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<tr>
<td>DOI</td>
<td>10.1021/es5006187</td>
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<tr>
<td>Publisher</td>
<td>American Chemical Society</td>
</tr>
<tr>
<td>Version</td>
<td>Accepted Manuscript</td>
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Evidence of Remediation-Induced Alteration of
Subsurface Poly- and Perfluoroalkyl Substance (PFAS)
Distribution at a Former Firefighter Training Area

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ABSTRACT: Poly- and perfluoroalkyl substances (PFASs) are a class of fluorinated chemicals that are utilized in firefighting and have been reported in groundwater and soil at several firefighter training areas. In this study, soil and groundwater samples were collected from across a former firefighter training area to examine the extent to which remedial activities have altered the composition and spatial distribution of PFASs in the subsurface. Log K_{oc} values for perfluoroalkyl acids (PFAAs), estimated from analysis of paired samples of groundwater and aquifer solids, indicated that solid/water partitioning was not entirely consistent with predictions based on laboratory studies. Differential PFAA transport was not strongly evident in the subsurface, likely due to remediation-induced conditions. When compared to the surface soil spatial distributions, the relative concentrations of perfluorooctane sulfonate (PFOS) and PFAA precursors in groundwater strongly suggest that remedial activities altered the subsurface PFAS distribution, presumably through significant pumping of groundwater and transformation of precursors to PFAAs. Additional evidence for transformation of PFAA precursors during remediation included elevated ratios of perfluorohexane sulfonate (PFHxS) to PFOS in groundwater near oxygen sparging wells.
INTRODUCTION. Poly and perfluoroalkyl substances (PFASs) have been produced in large quantities since the 1950s.\textsuperscript{1} Some of these substances, such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), have been detected at elevated concentrations in groundwater at fire fighter training areas\textsuperscript{2–5} as a result of repeated application of aqueous film forming foams (AFFFs) during firefighter training exercises. AFFFs are known to contain multiple classes of PFASs,\textsuperscript{6} and recent studies document the presence of a wide variety of presumed perfluoroalkyl acid (PFAA) precursors, as well as PFAAs such as perfluorinated sulfonates and some carboxylates, in various AFFF formulations.\textsuperscript{3,7,8} Given that the concentrations of PFOS and PFOA at these sites are frequently above the Provisional Health Advisory (PHA) levels recently issued by the U.S. Environmental Protection Agency (EPA) for drinking water (200 ng/L and 400 ng/L for PFOS and PFOA, respectively),\textsuperscript{9} concerns have arisen with respect to the scope and extent of groundwater contamination at former fire fighter training areas. This concern is also partially driven by the fact that PFAAs are very resistant to chemical and biological transformation,\textsuperscript{10–15} and some PFAAs are very difficult to remove from water using conventional treatment technologies.\textsuperscript{16–18}

Until the 1990s, waste fuels and extinguishing agents (such as AFFF) were employed during firefighter training activities and were released into the environment without treatment. These releases often occurred repeatedly over many years, leading to large amounts of contaminants (fuels, residual chlorinated solvents, and AFFF) infiltrating into the subsurface. Many of these training sites have undergone extensive remedial activities to address fuel and/or chlorinated solvent contamination, but the extent to which these remedial activities have impacted PFASs remains unclear. In particular, concerns have arisen about the potential biological transformation of polyfluoroalkyl precursors present in AFFF, which may, in fact, lead to higher levels of PFAAs.\textsuperscript{3,7,15}

Given the interest in PFAA contamination at firefighter training areas, understanding the common characteristics of both treated and untreated AFFF-impacted sites is a pressing need. While PFAA
groundwater plumes have been detected at several sites\textsuperscript{2,19,20} an extensive examination of the spatial
distribution of the full suite of identified PFASs at firefighter training areas, particularly in relation to
co-contaminants and co-contaminant remediation, has not yet been conducted. PFAS are often
simultaneously released with fuel components and chlorinated hydrocarbons, and as a result, PFAS
subsurface plumes would be expected to share some similarities with other co-released contaminant
plumes. However, differential transport of PFASs (relative to each other and to fuel and solvent
components) would also be expected due to their unique sorption properties and transformation
reactivities. Though laboratory-derived sorption constants have been measured for many PFAAs, and
even some PFAA precursors,\textsuperscript{21–23} it is unclear how representative the laboratory-derived values are of
field conditions. Moreover, the potential in situ formation of PFAA from precursors as a result of
remedial activities (e.g., biosparging) may significantly impact the spatial distribution of PFASs in the
subsurface at contaminated sites.

