2016

Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants

Xindi C. Hu

David Q. Andrews

Andrew B. Lindstrom

Thomas A. Bruton

Laurel A. Schaider

See next page for additional authors

Citation/Publisher Attribution

Hu, X. C., Andrews, D. Q., Lindstrom, A. B., Bruton, T. A., Schaider, L. A., Grandjean, P., Lohmann, R., Carignan, C. C., Blum, A., Balan, S. A., Higgins, C. P., & Sunderland, E. M. (2016). Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants. *Environ. Sci. Technol. Lett., 3*(10), 344-350.
Available at: http://dx.doi.org/10.1021/acs.estlett.6b00260

Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants

Authors

Xindi C. Hu, David Q. Andrews, Andrew B. Lindstrom, Thomas A. Bruton, Laurel A. Schaider, Philippe Grandjean, Rainer Lohmann, Courtney C. Carignan, Arlene Blum, Simona A. Balan, Christopher P. Higgins, and Elise M. Sunderland

This is a pre-publication author manuscript of the final, published article.

Detection of poly- and perfluoroalkyl substances (PFASs) in U.S. drinking water linked to industrial sites, military fire training areas and wastewater treatment plants

Author Contributor List:

Xindi C. Hu[*,1,2], David Q. Andrews[3], Andrew B. Lindstrom[4], Thomas A. Bruton[5], Laurel A. Schaider[6], Philippe Grandjean[1], Rainer Lohmann[7], Courtney C. Carignan[1], Arlene Blum[5,8], Simona A. Balan[9], Christopher P. Higgins[10], Elsie M. Sunderland[1,2]

[1] Harvard T.H. Chan School of Public Health, Boston, Massachusetts 02215, United States

[2] Harvard John A. Paulson School of Engineering and Applied Sciences, Cambridge, Massachusetts 02138, United States

[3] Environmental Working Group, Washington, D.C. 20009, United States

[4] U.S. Environmental Protection Agency, National Exposure Research Laboratory, Research Triangle Park, North Carolina 27711, United States

[5] University of California at Berkeley, Berkeley, California 94720, United States

[6] Silent Spring Institute, Newton, Massachusetts 02460, United States

[7] University of Rhode Island, Narragansett, Rhode Island 02882, United States

[8] Green Science Policy Institute, Berkeley, California 94705, United States

[9] California Department of Toxic Substances Control, 1001 I Street, Sacramento, California 95814, United States (Formerly at the Green Science Policy Institute, Berkeley, California 94705, United States)

[10] Colorado School of Mines, 1500 Illinois St, Golden, Colorado 80401, United States

Corresponding Author:

*Phone: 1-617-384-8839. E-mail: xhu@mail.harvard.edu. Mail: 128 Pierce Hall, Harvard University, Cambridge, Massachusetts, United States 02138.

Notes:

The authors declare no competing financial interest.

Abstract

Drinking water contamination with poly- and perfluoroalkyl substances (PFASs) poses risks to the developmental, immune, metabolic, and endocrine health of consumers. We present a spatial analysis of 2013-2015 national drinking water PFAS concentrations from the U.S. Environmental Protection Agency's (US EPA) third Unregulated Contaminant Monitoring Rule (UCMR3) program. The number of industrial sites that manufacture or use these compounds, military fire training areas, and wastewater treatment plants are all significant predictors of PFAS detection frequencies and concentrations in public water supplies. Among samples with detectable PFAS levels, each additional military site within a watershed's 8-digit hydrologic unit is associated with a 20% increase in PFHxS, a 10% increase in both PFHpA and PFOA, and a 35% increase in PFOS. The number of civilian airports with personnel trained in the use of aqueous film-forming foams (AFFFs) is significantly associated with the detection of PFASs above the minimum reporting level. We find drinking water supplies for 6 million U.S. residents exceed US EPA's lifetime health advisory (70 ng/L) for PFOS and PFOA. Lower analytical reporting limits and additional sampling of smaller utilities serving <10,000 individuals and private wells would greatly assist in further identifying PFAS contamination sources.

Introduction

Poly- and perfluoroalkyl substances (PFASs) are a large group of persistent anthropogenic chemicals used in industrial processes and commercial products over the past 60 years.[1] Widespread use and extreme resistance to degradation have resulted in the ubiquitous presence of these compounds in the environment. The 2011-2012 U.S. National Health and Nutrition Examination Survey reported detectable serum PFAS concentrations in virtually all individuals (97%).[2, 3] Human PFAS exposure has been linked to cancer, elevated cholesterol, obesity, immune suppression, and endocrine disruption.[4-6] Health concerns in the early 2000s prompted manufacturers in Europe and North America to phase out production of some long-chain PFASs.[7-10] Declines in production of these compounds have been offset by increases in developing regions such as Asia.[8] Limited available data suggest widespread exposure to replacement (short-chain) PFASs may also adversely affect human health.[11, 12]

Human PFAS exposure includes dietary sources, household dust, air, and drinking water.[13, 14] Exposure from drinking water is a serious concern due to the high aqueous solubility of many PFASs.[15, 16] Relatively low PFAS concentrations can lead to elevated exposures in the general population.[17] Elevated PFAS concentrations in U.S. drinking water have been reported in numerous regions,[15, 16, 18, 19] especially near industrial sites that produce or use them.[6, 16, 20] For example, perfluorooctanoic acid (PFOA) concentrations 190-fold higher than the lifetime health advisory (70 ng/L) recommended by the U.S. Environmental Protection Agency (US EPA)[21] were measured in drinking water near a fluorochemical facility in Washington, West Virginia where PFOA was used in fluoropolymer production.[18]

