

PAPER



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PFAS soil and groundwater contamination via industrial airborne emission and land deposition in SW Vermont and Eastern New York State, USA†

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In order to understand the extent to which airborne PFAS emission can impact soil and groundwater, we conducted a sampling campaign in areas of conserved forest lands near Bennington, VT/Hoosick Falls, NY. This has been home to sources of PFAS air-emissions from Teflon-coating operations for over 50 years. Since 2015, the Vermont and New York Departments of Environmental Conservation have documented ~1200 residential wells and two municipal water systems across a 200 km² area contaminated with perfluorooctanoic acid (PFOA). Given the large areal extent of the plume, and the fact that much of the contaminated area lies up-gradient and across rivers from manufactures, we seek to determine if groundwater contamination could have resulted primarily from air-emission, land deposition, and subsequent leaching to infiltrating groundwater. Sampling of soils and groundwater in the Green Mountain National Forest (GMNF) downwind of factories shows that both soil and groundwater PFOA contamination extend uninterrupted from inhabited areas into conserved forest lands. Groundwater springs and seeps in the GMNF located 8 km downwind, but >300 meters vertically above factories, contain up to 100 ppt PFOA. Our results indicate that air-emitted PFAS can contaminate groundwater and soil in areas outside of those normally considered down-gradient of a source with respect to regional groundwater flow.

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Environmental significance

Poly- and perfluoroalkyl substances (PFAS) are a class of widely used chemicals of emerging environmental concern. Most instances of PFAS contamination have resulted from direct land applications at industrial sites, locations of fire-fighting foam use, or biosolids application. In these cases, groundwater contamination typically migrates in the direction of regional groundwater flow. Where PFAS contamination results from airborne emission, contamination needs to be investigated in areas outside of those normally considered at-risk relative to the location of manufacturing facilities. In our study area, >200 km² of upland regions may have been contaminated by airborne PFAS emission.

Introduction

Poly- and perfluoroalkyl-substances (PFAS) are contaminants of emerging widespread concern. They have been used to apply non-stick, water repellant, and stain resistant coatings to a wide range of manufactured products since the 1950's.¹ PFAS have been found to be bioaccumulative, and have been linked by epidemiological and animal-based studies to a wide range of health issues, including kidney and testicular cancers,^{2,3} ulcerative colitis,⁴ thyroid disease,^{5,6} and immunological problems.⁷ PFAS are present in the blood serum of nearly all people and animals.^{8–14} Blood serum levels in people are highly variable and dependent on proximity to manufacturers, military bases, or

other point sources.^{11,15} Primary exposure pathways are through drinking water, eating contaminated food, food packaging, exposure to other products manufactured using PFAS, and/or occupational exposure.^{16–21} PFAS are highly persistent in the environment and have been found in soil, lakes, rivers, and oceans in all corners of the globe, including polar regions.^{22–30} PFAS are not broken down by any known natural process, and can be transported as anions in surface water or groundwater, through the atmosphere as dust and/or aerosols, and may be mobilized as aerosols from sea spray.^{3,31} The qualities of many PFAS – bioaccumulative, highly persistent, and mobile – pose new questions to environmental science and regulation.

This study seeks to test the hypothesis that airborne PFAS emissions from manufactures in southwest Vermont and eastern New York State contaminated soil and groundwater at significant distances (>8 km) from emission sources. Air emission of PFAS has been shown to have impacted water from manufacturers in West Virginia^{32,33} and North Carolina.³⁴

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However, the scale at which impacts can occur is debated. Early modelling and sampling studies indicated limited PFAS deposition more than a few kilometers from the source,^{32,35} while more recent sampling has suggested that air deposition can impact water >10 km from sources.^{34,36} Addressing this question is difficult because of the pervasive nature of PFAS contamination and the multiple pathways by which it can be introduced to the environment. Our study area is an ideal case to address this question because of the large areas of conserved lands in the Green Mountain National Forest downwind of emissions sources, within which point-source contamination is very unlikely to have occurred. We collected soil and groundwater samples from regions with specific spatial relations to air-emission sources and ran pairwise statistical tests on data to examine spatial patterns of contamination and delineate any signature of an air-deposition plume.

Site history and description

The Bennington/Hoosick region's industrial history stretches back to the 1800's, when mills were built in river valleys. The surrounding uplands were developed largely for agricultural use. Several of the riverside industrial sites were repurposed as plastics manufacturers in the second half of the 20th Century. The most significant of these are the McCaffrey Street factory in Hoosick Falls, NY, which operated from 1956 to present, ChemFab in North Bennington, VT, which operated from 1978 until 2002, and Taconic Plastics in Petersburg, NY, which has operated from 1961 to present. All three factories utilized dispersions containing ammonium perfluorooctanoate, which was vaporized during a baking step at ~300 °C and released from smokestacks as PFOA and other PFAS. Many of the region's PFAS-contaminated wells are in the uplands surrounding the factories in river valleys. Because the factories all lie in valley bottoms (groundwater discharge points), it is extremely unlikely for contamination to migrate from factory sites to uplands *via* groundwater flow.

PFOA contamination was discovered in the Hoosick Falls village water supply wells in 2015 at concentrations ranging from 400 to 600 ppt. Subsequent investigations conducted by the New York and Vermont Departments of Environmental Conservation have now discovered PFOA in over 1200 residential wells over an area of >200 km² across the region (Fig. 1).

