research in the Farmington River basin focused on GWD nitrogen loading. It lays a foundation for future research on the ecological and public health implications of contaminated baseflows in the Farmington River watershed and more broadly informs the implications of impaired GWDs for SW quality.

Objective(s)

The objectives of this project where to 1) characterize PFAS concentrations and mixture compositions in GWDs and SWs in streams representative of the Farmington River watershed and 2) investigate the potential for spatiotemporal variation in PFAS concentrations and compositions at specific locations of GWD to SW resources.

Results/Discussion

Overview of approach:

Our study included 24 sites (Fig. 1) sampled for a combination of GWD and SW samples between 2021-2022 and analyzed for a suite of 14 PFAS compounds, and including some preliminary samples collected from the mainstem of the Farmington River in 2020. Our sites are representative and spatially distributed across the watershed to capture variation in surrounding land cover; cold-water habitats as previously identified by the Connecticut Department of Energy and Environmental Protection; and proximity to "potential PFAS sources" as facilities that have categorically been associated with the potential to load PFAS to the environment (e.g., fire-fighting training facilities). Importantly, these locations have not been confirmed as contributors of PFAS to the environment and investigating them as PFAS sources was beyond the scope of this project. Rather, we used information about their locations to guide our sampling for where we might identify PFAS in the watershed. We prioritized streams that were wadeable, had public access, and where we were able to confirm the presence of groundwater discharges. Of the 24 sites included in this study, 17 were majority forested, 1 was majority agriculture, and 5 were majority developed. Fourteen of the 24 sites had at least one potential PFAS source within the upper catchment area as defined by the United States Geological Survey (USGS) StreamStats application (Ries et al., 2017).

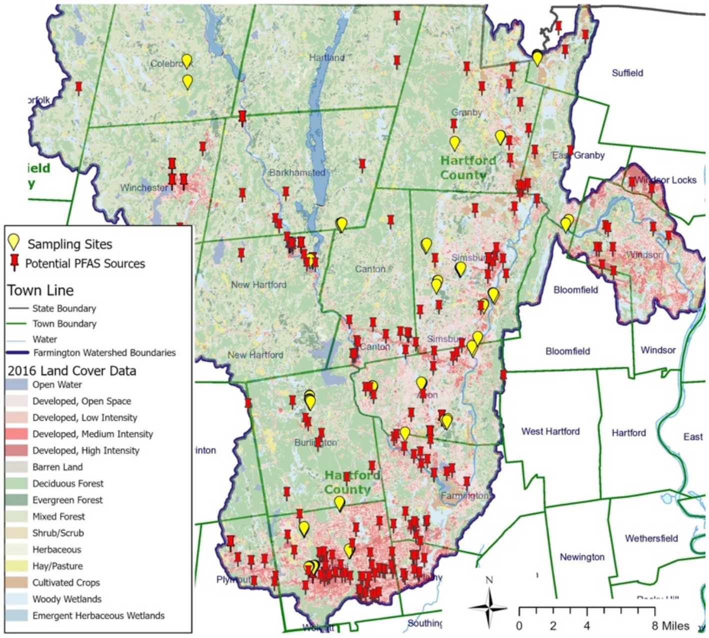

Fig. 1: *Map of sample sites (yellow pins), potential PFAS source sites (red pins), and land cover (NLCD 2016) in the Farmington River Watershed.*

We identified groundwater seeps by handheld thermal infrared imaging (TIR) surveys based on colder temperature profiles of groundwater seeps (9 -15°C) compared to surface waters (>16 °C) according to previously established methods (Barclay et al., 2020; Briggs et al., 2020). Field blanks were collected by passing deionized (DI) water through the sampling apparatus into a 250 mL HDPE bottle in the field prior to collecting field samples. Groundwater discharge samples were collected from identified seeps using a PushPoint sampler (MHE Products, 24" long x ¼" diameter) inserted 20 cm into the sediment. We extracted groundwater discharge through the sampling apparatus using a 60 mL luer-lock syringe (Fisher) and Tygone tubing (Saint Gobain) and discarded until the water ran clear. Samples were collected in 250 mL polypropylene copolymer (PPCO) bottles. We rinsed the sampling apparatus between sampling sites with deionized H_2O (DI water). SW samples were collected ~10 cm below water surface along each groundwater sampling transect. We recorded ancillary variables including GWD and SW temperatures, GWD seep extents, stream width, GPS locations, and substrate characteristics for each sample site. Samples were stored on ice for transport to the University of Connecticut (UConn, Storrs, CT, USA) and refrigerated them at 4°C prior to preparation for chemical analysis.

