Article

PFAS assessment in fish – samples from Illinois waters

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Abstract: Per- and Polyfluoroalkyl substances (PFAS) have been widely used in pesticide production, electroplating chemical industry, packaging, paper making, clean energy materials, and other industries. This study documented fish tissues in four target water bodies (16 sampling points) in Illinois collected during 2021-22. Concentrations of 17 PFASs were determined in nine fish species collected from four waterways/aquatic systems in the northwest corner of Illinois for the assessment of potential health risks. At least four PFAS (PFHxA, PFHxS, PFOS, and PFBS) were detected at each site. Across all waterbodies and sampling locations, the mean of the total (∑) PFAS levels varied from 7.32 to 335.05 ng/g wet weight (ww) in 2021 and from 13.19 to 146.13 ng/g wet weight (ww) in 2022. In individual fish fillet, the total PFAS ranged from 6.76 to 191.21 ng/g ww in 2021 samples and 1.39 ng/g ww to 37.50 ng/g ww in 2022 samples. The most abundant compound in each species was PFOS in 2021 and PFHxA in 2022, which accounted for 21.25 to 77.53% of the total PFASs. On an average, levels of PFOS in almost all fish were high enough to trigger fish consumption recommendations. More research is needed to further assess the sources and accumulation of PFAS in aquatics and the potential risk to the environment.

Keywords: PFAS; fish samples; risk assessment; 2021-22; Illinois waters; risk analysis

1. Introduction

Per- and Polyfluoroalkyl substances (PFAS) are a class of organic compounds wherein the hydrogen atoms in the carbon chain of aliphatic hydrocarbons are replaced by all or more fluorine atoms (Evich et al., 2022). Due to their high C-F bond energy, chemical stability, long half-life in the environment, bioenrichment, and ability to migrate to long distances, these chemicals are considered as persistent organic pollutants and have attracted much attention in the field of environmental pollution research (Zhang et al., 2022). Because of its hydrophobicity and high chemical stability, PFAS has been widely used in pesticide production, electroplating, packaging, paper making, and electronic among other industries. PFAS compounds have raised significant concerns regarding their potential impact on human and animal health (Solan et al., 2023; Wen et al., 2022). The impact of PFAS on both the ecosystem and human health receptors could be influenced by its characteristics and the concentration present in the environment.

The multi-agency distribution and ecological effects of legacy PFOS and PFOA have been examined (Anderko and Pennea, 2020; Rahman et al., 2014). Pham et al. found that PFOS and PFOA in the surface water of the Dianchuan Basin in Japan, reached up to 123 ng/L and 260 ng/L, respectively (Lein et al., 2008). The U.S. Environmental Protection Agency (EPA) noted that PFOS and PFOA in soils was likely to be a major source of PFAS (Renner, 2009). PFAS levels in drinking water in Australia was detected at 16 ng/L and 9.7 ng/L (Thompson et al., 2011) of PFOS and PFOA, respectively. PFOS and PFOA were detected in all serum samples (from 105 Danish men) and the level was negatively related to the number and quality of their sperm (Joensen et al., 2009). The stable chemical properties of PFAS is reflective of its long residual time in the environment with potential to migrate long distances through foreign flow and atmospheric conversion, reaching North and South Pole (Yeung et al., 2017). PFAS tests performed in 19 major water systems in China shows the highest levels of short-chain omnin fluorine sulfonic acid PFBS and full fluoride carboxylic acid PFOA (Wang et al., 2016). In the Great Lakes of North America, the ring-shaped whole fluorophyttel-alcoholic sulfonic acid was detected at a concentration similar to that of PFOS (De Silva et al., 2011).

In the top predato lake trout (*Salvelinus namaycush*) of the Great Lakes, the main PFAS observed was PFOS at concentrations as high as 121 ± 14 ng/g (Furdui et al., 2007), and PFOA (0.65– 5.5 ng/L) (De Silva et al., 2011). Although the general population is exposed to low levels of PFAS from various sources such as food and consumer products,

individuals can be exposed to higher levels near contaminated sites by consuming contaminated food or polluted drinking water (Fujii et al., 2015; Post et al., 2012). Certain PFAS, notably PFOS and long-chain perfluoroalkyl carboxylates (PFCAs), such as perfluoroundecanoic acid (PFUnA; C11), can accumulate in tissues (Labadie and Chevreuil, 2011). Numerous studies have reported the presence of PFAS in the environment and wildlife (Barbo et al., 2023; Evich et al., 2022; Fair et al., 2019). Among the PFAS detected, PFOS is generally the most prevalent and found in the highest concentrations in fish, although other PFAS are also frequently observed (Houde et al., 2011). Delinsky et al. (Delinsky et al., 2010) conducted a statewide study of Minnesota lakes and several Upper Mississippi River locations, while Fair et al. (Fair et al., 2019) evaluated fish collected from the Charleston Harbor and tributaries in South Carolina. The reported levels in the Great Lakes (Stahl et al., 2023) were generally lower than the Minnesota River (Lin et al., 2021), substantially lower than urban rivers in America (Coy et al., 2022; Goodrow et al., 2020; MacGillivray, 2021). There is limited to no information on PFAS contamination in fish from water bodies across Illinois. To conduct a comprehensive risk analysis, it is necessary to obtain data on PFAS levels by species from specific rivers and tributaries.

The objectives of this study were: 1) to conduct an initial assessment of the occurrence of 17 PFAS, their distribution, and risk in the nine fish species from local Illinois rivers collected in 2021 and 2022, 2) to determine the potential risks of PFAS, and 3) to estimate the dietary PFAS exposure due to fish consumption. The findings of this study could shed light on the types of PFAS compounds in fish obtained from water bodies around the state. In the long-term with periodic samples, these could aid local agencies in efficient management/mitigation of human exposure risks.

