SUPPORTING INFORMATION

Perfluoroalkyl and Polyfluoroalkyl Substances in Groundwater Used as a Source of Drinking Water in the Eastern United States

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S1. PFAS Sampling Protocols

Standard U.S. Geological Survey (USGS) protocols were used to collect groundwater samples from the wells prior to any treatment, blending, or pressure tanks;[1,2] thus, the chemistry of these samples may not represent the water used for human consumption in some instances.

For each PFAS sample, two 250-mL high-density polyethylene (HDPE) containers were filled and sent to the SGS Laboratory in Orlando, Florida for analysis. Samples were unfiltered and kept chilled between sample collection and arrival at the SGS Laboratory. PFAS samples were the last samples to be collected at each well.

Accessible Spigots. At many locations, direct filling of the sample bottles from a spigot was possible. For these samples, all standard sample tubing and equipment was disconnected, the spigot was turned on, and the flow rate adjusted to about 500 mL/min. Each 250-mL HDPE bottle was rinsed one time and then filled, leaving some head space. Samples were placed in a plastic bag and put in a cooler with ice. For field blanks, Optima^{TM} HPLC-grade water was brought near the source spigot and blank bottles were rinsed and filled in the same manner as sample bottles.

Inaccessible Spigots. In some locations, the source spigots were not accessible to directly fill the sampling containers. All standard sample tubing and equipment was disconnected. A Tuff-Lite^{TM} adapter was fitted with a stainless steel Swagelok^{TM} fitting and connected to the well spigot. New pre-cleaned HDPE tubing was attached to the Swagelok^{TM} fitting on one end and into the top of a sample-processing chamber bag on the other end, ensuring the tubing did not contact anything in the environment. All equipment was pre-cleaned before use (see Cleaning Equipment sections). The water was turned on and set at a flow rate of about 500 mL/min. The tubing was flushed at this flow rate for two minutes for every 10 feet of tubing. Each 250-mL HDPE bottle was rinsed one time and then filled, leaving some head space. Samples were placed in a plastic bag and put in a cooler with ice. After samples were collected, the Tuff-Lite^{TM} adapter, HDPE tubing, and stainless-steel ferrules were disposed of. The stainless-steel nut used to connect the HDPE tubing to the stainless-steel fitting was saved and rinsed with deionized water (DIW).

To collect field blanks, the sample equipment was cleaned as specified in the Cleaning Equipment sections. Optima™ water was poured through the equipment, and then blanks were collected in a processing chamber. Blank bottles were rinsed and filled in the same manner as sample bottles.

In cases where the sample must contact material other than already specified, a blank was collected by exposing the Optima™ water to the extra material and sent to SGS.

Monitoring Wells. Monitoring wells that did not have a dedicated pump were sampled with a Fultz™ pump that was modified to contain new HDPE tubing and Delrin gears instead of Teflon gears. To collect field blanks, the sample equipment was cleaned as specified in the Cleaning Equipment sections, Optima™ water was pumped through the equipment, and then blanks were collected in a processing chamber. Blank bottles were rinsed and filled in the same manner as sample bottles.

Cleaning Equipment for Inaccessible Spigots. To clean the equipment prior to use, a 0.1% Liquinox™ solution in deionized water (DIW) was used to rinse the Tuff-Lite™ adapter, Swagelok™ fittings, and HDPE tubing (approximately one tubing volume). The sampling equipment was then rinsed thoroughly with DIW to remove the Liquinox™, followed by a rinse with ACS grade methanol (approximately one tubing volume for HDPE tubing), and finally an Optima™ blank water rinse (approximately three tubing volumes for HDPE tubing).

Cleaning Equipment for Monitoring Wells. The Fultz™ pump, HDPE tubing, and Delring gears were cleaned by circulating 0.1% Liquinox in DIW for about 3 minutes at 2 L/min to achieve a three-tubing-volume flush. DIW was then used to remove the Liquinox™, followed by one tubing volume of methanol and three tubing volumes of Optima™ blank water.

S2. PFAS Analytical Methods

Following arrival at SGS Laboratory, samples were refrigerated at ≤6°C until extraction within the holding time of 28 days from sample collection. Samples were spiked with isotopically labelled standards, and the entire sample was extracted utilizing a weak anion exchange (W-AX) solid phase extraction (SPE) cartridge. A method blank, a reagent spike, a matrix spike, and a matrix spike duplicate or sample duplicate were extracted with each batch of 20 samples. The SPE cartridges were eluted with a basic methanol solution and concentrated to 1 ml. The methanol extracts were analyzed within 40 days from sample extraction.

