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Source attribution of poly- and perfluoroalkyl substances (PFASs) in surface waters from Rhode Island and the New York Metropolitan Area

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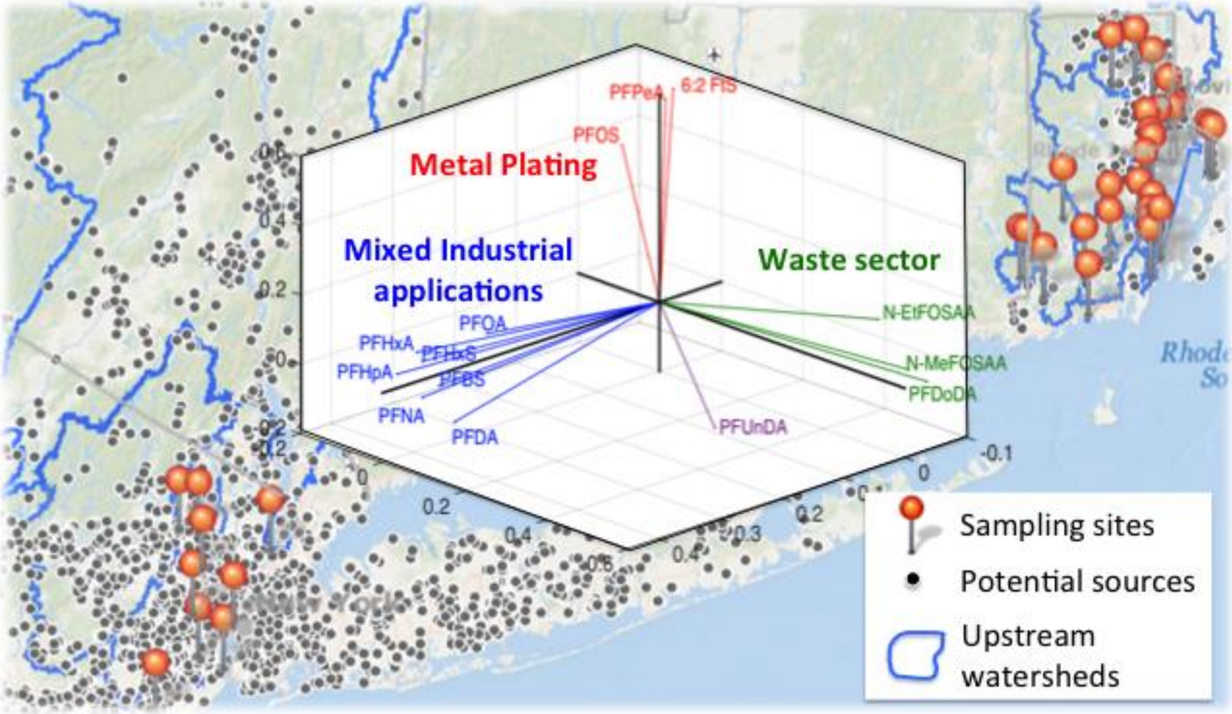
TOC Art


Metal Plating
PFPeA
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Waste sector
N-EtFOSAA
N-MeFOSAA
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Rhode
Sampling sites
Potential sources
Upstream watersheds

Abstract

Exposure to poly and perfluoroalkyl substances (PFASs) has been associated with adverse health effects in humans and wildlife. Understanding pollution sources is essential for environmental regulation but source attribution for PFASs has been confounded by limited information on industrial releases and rapid changes in chemical production. Here we use principal component analysis (PCA), hierarchical clustering, and geospatial analysis to understand source contributions to 14 PFASs measured across 37 sites in the Northeastern United States in 2014. PFASs are significantly elevated in urban areas compared to rural sites except for perfluorobutane sulfonate (PFBS), N-methyl perfluorooctanesulfonamidoacetic acid (N-MeFOSAA), perfluoroundecanate (PFUnDA) and perfluorododecanate (PFDoDA). The highest PFAS concentrations across sites were for perfluorooctanate (PFOA, 56 ng L^{-1}) and perfluorohexane sulfonate (PFOS, 43 ng L^{-1}) and PFOS levels are lower than earlier measurements of U.S. surface waters. PCA and cluster analysis indicates three main statistical groupings of PFASs. Geospatial analysis of watersheds reveals the first component/cluster originates from a mixture of contemporary point sources such as airports and textile mills. Atmospheric sources from the waste sector are consistent with the second component, and the metal smelting industry plausibly explains the third component. We find this source-attribution technique is effective for better understanding PFAS sources in urban areas.

Introduction

Exposure to poly- and perfluoroalkyl substances (PFASs) has been associated with many negative health outcomes including compromised immune function, metabolic disruption, obesity, and altered liver function.[1] PFASs in surface waters are an emerging concern for U.S. public water supplies and long-chain compounds bioaccumulate in aquatic food webs, posing health risks to seafood consumers.[2-6] Production of PFASs and their precursors has shifted dramatically over the last two decades toward shorter-chain and polyfluorinated species.[7] Diverse point sources and atmospheric deposition of some PFASs confounds understanding of the dominant contributors to contamination in the aquatic environment. Regulatory databases such as the U.S. EPA's Facility Registry Survey (FRS)[8] and the Toxic Release Inventory[9] presently contain limited to no information on magnitudes of PFASs released to the environment.

Multivariate statistical analyses based on chemical composition profiles can be a powerful tool for diagnosing contamination sources, as illustrated for many other organic contaminants.[10] Principal components analysis (PCA) provides information on interrelationships among various chemicals and is useful for deriving common source profiles. Two-way hierarchical clustering can be used as a confirmatory analysis of PCA by generating a flexible number of subgroups of similar sites (those affected by a common source type) without dictating the number of clusters *a priori.* Clustering of compounds identifies chemicals that co-occur to form a unique signature. These techniques have not been routinely applied to interpret PFAS contamination and show potential for interpreting sources in surface water and seawater.[4,11]

Here we combine PCA and hierarchical clustering of PFAS profiles measured in surface waters from 37 rivers, streams and estuaries in the Northeastern United States with geospatial analysis of potential sources. Few measurements are available for PFASs in U.S. surface waters over the past five years and the importance of different sources is poorly understood. Source regions for air pollution are commonly identified using back trajectories.[12,13] We apply an analogous approach for identifying sources of aquatic pollution based on hydrological distances within a watershed. The main objective of this study is to identify major sources of surface water PFAS contamination in diverse watersheds using information on chemical composition and geospatial analytical tools that consider surface hydrology.

Methods

Sample collection and analysis

We collected surface water samples from rivers/creeks and estuaries at approximately 1 m depth at 28 sites in the state of Rhode Island (RI) in June, 2014 and 9 sites the New York Metropolitan Area (NY/NJ) in October, 2014 (Figure 1). A complete description of sampling sites is provided in the Supporting Information (SI Table S1). Precipitation and flow rates in rivers tend to be higher in June, potentially resulting in enhanced dilution and a low bias for some PFASs measured in RI rivers compared to NY/NJ.

Samples were stored in one-liter pre-rinsed polypropylene bottles at -20 °C and thawed at room temperature. Each sample was shaken vigorously for homogenization before subsampling 500 ml for the analysis of 21 PFASs. Each unfiltered sample was spiked with 20 μL of a 0.1 ng μL^{-1} mass labeled PFAS mixture (Wellington; Guelph, Canada; individual compounds are listed in Table S2) as internal standards for quantification. PFASs were extracted using an Oasis Wax solid phase extraction (SPE) cartridge (6 mL, 150 mg sorbent) following the method of Taniyasu et. al.[14] (see SI Section S1 for details). A nitrogen evaporator (ZIPVAP) was used to concentrate the extract to 1 mL (methanol: water; v:v = 1:1).

Sample detection for 21 native PFASs (Tables S2, S3) was performed using an Agilent 6460 LC-MS/MS equipped with an online-SPE system (Agilent 1290 Infinity Flex Cube) in dynamic multiple reaction mode (sample chromatogram in Figure S1). At least one negative control (field or procedural blank) and one positive control (spiked with 2 ng of the 21 PFASs in 500 ml water) were included in every extraction batch. Whole method recovery tested using the positive controls was 70-120% for all but 4 PFASs that ranged from 60-70%, which is comparable to recoveries reported by previous studies.[3,14,15]. The 4 PFASs are perfluoropentanate (PFPeA), perfluoroheptanate (PFHpA), N-methyl perfluorooctanesulfonamidoacetic acid (MeFOSAA) and N-ethyl perfluorooctanesulfon-amidoacetic acid (EtFOSAA). Potential analyte loss during sample preparation was corrected using internal standards spiked prior to sample extraction. The limit of detection (LOD, Figure S2) was defined as equivalent to the blank plus the concentration corresponding to a signal-to-noise ratio of three. Variability between duplicates obtained at two sites was <20%. PFASs in five field blanks (HPLC grade water) prepared following the sample preparation procedure were all below the LOD.

We quantified branched isomers for perfluorooctanate (PFOA), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS), N-MeFOSAA and N-EtFOSAA using calibration standards for the linear isomers, assuming the same instrumental response factor (Table S3). Seven compounds namely perfluorododecane sulfonate (PFDS), 8:2 fluorotelomer sulfonate (8:2 FTS), perfluorooctane sulfonamide (FOSA), and PFCAs with more than 12 carbon atoms) were detected in less than half of samples and were excluded from additional statistical analysis (see Table S2 for details). For the 14 PFASs that had detection frequencies of greater than 60% (Table S2), we used the Robust Regression on Order Statistics approach for censored log-normally distributed environmental data described by Helsel[16] to assign values to samples with concentrations below the LOD.

Statistical and spatial analysis

We used principal components analysis (PCA) and hierarchical clustering to group sites with statistically distinct PFAS composition profiles. PCA was performed using MATLAB's Statistics Toolbox (MathWorks, Inc.) on normalized (z-score to remove the effect of concentration difference at different sites) PFAS concentration data. The inverse of variances of the data were used as variable weights and varimax rotation was applied to interpret the meaning of extracted principal components. Hierarchical Cluster analysis was conducted using the hclust function in the R statistical computing package (version 3.1.3).

We characterized the watershed for each freshwater sampling site using the U.S. Geological Survey's (USGS) National Elevation Dataset (3 arc-second for site 15 and 16 and 1 arc-second for others) and the Hydrologic Tool in ArcGIS Pro 1.2 and ArcGIS online. Estuarine sampling sites were excluded from the geospatial analysis due to the confounding influence of tidal waters diluting potential source profiles. Population within each watershed was based on ESRI's U.S. Demographic Database.[17] We used the USGS's StreamStats database (version 4)[18] to characterize water flow rates for each location and to compute mass flow (kg/yr) of PFASs at each site and per-capita mass flows (kg/person/yr).

