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Statewide Surveillance and Mapping of PFAS in Florida Surface Water

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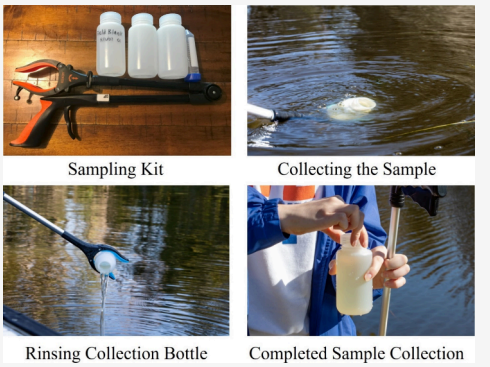
ABSTRACT: Florida's water bodies are vital for drinking, agriculture, recreation, tourism, and climate resilience. The monitoring of water quality is critical for the state, with consequences for both human health and the economy. This work describes our statewide monitoring of per- and polyfluoroalkyl substances (PFAS) within a myriad of water bodies in Florida to establish a PFAS baseline and determine hotspots. Surface water samples were obtained between April 2020 and December 2021, from 2323 sites, via crowdsourcing from all 67 counties in Florida and were subsequently analyzed for 50 PFAS via high-performance liquid chromatography-tandem mass spectrometry. The mean concentration of ∑PFAS across Florida was 29 ng/L, with a maximum ∑PFAS concentration of 3048 ng/L. Moreover, 23 counties reported perfluorooctanoic acid and perfluorooctanesulfonic acid levels over the EPA's maximum contaminant level of 4 ng/L, with 915 and 920 sites over the limit across the state, respectively. Data was organized by site coordinates, and predictive heat maps highlighting regions of concern were created. First attempts were made to identify possible PFAS pollution sources by overlaying suspect entities (airports, military installations, and wastewater treatment plants), in addition to relating data to historical pollution spill notifications (e.g., wastewater influent, effluent, and sludge).



KEYWORDS: *PFAS, surface water, wastewater treatment plants, statewide mapping, crowdsourcing, LC-MS/MS*

1. INTRODUCTION

Ranking third in the United States (US) by water area, with over 12,000 mi^2 of coastline and inland waterways,[1] the state of Florida relies heavily on its various water bodies for economic growth and stability—from the agriculture industry and fisheries, to ecotourism and even drinking water bottling from natural springs.[2,3] Florida's water bodies are both vast and complex, with a diverse array of water environments. The water itself ranges on all gradients between saltwater and freshwater, while water locationality includes unique environments spanning from intercoastal areas, the Gulf of Mexico/Atlantic Ocean, springs, and aquifers. Beyond their economic importance, these water bodies are primary habitats for Florida's abundance of aquatic wildlife, which includes a variety of endemic species like manatees, alligators, dolphins, and sea turtles, among others, all of which help bring more than 100 million tourists into the state each year.[4,5] Recreational fishing in Florida is a multibillion dollar industry, and approximately 100 million pounds of commercially harvested seafood is caught and sold in Florida each year.[6]

Along with the continued growth of Florida tourism, the overall population of Florida continues to grow, reaching over 22.5 million people in 2023 and ranking Florida as the third most populous state in the US.[7] This continually increasing flux of people poses an expanding threat to Florida's water bodies, stemming from increased industrialization, urbanization, and the resulting pollution.[8] Florida has previously experienced several types of pollution concerns, with notable examples including eutrophication, pesticide and herbicide use (e.g., glyphosate), and the unintended release of heavy metals and fecal material.[9−12] The concern over water quality is further emphasized by recent initiatives of the Florida government, with 210 million US dollars awarded to the Water Quality Improvement Grant Program;[13] these efforts are

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aimed at protecting Florida's most invaluable, but vulnerable, resource.

Per- and polyfluoroalkyl substances (PFAS) are a class of more than 12,000 anthropogenic chemicals which generally consist of a hydrophobic fluorinated tail and a hydrophilic functional headgroup, imbuing these chemicals with versatility within many industrial applications, including food packaging materials, textiles, consumer goods, and cosmetics.[14,15] Of the many PFAS sources destined for environment release, the most notable example is the use of aqueous film forming foams (AFFFs), which are commonly used as fire suppressants at aviation facilities and military installations.[16−24] PFAS are thermodynamically robust due to the strength of the carbon−fluorine bond, providing persistence and stability, which prevents them from readily biodegrading.[25] Other common sources of PFAS released into surface water are influent/effluent from wastewater treatment, fluorochemical manufacturing facilities, and runoff.[26−30] Once released into the environment, these chemicals have been shown to infiltrate and bioaccumulate in a variety of flora and fauna, leading to their ubiquity worldwide. This widespread presence has led to serious concerns about human and wildlife health, as mounting evidence is indicating that exposure to these PFAS lead to a myriad of adverse health-related effects.[31−34]

In recent years, the growing concern around PFAS has sparked numerous monitoring and/or surveillance studies focusing on mapping the locations of where these "forever chemicals" are present.[35−42] Several agencies, environmental organizations, and publications have highlighted areas suspected to have PFAS contamination, but most of the surface water research to date has been confined to region-specific reports or locations near known PFAS sources.[43−50] Despite these efforts, PFAS levels in most of Florida's waters are still unknown, representing a significant research gap regarding their abundance in these interconnected water bodies. In this study, we employed crowdsourcing to obtain a comprehensive statewide profile of PFAS in Florida waterbodies (n = 2323). By engaging college students and local community stakeholders, we created a network beneficial to all parties, gaining intimate knowledge of many of the sampling sites and establishing a pipeline to be able to inform samplers of the results and issues related to overall water quality. The primary objective of this study was to provide a heat map of PFAS concentrations within the state of Florida, highlighting hotspots which require further attention. Additionally, these hotspots were compared to historical pollution-spill data collected by the Florida Department of Environmental Protection (FDEP). These preliminary visual analyses of elevated PFAS sites and spill locations suggest that raw sewage and both treated and untreated wastewater spills are possible significant contributors to the levels of PFAS that are impacting Florida water bodies. Moreover, mass loading calculations (e.g., amount of actual material) were estimated for perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) based on the provided spill data.

