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Levels, profiles and distribution of perfluoroakyl substances in groundwater in Bac Ninh province, Viet Nam

Phung Thi Vi[1], Nguyen Thuy Ngoc[2], Nguyen Thanh Dam[1], Pham Hung Viet[1], Duong Hong Anh[1, 2, *]

[1]*Key Laboratory of Analytical Technology for Environment Quality and Food Safety Control (KLATEFOS), University of Science, Vietnam National University, 334 Nguyen Trai, Thanh Xuan, Ha Noi, Viet Nam*

[2]*Research Centre for Environmental Technology and Sustainable Development (CETASD), University of Science, Vietnam National University, 334 Nguyen Trai, Thanh Xuan, Ha Noi, Viet Nam*

[*]Emails: duonghonganh@hus.edu.vn

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Abstract. Paper-making is one of the potential sources of per- and polyfluoroalkyl substances (PFASs) contamination in groundwater. In this study, 12 PFASs in groundwater were analyzed during the dry season (n = 18) and the rainy season (n = 22) in Phong Khe (Bac Ninh), the largest paper-making village in Northern Viet Nam. The results showed that the total PFAS concentrations ranged from non-detectable levels to 15.06 ng/L during the dry season and from non-detectable levels to 9.92 ng/L during the rainy season. The short-chain PFASs ($C < 9$) were more commonly detected in groundwater compared to long-chain PFASs. While perfluorohexane sulfonic acid and perfluorooctanesulfonic acid were predominant in groundwater samples during the dry season, perfluorooctanoic acid, perfluorohexanoic acid, and perfluoroheptanoic acid contributed significantly to the composition of PFASs during the rainy season. Although PFASs have not posed a health risk through groundwater consumfption, future research is needed to investigate further their levels and distribution in different environmental compartments within other potential craft villages.

Keywords: paper making village, groundwater, perfluoroalkyl substances, PFCAs, PFSAs.

Classification numbers: 3.2.1.

1. INTRODUCTION

Perfluoroalkyl substances are aliphatic substances for which hydrogen atoms attached to carbon atoms have been fully replaced with fluorine atoms [1], hereinafter referred to as PFASs. Due to their molecular structure, these compounds possess unique properties, such as both water and oil-repellent characteristics, as well as low thermal stability and surface tension [2]. Since the 1950s, the PFASs have found widespread applications in various industries, including paper production, textiles, food packaging, dyeing, consumer products, electroplating, and fire-fighting foam productionz. Through manufacturing and use, the PFASs can be released into the environment, leading to contamination of the air, soil, and water. Research over the decades has revealed the presence of PFASs in various environmental components such as surface water, drinking water, groundwater [3], air [4], sediments, and organisms [5]. Importantly, the PFASs have been linked to adverse health effects, including fetal weight, testicular cancer, kidney cancer, and thyroid dysfunction [6]. Among thousands of chemicals in the PFASs group, perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS) and perfluorohexane sulfonic acid (PFHxS), belonging to the perfluoroalkyl acids (PFAAs) subgroup, are the most extensively studied due to their toxicity and persistence in both the environment and the human body. For this reason, the PFOS, PFOA, and PFHxS were listed as persistent organic pollutants (POPs) under the Stockholm Convention in 2009, 2019, and 2022, respectively [7].

Groundwater accounts for 30 % of the world's freshwater reserves and supplies roughly one-third of the freshwater consumed by humans, and in some regions of the world, it is the only source of drinking water. The groundwater typically has a more stable composition and lower levels of chemical and biological pollution compared to surface water. However, the groundwater can also become contaminated through urban, commercial, industrial, and agricultural activities. While some contaminants can be removed from groundwater through natural processes like self-purification and filtration through the soil, highly eliminating POPs like PFASs can take many decades or even longer [8]. Notably, due to their excellent water solubility and environmental persistence, oceans, groundwater, and surface water are major reservoirs of these compounds worldwide. The presence of PFASs in wastewater affects the quality of surface and groundwater, the two primary sources of drinking water worldwide [9].

The Phong Khe paper-making village (Bac Ninh province, Viet Nam) covers an area of 12.7 hectares and hosts over 300 production facilities, mainly producing various types of paper products, including sanitary paper, poonah paper, writing paper, carton, and joss paper. Approximately 250,000 tons of paper are produced annually in this area, with an estimated wastewater flow of 130,000 m^3/year. Among these facilities, Phong Khe 1 and Phong Khe 2 industrial clusters have nearly 150 production facilities with a daily capacity of 100 tons of paper. For several years, wastewater, emissions, and solid waste from the paper-making activities in the Phong Khe paper-making village have not been adequately collected and treated, leading to severe pollution of the Ngu Huyen Khe and Cau rivers. A study by Vi *et al.* detected concentrations of eight PFASs in surface water in the Phong Khe paper-making village ranging from 7.74 to 58.2 ng/L, with an average concentration of 13.9 ng/L [10]. The research results indicate a potential risk of the PFASs contamination in other environmental components, such as sediments and groundwater.