Many civilian airports and military fire training areas have been contaminated by PFASs contained in aqueous film-forming foams (AFFFs) that are widely used during firefighting training activities. Groundwater and surface waters surrounding these sites containing PFAS concentrations that are three to four orders of magnitude higher than the US EPA health advisory level for drinking water have been reported.[22, 23] Wastewater treatment plants (WWTPs) are another important PFAS source because these compounds are not removed by standard treatment methods[24] and labile precursors biodegrade, increasing concentrations in effluent relative to influent.[25, 26] Land application of approximately half of the biosolids generated by WWTPs may contribute to human exposure through subsequent contamination of water, food, livestock, and wildlife.[27]

Understanding nation-wide PFAS exposures from drinking water is important for identifying potentially vulnerable populations. However, previous studies have mainly focused on individual point sources of PFAS contamination and site-specific drinking water exposures.[15, 16] Here we develop a statistical framework for investigating whether increased PFAS concentrations in drinking water are associated with the number of point sources within a watershed (represented by an 8-digit hydrologic unit code, from here on abbreviated HUC). We used publicly available drinking water concentration data for six PFASs from the US EPA's third Unregulated Contaminant Monitoring Rule (UCMR3), including: perfluorobutane sulfonic acid (PFBS), perfluorohexane sulfonic acid (PFHxS), perfluoroheptanoic acid (PFHpA), PFOA, perfluorooctane sulfonic acid (PFOS), and perfluorononanoic acid (PFNA) (Table S1).[28] We discuss the utility of the UCMR3 database for identifying PFASs sources to U.S. drinking water supplies, locations of vulnerable populations, and priorities for future monitoring.

Methods

Drinking water data

Our analysis included analytical results for six PFASs in 36,149 drinking water samples from the US EPA's UCMR3 program collected between January 2, 2013 and December 9, 2015.[28] Samples cover all 4,064 public water supplies serving > 10,000 individuals. Data are also available for 800 public water supplies serving <10,000 individuals but this represents only a small fraction (0.5%) of the 144,165 in this category. Minimum reporting levels (MRLs) for the six PFASs analyzed are listed in Table S1.

One limitation of the UCMR3 database is that national data on system intakes for public water supplies are classified,[29] making it difficult to place them within a specific hydrological network. We therefore extracted the zip codes for areas served and aggregated data within 8-digit HUCs[30] to capture the most detailed hydrologic information that exceeds the spatial resolution of PFAS data (zip code areas). We used the highest reported PFAS concentrations when multiple systems were located within a single zip code and/or when multiple zip code areas were located within the same HUC.

PFAS point sources

Our spatial analysis (Figure S1) included point source information for: (a) 16 industrial sites listed in the US EPA's 2010/2015 PFOA Stewardship Program (Table S2);[31] (b) 8572 WWTPs;[32] (c) 290 military fire training areas that contain 664 military fire training sites;[33] and (d) 533 civilian airports that are compliant with Title 14 Code of Federal Regulations, Part 139 for personnel trained in the use of AFFF (from here on referred to as "AFFF certified airports").[34] PFASs produced and/or used vary across industrial sites and not all compounds were associated with all sites. For example, a fluorochemical manufacturing facility in Decatur, Alabama, produced both PFOS and PFOA,[35] while only PFOA was used in the manufacturing process of another fluorochemical production facility in Parkersburg, West Virginia.[36] We conducted a sensitivity analysis to examine the potential production misclassification bias by limiting industrial sites to include the ones that only produced or used each specific compound (Table S3). We used the Google Maps application program interface (API) to geocode coordinates based on addresses. Potentially important PFAS sources such as landfills, biosolids, and small industrial PFAS users could not be included in this analysis because comprehensive geospatial data are not available.

Spatial and statistical analysis

We used ArcMap 10.3.1 (ESRI) to explore statistical differences between the number of point sources in 8-digit HUCs with PFAS levels above and below detection. We developed a multivariate spatial regression model for watersheds with detectable PFASs that adjusts for correlations and co-location among point sources. A natural log transformation was used to normalize the distribution of individual PFASs. PFNA and PFBS were excluded from the spatial regression analysis due to low detection frequency (15 and 14 out of 1601 watersheds, respectively). We used Moran's I statistic to test for spatial dependence in the model residuals from an ordinary least square (OLS) regression and correct for spatial dependence in the final spatial regression model. Akaike Information Criterion[37] was used to compare the OLS and spatial regression models, where a lower value implies a better model fit. A series of cross-validation tests were also completed to assess the predictive capacity and stability of the final set of models. The OLS and spatial regression models were constructed using GeoDa 1.6 software,[38] and cross-validation was implemented in R version 3.1.3.

Results and Discussion

PFASs in U.S. drinking water

PFASs were detected at or above the MRLs in 194 out of 4,864 public water supplies, serving 16.5 million residents in 33 different states, three American territories (American Samoa, Northern Mariana Islands and Guam), and the Salt River Pima-Maricopa Indian Community. Drinking water from 13 states accounted for 75% of detections, including, by order of frequency of detection: California, New Jersey, North Carolina, Alabama, Florida, Pennsylvania, Ohio, New York, Georgia, Minnesota, Arizona, Massachusetts and Illinois (Figure 1). Detection frequencies for PFASs across the 4,864 public water supplies were 2.2% for PFOA, 2.0% for PFOS, 1.7% for PFHpA, 1.1% for PFHxS, and <0.003% for others.

Many detectable PFAS concentrations in the UCMR3 database are above chronic drinking water and water quality standards for other regions (i.e., surface water European Union: PFOS <1 ng/L; drinking water Sweden: sum of 7 PFASs < 90 ng/L; ground water State of New Jersey: PFNA <10 ng/L; drinking water State of Vermont: sum of PFOS and PFOA <20 ng/L).[39-42] A recent analysis developed a benchmark-dose for immunotoxicity in children and suggested a drinking water limit of approximately 1 ng/L for PFOS and PFOA.[26] Data from rodents that measured sensitive endpoints such as mammary gland development support a similar level.[26]

Six million people were served by 66 public water supplies that have at least one sample at or above the US EPA's 2016 health advisory for PFOS and PFOA (70 ng/L individually or combined). Concentrations ranged as high as 349 ng/L for PFOA, 1,800 ng/L for PFOS, and 56 ng/L for PFNA.