PFAS in the groundwater samples were analyzed using a modified version of U.S. Environmental Protection Agency (EPA) Method 537.1,[3] as briefly described here. Extracts were analyzed for PFAS using an Agilent Technologies 1260 high performance liquid chromatography (HPLC) system coupled to an Agilent Technologies 6470A tandem mass spectrometer (MS/MS) with negative electrospray ionization. Four µL of extract were injected onto the LC-MS/MS, and the peaks were separated using an Agilent Technologies Poroshell (120 EC C18 2.7 µm, 100 x 2.1 mm ID). Ultra-high purity nitrogen gas was used in the collision cell. Quantification was completed using isotope dilution and a minimum 5-point calibration curve with $r^2 \geq 0.99$. The calibration curve was validated using an initial calibration verification standard that is prepared from a source different than the calibration curve and was required to be within ±30% of the calculated concentration. Continuing calibration verification (CCV) standards were run throughout the sample run and were required to be within ±30% (for mid-level CCV standards) or ±50% (for low-level CCV standards) of the calculated concentration. Calibration standards for Perfluorooctane sulfonate (PFOS), Perfluorohexane sulfonate (PFHxS), N-Ethyl perfluorooctanesulfonamidoacetate (N-EtFOSAA), and N-Methyl

perfluorooctanesulfonamidoacetate (N-MeFOSAA) included both branched and linear

compounds. A technical standard was used to confirm the location of the branched

perfluorooctanoate (PFOA) isomers. For all PFAS, even when calibration standards include only

linear isomers, the sum of branched and linear isomers is reported, provided the primary and

secondary transition masses are present.

The PFAS data are listed in Table S2 and are also available in ref. 4 of this Supporting

Information.

S3. PFAS Quality-Control Data and Assessment

Assessment of quality-control (QC) data for the PFAS included in this study incorporated

data from field and laboratory samples, listed in Tables S3-S6 and available in a USGS

data release.[4] Rigorous QC was essential because PFAS sources are widespread and

include items, such as clothing and equipment, that can be present at a field site during sample

collection. Quality-control samples collected by field crews consisted of blanks (equipment,

field, and source solution), matrix spikes prepared by the USGS National Water Quality

Laboratory (NWQL) for analysis by SGS Laboratory, and field replicates. Laboratory QC data

were available from SGS Laboratory for routine method blanks, reagent (blank) spikes, matrix

spikes, and matrix spike duplicates or sample duplicates; commonly, results were also reported

for instrument blanks. Blank samples provided information on bias; spike samples provided

information on bias and (or) variability; and replicate samples provided information on

variability.

Field QC samples. Blank samples were collected by field crews following procedures described

in Section S1, using Optima^{TM} high purity blank water (Table S3). Equipment blanks for HDPE

tubing and associated fittings—and for sampling pumps as needed for collection of groundwater

samples from wells without dedicated pumps—typically were collected in a local (non-analyzing) laboratory before field sampling began to evaluate the suitability of the equipment and equipment cleaning protocols for the established data-quality requirements. Source solution blanks were collected in the same laboratory environment by pouring blank water directly into a sample bottle to verify that the blank water used to collect the equipment and field blanks had no detectable concentrations of PFAS. Field blanks were collected at selected sampling sites in a manner comparable to collection of a groundwater sample to evaluate the potential for the various aspects of sample collection, field processing, preservation, transportation, and laboratory handling to be sources of contamination.[5]

Because each state typically had its own sampling crew(s), equipment and field blanks were distributed to ensure that each state collected at least one equipment blank (if there was a potential need to use HDPE tubing and (or) a sampling pump at any sampling sites), one source solution blank, and one field blank. States were assigned to collect two field blanks if they were using HPDE tubing and (or) a sampling pump at one or more sampling sites, as opposed to directly filling sample containers from existing spigots at every site. A total of 40 blanks (11 equipment, 12 source solution, and 17 field) were collected. No PFAS were detected in equipment or source solution blanks, and only perfluorobutanoate (PFBA) was detected in any field blanks. The one PFBA detection of 4.6 ng/L was reported for a field blank that was analyzed in a sample batch with a method blank detection of 3.7 ng/L; consistent with the treatment of PFBA detections reported for groundwater samples in this same batch (see Section *Laboratory QC Samples*), the field blank detection was flagged as likely being affected by contamination at the laboratory, and the reported concentration was qualified with the remark code "<".

Matrix spikes that consisted of groundwater samples spiked at the NWQL with known concentrations of 14 PFAS for analysis by SGS were collected to estimate any positive or negative bias that might result from method performance or effects of the sample matrix (Table S4). A total of 18 groundwater samples collected from two well networks between July 31, 2019 and September 12, 2019 were spiked in late February 2020 at the NWQL and analyzed in early March 2020 at SGS Laboratory. The expected concentration of most PFAS in spiked samples was 80 ng/L, but expected concentrations were slightly less for perfluorobutane sulfonate (PFBS) (70.8 ng/L), PFHxS (73.2 ng/L), and PFOS (74.1 ng/L). Median recovery values for ten of the fourteen PFAS were within the range of 81.0 to 97.5% (Table S4), indicating the potential for a minor negative bias, which could result in slight underreporting of groundwater concentrations. The median recovery values for N-Ethylperfluorooctane sulfonamidoacetate (N-EtFOSAA), Perfluorononanoate (PFNA), and Perfluorohexanoate (PFHxA) were between 71.9 and 79.9%, indicating the potential for moderate underreporting of groundwater concentrations. The median recovery for Perfluorotridecanoate (PFTrDA) was 111%, indicating the potential for a minor positive bias. This potential for positive bias had no consequence for this study because PFTrDA was not detected in any of the groundwater samples. Matrix spikes are not ideally suited for evaluation of variability (that is, solely random measurement error) because differences in environmental sample matrices can affect laboratory performance for some compounds. Nevertheless, examination of relative standard deviations (RSDs) for these spikes can provide useful information about which PFAS are more likely than others to be affected by matrix characteristics in addition to random measurement error. The RSD was 9.3% or less for all PFAS except PFOA (RSD 20.2%), which had one

instance of very low recovery (22.9%) that may have been at least partly associated with

a fairly large environmental concentration (55 ng/L) relative to the spiked concentration.