Additionally, the high demand for groundwater use for domestic purposes by local people in this area can lead to the risk of PFASs exposure. However, there has been no research published in Viet Nam regarding the levels of the PFASs contamination in groundwater in such specific regions. Based on these practical concerns, this study aims to understand the presence, composition, and sources of PFASs in groundwater during the dry and rainy seasons in the Phong Khe paper-making village. Using the research findings, potential health risks posed by PFASs through groundwater consumption will be assessed.

2. MATERIALS AND METHODS

2.1. Reagents

A standard mixture containing 17 PFASs, including perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUdA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA), perfluorooctadecanoic acid (PFODA), potasium salts of perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), and perfluorooctane sulfonate (PFOS), was purchased from Wellington Laboratories Inc. in Canada. Additionally, a surrogate mixture containing mass-labeled (^{13}C) perfluoroalkyl carboxylic acids (PFCAs) (C6, C8, C9, C10, C11, C12) and mass-labeled (^{18}O, ^{13}C) perfluoroalkyl sulfonic acids (PFSAs) (C6, C8) was obtained from Wellington Laboratories Inc. in Canada.

Oasis WAX plus short cartridges (225 mg, 60 µm) were sourced from Waters Corp. in the USA. Furthermore, methanol, ammonium acetate (97 %), ammonium solution (25 %), and acetic acid (99.9 %) were procured from Sigma-Aldrich in the USA.

2.2. Sample collection and pretreatment

Groundwater samples were collected during the dry season and the rainy season from household wells around the Phong Khe industrial cluster in 2022 (sampling locations are shown in Figure 1).

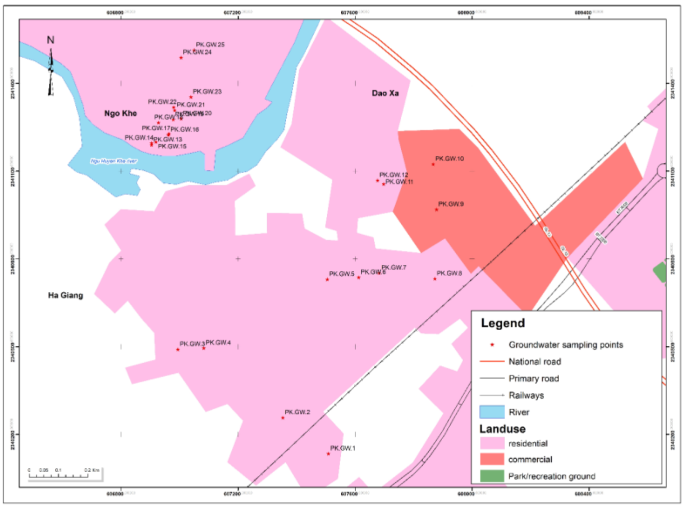

Figure 1. Sampling sites at Phong Khe paper-making village.

Due to the time of sampling, groundwater volume of wells and consent of households, the number of samples in the dry season and the rainy season were different. Eighteen groundwater samples were taken in the dry season (April), including PK.GW.01; 02; 05; 07 - 12; 14; 15; 17; 19; 22-25, and twenty-two samples were collected in the rainy season (September), including PK.GW.01-07; 09-13; 16; 17; 23; 25. Sampling points from PK.GW.01 - PK.GW.12 were taken between the southern part of the Ngu Huyen Khe River, where most production facilities are concentrated. Points from PK.GW.13 - PK.GW.25 were collected from the northern part of the river, where mainly households without paper production facilities are located. Sampling collection and storage were carried out according to TCVN 6663-11:2011 (ISO 5667-11:2009) - Water quality - Sampling - Part 11: Guidance on sampling of groundwaters [11]. Briefly, 1.5 L polyethylene terephthalate bottles were cleaned and rinsed with methanol and then used for sample collection. Groundwater samples were taken from wells with depths ranging from 30 to 70 meters. These groundwater samples were then transferred into PET bottles, stored in coolers, and transported to the laboratory.

The water sample pretreatment procedure consisted of the following steps based on ISO 25101:2009 [12] with minor modifications of the laboratory (Figure 2). Firstly, the sample was filtered through 0.45 µm glass fiber filter (Whatman, USA), and 25 µL of a 100 µg/L surrogate solution (SR) was added into 500 mL of filtered groundwater. Next, the WAX cartridge was conditioned successively with 4 mL of 0.1 % ammonia/methanol solution (v/v), 4 mL of methanol, and 4 mL of deionized water. Subsequently, 500 mL of the groundwater sample was loaded onto the cartridge at a flow rate of 2 - 3 drops/second. Then, 4 mL of 25 mmol/L acetate buffer solution (pH 4) was passed through the cartridge to remove impurities. The analytes were eluted with 4 mL of methanol and 4 mL of 0.1 % ammonia/methanol solution. The eluate was then evaporated to 1 mL using nitrogen gas and filtered through a 0.2 µm nylon filter before analysis on an LC-MS/MS instrument.