Geologic setting

Bennington and Hoosick Falls both lie within river valleys to the west of the Green Mountains (Fig. 1). The valley bottoms are filled with variable-thickness alluvial and fluvial gravels, while valley sides and hilltops are generally covered by variable-thickness (0–50 m thick) glacial till.³⁷ Bedrock beneath unconsolidated materials in the valleys and hills of Bennington/Hoosick region is dominantly a mixture of dolomitic limestone, phyllite, with minor quartzite. All bedrock formations are highly fractured, faulted, and folded.³⁸ Thus bedrock permeability is highly dependent on local structures, and is extremely heterogeneous and non-isotropic.³⁸ Bedrock beneath the Green Mountains is highly deformed quartzite and gneiss, the

permeability of which is highly dependent on local fractures. Bedrock in the Green Mountains is covered by a very thin (0–5 m thick) layer of sandy, rocky till.

Most private wells in the PFAS-impacted region are completed within the dolomite and/or phyllite bedrock units. However, several private wells and the Village of Hoosick Falls public wells are completed within the alluvial/fluvial gravel formations in valley bottoms. The degree of PFAS contamination in wells is highly variable spatially, with uncontaminated wells occurring within 200 meters of wells with over 1000 ppt PFOA (Fig. 1). Kim *et al.*³⁹ have hypothesized that the variability is in part due to the fracture-controlled nature of groundwater flow in the bedrock aquifer and possible groundwater recharge to some rock units occurring from distant sources along very low flow paths.

Methods

Study design and sampling

The ubiquitous nature of PFAS contamination raises the question: how does one differentiate locally air-emitted PFAS contamination from “baseline” PFAS levels caused by long-range air transport, while also considering the possibility of undocumented point sources? This question has significant legal importance in the Bennington/Hoosick Falls area, as regulators and courts are assessing responsibility and liability for the water contamination. We designed a sampling strategy to take advantage of the large areas of conserved forestland surrounding Bennington; many of these lands, including the Green Mountain National Forest have been conserved since prior to the first synthesis of PFAS. Prevailing wind patterns are dominantly west-to-east with a secondary peak wind direction out of the southeast (Fig. 1 inset). We divided our sample collection sites into five regions relative to these wind patterns:

(1) Bennington local – water sources and soil near PFAS industrial sites in Bennington; hypothesized to be impacted by air emission.

(2) Downwind – samples from the Green Mountain National Forest directly east of emitters in Bennington and Hoosick Falls; hypothesized to be impacted to by air emission.

(3) North of Main Wind Pattern – samples from the Green Mountain National Forest and other conserved forestlands that are north of the west-to-east wind pattern from the known emitters; hypothesized to be not impacted by air emission (*i.e.* background).

(4) Local Upwind – samples from the Pittsfield State Forest, directly upwind of known emitters in Bennington and Hoosick Falls; hypothesized to be not impacted to by air emission (*i.e.* background).

(5) Far Afield – samples collected from conserved forestlands more than 50 km distant from known industrial sites; hypothesized to be not impacted to by air emission (*i.e.* background).

We selected soils sampling sites in order to minimize the chance that any PFAS could have been applied directly to land by human activities. All sampling sites were either within the Green Mountain National Forest, New York DEC forest preserve or state forest land, or other protected tracts of private or state-