The detection frequency in drinking water sourced from groundwater was more than twice that from surface water (Table S4). Long-chain PFASs[43] (PFHxS, PFOS, PFOA, PFNA) were more frequently detected in groundwater and short-chain compounds (PFHpA, PFBS) were detected more frequently in surface waters. This may be due to both the original mode of environmental release (as an aerosol, application to soil, aqueous discharge) and the inverse relationship between PFAS mobility and chain length.[44] The MRLs (10-90 ng/L) in the UCMR3 database are up to two orders of magnitude higher than the limit of quantitation in most published studies,[45-49] and more than 10 times higher than the drinking water limit (1 ng/L) suggested by human and animal studies.[26, 50] Since PFASs are detectable in virtually all parts of the environment,[5, 7, 9, 13, 14, 20, 44, 51] we infer that the large fraction of samples below reporting limits (Table S4) is driven in part by high MRLs.

Sources surrounding locations with detectable PFASs

Our analysis indicates point sources are significantly more abundant in HUCs with detectable PFASs (two-sided t-test, p<0.05, Table 1, Figure S2). This includes drinking water samples from 1601 of the 2158 total U.S. HUCs. For example, HUCs with detectable PFOA levels (8% of the total) have more industrial sites, military fire training areas, AFFF certified airports, and WWTPs than those with concentrations below detection. These trends are observable across all PFASs. Similarly, HUCs with point sources have higher detection frequencies for PFASs (Table S5). For example, 10.4% of the HUCs with no military fire training areas have a detection of any PFAS, but this percentage increases to 28.2% for HUCs with at least one. One caveat is that imprecise information on public water supply intakes can cause misclassification bias. Systems that draw water upstream from point sources, such as Minneapolis and St. Paul in Minnesota, may not actually be affected as indicated the by aggregated spatial analysis.

Results of the spatial regression model

Spatial regression modeling explains 38-62% of the variance in drinking water concentrations for the four PFASs considered (Table 2). Each additional industrial site within a HUC is associated with an 81% increase in PFOA ($p<0.001$), which is the strongest statistical association across compounds and point sources. Increasing PFOS concentrations are positively associated with the number of industrial sites but this relationship is not statistically significant ($p=0.124$). The small number of sites that have manufactured or used PFOS likely accounts for the lack of a statistically significant relationship.

The number of military fire training areas within each HUC is positively associated with increasing levels of all PFOS, PFOA, PFHxS and PFHpA, and is statistically significant for PFHxS ($p=0.045$) and PFOS ($p=0.007$). Each additional military fire training area within the same HUC is associated with a 20% increase in PFHxS ($p=0.002$), 10% increase in PFHpA ($p=0.155$), 10% increase in PFOA ($p=0.111$) and 35% increase in PFOS ($p<0.001$). AFFFs typically contain relatively high concentrations of PFOS and PFHxS and their polyfluorinated precursors compared to other perfluorinated carboxylates,[23, 52-54] which is consistent with these statistical results.

We find a small but significant increase in PFOS and PFOA (2%, $p<0.01$) with each additional WWTP within the same HUC. This is consistent with the greater abundance but smaller quantities of PFASs released by WWTPs.[55] Similarly, results from Valsecchi et al. [51] show PFAS releases from WWTPs are important but less significant than fluoropolymer manufacturing facilities in Italy. The number of WWTPs may also be a proxy for other population-driven PFAS sources.

The number of AFFF certified airports is not significantly associated with PFAS concentrations in the current dataset. This may reflect misclassification bias because the certification used to identify airports indicates eligibility but not actual use of AFFF. The UCMR3 database contains limited data for smaller drinking water systems where localized reports of contamination from airports have been most abundant.[22, 56]

Current data limitations and future monitoring efforts

The UCMR3 database has several limitations that restrict its predictive power for identifying U.S. drinking water supplies likely to contain elevated levels of PFASs. Classification of geospatial data on intakes for public water supplies limits the spatial resolution of the current dataset and associated statistical models to a radius of 50 km (median radius of watersheds).[57, 58] Many of the impacted drinking water systems are groundwater systems and contaminated groundwater plumes are often much smaller than 50 km.[23, 53, 59]

Geospatial data are lacking for many potentially important PFAS point sources such as a wide-range of industries, landfills, biosolids application, and other AFFF-impacted sites where relatively smaller volumes of AFFF were released[27, 54, 60-67] Data on PFAS releases from smaller industrial facilities (e.g., plastics, textiles, paper, lubricants) are usually withheld as confidential business information and little information on airborne emissions is available for characterizing the importance of atmospheric releases and potential long-range transport. For example, biosolids application resulted in one of the largest PFAS drinking water contamination in Europe[68] but could not be included in this analysis because U.S. use data are not available on a national scale.

Sources not included in our spatial analysis are represented by the highly significant lambda (λ) coefficients (Table 2). Areas with high model residuals (greater than 1.5 standard deviation) mean that current information on sources cannot fully explain the high observed PFAS concentrations. The map of model residuals (Figure S3) can thus be used to guide high priority sampling regions in future work.

We found statistically greater abundance of point sources in watersheds with detectable PFASs, including AFFF certified airports. However, multivariate spatial regression models did not show a significant association between AFFF certified airports and concentrations of PFASs in nearby drinking water. Other studies have reported elevated PFAS concentrations in groundwater wells adjacent to AFFF certified airports.[22] Small drinking water systems and private wells may be disproportionately affected by PFASs originating from AFFF use at civilian airports but representative data for these small drinking water systems are not included in the UCMR3 program.[69]

Approximately 44.5 million U.S. individuals rely on private drinking water wells[70] and 52 million individuals rely on smaller public water supplies (< 10,000 served). The UCMR3 program includes 0.5% testing incidence for smaller public water supplies[71] and no testing of private wells, meaning that information on drinking water PFAS exposures is therefore lacking for almost 1/3 of the U.S. population.