All samples were prepared and analyzed with industry standard clean field techniques at UConn's Center for Environmental Sciences and Engineering within two weeks of sample collection and analyzed for 14 PFAS compounds (Table 1) using a modified version of U.S. EPA Method 537 for waters. All quality control and field-collected samples were analyzed using a Waters Acquity™ UPLC® coupled with an Acquity™ TQD™ tandem mass spectrometer (Waters Co., Milford, MA) fitted with a PFAS conversion kit. The detection and quantification of analytes and surrogate compounds was performed in negative ESI- MS/MS mode (MRM) using the Waters IntelliStart™ software for analyte signal optimization. Statistical analysis for obtaining calibration and quantification results for all compounds were run using Waters QuanLynx™included in the MassLynx™ software v.4.2.

Table 1: List of PFAS analyzed

Compound	**Acronym**	**Chain length**
Perfluorohexanoic acid	PFHxA	6
Perfluoroheptanoic acid	PFHpA	7
Perfluorooctanoic acid	PFOA	8
Perfluorononanoic acid	PFNA	9
Perfluorodecanoic acid	PFDA	10
Perfluoroundecanoic acid	PFUnDA	11
Perfluorododecanoic acid	PFDoDA	12
Perfluorotridecanoic acid	PFTrDA	13
Perfluorotetradecanoic acid	PFTeDA	14
Perfluorobutanesulfonic acid	PFBS	4
Perfluorohexanesulfonic acid	PFHxS	6
Perfluorooctanesulfonic acid	PFOS	8
2-(N-Ethyl perfluorooctane sulfonamido) acetic acid	NEtFOSAA	12
2-(N-Methyl perfluorooctane sulfonamido) acetic acid	NMeFOSAA	11

Objective 1 - characterize PFAS concentrations and mixture compositions in GWDs and SWs in streams representative of the Farmington River watershed:

PFAS were detected in at least one sample for all but two of the 24 sites surveyed. Seven of the 14 compounds analyzed (PFBS, PFHxA, PFHpA, PFHxS, PFOA, PFOS, PFNA) were detected in at least one sample across our study system and period and are the focus of the analyses that follow. The seven compounds for which we had no detections (PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, N-EtFOSAA, N-MeFOSAA) are all long-chain compounds with carbon chain lengths > 10 and are classified as either perfluorocarboxylic acids (PFCAs) or precursors, which are characterized by higher hydrophobicity and binding to particles (Ahrens & Bundschuh, 2014). Average site-specific individual compound concentrations ranged from below detection limit (BDL) to 0.181 ng mL^{-1} and average $\sum_7$PFAS concentrations per site and sample type ranged from BDL to 0.24 ng mL^{-1}. Among samples for which we measured detectable PFAS concentrations, average detected $\sum_7$PFAS concentrations were 0.024 ± 0.06 (SD) ng mL^{-1} in GWD samples (n = 48) and 0.018 ± 0.04 ng mL^{-1} for SW samples (n = 25). The U.S. EPA and CT's Department of Public Health (CT DPH) both set health advisory levels of 70 ppt (0.07 ng mL^{-1}) for drinking water, with the U.S. EPA's threshold reflecting the sum concentrations of PFOA and PFOS and CT DPH's threshold reflecting the sum concentrations of PFOA, PFOS, PFNA, PFHxS, and PFHpA (CT DPH, 2022; U.S. EPA, 2022). Five percent of our samples (n = 10/186) exceeded both of these thresholds.

Across study sites, the number of PFAS compounds detected and their proportional contributions to the $\sum_7$PFAS concentrations varied (Fig. 2). PFHxA, PFOA, and PFOS were the three most commonly detected PFAS compounds in our analysis and they were detected together at 45% of study sites (n = 11/24). PFOA and PFOS were detected at >50% of the sites regardless of sample type. PFOA and PFOS have attracted the most attention in the scientific and regulatory community. Introduced in the 1940s, PFOA and PFOS are now considered legacy PFAS compounds because they were voluntarily phased out between 2000 and 2002 and added to the Stockholm Convention on Persistent Organic Chemicals list of industrial persistent organic pollutants in 2009 and 2019, respectively (Boisvert et al. 2019; Houde et al. 2011; Schulz, Silva, and Klaper 2020; Wang et al. 2017). In the Farmington River watershed, potential sources of these compounds include municipal landfill leachates (Hepburn et al., 2019), fire training areas, and wastewater treatment plants (Hu et al., 2016) which have been shown to be persistent sources of PFOA and PFOS to the environment. The common co-occurrence of PFHxA with PFOS and PFOA in our samples is consistent with earlier findings that PFHxA and PFOA have similar mobility from biosolids (Lindstrom et al., 2011).

