

Evidence of Remediation-Induced Alteration of Subsurface Poly- and Perfluoroalkyl Substance (PFAS) Distribution at a Former Firefighter Training Area

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1 Evidence of Remediation-Induced Alteration of
2 Subsurface Poly- and Perfluoroalkyl Substance (PFAS)
3 Distribution at a Former Firefighter Training Area

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20 ABSTRACT: Poly- and perfluoroalkyl substances (PFASs) are a class of fluorinated chemicals that are
21 utilized in firefighting and have been reported in groundwater and soil at several firefighter training
22 areas. In this study, soil and groundwater samples were collected from across a former firefighter
23 training area to examine the extent to which remedial activities have altered the composition and
24 spatial distribution of PFASs in the subsurface. Log K_{oc} values for perfluoroalkyl acids (PFAAs),
25 estimated from analysis of paired samples of groundwater and aquifer solids, indicated that solid/water
26 partitioning was not entirely consistent with predictions based on laboratory studies. Differential
27 PFAA transport was not strongly evident in the subsurface, likely due to remediation-induced
28 conditions. When compared to the surface soil spatial distributions, the relative concentrations of
29 perfluorooctane sulfonate (PFOS) and PFAA precursors in groundwater strongly suggest that remedial
30 activities altered the subsurface PFAS distribution, presumably through significant pumping of
31 groundwater and transformation of precursors to PFAAs. Additional evidence for transformation of
32 PFAA precursors during remediation included elevated ratios of perfluorohexane sulfonate (PFHxS) to
33 PFOS in groundwater near oxygen sparging wells.

34 INTRODUCTION. Poly and perfluoroalkyl substances (PFASs) have been produced in large
35 quantities since the 1950s.¹ Some of these substances, such as perfluorooctane sulfonate (PFOS) and
36 perfluorooctanoic acid (PFOA), have been detected at elevated concentrations in groundwater at fire
37 fighter training areas²⁻⁵ as a result of repeated application of aqueous film forming foams (AFFFs)
38 during firefighter training exercises. AFFFs are known to contain multiple classes of PFASs,⁶ and
39 recent studies document the presence of a wide variety of presumed perfluoroalkyl acid (PFAA)
40 precursors, as well as PFAAs such as perfluorinated sulfonates and some carboxylates, in various
41 AFFF formulations.^{3,7,8} Given that the concentrations of PFOS and PFOA at these sites are frequently
42 above the Provisional Health Advisory (PHA) levels recently issued by the U.S. Environmental
43 Protection Agency (EPA) for drinking water (200 ng/L and 400 ng/L for PFOS and PFOA,
44 respectively),⁹ concerns have arisen with respect to the scope and extent of groundwater contamination
45 at former fire fighter training areas. This concern is also partially driven by the fact that PFAAs are
46 very resistant to chemical and biological transformation,¹⁰⁻¹⁵ and some PFAAs are very difficult to
47 remove from water using conventional treatment technologies.¹⁶⁻¹⁸

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

56 Given the interest in PFAA contamination at firefighter training areas, understanding the common
57 characteristics of both treated and untreated AFFF-impacted sites is a pressing need. While PFAA

58 groundwater plumes have been detected at several sites^{2,19,20} an extensive examination of the spatial
59 distribution of the full suite of identified PFASs at firefighter training areas, particularly in relation to
60 co-contaminants and co-contaminant remediation, has not yet been conducted. PFAS are often
61 simultaneously released with fuel components and chlorinated hydrocarbons, and as a result, PFAS
62 subsurface plumes would be expected to share some similarities with other co-released contaminant
63 plumes. However, differential transport of PFASs (relative to each other and to fuel and solvent
64 components) would also be expected due to their unique sorption properties and transformation
65 reactivities. Though laboratory-derived sorption constants have been measured for many PFAAs, and
66 even some PFAA precursors,²¹⁻²³ it is unclear how representative the laboratory-derived values are of
67 field conditions. Moreover, the potential in situ formation of PFAA from precursors as a result of
68 remedial activities (e.g., biosparging) may significantly impact the spatial distribution of PFASs in the
69 subsurface at contaminated sites.

70 While groundwater PFAS contamination has been documented at firefighter training areas, little data
71 exist on the extent of surface soil PFAS contamination at these sites. At one AFFF-impacted site in
72 Flesland, Norway, burn pit samples had PFOS concentrations as high as 273 µg/kg.²⁴ Current EPA soil
73 screening levels for PFASs are quite high (16,000 µg/kg for PFOA and 6,000 µg/kg for PFOS), as they
74 are meant to be protective of direct human exposure⁹ and are not necessarily protective of the
75 ecosystem. However, the extent to which AFFF-impacted sites have soil concentrations above the EPA
76 screening levels remains unclear.

