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Article

Sources and Pathways of PFAS Occurrence in Water Sources: Relative Contribution of Land-Applied Biosolids in an Agricultural Dominated Watershed

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Cite This: https://doi.org/10.1021/acs.est.4c09490

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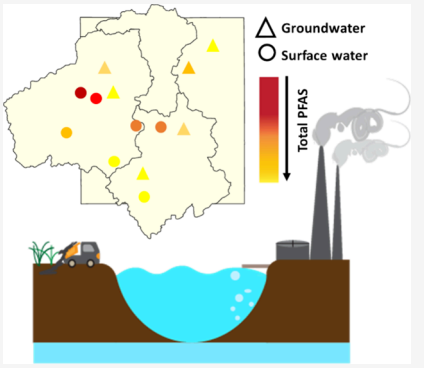
ABSTRACT: This study evaluated PFAS occurrence in rural well water and surface water relative to land application of biosolids in a tile-drained agriculture-dominated watershed. Spatial data were used to identify potentially vulnerable rural wells based on their proximity to biosolid-permitted land and location with respect to groundwater flow. Water was collected from 103 private wells in Greater Tippecanoe County Indiana and 168 surface water locations within the Region of the Great Bend of the Wabash River watershed. Overall, results indicate that surface water ($\sum$PFAS $\leq$ 169.4 ng/L) is more vulnerable to PFAS contamination than well water ($\sum$PFAS $\leq$ 15.7 ng/L). Short-chain perfluoroalkyl acids made up 72% of the $\sum$PFAS in both water sources. Nonetheless, long-chain homologues were detected more frequently in surface water (94%) than well water (82%). Hierarchical cluster analysis identified biosolid-applied fields, WTTPs, and industrial discharges as PFAS sources in first-order streams with high $\sum$PFAS. Temporal trends revealed an inverse relationship between streamflow and concentrations in surface water sites impacted by point discharges and vice versa for diffuse sources, thereby providing complementary evidence of potential sources. The well water data set did not show a distinct spatial trend between $\sum$PFAS and distance from biosolid application or well characteristics.



KEYWORDS: *groundwater vulnerability, rural wells, surface water, temporal trend, perfluoroalkyl acids, subsurface drainage, tile drainage*

1. INTRODUCTION

Land application of biosolids has been linked to water quality impairments from elevating levels of anthropogenic chemicals in associated hydrological networks. Among the chemicals of concern are per- and polyfluoroalkyl substances (PFASs), a family of several thousand chemicals with one or more fully fluorinated carbon atoms attached to another nonfluorinated polar group-containing moiety. Growing evidence of long-term PFAS threats to human and ecosystem health even at very low concentrations has resulted in regulations to reduce the risk of exposure.[1−3] Recently, the US EPA set enforceable maximum contaminant levels (MCLs) in drinking water for six PFASs starting in 2029.[4] PFOA and PFOS have MCLs of 4 ng/L, PFHxS, PFNA, and HFPO-DA (aka GenX) 10 ng/L, PFBS at 1000 ng/L, and a hazard index for two or more of the latter four PFASs. These compounds and other PFASs and have been used extensively in various industrial applications and consumer goods based on their exceptional stability and amphiphilic chemical properties.[5,6] The ubiquitous use of PFASs is reflected by their consistent detection in wastewater treatment influents, effluents, and residuals including biosolids,[7−9] all of which present pathways for PFAS redistribution in aquatic environments.[10] Industrial discharges, atmospheric deposition, manufacturing, use, and disposal of PFAS-associated products are also important environmental sources of PFAS, thus necessitating an in-depth evaluation of biosolid contribution to PFAS exposure.

PFASs released from source zones during weathering and drainage events are delivered either via suspended solids in runoffs to surface waters or via leaching to groundwater.[11−13] Within each PFAS class, differences in the perfluorocarbon chain length regulate transport outcomes. Short-chain PFASs ($CF_{2,3}$ < 6) are relatively more mobile and thus more susceptible to leaching compared to the longer-chain homologues.[14,15] However, the mechanisms driving the surface and subsurface transport of PFAS from and within diffuse source zones are complex and vary substantially over spatiotemporal scales.[16,17] For instance, the presence of artificial drainage systems, such as subsurface tile drains prevalent in the Midwest agricultural landscape, might alter PFAS transport dynamics. Gottschall et al.[18] detected PFOS and PFOA with maximum concentrations of 17 and 12 ng/L,

Received: September 6, 2024
Revised: December 20, 2024
Accepted: December 23, 2024

respectively, in tile drains installed in a biosolid-applied field. Other non-PFAS tile-drained field studies have shown that instead of vertical migration, agrochemicals including pesticides and inorganic fertilizers bypass the soil network and move horizontally through the tile drainage into receiving water bodies.[19−22] In addition to hydrology, groundwater vulnerability to contamination is moderated by regional aquifer systems;[23] therefore, a local approach is required to better understand the causative factors for PFAS contamination especially within a regulatory framework context.

While several studies have evaluated the environmental occurrence of PFAS, the relative contribution of biosolids to PFAS in water sources is poorly understood, partly due to knowledge gaps in tracing and connecting diffuse sources of PFAS to contamination of water sources.[24] The concept of critical source areas (CSAs) typically adopted for nonpoint source studies[25−27] could be a useful approach to evaluate PFAS flow paths. Identification of the CSA typically involves narrowing source zones to units disproportionately responsible for contamination in connected ecosystems, which further underscores the importance of identifying factors that drive PFAS release and mobilization within a region. In addition to inadequate forensic tools, environmental occurrence studies have largely focused on primary PFAS sources, such as aqueous film forming foams (AFFFs) and industrial discharges. For example, Johnson et al.[28] reviewed 96 studies for PFAS distribution in groundwater of which AFFF-impacted sites made up 32% of known sources, 18% in locations impacted by PFAS manufacturing and industrial activities, and only 3% for biosolid application sites. Moreover, in the biosolid sites, only one study evaluated PFAS mobilization to drinking wells beyond the biosolid application site.