While groundwater PFAS contamination has been documented at firefighter training areas, little data
exist on the extent of surface soil PFAS contamination at these sites. At one AFFF-impacted site in
Flesland, Norway, burn pit samples had PFOS concentrations as high as 273 μg/kg.\textsuperscript{24} Current EPA soil
screening levels for PFASs are quite high (16,000 μg/kg for PFOA and 6,000 μg/kg for PFOS), as they
are meant to be protective of direct human exposure\textsuperscript{9} and are not necessarily protective of the
ecosystem. However, the extent to which AFFF-impacted sites have soil concentrations above the EPA
screening levels remains unclear.

Lastly, though the focus of regulatory interest of the U. S. Environmental Protection Agency is
primarily on the PFAAs,\textsuperscript{25} there is a growing awareness of the potential importance of PFAA
precursors, which are present in AFFF. Though perfluorocarboxylates constitute a small fraction of the
total fluorochemical load in most AFFF formulations,\textsuperscript{7,8} there is strong evidence that many PFAA
precursors may be transformed to PFAAs upon release to the environment.\textsuperscript{7} This may be particularly
true if the subsurface microbial activity has been stimulated to enhance the natural attenuation of co-
contaminants. Some of the aforementioned PFAA precursors have recently been detected in
groundwater at AFFF-impacted sites, but their spatial distribution, particularly in relation to the
PFAA plumes and the co-contaminant plumes, remains unknown. Given their likely ability to undergo
stronger sorption due to their often zwitterionic or cationic nature, these PFAA precursors are expected
to be significantly less mobile than their transformation products.

The objective of this study was to evaluate whether site remediation activities significantly altered
the composition and distribution of PFASs at an AFFF-impacted fire fighter training area by
conducting an in-depth site assessment of groundwater and soil PFAS contamination. To address this
question, groundwater, aquifer solids, and surface soil samples were collected and analyzed for select
PFASs to enable the generation and analysis of plume maps. These maps were used to compare the
relative distribution of contaminants at the site as well as the predicted extent based on laboratory-
derived transport data. Direct analysis of recently identified PFAA precursors in groundwater was also
performed, and a recently-developed precursor oxidation assay was enlisted to help identify the
extent of potential PFAA formation in the subsurface. Paired groundwater and aquifer solids samples
enabled the determination of field-based solid-water distribution coefficients (i.e., apparent $K_d$ values)
for several PFAAs. By creating a conceptual model of the site and determining the extent of PFAS
contamination, this approach may provide a basis for determining the potential extent of contamination
and impact of remediation efforts at similar sites.
MATERIALS AND METHODS.

Site Description. The former firefighter training area Figure 1) at Ellsworth Air Force Base (South Dakota, USA) is located in a semi-arid climate. From 1942 to 1990 the fire training area consisted of a 36.5 m diameter unlined, bermed burn pit. Typical firefighter training activities included dispersing waste (contaminated) oils, solvents, and fuels until the ground was saturated, igniting, and subsequently extinguishing the fire using various extinguishing fluids such as AFFF. Precipitation and/or spent fuel was allowed to pool in the burn pit until it either evaporated or infiltrated the subsurface.27

In 1988 and 1989, a preliminary site investigation indicated that the soil, soil vapor, and groundwater were contaminated with volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), pesticides, hydrocarbons, chlorinated solvents and dioxin/furans.28 In 1990, firefighter-training activities were suspended and the site was listed on the National Priority List (NPL). Due to the high concentrations of contaminants at the site, several different remedies were utilized including soil vapor extraction (SVE), groundwater pump and treat, and installation of a dual phase extraction trench using

Figure 1. Aerial schematic of the former fire training area at Ellsworth Air Force Base. Specifically identified are the location of the former burn pit, the extents of the historical benzene plumes, the former site of discharge for the pump and treat system, and the two in-situ reductive treatment (IRT) walls. Oxygen infusion into groundwater continues at the wells denoted with yellow triangles. The southeastern groundwater flow is also indicated.
various wells (Figure 1, Figure S1). Groundwater treatment, which occurred periodically from 1996 to 2011, included oil-water separation, filtration, air stripping, and granulated activated carbon adsorption,\textsuperscript{29} with re-injection or surface water discharge at various locations adjacent to the site. In November 2011, this treatment system was shut down. The groundwater at the site is currently being treated by bioventing and oxygen infusion at several wells (Figure 1).

