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Evaluation of a national data set for insights into sources, composition, and concentrations of per- and polyfluoroalkyl substances (PFASs) in U.S. drinking water☆

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ABSTRACT

The United States Environmental Protection Agency (USEPA) completed nationwide screening of six perfluoroalkyl substances in U.S. drinking water from 2013 to 2015 under the Third Unregulated Contaminant Monitoring Rule (UCMR3). UCMR3 efforts yielded a dataset of 36,139 samples containing analytical results from >5000 public water systems (PWSs). This study used UCMR3 data to investigate three aspects of per- and polyfluoroalkyl substances (PFASs) in drinking water: the occurrence of PFAS and co-contaminant mixtures, trends in PFAS detections relative to PWS characteristics and potential release types, and temporal trends in PFAS occurrence. This was achieved through bivariate and multivariate analyses including categorical analysis, concentration ratios, and hierarchical cluster analysis. Approximately 50% of samples with PFAS detections contained $\geq$2 PFASs, and 72% of detections occurred in groundwater. Large PWSs (>10,000 customers) were 5.6 times more likely than small PWSs ($\leq$10,000 customers) to exhibit PFAS detections; however, when detected, median total PFAS concentrations were higher in small PWSs (0.12 μg/L) than in large (0.053 μg/L). Bivariate and multivariate analyses of PFAS composition suggested PWSs reflect impacts due to firefighting foam use and WWTP effluent as compared to other source types for which data were available. Mann-Kendall analysis of quarterly total PFAS detection rates indicated an increasing trend over time ($p = 0.03$). UCMR3 data provide a foundation for tiered design of targeted sampling and analysis plans to address remaining knowledge gaps in the sources, composition, and concentrations of PFASs in U.S. drinking water.

1. Introduction

The occurrence of per- and polyfluoroalkyl substances (PFASs) in the environment is a critical concern due to prevalence of use and release (Buck et al., 2011; Prevedouros et al., 2006), concerns about toxicity (DeWitt, 2015; Lau et al., 2007; USEPA, 2016b, 2016a), and known exposures (Braun et al., 2016; Frisbee et al., 2010). PFASs have been used in a wide variety of products and applications due to their unique chemistry that includes surface activity, resistance to chemical and biological degradation, and both hydro- and oleophobicity. PFAS applications and products include fluoropolymer manufacturing, stain and water repellant coatings, and certain classes of firefighting foams called aqueous film forming foams (AFFF) (Buck et al., 2011; Kissa, 2001). Resistance to degradation also causes the environmental persistence of some PFASs (Krafft and Riess, 2015) such perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS), which are considered recalcitrant (Merino et al., 2016; USEPA, 2016a; USEPA, 2016b). Persistent PFASs are not expected to degrade when discharged to water, air, or soil.

To date many studies have focused on perfluoroalkyl substances, particularly PFOA and PFOS. Perfluoroalkyl substances are recalcitrant and contain an alkyl tail with all carbons bonded to fluorine. There are also a wide range of polyfluoroalkyl substances, which still have at least one perfluoroalkyl moiety (C_nF_{2n+1}) but also contain carbons bonded to hydrogen, and these compounds are capable of transformation in the environment (Buck et al., 2011). Polyfluoroalkyl substances are sometimes referred to as precursors because of their ability to transform to recalcitrant, perfluoroalkyl terminal endpoints following release in the environment (Harding-

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Marjanovic et al., 2015; Mejia Avendaño and Liu, 2015; Knepper and Lange, 2012). Release of a single precursor may result in formation of multiple intermediate PFAS transformation products with different perfluoroalkyl endpoints. This process may lead to increases in perfluoroalkyl substance concentrations with time and/or distance from the release source (Ahrens and Bundschuh, 2014; Weber et al., 2017). It is unlikely that any PFAS-impacted site will be characterized by a single PFAS species; rather, it is expected that there will invariably be mixtures of PFAS involved. These PFAS mixtures will likely be found in the environment for reasons ranging from multiple sources present in a region, the general use of PFASs as mixtures even in a single product (e.g., AFFF), and finally the changes in commonly used PFASs over time such as those precipitated by the phase-out of PFOS and PFOA in the U.S. and other countries (Buck et al., 2011; CONCAWE, 2016). PFASs may also co-occur in with other (i.e. non-PFAS) contaminants. For example, application of AFFF to fuel fires has led to groundwater plumes containing PFASs and hydrocarbon constituents (McGuire et al., 2014).

It is possible to gain insights regarding sources of PFAS releases based on composition, concentrations, and temporal trends observed in occurrence data. For example, perfluoroalkyl carboxylates (PFCAs) such as PFOA have been used widely as manufacturing aids in the fluoropolymer industry, whereas perfluoroalkyl sulfonates (PFSAs) such as PFOS were a major component of some formulations of AFFF (Houtz et al., 2013; Prevedouros et al., 2006). Some AFFF formulations contain precursors that can generate PFCAs following release, and other precursors used in surface protection products may generate PFSAs (Harding-Marjanovic et al., 2015; Mejia Avendaño and Liu, 2015; Rhoads et al., 2008). Additionally, PFAS use has changed over time (Houtz et al., 2013; Wang et al., 2013). Long chain PFASs, defined by USEPA as PFSAs $\geq$ perfluorohexane sulfonate (PFHxS) and PFCAs $\geq$ PFOA and their precursors, have been phased out in favor of short chained PFASs and replacement products such as ADONA and GenX (Wang et al., 2013). In addition, different sources release different PFAS mixtures to different primary aqueous environments. Manufacturing releases often occur to surface water bodies, though groundwater impacts through historical disposal practices or atmospheric deposition are possible (Davis et al., 2007; Oliaei et al., 2013). Applications of AFFF occur at or near the land surface, leading to potential for migration through the subsurface to groundwater aquifers though some overland flow to surface water bodies may occur.

