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Research Article

Distribution of perfluoroalkyl substances (PFASs) in the water of the Bac Hung Hai River, Van Giang district, Hung Yen province, Vietnam

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Abstract: This study investigated and evaluated the quality of PFASs in the water of the Bac Hung Hai River passing through Van Giang district, Hung Yen, Vietnam. PFASs concentration in the river water samples were detected by using LC-MS/MS spectrum. The results showed that the studied river region contaminated PFASs. PFASs concentration ranged from 0.10 to 3.88 ng/l. The average concentrations of individual PFASs were PFBA 5.5, PFPeA 6.8, PFHxA 0.8, PFHpA 0.34, PFOA 0.16, PFNA 0.19, PFDA 0.036, PFHxA 1.34, PFOS 0.074, PFDS 0.037. The research results show that distribution of PFASs in the Bac Hung Hai River are not uniform and depend on the of discharge sources.

Keywords: PFASs contaminants; PFOA, PFOS, Bac Hung Hai; River pollution.

1. Introduction

Per– and polyfluoroalkyl substances (PFASs) are a group of anthropogenic compounds as new persistent organic pollutants (POPs) with special surface–active properties [1]. Their molecular contains both lipophilic and hydrophilic groups at both sides. PFASs are a diverse group of human-made chemicals used in a wide range of consumer and industrial products. Some PFASs, such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), have been more widely used and studied chemicals in the PFASs group. Many PFASs are resistant to grease, oil, water, and heat. For this reason, PFASs have been manufactured since the late 1940s [1–2] and used in a variety of applications including in stain and water–resistant fabrics and carpeting, cleaning products, paints, and fire–fighting foams, refrigerants, surfactants, and polymers and as components of pharmaceuticals, fire retardants, lubricants, adhesives, cosmetics, paper coatings, and insecticides. Certain PFASs are also authorized by the Food and Drug Administration (FDA) for limited use in cookware, food packaging, and food processing equipment. The concern about their presence in the environmental and potential human exposure is rising all over the world. A great number of studies have been available on the contaminations of PFASs in rivers, lakes, and ocean waters [3], and even in air [4–5], in dust [6]. PFASs have been investigated widely in fish of Europe and Asia, such as: Spain [7] Norway [8], Greece [9], Italy [10], Korea [11], and China [12]. The median PFOS contamination was found in river

water 14.4 ng/L (England), 5.5 ng/L (Singapore), 3.2 ng/L (Japan), and 1.7 ng/L (China). PFOA contamination (median) in river water was in the order of Japan (30.7 ng/L), England (10.6 ng/L), China (7.4 ng/L), Singapore (5.6 ng/L), and Vietnam (0.7 ng/L) [13]. PFASs found in ocean water were range from hundreds to thousands pg/L, such as in South China Sea 980–2640 pg/L [14].

PFASs related to environmental water in Vietnam have been concerned recently [15–18]. The occurrence of PFASs in surface water near waste recycling and disposal sites in Vietnam was reported [15–16]. The significant PFASs concentrations were found in leachate from the municipal dumping site and ambient water from the e-waste recycling site, suggesting such sites as potential contamination sources of PFASs in Vietnam. In Hanoi, PFASs contamination in river systems was studied at Nhue, To lich, Yen So, and Ho Tay Lake.

Van Giang district is located in the north of Hung Yen province, on the left bank of the Red River, 40 km from Hung Yen city to the north, 20 km from the center of Hanoi capital to the southeast. Wastewater sources such as wastewater and some solid wastes that may contain PFASs from domestic activities as well as industrial activities and pottery villages of residents here are concentrated into the Bac Hung Hai River. This is considered as one of the potential sources of PFASs pollution in the surface water environment. This research investigates the occurrence of PFASs in Bac Hung Hai River water. The PFASs in pretreated samples were analyzed using high performance liquid chromatography-tandem mass spectrometry (LC/MS-MS). The obtained results showed a sufficient picture of the distribution PFASs in river water and initial identification of contamination sources.