For all inland sites (non-estuarine), we acquired a list and geospatial data for plausible PFAS sources from the US EPA Facility Registry Service (FRS) database on facilities and sites subject to environmental regulation (see SI for the search criteria).[8] These include airports, facilities for metal plating/coating, printing, sewage treatment, waste management (including landfills), and manufacturers of semiconductor, textile, paint/coating/adhesive, ink, paper, and petroleum products. A caveat of this analysis is that not all facilities included in the FRS database necessarily release PFASs and the database may not comprehensively include all possible sources.

Hydrological distances of point sources from each sampling site were computed using the ArcGIS Trace Downstream tool. Within each watershed, we defined an indicator for the impact of potential point sources as a function of distance from sampling locations by assuming exponential decay in the source signature[19] (i.e., $impact = 1/e^d$, where d = hydrological distance, km). This approach provides additional information on plausible sources that complements multivariate statistical analysis but cannot be considered a quantitative estimate of contributions to sampling locations since magnitudes of PFAS discharges are not available.

Results and Discussion

Concentrations and spatial patterns

Figure 1 shows the compound specific composition and concentrations of PFASs measured in surface water samples as part of this work. Sampling sites in NY/NJ had much greater population density in upstream watersheds (10-43x) compared to RI but the highest concentrations of most PFASs were measured near the city of Providence, RI (Figure 1, Figure S2). The range of measured PFAS concentrations reported here are comparable or lower than U.S. surface waters from other regions collected between 2000-2009 (Table S4).[2,20-24]

All sites had detectable PFOA and PFNA and over 90% contained detectable PFHxS, PFOS, PFDA, and 6:2 FtS (Table S2, S3, Figure S2). The highest individual PFAS concentration across sites was PFOA (56 ng L^{-1}) at Site 31 (Passaic River, NJ). Highest concentrations of PFHxS (43 ng L^{-1}) and PFNA (14 ng L^{-1}) were measured at Site 5 (Mill Cove, RI). The maximum PFOS concentration (27 ng L^{-1}) was measured at Site 2 (Woonasquatucket

River, RI) within the City of Providence, RI. This is much lower than maximum levels reported in earlier studies of US surface waters that range between 43-244 ng L^{-1} (Table S4) and reflects the continued decline in environmental PFOS burdens in North America following elimination of production in 2002.[25,26]

Measured PFAS concentrations in urban regions were significantly higher (Wilcoxin rank sum test, $p<0.017$) than rural sites for all compounds except PFBS, N-MeFOSAA, PFUnDA and PFDoDA (Figure S3). Sites 1-9 in RI and Sites 29-37 in NY/NJ are all urban areas, defined by population densities of greater than 1000 individuals per square mile (2590 km^2), and population densities of greater than 500 individuals per square mile in surrounding census blocks.[27] We did not find a statistically significant correlation between total population in each upstream watershed and PFAS concentrations measured at each sampling site ($p=0.12$ to 0.95 across compounds). We derived per-capita discharges (Figure S4) using a similar approach as Pistocchi and Loos.[28] Highest median per-capita discharges (μg $person^{-1}$ day^{-1}) across compounds, in decreasing order, were for PFOA (27), PFHxA (14), PFHpA (10), PFOS (9), PFHxS (7), and PFNA (5) (Figure S4). These are lower than previously reported in Europe ca. 2007 (e.g., PFOA: 82 μg $person^{-1}$ day^{-1}, PFOS: 57 μg $person^{-1}$ day^{-1}).[28]

Source identification

Both hierarchical clustering and PCA identified three distinct groupings of PFASs (Figure 2a, b). The first component/cluster explains 46% of variability in the PCA and includes two major end products of the fluorochemical manufacturing industry (PFOA, PFNA), and a mix of other compounds: PFBS, PFHxS, PFHxA, PFDA. Site 5 (Mill Cove, RI) contains the highest summed PFASs across all sites and is dominated by this mixture of PFASs. PCA results suggest Site 5 is statistically similar to the Pawcatuck River, RI sampling locations (Sites 20, 19) and the

Passaic River, NJ (Site 31). However, these sites are grouped separately in the hierarchical clustering analysis (Figure 2b), suggesting some differences in source contributions.

Geospatial analysis of the watersheds for Sites 5, 19, 20 and 31 reveals a mixture of potential sources (Figure S5). For Site 5, the greatest source impact as a function of distance within the watershed is from T.F. Green Airport, the largest public airport in Rhode Island. Prior work indicates uses of AFFF in modern airports release diverse PFASs to downstream aquatic environments, including the compounds identified as part of the first PCA/cluster.[4,29-31] For Sites 19 and 20, textile mills in the upstream watersheds have the highest impact as a function of distance (Table S5). PFASs are used for water resistant coating in textiles and washing and disposal of wastewater at textile mills provides a vector for their entry to the aquatic environment. For Site 31, PCA scores suggest a mix of components 1-3 (Figure 2 c, d). This site also clusters differently than Sites 19 and 20 (Figure 2b). The FCA database indicates the watershed of Site 31 (Figure S5) contains diverse industrial sources that must account for this profile including metal plating, printing, a landfill, petroleum and coal products manufacturing. Overall, we conclude that the first PCA component and cluster of PFASs (PFOA, PFNA PFBS, PFHxS, PFHxA, PFDA) represents a mixture of contemporary sources including airports and textile mills.

The second component/cluster explains 19% of the variability in PFASs and includes two long-chain PFASs (PFUnDA and PFDoDA) and two precursors to PFOS (MeFOSAA and EtFOSAA) (Figure 2). PFUnDA and PFDoDA mainly originate from fluorotelomer alcohols or other fluototelomer based products.[32] Both N-MeFOSAA and N-EtFOSAA are intermediate degradation products from the volatile parent compound N-alkyl perfluorooctane sulfamideoethanol (FOSE) with PFOS as the final degradation product. This profile is most pronounced at Site 3 along the Woonasquatucket River in RI and is also evident at Site 1 (Slack's Tributary, RI) and Site 6 (Buckeye Brook, RI). For Site 3, the largest source impact based on distance is from a wastewater treatment plant 1 km upstream. No industrial facilities exist upstream of Sites 1 and 6. Landfill/waste management facilities are located within 2 km of all three sites but are not hydrologically connected to the sampling locations (Figure S5). Both landfills and wastewater treatment plants are known atmospheric sources of fluorotelomer alcohols and FOSE.[33] Concentrations of N-MeFOSAA, PFUnDA and PFDoDA were not spatially variable at most sites and only slightly elevated at Site 3, consistent with an atmospheric input pathway. We thus infer that this component is most likely attributable to sources from the waste sector.

The third component explains 15% of the variability in PFASs and includes PFPeA, PFOS, and 6:2 FTS. This component is most pronounced at Site 2 along the Woonasquatucket River, within the City of Providence, RI. GIS analysis of the watershed at this site reveals the presence of 14 metal coating/plating industries upstream (Figure 2d, Table S5, Figure S5). PFOS was historically used as a mist/fume control agent in metal plating, in surface coatings and as the major component in AFFFs for fighting petroleum related fire.[25,26,34] Some PFOS applications such as metal plating have been replaced by less stable fluorotelomer based chemicals such as 6:2 FtS,[35] which will eventually degrade into PFPeA and PFHxA (yields of 1.1% and 1.5% in activated sludge).[36] It is likely that PFHxA is not included in the cluster because other direct sources can contribute one order of magnitude more PFHxA than PFPeA.[37,38] We conclude that the distinct PFAS profile at Site 2 is can be explained by the metal plating industry.

Implications

Multivariate statistical tools such as PCA and hierarchical clustering of PFAS profiles combined with data on hydrological proximity of potential sources are useful for identifying sources of surface water contamination. We find aquatic transport pathways (hydrological distance and river flow directions) are critical for source identification. This contrasts many other persistent organic pollutants that are primarily transported atmospherically, allowing sources within a radius surrounding the sampling sites to be linked to concentrations.[39] We conclude that the approach demonstrated here for RI and NY/NJ has potential for diagnosing PFAS source contributions in urbanized regions with elevated concentrations and lacking specific information on the magnitude of PFAS discharges from diverse industries. Background PFAS concentrations at most rural sites in this study contain a mix of diverse source signatures that are not statistically distinguishable using these methods. This analysis could be refined in future applications by analyzing additional emerging short-chain PFASs and precursors to develop more unique chemical signatures for specific industries (i.e., those contributing to the first component/cluster).

Supporting Information

Supporting Information Available: Details on analytical methods, data analyses, supporting figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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References

