

2016

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

Xianming Zhang

Rainer Lohmann

University of Rhode Island, rlohmann@uri.edu

See next page for additional authors

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Citation/Publisher Attribution

Zhang, X., Lohmann, R., Dassuncao, C., Hu, X. C., Weber, A. K., Vecitis, C. D., & Sunderland, E. M. (2016). Source Attribution of Poly- and Perfluoroalkyl Substances (PFASs) in Surface Waters from Rhode Island and the New York Metropolitan Area. *Environ. Sci. Technol.*, 3(9), 316-321.

Available at: <http://dx.doi.org/10.1021/acs.estlett.6b00255>

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Authors

Xianming Zhang, Rainer Lohmann, Clifton Dassuncao, Xindi C. Hu, Andrea K. Weber, Chad D. Vecitis, and Elsie M. Sunderland

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

3 *Xianming Zhang^{†‡*}; Rainer Lohmann[§]; Clifton Dassuncao^{†‡}; Xindi C. Hu^{†‡}; Andrea K. Weber[†];*
4 *Chad D. Vecitis[†]; Elsie M. Sunderland^{†‡}*

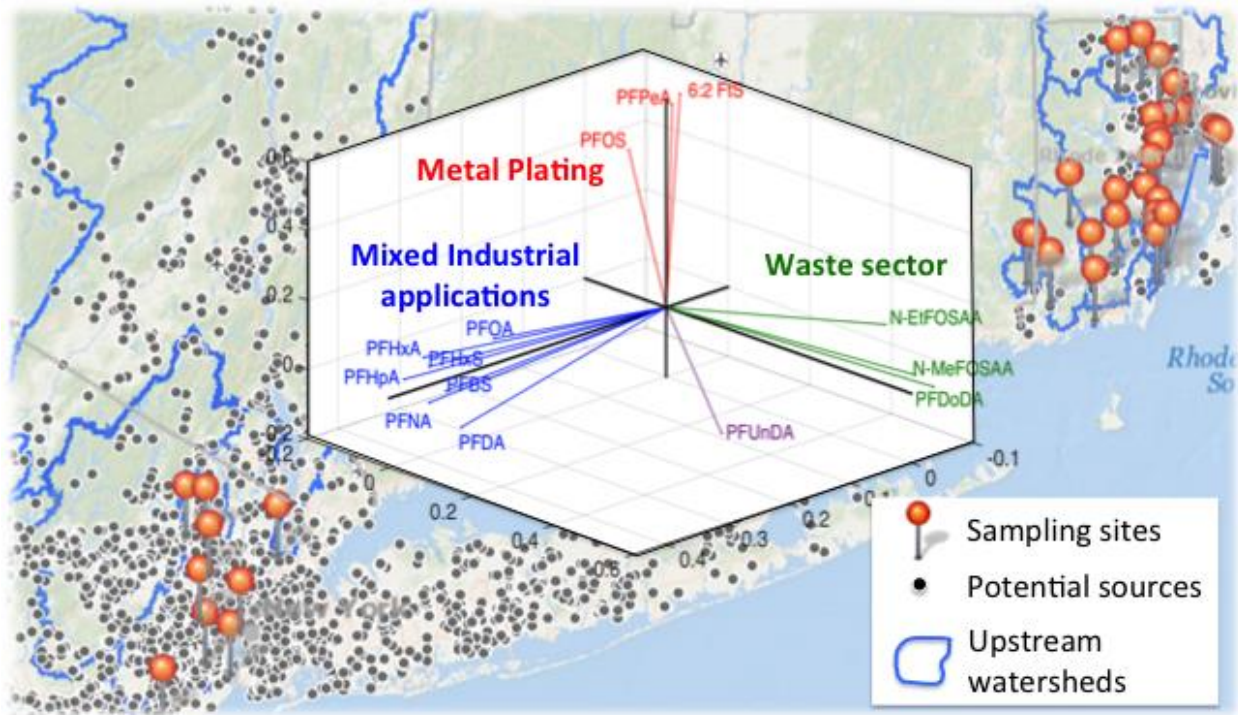
5 [†] Harvard John A. Paulson School of Engineering and Applied Sciences, Harvard University,
6 Cambridge MA USA 02138