2. MATERIALS AND METHODS

2.1. Framework for Crowdsourcing Water Collection. To provide an efficient statewide collection of surface water samples in Florida, a water collection program, consisting of two crowdsourcing cycles, was implemented. The first crowdsource cycle engaged undergraduate students (n = 126) at the University of Florida via social media outreach. The second cycle of water sampler recruitment focused on engaging citizen scientists and environmentally focused organizations within the state (n = 78). All samplers were provided sampling kits (Supporting Information Figure S1) and a sampling protocol (Supporting Information 1), which highlighted how to collect the surface water sample and avoid sample contamination. Each sampler collected between 1 and 61 surface water samples. Site selection was determined via consultation with each sampler and incorporated several aspects, such as safety, cost, proximity to pollution sources, and overall geographical representation. While some sites in proximity to potential pollution sources were targeted, maximizing geographical coverage of Florida remained one of the main objectives in this study. In addition to written instructions, we also provided a YouTube training video to supplement sampler training. Once collected, each sampler shipped or delivered the surface water back to our laboratory and relayed sampling details, which included time, date, GPS coordinates, and photos of the waterbody sampled. By utilizing crowdsourcing, we were able to collect 2323 surface water samples in all 67 counties in Florida (map of Florida counties shown in Supporting Information Figure S2), allowing the generation of a wider PFAS profile across the state. The recording of basic water quality parameters (e.g., suspended solid concentration) was attempted early in the study but concerns regarding measurement consistency halted continued measurement. Future crowdsourcing efforts by our laboratory are revisiting how to better obtain these measurements using the crowdsourcing strategy.

2.2. Sample Collection of Surface Water. Surface water (fresh-, salt-, and brackish water) was collected in 250 mL high density polyethylene (HDPE) bottles throughout Florida (n = 2323; Supporting Information Figure S2B; coordinates listed in Supporting Information Table S1). Sampling occurred between April 2020 to the end of December 2021. In each sampling kit, a grabber tool was provided to avoid sample contamination. Each HDPE bottle was rinsed three times before collection of the surface water sample. Each sampler was also provided with one field blank, which consisted of one 250 mL HDPE bottle filled with Optima water (Fischer Scientific) and one empty/clean HDPE bottle. In the field, samplers were instructed to transfer the contents from the full bottle to the empty bottle. Field blanks were included to test possible PFAS contamination during the sampling and shipping process. Once all water samples arrived at the laboratory, they were stored at −20 °C until extraction. While samples experienced identical storage conditions, they were stored for variable time periods depending on the randomized order in which they were extracted; this could have impacted signal intensity for select PFAS in samples analyzed later in the study. Monitoring the stability of PFAS standards in synthetic calibration samples, which were stored under identical conditions for the duration of this study, helped demonstrate the stability of the target analytes throughout the study.

2.3. Surface Water Extraction. The overall PFAS analysis workflow has been validated in previous work.[51,52] In brief, the pH of each sample was adjusted to approximately 3 using glacial acetic acid (Fischer Scientific). Samples were subsequently spiked with 25 μL of an isotopically labeled PFAS internal standard (IS) mixture (made by dilution of 2 mL Wellington Laboratories MPFAC-24ES in 25 mL of optima methanol). This mixture contained 19 isotopically labeled PFAS standards (dilution and concentrations can be found in

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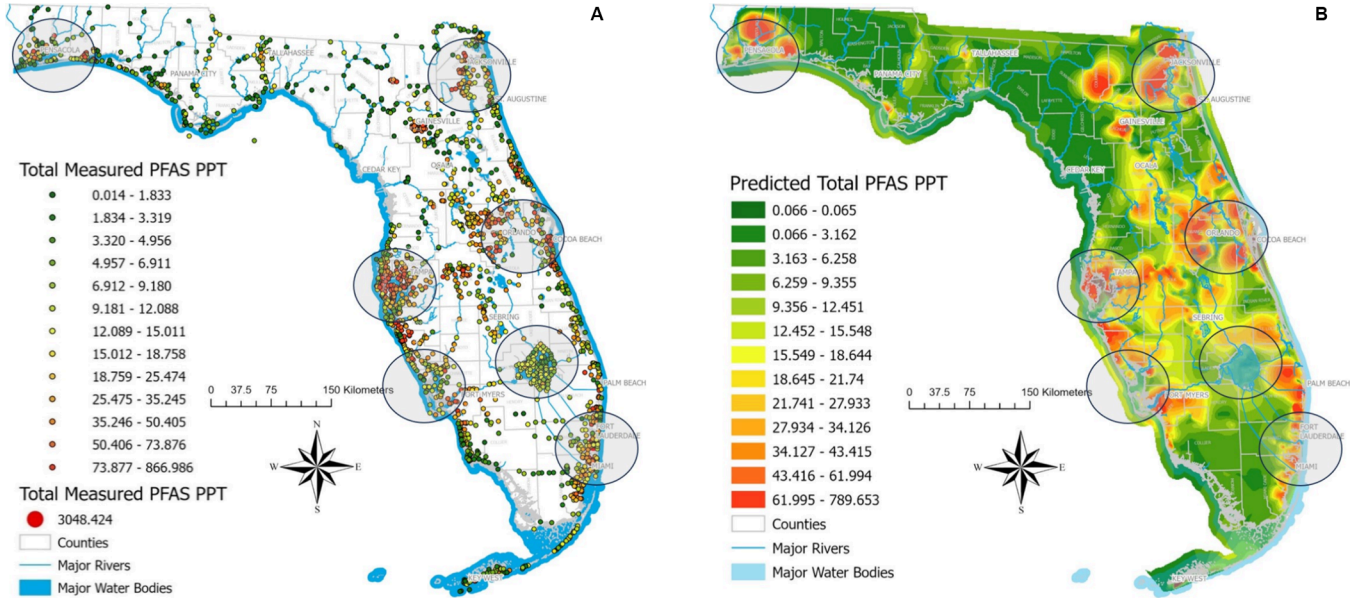

Figure 1. (A) Map of Florida with dots representing all surface water sampling sites with quantifiable levels of PFAS (n = 2056). Dot color corresponds to the measured ΣPFAS concentration, according to the key. Six regions (light gray circles) with high densities of yellow/red circles, indicating elevated levels of ΣPFAS, are highlighted. (B) Predictive heat map of Florida PFAS levels based on the measured ΣPFAS concentrations of the surface water samples. These predictions are extrapolated from surface water values and do not intend to describe land PFAS values.

