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Municipal and Industrial Wastewater Treatment Plant Effluent Contributions to Per- and Polyfluoroalkyl Substances in the Potomac River: A Basin-Scale Measuring and Modeling Approach

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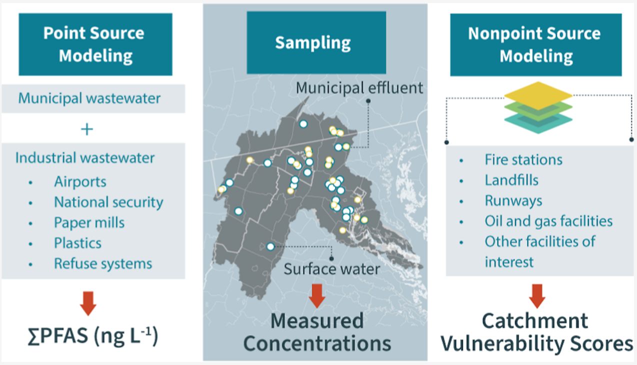

ABSTRACT: Managing per- and polyfluoroalkyl substances (PFAS) in water resources requires a basin-scale approach. Predicted environmental concentrations (PEC) and stream-vulnerability scores for PFAS were determined for the Potomac River watershed in the eastern United States. Approximately 15% of stream reaches contained municipal and/or industrial wastewater treatment plant (WWTP) discharges that are presumptive PFAS sources, comprising from <1 to >90% of streamflow. Mean annual PEC, based on the summed concentrations of eight PFAS detected in WWTP effluents ($\Sigma PFAS_{PEC}$), for all stream reaches in the watershed was 3.8 ng L^{-1}, and stream reaches impacted by WWTP had perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS) PEC of 0.39 and 0.14 ng L^{-1}. For locations where measured-environmental concentrations (MEC) were determined, municipal and industrial WWTP contributed 7.8% (0 to 65%) of the total annual streamflow and MEC were greater than PEC in 99% of the samples, indicating additional potential PFAS sources. The mean $\Sigma PFAS_{PEC}$ was 9.1 ng L^{-1} compared to a mean sum of PFAS MEC of 34 ng L^{-1}. Under mean-August low-flow, 17% and 9.4% of the water-supply intakes had maximum PFOA and PFOS PEC exceeding drinking water maximum contaminant levels.

KEYWORDS: *per- and polyfluoroalkyl substances, geospatial modeling, accumulated wastewater, stream vulnerability score, de facto reuse, predicted environmental concentrations, measured environmental concentrations*

■ INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) in the aquatic environment present a water resource management challenge because of the complexity of the chemical classes represented, diversity of uses, geospatial distribution of potential sources, range of physicochemical characteristics and environmental behaviors, variable biological effects, and degree of hydrologic interconnectivity of surface water and groundwater.[1] The term PFAS incorporates many classes of synthetic organic chemicals that contain carbon−fluorine bonds[2] and have widespread commercial applications and environmental occurrence.[3] Although thousands of PFAS are in current use,[4] only a small subset of approximately 40 compounds are routinely measured, and even fewer have been characterized with respect to environmental exposure pathways, fate and transport, and biological effects, resulting in uncertainty of occurrence and potential impacts.[1,5] In environmental waters, PFAS generally occur as mixtures of perfluoroalkyl acids (PFAA), including perfluoroalkyl carboxylates (PFCA) and perfluoroalkyl sulfonates (PFSA), as well as precursor compounds that can undergo transformations to form PFAA.[1,6] Depending on the source of contamination, PFAS can co-occur with a variety of other natural and synthetic organic and inorganic compounds; thus, it is important to measure ancillary water quality constituents to further characterize sample composition.[7] In the absence of specific data on PFAS, such co-occurring constituents can be used as "proxies" for evaluating potential sources and occurrence in streams. For example, fluorescent dissolved organic matter can be used to characterize relationships between water quality, land use, and wastewater infrastructure,[8] and can indicate potential PFAS contamination.

The diverse domestic, commercial, industrial, and agricultural uses of PFAS[4] can result in multiple inputs along a hydrological

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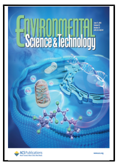

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flow path, and water composition can provide insight into current and legacy sources.[7] Known and presumptive PFAS sources include wastewater treatment plants (WWTP), septic systems, biosolids-amended fields, landfills, fire-training areas at military installations and airports, PFAS production and handling facilities, hazardous waste sites, oil and gas production, agriculture activities, transportation, and mining.[3] These sources can be identified by North American Industry Classification System (NAICS) or Standard Industrial Classification (SIC) codes.[3,9−11] However, a limitation in geospatial modeling efforts is the lack of high-quality geolocation information for many potential PFAS contamination sources, and many PFAS sources, such as municipal biosolids, do not have NAICS or SIC codes. Municipal WWTP receive PFAS from multiple sources, including domestic use, industrial laundries, car washes, manufacturing facilities, hospitals, and landfill leachate,[12,13] and are a continuous point-source for loading to surface waters.[14−16] Industrial WWTP discharges to surface waters and sewer systems are additional PFAS point-sources, but effluent compositions are more variable than for municipal WWTP.[17−23] The link between PFAS occurrence in water and emissions from presumptive sources can involve discharge to streams, discharge to the atmosphere, atmospheric transport and deposition, surface water runoff, infiltration and vadose zone transport, advective-dispersive groundwater transport, and groundwater/surface water interactions.[24−27] These multiple pathways can complicate the assessment of surface waters impacted by indirect sources, such as groundwater PFAS inputs.[28,29] Because of the widespread nature of PFAS contamination, geospatial scaling and flow-path analysis are essential for addressing the large number of presumptive PFAS sources and providing hydrological context.

Occurrence of PFAS in WWTP influents and effluents has been established in many studies across the world[5] and compositions and concentrations have shifted over time,[15,30] resulting in the need to continually reassess potential loading. A recent study of PFAS in 38 WWTP from 23 states in the United States (U.S.) reported a mean (±one standard deviation) sum of measured environmental concentrations ($\Sigma PFAS_{MEC}$) of 98 ± 28 ng L^{-1} for influents and 80 ± 24 ng L^{-1} for effluents.[31] Similar results were observed in samples from nine WWTP across the U.S. with mean $\Sigma PFAS_{MEC}$ of 93 ng L^{-1} for influents and 114 ng L^{-1} for effluents.[32] A recent investigation of 13 WWTP from the San Francisco, California area[13] reported that perfluoropentanoate (PFPeA), perfluorohexanoate (PFHxA), and perfluorooctanoate (PFOA) were detected in all influent and effluent samples, with PFHxA having the highest median effluent concentration (15 ng L^{-1}), and a median effluent $\Sigma PFAS_{MEC}$ of 37 ng L^{-1}. A study of six WWTP in New Hampshire[14] had influent and effluent $\Sigma PFAS_{MEC}$ that ranged from 30 to 198 ng L^{-1}. A survey of 27 WWTP across Canada[33] reported higher $\Sigma PFAS_{MEC}$ in facilities receiving landfill leachate and little change in perfluorooctanesulfonate (PFOS) concentrations over time, despite regulatory actions and industry phase-out. A study of two U.S. WWTP[34] reported that transformation of precursors into short-chain PFAA by biological treatment and the partitioning of long-chain PFAS into sludge are key factors determining their fate in WWTP.

In general, WWTP effluents have greater concentrations of PFAA than influents, a greater abundance of PFCA than PFSA, and shorter fluorocarbon chain lengths. Although PFAS exhibit considerable temporal variability at multiple scales (hours, days, months, years, and decades),[15,16,30,35,36] municipal WWTP effluent concentrations and composition fall within a relatively narrow range despite differences in facility location, size, discharge, and treatment. Total oxidizable precursor (TOP) analysis has shown that WWTP influents can have greater abundance of precursor compounds not quantified by targeted compound analysis than PFAA.[1,5,13−15,30−34] Effluent TOP analysis indicates lower proportions of precursors relative to influents, attributed to precursor removal by biotransformation and sorption during treatment.

