

1 **Supporting Information**

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

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50 **Section S1: Supplemental Information on Methods**

51 **Sample Preparation and Instrumental Analysis**

52 PFASs were extracted from water samples using Oasis Wax (6 ml, 150 mg sorbent) solid phase
53 extraction (SPE) cartridges following the method of Taniyasu et al.¹ Each 500 ml water sample was
54 passed through a preconditioned Oasis Wax (6 ml, 150 mg sorbent) weak ion exchange SPE cartridge
55 mounted on a vacuum manifold at a flow rate of ~1 drop/s. Target analytes were eluted off the
56 cartridges using 6 ml 0.1% NH₄OH in methanol and collected in 15 ml centrifuge tubes (Corning). The
57 extracts were concentrated to 0.5 ml under a gentle stream of high purity nitrogen (5.0 grade),
58 centrifuged at 5000 rpm for 10 minutes, and transferred 1.5 ml polypropylene auto-sampler vials
59 (Microsolv). Before instrumental analysis, 0.5 ml water was added to each sample and vortex mixed.

60 A 300 µL aliquot of each sample was injected and loaded to an Agilent Zorbax SB-Aq
61 (4.6×12.5mm; 5µm) online SPE column with 0.85 ml 0.1% (v:v) formic acid at a flow rate of 1
62 ml/min. Following sample loading, the SPE were eluted and load the analytes to an Agilent Poroshell
63 120 EC-C18 (3.0×50mm; 2.7µm) reverse phase HPLC column. Methanol and water containing 2 mM
64 ammonium acetate were used as mobile phases (flow rate: 0.5 ml/min). Starting from 3% methanol,
65 the elution gradient was linearly increased to 61% in 7 minutes, held for 1 minute, then linearly
66 increased to 100% methanol in 3 min, and was kept until the end of the sample run (14 min).

67 The tandem mass spectrometer equipped with an electrospray ionization source was operated in
68 negative ion mode. Dynamic multiple reaction monitoring (dMRM) mode was used for data
69 acquisition in order to increase sensitivity. The collision gas was 5.0 grade N₂. Optimized MS
70 parameters are as follows: source temperature, 300 °C; capillary voltage, -3.8 kV; nitrogen nebulizer
71 gas, 45 psi and 13 L/min. Methanol was injected and passed through the system to eliminate any
72 potential carry-over after every sample (or calibration standard).

73 Shorter chain PFASs such as PFBA and 4:2 FtS were not analyzed due to their low retention on

74 the C-18 reverse phase HPLC column, which would result in a low accuracy.² A different analytical
75 method (e.g., using a normal phase HPLC column) that can accurately measure those shorter chain
76 PFASs is needed to detect these compounds and represents a limitation of the present analysis.

77 **Data analysis**

78 Helsel² suggests statistical inference bias may occur for data with detection frequencies of less
79 than 30%. PFASs with detection frequencies of 60-70% are included here because they are important
80 for source identification. We tested results of principal component analysis with and without PFASs
81 with low detection frequencies (60-65%: PFPeA, PFHpA, PFDoDA) and find no significant changes in
82 PCA scores (Wilcoxon signed rank tests ($p=0.06-0.5$) and clustering included in the main results of
83 this work.

84 Potential industrial PFAS point sources were retrieved from the US EPA Facility Registry
85 Service (FRS) database and used in the geospatial analysis conducted as part of this research. Filtering
86 of the database was based North American Industry Classification System (NAICS) codes. Facilities
87 and their coordinates were retrieved based on the following NAICS codes: Sewage treatment facilities
88 (22132); textile mills (313); paper manufacturing (322); printing and related support activities (323);
89 petroleum and coal products manufacturing (324); paint, coating, and adhesive manufacturing (3255);
90 printing ink manufacturing (32591); metal coating, engraving, heat treating and allied activities (3328);
91 semiconductor manufacturing (3344); airport operation (48811); waste management and remediation
92 (562)

93 **Section S2: Supporting Tables and Figures**

94 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 | Woonasquacket River | N | Urban | Metal coating/plating | 06/19/2014 | -71.44 | 41.82 |
| 3 | Woonasquacket 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 |