Supporting Information Table S2). The SPE method used Strata-XL-AW 100 μm Polymeric weak-anionic exchange 500 mg/6 mL cartridges (Phenomenex, Torrence, CA), and has been published previously.[48] For detailed SPE protocol, see Supporting Information 2.

2.4. Mass Spectrometric Determination of PFAS in Surface Water. A Thermo Scientific Vanquish ultrahigh performance liquid chromatography system coupled with a Thermo Scientific Quantis triple quadrupole mass spectrometer (via electrospray) was employed to target 50 PFAS (full names with associated abbreviations in Supporting Information Table S3; PFAS standards obtained from Synquest Laboratories and Oakwood Chemical were given internal abbreviations also defined in this table) in surface water extracts, including both linear and branched isomers of PFOS, noted further as ΣPFOS. For chromatographic separation, a Phenomenex Gemini C-18 column (particle size: 3 μm, column dimensions: 100 mm × 2 mm) was employed and was fitted with a Phenomenex SecurityGuard cartridge (Gemini C-18 4 × 2 mm ID). The liquid chromatography system was also fitted with a Thermo Scientific Vanquish PFAS Replacement Kit, which included a Thermo Scientific Acclaim 120 C-18 (3 μm, 4.6 × 50 mm) delay column and PFAS-free plumbing and hardware to minimize background. The gradient method employed two mobile phases: (A) water and (B) methanol, both containing 5 mM ammonium acetate, set at a constant flow rate of 0.5 mL/min. The elution gradient was as follows: 0−1.0 min 90% B,1−2.5 min in 35% B, 2.5−17.5 min 5% B, 17.5−17.51 min 0% B, 17.51−22.5 min 0% B, 22.5−22.51 min 90% B, 22.51−37 min 90% B. The mass spectrometer was operated in negative polarity mode and each PFAS was measured using scheduled selected reaction monitoring (SRM) acquisition mode. Each PFAS had two SRM transitions (when possible), the most intense transition was used for quantitation, while the second transition was used for confirmation. The mass spectrometer had optimized source parameters set to spray voltage −3000 kV, sheath gas 60 arb, auxiliary gas 5 arb, sweep gas 1 arb, ion transfer tube temperature 325 °C and a vaporizer temperature of 350 °C (HPLC−MS/MS parameters detailed in Supporting Information Table S4). For each PFAS (and PFAS IS), optimized fragmentation voltages and collision energies are shown in Supporting Information Table S5. The total run time for the method was 37 min.

2.5. Data Processing. Surface water extracts, field blanks, method blanks, solvent blanks, and calibrants were randomly queued in the mass spectrometric sequence. Method blanks were prepared in the laboratory by transferring 250 mL of Optima water into clean HDPE bottles and were extracted following the protocol described above for surface water extraction. Solvent blanks were prepared by aliquoting 200 μL of Optima methanol (Fischer Scientific) into polypropylene vials at the time of instrument analysis; they were injected after every five samples in the queue to monitor potential PFAS carryover from sample to sample throughout the sequence. Each batch sequence consisted of approximately 200 surface water and field blank extracts, five method blanks, and a 14-level calibration curve run in triplicate (subsequently averaged). Data processing and peak integration were performed using Xcalibur v.4.1 software (Thermo Fisher Scientific). All PFAS quantitation was achieved using our developed open source PFAS Automated Quantitation (PAQ) workflow (additional information and Github link found in Supporting Information 3). For each detected PFAS, quantitation was achieved via isotope dilution over the calibration range of 0.0094 to 107 ng/mL (full list of target calibration point concentrations found in Supporting Information Table S6). Each PFAS, with its corresponding IS used for quantitation, is listed in Supporting Information Table S3. Each PFAS in the calibration curve was obtained from either Wellington Laboratories, Synquest Laboratories, or Oakwood Chemical (for complete list of vendor/PFAS acquisition, see Supporting Information Table S3). All calibration curves generated for quantitation had an R^2 value >0.99. The resultant

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Table 1. Concentrations and Frequencies of Individual PFAS (and Sum, Σ) across the State of Florida[a]

PFAS	frequency detection	frequency quantified	frequency by county	mean (ng/L)	max (ng/L)	median (ng/L)
PFOA	94%	83%	100%	5	81	3
PFBS	65%	64%	93%	5	48	4
PFHxA	61%	61%	82%	6	180	4
PFNA	54%	39%	96%	2	352	1
PFOS	53%	48%	91%	10	1135	6
PFHpA	53%	44%	87%	5	84	4
PFHxS	50%	17%	94%	17	365	12
PFDA	33%	16%	90%	2	27	2
Syn35	24%	1%	75%	6	24	5
PFHxPA	16%	14%	54%	15	322	10
FBSA	11%	11%	42%	5	85	5
Syn32	9%	6%	21%	1	7	1
PFPrS	5%	3%	51%	5	24	4
PFUdA	4%	4%	42%	3	114	2
PFPeS	3%	0%	36%	29	58	20
4_2FTS	3%	0%	25%	1	1	1
PFDoA	3%	2%	25%	1	4	1
PFECHS	3%	0%	31%	2	5	2
FHxSA	2%	2%	27%	19	320	10
Oak6	2%	0%	22%	1	3	1
Syn34	2%	NA	24%	NA	NA	NA
P4MOA	2%	0%	13%	4	12	2
ΣPFAS	**NA**	**NA**	**NA**	**29**	**3048**	**13**

[a]Data for all sampling sites (n = 2323) sorted by detection frequency. Excluding those PFAS with less than 30 detection hits (<2% of samples). The complete list of PFAS summary data can be found in Supporting Information Table S9. Peaks determined to be < LOD or < LOQ were not utilized in calculating the mean or median concentrations. However, peaks LOD < x < LOQ were used in calculating detection frequency. Internal laboratory abbreviations defined as perfluoro-3,7-dimethyloctanoic acid (Syn35), 7H-perfluoro-4-methyl-3,6-dioxaoctanesulfonic acid (Syn32), 7H-dodecafluoroheptanoic acid (Oak6), and perfluorobutanesulfinic acid (Syn34).