To aid in filling the current data gap in the relationship between biosolid land application and PFAS contamination, this study investigated PFAS occurrence in water sources relative to land application of biosolids in an agriculture-dominated watershed. In collaboration with the Wabash River Enhancement Corporation (WREC), we collected surface water from 168 locations within the Great Bend region of the Wabash River watershed. We also established a network of citizen science in Greater Tippecanoe County Indiana to conduct reconnaissance sampling of 103 private wells in locations in areas where land application of biosolids occurs. We targeted 48 PFASs and coupled chemical data with spatial analysis to explore the following objectives: (i) evaluate patterns of PFAS occurrence in water sources and implications for regulatory guidelines, (ii) identify potential sources of PFAS, (iii) evaluate the contribution of land-applied biosolids, and (iv) identify landscape and environmental factors driving PFAS contamination in water sources in the study region.

2. METHODS

2.1. Study Area Hydrogeology. The study was conducted in a predominantly agricultural landscape of Tippecanoe County (Figure 1) that lies primarily in sections of Burnett, Kickapoo, and Wea Creek watersheds (together known as the Region of the Great Bend of the Wabash River watershed).

Parts of Fountain, Montgomery, and Warren Counties in this region drain into the Wabash River, which flows southwestward through northern Indiana. Within the region, the glacial aquifer system is the main source of drinking water for individual homes in rural communities that are not

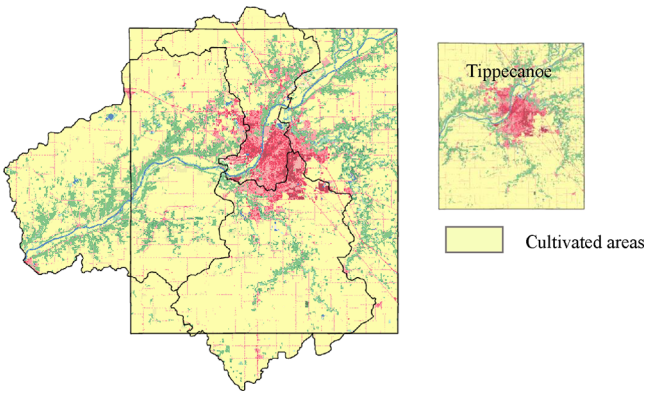


Figure 1. Land cover distribution of study area (Region of the Great Bend watershed and Tippecanoe County) extracted from the national landcover database.

connected to a public water supply. Most of the wells are completed in the Iroquois/Tipton complex aquifer system that consists of discontinuous sand, clay, and gravel layers overlain by up to 100 ft of till cap. Saturated aquifer materials are typically 20 to 50 ft thick, and most domestic wells are within the 70−135 ft depth range with static water levels of 30 to 70 ft. Few wells in portions of the aquifer that overlie the Teays Bedrock Valley System have depths between 80 to 180 ft. Groundwater vulnerability to contamination is generally low except in shallow aquifers with thin or nonexistent surficial clay deposits. Soils of glacial until origin found in this area are mostly moderately to poorly drained silt loams and silty clay loams. Consequently, subsurface tile drains are heavily relied on for corn and soybean cultivation. These drainage networks alter groundwater flow paths by redirecting soil water from high or perched water tables to receiving ditches and streams, thereby playing a key role in the environmental fate and transport of chemicals at a watershed scale.

2.2. Potential PFAS Sources and Pathways. Biosolids are widely used as fertilizer supplements in parts of Tippecanoe County and to a much lesser extent in the rest of the watershed. According to Indiana Department of Environmental Management (IDEM) spatial data records, 39,055 acres have permits for biosolid application in the watershed, of which only 9430 acres have received biosolids in the past 20 years (Figure S1). The biosolids are applied based on plant-available nitrogen (N) needs with an average rate of 2.32 ton/acre (dry weight) on either the surface or subsurface injected depending on the biosolid moisture content. Application is typically in late fall after harvest or spring before planting, in line with organic fertilizer management practices.[29] In this study, we collected surface water samples from first-order streams draining from biosolid-receiving fields in addition to samples from the Wabash River and its tributaries. Some of the waterbodies we sampled also received discharges from sanitary plants and industries operating in the area. As of 2023, over 300 national pollutant discharge elimination system (NPDES) permits were active in the watershed, including six combined sewage overflows (CSOs), most of which discharge into streams and ditches in the eastern part of the watershed. Historically, organic contaminants, including polychlorinated biphenyls, in the Wabash River were attributed to waste influent discharged into Wea Creek from an aluminum manufacturing industry. Other industrial NPDES permits in the area include pharmaceutical, food processing, metal

https://doi.org/10.1021/acs.est.4c09490
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coating, and allied services. We also sampled private drinking wells in areas with records of biosolid application in addition to wells located far from land application sites to determine regional baseline concentrations. Using a potentiometric surface map, we determined the downstream distance of wells from a land application site (additional details in the SI). Sixty-six percent of the wells sampled were within 2 km of an application site with the nearest well located 0.05 km from a biosolid-receiving field.

2.3. Sample Collection and PFAS Analysis. Surface water was collected by grab sampling in 250 mL of high-density polyethylene (HDPE) bottles from 168 locations that are part of an ongoing WREC water quality management effort. Of all the samples, 91 were in small streams close to biosolid-applied fields, 55 in wastewater treatment plant (WWTP)/industrial effluent associated streams, 12 in major tributaries of Wabash River, and 6 longitudinal sampling along the river. Thirty-seven locations with perennial or intermittent flow conditions were sampled during the spring and summer months to investigate the impact seasonal variation on PFAS concentrations. Private well owners from 103 households were recruited to collect untreated well water samples in 250 mL HDPE bottles in duplicates from a hydrant or spigot outside their homes. An example of sample collection procedures sent to participants is provided in the SI. Briefly, participants were instructed to flush the water sitting in the well column by running their tap for at least 10 min before sampling to ensure that samples were representative of groundwater matrix. Participants were also provided with field blanks (HPDE bottles filled with nanopure water) and were instructed to leave the bottles opened during sampling. After collection, samples were packed in a Styrofoam box along with double-bagged ice packs and shipped to Purdue where they were stored immediately at −20 °C until processing and PFAS analysis.