7 [‡] Department of Environmental Health, Harvard T.H. Chan School of Public Health, Harvard
8 University, Boston MA USA 02115

9 [§] Graduate School of Oceanography, University of Rhode Island

10 *Corresponding author:

11 Xianming Zhang, E-mail: xmzhang@seas.harvard.edu; Tel: 617-495-2893



14 **Abstract**

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

32 **Introduction**

33 Exposure to poly- and perfluoroalkyl substances (PFASs) has been associated with many
34 negative health outcomes including compromised immune function, metabolic disruption,
35 obesity, and altered liver function.¹ PFASs in surface waters are an emerging concern for U.S.
36 public water supplies and long-chain compounds bioaccumulate in aquatic food webs, posing
37 health risks to seafood consumers.²⁻⁶ Production of PFASs and their precursors has shifted
38 dramatically over the last two decades toward shorter-chain and polyfluorinated species.⁷
39 Diverse point sources and atmospheric deposition of some PFASs confounds understanding of
40 the dominant contributors to contamination in the aquatic environment. Regulatory databases
41 such as the U.S. EPA's Facility Registry Survey (FRS)⁸ and the Toxic Release Inventory⁹
42 presently contain limited to no information on magnitudes of PFASs released to the environment.

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

53 Here we combine PCA and hierarchical clustering of PFAS profiles measured in surface
54 waters from 37 rivers, streams and estuaries in the Northeastern United States with geospatial

55 analysis of potential sources. Few measurements are available for PFASs in U.S. surface waters
56 over the past five years and the importance of different sources is poorly understood. Source
57 regions for air pollution are commonly identified using back trajectories.^{12,13} We apply an
58 analogous approach for identifying sources of aquatic pollution based on hydrological
59 distances within a watershed. The main objective of this study is to identify major sources of
60 surface water PFAS contamination in diverse watersheds using information on chemical
61 composition and geospatial analytical tools that consider surface hydrology.

62 **Methods**

63 *Sample collection and analysis*

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

70 Samples were stored in one-liter pre-rinsed polypropylene bottles at -20 °C and thawed to
71 room temperature. Each sample was homogenized by shaking vigorously before subsampling
72 500 ml for the analysis of 21 PFASs. Each unfiltered sample was spiked with 20 µL of a 0.1 ng
73 µL⁻¹ mass labeled PFAS mixture (Wellington; Guelph, Canada; individual compounds are listed
74 in Table S2) as internal standards for quantification. PFASs were extracted using an Oasis Wax
75 solid phase extraction (SPE) cartridge (6 mL, 150 mg sorbent) following the method of Taniyasu
76 et. al.¹⁴ (see SI Section S1 for details). A nitrogen evaporator (ZIPVAP) was used to concentrate
77 the extract to 1 mL (methanol: water; v:v = 1:1).

78 Sample detection for 21 native PFASs (Tables S2, S3) was performed using an Agilent
79 6460 LC-MS/MS equipped with an online-SPE system (Agilent 1290 Infinity Flex Cube) in
80 dynamic multiple reaction mode (sample chromatogram in Figure S1). At least one negative
81 control (field or procedural blank) and one positive control (spiked with 2 ng of the 21 PFASs in
82 500 ml water) were included in every extraction batch. Whole method recovery tested using the
83 positive controls was 70-120% for all but 4 PFASs that ranged from 60-70%, which is
84 comparable to recoveries reported by previous studies.^{3,14,15} The 4 PFASs are perfluoropentanoate
85 (PFPeA), perfluoroheptanoate (PFHpA), N-methyl perfluorooctanesulfonamidoacetic acid
86 (MeFOSAA) and N-ethyl perfluorooctanesulfon-amidoacetic acid (EtFOSAA). Potential analyte
87 loss during sample preparation was corrected using internal standards spiked prior to sample
88 extraction. The limit of detection (LOD, Figure S2) was defined as equivalent to the blank plus
89 the concentration corresponding to a signal-to-noise ratio of three. Variability between duplicates
90 obtained at two sites was <20%. Concentrations of PFASs in five field blanks (HPLC grade
91 water) prepared following the sample preparation procedure were all below the LOD.

