

Contamination Of Perfluorinated Compounds In Sediment of The Cau River, Vietnam

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Research Article

Keywords: Perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), sediment core, Vietnam, Cau river

Posted Date: June 15th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-573006/v1>

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Abstract

Perfluorooctane sulfonate (PFOS) and Perfluorooctanoic acid (PFOA) are recognized as emerging environmental pollutants because of their high persistence in various environmental matrices and toxic effects on humans and animals. In Vietnam, PFOA and PFOS have been detected in surface water and sediment in recent studies. The objectives of this study were to evaluate the occurrence of PFOS and PFOA in the sediment of the Cau river, Thai Nguyen city to determine the partition coefficient between water and sediment, and to elucidate the environmental factors affecting the sorption of PFOS and PFOA to sediment. The concentration of PFOS and PFOA in surface sediment ranged from 1.19 ng/g to 4.73 ng/g and 0.17 ng/g to 1.78 ng/g, respectively, with the highest concentrations, are recorded in the areas that receiving wastewater from domestic and industrial activities. Depending on the depth, the total concentrations of PFOS and PFOA ranged from 8.41 to 19.25 ng/g and tended to decrease with increasing sediment depth. The concentrations in the surface sediments are lower than the second layer, indicating a downward trend in the use and consumption of these compounds in recent years. The water-sediment distribution coefficient (K_d) is relatively different for PFOS and PFOA, with log K_d values ranged from 1.31–1.86 and 0.08–1.31 for PFOS and PFOA, respectively. This study also confirms that the total organic carbon content is the physicochemical property that significantly affected the adsorption to sediments of PFOS and PFOA. No apparent relation was found between PFOS, PFOA concentration in sediment and clay content nor sediment particle size.

Introduction

Perfluorinated Compounds (PFCs) are fully man-made compounds manufactured since the 1950s. PFCs are widely distributed and have been found globally in many environmental components. PFCs have unique and useful properties such as stability, chemically inert, water-repellent, and non-biodegradable, so they are used in many industries and consumer products. The sources of PFCs into the environment include waste from industry, consumer products, disposal sites, and sewage treatment plants (Cheremisinoff 2017). These compounds have also been known to be toxic and bioaccumulative compounds. Numerous publications allude to the negative effects of PFCs on human health based on a correlation that exists between PFCs exposure and pathologies such as high cholesterol levels, thyroid problems, high blood pressure during pregnancy, and kidney and testicular cancer (Lau et al. 2007, Public Health of England 2009, Rayne et al. 2009, DeWitt 2015). PFCs are proposed as a new class of “Persistent Organic Pollutants – POPs”, and PFOS which is one of the most representative was added to the Stockholm Convention as a new POPs in 2009.

The occurrences of PFC in the environment is mainly in the following forms: (1) soluble in water; (2) adsorption onto solid particles in air and water; (3) deposition in sediments and soil; and (4) bioaccumulate in animal and human bodies (Cheremisinoff 2017). Studies on PFC contamination have recorded the presence of PFC in water and sediments with concentrations ranging from ppb to ppm (Becker et al. 2008, Bao et al. 2009, Bao et al. 2010, Gomez et al. 2011, Li et al. 2011, Pico et al. 2012, Lam et al. 2014). The fate of PFC in water and sediment depends on sediment-water distribution. Such distribution is very complex and depends on the physicochemical characteristics of the compound, properties of the water column, and sediment. Evaluating the distribution of PFCs is necessary to understanding the transport and transform mechanism of these compounds in the environment.

Like other developing countries, Vietnam has manufactured and used a relatively large amount of PFCs, but the inventory program for POP compounds including PFCs has received attention only in recent years. The first study on PFOS and PFOA in surface water in Vietnam was in 2007, in which PFOS and PFOA were detected at the highest concentration at 6.6 ng/L and 1.27ng/L, respectively in the rivers, waste canals, and lakes in the Hanoi area (Lien 2007). The study of Pham et. al has recorded the contamination of PFOS and PFOA in the effluent canals of the textile

and dyeing traditional villages in Hanoi, Bac Ninh in the range of 7.68 ng/L to 11.5 ng/L, in which PFOS and PFHxA are the predominant pollutants (Phạm et al. 2017). The first nationwide investigation of the contamination of 16 PFCs in urban canals was conducted in the four largest cities of Vietnam (Hanoi, Hue, Da Nang, and Ho Chi Minh City) by Duong et al. (Duong et al. 2015). The results showed that PFOS, PFOA, and PFNA were the typical pollutants with the highest concentration of 5.3ng/L, 18ng/L, and 0.93ng/L respectively. The study by Lam et. al was found the highest concentrations of PFOA (53.5 ng/L) and PFOS (40.2 ng/L) in a surface water sample from a cannal that receives wastewater treatment plant and PFOS and PFHxS were the predominant PFASs in sediments (Lam et al. 2017). Up to now, the data of PFC contamination in sediment are limited in Vietnam.