concentration of each PFAS was normalized to the mass of the extracted samples, providing ng PFAS/g water. All resultant quantified data can be found in Supporting Information Table S7. Limits of detection (LOD) and limits of quantitation (LOQ) for each PFAS were visually curated for each extract using the signal-to-noise defined as 3x for LOD and 10x for LOQ. All blanks (field and method) were assessed for background contamination and the mean of any background signal for a given PFAS was subtracted from all sample extracts prior to quantitation (Supporting Information Table S8). A geographic information system (ESRI's ArcGIS Pro (AGP) version 3.1.3) was used to spatially analyze the data and produce a predictive heat map (more details found in Supporting Information 4). In brief, predictive heat maps, using the Natural Neighbors interpolation method, were generated for ΣPFAS (Figure 1B), as well as for PFBS, PFHxA, PFHpA, PFOA, ∑PFOS, and PFNA (Supporting Information Figures S3B−S8B). These predictive heat maps were created by interpolating each point's ΣPFAS (or individual PFAS concentration), in addition to those points in close proximity (and distance). Thus, these maps highlight suspected areas of concern for high PFAS levels. It should be noted, these prediction values do not intend to describe land values and should only be considered for those water bodies within the shaded area.

3. RESULTS AND DISCUSSION

3.1. Efficacy of Citizen Sampling. PFAS are ubiquitous, and there have been several publications and sampling guides that have highlighted how to properly collect samples while minimizing PFAS contamination via supplies, clothing, and personal care products,[53−55] one of which (Pace Analytical) was distributed to samplers prior to sampling. Due to the robust inclusion of >200 individual samplers of varying skill, it was imperative to have each sampler prepare a field blank sample during the collection of their surface water samples. Field blanks were processed in parallel to the surface water samples. In total, 195 field blanks were extracted and analyzed with five PFAS quantified (>LOQ) in at least one field blank sample (percent of samples with quantified PFAS levels): perfluorobutanesulfonic acid (PFBS, 9%), 7H-perfluoro-4-methyl-3,6-dioxaoctanesulfonic acid (Syn32, 5%), pefluorohexanoic acid (PFHxA, 2%), perfluorononanoic acid (PFNA, 1%), and 9H-hexadecafluorononanoic acid (Oak10, 1%). Method blanks (no field collection component) were extracted also alongside surface water samples. A total of 73 method blanks were analyzed and three PFAS were quantified (>LOQ, percent of samples with quantified levels): PFBS (4%), Syn32 (5%), and 7H-dodecafluoroheptanoic acid (Oak6, 1%). In addition to field and method blanks, over 530 solvent blanks were injected across all batches to monitor potential carryover between injections. No PFAS were detected (>LOD) in any solvent blank.

3.2. Summary of Data by PFAS. In this study, 2323 surface water samples were collected across Florida and analyzed for 50 PFAS. Overall, 33 PFAS, shown in Table 1 (full summary statistics can be found in Supporting Information Table S9), were detected (>LOD) in at least one sample. Of these 33 PFAS, 31 were quantifiable (>LOQ) in at least one sample. Table 1 shows the concentrations (ng/L) and frequencies of individual PFAS (and sum, Σ) within the sample set. The mean (±standard deviation) ΣPFAS across

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the Florida sample set was 29 (±80) ng/L. The maximum ΣPFAS for a collected sample was 3,048 ng/L (found in Broward County), while the median ΣPFAS for all samples was 13 ng/L. Overall, there were 11 PFAS that were detected (>LOD) with a frequency above 10% for all samples analyzed, with all but one (perfluoro-3,7-dimethyloctanoic acid, Syn35) also above the 10% frequency for quantification (>LOQ). For brevity, we decided to focus our data interpretation on individual PFAS detected in >50% of the samples, which included PFBS, PFHxA, perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), and PFNA (Table 1). Coincidentally, not only were these six PFAS abundant by concentration, but they were also abundant across the state, as all of these PFAS were detected >82% of the Florida counties, with PFOA found in all 67 counties. The complete profile of all PFAS detected across the state is found in Supporting Information Table S9.

3.3. Comparison of Data to EPA MCLs. As PFAS continue to expand as an environmental and human health threat, with a concomitant increase in public awareness and concern, government regulations regarding PFAS are constantly evolving. For example, over the duration of this project and to date, nonenforceable EPA drinking water guidance levels for PFOA and PFOS went from 70 ng/L (either individual or combined) to the current enforceable Maximum Contaminant Levels of 4 ng/L of PFOA or PFOS. This was a significant development for this study, as there was an increase in the number of samples exceeding EPA levels, shown in Table 2. For PFOA, there were 915 samples (39% of samples tested) measured over the 4 ng/L limit, while for PFOS, there were 920 samples (40% of the samples tested) measured over the 4 ng/L limit. Moreover, the mean concentrations of both PFOA and PFOS across all samples collected were above this regulatory limit, at 5 and 10 ng/L respectively (Table 1). Although these MCLs are based on drinking water regulations by the US EPA, these limits can be used as a guideline for what are acceptable levels in surface water until federal guidelines are established specific to surface waters. The Florida county with the most values above the MCLs for both PFOA and PFOS was Pinellas (Table 2), and 6 of the top 7 counties, by number of samples above the MCLs, were in common for both PFOA and PFOS (Pinellas, Hillsborough, Miami-Dade, Brevard, Alachua, and Sarasota). In total, 27 and 24 counties, for PFOA and PFOS, respectively, had >10 samples with concentrations above the MCLs. In addition to MCLs, the EPA has released several analytical workflows, most recently EPA Method 1633,[56] which is designed to monitor 40 PFAS, many of which were included in this study. However, this study monitored 17 PFAS not currently part of EPA methods. Of these 17, seven were detected (>LOD), most notably perfluorobutane sulfanomide (FBSA) and perfluorohexylphosphonic acid (PFHxPA), which were detected in over 10% of samples. The full list can be found in Supporting Information 5 and summary statistics of the seven detected are included in Supporting Information Table S9.

3.4. Summary of Data by Florida County. One of the primary objectives of the study was to identify PFAS hotspots (i.e., areas of concern) that warrant both additional testing and a management plan for mitigation and/or remediation. Since geographical coordinates accompanied the collected surface water, distribution maps were created to show the density of samples collected and their corresponding PFAS levels. The map shown in Figure 1A presents all samples across Florida where quantifiable levels (>LOQ) were measured. Each dot represents a sampling location, and the color of the dot reflects the measured ΣPFAS concentrations at each site. For the color scheme, all ΣPFAS were organized into 13 color bins (gradient from green to red, each bin had the same number of coordinates). The brightest red correlated to those locations which had ΣPFAS concentrations from 74 to 867 ng/L, with the three highest red circles found in Broward (3048 ng/L), Duval (867 ng/L), and Osceola (524 ng/L) counties.