In contrast to extensive data on municipal WWTP as sources of PFAS, there is a dearth of information on industrial WWTP loading despite widespread PFAS use in many manufacturing processes.[4] The limited studies available indicate that industrial WWTP can have PFAS concentrations much greater than municipal WWTP. For example, pulp and paper mill, textile manufacturing, food production, and electronics fabrication WWTP effluents have been reported to contain >100 ng L^{-1} PFAS.[17−23] In addition to municipal and industrial WWTP point sources, there are many non-point sources that can contribute PFAS to surface waters, including stormwater runoff, land application of municipal and industrial biosolids, use of pesticide formulations, discharge of groundwater contamination plumes derived from AFFF use at fire-training areas, landfills, and atmospheric deposition. Due to the diffuse and episodic nature of non-point source inputs, quantification of corresponding environmental loading can be difficult.

Recent studies in the U.S. have reported PFAS concentrations in river waters.[7,37−40] A statewide study in Pennsylvania measured PFAS at 161 stream sites[37] with 76% of the samples having one or more PFAS detected, and PFPeA, PFHxA, PFOA, perfluorobutanesulfonate (PFBS), and PFOS were the most frequently detected compounds. The median $\Sigma PFAS_{MEC}$ was 3.8 ng L^{-1} and concentrations ranged from < MDL to 102 ng L^{-1}. A statewide study in Alabama[38] detected PFPeA, PFHxA, perfluoroheptanoate (PFHpA), PFOA, PFBS, and PFOS in 88% of 74 river water samples with a mean $\Sigma PFAS_{MEC}$ of 33 ng L^{-1} and a maximum of 237 ng L^{-1}; PFPeA was the most frequently detected and highest concentration PFAS (2.1 to 55 ng L^{-1}). In North Carolina, PFAS were measured in river samples upstream and downstream of a major PFAS manufacturing facility.[39] Perfluorobutanoate (PFBA), PFPeA, PFHxA, PFHpA, PFOA, and PFOS, constituted 89% of the $\Sigma PFAS_{MEC}$ at the upstream site. The downstream site had a distinctly different composition with more compounds and higher concentrations due to groundwater discharges, reflecting the impact of the manufacturing facility.[28] In a study of two watersheds in Nevada,[40] mean $\Sigma PFAS_{MEC}$ concentrations were 442 and 2234 ng L^{-1}, greater than most other studies, with the predominant compounds being PFPeA, PFHxA, PFOA, and PFBS.

Water reuse and the corresponding contribution to streamflow is an increasingly important component of the modern hydrological cycle,[41−45] providing continuous inputs of water and contaminants to surface waters and raising concerns about PFAS loading from WWTP discharges.[16] De facto water reuse is defined as the presence of municipal WWTP effluent in drinking-water supplies, and can provide an important human PFAS exposure pathway through direct consumption.[46] The de facto reuse exposure pathway originates at the source intakes for domestic- or commercial-use public or private water supplies, which may contain PFAS from upstream inputs. During domestic and commercial activities, PFAS can be contributed by consumer product use and industrial chemicals, which are disposed of down-the-drain. Sewer networks collect and transport sewage to WWTP where treatment typically does not completely remove

PFAS. Treated WWTP effluents containing PFAS are discharged back to surface water sources for downstream water supplies, continuing the de facto reuse cycle. During water reuse, there are many opportunities for PFAS introduction but few means for removal. Primary control points are water treatment prior to public-supply distribution, and municipal and industrial wastewater treatment before discharge to streams.

Because PFAS have a wide range of potential adverse effects on human[46] and ecosystem[47] health, they have been regulated in the U.S. to control their occurrence in drinking water[48] and protect aquatic ecosystems.[49] Understanding the magnitude of potential PFAS contamination requires a basin-scale approach to address the effects of water reuse on water quality, and models have been developed for screening-level assessment of contaminants, such as endocrine disruptors,[50] pharmaceuticals,[51] consumer products,[52,53] pesticides,[54] and PFAS.[55−57] A major challenge in modeling the fate of PFAS in surface waters is the diversity of molecular structures and compound classes present, which result in a range of physicochemical characteristics that control environmental behavior. These characteristics include ionization (speciation), volatilization, sorption, photolysis, bioconcentration, and biodegradation and can impart resistance to chemical, biological, and physical degradation, resulting in environmental persistence.[58−60] The low acid-dissociation constants of PFAA cause them to occur as water-soluble anions,[61] facilitating their aqueous transport. Long-chain PFAA (e.g., >7 fluorocarbons) are more strongly influenced by sorption processes than short-chain compounds (≤7 fluorocarbons), which have lower tendency to interact with sediments[62] or bioconcentrate in organisms.[63,64] Biodegradation processes typically are not effective for removing PFAS during short residence times.[60] Although PFAS discharged to streams can be subjected to additional transformation processes, degradation can be negligible and attenuation primarily attributed to physical mixing and dilution.

Despite the known occurrence of PFAS in WWTP discharges and the potential to contaminate receiving waters, there have been limited basin-scale investigations that develop models to determine the cumulative impacts of water reuse from multiple WWTP sources. Most investigations focus on PFAS occurrence within individual facilities and transformation and removal processes during various treatment stages. Likewise, investigations in surface waters typically focus on occurrence and partitioning between water, sediment, and biota.

An early effort to develop a model to assess PFAS at the catchment scale[55] focused on the Aire (282 km^2) and the Calder (341 km^2) River basins in the United Kingdom. A general linear river model was developed that compartmentalized segments into moving water, stagnant water, and surficial sediment layers, and incorporated advective- and reactive-transport processes. Estimates of PFOS concentrations for each stream segment were based on population density, point-source discharges from individual WWTP, population served by the WWTP, treatment type, and per capita emission (27 μg person^{-1} day^{-1}). Modeled and measured PFOS concentrations demonstrated that spatial concentration trends could be predicted based on population-derived inputs: however, the modeled concentrations were overestimated, suggesting that MEC cannot be accurately predicted using a single per capita emission rate and population density. Although other sources were recognized as important, the majority of PFAS emissions were attributed to municipal WWTP discharges.

Another modeling study[56] assessed PFOS and PFOA in the Danube River (801,463 km^2) in Europe using a chemical fate and transport model to estimate emissions based on population density, WWTP contributions, regional gross domestic product, and combinations thereof. Predicted PFOS and PFOA concentrations were compared with measured values, and results from the mixed emission inputs were close to measured values; the poorest agreement was for population-based estimates. Uncertainty and variability in PFAS sources and emission were major challenges to PFAS-concentration predictions at the catchment scale.

More recently, highly parameterized models to predict the occurrence and fate of PFAS have been developed.[24−28] All of the models involve synthesizing PFAS-source data, capturing relevant transport avenues, calibrating and validating using observational data, and coupling separate models to simulate surface water, groundwater, and water-quality processes. Shortcomings included uncertainty and variability in multiple PFAS source emissions, availability of empirical input data for model parameters, variable physicochemical characteristics of different PFAS, uncertainty in leaching from land surface to aquifers, simulation of groundwater/surface water interactions, coupling multiple models, and identifying point and nonpoint sources across watersheds. Because it is difficult to provide complete and reliable input data for highly parameterized models at large geographic scales, there is a need for robust screening-level models based on readily available geolocation data to provide assessment of potential PFAS contamination, identify presumptive sources, understand fate and transport, and determine data gaps.

A modeling and measuring approach[65] is required to address complex water contamination issues in areas affected by de facto water reuse. Here, two screening-level models were employed to assess cumulative PFAS contamination from upstream municipal and industrial WWTP discharges for all stream segments in the Potomac River watershed (U.S.). Predicted environmental concentrations (PEC) were used to evaluate potential PFAS exposure pathways and effects on aquatic organisms and human health. An accumulated wastewater (ACCWW) model[50,52−54] was used to identify potential municipal and industrial WWTP sources and loading, estimate the proportion of de facto water reuse in source waters, and calculate PEC for each stream segment. The PEC were compared to MEC from discrete surface water samples to validate the modeling approach. Additional presumptive PFAS sources without direct hydrological connectivity, and their potential impact on streamwater quality, were evaluated using the Water Sensing and Hydrology for Environmental Decision Support (WaterSHEDS) model[66] to determine stream-vulnerability scores for each catchment in the watershed.

