Public Comment
Proposed Recycled Water Policy Amendment
Deadline: 9/10/18 by 12 noon

September 9, 2018

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9-9-18
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Felicia Marcus, Chair
Members of the State Water Resources Control Board
1001 I Street, 24th Floor,
Sacramento, CA 95814
Submitted via email to Jeanine Townsend, Clerk of the Board

Dear Chair Marcus and Members of the Board:

Thank you for this opportunity to provide written comment on the revised proposed amendment, adding PFOS and PFOA to the Policy for Water Quality Control for Recycled Water. While this letter's signatories applaud the idea of looking at PFOS and PFOA in recycled water, limiting the amendment to include only these two out of thousands of known per- and polyfluorinated (PFAS) chemicals addresses just the tip of the iceberg and would be a disservice to the public and environment. We strongly urge the Board instead to view PFASs as a class of chemicals and amend the recycled water policy accordingly. At minimum the policy should require monitoring for the PFAS chemicals that can be accurately detected by EPA Method 537 v1.1 (EPA Document #: EPA/600/R-08/092) with the inclusion of branched PFOA isomers in the quantitation of PFOA. This would enable the quantification and reporting of 18 PFAS chemicals, including PFOS, PFOA, and the two other PFASs –PFHxS and PFHpA-detected in California drinking water sources through the UCMR3.[1] In addition, the policy should direct monitoring to include an expanded list of PFAS chemicals as EPA or the state expands its technical capability for detection in the future.[2]

There are an estimated 4730 PFAS chemicals in commercial use world-wide, both in consumer products and industrial processes. Our current understanding of contamination of California water and the population at large is limited. For instance, the UCMR3 program only tested for 6 PFAS chemicals nation-wide and at relatively high levels. However, as over 40 years of data has demonstrated, PFAS such as PFOA, PFOS, and related chemicals, are extremely persistent, mobile in water, accumulate in the human body, and are associated with a wide array of environmental and human health impacts including cancer, immunotoxicity, liver toxicity, developmental disorders, and high cholesterol.[3] The chemical industry's response to these issues has been to replace the long chained chemicals with shorter chained versions (less than 8 fluorinated carbon atoms). Unfortunately, emerging science is coalescing on a conclusion that these chemicals, though less studied and not currently regulated, are

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[1] *"In September of 2016, EPA issued a Technical Advisory informing of the possible under-reporting of PFOA when adhering to EPA 537 as originally written and recommending expansion of the integration window to account for branched isomers of PFOA".* See https://www.eurofinsus.com/environment-testing/laboratories/eurofins-eaton-analytical/services/pfas-testing-in-water/analytical-method/

[2] Methods currently under exploration, such as Total Oxidizer Precursor (TOP) assay should be explored to screen for the presence of PFAS compounds.

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also extremely resistant to environmental degradation.[4] In addition, independent researchers have raised a concern that greater amounts of short chained PFASs replacements may be required to serve the same purposes in products and processes, thus raising levels in water and other environmental media.[5]

Monitoring recycled water for a full array of PFAS is important to human health whether the water is used for potable or non-potable purposes given the persistence of these chemicals in the environment. In fact, PFHxS, which has been detected in 7 California drinking water sources at or over 30 parts per trillion, has a longer half life in the human body than PFOA and PFOS. According to the CDC, PFOA is retained from 2 to 4 years and PFOS from 5 to 6 years in the body. PFHxS is retained in the body from 8 to 9 years.[6] In addition, the Centers for Disease Control the CDC has generated a minimal risk level (MRL) for PFHxS based on hepatic and thyroid effects. Clearly, ignoring the presence of this chemical, along with other toxic PFASs is not adequately health protective.[7]

While there is limited evidence that some shorter chained PFAS may not remain in the human body as long as their larger cousins, the emerging science points to their being toxic at the cellular level and there have been studies indicating that they collect not only in blood and urine, but in the organs of humans and animals. This emerging science, along with that of short chained PFAS persistence in the environment has led scientists from around the world to call for the eradication of PFAS except in the essential products and processes, and for collection of data to identify and monitor the presence of all PFASs in the environment. As warned in the 2015 Madrid Statement, "increasing use of fluorinated alternatives will lead to increasing levels of stable perfluorinated degradation products in the environment, and possibly also in biota and humans. This would increase the risks of adverse effects on human health and the environment".[8] Since PFAS restrictions on short chained PFAS has not been forthcoming, failure to monitor for them in recycled water would likely result in their continued presence in California's environment and could perpetuate the harm that they cause to humans, as well as to water, soil, and air quality.

Wastewater and ground and surface waters influenced by recycled water are particularly vulnerable to contamination from a broad array of PFASs.[9] A spatial analysis of the 2013-2015 national drinking water PFAS concentrations from the UCMR3 program has correlated levels of PFAS in water above the MRL with wastewater facilities, in addition to industrial and military sites, and airports.[10] Industrial discharges, contaminated household dust, and consumer products contribute to the PFAS contamination flowing from wastewater treatment facilities. Given the replacement of PFOA and PFOS with alternative PFAS chemicals in consumer products and other applications, we can expect

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[4] U.S EPA. "Basic Information on PFAS.", https://www.epa.gov/pfas/basic-information-pfas. California Environmental Protection Agency, Department of Toxic Substances Control, Safer Consumer Products Program, *Product-chemical profile for perfluoroalkyl and polyfluoroalkyl substances in carpets and Rugs*, Feb. 2018, https://www.dtsc.ca.gov/SCP/upload/Product-Chemical-Profile-PFAS-Carpets-and-Rugs.PDF

[5] Madrid Statement on poly- and perfluorinated alkyl substances (PFAS). 2015. https://ehp.niehs.nih.gov/doi/10.1289/ehp.1509934

[6] An Overview of Perfluoroalkyl and Polyfluoroalkyl Substances and Interim Guidance for Clinicians Responding to Patient Exposure Concerns, https://www.atsdr.cdc.gov/pfc/docs/pfas_clinician_fact_sheet_508.pdf.

[7] https://www.atsdr.cdc.gov/mrls/pdfs/atsdr_mrls.pdf, page 13

[8] Ibid

[9] Pumlee MH,, Larabee J., Reinhard M. Perfluorochemicals in Water Reuse, *Chemosphere* 72 (2008) 1541-1547.