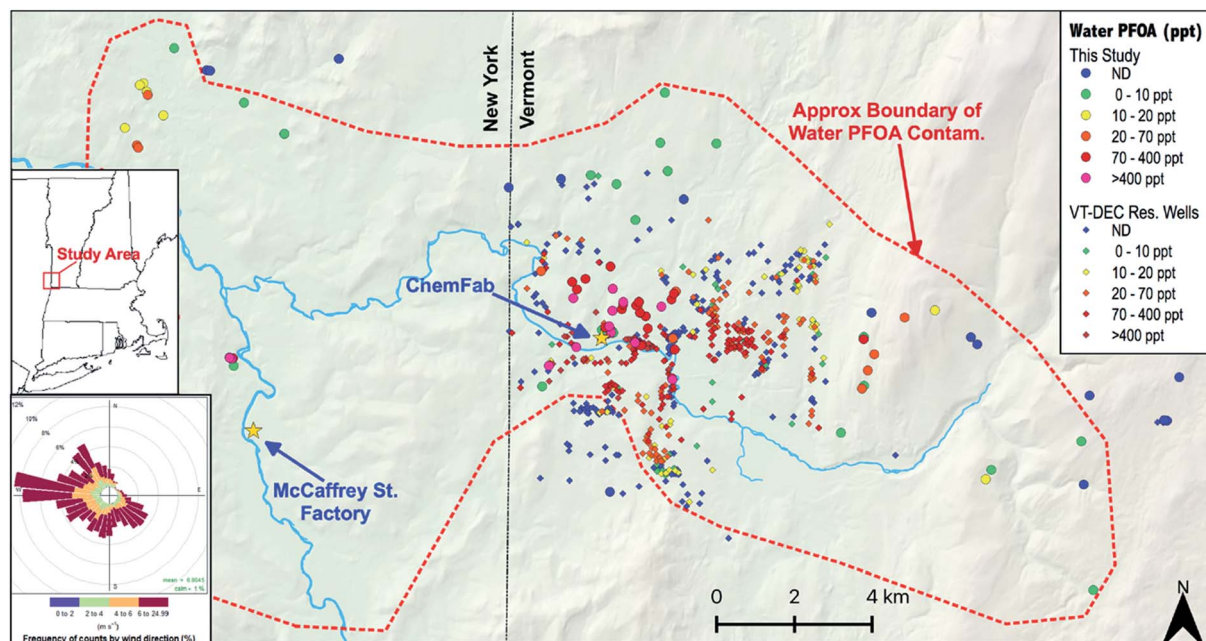


Fig. 1 Map of PFAS-impacted region surrounding Bennington, VT and Hoosick Falls, NY. Locations and ranges of groundwater PFOA concentrations are indicated for samples analyzed for this study, along with analyses compiled from the Vermont Department of Environmental Conservation and Site Investigation Reports prepared for St. Gobain Performance Plastics. Few analytical results are publicly available on the New York side of the plume because of privacy concerns raised by New York state government. The boundary of the plume within New York is estimated from general area maps provided by the NY Department of Environmental Conservation. In all, approximately 1200 private and public wells have been contaminated over an area exceeding 200 km². Inset Wind Rose diagram is based on daily two-minute maximum wind direction recorded at the Morse State Airport in Bennington for the period January 1 1998 through July 31 2018. This data includes a daily maximum two-minute average wind speed and direction (7162 records). This two-minute average maximum wind is taken to represent the wind during any given day that is most likely to transport PFAS aerosols from points of emission. The wind speed and directions were analyzed with the "Openair" package within the "R" environment.³⁸ The dominant aerosol transport direction should be from west to east, with some secondary transport from south-southeast to north-northwest.

owned land in VT and NY. Sample sites were accessed *via* foot and are located at least 200 meters from a road or 50 meters from a hiking trail. Sample locations were selected in clusters in order to achieve representative coverages from specific regions.

Soil samples were collected with a one-inch-diameter, 16-inch long, stainless steel push sampler. At each site, the sampler was driven to refusal depth (generally 12 to 16 inches) at four to eight locations within a five-square-meter area. The soil was then thoroughly homogenized in a stainless-steel bowl before being transferred into sample containers provided by Eurofins labs.

Groundwater seeps were sampled by driving a 0.5 cm diameter stainless steel mini-well into the center of the seep, then drawing water from the well with a 250 ml polyethylene syringe. The water was then decanted from the syringe into two 250 ml Trimza-treated sample bottles provided by Eurofins labs. Springs and surface water samples were collected from the source with a 500 ml polyethylene beaker, and then transferred to two 250 ml Trizma-treated sample bottles provided by Eurofins labs.

Full details of sampling and analysis procedures are included in ESI-1.[†]

Data analysis/statistics

Interpretation of our analytical results hinges on determining if there is a statistically significant difference between PFAS concentrations in our five sampling regions. We conducted statistical analysis of PFOA and PFOS. Analysis results returned below detection limits were not included in statistical comparisons. Significant outliers were also excluded from statistical analysis so that sample groups would better approximate a normal distribution. For analytical results that were below the 95% confidence quantification limit, the estimated value from the lab is used in our statistical comparisons. In comparing PFOA and PFOS concentrations between sampling regions, we first ran a one-way ANOVA (analysis of variance) test to determine if there is a statistically significant difference between the mean values of any of the groups. If the ANOVA test rejected the null hypothesis, meaning that there is a statistically significant difference between groups, we proceeded to run a Tukey-HSD (Honestly Significant Difference) pairwise test, which compares sample-group means with a studentized range with a 95% confidence interval for the entire sample set. All statistical analyses were conducted using the "Statsmodel" package in Python. All code and output are included in ESI-3.[†]

Data quality

Duplicate sampling. Over the course of this study, we collected five duplicate water samples and one duplicate soil sample in order to test the consistency of laboratory results. Duplicate water samples were collected by simply filling additional sample bottles from the same source. Duplicate soil samples were collected by filling additional samples bottles from the stainless-steel bowl following homogenization. Full data from the duplicate sampling is included in supplementary information ESI-1.†

Repeat water sampling. Monitoring wells on the Bennington College campus and several residential wells were sampled multiple times over this course of this investigation to study the temporal variability of PFAS concentrations. The results also provide a reasonable test of the quality of our sampling techniques and the consistency of laboratory results. Results were very consistent between sampling events, with the PFOA concentration of water sources varying less than 20% between most sampling events; see data and graphs in ESI-5.†

Sequence analysis of soil samples. One concern with our study design is the possibility of cross-contamination between soil samples because we used the same equipment at each sample site. Though we carefully cleaned the equipment between each site, influence of prior samples on each result is still a concern. To test for this effect, we plotted the PFOA and PFOS concentrations in the sequence that they were collected with color codes for the sampling region (see ESI-2 Fig. 1†). Visual examination of these plots does not suggest any influence of a prior sample on the result of subsequent samples. There is no smearing effect apparent after high- or low-concentration samples, and the dominant influence on the PFOA concentration is the region from which the sample was collected.

Comparison between multiple soils studies. We have compiled analysis data from additional PFAS soil studies conducted in the Bennington, VT region to test that data collected in this study is consistent with the results of other sampling and analysis techniques. These include:

(1) Samples collected by the Vermont Dept. of Environmental Conservation (VT-DEC) around the North Bennington area impacted by the ChemFab factory contamination (<https://dec.vermont.gov/commissioners-office/pfoa>).