77 Lastly, though the focus of regulatory interest of the U. S. Environmental Protection Agency is
78 primarily on the PFAAs,²⁵ there is a growing awareness of the potential importance of PFAA
79 precursors, which are present in AFFF. Though perfluorocarboxylates constitute a small fraction of the
80 total fluorochemical load in most AFFF formulations,^{7,8} there is strong evidence that many PFAA
81 precursors may be transformed to PFAAs upon release to the environment.⁷ This may be particularly

82 true if the subsurface microbial activity has been stimulated to enhance the natural attenuation of co-
83 contaminants. Some of the aforementioned PFAA precursors have recently been detected in
84 groundwater at AFFF-impacted sites,^{3,4} but their spatial distribution, particularly in relation to the
85 PFAA plumes and the co-contaminant plumes, remains unknown. Given their likely ability to undergo
86 stronger sorption due to their often zwitterionic or cationic nature, these PFAA precursors are expected
87 to be significantly less mobile than their transformation products.⁷

88 The objective of this study was to evaluate whether site remediation activities significantly altered
89 the composition and distribution of PFASs at an AFFF-impacted fire fighter training area by
90 conducting an in-depth site assessment of groundwater and soil PFAS contamination. To address this
91 question, groundwater, aquifer solids, and surface soil samples were collected and analyzed for select
92 PFASs to enable the generation and analysis of plume maps. These maps were used to compare the
93 relative distribution of contaminants at the site as well as the predicted extent based on laboratory-
94 derived transport data. Direct analysis of recently identified PFAA precursors in groundwater was also
95 performed, and a recently-developed precursor oxidation assay²⁶ was enlisted to help identify the
96 extent of potential PFAA formation in the subsurface. Paired groundwater and aquifer solids samples
97 enabled the determination of field-based solid-water distribution coefficients (i.e., apparent K_d values)
98 for several PFAAs. By creating a conceptual model of the site and determining the extent of PFAS
99 contamination, this approach may provide a basis for determining the potential extent of contamination
100 and impact of remediation efforts at similar sites.

101

102 MATERIALS AND METHODS.

103 *Site Description.* The former firefighter training area (Figure 1) at Ellsworth Air Force Base (South
104 Dakota, USA) is located in a semi-arid climate. From 1942 to 1990 the fire training area consisted of a
105 36.5 m diameter unlined, bermed burn pit. Typical firefighter training activities included dispersing
106 waste (contaminated) oils, solvents, and fuels until the ground was saturated, igniting, and
107 subsequently extinguishing the fire using various
108 extinguishing fluids such as AFFF. Precipitation
109 and/or spent fuel was allowed to pool in the burn
110 pit until it either evaporated or infiltrated the
111 subsurface.²⁷

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

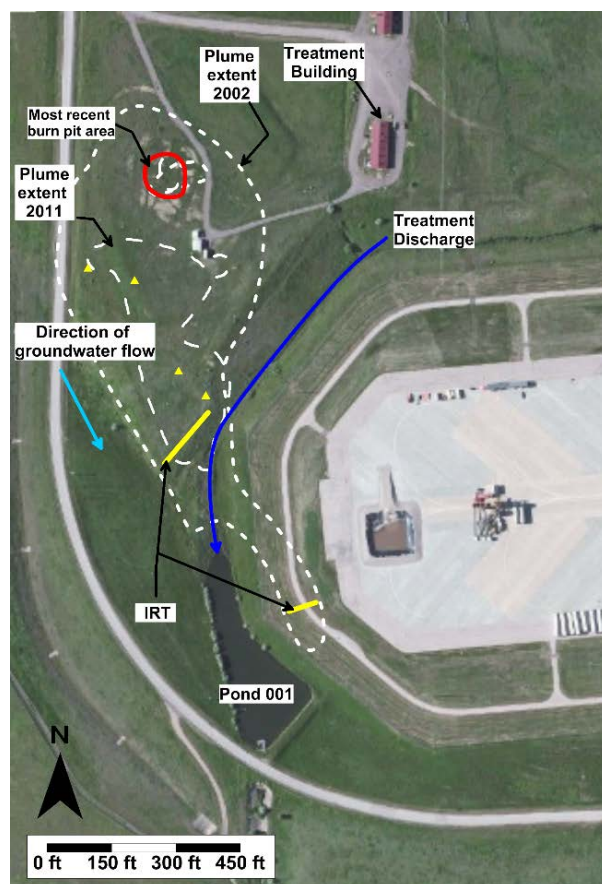


Figure 1. Aerial schematic of the former fire training area at Ellsworth Air Force Base. Specifically identified are the location of the former burn pit, the extents of the historical benzene plumes,^{36,37} the former site of discharge for the pump and treat system, and the two in-situ reductive treatment (IRT) walls. Oxygen infusion into groundwater continues at the wells denoted with yellow triangles. The southeastern groundwater flow is also indicated.