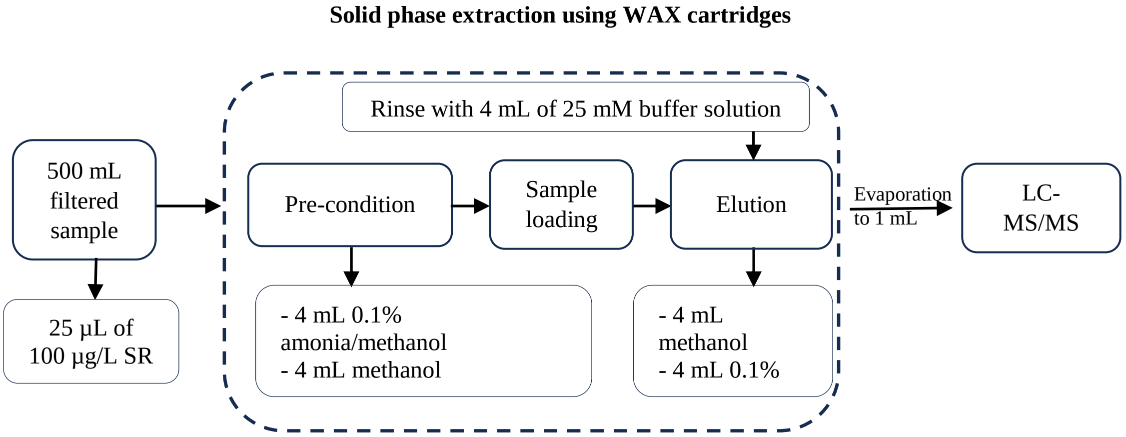

Figure 2. Scheme for pretreatment procedure of groundwater sample.

2.3. Instrumental analysis

The concentrations of PFASs in the extracts were determined using Liquid Chromatography Tandem Mass Spectrometry (LC-MS/MS 8040, Shimadzu, Japan) operating in electrospray negative ionization mode. Chromatographic separation was achieved using a Poroshell 120, EC-C18 column (2.1 mm I.D. × 150 mm L, 2.7 µm; Agilent Technologies, USA). The mobile phases consisted of 2 mmol/L ammonium acetate in methanol (9:1, v/v) (A) and methanol (B). The elution gradient was as follows: from 0 to 17 minutes, the composition of A was maintained at 50 %, then gradually decreased to 5 % A at 18 minutes, held for 4 minutes, and finally increased back to 50 % A over 5 minutes.

2.4. Quality assurance and quality control

A seven-point internal calibration curve ranging from 0.1 to 20 ng/mL of PFASs and 5 ng/mL of mass-labeled PFASs was constructed for all analytes with a linear regression coefficient of determination (R^2) > 0.997. When validating the method, the recoveries of PFAS substances spiked in real samples were calculated. The recoveries for PFASs ranged from 73 % to 114 %, except five PFASs (PFBA, PFHpA, PFHxDA, PFODA, and PFBS). These five PFASs showed low recoveries of 20 - 40 %, so the results of these compounds were not calculated. The limit of detection (LOD) and limit of quantification (LOQ) of individual analyte were determined as concentrations giving 3 and 10 times the signal-to-noise ratio (S/N), respectively. The LOD and LOQ values for PFASs in groundwater ranged from 0.04 ng/L to 0.18 ng/L and from 0.14 ng/L to 0.56 ng/L, respectively. Blank and QC samples (real samples were spiked with PFAS standards) were analyzed in each batch of samples (10 samples) to control contamination and sample loss during the sample treatment, and all blank samples were below LODs in this study.

2.5. Health risk assessment

In this study, hazard ratio (HR) was calculated to assess health risks posed to residents by PFASs through groundwater consumption. HR values greater than 1 indicate potential health risk. The equation for HR was shown as follows:

$$\text{HR} = \frac{EDI}{RfD} \tag{1}$$

where EDI: Estimated Daily Intakes (ng/kg.d), and RfD: oral reference dose (ng/kg.d). According to US Environmental Protection Agency, RfD for both PFOA and PFOS was 20 ng/(kg.d) and no RfDs were recommended for other PFASs [13]. For this reason, RfDs for PFOA and PFOS were used for PFCAs and PFSAs, respectively, in this study.

The equation for EDI was presented as below:

$$\text{EDI} = \frac{PFAS\ concentration\ \left(\frac{ng}{L}\right)\ x\ water\ daily\ consumption\ \left(\frac{L}{d}\right)}{Body\ weight\ (kg)} \tag{2}$$

Residents still use groundwater as domestic water in the study area, but the amount of groundwater directly entering the human body is difficult to determine. Therefore, to assess health risks, the amount of groundwater is calculated as the amount of drinking water consumed daily. Up to now, data on the daily intake of water by Vietnamese people has not been officially reported. To assume EDI, water daily intake and average body weight were estimated as 1.5 L and 60 kg, respectively.

3. RESULTS AND DISCUSSION

3.1. Levels of PFASs in groundwater in dry season and rainy season

Among the twelve analyzed PFASs, nine of them were detected in groundwater samples. The concentrations of these PFASs in groundwater during the rainy and dry seasons in the Phong Khe industrial cluster area are presented in Figure 3 and Figure 4. The total concentration of the 12 PFASs ranged from non-detectable to 15.06 ng/L during the dry season and from non-detectable to 9.92 ng/L during the rainy season. Although the average concentrations of PFASs were slightly higher during the dry season (average: 2.79 ng/L) compared to the rainy season (average: 2.71 ng/L), no statistically significant difference was found ($p < 0.05$). In general, the concentrations of PFCAs were higher than PFSAs, and long-chain PFCAs (C10 - C14) were almost non-detectable in both seasons. This result is consistent with findings in groundwater in rural areas of China [14].