2. Materials and Methods

2.1. Chemicals and reagents

MPFAC-2ES, a mixture containing 19 mass-labelled standards containing C_4-C_{14} PFCAs, C_4-C_{10} PFSAs, FOSA, N-MeFOSAA, N-EtFOSAA, as well as 4:2, 6:2, and 8:2FTS was purchased from Wellington Laboratories (Canada). Target compounds included four perfluorocarboxylic acids (PFBA, PFHxA, PFOA and PFDA) and three perfluorosulfonic acids (PFBS, PFHxS and PFOS). These compounds were purchased from Wellington Laboratories (Canada) and SynQuest Laboratories (USA). Detailed information is provided in Table S1. The stock solutions were prepared in methanol and kept in polypropylene (PP) tubes at 4°C. HPLC-grade methanol, with a purity of at least 99.9%, from Sigma-Aldrich (USA), was used as a solvent for HPLC analysis.

2.2. Study area

Based on their proximity to potential sources of PFAS and the likelihood of recreational and subsistence fishing, samples were collected from Rock River, Pecatonica River, Sugar River and Yellow Creek in Illinois (see **Figure 1** and Table S2). Rock River and Pecatonica Rivers are the larger streams, Sugar River and Yellow Creek are the smaller tributaries to the Pecatonica River, the four waterways/aquatic systems are in the northwest corner of Illinois.

The Rock River is a significant waterway in the state of Illinois. It stretches for approximately 299 miles, flowing through various cities and towns. The Rock River is one of Mississippi River's major tributaries and it merges near the city of Rock Island, Illinois. It has served as a vital transportation route for industries, commerce, and recreational activities. The combined waters of the Rock River and the Mississippi River have facilitated trade and transportation of goods, support various species of fish, birds, and other wildlife. The watersheds had varying land-use and land-cover compositions, range from agricultural dominance and forest dominance to heavy urbanization. Sampling activities were conducted during the period between October to November 2021 and July to November 2022 to collect relevant data and information.

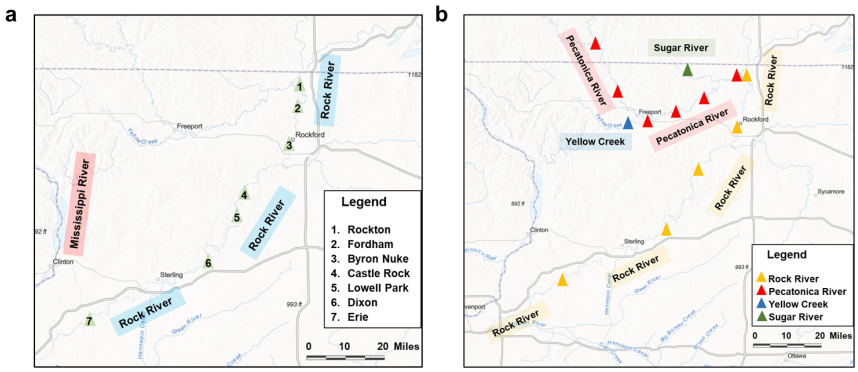

Figure 1. (a). Map showing 7 sampling sites located in Rock River from Illinois, USA (2021). **(b).** Map showing 13 sampling sites located in four major rivers from Illinois, USA (2022).

2.3. Sample collection(fish)

A total of 52 fish samples were collected from the Rock River in 2021 for fillet contaminant analysis. Seven fish species were collected: Bluegill (*Lepomis macrochirus*), Smallmouth Buffalo (*Ictiobus bubalus*), Common Carp (*Cyprinus carpio*), Sauger (*Sander canadensis*), Smallmouth Bass (*Micropterus dolomieu*), Walleye (*Sander vitreus*), and Channel Catfish (*Ictalurus punctatus*). Nine fish species with a total of 70 fish samples were collected in 2022 from four waterways/aquatic systems, the additional fish species collected in 2022 were, Black Crappie (*Pomoxis nigromaculatus*) and Northern Pilce (*Esox Lucius*). These species were selected to represent both pelagic and benthic environments, covering various trophic levels. The demographic information can be found in Table S3.

Fish samples were collected by the Illinois Department of Natural Resources (IL-DNR). To ensure sample integrity, each fish was individually wrapped in thick aluminum foil and then placed inside a sealed polyethylene bag. The samples were kept on ice for 3-6 hours before being frozen at -20°C. They remained frozen until they were ready for preparation and subsequent analysis.

2.4. Sample extraction and Instrumental analysis

Sample processing steps were adapted from other works (Fair et al., 2019; Valsecchi et al., 2021). In brief, methanol was used to extract PFAS from the fish fillet sample. Once an extra labeled standard (MPFAC-2ES) was added, PFAS were measured through liquid chromatography-mass spectrometry (LC-MS) using both internal and external standards, with calibration done at various concentration levels. LC-MS was provided by the Carver Metabolomics Core Facility of the Roy J. Carver Biotechnology Center, University of Illinois Urbana-Champaign. Using an Agilent 1260 Infinity II HPLC system (Agilent Technologies, Santa Clara, CA, USA), metabolites were separated with a Phenomenex Kinetex PS C18 100A (2.6µm, 100 x 4.6mm) column (Phenomenex, Torrance, CA, USA) via a gradient method consisting of mobile phase A: H2O+20mM ammonium acetate and mobile phase B: methanol running at a flow rate of 0.35 mL/min. The gradient was 0-2 min = 90% A; 2-10min = 0% A; 18.1-24min = 90% A. A Sciex 6500+ triple quadrupole MS (Sciex, Framingham, MA, USA) operating in negative ionization mode using multiple reaction monitoring (MRM) was used to screen for over 20 PFAS compounds.

