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STATE OF NEW MEXICO

DEPARTMENT OF ENERGY, MINERALS AND NATURAL RESOURCES

OIL CONSERVATION COMMISSION

IN THE MATTER OF PROPOSED
AMENDMENT TO THE COMMISSION'S
RULES TO ADDRESS CHEMICAL DISCLOSURE AND
THE USE OF PERFLUOROALKYL AND
POLYFLUOROALKYL SUBSTANCES AND
IN OIL AND GAS EXTRACTION,
19.15.2, 19.15.7, 19.15.14, 19.15.16 AND 19.15.25 NMAC CASE NO. 23580

WILDEARTH GUARDIANS,

Petitioner.

REBUTTAL TESTIMONY AND EXHIBITS
OF
DUSTY HORWITT
ON BEHALF OF
WILDEARTH GUARDIANS

November 12, 2024

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I. Introduction

My name is Dusty Horwitt, and I am offering this rebuttal testimony on behalf of WildEarth Guardians in response to parties' direct testimony offered by Janet Anderson and Stephen Richardson in the matter of proposed amendment to the commission's rules to address chemical disclosure and the use of perfluoroalkyl and polyfluoroalkyl substances in oil and gas extraction, 19.15.2, 19.15.7, 19.15.14, 19.15.16 AND 19.15.25 NMAC. Each direct testimony makes misleading statements that I would like to address below.

II. PFAS are exceptionally toxic.

On page three of her testimony, Anderson argues that in characterizing PFAS as "exceptionally toxic," WildEarth Guardians is "inaccurate and misleading." Similarly, Richardson argues on page 4 of his testimony that WildEarth Guardians' statement is "incorrect." Both experts say that some types of PFAS are not toxic and that there are thousands of PFAS, most of which "have little to no toxicity data available" in Anderson's words. Therefore, it is inaccurate to characterize the class of chemicals as "exceptionally toxic."

While it is true that most PFAS have undergone little or no testing for toxicity, it is also true that most PFAS for which significant toxicological data exist are exceptionally toxic and the public has reason to be concerned that other chemicals in this class could be found to be exceptionally toxic.

The Interstate Technology Regulatory Council (ITRC) tracks the regulation of PFAS in drinking water across the United States and shows that these regulations reflect the exceptional toxicity of PFAS for which significant toxicity data exist. The ITRC is a program of the Environmental Research Institute of the States, a nonprofit corporation affiliated with the Environmental

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Council of States, a national nonpartisan, nonprofit[1] whose members include the New Mexico Environment Department.[2] The ITRC shows that as of August 2024, the federal government and eight states had set drinking water standards for nine types of PFAS, though not every one of these governments regulated each type of PFAS. The states included Massachusetts, Michigan, New Hampshire, New Jersey, New York, Rhode Island, Vermont, and Wisconsin. The types of PFAS regulated include PFOA, PFOS, PFNA, PFHxS, PFHpA, PFDA, PFBS, PFHxA, and HFPO-DA (Gen X). In only one case, did the maximum contaminant levels allowed under these regulations exceed the parts per trillion range, meaning that the regulated substances are toxic at low and, in most cases, extremely low levels. That one case involved PFHxA under Massachusetts' regulations which is limited to 400 parts per billion in drinking water. For the other types of PFAS, maximum contaminant levels ranged from 420 parts per trillion for PFBS in Michigan to only four parts per trillion for PFOA and PFOS under the EPA's regulations.[3] EPA's maximum contaminant levels also include limits of 10 parts per trillion for PFNA, PFHxS, and HFPO-DA (Gen-X). EPA added a Hazard Index Maximum contaminant level for "any mixture containing two or more of PFNA, PFHxS, PFBS, and HFPO-DA." The agency explained that "[t]hese PFAS can often be found together in different mixtures and research shows that exposure to mixtures of these chemicals may have additive health impacts."

The maximum contaminant levels for individual PFAS in the state- and EPA drinking water standards are much lower than those of such well-known toxic substances as arsenic (10 parts per billion), benzene (five parts per billion), ethylbenzene (0.7 parts per million), toluene (one part per million), and xylenes (10 parts per million).[4] With a maximum contaminant level of just four parts per *trillion* under the EPA's standards, PFOA and PFOS are more than an order of magnitude more toxic than the most toxic substance listed above, benzene, which is a known

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human carcinogen. To put these figures into additional perspective, one measuring cup of benzene could contaminate about 11 *million* gallons of drinking water.[5] The same amount of PFOA under the EPA's standards could contaminate about 28 *billion* gallons of drinking water.[6] For comparison, average annual water use in Santa Fe was about 97 gallons per capita per day in 2023[7] or about three billion gallons per year for the population of about 89,000 people.[8] These data show that even small amounts of PFAS pollution can contaminate vast volumes of water.

The ITRC's research on PFAS indicates why relatively few of the thousands of PFAS are regulated with drinking water standards: there is very little toxicological data on most of the substances, as Anderson and Richardson acknowledge. The type of PFAS that are regulated are those with more toxicological data. The ITRC reports that the largest amount of toxicological data exists for PFOA and PFOS, with "considerable data" for "PFBA, PFHxA, PFNA, PFDA, PFBS, and the GenX chemicals HFPO-DA and its ammonium salt."[9] Almost all of the substances for which considerable data exists are regulated at very low concentrations under drinking water standards in the U.S., meaning that they are exceptionally toxic. Based on this pattern, we should be concerned about whether the thousands of PFAS for which toxicological testing data are lacking would also be found to be exceptionally toxic. These uncertainties highlight the need for full chemical disclosure under WildEarth Guardians' proposed regulations so that scientists and regulators can know what chemicals people might be exposed to through oil and gas operations and test those chemicals for toxicity if such tests are lacking.

III. PTFE is of concern

Anderson writes on page 5 of her testimony that "Some PFAS, such as the fluoropolymers including polytetrafluoroethylene (PTFE), are not water soluble and would not be expected to be found widespread in groundwater." Similarly, Richardson writes on page 5 of his testimony that "heavy molecular weight polymeric PFAS (or fluoropolymers), such as PTFE, are insoluble or poorly soluble in water and, therefore, will not appreciably migrate in a groundwater setting." These statements imply that PTFE, which has been disclosed as being used for fracking in oil and gas wells in New Mexico is not toxic, but that implication is not necessarily true.

While PTFE may be of less concern than other types of PFAS, it could still pose toxic risks. Scientists'[10] and environmentalists'[11] major concerns about PTFE and other so-called fluoropolymers are related less to these substances themselves, but rather to the associated impacts of their production, use, and disposal. The production of PTFE and other fluoropolymers relies on the use of other, highly toxic PFAS as production aids. As noted in a peer-reviewed study published in 2020, these other PFAS have included fluorosurfactants such as PFOA, whose risks and extraordinary toxicity are well known, and GenX, which is similarly harmful and has replaced PFOA in fluoropolymer production.[12] PTFE and other fluoropolymers may contain these more toxic PFAS fragments, and those fragments may leach out of the PTFE during use.[13] The authors of the 2020 paper noted that

"The levels of leachables…in individual fluoropolymer substances and products depend on the production process and subsequent treatment processes; a comprehensive global overview is currently lacking."[14]

This lack of data is another reason for full chemical disclosure in oil and gas operations, so that scientists can know what substances are being injected into oil and gas wells and assess these substances and their degradation products for toxicity.

IV. Claim that over 99 percent of fracking projects have not use PFAS is misleading

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Anderson claims on page 8 of her testimony that based on disclosures to FracFocus, "over 99% of hydraulic fracturing projects on record have used no such additives" referring to PFAS. Similarly, Richardson writes on page 3 about the two types of PFAS identified by Physicians for Social Responsibility as having been used in oil and gas wells in New Mexico. "According to FracFocus," he writes, "the use of these PFAS in hydraulic fracturing operations in New Mexico is very limited; only 2.2% and 0.38% of the over 9,000 FracFocus records between 2013 and 2023 referenced PTFE or FPEG, respectively." However, these statements are misleading. Anderson and Richardson are correct that very few of the hydraulic fracturing treatments in New Mexico reported to the FracFocus database have <u>disclosed</u> PFAS, but it is impossible to know how many oil and gas wells in New Mexico have been injected with PFAS because of the lack of full chemical disclosure. As my direct testimony makes clear, New Mexico does not require full disclosure of chemicals used in oil and gas wells. The state allows oil and gas well operators to withhold from the public the identity of fracking chemicals designated as trade secrets. In PSR's 2023 report about the use of PFAS in New Mexico's oil and gas wells, we found that more than 90 percent of the 9,000 wells fracked in New Mexico over a ten-year period disclosed the use of at least one trade secret chemical. These chemical identities are unknown to the public and could be PFAS. The state requires disclosure only of chemicals used in fracking and not those used in drilling which precedes fracking or in other methods of oil and gas extraction. At least some of these chemicals could be PFAS. And evidence from other states shows that the safety data sheets for chemical products which New Mexico requires to be used as the basis for fracking chemical disclosure often contain incomplete lists of chemicals. It is possible that some of the fracking chemicals unlisted on the safety data sheets could be PFAS. These chemicals would not be disclosed under New Mexico law and would therefore not be reported to FracFocus.

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V. Oil and gas extraction has impacted groundwater and surface water

Anderson writes on page 8 of her testimony, “With many thousands of hydraulic fracturing projects completed in the US, there is no evidence of ‘already impacted regions,’ where hydraulic fracturing has impaired groundwater or surface water, as stated by PSR.” This statement is misleading and refers to a 2021 report that I authored for Physicians for Social Responsibility about the use of PFAS in oil and gas wells nationally including some wells in New Mexico. Anderson may be making this statement based on a narrow interpretation of the term “fracking” in which fracking is defined solely as what happens deep underground when fluid injected under high pressure creates fractures to allow gas and oil to be accessed. Considering the multiple stages and complexity of oil and gas operations, it would be difficult to determine in any case of water pollution associated with oil and gas extraction that this particular portion of the process was responsible as opposed to the multiple other potential pathways of pollution associated with oil and gas extraction. Yet, it is clear that there are at least hundreds of documented cases in which oil and gas production operations have impacted water supplies whether during the fracking stage of production or during other stages. As we wrote in Physicians for Social Responsibility’s 2023 report about the use of PFAS in New Mexico’s oil and gas wells, “From the mid-1980s to 2003, the state’s Oil Conservation Division found almost 7,000 cases of soil and water contamination from oil and gas waste pits and 400 cases of groundwater contamination.[15] This evidence prompted the state to enact the “pit rule” in 2008 that prohibited those unlined pits that were most likely to cause contamination, strengthened the standards for pit liners, mandated that all pits have a permit, and banned new pits within certain distances of water resources and homes.[16] The Denver Post reported in 2012 that state data in Colorado revealed more than 350 cases of groundwater pollution resulting from more than 2,000

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spills from oil and gas operations over the past five years.[17] I am aware of additional cases of documented water pollution associated with oil and gas operations. If PFAS or other chemicals were used in these operations, it is possible that they could have leached into the impacted water supplies.

There may be many more cases of water pollution associated with oil and gas extraction that have not been documented, each of which could involve chemicals used in oil and gas wells. In a 2016 report about fracking and water contamination, EPA found that several "combinations of activities and factors are more likely than others to result in more frequent or more severe impacts" including "Spills during the management of hydraulic fracturing fluids and chemicals or produced water that result in large volumes or high concentrations of chemicals reaching groundwater resources."[18] But EPA added that "[i]n places where we know hydraulic fracturing water cycle activities have occurred, data to assess impacts are often either not collected or are not publicly available in accessible forms."[19] Another hurdle the EPA encountered in assessing the number and severity of cases of water contamination associated with fracking was the lack of full disclosure of chemicals used in the fracking process. "When chemicals are claimed as CBI [confidential business information]," EPA wrote, "there is no public means of accessing information on these chemicals. Furthermore, many of the chemicals and chemical mixtures disclosed, or those detected in produced water, lack information on properties affecting their movement, persistence, and toxicity in the environment should they be spilled. Better information on these chemicals would allow for a more robust evaluation of potential human health hazards posed, and thus a better understanding about the severity of impacts should the chemicals reach drinking water resources."[20] This lack of data identified by EPA is another reason to enact WildEarth Guardians' proposed regulations, so that regulators and scientists can better understand the severity of impacts to water supplies.

VI. Limiting a prohibition to intentionally added PFAS could place health at risk

Anderson writes on page 11 of her testimony that the definition of PFAS in WildEarth Guardians' proposed regulation should be limited to "intentionally added." However, this definition would be too limited to protect health and the environment. To be sure, PFAS in chemical products used in oil and gas wells is almost certain to be intentionally added because these products are made in laboratories or factories where ingredients are controlled. However, PFAS could be unintentionally present in what is likely to be the largest volume of fluid injected into oil and gas wells: water used for hydraulic fracturing.[21] This water can be obtained from groundwater, surface water, or reused wastewater from previously fracked oil and gas wells.[22] This water may have contaminants in it that were not intentionally added but infiltrated the water nonetheless due to runoff, spills, deposition through air, or because chemicals used in a prior fracking treatment made their way into wastewater being reused in a subsequent fracking treatment. Yet these contaminants may be just as harmful to health and the environment unintentionally added as they would be intentionally added. We know that PFAS has been found in water supplies across the nation,[23] including in New Mexico. Some of these levels can be exceptionally high, especially near military facilities such as Cannon and Holloman Air Force Bases. If water with high levels of unintentionally added PFAS were used in oil and gas wells, it would introduce PFAS into those wells and potentially into nearby ground- and surface water supplies. Therefore, the Commission should strongly consider extending the prohibition on PFAS use in oil and gas wells not only to intentionally added PFAS but also to unintentionally added PFAS, at least above a certain threshold. For example, the Commission could require any unintentionally added PFAS

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in water used in oil and gas wells to be at concentrations lower than maximum contaminant levels established for PFAS by EPA or other regulatory agencies. Such water would have to be tested for PFAS -- and other toxic chemicals -- before it could be injected into oil and gas wells.