A unique aspect of this study was integration of multiple tools to provide a holistic understanding of PFAS sources, occurrence, and exposure pathways at the basin scale. Most previous studies on PFAS in municipal WWTP have focused on occurrence and treatment processes at individual facilities without considering direct impacts on receiving water bodies or the larger hydrological context of aggregate upstream loading. The few available basin-scale studies on PFAS occurrence generally are not linked to contaminant sources and do not incorporate both municipal and industrial discharges. Highly parameterized models that capture detailed physicochemical and hydrological processes have intensive input data requirements. The present study provided a transferable approach using widely available hydrological and geospatial data on PFAS sources to systematically assess potential risks to aquatic ecosystem and human health, estimate PEC from WWTP discharges, determine stream vulnerability scores for sources without direct hydrological connectivity for every stream reach in the basin, and verify model results with direct measurements. Inclusion of ecosystem and public-water supply information enhanced understanding of source-to-receptor environmental health implications of PFAS and provided the hydrological context essential to water-resource managers and researchers.

■ METHODS

Study Location, Water Sampling, and PFAS Analysis. The Potomac River is a Strahler[67] seventh-order stream within the Chesapeake Bay watershed. Stream order is an indication of relative position in the hydrologic network and cumulative contribution to flow, with first-order streams representing small headwater tributaries, and incremental order increases at the confluence of equal-order streams (e.g., two sixth-order streams converge to form a seventh-order stream). The Potomac River watershed (Supporting Information Text S1 and Figure S1A) covers portions of Virginia, West Virginia, Pennsylvania, Maryland, and the District of Columbia (U.S.), and had a population of 6.89 million people.[68] During August and September 2022, 32 stream locations (Figure S1B and Table S1) were sampled based on their spatial distribution across the watershed, variable wastewater impacts, range of stream orders, land uses, stream access, and proximity to U.S. Geological Survey stream gages.[69] As part of a separate study focusing on the streams of Virginia during the same period,[70] water samples were collected from an additional 16 locations (Figure S1B and Table S1). In conjunction with the stream sampling, effluents from 18 municipal WWTP with variable sizes and treatment trains distributed across the watershed were sampled for PFAS analysis (Figure S1B and Table S2).[71] During the study period, the Potomac River watershed had 68 surface water sourced public water supplies serving approximately 4.5 million people (Table S3),[53] and 101 stream gages with a period of record >10 years (Table S4).[72] Stream gages were located near 16 sampling sites and annual hydrographs for nine of the gages provided flow context for water-quality sampling events (Figure S2).

Details of water sample collection, flow measurements, and chemical analyses are given in Texts S1 and S2. Stream discharge, field parameters, PFAS measurements, and ancillary constituent analysis (dissolved organic carbon, nutrients, major and trace elements, optical properties, pesticides, and pharmaceuticals) for all sampling events are presented elsewhere.[69] Supernatants from centrifuged unfiltered water samples collected in this study were analyzed for PFAS using direct-aqueous-injection liquid chromatography-tandem mass spectrometry (LC−MS/MS).[73] Unfiltered water samples for the Virginia stream study[70] were analyzed for PFAS by solid-phase-extraction LC−MS/MS using U.S. Environmental Protection Agency Method 1633.[74] Unfiltered municipal WWTP effluents[71] were analyzed by U.S. Environmental Protection Agency Method 1633.[74] Table S5 lists individual PFAS measured by each method, abbreviations used in this paper, and method detection limits (MDL) for the various laboratories.

Geospatial and Proxy Models. Two geospatial modeling approaches were developed using publicly available databases: one allowed calculation of percentage of accumulated wastewater effluent and PFAS PEC based on the hydrologic connection between streamflow and municipal and industrial WWTP discharges, and the other assessed contamination from PFAS sources not hydrologically connected to the streams. These models allowed evaluation of each stream reach in the Potomac River watershed without requiring technically and economically intractable universal collection and analysis of reach-specific water samples. Such screening-level assessments can be used to guide focused investigations.

The ACCWW model was limited to municipal and industrial WWTP sources (Texts S3 and S4) with georeferenced National Pollutant Discharge Elimination System (NPDES) permits and discharges reported in Discharge Monitoring Reports (DMR), and did not include other known or presumptive PFAS sources, including septic systems,[75,76] biosolids application sites,[77] and landfills.[78−80] The non-sewage PFAS-handling industry WWTP were identified by NAICS and SIC codes (Table S6), and the limited data available on PFAS loading for industrial discharges introduced greater uncertainty compared to municipal effluents. Available wastewater effluent PFAS concentration data for PFAS-handling sources are limited to industries, such as pulp and paper mills (SIC code 2621) and refuse systems (SIC code 4953).[17] Because of the lack of specific data, effluents for other PFAS-handling industries were assigned the same concentrations as municipal WWTP effluents for PEC calculations.

The ACCWW model[50,52−54] was used to determine the percentage of streamflow derived from all upstream municipal and industrial WWTP discharges for all 14,885 National Hydrography Data set Plus Version 2 (NHDPlus V2)[81] stream segments in the nontidal portion of the Potomac River watershed (Text S4). Across the U.S., 57,412 presumptive point and non-point PFAS sources with the potential to contaminate surface waters have been identified (49,145 industrial facilities, 4255 municipal wastewater treatment plants, 3493 current or former military sites, and 519 major airports).[11] There were 276 municipal and PFAS-handling industrial WWTP outfalls in the Potomac River watershed. These sites can be further categorized based on the 24 PFAS-handling industry sectors with NAICS or SIC codes listed in the U.S. Environmental Protection Agency Enforcement and Compliance History Online PFAS Analytics tool.[3] Percentage of wastewater contributed by all upstream WWTP was calculated using the NHDPlus V2 estimated runoff method mean monthly streamflows and the mean monthly NPDES municipal and industrial discharges from the DMR.[3] Locations where WWTP discharges occurred were linked to NHDPlus V2 common identifiers (COMID) and used for flow routing and calculation of ACCWW. After determining percentage ACCWW for each COMID, PEC were calculated for specific PFAS frequently detected in the municipal WWTP effluents using the median (e.g., 50th percentile), fifth percentile, and 95th percentile concentrations and reported discharges for the municipal WWTP (NAICS code 221320; SIC code 4952). Similar PEC calculations were made for industrial WWTP discharges from known or suspected PFAS-handling facilities in the watershed using reported industry specific data[17] or PFAS concentration data obtained from the municipal WWTP sampled in this study. Based on reported PFAS fate during municipal[14] and industrial[23] WWTP treatment, and compound physicochemical characteristics (Table S7),[59] the screening-level assessment assumed that PFAS were not removed by in-stream chemical or biological processes.

The ACCWW model was linked to the U.S. Geological Survey stream gage network, and for each gage, mean monthly streamflow, municipal WWTP discharges, industrial WWTP discharges (all other NAICS and SIC codes), percentage of streamflow contributed by WWTP discharges, estimated

