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# Spatial and seasonal changes in levels of perfluoroalkyl acids (PFAAs) in surface water and sediment from a typical paper-making area in Vietnam

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# Abstract

Perfluoroalkyl acids (PFAAs) have been increasingly reported in the aquatic environment but integrated evidence linking their occurrence in surface water and sediment in potential source areas for paper-making activities remains limited. This study reported the levels, spatial and seasonal changes of selected PFAAs in surface water (n = 40) and sediment (n = 25) from Phong Khe, the largest paper-recycling area in Vietnam. PFAA compounds with carbon number ≤ 8, which showed the highest detection frequencies in both seasons, also exhibited the highest concentrations in surface water. Concentrations of PFOS in more than 70% of surface water samples exceeded the environmental quality standard of the European Union. Total PFAA concentrations measured in sediments in Phong Khe during the dry season ranged from 0.03 to 6.32 ng/g, with a mean of 1.73 ng/g and a median of 0.88 ng/g. The results showed a spatially consistent change in levels of PFAAs with increasing distance from the discharge sources, following the order: drainage channels > Ngu Huyen Khe River > Cau River. In contrast to surface water, sediment samples exhibited higher detection frequencies and greater relative contributions from long-chain PFAAs than from short-chain homologues. Although ecological risks were generally within acceptable thresholds, some sensitive species, such as *Chironomus plumosus*, still showed low to moderate risk. Source apportionment using PCA suggested seasonal differences in the sources and controlling factors of PFAAs in surface water.


# 1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a large group of fluorinated aliphatic substances, widely referred to as “forever chemicals” due to their exceptional persistence in the natural environment. These substances are characterized by both hydrophobic and oleophobic properties, together with high thermal and chemical stability attributable to the presence of the strong C-F bond in their molecular structures (Buck et al., 2011). Owing to these unique properties, PFASs have been extensively used for more than 60 years across a wide range of industrial and consumer applications, including water-repellent textiles, firefighting foams, non-stick cookware, and particularly paper-based packaging and paper manufacturing processes (Gaines, 2023; Lindstrom et al., 2011). Among the diverse PFAS family, perfluoroalkyl acids (PFAAs) are of particular interest as an important subgroup, as they are often regarded as the most stable and persistent terminal transformation and degradation products formed from a wide range of other PFAS precursors in the environment (Li et al., 2022).

Based on their functional groups, PFAAs are commonly classified into two major groups: perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) (Hua et al., 2021; Lindstrom et al., 2011). Their widespread release and persistence in the environment have raised great concerns of ecosystems and human health. Previous studies reported that the adverse human health effects associated with PFAA exposure include: immunotoxicity (reduced vaccine antibody response, asthma), cardiovascular effects (hypertension), carcinogenicity (including breast, liver, testicular, and kidney cancers), hepatotoxicity (alterations in serum enzymes/bilirubin and elevated cholesterol), endocrine disruption (thyroid disease), reproductive toxicity (reduced fertility), and developmental toxicity (decreased birth weight) (Radke et al., 2022; Jiaxin Zhang et al., 2025; Di Nisio et al., 2019; Fenton et al., 2021; Manojkumar et al., 2023). Consequently, perfluorooctane sulfonic acid (PFOS) and its salts were listed as persistent organic pollutants (POPs) in Annex B of the Stockholm Convention in 2009, then perfluorooctanoic acid (PFOA) and perfluorohexane sulfonic acid (PFHxS) were added to Annex A in 2019 and 2022, respectively (UNEP, 2009; 2019; 2022). The phase-out of long-chain (legacy) PFAAs has driven a shift toward the use of short-chain alternatives (e.g., PFBA and PFBS) and other emerging substitutes (e.g., HFPO-DA/GenX and F-53B) (Zhang et al., 2020). However, these replacement compounds are also being increasingly detected in the environment. In parallel, many countries worldwide have issued regulations to control the occurrence of PFAAs in

the environment and in public drinking-water supplies. For example, the United States finalized a new national drinking water regulation in 2024 that set Maximum Contaminant Levels (MCLs) of 4 ng/L for PFOA and PFOS, and 10 ng/L for PFNA, PFHxS, and HFPO-DA (GenX), reflecting government efforts toward low allowable concentrations (EPA, 2024).

Aquatic environments are considered as major reservoirs for PFAAs, with surface water playing a critical role in transporting them from land emission sources to the ocean. Additionally, sediment also strongly influences how PFAAs move and persist in water bodies, they do not only serve as natural sinks that accumulate contaminants particularly long-chain PFAAs but also act as potential secondary sources that can release pollutants back into the aqueous phase (Prevedouros et al., 2006; Shang et al., 2023). The partitioning behavior of PFAAs between water and sediment is influenced by many factors like carbon-chain length, salinity, and organic carbon content (Higgins et al., 2005; Ahrens et al., 2016; Hua et al., 2021). Therefore, comprehensive investigation of PFAAs in surface water and sediment is essential for assessing contamination levels and ecological risks since benthic organisms and aquatic biota can bioaccumulate these substances from sediments, thus allowing their transfer through food webs and eventually posing threats to human health.

Industrial and traditional craft-village production are potential sources for PFAA emissions, but they remain insufficiently investigated in many developing countries. The rapid development and expansion of production scale in some craft villages in Vietnam in recent years have led to serious environmental pollution issues. The Phong Khe paper-making area in Bac Ninh is a typical example. This is the largest paper-making area in Vietnam, providing a variety of paper products for the domestic market. Although there has been a centralized wastewater treatment plant here, many production facilities, in an effort to reduce costs, intentionally discharged untreated wastewater directly into the environment, causing severe pollution in the surrounding area, including the Ngu Huyen Khe and Cau River (Phung et al., 2025). Notably, in the paper production industry, PFAAs have been commonly used to improve the water- and oil-repellent properties of paper (Hoang et al., 2023). Due to their high-water solubility and low volatility, the aquatic environment has been the primary reservoir of PFAAs. Consequently, surface water and sediment were susceptible to contamination by PFAAs. Notably, data about occurrence of PFAAs in environmental compartments in potential sources like paper-making production in Vietnam has not been comprehensively reported before. Therefore, this study aims to investigate the profiles and contamination levels of PFAAs in the environment, explore spatial and seasonal changes in levels of PFAAs in surface water and sediment in this study area, and assess ecological risks to living organisms.

## 2. Materials and methods

# 2.1. Study area

It was the fact that many production facilities in Phong Khe still deliberately discharged untreated effluent directly into drainage channels. The drainage channels conveyed the wastewater straight to the Ngu Huyen Khe River, the primary receiving water body for the area's discharges. The Ngu Huyen Khe River is a tributary of the Duong River; it flows through Bac Ninh Province and ultimately empties into the Cau River. A total of sixty-five environmental samples were taken in dry season and rainy season. Forty surface water samples (Fig. 1) were collected, including six samples from the Cau River (PK.SW.01 to PK.SW.06), nine samples from the Ngu Huyen Khe River (PK.SW.07 to PK.SW.15), and five samples from the drainage channels in the Phong Khe area (PK.SW.16 to PK.SW.20) in both dry (April) and rainy season (September) in 2020. The samples were collected using a scoop and transferred into 1.5 L polyethylene terephthalate bottles, which had been cleaned and rinsed with methanol. The samples were then

stored in a cooler with dry ice and transported to the laboratory. Twenty-five sediment samples were taken from the same locations as the surface water sampling points. The samples were collected using a scoop, wrapped in aluminum foil, stored in a cooler with dry ice, and transported to the laboratory. Due to the water level of sampling points, the number of sediment samples in dry season and rainy season was different.

## 2.2. Chemicals

The standards of seventeen PFAAs, including perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA), perfluorooctadecanoic acid (PFODA), potasium salts of perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS), and perfluorodecane sulfonate (PFDS) were purchased from Wellington Laboratories (Ontario, Canada). $^{13}C$- or $^{18}O$-labeled PFAAs were used as surrogates (MPFAC-MXA) were Wellington Laboratories (Ontario, Canada). Methanol, acetic acid (≥ 99%), ammonia solution (25%), ammonium acetate (≥ 97%), and sodium hydroxide were purchased from Sigma-Aldrich (St Louis, MO, USA). Oasis WAX solid phase extraction cartridges were purchased from Waters (225 mg, MA, USA). Water for sample preparation was obtained from a Milli-Q system (Millipore, Milford, MA, USA).

## 2.3. Sample preparation

The sample treatment for surface water was conducted in accordance with ISO 21675:2019 (ISO, 2019), with minor modifications. Surface water samples were filtered using 0.45 μm glass fibre filters (GF/C, Whatman) and spiked with 25 μL of 100 μg/L of surrogates containing isotopically labelled PFAAs. The SPE was performed using an Oasis WAX cartridge. The cartridge was preconditioned with 4 mL of 0.1% ammonium hydroxide in methanol, 4 mL of methanol, and 4 mL of deionized water. After loading the sample at one drop per second speed, the cartridge was washed with 4 mL of 25 mM ammonium acetate buffer at pH 4. The target PFAAs were eluted with 4 mL of methanol, followed by a sequence of 4 mL of 0.1% ammonium hydroxide in methanol. The eluent was then concentrated to 1 mL under a gentle nitrogen stream, passed through 0.2 μm nylon filters, and stored at 4$^{o}$C before instrumental analysis.

For sediment samples, the sample treatment was conducted following the method described in (Higgins et al., 2005) with minor modifications. Briefly, 5 g of wet sediment sample was weighed into a 50 mL polypropylene (PP). Then, 25 μL of a 100 ng/mL surrogate solution, and 20 mL of methanol were added into the sample tube. Next, the tube was shaked thoroughly using a vortex mixer for one minute, sonicated for 15 minutes at 60°C, and centrifuged at 1500 rpm for five minutes. The supernatant was transfered into another PP centrifuge tube. The extraction process was repeated three times. The combined extracts were concentrated using a rotary evaporator to 5 mL, then deionized water was added to obtain a concentration containing of 20% v/v methanol in deionized water. The SPE procedure for the solution of sediment extract was the same as that described for the water sample.

## 2.4. Instrumental analysis

The target PFAAs were analyzed by a liquid chromatography–tandem mass spectrometry system (LC-MS/MS 8040, Shimadzu, Japan) operated under electrospray negative ionisation (ESI) mode. Separation of PFAAs was performed on a Poroshell 120, EC-C18 (2.1 mm I.D. × 150 mm L, 2.7 μm; Agilent Technologies, USA) with the mobile phases consisting of solvent A: 2 mmol/L ammonium acetate in methanol (9:1, v/v), and solvent B:

methanol at a flow rate of 0.25 mL min. A gradient program was given as follows: 50% B for 2 minutes, continuously increased to 95% B in 16 minutes, held for 4 minutes, and then decreased to 50% B for 3 minutes. MRM parameters of analytes were presented in Table S1 in the Supplementary Information.