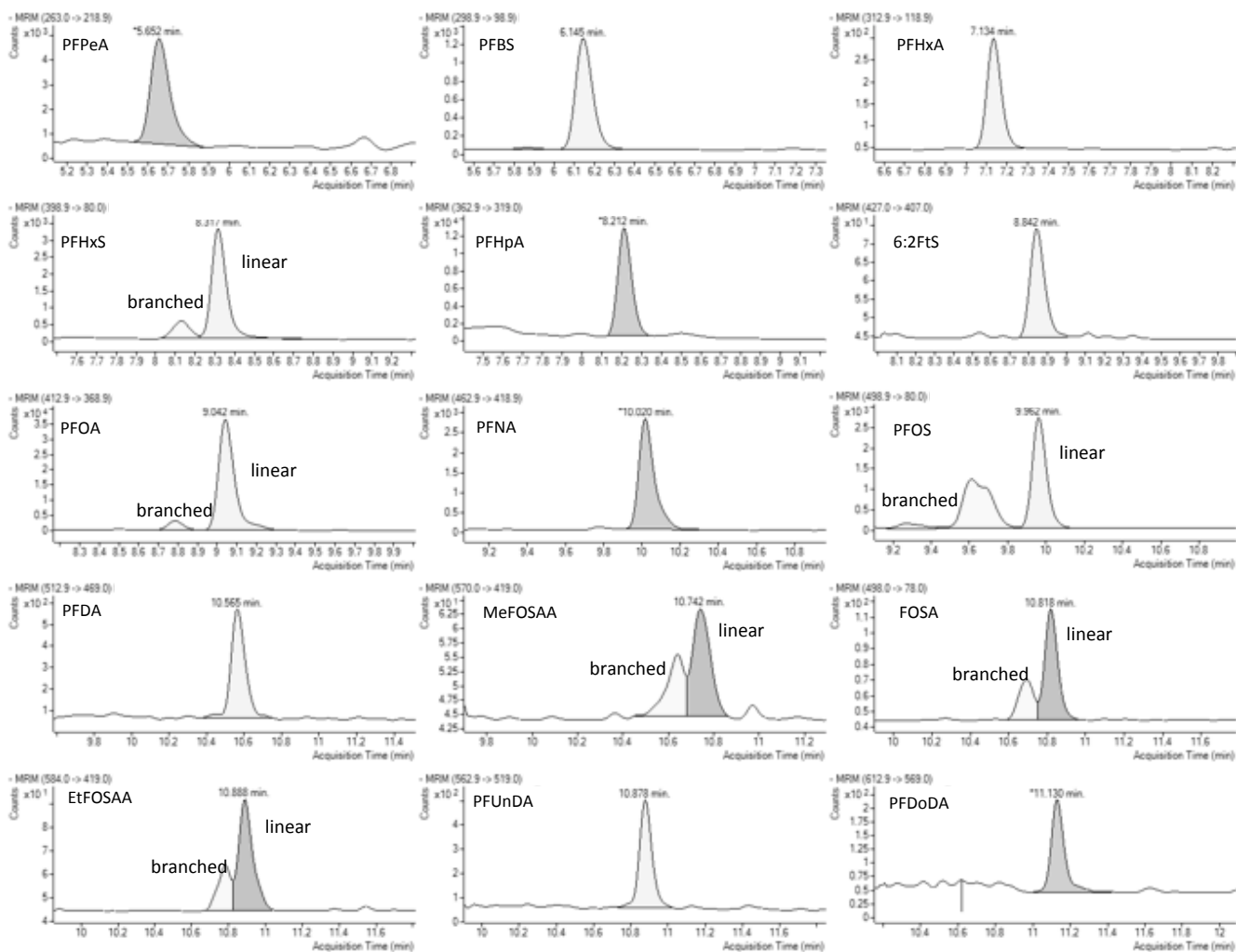
| Site | Location | Coastal | Urban/Rural | Potential sources | Date | Longitude | Latitude |
|------|---------------------------------------|---------|-------------|--|------------|-----------|----------|
| | River Lakeside Dr. | | | | 2014 | | |
| 15 | Narrow River | N | Rural | 2.5 km downstream of 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 | Chickasheem 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 occurred 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 |