Sequential replicate samples were collected, processed, and analyzed in a manner

allowing them to be considered essentially identical in composition and how they were analyzed;

these pairs of samples are intended to estimate variability of analytical results caused by random

measurement error (Table S5).[5] Eighteen replicate pairs were collected for PFAS. Preliminary

analysis of replicate pairs showed large enough differences for one pair that a mix-up of the

primary groundwater sample with some other sample was suspected; resampling of this well in

2020 resulted in no PFAS detections, which was consistent with results of the original replicate

sample and confirmed that the multiple PFAS detections reported for the original primary

groundwater sample likely were erroneous. This replicate pair was dropped from

further investigation of variability associated with the analytical method, leaving 17 pairs. Of the

24 PFAS compounds, only PFBA and perfluoropentanoate (PFPeA) had any instances

of inconsistent detections (that is, a detection in one sample of the replicate pair but not the

other), and in only one pair each; in both cases, the concentration of the reported

detection was below the reporting level. Because no PFAS compound had more than seven

replicate pairs with consistent detections, robust analysis could not be performed for variability

in reported concentrations. However, relative percent differences (RPDs) in concentrations

were all 18.2% or less (and commonly less than 10%), except for PFHxS concentrations in one

sample pair, which had an RPD of 30.8% but an absolute difference of only 0.4 ng/L. Therefore,

variability in detection and concentration were determined to be low.

Laboratory QC samples. SGS Laboratory routinely monitors method performance using four of

five possible types of QC (control) samples that are prepared and analyzed with each batch of no

more than 20 samples. These samples include laboratory method blanks, reagent (blank) spikes, matrix spikes, and matrix spike duplicates or sample duplicates (Tables S4 and S6); results were supplied by SGS Laboratory in a spreadsheet format for all QC sample types except sample duplicates, for which results were supplied in .pdf files. The specific uses of these QC samples, and summaries of QC sample results for the 88 prep batches pertaining to the analytical batches in which groundwater samples for this study were included, are discussed in this section.

A laboratory method blank is intended to monitor for interferences and possible contamination of samples with method analytes during preparation. In some cases, SGS Laboratory also supplied results for instrument blanks (results were provided in .pdf files and are not included in the USGS data release), presumably used to monitor for carryover of compounds between samples. For this study, method and instrument blanks (together, laboratory blanks) were examined to characterize the potential for contamination of groundwater samples during laboratory processing and analysis. PFAS that were detected in at least one laboratory blank were: PFOS (1 method blank, 3.7 ng/L), PFBA (5 method blanks, 2.9 to 3.9 ng/L in batches with reported groundwater detections and 10.1 to 13.6 ng/L in batches without reported groundwater detections), and 6:2 Fluorotelomer sulfonate (6:2 FTS) (1 instrument blank, 5.8 ng/L). A total of 15 PFBA detections in groundwater samples in two analytical batches (range 2.0 to 15 ng/L) and one 6:2 FTS detection in a groundwater sample in one analytical batch (2.2 ng/L) had concentrations less than 10 times the concentration of the associated laboratory blank, so the reported groundwater concentrations for those compounds in those samples were qualified with the remark code "<".

A laboratory reagent spike is intended to evaluate method performance in a clean matrix that does not include potentially interfering compounds. The laboratory reagent spikes

analyzed in the same batches as groundwater samples included in this study consistently

met acceptance criteria, which typically required recovery to fall within a range of about 70 to

130%. Recovery for PFTrDA was above acceptance criteria for one prep batch (145%), and

recovery for Perfluorodecane sulfonate (PFDS) was below acceptance criteria for six prep

batches (62 to 69%). Median recovery values ranged from 92 to 100% for all PFAS except

PFDS (which had a median recovery of 85%) (Table S2), indicating generally little bias in blank

water. RSDs were below 13% for all PFAS and were below 10% for all PFAS except PFDS

and PFTrDA, indicating low variability in recovery.

　　A laboratory matrix spike is intended to evaluate method bias in environmental matrices,

which may include potentially interfering compounds. Some laboratory matrix spikes analyzed

by SGS Laboratory in batches that included samples analyzed for this study were

prepared using samples from other customers, which might not closely approximate matrices that

are characteristic of the groundwater sampled for this study. However, the overall dataset

of laboratory matrix spikes from these batches can still provide useful information about method

performance in environmental matrices and about which PFAS are more likely than others to be

affected by matrix characteristics. Matrix spikes generally met the typical acceptance criteria of

70 to 130% (negative recovery values, which appeared likely to have resulted from much lower

spiked concentrations than groundwater concentrations, were excluded from this summary

analysis). Although more recovery values outside acceptance criteria were observed for

laboratory matrix spikes than for reagent spikes, median recovery values ranged from 90 to

103% for all PFAS except PFDS (which had a median recovery of 87%) (Table S2), indicating

generally little bias in groundwater matrices.