Table 2. Top Counties for Hits above the Maximum Contaminant Levels for PFOA and PFOS (4 ng/L for Both)[a,b]

county	no. samples> 4 ng/L PFOA	county	no. samples > 4 ng/L PFOS
Pinellas (*n* = 120)	84 (70%)	Pinellas (*n* = 120)	100 (83%)
Hillsborough (*n* = 89)	61 (69%)	Miami-Dade (*n* = 104)	71 (68%)
Brevard (*n* = 88)	56 (64%)	Sarasota (*n* = 91)	64 (70%)
Orange (*n* = 57)	49 (86%)	Brevard (*n* = 88)	61 (69%)
Alachua (*n* = 80)	48 (60%)	Hillsborough (*n* = 89)	62 (70%)
Miami-Dade (*n* = 104)	48 (46%)	Alachua (*n* = 80)	49 (61%)
Sarasota (*n* = 91)	47 (52%)	Monroe (*n* = 95)	49 (52%)
Palm Beach (*n* = 113)	43 (38%)	Orange (*n* = 57)	37 (65%)
Polk (*n* = 57)	43 (75%)	Okaloosa (*n* = 49)	38 (78%)
Broward (*n* = 63)	36 (57%)	Palm Beach (*n* = 113)	36 (32%)
Volusia (*n* = 58)	30 (52%)	Duval (*n* = 59)	31 (53%)
Lee (*n* = 50)	28 (56%)	St. Johns (*n* = 62)	30 (48%)
Duval (*n* = 59)	27 (46%)	Lee (*n* = 50)	26 (52%)
Collier (*n* = 98)	23 (23%)	Volusia (*n* = 58)	23 (40%)
St. Johns (*n* = 62)	22 (35%)	Broward (*n* = 63)	18 (29%)
Martin (*n* = 41)	20 (49%)	Manatee (*n* = 43)	18 (42%)
Seminole (*n* = 22)	20 (91%)	Polk (*n* = 57)	18 (32%)
Osceola (*n* = 26)	17 (65%)	Highlands (*n* = 25)	17 (68%)
Lake (*n* = 42)	16 (38%)	Martin (*n* = 41)	16 (39%)
Clay (*n* = 18)	15 (83%)	Osceola (*n* = 26)	16 (62%)
Pasco (*n* = 32)	15 (47%)	Clay (*n* = 18)	14 (78%)
Escambia (*n* = 52)	14 (27%)	Nassau (*n* = 42)	12 (29%)
Highlands (*n* = 25)	13 (52%)	Collier (*n* = 98)	10 (10%)
Manatee (*n* = 43)	13 (30%)	Lake (*n* = 42)	10 (24%)
Nassau (*n* = 42)	13 (31%)		
Charlotte (*n* = 49)	12 (24%)		
Okaloosa (*n* = 49)	10 (20%)		

[a]Percentages indicate the ratio of Hits above the MCL to the total number of samples collected in each respective county. [b]Only shown are counties with at least 10 hits. For the complete list of counties and hits above 4 ng/L, please see Supporting Information Table S11.

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Table 3. PFAS Concentration (ng/L) by Florida County[a]

Florida county	no of samples	max ΣPFAS (ng/L)	mean ΣPFAS (ng/L)	standard deviation ΣPFAS (ng/L)	median ΣPFAS (ng/L)	no. unique PFAS[b]	Florida county	no of samples	max ΣPFAS (ng/L)	mean ΣPFAS (ng/L)	standard deviation ΣPFAS (ng/L)	median ΣPFAS (ng/L)	no. unique PFAS[b]
Alachua	80	411	56	74	49	19	Lee	50	141	32	29	22	21
Baker	10	NA	NA	NA	NA	4	Leon	21	42	10	11	5	14
Bay	41	279	16	49	4	15	Levy	16	NA	NA	NA	NA	4
Bradford	4	32	20	10	20	8	Liberty	3	19	11	8	11	9
Brevard	88	239	50	41	51	17	Madison	5	9	5	5	5	9
Broward	63	3048	71	385	16	19	Manatee	43	101	21	24	10	12
Calhoun	6	15	6	6	2	9	Marion	29	40	12	11	11	14
Charlotte	49	152	15	23	9	12	Martin	41	25	8	6	5	8
Citrus	35	15	15	15	15	4	Miami-Dade	104	86	24	21	18	17
Clay	18	141	46	43	29	14	Monroe	95	226	15	29	8	23
Collier	98	88	14	18	6	15	Nassau	42	90	16	22	4	15
Columbia	14	170	26	45	13	16	Okaloosa	49	185	31	42	12	18
DeSoto	8	29	22	7	22	9	Okeechobee	12	21	12	4	14	6
Dixie	14	5	3	3	3	4	Orange	57	133	36	26	26	20
Duval	59	867	62	135	26	16	Osceola	26	524	55	99	39	20
Escambia	52	118	12	21	4	11	Palm Beach	113	465	27	52	13	20
Flagler	26	17	9	8	6	10	Pasco	32	76	15	17	8	12
Franklin	25	10	4	3	4	11	Pinellas	120	500	56	60	41	25
Gadsden	6	18	10	6	9	14	Polk	57	97	34	25	32	15
Gilchrist	6	3	1	1	1	7	Putnam	17	25	7	6	6	8
Glades	42	19	11	3	11	12	Santa Rosa	36	279	24	63	6	20
Gulf	28	79	10	17	4	10	Sarasota	91	115	29	28	20	20
Hamilton	6	10	3	3	1	8	Seminole	22	121	39	26	37	12
Hardee	1	31	31	31	31	6	St. Johns	62	311	22	45	12	19
Hendry	12	25	12	6	12	8	St. Lucie	21	47	19	14	16	13
Hernando	10	23	7	7	5	9	Sumter	11	57	23	17	22	9
Highlands	25	60	23	15	17	16	Suwannee	9	4	2	1	2	6
Hillsborough	89	354	42	53	28	22	Taylor	8	6	3	3	1	4
Holmes	4	1	1	0	1	2	Union	9	22	9	8	4	9
Indian River	28	12	7	3	7	8	Volusia	58	98	19	23	10	15
Jackson	11	21	5	8	1	9	Wakulla	24	18	6	5	3	12
Jefferson	7	3	1	1	1	4	Walton	18	29	6	9	4	12
Lafayette	7	1	1	0	1	4	Washington	8	2	1	0	1	4
Lake	42	49	17	9	15	17							

[a]Map of Florida Counties is shown in Supporting Information Figure S2. [b]Indicates that these PFAS were detected in at least one sample per county. Peaks determined to be < LOD or < LOQ were not utilized in calculating the mean or median concentrations.