2. Materials and methods

2.1. Materials

The mixture of PFASs (PFACMXB0614) and the mixture of Mass-Labeled PFASs (MPFACMXA0714) were purchased from Wellington Laboratories, Canada. HPLC-grade methanol was purchased from Merck, Germany, and other chemicals were of analytical reagent grade. Ammonium acetate was obtained from Wako Chemicals, Japan. Ultrapure water was delivered by a Direct-Q water purification system (Millipore, Japan).

2.2. Sample collection and preparation

Figure 1 shows the location of sampling sites. Fifteen river water samples were taken along the Bac Hung Hai River in March 2021. The water sample was pretreated according to the international standard ISO 25101:2009 with minor modifications [19]. Briefly, the water sample (500 mL) was filtered through a 47 mm glass fiber filters to separate suspended solids. An Oasis HLB (200mg) cartridge was preconditioned with 4mL of MeOH containing 0.1% ammonia followed by 4 mL of MeOH and 4 mL of deionized water. The water sample was then loaded through a WAX cartridge with a flow rate of 10 mL/min. The SPE cartridge was washed with 4 mL of 25 mM ammonium acetate and dried for 15min. Next, the target compounds in the cartridge were eluted with 4 mL of MeOH and 4 mL of 0.1% ammonia solution at a rate of 1 drop per second. The extract was concentrated to 1 under a gentle nitrogen stream. A 0.2 µm nylon membrane filter was used to filter the final eluate before LC-MS/MS analysis.

Figure 1. Sampling site in Bac Hung Hai River.

2.3. PFASs analysis

PFASs were analyzed by LC-MS/MS 8040, Shimadzu, Japan. The LC system was equipped with a column (Poroshell 120, EC.C18 (2.1 mm I.D. × 150 mm L, 2.7 µm) and guard column EC-C18, Agilent, USA. The mobile phase consisted of a binary mixture of A (2 $mM.L^{-1}$ ammonium acetate in water with methanol in a ratio of volume is 9 and 1) and solvent B (methanol) at flow rate of 0.25 $ml.min^{-1}$. The gradient, the start with 50% B in 2 min increased to 95% B for 18 min and linearly at 95% B for 4 min then ramped to 50%A for 5 min. Total running time was 29 min. The inject volume was 2µL. The MS system was running with an electrospray ionization source in negative mode (ESI) at 3.5kV.

3. Results and Discussions

3.1. PFASs concentrations in water samples

Figure 2 showed the total PFASs concentrations in all river water samples. They were detected in all studied samples in range from 1 ng/L to 38.8 ng/L. Comparison to PFASs concentration in the wastewater from the rivers which belong to the drainage systems of Hanoi city including Lu, Set, To Lich, Kim Nguu and Nhue Rivers and two urban large lakes as West Lake and Yen So Lake, was collected. The concentrations of PFASs were in arranged of 0.93 and 28 ng/L [20]. In Ha Dong silk weaving wastewater, the concentrations of PFASs were in arranged 2.94–12.64 ng/L, and those at Hoi Quan silk weaving wastewater were 4.77 to 17.66 ng/L [21]. The concentration of PFASs in surface water samples along the Bac Hung Hai River is slightly high.

There is a great difference between different sampling points. It proves that the water of Bac Hung Hai River is the reservoir of many waste sources with high concentration of pollution. Samples W1, W2, W3 with the appearance of PFASs were low because the location of these samples is the first part of Bac Hung Hai River, there are very few sources of impact but going deeper along the river. When we see the appearance of residential areas, restaurants, leather manufacturing companies, packaging... the more PFOA and PFOS appear and the concentration also varies.