1. Grandjean, P.; Andersen, E. W.; Budtz-Jorgensen, E.; Nielsen, F.; Molbak, K.; Weihe, P.; Heilmann, C., Serum vaccine antibody concentrations in children exposed to perfluorinated compounds. *Jama-J Am Med Assoc* **2012**, *307*, 391-397.
2. Post, G. B.; Louis, J. B.; Lippincott, R. L.; Procopio, N. A., Occurrence of Perfluorinated Compounds in Raw Water from New Jersey Public Drinking Water Systems. *Environ. Sci. Technol.* **2013**, *47*, 13266-13275.
3. Castiglioni, S.; Valsecchi, S.; Polesello, S.; Rusconi, M.; Melis, M.; Palmiotto, M.; Manenti, A.; Davoli, E.; Zuccato, E., Sources and fate of perfluorinated compounds in the aqueous environment and in drinking water of a highly urbanized and industrialized area in Italy. *J. Hazard. Mater.* **2015**, *282*, 51-60.
4. de Solla, S. R.; De Silva, A. O.; Letcher, R. J., Highly elevated levels of perfluorooctane sulfonate and other perfluorinated acids found in biota and surface water downstream of an international airport, Hamilton, Ontario, Canada. *Environ. Int.* **2012**, *39*, 19-26.
5. Hurley, S.; Houtz, E. F.; Goldberg, D.; Wang, M.; Park, J.; Nelson, D. O.; Reynolds, P.; Bernstein, L.; Anton-Culver, H.; Horn-Ross, P., Preliminary Associations between the Detection of Perfluoroalkyl Acids (PFAAs) in Drinking Water and Serum Concentrations in a Sample of California Women. *Environ. Sci. Technol. Letters* **2016**.
6. Happonen, M.; Koivusalo, H.; Malve, O.; Perkola, N.; Juntunen, J.; Huttula, T., Contamination risk of raw drinking water caused by PFOA sources along a river reach in south-western Finland. *Sci. Total Environ.* **2016**, *541*, 74-82.
7. Wang, Z. Y.; Cousins, I. T.; Scheringer, M.; Hungerbuhler, K., Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors. *Environ. Int.* **2013**, *60*, 242-248.
8. US EPA, Facility Registry Service (FRS). http://www.epa.gov/enviro/epa-frs-facilities-state-single-file-csv-download (accessed Nov 2015).
9. U.S. EPA, Toxics Release Inventory (TRI) Program. https://http://www.epa.gov/toxics-release-inventory-tri-program (accessed May 2016).
10. Johnson, G. W.; Ehrlich, R.; Full, W.; Ramos, S., *Principal components analysis and receptor models in environmental forensics*. Academic Press, San Diego, CA: 2002.
11. Benskin, J. P.; Ahrens, L.; Muir, D. C. G.; Scott, B. F.; Spencer, C.; Rosenberg, B.; Tomy, G.; Kylin, H.; Lohmann, R.; Martin, J. W., Manufacturing Origin of Perfluorooctanoate (PFOA) in Atlantic and Canadian Arctic Seawater. *Environ. Sci. Technol.* **2012**, *46*, 677-685.
12. Zhang, X.; Meyer, T.; Muir, D. C.; Teixeira, C.; Wang, X.; Wania, F., Atmospheric deposition of current use pesticides in the Arctic: snow core records from the Devon Island Ice Cap, Nunavut, Canada. *Environ Sci Process Impacts* **2013**, *15*, 2304-11.
13. Westgate, J. N.; Wania, F., On the construction, comparison, and variability of airsheds for interpreting semivolatile organic compounds in passively sampled air. *Environ. Sci. Technol.* **2011**, *45*, 8850-7.
14. Taniyasu, S.; Kannan, K.; So, M. K.; Gulkowska, A.; Sinclair, E.; Okazawa, T.; Yamashita, N., Analysis of fluorotelomer alcohols, fluorotelorner acids, and short- and long-chain perfluorinated acids in water and biota. *J. Chromatogr. A* **2005**, *1093*, 89-97.
15. D'eon, J. C.; Crozier, P. W.; Furdui, V. I.; Reiner, E. J.; Libelo, E. L.; Mabury, S. A., Perfluorinated Phosphonic Acids in Canadian Surface Waters and Wastewater Treatment Plant Effluent: Discovery of a New Class of Perfluorinated Acids. *Environ. Toxicol. Chem.* **2009**, *28*,

2101-2107.

16. Helsel, D. R., *Nondetects and data analysis : statistics for censored environmental data*. Wiley-Interscience: Hoboken, N.J., 2005; p xv, 250 p.

17. ESRI Demographics (2012) Population density in the United States. http://www.esri.com/data/esri_data (accessed May 2016).

18. U.S. Geological Survey StreamStats (version 4). http://ssdev.cr.usgs.gov/streamstats/ *(accessed May 2016).*

19. Sakurai, T.; Serizawa, S.; Kobayashi, J.; Kodama, K.; Lee, J. H.; Maki, H.; Zushi, Y.; Sevilla-Nastor, J. B.; Imaizumi, Y.; Suzuki, N.; Horiguchi, T.; Shiraishi, H., Temporal trends for inflow of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) to Tokyo Bay, Japan, estimated by a receptor-oriented approach. *Sci. Total Environ.* **2016**, *539*, 277-85.

20. Hansen, K. J.; Johnson, H. O.; Eldridge, J. S.; Butenhoff, J. L.; Dick, L. A., Quantitative characterization of trace levels of PFOS and PFOA in the Tennessee River. *Environ. Sci. Technol.* **2002**, *36*, 1681-1685.

21. Nakayama, S.; Strynar, M. J.; Helfant, L.; Egeghy, P.; Ye, X. B.; Lindstrom, A. B., Perfluorinated compounds in the Cape Fear Drainage Basin in North Carolina. *Environ. Sci. Technol.* **2007**, *41*, 5271-5276.

22. Konwick, B. J.; Tomy, G. T.; Ismail, N.; Peterson, J. T.; Fauver, R. J.; Higginbotham, D.; Fisk, A. T., Concentrations and patterns of perfluoroalkyl acids in Georgia, USA surface waters near and distant to a major use source. *Environ. Toxicol. Chem.* **2008**, *27*, 2011-2018.

23. Nakayama, S. F.; Strynar, M. J.; Reiner, J. L.; Delinsky, A. D.; Lindstrom, A. B., Determination of Perfluorinated Compounds in the Upper Mississippi River Basin. *Environ. Sci. Technol.* **2010**, *44*, 4103-4109.

24. Lasier, P. J.; Washington, J. W.; Hassan, S. M.; Jenkins, T. M., Perfluorinated chemicals in surface waters and sediments from northwest Georgia, USA, and their bioaccumulation in Lumbriculus variegatus. *Environ. Toxicol. Chem.* **2011**, *30*, 2194-201.

25. Paul, A. G.; Jones, K. C.; Sweetman, A. J., A first global production, emission, and environmental inventory for perfluorooctane sulfonate. *Environ. Sci. Technol.* **2009**, *43*, 386-392.

26. Armitage, J. M.; Schenker, U.; Scheringer, M.; Martin, J. W.; MacLeod, M.; Cousins, I. T., Modeling the Global Fate and Transport of Perfluorooctane Sulfonate (PFOS) and Precursor Compounds in Relation to Temporal Trends in Wildlife Exposure. *Environ. Sci. Technol.* **2009**, *43*, 9274-9280.

27. US Census Bureau (1995) Urban And Rural Definitions. http://www.census.gov/population/censusdata/urdef.txt (accessed June 2016).

28. Pistocchi, A.; Loos, R., A Map of European Emissions and Concentrations of PFOS and PFOA. *Environ. Sci. Technol.* **2009**, *43*, 9237-9244.

29. Ahrens, L.; Norström, K.; Viktor, T.; Cousins, A. P.; Josefsson, S., Stockholm Arlanda Airport as a source of per- and polyfluoroalkyl substances to water, sediment and fish. *Chemosphere* **2015**, *129*, 33-38.

30. Awad, E.; Zhang, X. M.; Bhavsar, S. P.; Petro, S.; Crozier, P. W.; Reiner, E. J.; Fletcher, R.; Tittemier, S. A.; Braekevelt, E., Long-Term Environmental Fate of Perfluorinated Compounds after Accidental Release at Toronto Airport. *Environ. Sci. Technol.* **2011**, *45*, 8081-8089.

31. Filipovic, M.; Woldegiorgis, A.; Norstrom, K.; Bibi, M.; Lindberg, M.; Osteras, A. H., Historical usage of aqueous film forming foam: A case study of the widespread distribution of

perfluoroalkyl acids from a military airport to groundwater, lakes, soils and fish. *Chemosphere* **2015**, *129*, 39-45.

32. Government of Canada, Chemical Substances: Long-Chain (C9-C20) Perfluorocarboxylic Acids (PFCAs), Their Salts, and Their Precursors http://www.chemicalsubstanceschimiques.gc.ca/challenge-defi/summary-sommaire/pfcaps-apfcsp-eng.php (accessed Nov 2015).

33. Ahrens, L.; Shoeib, M.; Harner, T.; Lee, S. C.; Guo, R.; Reiner, E. J., Wastewater Treatment Plant and Landfills as Sources of Polyfluoroalkyl Compounds to the Atmosphere. *Environ. Sci. Technol.* **2011**, *45*, 8098-8105.

34. Moody, C. A.; Field, J. A., Perfluorinated surfactants and the environmental implications of their use in fire-fighting foams. *Environ. Sci. Technol.* **2000**, *34*, 3864-3870.

35. Persistent Organic Pollutants Review Committee of UNEP (2012) Technical paper on the identification and assessment of alternatives to the use of perfluorooctane sulfonic acid, its salts, perfluorooctane sulfonyl fluoride and their related chemicals in open applications (UNEP/POPS/POPRC.8/INF/17/Rev.1).

36. Wang, N.; Szostek, B.; Buck, R. C.; Folsom, P. W.; Sulecki, L. M.; Gannon, J. T., 8-2 Fluorotelomer alcohol aerobic soil biodegradation: Pathways, metabolites, and metabolite yields. *Chemosphere* **2009**, *75*, 1089-1096.

37. Dauchy, X.; Boiteux, V.; Rosin, C.; Munoz, J. F., Relationship Between Industrial Discharges and Contamination of Raw Water Resources by Perfluorinated Compounds: Part II: Case Study of a Fluorotelomer Polymer Manufacturing Plant. *Bull. Environ. Contam. Toxicol.* **2012**, *89*, 531-536.

38. Butenhoff, J. L.; Kennedy, G. L., Jr.; Frame, S. R.; O'Connor, J. C.; York, R. G., The reproductive toxicology of ammonium perfluorooctanoate (APFO) in the rat. *Toxicology* **2004**, *196*, 95-116.

39. Khairy, M.; Muir, D.; Teixeira, C.; Lohmann, R., Spatial Distribution, Air-Water Fugacity Ratios and Source Apportionment of Polychlorinated Biphenyls in the Lower Great Lakes Basin. *Environ. Sci. Technol.* **2015**, *49*, 13787-97.

Figure Captions

Figure 1. Concentrations of PFASs measured in surface waters from Rhode Island and the New York Metropolitan Area. Full names of individual compounds are listed in Table S2. N-MeFOSAA and N-EtFOSAA are not shown but were detected in ~70% of the samples at concentrations <1 ng/L.

Figure 2. Multivariate statistical analysis of surface water data. Panel (A) shows loadings of principal components analysis (PCA) and Panels (C) and (D) show score plots for three components across sampling sites. Panel (B) compares PCA results to hierarchical clustering of compounds and sites. Sites with statistically distinct PFAS profiles are indicated on plots (C) and (D) and highlighted on the hierarchical clustering diagram. The three principal components together explain 80% of the variance in PFAS composition.

