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

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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.

183

184 **Results of the spatial regression model**

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

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

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

206 The number of AFFF certified airports is not significantly associated with PFAS
207 concentrations in the current dataset. This may reflect misclassification bias because the
208 certification used to identify airports indicates eligibility but not actual use of AFFF. The
209 UCMR3 database contains limited data for smaller drinking water systems where localized
210 reports of contamination from airports have been most abundant.[22, 56]
211
212 **Current data limitations and future monitoring efforts**
213 The UCMR3 database has several limitations that restrict its predictive power for
214 identifying U.S. drinking water supplies likely to contain elevated levels of PFASs.
215 Classification of geospatial data on intakes for public water supplies limits the spatial resolution
216 of the current dataset and associated statistical models to a radius of 50 km (median radius of
217 watersheds).[57, 58] Many of the impacted drinking water systems are groundwater systems and
218 contaminated groundwater plumes are often much smaller than 50 km.[23, 53, 59]
219 Geospatial data are lacking for many potentially important PFAS point sources such as a
220 wide-range of industries, landfills, biosolids application, and other AFFF-impacted sites where
221 relatively smaller volumes of AFFF were released[27, 54, 60-67] Data on PFAS releases from smaller
222 industrial facilities (e.g., plastics, textiles, paper, lubricants) are usually withheld as confidential
223 business information and little information on airborne emissions is available for characterizing
224 the importance of atmospheric releases and potential long-range transport. For example,
225 biosolids application resulted in one of the largest PFAS drinking water contamination in
226 Europe[68] but could not be included in this analysis because U.S. use data are not available on a
227 national scale.

228 Sources not included in our spatial analysis are represented by the highly significant
229 lambda (λ) coefficients (Table 2). Areas with high model residuals (greater than 1.5 standard
230 deviation) mean that current information on sources cannot fully explain the high observed
231 PFAS concentrations. The map of model residuals (Figure S3) can thus be used to guide high
232 priority sampling regions in future work.
233 We found statistically greater abundance of point sources in watersheds with detectable
234 PFASs, including AFFF certified airports. However, multivariate spatial regression models did
235 not show a significant association between AFFF certified airports and concentrations of PFASs
236 in nearby drinking water. Other studies have reported elevated PFAS concentrations in
237 groundwater wells adjacent to AFFF certified airports.[22] Small drinking water systems and
238 private wells may be disproportionately affected by PFASs originating from AFFF use at civilian
239 airports but representative data for these small drinking water systems are not included in the
240 UCMR3 program.[69]
241 Approximately 44.5 million U.S. individuals rely on private drinking water wells[70] and
242 52 million individuals rely on smaller public water supplies (< 10,000 served). The UCMR3
243 program includes 0.5% testing incidence for smaller public water supplies[71] and no testing of
244 private wells, meaning that information on drinking water PFAS exposures is therefore lacking
245 for almost 1/3 of the U.S. population.
246
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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	WWTP[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	9.4
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.

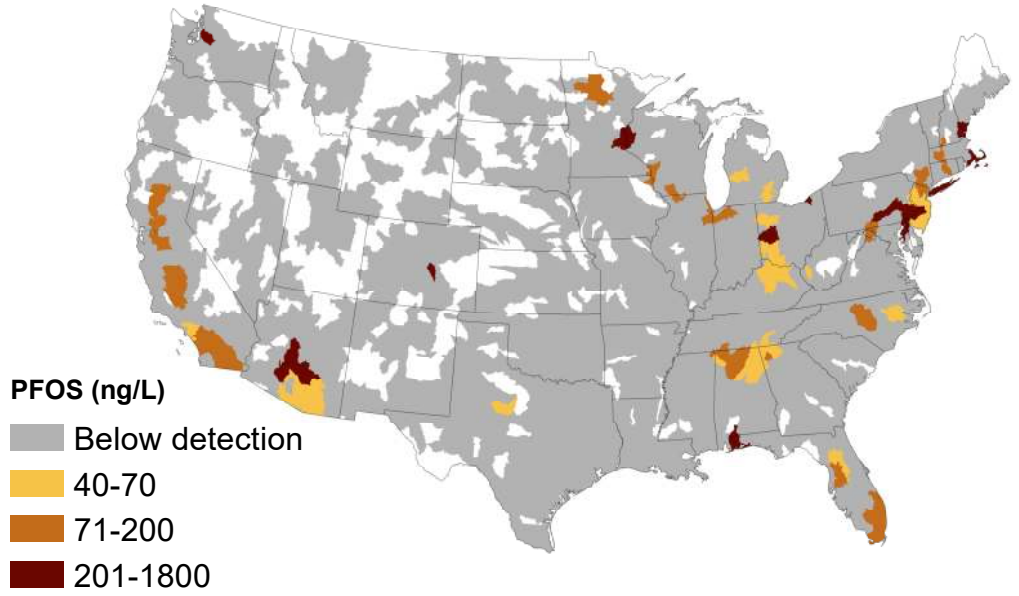
[c] Wastewater treatment plant.