Acknowledgements

We acknowledge financial support for research at Harvard from the Smith Family Foundation and a private donor. We thank Marcia Castro (Harvard) for her feedback on an earlier version of this manuscript and Jahred Liddie (Harvard) for his assistance with the sensitivity analysis. T.B.

was supported by the U.S. National Institute for Environmental Health Sciences (NIEHS) Superfund Research Program (Grant P42 ES004705) and the Superfund Research Center at University of California, Berkeley. This article was reviewed in accordance with the policy of the National Exposure Research Laboratory, U.S. Environmental Protection Agency, and approved for publication.

References:

1. Kissa, E., *Fluorinated surfactants and repellents*. 2nd ed.; CRC Press: 2001.
2. Lewis, R. C.; Johns, L. E.; Meeker, J. D., Serum Biomarkers of Exposure to Perfluoroalkyl Substances in Relation to Serum Testosterone and Measures of Thyroid Function among Adults and Adolescents from NHANES 2011–2012. *International Journal of Environmental Research and Public Health* **2015,** *12*, (6), 6098-6114.
3. US CDC *Fourth National Report on Human Exposure to Environmental Chemicals*; Centers for Disease Control and Prevention: United States, 2015.
4. Grandjean, P.; Andersen, E.; Budtz-Jørgensen, E.; et al., Serum vaccine antibody concentrations in children exposed to perfluorinated compounds. *JAMA* **2012,** *307*, (4), 391-397.
5. Braun, J. M.; Chen, A.; Romano, M. E.; Calafat, A. M.; Webster, G. M.; Yolton, K.; Lanphear, B. P., Prenatal perfluoroalkyl substance exposure and child adiposity at 8 years of age: The HOME study. *Obesity* **2015**, n/a-n/a.
6. Barry, V.; Winquist, A.; Steenland, K., Perfluorooctanoic acid (PFOA) exposures and incident cancers among adults living near a chemical plant. *Environ Health Perspect* **2013,** *121*, (11-12), 1313-1318.
7. Land, M.; de Wit, C. A.; Cousins, I. T.; Herzke, D.; Johansson, J.; Martin, J. W., What is the effect of phasing out long-chain per- and polyfluoroalkyl substances on the concentrations of perfluoroalkyl acids and their precursors in the environment? A systematic review protocol. *Environmental Evidence* **2015,** *4*, (1), 1-13.
8. OECD *Working Towards a Global Emission Inventory of PFASs:*; Environment Directorate, Organization for Economic Cooperation and Development: Paris, 2015.
9. Wang, Z.; Cousins, I. T.; Scheringer, M.; Buck, R. C.; Hungerbühler, K., Global emission inventories for C 4–C 14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: production and emissions from quantifiable sources. *Environment international* **2014,** *70*, 62-75.
10. Butenhoff, J. L.; Chang, S.-C.; Ehresman, D. J.; York, R. G., Evaluation of potential reproductive and developmental toxicity of potassium perfluorohexanesulfonate in Sprague Dawley rats. *Reproductive Toxicology* **2009,** *27*, (3), 331-341.
11. Birnbaum, L. S.; Grandjean, P., Alternatives to PFASs: Perspectives on the Science. *Environmental health perspectives* **2015,** *123*, (5), A104.

12. Caverly Rae, J. M.; Craig, L.; Slone, T. W.; Frame, S. R.; Buxton, L. W.; Kennedy, G. L., Evaluation of chronic toxicity and carcinogenicity of ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoate in Sprague–Dawley rats. *Toxicology Reports* **2015,** *2*, 939-949.

13. Vestergren, R.; Cousins, I. T., Tracking the Pathways of Human Exposure to Perfluorocarboxylates. *Environmental Science & Technology* **2009,** *43*, (15), 5565-5575.

14. D'Hollander, W.; de Voogt, P.; De Coen, W.; Bervoets, L., Perfluorinated Substances in Human Food and Other Sources of Human Exposure. In *Reviews of Environmental Contamination and Toxicology*, De Voogt, P., Ed. Springer New York: 2010; Vol. 208, pp 179-215.

15. Emmett, E. A.; Shofer, F. S.; Zhang, H.; Freeman, D.; Desai, C.; Shaw, L. M., Community exposure to perfluorooctanoate: relationships between serum concentrations and exposure sources. *J Occup Environ Med* **2006,** *48*, (8), 759-770.

16. Landsteiner, A.; Huset, C.; Williams, A.; Johnson, J., Biomonitoring for Perfluorochemicals in a Minnesota Community With Known Drinking Water Contamination. *Journal of Environmental Health* **2014,** *77*, (5), 14-19.

17. Hurley, S.; Houtz, E.; Goldberg, D.; Wang, M.; Park, J.-S.; Nelson, D. O.; Reynolds, P.; Bernstein, L.; Anton-Culver, H.; Horn-Ross, P.; Petreas, M., Preliminary Associations between the Detection of Perfluoroalkyl Acids (PFAAs) in Drinking Water and Serum Concentrations in a Sample of California Women. *Environmental Science & Technology Letters* **2016**.

18. Hoffman, K.; Webster, T. F.; Bartell, S. M.; Weisskopf, M. G.; Fletcher, T.; Vieira, V. M., Private Drinking Water Wells as a Source of Exposure to Perfluorooctanoic Acid (PFOA) in Communities Surrounding a Fluoropolymer Production Facility. In 2010.

19. Shin, H.-M.; Vieira, V. M.; Ryan, P. B.; Detwiler, R.; Sanders, B.; Steenland, K.; Bartell, S. M., Environmental Fate and Transport Modeling for Perfluorooctanoic Acid Emitted from the Washington Works Facility in West Virginia. *Environmental Science & Technology* **2011,** *45*, (4), 1435-1442.