A laboratory matrix spike duplicate or sample duplicate is intended to estimate variability and (or) bias of the analytical method in environmental matrices. As with laboratory matrix spikes, not all matrix spike duplicates or sample duplicates analyzed by SGS Laboratory in relevant batches were prepared using samples from this study, meaning that results might not all be strictly relevant. However, the overall results are still useful in estimating the magnitude of potential variability and (or) bias. Results for matrix spike duplicates, which were provided by SGS Laboratory in spreadsheet form, generally met the acceptance limit of 30 percent RPD. Mean RPDs were less than 13% for all PFAS except PFBA (24.2%) and PFDA (17.4%).

S4. Geospatial Datasets and Analysis

Spatial relations between PFAS detections in groundwater and proximity of the sampled wells to potential PFAS sources were examined in a geographic information system (GIS), using geospatial datasets from publicly available sources and from U.S. Government proprietary sources. The data sources and types are listed in Tables S7 and S8 and available in ref. 4. For most of the geospatial data, distances of the sampled wells to the nearest source types were determined in the GIS using locational information for the wells and potential PFAS sources. The GIS was also used to determine (1) percentages of urban, agricultural, and natural lands within 500-m buffers around the sampled wells, (2) N loading to septic systems in the 500-m buffers, and (3) distance to the nearest wastewater treatment plant.

Several regional-scale studies have shown that using 500-m circular buffers to assign land-use features to wells can reveal meaningful correlations between water-quality variables and land-use features.[6,7] Importantly, correlations derived from 500-m buffers are comparable to correlations derived from other buffer sizes (~250 to 2000 m) and shapes (circles, wedges,

upgradient-oriented semicircles).[6,7] It was shown that buffers of different sizes and shapes give similar correlation results because of spatial autocorrelation in land use.[6] Land use autocorrelation distances of up to 8 km have been reported,[6,7] such that buffer sizes within the autocorrelation distance can be expected to produce similar land use-water quality correlations. Moreover, 500-m buffers have been shown to reveal meaningful correlations between land-use features and a diverse group of water-quality variables: nitrate, pesticides, VOCs, and hormones and pharmaceuticals.[6,8-10] A primary reason for the applicability of the buffer approach to a variety of chemicals is that the buffer is used to assign land-use features to the well, not chemical properties. If a particular land-use feature (e.g., urban area) is a source of both VOCs and PFAS, one could expect to see correlations between percent urban area in the buffer and detection frequency of VOCs or PFAS.

S5. Boosted Regression Tree Modeling

Model Setup. PFAS concentrations reported as being less than a detection level were set to zero. Tenfold cross-validation tuning was employed to identify the model parameters that returned the most accurate model. Note that there are more data to pull from when tuning the model so 10-fold validations works, but much less data are available for the cross validation on the model testing dataset described in the Boosted Regression Tree Modeling section of the main text, hence 5-fold cross validation was used for that purpose. Because the model with the highest accuracy may be overfit to the model training data, and because models with lower complexity typically perform better when predicting to new data,[11] the simplest model within one standard error of the model with the highest accuracy was selected as the final model used for interpretation of results. The model output for training and testing datasets is a probability of PFAS detection, which ranges from 0-1. A probability threshold of 0.5 was used to evaluate

model performance. A probability less than 0.5 was considered a non-detect, and a probability greater than or equal to 0.5 was considered a detection. The threshold of 0.5 was chosen after evaluation of different probability thresholds (0.3, 0.4, 0.5, 0.6, and 0.7) because it provided excellent overall performance, as shown in the below table. Specifically, it provided good overall accuracy and the highest sensitivity for the testing (holdout) data. This is important because it reduces the likelihood of predicting a non-detect when there is a detection in the observed data.

	Training Data			Testing Data		
Probability Thresholds	Accuracy	Sensitivity	Specificity	Accuracy	Sensitivity	Specificity
0.3	0.83	0.97	0.65	0.74	0.96	0.52
0.4	0.91	0.96	0.85	0.82	0.96	0.68
0.5 (Chosen Threshold)	**0.91**	**0.93**	**0.89**	**0.84**	**0.96**	**0.72**
0.6	0.91	0.88	0.95	0.86	0.92	0.8
0.7	0.90	0.82	0.99	0.82	0.76	0.88

Investigation into Model Effects from Correlated Explanatory Variables and Data Censoring. Of the 57 potential predictor variables, specific conductance, total dissolved solids (TDS), and Ca were highly correlated (r>0.8), as were Mg and SO_4 (r>0.7), dissolved oxygen (O_2) and NO_3 (r>0.7), and distance to the nearest fire training area and distance to the nearest furniture/carpet manufacturer (r>0.7). Specific conductance, TDS, O_2, SO_4, and distance to the nearest furniture/carpet manufacturer were removed from the list of predictor variables and a new model was developed. Despite SO_4 being the sixth most important predictor variable in the original model (Figure 4), removing SO_4 and the other 4 input parameters produced results similar to the original model, with ^3H, distance to the nearest fire training facility, dissolved organic carbon (DOC), urban land use, and the sum of volatile-organic-compound (VOC) concentrations having high variable influence (ranks of 2, 3, 4, 5, and 7, respectively).