96 Table S2. Full names and acronyms of PFASs measured in surface waters, limits of detection (LOD),
 97 concentration ranges measured across sites, and percent of sites with detection. PFASs measured in
 98 >60% of samples analyzed in this study are highlighted in bold

| PFAS | Acronym | # of carbons | Internal standard | LOD (ng/L) | Range (ng/L) | Detect. % |
|---|------------------|--------------|---------------------------------------|--------------|------------------|-------------|
| <i>Perfluorocarboxylates</i> | | <i>PFCAs</i> | | | | |
| Perfluoropentanoate | PFPeA | C5 | ¹³ C ₂ -PFHxA | 0.38 | BD – 10 | 62% |
| Perfluorohexanoate | PFHxA | C6 | ¹³ C ₂ -PFHxA | 0.29 | BD–48 | 87% |
| Perfluoroheptanoate | PFHpA | C7 | ¹³ C ₄ -PFOA | 0.62 | BD–48 | 64% |
| Perfluorooctanoate | PFOA | C8 | ¹³ C ₄ -PFOA | 0.07 | 0.27 – 47 | 100% |
| Perfluorononanoate | PFNA | C9 | ¹³ C ₅ -PFNA | 0.04 | 0.07 – 14 | 100% |
| Perfluorodecanoate | PFDA | C10 | ¹³ C ₂ -PFDA | 0.03 | BD – 5.8 | 92% |
| Perfluoroundecanoate | PFUnDA | C11 | ¹³ C ₂ -PFUnDA | 0.02 | BD –1.9 | 77% |
| Perfluorododecanoate | PFDoDA | C12 | ¹³ C ₂ -PFDoDA | 0.02 | BD–2.6 | 64% |
| Perfluorotridecanoate | PFTrDA | C13 | ¹³ C ₂ -PFDoDA | 0.02 | BD–1.2 | 31% |
| Perfluorotetradecanoate | PFTeDA | C14 | ¹³ C ₂ -PFDoDA | 0.02 | BD0.4 | 18% |
| Perfluorohexadecanoate | PFHxDA | C16 | ¹³ C ₂ -PFDoDA | 0.01 | BD–0.2 | 26% |
| Perfluorooctadecanoate | PFODA | C18 | ¹³ C ₂ -PFDoDA | 0.08 | BD–0.4 | 8% |
| <i>Perfluoroalkane sulfonates</i> | | <i>PFSAs</i> | | | | |
| Perfluorobutane sulfonate | PFBS | C4 | ¹⁸ O ₂ -PFHxS | 0.08 | BD–6.2 | 85% |
| Perfluorohexane sulfonate | PFHxS | C6 | ¹⁸ O ₂ -PFHxS | 0.06 | BD – 35 | 90% |
| Perfluorooctane sulfonate | PFOS | C8 | ¹³ C ₄ -PFOS | 0.05 | BD – 23 | 95% |
| Perfluorododecane sulfonate | PFDS | C10 | ¹³ C ₄ -PFOS | 0.07 | BD–0.6 | 15% |
| 6:2 fluorotelomer sulfonate | 6:2 FtS | | ¹³ C ₂ -6:2 FtS | 0.003 | BD – 15 | 97% |
| 8:2 fluorotelomer sulfonate | 8:2 FtS | | ¹³ C ₂ -6:2 FtS | 0.4 | BD–0.8 | 41% |
| Perfluorooctane sulfonamide | FOSA | C8 | ¹³ C ₈ -FOSA | 0.02 | BD–0.2 | 41% |
| N-ethyl perfluorooctanesulfonamidoacetic acid | N-EtFOSAA | | D ₅ N-EtFOSAA | 0.001 | BD-9.9 | 67% |
| N-methyl perfluorooctanesulfonamidoacetic acid | N-MeFOSAA | | D ₅ N-MeFOSAA | 0.002 | BD-0.6 | 69% |

99 BD = below detection.



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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.