In most places, the site is underlain by clay loam and gravely sandy loam soils, possessing low to moderate permeability. The clay, sand, and gravel overburden ranges in thickness from 3 - 9 m below ground surface (bgs) and is underlain directly by Pierre Shale bedrock. During the period when samples were collected, the groundwater depth was 2 - 8 m bgs and flow rates at the site were estimated to range from 0.12 m/year in shale or clay to 1 m/year in the fractured shale. There are sparse and thin lenses of sand and gravel at the site where flow rates can reach 25 m/year, but most of the groundwater travels at the lower rates.

\textit{Sampling.} Groundwater and soil samples were collected during two field sampling campaigns in October 2011 and August 2012, with all sampling locations recorded via a hand-held global position system (GPS; Figures S2-S4). In October 2011, 17 temporary monitoring wells were drilled. Temporary wells were installed using a direct push technology drill and well sampling installation system. Solid phase samples were collected twice during the drilling, once at 0.6 m bgs (surface soil) and again at the water table (approximately 5 m bgs; aquifer solids). For the 17 temporary wells, each surficial soil and aquifer solid sample was separately homogenized and transferred to a methanol-rinsed high-density polyethylene (HDPE) bottles. Samples were also collected and preserved for VOCs,\textsuperscript{30} and total organic carbon (TOC) analyses\textsuperscript{31} according to standard protocols, for a subset of sampling locations. All sampling and drilling equipment was hand-cleaned and rinsed with clean deionized water and methanol between sampling locations.
During the August 2012 sampling event, a hand auger was used to collect surficial soil samples 0.2 – 0.3 m bgs. For several of the 34 sampling locations, resistance was met before reaching 0.2 m below the surface; at these locations, soil was collected at depths just above the resistive layer. As before, each soil sample was homogenized and collected in a methanol-rinsed, HDPE bottle.

Groundwater samples were collected during both field sampling campaigns, using either the newly installed temporary wells or existing wells. Prior to sample collection, the depth to groundwater was recorded. The wells were purged using a peristaltic or a bladder pump. To ensure samples collected were representative of the groundwater at that location, pH, temperature, oxidation-reduction potential, dissolved oxygen, and specific conductivity was measured continuously in-situ using a YSI multimeter (YSI Inc., Yellow Springs, Ohio, USA) until stabilized. Water samples were collected from within the screened interval of the wells using Tygon™ tubing. New Tygon™ tubing was used for each sampling location, and was discarded following sample collection. Four groundwater samples were collected at each location in 250 mL HDPE bottles that had been rinsed with methanol and Milli-Q™ water. Several groundwater samples were also collected at each location and appropriately preserved prior to analysis for VOCs, TOC, and inorganic cations. All soil and groundwater samples were shipped on ice overnight to the analytical laboratories. One groundwater field blank was collected during each sampling event using Milli-Q™ water supplied by CSM (EB-001 and EB-002). Laboratory blanks were also analyzed with each batch of water samples and used to set the limits of quantitation (LOQ) for each analyte: the LOQ was required to provide at least twice the signal observed in any laboratory blank for that batch of samples.

**Sample Analysis.** Samples were analyzed for PFASs (Table S1) at the Colorado School of Mines (CSM) and the University of California at Berkeley (UCB). The results of a subset of the groundwater samples analyzed at UCB were previously reported. Several samples were also analyzed for VOCs, TOC, and inorganic cations at CB&I Federal Services, Inc. Upon arrival at the laboratory, all samples
were stored at 4°C in the dark. At CSM, groundwater samples were analyzed for PFASs unfiltered using a direct-injection liquid chromatography tandem mass spectrometry (LC-MS/MS) method modified from Sepulvado et al.\textsuperscript{22} Briefly, samples were prepared for analysis by removing an aliquot of the groundwater (after vigorously shaking sample bottles by hand) and adding it to a prepared solution of 9% isopropanol (IPA) in Milli-Q\textsuperscript{™} water and a surrogate spiking solution (Table S2). Samples were then centrifuged at 17,000 RCF for 30 minutes and transferred to auto sampler vials for analysis. Samples were diluted as necessary up to 100 times.