VII. Chemophobia

On page 17 of her testimony, Anderson writes that "disclosure of the potential presence of a list of various chemicals in the environment does not serve to support improved public health unless the presence of each chemical on any such list is put into the context of technical information including which chemicals specifically the disclosure covers, the concentration(s) of each chemical listed, fate and transport of each chemical, potential for human exposure to each chemical, and potential specific adverse health effects from each chemical." Disclosure without taking these steps, she argues, "could cause unnecessary health effects, including, but not limited to, psychological effects."

Waiting for the development of such information before making chemical disclosure would be counterproductive. While detailed information about each chemical used in oil and gas wells would be valuable, neither the public, regulators, nor scientists should not have to wait for this level of disclosure in order to know what chemicals are going into oil and gas wells. After all, without knowing the full list of chemicals injected into wells, it would be impossible for scientists to develop the information Anderson recommends for each chemical. In addition, first responders might rush to emergencies at well sites only to be exposed unknowingly to harmful substances. Full disclosure of chemicals used in oil and gas wells would help advance science and protect health and the environment.

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In addition, there is no evidence that New Mexicans would suffer serious psychological effects from disclosure of lists of oil and gas chemicals because the state has been making public lists of fracking chemicals since 2012 and I am unaware of evidence that New Mexicans are reporting serious psychological effects. Residents concerned about seeing lists of chemicals could always choose not to view the lists without denying other residents' interest in knowing what chemicals could impact air, soil, and water.

This concludes my rebuttal testimony, which is accurate to the best of my knowledge.

/s/ Dusty Horwitt Date: November 12, 2024

Dusty Horwitt

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[1] Interstate Technology Regulatory Council. About us. Who We Are. Accessed November 7, 2024, at https://itrcweb.org/who-we-are/.

[2] The Environmental Council of the States. Our Members. Accessed November 7, 2024, at https://www.ecos.org/members/.

[3] Interstate Technology Regulatory Council. PFAS – Per- and Polyfluoroalkyl Substances. Fact Sheets: PFAS Water and Soil Regulatory and Guidance Values Table Excel File. Accessed November 4, 2024, at https://pfas-1.itrcweb.org/external-data-tables/.

[4] U.S. Environmental Protection Agency. National Primary Drinking Water Regulations. Accessed November 4, 2024, at https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations#two.

[5] EPA's maximum contaminant level for benzene is five parts per billion. U.S. Environmental Protection Agency. National Primary Drinking Water Regulations. Accessed November 4, 2024, at https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations#two. Parts per billion refers to milligrams per one thousand liters of water. U.S. Environmental Protection Agency. Environmental Science and Technology Briefs for Citizens. Center for Hazardous Substance Research. Understanding Units of Measurement. Accessed Aug. 7, 2023, at https://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.files/fileid/14285. One measuring cup contains approximately 237 milliliters. Exploratorium. Cooking Equivalents and Measures. Accessed Aug. 7, 2023, at https://www.exploratorium.edu/food/measurements. The density of benzene is 0.88 grams per milliliter. National Institutes of Health. National Library of Medicine. National Center for Biotechnology Information. PubChem. Perfluorooctanoic Acid. Density. Accessed Aug. 7, 2023, at https://pubchem.ncbi.nlm.nih.gov/compound/Benzene#section=Density.
Therefore, the mass of one measuring cup of benzene is 208.6 grams or 208,600 milligrams. This mass of benzene is 41,720 times greater than five milligrams (EPA's maximum contaminant level per thousand liters). In order to dilute the mass of the benzene in an equivalent volume of water, we multiplied 41,720 by 1,000. The result is 41,720,000 liters of water. There are 3.785 liters of water per gallon. U.S. Environmental Protection Agency. EPA Expo Box Unit Conversion Table. Accessed Aug. 7, 2023, at https://www.epa.gov/expobox/epa-expobox-unitconversion-table. Therefore, 41,720,000 liters of water is equal to more than 11 million gallons of water.

[6] EPA's maximum contaminant level for PFOA (and PFOS) is four parts per trillion. 89 Fed. Reg. 32532 (Apr. 26, 2024). Accessed Nov. 5, 2024, at https://www.govinfo.gov/content/pkg/FR-2024-04-26/pdf/2024-07773.pdf. Parts per trillion refers to milligrams per one million liters of water. U.S. Environmental Protection Agency. Environmental Science and Technology Briefs for Citizens. Center for Hazardous Substance Research. Understanding Units of Measurement. Accessed Aug. 7, 2023, at https://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.files/fileid/14285. One measuring cup contains approximately 237 milliliters. Exploratorium. Cooking Equivalents and Measures. Accessed Aug. 7, 2023, at https://www.exploratorium.edu/food/measurements. The density of PFOA is 1.8 grams per milliliter. National Institutes of Health. National Library of Medicine. National Center for Biotechnology Information. PubChem. Perfluorooctanoic Acid. Density. Accessed Aug. 7, 2023, at https://pubchem.ncbi.nlm.nih.gov/compound/Perfluorooctanoic-acid. Therefore, the mass of one measuring cup of PFOA is 426.6 grams or 426,600 milligrams. This mass of PFOA is 106,650 times greater than four milligrams (EPA's maximum contaminant level per million liters). In order to dilute the mass of the PFOA in an equivalent volume of water, we multiplied 106,650 by 1,000,000. The result is 106,650,000,000 liters of water. There are 3.785 liters of water per gallon. U.S. Environmental Protection Agency. EPA Expo Box Unit Conversion Table. Accessed Aug. 7, 2023, at https://www.epa.gov/expobox/epa-expobox-unitconversion-table. Therefore, 106,650,000,000 liters of water is equal to a bit more than 28 billion gallons of water.

[7] City of Santa Fe Water 2023 Annual Report. Accessed November 6, 2024, at https://santafenm.gov/City_of_Santa_Fe_Water_Annual_Report_2023_1.pdf.

[8] U.S. Census Bureau. Quick Facts. Santa Fe City, New Mexico. Accessed November 6, 2024, at https://www.census.gov/quickfacts/fact/table/santafecitynewmexico,US/PST045223 (showing that Santa Fe's population in 2023 was about 89,000 people. Santa Fe's yearly water consumption is calculated by multiplying per capita per day water consumption for 2023, 97 gallons, by 89,000 people, by 365 days).

[9] Interstate Technology & Regulatory Council. Technical/Regulatory Guidance. Per- and Polyfluoroalkyl Substances, at 157-158. Accessed November 4, 2024, at https://pfas-1.itrcweb.org/wp-content/uploads/2023/12/Full-PFAS-Guidance-12.11.2023.pdf.

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[10] WG Ex. 95 Rainer Lohmann et al. Are Fluoropolymers Really of Low Concern for Human and Environmental Health and Separate from Other PFAS? Environmental Science & Technology 2020, 54, 12820-12828, 12821-2. Accessed Sept. 5, 2022, at https://pubs.acs.org/doi/10.1021/acs.est.0c03244.
[11] Safer States et al. PFAS polymers pose serious health and environmental threats. Accessed Sept. 5, 2022, at https://www.nrdc.org/sites/default/files/pfas-polymer-fs.pdf.
[12] WG Ex. 95 Rainer Lohmann et al. Are Fluoropolymers Really of Low Concern for Human and Environmental Health and Separate from Other PFAS? Environmental Science & Technology 2020, 54, 12820-12828, 12821-12822. Accessed Sept. 5, 2022, at https://pubs.acs.org/doi/10.1021/acs.est.0c03244.
[13] WG Ex. 95 Rainer Lohmann et al. Are Fluoropolymers Really of Low Concern for Human and Environmental Health and Separate from Other PFAS? Environmental Science & Technology 2020, 54, 12820-12828, 12823. Accessed Sept. 5, 2022, at https://pubs.acs.org/doi/10.1021/acs.est.0c03244.
[14] WG Ex. 95 Rainer Lohmann et al. Are Fluoropolymers Really of Low Concern for Human and Environmental Health and Separate from Other PFAS? Environmental Science & Technology 2020, 54, 12820-12828, 12823. Accessed Sept. 5, 2022, at https://pubs.acs.org/doi/10.1021/acs.est.0c03244.
[15] Laura Paskus. New Mexico's "Fracking" Legacy. KUNM (July 11, 2012). Accessed Dec. 23, 2022, at https://www.kunm.org/localnews/2012-07-11/new-mexicos-fracking-legacy.
[16] N.M. Reg. Vol. XIX, No. 11 (June 16, 2008) 372-384. Accessed February 16, 2023, at https://www.srca.nm.gov/nmac/nmregister/pdf/xix11.pdf.
[17] Bruce Finley, "Drilling Spills Reaching Colorado Groundwater; State Mulls Test Rules," The Denver Post, December 8, 2012, sec. Environment, http://www.denverpost.com/environment/ci_22154751/drilling-spills-reaching-colorado-groundwater-state-mulls-test#ixzz2EihHU2fg.
[18] WG. Ex. 34 U.S. Environmental Protection Agency. Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Water Cycle on Drinking Water Resources in the United States, at ES-3. Accessed November 8, 2024, at https://cfpub.epa.gov/ncea/hfstudy/recordisplay.cfm?deid=332990.
[19] WG. Ex. 34 U.S. Environmental Protection Agency. Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Water Cycle on Drinking Water Resources in the United States, at 10-25. Accessed November 8, 2024, at https://cfpub.epa.gov/ncea/hfstudy/recordisplay.cfm?deid=332990.
[20] WG. Ex. 34 U.S. Environmental Protection Agency. Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Water Cycle on Drinking Water Resources in the United States, at 10-25. Accessed November 8, 2024, at https://cfpub.epa.gov/ncea/hfstudy/recordisplay.cfm?deid=332990.
[21] WG. Ex. 34 U.S. Environmental Protection Agency. Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Water Cycle on Drinking Water Resources in the United States, at ES-12. Accessed November 8, 2024, at https://cfpub.epa.gov/ncea/hfstudy/recordisplay.cfm?deid=332990.
[22] WG. Ex. 34 U.S. Environmental Protection Agency. Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Water Cycle on Drinking Water Resources in the United States, at ES-12, 4-5. Accessed November 8, 2024, at https://cfpub.epa.gov/ncea/hfstudy/recordisplay.cfm?deid=332990.
[23] WG. Ex. 96 Kelly L. Smalling et al. Per- and polyfluoroalkyl substances (PFAS) in United States tapwater: Comparison of underserved private-well and public-supply exposures and associated health implications. Environment International, Vol. 178 (Aug. 2023), 108033. Accessed November 8, 2024, at https://www.sciencedirect.com/science/article/pii/S0160412023003069?via%3Dihub.

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Policy Analysis

Are Fluoropolymers Really of Low Concern for Human and Environmental Health and Separate from Other PFAS?

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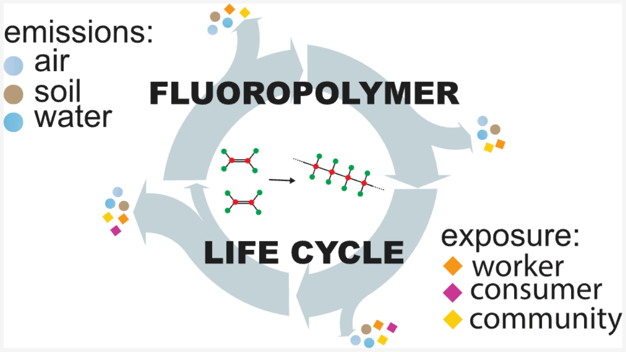

ABSTRACT: Fluoropolymers are a group of polymers within the class of per- and polyfluoroalkyl substances (PFAS). The objective of this analysis is to evaluate the evidence regarding the environmental and human health impacts of fluoropolymers throughout their life cycle(s). Production of some fluoropolymers is intimately linked to the use and emissions of legacy and novel PFAS as polymer processing aids. There are serious concerns regarding the toxicity and adverse effects of fluorinated processing aids on humans and the environment. A variety of other PFAS, including monomers and oligomers, are emitted during the production, processing, use, and end-of-life treatment of fluoropolymers. There are further concerns regarding the safe disposal of fluoropolymers and their associated products and articles at the end of their life cycle. While recycling and reuse of fluoropolymers is performed on some industrial waste, there are only limited options for their recycling from consumer articles. The evidence reviewed in this analysis does not find a scientific rationale for concluding that fluoropolymers are of low concern for environmental and human health. Given fluoropolymers' extreme persistence; emissions associated with their production, use, and disposal; and a high likelihood for human exposure to PFAS, their production and uses should be curtailed except in cases of essential uses.

1. INTRODUCTION

The class of per- and polyfluoroalkyl substances (PFAS) consists of polymers and nonpolymers.[1] Most regulatory and academic attention so far has focused on the nonpolymeric PFAS, either perfluorinated or polyfluorinated alkyl substances. Within the groups of polymeric PFAS, there are fluoropolymers, side-chain fluorinated polymers, and poly- or perfluoropolyethers.

As defined by Buck et al., "fluoropolymers" represent a distinct subset of fluorinated polymers, based on a carbon-only polymer backbone with F atoms directly attached to it, e.g., polytetrafluoroethylene (PTFE); though some fluoropolymers also have Cl or O directly attached to the backbone.[1] In this analysis, we focus on fluoropolymers, but do not assess concerns about other fluorinated polymers, namely, side-chain fluorinated polymers, and poly- or perfluoropolyethers. Previous studies have already documented that side-chain fluorinated polymers can decompose and release nonpolymeric PFAS to the environment;[2] otherwise, they present similar challenges as discussed for fluoropolymers below.