125 various wells (Figure 1, Figure S1). Groundwater treatment, which occurred periodically from 1996 to
126 2011, included oil-water separation, filtration, air stripping, and granulated activated carbon
127 adsorption,²⁹ with re-injection or surface water discharge at various locations adjacent to the site. In
128 November 2011, this treatment system was shut down. The groundwater at the site is currently being
129 treated by bioventing and oxygen infusion at several wells (Figure 1).

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

137 *Sampling.* Groundwater and soil samples were collected during two field sampling campaigns in
138 October 2011 and August 2012, with all sampling locations recorded via a hand-held global position
139 system (GPS; Figures S2-S4). In October 2011, 17 temporary monitoring wells were drilled.
140 Temporary wells were installed using a direct push technology drill and well sampling installation
141 system. Solid phase samples were collected twice during the drilling, once at 0.6 m bgs (surface soil)
142 and again at the water table (approximately 5 m bgs; aquifer solids). For the 17 temporary wells, each
143 surficial soil and aquifer solid sample was separately homogenized and transferred to a methanol-
144 rinsed high-density polyethylene (HDPE) bottles. Samples were also collected and preserved for
145 VOCs,³⁰ and total organic carbon (TOC) analyses³¹ according to standard protocols, for a subset of
146 sampling locations. All sampling and drilling equipment was hand-cleaned and rinsed with clean
147 deionized water and methanol between sampling locations.

148 During the August 2012 sampling event, a hand auger was used to collect surficial soil samples 0.2 –
149 0.3 m bgs. For several of the 34 sampling locations, resistance was met before reaching 0.2 m below
150 the surface; at these locations, soil was collected at depths just above the resistive layer. As before,
151 each soil sample was homogenized and collected in a methanol-rinsed, HDPE bottle.

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

168 *Sample Analysis.* Samples were analyzed for PFASs (Table S1) at the Colorado School of Mines
169 (CSM) and the University of California at Berkeley (UCB). The results of a subset of the groundwater
170 samples analyzed at UCB were previously reported.³ Several samples were also analyzed for VOCs,
171 TOC, and inorganic cations at CB&I Federal Services, Inc. Upon arrival at the laboratory, all samples

172 were stored at 4°C in the dark. At CSM, groundwater samples were analyzed for PFASs unfiltered
173 using a direct-injection liquid chromatography tandem mass spectrometry (LC-MS/MS) method
174 modified from Sepulvado et al.²² Briefly, samples were prepared for analysis by removing an aliquot
175 of the groundwater (after vigorously shaking sample bottles by hand) and adding it to a prepared
176 solution of 9% isopropanol (IPA) in Milli-Q™ water and a surrogate spiking solution (Table S2).
177 Samples were then centrifuged at 17,000 RCF for 30 minutes and transferred to auto sampler vials for
178 analysis. Samples were diluted as necessary up to 100 times.

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

188 At UCB, aqueous samples were processed in a manner similar to CSM. Samples were received on
189 ice and stored at 4° C until analysis, which occurred within two months of sampling. Groundwater
190 samples were inverted five times to ensure adequate mixing before subsampling. A 500 µL aliquot of
191 groundwater, taken from 6 cm below the sample surface, was added to 500 µL of methanol in a 2-mL
192 microcentrifuge tube. Samples were centrifuged at 15,000 rpm for 5 minutes. Each groundwater
193 sample was initially analyzed at 2.5 times dilution, with additional dilutions performed as needed. The
194 analytical method is described in Houtz and Sedlak,²⁶ though newly identified polyfluorinated
195 compounds identified by Place and Field⁷ (particularly fluorohexanesulfonamide (FHxSA), 6:2

196 fluorotelomer sulfonate (6:2 FtS), and 8:2 fluorotelomer sulfonate (8:2 FtS; Table S1)) were added to
197 the analytical protocol and measured.³ All samples were analyzed in duplicate.