2.5. Quality assurance and quality control (QA/QC)

To minimize laboratory contamination, only glass, metal, Teflon materials were used. Metabolites were quantified with Sciex Analyst software using 5- to 7-point calibration curves adjusted for stable-isotope labeled internal standards (Wellington Laboratories, Guelph, ON). A delay column (Halo PFAS delay column, 2.7 µm, 4.6 mm x 50 mm; Advanced Materials Technology, Wilmington, DE, USA) was placed between the mobile phase mixer and sample injector to momentarily trap any system related PFAS interferences due to tubing or mobile phase. Blanks were periodically analyzed throughout the sequence to test for the presence of PFAS contamination. QCs were run to assess reproducibility of quantitation at varying concentrations.

2.6. Risk assessment

In this study, the Risk Quotient (RQ) method was used to evaluate the ecological risk degree of PFAS in fish. RQ is the ratio of the measured environmental concentration (MEC, in ng/L) and the predicted non-effect concentration (PNEC, in ng/L) of the actual sample and calculated using the formula:

$$RQ = \frac{MEC}{PNEC} \tag{1}$$

$$PNEC = \frac{EC50(LC50)}{AF} \tag{2}$$

Where: PNEC was obtained from toxicological data. LC50 was the lowest 50% lethal concentration (ng/L) obtained by toxicological tests across organisms. EC50 was the minimum 50% effective concentration (ng/L) obtained by toxicological tests across organisms. AF is the EC50 value of the assessment factor (three trophic levels (algae, crustacea, fish)). Ecological toxicology data was obtained from the US EPA's Integrated Risk Information System (IRIS) database at https://www.epa.gov/iris.

The risk stratification criteria for each PFAS are as follows:

RQ < 0.01, no risk;
0.01 ⩽ RQ < 0.1, low risk;
0.10 ⩽ RQ < 1.00, medium risk;
RQ ⩾ 1.00, high risk.

2.7. Fish consumption

Based on national and local fish consumption, we analyzed the impact of consuming fish on human exposure to PFAS. The daily trigger concentration (DTC) (Eq. (3)) is the ratio of Reference Dose (RfD; the daily dose in ng/kg/day expected without risk from lifetime exposure) multiplied by average body weight (BW, assuming an average body of 70 kg), then divided by meal size(g).

$$Daily\ trigger\ concentrtion\left(\frac{ng}{g}\right) = \frac{RfD(ng/kg/day)*Body\ Weight(kg)}{Meal\ size(g)} \quad (3)$$

Where: Body weight = 70 kg; Meal size = 227 g.

3. Results and discussion

3.1 Concentration and composition of PFAS in fish

Figure 2 presents PFAS contamination in fish from Rock River, Pecatonica River, Sugar River and Yellow Creek in 2021 and 2022. **Figure 2a** and **2c** provide the absolute value of PFAS concentration in ng/g. **Figure 2b** and **2d** are the mean percentage composition of different PFAS in sampling sites. **Figure 2a** and **2b** show that the highest concentration in 2021 is PFBS, followed by PFOS and PFHxS. **Figure 2c** and **2d** show that the highest concentration in 2022 is PFHxA, followed by PFOS among the seventeen PFAS. Among the four watersheds, almost all sampling sites of Rock River have the highest PFAS concentration. The results of PCA analysis also indicated that samples from Rock River had the most significant contribution to PFAS (**Figure 2f** and Table S7). Among all the Rock River sites, Rockton contributed the most in both 2021 and 2022 (**Figure 2g** and **2h**). Pecatonica River had the lowest PFAS concentration and the fewest types of PFAS compounds. In the samples analyzed, PFOA was not detected from samples in Pecatonica River, despite being frequently reported in fish tissue in the existing literature.

The concentrations of PFAS vary widely in fish tissues in samples obtained from different sites, with some sites having much higher concentrations than others. Byron Nuke has the highest concentration of PFBS and PFOS in 2021, while PFHxS and PFOA are relatively high in samples from Erie. In 2022, Rockton has a relatively high concentration of PFHxA and PFOA, while Harrison has a relatively high concentration of PFHxS. The concentration of PFHxA in samples from Rockton was 62.26 ng/g, while those from Forest Preserve recorded only 3.97 ng/g. This could be due to differences in the sources of PFAS and their potential spread. The PFAS with the highest concentration in the samples is PFHxA, with a maximum concentration of 62.26 ng/g found in samples obtained from Rockton, followed by PFOS with a maximum concentration of 39.32 ng/g found in those from Erie. The PFAS with the lowest concentration in the samples is 8:2 FTS and EtFOSA, which is not detected in any of the sites.

These findings are in line with previous studies that also report PFHxA and PFOS as the most commonly detected PFAS (Bai and Son, 2021; East et al., 2021; Johnson, 2022). However, the present study differs from these studies in that it reports a higher concentration of PFHxA than PFOS, while the converse was observed in other studies. This difference could be due to variations in the sources and pathways of PFAS contamination, which can vary depending on the location and surrounding conditions. It should be noted that there is a factory on the side of Rock River near the Mississippi River, a Fire Department in Rockton and a Metal Company in Dixon, as well as some towns with a population of more than 7000.