(2) Samples collected for preparation of the *Draft Conceptual Site Model Site Investigation Report* prepared by Barr Engineering on behalf of St. Gobain Performance Plastics; samples collected around the Bennington region impacted by ChemFab (<https://anrweb.vt.gov/PubDocs/DEC/PFOA/Conceptual%20Site%20Model%20Site%20Investigation/DRAFT-CSM-Site-Investigation-Report-text-only-FEB2018.pdf>).

(3) Samples collected in a forested region of Bennington by a contractor for a solar developer as part of the permitting process for a solar farm on the site (<https://epuc.vermont.gov/?q=node/64/127312/FV-PFEXAFF-PTL>).

(4) PFAS soil background study across Vermont commissioned by VT-DEC (<https://anrweb.vt.gov/PubDocs/DEC/PFOA/>

Soil-Background/PFAS-Background-Vermont-Shallow-Soils-03-24-19.pdf).

The samples from these studies were collected in vertical profiles at varying depths at each site. We have averaged results from the top 18 inches in each depth profile in order to provide the most direct comparison to the results of our sampling technique. We have also divided our samples into sets of the impacted areas (Bennington Local and Downwind regions), and the sampling regions that we hypothesize to not be impacted by local air deposition (North of Wind Pattern, Upwind, and Far-Afield).

With the exception of the Barr Site Investigation,⁴⁰ our data is consistent with these other investigations. A Tukey–Kramer pairwise test between the sample groups (see ESI-2 Fig. 4 and 5†) shows that dry soil PFOA concentrations from impacted areas of our study are not significantly different from those of the initial VT-DEC samples or the sampling done on the proposed Apple-Hill solar farm, but they are significantly different those of the Barr Site Investigation. The Barr samples are also significantly lower than those of the VT-DEC and Apple-Hill studies. Dry soil PFOA concentrations in the peripheral (non-impacted) samples of our study are not significantly different from those in the Vermont Soil Background study, or those of the Barr Site Investigation. Dry soil perfluorooctanesulfonate (PFOS) concentrations were not significantly different between any of the studies.

The lower dry soil PFOA concentrations from the Barr Site Investigation relative to those of our study and the other two studies may be due to sampling techniques and/or the land cover of the sampling sites. Our study, the VT-DEC samples, and the Solar-Farm samples were collected with hand-operated soil probes, while the Barr samples were collected from boreholes during drilling with a casing-advance rotary technique that involved significant amounts of water pumped down the hole. The sample sites from the Barr Investigation were also almost entirely in areas of developed land cover, with disturbed soils, while the other studies' sites were more commonly located in forestland or grassland. These differences are further addressed in the Discussion section below.

Results/discussion

PFAS distribution in surface soils

Soil sampling results (included in ESI-4†) support our hypothesis that the Bennington Local and Downwind regions were impacted by air deposition from local PFAS air emitters. Dry soil PFOA concentrations mapped in Fig. 2 and 3 and graphed in Fig. 4 exhibit distinctly higher concentrations in the Bennington Local and Downwind regions relative to the three peripheral sampling regions. The mean values of soil PFOA concentration in the Local (5.6 ppt) and Downwind (4.3 ppt) regions is higher than the mean soil PFOA in the other three sampling regions (North = 1.33 ppb, Upwind = 1.16 ppb, Far = 0.62 ppb).

One-way ANOVA showed a statistically significant difference between soil dry PFOA concentration in the five sampling areas; $F(4,60) = 7.383$, $p = 0.000038$. The Tukey-HSD pairwise test indicates that the mean soil PFOA concentration in the Local