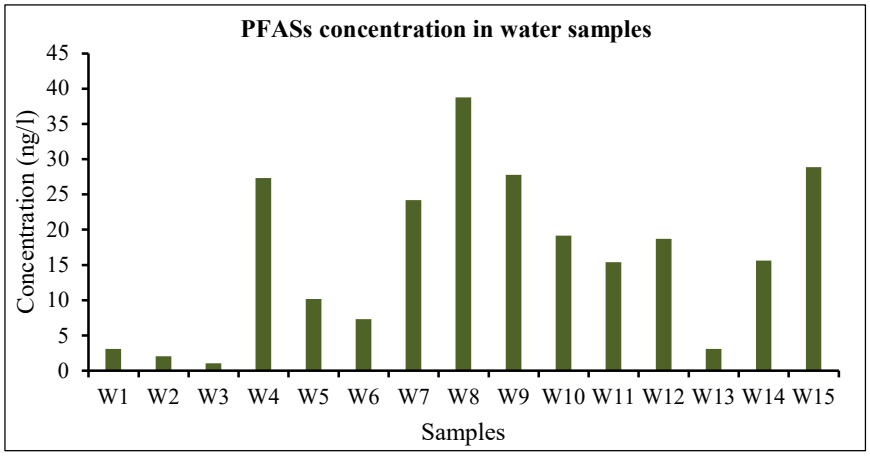

Figure 2. PFASs concentration in Bac Hung Hai River water samples.

It is the production activities of people, companies, industrial parks, and daily life that are not strictly managed, so the discharge of wastewater directly into the Bac Hung Hai River has led to the presence of toxic compounds. The highest concentration at position W8 reached 38.8 ng/L and then samples W4, W7, W9, W10, W11, W12, W14 and W15 also had high concentrations. The lowest at position W3 reached 1 ng/L.

3.2. PFOA and PFOS concentrations

The occurrence of PFOA showed frequency in all studied samples. There are many locations where PFOS is not found but PFOA is present, even PFOA is at high concentration. At sample W15, the highest occurrence of 2 substances was PFOA 0.42 ng/L and PFOS 0.38 ng/L. PFOS and PFOA concentration in other locations were showed in Table 1. In this study, the compound concentration of PFOA reached 0.044–0.42 ng/L and PFOS reached 0.06–0.38 ng/L. The surface water in Da Nang, Ho Chi Minh City and Bui Dau e-waste recycling craft village have much higher PFOA content than the study area of Bac Hung Hai River flowing through Van Giang district area.

For surface water in Hue, there are very small concentrations of PFOA and PFOS, indicating that there are very few impact sources containing this compound at those sampling locations. For the low PFOS concentration in Hanoi and Hung Yen, the PFOA concentration in the Bac Hung Hai River water flowing through the Van Giang district area was four times higher than the PFOA concentration in the river water in the Hanoi area.

The concentration of PFOA in the surface water of a waste recycling craft village in Hung Yen is nearly 90 times higher than the concentration of PFOA in the water of Bac Hung Hai River that we obtained.

Table 1. PEOS and PFOA concentrations through studies in provinces/cities.

Location	Samples	PFOS (ng/L)	PFOA (ng/L)	Ref.
Hanoi	River water	ND – 0.14	ND – 1.00	[22]
	Urban lake water	0.17–0.81	1.4 – 6.6	
	Wastewater channel	ND – 1.3	ND – 6.1	
Hung Yen	Surface water	ND – 0.8	ND – 4.1	[16]
	Surface water of Dong Mai craft village	ND – 2.7	2.5 – 5.6	
	Surface water of Bui Dau craft village	ND – 1.8	3.3 – 35	
Da Nang	Surface water	ND – 3.8	ND–104.5	[23]

Location	Samples	PFOS (ng/L)	PFOA (ng/L)	Ref.
Ho Chi Minh	Surface water	ND – 5.3	0.21 – 18	[18]
Hue	Surface water	ND – 0.19	0.09–0.32	

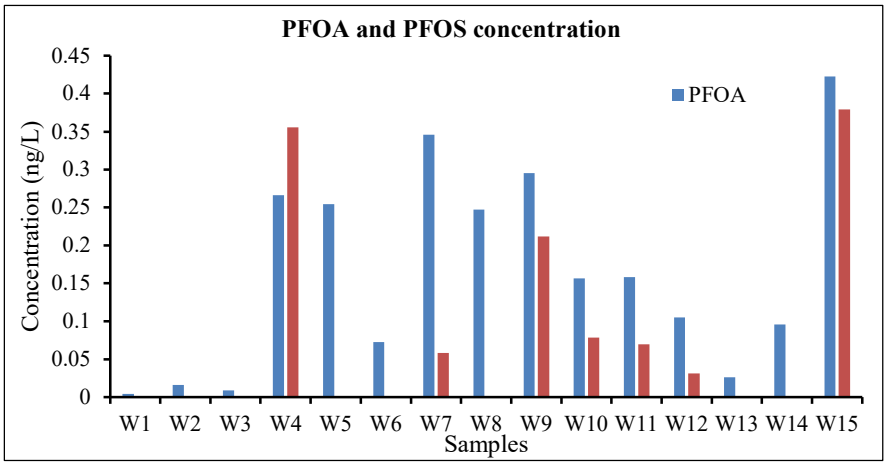

Figure 3. PFOA and PFOS concentration in Bac Hung Hai River water samples.