It can be observed that PFCAs are more soluble in water than PFSAs. For example, at 25°C, PFOA (C8), which belongs to the PFCA group, has a solubility of about 9,500 mg/L, while PFOS (C8), belonging to the PFSA group, has a lower solubility of 680 mg/L, nearly 14 times less than PFOA [15]. In addition, PFSAs exhibited higher distribution coefficients (K_d)

than PFCAs, indicating that PFSAs tend to be adsorbed by sediment [16] while the PFCAs tend to be retained in water. Regarding the PFCA group, compounds with shorter carbon chain lengths are more soluble and persistent than compounds with longer carbon chains [17]. This may explain why long-chain compounds were nearly absent or found at very low concentrations in groundwater samples in the study area. Additionally, the input source of PFASs might include raw materials in production that do not contain long-chain compounds. Among the three PFSAs analyzed, including PFHxS, PFOS, and PFDS, PFDS (C10) was not detected in any groundwater samples during both the rainy and dry seasons. Samples from PK.GW.01 to PK.GW.12 (average concentration during dry season: 3.81 ng/L, rainy season: 3.83 ng/L) were collected from wells located south of the Ngu Huyen Khe River, primarily in areas with manufacturing facilities. Samples from PK.GW.13 to PK.GW.25 (average concentration during dry season: 1.52 ng/L, rainy season: 1.25 ng/L) were collected from wells located to the north, mainly in households' areas that are not involved in manufacturing activities but are influenced by manufacturing activities of paper production companies along the Ngu Huyen Khe river. According to the t-test results, there was a statistically significant difference in the total concentrations of PFASs when comparing the sample group from PK.GW.01 to PK.GW.12 and the sample group from PK.GW.13 to PK.GW.25 ($p < 0.05$).

During the dry season, the PFASs were found in all groundwater samples except for samples PK.GW.06, PK.GW.23, and PK.GW.25. The total concentration of PFSAs ranged from non-detectable to 1.57 ng/L, while the total concentration of PFCAs ranged from non-detectable to 14.3 ng/L. The highest PFASs concentration was detected in sample PK.GW.02, which was collected from the deepest well in the study (70 m) at a paper recycling facility. Groundwater samples in the Phong Khe industrial cluster area were taken from wells with depths ranging from 25 to 40 m, except for sample PK.GW.02. PFCAs were found in sample PK.GW.02 during the dry season, accounting for up to 95 % of the total PFASs concentration, indicating that this point may be influenced by a source containing PFCAs. During the rainy season, the total concentration of PFSAs ranged from non-detectable to 0.82 ng/L, and the total concentration of PFCAs ranged from non-detectable to 9.92 ng/L. Figure 4 shows that PFSAs were only detected in samples PK.GW.09 and PK.GW.11. Notably, only three PFCAs, including PFHxA, PFHpA, and PFOA, were detected in groundwater samples. No PFASs were detected in samples PK.GW.18, PK.GW.19, PK.GW.20, PK.GW.21, PK.GW.22, and PK.GW.24 during the rainy season. However, during the dry season, the PFHxS was detected in samples PK.GW.19, PK.GW.22, and PK.GW.24 at low concentrations of 0.75 ng/L, 1.7 ng/L, and 1.27 ng/L, respectively. Conversely, no PFASs were detected in samples PK.GW.06, PK.GW.23, and PK.GW.25 during the dry season, but they were found during the rainy season with total concentrations of 5.58 ng/L, 0.58 ng/L, and 3.78 ng/L, respectively.

Among the PFASs, the PFOA was detected more frequently than others in 12 out of 18 groundwater samples during the dry season and 14 out of 22 samples during the rainy season. The concentration of PFOA ranged from non-detectable to 2.74 ng/L (average: 0.89 ng/L). Compared to other studies (Table 1), the average PFOA value is three times higher than those obtained from a study conducted in two major cities in Viet Nam (Ha Noi and Ho Chi Minh City) [18] and India [19], and similar to the levels of PFOA found in groundwater in China [20], Malta [21], France [22], and Australia [23]. However, the PFOA levels are lower than those found in groundwater in the Nakdong River basin in South Korea [24], landfill sites in Thailand [25], and rural areas of China [14].