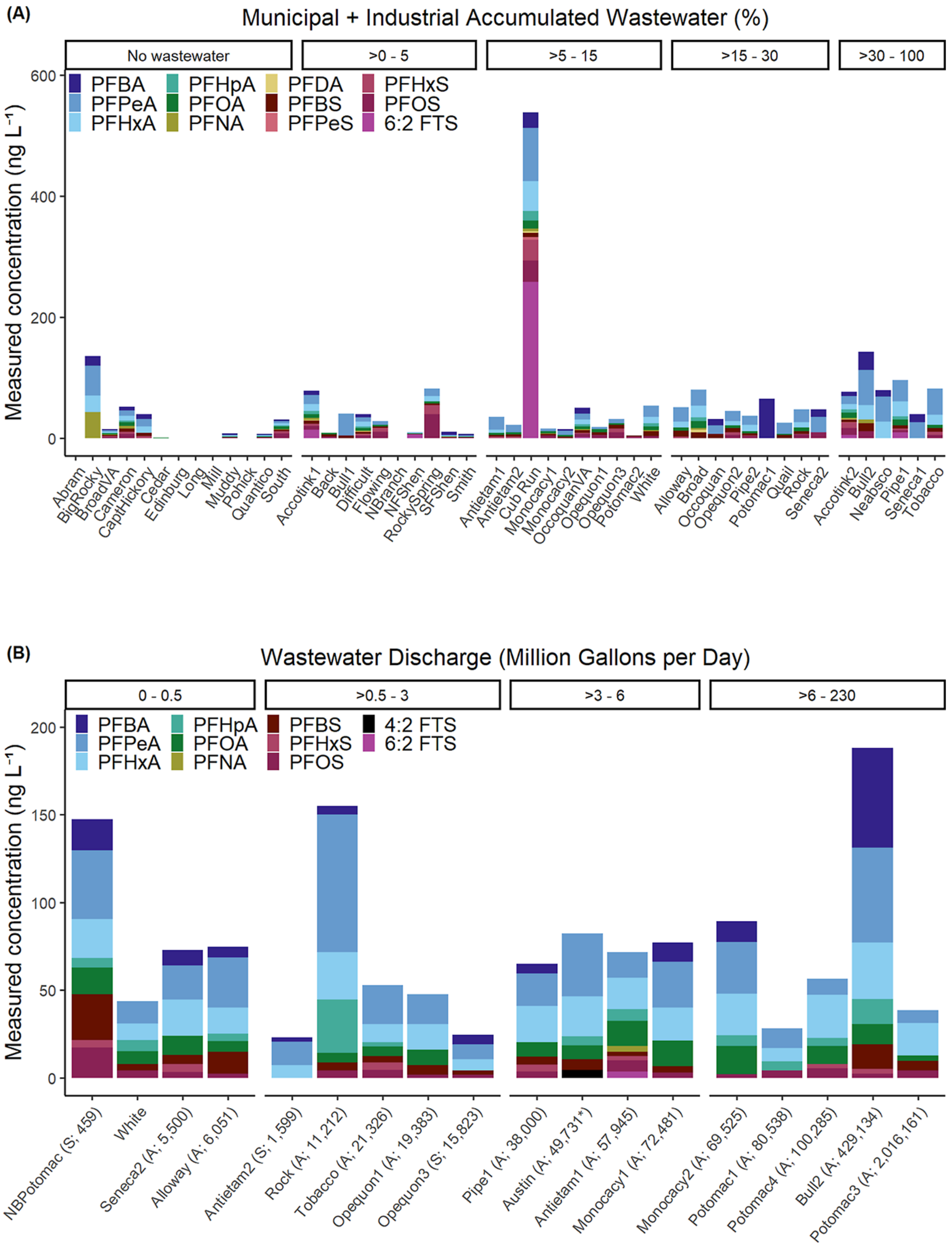

Figure 1. Distribution of measured per- and polyfluoroalkyl substances concentrations in the Potomac River watershed (A) river water samples, and (B) municipal wastewater treatment plant (WWTP) effluents. [Panel A includes 32 stream sites sampled in this study[69] and 16 stream sites sampled in Virginia in a concurrent study;[70] panel B includes 18 municipal WWTP sampled in a concurrent study;[71] stream sites are sorted by increasing percentage of mean-August accumulated municipal-plus-industrial wastewater; WWTP sites sorted by discharge; see Tables S1 and S2 for stream and municipal WWTP site information; see Tables S9 and S11 for individual compound concentrations; information shown in parentheses after WWTP site name is treatment type (A, advanced; S, secondary) and population served, and were not reported for White; * population data are from 2012 and for all other sites are from 2022].

monthly PFAS PEC, and estimated monthly PFAS loads were calculated for water year 2022 to 2024 (Text S4).[82]

The WaterSHEDS model[66] was used to assess additional presumptive PFAS sources including those without discharge information (Text S5, Figure S3, and Table S8). The model determined stream-vulnerability scores (rather than percentage of accumulated wastewater and PEC) based on a limited number of presumptive PFAS sources and the hydrologic network from NHDPlus High Resolution.[83] Presumptive PFAS sources within the watershed were assigned relative weights based on their industries.[9] The presence of presumptive sources upstream from each flowline, their relative industry weighting, and distance from the flowline were used to estimate a vulnerability score from 0 to 1 for each stream reach. A vulnerability score of 0 indicates the absence of presumptive PFAS sources in the contributing catchment, and a score of 1 indicates the presence of many high-weighted potential sources near the stream segment of interest.

A statistical-proxy model and principal-component analysis (PCA) were used to assess the relationships between chemical, hydrological, and geospatial data sets (Text S6) and potential influences on PFAS contamination. Landscape characteristics relevant to presumptive PFAS sources (Figure S1B and Table S1) included geology, hydrology, land use, population density, and industrial and agricultural activities. Ancillary water quality measurements[69] and landscape characteristics were used to develop stepwise regression models that provided an additional means to predict PFAS concentrations.

RESULTS AND DISCUSSION

Measured Concentrations in River Water and WWTP Effluents. Surface-water samples were collected from 48 sites distributed across the watershed that covered a gradient of stream orders and ACCWW (Table S1). Seventeen of the 40 PFAS measured (note different sample sets had different analyte numbers; Table S5) were detected in river water and generally occurred as mixtures (Text S7 and Tables S9 and S10). Results for the 12 most frequently detected PFAS are presented in Figure 1A. There was a trend of increasing PFAS concentration with increasing accumulated wastewater (Figure S4) with several notable exceptions that had elevated concentrations but low percentages of accumulated wastewater (Big Rocky, Accotink 1, Rocky Spring, and Cub Run). These sites also had different PFAS compositions than typical municipal WWTP impacted sites. Perfluoropentanoate was the most frequently detected PFAS (79%) and had the highest mean concentration (19 ± 18 ng L^{-1}). Perfluorobutanesulfonate was the next most frequently detected compound (75%) but had lower concentrations (4.3 ± 2.9 ng L^{-1}). Perfluorobutanoate and PFHxA had the next highest concentrations after PFPeA (12 ± 14 and 12 ± 11 ng L^{-1}, respectively) but lower detection frequencies (44 and 56%, respectively). Other frequently detected compounds were PFOA (65% detection; 4.3 ± 3.0 ng L^{-1}), PFOS (58% detection; 7.1 ± 9.2 ng L^{-1}), and perfluorohexanesulfonate (PFHxS; 44% detection; 5.3 ± 7.3 ng L^{-1}). Perfluorononanoate (PFNA) was detected in 31% of samples (5.0 ± 11 ng L^{-1}). Perfluoroheptanoate also was detected in 31% of samples (3.9 ± 4.0 ng L^{-1}). Perfluorodecanoate (PFDA), perfluoroundecacoate (PFUnDA), perfluoropentanesulfonate (PFPeS), perfluoroheptanesulfonate (PFHpS), and the precursors 6:2 fluorotelomer sulfonate (6:2 FTS), 8:2 fluorotelomer sulfonate, perfluorooctane sulfonamide, and perfluoro-3-methoxypropanoate were detected with low frequency (<20%). The $\Sigma PFAS_{MEC}$ ranged from 0.5 to 546 ng L^{-1} (55 ± 84 ng L^{-1}) and increased with increasing ACCWW (Spearman correlation = 0.60, p value ≤ 0.0001, n = 48).

Eleven of the 30 PFAS measured were detected in municipal WWTP effluent samples (Text S7 and Tables S11 and S12). Figure 1B shows that concentrations and compositions for most of the WWTP effluents were relatively consistent, but there was considerable variability between sites. Three of the sites had much higher concentrations than the others, suggesting additional non-domestic PFAS sources, such as inputs from landfill leachate[12,33] or industrial discharges[13] (seven of the WWTP had industrial pretreatment programs; Table S2). Although detected in streamwater, PFDA and PFPeS were not detected in WWTP effluent. The most frequently detected PFAS in effluent were PFPeA (100% detection; 25 ± 18 ng L^{-1}), PFHxA (100% detection; 18 ± 7.4 ng L^{-1}), PFOS (89% detection; 4.4 ± 3.7 ng L^{-1}), PFOA (83% detection; 9.7 ± 4.1 ng L^{-1}), PFBS (77% detection; 7.1 ± 6.4 ng L^{-1}), PFBA (56% detection; 13 ± 16 ng L^{-1}), and PFHpA (61% detection; 8.3 ± 7.9 ng L^{-1}). The $\Sigma PFAS_{MEC}$ for compounds detected in the effluents ranged from 23 to 190 ng L^{-1} (74 ± 46 ng L^{-1}). No clear relationships were observed between WWTP effluent PFAS concentrations and population served.