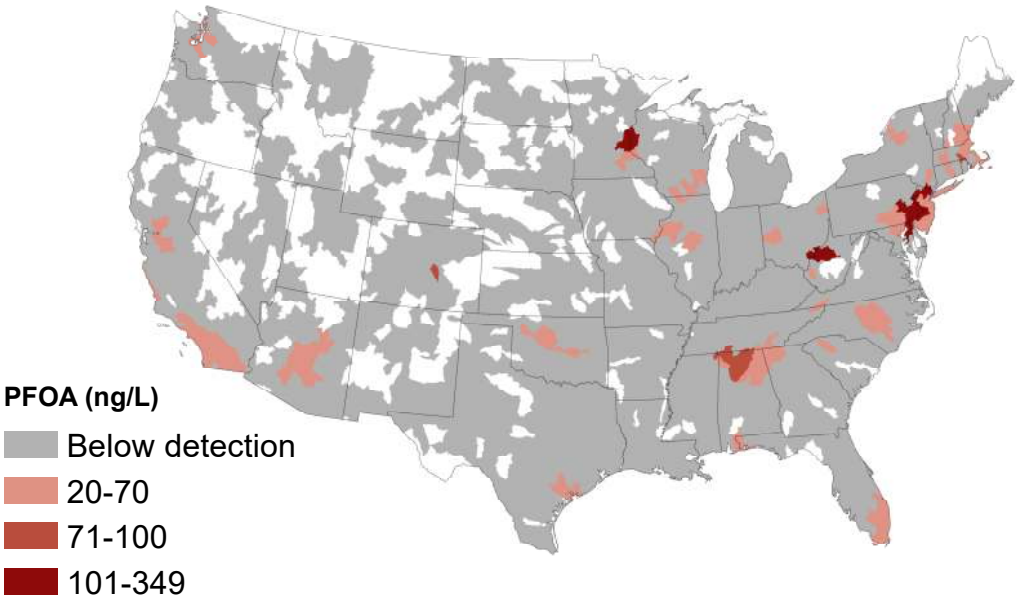
[d] Two-sample t-test *p-values*.

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.





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535 Figure 1. Hydrologic unit codes (8-digit HUCs) used as a proxy for watersheds with detectable

536 PFOA and PFOS in drinking water measured in the US EPA's UCMR3 program (2013-2015).

537 Blank areas represent regions where no data are available.

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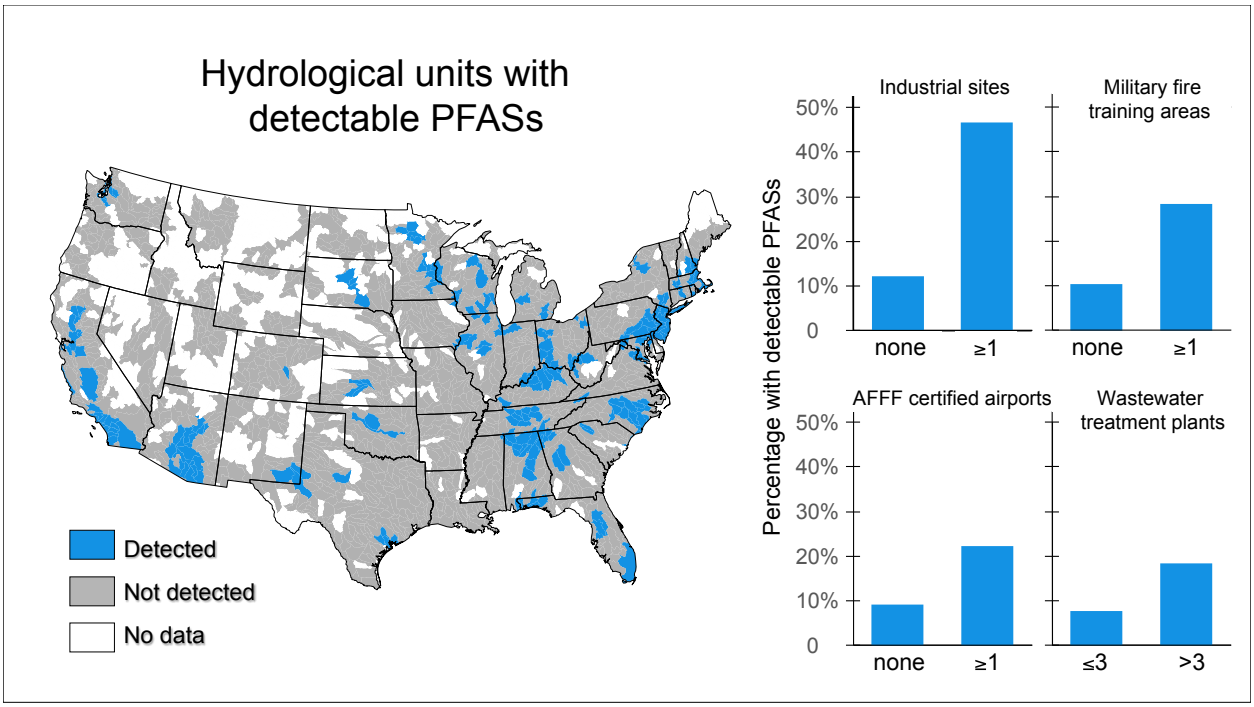

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