3.3. Composition profiles of various PFASs in water samples

PFASs were detected mostly in water samples. The composition profiles of PFASs are presented in figure 4, 5. Six perfluoroalkylcarboxylic acids (PFBA, PFPeA, PFHxA, PFHpA, PFOA, and PFNA) were found in all studied samples. The content of PFBA and PFPeA were found with the highest concentration among PFASs compounds. The difference between the content of PFASs compounds was explained for the composition of wastewater from industrial, production, business, domestic, medical, and livestock zones in different locations.

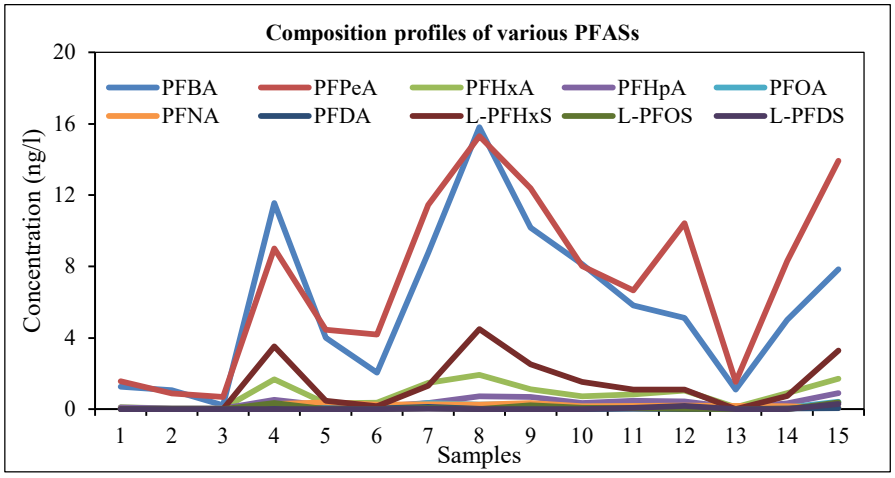

Figure 4. Composition profiles of various PFASs in Bac Hung Hai River water samples.

The PFASs that accounted for the highest percentage among the 10 analytes were PFBA at 36.4%, PFPeA 44.7%, PFDA 8.3%, PFHxA 5.1%. In general, the components detected with high content are pefloankyl acids with low number of carbon atoms in the molecule from C4, C5, indicating that the PFASs are from wastewater of residential and industrial zones.

Most of the compounds PFBA and PFPeA account for a high proportion and they occur at sample locations affected by many sources of direct discharge into the Bac Hung

Hai River. Typically, at sample location W4, W7, W8, W9, W10, the presence of these two compounds was very high due to waste sources from industrial parks, people's livelihoods, craft villages and many other sources. Short-chain PFASs were much more dominant than long-chain PFASs in Bac Hung Hai River water. Comparison with EU regulations for 25 ng/L PFOA threshold, PFASs contamination in the studied region is mostly within the threshold [24].

Aquatic studies and data for surface water in Denmark and other European countries most of the data are for PFOS, PFOA and other long-chain PFAS and some data are available for compounds short chains such as PFBS, PFHxS, PFBA, PFPeA and PFHxA were detected in many seafood samples. Usually, concentrations range from levels similar to PFOS or PFOA to one order of magnitude lower. The presence of shorter-chain compounds in the medium is explained by replacing long-chain compounds with shorter-chain substitutes.

In the Atlantic, PFASs concentrations were significantly higher in the North Atlantic than in the Central and South Atlantic. ΣPFAS concentrations decreased from 2007 to 2010 in the North and Mid-Atlantic mainly due to decreased PFOA/PFOS concentrations while such short-chain PFAS such as PFBS, PFHxA and PFHxS showed no such trend.