Figure 1

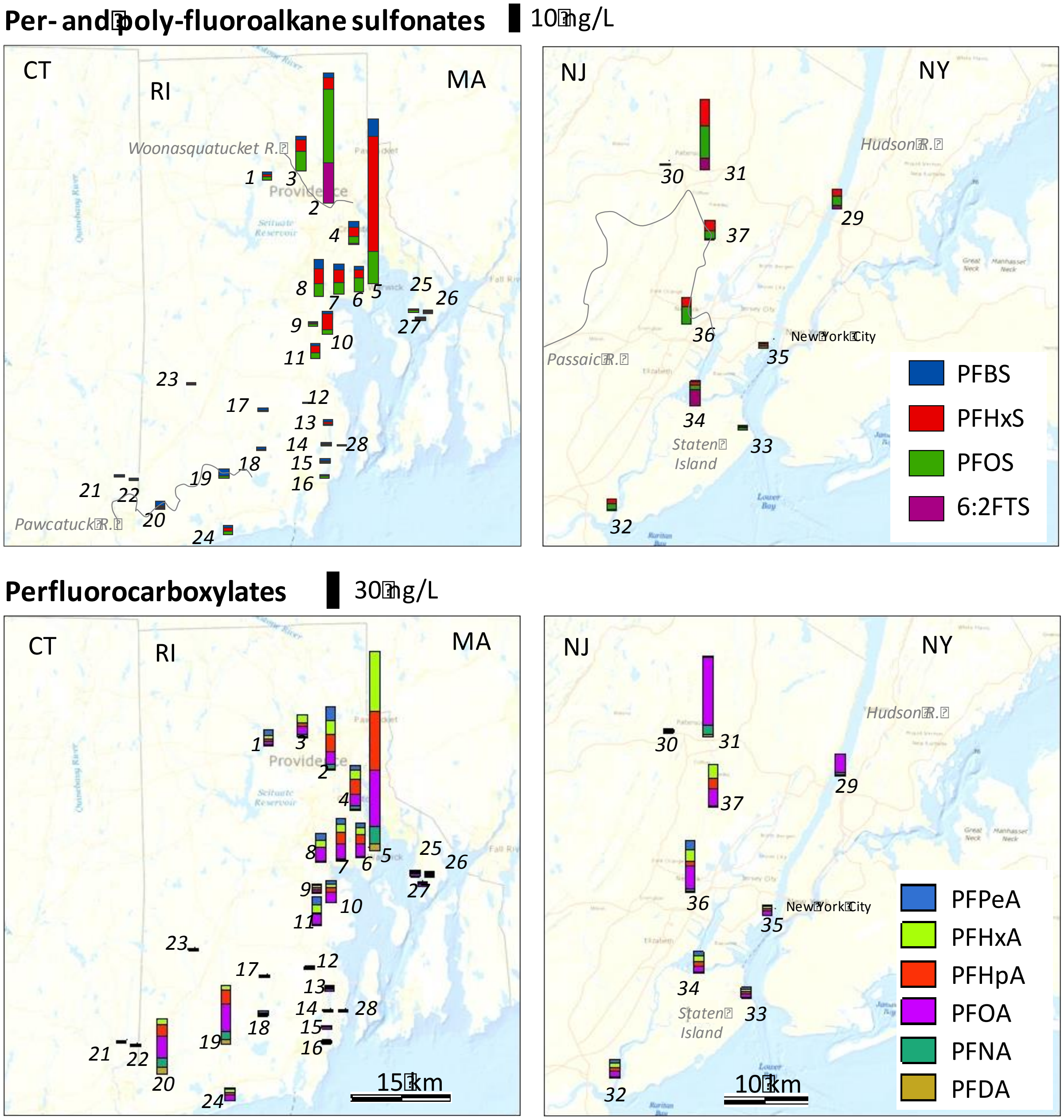
Per- and poly-fluoroalkane sulfonates
10 ng/L
CT
RI
MA
Woonasquatucket R.
Providence
Scituate Reservoir
Pawcatuck R.
NJ
NY
Hudson R.
Passaic R.
New York City
Staten Island
Lower Bay
PFBS
PFHxS
PFOS
6:2FTS
Perfluorocarboxylates
30 ng/L
15 km
10 km
PFPeA
PFHxA
PFHpA
PFOA
PFNA
PFDA
1
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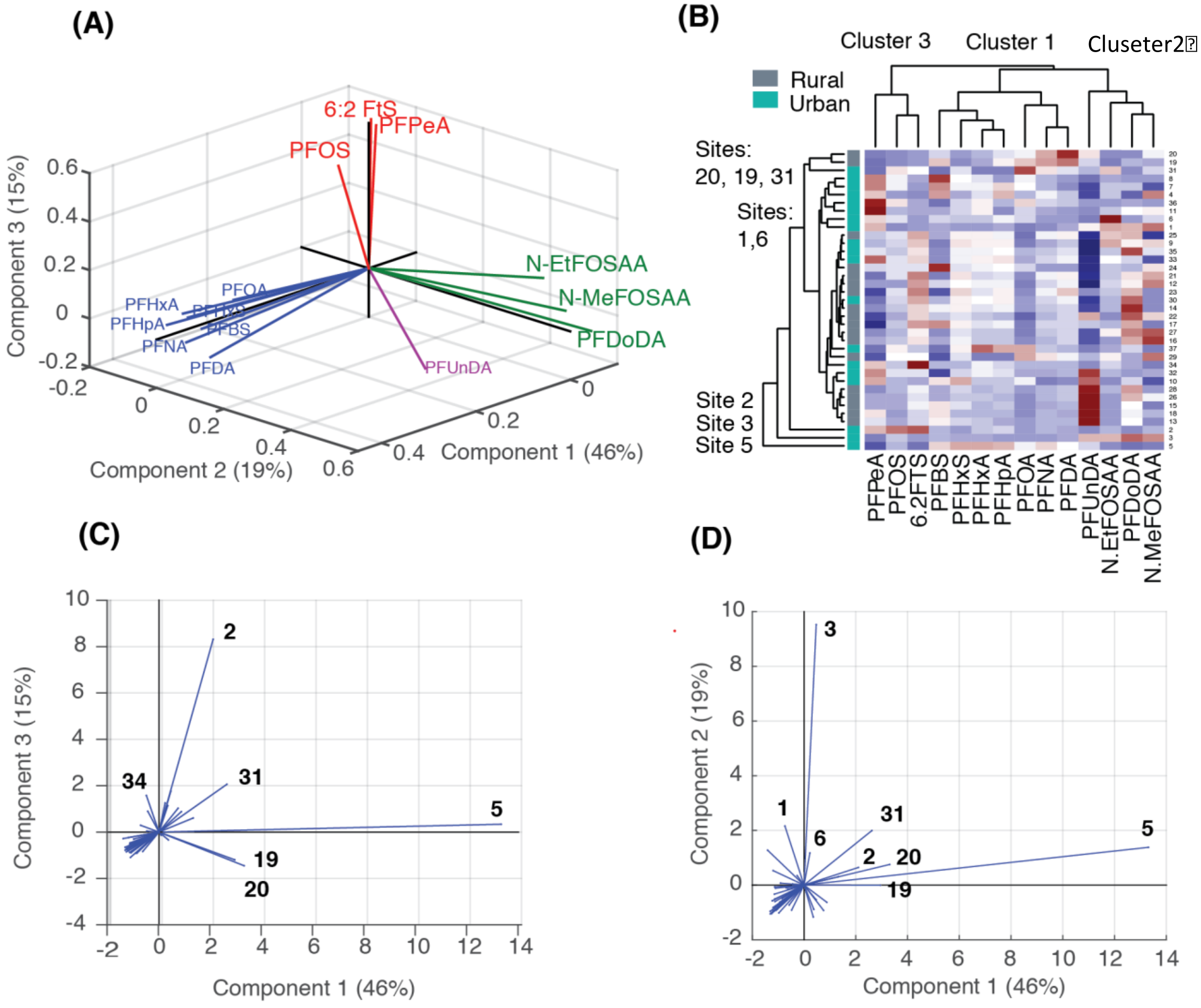
Figure 2


(A)
6:2 FtS
PFPeA
PFOS
N-EtFOSAA
N-MeFOSAA
PFDoDA
PFUnDA
PFHxA
PFOA
PFHxS
PFHpA
PFBS
PFNA
PFDA
Component 3 (15%)
0.6
0.4
0.2
0
-0.2
-0.2
0
0.2
0.4
0.6
Component 2 (19%)
0.4
0.2
0
Component 1 (46%)
(B)
Cluster 3
Cluster 1
Cluseter2
Rural
Urban
Sites:
20, 19, 31
Sites:
1,6
Site 2
Site 3
Site 5
PFPeA
PFOS
6.2FTS
PFBS
PFHxS
PFHxA
PFHpA
PFOA
PFNA
PFDA
PFUnDA
N.EtFOSAA
PFDoDA
N.MeFOSAA
(C)
Component 3 (15%)
Component 1 (46%)
2
34
31
5
19
20
10
8
6
4
2
0
-2
-4
-2
0
2
4
6
8
10
12
14
(D)
Component 2 (19%)
Component 1 (46%)
3
1
6
31
2
20
5
19
10
8
6
4
2
0
-2
-2
0
2
4
6
8
10
12
14

Supporting Information

Concentrations and source attribution of poly- and perfluoroalkyl substances (PFASs) in surface waters from the Northeastern U.S.

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Number of pages: 20
Number of tables: 5
Number of figures: 5

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Section S1: Supplemental Information on Methods

Sample Preparation and Instrumental Analysis

PFASs were extracted from water samples using Oasis Wax (6 ml, 150 mg sorbent) solid phase extraction (SPE) cartridges following the method of Taniyasu et al.[1] Each 500 ml water sample was passed through a preconditioned Oasis Wax (6 ml, 150 mg sorbent) weak ion exchange SPE cartridge mounted on a vacuum manifold at a flow rate of ~1 drop/s. Target analytes were eluted off the cartridges using 6 ml 0.1% NH_4OH in methanol and collected in 15 ml centrifuge tubes (Corning). The extracts were concentrated to 0.5 ml under a gentle stream of high purity nitrogen (5.0 grade), centrifuged at 5000 rpm for 10 minutes, and transferred 1.5 ml polypropylene auto-sampler vials (Microsolv). Before instrumental analysis, 0.5 ml water was added to each sample and vortex mixed.

A 300 µL aliquot of each sample was injected and loaded to an Agilent Zorbax SB-Aq (4.6×12.5mm; 5µm) online SPE column with 0.85 ml 0.1% (v:v) formic acid at a flow rate of 1 ml/min. Following sample loading, the SPE were eluted and load the analytes to an Agilent Poroshell 120 EC-C18 (3.0×50mm; 2.7µm) reverse phase HPLC column. Methanol and water containing 2 mM ammonium acetate were used as mobile phases (flow rate: 0.5 ml/min). Starting from 3% methanol, the elution gradient was linearly increased to 61% in 7 minutes, held for 1 minute, then linearly increased to 100% methanol in 3 min, and was kept until the end of the sample run (14 min).

The tandem mass spectrometer equipped with an electrospray ionization source was operated in negative ion mode. Dynamic multiple reaction monitoring (dMRM) mode was used for data acquisition in order to increase sensitivity. The collision gas was 5.0 grade N_2. Optimized MS parameters are as follows: source temperature, 300 °C; capillary voltage, -3.8 kV; nitrogen nebulizer gas, 45 psi and 13 L/min. Methanol was injected and passed through the system to eliminate any potential carry-over after every sample (or calibration standard).