Unfiltered water samples were spiked with mass-labeled surrogates, processed with solid phase extraction (SPE) using Waters Oasis prime HLB 500 mg 6 cc cartridges that were preconditioned sequentially with 20 mL of methanol and 10 mL of nanopure water, and placed in an EZPFC SPE manifold. Surrogate spikes consisted of 200 μL of 25 ng/mL isotopic mass-labeled PFAS (detailed in the Supporting Information, Table S1) and 625 μL of 8 M NH_4OAc solution. Extracted samples were concentrated to 300 μL under N_2 gas and diluted to 600 μL with nanopure water prior to injection. PFASs were analyzed using a Shimadzu ultrahigh performance liquid chromatography (uPLC) system coupled to a Sciex 5600+ quadrupole time-of-flight mass spectrometer operated in negative electrospray ionization with SWATH data acquisition as described in our previous study[30] and briefly detailed in the SI.

2.4. Quality Assurance (QA) and Quality Control (QC). Two laboratory blanks and matrix spike samples were included in each extraction batch to account for contamination during processing and recovery, respectively. All QAQC samples contained the same amount of stock surrogate solution as the samples, and matrix spiked samples contained 5 ng of native PFAS stock solution. A separate spike check sample was added and directed to an LC injection vial. Average individual PFAS concentrations with concentrations within ≤20 covariance (COV) in laboratory blanks were subtracted from samples. Target PFASs that were present in both laboratory blanks greater than the limits of quantitation (LOQs) were excluded from further analysis. Processed and nonprocessed spiked samples within ±30% of each other was considered acceptable recovery. For each analyte, the limit of detection (LOD) was determined as the average lowest concentration on the calibration curve for 10 batches of injections, and LOQ was defined as 3× LOD. Additional details on recovery and LOQ for each analyte are provided in Table S2.

2.5. Geospatial and Statistical Analysis. Spatial clustering of PFAS concentrations in sampling locations was calculated using Moran's *I* spatial autocorrelation test with an inverse distance and row standardized weight matrix. Data sets with positive autocorrelation were explored further for patterns of occurrence with hierarchical cluster analysis in the R statistical software. We also assessed plausible pathways of PFAS transport to surface water by qualitatively comparing differences in concentrations based on the distance of the waterbody from potential diffuse sources (calculated with ArcGIS Pro) and the density of point discharges in sampling locations.

A bivariate correlation analysis followed substitution of censored data with a maximum likelihood estimation method (details in the SI) to evaluate the relationship between total PFAS concentration in private wells and possible predictor variables. The variables included distance to land application, well characteristics (static water level and well depth), and hydrological classification of soils at the well location or source zone. Well distance from the closest upstream land application site was calculated along the path of groundwater flow paths from lines of potentiometric surface maps using ArcGIS. Data on well characteristics and hydrologic classification of soils were extracted from Indiana Department of Environmental Management (IDEM) records. The analysis was restricted to samples with complete well characteristic data sets given that variables such as well depth cannot be accurately interpolated.

3.0. RESULTS AND DISCUSSION

3.1. PFAS in Well and Surface Waters. Out of 51 targeted PFASs, 14 were detected above the LOQ in one or more water samples. At least one PFAS was detected above the LOD in 90 and 84% of the surface water and well water samples, respectively; however, none of the samples had more than 10 targeted PFASs of quantifiable concentration. The distribution of perfluoroalkyl acids (PFAAs) was similar between water sources, with perfluoroalkyl carboxylates (PFCAs) making up 67 and 63% and perfluorosulfonic acids (PFSAs) comprising 29 and 27% in surface water and well water, respectively. Among PFCAs, PFPeA, PFHxA, PFHpA, and, to a lesser extent, PFOA were detected frequently in both surface water and groundwater. The prevalence of these PFASs in aqueous environmental matrices has been reported in numerous studies[10,16,31] and attributed to their relative mobility, persistence, and being terminal metabolites of telomer PFAS.[32,33] PFBS, PFHxS, and PFOS were the major PFSAs in all water samples with surface water having higher proportions of PFOS (68%) compared to well water (48%). Other PFAAs detected in quantifiable concentrations in at least one water sample were PFBA, PFPeS, PFNA, PFDoA, and PFDA, while PFDA, PFUdA, and PFDS were generally < LOD. FBSA and EtFOSAA, two electrochemically derived precursors to PFSAs, were detected in 11 and 3%, respectively, of surface water sampling locations. These sample locations may be impacted by specific point sources of PFAS, given that these compounds were rarely detected in the rest of the study area.