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

| Site | PFPeA | PFHxA | PFHpA | PFOA ^a | PFNA | PFDA | PFUnDA | 106 107 |
|------|-------|-------|-------|-------------------|-------|------|--------|------------|
| 1 | 4550 | 2191 | 2409 | 2363 | 390 | 405 | 607 | 108 |
| 2 | 10357 | 12137 | 13577 | 8832 | 3134 | 1133 | 308 | 109 |
| 3 | <LOD | 6310 | 3371 | 5236 | 1476 | 894 | 1853 | 110 |
| 4 | 4228 | 7337 | 12301 | 7546 | 2735 | 957 | 114 | 111 |
| 5 | <LOD | 48414 | 48159 | 36806 | 13986 | 5625 | 1286 | 112 |
| 6 | 4359 | 5408 | 7640 | 8455 | 733 | 367 | 167 | 113 |
| 7 | 4828 | 6715 | 9236 | 10080 | 1275 | 205 | 46 | 114 |
| 8 | 5611 | 5649 | <LOD | 9237 | 923 | 176 | 48 | 115 |
| 9 | 927 | 1562 | 1597 | 1972 | 336 | 127 | 97 | 116 |
| 10 | 3064 | 2987 | 3090 | 6978 | 308 | 125 | <LOD | 117 |
| 11 | 6361 | 6678 | <LOD | 6905 | 799 | 226 | 177 | 118 |
| 12 | 555 | 565 | <LOD | 849 | 165 | 59 | 38 | 119 |
| 13 | 1413 | 1170 | <LOD | 1480 | 253 | 104 | <LOD | 120 |
| 14 | <LOD | 665 | <LOD | 663 | 104 | <LOD | 33 | 121 |
| 15 | 732 | 556 | <LOD | 851 | 136 | 31 | <LOD | 122 |
| 16 | 631 | 543 | <LOD | 946 | 174 | 87 | 62 | 123 |
| 17 | 681 | 550 | <LOD | 898 | 155 | 59 | 62 | 124 |
| 18 | 2138 | 663 | <LOD | 1006 | 293 | <LOD | <LOD | 125 |
| 19 | <LOD | 3740 | 11793 | 18974 | 6182 | 3808 | 482 | 126 |
| 20 | <LOD | 4138 | 9728 | 14985 | 7235 | 5824 | 888 | 127 |
| 21 | <LOD | <LOD | <LOD | 586 | 232 | 73 | 41 | 128 |
| 22 | <LOD | 493 | <LOD | 708 | 206 | 83 | <LOD | 129 |
| 23 | <LOD | <LOD | <LOD | 640 | 200 | 152 | 97 | 130 |
| 24 | 1221 | 2121 | 2479 | 3784 | 260 | 52 | 55 | 131 |
| 25 | 843 | 1214 | 897 | 1320 | 400 | 169 | 97 | 132 |
| 26 | 821 | 964 | 751 | 1014 | 323 | 134 | <LOD | 133 |
| 27 | 617 | 900 | 800 | 1170 | 355 | 166 | 78 | 134 |
| 28 | <LOD | <LOD | <LOD | 267 | 74 | 38 | <LOD | 135 |
| 29 | <LOD | <LOD | <LOD | 11862 | 2188 | 685 | 257 | 136 |
| 30 | <LOD | 815 | 947 | 871 | 151 | 59 | 28 | 137 |
| 31 | <LOD | <LOD | <LOD | 47254 | 6658 | 2154 | 464 | 138 |
| 32 | 3032 | 3529 | 3226 | 3738 | 601 | 301 | <LOD | 139 |
| 33 | 1870 | 1802 | 1907 | 2020 | 363 | 182 | 49 | 140 |
| 34 | 3434 | 5188 | 3431 | 4049 | 726 | 347 | 115 | 141 |
| 35 | 1111 | 1710 | 1852 | 2805 | 411 | 211 | 59 | 142 |
| 36 | 7998 | 9277 | 3426 | 15137 | 2022 | 719 | 238 | 143 |
| 37 | <LOD | 10901 | 8455 | 11335 | 757 | 152 | 79 | 144 |