Effects to the model arising from data censoring of explanatory variables were also evaluated. In the original model, any data value that was not flagged as a non-detect was included, even if that value was flagged as estimated, below the reporting level, or below the method detection level. To test whether an alternate method of data censoring affected the model, all data less than the maximum reporting level (the censoring value) was set to zero. The model was not significantly affected, and produced results with ^{3}H, distance to the nearest fire training facility, DOC, and urban land use as the first, second, third, and fourth highest variable influence, respectively. The VOC sum was no longer an important variable, likely due to the large effect this censoring had on VOC concentrations.

S6. References

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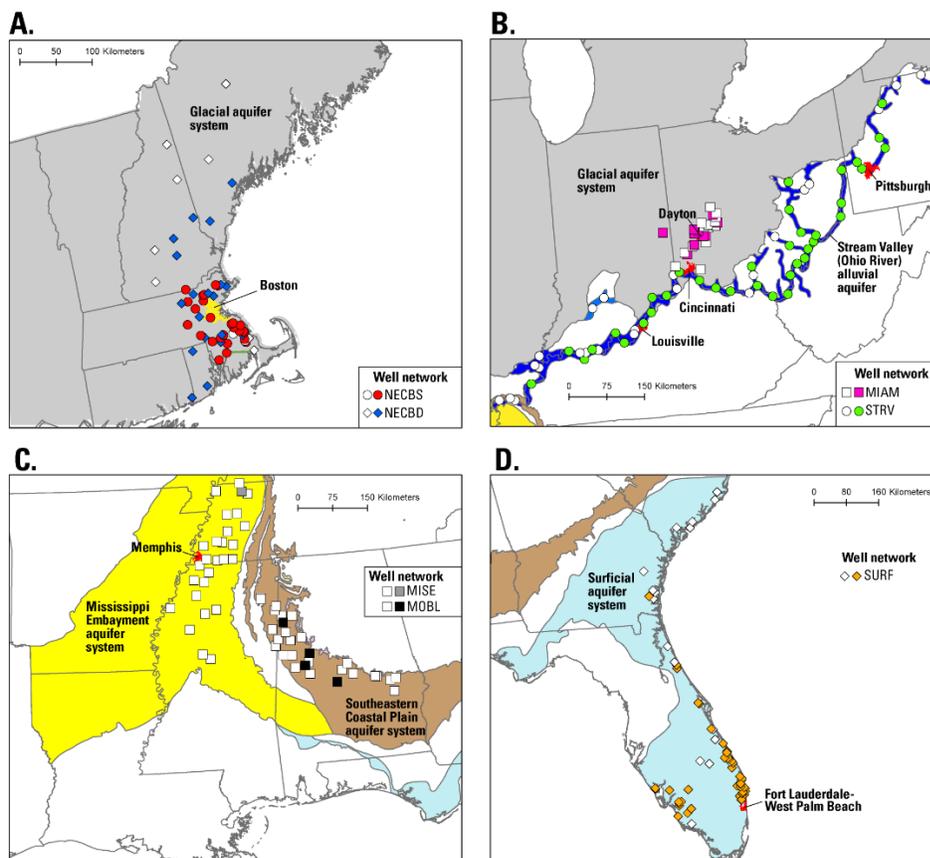
Figures