The group of fluoropolymers is dominated by PTFE; combined with fluorinated ethylene propylene (FEP), perfluoroalkoxy alkanes (PFA), ethylene tetrafluoroethylene (ETFE), and other tetrafluoroethylene-copolymers; they account for around 75% of the fluoropolymer market.[3] Other important fluoropolymers include polyvinylidene fluoride (PVDF), polyvinyl fluoride (PVF), and fluoroelastomers. One additional fluoropolymer that is discussed in this policy analysis is the functionalized fluoropolymer Nafion (produced by Chemours), which is a tetrafluoroethylene-based fluoropolymer−copolymer incorporating perfluorovinyl ether groups terminated with sulfonate groups. A review by Gardiner includes a more complete overview of the different types of fluoropolymers.[4] Industry produced 320 300 tonnes of fluoropolymers in 2018,[5] and production is steadily increasing.[4] By 2018, the global fluoropolymer industry was expected to be at $10 billion per annum.[4]

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Here, we evaluate the evidence regarding the environmental and health impacts of fluoropolymers. Our analysis was prompted by a recent suggestion that fluoropolymers should be considered as polymers of low concern (PLC).[3] According to the Organization for Economic Cooperation and Development (OECD), "polymers of low concern are those deemed to have insignificant environmental and human health impacts."[6] The PLC status of a material leads to exemptions for manufacturers from requirements under the legal chemicals management frameworks in some jurisdictions.[7] In recognition of the potential risks posed by PFAS-related polymers, the U.S. Environmental Protection Agency (EPA) has denied PLC exemptions for side-chain fluorinated polymers but has not acted on fluoropolymers per se.[8]

We here distinguish between fluoropolymer substances, fluoropolymer products, and fluoropolymers in finished articles. A fluoropolymer substance such as PTFE, FEP, and PFA is a material of known chemical structure. A fluoropolymer product is the actual material produced and sold by a chemical manufacturer (e.g., Chemours, Solvay, Daikin, Asahi Glass, etc.), it comes in different grades (e.g., Teflon-granulate, Teflon-fine powder, etc.), and may contain impurities from the production process. These fluoropolymer products are sold to manufacturers of finished articles (e.g., PTFE tape, waterproof clothing with a PTFE membrane, PTFE-coated cookware, etc.) who incorporate the fluoropolymer products in their finished articles. The distinction is important, as there are many different processes of making fluoropolymer products. For example, some fluoropolymers do not require PFAS-based processing aids in their manufacture by suspension polymerization (e.g., granular PTFE), whereas other fluoropolymers (e.g., fine powder PTFE and PVDF) are manufactured using PFAS-based processing aids during emulsion polymerization. Fluoropolymers are also diverse in how they are produced (as granulates, fine powders, or aqueous dispersions, through emulsion or suspension polymerization, with different grades), shipped, and used, which renders generic judgements on their behavior and characteristics difficult.

Recently, polymers have been under increased regulatory scrutiny. In 2019, the industry-led European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) developed a Conceptual Framework for Polymer Risk Assessment ("CF4Polymers")[9] and, in 2020, the European Commission contracted a study to propose criteria for the identification of polymers requiring registration (PRR) under REACH ("the Wood report").[10] CF4Polymers provides guiding elements to be considered in assessing potential ecological and human health hazards and risks posed by polymer substances. Unlike the PLC concept, CF4Polymers also considers specific life cycle stages of polymer products and their associated routes of exposure. CF4Polymers thus appears sufficiently flexible to allow consideration of potential chemical hazards at each life stage of a fluoropolymer. However, the authors of the CF4Polymers framework support the PLC approach as a means of streamlining polymer risk assessments. They specifically support the findings of Henry et al.[3] and state that they are "...unaware of scientific evidence to justify generally assigning fluoropolymers the same level of regulatory concern as other PFAS."[9] The Wood Report notes that side-chain fluorinated polymers "can potentially lead to the formation of PFAS substances as a result of degradation," but considers fluoropolymers as PLCs, following the recommendations of Henry et al.[3]

The PLC concept is currently derived from the characteristics of substances and articles but does not cover problems occurring during production and disposal. Specific fluoropolymer articles could hence technically meet the definitions of a PLC, but still pose significant concerns to human health and the environment due to emissions occurring during the life cycle (Figure 1). A well-known case where this occurs is the release of processing aids during the manufacture of some fluoropolymers (such as PTFE, FEP, PFA, PVDF, and some fluoroelastomers). The pollution caused by emissions of low-molecular-weight PFAS used as polymer processing aids (i.e., emulsifiers, dispersants, and surfactants at large) for the manufacture of some types of fluoropolymers has received considerable attention.[11−13]

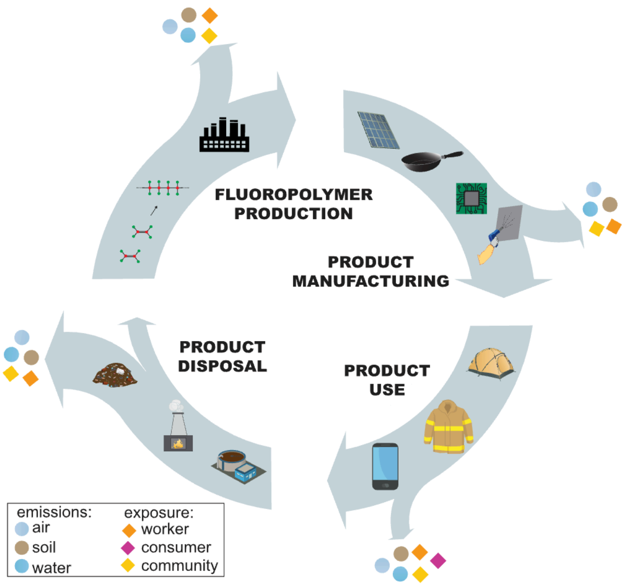

Figure 1. Conceptual diagram of PFAS emissions during fluoropolymer production, product manufacturing, and disposal.

In this article, we identify concerns for environmental and human health resulting from emissions during fluoropolymer production, processing, and disposal. We first review the link between some types of fluoropolymers and PFAS emissions and then turn to more general concerns associated with (fluoro)polymers.

2. HISTORY OF POLLUTION FROM FLUOROPOLYMER PRODUCTION IS CLOSELY TIED TO USE OF PFAS AS POLYMER PROCESSING AIDS

Low-molecular-weight PFAS have been used for decades as emulsifiers in the polymerization of some types of fluoropolymer substances. The resulting long-term exposure of production workers, the environment, and nearby neighborhoods to high levels of PFAS polymer processing aids by fluoropolymer manufacturers is now well documented and has driven much of the initial action on PFAS control.[14−21]

Historically, the most widely used polymer processing aids were the ammonium salts of perfluorooctanoic acid (PFOA) and perfluorononanoic acid (PFNA).[22,23] The majority of PFOA and PFNA now in the global environment is a result of

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the historical use of salts of these substances as processing aids.[22,24] As a consequence of human and environmental health concerns, under the U.S. EPA 2010/15 Stewardship Program, eight major manufacturers phased out PFOA/PFNA in their fluoropolymer production.[25] Many other manufacturers, though, still utilize PFOA as a processing aid; PFOA emissions have, for example, now widely polluted the Asian (especially Chinese) environment.[26] These Asian emissions are being discharged into the atmosphere, rivers, and oceans in large quantities and are causing additional global-scale pollution.[26]

3. SUBSTITUTE FLUOROPOLYMER PROCESSING AIDS RAISE SIMILAR CONCERNS

Fluoropolymer producers in industrialized countries have moved to substitute PFOA and PFNA in polymer production with structurally similar alternatives such as per- and polyfluoroalkylether carboxylic acids (PFECAs).[23,27,28] These PFECAs are not technically classified as "long-chain" perfluoroalkyl acids (PFAAs) like PFOA and PFNA, but they have similar physical and chemical properties (including surfactancy and resistance to degradation) when compared with the original emulsifiers.[28]

One example is the substitution by Chemours of the ammonium salt of PFOA with the ammonium salt of hexafluoropropylene oxide dimer acid (HFPO-DA, CAS 62037-80-3, or GenX; Figure 2a) for PTFE production. When released into the environment, the ammonium salt of HFPO-DA dissociates to HFPO-DA, which due to similarly high persistence and mobility as its predecessor PFOA, accumulates in surface water, groundwater, and soil.[29,30] HFPO-DA has also been observed in surface water and drinking water in areas where it is produced, e.g., in North Carolina[31] and The Netherlands.[14] HFPO-DA does not bioaccumulate in animals to the same extent as PFOA[32] but has been added to the E.U.'s Candidate List of Substances of Very High Concern (SVHC) due to an equivalent level of concern about its very high persistence, mobility in water, potential for long-range transport, accumulation in plants, and observed effects on human health and the environment.[33]

In another example, PFNA or, more specifically, its ammonium salt, has been substituted with salts of another PFECA (CAS 329238-24-6; Figure 2b).[28] The dissociated PFECA has since been detected in the surface water near a fluoropolymer production facility in Italy[34] and in the soil,[35] surface, and groundwater near a similar PVDF facility in West Deptford, New Jersey (U.S.).[36] Another replacement polymer processing aid, cC604, is the ammonium salt of [perfluoro-{acetic acid, 2-[(5-methoxy-1)] (Figure 2c). cC604 has been detected in surface and groundwater in the Veneto region in Italy.[37] Also, ammonium 4,8-dioxa-3H-perfluorononanoate (CAS 958445-44-8, ADONA; Figure 2d) is a PFECA processing aid that has been detected in the Rhine River in Germany[38] and in the blood of individuals living near a fluorochemical production facility in this area.[39]

These examples demonstrate the similar concern between legacy and replacement fluoropolymer processing aids mentioned above in terms of environmental exposure, bioaccumulation, and toxicity (see also section 6 below).[40,41] Many more PFAS with similar structures have been patented for possible use as fluoropolymer processing aids.[42−44] Thus, even if individual processing aids are banned, many other PFAS are available with the same functionality and similar concerns with respect to persistence and human health effects. 3M claimed that modern containment technologies recapture approximately 98% of polymer processing aids such as PFOA and others,[45] but losses of 2% are still of concern given their persistence and related properties. Moreover, independent data are not available to support this claim.

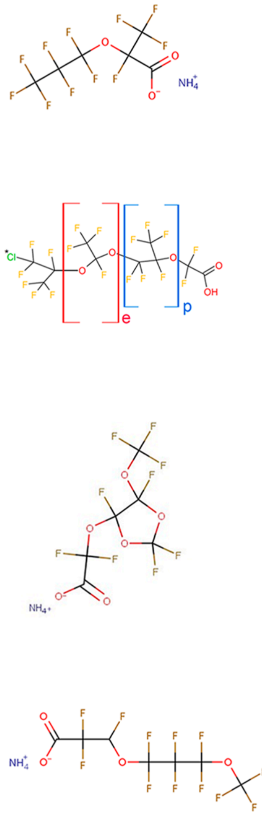

Figure 2. Structures of replacement fluoropolymer processing aids detected in the environment. (a) Ammonium salt of hexafluoropropylene oxide dimer acid (HFPO-DA, CAS 62037-80-3, or "GenX") detected in the environments of North Carolina and The Netherlands. (b) Functionalized PFPE reported in Wang et al. (CAS 329238-24-6) now observed in the Bormida River (Italy) and New Jersey. Note, the e = ethyl group can range from 0−2 units and p = propyl group can range from 1−4 units with the ethyl group most likely being closest to the chlorine. Additionally, the chlorine can be on the terminal carbon as shown or on the C2 position as $CF_3CF(Cl)CF_2{-}O$. (c) Perfluoro{acetic acid, 2-[(5-methoxy-1,3-dioxolan-4-yl)oxy]}, ammonium salt (CAS No 1190931-27-1; cC604), now observed in ground- and surface water in the Veneto region (Italy). https://echa.europa.eu/substance-information/-/substanceinfo/100.207.411. (d) Ammonium 4,8-dioxa-3H-perfluorononanoate (CAS 958445-44-8; ADONA) detected in the Rhine River and serum samples.

4. MONOMER, OLIGOMER, AND SYNTHESIS BYPRODUCT EMISSIONS DURING THE PRODUCTION OF FLUOROPOLYMERS

Fluoropolymers are made of one or several types of monomers. During the synthesis, incomplete polymerization will result in residual monomers and oligomers and smaller "polymers" with up to about 100 monomer units. These and other synthesis byproducts are not bound to the polymers and may be released to air upon heating during manufacturing and processing (including sintering) and to water through wastewater

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streams.[11,15] For example, a series of polyfluoroalkyl carboxylic acids were discovered near Decatur, Alabama (U.S.), each differing by one 1,1-difluoroethene, CF_2CH_2, unit, which was likely used as a building block for production of PVDF at that site.[15] Chemours discovered more than 250 unknown, potentially unique, PFAS in their wastewater in North Carolina.[46] Many ultra-short-chain fluorinated byproducts are highly volatile and therefore difficult to remove in filters or liquid scrubber baths. An example is trifluoromethane (CHF_3), which has a boiling point of −82.1 °C and belongs to the group of hydrofluorocarbon (HFC) gases (HFC-23); it has a 100-year global warming potential of 12 400 relative to CO_2.[47]

Little is known about emissions of airborne fluoropolymer particles and oligomers, another potential source of PFAS in the atmosphere. Henry et al. specified the particle size in fluoropolymer powders to vary between 50 and 250 μm, larger than the harmful particle sizes of PM10 and PM2.5 (10 and 2.5 μm) in terms of harm caused by inhalation.[3] However, fluoropolymer particles vary in size[48] and may contain and transport residual monomers/oligomers long distances from their emission sources.

Various PFAS oligomers were recently detected in the stack emission samples collected from a fluorochemical production site.[49] A wide range of byproducts of the functionalized fluoropolymer Nafion have been observed in the environment, fish,[50] and birds[51] downstream of this facility. Moreover, a recent study involving the residents of Wilmington, North Carolina found that the majority have Nafion Byproduct 2 (99%) and other related PFAS in their blood serum as a result of consuming contaminated drinking water in this region.[52] These Nafion-related compounds could be the result of manufacturing discharges[12] or losses resulting from Nafion use over time.[53,54] It is noted that Nafion probably does not meet the PLC criteria because it has a reactive functional group that can be lost under its harsh use conditions.

5. LEACHING OF LOW-MOLECULAR-WEIGHT PFAS FROM FLUOROPOLYMERS DURING PROCESSING AND USE

Linked to the use of PFAS as production processing aids (see above), there are concerns regarding the remaining low molecular weight PFAS in fluoropolymers after production. For example, Henry et al. argued that fluoropolymers are not toxic, based on a data set that was restricted only to a few fluoropolymer substances, typically >100 000 Da.[3] Concentrations of leachable components reported for those specific fluoropolymer products, particularly a PTFE fine powder, were labeled "very low" at 1 ppm (i.e., 1 mg/kg),[3] though earlier studies reported concentrations of 1−10 ppm in PTFE fine powder and much higher in PTFE aqueous dispersion (see SI in Wang et al.[24]). Similar levels of PFAAs (0.3−24 ppm) were found in personal care articles that contained PTFE fine particles (assuming the cosmetics contained 1% PTFE, the range of leachables is 0.3−24 ppm; if the total organofluorine measurements represented PTFE fine powder, then the range of PFAA-leachables is 15−1000 ppm).[55] Residuals of 1 ppm may have significant toxicological relevance, given the recently proposed drinking water guidelines for some PFAS set at 10−100 ng/L in different countries.[56,57] The levels of leachables (e.g., processing aids, synthesis byproducts and oligomers) in individual fluoropolymer substances and products depend on the production process and subsequent treatment processes; a comprehensive global overview is currently lacking.