92 We quantified branched isomers for perfluorooctanoate (PFOA), perfluorohexane
93 sulfonate (PFHxS), perfluorooctane sulfonate (PFOS), N-MeFOSAA and N-EtFOSAA using
94 calibration standards for the linear isomers, assuming the same instrumental response factor
95 (Table S3). Seven compounds namely perfluorododecane sulfonate (PFDS), 8:2 fluorotelomer
96 sulfonate (8:2 FTS), perfluorooctane sulfonamide (FOSA), and perfluorocarboxylates with more
97 than 12 carbon atoms) were detected in less than half of samples and were excluded from
98 additional statistical analysis (see Table S2 for details). For the 14 PFASs that had detection
99 frequencies of greater than 60% (Table S2), we used the Robust Regression on Order Statistics

100 approach for censored log-normally distributed environmental data described by Helsel¹⁶ to
101 assign values to samples with concentrations below the LOD.

102 *Statistical and spatial analysis*

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

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

118 For all inland sites (non-estuarine), we acquired a list and geospatial data for plausible
119 PFAS sources from the US EPA Facility Registry Service (FRS) database on facilities and sites
120 subject to environmental regulation (see SI for the search criteria).⁸ These include airports,
121 facilities for metal plating/coating, printing, sewage treatment, waste management (including
122 landfills), and manufacturers of semiconductor, textile, paint/coating/adhesive, ink, paper, and

123 petroleum products. A caveat of this analysis is that not all facilities included in the FRS
124 database necessarily release PFASs and the database may not comprehensively include all
125 possible sources.

126 Hydrological distances of point sources from each sampling site were computed using the
127 ArcGIS Trace Downstream tool. Within each watershed, we defined an indicator for the impact
128 of potential point sources as a function of distance from sampling locations by assuming
129 exponential decay in the source signature¹⁹ (i.e., $impact = 1/e^d$, where d = hydrological distance,
130 km). This approach provides additional information on plausible sources that complements
131 multivariate statistical analysis but cannot be considered a quantitative estimate of contributions
132 to sampling locations since magnitudes of PFAS discharges are not available.

133 **Results and Discussion**

134 *Concentrations and spatial patterns*

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

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

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

150
151 Measured PFAS concentrations in urban regions were significantly higher (Wilcoxin rank
152 sum test, $p < 0.017$) than rural sites for all compounds except PFBS, N-MeFOSAA, PFUnDA and
153 PFDoDA (Figure S3). Sites 1-11 in RI and Sites 29-37 in NY/NJ are all urban areas, defined by
154 population densities of greater than 1000 individuals per square mile (2590 km²), and population
155 densities of greater than 500 individuals per square mile in surrounding census blocks.²⁷ We did
156 not find a statistically significant correlation between total population in each upstream
157 watershed and PFAS concentrations measured at each sampling site ($p = 0.12$ to 0.95 across
158 compounds). We derived per-capita discharges (Figure S4) using a similar approach as Pistocchi
159 and Loos.²⁸ Highest median per-capita discharges ($\mu\text{g person}^{-1} \text{ day}^{-1}$) across compounds, in
160 decreasing order, were for PFOA (27), PFHxA (14), PFHpA (10), PFOS (9), PFHxS (7), and
161 PFNA (5) (Figure S4). These are lower than previously reported in Europe ca. 2007 (e.g., PFOA:
162 $82 \mu\text{g person}^{-1} \text{ day}^{-1}$, PFOS: $57 \mu\text{g person}^{-1} \text{ day}^{-1}$).²⁸