Accumulated Wastewater Model. During 2022, 228 permitted municipal WWTP outfalls were included in the DMR for facilities discharging to the nontidal Potomac River watershed (Text S8, Figure S5A, and Table S13), affecting 3646 km (14%) of the 26,668 km stream network. Although 372 permitted industrial WWTP outfalls were reported in the DMR for the watershed, only 48 included outfalls with NAICS and SIC codes for potential PFAS-handling sectors (Figure S5B andTables S6 and S14). Basin-wide municipal-plus-industrial accumulated wastewater ratios were lower under mean-annual flow (Figure S5C) than mean-August flow (Figure S5D). Municipal-plus-industrial WWTP discharges to the Potomac River upstream from the confluence with the Monocacy River contributed 2.8 and 12% of the total flow under mean-March (high-flow) and mean-August (low-flow) conditions, respectively. Municipal discharges contributed 30% of the total wastewater flow and industrial discharges contributed 70%. The largest industrial WWTP discharge in the watershed was a thermoelectric power plant (SIC code 4911): however, because it discharged to a recirculating reservoir and there was no information on PFAS use, this facility was excluded from further analysis. The next largest industrial WWTP was a pulp and paper mill (SIC code 2621) which discharged to the North Branch Potomac River and was responsible for 64% of the total industrial wastewater flow in the watershed. First- and second-order streams comprised 80% of the river network, had 122 municipal and 260 (only 23 were considered PFAS handling facilities) industrial WWTP discharges, and received 29% of the total WWTP flow. Some first- and second-order streams had >99% ACCWW under low-flow conditions. Approximately one-half of the third- to seventh-order streams contained municipal and industrial WWTP effluent, but the corresponding ACCWW did not exceed 65% under low-flow conditions.

Loading rates for PFAS from individual WWTP can be highly variable and are influenced by the nature of the wastewater sources, specific treatment trains, and seasonal effects.[14,15,35] In contrast to municipal wastewater contaminants such as pharmaceuticals and sucralose, which can be estimated from individual per capita use,[51−53,55,57] PFAS are used in many consumer and industrial products[4] and loads are difficult to estimate a priori from population served. Municipal and industrial WWTP derived PFAS PEC were calculated using estimated streamflow from NHDPlus V2, WWTP effluent discharges from DMR (Tables S13 and S14), and the median, fifth percentile, and 95th percentile PFAS concentrations measured in the municipal WWTP effluents (Table S11). While it is known that PFAS concentrations in municipal WWTP can vary temporally,[15,35,36] the measured effluent PFAS concentrations in this study represent a single point in time for the individual facilities. However, the diversity of facilities sampled provided a representative distribution of PFAS concentrations. The estimated median $\Sigma PFAS_{MEC}$ WWTP loading for the Potomac River watershed was 51 μg $capita^{-1}$ day^{-1} (ranged from 11 to 150 μg $capita^{-1}$ day^{-1}), consistent with values reported for other municipal facilities (Table S15). Based on the limited data reported in the literature, industrial WWTP effluents also are potential sources of PFAS (Table S16).

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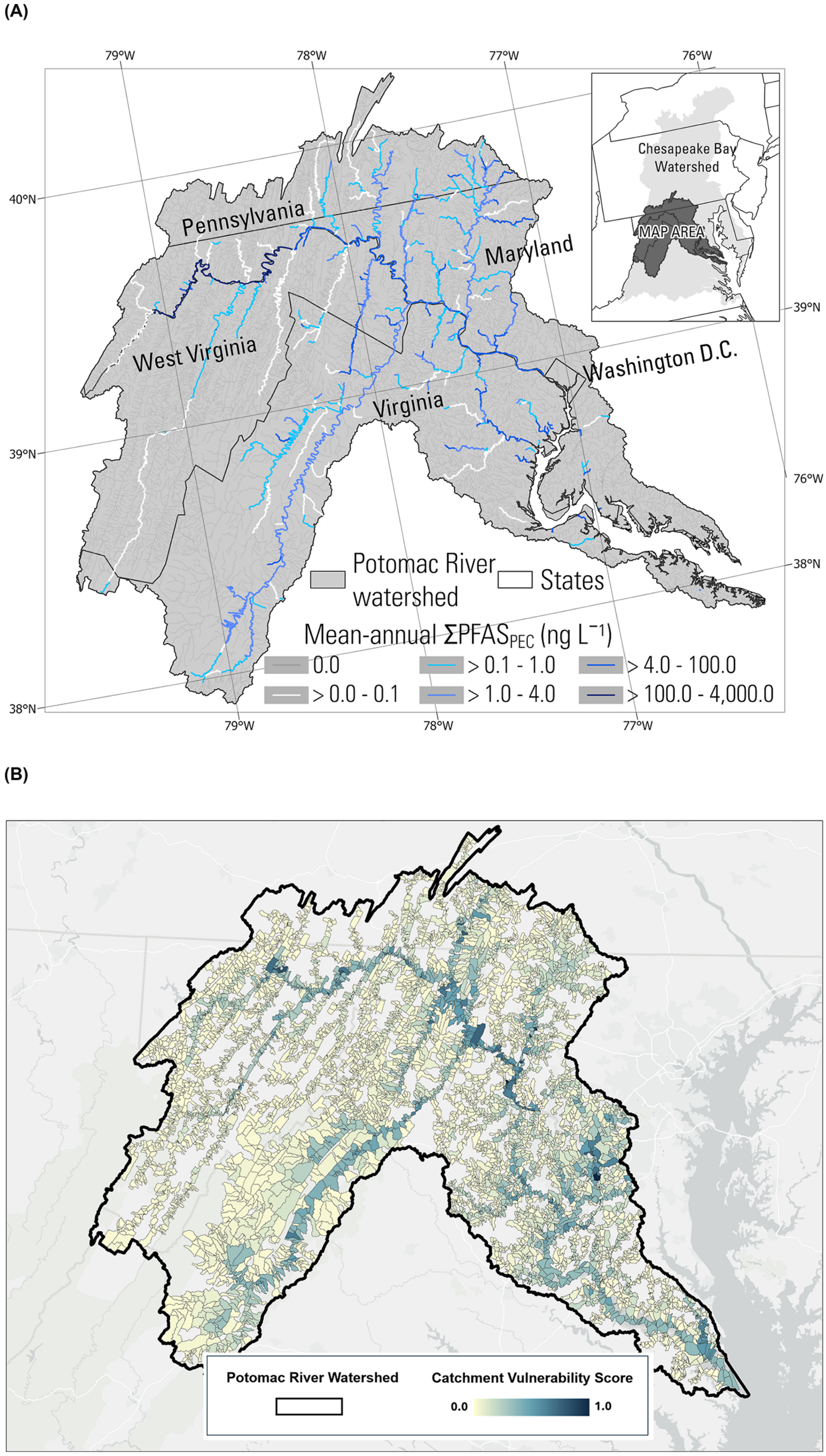

Figure 2. Maps of the Potomac River watershed showing (A) predicted environmental concentrations (PEC) determined by the Accumulated Wastewater model[54] for the sum of eight per- and polyfluoroalkyl substances ($\sum\mathrm{PFAS}_{\mathrm{PEC}}$) sourced from municipal and industrial wastewater treatment plant (WWTP) discharges, and (B) catchment vulnerability scores determined by the Water Sensing and Hydrology for Environmental Decision Support model.[66] [PEC calculations based on mean annual streamflow, mean annual WWTP discharge, and median WWTP effluent concentrations].