Soil and aquifer solids samples were extracted as per Sepulvado et al.\textsuperscript{22} Several minor adjustments were made for analysis of samples in which high levels of PFAAs were present. Specifically, the amount of soil extracted was decreased (limited to 0.1 g), the amount of surrogate spiking solution added to the soils was increased, and the soil extracts were diluted prior to analysis. At CSM, all groundwater and soil samples were analyzed on an AB Sciex 3200 Tandem Mass Spectrometer (AB Sciex, Ontario), with quantitation performed using Analyst Software (ABSciex). When analyzing both the groundwater and soil samples, 20% of all samples were run in triplicate. Analytical variability (expressed as percent relative standard deviation) was, on average, 22% for all solid samples and 33% for all groundwater samples.

At UCB, aqueous samples were processed in a manner similar to CSM. Samples were received on ice and stored at 4°C until analysis, which occurred within two months of sampling. Groundwater samples were inverted five times to ensure adequate mixing before subsampling. A 500 µL aliquot of groundwater, taken from 6 cm below the sample surface, was added to 500 µL of methanol in a 2-mL microcentrifuge tube. Samples were centrifuged at 15,000 rpm for 5 minutes. Each groundwater sample was initially analyzed at 2.5 times dilution, with additional dilutions performed as needed. The analytical method is described in Houtz and Sedlak,\textsuperscript{26} though newly identified polyfluorinated compounds identified by Place and Field\textsuperscript{7} (particularly fluorohexanesulfonamide (FHxSA), 6:2
fluorotelomer sulfonate (6:2 FtS), and 8:2 fluorotelomer sulfonate (8:2 FtS; Table S1)) were added to the analytical protocol and measured. All samples were analyzed in duplicate.

Of particular interest in understanding the relative importance of PFAA precursors at AFFF-impacted sites is the advent of a novel characterization technique whereby PFAA precursors are transformed by oxidation with hydroxyl radical to more easily measured perfluorocarboxylates. When applied to a series of spatially-varied groundwater samples, this technique may enable a preliminary delineation of a “precursor” plume, even if those PFAA precursors cannot be directly measured. To this end, UCB also oxidized groundwater samples with hydroxyl radical to convert precursors in the aqueous samples to perfluorocarboxylates, as described in Houtz et al. Duplicate 3 mL aliquots of each sample were diluted by 50% in a persulfate and NaOH stock solution in 7-mL HDPE tubes. Samples were transferred to vials containing 60 mM potassium persulfate and 125 mM NaOH and were reacted for 6 hours at 85°C. Samples were brought to room temperature, neutralized with concentrated HCl to a pH value between 4 and 10, and amended with 1 mL methanol to enhance dissolution of PFASs. An aliquot of each reacted solution was removed for LC-MS/MS analysis. While the formation potential for each perfluorocarboxylate (i.e., ΔPFOA) in each sample was determined as the difference between the level of each perfluorocarboxylate measured before and after oxidation, the total oxidizable precursor concentration for each sample was estimated by the sum of the formation potentials of each perfluorocarboxylate (i.e., ΔPFOA + ΔPFHpA+..., etc.).

VOCs in soil samples were determined using EPA Method 5035 with a methanol extraction. Soil samples were then analyzed using EPA Method 5030; this method combines an aliquot of the extract from 5035 with organic-free reagent water in the purging chamber and is then analyzed by purge-and-trap GC/MS. VOC concentrations in groundwater samples were analyzed using EPA Method 8260, which analyzes for VOCs using a purge-and-trap GC/MS. Groundwater and soil samples were analyzed for organic carbon content using EPA Methods 5310 B, C and D. These methods use high
temperature combustion (method B), persulfate, and/or UV (methods C and D), depending on the amount of TOC in the sample.\textsuperscript{32} Groundwater samples analyzed for VOCs were shipped to the lab in 40 mL glass vials with polytetrafluoroethylene lined screw caps, with HCl as a preservative. Groundwater samples were also analyzed for inorganic ions using ion chromatography as outlined in EPA Method 300.\textsuperscript{33}

\textit{Spatial Analysis and Modeling.} Concentration maps of the various PFASs were created from results of groundwater, surface soil, and aquifer solids analyses using GPS data. Kriging\textsuperscript{34} interpolation of concentrations between sampling locations, and subsequent contour maps, were created using Surfer 11 (Golden Software, Golden, Colorado, USA). The interpolated spatial distributions of PFAAs in the field were compared to predictive contaminant transport simulations. Limited numerical simulations of PFAA transport in a simulated aquifer were carried out with HYDRUS-2D\textsuperscript{34}, using laboratory-derived sorption constants and modeling parameters chosen to be representative of the hydrology at the site. Additional details on the modeling of the simulated aquifer can be found in the Supporting Information.