The concentrations of individual PFAS can vary widely even within the same site which could be due to differences in the chemical properties of each PFAS and their spread in the environment (Nguyen et al., 2020). For example, at the Winslow site, the PFAS concentration in the collected samples ranges from 0 for PFHpA to over 4 ng/g for PFPeA. This could be due to differences in the chemical properties of each PFAS, which can affect the nature of spread in the environment. Some PFAS are more prevalent in specific sites. PFHxA, PFHxS, PFOS, and PFBS were present in all sites. Meanwhile, PFBA is only present in samples from Winslow and PFNA is only present in samples from Winnebago. The samples with the most types of PFAS detected are from the site in Dixon (12), followed by Rockton (10), Fordham Twz (10) and Macktown (10). Over 10 types of PFAS were noted from these sites. The site with the least type of PFAS detected

is Harrison and Damascus Landing, where only 5 types of PFAS detected in the samples. The percentage of PFAS in each site varied. In Freeport, PFHxA accounted for 77.53% of the total PFAS detected, while in Damascus Landing, PFHxA accounted for 21.25% of the total PFAS detected. In Forest Preserve, MeFOSA accounts for 36.35% of the total PFAS detected, followed by PFHxA and PFOS with 30.07% and 22.73%, respectively from the fish samples.

To explain the possible common origin of different PFAS, correlation analysis of the target compounds was performed. Because the variables did not conform to the normal distribution, Spearman rank correlation was selected for analysis, and the results are shown in **Figure 2e** and **2f**. PFOS and PFOSA, PFTrDA and PFUdA had a significant positive correlation, and the number of carbon chains was almost the same, indicating that they might have a similar origin. PFOSA, a precursor of PFOS, had a correlation coefficient as high as 0.86. The short-chain PFAS with the highest contribution rate, PFHxA, was positively correlated with PFOA, PFOSA, PFHxS and PFBS, but not with other compounds, suggesting that PFHxA might have a relatively stable source of contamination. There is a strong correlation between long-chain PFAS and short-chain PFAS, hinting that they might come from the same pollution source, on the other hand, the long-chain PFAS could be converted into short-chain PFAS by long-distance migration and decomposition (Neuwald et al., 2022). In general, longer-chain PFAS tend to be more toxic and bioaccumulative in humans and other mammals (Lau, 2012), with their solubility in water decreasing as the length of their carbon chain increases (Armitage et al., 2009).

The differing types of PFAS detected in the same sampling sites between 2021 and 2022 may be the result of a complex interplay between environmental, anthropogenic, and methodological factors. Natural variations in environmental conditions between 2021 and 2022 can impact the mobility, transport, and degradation of PFAS compounds. Different pollution sources, industrial activities, and human behavior can introduce a variety of PFAS compounds into the environment. The presence and types of PFAS compounds can also be influenced by the composition of aquatic ecosystems, including the diversity of species and their behaviors.

In summary, the concentration and types of PFAS in fish samples from the 16 sites in Illinois vary. The PFAS with the highest and lowest concentrations are PFHxA and PFOS, respectively. The samples with the most types of PFAS detected is from Dixon, and the site with the least types of PFAS detected is Lowell Park in 2021 and Harrison in 2022. The percentage of PFAS in each site also varies, with PFHxA, PFHxS, PFOS and PFBS, and PFOSA being the most common. Overall, the present study adds to the existing literature on PFAS contamination in fish by providing an inclusive analysis of PFAS levels and composition in the four major rivers in Illinois. The findings have important implications for public health and environmental policy, as PFAS contamination in fish can have adverse effects on human health and the ecosystem. The present study highlights the need for continued monitoring and regulation of PFAS contamination in aquatic environments, particularly in areas where the concentration of these compounds is high.