Figure S1. Locations of aquifer systems and well networks. Wells shown with white symbols indicate PFAS were not detected, and those shown with other colored symbols indicate PFAS were detected.
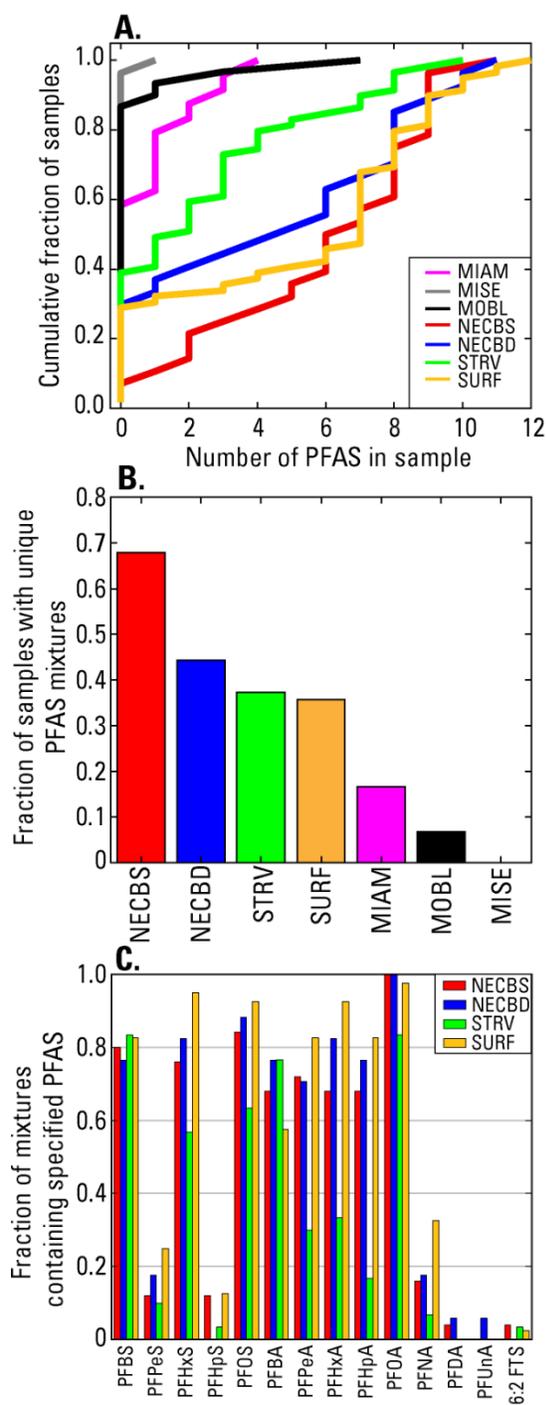
Figure S2. (A) Cumulative fraction of samples that contain one or more PFAS, (B) fraction of samples with unique PFAS mixtures, and (C) fraction of mixtures that contain specified PFAS. In (C), only the top four networks with respect to fractions of samples containing one or more PFAS are considered.
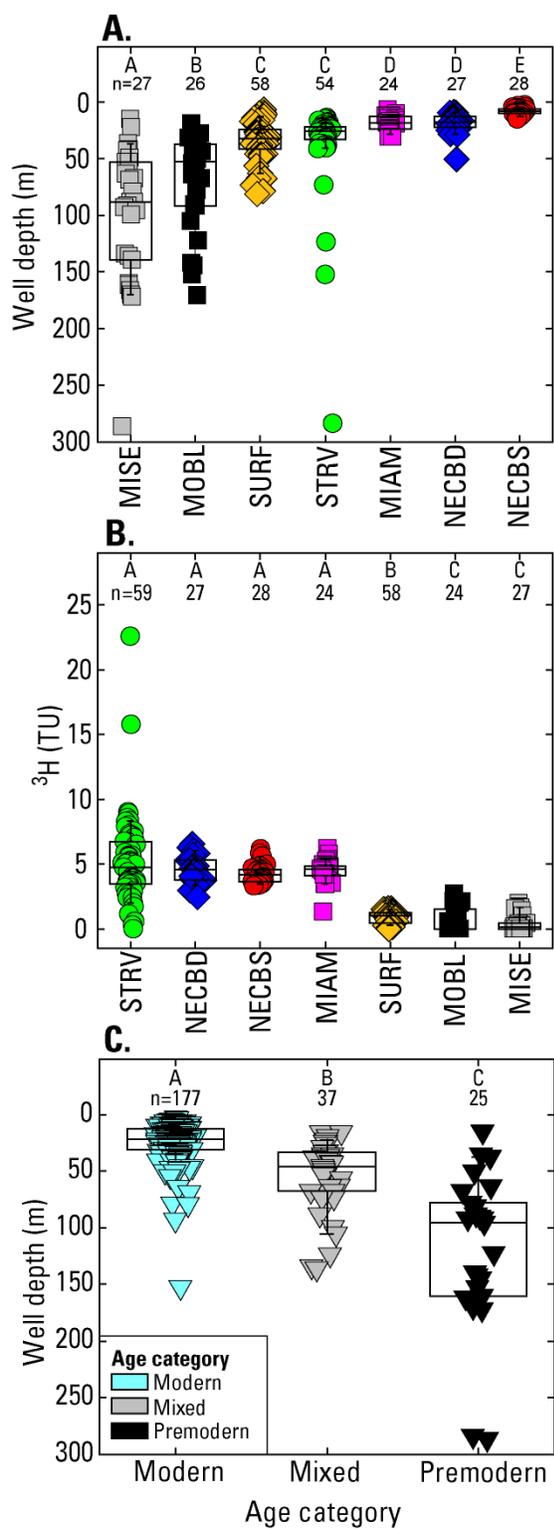
Figure S3. (A) Well depths, (B) ^{3}H concentrations, and (C) wells depths in relation to age category. Boxes represent 25th, 50th, and 75th percentiles, whiskers represent 10th and 90th

percentiles, n is number of samples; in each panel, networks or age categories with different letters at the top of the panel have significantly different values based on Kruskal-Wallace and Mann-Whitney tests and α=0.05.

Figure S4. (A) O_2 concentrations; (B) pH values; concentrations of (C) total dissolved solids, (D) DOC, (E) Ca+Mg, and (G) Mn+Fe; and (F) Ca+Mg/Cl mass ratios in groundwater. Boxes represent 25th, 50th, and 75th percentiles, whiskers represent 10th and 90th percentiles, n is number of samples; in each panel, networks with different letters at the top of the panel have significantly different values based on Kruskal-Wallace and Mann-Whitney tests and α=0.05. In (G), RL is reporting level.