Fluoropolymer-coated food contact materials (e.g., metal cookware), if not properly pretreated, could lead to the leaching of nonpolymeric PFAS residuals into food during the use phase. Processing aids are known to leach from fluoropolymer articles, for example in chromatographic instrumentation, causing a consistent background signal in analytical chemistry at the ppt level[58,59]

Further, Henry et al. state that the low residual levels found in the finished PTFE products that they tested are due in large part to "aggressive" steps taken to wash out residuals and drive off volatiles.[3] Such aggressive treatment raises the question of how these residuals and volatiles are captured and their releases controlled or if production byproducts become air or water emissions with potential for human exposure. There is evidence that the drying step (sintering) of fluoropolymers has led to substantial emissions to air of processing aids at sites of PTFE production (West Virginia (US)[29] and The Netherlands) and use sites in the US (North Bennington, VT; Merrimack, NH; Hoosick Falls, NY).[60−62]

6. TOXICITY OF FLUOROPOLYMER PROCESSING AIDS, MONOMERS, AND OLIGOMERS

Legacy processing aids (i.e., PFOA, PFNA) used to manufacture fluoropolymers are linked to a wide range of health effects in experimental animal models (causative) and humans (associative), including certain types of cancer, immunotoxicity, reproductive and developmental toxicity, liver toxicity, and thyroid disease.[63] The production of many fluoropolymers still requires the use of PFAS as surfactants or as monomers, which causes releases to the environment during manufacture, and thus may pose a risk to human health and the environment (see also point 9 below). A replacement processing aid, HFPO-DA, shows a similar toxic potency in rodents to that of PFOA,[41] but its pharmacokinetics in humans is less certain.[64] Few reviews have been published regarding the potential toxicity of other replacement PFECAs, such as ADONA[65,66] or the PFECA CAS 329238-24-6,[67] but these replacement chemicals need to have similar properties to work and are as environmentally persistent as the original polymer processing aids.[40]

7. PENETRATION OF CELL MEMBRANES BY MACROMOLECULES

While not specific to fluoropolymers, the PLC status is partially based on a mass-based cutoff for cellular uptake (MW of >1000 Da or 10 000 Da, depending on reactive functional groups). This was summarized by Henry et al., who advocated for the PLC status of some fluoropolymers by suggesting "polymers are too large to penetrate cell membranes."[3] This position is not currently supported by the scientific literature related to the bioavailability of similarly sized micro- and nanoplastics of fluorine-free polymers. Nearly a decade ago, Jiang et al. showed that polystyrene nanoparticles of about 100 nm diameter are easily able to enter stem cells.[68] Similarly, Pitt et al. reported that 42 nm polystyrene nanoparticles were present in tissue and organs of maternally and coparentally exposed F1 embryos/larvae, proving membrane crossing capabilities of polymer nanoparticles.[69] Polymer nanoparticles with molecular weights between 12 000 and 21 000 Da have been used to deliver chemotherapeutic drugs to cancer cells,[70] and those on the order of tens of nanometers in size have been found to enter cells and eventually even cell nuclei.[71,72]

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Furthermore, Geiser et al. showed that inhaled spherical microparticles of Teflon were able to migrate into the surface lining layer of hamster alveoli, where interactions with lung cells could occur.[73] Many fluoropolymer substances are marketed in the form of suspensions with submicron fluoropolymer particle sizes (see, e.g. https://www.teflon.com/en/products/dispersions), thus, release of bioavailable fluoropolymer particles is plausible. On the basis of such emerging evidence from environmental and medical research on diverse macromolecules,[74] a blanket statement that polymers cannot enter cells is factually inaccurate.

It is recognized that the global production of fluoropolymers (though not insignificant at 320 000 tonnes in 2018,[5] and increasing[4]) is relatively low in volume (at ~0.1%) compared to global production of plastics (300 million tonnes in 2018[75]). However, detection of PTFE microparticles in Mediterranean fish and remote Arctic Ocean sediment samples demonstrates their global presence, albeit representing a small fraction of all detected microplastics.[76,77] We note that the occurrence, exposure to, and toxicity of nanoplastics is an area of ongoing research with many unknowns.[78]

8. PERSISTENCE AND DISPOSAL OF FLUOROPOLYMERS

Fluoropolymers are extremely persistent under environmental conditions,[45] which, in the same way as for other polymers, can lead to a wide array of issues, particularly with respect to disposal of fluoropolymer-containing wastes and products.[79] Current concern over microplastics present in the oceans provides an example of why the manufacture of polymers likely to be released into the environment should ideally be curtailed.[80] Hence, production of persistent polymers, such as the highly persistent fluoropolymers, should occur only in time-limited essential use categories, i.e., critical for the safety, health, and functioning of society.

On the industrial scale, recycling of clean PTFE waste or scraps generated during production is already happening, often by converting these into PTFE micropowder (so-called fluoroadditives) and then using them to reduce wear rate and friction.[81] This has the unintended consequence of spreading fluoropolymers into more uses, and complicating any efforts of controlling and reducing their losses from the technosphere. More recently, a pilot-scale industrial high-temperature recycling process (vacuum pyrolysis) to regenerate gas-phase monomers from end-of-life industrial-scale fluoropolymer products has been established.[82]

On the other hand, the recycling of fluoropolymers in consumer articles is not well established, as those fluoropolymers are typically contaminated by other substances and fillers, which makes recycling difficult.[82,83] Fluoropolymers applied to metal articles (e.g., nonstick frying pans) might end up in metal recycling streams, leading to their uncontrolled breakdown in metal smelters at high temperatures.

Commercial bakeries regularly remove fluoropolymer coatings from their baking forms after 12−24 months of use either via burning or blasting, with unknown emissions of PFAS and fluoropolymer particles to air, water, and soil, and then have the forms recoated. In Sweden alone, for example, every year some 20 000 baking pans are "recoated" with a total baking surface of 500 000 m^2. Stripping the old coating is performed by either "burning off" at 450 °C for 4−5 h to "break down" the coating followed by grit blasting or by water blasting at 1500 bar; it is unclear whether emissions are controlled.[84]

Landfilling of fluoropolymers leads to contamination of leachates with PFAS and can contribute to releases of plastics and microplastics. Even with an exceptional chemical and thermal stability, fluoropolymer particles will be disintegrated into microplastics by weathering and physical stress, which enables further dispersion and increased bioavailability.[85,86] Storage in abandoned mines and oil extraction fields is an option not routinely explored (except when court-ordered, see below) but is costly and logistically complicated.

The remaining option for the disposal of fluoropolymers is incineration; its effectiveness to destroy PFAS and the tendency for formation of fluorinated or mixed halogenated organic byproducts is not well understood.[87]

Tetrafluoromethane and perfluoroethane have been identified as very stable combustion byproducts from the incineration of fluorine-containing waste, but given the extra stability of perfluorinated radicals, larger molecules might also be formed as a result of incomplete combustion.[87,88] PTFE can produce PFCAs (including trifluoroacetic acid (TFA)) and other fluorinated compounds when heated to temperatures between 250 and 600 °C (relevant for uncontrolled burning).[89−91] Myers et al. identified multiple thermal decomposition products of polychlorotrifluoroethylene (PCTFE), a common fluoropolymer, including 29 perhalogenated carboxylic acid groups and 21 chlorine/fluorine-substituted polycyclic aromatic hydrocarbon groups, such as mixed halogenated benzenes and naphthalenes.[92]

It is currently unclear whether typical municipal solid waste incinerators can safely destroy fluoropolymers without emissions of harmful PFAS and other problematic substances.[87] There is evidence that PFOA itself is not thermally stable at elevated temperatures[93] or produced in high-temperature (>1000 °C) incineration of fluorotelomer based articles.[94,95] Combustion within an optimized waste incinerator (870 °C, 4 s residence time of 0.3% PTFE by weight), as opposed to the less strict 850 °C and 2 s required in the E.U. for municipal solid waste incinerators[96] yielded inconclusive results with respect to stack emissions of PFAS.[97] PFOA was regularly detected in the exhaust, but the study was marred by elevated blanks. The authors were only able to account for 56−78% of the fluorine mass balance during incineration, meaning that a wide variety of other PFAS could have been released.[97] In any case, municipal waste incinerators can only tolerate limited amounts of fluoropolymers due to the corrosive nature of the hydrogen fluoride released during the fluoropolymers' thermal decomposition.[45]

9. CAN FLUOROPOLYMERS BE CONSIDERED SEPARATELY FROM THE USE OF PFAS AS PROCESSING AIDS?

For current manufacturing processes, it has not been clearly demonstrated that those fluoropolymer products that are made using emulsion polymerization (in contrast to suspension polymerization) can be produced without the use and emissions of PFAS as processing aids. For example, after discovery of widespread PFAS contamination of the Cape Fear watershed resulting from the use as various PFAS, including HFPO-DA, as processing aids in the production of fluoropolymers, a "zero" emission policy to water was mandated in North Carolina.[13] This includes the capture of PFAS-containing liquid processing waste, which is now moved out of the state for deep well injection,[98] merely relocating the environmental concern and creating the possibility of spills and

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leaking. In Dordrecht (Netherlands), regulations exist for air emissions (which are now restricted to 450 kg/y), direct (surface water) emissions (recently restricted to 5 kg/y), and indirect emission to a local waste water treatment plant (recently restricted to 140 kg/y, it was 2 tonnes/y in 2018 and 6 tonnes/y in 2017).[14] A report to the Nordic Council compiled additional production and release estimates for various per- and polyfluoroalkylethers.[99] Emulsion polymerization processes with much reduced PFAS use,[100] or without the use of PFAS,[44,101] as processing aids have been developed, but it is unclear whether they will be implemented industry-wide. A phase-out of all PFAS as fluoropolymer processing aids would be a vast improvement but would not address the current problems associated with impurities, as well as a lack of recycling and disposal.

10. ARE FLUOROPOLYMERS POLYMERS OF LOW OR HIGH CONCERN?

The concerns we present above suggest that there is no sufficient evidence to consider fluoropolymers as being of low concern for environmental and human health. The group of fluoropolymers is too diverse to warrant a blanket exemption from additional regulatory review. Their extreme persistence and the emissions associated with their production, use, and disposal result in a high likelihood for human exposure as long as uses are not restricted. Concluding that some specific fluoropolymer substances are of low concern for environmental and human health can only be achieved by narrowly focusing on their use phase, as was done by Henry et al.[3]

Ideally, the assessment and management of fluoropolymer products would consider the complete life cycle including associated emissions during production and disposal, as described above (see also Figure 1). The ECETOC CF4Polymers was an improvement over the early OECD PLC criteria by introducing life cycle considerations in polymer risk assessment, and it is recommended that these approaches are applied rather than focusing narrowly on the use phase. Monitoring emissions of harmful volatile and particulate PFAS at manufacturing and incineration sites is urgently needed. Furthermore, mapping of all industrial activities that produce, process, and dispose/incinerate fluoropolymers would allow for targeted monitoring of potentially contaminated sites and protection of potentially exposed communities.

Further, there is no scientific basis to separate and subsequently remove fluoropolymers from discussions of other PFAS as a class or in terms of their impacts on human or environmental health. The conclusion that all fluoropolymers are of low concern, simply based on tests on limited substances of four types of fluoropolymers,[3] ignores major emissions linked to their production and large uncertainties regarding their safe end-of-life treatment.

In addition, there is only very limited information on the compositions, grades, etc. of the fluoropolymer products on the market. Not all fluoropolymer products meet the OECD PLC criteria, as suggested by Henry et al. in the conclusions of their paper; for example, functionalized fluoropolymers do not meet the criteria (e.g., Nafion) due to the presence of reactive functional groups. It would anyway be impossible to verify if all fluoropolymer products were PLC or not with the information available in the public domain. If PLC is part of a regulatory framework, PLC assessment should be performed on a product-by-product basis because various grades and commercial products of fluoropolymers may or may not meet the PLC criteria. For example, a PTFE product made in China cannot be assumed to be equivalent to the PTFE products tested by Henry et al.[3] Our recommendation is to move toward the use of fluoropolymers in closed-loop mass flows in the technosphere and in limited essential-use categories, unless manufacturers and users can eliminate PFAS emissions from all parts of the life cycle of fluoropolymers.

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Notes

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Per- and polyfluoroalkyl substances (PFAS) in United States tapwater: Comparison of underserved private-well and public-supply exposures and associated health implications

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ABSTRACT

Drinking-water quality is a rising concern in the United States (US), emphasizing the need to broadly assess exposures and potential health effects at the point-of-use. Drinking-water exposures to per- and poly-fluoroalkyl substances (PFAS) are a national concern, however, there is limited information on PFAS in residential tapwater at the point-of-use, especially from private-wells. We conducted a national reconnaissance to compare human PFAS exposures in unregulated private-well and regulated public-supply tapwater. Tapwater from 716 locations (269 private-wells; 447 public supply) across the US was collected during 2016–2021 including three locations where temporal sampling was conducted. Concentrations of PFAS were assessed by three laboratories and compared with land-use and potential-source metrics to explore drivers of contamination. The number of individual PFAS observed ranged from 1 to 9 (median: 2) with corresponding cumulative concentrations (sum of detected PFAS) ranging from 0.348 to 346 ng/L. Seventeen PFAS were observed at least once with PFBS, PFHxS and PFOA observed most frequently in approximately 15% of the samples. Across the US, PFAS profiles and estimated median cumulative concentrations were similar among private wells and public-supply tapwater. We estimate that at least one PFAS could be detected in about 45% of US drinking-water samples. These detection probabilities varied spatially with limited temporal variation in concentrations/numbers of PFAS detected. Benchmark screening approaches indicated potential human exposure risk was dominated by PFOA and PFOS, when detected. Potential source and land-use information was related to cumulative PFAS concentrations, and the number of PFAS detected; however, corresponding relations with specific PFAS were limited likely due to low detection frequencies and higher detection limits. Information generated supports the need for further assessments of cumulative health risks of PFAS as a class and in combination with other co-occurring contaminants, particularly in unmonitored private-wells where information is limited or not available.