\textbf{RESULTS}

\textit{Surface Soil.} For most PFAAs, surface soil (0-0.6 m bgs) contamination was primarily centered around the former burn pit (i.e., the historical source zone; Figure 2 and Figure S5), although elevated concentrations of most PFAAs were apparent across a much broader area. PFOS surface soil levels reached 36,000 µg/kg around the burn pit (Table S3). The spatial distribution of PFAAs was similar to the reported spatial distributions of fuel hydrocarbons in the surface soil during the original remedial investigation in 1993.\textsuperscript{28} Surface soil contamination was similar for the majority of the PFAAs; high concentrations in the surface soil seemed to be contained to the burn pit area. Several soil samples at the site were also analyzed for VOCs and organic carbon content (Tables S4-S5) in addition to PFAAs. Surface soil samples showed high levels of VOCs in the burn pit area, as would be expected. The
fraction of organic carbon ($f_{oc}$) of the surface soil samples ranged from about 0.6% to 5.5%, with higher concentrations in the burn pit area (Table S5).

**Aquifer Solids.** Solids samples were also collected at the water table during the installation of the temporary monitoring wells. The areal extent of contamination of the aquifer solids (Figure S6) was similar to the areal extent of contamination in the groundwater (Figure 3, Figure S7). High PFAA levels were observed in aquifer solids near the burn pit. However, with the exception of PFBA, the highest levels (Table S6) were observed downgradient from the burn pit (Sample S10D; Figure S6), and very close to the center of the current benzene groundwater plume. Analysis of the aquifer solids suggested that most of the mass of PFAAs remains within the existing (as of 2011) benzene groundwater plume. The notable exception was PFOS, for which the elevated aquifer solids concentrations extended to the east of the benzene plume (Figure S6).

**Groundwater.** Similarly to the spatial distribution of PFAAs in aquifer solids, most of the contamination of PFAAs in groundwater was located within the historical benzene plume (Figure S7). However, while PFOS was present in high concentrations within the benzene plume, the highest PFOS...
concentrations in groundwater were found to the east of the burn pit (Figure 3C; Table S7). In addition, based on the relative extent of the groundwater plumes alone, there was no strong evidence for differential transport of different chain-length perfluorocarboxylates or perfluorinated sulfonates, which are known to undergo chain-length dependent sorption\textsuperscript{21,23}. For example, the results of the HYDRUS-2D modeling (Figure S8) indicate that PFHxA should have traveled farther and have a larger plume distributions than PFOA 22 years after releases have ceased due to its weaker sorptive potential.

**Groundwater PFAA Precursor Plumes.** Whether measured directly or indirectly through the oxidative precursor assay (Table S8), a delineation of potential PFAA precursors can provide an indication as to the zones in which concentrations of PFAAs could increase without new AFFF releases. As seen in Figure 4A, the area with the highest total PFAA precursor concentration was to the east of the burn pit, the same area where high PFOS groundwater concentrations were seen. This pattern was even more evident when the formation potential of individual perfluorocarboxylates (i.e.,

**Figure 3.** PFAA contamination in groundwater of (A) PFHxA, (B) PFOA, and (C) PFOS. Dashed red lines illustrate the bounds of the data, dashed white lines indicate the extent of the historic (2002) benzene plume, blue circles represent groundwater sample locations and yellow triangles represent current oxygen infusion wells.
\[ \Delta \text{PFHxA}, \Delta \text{PFHpA} \] were mapped (Figure S9), though the formation potential of the shortest carboxylate (\( \Delta \text{PFBA} \)) was also elevated within the benzene plume. However, this eastern PFAS source zone became evident again when the spatial distribution of specific precursors were examined (Figure 4B, Figure S10).