^aLinear isomers with calibration standards for quantification

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

| Site | PFBS | PFHxS ^a | PFOS ^a | 6:2 FtS | MeFOSAA ^a | EtFOSAA ^a | PFDoDA ^a | 148 |
|------|------|--------------------|-------------------|---------|----------------------|----------------------|---------------------|-----|
| 1 | 669 | 864 | 777 | 15 | 241 | 348 | 618 | 149 |
| 2 | 1652 | 3758 | 23226 | 15292 | 147 | 278 | 89 | 150 |
| 3 | 1327 | 3583 | 5868 | 55 | 610 | 937 | 2598 | 151 |
| 4 | 2290 | 2558 | 2185 | 380 | 227 | 152 | 28 | 152 |
| 5 | 6181 | 35022 | 9804 | 239 | 113 | 240 | 117 | 153 |
| 6 | 1087 | 2637 | 4127 | 24 | 90 | 694 | 96 | 154 |
| 7 | 2102 | 4130 | 3743 | 30 | <LOD | 122 | <LOD | 155 |
| 8 | 3355 | 4664 | 3937 | 9 | 23 | 53 | 23 | 156 |
| 9 | 296 | 695 | 735 | 26 | 38 | 65 | 61 | 157 |
| 10 | 1161 | 5075 | 1477 | 8 | <LOD | 36 | <LOD | 158 |
| 11 | 546 | 2418 | 1822 | 5 | 106 | 94 | 313 | 159 |
| 12 | 278 | <LOD | <LOD | <LOD | 43 | 14 | 25 | 160 |
| 13 | 889 | 645 | 347 | 6 | <LOD | <LOD | <LOD | 161 |
| 14 | 368 | 476 | 176 | <LOD | <LOD | <LOD | <LOD | 162 |
| 15 | 705 | 421 | 180 | 10 | <LOD | <LOD | <LOD | 163 |
| 16 | 226 | 323 | 488 | 3 | 82 | <LOD | 131 | 164 |
| 17 | 466 | 372 | 334 | 7 | 82 | <LOD | 131 | 165 |
| 18 | 973 | 208 | <LOD | 10 | 27 | <LOD | <LOD | 166 |
| 19 | 2485 | <LOD | 509 | 10 | 60 | <LOD | 194 | 167 |
| 20 | 1465 | 361 | 612 | 4 | 159 | 24 | 35 | 168 |
| 21 | 92 | <LOD | 290 | 10 | 34 | <LOD | 24 | 169 |
| 22 | 341 | 133 | 292 | 13 | 39 | <LOD | <LOD | 170 |
| 23 | <LOD | 143 | 238 | 12 | <LOD | <LOD | 42 | 171 |
| 24 | 1185 | 916 | 1198 | 6 | 55 | 46 | 41 | 172 |
| 25 | 281 | 343 | 626 | 16 | <LOD | 49 | <LOD | 173 |
| 26 | 254 | 282 | 437 | 12 | 47 | <LOD | <LOD | 174 |
| 27 | 229 | 320 | 460 | 22 | 80 | 58 | <LOD | 175 |
| 28 | 131 | <LOD | 161 | 4 | <LOD | <LOD | <LOD | 176 |
| 29 | <LOD | 2149 | 2835 | 1087 | 160 | 148 | 59 | 177 |
| 30 | 220 | 224 | 244 | 69 | <LOD | <LOD | <LOD | 178 |
| 31 | <LOD | 8526 | 9988 | 4377 | 166 | 593 | 99 | 179 |
| 32 | <LOD | 1390 | 1929 | 464 | 32 | 59 | 25 | 180 |
| 33 | 226 | 408 | 755 | 58 | <LOD | 48 | 31 | 181 |
| 34 | 467 | 963 | 1661 | 5918 | <LOD | 92 | 34 | 182 |
| 35 | 278 | 640 | 790 | 82 | 33 | 31 | <LOD | 183 |
| 36 | <LOD | 3087 | 5384 | 89 | 40 | 57 | 99 | 184 |
| 37 | <LOD | 3162 | 2748 | 43 | <LOD | 18 | 128 | 185 |

^aLinear isomers with calibration standards for quantification

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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 |

^aBranched isomers were quantified based on peak areas assuming the same response factors as the linear isomers.