1. Introduction

The quality and sustainability of drinking-water are rising concerns in the United States (US) because of population-driven water demands, increasing contamination of drinking-water resources, and a growing understanding of potential human-health consequences associated with

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exposures to contaminants. Per- and poly-fluoroalkyl substances (PFAS), "forever chemicals," are a class consisting of thousands of substances (Glüge et al., 2020) that are national/global human-health concerns due to environmental prevalence and persistence, toxicity, and human exposures through water and food (Evich et al., 2022; Sunderland et al., 2019; Tokranov et al., 2021). Legacy long-chain perfluoroalkyl acids (PFAAs) include perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), which are historically two of the most widely used and studied chemicals in the PFAS group (Tokranov et al., 2021). Due to their persistence, toxicity and bioaccumulation potential, actions have been taken voluntarily by industries and regulators worldwide to reduce the release of PFAAs including PFOA, PFOS and perfluorohexane sulfonic acid (PFHxS) (Butenhoff et al., 2009; Wang et al., 2015; Wang et al., 2013). Legacy PFAAs have been replaced by shorter chain analogues (C3-C6) such as perfluorobutanoic acid (PFBA), perfluorobutane sulfonic acid (PFBS), and perfluorohexanoic acid (PFHxA) as well as perfluoroether carboxylic acids (Bao et al., 2018; Li et al., 2020; Wang et al., 2015). These replacement PFAS are considered less bioaccumulative but still have the potential to persist in the environment and are quickly becoming the dominant PFAS in aquatic ecosystems (Wang et al., 2015; Wang et al., 2013). For example in chemical and product manufacturing in the US, two of the replacement products for PFOA and PFOS are the hexafluoropropylene oxide dimer acid (HFPO-DA or GenX) and PFBS, respectively (U.S. Environmental, 2022a).

PFAS are also widely-documented in human plasma (Hu et al., 2019) and can be maternally transferred pre- and post-natal (Bach et al., 2016; Blake and Fenton, 2020). Some PFAS have also been linked with human developmental, metabolic, and immune disorders as well as certain types of cancers (Barry et al., 2013; Grandjean and Budtz-Jørgensen, 2013; Liu et al., 2018). Potential pathways to drinking-water resources are diverse, including biosolids application, outdoor products (e.g., ski waxes), industrial releases, firefighting foams, and discharges from wastewater treatment, septic, stormwater, and landfill systems (Houtz et al., 2013; Kurwadkar et al., 2022; Masoner et al., 2019; Masoner et al., 2020; Salvatore et al., 2022; Sims et al., 2022). PFAS have been detected globally in surface and groundwater drinking–water resources (Evich et al., 2022) and in public drinking–water supplies prior to distribution (Andrews and Naidenko, 2020; Domingo and Nadal, 2019; Hu et al., 2016; McMahon et al., 2022).

In the US, publicly–available large national (e.g., U.S. Environmental Protection Agency's Third Unregulated Contaminant Monitoring Rule (UCMR3) (U.S. Environmental Protection Agency, 2022b) and state-specific databases comprise results from samples collected from public drinking-water treatment plants after treatment and prior to distribution, an approach which does not account for distribution-system changes that can affect consumer exposures at the tap (e.g., (Chen et al., 2019; Li et al., 2022; Mohammadi et al., 2022). Currently, limited information exists on drinking-water PFAS concentrations at the point of exposure (i.e., point-of-use tapwater) in public-supply and especially in unregulated and generally unmonitored private-wells. Private-well owners make up about 13–14% of the US population (Dieter et al., 2018) and previous research has documented a range of contaminant concerns in unregulated/unmonitored private-well drinking-water (Bradley et al., 2021a; Charrois, 2010; Focazio et al., 2006). Because the burden of private-well maintenance and monitoring falls on the owner (U.S. Environmental Protection Agency, 2023c), private-well water quality information remains scarce and typically is limited to only a few contaminants (e.g., coliform bacteria), due to high analytical costs, confusion of aesthetic quality (taste, odor) with safety, and a range of socioeconomic factors (Seltenrich, 2017; Zheng and Flanagan, 2017). This circumstance leads to the increased probability of unrecognized contaminant exposures (Zheng and Flanagan, 2017) and adverse health effects to private-well dependents (American Academy of Pediatrics, 2009) and illustrates the continued need for comparable assessments in both private-wells and public-supply at the point-of-use. For PFAS, such assessments are essential for quantifying population-level drinking-water exposures, identifying at-risk or contaminated water sources or systems, and determining potential human-health implications, especially for vulnerable subpopulations (Andrews and Naidenko, 2020).

PFAS regulations are changing rapidly in the US as a growing number of increasingly strict state and federal drinking-water guidelines/benchmarks have been established over the last 20 years (Interstate Technology Regulatory Council, 2022; Post, 2021; U.S. Environmental Protection Agency, 2023b). However, there currently are no final enforceable national drinking-water standards (e.g., maximum contaminant level [MCL]) for PFAS in the US and some states over the last few years have adopted their own enforceable MCLs for several PFAS (Interstate Technology Regulatory Council, 2022). In March 2023 U.S. Environmental Protection Agency (EPA) released, for public comment, proposed MCLs of 4 ng/L and MCLGs (maximum contaminant level goal) of zero for PFOA and PFOS. MCLGs are non-enforceable health goals established to protect vulnerable subpopulations irrespective of treatment technology, cost, and limits of detection. Further, any contaminant considered a likely or known carcinogen receives an MCLG of zero (U.S. Environmental Protection Agency, 2023b). A hazard index approach was also proposed to regulate PFHxS, GenX, PFNA, and PFBS. This approach considers the health-based values for PFHxS (9 ng/L), GenX (10 ng/L), PFNA (10 ng/L), and PFBS (2000 ng/L) to determine if the combined individual hazard quotient values pose a potential risk (U.S. Environmental Protection Agency, 2023b; U.S. Environmental Protection Agency, 2020). Significant shifts in guidelines to be more stringent are due primarily to improved information on potential health effects and exposure of sensitive subgroups such as infants through drinking-water (Post, 2021) indicating the need for more robust regional and national assessments of drinking-water with an emphasis on downstream exposure at the point-of-use especially as new proposed MCLs are promulgated in the US.

The U.S. Geological Survey (USGS) has been conducting ongoing national research on the potential for human exposures (both home and workplace) from natural and man-made tapwater contaminants, including PFAS (Bradley et al., 2020; Bradley et al., 2018; Bradley et al., 2023a; Bradley et al., 2021a; Bradley et al., 2021b; Bradley et al., 2023b). To better understand human exposure to PFAS at the point-of-use, we conducted a standardized analytical survey of PFAS nationally using a network of volunteers and combined this new data with tapwater samples collected previously by our research team to maintain consistency in data collection/processing. The overall objectives of the study were to (1) directly compare PFAS exposure in regulated public-supply tapwater to tapwater from unregulated private-wells, (2) provide information on potential aggregated human-health effects of PFAS using health-based screening tools, and (3) identify potential landscape-scale drivers of PFAS contamination in tapwater.

2. Material and methods

2.1. Site selection and sample collection

This nationwide pilot assessment included 716 tapwater samples collected from residences, businesses, and drinking-water treatment plants across the US (Figure S1) from 2016 to 2021. Of these, 409 tapwater samples were collected at the point-of-use in 2021 from 155 unregulated private–well and 252 regulated public–supply locations in all 50 states, the District of Columbia, Puerto Rico, and the US Virgin Islands (Fig. 1, Figure S1) using a network of volunteers. Sampling locations were selected based on a presumptive–impact gradient approach wherein we identified locations in low (leveraged National Park Service/US Fish and Wildlife Service colleagues/sites), median (general outreach to colleagues and community volunteers, etc.), and high (targeted samples near reported PFAS sources based on geospatial information) human–impacted areas. Three locations (2 private-wells and 1 public-supply) were also sampled repeatedly (0, 0.5, 6, 12 and 24 h on day 1, daily for 7 days and then at least weekly for up to 2 months) to

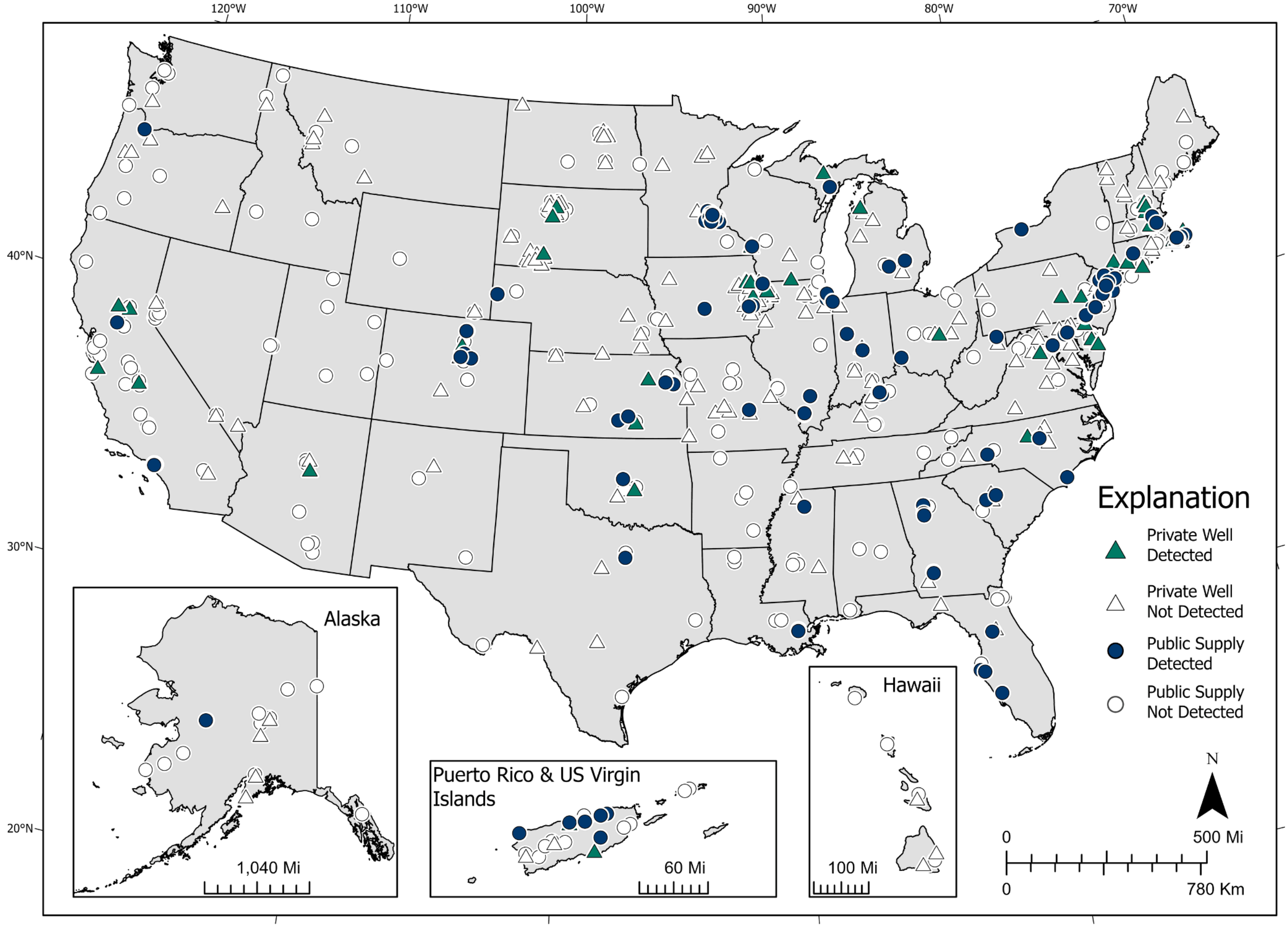

Fig. 1. Per- and polyfluoroalkyl substances (PFAS) detections in point-of-use tapwater collected from public-supply (blue circles) and private-wells (green triangles) across the United States including Puerto Rico and the U.S Virgin Islands. Samples with no detections are represented by open circles (public-supply) and triangles (private-wells). Tapwater samples were collected from 716 locations from 2016 to 2021. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

assess temporal changes in PFAS concentrations and profiles. Each volunteer was shipped a small cooler containing detailed instructions, and sampling supplies (gloves, two sets of three 2–mL polypropylene centrifuge tubes, and an ice pack). Instructions directed participants to rinse each tube three times, then fill half full, cap and chill until shipment. Samples were collected one time between July and December 2021 with sampling times varying throughout the day and without precleaning, screen removal or flushing of the sample tap. We requested samples from households without point of entry treatment and from faucets without a point-of-use treatment system (note, 1 location reported treatment after the sample was collected). All samples (three centrifuge tubes per sample) were collected in duplicate, and one set was frozen for archival.

PFAS data from an additional 307 tapwater samples (112 private-wells and 195 public-supply) collected as part of the USGS point-of-use tapwater research effort between 2016 and 2021 were also included herein (Table S1). USGS point-of-use tapwater research is conducted modularly with individual community-based studies (designed to address community priorities and support public-health decisions by individuals, communities, and public-health agencies) informing a national perspective in aggregate. Tapwater sampled in 2016 were collected in three 15-mL Falcon tubes, shipped on ice to the EPA National Exposure Research Laboratory (NERL) and extracted onto a solid phase extraction cartridge (SPE) prior to analysis based on methods described previously (Romanok et al., 2018c; Strynar, 2017; Strynar et al., 2015). Tapwater sampled 2017–2018 were collected in 15-mL Falcon tubes and shipped on ice to the Colorado School of Mines (CSM) laboratory where they were prepared for analysis based on previously published methods (Murray et al., 2019). All tapwater samples collected 2019–2021 were sent to the USGS National Water Quality Laboratory (NWQL) in three 2-mL polypropylene centrifuge tubes that had been rinsed three times prior to sampling, placed in a whirl pack bag and shipped on ice to the laboratory where they were stored frozen prior to analysis (Kolpin et al., 2021; Romanok et al., 2018c). Detailed information on previous study designs, site selection and sample collection are provided elsewhere (Bradley et al., 2020; Bradley et al., 2018; Bradley et al., 2021b; Bradley et al., 2022; Romanok et al., 2018c.