Interestingly, the Broward site was collected in the immediate proximity of Fort Lauderdale International Airport. Distribution maps for the six most abundant PFAS (PFBS, PFHxA, PFHpA, PFOA, ∑PFOS, and PFNA) are found in Supporting Information Figures S3A–S8A. Upon examination of the distribution maps, a more detailed analysis of the presence of PFAS within Florida counties was performed. Table 3 shows the number of samples, the max/mean ∑PFAS concentration (ng/L), and the number of unique PFAS detected across all Florida counties. The top-3 Florida counties, by highest number of unique PFAS detected in at least one surface water sample, were: Pinellas (25) > Monroe (23) > and Hillsborough (22). The top-5 counties with the most individual PFAS on average per sample were: Pinellas (9.0) > Osceola (8.4) > Sarasota (8.0) > Hillsborough (7.8) > Orange (7.6). By calculating the mean ΣPFAS for each county, the top-5 counties with the highest ΣPFAS means were: Broward (mean: 71 ng/L, median 16 ng/L) > Duval (mean: 62 ng/L, median: 26 ng/L) > Pinellas (mean: 56 ng/L, median: 41 ng/L) > Alachua (mean: 56 ng/L, median: 49 ng/L) > Osceola (mean: 55 ng/L, median: 39 ng/L). The counties which appeared to have the lowest mean ΣPFAS concentrations (along with their maximum ΣPFAS concentration in parentheses), the bottom-5 were: Holmes (1 ng/L) < Lafayette (1 ng/L) < Jefferson (3 ng/L) < Gilchrist (3 ng/L) < Washington (2 ng/L), all located within or connected to the Florida panhandle region. Levy county detected (>LOD) four unique PFAS but did not measure (>LOQ) any PFAS in the 12 samples collected. All counties which ranked in the top ten for lowest mean ΣPFAS concentration had at least four samples collected within the county.

3.5. Predictive Heat Maps for Σ and Individual PFAS.

A brief examination of Figure 1A yielded regions (light gray circles) that had a higher density of yellow/red circles, indicating elevated levels of ΣPFAS. These regions included Pensacola, Jacksonville, Tampa Bay, Orlando/Cocoa Beach, Sarasota/Fort Myers, Lake Okeechobee and Miami/Fort Lauderdale. These same hotspots garnered red shading in the ΣPFAS prediction maps (except for Lake Okeechobee), as shown in Figure 1B. The ΣPFAS prediction maps also aligned with the respective county ΣPFAS concentrations shown in Table 3 (counties within the gray circles). To further examine

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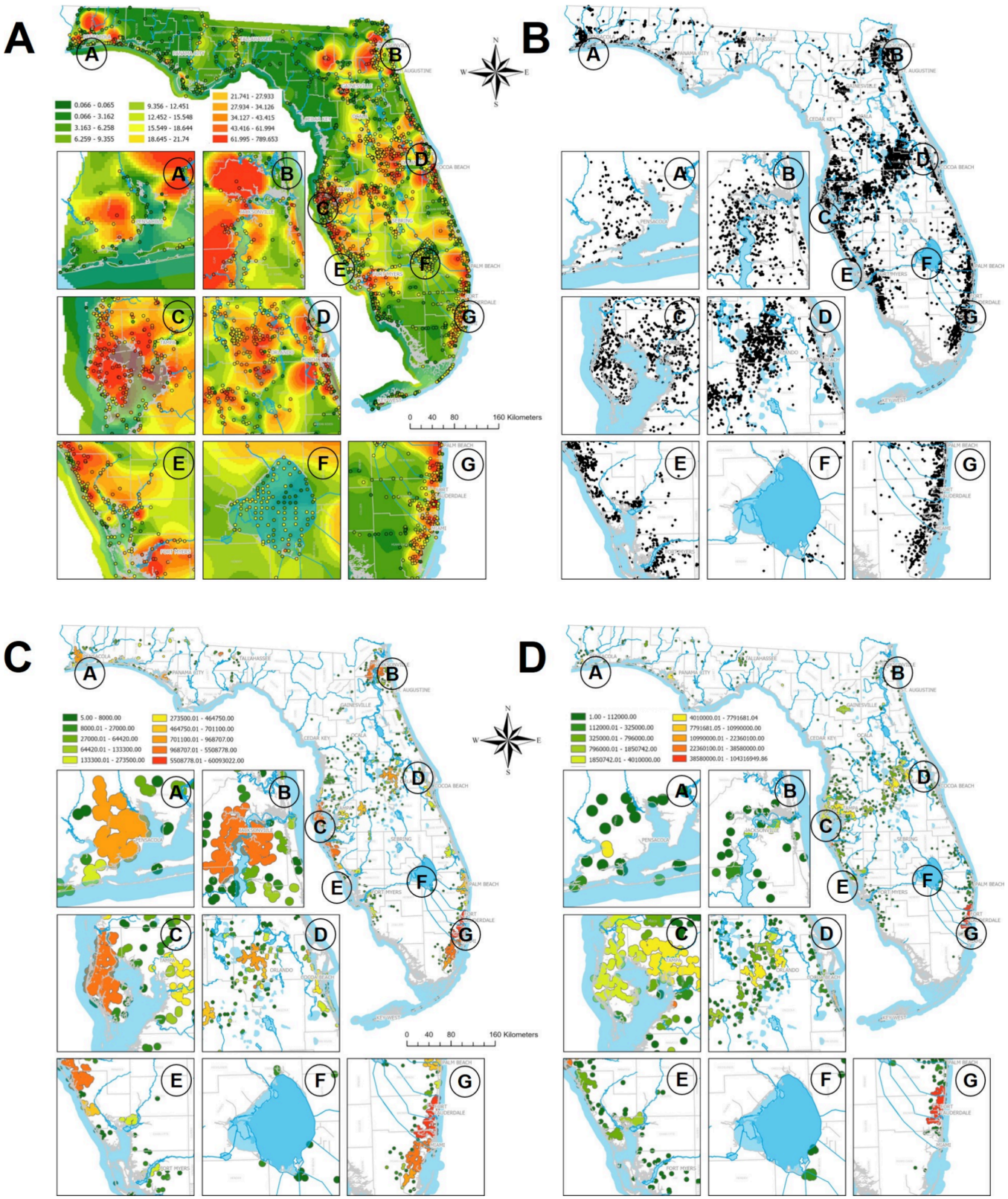

