

Supplementary Information ESI-1: Detailed sampling and Analysis Methods

Supplemental data to accompany "PFAS soil and groundwater contamination via industrial airborne emission and land deposition in SW Vermont and Eastern New York State, USA"

Sampling Areas & Study Design

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 in the region. 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
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
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

Soil Sampling and Analysis

Site Selection: We selected soils sampling sites in order to minimize the chance that any PFAS compounds 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-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 areas.

Sample Collection: We collected the samples 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. Samples were removed from the sample tube and placed into a stainless steel bowl. The samples in the bowl were then thoroughly homogenized via hand mixing before being placed into two 250 ml polyethylene

bottles (provided by Eurofins Labs). The purpose of the homogenization step was to attempt to obtain a representative sample, given that the distribution of PFAS in soil is likely heterogeneous. PFAS is more likely to adsorb to some soil components than to others, particularly in soils in which there is an uneven distribution of organic and mineral matter. Because for this study we were more interested in large scale spatial patterns than fine-scale variation, we determined that the homogenization step was a reasonable way to achieve bulk average sampling. Samplers wore nitrile gloves, avoided wearing synthetic-fabric clothing, and kept food wrappers away from sampling equipment. All sampling equipment was thoroughly decontaminated with North Bennington, Vermont tap water (regularly tested as PFAS-free) between each site. Samples were stored on ice and/or in a refrigerator before shipping to Eurofins Lancaster Laboratory.

Soil Sample Analysis: Soil samples were analyzed for 14 PFAS compounds at Eurofins Labs using a version of EPA Method 537 modified for soil. A methanol-based spike of C13 and deuterium-isotopically labeled analogs of the target PFAS compounds was added to a one-gram portion of each soil sample. These compounds serve as extraction standards for the quantitative analysis. A base modified organic solvent solution was then added to each soil sample, and the mixture was sonicated and agitated for one hour. The samples were then centrifuged, and aliquots of the solvent supernatants were removed and concentrated to near dryness. One milliliter of methanol was then added to each sample, and the extracts were placed in an auto-sampler vial. To each sample extract was added a one-milliliter methanol-based solution that contains several other C13-labeled analogs. These are used as injection standards for instrumental and quantitative analysis. The resulting solution was analyzed by LC/MS/MS (Triple Quadrupole mass spectrometer). A method blank with extraction standards was run with each batch of samples. A Matrix Spike/Duplicate was also performed with each extraction batch. These are replicate portions of a given sample that are spiked with both the extraction standards as well as the native compounds. Calibration verification samples were run between every batch of ten field samples, and instrument blanks were run between every ten samples. Laboratory analysis and QA/QC reports are included in ESI.

Total organic carbon in soil samples was also analyzed by Eurofins Lancaster Labs based on method SW-846 9060A. Inorganic carbon was first removed from the samples by lowering the pH of the soil to 2 by adding 1:1 phosphoric acid. The remaining carbon fraction was then oxidized to CO₂ and measured by a nondispersive infrared detector.

Water Sampling and Analysis

Water sampling in the Green Mountain National Forest and other remote areas: The Green Mountain National Forest is largely uninhabited, and thus contains very few wells from which groundwater may be sampled. We searched for and sampled springs and seeps, which are natural points of groundwater discharge. In areas where we could not locate springs or seeps, we collected water from wetlands and/or creeks, which represent a mixture of discharging groundwater and recently precipitated surface runoff. Thus, PFAS detected in these sources represents a minimum value of the groundwater PFAS concentration there. 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. Where springs and surface water was sampled, samples were collected from the source in a 500 ml polyethylene beaker, and then transferred to two 250 ml Trimza-treated sample bottles provided by Eurofins labs. Personnel wore nitrile gloves while sampling, and took precautions to wear non-synthetic clothing and limit exposure to food packaging material. Samples were shipped to Eurofins Eaton Laboratory within the 48-hour hold time.

Monitoring wells on Bennington College campus: Seven monitoring wells on the Bennington College campus, immediately downwind of the ChemFab factory, were sampled multiple times during this study. Monitoring wells were sampled with a stainless steel well bailer. Each well was initially bailed until either no more water could be retrieved or two well-volumes of water had been withdrawn. After each well had recovered, the sample was extracted with the bailer and decanted directly into two 250 ml Trimza-treated sample bottles provided by Eurofins labs. Samples were shipped to Eurofins Eaton Laboratory within the 48-hour hold time.

Domestic Water Wells: Several domestic water wells were also sampled in the Bennington area as part of this study. These samples were collected in accordance with EPA Method 531.1. Samples were decanted directly from the home's pressure tank outflow into two 250 ml Trimza-treated sample bottles provided by Eurofins labs after running the water until its temperature had stabilized. Personnel wore nitrile gloves while sampling and took precautions to wear non-synthetic clothing and limit exposure to food packaging material. Samples were shipped to Eurofins Eaton Laboratory within the 48-hour hold time.

Water Sample Analysis: Water samples were analyzed for 14 PFAS compounds at Eurofins Eaton Laboratory using EPA Method 537.1. Water samples (250 ml) were fortified with method surrogates, then the entire volume of each sample bottle was passed through a solid-phase extraction cartridge. The analytes were then eluted from the cartridges by pulling 4 mL of methanol through each cartridge and transfer tube. The extract was concentrated to dryness and then adjusted to a 1 mL volume. The resulting solution was transferred to an autosampler vial that was analyzed by LC/MS/MS operated in negative electrospray ionization (ESI) mode. Separation and detection were performed using a Thermo Scientific Accela autosampler and quaternary U-HPLC pump equipped with TSQ Quantum Access Triple Quadrupole mass spectrometer. Laboratory analysis and QA/QC reports are included in ESI.