Shorter chain PFASs such as PFBA and 4:2 FtS were not analyzed due to their low retention on the C-18 reverse phase HPLC column, which would result in a low accuracy.[2] A different analytical method (e.g., using a normal phase HPLC column) that can accurately measure those shorter chain PFASs is needed to detect these compounds and represents a limitation of the present analysis.

Data analysis

Helsel[2] suggests statistical inference bias may occur for data with detection frequencies of less than 30%. PFASs with detection frequencies of 60-70% are included here because they are important for source identification. We tested results of principal component analysis with and without PFASs with low detection frequencies (60-65%: PFPeA, PFHpA, PFDoDA) and find no significant changes in PCA scores (Wilcoxson signed rank tests (p=0.06-0.5) and clustering included in the main results of this work.

Potential industrial PFAS point sources were retrieved from the US EPA Facility Registry Service (FRS) database and used in the geospatial analysis conducted as part of this research. Filtering of the database was based North American Industry Classification System (NAICS) codes. Facilities and their coordinates were retrieved based on the following NAICS codes: Sewage treatment facilities (22132); textile mills (313); paper manufacturing (322); printing and related support activities (323); petroleum and coal products manufacturing (324); paint, coating, and adhesive manufacturing (3255); printing ink manufacturing (32591); metal coating, engraving, heat treating and allied activities (3328); semiconductor manufacturing (3344); airport operation (48811); waste management and remediation (562)

Section S2: Supporting Tables and Figures

Table S1. Surface water sampling dates, site locations and description.

Site	Location	Coastal	Urban/Rural	Potential sources	Date	Longitude	Latitude
1	Slack's Tributary	N	Urban	No hydrologically connected point sources; a landfill is located 1.9 km to the north	06/19/2014	-71.55	41.85
2	Woonasquatucket River	N	Urban	Metal coating/plating	06/19/2014	-71.44	41.82
3	Woonasquatucket River (Greystone pond)	N	Urban	Wastewater treatment plant, printing activity	06/19/2014	-71.49	41.87
4	Pawtuxet River	N	Urban	Metal coating/plating, semiconductor manufacturing	06/19/2014	-71.40	41.77
5	Brook at Mill Cove	N	Urban	T.F. Green State Airport ~5km upstream	06/19/2014	-71.38	41.71
6	Buckeye Brook	N	Urban	No hydrologically connected point sources; a landfill is located 2.3 km to the west	06/19/2014	-71.39	41.70
7	Southern Creek	N	Urban	No hydrologically connected point sources	06/19/2014	-71.42	41.70
8	Mill Brook	N	Urban	One semiconductor manufacturer making thin film components, networks, and arrays on ceramic and silicon; one company conducting waste management providing service on hazardous waste removal, hazardous waste transportation, oil tank hazardous waste disposal (https://www3.epa.gov/region1/removal-sites/BradfordPrintingFinishing.html)	06/19/2014	-71.46	41.70
9	EG Town Dock	Y	Urban	Estuary of Greenwich Cove; next to an e-waste recycling company	06/19/2014	-71.45	41.65
10	Hunt River	Y	Urban	Two semiconductor manufacturers and one printing company	06/19/2014	-71.44	41.64
11	Sand Hill Brook (Saw Mill Pond Inlet)	N	Urban	A municipal waste transfer station and paint, coating, adhesive manufacturing	06/19/2014	-71.47	41.61
12	Secret Lake-Oak Hill Brook	N	Urban	A legacy landfill site is approximately 2 km to the west of this site	06/19/2014	-71.48	41.55
13	Narrow River Stuart Stream	N	Rural	Outlet of Carr Pond	06/19/2014	-71.44	41.52
14	Narrow	N	Rural	3 km downstream of site 13	06/19/	-71.45	41.49

Site	Location	Coastal	Urban/Rural	Potential sources	Date	Longitude	Latitude
	River Lakeside Dr.				2014		
15	Narrow River	N	Rural	2.5 km downstream of site 14	06/19/2014	-71.45	41.47
16	Narrow River	N	Rural	2 km downstream of site 15	06/19/2014	-71.45	41.45
17	Queens River	N	Rural	One river branch upstream of Pawcatuck River (background site)	06/19/2014	-71.56	41.54
18	Chickasheen Brook	N	Rural	River branch upstream of Pawcatuck River; a manufacturer of uninterruptible power supplies, electronics peripherals and data center products is downstream	06/19/2014	-71.56	41.49
19	Pawcatuck River	N	Rural	Where Beaver River merges into Pawcatuck River; a manufacture of military, tactical, and performance synthetic and synthetic blend textiles ~1 km upstream	06/19/2014	-71.63	41.45
20	Pawcatuck River	N	Rural	Adjacent to Bradford Printing & Finishing facility, a textile finishing plant from 1911 until 2012; a large fire occurred in 2007; heavy flooding occured in 2010; another fire occurred in 2012; Several hundred containers of highly flammable liquid, dyes and unknown compounds were stored next to each another and many containers were visibly leaking in 2012.[3]	06/19/2014	-71.75	41.41
21	Green Falls River	N	Rural	Background site; no upstream industrial facilities recorded in FRS database	06/19/2014	-71.82	41.45
22	Green Falls River	N	Rural	~ 2 km downstream of site 21 where Parmenter Brook merges into Green Falls River; no upstream industrial facilities recorded in FRS database	06/19/2014	-71.80	41.44
23	Fall River	N	Rural	Background site; no upstream industrial facilities recorded in FRS database	06/19/2014	-71.69	41.58
24	Allen Cove - Inflow (Green Hill Pond)	N	Rural	Close to Charlestown beach; residential area	06/19/2014	-71.62	41.37
25	Bristol Harbor	Y	Rural	Coastal site; east shore of Bristol Harbor	06/19/2014	-71.29	41.67
26	Bristol Harbor	Y	Rural	Coastal site; east shore of Bristol Harbor	06/19/2014	-71.28	41.67
27	Bristol Harbor	Y	Rural	Coastal site; west shore of Bristol Harbor	06/19/2014	-71.27	41.66
28	South Ferry Rd Pier	Y	Rural	Coastal site; Narragansett Bay	06/19/2014	-71.42	41.49

Site	Location	Coastal	Urban/Rural	Potential sources	Date	Longitude	Latitude
	Dock						
29	Hudson River	N	Urban	There are a sewage treatment plant, a plastic bag manufacturing and printing company, a printing ink manufacture, and a floor coating manufacture within 10 km upstream along the river	10/24/ 2014	-73.93	40.87
30	Passaic River	N	Urban	West Paterson Recycling Center 2.5 km upstream	10/24/ 2014	-74.19	40.91
31	Passaic River	N	Urban	Highly industrialized between 30 and 31, including paint, coating, adhesive manufacturing, textile mills, printing ink manufactures, paper manufacturers; semiconductor manufactures and metal coating/plating companies.	10/24/ 2014	-74.13	40.91
32	Harbortown Rd, NJ	Y	Urban	At the mouth of a tidal strait and a kill separating Staten Island, New York City from mainland New Jersey; some petroleum/coal related industrials within 2 km upstreams	10/25/ 2014	-74.25	40.52
33	Lower NY Harbor	Y	Urban	A printing ink manufacture 1 km away	10/25/ 2014	-74.06	40.62
34	Staten Island NY	N	Urban	A company with printing activity; a paint, coating, adhesive manufacture, and a paper manufacture within 1.5 km upstream	10/25/ 2014	-74.13	40.64
35	Hudson River	Y	Urban	Morris Canal close to Jersey city; two companies on Paint, coating, adhesive manufacturing 1 km away	10/26/ 2014	-74.04	40.71
36	Passaic River	N	Urban	Close to the city of Newark and the airport; highly industrialized area; Newark wastewater treatment plant is 2.5 km upstream	10/26/ 2014	-74.15	40.73
37	Passaic River	N	Urban	Upstream of site 36; highly industrial area; within 1 km upstream there is a company related to metal plating and a textile mill.	10/26/ 2014	-74.12	40.83

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Table S2. Full names and acronyms of PFASs measured in surface waters, limits of detection (LOD), concentration ranges measured across sites, and percent of sites with detection. PFASs measured in >60% of samples analyzed in this study are highlighted in bold

PFAS	Acronym	# of carbons	Internal standard	LOD (ng/L)	Range (ng/L)	Detect. %
Perfluorocarboxylates	*PFCAs*					
Perfluoropentanate	**PFPeA**	**C5**	$^{13}\mathrm{C}_2$-PFHxA	**0.38**	**BD – 10**	**62%**
Perfluorohexanate	**PFHxA**	**C6**	$^{13}\mathrm{C}_2$-PFHxA	**0.29**	**BD–48**	**87%**
Perfluoroheptanate	**PFHpA**	**C7**	$^{13}\mathrm{C}_4$-PFOA	**0.62**	**BD–48**	**64%**
Perfluorooctanate	**PFOA**	**C8**	$^{13}\mathrm{C}_4$-PFOA	**0.07**	**0.27 – 47**	**100%**
Perfluorononanate	**PFNA**	**C9**	$^{13}\mathrm{C}_5$-PFNA	**0.04**	**0.07 – 14**	**100%**
Perfluorodecanate	**PFDA**	**C10**	$^{13}\mathrm{C}_2$-PFDA	**0.03**	**BD – 5.8**	**92%**
Perfluoroundecanate	**PFUnDA**	**C11**	$^{13}\mathrm{C}_2$-PFUnDA	**0.02**	**BD –1.9**	**77%**
Perfluorododecanate	**PFDoDA**	**C12**	$^{13}\mathrm{C}_2$-PFDoDA	**0.02**	**BD–2.6**	**64%**
Perfluorotridecanate	PFTrDA	C13	$^{13}\mathrm{C}_2$-PFDoDA	0.02	BD–1.2	31%
Perfluorotetradecanate	PFTeDA	C14	$^{13}\mathrm{C}_2$-PFDoDA	0.02	BD0.4	18%
Perfluorohexaadecanate	PFHxDA	C16	$^{13}\mathrm{C}_2$-PFDoDA	0.01	BD–0.2	26%
Perfluorooctadecanate	PFODA	C18	$^{13}\mathrm{C}_2$-PFDoDA	0.08	BD–0.4	8%
Perfluoroalkane sulfonates	*PFSAs*					
Perfluorobutane sulfonate	**PFBS**	**C4**	$^{18}\mathrm{O}_2$-PFHxS	**0.08**	**BD–6.2**	**85%**
Perfluorohexane sulfonate	**PFHxS**	**C6**	$^{18}\mathrm{O}_2$-PFHxS	**0.06**	**BD – 35**	**90%**
Perfluorooctane sulfonate	**PFOS**	**C8**	$^{13}\mathrm{C}_4$-PFOS	**0.05**	**BD – 23**	**95%**
Perfluorododecane sulfonate	PFDS	C10	$^{13}\mathrm{C}_4$-PFOS	0.07	BD–0.6	15%
6:2 fluorotelomer sulfonate	**6:2 FtS**		$^{13}\mathrm{C}_2$-6:2 FtS	**0.003**	**BD – 15**	**97%**
8:2 fluorotelomer sulfonate	8:2 FtS		$^{13}\mathrm{C}_2$-6:2 FtS	0.4	BD–0.8	41%
Perfluorooctane sulfonamide	FOSA	C8	$^{13}\mathrm{C}_8$-FOSA	0.02	BD–0.2	41%
N-ethyl perfluorooctanesulfon-amidoacetic acid	**N-EtFOSAA**		D_5 N-EtFOSAA	**0.001**	**BD-9.9**	**67%**
N-methyl perfluorooctanesulfon-amidoacetic acid	**N-MeFOSAA**		D_5 N-MeFOSAA	**0.002**	**BD-0.6**	**69%**

BD = below detection.