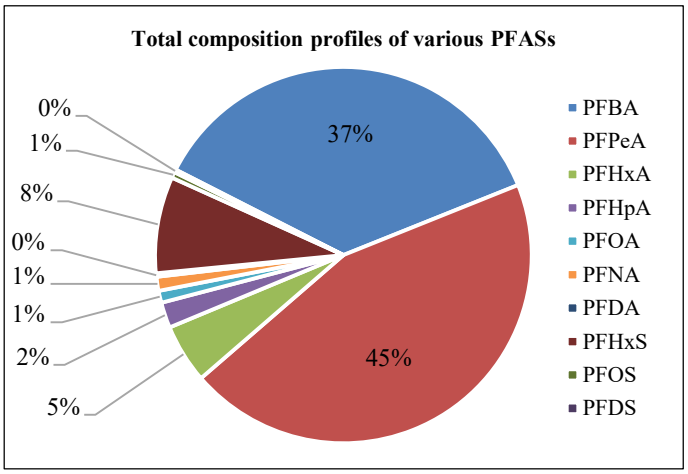

Figure 5. Percentage of various PFASs in Bac Hung Hai River water samples.

3.4. Identification of pollution sources

According to the actual survey, from the beginning of the river to the end point where samples are taken in Van Giang district, there are many sources of pollution affecting the river water. Main sources of pollution: industrial waste, services, healthcare, agricultural production, livestock, daily life activities, Kieu Ky landfill.

At the sample location W1, W2, W3 is affected by the waste source of the people of Xuan Quan commune and the people of Bat Trang Village. Sample location W4 is the main source of pollution originating from industrial, service, craft villages and people's wastewater along the Cau Bay River basin flowing through Xuan Thuy culvert along with about 50 facilities in the area discharging wastewater into Bac Hung Hai channel and Kieu Ky landfill. Sample W5 is affected by medical waste from Bay Hospital and from Cau Chua residential area. The location of the W6 sample is influenced by the waste source from the plastic and paint industry. At the sample location W7 is affected by waste sources of Tan Quang industrial cluster, service restaurants. The location of the sample W8 is affected by wastewater from industrial parks producing paper, paperboard, plastic, carton packaging, animal feed, mechanical engineering and waste sources from residential areas. Sample W9 is affected by residential waste, seafood processing, motor vehicle maintenance and repair, and waste from Dong Than market. Sample W10 is affected by wastes from

plastic, neoprene, scrap recycling and residential areas. Sample W11 is affected by wastewater from Bao Dap residential area and wastewater from Cau Kenh. Sample W12 is the wastewater of the whole Bao Da area, including all business and production activities of the people. Sample W13 is less affected by domestic waste. Sample W14 was the waste source of residential area and Bat Trang pottery village. Sample W15 was taken at the Xuan Cau bridge where it is affected by domestic waste, agricultural production, animal husbandry and services.

Thereby, it is found that the source of wastewater pollution from industrial parks and wastewater from residential areas is mainly along the Bac Hung Hai River in Van Giang district, Hung Yen province.

4. Conclusion

The distribution of PFASs concentration along the Bac Hung Hai River is uneven, which showed that each location and each area has different waste sources, leading to different concentrations of PFASs. The average ng/L concentrations of PFBA 5.5, PFPeA 6.8, PFHxA 0.8, PFHpA 0.34, PFOA 0.16, PFNA 0.19, PFDA 0.036, PFHxA 1.34, PFOS 0.074, PFDS 0.037 compared with EU regulations are mostly within the threshold for EU regulations. Bac Hung Hai River water flowing through Van Giang district, Hung Yen province contains mainly PFBA and PFPeA compounds. The total content of PFCs in water samples collected along the Bac Hung Hai River, the section running through Van Giang district, Hung Yen province ranged from 1 ng/L to 38.8 ng/L. This finding shows that it is the waste sources from production activities, industrial parks and domestic activities that are the main causes for the presence of these PFASs.

Author Contributions: The experiment was conducted by L.A.P.T., B.V.L., H.T.D. The paper was written by H.T.D., L.A.P.T.

Conflicts of Interest: The authors declare no conflict of interest.

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