[10] Hu XC, et al., 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*. 2016, 3, 344-350.

contamination of wastewater effluent with multiple PFAS compounds beyond PFOA and PFOS. Testing of WWTP effluent used for recycling in California detected 14 PFAS compounds.[11]
Finally, we would point out to the Board that the rise in shorter chain length PFAS chemicals complicates the state's ability to treat water. While activated carbon, ion exchange, and high pressure membranes have been effective in removing PFOA and PFOS[12], less is understood about the removal of smaller PFAS molecules or combinations of PFAS in the same water source. Evidence exists, however, that shorter chained PFAS are PFASs such as PFHxA, PFBA, PFPeA are more difficult to remove effectively.[13] Consequently, it is essential to gain as comprehensive a picture as possible of what is present in recycled water to avoid poor management and treatment decisions that would have to be revisited at great expense later on.

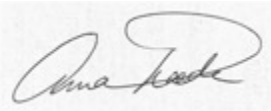
To summarize:

- PFASs *as a class* persist in the environment, and are thus labeled as 'forever" chemicals
- Health impacts are being demonstrated well beyond PFOA and PFOS
- Drinking water and food contaminated with PFAS, including but not limited to PFOA and PFOS pose a threat to human health.
- Recycled water, used for both non-potable and potable uses, is particularly vulnerable to contamination from the vast array of PFAS chemicals used in commerce.
- We cannot "guess" what chemicals may impact recycled water given the lack of data on what PFASs are used in the state. Consequently, it is necessary to use the best technology possible to monitor for a wide array of these chemicals to protect human health and the environment.

By focusing solely on PFOA and PFOS, we risk allowing other similarly dangerous PFASs to enter the environment and, as the state ultimately moves toward potable reuse, into human bodies. For these reasons the recycled water policy must be inclusive of the entire class of these toxic chemicals, monitor for the greatest number of PFAS that is technically possible, and continue to develop and implement greater monitoring and treatment technologies in response to this world-wide problem.

Sincerely,

Andria Ventura
Toxics Program Manager
Clean Water Action



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[11] https://www.ncbi.nlm.nih.gov/pubmed/18547612
[12] https://www.epa.gov/sciencematters/reducing-pfas-drinking-water-treatment-technologies
[13] McCleaf p., et al., Removal efficiency of multiple poly-and perfluoroalkyl substances (PFASs) in drinking water using granular activated carbon (GAC) and anion exchange (AE) column tests. *Water Res.* 2017, 1; 120:77-87.

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Chemosphere 72 (2008) 1541–1547

Contents lists available at ScienceDirect

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Perfluorochemicals in water reuse

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ARTICLE INFO

Article history:
Received 16 January 2008
Received in revised form 17 April 2008
Accepted 18 April 2008
Available online 10 June 2008

Keywords:
PFOS
PFOA
Reclaimed wastewater
Wetland
Toxicity

ABSTRACT

Faced with freshwater shortages, water authorities are increasingly utilizing wastewater reclamation to augment supplies. However, concerns over emerging trace contaminants that persist through wastewater treatment need to be addressed to evaluate potential risks. In the present study, perfluorinated surfactant residues were characterized in recycled water from four California wastewater treatment plants that employ tertiary treatment and one that treats primary sewage in a wetland constructed for both treatment and wildlife habitat. Effluent concentrations were compared with surface and groundwater from a creek where recycled water was evaluated as a potential means to augment flow (Upper Silver and Coyote Creeks, San Jose, CA). In the recycled water, 90–470 ng/l perfluorochemicals were detected, predominantly perfluorooctanoate (PFOA; 10–190 ng/l) and perfluorooctanesulfonate (PFOS; 20–190 ng/l). No significant removal of perfluorochemicals was observed in the wetland (total concentration ranged 100–170 ng/l across various treatment stages); in this case, 2-(*N*-ethylperfluorooctanesulfonamido) acetic acid (*N*-EtFOSAA), perfluorodecanesulfonate (PFDS), and PFOS were dominant. Though there is currently no wastewater discharge into the creeks, perfluorochemicals were found in the surface water and underlying groundwater at a total of 20–150 ng/l with PFOS and PFOA again making the largest contribution. With respect to ecotoxicological effects, perfluorochemical release via recycled water into sensitive ecosystems requires evaluation.

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1. Introduction

With ecosystems increasingly stressed by the shortage of freshwater, treated wastewater effluent is a promising water resource for the augmentation of water-starved environments. Historically, release of treated wastewater to surface water has been commonplace given the lack of alternatives. Water recycling, however, requires consideration of a complex set of benefits and risks at sites where a natural source (rain, groundwater, rivers) is replaced or augmented with tertiary effluent. Considerations include ecological effects and contamination of potable aquifers with potentially harmful organic contaminants.

Perfluorochemicals represent one such group of contaminants. They are used in a variety of materials such as food packaging, paints, and lubricants (Kissa, 1994) and have been detected in wastewater (Alzaga and Bayona, 2004; Boulanger et al., 2005; Schultz et al., 2006; Sinclair and Kannan, 2006; Loganathan et al., 2007), surface water (Hansen et al., 2002; Moody et al., 2002; Boulanger et al., 2004; Boulanger et al., 2005; Simcik and Dorweiler, 2005; Rostkowski et al., 2006; Sinclair et al., 2006; Skutlarek et al., 2006; McLachlan et al., 2007; So et al., 2007), groundwater (Moody et al., 2003; Schultz et al., 2004), drinking water (Harada et al., 2003; Skutlarek et al., 2006; Paustenbach et al., 2007), and rain (Loewen et al., 2005; Scott et al., 2006). Table 1 summarizes the aquatic occurrence of two commonly detected perfluorochemicals, perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS).

Laboratory studies demonstrate that mammals readily absorb PFOA and PFOS during oral and inhalation exposures. They tend to distribute to the blood serum and the liver and can cross the blood-brain and placental barriers (Lange et al., 2006). Although research shows that PFOA, perfluorononanoate (PFNA), and PFOS are not estrogenic (Maras et al., 2006), high doses of PFOA and PFOS lead to mortality while lower doses result in hepatotoxic, immunotoxic, neurotoxic, and behavioral effects (Lange et al., 2006). When present in a mixture, PFOS may enhance the toxicity of other compounds by increasing cell membrane permeability (Hu et al., 2003; Jernbro et al., 2007). Perfluorochemicals bioaccumulate and have been detected in biota around the world, including fish, seals, minks, albatross, bald eagles, polar bears, and humans (Giesy and Kannan, 2002; Schultz et al., 2003). Typical concentrations of PFOA and PFOS in the serum of non-occupationally exposed humans are 3–35 and 7–82 μg/l, respectively (Hansen et al., 2001; Kannan et al., 2004). These levels are concerning given that adverse effects have been observed in rats at levels (370 μg/l PFOA) which differ from humans by less than a safety factor of 100 (Butenhoff et al., 2004; Lange et al., 2006). Wildlife monitoring studies for high trophic levels report PFOS concentrations of 8–242 μg/l serum in ringed seals (Kannan et al., 2001a), 3–34 μg/l