Relationships between soil and groundwater. Field-based solid-water distribution coefficients (\( K_d \) values) were calculated for a limited number of sample pairs based on availability of groundwater and aquifer solids data (Table S9). These values were calculated from the measured soil concentrations (adjusted for moisture content and resultant aqueous PFAA levels) and measured groundwater concentrations. The resulting log \( K_d \) values (L/kg\(_{dw}\)) from seven locations were also normalized to the fraction of organic carbon of the soil (\( f_{oc} \)) to obtain \( K_{oc} \) (L/kg\(_{oc}\)) values. The average log \( K_d \) values and average log \( K_{oc} \) values are presented in Table 1, as are the ranges of values observed. For these samples, \( f_{oc} \) values ranged from 0.00121 to 0.0135 and reflect any organic carbon associated with any

![Figure 4](image_url)

**Figure 4.** Evidence of PFAA precursors and precursor transformation potential in groundwater: (A) total molar concentration of PFAA precursors measured by the oxidation assay, (B) FHxSA, a C6 sulfonamide; and (C) the ratio of PFHxS to PFOS. Blue dots represent the location of groundwater samples, yellow triangles show the location of oxygen infusion, and red lines show the bounds of the data.
organic contaminants in the soil (i.e., non-aqueous phase liquids; NAPLs) in addition to naturally-occuring organic carbon, although these levels are quite low in comparison to the total f_{oc}. Others have observed an impact of NAPLs and other co-contaminants on the sorption potential of PFAAs, though effects are dependent on soil type, the type of PFAA, and the level of the PFAA.22

Table 1. Field-based partition coefficients and ranges for PFAAs included in this study.

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<th>Avg Log K_d (± SD, n = 7)</th>
<th>Log K_d Range</th>
<th>Avg Log K_oc (± SD, n = 7)</th>
<th>Log K_oc Range</th>
<th>Log K_oc (literature)</th>
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<td>PFBA</td>
<td>-0.25 ± 0.87</td>
<td>-1.64 - 0.84</td>
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<td>PFPeA</td>
<td>-0.57 ± 0.62</td>
<td>-1.42 - 0.23</td>
<td>1.85 ± 0.70</td>
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<td>PFHxA</td>
<td>-0.36 ± 0.59</td>
<td>-1.16 - 0.40</td>
<td>2.06 ± 0.67</td>
<td>1.33 - 3.01</td>
<td>1.91^{22}, 1.31^{23},</td>
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<td>PFHpA</td>
<td>-0.37 ± 0.46</td>
<td>-1.05 - 0.17</td>
<td>2.04 ± 0.48</td>
<td>1.34 - 2.71</td>
<td>2.19^{22}, 1.63^{23},</td>
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<td>PFOA</td>
<td>-0.19 ± 0.47</td>
<td>-0.68 - 0.52</td>
<td>2.22 ± 0.71</td>
<td>1.33 - 3.13</td>
<td>2.06^{21}, 2.31^{22},</td>
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<td>PFBS</td>
<td>-0.36 ± 0.64</td>
<td>-1.08 - 0.46</td>
<td>2.06 ± 0.77</td>
<td>1.11 - 3.07</td>
<td>1.79^{23}</td>
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<td>PFHxS</td>
<td>-0.14 ± 0.53</td>
<td>-0.80 - 0.61</td>
<td>2.28 ± 0.70</td>
<td>1.30 - 3.22</td>
<td>2.72^{22}, 2.05^{23},</td>
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<td>PFOS</td>
<td>0.72 ± 0.49</td>
<td>0.16 - 1.58</td>
<td>3.14 ± 0.66</td>
<td>2.28 - 4.19</td>
<td>2.57^{21}, 3.34^{22},</td>
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DISCUSSION

*Field-based K_oc values.* The field-based log K_oc values determined in this study are, to the best of our knowledge, the first field-based log K_oc values determined for PFAAs. While the trends within the perfluorinated sulfonates (i.e., Δ logK_oc of ~ 0.9 between PFHxS and PFOS; Table 1) were consistent with previously observed chain-length dependent trends,^{21,23,35,36} there were some inconsistencies between the trends in the field-derived average log K_oc values for the perfluorocarboxylates and previous observations. The lack of clear chain-length dependent trends for the perfluorocarboxylates was even apparent when results were limited to log K_oc values determined from individual wells (Table S9). Given the general consistency of chain-length dependent trends in the laboratory and modeling studies, these data suggest that the field-based data for the perfluorocarboxylates may potentially be biased due to the presence of perfluorocarboxylate precursors. For example, if perfluorocarboxylate precursors were chemisorbed to the organic matter within the solid phase and were sensitive to base-
catalyzed hydrolysis, then the measured solid phase concentrations of certain perfluorocarboxylates might have been slightly elevated relative to what should have been in equilibrium with the aqueous phase due to the basic methanol extraction process (resulting in an artificially high $K_{oc}$ value). This is supported by the fact that the only paired samples that were somewhat consistent with chain length trends (i.e., $\Delta \log K_{oc}$ of ~ 1 between PFHxA and PFOA at Tmp 11; Table S9) also had minimal levels of precursors, as measured by the oxidation assay (Table S8). While somewhat speculative, these data represent one of the first suggestions as to the important role of PFAA precursors in the distribution of PFAAs in the subsurface at AFFF-impacted sites. Alternatively, the lack of clear trends for the perfluorocarboxylates may have been due to a lack of equilibrium between the two phases, though this is less likely for the shorter chain perfluorocarboxylates than the perfluorosulfonates.36