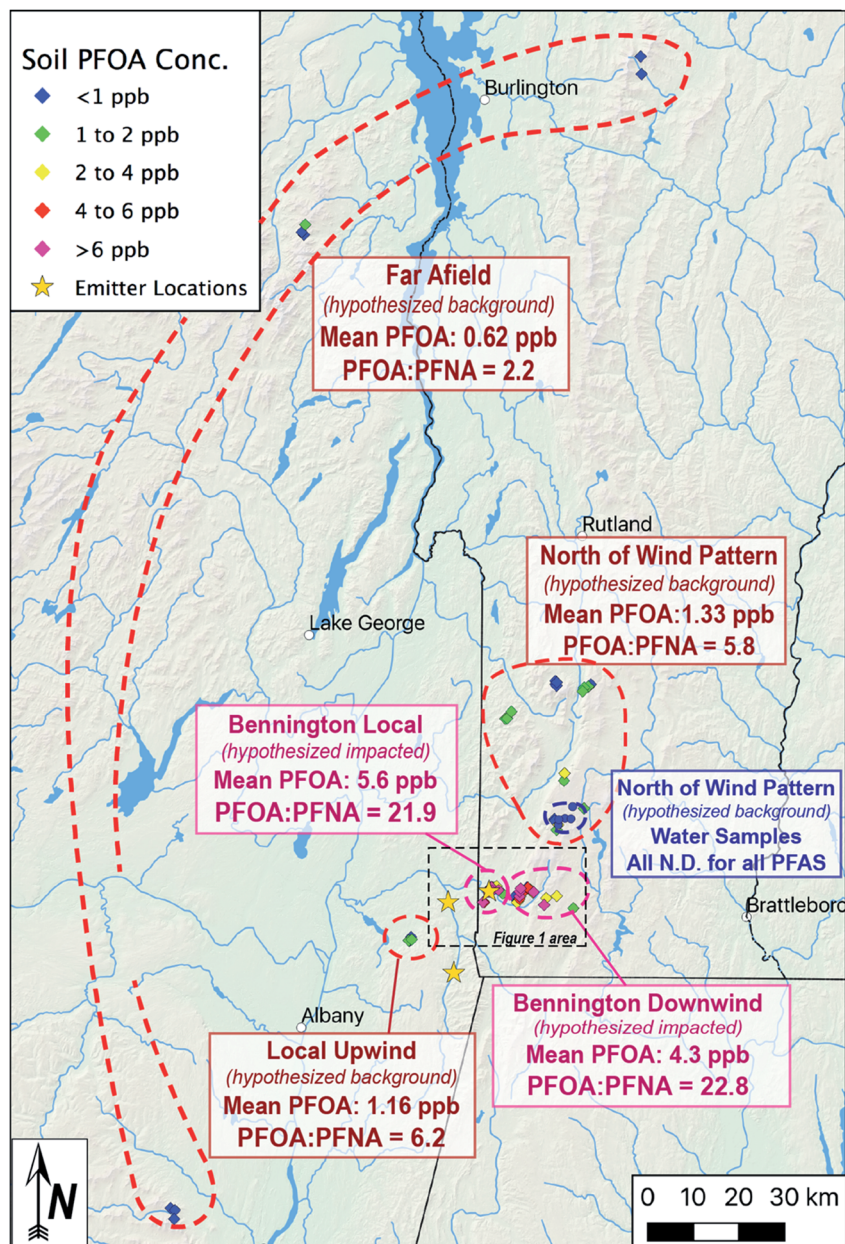


Fig. 2 Map showing all dry soil PFOA concentrations selected water concentrations analyzed for this study. Sample sites are divided into regions in relation to manufacturers that emitted airborne PFOA in Bennington and Hoosick Falls: (1) Bennington Local, (2) Downwind, (3) North of Wind Pattern, (4) Upwind, and (5) Far-afield. All samples were collected from forest landscapes on conserved lands with minimal human disturbance.

and Downwind regions is statistically significantly higher than that of the North of Wind Pattern and Far-Afield regions, though not significantly higher than the Upwind region (see ESI-4 Fig. 12†), even though the mean PFOA concentration in the Upwind region is much lower than that of the North region. We were only able to collect four samples in the Upwind area, and thus the confidence range around the Upwind PFOA mean is much wider, which likely contributed to the failed test for statistical difference.

The mean values of soil PFOS concentration (Fig. 4) in the Local (1.8 ppt) and Downwind (0.66 ppt) regions is not apparently different from the mean soil PFOS in the other three

sampling regions (North = 0.76 ppb, Upwind = 0.55 ppb, Far = 0.61 ppb). One-way ANOVA showed that there is not a statistically significant difference between soil dry PFOS concentration in the five sampling areas; $F(4,60) = 0.355$, $p = 0.839$. Because PFOS was claimed to not have been used by local industries, this pattern further supports our hypothesis of soil impacts from local air emitters.

PFHpA was detected in 74% of samples in the downwind area, but only 29% of samples from other areas, and PFHxA was detected in 53% of the downwind samples, but only 10% of the samples from the other regions.

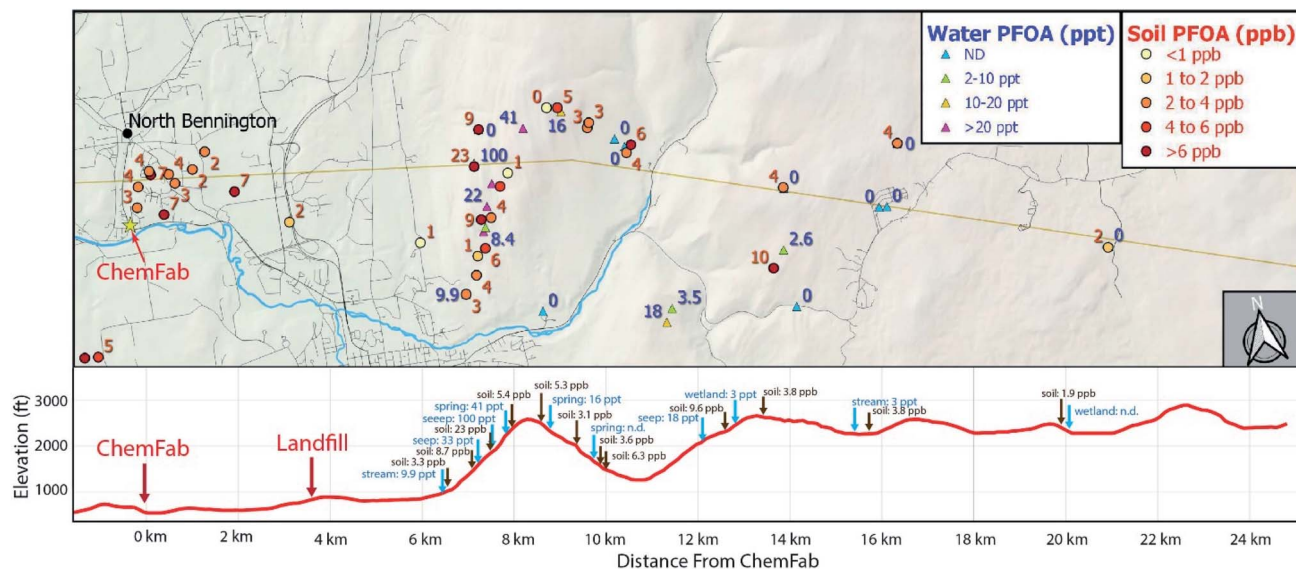


Fig. 3 Detail map and profile section of soil and water PFOA concentrations in the downwind-of-emitters sampling areas within the Green Mountain National Forest. Line of profile on map is shown in yellow. The profile shows elevated soil and water PFOA levels in regions up-gradient, though down-wind, of possible PFOA point sources.