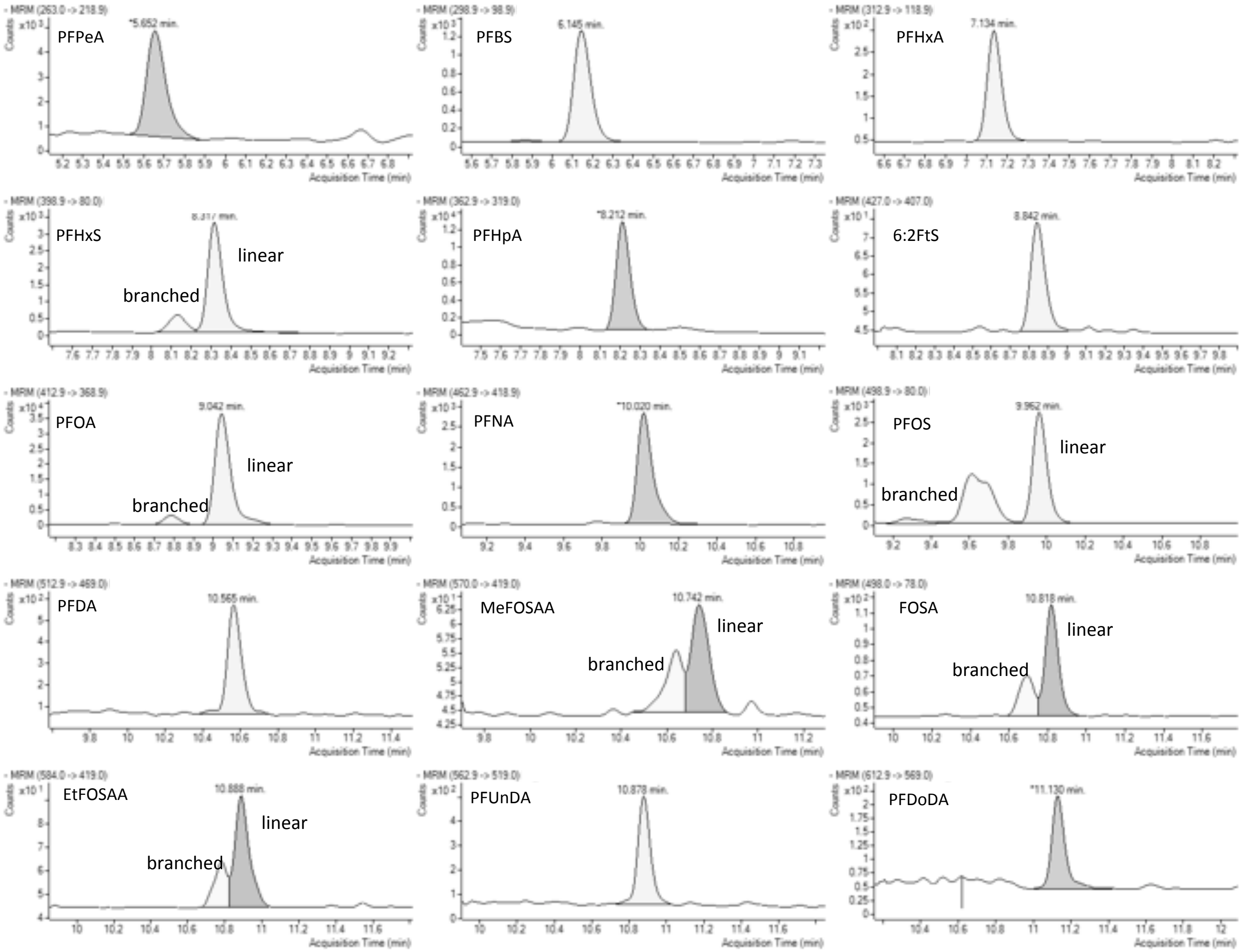

Figure S1. Chromatograms of PFASs in a sample analyzed using an Agilent 6460 LC-MS/MS equipped with an online-SPE system (Agilent 1290 Infinity Flex Cube) in dynamic multiple reaction mode.

Table S3a. Concentrations (pg/L) of poly- and perfluoroalkyl substances with detection frequency greater than 60%.

Site	PFPeA	PFHxA	PFHpA	PFOA[a]	PFNA	PFDA	PFUnDA
1	4550	2191	2409	2363	390	405	607
2	10357	12137	13577	8832	3134	1133	308
3	<LOD	6310	3371	5236	1476	894	1853
4	4228	7337	12301	7546	2735	957	114
5	<LOD	48414	48159	36806	13986	5625	1286
6	4359	5408	7640	8455	733	367	167
7	4828	6715	9236	10080	1275	205	46
8	5611	5649	<LOD	9237	923	176	48
9	927	1562	1597	1972	336	127	97
10	3064	2987	3090	6978	308	125	<LOD
11	6361	6678	<LOD	6905	799	226	177
12	555	565	<LOD	849	165	59	38
13	1413	1170	<LOD	1480	253	104	<LOD
14	<LOD	665	<LOD	663	104	<LOD	33
15	732	556	<LOD	851	136	31	<LOD
16	631	543	<LOD	946	174	87	62
17	681	550	<LOD	898	155	59	62
18	2138	663	<LOD	1006	293	<LOD	<LOD
19	<LOD	3740	11793	18974	6182	3808	482
20	<LOD	4138	9728	14985	7235	5824	888
21	<LOD	<LOD	<LOD	586	232	73	41
22	<LOD	493	<LOD	708	206	83	<LOD
23	<LOD	<LOD	<LOD	640	200	152	97
24	1221	2121	2479	3784	260	52	55
25	843	1214	897	1320	400	169	97
26	821	964	751	1014	323	134	<LOD
27	617	900	800	1170	355	166	78
28	<LOD	<LOD	<LOD	267	74	38	<LOD
29	<LOD	<LOD	<LOD	11862	2188	685	257
30	<LOD	815	947	871	151	59	28
31	<LOD	<LOD	<LOD	47254	6658	2154	464
32	3032	3529	3226	3738	601	301	<LOD
33	1870	1802	1907	2020	363	182	49
34	3434	5188	3431	4049	726	347	115
35	1111	1710	1852	2805	411	211	59
36	7998	9277	3426	15137	2022	719	238
37	<LOD	10901	8455	11335	757	152	79

[a] Linear isomers with calibration standards for quantification

Table S3b. Concentrations (pg/L) of poly- and perfluoroalkyl substances with detection frequency greater than 60%.

Site	PFBS	PFHxS[a]	PFOS[a]	6:2 FtS	MeFOSAA[a]	EtFOSAA [a]	PFDoDA
1	669	864	777	15	241	348	618
2	1652	3758	23226	15292	147	278	89
3	1327	3583	5868	55	610	937	2598
4	2290	2558	2185	380	227	152	28
5	6181	35022	9804	239	113	240	117
6	1087	2637	4127	24	90	694	96
7	2102	4130	3743	30	<LOD	122	<LOD
8	3355	4664	3937	9	23	53	23
9	296	695	735	26	38	65	61
10	1161	5075	1477	8	<LOD	36	<LOD
11	546	2418	1822	5	106	94	313
12	278	<LOD	<LOD	<LOD	43	14	25
13	889	645	347	6	<LOD	<LOD	<LOD
14	368	476	176	<LOD	<LOD	<LOD	<LOD
15	705	421	180	10	<LOD	<LOD	<LOD
16	226	323	488	3	82	<LOD	131
17	466	372	334	7	82	<LOD	131
18	973	208	<LOD	10	27	<LOD	<LOD
19	2485	<LOD	509	10	60	<LOD	194
20	1465	361	612	4	159	24	35
21	92	<LOD	290	10	34	<LOD	24
22	341	133	292	13	39	<LOD	<LOD
23	<LOD	143	238	12	<LOD	<LOD	42
24	1185	916	1198	6	55	46	41
25	281	343	626	16	<LOD	49	<LOD
26	254	282	437	12	47	<LOD	<LOD
27	229	320	460	22	80	58	<LOD
28	131	<LOD	161	4	<LOD	<LOD	<LOD
29	<LOD	2149	2835	1087	160	148	59
30	220	224	244	69	<LOD	<LOD	<LOD
31	<LOD	8526	9988	4377	166	593	99
32	<LOD	1390	1929	464	32	59	25
33	226	408	755	58	<LOD	48	31
34	467	963	1661	5918	<LOD	92	34
35	278	640	790	82	33	31	<LOD
36	<LOD	3087	5384	89	40	57	99
37	<LOD	3162	2748	43	<LOD	18	128

[a] Linear isomers with calibration standards for quantification

Table S3c. Concentrations (pg/L) of branched isomers[a] of poly- and perfluoroalkyl substances

Site	br-PFHxS	br-PFOA	br-PFOS	br-MeFOSAA	br-EtFOSAA
1	201	550	181	56	81
2	695	1635	4298	27	51
3	777	1135	1272	132	203
4	590	1741	504	52	35
5	8228	8647	2303	27	56
6	481	1542	753	<17	127
7	741	1808	671	<17	22
8	896	1775	756	<17	<12
9	<64	114	<51	<17	<12
10	982	1350	286	<17	<12
11	483	1378	364	21	19
12	<64	249	<51	<17	<12
13	76	174	<51	<17	<12
14	76	106	<51	<17	<12
15	<64	125	<51	<17	<12
16	<64	146	75	<17	<12
17	<64	118	<51	<17	<12
18	<64	151	<51	<17	<12
19	<64	3015	81	<17	<12
20	78	3250	133	35	<12
21	<64	74	<51	<17	<12
22	<64	<68	<51	<17	<12
23	<64	<68	<51	<17	<12
24	164	678	215	<17	<12
25	80	306	145	<17	<12
26	93	333	144	<17	<12
27	<64	227	89	<17	<12
28	<64	284	171	<17	<12
29	471	2602	622	35	32
30	<64	193	54	<17	<12
31	1578	8745	1848	31	110
32	294	790	408	<17	12
33	113	557	208	<17	13
34	176	739	303	<17	17
35	158	691	195	<17	<12
36	539	2660	953	<17	<12
37	700	2512	609	<17	<12

[a] Branched isomers were quantified based on peak areas assuming the same response factors as the linear isomers.