20. US CDC, Perfluorochemical Serum Sampling in the vicinity of Decatur, Alabama, Morgan, Lawrence, and Limestone Counties. In 2013.

21. US EPA, Lifetime Health Advisories and Health Effects Support Documents for Perfluorooctanoic Acid and Perfluorooctane Sulfonate. In 2016.

22. Ahrens, L.; Norstrom, 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*, 33-8.

23. Moody, C. A.; Hebert, G. N.; Strauss, S. H.; Field, J. A., Occurrence and persistence of perfluorooctanesulfonate and other perfluorinated surfactants in groundwater at a fire-training area at Wurtsmith Air Force Base, Michigan, USA. *J Environ Monit* **2003,** *5*, (2), 341-5.

24. Schultz, M. M.; Higgins, C. P.; Huset, C. A.; Luthy, R. G.; Barofsky, D. F.; Field, J. A., Fluorochemical mass flows in a municipal wastewater treatment facility. *Environmental science & technology* **2006,** *40*, (23), 7350-7357.

25. Loganathan, B. G.; Sajwan, K. S.; Sinclair, E.; Senthil Kumar, K.; Kannan, K., Perfluoroalkyl sulfonates and perfluorocarboxylates in two wastewater treatment facilities in Kentucky and Georgia. *Water Res* **2007,** *41*, (20), 4611-20.

26. Post, G. B.; Cohn, P. D.; Cooper, K. R., Perfluorooctanoic acid (PFOA), an emerging drinking water contaminant: a critical review of recent literature. *Environmental research* **2012,** *116*, 93-117.

27. Lindstrom, A. B.; Strynar, M. J.; Delinsky, A. D.; Nakayama, S. F.; McMillan, L.; Libelo, E. L.; Neill, M.; Thomas, L., Application of WWTP biosolids and resulting perfluorinated compound contamination of surface and well water in Decatur, Alabama, USA. *Environmental science & technology* **2011,** *45*, (19), 8015-8021.

28. US EPA Third Unregulated Contaminant Monitoring Rule. https://http://www.epa.gov/dwucmr/occurrence-data-unregulated-contaminant-monitoring-rule - 3 (2016-05-23),

29. US EPA Why is only certain information made available to the public (PWS ID), but not facility location information (longitude and latitude)? https://safewater.zendesk.com/hc/en-us/articles/212078697-Why-is-only-certain-information-made-available-to-the-public-PWS-ID-but-not-facility-location-information-longitude-and-latitude-

30. USGS 1:250,000-scale Hydrologic Units of the United States. http://water.usgs.gov/GIS/metadata/usgswrd/XML/huc250k.xml

31. US EPA Per- and Polyfluoroalkyl Substances (PFASs) under TSCA. https://http://www.epa.gov/assessing-and-managing-chemicals-under-tsca/and-polyfluoroalkyl-substances-pfass-under-tsca

32. US EPA, Database associated with the Clean Watersheds Needs Survey (CWNS) 2008 Report to Congress. https://http://www.epa.gov/cwns/clean-watersheds-needs-survey-cwns-2008-report-and-data (accessed March 2014). **2008**.

33. US DoD DoD Inventory of Fire/Crash Training Area Sites (as of the end of FY 2014). https://assets.documentcloud.org/documents/2647381/List-of-Fire-amp-Crash-Training-Areas-EOY14.pdf (12-23),

34. FAA, Programs for Training of Aircraft Rescue and Firefighting Personnel. In U.S. Department of Transportation Federal Aviation Administration, AC No: 150/5210-17C, 2015.

35. 3M, Map, 3M-Decatur Manufacturing Facility. In *US EPA docket AR226-1484*, US Environmental Protection Agency: Washington, DC, 2003.

36. DuPont, DuPont Telomer Manufacturing Sites: Environmental Assessment of PFOA Levels in Air and Water. In *US EPA docket AR226-1534*, Agency, U. E. P., Ed. Washington, DC, 2003.

37. Akaike, H., A new look at the statistical model identification. *Automatic Control, IEEE Transactions on* **1974,** *19*, (6), 716-723.

38. Anselin, L.; Syabri, I.; Kho, Y., GeoDa: an introduction to spatial data analysis. *Geographical analysis* **2006,** *38*, (1), 5-22.

39. Livsmedelsverket, Riskhantering - PFAS i dricksvatten och fisk. In Swedish National Food Agency. Retrieved from http://www.livsmedelsverket.se/livsmedel-och-innehall/oonskade-amnen/miljogifter/pfas-poly-och-perfluorerade-alkylsubstanser/riskhantering-pfaa-i-dricksvatten/, 2016.

40. NJ DEP Ground Water Quality Standards - Class IIA by Constituent. http://www.nj.gov/dep/standards/ground water.pdf Accessed Feb 18 2016

41. EU, Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. In EU Environmental Quality Standards, 2013.

42. Vermont Perfluorooctanoic acid (PFOA) and Perfluorooctanesulfonic acid (PFOS) Vermont Drinking Water Health Advisory. https://anrweb.vt.gov/PubDocs/DEC/PFOA/PFOA%20-%20PFOS%20Health%20Advisories/Vermont/PFOA_PFOS_HealthAdvisory_June_22_2016.pdf

43. Buck, R. C.; Franklin, J.; Berger, U.; Conder, J. M.; Cousins, I. T.; de Voogt, P.; Jensen, A. A.; Kannan, K.; Mabury, S. A.; van Leeuwen, S. P. J., Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins. *Integrated Environmental Assessment and Management* **2011,** *7*, (4), 513-541.

44. Bergström, S., Transport of per-and polyfluoroalkyl substances in soil and groundwater in Uppsala, Sweden. **2014**.

45. Thompson, J.; Eaglesham, G.; Mueller, J., Concentrations of PFOS, PFOA and other perfluorinated alkyl acids in Australian drinking water. *Chemosphere* **2011,** *83*, (10), 1320-1325.