198 Of particular interest in understanding the relative importance of PFAA precursors at AFFF-
199 impacted sites is the advent of a novel characterization technique whereby PFAA precursors are
200 transformed by oxidation with hydroxyl radical to more easily measured perfluorocarboxylates.²⁶
201 When applied to a series of spatially-varied groundwater samples, this technique may enable a
202 preliminary delineation of a “precursor” plume, even if those PFAA precursors cannot be directly
203 measured. To this end, UCB also oxidized groundwater samples with hydroxyl radical to convert
204 precursors in the aqueous samples to perfluorocarboxylates, as described in Houtz et al.³ Duplicate 3
205 mL aliquots of each sample were diluted by 50% in a persulfate and NaOH stock solution in 7-mL
206 HDPE tubes. Samples were transferred to vials containing 60 mM potassium persulfate and 125 mM
207 NaOH and were reacted for 6 hours at 85°C. Samples were brought to room temperature, neutralized
208 with concentrated HCl to a pH value between 4 and 10, and amended with 1 mL methanol to enhance
209 dissolution of PFASs. An aliquot of each reacted solution was removed for LC-MS/MS analysis.
210 While the formation potential for each perfluorocarboxylate (i.e., Δ PFOA) in each sample was
211 determined as the difference between the level of each perfluorocarboxylate measured before and after
212 oxidation, the total oxidizable precursor concentration for each sample was estimated by the sum of the
213 formation potentials of each perfluorocarboxylate (i.e., Δ PFOA + Δ PFHpA+..., etc.).

214 VOCs in soil samples were determined using EPA Method 5035 with a methanol extraction. Soil
215 samples were then analyzed using EPA Method 5030; this method combines an aliquot of the extract
216 from 5035 with organic-free reagent water in the purging chamber and is then analyzed by purge-and-
217 trap GC/MS.³² VOC concentrations in groundwater samples were analyzed using EPA Method 8260,
218 which analyzes for VOCs using a purge-and-trap GC/MS.³⁰ Groundwater and soil samples were
219 analyzed for organic carbon content using EPA Methods 5310 B, C and D. These methods use high

220 temperature combustion (method B), persulfate, and/or UV (methods C and D), depending on the
221 amount of TOC in the sample.³² Groundwater samples analyzed for VOCs were shipped to the lab in
222 40 mL glass vials with polytetrafluoroethylene lined screw caps, with HCl as a preservative.
223 Groundwater samples were also analyzed for inorganic ions using ion chromatography as outlined in
224 EPA Method 300.³³

225 *Spatial Analysis and Modeling.* Concentration maps of the various PFASs were created from results
226 of groundwater, surface soil, and aquifer solids analyses using GPS data. Kriging³⁴ interpolation of
227 concentrations between sampling locations, and subsequent contour maps, were created using Surfer
228 11 (Golden Software, Golden, Colorado, USA). The interpolated spatial distributions of PFAAs in the
229 field were compared to predictive contaminant transport simulations. Limited numerical simulations
230 of PFAA transport in a simulated aquifer were carried out with HYDRUS-2D³⁴, using laboratory-
231 derived sorption constants and modeling parameters chosen to be representative of the hydrology at the
232 site. Additional details on the modeling of the simulated aquifer can be found in the Supporting
233 Information.

234 RESULTS

235 *Surface Soil.* For most PFAAs, surface soil (0-0.6 m bgs) contamination was primarily centered
236 around the former burn pit (i.e., the historical source zone; [Figure 2](#) and [Figure S5](#)), although elevated
237 concentrations of most PFAAs were apparent across a much broader area. PFOS surface soil levels
238 reached 36,000 µg/kg around the burn pit ([Table S3](#)). The spatial distribution of PFAAs was similar to
239 the reported spatial distributions of fuel hydrocarbons in the surface soil during the original remedial
240 investigation in 1993.²⁸ Surface soil contamination was similar for the majority of the PFAAs; high
241 concentrations in the surface soil seemed to be contained to the burn pit area. Several soil samples at
242 the site were also analyzed for VOCs and organic carbon content ([Tables S4-S5](#)) in addition to PFAAs.
243 Surface soil samples showed high levels of VOCs in the burn pit area, as would be expected. The