163 ***Source identification***

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

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

172 Geospatial analysis of the watersheds for Sites 5, 19, 20 and 31 reveals a mixture of
173 potential sources (Figure S5). For Site 5, the greatest source impact as a function of distance
174 within the watershed is from T.F. Green Airport, the largest public airport in Rhode Island. Prior
175 work indicates uses of AFFF at modern airports release diverse PFASs to downstream aquatic
176 environments, including the compounds identified as part of the first PCA/cluster.^{4,29-31} For Sites
177 19 and 20, textile mills in the upstream watersheds have the highest impact as a function of
178 distance (Table S5). PFASs are used for water resistant coating in textiles and washing and
179 disposal of wastewater at textile mills provides a vector for their entry to the aquatic
180 environment. For Site 31, PCA scores suggest a mix of components 1-3 (Figure 2 c, d). This site
181 also clusters differently than Sites 19 and 20 (Figure 2b). The FRS database indicates the
182 watershed of Site 31 (Figure S5) contains diverse industrial sources that must account for this
183 profile including metal plating, printing, a landfill, petroleum and coal products manufacturing.
184 Overall, we conclude that the first PCA component and cluster of PFASs (PFOA, PFNA PFBS,
185 PFHxS, PFHxA, PFDA) represents a mixture of contemporary sources including airports and
186 textile mills.

187 The second component/cluster explains 19% of the variability in PFASs and includes two
188 long-chain PFASs (PFUnDA and PFDoDA) and two precursors to PFOS (N-MeFOSAA and N-
189 EtFOSAA) (Figure 2). PFUnDA and PFDoDA mainly originate from fluorotelomer alcohols or
190 other fluototelomer based products.³² Both N-MeFOSAA and N-EtFOSAA are intermediate
191 degradation products from the volatile parent compound N-alkyl
192 perfluorooctansulfonamidoethanol (FOSE) with PFOS as the final degradation product. This

193 profile is most pronounced at Site 3 along the Woonasquatucket River in RI and is also evident
194 at Site 1 (Slack's Tributary, RI) and Site 6 (Buckeye Brook, RI). For Site 3, the largest source
195 impact based on distance is from a wastewater treatment plant 1 km upstream. No industrial
196 facilities exist upstream of Sites 1 and 6. Landfill/waste management facilities are located within
197 2 km of all three sites but are not hydrologically connected to the sampling locations (Figure S5).
198 Both landfills and wastewater treatment plants are known atmospheric sources of fluorotelomer
199 alcohols and FOSE.³³ Concentrations of N-MeFOSAA, PFUnDA and PFDoDA were not
200 spatially variable at most sites and only slightly elevated at Site 3, consistent with an atmospheric
201 input pathway. We thus infer that this component is most likely attributable to sources from the
202 waste sector.

203 The third component explains 15% of the variability in PFASs and includes PFPeA,
204 PFOS, and 6:2 FTS. This component is most pronounced at Site 2 along the Woonasquatucket
205 River, within the City of Providence, RI. GIS analysis of the watershed at this site reveals the
206 presence of 14 metal coating/plating industries upstream (Figure 2d, Table S5, Figure S5). PFOS
207 was historically used as a mist/fume control agent in metal plating, in surface coatings and as the
208 major component in AFFFs for fighting petroleum related fire.^{25,26,34} Some PFOS applications
209 such as metal plating have been replaced by less stable fluorotelomer based chemicals such as
210 6:2 FtS,³⁵ which will eventually degrade into PFPeA and PFHxA (yields of 1.1% and 1.5% in
211 activated sludge).³⁶ It is likely that PFHxA is not included in the cluster because other direct
212 sources can contribute one order of magnitude more PFHxA than PFPeA.^{37,38} We conclude that
213 the distinct PFAS profile at Site 2 is can be explained by the metal plating industry.