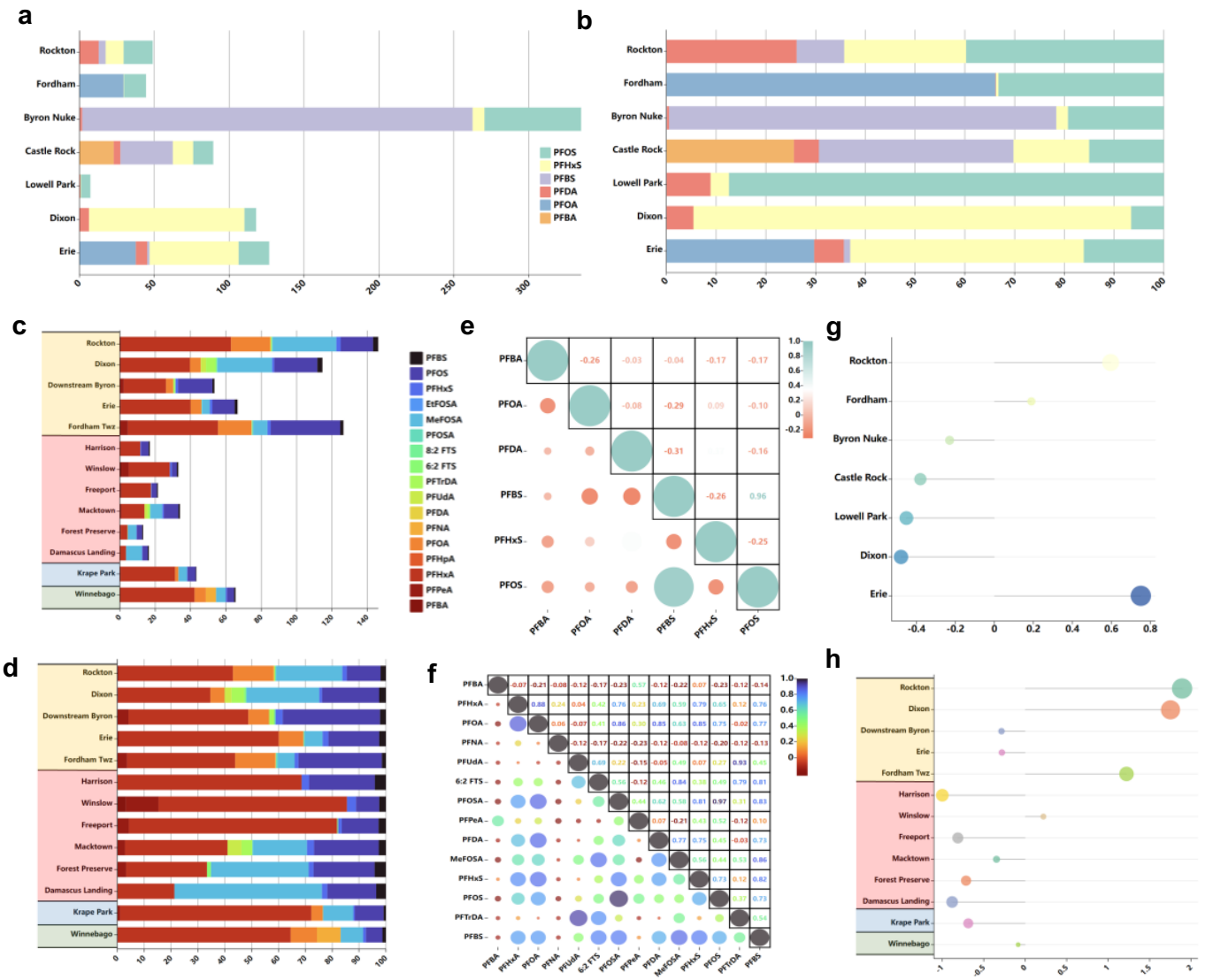

Figure 2. (a). Concentration and composition of PFAS in samples from Rock River (2021), **(b).** Mean percentage composition of different PFAS in samples from 7 sites (2021)**, (c).** Concentration and composition of PFAS in samples from four major rivers from Illinois (2022), **(d).** Mean percentage composition of different PFAS detected in samples from 13 sites (2022). Correlation analyses between individual PFAS in 2021 **(e)** and 2022 **(f)** samples. Principal Component Analysis (PCA) score across samples obtained from sampling sites in 2021 **(g)** and 2022 **(h)**.

3.2 Comparison of PFAS in fish species

PFAS are persistent in the environment and can accumulate in the food chain, and several studies have noted its accumulation in fish. **Figure 3** presents data on the content and PFAS compounds present in 9 fish types, including Bluegill, Smallmouth Buffalo, Common Carp, Sauger, Smallmouth Bass, Walleye, Black Crappie, Channel Catfish, and Northern Pilce, collected from various water bodies in Illinois. Number of individual fish collected and analyzed at each site can be found in Table S4 and S5.

The analysis of PFAS in the fish samples was conducted by LC-MS. **Figure 3a** showed that the total PFAS concentration in the 2021 caught fish ranged from 6.76 to 191.21 ng/g wet weight (ww) in common carp. Among fish at different food chain levels, bluegill had the lowest total PFAS content, and Channel Catfish the highest total PFAS content, indicating that PFAS can accumulate in order based on the food chain level. The Pearson correlation coefficient also supports this conclusion, and BLG is significantly positively correlated with CCF and SMB **(Figure 3b)**. **Figure 3c** showed that in 2022, all the fish samples contained various types of PFAS, and the total concentration ranged from 1.39 ng/g ww to 37.50 ng/g ww in common carp. The average total PFAS concentration across all the fish species was 12.46 ng/g ww. The higher its level in the food chain, the higher the PFAS content of fish. The correlation matrix in **Figure 3d** also

indicates that the total PFAS content in different fish species satisfies the food chain cumulative effect. The fish with the highest total PFAS concentration was Sauger, with a level of 29.33 ng/g wet weight, followed by Smallmouth Buffalo (25.62 ng/g) and Channel Catfish (17.96 ng/g). The fish with the lowest total PFAS concentration was Walleye, with a concentration of 3.97 ng/g wet weight.