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doi:10.1016/j.chemosphere.2008.04.057

Table 1
Summary of perfluorochemical occurrence in wastewater, freshwater, and drinking water

Site and location	PFOA (ng/l)	PFOS (ng/l)	Other perfluorochemicals detected	Source of perfluorochemicals[a]	References
Wastewater effluent					
2 WWTPs (Catalonia, Spain)	<100–4300	n.m.	PFDA (50-8170)	Domestic and industrial influents	Alzaga and Bayona, 2004
WWTP (Iowa City, Iowa, USA)	22	26	*N*-EtFOSAA (3.6 ng/l)	Domestic influent (no known manufacturing or industrial perfluorochemical source)	Boulanger et al., 2005
10 WWTPs (USA)	3–97	1–130	PFBS, PFHxS, 6:2 FtS, PFHxA, PFNA, PFDA, FOSA	Domestic, industrial, and commercial influents	Schultz et al., 2006
6 WWTPs (New York, USA)	58–1050	3–68	PFHxS, PFNA, PFDA, PFUnDA, 8:2 FTCA, 8:2 FTUCA	Domestic, industrial, and commercial influents	Sinclair and Kannan, 2006
Reclaimed wastewater, 4 WWTPs (California, USA)	12–185	20–187	PFHxS, PFDS, PFHxA, PFHpA, PFNA, PFDA, 6:2 FtS, FOSA, *N*-EtFOSAA	Domestic, industrial, and commercial influents	present study, 2007
Surface water					
Tennessee river (Decatur, AL, USA) upstream and downstream of fluorochemical manufacturing facility	Upstream: <25; Downstream: <25–513	Upstream: 17-53; Downstream: 30–140	n.m.	Fluorochemical manufacturing facility	Hansen et al., 2002
Etobicoke Creek (Toronto, Ontario, Canada) upstream and downstream of fluorochemical spill over time	Upstream: n.d.-33; downstream: n.d.-10 600	Upstream: n.d.; downstream: n.d.-995 000	PFHxS	Accidental spill of aqueous film-forming foams (AFFFs)	Moody et al., 2002
Lake Erie and Lake Ontario (USA), urban and remote locations	27–50	21–70	*N*-EtFOSAA (4.2–11 ng/l), FOSA (0.6–1.3 ng/l), PFOSulfinate (n.d.-17 ng/l)	Not stated	Boulanger et al., 2004
River (Iowa City, Iowa, USA)	8.7	23	*N*-EtFOSAA (1.2 ng/l)	Wastewater effluent	Boulanger et al., 2005
"Remote" lakes (Lake Superior, Minnesota, USA; Voyageurs National Park lakes, Canada)	0.1–0.7	n.d.-1.2	PFHxA, PFHpA, PFNA	Atmospheric deposition	Simcik and Dorweiler, 2005
"Urban" waters (3 lakes in Minneapolis and Minnesota River in Minnesota, USA)	0.5–19	2.4–47	PFHxA, PFHpA, PFNA, PFDA	Urban location, runoff, and wastewater discharge	Simcik and Dorweiler, 2005
Lake Michigan (USA)	0.3–3.4	0.9–3.1	PFHpA	Non-atmospheric sources	Simcik and Dorweiler, 2005
Streams, lake in Shihwa and Banweol industrial areas, South Korea	0.9–62	2.2–651	PFBS, PFHxS, FOSA, PFHxA, PFHpA, PFDA	Local industrial sources	Rostkowski et al. (2006)
Surface waters of New York state, USA	<0.5–7.4	<0.8–756	PFHxS	Industrial and municipal wastewater effluent	Sinclair et al., 2006
Rhine river, Moehne river, and their tributaries (Germany)	2–48 (Rhine); 11–33 900 (Moehne)	2–26 (Rhine); 2–5900 (Moehne)	PFBS, PFBA, PFPnA, PFHxA, PFHpA	Superficial run-off from waste materials applied to agricultural areas upstream; wastewater discharge	Skutlarek et al., 2006
Tributaries of the Pearl and Yangtze Rivers (China)	0.85–260	<0.01–99	PFBS, PFHxS, FOSA, PFHxA, PFHpA, PFNA, PFDA, PFUnA	Industrial and municipal wastewater effluent	So et al., 2007
European rivers including Po, Rhine, Danube, Elbe, Oder, Seine, and Loire	200 (Po River) <0.65–23 (other rivers)	n.m.	PFHxA, PFHpA, PFNA	Fluoropolymer manufacturing facilities present in Po watershed; wastewater effluent is a likely source for the other rivers	McLachlan et al., 2007
Constructed wetland receiving reclaimed wastewater (California, USA)	9–14	19–29	PFHxS, PFDS, PFHxA, PFHpA, PFNA, PFDA, FOSA, *N*-EtFOSAA	Wastewater effluent	Present study, 2007
Upper Silver and Coyote Creeks (San Jose, CA, USA)	8–36	5–56	PFHxS, PFDS, PFHxA, PFHpA, PFDA, FOSA, *N*-EtFOSAA	Urban location, runoff, and atmospheric deposition	Present study, 2007
Groundwater					
Wurtsmith air force base (Michigan, USA)	8000–105 000	4000–110 000	PFHxS, PFHxA	Past fire-training exercises using AFFFs	Moody et al., 2003
Wurtsmith (Michigan, USA) and Tyndall (Florida, USA) Air Force Bases	3000–6 570 000	4000–2 300 000	4:2 FtS, 6:2 FtS, 8:2 FtS	Past fire-training exercises using AFFFs	Schultz et al., 2004
Monitoring wells near Upper Silver and Coyote Creeks (San Jose, CA, USA)	n.d.-18	19–87	PFHxS, PFDS, PFHxA, PFHpA, PFDA, FOSA, *N*-EtFOSAA	Infiltration from overlying urban stream, possibly other sources	Present study, 2007
Rainwater					
Winnipeg, Manitoba, Canada	n.d.	0.6	FTCAs, FTUCAs	Degradation from volatile fluorotelomer alcohols and other precursors	Loewen et al., 2005

Table 1 (*continued*)