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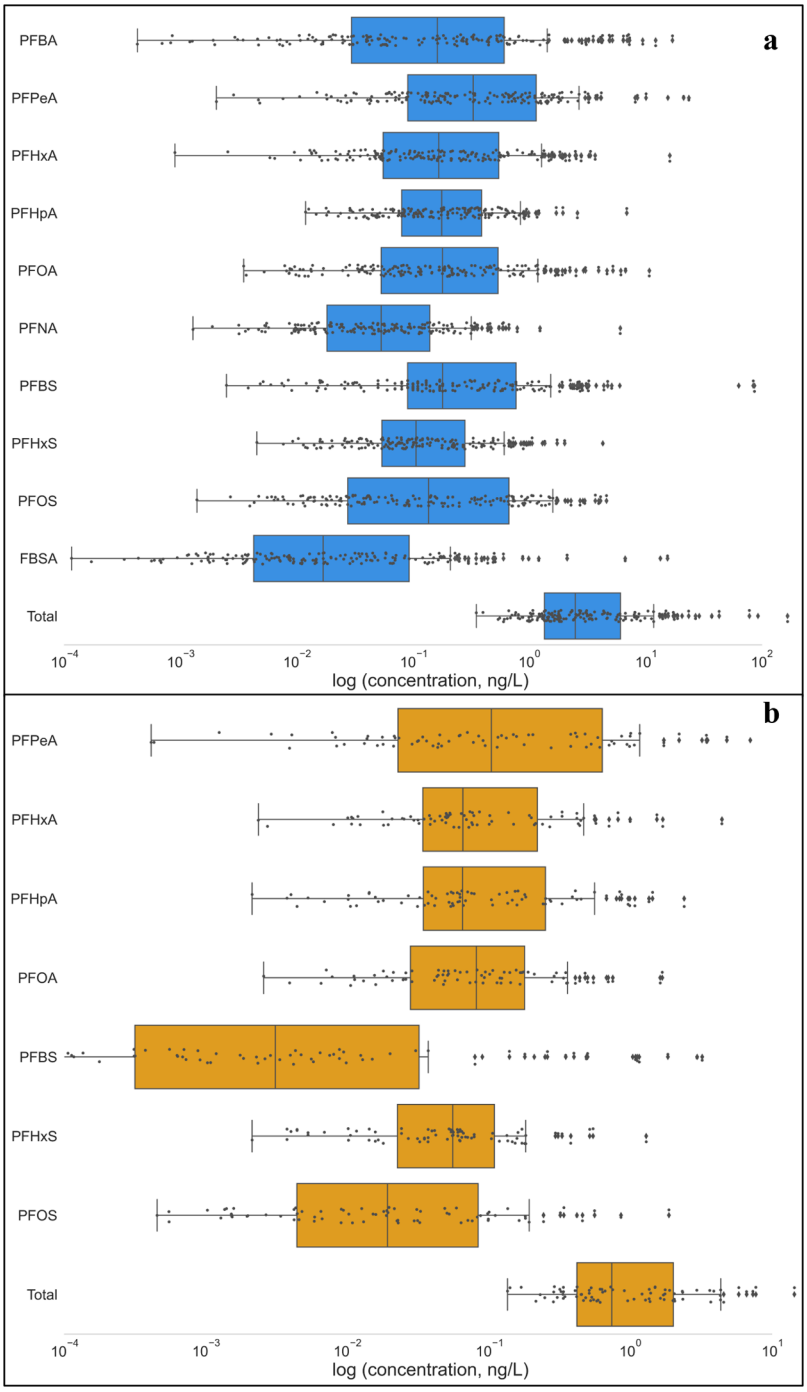

Figure 2. Concentrations of frequently detected PFAS as well as total concentration of PFAS in (a) surface water and (b) rural well water.

The maximum total PFAS concentration in surface water (169.5 ng/L) was higher than well water (15.7 ng/L) with over 90% of the wells having total concentrations <5 ng/L (Figure 2). A similar observation was reported in a study[34] conducted in an oil and gas producing region of the US where the average total PFAS concentration was 5 times lower in groundwater than surface water. In another study investigating PFAS occurrence across water sources in Sweden, the total maximum PFAS concentration in surface water was 13,000 ng/L, while that in groundwater was 6400 ng/L,[35] suggesting that even in heavily impacted areas, groundwater is relatively less vulnerable to contamination possibly due to protection from overlying aquifer materials. Nevertheless, in our study, median concentrations in surface water (2.6 ng/L) and well water (1.0 ng/L) are comparable, indicating similarity in concentrations for both water sources except for the hotspot surface water locations that are disproportionately impacted directly by PFAS discharges.

Among all the PFASs across all samples, PFBS had the highest maximum concentration of 87 ng/L followed by 24 ng/L for PFPeA and 17 ng/L for PFBA, all of which were in surface water samples. PFOA and PFOS concentrations in well water were below the proposed EPA MCL of 4 ng/L, suggesting that potential exposure to these two PFAS of concern is low for households that depend on well water in the study area. Statewide monitoring of PFAS in public water

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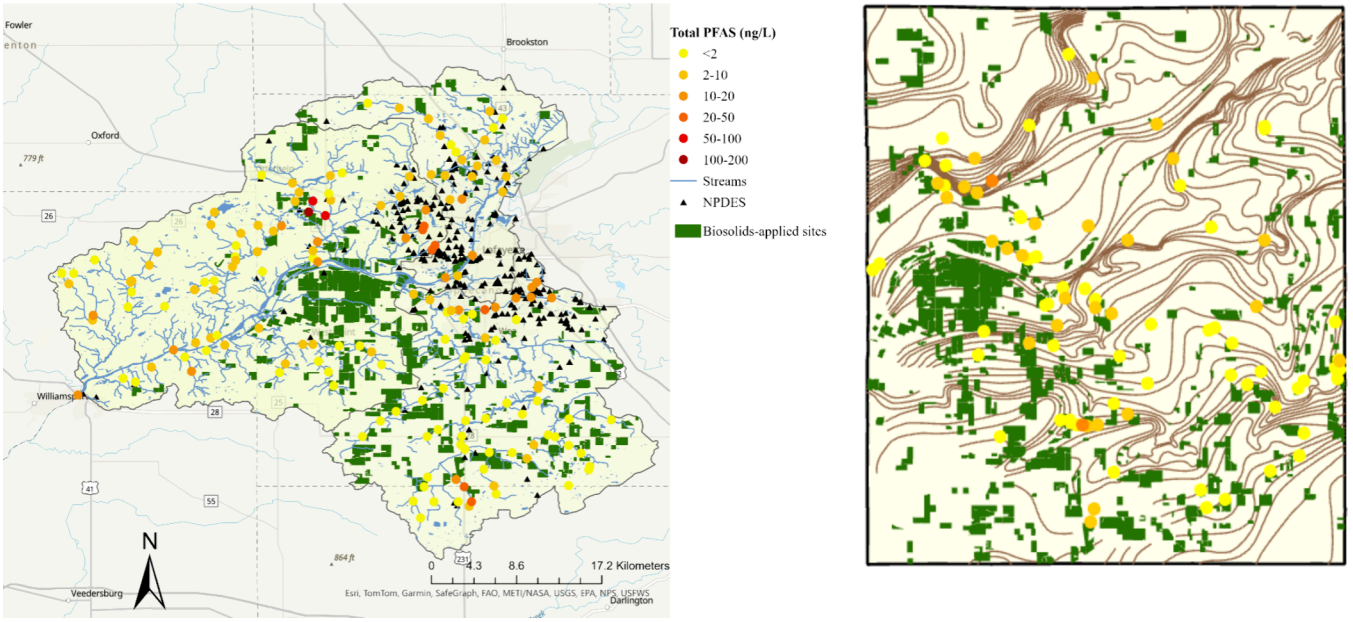

Figure 3. Spatial snapshot of total PFAS concentrations in surface water (left) and well water (right).