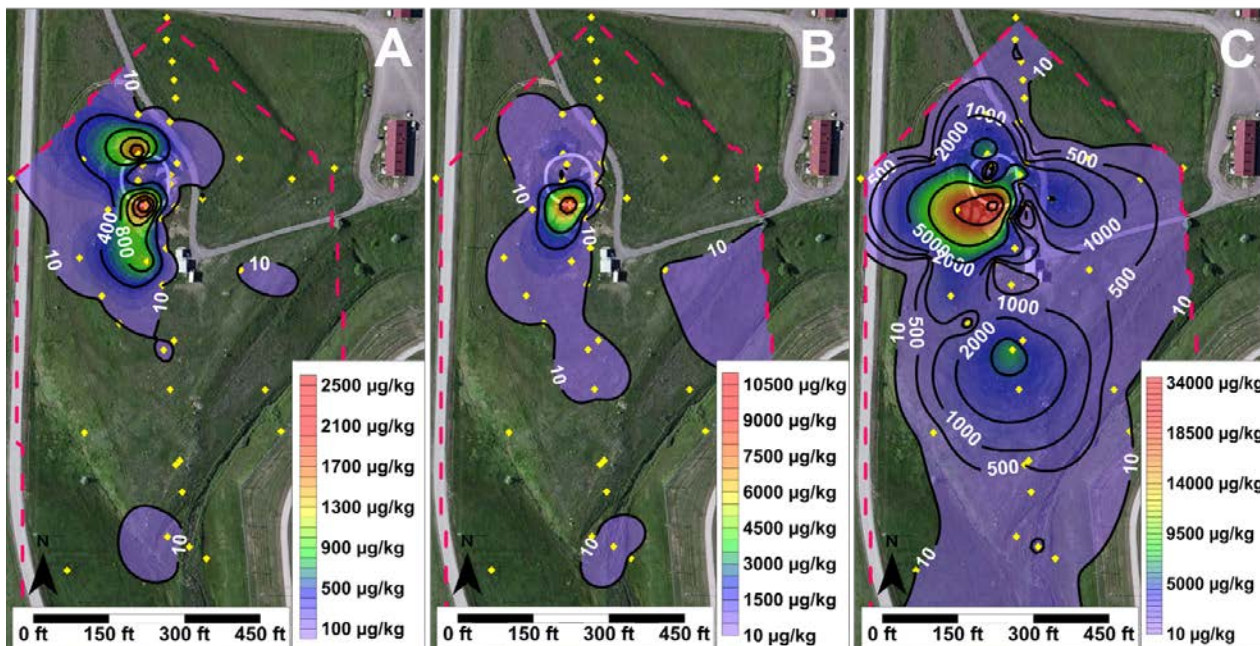


Figure 2 - Extents of surface soil PFAA contamination for (A) PFHxA, (B) PFOA, and (C) PFOS. Yellow symbols represent soil sample locations and red lines illustrate the bounds of the data.

244 fraction of organic carbon (f_{oc}) of the surface soil samples ranged from about 0.6% to 5.5%, with
 245 higher concentrations in the burn pit area (Table S5).

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

255 *Groundwater.* Similarly to the spatial distribution of PFAAs in aquifer solids, most of the
 256 contamination of PFAAs in groundwater was located within the historical benzene plume (Figure S7).
 257 However, while PFOS was present in high concentrations within the benzene plume, the highest PFOS

258 concentrations in groundwater were found to the east of the burn pit (Figure 3C; Table S7). In addition,
259 based on the relative extent of the groundwater plumes alone, there was no strong evidence for
260 differential transport of different chain-length perfluorocarboxylates or perfluorinated sulfonates,
261 which are known to undergo chain-length dependent sorption.^{21,23} For example, the results of the
262 HYDRUS-2D modeling (Figure S8) indicate that PFHxA should have traveled farther and have a
263 larger plume distributions than PFOA 22 years after releases have ceased due to its weaker sorptive
264 potential.