2.2. Analytical methods and quality assurance

Across all studies, PFAS were analyzed by three different laboratories: 1) EPA National Exposure Research Laboratory (NERL, 1 study, 26 samples) in 2016, 2) Colorado School of Mines (CSM, 3 studies, 82 samples) in 2017–2018, and 3) USGS National Water Quality Laboratory (NWQL, 6 studies, 608 samples) in 2019–2021, using previously published methods (Supplemental Information; Tables S1-S2). Potential effects (e.g., bias) associated with the use of different laboratories with varying detection limits and number/types of PFAS analyzed was addressed during statistical analysis.

The EPA NERL (Strynar, 2017; Strynar et al., 2015) method included the analysis of 10 PFAS that were first extracted onto a solid phase extraction (SPE) cartridge, eluted with methanol/ammonia solution and

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analyzed by ultra-high performance liquid chromatography (UPLC)-tandem mass spectrometry (MS/MS) operated in negative electrospray ionization (ESI) mode. The CSM method (Murray et al., 2019) included the analysis of 28 and 44 PFAS (Tables S2 and S3) using liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QToF-MS) in negative electrospray ionization (ESI-) mode. The USGS method (Kolpin et al., 2021) included the analysis of 34 total PFAS (including PFOS and PFHxS reported separately as branched and linear) by matrix-modified samples and direct aqueous injection-liquid chromatography/tandem mass spectrometry (DAI-LC/MS/MS) with isotope-dilution quantification. Data were acquired in dynamic multiple reaction monitoring (dMRM) mode with two transitions per analyte for confirmation (except for PFBA and PFPeA that only had one confirming ion).

Method detection limits ranged from 0.1 to 61.8 ng/L depending on compound and laboratory (Table S3). Known bias associated with the variability in laboratory detection limits was accounted for in the selection of statistical models. Quantitative ($\geq$limit of quantitation (LOQ)) and semi-quantitative (between LOQ and long-term method detection limit, LMDL) results were treated as detections. Quality-assurance/quality-control included analyses of field blanks and stable isotope surrogates. The median surrogate recovery for PFAS across all studies and laboratories was 103% (interquartile range (IQR): 93–116%) and the median matrix spike recovery ($N = 84$) was 107% (IQR: 96–117%). For detailed information on PFAS recoveries by individual and study see Table S1 for links to all available data. Field blanks from the nine individual studies conducted 2016–2021 are detailed in the supporting information section and elsewhere (Bradley et al., 2020; Bradley et al., 2018; Bradley et al., 2023a; Bradley et al., 2021a; Bradley et al., 2021b; Bradley et al., 2022; Romanok and Bradley, 2021; Romanok and Bradley, 2018; Meppelink et al., 2022; Romanok et al., 2019; Romanok et al., 2018a; Romanok et al., 2018b; Romanok et al., 2023b; Romanok et al., 2023a; Romanok et al., 2022). For the new samples collected by our volunteer network, field blanks were collected by 47 volunteers selected at random from 37 states in 2021. PFBA was the only PFAS detected (one blank sample, 72.3 ng/L), resulting in the censoring of one value (52.1 ng/L) from the associated environmental sample (Romanok et al., 2023c).

2.3. Geospatial analysis

The geospatial analysis joined the 716 sample site locations with numerous geospatial layers and rasters to provide more detailed information regarding each sample site (Seawolf et al., 2023). The datasets included: sources listed in the EPA ECHO (Enforcement and Compliance History Online) Database as potential PFAS environmental release sites including broad categories such as airports, industry, waste management, oil and gas, and department of defense; land-use classes from both the National Land Cover Database (NLCD) and Coastal Change Analysis Program (C-CAP) (Seawolf et al., 2023; Multi-Resolution Land Characteristics Consortium, 2011; National Oceanic and Atmospheric Administration, 2022). A five-km spatial buffer was established around each sample site as a means of capturing the number of PFAS in close proximity to the sampling location and to calculate an average distance to source. Within that buffer each sample site was joined with proximal PFAS sources identified from the EPA ECHO dataset. This join resulted, for many sites included, in multiple potential PFAS sources proximal to each sample site.

We also performed a spatial analysis of the NLCD and C-CAP datasets around each sample site, collecting land use data within the five-km buffer. NLCD data from 2011 was used for both the continental US and Alaska. C-CAP data was available for the Hawaiian Islands. For the island of Hawaii, Maui, and Kuai we used C-CAP data from 2010. For the island of Oahu, C-CAP data from 2011 was used. C-CAP data from 2010 was used for the island of Puerto Rico and for the island of St. Thomas, C-CAP data from 2012 was used. Merging the C-CAP dataset with NLCD was not problematic. We followed the convention outlined in Table S4 to convert C-CAP classes to NLCD classes.

2.4. Statistical analysis

Three different Bayesian hierarchical statistical modeling approaches – employing different distributional assumptions – were used to accommodate the unique aspects of the three primary goals of the analysis. The modeling approaches included (1) a hierarchical regression model to accommodate left-censored observations (observations below detection limits) for individual PFAS (Qian et al., 2004; Wu et al., 2011); (2) a hierarchical Tweedie compound Poisson linear model to model the total PFAS data, which included skewed continuous observations of total PFAS concentrations and many sites with no PFAS detections (i.e., there is zero inflation); and (3) a hierarchical negative binomial regression to model the number of compounds detected at each site. Each of these three modeling approaches are discussed in more detail below and in the Supplemental Information section 1.2.

The Bayesian hierarchical approach to accommodating left-censored data that we employ is robust, and simulation studies have shown it performs well for recovering true contaminant distributions and can handle relatively high proportions of left-censored observations in the dataset (Qian et al., 2004; Stow et al., 2018). For each modeling approach, we fitted two models, a source model that evaluated potential differences between tapwater sources (private or public) and a geospatial model, in which some of the landscape properties hypothesized to influence PFAS concentrations and occurrence were included as predictor variables. For the source model, tapwater source was included as an indicator variable, with public-supply tapwater as the reference cell. For the geospatial models, we included those predictors that were not highly correlated with one another ($r < 0.60$). The final set of geospatial predictors included the proportion of total developed land, developed open land, cultivated agricultural land, and pasture agricultural land, along with the average distance to the nearest EPA ECHO site. All predictor variables were standardized (mean = 0, standard deviation = 1) prior to analysis. Because land use geospatial variables were highly skewed, they were logit-transformed prior to standardization. For individual PFAS analysis, we limited statistical analysis to those compounds that were measured above their respective detection limits in at least 5% of sites, resulting in inclusion of 8 compounds (PFBA, PFBS, PFHxA, PFHxS, PFOA, PFOS, PFPeA, PFPeS). We chose 5% of the sites as a cutoff because this provided enough observations that were recorded above the detection limit to allow for meaningful inferences of estimated parameters (i.e., lower than 5% resulted in very little information on concentrations above the detection limit to inform parameter estimates). The study, from which data were collected was included as a random effect in all models. All estimated parameters are reported using the posterior mean and 95% credible intervals (CRIs). The code for Bayesian model fitting and posterior inference is available at https://doi.org/10.5066/P9MCYEVS.

2.5. Screening-level assessment

A screening-level assessment (Goumenou and Tsatsakis, 2019; U.S. Environmental Protection Agency, 2011) of potential cumulative biological activity of available individual PFAS in each tapwater sample was conducted using two analogous bioactivity-weighted approaches (Σ_{EAR}, Σ_{TQ}) as described previously (Blackwell et al., 2017; Bradley et al., 2019; Bradley et al., 2018). The EAR approach is a considered a high-level screening of the potential for molecular-scale vertebrate effects to complement the Hazard Index (i.e., TQ) approach. The ToxCast vertebrate-centric *in vitro* effects library was specifically assembled to inform the potential for human biological effects (Blackwell et al., 2017). The ToxEval version 1.3.0 (De Cicco et al., 2018) was used to sum (non-interactive, concentration addition model, e.g., (Altenburger et al., 2018; Cedergreen et al., 2008; Stalter et al., 2020)) individual exposure activity ratios (EAR) from the Toxicity ForeCaster (ToxCast, high-throughput screening data (U.S. Environmental Protection Agency, 2022c) to estimate sample-specific cumulative EAR (∑EAR) (Blackwell et al., 2017; Bradley et al., 2018). EAR is the ratio of the detected concentration in the sample to the activity concentration at cutoff (ACC) obtained from the ToxCast database. The ACC estimates the point of departure concentration at which a defined threshold of response (cutoff) is achieved for a given biological activity and is less prone to violations of relative potency assumptions (Blackwell et al., 2017). ACC data in the ToxEval v1.3.0 employed in the present study were from the August 2022 invitroDBv3.5 release of the ToxCast database including updated bioactivity information for individual PFAS (U.S. Environmental Protection Agency, 2022c). Non-specific-endpoint, baseline, and unreliable response-curve assays were excluded (Blackwell et al., 2017; Bradley et al., 2018). ∑EAR results are summarized in Table S10.

Because the ∑EAR approach was limited to 11 individual PFAS in ToxCast, an analogous human-health-based assessment (Goumenou and Tsatsakis, 2019; U.S. Environmental Protection Agency, 2012; U.S. Environmental Protection Agency, 2011) using available federal, state or international human-health benchmarks for 15 individual PFAS was also conducted to sum the toxicity quotient (TQ; ratio of detected concentration to corresponding health–based benchmark) of individual detections to estimate sample-specific cumulative TQ (∑TQ) (Corsi et al., 2019). A precautionary screening–level approach was employed based on the most protective human-health benchmark (i.e., lowest benchmark concentration) available (Interstate Technology Regulatory Council, 2022). ∑TQ results and respective health–based benchmarks are summarized in Tables S10 and S5, respectively. Screening assessments were conducted in the program R version 3.6.1 (R Development Core Team, 2019). Differences (centroids and dispersions) among sample types (private-wells and public-supply) for Σ_{EAR} and Σ_{TQ} were assessed by one-way PERMANOVA (n = 9999 permutations) on Euclidean distance (Hammer et al., 2001).

3. Results and discussion

3.1. Spatial and temporal assessments of PFAS exposure in tapwater

In the US and globally, limited information is available on PFAS in point-of-use tapwater, with most drinking-water studies focused on samples from source waters (McMahon et al., 2022; Sims et al., 2022) or pre-distribution samples from community water supplies (Andrews and Naidenko, 2020; Hu et al., 2016; Kurwadkar et al., 2022; Li et al., 2022; McMahon et al., 2022; Neuwald et al., 2022; Post et al., 2013), largely omitting distribution system factors (e.g., plumbing material with PFAS or sorption/degradation in the supply network; (Mohammadi et al., 2022) and a notable paucity of data available for private-wells across the US. To address this gap, we utilized targeted analysis of up to 44 PFAS in point-of-use tapwater from 269 private-wells and 447 public-supply collected 2016–2021 as fractional indicators of the presumptive 8000 + PFAS contaminant (U.S. Environmental Protection Agency, 2022a) (Fig. 1, Figure S1, Table S1). Consistent with other studies and large datasets focused on public–supply tapwater (Hu et al., 2016; Li et al., 2022; McMahon et al., 2022; Post et al., 2013), at least one PFAS was observed in 30% (237 of the 716) of the tapwater samples collected throughout the US (Fig. 1, Figure S2). Based on data from the UCMR3, about 4% of US drinking-water treatment plants tested had detectable PFAS but the breadth of contamination was likely missed due to high detection limits (10–90 ng/L depending on individual PFAS) and a limited number of PFAS analyzed (Hu et al., 2016). More recently, assuming lower detection limits, Andrews and Naidenko (2020) estimated that approximately half the US population likely receive water with PFOA/PFOS concentrations<1 ng/L, but this information has yet to be validated fully with field data particularly at the point-of-use. In our study, seventeen PFAS were detected at least once and, apart from perfluoropropane sulfonic acid (PFPrS), all detected PFAS were analyzed in > 600 samples (Table S2). Reporting limits for the PFAS observed in the current study varied by laboratory and ranged from 0.1 to 20 ng/L (Table S3). The most frequently detected PFAS analyzed by all laboratories included PFBS (16%), PFHxS (15%), and PFOA (14%), similar to results reported by others for drinking-water resources (surface water intakes or groundwater wells) or community water supplies (Andrews and Naidenko, 2020; Boone et al., 2019; McMahon et al., 2022; Post et al., 2013; Teymoorian et al., 2023). The number of individual PFAS observed ranged from one to nine (median of two) with detected concentrations ranging from 0.025 to 319 ng/L (median: 2.88 ng/L) and corresponding cumulative PFAS concentrations (sum of 16 detected PFAS) ranging from 0.348 to 346 ng/L (median: 7.00 ng/L; Table S10). As expected, sites classified as 'low' impact had the lowest prevalence of PFAS compared to sites near known PFAS sources, whereas PFAS varied widely among sites classified as 'medium.'.

At least one PFAS was detected in 20% of private-well (55/269) and 40% of the public-supply (182/447) samples collected throughout the US. A similar pattern was reported in groundwater from the eastern US, in which 60% of the public-supply wells and 20% of monitoring wells contained at least one PFAS (McMahon et al., 2022). Median cumulative PFAS concentrations (estimated considering detection limits and including study as a random effect) were comparable between public-supply (median = 7.1 ng/L [95% CRI = 2.3, 17.1]) and private–well point-of-use tapwater (median = 8.2 ng/L [95% CRI = 2.6, 20.5]; Fig. 2). Similarly, considering only PFAS with > 5% detections, we observed no differences in estimated median concentrations of individual PFAS or in the number of detected individual PFAS between public-supply and private-well point-of-use tapwater samples (Fig. 2, Tables S7-8). We chose 5% as a cutoff because this provided enough observations above the detection limit to allow for meaningful inferences of estimated parameters. Based on model predictions (Figure S3), the probability of not detecting PFAS above our detection limits ranged from approximately 25% in urban centers (e.g., Chicago) or areas with a known history of PFAS contamination (e.g., Cape Cod (Bradley et al., 2021a)) to > 75% in rural areas (e.g., Northern Plains (Bradley et al., 2022)). Figure S3 illustrates the spatial (among-study) variability that exists in PFAS occurrence (and concentration, not shown) quantified by the study random effect included in all models to account for variability in detection limits and the difference in numbers of PFAS included in each method (Tables S7-8, S10-11). Across all studies, the probability of detecting one PFAS was approximately 18%, with a marked decrease in probability with increasing number of detected compounds; no differences were observed between public-supply and private-well samples (Fig. 3).