Predicted and Measured Concentrations. Municipal WWTP discharges impacted 14% of the Potomac River watershed stream segments, and PEC were calculated for the eight PFAA (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFBS,

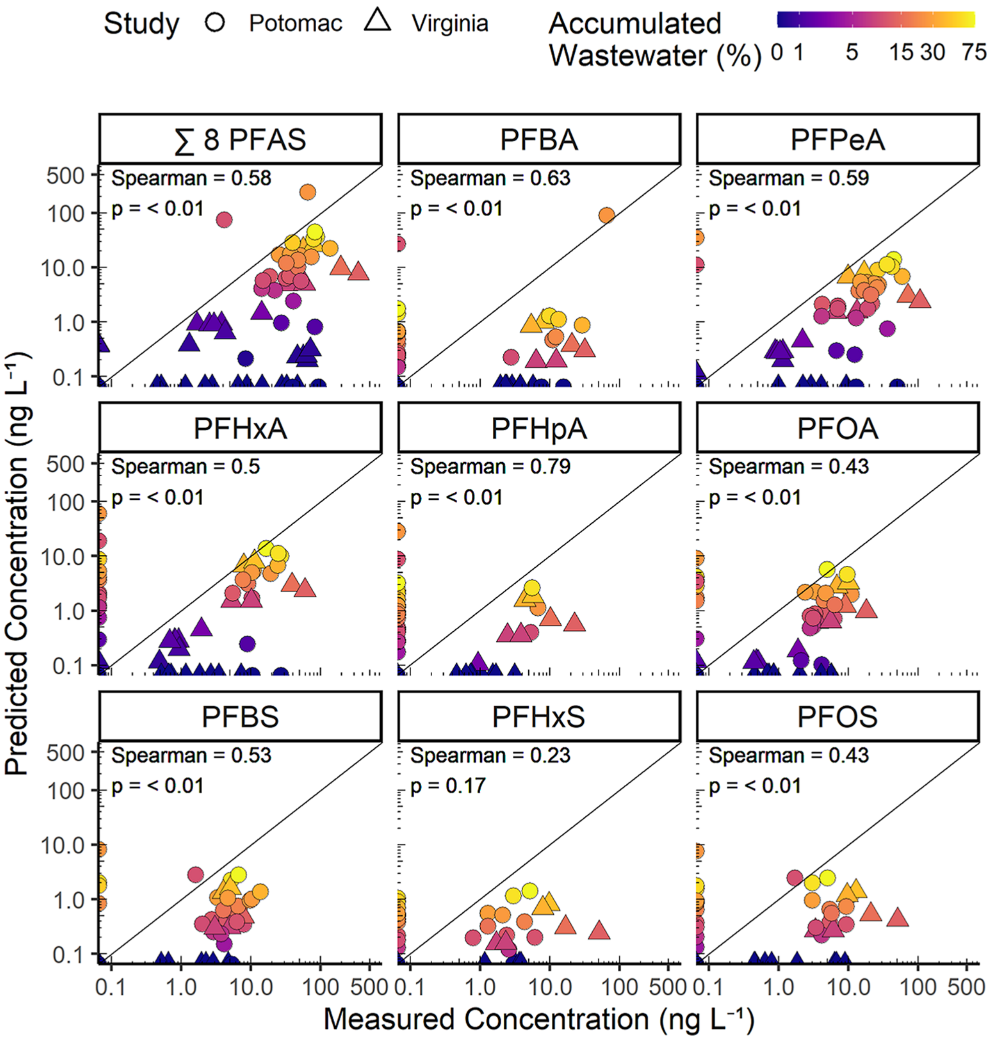

Figure 3. Plots of measured environmental concentrations versus predicted environmental concentrations for the sum of eight perfluoroalkyl substances (∑ 8 PFAS) and the individual compounds for municipal-plus-industrial wastewater treatment plants. [Plots show Spearman correlation coefficients and probability values; see Table S5 for compound abbreviations; see Tables S9 and S18 for individual compound concentrations; Potomac, samples measured in this study;[69] Virginia, samples measured in concurrent study;[70] values that plot on the *x*-axis represent samples with no accumulated wastewater (ACCWW) resulting in predicted environmental concentrations of zero; values that plot on the *y*-axis have ACCWW predicted concentrations, but measured concentrations are below method detection limits.].

PFHxS, and PFOS) most frequently detected in the effluents (Table S11). Uncertainty in the assumption that all municipal WWTP discharged the same median PFAS composition over time was addressed using the fifth and 95th percentile effluent concentrations as input to the PEC model. The PFAS PEC for municipal and municipal-plus-industrial WWTP discharging into stream segments where MEC also were determined are presented in Tables S17 and S18, respectively. The full set of PEC calculations for all stream segments are reported elsewhere.[69] Basin-wide distributions for the sum of the eight PFAS PEC ($\Sigma PFAS_{PEC}$) for municipal-plus-industrial WWTP discharges under mean-annual flow are shown in Figure 2A. Distributions for PFOA, PFHxS, and PFOS are shown in Figure S6.

Because municipal and industrial WWTP discharges are continuous PFAS point-sources, MEC and PEC were significantly correlated with municipal-plus-industrial ACCWW, except for PFHxS (Figure 3). Although samples with >1% ACCWW typically exhibited higher PFAS MEC than PEC (98% of results with detected PFAS), 62% of sites with no ACCWW had PFAS detections, suggesting contributions from non-WWTP sources. When only municipal ACCWWwas considered (Figure S7), agreement between MEC and PEC was not as good as when municipal-plus-industrial ACCWW was considered. For municipal-plus-industrial WWTP, MEC exceeded PEC in 99% of the samples, and PEC accounted for 12 and 2% of the mean and median MEC, respectively. The mean and median $\Sigma PFAS_{PEC}$ (using median WWTP effluent concentrations) at locations with MEC were 9.1 and 0.4 ng L^{-1}, respectively, lower than the mean and median $\Sigma PFAS_{MEC}$ (34 and 26 ng L^{-1}, respectively). The mean $\Sigma PFAS_{PEC}$ using the fifth percentile WWTP effluent concentrations was lower (3.0 ng L^{-1}), while the mean $\Sigma PFAS_{PEC}$ using the 95th percentile concentration was higher (28 ng L^{-1}) and approached the mean $\Sigma PFAS_{MEC}$. These results suggest that either the WWTP effluent concentrations were higher than the median values used in the model or that there were other PFAS sources.

Stream and Effluent Loads. Establishing hydrological connectivity between landscape sources and stream reach processes provided a means to evaluate exposure pathways. Because stream concentration-discharge relationships often

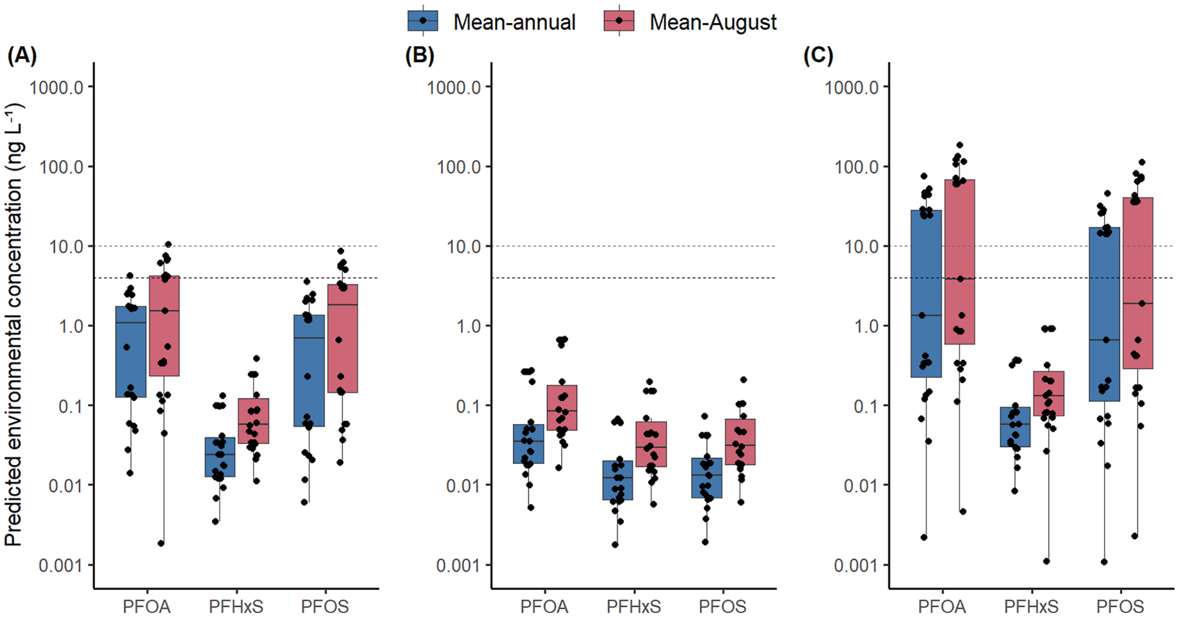

Figure 4. Predicted environmental concentrations (PEC) for perfluorooctanoate (PFOA), perfluorohexanesulfonate (PFHxS), and perfluorooctanesulfonate (PFOS) at public water supply surface water sources in the Potomac River watershed under mean-annual and mean-August flow conditions using (A) median measured wastewater treatment plant (WWTP) effluent concentrations, (B) fifth percentile measured WWTP effluent concentrations, and (C) 95th percentile measured WWTP effluent concentrations. [Dashed horizontal lines represent drinking water maximum contaminant levels of 4.0 ng L^{-1} (black) for PFOA and PFOS and 10 ng L^{-1} (gray) for PFHxS;[48] boxplots represent the 25th, 50th, and 75th percentiles while whiskers extend to the largest value no greater than 1.5 times the interquartile range; PEC greater than 0.001 ng L^{-1} are plotted as points; 39 of the 68 source waters were located on stream reaches with no municipal or industrial WWTP discharges and therefore are not included in the figure].