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

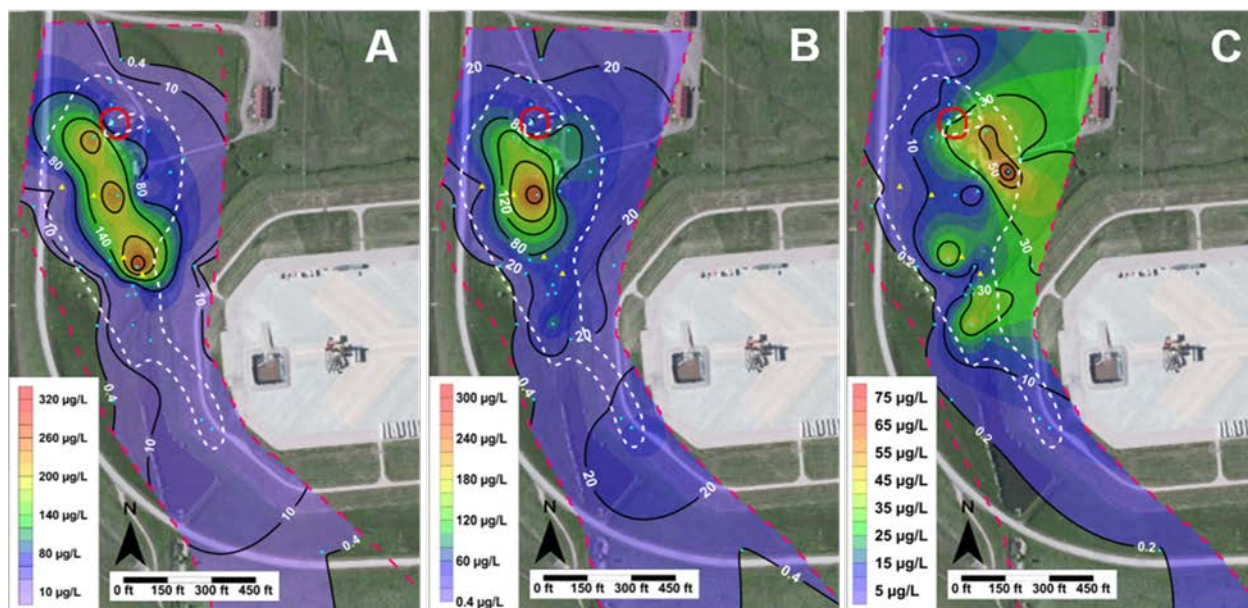


Figure 3. PFAA contamination in groundwater of (A) PFHxA, (B) PFOA, and (C) PFOS. Dashed red lines illustrate the bounds of the data, dashed white lines indicate the extent of the historic (2002) benzene plume, blue circles represent groundwater sample locations and yellow triangles represent current oxygen infusion wells.

271 Δ PFH_xA, Δ PFHpA) were mapped (Figure S9), though the formation potential of the shortest
272 carboxylate (Δ PFBA) was also elevated within the benzene plume. However, this eastern PFAS source
273 zone became evident again when the spatial distribution of specific precursors were examined (Figure
274 4B, Figure S10).

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

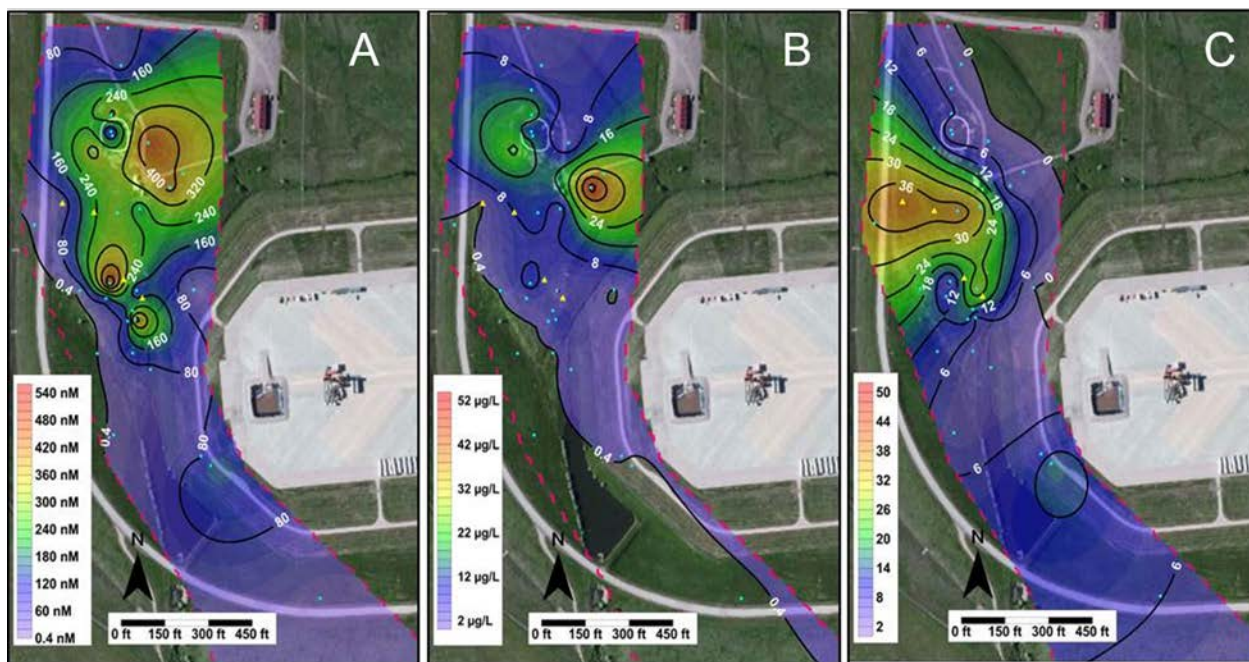


Figure 4. Evidence of PFAA precursors and precursor transformation potential in groundwater: (A) total molar concentration of PFAA precursors measured by the oxidation assay, (B) FHxSA, a C6 sulfonamide; and (C) the ratio of PFHxS to PFOS. Blue dots represent the location of groundwater samples, yellow triangles show the location of oxygen infusion, and red lines show the bounds of the data.