Figure 2. (A) Predictive heat map for ΣPFAS, (B) Map of Florida with all reported spill locations by the FDEP between 2017 and 2022, (C) Map of Florida with reported raw sewage spills (in gallons), and (D) Map of Florida with reported untreated/partially treated wastewater spilled (in gallons). All maps include regional inserts around (A) Pensacola, (B) Jacksonville, (C) Tampa Bay, (D) Orlando/Cocoa Beach, (E) Sarasota/Ft Myers, (F) Lake Okeechobee, and (G) Miami/Ft Lauderdale.

the most impacted regions, expanded views of (A) Pensacola, (B) Jacksonville, (C) Tampa Bay, (D) Orlando/Cocoa Beach, (E) Sarasota/Ft Myers, (F) Lake Okeechobee and (G) Miami/Ft Lauderdale, for ΣPFAS prediction map (Figure 2A) and individual PFAS (PFBS, PFHxA, PFHpA, PFOA, PFOS, and PFNA, Supporting Information Figures S3C–

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S8C), were generated. These maps serve as the first critical guides to unraveling the distribution of PFAS across the state and their fate and transport within different water bodies, with the ultimate goal of identifying potential sources.

3.6. Overlaying PFAS Data with Historical Florida Spill Data. Using this robust data set and wide geographic footprint, we aimed to provide preliminary explanations for the presence of PFAS hotspots by visually comparing the geographical locations of the resultant ∑PFAS values to other available spatial data throughout Florida. For example, when comparing the hotspot locations on the ΣPFAS prediction map (Figure 2, inserts A−G) to a map of Florida population levels (Supporting Information Figure S9), it is shown that these hotspots are among the higher populated areas. Visual comparisons between the resultant PFAS data and multiple potential contamination sources were conducted separately (i.e., without considerations for more than one source per each comparison) Looking for associations with specific anthropogenic activities led to a comparison to the presence of sites which potentially use AFFFs. As shown in Supporting Information Figure S10 (Figure S11 showing density per km^2), there appears to be an abundance of airports across the state (n = 925 site locations), with potentially a modest visual elevation of the number of airports in these same hotspots; however, there also appear to be several airports in areas with lower PFAS levels. Military installations also use AFFFs (n = 47 polygon facilities, Supporting Information Figure S10, orange shaded regions); however, after comparing the geographical PFAS results from this study with mapped military installations in Florida, their presence likely only reflects high levels locally and is not assumed to be the only source for the statewide levels observed in Florida. In contrast, while military installations comprise a small geographic footprint, the presence of wastewater treatment plants (WWTPs) are widespread across the state (Supporting Information Figure S12, with Figure S13 showing density per km^2). There are approximately 2793 wastewater site locations, comprised of domestic, industrial, phosphate, and power plant programs. Like the use of AFFFs, WWTPs have also been implicated as a significant source for PFAS release into the environment.[57] It is well documented that the vast majority of WWTPs do not effectively remove PFAS during treatment.[58,59] A number of these WWTPs are permitted to directly discharge a fraction of or all of their treated wastewater into nearby surface water[60] or reuse the wastewater for irrigation or agricultural purposes.[61] Both scenarios would likely contribute to the mass loading of PFAS into surrounding waterways.

Since 2017, the FDEP has documented every pollution-based spill, as self-reported by local entities. This information is publicly available at https://prodenv.dep.state.fl.us/DepPNP/reports/viewIncidentDetails?page=1 (accessed January 26, 2024).[62] Exporting all pollution notices prior to 2022 (up to last surface water sample collected in this study), we found a total of 7395 spills with GPS coordinates (this is after removing duplicates and citations with inaccurate coordinates). Over these 7395 spills, approximately 78% of these listed estimated volumes (in gallons) for what was spilled. The spill type and amount were tallied from the incident reports and organized into five categories (with number of incidents prior to 2022): raw sewage (2152), untreated/partially treated wastewater (1936), treated wastewater (755), solids (sludge/biosolids, 111), and various liquids (e.g., fuel, 765, liquid which did not fit into the other four categories). Summing all the estimated spills per category (in gallons), resulted in high volumes spilled: raw sewage (104 million gallons), untreated/partially treated wastewater (341 million gallons), treated wastewater (970 million gallons), solids/sludge (2.3 million gallons), and various liquids (10 million gallons). Note that within these incident reports, a significant contributor to spills occurrence was large episodic weather events, such as hurricanes, flooding and overflows. A map that shows all spill locations (prior to 2022) is shown in Figure 2B.

Most interestingly, the spill points are largely associated with the most elevated (red) positions within the prediction map (Figure 2A). This was further supported by examining the insets for the same hotspot locations on Figure 2B, where the highest predictions of ΣPFAS also had the highest density of spills. Beyond the number and locations of spills, we also quantitatively analyzed the spills by location visually by creating polygon density heat maps. As shown in Figure 2C, the amount of raw sewage spilled (in gallons) is shown with polygon gradients. Each polygon was created by buffering each spill point by 2000 m and calculating aggregated summary statistics for all points within the buffer. The size of the polygon shows the number of points around it and the color of the polygon shows the amount spilled. As shown, several of the same regions where elevated PFAS levels were measured also had a higher volume of raw sewage spilled. For example, in Pinellas and Duval Counties (Figure 2C, insets B and C), the polygons are dark orange and encapsulate the range of 1−5 million gallons spilled within those highlighted areas, while in Miami-Dade (Figure 2C, inset G), there are red locations, which correlates to >60 million gallons. For untreated/partially treated wastewater (Figure 2D), these same hotspots are also noted, with Pinellas County (1−7 million) and Miami-Dade (>104 million). Maps showing treated wastewater, solids, and various liquids and the quantity spilled across Florida are found in Supporting Information Figures S14−S16. These spills are much more scattered and, while their presence is still significant locally, we do not hypothesize these spills are as impactful to PFAS levels as raw sewage and untreated wastewater.