Site and location	PFOA (ng/l)	PFOS (ng/l)	Other perfluorochemicals detected	Source of perfluorochemicals[a]	References
4 urban sites (2 USA, 2 Canada) and 5 rural/remote sites (2 USA, 3 Canada)	<0.1–89 (urban); <0.1–10 (rural)	n.m.	TFA, PFPrA, PFBA, PFPnA, PFHxA, PFHpA, PFNA, PFDA, PFUnA, PFDoA, FTCAs, FTUCAs	Degradation from volatile fluorotelomer alcohols	Scott et al., 2006
Drinking water					
Japan (four cities)	n.m.	0.1–51	n.m.	Sourced from Tama River	Harada et al., 2003
Ruhr area (Germany)	n.d.-519	n.d.-22	PFBS, PFBA, PFPnA, PFHxA, PFHpA	Sourced from rivers contaminated by land application of waste materials, see above	Skutlarek et al., 2006
Outside the Ruhr area (Germany), Paris (France), Hampshire (Great Britain)	n.d.-4 (outside Ruhr); n.d. (Paris, Hampshire)	n.d.-6 (outside Ruhr); n.d. (Paris, Hampshire)	PFPnA, PFHxA	Not stated	Skutlarek et al., 2006
West Virginia, USA measured over 1984–2004	58-4800	n.m.	n.m.	Sourced from groundwater contaminated by nearby Dupont facility	Paustenbach et al., 2007

[a] Known or suggested by authors of study.

blood in albatross (Kannan et al., 2001b), and 0.8–74 μg/l serum in red panda (Dai et al., 2006). Morikawa et al. (2006) report both the serum and aquatic concentrations of PFOS for turtles collected in a Japanese river, reporting 2–486 μg/l in the serum and 3–37 ng/l in the nearby water.

Because of the persistence of perfluorochemicals in wastewater treatment (Boulanger et al., 2005; Schultz et al., 2006; Sinclair and Kannan, 2006) and their expected bioaccumulation, the occurrence of these compounds must be considered in wastewater and wastewater reclamation, especially where humans or wildlife may be exposed. To this end, a range of perfluorochemicals (Fig. 1) were determined in recycled water and in two unique water recycling operations: a wetland constructed using wastewater for both treatment and habitat creation, and an urban stream evaluated for flow augmentation using recycled water. Results are interpreted based on literature evaluations of perfluorochemical toxicity.

2. Experimental

Reclaimed wastewater was collected in June 2007 from four California (USA) wastewater treatment plants (WWTP 1, 2, 3, and 4) that produce tertiary treated effluent for landscape irrigation and other reuse purposes. Grab samples were collected following tertiary treatment.

Water samples were also collected from a constructed wetland (California, USA) that receives primary treated wastewater

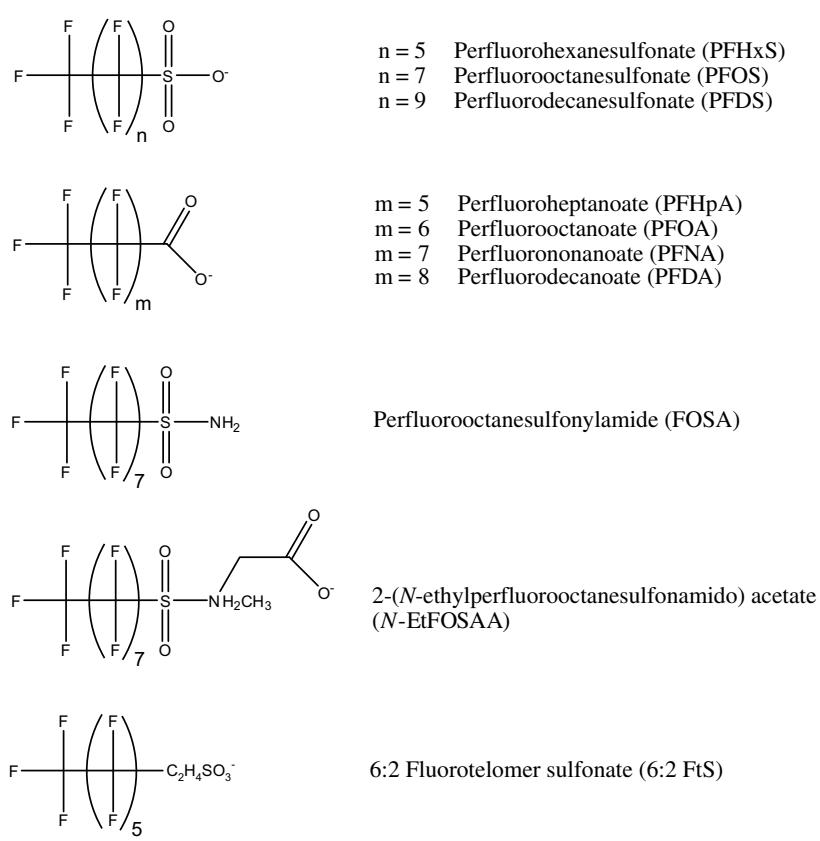

Fig. 1. Perfluorochemicals monitored in the present study.