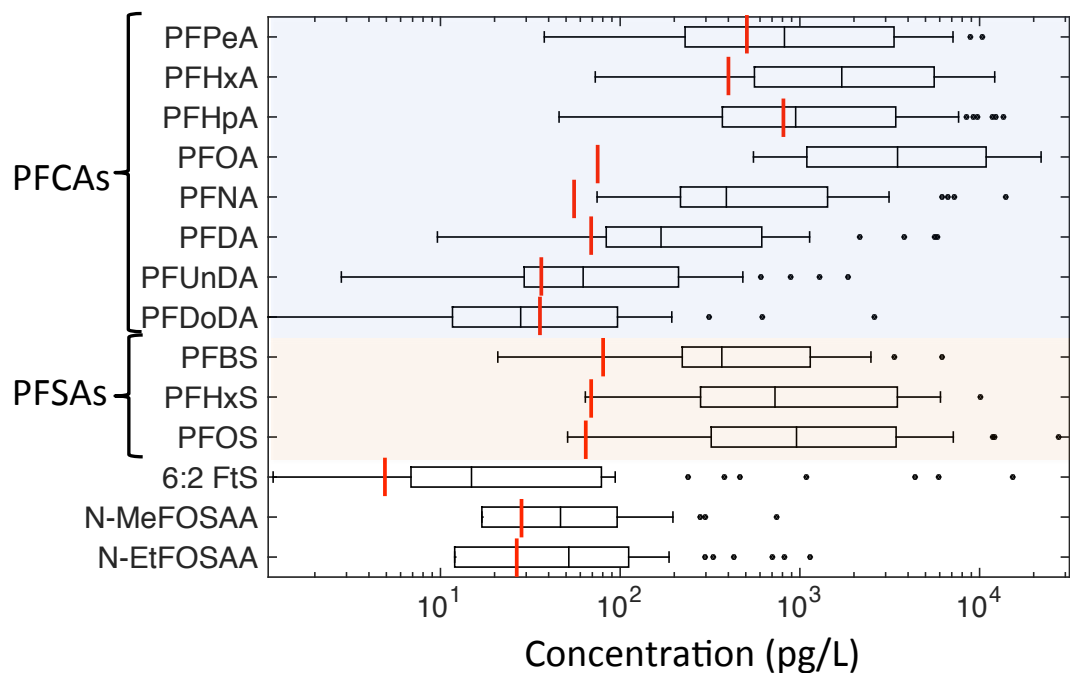
192 Table S4. PFAS concentrations measured in U.S. surface waters in this study and previous work.

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 |
| Georgia (n=11, 2006) ⁶ | | 23 | 329 | 287 | 194 | 120 | 52.1 | 4.46 | 9.41 | 35.1 | 132 |
| | | | | 3 | <0.6 | <0.1 | <0.1 | | | | 1 |
| | | | | 238 | 5.6 | 2.1 | <0.1 | | | | 6 |
| Upper Mississippi River Basin (n=177, 2008) ⁷ | | | | 1150 | 369 | 131 | 99 | | | | 318 |
| | <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 |
| Georgia (n=8, 2008) ⁸ | 31.5 | 53.4 | 90.2 | 125 | 72.9 | 42 | 29.1 | 24.7 | 84.1 | 169 | 245 |
| | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL |
| | 57 | 68 | 46 | 102 | 21 | 25 | | | 124 | 13 | 150 |
| New Jersey (n=12, 2009) ⁹ | 149 | 149 | 100 | 204 | 46 | 46 | | | 260 | 31 | 321 |
| | <5 | <5 | <5 | <5 | <5 | <5 | | | <5 | <5 | <5 |
| | <5 | <5 | <5 | 11 | <5 | <5 | | | <5 | <5 | <5 |
| Rhode Island and New York Metropolitan Region (n=37, 2014, this study)* | 15 | 17 | 10 | 100 | 19 | ND | | | 6 | 46 | 43 |
| | <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 |

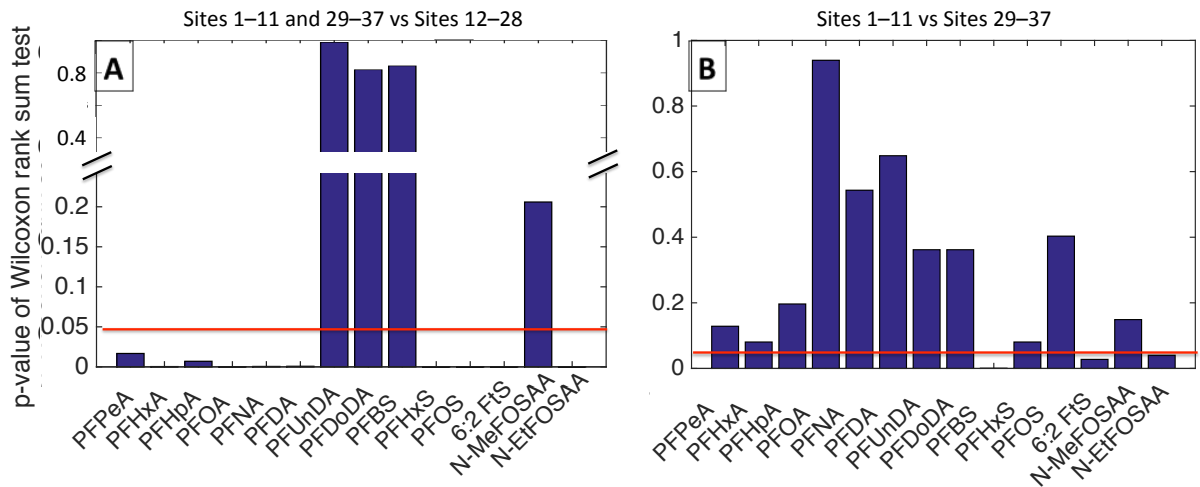
193 *PFOA, PFHxS and PFOS reported here include both linear and branched isomers. The branched
194 isomers were quantified based on peak areas assuming the same response factors as the linear isomers