## 2.5. Calculation of Partition Coefficients

In this study, the sediment - water partition coffecients was typically used to investigate the behavior of PFAAs in their splitting in both dissolved and solid stages (Hua et al., 2021). The equation is as followed:

$K_d = \frac{C_{sediment}}{C_{water}}$

Where $C_{sediment}$ and $C_{water}$ are the concentrations of individual PFAAs in the sediment and surface water (ng/g and ng/L), respectively. $LogK_d$ was commonly used to reflect the distribution between different phases, larger $logK_d$ indicates that the compound tends to adhere to the sediment.

## 2.5. Ecological assessment

In this study, the ecological risk quotient (RQ) was evaluated based on the ratio of the Measured Environmental Concentration (MEC) to the Predicted No-Effect Concentration (PNEC) (Wang et al., 2025), as described in Eq. (1). The lowest PNEC value was used for calculations for each species:

$RQ = \frac{\mathrm{MEC}}{\mathrm{PNEC}}$ (1)

Three levels of risk were assessed based on the RQ value, which include: no risk when RQ < 0.01, low risk when RQ is between 0.01 and 0.1, medium risk when RQ is between 0.1 and 1, and high risk when RQ > 1. Additionally, the PNEC value is determined through an assessment factor (AF) using the following equation:

$PNEC = \frac{\mathrm{NOEC\ or\ EC50}}{\mathrm{AF}}$ (2)

Where NOEC is No Observed Effect Concentration, and EC50 is half maximal Effective Concentration.

## 2.6. Quality assurance and quality control (QA/QC)

Quantification was performed using an internal standard calibration curve of six calibration points in the concentration range from 0.5 ng/mL to 20 ng/mL. For quality control and assurance, the procedural blanks and matrix spikes were analyzed after every 10 samples to control the possible loss of each PFAA and background contamination, and no contamination was found in the procedural blanks. The detection limit and quantification limit of the device were determined as the concentrations for signal-to-noise ratios of 3 and 10, respectively. The quantification limits of the method (MQLs) of PFAAs were 0.06–0.66 ng/L for surface water, and 0.01–0.06 ng/g for sediment samples. Recoveries of surrogates ranged of 87% to 112% and 80% to 121% in water samples and sediment samples, respectively. Target compounds with recoveries below 70% were not reported.

Table 1
Detected frequency (DF - %), concentration levels, medians and means (ng/L) of PFAAs in surface water in two seasons

| No | Compounds | Dry season | | | | | Rainy season | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | DF (%) | Min | Max | Median | Mean | DF (%) | Min | Max | Median | Mean |
| 1 | PFHxA | 100 | 0.45 | 15.93 | 3.65 | 4.59 | 85 | < MQL | 12.23 | 1.97 | 3.47 |
| 2 | PFHpA | 90 | < MQL | 1.86 | 0.26 | 0.51 | 80 | < MQL | 4.81 | 1.10 | 1.59 |
| 3 | PFOA | 100 | 0.24 | 16.25 | 3.20 | 4.40 | 85 | < MQL | 13.34 | 2.40 | 3.89 |
| 4 | PFNA | 100 | 0.14 | 3.32 | 1.08 | 1.20 | 15 | < MQL | 3.34 | < MQL | 0.31 |
| 5 | PFDA | 0 | < MQL | < MQL | < MQL | < MQL | 30 | < MQL | 2.76 | < MQL | 0.37 |
| 6 | PFUnDA | 10 | < MQL | 0.77 | < MQL | 0.07 | 10 | < MQL | 2.07 | < MQL | 0.15 |
| 7 | PFDoDA | 20 | < MQL | 0.41 | < MQL | 0.06 | 30 | < MQL | 4.00 | < MQL | 0.84 |
| 8 | PFTrDA | 0 | < MQL | < MQL | < MQL | < MQL | 5 | < MQL | 0.62 | < MQL | 0.03 |
| 9 | PFTeDA | 10 | < MQL | 0.66 | < MQL | 0.05 | 20 | < MQL | 2.97 | < MQL | 0.37 |
| 10 | PFHxS | 85 | < MQL | 6.30 | 3.09 | 3.12 | 70 | < MQL | 12.96 | 0.52 | 2.77 |
| 11 | PFOS | 100 | 0.79 | 3.64 | 2.13 | 2.07 | 85 | < MQL | 3.21 | 1.72 | 1.65 |
| 12 | PFDS | 40 | < MQL | 63.54 | < MQL | 6.72 | 5 | < MQL | 0.62 | < MQL | 0.03 |
| | **Sum PFAAs** | | **2.32** | **88.38** | **15.98** | **22.77** | | | **50.13** | **8.35** | **15.47** |
| | **Sum PFCAs** | | **1.51** | **37.12** | **8.82** | **10.88** | | | **39.65** | **5.56** | **11.02** |
| | **Sum PFSAs** | | **0.81** | **73.23** | **6.05** | **11.89** | | | **15.18** | **2.78** | **4.45** |

## 2.7. Data analysis

All concentration calculations in the study were performed using Microsoft Excel 365 (Microsoft, USA). In addition, statistical analyses including Shapiro-Wilk, Pearson, ANOVA, and PCA were conducted using SPSS software (version 27.0, IBM, USA).

## 3. Results and discussion

## 3.1. Spatial and seasonal changes in levels of PFAAs in surface water

### 3.1.1. Detection frequencies and concentrations of PFAAs in surface water

The detection frequency (%), concentration range, median, and mean (ng/L) of PFAAs in surface water for the two seasons are presented in Table 1. Concentrations of PFAA compounds in surface water (ng/L) were shown in Table S2 in the Supplementary Information. Overall, C6 – C8 PFAAs were the most frequently detected compounds in surface water collected in Phong Khe, and their detection frequencies in the dry season were higher than those in the rainy season. PFHxA, PFOA, and PFOS exhibited the highest detection frequencies in both seasons and were detected in all surface water samples collected during the dry season. The next most frequently detected compounds were PFHpA (85.0%) and PFHxS (77.5%). Notably, PFNA was detected in all surface water samples in dry season; however, it was found in only 15% of samples in rainy season, resulting in an overall detection frequency of 57.5% in both seasons. Other compounds exhibited detection frequencies below 50%, with PFTrDA being the lowest (2.5%), followed by PFUnDA (10.0%), PFDA and PFTeDA (15.0%), PFDS (22.5%), and PFDoDA (25.0%).

PFAA compounds with carbon number ≤ 8, which showed the highest detection frequencies in both seasons, also exhibited the highest concentrations in surface water. Specifically, the mean concentration of PFOA across the two seasons was 4.14 ng/L (median: 2.58 ng/L; concentration range: < MQL – 16.25 ng/L), followed by PFHxA (mean: 4.03 ng/L; median: 2.05 ng/L; range: < MQL – 15.93 ng/L), PFHxS (mean: 2.94 ng/L; median: 1.27 ng/L; range: < MQL – 12.96 ng/L), PFOS (mean: 1.86 ng/L; median: 2.01 ng/L; range: < MQL – 3.64 ng/L), and PFHpA (mean: 1.05 ng/L; median: 0.76 ng/L; range: < MQL – 4.81 ng/L). Overall, short-chain PFAAs were detected in surface water in Phong Khe area with higher detection frequencies and concentrations than long-chain PFAAs (≥ C9). This

result is reasonable and consistent with variations in the aqueous solubility of PFAAs. Long-chain PFAAs have substantially lower solubility than short-chain compounds; they more readily precipitate with metal cations in solution and tend to accumulate primarily in sediment (Buck et al., 2011). For compounds with the same carbon number, PFCAs generally occurred at higher frequencies and higher concentrations than PFSAs, except for PFDS, as discussed above. This is because PFSAs have higher soil organic carbon – water partition coefficients ($K_{oc}$) than PFCAs, indicating that PFSAs tend to be more strongly sorbed to soils and sediments (Arslan and Gamal El-Din, 2021), whereas PFCAs are more likely to remain in the aqueous phase.

### 3.1.2. Spatial changes in levels of PFAAs in surface water

The results showed that PFAA concentrations measured in surface water samples collected from drainage channel were also higher than those in the Ngu Huyen Khe River and the Cau River (Fig. 2). This finding was consistent with the spatial arrangement of the sampling locations relative to the craft village: the drainage channels received wastewater directly from the production area of Phong Khe, followed by the Ngu Huyen Khe River, while the Cau River was located farthest from the discharge sources. Considering both seasons, the median of total PFAA concentration in surface water collected in the drainage channels was 41.69 ng/L (mean: 45.12 ng/L; range: 22.18–88.38 ng/L), whereas the median values for the Ngu Huyen Khe River and the Cau River were 9.39 ng/L (mean: 15.30 ng/L; range: 6.72–49.02 ng/L) and 2.41 ng/L (mean: 3.18 ng/L; range: < MQL – 9.42 ng/L), respectively. The sampling point PK.SW.17 showed an abnormally high total PFAA concentration (88.38 ng/L) in a

dry-season sample collected from a drainage channel near the centralized paper-production area. Notably, the concentration of PFDS reached 63.54 ng/L, suggesting that a site-specific source influencing dry-season wastewater at this location may be associated with PFDS.

A Kruskal–Wallis H test was used to evaluate differences in total PFAA concentrations among three sampling locations: the Cau River (n = 12), the Ngu Huyen Khe River (n = 18), and drainage channels (n = 10). The results indicated that differences in total PFAA concentrations were statistically significant for all pairwise comparisons (Cau River - drainage channels: $p < 0.001$; Cau River – Ngu Huyen Khe River: $p = 0.009$; and Ngu Huyen Khe River – drainage channels: $p = 0.010$). Similar statistically significant differences ($p < 0.05$) were also observed for total PFCAs and total PFSAs in drainage channel samples compared with those from the Ngu Huyen Khe and Cau rivers.