PFASs are unregulated at the federal level, though USEPA has issued non-enforceable lifetime health advisories (LHAs) for the sum of PFOA and PFOS of 0.07 μg/L in drinking water (USEPA, 2016a; USEPA, 2016b). To inform the need for a federal drinking water maximum contaminant levels (MCL) for unregulated compounds, USEPA compiles information on occurrence in U.S drinking water via the Unregulated Contaminant Monitoring Rule (UCMR). Under this rule, certain public water systems (PWSs) monitor for a designated list of unregulated contaminants during a three-year period. The most recent round of monitoring, labeled UCMR3, included PFOA, PFOS, and 4 additional PFASs. The publicly-accessible UCMR3 dataset was available by mid-2016. Formal regulatory determinations based on UCMR data generally occur several years after monitoring is completed (Roberson and Eaton, 2014). PFASs are currently regulated at the state level in some regions (e.g. New Jersey, Vermont). Regulations typically target PFOA and/or PFOS, but have been developed for other PFASs in some areas (i.e. NCDHHS, 2017). Additionally, regulation of PFAS mixtures may become more common as studies are completed on mixture toxicity. For example, only limited studies to date have investigated the potential for synergistic effects of PFAS mixtures (Carr et al., 2013; Wolf et al., 2014).

Multiple studies examined PFAS occurrence data generated by UCMR3 monitoring (Hu et al., 2016; Suthersan et al., 2016). One study concluded that 6 million U.S residents were being served by PWSs with PFOA and PFOS concentrations that exceeded the LHA in one or more samples (Hu et al., 2016). Additionally, positive correlations were identified between numbers of potential PFAS point sources within specific regions and PFAS detections within those areas (Hu et al., 2016). This work concluded that industrial sources represented the highest per source contribution, but minor sources, including wastewater treatment plants (WWTPs) that are more numerous, likely also represent a significant cumulative contribution. A recent evaluation of UCMR3 data focused on 1,4-dioxane occurrence concluded PFAS detections were significantly correlated with 1,4-dioxane detections. However, detection rates for all PFASs were much lower than the detection rate for 1,4-dioxane and several other UCMR3 contaminants (Adamson et al., 2017).

Knowledge gaps remain regarding sources, occurrence, and fate of PFASs in the environment, and UCMR3 data can be further leveraged towards providing insights into some of these key questions. The UMCR3 dataset for PFASs is unique because it includes data on PFAS mixtures from PWSs of various sizes, from multiple source water types (e.g. surface water, groundwater), over a broad geographic distribution, and over a three-year period. The objective of the current study was to use UCMR3 data to advance understanding of PFASs in U.S drinking water by addressing three primary hypotheses: 1) due to complex chemistry and usage history for PFAS-containing products, multiple PFASs will be present whenever detected in a drinking water supply, and are likely to be correlated with other co-contaminants; 2) concentration and relative abundance of PFASs detected in drinking water are a function of PWS characteristics (i.e. source water type, system size) and serve as indicators of the source of PFAS contamination; 3) temporal trends in PFAS occurrence reflect their recalcitrance and changes in use and source control of these compounds. Lastly, the results of the study were used to investigate the extent to which the UCMR3 dataset is a general representative proxy for PFAS occurrence in U.S. drinking water.

2. Methods

2.1. Data sources

This study relied on publicly available data collected to support USEPA's UCMR3 efforts (USEPA, 2012). UCMR3 data contains PWS information and compound analytical results for >73,000 drinking water samples collected 2013–2015 from >5000 PWSs. System information includes PWS identification, state, zip code, system size, and water source type for each drinking water sample collected. PWSs size was designated as either large (serving populations >10,000) or small (serving populations $\leq$ 10,000). Water sources were specified as groundwater, groundwater under the influence of surface water, surface water, or mix. Sampling and analysis of 6 PFASs (Table 1) and 15 additional compounds was mandatory for all large PWSs in the U.S., but only a subset of smaller PWSs. Each PWS sampled for at least one year, yielding 36,139 samples analyzed for PFASs. Minimum reporting limits (MRLs) were specified to ensure each PWS generated uniform occurrence data (Table 1). A complete description of the UCMR3 sampling and analysis protocol can be found in USEPA (2016), and a summary of the process is provided in Adamson et al. (2017). Information regarding population size served by specific PWSs was identified in the USEPA Safe Drinking Water Information System (SDWIS, https://ofmpub.epa.gov/apex/sfdw/f?p=108:200::::::).

2.2. Regulatory limits

To provide perspective on PFAS impacts in U.S. drinking water,