Our Local and Downwind samples have an average PFOA : PFNA ratio of 21.9 and 22.8 respectively, while average ratios in the other three sampling areas are much lower; North PFOA : PFNA = 5.8, Upwind PFOA : PFNA = 6.2, and Far Afield PFOA : PFNA = 2.2 (Fig. 2). Globally, the PFAS air deposition on soils likely occurs *via* a combination of direct PFAS deposition,⁴¹ and long-range-transport of volatile precursor compounds, including fluorotelomer alcohols (FTOH) followed by oxidation to PFAS in aquatic, atmospheric, or biologic media.^{42–45} Data compiled by Rankin *et al.*²⁵ from other sources suggests that the range of FTOH oxidation reactions should produce PFOA : PFNA ratios between 1 : 1 and 6 : 1, while direct air

deposition of PFOA may produce PFOA : PFNA ratios greater than 8 : 1 because PFOA was used much more commonly in industrial processes than PFNA. The higher PFOA : PFNA ratio in the Local and Downwind regions relative to other sampling regions further supports our hypothesis that local industrial emissions source of direct air deposition in the region downwind of industrial emitters in Bennington and Hoosick Falls.

An area of at least 200 km² has been contaminated to a level of between 5 and 6 ppb dry soil PFOA by industrial emitters in the Bennington/Hoosick Falls area, which corresponds to roughly 1000 kg of PFOA sequestered in soils. This likely represents only a small fraction of the total PFOA used during

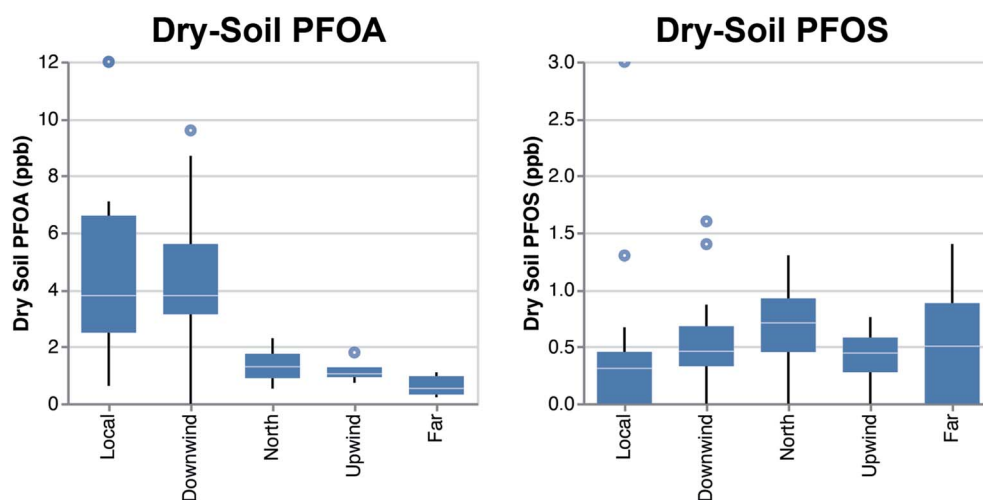


Fig. 4 Box plots of dry soil PFOA and PFOS concentrations; subdivided by the sampling regions delineated in Fig. 2. Soil PFOA concentrations are distinctly higher in the downwind from emitters area than in the other three sample regions, while the soil PFOS concentrations are broadly similar across all sample regions.

the region's manufacturing history. Our results represent a minimum extent of the plume; additional work is needed to delineate its full extent. The size of the Bennington/Hoosick soil plume is roughly similar to the reported size of a soil and groundwater PFOA plume near Merrimack, New Hampshire, which is where ChemFab relocated to from North Bennington in 2002.⁴⁶

Groundwater PFAS distribution

PFOA concentrations in water samples through the Bennington valley (ESI-5†) are highly variable, ranging from non-detect to 3100 ppt. Both the range and variability are consistent with water sampling of domestic wells performed by VT-DEC (Fig. 1). Groundwater samples in the Downwind region of the Green Mountain National Forest ranged from non-detect in several springs to 100 ppt from a groundwater seep located ~6.5 km from ChemFab (Fig. 3). Several other groundwater seeps and springs located between 6 and 8 km downwind of ChemFab ranged in concentration from 6 to 41 ppt. This area on the west-facing slope of the Green Mountains contains no roads or human habitation, and is 200 to 800 vertical meters above (up-gradient) known PFOA emission sources. Thus, the only reasonable explanation for water contamination there is PFOA leaching from soil that was contaminated by air deposition.

A cluster of water samples collected from the North-of-Wind-Pattern region of the Green Mountain National Forest was below detection limits for PFOA and all other PFAS analytes. This is consistent with lower soil PFOA levels detected in this area, and thus provides a control that further supports the hypothesis that groundwater contamination in the Downwind region is a result of air deposition from the local industries.