When examining the spatial variation of individual contaminants by sampling sites, the five PFAAs with detection frequencies > 50% in both seasons (PFHxA, PFHpA, PFOA, PFHxS, and PFOS) consistently exhibited concentrations in the following order: drainage channels > Ngu Huyen Khe River > Cau River (Fig. 3). Differences in the concentrations of these compounds between samples from the Cau River and the other two locations were statistically significant ($p < 0.05$), except for PFHpA (Cau River – drainage channels: $p = 0.080$) and PFHxS (Cau River – Ngu Huyen Khe River: $p = 0.207$). In contrast, with the exception of PFHpA ($p = 0.016$) and PFHxS ($p = 0.002$), differences between the Ngu Huyen Khe River and drainage channel groups were not statistically significant ($p > 0.05$). These results further confirm the influence of paper-production activities on the occurrence of PFAAs in surface water within the study area.

In this study, the total concentrations of PFAAs in surface water in the Phong Khe area ranged from < MQL – 88.38 ng/L (mean: 19.12 ng/L; median: 9.33 ng/L), which is higher than those previously reported for surface water in several craft villages in northern Viet Nam (range: 0.83–58.2 ng/L; mean: 10.68 ng/L; median: 12.40 ng/L) (Vi et al., 2015). In addition, the total PFAA concentrations in the Ngu Huyen Khe River were higher than those reported for surface water from major river systems in Viet Nam, including the Red, Dong Nai, Sai Gon, Mekong, Ma, Da Rang, Cai, and Quan Truong rivers (Lam et al., 2017; Duong et al., 2015), as well as the Day River (Phung et al., 2022). These findings suggest that paper recycling activities represent a PFAA emission source of concern, and that the Ngu Huyen Khe River, which is directly impacted by these discharges, exhibits elevated PFAA contamination.

In general, the total PFAA concentrations observed here were substantially lower than those reported for surface water in several river basins worldwide. Markedly higher surface-water PFAA concentrations have been reported in areas adjacent to industrial chemical manufacturing facilities, such as Changsu, China (7.0–489 ng/L) (Chen et al., 2016) and the Yuqiao River, China (5.8–120.9 ng/L) (Cao et al., 2019). Notably, the concentrations of compounds that are restricted (PFOS) and phased out (PFOA and PFHxS) under the Stockholm Convention in this study were far lower than those reported for certain hotspots elsewhere. The highest PFOA concentration reported in surface water from the Xiaoqing River, China (near an industrial zone) reached 320,000 ng/L (Joerss et al., 2020); concentrations in the Keya River, Taiwan (near an industrial zone) and the Nanmen River, Taiwan were 717 ng/L and 517.3 ng/L, respectively (Angela et al., 2010); and the Yodo River, Japan reached 2,600 ng/L (Lien et al., 2008) - all far exceeding the PFOA levels in this study (maximum: 16.25 ng/L). The maximum PFOS concentration in this study (3.64 ng/L) was comparable to PFOS concentrations reported for the Yuqiao River (5.54 ng/L) (Cao et al., 2019) and the Xiaoqing River (5.3 ng/L) (Joerss et al., 2020) in China, as well as the Ganges River (3.91 ng/L) (Yeung et al., 2009) in India; however, it was much lower than those reported for the Keya River (4,330 ng/L) and the Nanmen River (6,050 ng/L) in Taiwan (Angela et al., 2010), and the Yodo River (123 ng/L) in Japan (Lien et al.,

2008). Similarly, PFHxS concentrations in this study were lower than those reported in other studies worldwide. When compared with the European Union (EU) environmental quality standard for PFOS in surface water (0.65 ng/L), all dry-season samples exceeded this threshold, with 15 out of 20 samples exceeding it by more than twofold while 14 out of 20 samples in the rainy season also exceeded the EU standard. This indicates potential risks to the aquatic organisms, highlighting the need for ecological risk assessments.

## 3.1.3. Seasonal changes of PFAS levels in surface water

When assessing the effect of time (dry and rainy season) on the status of PFAA contamination in surface water in the Phong Khe area using the Wilcoxon signed-rank test, total PFAA concentrations in dry-season samples (mean: 22.77 ng/L; median: 15.98 ng/L) were significantly higher ($p = 0.028$) than those measured in rainy-season samples (mean: 15.47 ng/L; median: 8.349 ng/L) (Fig. 4). This difference was driven primarily by markedly higher total PFSA concentrations in dry-season samples (mean: 11.89 ng/L; median: 6.05 ng/L) compared with rainy-season samples (mean: 4.45 ng/L; median: 2.78 ng/L; $p = 0.012$), whereas the seasonal difference in total PFCA concentrations (means: 10.88 and 11.02 ng/L; medians: 8.82 and 5.56 ng/L for the dry and rainy seasons, respectively) was not statistically significant ($p = 0.236$).

When stratifying the data by sampling sites, no statistically significant seasonal differences were observed in total PFAA concentrations ($p > 0.05$) for samples from the Cau River or wastewater ditches between the dry season (means: 4.12 and 48.35 ng/L; medians: 3.10 and 41.32 ng/L, respectively) and the rainy season (means: 2.24 and 41.89 ng/L; medians: 1.21 and 42.05 ng/L, respectively). In contrast, total PFAA concentrations in the Ngu Huyen Khe River were significantly higher in the dry season (mean: 21.00 ng/L; median: 16.77 ng/L) than in the rainy season (mean: 9.61 ng/L; median: 8.04 ng/L; $p = 0.008$). The Ngu Huyen Khe River sites also exhibited statistically significant seasonal differences in both total PFCA ($p = 0.039$) and total PFSA ($p = 0.008$), with higher concentrations in the dry season (means: 14.11 and 6.89 ng/L; medians: 11.63 and 6.77 ng/L, respectively) compared with the rainy season (means: 6.95 and 2.66 ng/L; medians: 5.54 and 2.67 ng/L, respectively). By contrast, no significant seasonal differences ($p > 0.05$) in total PFCA or total PFSA were found for the Cau River samples. For wastewater-ditch samples, although total PFSA did not differ significantly between seasons ($p = 0.225$), total PFCA in the dry season (mean: 15.14 ng/L; median: 15.14 ng/L) was significantly lower ($p = 0.043$) than in the rainy season (mean: 29.85 ng/L; median: 28.38 ng/L).

These patterns indicate that the Ngu Huyen Khe River has hydrological characteristics that are different from those of the Cau River. The mean flow rate of the Ngu Huyen Khe River during the dry season (0.51 $m^3/s$) and rainy season (8.67 $m^3/s$) was significantly lower than the corresponding values for the Cau River (115.4 $m^3/s$ and 210.2 $m^3/s$). This difference can be explained by different catchment scales and hydrological regimes of the two rivers. Under low flow conditions, the Ngu Huyen Khe River had limited dilution capacity, resulting in generally higher contaminant concentrations in the dry season when discharge declined sharply. During the rainy season, however, rapid increases in flow could considerably alter contaminant levels due to more dilution and dispersion. In contrast, the Cau River, with larger and more stable flows, had greater capacity to dilute and disperse contaminants, and thus concentrations tend to show less significant seasonal variability. In general, these results suggest that atmospheric deposition (via rainfall) may exert a stronger influence on small-flow surface-water systems such as wastewater drainage channels and the Ngu Huyen Khe River, while its influence is likely less pronounced in larger water bodies such as the Cau River.

## 3.2. Spatial and seasonal changes in levels of PFAAs in sediment

# 3.2.1. Spatial changes in levels of PFAAs in sediment

Concentrations of PFAA compounds in sediment (ng/g) were presented in Table S3 in the Supplementary Information. Among PFAAs analyzed in sediment, detection frequencies ranged from 0% to 92%, clearly reflecting differences of these compounds in physicochemical properties and solid-phase sorption potential. Overall, short-chain PFCAs such as PFHxA, PFOA, and PFHpA were detected at very low frequencies (16%, 8%, and 4%, respectively), while PFNA was not detected in any sample. This pattern was likely attributable to the relatively high aqueous solubility and weak affinity of short-chain PFCAs for solid phases, resulting in preferential partitioning to the water column rather than accumulation in sediments (Higgins et al., 2005). In contrast, long-chain PFCAs, including PFDA, PFUnDA, PFDoDA, PFTrDA, and PFTeDA, exhibited significantly higher detection frequencies. Notably, PFTeDA showed the highest detection rate within this group (92%), followed by PFTrDA (64%) and PFDA (56%). This trend is consistent with a positive relationship between carbon-chain length and sediment accumulation, driven by increased hydrophobic interactions and enhanced sorption to organic matter. Within the PFSA group, PFHxS and PFDS were detected relatively frequently (both 60%), whereas PFOS showed a lower detection frequency (44%).

Total PFAA concentrations measured in sediments from the Cau River, the Ngu Huyen Khe River, and drainage channels in the Phong Khe area during the dry season ranged from 0.03 to 6.32 ng/g, with a mean of 1.73 ng/g and a median of 0.88 ng/g. PFCAs were the predominant contributors, accounting for 71.1% of total PFAAs in sediment, with a mean concentration of 1.23 ng/g (range: 0.03–5.06 ng/g; median: 0.65 ng/g). By comparison, total PFSAs ranged from < MQL to 1.296 ng/g, with mean and median values of 0.5 and 0.32 ng/g, respectively, representing 28.9% of total PFAAs. Similar to the dry-season surface-water samples, total PFAA concentrations in sediment were lowest in the Cau River (mean: 0.46 ng/g; median: 0.43 ng/g), followed by the Ngu Huyen Khe River (mean: 2.41 ng/g; median: 0.99 ng/g) and the drainage channels (mean: 2.03 ng/g; median: 2.30 ng/g) (Fig. 5). A Kruskal–Wallis H test was applied to examine differences in total PFAA concentrations among the three sampling sites (Cau River, n = 6; Ngu Huyen Khe River, n = 9; drainage channel, n = 5). The results indicated a statistically significant difference only for the Cau River – ditch comparison ($p = 0.048$), whereas the Cau River – Ngu Huyen Khe River comparison was borderline ($p = 0.052$) and the Ngu Huyen Khe River – channel comparison was not significant ($p = 1.000$). Significant differences were also observed for total PFSA concentrations between Cau River sediments and those from the Ngu Huyen Khe River and the drainage channels ($p = 0.046$ and $p = 0.029$, respectively), while differences in total PFCA across the locations were not statistically significant ($p > 0.05$). These findings differ somewhat from the surface-water results, where differences in total PFAA and PFCA between the Cau River and Ngu Huyen Khe River were statistically significant. Such discrepancies may reflect the influence of hydrodynamic transport, non-equilibrium partitioning of PFAAs between sediments and the overlying water column, legacy accumulation, and other biogeochemical processes.