result in decreasing concentrations with increasing discharge due to dilution effects, source apportionment of PFAS requires an understanding of mass loading to river basins.[16,31,39,84] Measured and predicted PFAS loads can be calculated by multiplying concentrations by streamflow (Text S2).[85] Mean-annual discharge during 2022 for the 16 stream gages ranged from 1.68 to 76.5 $m^3\ s^{-1}$ and instantaneous discharge measured at 26 sampling sites ranged from 0.02 to 133 $m^3\ s^{-1}$ (Table S1). Instantaneous PFAS load calculations (Text S8) were made at 19 of the 32 sites where PFAS were detected in water samples (Table S9) and instantaneous streamflows were measured (Table S1). Although results varied by site and compound, for the frequently detected PFAS, median measured stream loads ranged from 267 mg per day (mg d^{-1}) for PFBS to 627 mg d^{-1} for PFPeA. The median measured PFAS loads for the 18 WWTP (Table S11) ranged from 27 mg d^{-1} for PFBS to 252 mg d^{-1} for PFPeA.

The ACCWW model results were integrated with the U.S. Geological Survey stream gage network[72] (Table S4) to provide basin-wide assessment of PFAS. Using monthly streamflows and municipal-plus-industrial WWTP discharges from water year 2022 to 2024, the average monthly ACCWW percentage, PFAS PEC, and estimated PFAS loads at each stream gage were estimated.[82] Mean water year municipal-plus-industrial WWTP $\Sigma PFAS_{PEC}$ loads increased along the Potomac River from the upstream Steyer site (Figure S8A; station number 01595000; 0.06 kg per year, kg yr^{-1}) to the Paw Paw site (Figure S8B; station number 01610000; 47 kg yr^{-1}) to the downstream Little Falls Pump Station site (Figure S8C; station number 01646500; 68 kg yr^{-1}). The elevated PFAS PEC at the Little Falls Pump Station site (which discharges into the Chesapeake Bay tidal zone) during the low-flow period from July to December 2023, which was the 11th lowest average streamflow during these months out of 95 years of record (12th percentile), illustrated the temporal relationship between streamflow and water concentrations.

Landscape Sources. The WaterSHEDS model assessed additional presumptive PFAS sources distributed across the landscape to determine stream-vulnerability scores (Figure 2B) based on contributing sources, weighting factors, and distance from source to stream flowline (Texts S5 and S9 and Figure S3). Seventy-three percent of the flowlines had vulnerability scores ≤0.05, indicating a low likelihood of PFAS contamination. The mean vulnerability score for the remaining 27% of flowlines was 0.15 (Figure S9A), the median vulnerability score was 0.13, and the maximum vulnerability score was 0.66, the latter suggesting a substantial potential for PFAS contamination. Because the vulnerability scores do not have direct hydrological connectivity between source discharges and streamflow, they do not provide insight into concentrations or loads. Vulnerability scores increased with increasing stream order (Figure S9B), indicating that there were more accumulated upstream presumptive PFAS sources, the upstream presumptive PFAS sources were weighted heavily, or the sources were located closer to the stream segment.

Vulnerability scores complement the ACCWW by identifying areas with potential for contamination. For example, the highest $\Sigma PFAS_{MEC}$ (Figure 1A) occurred at the Cub Run site, a second-order stream with no municipal WWTP inputs. However, Cub Run had 14% mean-annual ACCWW when industrial WWTP were included. The PFAS composition at this site exhibited a high abundance of 6:2 FTS precursor, suggesting a nonmunicipal WWTP source. Most of the drainage area for Cub Run consists of an international airport, with associated fire-training areas that use AFFF, and concentrated industrial activities. The 16 PFAS sources within the catchment resulted in a vulnerability score of 0.23 (Figure S10A). The Big Rocky Run site, a second-order stream, had the third highest $\Sigma PFAS_{MEC}$ concentration and a high abundance of PFNA, but there were no municipal or industrial WWTP discharges. The three PFAS sources resulted in a vulnerability score of 0.10 (Figure S10B). The Paw Paw site, located on the fifth-order reach of the mainstem Potomac River, had 2939 potential PFAS sources, including a pulp and paper mill, that resulted in a vulnerability score of 0.25 (Figure S10C). Although the $\Sigma PFAS_{MEC}$ was low, this site had a unique composition dominated by PFBA (Figure 1A and Table S9), which has been reported as characteristic of paper mill activities.[17] Abram Creek, a third-order stream, had no PFAS detections and no upstream municipal WWTP, but 16 potential sources resulted in a vulnerability score of 0.17 (Figure S10D). Edinburgh Run, a first-order stream, had no detectable PFAS, no municipal WWTP, and only four potential sources, resulting in a vulnerability score of 0.03 (Figure S10E). In general, sites with vulnerability scores <0.10 had limited PFAS detections, whereas sites with scores >0.20 had measurable PFAS concentrations.

De Facto Water Reuse, Drinking Water PFAS Exposure, and Human Health. Recent studies comparing public water supply source water (surface water and groundwater), treated predistribution drinking water without PFAS-specific treatment, and residential tapwater across the U.S.[86−88] have shown widespread occurrence of PFAS and minimal concentration changes during treatment. An assessment of PFAS concentrations in source-water and predistribution drinking water at 25 treatment facilities in the U.S. indicated minimal removal by standard treatment technologies.[89,90] These findings indicate that in the absence of advanced treatment, PFAS concentrations (measured or predicted) at the source water intake provide reasonable estimates of potential human exposure through drinking-water.

Four of the six PFAS with drinking water maximum contaminant levels (MCL)[48] were detected in Potomac River watershed stream samples (PFOA and PFOS have MCL of 4.0 ng L^{-1}; PFNA and PFHxS have MCL of 10 ng L^{-1}). Source water samples collected near one drinking water intake (n = 5) had PFOA and PFOS mean MEC of 0.83 ± 0.70 and 0.71 ± 0.31 ng L^{-1}, respectively, which did not exceed the drinking water MCL. Only one of the five samples had a detection of PFNA (0.78 ng L^{-1}), and PFHxS was not detected.

The ACCWW model was used to assess de facto reuse in surface water sources for 68 public water supplies in the watershed (41 source waters had no upstream municipal or industrial WWTP discharges), and PFAS PEC are presented in Table S3. A threshold value of 1% municipal WWTP de facto reuse has been associated with adverse impacts on public water supplies.[44,91] Under mean-annual and mean-March flow, 26% of the source waters exceeded 1% ACCWW (municipal-plus-industrial), and under mean-August conditions, 32% exceeded 1%. Maximum municipal-plus-industrial ACCWW under mean-annual, mean-March, and mean-August conditions were 12, 7.5, and 28%, respectively. The PEC calculated from median measured WWTP effluent concentrations for PFOA, PFHxS, and PFOS in stream reaches with public water supply intakes ranged from <0.01 to 10 ng L^{-1}, with the greatest values occurring during mean-August flow (Figure 4A) when PFOA and PFOS concentrations exceeded MCL in 15 and 7% of the source waters, respectively. The PFHxS PEC did not exceed 25% of the MCL under either flow condition. The fifth percentile PEC for PFOA, PFHxS, and PFOS ranged from <0.01 to 0.66 ng L^{-1}, with the greatest values occurring during mean-August flow (Figure 4B), but no concentrations exceeded MCL. The 95th percentile PEC for PFOA, PFHxS, and PFOS ranged from <0.01 to 183 ng L^{-1}, and during mean-August flow (Figure 4C) PFOA and PFOS exceeded MCL in 16% of the source waters. These results indicated potential for human exposures from drinking water across the Potomac River watershed.