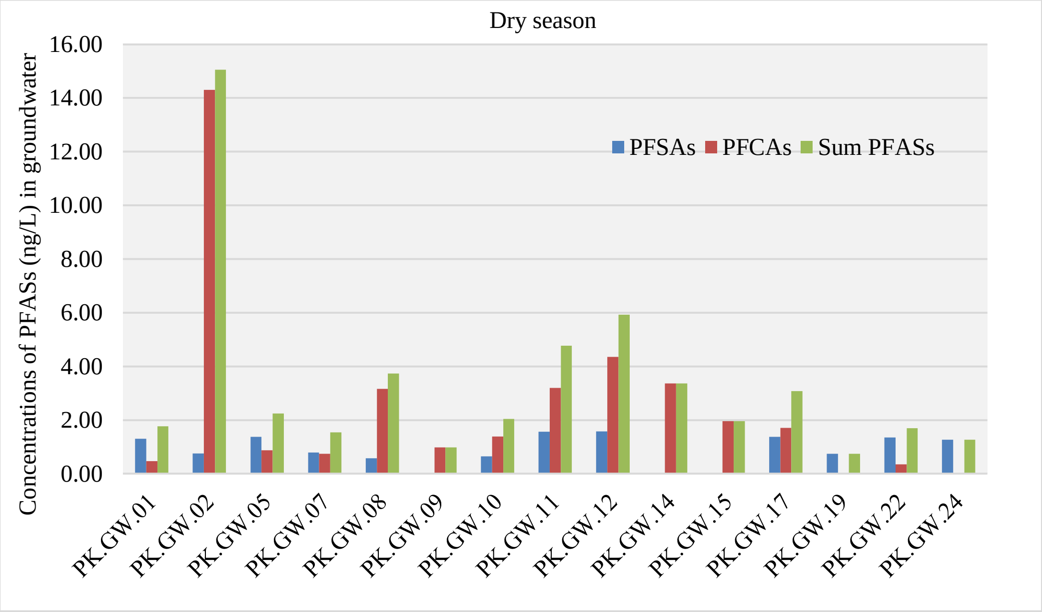

Figure 3. Concentrations of PFASs (ng/L) in groundwater in dry season.

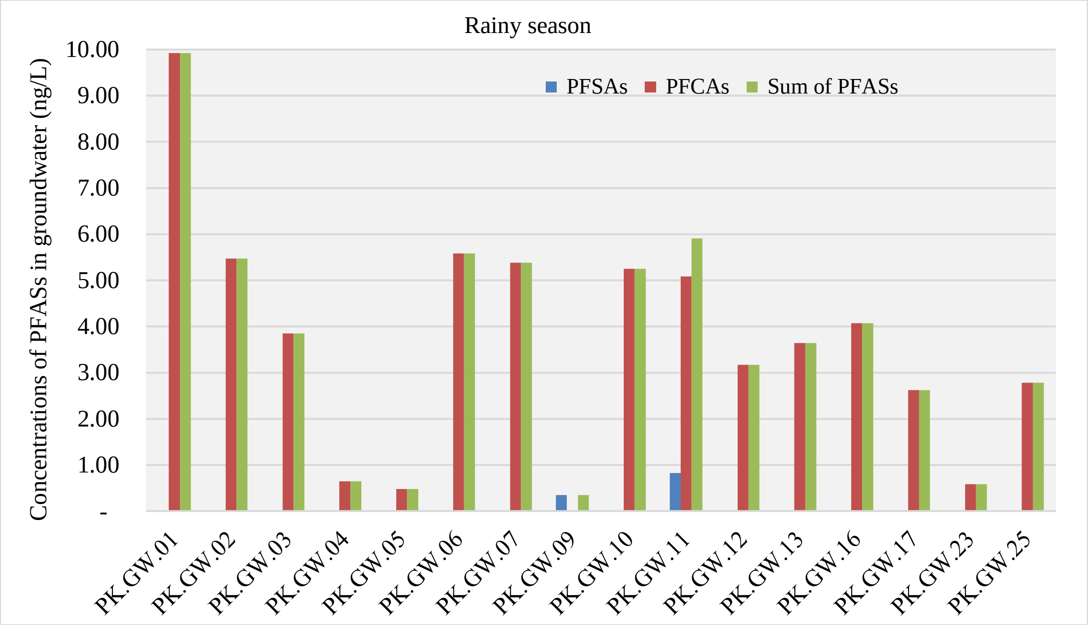

Figure 4. Concentrations of PFASs (ng/L) in groundwater in rainy season.

Two other common compounds in this study, the PFHxA and PFHpA, had concentrations ranging from non-detectable to 6.19 ng/L (average: 1.11 ng/L) and from non-detectable to 6.81 ng/L (average: 0.79 ng/L), respectively. These values are lower by a factor of 20 compared to results found in groundwater near a fluorine production industrial area in China σ, and lower by a factor of 6 compared to urban areas in Japan [35]. In other studies, PFOS was often detected in groundwater, but in this study, the PFOS had a low detection frequency with concentrations ranging from non-detectable to 0.69 ng/L (average: 0.15 ng/L). The PFHxS, another compound listed in the Stockholm Convention, was found in this study from non-detectable to 0.90 ng/L with a detection frequency of 30 %, higher than the concentrations detected in the Yuquiao reservoir, China [20] and Ganges river basin, India [19]. However, this compound was at much lower levels than those found in groundwater in France [22] and Australia [23]. Overall, the concentrations of each PFASs compound are much lower compared to levels found in groundwater at landfill sites in Thailand [25], rural areas in China [14], urban areas in Japan [27], and the United States [28].

Table 1. Comparison of PFAS levels (ng/L) in groundwater with other studies.