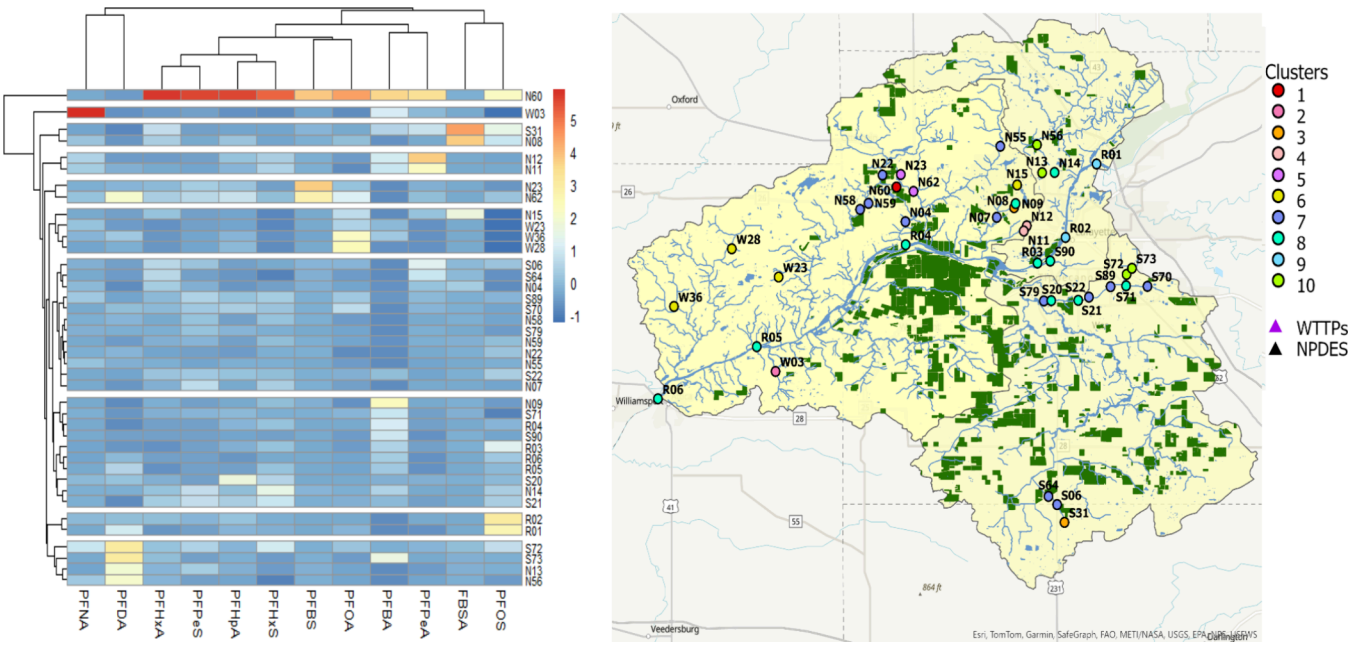

Figure 4. Hierarchical cluster analysis performed on standardized PFAS data (high values are in in red; low values are in blue) for compounds detected in ≥20% of surface water sites. Ten distinct clusters were identified in sites with total PFAS above the median concentration.

systems (PWS) is ongoing,[36] and current results detected PFOA and PFOS above the proposed MCLs in 20 untreated water sources. However, only 10 facilities exceeded the MCLs in treated water for PFOA (max 11 ng/L) and/or PFOS (max 7.8 ng/L), indicating that water treatment systems are effective in reducing total PFAS concentrations in drinking water available to the public. Still, the elevated levels of PFAS in untreated water reveal the potential risk of exposure; therefore, in addition to monitoring PWS, a comprehensive statewide assessment of private wells should be undertaken especially in areas with unglaciated aquifer systems. For surface water in this study, the highest concentration of PFOA and PFOS measured was 6.8 and 4.6 ng/L, respectively. While these values are above EPA's MCLs, surface water in this watershed does not serve as a drinking water source. However, contaminated locations could potentially impact downstream public water supplies or provide a pathway for exposure via fish consumption.

3.2. Spatial Pattern in Surface Water. PFAS distribution in surface water was spatially clustered (Moran *I* test, p value < 0.05), suggesting that PFAS contamination in the watershed is driven by location-specific activities. Total PFAS concentrations above the median were often detected in the urbanized northeastern part of the watershed where point discharges are heavily present, including NPDES, CSOs, and WWTPs (Figure 3). In these locations, perhaps pretreating effluents might reduce PFAS loads being discharged into surface water. In contrast, over 80% of the streams in the more agriculturally

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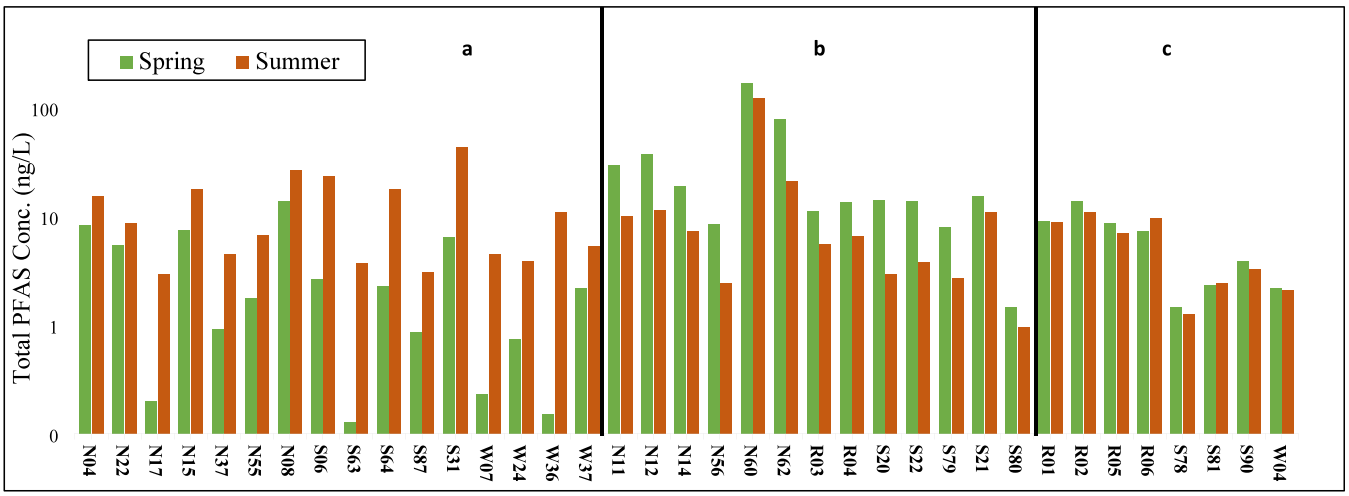