■ ECOSYSTEM AND HUMAN HEALTH CONSIDERATIONS

Although much of the current PFAS effects research focuses on drinking water exposure and human health,[46,48] aquatic ecotoxicity[47,49] and potential human exposure through fish consumption[92−95] also are concerns. National aquatic life ambient water quality criteria have been established for PFOA and PFOS, with acute criterion maximum concentrations of 3,100,000 and 71,000 ng L^{-1}, respectively, and chronic criterion continuous concentrations of 100,000 and 250 ng L^{-1}, respectively.[49] The maximum concentrations of PFOA and PFOS measured in the municipal WWTP effluent samples were 16 and 17 ng L^{-1}, respectively, indicating that even under 100% de facto reuse conditions, levels would be below U.S. Environmental Protection Agency aquatic toxicity thresholds.

Using maximum measured streamwater concentrations for PFOA, PFNA, PFHxS, and PFOS (Table S9) and fish bioconcentration factors of 14, 55, 110, and 220 L kg^{-1}, respectively,[63] estimated whole organism tissue concentrations were 0.15, 2.5, 1.5, and 8.7 $\mu g\ kg^{-1}$. Maryland Department of the Environment and Maryland Department of Health[96] fish screening values for PFOA, PFNA, PFHxS, and PFOS were 3.6, 3.6, 24, and 2.4 $\mu g\ kg^{-1}$, respectively; these screening levels equate to fish consumption reference doses of 3.0×10^{-6}, 3.0×10^{-6}, 2.0×10^{-5}, and 2.0×10^{-6} mg kg^{-1} day^{-1}, respectively. Fish consumption reference dose values from the Virginia Department of Environmental Quality and Virginia Department of Health[97] are 1.5×10^{-9} mg kg^{-1} day^{-1} for PFOA and 7.9×10^{-9} mg kg^{-1} day^{-1} for PFOS. In the current study, only PFOS had estimated fish tissue concentrations exceeding screening levels or fish consumption reference doses.

■ RESOURCE MANAGEMENT TOOLS

The occurrence, fate, and effects of PFAS in the aquatic environment are complex, multidimensional, and dynamic. This integrated basin-scale modeling and measuring approach provided multiple lines of evidence to assess PFAS occurrence from presumptive sources and determined relationships between landscape and hydrological factors to assess potential exposure in both sampled and unsampled stream reaches. Because water reuse is an intrinsic component of the modern hydrological cycle, the interconnected nature of landscape sources and exposure pathways need to be considered to protect ecosystem and human health. For example, identifying source water locations and flow conditions where PFAS concentrations at public water supply intakes might exceed MCL thresholds could inform operation of drinking water treatment facilities.

Contamination of water resources involves mixtures of co-occurring chemicals derived from multiple sources. Ancillary water quality data should be considered an integral component for assessment of target contaminants, such as PFAS, to provide chemical context for ranking relative risks from simultaneous exposure to multiple chemicals.[52,98] Ancillary data also can provide "proxy" measurements for PFAS occurrence attributed to sources, such as municipal WWTP discharges. For example, optical properties (light absorption and fluorescence) of water samples have been used to identify stream reaches impacted by municipal WWTP and septic systems.[7,8,99] Optical property measurements can be used to confirm the presence of wastewater, with attendant PFAS, and develop statistical models to estimate contaminant levels (Text S10). Optical property-based proxy models (Figure S11 and Tables S19−S21) were used to estimate PFAS concentrations when MEC values were < MDL. Analytical-interference elevated MDL can introduce uncertainty into interpretations by implying no contamination. As shown in Figure S12, applying the optical property proxy model indicates that samples with individual PFAS levels < MDL could have substantial $\Sigma\text{PFAS}_{\text{MEC}}$. Multiple lines of evidence provide a means for evaluating uncertainty in complex sample matrices.

The diverse relationships between landscape variables, surface water PFAS concentrations, and co-occurring constituents were assessed using PCA (Figure S13). Three principal components accounted for 60% of the variability in the combined data with 49% attributed to the first two components alone (Figure S13). The first component (27%) represented a rural to urban land-use gradient, whereas the second component (22%) discriminated between municipal wastewater indicators and non-sewage urban source indicators, presumed to be due to runoff from impervious surfaces and other industrial-like sources that can vary spatially. A more comprehensive PCA assessment of the full Potomac River chemical data set[69] showed similar relationships with other constituents associated with WWTP, such as trace elements, pharmaceuticals, and pesticides.[54] Similar PCA relationships between PFAS and urban land use also have been observed in other studies.[7]

Although publicly available geospatial data on WWTP discharges can be used to identify presumptive PFAS sources that have NPDES permits, other presumptive sources without associated discharge data, including current and formerly used Department of Defense sites, airport runways, landfills, fire stations, and oil and gas operations, were not included. Many other potential non-point PFAS sources without available geospatial data also were not considered, including septic systems,[75,76] pesticide applications,[73,100] construction material disposal,[101] recreation activities,[102,103] municipal biosolids,[77] and urban stormwater runoff.[104]

Because there are multiple definitions of PFAS, such as the requirement of either a single fluorocarbon unit or repeating fluorocarbon units,[1,105] many fluorochemical compound classes, including fluoropesticides[106] and fluoropharmaceuticals,[107] typically are not considered when assessing PFAS. In contrast to commercial and industrial PFAS designed to repel water and oil or to have resistance to thermal and biological degradation, fluoropesticides and fluoropharmaceuticals are designed for specific biological activity. For example, in a companion study,[54] the fluoroinsecticide fipronil (containing two trifluoromethyl moieties) was detected in >50% of the water samples, and the mean concentration ($22\ \text{ng L}^{-1}$) exceeded the chronic freshwater invertebrate aquatic life benchmark ($11\ \text{ng L}^{-1}$) and the median concentration ($8.6\ \text{ng L}^{-1}$) approached the benchmark. Although the mean and median PFOS PEC (7.8 and 5.0 ng L^{-1}, respectively) exceeded the drinking water MCL[48] of 4.0 ng L^{-1} they were below freshwater aquatic life water quality criteria (250 and 71,000 ng L^{-1}, respectively).[49]

This integrated investigation developed tools to provide a basin-scale perspective on PFAS contamination arising from de facto water reuse and highlighted the diverse sources of PFAS, their hydrologic connection to surface water systems, and potential ecosystem and human exposure pathways. A screening-level modeling approach was used to develop predicted PFAS concentrations resulting from municipal and industrial WWTP discharges, and vulnerability scores that incorporate other landscape-based sources, for all stream segments within the watershed. The modeling results were verified using measurements from discrete water samples, and comparisons of PEC and MEC were used to identified areas potentially impacted by non-WWTP sources. The PFAS vulnerability scores allowed assessment of a broad range of presumptive sources, including those without discharge data, providing characterization of potential ecosystem and human health risks. This novel multitiered investigation developed a systematic understanding of known or suspected sources of PFAS contamination and a basin-scale hydrological context for assessment of source-to-receptor exposure pathways. Because the screening-level models are based on publicly available geospatial information, the approach has broad applicability to other basins to identify areas of concern and can be used to inform research and monitoring activities. Addressing de facto water reuse, and associated introduction of PFAS into public water supply sources, is a water resource management priority requiring knowledge of upstream presumptive sources and spatial and temporal loading trends. The modeling tools presented here are adaptable to other watersheds and can be up- or down-scaled to address a variety of water-quality issues and can be applied to contaminants other than PFAS.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.4c12167.

> Supporting Information consists of 40 pages, including 10 text sections, 13 figures, and 21 data tables describing sampling, analysis, modeling, and results. Texts S1 to S6 describe methods including site selection, sampling, chemical analysis, and model development. Texts S7 to S10 describe results from the measuring and modeling efforts. Figures S1 to S3 show site locations, hydrographs, and the WaterSHEDS model framework. Figures S4 to S13 present modeling results and statistical analysis (PDF)
>
> Tables S1 to S4 present information on stream and WWTP sampling sites, public-water supplies, and U.S. Geological Survey stream gages. Tables S5 to S8 present information on PFAS analysis, physicochemical characteristics, presumptive sources, and input data for the WaterSHEDS model. Tables S9 to S12 present results and quality assurance from discrete sample analyses. Tables S13 to S16 present information on municipal and industrial WWTP in the watershed and PFAS loading. Tables S17 and S18 present PEC results for stream reaches where discrete water samples were collected. Tables S19 to S21 present variables used in developing statistical models and principal component analysis and results (XLSX)

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Notes

The authors declare no competing financial interest.

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