Due in large part to funding constraints and prioritization of population-relevant reconnaissance of a range of exposure points within a given community, point-of-use tapwater exposure studies conducted to date (Bradley et al., 2020; Bradley et al., 2018; Bradley et al., 2023a; Bradley et al., 2021a; Bradley et al., 2021b; Bradley et al., 2023b) typically have employed a one-time spatial–synoptic approach, which provides limited to no insight into point-of-use tapwater temporal variability. To address this data gap, PFAS samples were collected temporally at 3 of the residential locations (2 private-wells, 1 public-supply). The rural, private–well location in South Carolina had no PFAS detected during three months of sampling. PFAS were detected at the suburban public-supply and private-well locations in New Jersey, and cumulative detected concentrations were generally stable (hourly increasing to weekly samples) over 3 months (Figures S4, S5). In light of the near-detection-limit concentrations of several individual PFAS detections, the observed variabilities in detections of some individual PFAS and in per-sample cumulative PFAS detections (Figure S4) were likely due more to method–sensitivity limitations (Teymoorian et al., 2023) than to short-term changes in drinking-water resources. New Jersey (NJ), one of the more proactive states regarding PFAS regulation, has established enforceable NJ-MCLs for three PFAS including PFOA (14 ng/L), PFNA (13 ng/L) and PFOS (13 ng/L) (New Jersey Department of Environmental Protection, 2022a) and has added PFOA, PFOS and PFNA

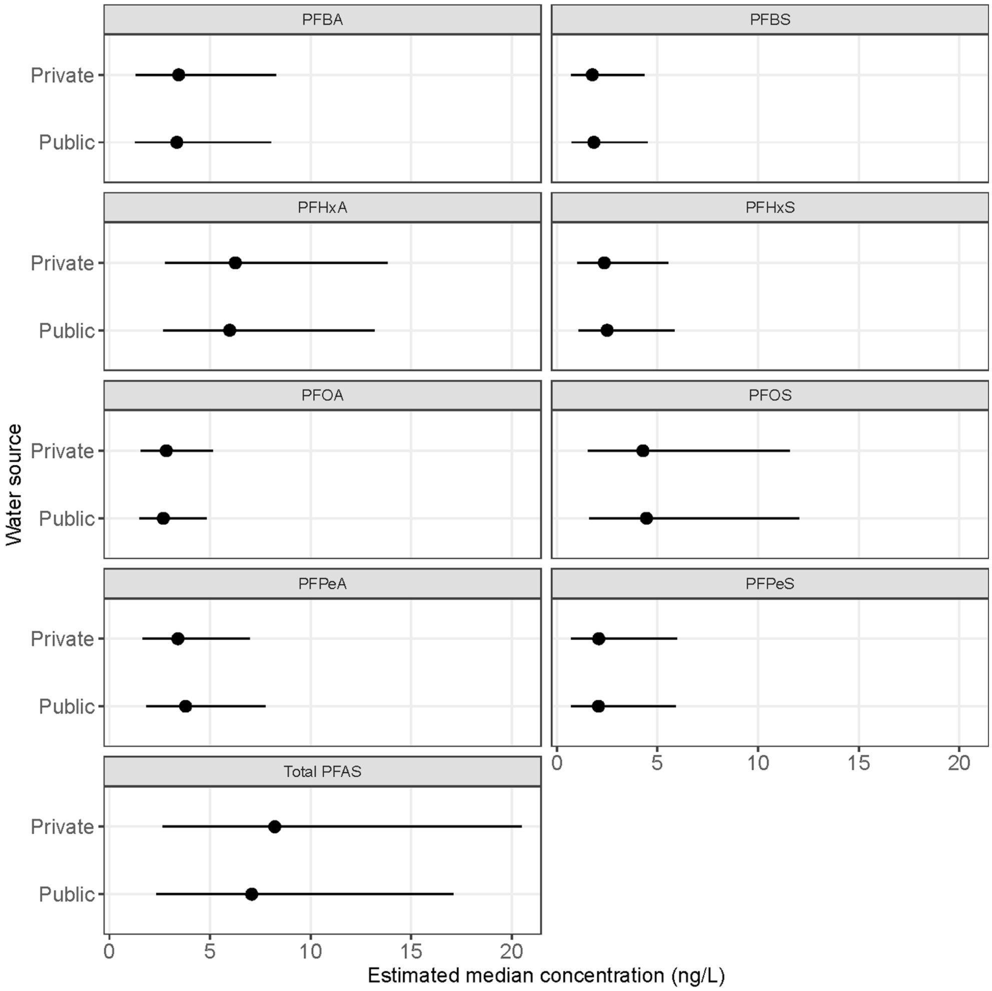

Fig. 2. Estimated median concentrations (ng/L) of select per- and polyfluoroalkyl substances (PFAS) and cumulative PFAS in private-wells and public-supply samples. Circles are posterior means and horizontal lines are 95% credible intervals.

to the Private-well Testing Act, which requires homeowners to test potable wells prior to sale and landlords to test their well water and report results to the tenant once every five years (New Jersey Department of Environmental Protection, 2022b). None of the detections in either location exceeded NJ-MCLs. These results further support the need for continued monitoring of PFAS in point-of-use tapwater from residential private-wells as well as for continued temporal assessments to accurately assess PFAS exposures at the point-of-use more broadly.

3.2. *Comparison to proposed US drinking water regulations*

Newly proposed MCLs for PFOA (4 ng/L) and PFOS (4 ng/L) were released in March 2023 by EPA as part of the National Primary Drinking-water Standards Rule (U.S. Environmental Protection Agency, 2023b). The proposed MCL for PFOS was below the reporting limit for two of the three laboratories (CSM:1.3 ng/L, NERL: 5.0 ng/L and USGS: 7.4 ng/L; Table S3) used during this study; consequently, our estimates of samples exceeding the proposed MCL should be considered conservative. The reporting limit for PFOA was above the proposed MCL for only one laboratory (CSM: 1.3 ng/L, NERL: 5 ng/L, USGS: 2.0 ng/L; Table S3) in which the least number of samples were analyzed (26/716; Table S1). Proposed MCLs for PFOA and PFOS were exceeded in 6.7% and 4.2%, respectively, of all tapwater samples collected but were exceeded in 48% (48 of 99) and 70% (30 of 43), respectively, of tapwater samples when detected. Further, proposed MCLs for PFOA and PFOS were exceeded in 63% and 67%, respectively of the private-well tapwater samples and in 44% and 77%, respectively of the public-supply tapwater samples, when detected. The proposed MCLG (zero) (U.S. Environmental Protection Agency, 2023b) was de facto exceeded in every sample in which PFOS and PFOA was detected (private-well: 15 and 24, respectively; public-supply: 28 and 75, respectively). Further, to account for dose additive noncancer effects of PFBS, PFNA, PFHxS, GenX, EPA proposed an MCL for the mixture of these four PFAS based on a hazard index approach (U.S. Environmental Protection Agency, 2020). The proposed hazard index of 1 for the sum of the toxicity quotient (measured concentration/health-based value) for PFBS + PFNA + PFHxS + GenX was exceeded in 4.6% of tapwater collected.

3.3. *Aggregated screening-level assessments*

We also used two bioactivity weighted screening approaches Σ_{EAR} and Σ_{TQ} to provide insight into the potential aggregated (sum of all PFAS) effects. These approaches are limited by the availability of weighting factors (ToxCast ACC and health-based benchmarks, respectively) and mixture effects are estimated by assuming concentration addition (Cedergreen, 2014). The Σ_{EAR} approach has been used effectively in other studies as a protective (conservative) screening tool to asses drinking-water exposure risk to organic contaminant mixtures because it leverages response relations for>9000 organic chemicals across over 1000 standardized vertebrate cell lines (Kavlock et al., 2012; Kavlock et al., 2008; Richard et al., 2016). Contaminant bioactivity ratios were aggregated across all ToxCast endpoints available for

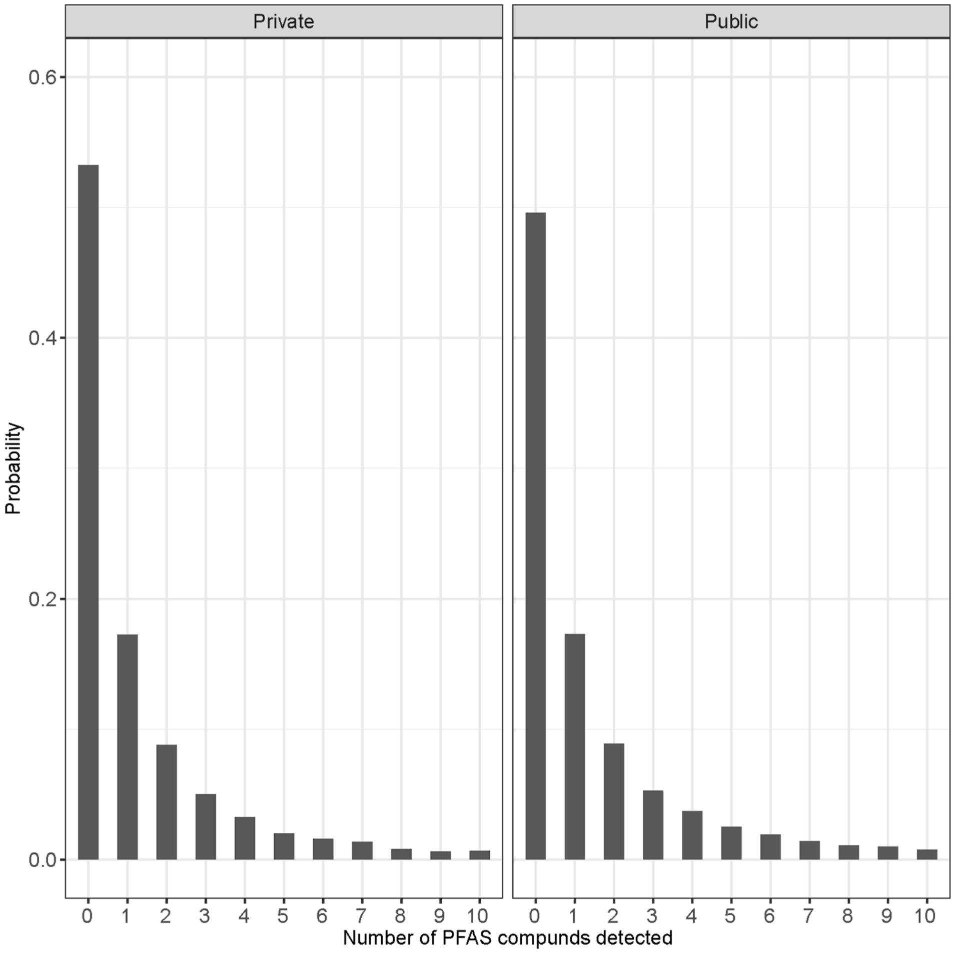

Fig. 3. The predicted posterior probability of detecting 1 – 10 per- and polyfluoroalkyl substances (PFAS) in private-well and public water-supply tapwater.

individual PFAS without restriction to recognized modes of action to provide a precautionary lower-bound estimate of in vivo adverse-effect levels (Paul Friedman et al., 2020), however, this approach may not accurately reflect apical effects (Blackwell et al., 2017; Schroeder et al., 2016). Further, for PFAS, the approach has the potential to underestimate exposure risk because only 11 of the detected compounds had exact Chemical Abstract Services number matches in the ToxCast™ database and only six (PFOS, PFOA, PFNA, PFHpA, PFBA, PFHxS) of these had EAR exceeding our lowest threshold for consideration ($>$0.00001). The $\sum_{\mathrm{TQ}}$ approach targets apical human-health effects, is notably constrained to recognized (i.e., benchmarked) health concerns and was used herein to estimate cumulative effects from a broader suite of PFAS (15 with established health-based benchmarks; Table S5) (Interstate Technology Regulatory Council, 2022). Lastly, it is important to note, the EAR approach is based on measured endpoint-specific activity cutoff concentrations, whereas the human-health benchmarks used in the TQ approach generally include a margin of safety (margin of exposure).

None of the samples exceeded a $\Sigma_{\mathrm{EAR}} > 1$, a value which indicates cumulative exposure at concentrations capable of modulating molecular endpoints *in vitro,* and we observed no systematic differences in Σ_{EAR} between private–well and public–supply locations (Fig. 4). However, 65 tapwater samples exceeded the $\Sigma_{\mathrm{EAR}} = 0.001$ precautionary screening level of potential concern (yellow line, Fig. 4; Table S10) for molecular effects described previously (Bradley et al., 2018). For PFAS and PFOA, which proposed MCLGs of zero, EPA's interim health advisory levels released in 2022 (U.S. Environmental Protection Agency, 2022a) were used as the benchmark value (Table S5). Σ_{TQ} values were higher in private–well tapwater samples compared to public–supply ($p = 0.0015$), and 124 samples overall had $\Sigma_{\mathrm{TQ}} > 1$ (Fig. 4, Table S10), indicating a high probability of aggregated risk when considering exposures to all observed PFAS with an available benchmark. As expected, given their proposed MCLG of zero (U.S. Environmental Protection Agency, 2023b), Σ_{TQ} results were driven by PFOA and PFOS, when detected. Simultaneous detection of multiple PFAS is consistent with other drinking-water (Andrews and Naidenko, 2020; Boone et al., 2019; Hu et al., 2016) and tapwater studies (Bradley et al., 2020; Bradley et al., 2018; Bradley et al., 2021b) in the US. The results of precautionary Σ_{EAR} and Σ_{TQ} assessments by this group indicate that the potential for human-health effects from contaminant exposures (including PFAS) through drinking-water are common and comparable in private-well and public-supply tapwater (Bradley et al., 2020; Bradley et al., 2018; Bradley et al., 2021a). Information generated by this study and elsewhere indicates the need for further assessments of cumulative health exposure risks of PFAS mixtures (Kwiatkowski et al., 2020) and of PFAS in combination with other organic and inorganic contaminants of concern, particularly in unmonitored/unregulated private-wells where information is limited or not available.