283 organic contaminants in the soil (i.e., non-aqueous phase liquids; NAPLs) in addition to naturally-
 284 occurring organic carbon, although these levels are quite low in comparison to the total f_{oc} . Others have
 285 observed an impact of NAPLs and other co-contaminants on the sorption potential of PFAAs, though
 286 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.

Analyte	Avg Log K_d (\pm SD, n = 7)	Log K_d Range	Avg Log K_{oc} (\pm SD, n = 7)	Log K_{oc} Range	Log K_{oc} (literature)
PFBA	-0.25 \pm 0.87	-1.64 - 0.84	2.17 \pm 1.10	0.55 - 3.45	1.88 ²³
PFPeA	-0.57 \pm 0.62	-1.42 - 0.23	1.85 \pm 0.70	0.99 - 2.84	1.37 ²³
PFHxA	-0.36 \pm 0.59	-1.16 - 0.40	2.06 \pm 0.67	1.33 - 3.01	1.91 ²² , 1.31 ²³ ,
PFHpA	-0.37 \pm 0.46	-1.05 - 0.17	2.04 \pm 0.48	1.34 - 2.71	2.19 ²² , 1.63 ²³ ,
PFOA	-0.19 \pm 0.47	-0.68 - 0.52	2.22 \pm 0.71	1.33 - 3.13	2.06 ²¹ , 2.31 ²² , 1.89 ²³
PFBS	-0.36 \pm 0.64	-1.08 - 0.46	2.06 \pm 0.77	1.11 - 3.07	1.79 ²³
PFHxS	-0.14 \pm 0.53	-0.80 - 0.61	2.28 \pm 0.70	1.30 - 3.22	2.7 ²² , 2.05 ²³ ,
PFOS	0.72 \pm 0.49	0.16 - 1.58	3.14 \pm 0.66	2.28 - 4.19	2.57 ²¹ , 3.34 ²² , 2.80 ²³

287

288 DISCUSSION

289 *Field-based K_{oc} values.* The field-based log K_{oc} values determined in this study are, to the best of our
 290 knowledge, the first field-based log K_{oc} values determined for PFAAs. While the trends within the
 291 perfluorinated sulfonates (i.e., Δ log K_{oc} of \sim 0.9 between PFHxS and PFOS; **Table 1**) were consistent
 292 with previously observed chain-length dependent trends,^{21,23,35,36} there were some inconsistencies
 293 between the trends in the field-derived average log K_{oc} values for the perfluorocarboxylates and
 294 previous observations. The lack of clear chain-length dependent trends for the perfluorocarboxylates
 295 was even apparent when results were limited to log K_{oc} values determined from individual wells (**Table**
 296 **S9**). Given the general consistency of chain-length dependent trends in the laboratory and modeling
 297 studies, these data suggest that the field-based data for the perfluorocarboxylates may potentially be
 298 biased due to the presence of perfluorocarboxylate precursors. For example, if perfluorocarboxylate
 299 precursors were chemisorbed to the organic matter within the solid phase and were sensitive to base-

300 catalyzed hydrolysis, then the measured solid phase concentrations of certain perfluorocarboxylates
301 might have been slightly elevated relative to what should have been in equilibrium with the aqueous
302 phase due to the basic methanol extraction process (resulting in an artificially high K_{oc} value). This is
303 supported by the fact that the only paired samples that were somewhat consistent with chain length
304 trends (i.e., $\Delta \log K_{oc}$ of ~ 1 between PFHxA and PFOA at Tmp 11; [Table S9](#)) also had minimal levels
305 of precursors, as measured by the oxidation assay ([Table S8](#)). While somewhat speculative, these data
306 represent one of the first suggestions as to the important role of PFAA precursors in the distribution of
307 PFAAs in the subsurface at AFFF-impacted sites. Alternatively, the lack of clear trends for the
308 perfluorocarboxylates may have been due to a lack of equilibrium between the two phases, though this
309 is less likely for the shorter chain perfluorocarboxylates than the perfluorosulfonates.³⁶

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

320 Importantly, most PFAA groundwater plumes were spatially similar to the historical benzene plume.
321 These data initially suggest that sampling existing monitoring wells within co-contaminant fuel plumes
322 may provide a very good indication as to the center of mass for most PFAA groundwater plumes at
323 AFFF-impacted fire fighter training areas. This is corroborated by the aquifer solids data, which

324 indicated elevated concentrations both within and to the east of the existing benzene plume (Figure
325 S5). However, the PFOS data and the precursor data strongly suggest that a conceptual model of co-
326 located PFAA and co-contaminant (i.e., benzene) plumes is overly simplistic.