Figure 5. Seasonal trends in surface water sites sampled temporally show higher PFAS concentrations in (a) summer sampling and (b) spring sampling and (c) no distinct temporal trends between summer and spring sampling.

dominated southern part of the watershed had total concentrations <2 ng/L. While land application is active in this area, 90% of the agricultural fields have received biosolids only twice over the past 20 years (Figure S3). Nevertheless, even at a higher frequency, land application of biosolids rarely resulted in PFAS contamination as demonstrated by the negligible concentrations in streams with hydrological connection to biosolid-receiving fields except for three locations (N23, N60, and N62). These three locations receive drainage directly from agricultural fields that have received biosolids since the 1980s with nearly annual application over the past two decades. Total PFAS concentrations at these locations were 93.6, 169.5, and 79.2 ng/L respectively. PFOA concentrations were 1.8, 10.8, and 4.0 ng/L, and PFOS concentrations were 0.7, 3.7, and 1.5 ng/L. While these are relatively high concentrations compared to the rest of the watershed, PFOS levels are all below the proposed EPA drinking water standards, and PFOA exceeds the limit in only one location. Also, the total concentrations are lower than those previously reported in surface water linked to primary sources including AFFF,[37,38] landfill leachates,[35] and industrial discharges.[39] Surface water studies focusing on biosolid-applied sites are limited. Lindstrom et al.[40] reported total concentrations of up to 30,000 ng/L in surface water associated with land application of industrial-impacted biosolids. In another study, biosolids applied to agricultural fields were linked to PFAS contamination in the upper Moehne River in Heidelberg, Germany, with a maximum total concentration of 4,348 ng/L (seven PFASs with 83% being PFOA).[41] The variation in the extent of contamination reported in both studies as well in our study is likely due to differences in PFAS concentrations in applied biosolids that largely hinge on wastewater influent sources.[42] Hierarchical cluster analysis identified PFAS co-occurrence trends and spatial clustering of sites (Figure 4). The main PFAS grouping included short-chain (PFBA, PFBS, PFPeA, PFPeS, PFHxA, and PFHpA) and long-chain (PFHxS and PFOA) PFAAs frequently detected together in both rural and urban sites, suggesting multiple sources of these compounds to surface water. Site N60, which had the highest concentrations for all but one of these PFAAs, receives tile drain discharges from an active biosolid-applied field with yearly application for over 20 years. The site is likely impacted by short-chain PFAAs that leached into tile drains following land application of biosolids in addition to surface runoff of long-chain PFAS sorbed to the soil.[12] Additionally, in the early 2000s, biosolids were applied at ∼30 dry tons/acre, which is >10× the regular application rate. This high rate was a result of the biosolids having low plant-available N; thus, high rates were required to achieve the requisite N levels for corn cultivation. This high loading rate could have led to PFAS accumulation in the soil and subsequent gradual release into the environment. Therefore, it is possible that our current observation in site N60 is a combination of short- and long-term PFAS transport outcomes from current and historical applications. The high biosolid application rate triggered by low plant-available N points to the potential benefit of using high N/PFAS ratio criteria for guiding best management toward the beneficial reuse of biosolids.[43] Although not grouped together in the hierarchical clustering analysis, the proximity and similarity in PFBS profiles between sites N60, N23, and N62 suggest that these sites were likely impacted by the same source. More so, surface water from the three sites is hydrologically connected to agricultural fields that receive biosolids at similar loading rates and is generated from the same WWTPs based on IDEM records. Site N60 is 0.05 km from the source, while N23 and N62 are 0.7 and 1.9 km, respectively; therefore, the proximity to the source might explain the differences in concentrations between these three sites. Another potential source is the use of AFFF as observed in cluster 4 sites (N11 and N12) that are located within ∼0.3 km from a small airport with a nearby undisclosed fire training site. The elevated levels of PFAAs in both sites might be explained by the historical release of AFFF as observed in several studies.[44,45] PFNA and PFDA, both long-chain PFCAs, constituted another grouping, especially in cluster 10. Sites N13 and N56 are near NPDES discharges from the upstream building and construction industries. PFAS used in different construction materials including cements, roofs, cables, hoses, and gaskets to promote stability and durability[5,46] can end up in surface water via wastewater disposal. Sites S72 and S73 are downstream numerous point discharges from multiple activities including metal coating, aluminum, and heavy machinery manufacturing, further underscoring the diverse nature of PFAS sources.

https://doi.org/10.1021/acs.est.4c09490
Environ. Sci. Technol. XXXX, XXX, XXX−XXX