Country	PFOA	PFOS	PFHxS	Areas	References
Viet Nam	ND - 2.74 (0.89)	ND - 0.69 (0.15)	ND - 0.9 (0.22)	Craft village	This study
Viet Nam	ND - 4.5 (0.34)	0.19 - 8.2 (0.27)	ND-6 (2.27)	Urban	[18]
Thailand	0.65 - 34.96 (8.32)	0-25.88 (3.59)	ND - 3.73 (0.31)	Landfills	[25]
China	7-175.2 (77.17)	< 0.5 - 37 (19.2)	< 0.5 - 1.9 (0.13)	Rural	[14]
China	ND-5.11 (0.8)	ND - 0.5 (0.17)	ND-0.23 (0.09)	Yuquiao reservoir	[20]
India	ND-0.76 (0.46)	ND - 1.13 (0.16)	ND-0.08 (0.02)	Ganges river basin	[19]
Korea	ND-6.72 (2.9)	ND - 2.35 (0.2)	ND - 10.39 (2.8)	Nakdong river basin	[24]
Japan	< 0.25 - 1800 (8.5)	< 0.25 - 990 (5.7)	ND - 56 (3.1)	Urban	[27]
Malta	0 - 8.03 (1.46)	0-2.63 (0.48)	(0.61)	Nationwide	[21]
France	Max:14 (1.10)	Max: 38 (2.4)	Max: 143 (4.6)	Industrial, urban, agricultural and rural	[22]
USA	ND - 31	ND-12	ND-10	Urban	[28]
Australia	< 0.09 - 6.9 (2.2)	< 0.03 - 34 (11)	<0.03 - 18 (5.9)	Agricultural (recycled water from wastewater treatment plant)	[23]

3.2. Distribution profiles of PFASs

The three most commonly detected the PFAS compounds in groundwater were the PFOA (detection frequency: 65 %), PFHxA (60 %), and PFHpA (58 %). The average concentrations and contribution percentage to total PFASs of these compounds were 0.63 ng/L (22.6 %), 0.75 ng/L (26.9 %), and 0.61 ng/L (21.9 %) during the dry season, and 1.11 ng/L (41.0 %), 0.83 ng/L (30.6 %), and 0.56 ng/L (20.7 %) during the rainy season, respectively. The composition of PFAS compounds in groundwater during the two seasons is presented in Figure 5 and Figure 6. Six PFAS compounds, including the PFDA, PFUdA, PFDoA, PFTrDA, PFTeDA, and PFDS, were not detected in groundwater samples during the dry season, while four PFAS compounds, including the PFNA, PFDA, PFUnDA, and PFDS, were not found during the rainy season. Although the study detected the presence of PFDoDA, PFTrDA, PFTeDA, PFHxS, and PFOS during the rainy season, their occurrence frequencies were low, around 5 %. During the dry season, the PFHxS was only detected in sample PK.GW.19, while during the rainy season, samples PK.GW.04 and PK.GW.05 only showed the presence of PFOA, and sample PK.GW.23 only showed the PFHxA. A common factor among these groundwater samples is that they were either collected from paper production households (samples PK.GW.04 and PK.GW.05) or near paper production companies (PK.GW.19 and PK.GW.23). However, it is challenging to explain why only one PFAS compound was detected in some samples because the composition of PFASs in groundwater at these sampling points varies between the two seasons.

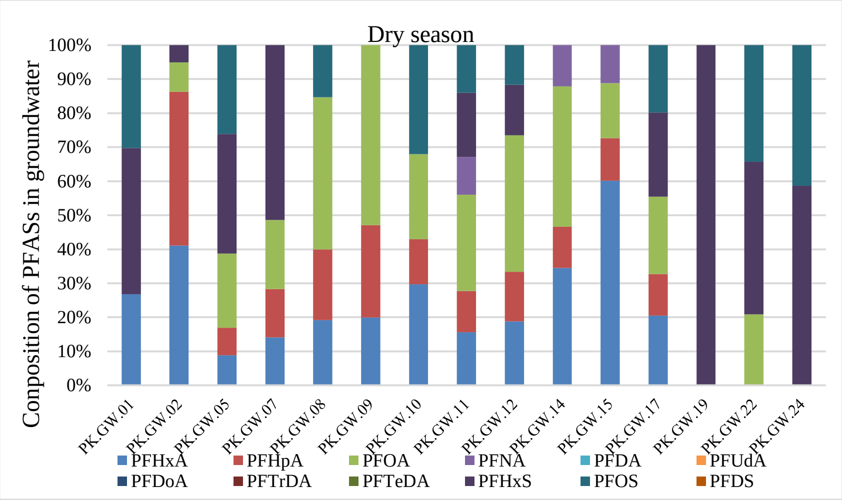

Figure 5. Composition of PFASs in groundwater in dry season.

While the PFCAs C6-C8 were present in most samples, the long-chain PFCAs (C9-C14) and PFSAs made up a very small proportion of the groundwater samples. In a published study, the number of PFASs detected in groundwater was lower than in surface water and soil, and the long-chain PFASs were almost not found in groundwater. This can be explained by the fate of PFASs in groundwater being significantly influenced by carbon chain length and functional groups (carboxylic COO^- and sulfonic SO_3^-). The anionic groups in PFCAs and PFSAs make the PFASs highly soluble in water, while their ability to adsorb into soil and sediment depends on the carbon chain length. The Long-chain PFCAs and PFSAs have lower water solubility compared to the short-chain PFCAs and tend to be strongly adsorbed onto soil surfaces or accumulated through the infiltration process [29]. This also makes groundwater more prone to accumulating the short-chain PFASs than surface water.