Figure S5. (A) Number of potential PFAS sources less than 5 km from the sampled wells and (B) N input to septic systems in 500-m buffers around the sampled wells. Data are listed in Table S8. Boxes represent 25th, 50th, and 75th percentiles, whiskers represent 10th and 90th percentiles, n is number of samples; in each panel, networks with different letters at the top of the panel have significantly different values based on Kruskal-Wallace and Mann-Whitney tests and $\alpha=0.05$.
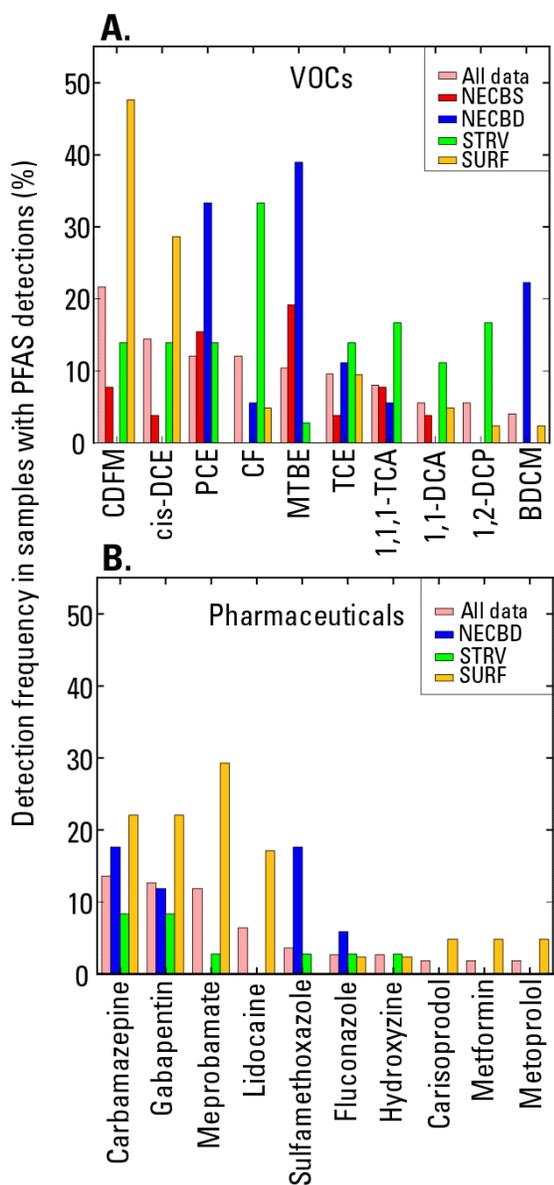
Figure S6. Detection frequencies for (A) VOCs and (B) pharmaceuticals in samples with PFAS detections, showing only the top ten detected VOCs and pharmaceuticals. In (A), CDFM is chlorodifluoromethane; cis-DCE is cis-1,2-dichloroethene; PCE is tetrachloroethene; CF is chloroform; MTBE is methyl tert-butyl ether; TCE is trichloroethene; 1,1,1-TCA is 1,1,1-trichloroethane; 1,1-DCA is 1,1-dichloroethane; 1,2-DCP is 1,2-dichloropropane; and BDCM is bromodichloromethane;. In (B), there are no data for NECBS.
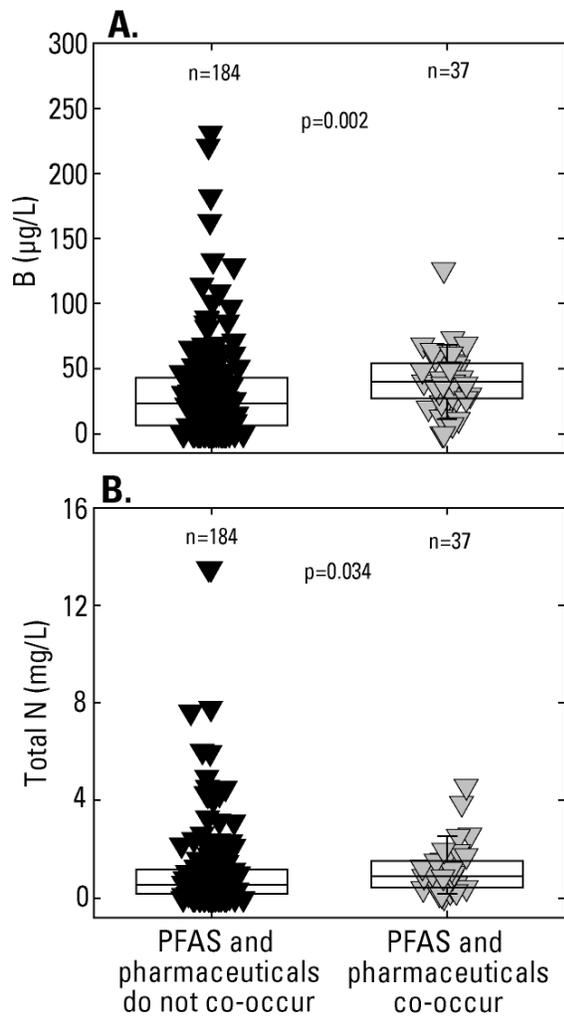