PFOA water contamination appears to extend less far (~8 km) from the air emitters than the anomalously high soil concentrations (Fig. 3 and 5). We detected PFOA in several

springs and seeps beyond the westernmost ridge of the Green Mountains, but the values are relatively low. The extent and scope of air-deposited PFAS in our study appears to be less than that documented by Galloway *et al.*³⁶ from the Washington Works plant in West Virginia. These investigators found PFOA in surface waters >10 ppt at distances up to 30 km from the emission source. The primary difference between these sites may be in the mass of PFOA vapors emitted per year. The Washington Works factory was DuPont's primary Teflon production center; the Bennington/Hoosick manufacturers are relatively small by comparison.

Groundwater contamination via airborne PFAS deposition

Drinking water is an important human exposure pathway for PFAS,^{21,47} thus we are primarily concerned with the transference of air-deposited PFAS from soil to groundwater. While our results indicate that air-emitted PFAS can impact groundwater, a fundamental question remains for environmental professionals: what soil concentration is necessary for PFOA to begin leaching from soil to infiltrating groundwater? Our dataset does not offer a clear-cut answer to this question. The degree of soil PFOA contamination in the Green Mountain National Forest is on the same order as that in the Bennington Valley. However, groundwater PFOA concentrations fall to non-detect values with greater distance east in the mountains where the soil PFOA concentration is still in the 4–6 ppb range (Fig. 4 and 5).

Insights may lie in the nature of the soils themselves. The undisturbed forest soils in the Green Mountains have significantly higher organic carbon content than the human-disturbed soils in the Bennington Valley (see data in ESI-4†). Experimental studies suggest that higher organic carbon content causes higher PFAS retention in soils *via* electrostatic interactions.^{48–55} Miao *et al.*⁵³ and Li *et al.*⁵⁵ both demonstrate positive, though not particularly strong, correlations between organic carbon

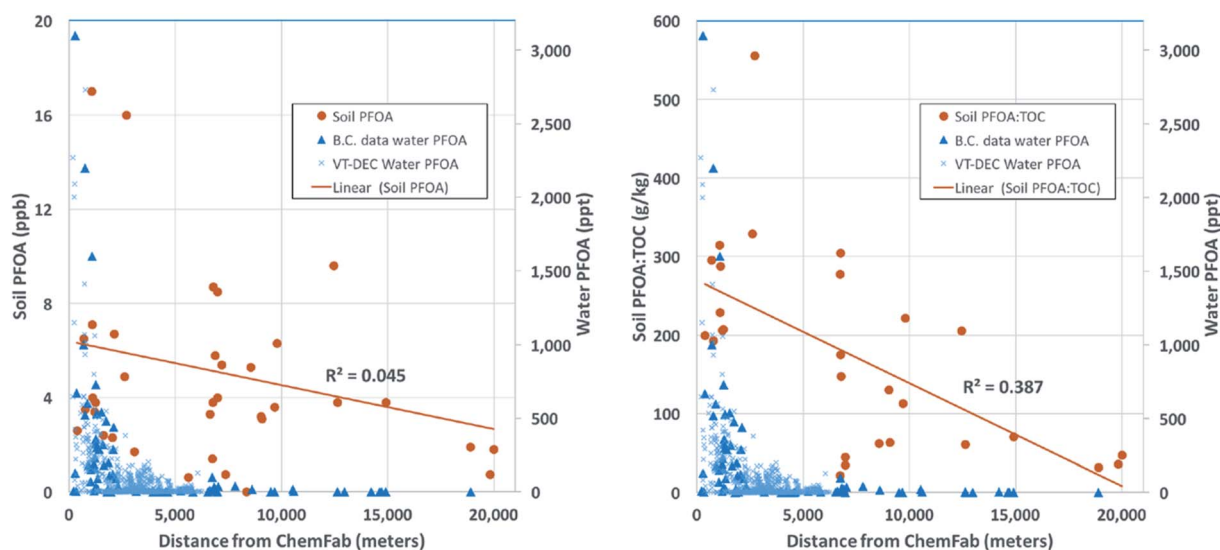


Fig. 5 Graphs of PFOA water and soil concentrations vs. sample location distance from ChemFab source of air emission. Water concentration from this study are plotted as triangles and those from VT-DEC domestic well sampling are plotted as "X's". Soil PFOA concentration on the right graph have been normalized to Total Organic Carbon, which shows a more pronounced decrease with distance from ChemFab.

content and PFAS soil retention, with the effect being strongest for longer chain PFAS. Some of the highest PFOA soil concentrations found in our study come from very organic-rich soils on the west slope of the Green Mountains, ~6.5 km to the east and 1000 vertical feet above the ChemFab factory. This includes significant outlier soil PFOA concentrations of 23 ppb, collected in 2018, and 96 ppb when we resampled the same site in 2019. When soil and water PFOA level are plotted *vs.* distance from ChemFab (Fig. 5a), it is apparent that water PFOA concentration decreases dramatically with distance from the factory, while soil PFOA remains high to much larger distances (into the Green Mountains). If soil PFOA is normalized to total organic carbon (Fig. 5b), a more regular linear relationship between distance and concentration emerges.

Soil pH is also a possible factor in PFAS retention, with adsorption decreasing at higher pH due to the surface charge on soils becoming less positive under alkaline conditions.^{55,56} These laboratory results are consistent with our observation of high PFOA retention in the Green Mountain soils, which are above quartzo-feldspathic bedrock (low pH), while the valley soils are above carbonate bedrock (high pH).