Additionally, FBSA and PFOS were grouped together (Figure 4) primarily due to the chemical profiles observed in cluster 3 (sites S31 and N08). In both sites, FBSA (15.5 and 13.5 ng/L, respectively) was detected at higher concentrations than PFOS (2.9 and 2.3 ng/L, respectively) possibly due to changes in the industrial use of long-chain PFASs over the past decade. Chu and Letcher[47] identified FBSA as a metabolite of *N*-methyl-perfluorobutanesulfonyl [$C_4F_9SO_2N(CH_3)$], which is a short-chain fluorinated surfactant used in Scotchgard products as an alternative to *N*-ethyl-perfluorooctaneslfonyl ($C_8F_{17}SO_2N(C_2H_5)$, a PFOS precursor). In another study, FBSA was reported as a short-chain substitute for PFOS in semiconductor production.[48] Site N08 is located ∼2 km downstream of a computer chip manufacturing company. Although the hydrological connection between N08 and the computer chip factory is unclear, at site N15, also downstream from the same company, elevated FBSA concentrations were observed indicating that the chip manufacturing is the likely source. Site S31 is impacted by wastewater discharge from a WWTP located <0.5 m upstream. The WTTP effluent typically comprises a suite of PFASs including sulfonamido derivatives such as FBSA[49,50] and can therefore be linked to the chemical profile at this site. Sites S06 and S64, which are ∼0.1 and 0.2 km downstream of S31, had different chemical profiles likely due to PFAS dilution along the stream. Similarly, dilution might explain the clustering pattern along the Wabash River in which sites with elevated PFOS concentrations (R01 and R02) located between three WWTP outfalls were separated from diluted downstream river sites (R03, R04, R05, and R06). Sorption to river sediment and bioaccumulation in biota are other potential attenuation pathways along the river reach.[13]

3.3. Seasonal Trends in Surface Water. PFAS concentrations were highest in the summer for 46% of sites sampled temporally, with all sites but one recording ∼2× more total concentrations in the summer compared to the spring (Figure 5). Such observations are typical for effluent-dominated or -influenced streams during low-flow conditions.[51−53] This also was evident for headwaters in our study impacted by point sources from industrial discharge (N08 and N15) or WWTP effluents (S06, S31, and S64). Although streamflow was not measured, changes in flow conditions were inferred from rainfall data and stream gauges placed in the Wabash River within the watershed (Figure S4). Average flow in the summer and spring was 2300 and 10000 f^3/s, respectively. Summer sampling followed periods of little to no precipitation resulting in insufficient flow to dilute point discharges and thereby resulted in higher PFAS concentrations. In the spring, high streamflow can dilute PFAS concentrations in point discharges or increase concentrations via surface runoff in locations impacted by nonpoint sources. Preferential flow through tile drains can also increase PFAS export to ditch networks during storm events, resulting in a direct relationship between streamflow and concentrations. This transport dynamic was observed at sites N60 and N62, both of which directly receive tile drainage from biosolid amended fields. Sites associated with AFFF use for fire training activities (N11 and N12) also had higher concentrations in the spring than in the summer possibly due to surface runoff. Interestingly, sites R03 and R04 along the Wabash River also had elevated PFAS concentrations in the spring. Unlike other sampling locations on the river, both sites are flanked by biosolid-receiving fields and thereby impacted by both nonpoint and upstream point sources. During intense storm events, PFASs sorbed to soils are most likely transported to surface water via suspended solids even in tile-drained fields that are subject to preferential flow as previously reported by Gall et al.[54] In such scenarios, concentrations are often highest immediately after source application, which aligns with the spring timeline for biosolid application in the watershed. The relationship between flow conditions and concentrations can be nonlinear as observed in sites S21 and S22. Both sites are likely impacted not by nonpoint sources but rather by upstream ephemeral headwaters that receive point discharges but only have flowing water in the spring, hence resulting in elevated PFAS levels during spring sampling. For the remaining sites, there were no clear temporal trends possibly due to increased downstream dilution for sites S78, S81, and S90 or sustained concentrations from year-round equitable flow conditions for sites along the river (R01, R02, R05, and R06).

3.4. Pattern of Occurrence in Groundwater. Spatial autocorrelation implemented with Moran *I* did not confirm any relationship between the PFAS concentration in individual wells and the average PFAS concentration in neighboring wells ($p > 0.05$). The high p value and z score of 0.62 clearly signify the absence of geospatial clustering for PFAS concentrations in wells, thereby implying a random distribution of concentrations relative to landscape factors. Bivariate correlation analysis corroborates similar findings between PFAS concentrations in wells and explanatory variables, including well depth, static water level, and distance to upstream sources. None of the variables showed a significant relationship with PFAS concentrations in wells (Table S4 and Figure S5). This suggests that differences in PFAS concentrations in this study cannot be explained by a generalized model and that transport from potential sources to groundwater is location specific. Statistical models that identify drivers of PFAS concentrations in groundwater have been reported in statewide or regional studies.[55−57] The data analyzed in these studies cover a range of heterogeneous landscapes and hydrological characteristics typical of a large study area and thus capture the variability necessary for most regression models. Such transport models can inform risk assessment at a large scale; however, they sometimes have limitations at capturing location-specific nuances. For example, the well in our study with the highest total PFAS concentration is ∼0.9 km from an upstream biosolid-applied field, with a total well depth of 43 m and 1.5 m static water level. Although the distance to the upstream location might play a role in this case, aquifer characteristics appear to be more critical considering that the well was completed in parts of the Till Veneer aquifer system where protective clay layers are thin or absent. With coarse aquifer media and a high-water table, this well is likely susceptible to advective flow of PFAS from overlying surface sources compared with other wells with similar characteristics but completed in parts of the glacial aquifer system with more restrictive layers. Such aquifers with low hydraulic conductivity and transmissivity in this area have been reported to contain substantial proportions of groundwater that dates from the 1940s to 1950s,[58] a period that precedes the proliferation of PFAS use. In addition to geological factors, the prevalence of subsurface drainage in the study mediates transport of chemicals to groundwater; rather than vertical transport, soil porewater is redirected to ditches and other waterbodies. This alteration in drainage might explain why the distance from upstream sources as a factor was not apparent in well water.

https://doi.org/10.1021/acs.est.4c09490
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Also, observed concentrations in wells near impacted surface water sites associated with known PFAS sources were comparable to other well water samples, indicating that groundwater in this area is generally protected from contamination. Moreover, gaining streams are prevalent in the watershed; therefore, PFAS-impaired surface water is unlikely to impact groundwater. Nonetheless, detectable levels of PFASs in approximately 83% of the wells are indicative of the ubiquitous presence of PFASs in the environment. Additional sampling throughout the state that reflects a wider geological spectrum, land use and cover, and potential PFAS sources is necessary to adequately identify causative factors for PFAS contamination in groundwater.