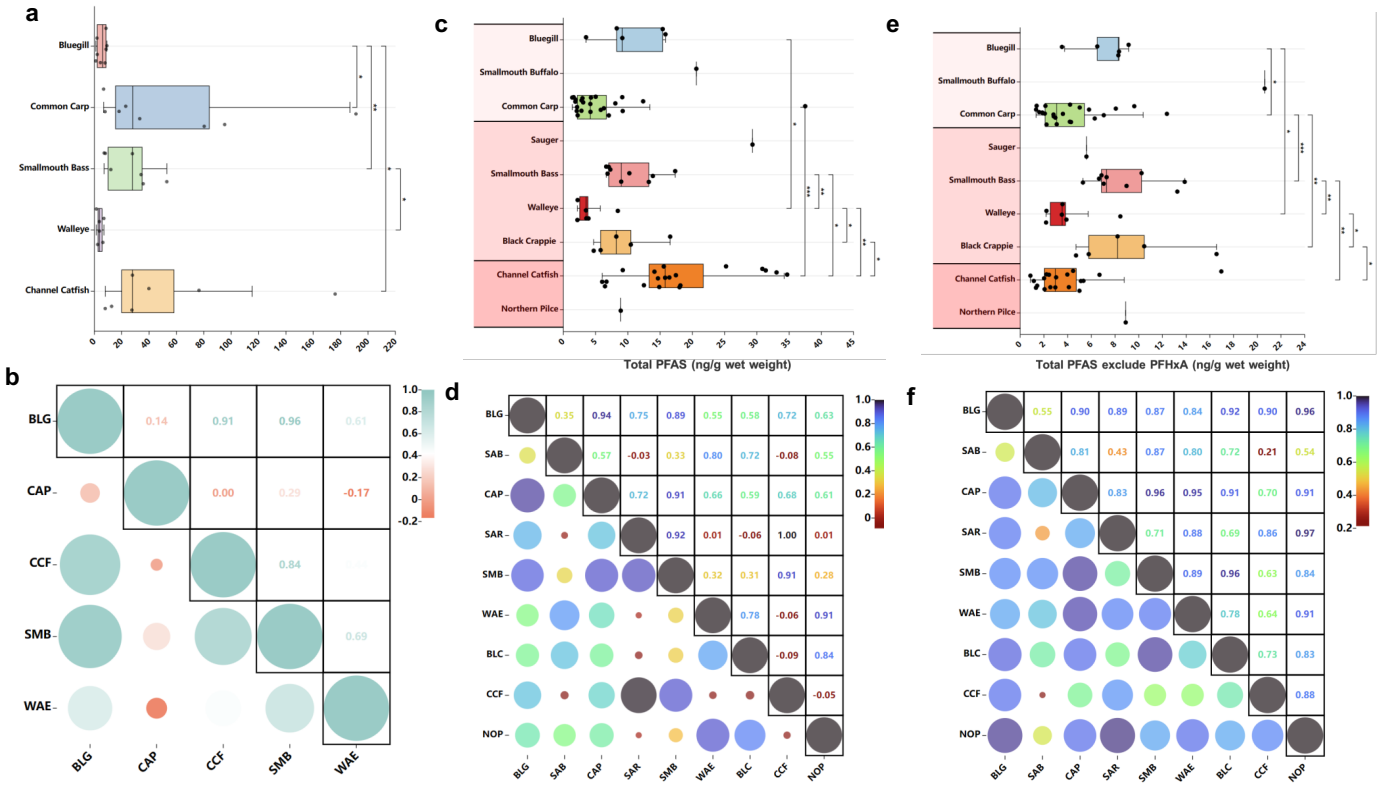

Figure 3. Box-whisker plot of the concentration of total PFAS in five fish species (a. 2021, c. 2022). Correlation matrix of PFAS (total) for five fish species (b. 2021, d. 2022). **(e).** Box-whisker plot of PFAS (exclude PFHxA) concentration in nine fish species (2022). **(f)** Correlation matrix of PFAS (exclude PFHxA) for the nine fish species (2022).

In terms of the range of PFAS detected, fish with high trophic levels have a higher number of PFAS accumulated. Channel Catfish shows a relatively high diversity of the types of PFAS, with 13 types of PFAS detected. This indicates that these fish have been exposed to multiple sources of PFAS contamination. In contrast, Bluegill and Common Carp showed the lowest diversity, with only 11 types of PFAS detected in each fish. Both the carbon chain length and anionic group (carboxylate or sulfonate) of PFAS determine their potential for bioaccumulation in fish tissue. Generally, the longer the fluorinated carbon chain in the PFAS, the higher the potential for bioaccumulation in fish (Goodrow et al., 2020). Sulfonates have a higher bioaccumulation potential than carboxylates with the same fluorinated carbon chain length (Martin et al., 2003). PFOA and PFOSAs with eight or more fluorinated carbons (PFTrDA and 6:2 FTS and longer) are more likely to bioaccumulate in fish. However, even shorter chain compounds can accumulate less and may be present in fish tissue (Conder et al., 2008). PFOS is one of the most abundant PFAS seen in fish (Fair et al., 2019). In general, PFOS being more toxic than PFOA is the most concerning, given its common occurrence in the environment, propensity for bioaccumulation in fish tissues, and potential human health risks (Christensen et al., 2017).

Since PFHxA accounts for the most significant proportion of all PFAS, we counted PFAS other than PFHxA, as shown in **Figure 3e and 3f**. These results showed no significant cumulative effect of PFAS at different food chain levels after excluding PFHxA data, and their correlation coefficient was found to be very high. Thus, it is likely that PFHxA easily accumulates in the body mass of organisms and is transmitted through the food chain. PFAS are persistent in the environment and have been found to accumulate in the food chain, including fish, posing potential risks to human health.

3.3 Potential risk of PFAS

The Risk Quotient method has been widely used to evaluate the ecological risk of organic pollutants to aquatic ecosystems. The ecotoxicology data of PFAS were obtained from the EPAECTOX database (2022) and the predicted non-effect concentration (PNEC) was calculated. Table S8 summarizes the PNEC data of PFAS. The measured PFAS concentration was divided by the PNEC value to obtain the RQs value of PFAS for fish at each sampling site in Illinois.