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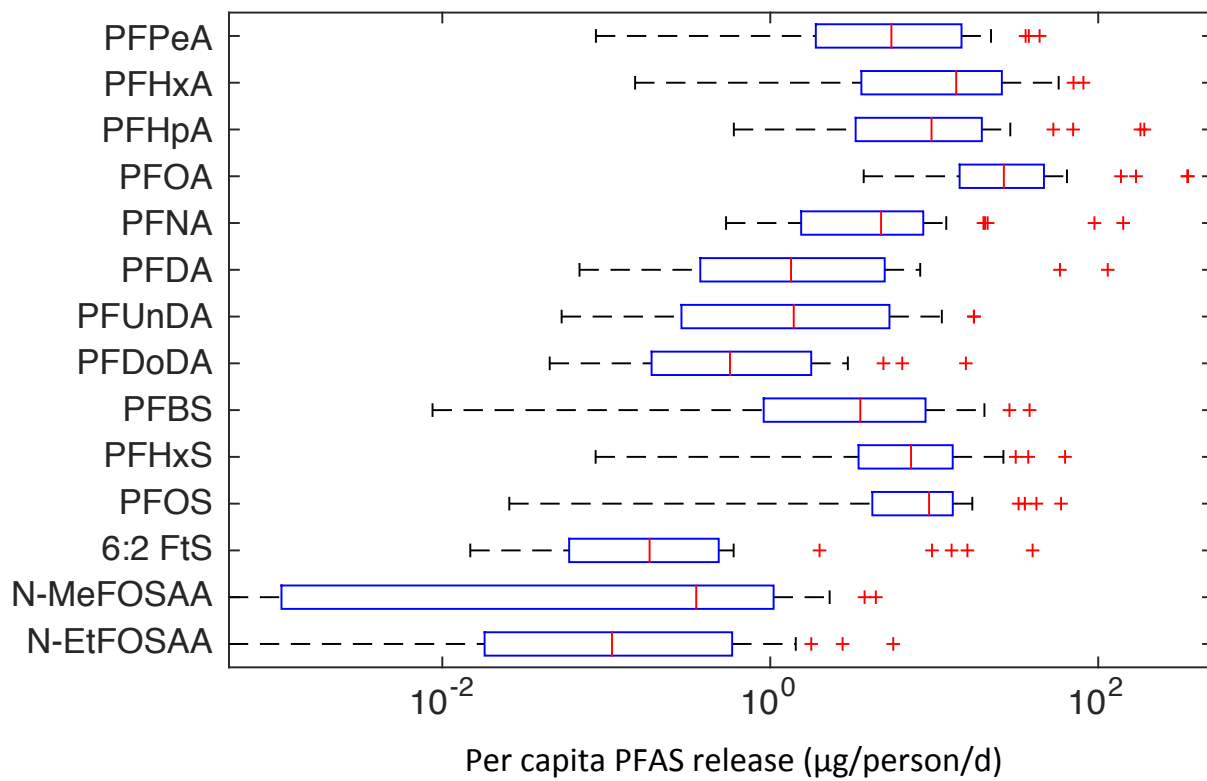
Figure S2. Concentrations of 14-PFASs measured in 37 rivers and estuaries in Rhode Island (RI) and the New York Metropolitan area (NY/NJ). The limit of detection (LOD) for each compound is shown as a red bar. Those below detection are assigned values based on the robust ROS (Regression on Order Statistics)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