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

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

347 (Figure 2), though historical data from the site suggest there may have been surface fill placed in this
348 area,³⁴ potentially masking a surface soil signal.

349 An alternative explanation for the eastern source zone, and one with important implications, is that
350 hydrologic and biogeochemical alterations to the subsurface as a result of remediation activities are
351 responsible for the current spatial PFAS distribution. This explanation hinges on the fact that this
352 eastern area was initially also contaminated with benzene,²⁸ though the present plume boundary now
353 excludes this area. In addition, neither significant pumping of groundwater nor stimulation of
354 subsurface microbial populations through oxygen infusion appears to have occurred in this eastern area
355 (Figure S1): both types of activities have occurred in the main benzene plume. The lack of oxygen
356 infusion in this eastern area may explain why the perfluorocarboxylates, likely terminal products of
357 aerobic transformations of some PFAA precursors, are not elevated in this area. In contrast, many
358 PFAA precursors, such as FHxSA and the FtSs (which are generally considered intermediate
359 degradation products of AFFF-components), are still present in this area, suggesting some partial
360 transformation of AFFF components has occurred. As the transport potential of both PFOS and PFAA
361 precursors is generally expected to be significantly less^{7,22} than many of the perfluorocarboxylates, the
362 fact that extensive pumping occurred within the main benzene plume would suggest that the relative
363 levels of PFOS in the main benzene plume should be elevated, at least compared to the
364 perfluorocarboxylates, *if* PFOS and the perfluorocarboxylates were co-released. Given that the
365 opposite is true (i.e., the perfluorinated carboxylate signal is relatively stronger in the area subjected to
366 extensive pumping), this suggests releases of PFOS and the perfluorocarboxylates to the groundwater
367 was *not* contemporaneous.

368 This alternative explanation would, in fact, suggest that the levels of perfluorocarboxylates in the
369 subsurface, particularly within the current benzene plume, are primarily a result of the *in situ*
370 transformation of less mobile PFAA precursors to the perfluorocarboxylates within the benzene plume.

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

378 The potential for alteration in PFAS signals in groundwater due to remedial activities is most clearly
379 illustrated in [Figure 4C](#). In this figure, the spatial distribution of the ratio of PFHxS to PFOS in
380 groundwater is plotted, and a significant increase in the ratio (up to 50:1) is observed. Analysis of
381 AFFF containing these compounds suggests the ratio in the AFFF itself was closer to 1:10, though
382 some variation over the years and formulations is expected.^{3,4} If differential transport was occurring
383 (average log K_{oc} for PFHxS is 2.28 vs 3.14 for PFOS; [Table 1](#)), the ratio would be expected to increase
384 (continually) downgradient.²³ Instead, the ratio increases downgradient from the burn pit, and then
385 *decreases*. Alternatively, if *in situ* generation of PFHxS was occurring, this could also lead to an
386 increase in the PFHxS:PFOS ratio. Given the near absence of at least one suspected PFHxS precursor
387 in this area ([Figure 4B](#)) and the fact that this area of elevated PFHxS:PFOS ratios is in the immediate
388 vicinity of the wells where significant oxygen infusion has occurred ([Figure 1](#)), the *in situ* generation
389 of PFHxS from PFAA precursors due to aerobic biological processes is the likely explanation, though
390 more research is needed to verify this expected change in ratios as a result of AFFF degradation. It
391 should be noted that FOSA, the PFOS analog to FHxSA, has been shown to form PFOS under aerobic
392 (activated sludge) conditions.³⁵ In addition, it is possible that this presumed production of PFHxS from
393 precursors could have occurred naturally as a result of natural attenuation of the precursors in the
394 groundwater, though the biosparging would likely have accelerated this presumably aerobic process.

395 *Implications.* If the hydrological and biogeochemical explanation of the inconsistencies in the PFOS
396 contamination, spatial distribution of PFH_xS:PFOS ratios, and the distribution of aqueous PFAA
397 precursors is valid, this has major implications with respect to AFFF-impacted sites. Notably, this
398 would imply that the elevated PFOS levels to the east of the burn pit may be more representative of
399 conditions at a site that has not undergone remediation. Moreover, the PFAA precursor and
400 perfluorocarboxylate data from this area of the site would suggest that simply analyzing groundwater
401 samples for perfluorocarboxylates (and not employing the assay developed by Houtz et al.³) would
402 obscure the actual potential for perfluorocarboxylate contamination, particularly for a site that has not
403 undergone remediation. This latter point is particularly crucial as additional AFFF-impacted sites are
404 investigated with respect to PFAS contamination.

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