Spatial groundwater plume comparisons. Consistent with the lack of clear trends in the log $K_{oc}$ data for the perfluorocarboxylates, despite laboratory-based evidence for differential sorption of PFAAs depending on the chain-length,21,22 there was no strong evidence for differential transport of PFAAs in the groundwater (Figure 3, Figure S7). Indeed, for most of the PFAAs investigated at this site, elevated levels in the groundwater could be roughly approximated by the location of the historical (and/or current) benzene plume (Figure 1). For comparison, the HYDRUS-2D simulations for PFHxA and PFOA transport based on advection and dispersion alone are presented in Figure S8. The ~4 fold difference in their $K_d$ values should have led, under ideal conditions, to a ~2 fold difference in their plume centers of mass after 22 years of transport following 25 years of continual release (Figure S8c,d). Instead, both PFHxA and PFOA plumes mostly overlapped (Figure 3).

Importantly, most PFAA groundwater plumes were spatially similar to the historical benzene plume. These data initially suggest that sampling existing monitoring wells within co-contaminant fuel plumes may provide a very good indication as to the center of mass for most PFAA groundwater plumes at AFFF-impacted fire fighter training areas. This is corroborated by the aquifer solids data, which
indicated elevated concentrations both within and to the east of the existing benzene plume (Figure S5). However, the PFOS data and the precursor data strongly suggest that a conceptual model of co-located PFAA and co-contaminant (i.e., benzene) plumes is overly simplistic.

**Spatial surface soil distributions.** Elevated concentrations of PFAAs around the burn pit area were expected in surface soil due to direct application of AFFF at this location. Though the soils in the burn pit area were treated with SVE to remove VOCs and SVOCs from the vadose zone, these technologies likely did not result in decreased PFAA levels (though historical soil samples for PFAA analysis are not available). While contaminated groundwater at AFFF-impacted sites will likely be the primary risk driver (as opposed to contaminated soil), effects on wildlife, possibly as a result of contaminated soil and water, are worth considering in light of previous studies.\(^{37–39}\) Moreover, the disconnect between the surface soil and groundwater spatial distributions of PFOS (Figure 2C and Figure 3C) again suggests that remedial activities have altered the PFAA composition and distributions in the subsurface.

**Likely explanations for the spatial distribution of PFOS and PFAA precursors in groundwater.** While several things could possibly explain the spatial distributions observed at Ellsworth AFB, we suggest two possible explanations for the spatial patterns observed in the aquifer solids PFOS data (Figure S5), groundwater PFOS data (Figure 3C), the total PFAA precursors data (Figure 4A), and the chemical-specific precursor data (i.e., FxHSA; Figure 4B). The first possible explanation is that there was a second spatial source of PFASs to the subsurface (in addition to the co-release with the fuel within the burn pit). Given the higher concentrations, this would likely be a repeated release scenario, perhaps related to the firefighter training activities. For example, cleaning of AFFF-contaminated equipment might have occurred in a second location outside of the burn pit. This is not supported, however, by the surface soil data. No elevated surface soil concentrations are observed in this area.
(Figure 2), though historical data from the site suggest there may have been surface fill placed in this area, potentially masking a surface soil signal.