In contrast to surface water, sediment samples exhibited higher detection frequencies and greater relative contributions from long-chain PFAAs than from short-chain homologues. Across all locations, PFTeDA showed the highest detection frequency (90%), followed by PFTrDA (80%), PFDS (75%), and PFDA (65%). This pattern was consistent with partitioning behavior of sediment–water phase, as long-chain PFAAs typically exhibited stronger affinity for sediments and substantially higher distribution coefficients ($K_d$) than short-chain compounds. A similar tendency was observed when comparing PFSAs and PFCAs, with PFSAs showing higher detection frequencies than their PFCA counterparts with the same carbon number (PFHxS: 65% vs. PFHxA: 20%; PFOS: 30% vs. PFOA: 5%). On average, the combined concentration of the four frequently detected long-chain compounds (PFDA, PFTrDA, PFTeDA, and PFDS) was 1.37 ng/g, accounting for 79.5% of total PFAAs measured in sediments. Within

each group, the sum of PFDA, PFTrDA, and PFTeDA (mean: 1.11 ng/g) represented 90.7% of total PFCAs, while PFDS (mean: 0.26 ng/g) accounted for 52.2% of total PFSAs.

Concentrations of several high-frequency PFAAs detected in dry-season sediment samples from the Phong Khe area are presented in Fig. 6. Comparisons of PFDA, PFTrDA, PFHxS, and PFDS concentrations between sediments from the Ngu Huyen Khe River and the drainage channeles using the Mann–Whitney U test indicated no statistically significant differences between the two site categories ($p > 0.05$). Likewise, a Kruskal–Wallis test showed no significant differences in PFTeDA concentrations among the three sampling-site categories ($p > 0.05$).

Owing to their physicochemical properties, most PFAAs preferentially remain in the aqueous phase rather than sorb onto solids; consequently, PFAA concentrations in sediments are generally reported at relatively low levels (Nakata et al., 2006). In the present study, total PFAA concentrations in 20 dry-season sediment samples ranged from 0.034 to 6.32 ng/g (mean: 1.73 ng/g). Compared with other studies conducted in Viet Nam, these levels were higher than those reported for sediment from the Cai River and Quan Truong River (< MQL to 1.41 ng/g) (Lam et al., 2017), the Nhue and Day Rivers (0.06 − 2.6 ng/g) (Phung et al., 2022), West Lake (10 PFAAs; 0.03–0.26 ng/g), and Yen So Lake (10 PFAAs; 0.08–2.01 ng/g) (Nguyen et al., 2018). Overall, the concentrations observed in this study were comparable to those reported for the Yuqiao River sediments (0.232–1.210 ng/g) (Cao et al., 2019), the Jiulong River in China (0.24–1.9 ng/g) (Lin et al., 2022), and river/lake sediments in Korea (0.35 [0.03–1.09] ng/g) (Lam et al., 2014), but were remarkably lower than those reported for the Truckee River (1.8–183.8 ng/g) and Las Vegas Wash in the United States (3.9–134.2 ng/g) (Bai and Son, 2021), as well as the Victoria River in Kenya (1.4–99.1 ng/g) (Ssebugere et al., 2020).

## 3.2. Seasonal changes in levels of PFAAs in sediment

Because high levels and strong flow of surface water during the rainy season made river-sediment sampling technically challenging, only sediment samples from drainage channels in the Phong Khe area were collected in the rainy season. Notably, total PFAA concentrations - encompassing both total PFCAs and total PFSAs in sediment in rainy-season channel were substantially higher than those measured in sediment in dry season (Fig. 7).

Specifically, in the rainy season, total PFAAs ranged from 2.74 to 11.82 ng/g, with mean and median values of 6.06 and 3.94 ng/g, respectively. By comparison, as reported above, total PFAAs in the dry season ranged from 0.74 to 3.00 ng/g, with a mean of 2.02 ng/g and a median of 2.32 ng/g. A Wilcoxon signed-rank test indicated that the seasonal difference in total PFAAs in channel sediments was statistically significant ($p = 0.043$). This pattern was primarily driven by PFCAs, which contributed the majority to total PFAAs (63.7% in the dry season and 88.2% in the rainy season). Consistently, paired t-test results showed that total PFCA concentrations in sediment in rainy season were significantly higher than those in sediment in dry season ($p = 0.036$). In contrast, the seasonal difference in total PFSAs was not statistically significant, with mean concentrations of 0.73 ng/g in the dry season and 0.72 ng/g in the rainy season ($p = 0.500$).

When examining individual PFAAs in sediment collected from the drainage channels across seasons, the overall increase in total PFAAs was largely attributable to PFDoDA. This compound was detected infrequently and at low levels in the dry season (2/6 samples; < MQL – 0.18 ng/g), whereas it was detected in 100% of rainy-season sediment samples at markedly higher concentrations (2.22–8.81 ng/g; mean: 3.90 ng/g). This observation was consistent with the seasonal variation of PFDoDA in surface water, where both detection frequency and concentration in the drainage channel in rainy season (100% and 2.87 ng/L) were far higher than in the dry season

(40% and 0.08 ng/L). Collectively, these results suggested a substantial contribution from a PFDoDA - rich emission source that became apparent only during the rainy season in the study area.

## 3.3. Partition water – sediment

The distribution coefficient between the aqueous phase and sediment ($logK_d$) is an important parameter for evaluating the adsorptive affinity of PFAAs in aquatic environments. In this study, $logK_d$ values of PFAAs were determined at various sampling sites. The results showed that $logK_d$ ranged from 0.56 to 3.97, indicating considerable variability in phase partitioning among compounds. Carbon chain length exhibited a clear influence on $logK_d$. The $logK_d$ values of short-chain PFAAs such as PFHxA (0.56–2.04) and PFHpA (1.79–2.51) were markedly lower than those of PFUnDA (2.04–3.97) and PFTeDA (1.91–3.23). Similarly, the $logK_d$ of PFHxS was lower than that of PFOS. These findings showed the trend of increasing hydrophobicity and adsorption with increasing carbon chain length. However, several exceptions were observed in several samples. For example, the $logK_d$ of PFOS in some samples exceeded that of PFDS, or the $logK_d$ of PFUnDA was higher than that of PFDoDA and PFTeDA. This indicates the influence of functional groups and steric hindrance. When the PFAA chain becomes excessively long, steric effects may limit access to small and narrow adsorption sites within sedimentary organic matter, some of which are more suitable for capturing smaller molecules. The combined effects of steric hindrance and hydrophobic interactions likely account for these exceptions (Kuroda et al., 2014). The variations in $logK_d$ across samples suggested that adsorption was not driven by a single mechanism, but rather by the complex interplay of multiple factors, including sediment composition, organic carbon content, pH, salinity, and PFAA molecular structure (Hepburn et al., 2019).

Regarding functional groups, PFSAs (e.g., PFOS, PFDS, PFHxS) generally exhibited stronger adsorption than PFCAs with the same carbon number. This was attributed to the larger size, higher polarity, and stronger binding affinity of sulfonate groups to mineral surfaces and sedimentary organic matter, resulting in increased interactions with the sediment phase. These findings are consistent with (Ahrens et al., 2011), who reported higher log $K_d$ values for PFOS than for PFOA in sediments, further demonstrating the preferential accumulation of PFSAs compared to PFCAs.

When comparing $logK_d$ values of samples collected from drainage channels in two seasons, higher values were observed during the rainy season, particularly for long-chain PFAAs such as PFTeDA, PFDS, and PFOS. This difference can be explained by the relatively stable concentrations of these compounds in sediments across seasons, while concentrations in surface water were higher during the dry season than the rainy season.

## 3.4. Ecological risk assessment

In this study, acute toxicity values (LC50 and EC50) and chronic toxicity thresholds (NOEC/LOEC) for PFAAs were compiled from previous studies and are presented in Table S4 of Supplementary Information. Ecological risk assessment was not determined for PFAAs in sediment because of its limited number of samples in rainy seasons. Due to low detection frequencies or limited toxicity data, ecological risk quotient (RQ) values in surface water were not calculated for PFTrDA, PFTeDA, PFHxS, and PFDS. The calculated RQ values for PFAAs in surface water across all sampling sites in the Phong Khe area (Cau River, Ngu Huyen Khe River, and drainage channels) are summarized in Table 2. The ecological risk assessment results indicated that most values fell within the acceptable threshold for aquatic organism groups, as indicated by the green color coding in the dataset.

For PFHxA, PFHpA, and PFOS; RQ values at all sampling groups during both dry and rainy seasons were below 0.01, suggesting negligible risk to the evaluated aquatic species, including the zooplankton *Daphnia magna*, *Moina macrocopa*, *Moina micrura*, and *Brachionus calyciflorus*. However, certain compounds such as PFOA, PFNA, PFDA, and PFUnDA began to exceed ecological safety thresholds for some sensitive species, as indicated by orange-coded cells corresponding to low-to-moderate risk levels. Notably, *Chironomus plumosus* consistently exhibited low to moderate risk levels (RQ = 0.02–0.1) for PFOA in the Ngu Huyen Khe River and drainage canal during both seasons; low risk levels (RQ = 0.01–0.02) for PFNA were observed in the Cau River and Ngu Huyen Khe River during the dry season, and in the drainage canal during both seasons. PFDA and PFUnDA in the drainage canal during the rainy season also posed low ecological risk to *Chironomus plumosus*. Additionally, PFOA in the Ngu Huyen Khe River (dry season) and in the drainage channel (both seasons) demonstrated low risk potential for the crustacean *Moina micrura*. The present study further indicated low ecological risk posed by PFUnDA to *Cyprinus carpio* at all sites except the Cau River during the dry season.