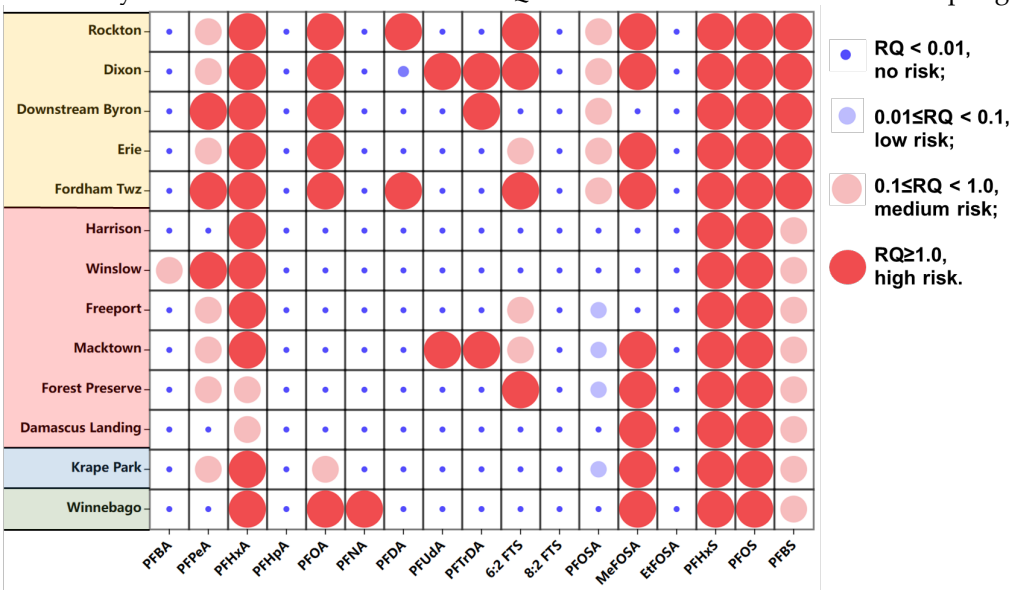

Figure 4. Ecological risk of PFAS from the analysis of fish samples (2022).

It can be concluded from **Figure 4** that PFHxS and PFOS have a higher risk of accumulation in fish in all 13 sampling points of the four water bodies in 2022, the proportion of high risk was 100%, which could lead to adverse effects of fish health, the environment, and potentially pose a risk to human health. PFHxA had a higher risk of accumulation in a vast majority of sampling sites. PFAS with low and no risk includes PFBA, PFHpA, and PFOSA, which have low or no effect on fish. PFBS was at high risk at all sampling sites in Rock River, whereas it was in the medium risk category in the other three waterbodies. The reason may be due to differences in the physicochemical properties of PFBS in different water bodies. For example, differences in pH, temperature, and dissolved organic matter can influence the behavior and toxicity of PFAS compounds in aquatic environments (Lyu and Brusseau, 2020; Nguyen et al., 2020). Further research is needed to understand the factors that influence the behavior of PFAS in different water bodies and its transport.

Among water bodies, Rock River had the highest number (up to 11) of high-risk PFAS species as evaluated from the samples analyzed. This was followed by Pecatonica River with eight species. The Yellow River had the lowest number of high-risk PFAS, with only four types. In Rock River, up to five PFAS (PFHxA, PFHxS, PFOS, PFOA and PFBS) were identified as high risk at all sampling points, while only two PFAS (PFHxS and PFOS) were identified as high risk at all sampling points in Pecatonica River. The potential risks associated with PFAS exposure are of growing concern, and the findings of this study provide important insights on the risks posed by PFAS to fish in Illinois. Our results indicate that certain PFAS compounds pose a significant risk to fish, with PFHxS and PFOS being the most toxic.

3.4 Fish consumption advisories

One potential pathway of PFAS exposure in humans is through the consumption of contaminated fish. In Illinois, the Department of Public Health has established fish consumption advisory triggers for several PFAS compounds, including PFBS, PFHxA, PFOS, PFNA, PFOA, and PFHxS on https://epa.illinois.gov/. These advisory triggers are based on the US Environmental Protection Agency's RfD and are intended to provide guidance to consumers on safe levels of fish consumption (Cordner et al., 2019).

Table 1. Illinois PFAS fish Consumption Advisory Triggers (ng/g) (Goodrow et al., 2020)

Consumption frequency (meal)	PFBS	PFHxA	PFOS	PFNA	PFOA	PFHxS
RfD ($ng/kg/day$)	320	83000	1.7	3.3	2.7	16

Unlimited (daily)	⩽98.68	⩽25594.71	⩽0.52	⩽1.02	⩽0.83	⩽4.93
Weekly	⩽690.7	⩽179163	⩽3.67	⩽7.12	⩽5.83	⩽34.54
Monthly	⩽2960	⩽767841	⩽156	⩽30	⩽25	⩽148
Once every 3 months	⩽8881	⩽2303524	⩽47	⩽91.59	⩽74.93	⩽444
Yearly	⩽36017	⩽9342070	⩽191	⩽371	⩽304	⩽1801
Do not eat	>36017	>9342070	>191	>371	>304	>1801

Table 1 shows the fish consumption advisory triggers for PFAS in Illinois, based on the frequency of fish consumption and the RfD for each compound. The advisory triggers are given in units of nanograms per gram (ng/g) of fish tissue. According to the advisory triggers, individuals who consume fish daily should limit their consumption of fish containing PFAS. The average levels of PFAS across all nine fish species and 16 sites were above the advisory triggers for safe fish consumption. The level of advisory ranged from consuming fish no more than once a week to no more than once a year. The advisory triggers were mainly based on concentrations of PFOS.

In conclusion, the fish consumption advisory triggers for PFAS in Illinois provide important guidance to consumers on safe levels of fish consumption. By limiting the consumption of fish containing PFAS to levels below the advisory triggers, consumers can help protect their health and reduce exposure to these harmful chemicals. However, ongoing research and monitoring are needed to better understand the risks of PFAS exposure and to develop more effective strategies for managing these contaminants in the environment.

3.5 Policy implication

Based on the data provided, a need for regulation and monitoring of PFAS levels in water sources is imminent. Given the potential risks associated with PFAS exposure, a statewide monitoring program to track PFAS levels in the environment and in fish and wildlife, such as the PFAS Strategic Roadmap released by U.S. EPA in 2021 could be proposed. This could help identify problem areas and inform future policy decisions.

The high levels of PFAS detected in some fish samples suggest that there may be health risks associated with consuming certain types of fish. Guidance and advisories for fish consumption are important to inform the public on the potential risks to provide guidance on safe levels of consumption. It may be beneficial to conduct education and outreach programs to inform the public about the risks associated with PFAS exposure and the potential health effects of consuming contaminated fish. This could also help raise awareness on the importance of safe methods for disposing PFAS-containing products. Overall, the goal should be to minimize the amount of PFAS that enters the environment and to mitigate the health risks associated with exposure to these chemicals. By working together to develop and implement effective policies and strategies, we can protect the health and well-being of both current and future generations.