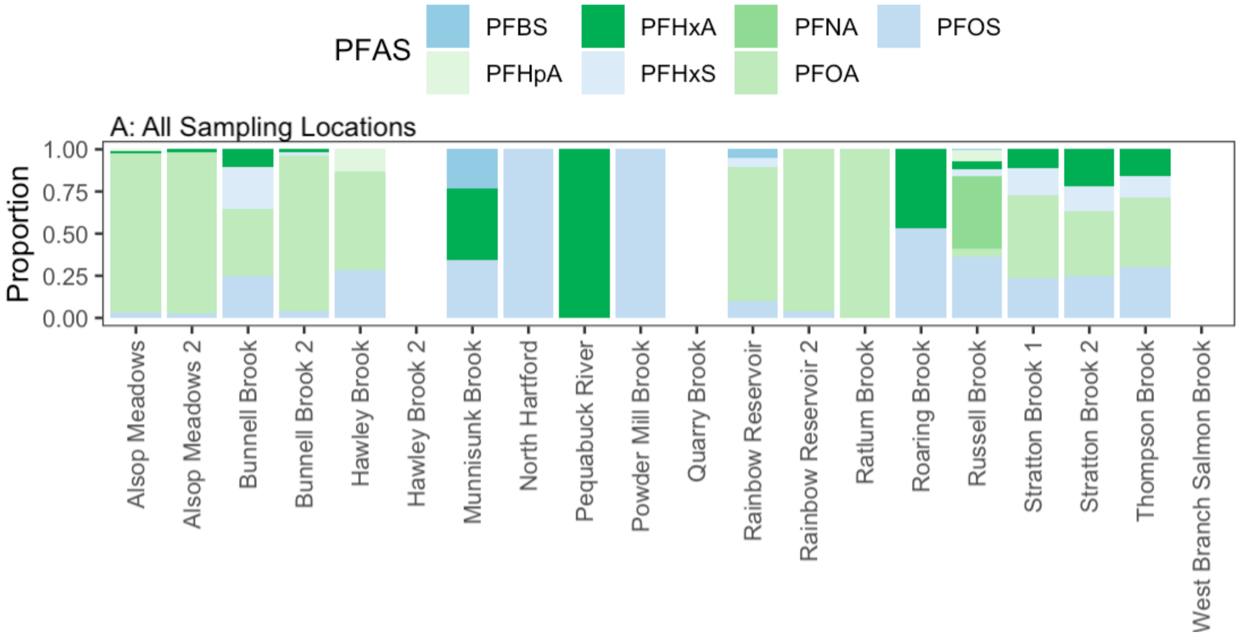

Fig. 2: *Average GWD PFAS compositions as compound-specific contributions to* $\sum_7$PFAS concentrations *across sampling locations.*

Objective 2 - Investigate the potential for spatiotemporal variation in PFAS concentrations and compositions at specific GWD locations:

Spatial variation: We investigated variation in PFAS concentrations in GWDs at two spatial scales: a) among discrete GWDs distributed along the sampling reach of a given sampling site (i.e., to inform spatial variation at the stream site level) and b) within an individual GW seep face where GWD to SW spanned a distance of > 10m. The two seep faces sampled in this study extended 22.5m whereas the spatial extent of discrete GWDs ranged from 0.3 – 8.3m. We observed considerable variation in both PFAS concentrations and mixture compositions among discrete GWDs distributed within a given stream site. Depending on the site, individual compounds were detected in n=0-7 GWD samples, such that the composition of PFAS mixtures also varied among the GWDs sampled from a given stream site. We also observed variation within spatially-extensive GWD seep faces (>10m in stream bank length), such that different PFAS concentrations and compositions were measured in subsamples collected along the spatial extent of a single GWD plume. For example, four compounds (PFBS, PFHpA, PFHxA, and PFHxS) were only detected in a single subsample collected from within a given seep face.

Temporal variation: We investigated temporal variation in GWD using data from five spatially-extensive seeps distributed among two sampling sites (Alsop Meadows and Rainbow Reservoir) in the Farmington River mainstem, where samples were collected from the same set of discrete sampling locations along a defined seep face in both July and October 2020. At both sites, we detected a higher number of individual compounds in July than in October. PFOA and PFOS were the most commonly detected compounds, but were inconsistently detected across sampling events. For example, PFOA was only detected during both sampling events at one of the five seep faces and average concentrations in October were 9.3 times higher than in July. At the two seep faces where PFOS was detected in both July and October 2020, concentrations were 1.3-2.4 times higher in July than October.

These results collectively indicate that GWDs represent complex and variable sources of PFAS to SW habitats and point to the need for sampling strategies designed to capture spatiotemporal variation to best characterize the exposure scenarios for resident biota.

Conclusions

This study provides an initial evaluation of PFAS in GWD in streams representative of the Farmington River watershed in CT. Our results demonstrate that PFAS are commonly detected within this watershed, including at sites without a previously-identified potential upstream point source. This indicates the possibility of diffuse non-point sources of PFAS with measurable impact on freshwater resources. In almost all cases, detected concentrations fell below established drinking water thresholds. These results also highlight that PFAS inputs via GWD vary in space and time, such that discrete samples or sampling events are unlikely to be representative of longer-term concentrations and exposure levels for aquatic biota in groundwater dependent ecosystem habitats.

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