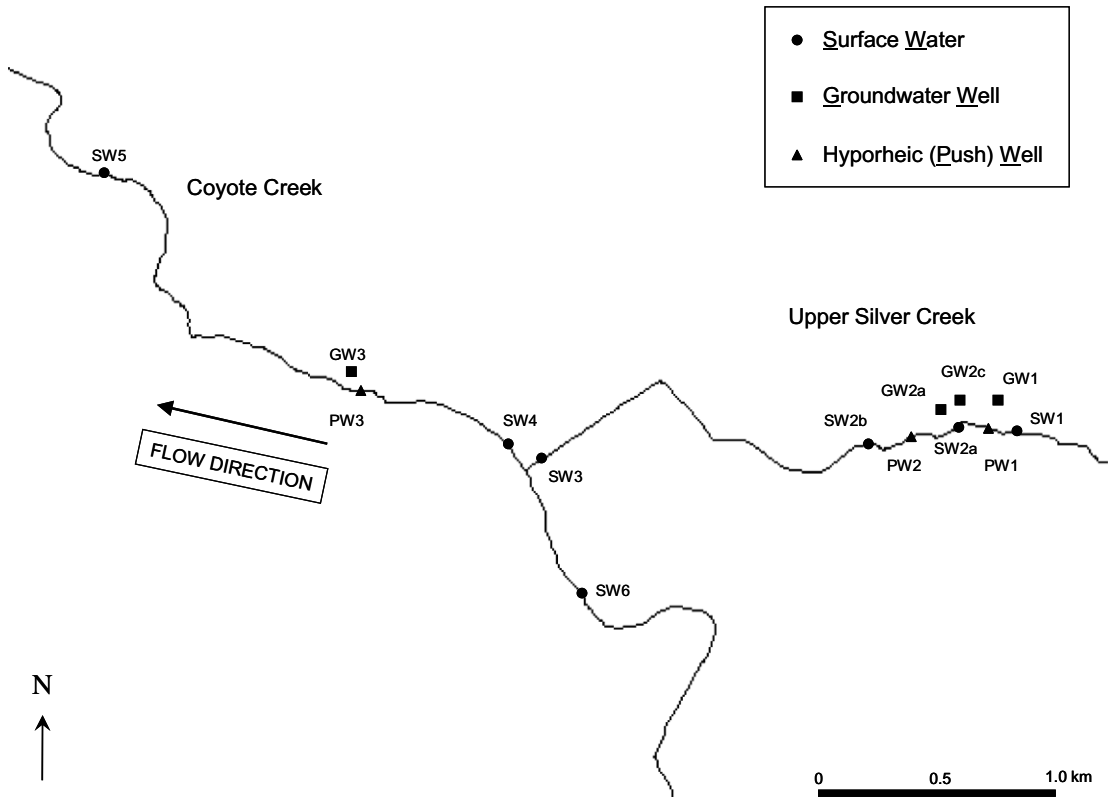

Fig. 2. Map of San Jose (CA) creek study reach, indicating surface water, groundwater, and hyporheic zone (push well) sampling sites. Creek flows northwest, eventually reaching the San Francisco Bay.

Table 2
Perfluorochemicals (ng/l) in reclaimed wastewater from four California treatment plants and in consecutive stages of a constructed wetland for wastewater treatment and wildlife habitat

Sample	PFHxS	PFOS	PFDS	PFHpA	PFOA	PFNA	PFDA	6:2 FtS	FOSA	*N*-EtFOSAA	Total PFCs
Reclaimed wastewater											
WWTP 1[a]	24	38	9.0	8.8	36	n.d. (<10)	11	11	2.8	11	150
WWTP 2[b]	17	190	n.d. (<2)	13	180	32	7.5	n.d. (<4)	3.2	23	470
WWTP 3[c]	6.5	20	n.d. (<2)	21	190	14	11	n.d. (<4)	4.8	5.5	270
WWTP 4[d]	8.0	42	3.3	5.6	12	n.d. (<10)	n.d.	n.d. (<4)	2.1	12	90
Constructed wetland using primary treated wastewater											
Oxidation pond influent	3.4	23	36	n.d. (<4)	14	9.1	3.4	n.d. (<4)	8.8	48	150
Oxidation pond effluent	3.2	21	23	n.d. (<4)	13	7.8	n.d. (<2)	n.d. (<4)	6.9	69	140
Treatment marsh effluent	3.0	25	29	n.d. (<4)	12	5.4	n.d. (<2)	n.d. (<4)	6.9	59	140
Enhancement marsh 1 influent	3.2	23	14	n.d. (<4)	11	3.3	n.d. (<2)	n.d. (<4)	5.3	40	100
Enhancement marsh 1 effluent	3.3	19	10	16	9.1	3.0	n.d. (<2)	n.d. (<4)	4.5	41	110
Enhancement marsh 3 effluent	3.2	29	36	n.d. (<4)	11	3.5	n.d. (<2)	n.d. (<4)	7.4	85	170

Values are the mean of duplicate samples (mean percent difference between duplicate samples was 21%).
[a] Tertiary treatment via dual media filtration and chlorination, followed by polymer treatment and repeated filtration for reclaimed wastewater.
[b] Tertiary treatment via dual media filtration and chloramination, followed by additional chloramination for reclaimed wastewater.
[c] Tertiary treatment via dual media filtration and chlorination.
[d] Tertiary treatment via fixed growth reactor (ammonia removal), flocculation, dual media filtration, and chlorination, followed by additional flocculation, dual media filtration, and chlorination for reclaimed wastewater.

(clarification and solids digestion) and discharges to the ocean. In addition to fulfilling treatment requirements for discharge, the wetland provides community recreation and wildlife habitat. Grab samples were taken in February 2006 from treatment stages including the oxidation ponds, treatment marshes, and enhancement marshes. Chlorination and dechlorination occur prior to the enhancement marshes. The hydraulic retention time of each stage varies from 1 to 2 months for the oxidation ponds, approximately 2 days for the treatment marshes, and nearly 10 days for the enhancement marshes.

In addition, grab samples of surface water were collected from several sites along Coyote Creek and a tributary, Upper Silver Creek, over a reach (Fig. 2) of approximately 5 km in San Jose, CA (USA) in May 2006 and June 2007. The Santa Clara Valley Water District (San Jose, CA, USA) was investigating the site for a potential flow augmentation with reclaimed wastewater; perfluorochemicals were evaluated in the creeks and reclaimed wastewater (from WWTP 2) to characterize baseline conditions. Nearby groundwater samples were obtained from four monitoring wells (GW1, 2a, 2c, and 3) installed to depths of 5–10 m. Depth-to-water ranged 2–5 m for the four wells. Very shallow "push" wells (PW1, 2, and 3) were also installed in or adjacent to the creek. The push wells were installed at a depth of just 0.6–0.9 m to capture young groundwater in the hyporheic zone, a region in which surface

and groundwater exchange and flow velocity, relative to the surface, is reduced by orders of magnitude (Hoehn and Cirpka, 2006). In order to use temperature as a tracer for hydraulic residence time (Anderson, 2005), temperature monitors were installed at selected surface water sites and in push wells. The results from this survey represent background, pre-augmentation conditions for the site.

Samples and blanks were analyzed by direct, large-volume injection using liquid chromatography-tandem mass spectrometry (Higgins et al., 2005; Schultz et al., 2006). Analytical details may be found in the supplementary information.

3. Results

3.1. Perfluorochemicals in four reclaimed wastewaters

Perfluorochemicals were measured in reclaimed wastewater from four California treatment plants. Following primary and secondary treatment, the reclaimed wastewaters were treated using the tertiary treatments listed in Table 2. Nearly all of the perfluorochemicals monitored were detected in all wastewaters (Table 2). As evidenced by the detections, perfluorochemicals persisted beyond the tertiary treatment steps. Summing the ten perfluorochemicals, the total concentration ranged from 90 to 470 ng/l across the effluents. PFOS and PFOA made the largest contributions to the total, at 7.6–46% and 13–68%, respectively. The perfluorochemical concentrations are consistent with reports for other municipal wastewaters (Table 1), which vary between plants (Alzaga and Bayona, 2004; Boulanger et al., 2005; Schultz et al., 2006; Sinclair and Kannan, 2006).