**Table 2: Risk quotient (RQ) values of PFAA compounds for aquatic organisms**

| Compounds | Species | Cau River | | Ngu Huyen Khe River | | Drainage channel | |
|---|---|---|---|---|---|---|---|
| | | Dry season | Rainy season | Dry season | Rainy season | Dry season | Rainy season |
| PFHxA | *Daphnia magna* | $7.9 \times 10^{-7}$ | $5.99 \times 10^{-7}$ | $4.88 \times 10^{-6}$ | $1.92 \times 10^{-6}$ | $7.3 \times 10^{-6}$ | $8.04 \times 10^{-6}$ |
| | *Brachionus calyciflorus* | $5.91 \times 10^{-6}$ | $4.49 \times 10^{-6}$ | $3.66 \times 10^{-5}$ | $1.44 \times 10^{-5}$ | $5.47 \times 10^{-5}$ | $6.02 \times 10^{-5}$ |
| PFHpA | *Daphnia magna* | $3.43 \times 10^{-7}$ | $2.99 \times 10^{-7}$ | $8.92 \times 10^{-7}$ | $1 \times 10^{-6}$ | $1.53 \times 10^{-7}$ | $3.67 \times 10^{-6}$ |
| PFOA | *Brachionus calyciflorus* | $6.95 \times 10^{-4}$ | $5.09 \times 10^{-4}$ | $5.99 \times 10^{-3}$ | $1.77 \times 10^{-5}$ | $3.05 \times 10^{-3}$ | $7.55 \times 10^{-3}$ |
| | *Chironomus plumosus* | $8.87 \times 10^{-3}$ | $6.49 \times 10^{-3}$ | 0.08 | 0.02 | 0.04 | 0.1 |
| | *Chydorus sphaericus* | $4.94 \times 10^{-6}$ | $3.61 \times 10^{-6}$ | $4.25 \times 10^{-5}$ | $1.26 \times 10^{-5}$ | $2.17 \times 10^{-5}$ | $5.36 \times 10^{-5}$ |
| | *Cipangopaludina cathayensis* | $1.17 \times 10^{-6}$ | $8.59 \times 10^{-7}$ | $1.01 \times 10^{-5}$ | $3 \times 10^{-6}$ | $5.15 \times 10^{-6}$ | $1.27 \times 10^{-5}$ |
| | *Cyclops sp.* | $1.24 \times 10^{-6}$ | $9.08 \times 10^{-7}$ | $1.07 \times 10^{-5}$ | $3.17 \times 10^{-6}$ | $5.45 \times 10^{-6}$ | $1.35 \times 10^{-5}$ |
| | *Limnodrilus hoffmeisteri* | $1.53 \times 10^{-6}$ | $1.12 \times 10^{-6}$ | $1.32 \times 10^{-5}$ | $3.9 \times 10^{-6}$ | $6.72 \times 10^{-6}$ | $1.66 \times 10^{-5}$ |
| | *Macrobrachium nipponense* | $2.37 \times 10^{-6}$ | $1.73 \times 10^{-6}$ | $2.04 \times 10^{-5}$ | $6.04 \times 10^{-6}$ | $1.04 \times 10^{-5}$ | $2.57 \times 10^{-5}$ |
| | *Moina macrocopa* | $4.37 \times 10^{-6}$ | $3.2 \times 10^{-6}$ | $3.76 \times 10^{-5}$ | $1.11 \times 10^{-5}$ | $1.92 \times 10^{-5}$ | $4.74 \times 10^{-5}$ |
| | *Moina micrura* | $1.83 \times 10^{-3}$ | $1.34 \times 10^{-3}$ | 0.02 | $4.67 \times 10^{-3}$ | 0.01 | 0.02 |
| | *Neocaridina denticulata* | $1.54 \times 10^{-6}$ | $1.13 \times 10^{-6}$ | $1.33 \times 10^{-5}$ | $3.93 \times 10^{-6}$ | $6.76 \times 10^{-6}$ | $1.67 \times 10^{-5}$ |
| | *Cyprinus carpio* | $4.35 \times 10^{-5}$ | $3.18 \times 10^{-5}$ | $3.74 \times 10^{-4}$ | $1.11 \times 10^{-4}$ | $1.91 \times 10^{-4}$ | $4.72 \times 10^{-4}$ |
| PFNA | *Daphnia magna* | $3 \times 10^{-3}$ | | $4.17 \times 10^{-3}$ | $2.79 \times 10^{-4}$ | $3.34 \times 10^{-3}$ | $2.59 \times 10^{-3}$ |
| | *Chironomus plumosus* | 0.01 | | 0.02 | $1.16 \times 10^{-3}$ | 0.01 | 0.01 |
| | *Chydorus sphaericus* | $4.32 \times 10^{-5}$ | | $6 \times 10^{-5}$ | $4.01 \times 10^{-6}$ | $4.81 \times 10^{-5}$ | $3.72 \times 10^{-5}$ |
| PFDA | *Daphnia magna* | | $2.71 \times 10^{-7}$ | | $2.78 \times 10^{-7}$ | | $1.46 \times 10^{-6}$ |
| | *Chironomus plumosus* | | $2.15 \times 10^{-3}$ | | $2.21 \times 10^{-3}$ | | 0.01 |
| | *Chydorus sphaericus* | | $5.09 \times 10^{-6}$ | | $5.22 \times 10^{-6}$ | | $2.74 \times 10^{-6}$ |
| PFUnDA | *Daphnia magna* | | $1.16 \times 10^{-7}$ | $2.18 \times 10^{-7}$ | $8.71 \times 10^{-8}$ | $4.46 \times 10^{-7}$ | $8.94 \times 10^{-7}$ |
| | *Chironomus plumosus* | | $6.99 \times 10^{-4}$ | $1.31 \times 10^{-3}$ | $5.24 \times 10^{-4}$ | $2.69 \times 10^{-3}$ | 0.01 |
| | *Chydorus sphaericus* | | $1.15 \times 10^{-5}$ | $2.16 \times 10^{-5}$ | $8.64 \times 10^{-6}$ | $4.43 \times 10^{-5}$ | $8.88 \times 10^{-5}$ |
| | *Cyprinus carpio* | | 0.01 | 0.01 | 0.01 | 0.03 | 0.05 |
| PFOS | *Moina macrocopa* | $5.47 \times 10^{-5}$ | $3.88 \times 10^{-5}$ | $1.42 \times 10^{-3}$ | $1.28 \times 10^{-4}$ | $1.4 \times 10^{-4}$ | $9.99 \times 10^{-5}$ |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | *Moina micrura* | $1.79 \times 10^{-3}$ | $1.27 \times 10^{-3}$ | $4.63 \times 10^{-3}$ | $4.19 \times 10^{-4}$ | $4.57 \times 10^{-3}$ | $3.26 \times 10^{-3}$ |
| | *Daphnia magna* | $4.2 \times 10^{-5}$ | $2.98 \times 10^{-5}$ | $1.09 \times 10^{-4}$ | $9.84 \times 10^{-5}$ | $1.07 \times 10^{-4}$ | $7.66 \times 10^{-5}$ |
| | *Brachionus calyciflorus* | $1.59 \times 10^{-5}$ | $1.13 \times 10^{-5}$ | $4.12 \times 10^{-5}$ | $3.73 \times 10^{-5}$ | $4.07 \times 10^{-5}$ | $2.9 \times 10^{-5}$ |

**Note:** No risk; Low risk; Moderate risk

Among the three sampling locations, RQ values > 0.01 were most frequently detected in the drainage canal during both dry and rainy seasons, particularly for *Chironomus plumosus* (PFOA, PFNA, PFDA, and PFUnDA), *Moina micrura* (PFOA), and *Cyprinus carpio* (PFUnDA). This pattern indicated greater risk in shallow, stagnant water bodies because PFAAs can accumulate more easily and the reservoir has limited capacity to dilute them across seasons. The Ngu Huyen Khe River ranked second, exhibiting low risk levels for sensitive aquatic organisms but at lower frequencies. In contrast, the Cau River - located farther from pollution sources - showed minimal ecological risk associated with PFAAs. A study by (Lin et al., 2022) reported that PFHxA, PFOA, PFNA, and PFOS posed negligible ecological risk to aquatic organisms in Dongshan Bay, China. In the Yellow River (China), PFBA, PFPeA, PFHxA, and PFHpA did not pose ecological risk, whereas PFOA exhibited high risk to *Chironomus plumosus* (RQ = 1.96) and *Chironomus riparius* (RQ = 1.96). Several studies have also reported low ecological risks of PFBA, PFPeA, PFOA, and PFBS to coastal ecosystems in southern China (Qi Wang et al., 2019).

# 3.5. Source Apportionment of PFAAs

Principal Component Analysis (PCA) is a simple, effective, and widely used multivariate statistical tool for reducing dataset complexity and identifying latent variables. In this study, PCA was employed to examine the relationships between PFAA concentrations and surface water sample groups collected from the Phong Khe area during both the rainy and dry seasons. Additionally, source apportionment of PFAAs in sediment was not determined due to its limited number of samples in rainy seasons.

Among the 40 analyzed surface water samples, long-chain PFAAs with carbon chain lengths > 9 (including PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, and PFDS) were detected at a frequency below 50%. Therefore, the dataset used for PCA comprised five compounds: PFHxA, PFHpA, PFOA, PFHxS, and PFOS. Five principal components were initially determined using PCA with varimax rotation, with the first two components explaining 83.8% of the total variance in the dataset. Specifically, PC1 included PFHxS and three PFCAs (PFHxA, PFHpA, and PFOA), accounting for 66.0% of the total variance. In contrast, PC2 comprised PFHxA and PFOS, explaining 17.8% of the total variance. The eigenvalues of PC1 and PC2 were 3.285 and 0.903, respectively. Together with the scree plot, these results indicated that retaining two principal components was appropriate.

For PC1, PFHpA exerted the strongest influence, with a loading coefficient of 0.912, while PFHxS and PFOA showed comparable contributions, with loadings of 0.818 and 0.812, respectively. For PC2, PFOS had the dominant influence, with a loading of 0.951, whereas PFHxA exhibited a moderate loading of 0.512. The two-dimensional score plot shown in Fig. 8 reveals relatively distinct clustering patterns among surface water samples from different sampling groups. While no clear seasonal separation was observed for Cau River samples, Ngu Huyen Khe River samples were distributed across both sides of PC2, and drainage canal samples were separated along PC1. These patterns suggested seasonal differences in the sources and/or controlling factors of PFAAs in surface water.

## Conclusions

Paper-making activities were identified as a potential source of PFAA contamination to the aquatic environment. Levels and fates of PFAAs were driven by characteristics of discharge, carbon-chain length and hydrology: short-chain PFAAs (C ≤ 8) dominated surface water, whereas long-chain PFAAs preferentially accumulated in sediments, consistent with increasing $\log K_d$ with carbon-chain length. Seasonally, surface-water concentrations were higher in the dry season (dilution-driven), while sediment burdens in drainage channels increased in the rainy season due to high levels of PFDoDA. Although overall ecological risk was generally acceptable, PFOS exceedances of the EU EQS and PFOA/PFNA-related risks to sensitive species highlighted the need for stricter wastewater control, sediment management, and PFAA-specific monitoring and regulation in craft villages in developing countries like Vietnam.

## Declarations

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**Author contributions** All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Thi Vi Phung, Thuy Ngoc Nguyen, Thanh Dam Nguyen, Hung Viet Pham, Dinh Quang Phan, Huu Tuyen Le, Hong Anh Duong. The first draft of the manuscript was written by Thi Vi Phung and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

**Data availability** Data is provided within the supplementary information file.

**Competing interests** The authors declare that they have no competing interests.

**Ethics approval** This is an observational study for which no ethical approval is required.

**Consent to participate** Not applicable.

**Consent for publication** All authors agreed to the publication and approved the final version.

**Informed consent** Samples of human beings or animals were not used for this study. Instead, the experiments were conducted on soil samples, and hence no consent statement is needed for this study.