46. Taniyasu, S.; Kannan, K.; Wu, Q.; Kwok, K. Y.; Yeung, L. W. Y.; Lam, P. K. S.; Chittim, B.; Kida, T.; Takasuga, T.; Tsuchiya, Y.; Yamashita, N., Inter-laboratory trials for analysis of perfluorooctanesulfonate and perfluorooctanoate in water samples: Performance and recommendations. *Analytica Chimica Acta* **2013,** *770*, 111-120.

47. Eriksson, U.; Kärrman, A.; Rotander, A.; Mikkelsen, B.; Dam, M., Perfluoroalkyl substances (PFASs) in food and water from Faroe Islands. *Environmental Science and Pollution Research* **2013,** *20*, (11), 7940-7948.

48. 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. *Science of The Total Environment* **2016,** *541*, 74-82.

49. Munoz, G.; Vo Duy, S.; Budzinski, H.; Labadie, P.; Liu, J.; Sauvé, S., Quantitative analysis of poly- and perfluoroalkyl compounds in water matrices using high resolution mass spectrometry: Optimization for a laser diode thermal desorption method. *Analytica Chimica Acta* **2015,** *881*, 98-106.

50. Grandjean, P.; Budtz-Jorgensen, E., Immunotoxicity of perfluorinated alkylates: calculation of benchmark doses based on serum concentrations in children. *Environmental Health* **2013,** *12*, (1), 35.

51. Valsecchi, S.; Rusconi, M.; Mazzoni, M.; Viviano, G.; Pagnotta, R.; Zaghi, C.; Serrini, G.; Polesello, S., Occurrence and sources of perfluoroalkyl acids in Italian river basins. *Chemosphere* **2015,** *129*, 126-134.

52. Hebert, G. N.; Odom, M. A.; Craig, P. S.; Dick, D. L.; Strauss, S. H., Method for the determination of sub-ppm concentrations of perfluoroalkylsulfonate anions in water. *Journal of Environmental Monitoring* **2002,** *4*, (1), 90-95.

53. Houtz, E. F.; Higgins, C. P.; Field, J. A.; Sedlak, D. L., Persistence of perfluoroalkyl acid precursors in AFFF-impacted groundwater and soil. *Environmental science & technology* **2013,** *47*, (15), 8187-8195.

54. Anderson, R. H.; Long, G. C.; Porter, R. C.; Anderson, J. K., Occurrence of select perfluoroalkyl substances at U.S. Air Force aqueous film-forming foam release sites other

than fire-training areas: Field-validation of critical fate and transport properties. *Chemosphere* **2016,** *150*, 678-85.

55. Sinclair, E.; Kannan, K., Mass Loading and Fate of Perfluoroalkyl Surfactants in Wastewater Treatment Plants. *Environmental Science & Technology* **2006,** *40*, (5), 1408-1414.

56. Schaider, L. A.; Rudel, R. A.; Ackerman, J. M.; Dunagan, S. C.; Brody, J. G., Pharmaceuticals, perfluorosurfactants, and other organic wastewater compounds in public drinking water wells in a shallow sand and gravel aquifer. *Science of The Total Environment* **2014,** *468–469*, 384-393.

57. Pascual, P.; Stiber, N.; Sunderland, E., Draft guidance on the development, evaluation, and application of regulatory environmental models. *The Council for Regulatory Environmental Modeling. Office of Science Policy, Office of Research and Development. US Environmental Protection Agency, Washington DC* **2003**.

58. NRC, *Models in Environmental Regulatory Decision Making. National Research Council.Committee on Models in the Regulatory Decision Process*. National Academies Press: 2007.

59. Houtz, E. F.; Sutton, R.; Park, J.-S.; Sedlak, M., Poly- and perfluoroalkyl substances in wastewater: Significance of unknown precursors, manufacturing shifts, and likely AFFF impacts. *Water Research* **2016,** *95*, 142-149.

60. 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. *Environmental Toxicology and Chemistry* **2008,** *27*, (10), 2011-2018.

61. Clara, M.; Scheffknecht, C.; Scharf, S.; Weiss, S.; Gans, O., Emissions of perfluorinated alkylated substances (PFAS) from point sources--identification of relevant branches. *Water science and technology* **2008,** *58*, (1), 59.

62. Zhang, C.; Peng, Y.; Niu, X.; Ning, K., Determination of perfluoroalkyl substances in municipal landfill leachates from Beijing, China. *Asian Journal of Chemistry* **2014,** *26*, (13), 3833.

63. Busch, J.; Ahrens, L.; Sturm, R.; Ebinghaus, R., Polyfluoroalkyl compounds in landfill leachates. *Environmental Pollution* **2010,** *158*, (5), 1467-1471.

64. Huset, C. A.; Barlaz, M. A.; Barofsky, D. F.; Field, J. A., Quantitative determination of fluorochemicals in municipal landfill leachates. *Chemosphere* **2011,** *82*, (10), 1380-1386.

65. Blaine, A. C.; Rich, C. D.; Hundal, L. S.; Lau, C.; Mills, M. A.; Harris, K. M.; Higgins, C. P., Uptake of perfluoroalkyl acids into edible crops via land applied biosolids: Field and greenhouse studies. *Environmental science & technology* **2013,** *47*, (24), 14062-14069.

66. Sepulvado, J. G.; Blaine, A. C.; Hundal, L. S.; Higgins, C. P., Occurrence and fate of perfluorochemicals in soil following the land application of municipal biosolids. *Environmental science & technology* **2011,** *45*, (19), 8106-8112.

67. Rich, C. D.; Blaine, A. C.; Hundal, L.; Higgins, C. P., Bioaccumulation of perfluoroalkyl acids by earthworms (Eisenia fetida) exposed to contaminated soils. *Environ Sci Technol* **2015,** *49*, (2), 881-8.