3.2. Perfluorochemicals in a constructed wetland receiving primary treated wastewater

Perfluorochemicals were also measured at various treatment stages of a constructed wetland sustained using wastewater. All ten perfluorochemicals were detected (Table 2), with the exception of 6:2 FtS, which was not detected at any stage. No significant removal of the perfluorochemicals was observed across wetland treatment. Although PFOA and PFOS are often found in the highest concentrations compared to other perfluorochemicals in wastewaters, in this case PFDS and 2-(*N*-ethylperfluorooctanesulfonamido) acetic acid (*N*-EtFOSAA) were found at greater concentrations. According to a recent study by Rhoads et al. (2008), higher concentrations of *N*-EtFOSAA rather than PFOS in wastewater effluent are expected given the biodegradation kinetics of 2-(*N*-ethylperfluorooctanesulfonamido) ethanol (*N*-EtFOSE), a precursor to *N*-EtFOSAA that is used in protective paper coatings. *N*-EtFOSAA then biodegrades to PFOS, but more slowly. Few monitoring studies include PFOS-precursors like *N*-EtFOSAA; Boulanger et al. detected 3.6±0.2 ng/l *N*-EtFOSAA in WWTP effluent compared to 26±2.0 ng/l PFOS (2005). Because PFOS and PFOA are directly discharged to treatment plants (Prevedouros et al., 2006), their concentrations in most wastewaters may exceed precursors.

3.3. Perfluorochemicals in an urban creek and groundwater

Perfluorochemicals were detected in an urban stream evaluated for flow augmentation using reclaimed wastewater, as well as in the underlying groundwater (Table 3). Upper Silver Creek sites (2007) showed a range of 126–145 ng/l total perfluorochemicals. This would increase to approximately 300 ng/l during augmentation with reclaimed wastewater (WWTP 2) given a flow regime of equal parts wastewater and surface flow.

The concentrations found downstream of the confluence of Upper Silver and Coyote Creeks are a result of mixing of the upstream contributions: downstream PFOS and PFOA levels are within 10–30% of those predicted using flow measurements (data not shown). The source of perfluorochemicals to these two creeks is unknown, but is likely to be a combination of atmospheric deposition of volatile precursors (Ellis et al., 2004; Simcik and Dorweiler, 2005; Martin et al., 2006) and surface runoff. There is currently no known upstream wastewater discharge into either creek. Results are consistent with the urban surface water sites characterized by Simcik and Dorweiler (2005), which ranged from 2–47 ng/l PFOS to 0.5–20 ng/l PFOA (compared to remote sites with n.d.-1.2 ng/l PFOS and n.d.-0.7 ng/l PFOA).

The concentrations detected in the hyporheic zone were typically consistent with the nearby creek water (Table 3), indicating that the hyporheic zone was supplied by the overlying creek and that negligible perfluorochemical attenuation occurred in the hyporheic zone. Analysis of temperature data for select sites indicated a hyporheic residence time of 15–60 min (Hoehn et al., 2007). No significant attenuation was expected in the hyporheic zone, nor with distance downstream, as the perfluorochemicals monitored resist biodegradation and sorption is limited (Giesy and Kannan, 2002; Prevedouros et al., 2006).

Groundwater wells near the creeks showed perfluorochemical detections in all samples and generally on the order of the creek concentrations. PFOS ranged 19–192 ng/l and PFOA n.d.-22 ng/l in the four groundwater wells monitored in 2006 and 2007. The source of perfluorochemicals to the groundwater is not entirely clear. Although head measurements indicate that the stream is a losing stream, the groundwater sampled is not necessarily recharged from the creek alone. For instance, urban rain (Table 1) may be a source of perfluorochemicals to the aquifer, or potentially septic systems located upstream. Additionally, a nearby golf course

Table 3
Range of perfluorochemical (ng/l) concentrations measured in an urban creek and groundwater in San Jose, CA during the dry months of 2006 and 2007

	PFHxS		PFOS		PFDS		PFHpA		PFOA		PFDA		FOSA		*N*-EtFOSAA	
	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07
Detection limit	4	2	10	2	21	2	4	2	4	4	21	2	21	2	21	4
Upper silver creek surface water (sites 1, 2a, 2b, 3)[a]	n.d.	8.3–12	27–38	41–56	n.d.	3.1–36	n.d.	7.7–12	10–15	27–36	n.d.	11–19	n.d.	2.3–3.5	n.d.	n.d.-10
Coyote creek surface water (sites 4, 5, 6)	n.d.	2.3–3.8	9.3–20	4.8–25	n.d.-44	3.4–18	n.d.	n.d.-4.7	n.d.	8.0–13	n.d.	6.0–13	n.d.	n.d.-2.4	n.d.-31	n.d.-24
Hyporheic zone (3 wells)[b]	n.d.	3.8–10	44–58	25–48	n.d.	5.7–15	n.d.	7.3–8.1	10–23	22–28	n.d.	13–19	n.d.	2.9–4.3	n.d.	6.2–10
Groundwater (4 wells)	n.d.-11	4.0–17	31–192	19–87	n.d.	n.d.-3.3	n.d.	n.d.-4.8	n.d.-22	n.d.-18	n.d.	n.d.-10	n.d.	n.d.-3.7	n.d.-26	n.d.

PFNA and 6:2 FtS were also monitored but were not detected above detection limits of 4 and 10 ng/l in May 2006 and 10 and 4 ng/l in June 2007, respectively.
[a] Surface water site 2a was not monitored in May 2006.
[b] Hyporheic well 1 was not monitored in June 2007, hyporheic well 3 was not monitored in May 2006.