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## Figures

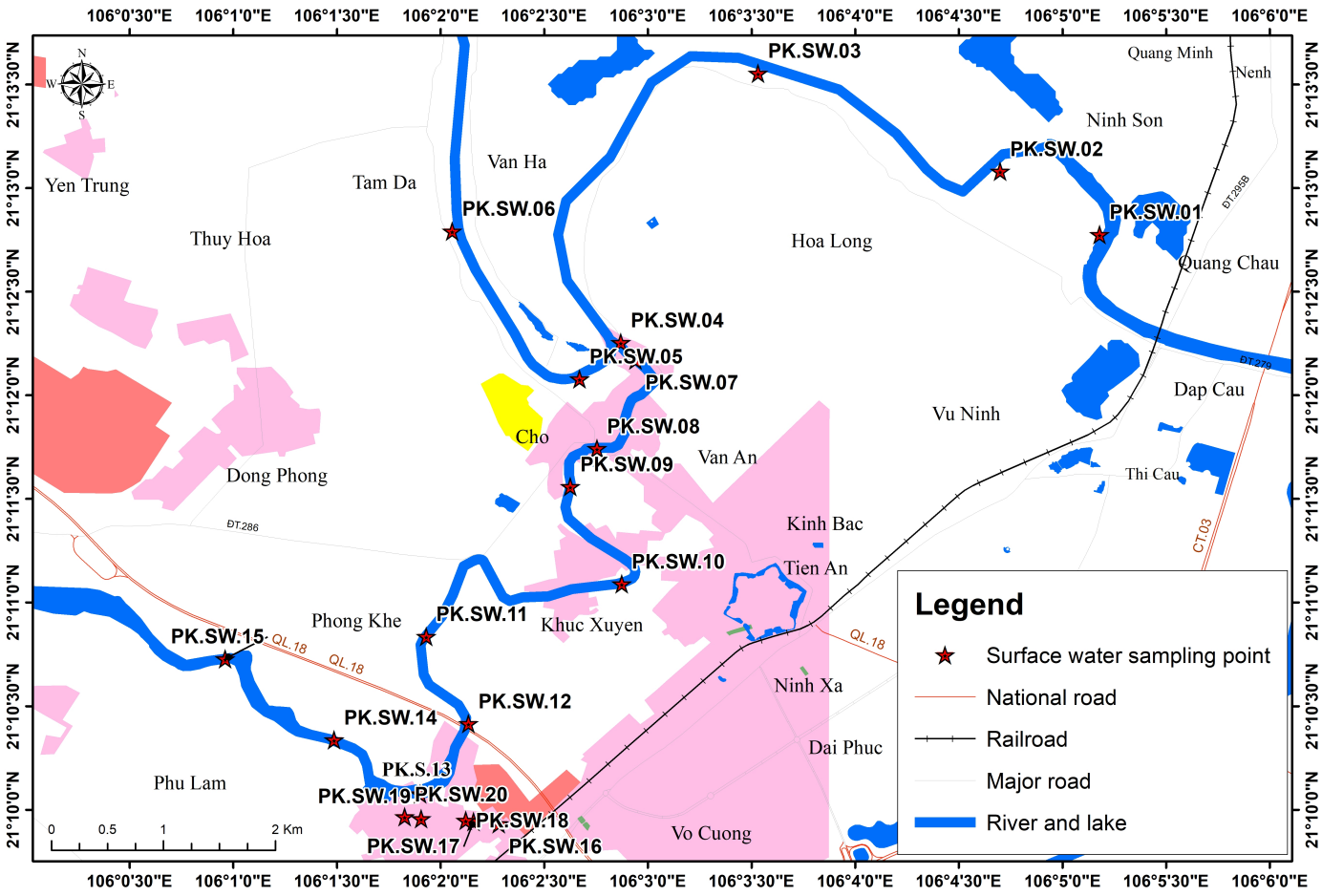



**Figure 1**

**Sampling points of surface water and sediment samples**

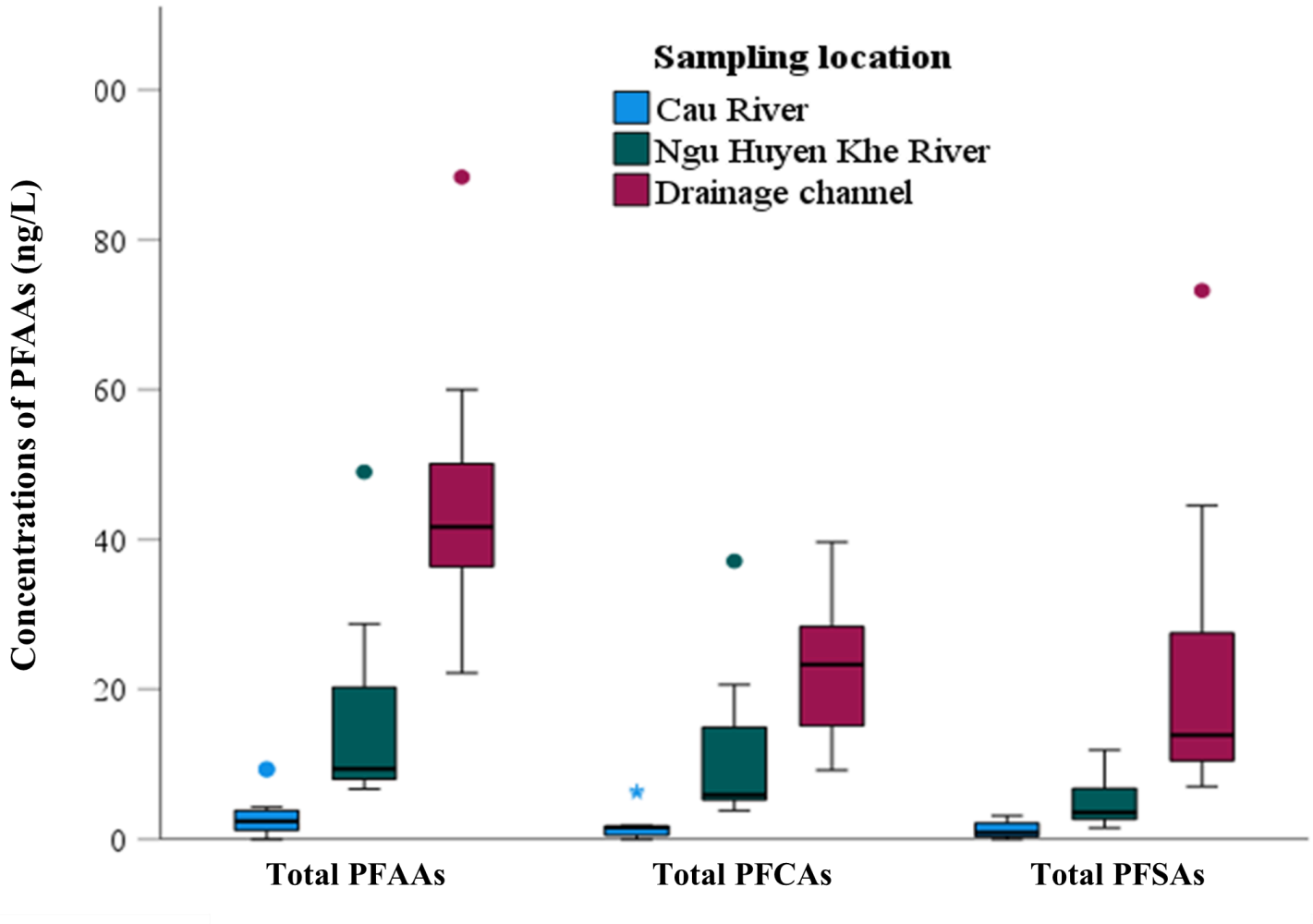



Figure 2

**Comparison of total PFAA, PFCA, and PFSA concentrations in surface water in both seasons among different sampling locations in the study area**