68. Hölzer, J.; Midasch, O.; Rauchfuss, K.; Kraft, M.; Reupert, R.; Angerer, J.; Kleeschulte, P.; Marschall, N.; Wilhelm, M., Biomonitoring of Perfluorinated Compounds in Children and Adults Exposed to Perfluorooctanoate-Contaminated Drinking Water. *Environmental Health Perspectives* **2008,** *116*, (5), 651-657.

69. Minnesota Pollution Control Agency. Report of Investigation Activities at Select Firefighting Foam Training Areas and Foam Discharge Sites in Minnesota. In St.Paul, Minnesota, 2010.

70. Maupin, M. A.; Kenny, J. F.; Hutson, S. S.; Lovelace, J. K.; Barber, N. L.; Linsey, K. S. *Estimated use of water in the United States in 2010*; 2330-5703; US Geological Survey: 2014.

71. US EPA, Factoids: Drinking Water and Ground Water Statistics for 2009. In US Environmental Protection Agency Office of Water, Washington, DC., 2009.

Table 1. Mean abundance of point sources within 8-digit hydrologic unit codes (HUCs) with drinking water PFAS concentrations above and below method reporting limit in the UCMR3 program.

Compound	Mean abundance[a] within 8-digit hydrologic unit codes			
	Major industrial sites[b]	Military fire training areas	AFFF certified airports	WWTPs[c]
PFBS				
<90 ng/L (n=1587)	0.01	0.15	0.29	4.9
>90 ng/L (n=14)	0.21	0.71	0.50	14.6
p-value[d]	*0.206*	*0.105*	*0.148*	*0.069*
PFHxS				
<30 ng/L (n=1507)	0.01	0.13	0.27	4.8
>30 ng/L (n=94)	0.06	0.60	0.63	8.8
p-value	*0.056*	*<0.001*	*<0.001*	*<0.001*
PFHpA				
<10 ng/L (n=1509)	0.01	0.13	0.26	4.7
>10 ng/L (n=92)	0.09	0.57	0.67	9.7
p-value	*0.016*	*<0.001*	*<0.001*	*<0.001*
PFOA				
<20 ng/L (n=1473)	0.01	0.13	0.26	4.6
>20 ng/L (n=128)	0.05	0.52	0.56	9.5
p-value	*0.038*	*<0.001*	*<0.001*	*<0.001*
PFOS				
<40 ng/L (n=1487)	0.01	0.13	0.26	4.7
>40 ng/L (n=114)	0.05	0.54	0.57	8.9
p-value	*0.064*	*<0.001*	*<0.001*	*<0.001*
PFNA				
<20 ng/L (n=1586)	0.01	0.15	0.28	4.9
>20 ng/L (n=15)	0.13	1.13	1.13	20.1
p-value	*0.366*	*0.014*	*0.008*	*0.067*

[a] Mean abundance is calculated as the mean numbers of point sources within HUCs with PFASs above or below-detection.

[b] Only the major industrial sites participating in US EPA 2010/2015 PFOA Stewardship Program were included.

[c] Wastewater treatment plant.

[d] Two-sample t-test *p-values*.

Table 2. Spatial regression models for drinking water PFAS concentrations as a function of abundance of point sources.

Compound	Major industrial sites[a]	MFTAs[b]	AFFF certified airports	WWTPs[c]	λ[d]	R^2
PFHxS						
Coefficient[e]	24%	20%	-13%	1%	94%	0.62
p-value[f]	*0.249*	*0.002*	*0.073*	*0.045*	*<0.001*	
PFHpA						
Coefficient	10%	10%	-2%	0.5%	72%	*0.40*
p-value	*0.569*	*0.155*	*0.761*	*0.436*	*<0.001*	
PFOA						
Coefficient	81%	10%	-6%	2%	52%	*0.38*
p-value	*<0.001*	*0.111*	*0.353*	*0.006*	*<0.001*	
PFOS						
Coefficient	46%	35%	-6%	2%	79%	0.46
p-value	*0.124*	*<0.001*	*0.512*	*0.007*	*<0.001*	

[a] Only the major industrial sites participating in US EPA 2010/2015 PFOA Stewardship Program were included.

[b] MFTA = military fire training area.

[c] WWTP = wastewater treatment plant.

[d] Coefficient for the spatial error term characterizing spatial influence.

[e] Results have been transformed to reflect expected changes in drinking water concentrations per increase in the abundance of different sources. Positive coefficients in the results indicate increasing concentrations with increasing abundance of point sources within the same hydrologic unit.

[f] *p*-values for spatial error regression model. The spatial error term is used to incorporate spatial autocorrelation structures into a linear regression model.