3.4. Predicting exposure based on potential sources and land-use

The final model comparing tapwater PFAS concentrations to geospatial drivers included median distance to potential source (including airport, industry, waste management, oil and gas, and department of defense) and several land-use classifications (total developed, open developed, cultivated and pasture agriculture). The number of PFAS sources in a 5–km buffer around each site was highly correlated with developed land-use ($r = 0.66$) and was excluded from the model.

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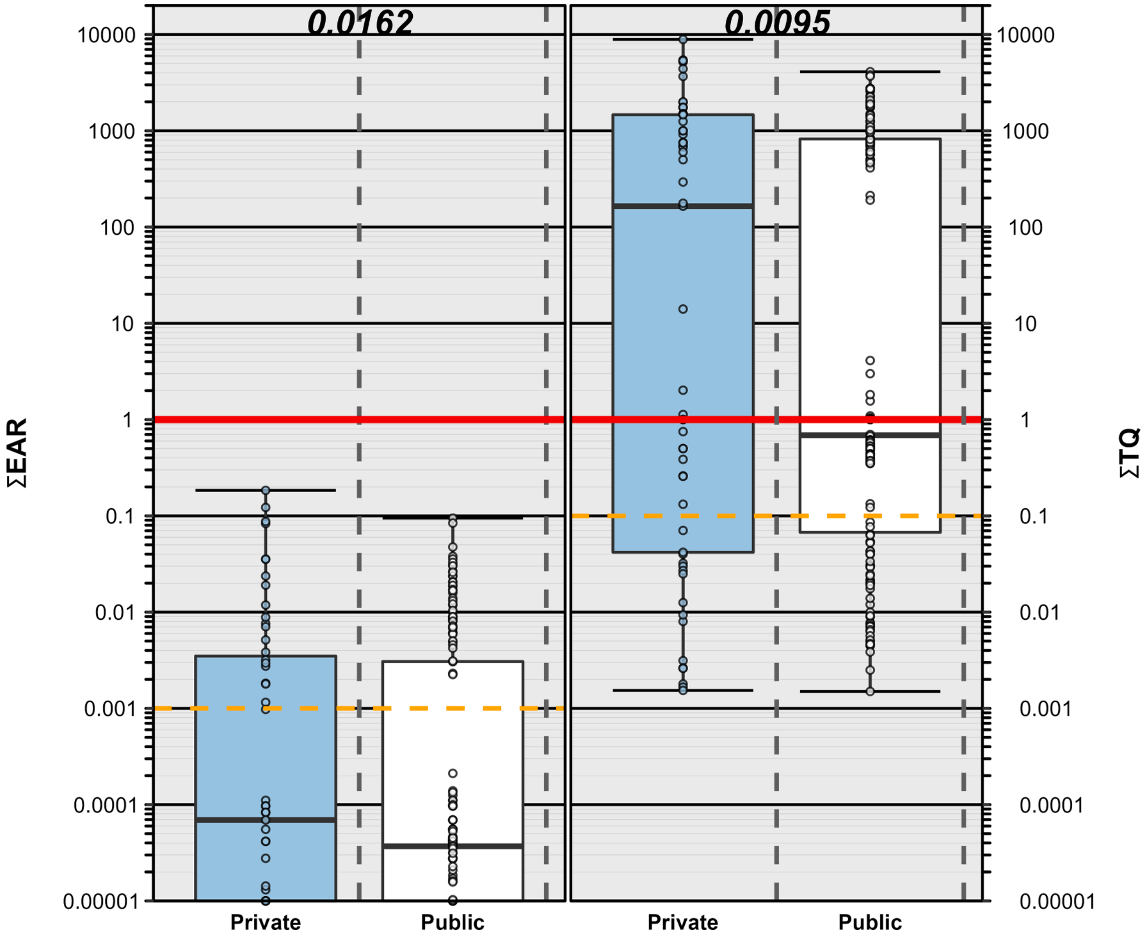

Fig. 4. Left. Cumulative maximum Exposure-Activity Ratios (∑EAR) across all assays for 9 individual per- and polyfluoroalkyl substances (PFAS) in ToxCast and detected in tapwater collected from public-supply and private-wells. Solid red and yellow lines indicate concentrations shown to modulate effects *in vitro* and effects-screening-level thresholds (EAR = 1 and EAR = 0.001), respectively. Right. Human-health benchmark cumulative toxicity quotient (ΣTQ) for 15 PFAS listed in Table S5 and tapwater from public-supply and private-wells. Solid red and yellow lines indicate benchmark equivalent concentrations and effects-screening-level threshold of concern (TQ = 0.1), respectively. Boxes, centerlines, and whiskers indicate interquartile range, median, and 5th and 95th percentiles, respectively. Numbers above each boxplot pair indicate the permuted probability that the centroids and dispersions are the same (PERMANOVA; 9999 permutations). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Cumulative PFAS concentrations and the number of detected compounds increased with surrounding developed–land and decreased with increasing distance from probable source(s) (Fig. 5, Figure S6, Tables S10-11). However, for individual PFAS the distance to probable source(s) was not a strong predictor of concentration (Figure S7, Table S8). PFBS was the only PFAS which exhibited a positive relation with development and pasture agriculture and a negative relation with open development (commonly includes large-lot single-family housing units, parks, golf courses, and vegetation planted in developed settings for recreation, erosion control, or aesthetic purposes). Although biosolids application is a recognized source of PFAS to surface- and groundwaters in agricultural landscapes (Munoz et al., 2022; Sepulvado et al., 2011), in this study concentrations of PFBS, PFHxA, PFHxS, PFOA and PFOS decreased with increasing surrounding cultivated cropland. Further, for several compounds (PFBA, PFHxA, PFHxS and PFOA), concentrations decreased with increasing development, an unexpected result which suggests that point-of-use tapwater exposure to individual PFAS in our study is more closely associated with the type of PFAS sources (e.g., industry, airport, wastewater, etc., which are generally located at the edge of urban development and not in the highest residentially-developed areas) (Hu et al., 2016) rather than numbers of potential PFAS sources (Salvatore et al., 2022). Because our geospatial analysis was constrained to broad putative-source categories (e.g., military fire training areas, industrial, wastewater) and 90% of the corresponding potential sources were characterized as industrial, exploration of source-type/point-of-use tapwater exposure relationships was limited and merits further investigation. Further, most public-supply samples were collected at the tap not the treatment facility, indicating a distinct disconnect from PFAS source and drinking water resource. Despite these limitations, the real–world point-of-use tapwater PFAS concentration data compiled herein along a national gradient of presumptive contamination represents an important validation dataset to assess and tune putative-source PFAS contamination models, like that presented recently (Salvatore et al., 2022).

3.5. Implications and future directions

Approximately 40 million people in the US rely on private-wells for drinking-water (DeSimone et al., 2015; Dieter et al., 2018), most national testing programs, like the UCMR3 focused on community water supplies serving ≥ 10,000 consumers, do not include private-wells and rarely capture information from rural communities (52 million people rely on small water supplies serving < 10,000), indicating data on PFAS exposure and potential human-health effects is does not exist for over one-third of the US population (Hu et al., 2016). As noted previously, small public supplies and private-wells may be disproportionally affected by PFAS, emphasizing the value of studies like these focused broadly on point-of-use tapwater PFAS exposures, with an emphasis on

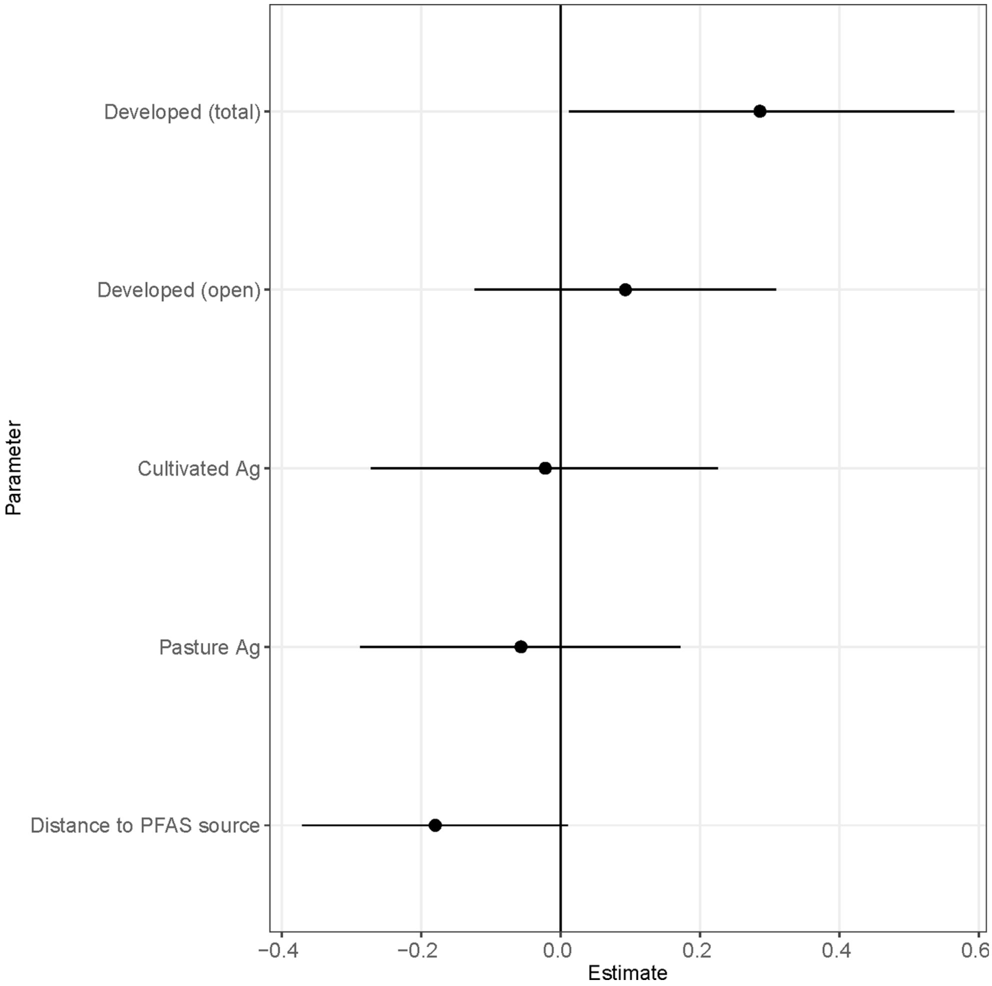

Fig. 5. Estimated effects of geospatial predictor variables on cumulative per- and polyfluoroalkyl substances (PFAS) concentrations. Circles are posterior means and horizontal lines are 95% credible intervals. Geospatial predictors with 95% credible intervals that overlap with zero are not considered statistically significant.

comparing exposures in private-wells with those directly from public-supply using similar sampling/analytical methods. Some of these gaps associated with PFAS in small community public supply facilities may be addressed by the UCMR5, currently underway in the US and expected to provide extensive information on PFAS in US drinking water for public-supply consumers in the next few years (U.S. Environmental Protection Agency, 2023a).

Modeled results indicate that on average at least one PFAS is detected in about 45% of US drinking-water samples. Results also indicate that 1) detection probabilities vary spatially (8% in rural areas up to > 70% in urban areas/areas with a known history of PFAS contamination), 2) drinking-water exposures may be more common in the Great Plains, Great Lakes, Eastern Seaboard, and Central/Southern California regions, and 3) temporal variations in concentrations/detections may be limited. Geospatial datasets and land-use information were correlated with both cumulative PFAS concentrations, and the number of PFAS detected; however, they were not often correlated with specific PFAS profiles due to the limited number of individual PFAS detected more than once using targeted approaches. Targeted PFAS analytes are only a fractional indicator of the 8000 + potential PFAS and the fraction of total organic fluorine captured by these targeted analyses is typically low in surface water (D'Agostino and Mabury, 2017; McDonough et al., 2019) and drinking-water (Jiao et al., 2022). Potential detection of one or more PFAS in US drinking-water combined with the paucity of information available on current use/ultra-short chain compounds (Neuwald et al., 2022) supports the continued need for point-of-use tapwater monitoring, with an emphasis on unmonitored private-wells and underserved communities on small community water supplies. To fully understand exposure and adequately determine risk to human-health, continued emphasis should be placed on 1) integrating geospatial datasets with PFAS data broadly to identify vulnerable regions/subpopulations, 2) expanding monitoring to include rural small–system and private–well dependent communities, and 3) expanding target and non-target analysis methods particularly in drinking-water monitoring programs in the US and globally.

CRediT authorship contribution statement

Kelly L. Smalling: Conceptualization, Formal analysis, Investigation, Methodology, Project administration, Visualization, Writing – original draft, Writing – review & editing. **Kristin M. Romanok:** Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing – review & editing. **Paul M. Bradley:** Formal analysis, Investigation, Methodology, Project administration, Writing – review & editing. **Mathew C. Morriss:** Investigation, Writing – review & editing. **James L. Gray:** Investigation, Writing – review & editing. **Leslie K. Kanagy:** Investigation, Writing – review & editing. **Stephanie E. Gordon:** Investigation, Visualization, Writing – review & editing. **Brianna M. Williams:** Investigation, Visualization, Writing – review & editing. **Sara E. Breitmeyer:** Visualization, Writing – review & editing. **Daniel K. Jones:** Writing – review & editing. **Laura A. DeCicco:** Investigation, Writing – review & editing. **Collin A. Eagles-Smith:** Investigation, Writing – review & editing. **Tyler Wagner:** Investigation, Formal analysis, Writing – review & editing.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All data are available. All data presented can be found in a series of USGS data releases (Meppelink et al., 2022; Romanok and Bradley, 2018; Romanok and Bradley, 2021; Romanok et al., 2022; Romanok et al., 2019; Romanok et al., 2023a; Romanok et al., 2023b; Romanok et al., 2023c). For links to the individual USGS data releases see Table S1.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2023.108033.

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