The first examination of the spill records focused on those that occurred prior to the end of surface water collections for this study. However, we also collected all spill information available up to January 26, 2024, to investigate how much more potential PFAS may have been released since our final water collection. There were a total of 10,959 spills noted since 2017, including 3564 (2022-*pres*) more than we reported above. For raw sewage, there were an additional 1185 spills, with the overall amount spilled almost doubled, at 202 million gallons. For untreated or partially treated wastewater, there were an additional 1,065 spills added, with the overall amount spilled of 516 million gallons. A map depicting all spill sites to date is shown in Supporting Information Figure S17, with an even more pronounced presence of spills in the PFAS hotspots previously highlighted above. Supporting Information Figures S18 and S19 show the polygon maps for raw sewage and untreated/partially treated wastewater, with the maps displaying more orange and red polygons than previously shown, reaching upward of 70 and 100 million gallons, respectively. One particular noteworthy change is the dramatic increase in untreated wastewater in the Orlando area (Supporting Information Figure S19, insert D). Maps highlighting the spill polygons for treated wastewater, solids/sludge, and

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various liquids are shown in Supporting Information Figures S20−S22.

The environmental risks associated with these spills were further analyzed in two ways: first, by assessing the acute risk of PFAS concentrations in surface water surpassing risk-based groundwater thresholds, and second, by examining the total mass load of PFAS emitted over time from these spills. Determining the acute risk involves comparing average concentrations of PFAS within spilled materials to risk-based thresholds for drinking water standards. For simplicity, only PFOA and PFOS were considered, given their abundance in wastewater bodies and relevance in regulations. Additionally, raw sewage and untreated wastewater were both assumed to be nonindustrial wastewater influent, i.e., wastewater being sent to a WWTP from a domestic source. A recent meta-analysis of PFAS within wastewater bodies provided data on the average concentrations of these compounds in nonindustrial impacted influent, effluent, and sludge, which was used for analysis.[57]

To assess the risk of direct exposure through spill events, concentrations of PFOA and PFOS in influent and effluent were compared to their respective risk-based drinking water thresholds. The average concentrations of PFOA within influent and effluent were reported to be 11 ng/L and 8.4 ng/L, respectively,[57] which are 2−3 times higher than the EPA's proposed drinking water standard of 4 ng/L.[63] This suggests that if a spill was significant and not adequately diluted through groundwater, there could be a risk of PFOA exposure exceeding risk-based thresholds for both treated and untreated wastewater. The risk associated with PFOS is even higher, with average concentrations in influent and effluent reported at 35 ng/L and 32 ng/L, respectively,[57] which is 8−9 times higher than the drinking water threshold of 4 ng/L. Given the presence of several private wells around Florida, it is not unreasonable to assume that certain populations could have their drinking water impacted by such spills. It is worth noting that many spill events occur during large storm events, which may lead to more dilution than typical wastewater, thus potentially reducing the risk of exposure to PFAS exceeding drinking water standards.

Furthermore, the release of wastewater influent, effluent, and sludge can introduce a mass of PFAS into the environment, which may continue to leach over time into both surface and groundwater. This estimation was calculated using reported concentrations of PFOA and PFOS in these matrices, with more detailed calculations provided in Supporting Information 6 (estimated mass load of PFOA and PFOS in Supporting Information Table S10). For PFOA, the documented spills represent an estimated mass of 60 g released between 2017 and the end of sampling in 2021, with an additional 15.5 g released between 2022 until January 2024. Notably, even more PFOS was released, with an estimated 277 g released between 2017 and the conclusion of surface water collections in this work, and 70 g released postsampling until 2024. Although sludge represents less than 1% of the volume spilled, it accounts for roughly 20% of the mass of PFOA spilled and 40% of PFOS spilled. This indicates that sludge spills may contribute significantly to PFAS loading in the surrounding environment; however, more work should be performed to better estimate the extent of PFAS contribution from sludge, in addition interrogating and comparing the contributions from other potential sources.

4. CONCLUSIONS

A significant gap of PFAS distribution currently exists for Florida, especially in surface water - a vital resource within the state. A total of 2323 water samples were analyzed, largely accomplished by crowdsourcing with concerned students and stakeholders across the state. Overall, with the written and video protocols and inclusion of field blanks, we believe crowdsourcing is an effective strategy for comprehensive sampling of surface water over wide geographical regions. The mean concentration of ∑PFAS across all 67 counties in Florida was 29 ng/L, with a maximum ∑PFAS concentration of 3048 ng/L for one site near the Fort Lauderdale International Airport. Moreover, 23 counties in Florida had 10 or more samples with PFOA and PFOS over the EPA's MCL of 4 ng/L for drinking water. Many of the determined PFAS hotspots were present in or near locations with recorded waste-spill data curated by the FDEP dating back to 2017. Based on our visual analyses, we believe raw sewage spills and untreated wastewater spills could potentially be significant point sources for PFAS across the state of Florida. Further studies would be required to determine the magnitude of these spills' contributions to PFAS in Florida surface water and how they compare to other known sources of PFAS influence as described by Hu et al. 2016 and Liddie et al. 2023.[64,65] These initial data points offer a first statewide baseline that can be utilized for future comparisons (e.g., from spills or episodic weather events). This study also aimed to create an avenue to disseminate PFAS information to impacted stakeholders, which we hope will lead to initiatives focused on motivating both state and local governments to increase the monitoring of PFAS across the state.

■ ASSOCIATED CONTENT

Data Availability Statement

Data will be provided in the Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.4c00272.

Supplemental tables (Tables S1−S11) are provided in the Excel File (XLSX)

Additional experimental details, materials, and methods can be found in the Supporting Information. Supplemental text (1−6) and figures (Figures S1−S22) are provided in the Word File. A table of contents of all Supporting Information can be found in the Word File (PDF)

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