The pollution due to the existence of PFCs in the environment in Vietnam has been recognized. However, these previous studies were only conducted in small or specific areas, not giving a general picture of the contamination of these compounds in environmental components. In particular, the level of PFCs in sediments as well as the distribution according to the depth of sediment, the partition between water and sediment have not been completely described and studied. This is one of the largest information gaps in the studies on PFCs in Vietnam. The objectives of this study are: (1) identify the contamination of PFCs in the sediment; (2) evaluate spatial and vertical distributions of PFCs in sediments and (3) evaluate the factors affecting the adsorption of PFCs on river sediments.

Materials And Methods

2.1 Study area

The Cau river is one of the five longest rivers in northern Vietnam that including Red river, Da river, Lo river, Cau river, and Day river, and is also one of the major river basins in Vietnam. It has a special geographical position, is diverse and rich in natural resources as well as a history of socio-economic development of the provinces in its basin. The Cau river basin has a total area of 6,030 km², with the mainstream of Cau river with a length of 290km. Cau river originates from the Tam Tao mountain area (with a height of 1,326m) flowing through Bac Kan, Thai Nguyen, Bac Ninh, and Bac Giang province and the endpoint is Pha Lai at Hai Duong province (Environmental Protection Committee of the Cau river basin 2019).

Among the provinces in the river basin, Thai Nguyen province has the most sources of discharges into the Cau river, mainly from production and business establishments, industrial parks, and craft-village (Environmental Protection Committee of the Cau river basin 2019). Thai Nguyen city is the most dynamically developed economic region of the province, is an old industrial center and concentrates mainly on industrial zones and large factories of the province. The main industries in Thai Nguyen include mining (coal, iron ore, lead-zinc, building stone, clay ...), metallurgical, mechanical engineering, construction materials, garments, paper and packaging industries, electric and electronic industries including the thermal power plant, agro-forestry processing industry such as tea, fruit, beer, beverage, mineral water (General Statistics Office 2020).

2.2 Sampling

The sampling campaign was carried out in Cau river flowing through Thai Nguyen city in October 2019. Five (5) sediment core were collected at depth of 30cm from M1 to M5 site in the Cau river (Fig. 1). The selected sites are based on evaluating contamination levels for upstream, downstream and the areas are received the wastewater from main canals/streams to the Cau river. The core samples were collected by using an acrylic tube with a length of 30cm. Thirty centimeters (30cm) long sediment core were sliced in segments of 5cm by using an acrylic slicer. Thus, each sediment core has six samples at different depths. All samples were transferred into polypropylene bags, stored in cool

conditions with ice, and brought back to the laboratory on the same day. All sampling tools and containers were pre-rinsed with methanol and MilliQ water before use.

2.3 Target compounds, chemicals, and equipment

Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoate Acid (PFOA) were selected as the target compounds for this study. They were representatives of the PFC group and usually detected at the highest concentration of all environmental components and their toxicity and bioaccumulation have been reported in many publications (Pico et al. 2012) (Becker et al. 2008) (Li et al. 2011) (Lam et al. 2014) (Gomez et al. 2011) (Pico et al. 2012).

Perfluoro-n-octanoic acid (PFOA-001S) and Perfluorooctane-n-sulfonic acid (PFOS-001S) standards were purchased from AccuStandard, Inc. (US). The mass labeled internal standards MPFOS (Sodium perfluoro-1-[1,2,3,4-¹³C₄] octane sulfonate) and MPFOA (Perfluoro-n-[1,2,3,4-¹³C₄] octanoic acid) were obtained from Wellington Laboratories Company (Canada). Methanol and acetonitrile solutions with HPLC grade were purchased from Merck (Germany). PFCs standard solutions were prepared in acetonitrile in MilliQ water (40:60 v/v). All the equipment involved in the study was pre-cleaned with methanol and MilliQ water.

2.4 Sample preparation and analysis

Sediment core samples were extracted by the accelerated solvent extraction method (ASE) according to the study of Kunacheva (Kunacheva et al. 2011). In the laboratory, sediment core samples were air-dried, weighted 0.2g into sample cell, spiked 10µg/L an internal standard mixture, and then inserted into ASE cells on an ASE 350 (Thermo Fisher Scientific Inc., Waltham, MA, US) for extraction. The methanol (LC/MS grade) was used as a solvent for the extraction. The extraction process ran two cycles under the pressure of 2000 psi and a temperature of 100⁰C. The final extracted (60-90mL) were diluted by MilliQ water into 1000mL and continued solid phase extraction by the following procedure. The extraction (1000mL) was filtered through GF/B filter papers (1µm, Whatman, UK), to remove suspended solids. The filtrates were passed through a Presep C-Agri (C18) cartridge (Wako, Japan) connected with an Oasis HLB cartridge (Water, US) at a flow rate of 10mL/min. Before loading the sample, the cartridges were preconditioned by 10mL of methanol and 20mL of MilliQ water, respectively. The target compounds in the dry cartridges were eluted by 4mL of methanol into a polypropylene tube. And then they were dried under the gentle nitrogen flow and reconstituted with 1mL of 40% acetonitrile in MilliQ water. The final extracted was analyzed by HPLC-MS/MS. Five microliters of the extracted sample were injected into the chromatography column. The mobile phase consists of (A) 5mM ammonium acetate in MilliQ water and (B) 100% acetonitrile. The separation process began with initial conditions of 50% (B), which was decreased to 10% (B) at 1.25 min, 10 % to 60% B from 1.25 min to 1.40 min, 60% B was held for 3.6 min, and finally at 50% (B) at a flow rate of 0.5 mL/min.