An alternative explanation for the eastern source zone, and one with important implications, is that hydrologic and biogeochemical alterations to the subsurface as a result of remediation activities are responsible for the current spatial PFAS distribution. This explanation hinges on the fact that this eastern area was initially also contaminated with benzene, though the present plume boundary now excludes this area. In addition, neither significant pumping of groundwater nor stimulation of subsurface microbial populations through oxygen infusion appears to have occurred in this eastern area (Figure S1): both types of activities have occurred in the main benzene plume. The lack of oxygen infusion in this eastern area may explain why the perfluorocarboxylates, likely terminal products of aerobic transformations of some PFAA precursors, are not elevated in this area. In contrast, many PFAA precursors, such as FHxSA and the FtSs (which are generally considered intermediate degradation products of AFFF-components), are still present in this area, suggesting some partial transformation of AFFF components has occurred. As the transport potential of both PFOS and PFAA precursors is generally expected to be significantly less than many of the perfluorocarboxylates, the fact that extensive pumping occurred within the main benzene plume would suggest that the relative levels of PFOS in the main benzene plume should be elevated, at least compared to the perfluorocarboxylates, if PFOS and the perfluorocarboxylates were co-released. Given that the opposite is true (i.e., the perfluorinated carboxylate signal is relatively stronger in the area subjected to extensive pumping), this suggests releases of PFOS and the perfluorocarboxylates to the groundwater was not cotemporaneous.

This alternative explanation would, in fact, suggest that the levels of perfluorocarboxylates in the subsurface, particularly within the current benzene plume, are primarily a result of the in situ transformation of less mobile PFAA precursors to the perfluorocarboxylates within the benzene plume.
In situ generation and “release” of perfluorocarboxylates would also help explain why there is no strong evidence for their differential transport: differing rates of in situ generation could potentially blur any differential perfluorinated carboxylate transport signal. This second potential explanation is important, in that it implies that the groundwater PFAS levels and composition in this eastern zone (relatively high PFOS, high PFAA precursors, low perfluorocarboxylates) are representative of the initial (i.e., pre-remediation) conditions at the site, whereas the levels within the current benzene plume are primarily a result of the various remedial activities conducted at the site.

The potential for alteration in PFAS signals in groundwater due to remedial activities is most clearly illustrated in Figure 4C. In this figure, the spatial distribution of the ratio of PFHxS to PFOS in groundwater is plotted, and a significant increase in the ratio (up to 50:1) is observed. Analysis of AFFF containing these compounds suggests the ratio in the AFFF itself was closer to 1:10, though some variation over the years and formulations is expected. If differential transport was occurring (average log Koc for PFHxS is 2.28 vs 3.14 for PFOS; Table 1), the ratio would be expected to increase (continually) downgradient. Instead, the ratio increases downgradient from the burn pit, and then decreases. Alternatively, if in situ generation of PFHxS was occurring, this could also lead to an increase in the PFHxS:PFOS ratio. Given the near absence of at least one suspected PFHxS precursor in this area (Figure 4B) and the fact that this area of elevated PFHxS:PFOS ratios is in the immediate vicinity of the wells where significant oxygen infusion has occurred (Figure 1), the in situ generation of PFHxS from PFAA precursors due to aerobic biological processes is the likely explanation, though more research is needed to verify this expected change in ratios as a result of AFFF degradation. It should be noted that FOSA, the PFOS analog to FHxSA, has been shown to form PFOS under aerobic (activated sludge) conditions. In addition, it is possible that this presumed production of PFHxS from precursors could have occurred naturally as a result of natural attenuation of the precursors in the groundwater, though the biosparging would likely have accelerated this presumably aerobic process.
Implications. If the hydrological and biogeochemical explanation of the inconsistencies in the PFOS contamination, spatial distribution of PFHxS:PFOS ratios, and the distribution of aqueous PFAA precursors is valid, this has major implications with respect to AFFF-impacted sites. Notably, this would imply that the elevated PFOS levels to the east of the burn pit may be more representative of conditions at a site that has not undergone remediation. Moreover, the PFAA precursor and perfluorocarboxylate data from this area of the site would suggest that simply analyzing groundwater samples for perfluorocarboxylates (and not employing the assay developed by Houtz et al.\textsuperscript{3}) would obscure the actual potential for perfluorocarboxylate contamination, particularly for a site that has not undergone remediation. This latter point is particularly crucial as additional AFFF-impacted sites are investigated with respect to PFAS contamination.

ACKNOWLEDGEMENTS. The authors thank the Air Force Center for Engineering and the Environment (BAA 689 and the Strategic Environmental Research and Development Program (SERDP ER2126 and ER 2128) for financial support for this project, as well as the NSF CO-AMP Bridge to the Doctorate Fellowship at Colorado School of Mines. In addition, the authors thank Dr. Kaneen Christensen for help with sampling, and Lisa Kudryk and Dr. Derrick Rodriguez for help with spatial analysis.

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