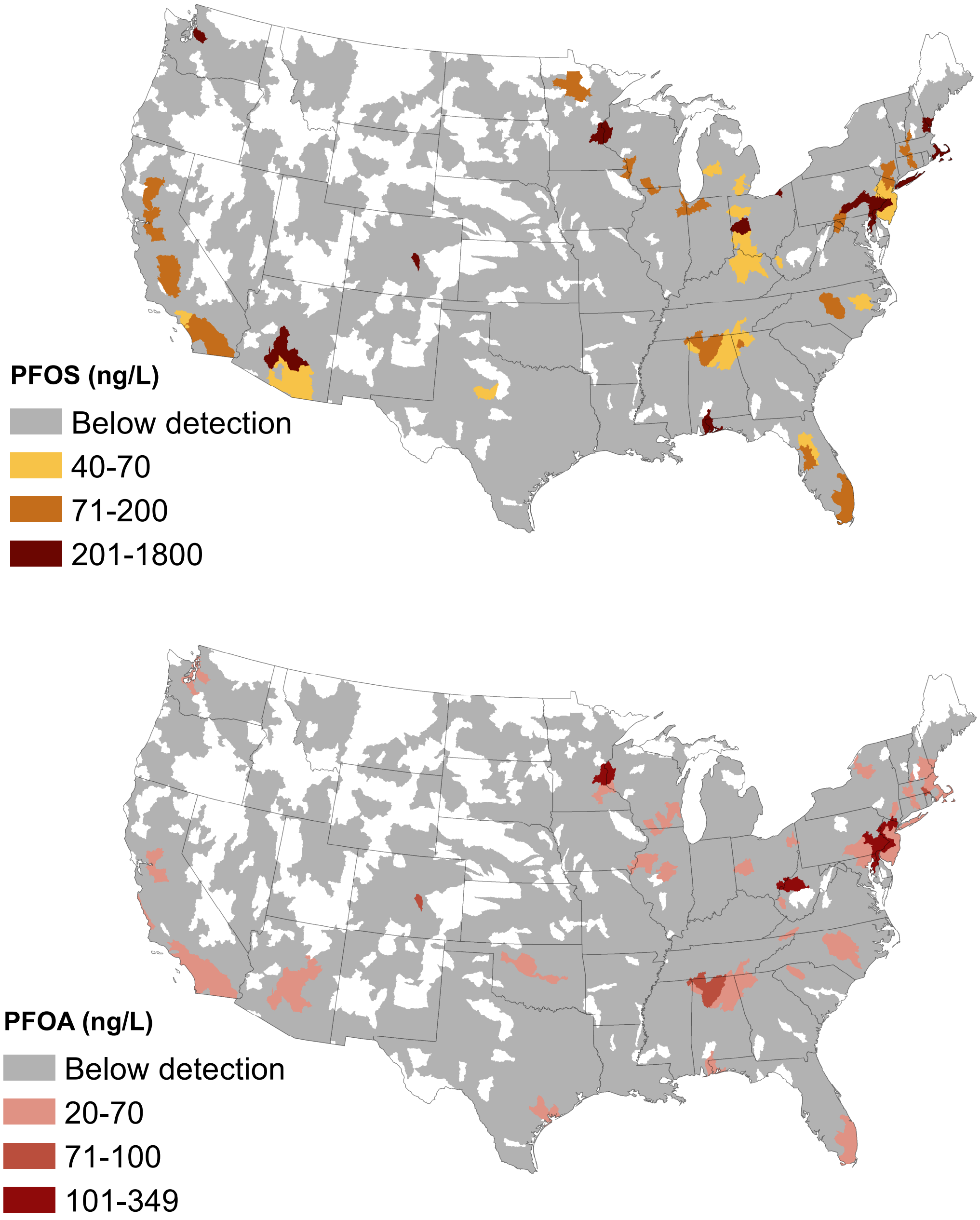
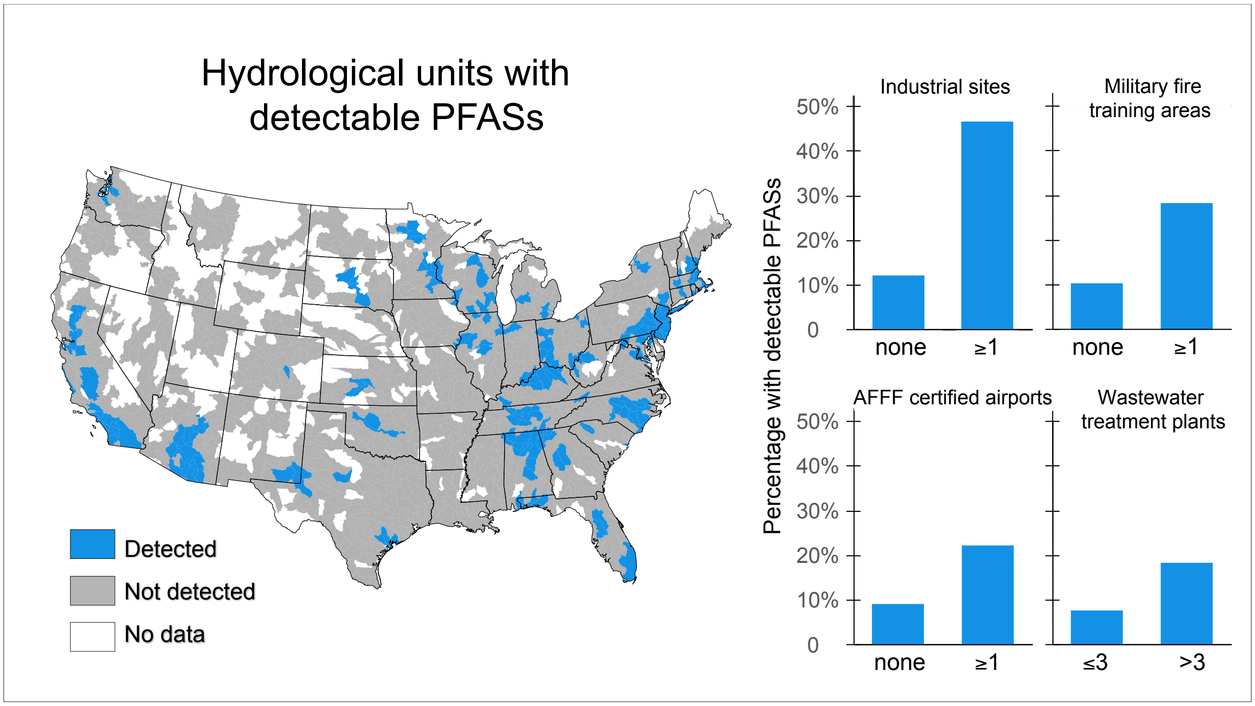


Figure 1. Hydrologic unit codes (8-digit HUCs) used as a proxy for watersheds with detectable PFOA and PFOS in drinking water measured in the US EPA's UCMR3 program (2013-2015). Blank areas represent regions where no data are available.


Hydrological units with detectable PFASs
Detected
Not detected
No data
Percentage with detectable PFASs
Industrial sites
Military fire training areas
AFFF certified airports
Wastewater treatment plants
50%
40%
30%
20%
10%
0
none
≥1
none
≥1
none
≥1
≤3
>3

TOC Art