The type of land cover/use may also have an effect on retention *vs.* leaching of PFAS from soil. In order to examine this relationship, we intersected soil sample location points from our study and the three other soil studies conducted in the Bennington area with the 2016 National Land Cover Dataset (NLCD), and binned the NLCD categories into “Forest”, “Grassland/Pasture”, and “Developed”, the last of which includes residential, commercial, and tilled agricultural land (Fig. 6). Soils in developed land areas are generally low in organic carbon, and may be subject to regular disturbance (*i.e.*, tilling & mowing), which could increase the tendency for them to leach rather than retain PFAS. The results of our sampling and the other three studies in the Bennington area show highest

PFOA in areas of forest cover, and lowest PFOA in developed land soils, with grassland/pasture being intermediate between the two. A Tukey-HSD pairwise test of these land use groups indicates that soils in forested land have statistically significant higher PFOA concentrations than those on developed land (see ESI-3 Fig. 9 and 10†).

Taken together, our observations indicate that multiple factors need to be considered when assessing the potential for PFAS to leach from soil to groundwater. It is likely that soil PFOA levels were higher in the Bennington valley while the ChemFab factory was active, and that a portion of that soil PFOA has subsequently leached to groundwater. In the Green Mountains and other forested areas, a higher fraction of the PFOA deposited on soils has been retained rather than leached.

Baseline soil PFAS contamination in the northeastern United States

Soil results from our sampling sites that are not directly downwind of the Bennington/Hoosick PFAS emitters may be indicative of baseline level of soil PFAS contamination in the northeast United States caused by long-distance air transport of PFAS and precursor chemicals. The mean values of major PFAS compounds from these sites are PFOA = 1.12 ppb, PFOS = 0.61 ppb. The mean values of our sites that are more remote from the Bennington/Hoosick emitters are PFOA = 0.62 ppb, PFOS = 0.53 ppb.

There are only a few published analyses with which to compare our soil results. Rankin *et al.*²⁵ analyzed PFAS soil levels in sites globally. The nearest soil sample site to the Bennington/Hoosick area this study is from Holderness, NH, which contained 1.2 ppb PFOA. This is broadly similar to many of our background results (average 1.12 ppb), but the PFOS concentration in this sample (1.8 ppb) is considerably higher than our downwind and background results. Other results

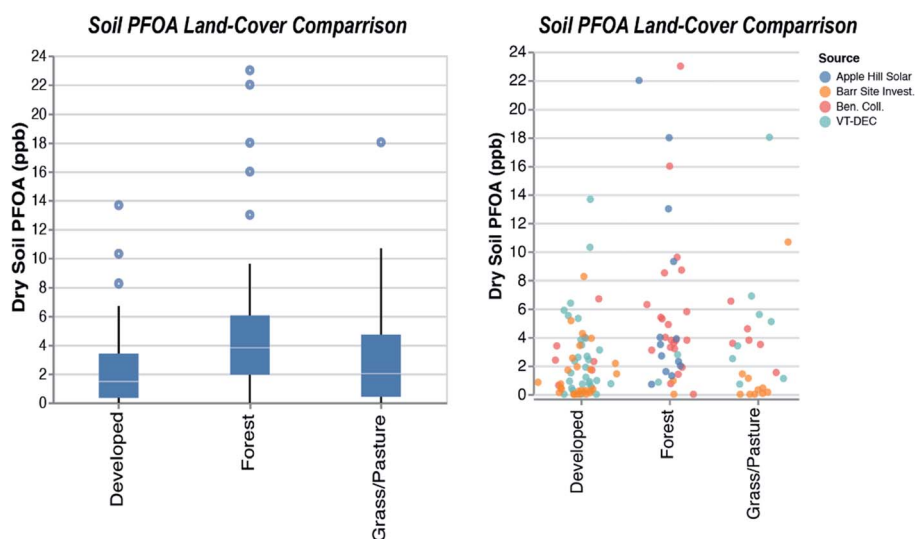


Fig. 6 Box-plot and jitter-plot of soil PFOA concentrations in the Bennington region divided by the land cover/use for each sampling point. Forest soils contain more PFOA than Grasslands or areas of developed/tilled land, indicating higher PFAS soil-retention and/or air-deposition in forested regions.

reported by Rankin *et al.* for sites near Cortland, NY and Penns Grove, NJ are generally similar to the Holderness site. Mejia-Avendaño *et al.*⁵⁷ reported on soils in Lac Megantic, Quebec that were contaminated with PFAS by AFFF application. This study included analyses of background soils away from the fire-fighting sites: PFOA = 0.250 ppb, and PFOS = 0.160 ppb. This area of southern Quebec is somewhat more remote from industrial regions of the northeastern US, which could account for the lesser contaminated soils there. Discrepancies in baseline levels between these studies could also be due to variations in local soil conditions (*i.e.* sorption capacity), local/regional contamination sources, or analytical techniques.

Conclusions and implications

PFAS soil sampling and analysis reveal a statistically significant enrichment of PFOA in areas local to, and downwind of factories that emitted PFAS to the atmosphere during baking of wet dispersions. Our results are further supported by higher PFOA : PFNA ratios in the local and downwind regions relative to peripheral areas. The presence of elevated PFOA in groundwater seeps and springs within the Green Mountain National Forest in the downwind region supports our hypothesis that air-emitted PFAS can cause groundwater contamination over large areas downwind of emission sites. Environmental investigations related to such manufacturing facilities need to expand in scope to consider regions downwind of emission sites, rather than being limited to areas in the down-gradient direction of groundwater flow.

Conflicts of interest

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