4. Conclusions

The widespread use of household and unregulated industrial practices, as well as fire training activities could generally result in the widespread distribution of PFAS. These chemicals are persistent in the environment, accumulate not only in fish, and pose a threat to human health. The levels of PFAS in almost all fish species tested at all locations in this study were high enough to warrant fish consumption advisories based on the Illinois PFAS RfD. Our study indicates that the presence of these compounds in fish may have an impact on human health based on accumulation. Given the numerous potential sources of PFAS in Illinois, further studies are warranted to comprehensively evaluate the occurrence and sources of PFAS throughout the state. Such additional information is crucial to better understand the distribution and potential risks of these compounds to the environment.

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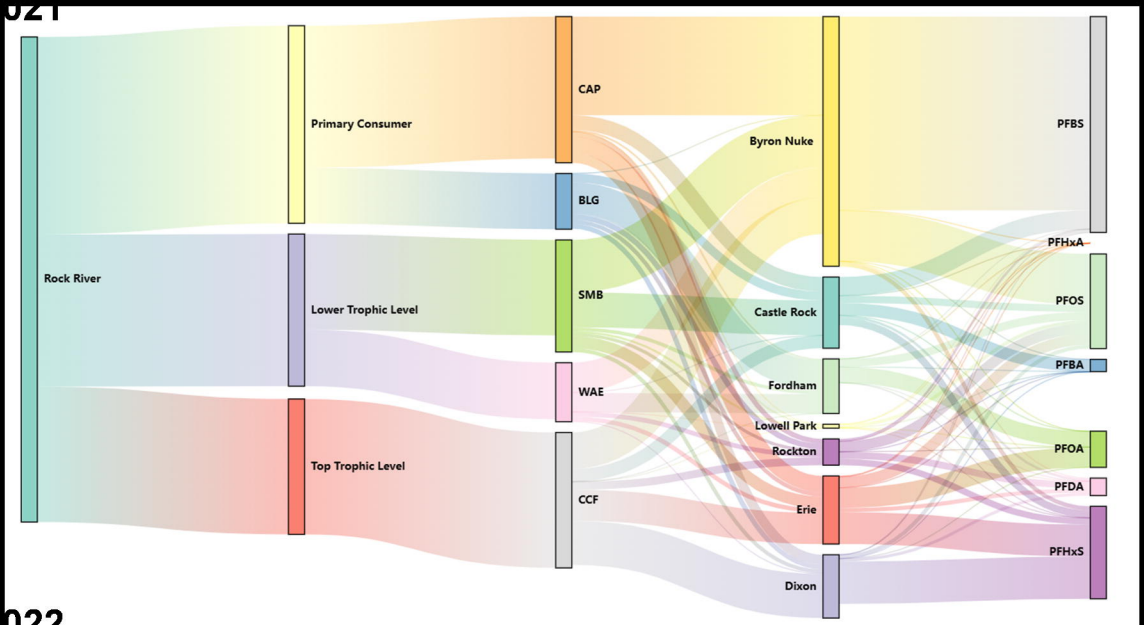
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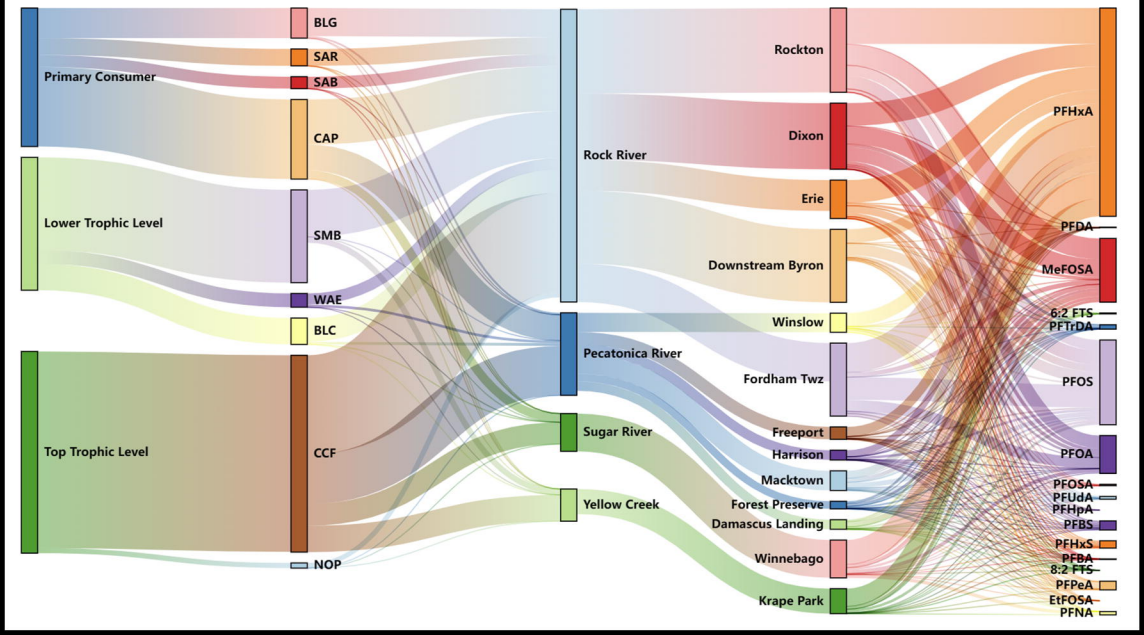
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