The Phong Khe paper-making village, with a history of paper production dating back hundreds of years, is continually growing in terms of scale, production volume, and paper types. In the past, this traditional paper village primarily produced poonah (without chemical treatment), which was used for traditional Vietnamese folk-art painting, especially for Dong Ho paintings. Today, the village has expanded its production to various industrial paper products to meet market demands, such as cardboard and school paper. However, these industrial products have a high potential for containing the PFASs added to make the paper water-resistant. Recent studies have indicated the presence of various PFASs in packaging materials and paper products [30]. Previously, the PFASs used in packaging were typically a mixture of C8, C10, and long-chain PFASs like C12. However, they have gradually been replaced by the short-chain PFASs, primarily C6 compounds, due to increasing legal pressure since the 2000s [31]. The results presented in Figure 5 and Figure 6 show that the C10 and C12 compounds were hardly detected, while the C6 and C7 compounds contributed largely to the composition of the PFASs in groundwater. This finding is consistent with the trend of using these compounds in the paper manufacturing sector. However, the compound C8 was still found in relatively high concentrations, suggesting a need for stricter control of input materials during the paper production process. Furthermore, a previous study on PFAS contamination levels in surface water in this area showed significantly higher total PFAS concentrations compared to a non-industrial reference area [10]. Therefore, wastewater pollution from industrial activities can be considered a primary source of the PFAS release into groundwater in this study area.

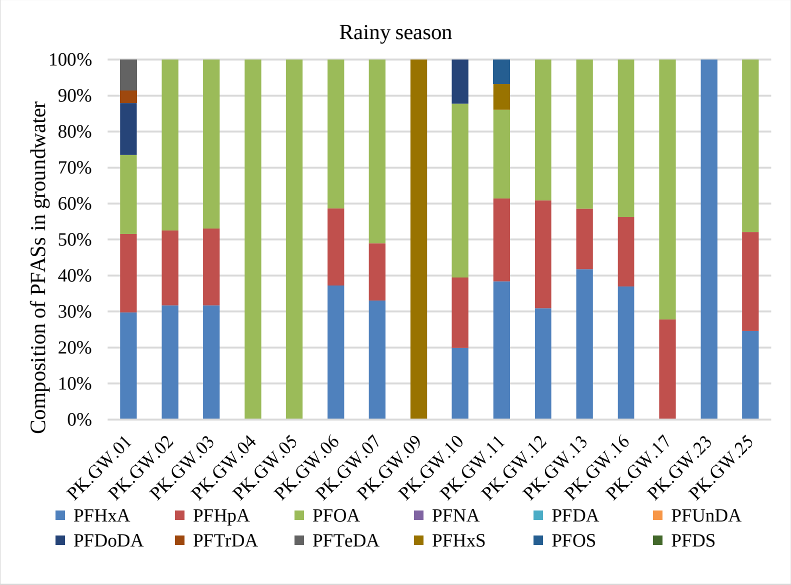

Figure 6. Composition of PFASs in groundwater in rainy season.

The composition of PFASs in environmental samples can provide information about the source of contamination to some extent. In previous study, certain ratios like PFOS/PFOA, PFHxA/PFOA, and PFHpA/PFOA have been used to determine potential PFAS sources [32]. Simcik *et al*. found that high concentrations of the PFHxA and PFHpA in surface water in remote areas indicated atmospheric decomposition (e.g., rainfall) as the primary source of these compounds. Meanwhile, higher PFOA concentrations in surface water in urban areas suggested non-atmospheric sources (e.g., wastewater) for the PFOA. Therefore, the PFHxA/PFOA and PFHpA/PFOA ratios can be used to identify the origins of various PFCAs. In this study, the average ratios of PFHxA/PFOA and PFHpA/PFOA were 0.65 and 0.50 in the dry season and 0.67 and 0.47 in the rainy season. It can be observed that both ratios in the two seasons are at similar levels, suggesting that the source of PFCAs derived from atmospheric deposition is insignificant, while non-atmospheric sources such as wastewater could be the origin of PFCAs. Furthermore, the previous report has indicated that the PFASs in groundwater may come from domestic wastewater (such as food packaging, cosmetics, pharmaceuticals, and human/animal urine/feces) and contamination from nearby industrial areas [14].

3.3. Principal Component Analysis (PCA)

Principal component analysis (PCA) is a simple, effective, and widely used multivariate analysis tool that reduces the complexity of data sets and uncovers latent variables. In this study, the PCA was applied to analyze the relationship between the concentration of PFASs and groups of groundwater samples collected from wells in the Phong Khe area in the rainy and dry seasons. Among the 22 wet-season and 18 dry-season samples analyzed, the long-chain PFAS, including PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA and PFDS, were almost undetectable (0 – 3/40 samples). Therefore, the data set used for the PCA analysis only included five substances: PFHxA, PFHpA, PFOA, PFHxS and PFOS.