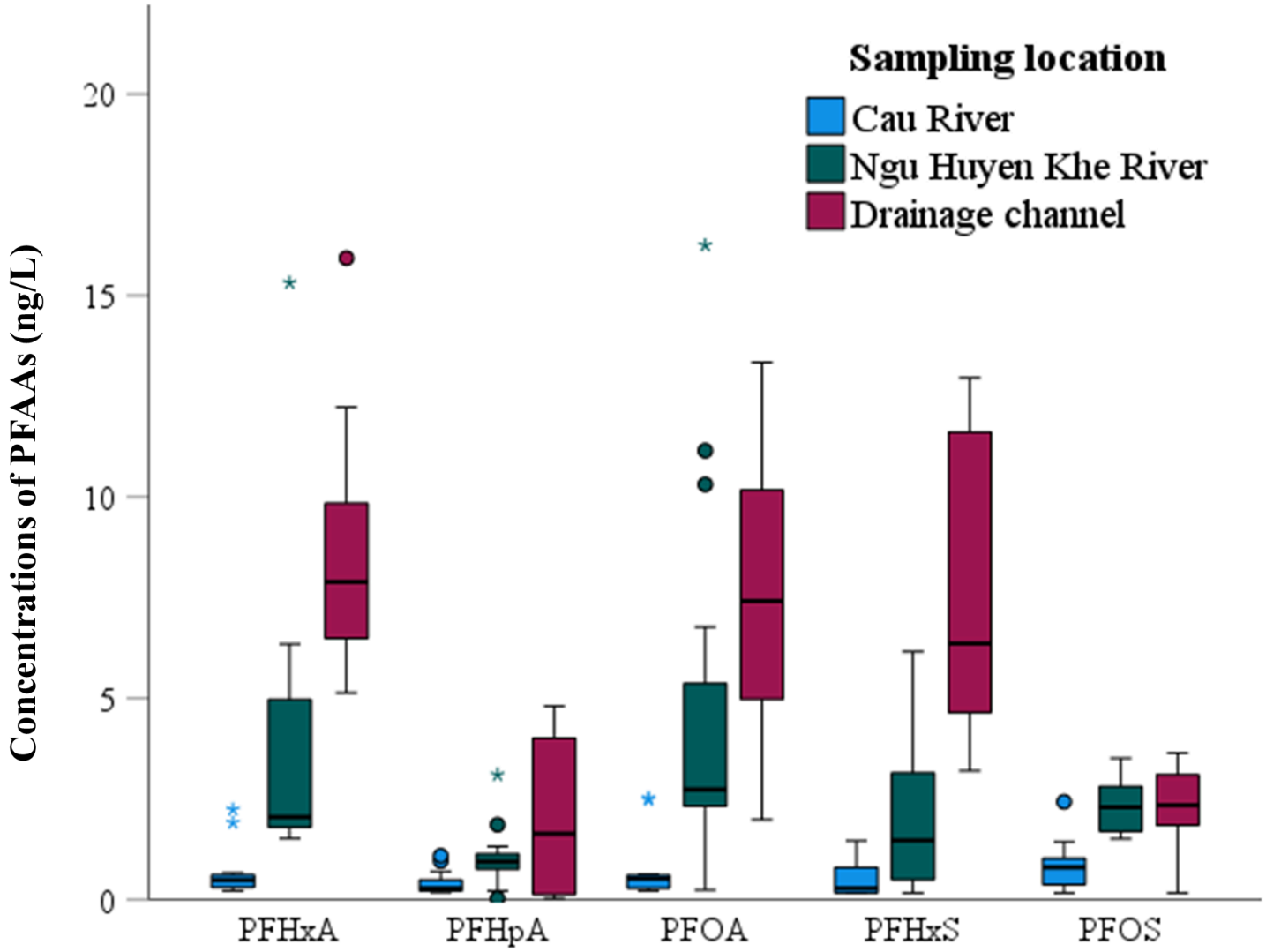



Figure 3

**Concentrations of the five major PFAAs in surface water across different sampling locations in the study area**

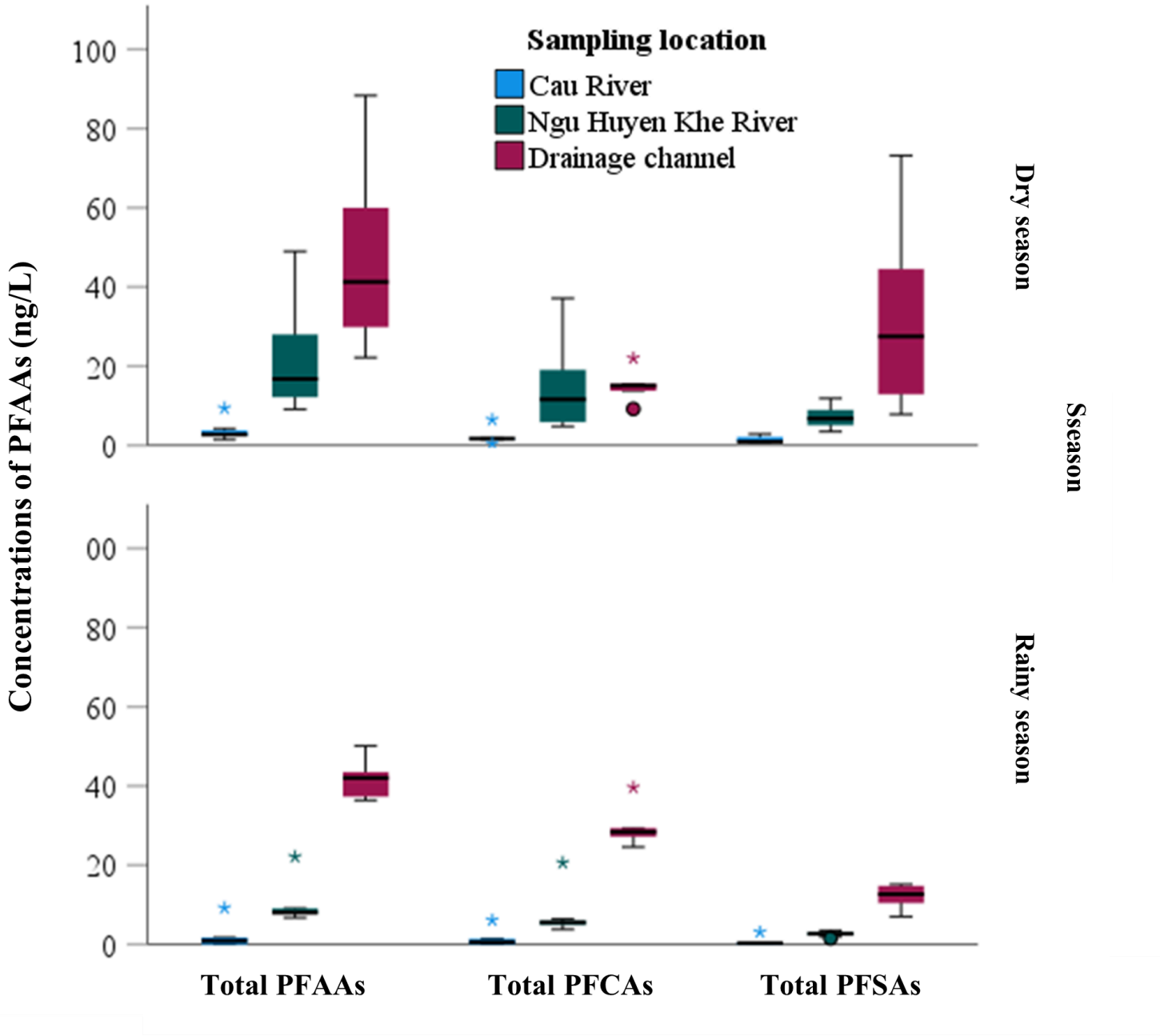



Figure 4

**Total concentrations of PFAAs, PFCAs, and PFSAs in surface water across the study area by sampling locations and seasons**

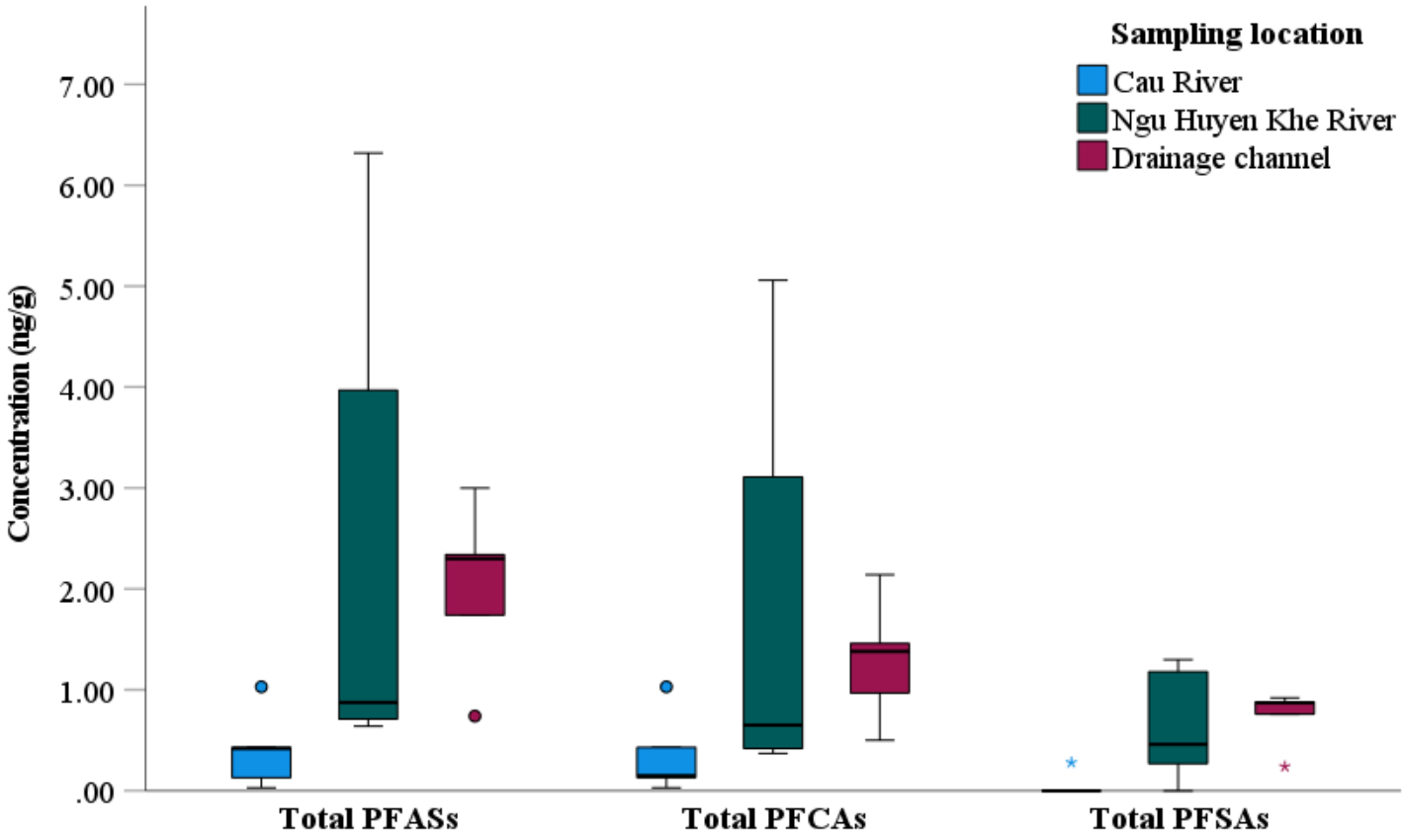



Figure 5

**Total concentrations of PFAAs, PFCAs, and PFSAs in sediment samples collected during the dry season in the Phong Khe area**