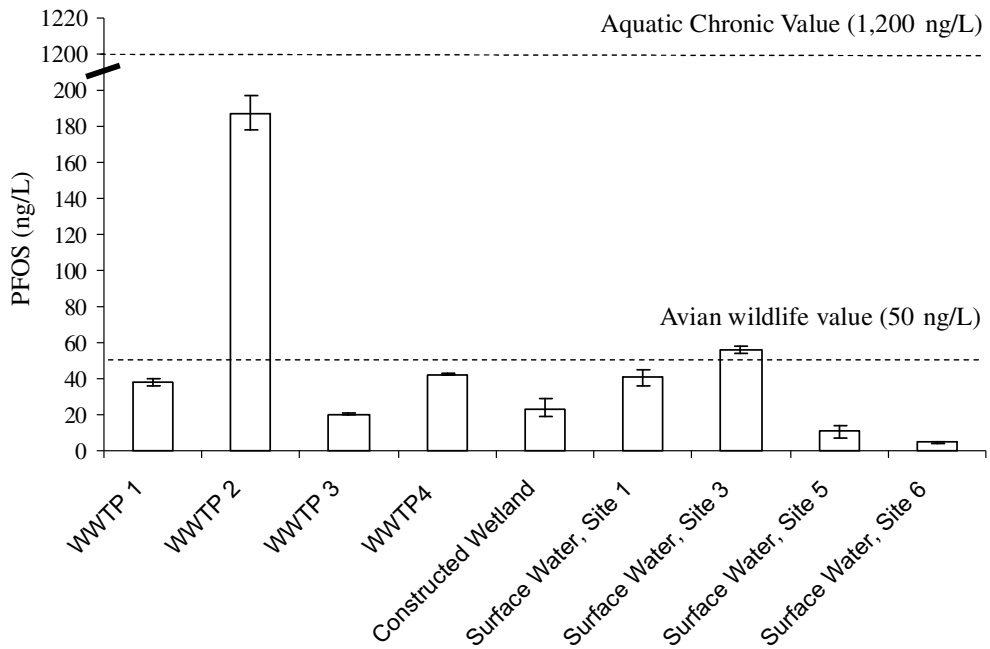

Fig. 3. Mean concentrations of PFOS in reclaimed wastewater (WWTP 1–4; June 2007, $n = 2$), a treatment and habitat wetland constructed using primary-treated wastewater (February 2006, mean of six treatment stages), and surface samples from an urban creek under consideration for stream flow augmentation with reclaimed wastewater (June 2007, $n = 2$). Error bars of mean values indicate the range. Threshold concentrations considered protective of aquatic and avian life are shown.

uses reclaimed wastewater for landscaping. Nevertheless, it is likely that the creek water is a significant source to the nearby groundwater given that the distribution and concentrations of the perfluorochemicals are consistent between surface and groundwater at the site. For example, perfluorohexanesulfonate (PFHxS), PFOS, PFDS, PFOA, and perfluorodecanoate (PFDA) were always or nearly always detected in the surface water, hyporheic zone, and groundwater (2007), whereas perfluoroheptanoate (PFHpA), perfluorooctane sulfonamide (FOSA), and *N*-EtFOSAA were detected only intermittently, and 6:2 FtS and PFNA were not present.

3.4. Implications of perfluorochemicals for water reuse

The potential contribution of water reuse projects to perfluorochemical exposure in humans will depend on the nature of the application and existing perfluorochemical background concentrations at the reuse site. No exposure to reclaimed wastewater is expected from drinking water given that in the US, recycled water is carried separately from potable water in clearly marked distribution systems.

Understanding the environmental risk requires analysis of perfluorochemical aquatic ecotoxicity at the ng/l-levels typically observed in reclaimed wastewater or at application sites. Perfluorochemical toxicity research is currently limited and must be extrapolated from laboratory organisms to complex ecosystems; however, suggested reference values provide some insight. Lowest observed effect concentrations (LOECs) for both acute and sub-chronic/chronic toxicity laboratory studies are greater than typical environmental concentrations (Lange et al., 2006), i.e. μg/l to mg/l-levels compared to ng/l-levels found in surface water, wastewater, and in water reuse sites characterized in the present study. A more conservative Tier II (potential risk) screening value of 1200 ng/l PFOS (aquatic chronic value) was determined by Beach et al. (2005) using EPA methodology by adjusting the lowest available LOEC, which is 70 times greater than the calculated aquatic chronic value. None of the reclaimed wastewaters or sites surveyed in this study exceed this screening value (Fig. 3).

For cases in which water recycling may expose organisms at upper trophic levels (i.e. wetland or stream flow enhancement), the fact that perfluorochemicals bioaccumulate in aquatic and terrestrial organisms (Giesy and Kannan, 2002; Schultz et al., 2003; Kannan et al., 2005) must be considered. The resulting tissue concentrations constitute an internal dose (Butenhoff et al., 2006), which may be more ecotoxicologically relevant than the aquatic perfluorochemical concentration. Taking into account bioaccumulation, Rostkowski et al. (2006) calculated a safe water concentration of 50 ng/l PFOS that is protective of trophic level IV avian species (avian wildlife value) that consume organisms in equilibrium with the water. Comparing this value to PFOS measured in the present study (Fig. 3), one of five reclaimed wastewaters (WWTP 2) and two of six urban creek sites (2b and 3) exceed this threshold. Assessment of the risk associated with recycled water projects is further complicated by the fact that perfluorochemicals are ubiquitous and thus are likely to be present at a site before application of reclaimed wastewater, as can be seen from the detections at the creek sites in the present study.

Compared to the global perfluorochemical burden from sources such as wastewater discharge and rain, water recycling plays only a limited role. Perfluorochemical occurrence is widespread and advanced wastewater treatment such as reverse osmosis or nanofiltration, while effective (Tang et al., 2006; Steinle-Darling and Reinhard, submitted for publication), may not be feasible for every situation. Furthermore, membrane technologies are nondestructive and typically produce brine that is released untreated. This brine is almost certain to contain perfluorochemicals at relatively high concentrations. Addressing the global perfluorochemical problem will require further research to predict the fate and toxicity of perfluorochemicals in the environment and an examination of source control.

Acknowledgements

Portions of this research were funded by the Santa Clara Valley Water District (SCVWD; California, USA), the California Department of Water Resources, the WateReuse Foundation, and the

National Science Foundation Graduate Research Fellowship program. We thank Alice Ringer and Sven Rosengreen (SCVWD), Eduard Hoehn (Eawag, Switzerland), Christopher P. Higgins, and Carlos Diaz. Any opinions, findings, conclusions, and recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of the sponsoring agencies.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2008.04.057.