Figure S7. Concentrations of (A) boron and (B) total nitrogen in samples with and without co-occurring detections of PFAS and pharmaceuticals. Boxes represent 25th, 50th, and 75th percentiles, whiskers represent 10th and 90th percentiles, n is number of samples, and p-values are based on the Mann-Whitney test (α=0.05).
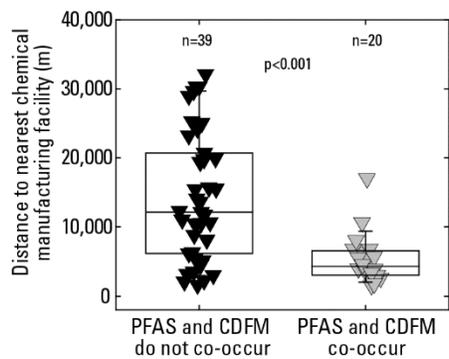
Figure S8. Distance to the nearest chemical manufacturing facility in the SURF network for samples that do and do not have co-occurring PFAS and CDFM detections. CDFM, chlorodifluoromethane. Boxes represent 25th, 50th, and 75th percentiles, whiskers represent 10th and 90th percentiles, n is number of samples, and p-values are based on the Mann-Whitney test (α=0.05).
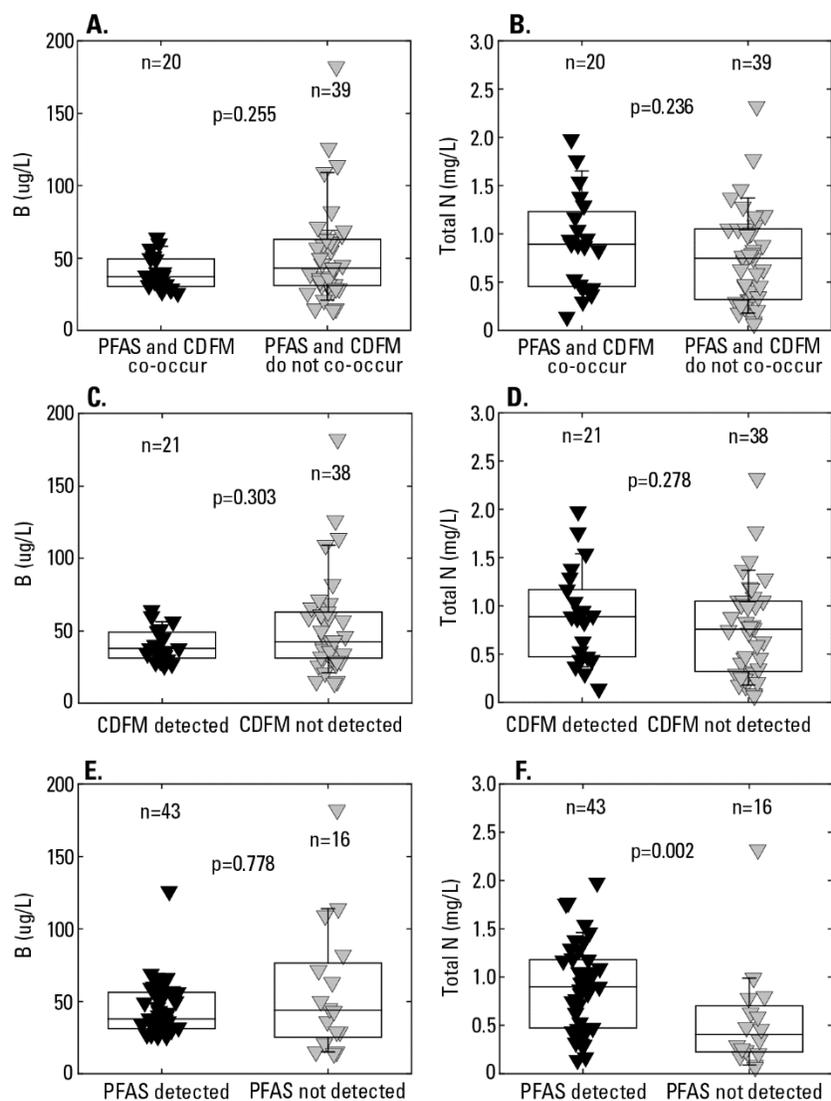
Figure S9. Concentrations of boron (A., C., and E.) and total nitrogen (B., D., and F.) in groundwater samples from the SURF network that (A.) do and (B.) do not have co-occurring detections of PFAS and CDFM; (C.) do and (D.) do not have CDFM detections; and (E.) do and (F.) do not have PFAS detections. Boxes represent 25th, 50th, and 75th percentiles, whiskers represent 10th and 90th percentiles, n is number of samples, and p-values are based on the Mann-Whitney test (α=0.05).