Table S4. PFAS concentrations measured in U.S. surface waters in this study and previous work.

PFASs, ng/L (minimum/median/maximum)

Location/ (sites, sampling year)	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS
Tennessee (*n*=40, 2000)[4]				<25							17
				<25							52
				598							144
North Carolina (*n*=11, 2006)[5]		<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
		5.14	14.8	12.6	5.7	13.2	5.67	1.95	2.46	5.66	28.9
		23	329	287	194	120	52.1	4.46	9.41	35.1	132
Georgia (*n*=11, 2006)[6]				3	<0.6	<0.1	<0.1				1
				238	5.6	2.1	<0.1				6
				1150	369	131	99				318
Upper Mississippi River Basin (*n*=177, 2008)[7]	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	0.71	1.59	2.16	2.07	0.71	0.71	0.71	0.71	0.71	0.71	3.01
	31.5	53.4	90.2	125	72.9	42	29.1	24.7	84.1	169	245
Georgia (*n*=8, 2008)[8]	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
	57	68	46	102	21	25			124	13	150
	149	149	100	204	46	46			260	31	321
New Jersey (*n*=12, 2009)[9]	<5	<5	<5	<5	<5	<5			<5	<5	<5
	<5	<5	<5	11	<5	<5			<5	<5	<5
	15	17	10	100	19	ND			6	46	43
Rhode Island and New York Metropolitan Region (*n*=37, 2014, this study)*	<0.4	<0.3	<0.6	0.3	0.1	<0.03	<0.03	<0.03	<0.08	<0.12	<0.10
	0.8	1.7	0.9	3.5	0.4	0.2	0.1	0.0	0.4	0.7	0.96
	10.4	48.4	48.2	56.0	14.0	5.8	1.9	2.6	6.2	43.0	27.5

*PFOA, PFHxS and PFOS reported here include both linear and branched isomers. The branched isomers were quantified based on peak areas assuming the same response factors as the linear isomers

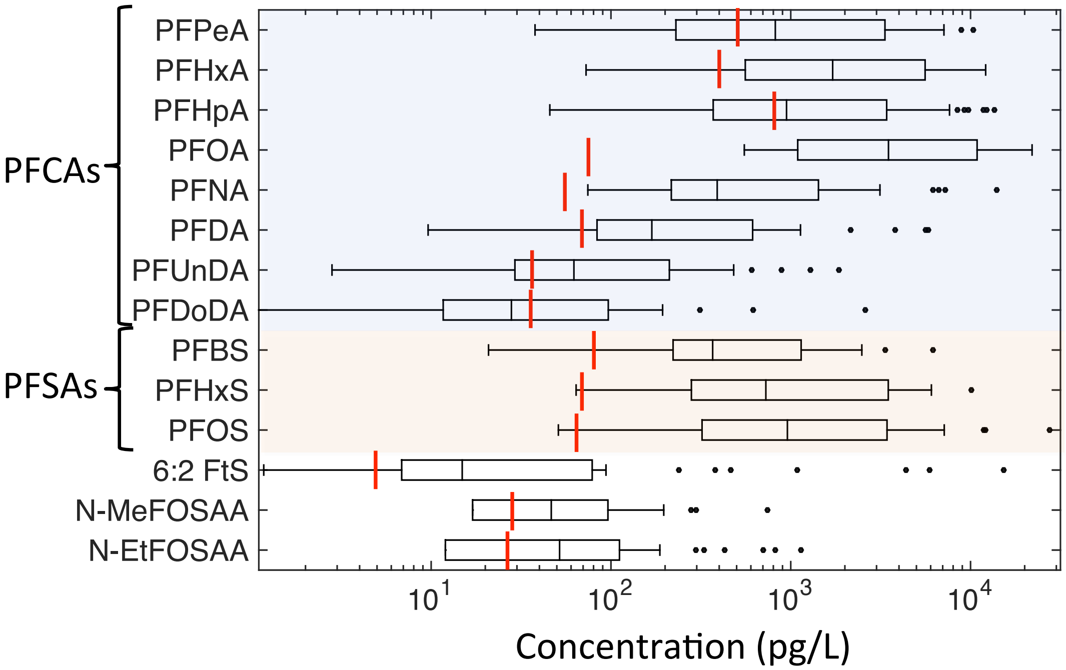

Figure S2. Concentrations of 14-PFASs measured in 37 rivers and estuaries in Rhode Island (RI) and the New York Metropolitan area (NY/NJ). The limit of detection (LOD) for each compound is shown as a red bar. Those below detection are assigned values based on the robust ROS (Regression on Order Statistics) approach for censored log-normally distributed environmental data as described by Helsel.[2]

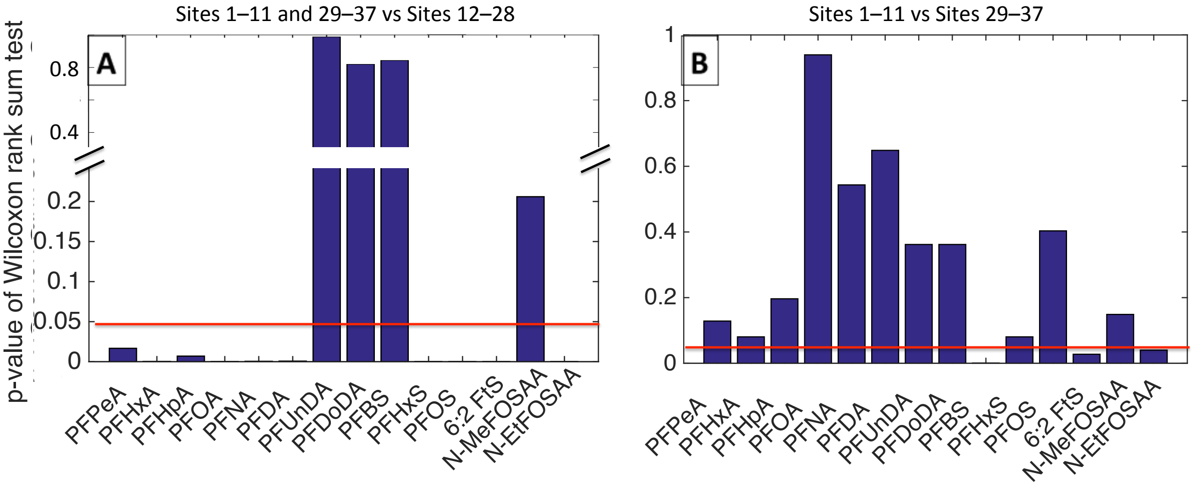

Figure S3. Significance levels for Wilcoxon rank sum tests comparing PFAS concentrations (a) between urban sites (RI sites 1–11 and NY/NJ sites 29–37) and rural sites 12-28 (b) RI sites 1–11 and NY/NJ sites 29–37. Red line denotes *p*=0.05, which we use to indicate statistical significance.

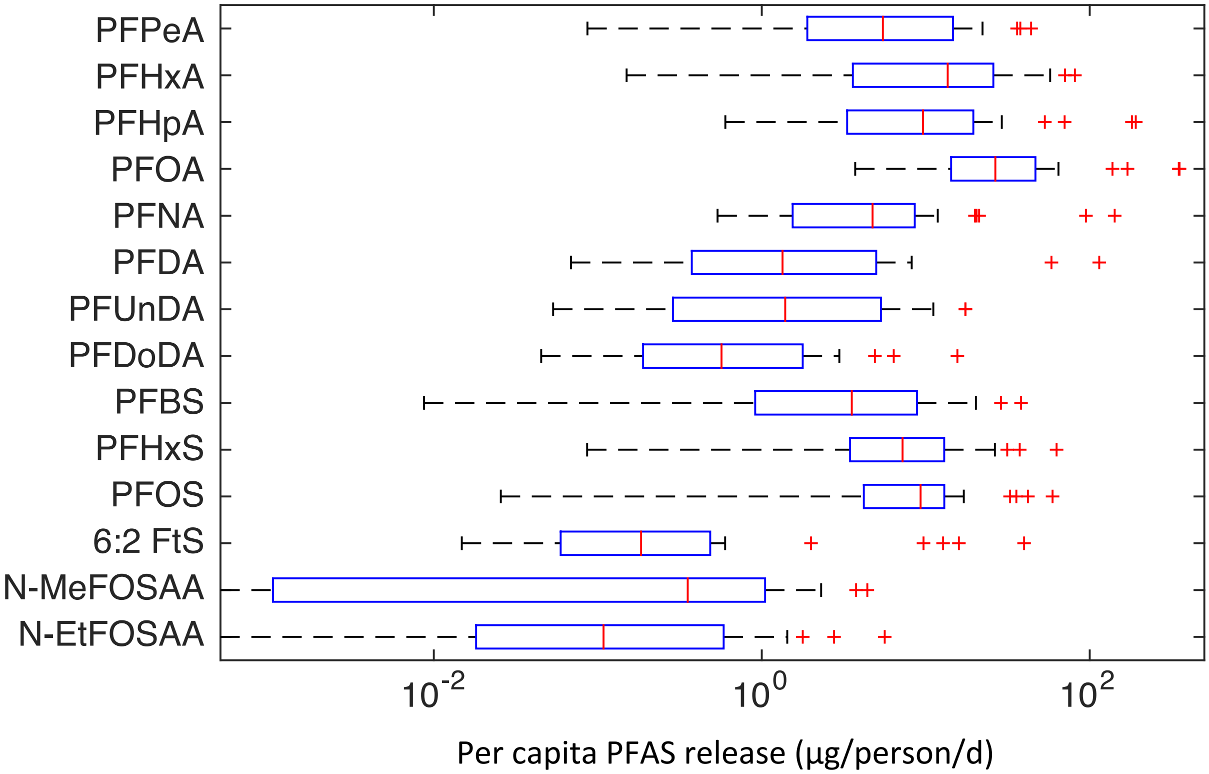

Figure S4. Per-capita release of PFAS (μg/person/d) estimated based on measured PFAS concentrations, water flow rate and upstream population at each sampling site.