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Environmental Science & Technology Letters

Letter

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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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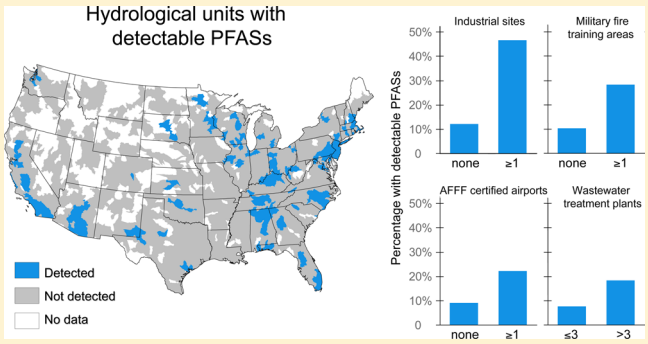
Supporting Information

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, the number of military fire training areas, and the number of 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 eight-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 is significantly associated with the detection of PFASs above the minimal 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 <10000 individuals and private wells would greatly assist in further identifying PFAS contamination sources.



INTRODUCTION

Poly- and perfluoroalkyl substances (PFASs) make up 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

Received: July 11, 2016
Accepted: July 22, 2016
Published: August 9, 2016

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DOI: 10.1021/acs.estlett.6b00260
Environ. Sci. Technol. Lett. 2016, 3, 344−350

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 because of 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, WV, 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 3−4 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 nationwide 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 eight-digit hydrologic unit code, hereafter 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 perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), perfluoroheptanoic acid (PFHpA), PFOA, perfluorooctanesulfonic acid (PFOS), and perfluorononanoic acid (PFNA) (Table S1).[28] We discuss the utility of the UCMR3 database for identifying sources of PFASs 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 36149 drinking water samples from the US EPA's UCMR3 program collected between January 2, 2013, and December 9, 2015.[28] Samples cover all 4064 public water supplies serving >10000 individuals. Data are also available for 800 public water supplies serving <10000 individuals, but this represents only a small fraction (0.5%) of the 144165 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 eight-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 (hereafter termed "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, AL, produced both PFOS and PFOA,[35] while only PFOA was used in the manufacturing process of another fluorochemical production facility in Parkersburg, WV.[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 eight-digit HUCs with PFAS levels above and below the level of 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 a low detection frequency (15 and 14 of 1601 watersheds, respectively). We used Moran's I statistic to test for spatial dependence in the model residuals from an ordinary least-squares (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 of 4864 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,

DOI: 10.1021/acs.estlett.6b00260
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New York, Georgia, Minnesota, Arizona, Massachusetts, and Illinois (Figure 1). Detection frequencies for PFASs across the 4864 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.

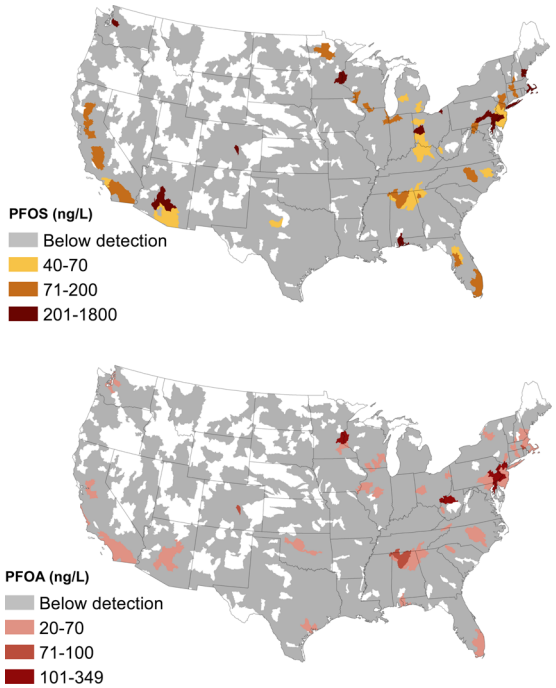

Figure 1. Hydrologic unit codes (eight-digit HUCs) used as a proxy for watersheds with detectable PFOA and PFOS in drinking water measured in the US EPA's UCMR3 program (2013−2015). Blank areas represent regions where no data are available.

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 seven PFASs, <90 ng/L; groundwater 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 end points 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, 1800 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, and PFNA) were more frequently detected in groundwater, and short-chain compounds (PFHpA and 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, and 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 2 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] Because 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 and 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 can be observed across all

Table 1. Mean Abundance of Point Sources within Eight-Digit Hydrologic Unit Codes (HUCs) with Drinking Water PFAS Concentrations above and below the Method Reporting Limit in the UCMR3 Program

	mean abundance[a] within eight-digit hydrologic unit codes			
compound	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	0.007

[a]The mean abundance is calculated as the mean number of point sources within HUCs with PFASs above or below the level of detection. [b]Only the major industrial sites participating in the US EPA's 2010/2015 PFOA Stewardship Program were included. [c]Wastewater treatment plant. [d]Two-sample t-test p-values.

DOI: 10.1021/acs.estlett.6b00260
Environ. Sci. Technol. Lett. 2016, 3, 344−350

Table 2. Spatial Regression Models for Drinking Water PFAS Concentrations as a Function of the 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's 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 an increasing abundance of point sources within the same hydrologic unit. [f]*p*-values for the spatial error regression model. The spatial error term is used to incorporate spatial autocorrelation structures into a linear regression model.

PFASs. Similarly, HUCs with point sources have higher detection frequencies for PFASs (Table S5). For example, the presence of a military fire training area within a HUC increases the frequency of detection of at least one PFAS from 10.4% to 28.2%. One caveat is that imprecise information about 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 by the 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 ($p = 0.002$), a 10% increase in PFHpA ($p = 0.155$), a 10% increase in PFOA ($p = 0.111$), and a 35% increase in PFOS ($p < 0.001$). AFFFs typically contain relatively high concentrations of PFOS and PFHxS and their polyfluorinated precursors compared to the concentrations of 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 of Valsecchi et al.[51] show PFAS releases from WWTPs are important but less significant than those from fluorochemical 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 data set. 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 data set 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, and lubricants) are usually withheld as confidential business information, and little information about 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 events 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 about 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 a 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.

DOI: 10.1021/acs.estlett.6b00260
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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 (<10000 served). The UCMR3 program includes 0.5% testing incidence for smaller public water supplies[71] and no testing of private wells, meaning that information about drinking water PFAS exposures is therefore lacking for almost one-third of the U.S. population.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00260.

Additional tables and figures (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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 the manuscript and Jahred Liddie (Harvard) for his assistance with the sensitivity analysis. T.A.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 the University of California, Berkeley. The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

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■ NOTE ADDED AFTER ASAP PUBLICATION

There was a text error in the Results and Discussion section in the version published ASAP August 9, 2016; the corrected version was published ASAP August 11, 2016.

DOI: 10.1021/acs.estlett.6b00260
Environ. Sci. Technol. Lett. 2016, 3, 344−350