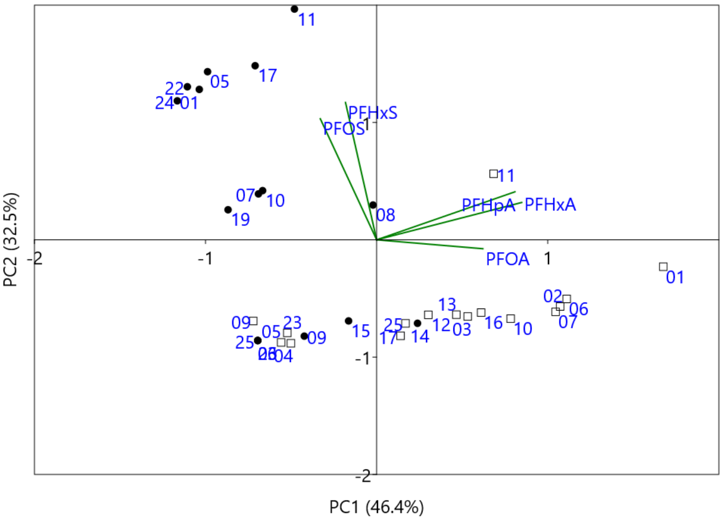

Figure 7. Result of PCA analysis for PFASs in both seasons (black dots represent wet-season samples, and black squares symbolize dry-season samples).

Five principal components were extracted using the unrotated PCA, with the first two explaining 78.9 % of the total dataset variance. Specifically, the PC1 comprised three PFCAs (PFHxA, PFHpA, and PFOA), explaining 46.4 % of the total variances. Conversely, the PC2 included only two PFSA compounds (PFHxS and PFOS), accounting for 32.5 % of the total variances. The eigenvalues of PC1 and PC2 were greater than 1, with values of 2.322 and 1.627, respectively, indicating that selecting PCA with only these two principal components was appropriate. In PC1, the PFHxA and PFHpA had the strongest influence, with loadings of 0.615 and 0.587, while the PFOA had a weaker influence, with a loading of 0.451. Contrarily, the PFHxS and PFOS had nearly equal influence in the PC2, with loading of 0.711 and 0.627, respectively.

The biplot in Figure 7 showed a relatively straightforward difference between the components of groundwater samples obtained during the dry and rainy seasons. Most dry-season samples were distributed along PC2, indicating that the PFSAs became dominant in groundwater during the dry season. Contrariwise, concentrations of the PFCAs were higher in groundwater samples of the rainy season. This suggested a difference in the source of PFASs in groundwater between the two seasons. A study by David, *et al*. showed that the PFCAs were detected most frequently in rainwater and accounted for an average of 83 % of the total PFASs in the samples [33]. Some other studies also indicated that the PFCAs were the main components in rainwater, highlighting the significant role of rainfall in generating the PFHxA, PFHpA, and PFOA in groundwater but having less contribution to the PFHxS and PFOS components [34]. Additionally, the composition of PFASs might be influenced by wastewater from paper recycling activities in the study area, and variations in wastewater characteristics and rainfall levels might result in higher levels of the PFHxS and PFOS during the dry season.

3.4. Human risk assessment

In this study, the average amount of PFASs absorbed into the human body and HR values through groundwater consumption were calculated based on the concentrations of PFASs found in the analyzed samples. The average total concentrations of PFCAs and PFSAs were 2.52 ng/L and 0.37 ng/L, respectively. The average EDI for adults from groundwater was 0.07 (ng/kg/day), with EDI values for PFOA and PFOS being 0.029 ng/kg/day and 0.004 ng/kg/day, respectively. The calculated HR values for total PFASs in this study were all less than one, indicating a low risk associated with the use of groundwater in the Phong Khe paper village area.

A previous study conducted in a river basin in India showed an EDI for the PFOA and PFOS in groundwater at a level of 0.04 ng/kg/day. In other studies in China, the EDI for PFOA and PFOS in groundwater was found to be 0.024 and 0.001 ng/kg/day, respectively [35]. Overall, the EDI values for both PFOA and PFOS in this study were similar to the values found in studies conducted in China and India and lower than the EDI values found in South Korea (EDI for PFOA was 0.07 ng/kg/day) [24]. However, the HR for non-cancer risk associated with the PFOA and PFOS was much lower than 1 for groundwater, indicating that exposure to these two compounds poses a low risk to the residents of Phong Khe paper-making village.

4. CONCLUSION

The results of this study in Phong Khe village provide the first information on the concentrations of PFAS compounds and their sources in groundwater in potentially polluted areas such as paper-making villages in Viet Nam. PFASs detected in groundwater primarily consisted of compounds with a carbon number < 9. The study found statistically significant differences in the concentrations of PFAS compounds in groundwater between the northern part of the Ngu Huyen Khe River, where mainly households without paper production facilities are located, and the southern part of the river, where most production facilities are concentrated. The source of PFCAs derived from atmospheric deposition is insignificant while non-atmospheric sources such as wastewater could be the origin of PFCAs. Furthermore, the sources of PFASs in groundwater in the study area may include industrial production activities in the village, atmospheric deposition, rainfall, and surface runoff.

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Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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