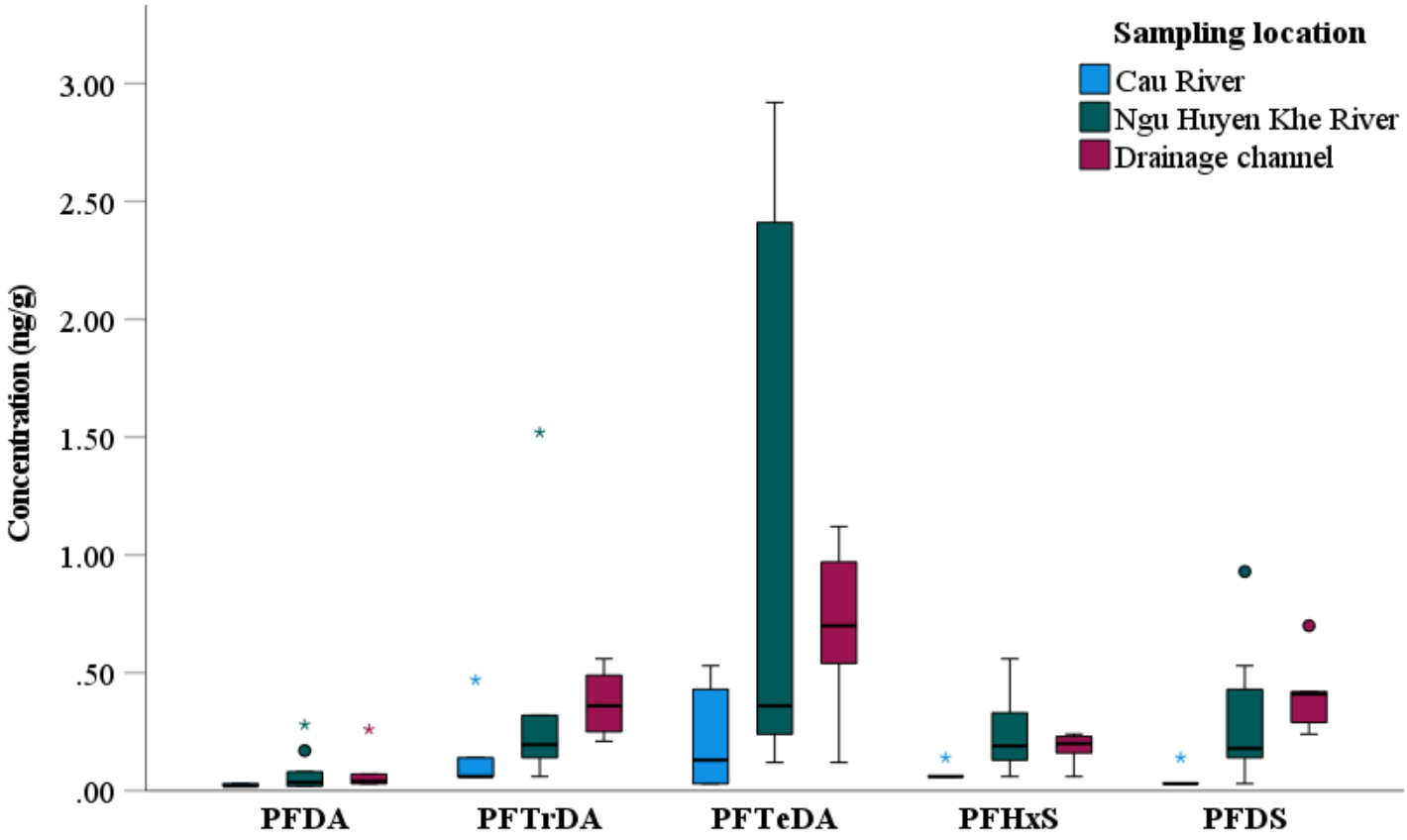



Figure 6

**Concentrations of selected frequently detected PFAAs in sediment samples collected during the dry season in the Phong Khe area**

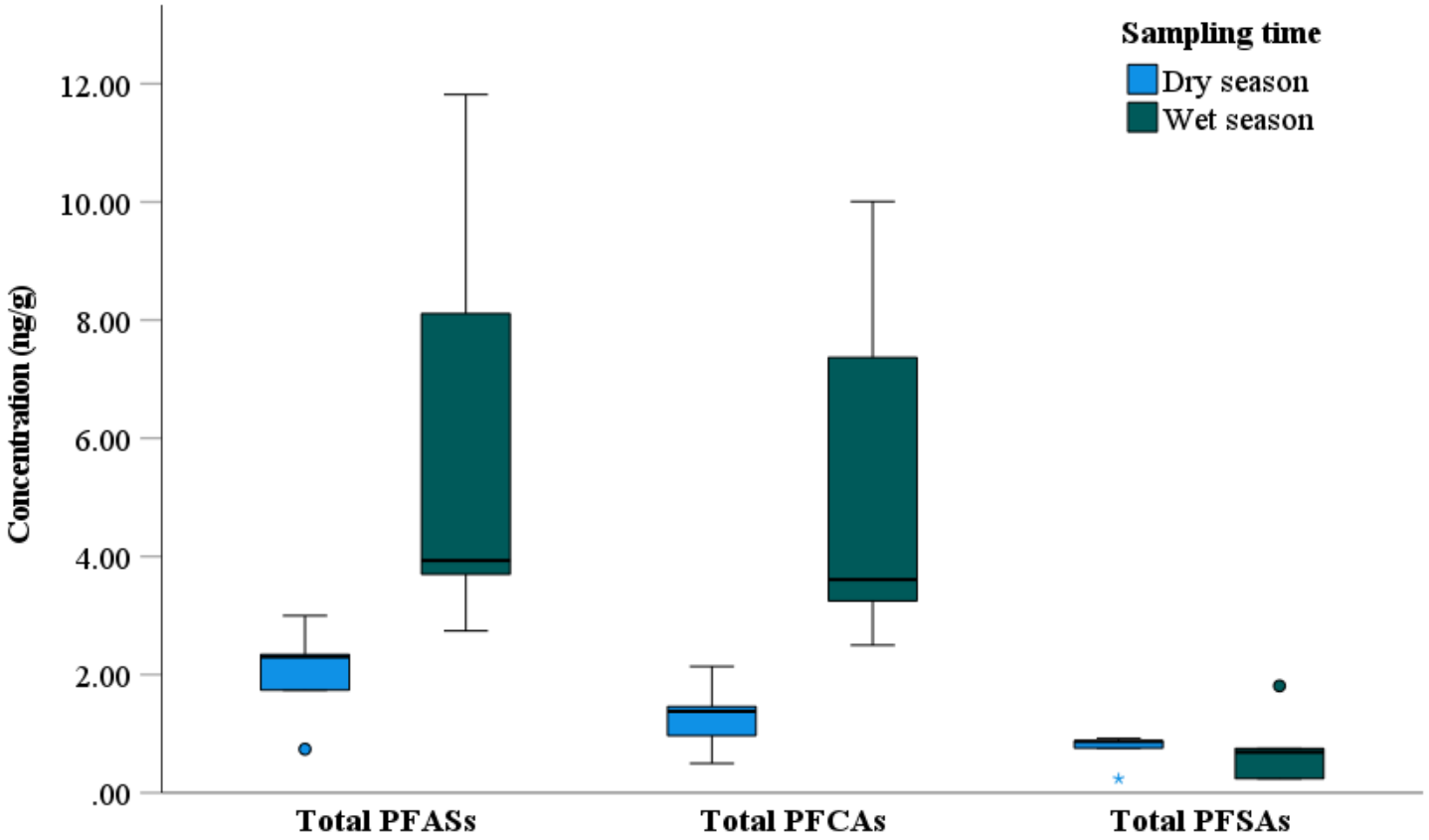



Figure 7

**Seasonal variation in total concentrations of PFAAs, PFCAs, and PFSAs in sediment samples collected from the drainage channels in the study area**

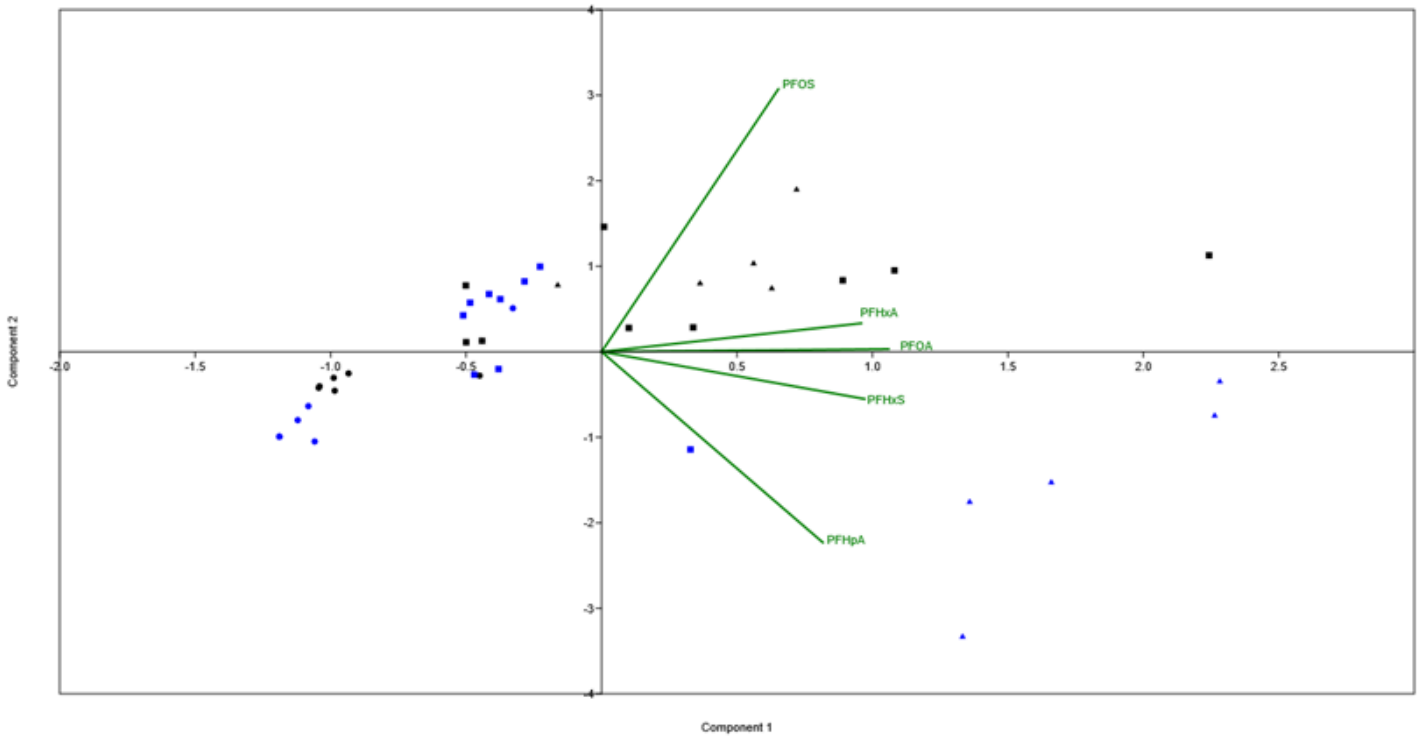



Figure 8

**PCA results for PFAAs in two seasons (circles represent Cau River samples, squares represent drainage channel samples, and triangles represent Ngu Huyen Khe River samples; black symbols indicate the dry season and blue symbols indicate the rainy season)**

## Supplementary Files

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- SupplementaryInformation.docx