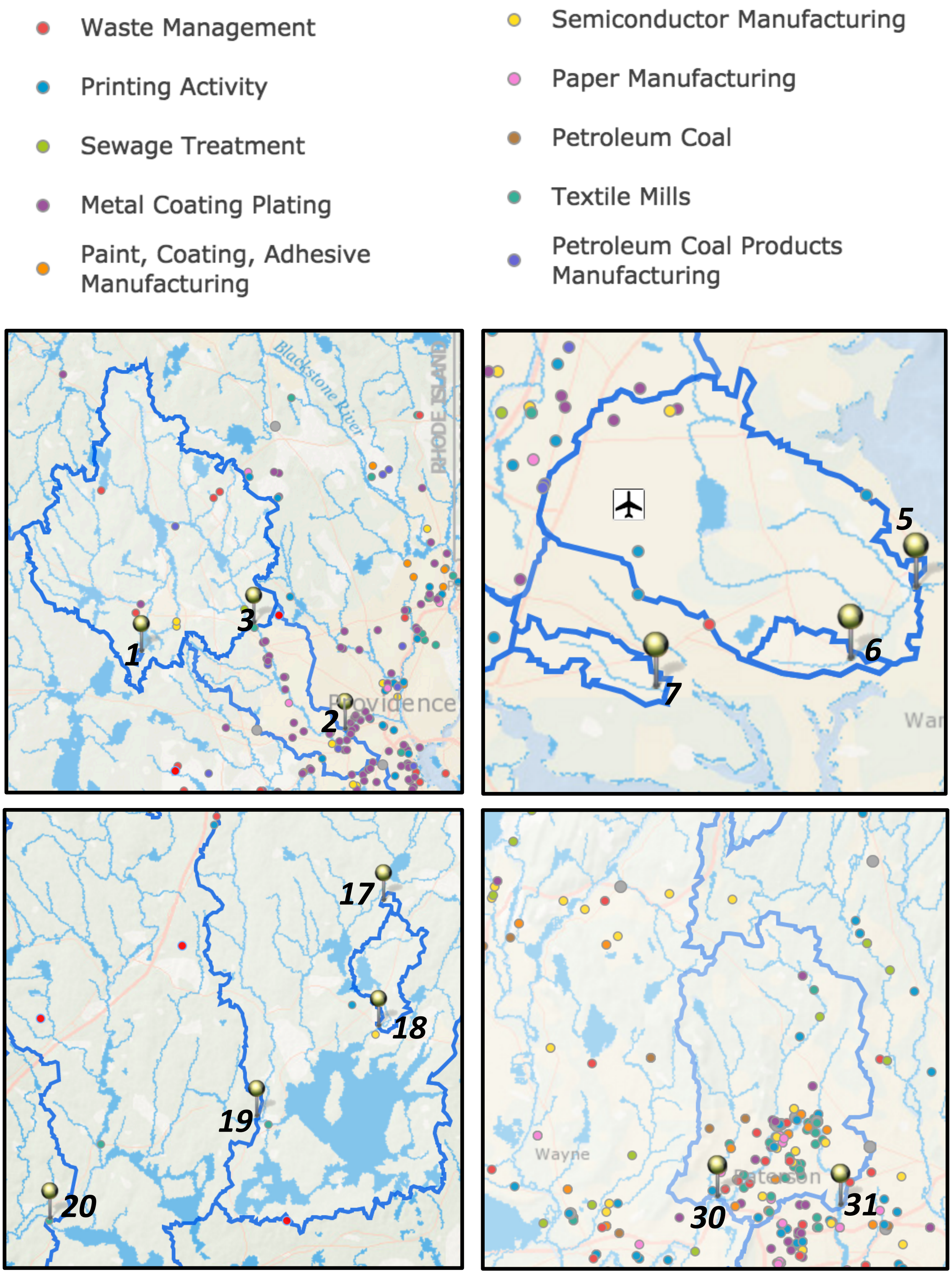

Figure S5. Maps showing sampling sites with distinct PFAS composition profiles, the upstream watersheds and the potential source contributions.

Table S5. Impact factors for potential PFAS sources in watersheds upstream of the non-estuarine sampling sites.

				Impact from facilities upstreams										
sites	Upstream Area (km^2)	Upstream Population	Upstream Population Density (Person/km^2)	Metal Coating Plating	Paint, Coating, Adhesive Manufacturing	Paper Manufacturing	Petroleum Coal Products Manufacturing	Printing Activity	Printing Ink Manufacturing	Semiconductor Manufacturing	Sewage Treatment	Textile Mills	Waste Management (incl. Landfills)	Airport
1	0.1	26	190											
2	124.4	87446	703	1.7E+00	3.7E-01	1.3E-02	2.6E-01	5.5E-05		5.1E-01		1.1E-01	5.5E-08	
3	97.6	24495	251	3.2E-04		1.7E-06				1.2E-06	3.7E-01		3.5E-04	
4	598.2	208255	348	1.3E-01	5.2E-04	1.7E-04	5.8E-04	5.5E-03	1.4E-08	2.8E-02	4.9E-03	1.7E-04	1.6E-01	
5	16.0	16509	1032	9.9E-04				3.0E-03					3.4E-04	4.1E-03
6	1.0	1174	1196											
7	1.4	1792	1306											
8	15.9	12476	783	7.1E-01			2.5E-04	6.1E-04		6.0E-01				
10	59.3	14886	251	4.4E-03	1.3E-03			9.1E-05		3.3E-04			3.0E-04	
11	5.5	1394	254		2.1E-01								6.9E-01	
12	0.6	123	218											
13	12.1	1951	161											
14	21.2	4811	226											
15	24.4	5870	240											
16	33.8	8835	262											
17	0.5	20	42											
18	10.2	746	73											
19	235.3	23112	98					2.0E-04		4.3E-05		3.9E-01		
20	561.1	43081	77			3.8E-15		4.8E-13		1.1E-13		9.1E-01		
21	0.01	1	69											
22	65.7	2647	40											
23	0.3	12	44											
29	12799.8	1994644	156	9.6E-02	1.4E+00	2.2E+00	4.9E-09	5.6E+00	2.0E+00	7.5E-02	3.6E+00	2.8E-01	1.8E+00	
30	2015.8	854842	424	1.2E-02	4.7E-03	6.5E-04	8.0E-04	9.8E-02	1.8E-05	6.3E-02	9.4E-04	3.8E-03	3.8E-04	
31	2090.0	1050694	503	3.2E-02	1.1E-01	2.6E-02	7.6E-04	4.2E-02	1.6E-01	1.2E-01	2.4E-04	1.6E-01	3.1E-02	
34	3345.1	3737691	1117	2.1E-01	5.2E-04	1.8E-01	6.2E-03	2.7E-01	1.5E-04	3.6E-01	2.9E-03	1.7E-01	6.1E-02	2.5E-04
36	2406.9	1903628	791	1.7E+00	3.5E-01	1.8E-01	4.2E-01	7.8E-01	7.6E-03	4.8E-02	6.0E-01	4.2E-02	7.0E-01	
37	2303.7	1494335	649	1.9E+00	5.5E-01	1.9E-01	8.0E-02	1.1E+00	3.7E-02	1.4E-01	1.3E-03	5.8E-01	5.7E-02	

*Facilities are based on the U.S. EPA Facility Registry Service database.[10] Impact of potential point sources as a function of distance from sampling locations by assuming exponential decay in the concentration (i.e., *Impact* = $1/e^d$, where d = hydrological distance, km)

References

1. Taniyasu, S.; Kannan, K.; So, M. K.; Gulkowska, A.; Sinclair, E.; Okazawa, T.; Yamashita, N., Analysis of fluorotelomer alcohols, fluorotelorner acids, and short- and long-chain perfluorinated acids in water and biota. *J. Chromatogr. A* **2005**, *1093*, 89-97.
2. Huset, C. A.; Barlaz, M. A.; Barofsky, D. F.; Field, J. A., Quantitative determination of fluorochemicals in municipal landfill leachates. *Chemosphere* **2011**, *82*, 1380-1386.
3. U.S. EPA, Waste Site Cleanup & Reuse in New England - Bradford Printing & Finishing https://www3.epa.gov/region1/removal-sites/BradfordPrintingFinishing.html (accessed Feb 2016). **2012**.
4. Hansen, K. J.; Johnson, H. O.; Eldridge, J. S.; Butenhoff, J. L.; Dick, L. A., Quantitative characterization of trace levels of PFOS and PFOA in the Tennessee River. *Environ. Sci. Technol.* **2002**, *36*, 1681-1685.
5. Nakayama, S.; Strynar, M. J.; Helfant, L.; Egeghy, P.; Ye, X. B.; Lindstrom, A. B., Perfluorinated compounds in the Cape Fear Drainage Basin in North Carolina. *Environ. Sci. Technol.* **2007**, *41*, 5271-5276.
6. Konwick, B. J.; Tomy, G. T.; Ismail, N.; Peterson, J. T.; Fauver, R. J.; Higginbotham, D.; Fisk, A. T., Concentrations and patterns of perfluoroalkyl acids in Georgia, USA surface waters near and distant to a major use source. *Environ. Toxicol. Chem.* **2008**, *27*, 2011-2018.
7. Nakayama, S. F.; Strynar, M. J.; Reiner, J. L.; Delinsky, A. D.; Lindstrom, A. B., Determination of Perfluorinated Compounds in the Upper Mississippi River Basin. *Environ. Sci. Technol.* **2010**, *44*, 4103-4109.
8. Lasier, P. J.; Washington, J. W.; Hassan, S. M.; Jenkins, T. M., Perfluorinated chemicals in surface waters and sediments from northwest Georgia, USA, and their bioaccumulation in Lumbriculus variegatus. *Environ. Toxicol. Chem.* **2011**, *30*, 2194-201.
9. Post, G. B.; Louis, J. B.; Lippincott, R. L.; Procopio, N. A., Occurrence of Perfluorinated Compounds in Raw Water from New Jersey Public Drinking Water Systems. *Environ. Sci. Technol.* **2013**, *47*, 13266-13275.
10. US EPA, Facility Registry Service (FRS). http://www.epa.gov/enviro/epa-frs-facilities-state-single-file-csv-download (accessed Nov 2015).