203

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

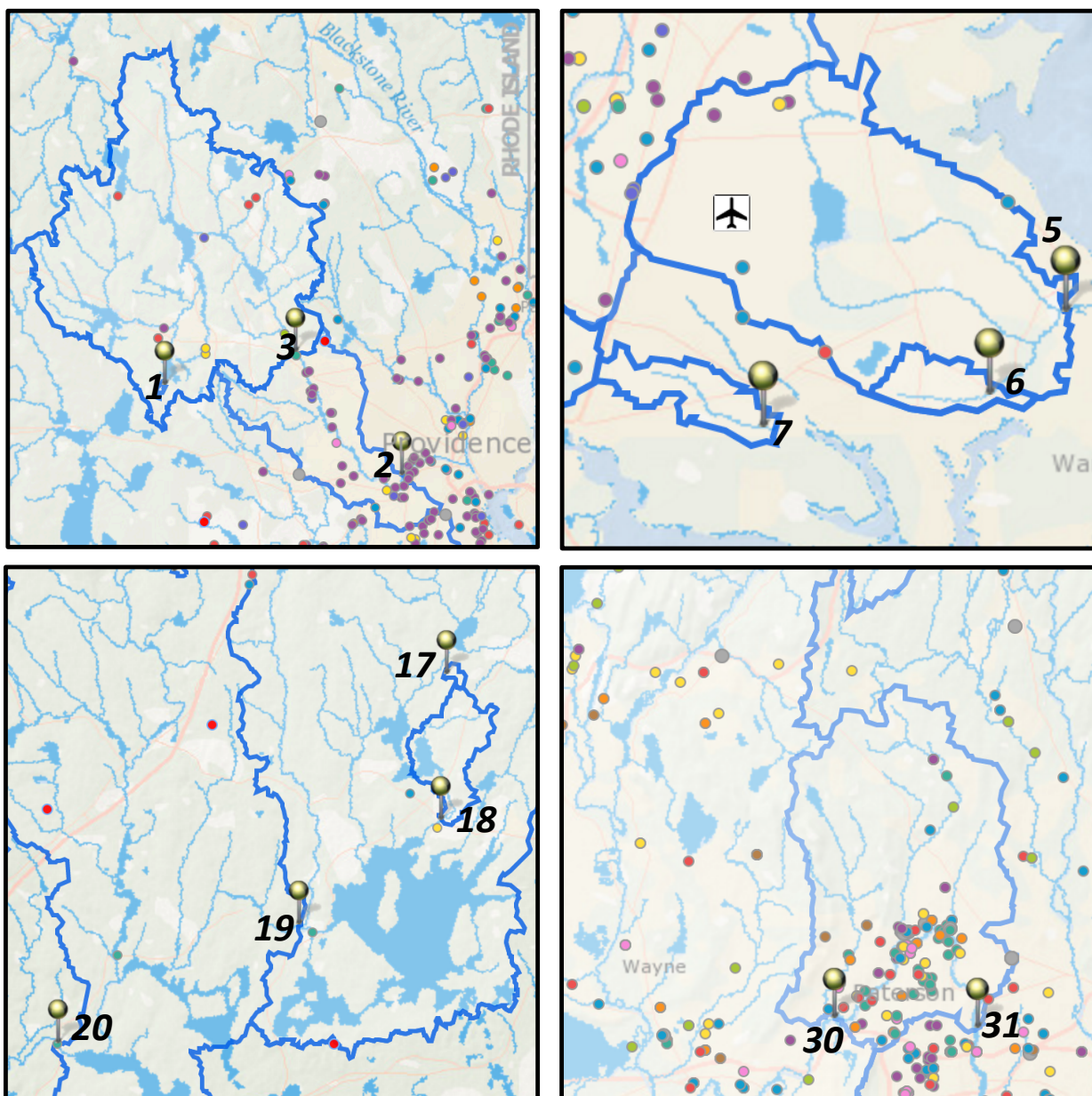
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210 Figure S4. Per-capita release of PFAS ($\mu\text{g}/\text{person}/\text{d}$) estimated based on measured PFAS
211 concentrations, water flow rate and upstream population at each sampling site.

- Waste Management
- Printing Activity
- Sewage Treatment
- Metal Coating Plating
- Paint, Coating, Adhesive Manufacturing
- Semiconductor Manufacturing
- Paper Manufacturing
- Petroleum Coal
- Textile Mills
- Petroleum Coal Products Manufacturing



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

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

| sites | Impact from facilities upstreams | | | | | | | | | | | | | |
|-------|----------------------------------|---------------------|---|-----------------------|--|---------------------|---------------------------------------|-------------------|----------------------------|-----------------------------|------------------|---------------|------------------------------------|---------|
| | 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 | |

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