3.5. Key Findings, Environmental Implications, and Study Limitations. PFAS contamination of surface waters and groundwater is often linked to industrial discharges and waste disposal and the use of AFFFs and landfill leachates. The potential impact of other sources such as land application of biosolids on water sources is unclear due to limited studies. In this study, we evaluated PFAS occurrence and pathways in surface water and private well water of a predominantly agricultural area in northern Indiana. Concentrations of quantifiable PFAS were generally higher in surface water compared to well water, and the site with the highest concentration was hydrologically connected to an active biosolid-applied field. This particular location is unlikely to be impacted by industrial sources due to the absence of NPDES discharges and likely represents the worst case scenario of PFAS contamination from biosolid applications in the study area. The field has frequently received biosolids over the past 20 years at a loading rate between 1.0 and 4.8 dry tons/acre except for an instance where biosolids were applied at ∼30 dry tons/acre. Elevated PFAS concentrations observed in agricultural-influenced headwaters are partly linked to subsurface tile drains typically employed in this region especially in poorly drained silty clay loam agricultural soils. These artificial drainage systems facilitate the horizontal transport of porewater from soils to agricultural ditches and surface water bodies and thereby are critical sources of PFASs in the study area. Additional studies in other subsurface tile-drained landscapes across the Midwest are required given the broader implications on surface water quality, ecosystem health, and human exposure. Such studies could monitor patterns of PFAS release from tile drains following the land application of biosolids.

Other locations with high surface water PFAS concentrations relative to other observations in the study area were in urbanized areas impacted by WWTPs and industrial discharges, as shown by spatial and temporal trends as well as hierarchical cluster analysis. As health and environmental concerns on PFAS escalate, multiple statistical and spatial tools such as those demonstrated in this study can provide complementary lines of evidence in identifying PFAS environmental sources and transport pathways especially in sites with multiple potential sources. The shift to shorter-chain alternatives is reflected by consistently higher concentrations of C_4 PFSAs (e.g., PFBS) and FASAs (e.g., FBSA) compared to longer-chain homologues. PFBS and other PFAAs were detected across all sites due to their ubiquitous use, while concentrations of the less-documented FBSA were elevated downstream from a computer hardware manufacturer that is a previously reported novel source.[47] Temporal trends in surface water sites provided additional evidence of the PFAS source and pathways. Sites associated with point discharges had peak concentrations in the summer when low streamflow is expected, while locations impacted by nonsource point release recorded higher concentrations in the spring. However, additional data are required for a robust interpretation of temporal trends in sites with no distinct trend or nonlinear patterns. Additionally, the contribution of specific sources in sites impacted by multiple NPDES associated with different industrial activities remains ambiguous. Future studies that expand on our current results might consider sampling at individual point of release to fine-tune source apportionment in sites with comingled sources.

Although PFAS concentrations in wells were relatively low and did not exceed the enforceable EPA MCLs, our results provide evidence of PFAS transport down the soil profile, but the impact from land application of biosolids and other sources is confounded by multiple interdependent transport factors. Overall, the glacial aquifer system protects groundwater from contamination in the study area, and subsurface drainage systems obscure transport pathways and source attribution, which highlight the importance of incorporating prevailing hydrogeological conditions into PFAS forensic studies. Nevertheless, the risk of contamination might increase when industrially impacted biosolids are applied to coarse-textured soils in areas with nonconfining aquifer material and a high-water table. Our current study area does not adequately capture a combination of these factors; therefore, more studies across diverse agricultural landscapes within the region are needed to sufficiently characterize causative factors driving PFAS transport to groundwater.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.4c09490.

Additional text explaining sampling and experimental methods, quality control, and data analysis, including supporting figures and tables (PDF)

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Notes

The authors declare no competing financial interest.

https://doi.org/10.1021/acs.est.4c09490
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ACKNOWLEDGMENTS

This study was funded primarily by the US EPA National Priorities program under EPA G20B113019085, Grant R84008201. Dr. Lee is also partially supported by USDA/NIFA Hatch Project 1006516. The work has not been formally reviewed by EPA. The views expressed in this document are solely those of the authors and do not necessarily reflect those of the Agency. EPA does not endorse any products or commercial services mentioned in this publication. The authors also thank Renee Hallstein and Angelly Guarin for their help in sample preparation, Brenda Stephanoff for assisting with biosolid application records, WREC for coordinating surface water sampling, Dr. Byron Jenkinson for providing guidance during preliminary well water sampling, and Dr. Heather Preisendanz for drafting well water sampling instructions.

ABBREVIATIONS

AFFFs: aqueous film forming foams
COV: covariance
CSA: critical source areas
EtFOSAA: *N*-ethylperfluoro-1-octanesulfonamidoacetic acid
FBSA: perfluoro-1-buctanesulfonamide
FOSA: perfluoro-1-octanesulfonamide
HDPE: high-density polyethylene
HFPO-DA: hexafluoropropylene oxide dimer acid (aka GenX)
IDEM: Indiana Department of Environmental Management
LOD: limit of detection
LOQ: limit of quantitation
MCL: maximum concentration level
MeFOSAA: *N*-methylperfluoro-1-octanesulfonamidoacetic acid
N: nitrogen
NPDES: national pollutant discharge elimination systems
PFAA: perfluoroalkyl acids
PFAS: per- and polyfluoroalkyl substances
PFBA: perfluorobutanoic acid
PFBS: perfluorobutanesulfonic acid
PFCAs: perfluoroalkyl carboxylic acids
PFDA: perfluorodecanoic acid
PFDS: perfluorodecanesulfonic acid
PFHpA: perfluoroheptanic acid
PFHxA: perfluorohexanoic acid
PFHxS: perfluorohexanesulfonic acid
PFNA: perfluorononanoic acid
PFOA: perfluorooctanoic acid
PFOS: perfluorooctanesulfonic acid
PFPeA: perfluoropentanoic acid
PFSAs: perfluoroalkanesulfonic acids
PFUdA: perfluoroundecanoic acid
QA: quality assurance
QC: quality control
SPE: solid phase extraction
uPLC/MS/MS: ultrahigh pressure liquid chromatography tandem mass spectrometry
WREC: Wabash River Enhancement Corporation
WWTP: wastewater treatment plant

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