214 **Implications**

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

228 **Supporting Information**

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

231 **ACKNOWLEDGMENTS**

232 We acknowledge financial support for this study from the Smith Family Foundation, the Harvard
233 John A. Paulson School of Engineering and Applied Sciences TomKat fund and the Harvard
234 NIEHS Center Grant (P30ES000002). X.Z. was partially supported by a Postdoctoral Fellowship
235 from the Natural Sciences and Engineering Research Council of Canada (PDF-437949-2013).
236 We thank Pete August (URI), Wenlu Zhao, Minggang Cai (Xiamen Univ.), Kirk Barrett

237 (Manhattan College) for assistance with sample collection and GIS data. We thank Linda Green
238 and Elizabeth Herron, University of Rhode Island Watershed Watch program
239 (<http://web.uri.edu/watershedwatch>) leaders as well as the many URI Watershed Watch
240 volunteer water quality monitors who collected water samples. RL acknowledges support from
241 the Hudson River Foundation (HRF 2011-5) and SERDP (ER-2538).

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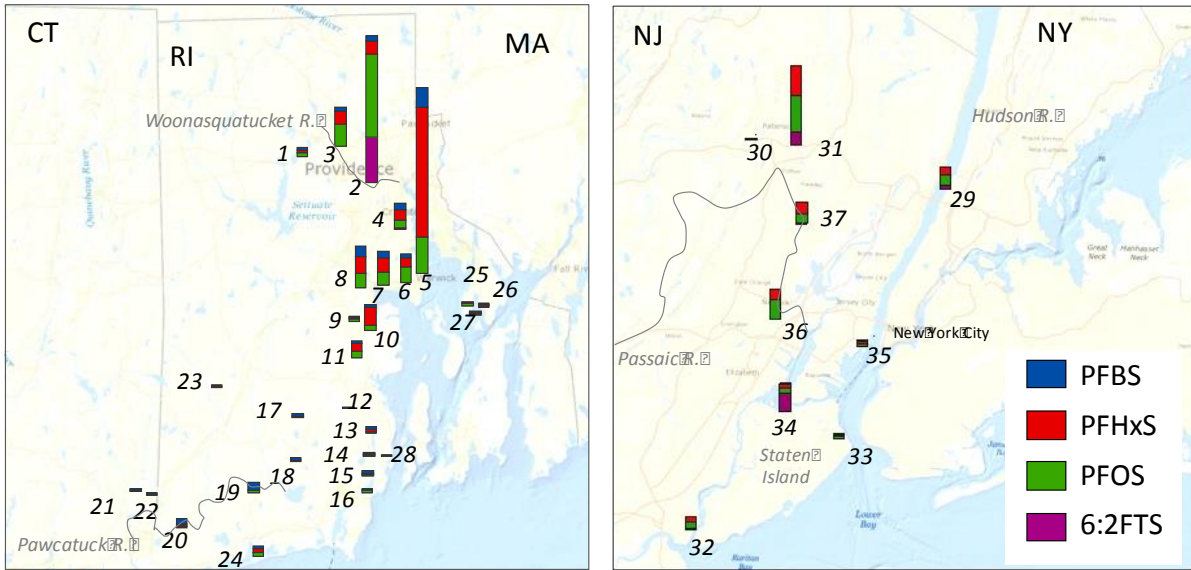
361

362 **Figure Captions**

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

367
368 **Figure 2.** Multivariate statistical analysis of surface water data. Panel (A) shows loadings of
369 principal components analysis (PCA) and Panels (C) and (D) show score plots for three
370 components across sampling sites. Panel (B) compares PCA results to hierarchical clustering of
371 compounds and sites. Sites with statistically distinct PFAS profiles are indicated on plots (C)
372 and (D) and highlighted on the hierarchical clustering diagram. The three principal components
373 together explain 80% of the variance in PFAS composition.

Per- and poly-fluoroalkane sulfonates 10 ng/L



Perfluorocarboxylates 30 ng/L