PFOS and PFOA in sediment samples were analyzed by using Agilent 6430A Triple Quadruple HPLC-MS/MS System (Agilent Technologies, US) with chromatography column Eclipse Agilent XDB-C18 (2.1 x 150 mm, 5µm narrow-bore). The total organic carbon contents in sediment were analyzed by using a Shimadzu TOC-Vcph analyzer combined with a solid sample module (SSM-5000A) heating at 900⁰C based on the NCEA-C-1282- Methods for the determination of total organic carbon (TOC) in soils and sediments. The clay content and particle size distribution of sediment were determined by the sieving method based on the guidelines ASTM C136-01- Standard test method for sieve analysis of fine and coarse aggregates and ASTM C117-17- Standard test method for materials finer than 75-µm (No. 200) sieve in mineral aggregates by washing.

2.5 Quality assurance and control

The calibration curves for quantification were based on five points ranging from 0.1 µg/L to 100 µg/L. The determination coefficient (R^2) of the linear calibration curves was more than 0.99. Limit of quantification (LOQ) was

calculated by the ratio of signal to noise (S/N) 10:1. The potential contamination was checked by the procedural blanks after every six samples. The analysis was replicated on all samples and the coefficient of variations of concentration was below 20%. The recovery rates were checked by spiking PFOS and PFOA internal standards (10 microgram/L) into the samples. The recovery results for all samples were in the range of 78.47% – 115.96%.

Results And Discussions

3.1 Spatial distributions in surface sediment of PFOS and PFOA

The measurement results of PFOS and PFOA concentrations in surface sediment (depth of 0–5 cm) in Cau river, Thai Nguyen are shown in Fig. 1. The concentrations of PFOS and PFOA in the surficial sediment (0-5cm of depth) are ranged from 1.19 ng/g to 4.73 ng/g and 0.17 ng/g to 1.78 ng/g, respectively. The largest value of total PSOS and PFOA concentration was recorded at site M3 (6.44 ng/g). This is the location where the river receives the discharge from the Thai Nguyen city wastewater treatment plant using activated sludge technology (Thai Nguyen city drainage and wastewater treatment project management unit 2008). Many previous studies have shown that only plants with advanced treatment technologies such as advanced oxidation processes (photolysis by UV, photocatalytic, ...), membrane filtration, and sonochemistry process is possible to effectively remove these compounds from the water environment, and activated sludge technology is not effective in the treatment of PFCs (Yao et al. 2014, Arvaniti et al. 2015). The second-highest concentration was observed at site M2, with a total concentration was 4.86 ng/g, in which the PFOS and PFOA contents were 3.07 ng/g and 1.78 ng/g, respectively. This is a central area of Thai Nguyen city, with a high population density, and several manufacturing facilities in this area. Meanwhile, the remaining sites are M1, M4, and M5 which are located upstream, the confluence of Cau River and main irrigation canal, and downstream of Cau River, respectively have the lower concentrations with total PFOS and PFOA concentration recorded at 1.37ng/g, 2.06ng/g, and 1.80ng/g, respectively. These results suggest that untreated or inefficiently treated domestic and industrial wastewater are the potential sources of PFOS and PFOA pollution to river sediments. This result is similar to conclusions in the studies by Bao et al and Pan et al (Bao et al. 2010, Pan et al. 2015).

The concentrations of target compounds in surface sediments of the Cau river were also compared with the worldwide levels and shown in Table 1. The results show that both PFOS and PFOA are typical pollutants, with concentrations often ranging from < 0.1 to 10 ng/g. The concentrations of both PFOS and PFOA in sediments of Cau river in Thai Nguyen are significantly higher than those observed in the world and some major rivers in Vietnam. The average concentration of PFOS and PFOA in the surface layer of Cau river was 2.66 ng/g and 0.84 ng/g, respectively. However, these values are still significantly lower than the recorded concentration in the Yellow river as the second-longest river in China with a populous area has many kinds of human activities with the mean PFOS concentration was reported as 198.81 ng/g (Wang et al. 2013). The difference in the concentration of PFOS and PFOA in river sediments can be explained by the different sources of pollutant discharge, wastewater treatment technologies, discharge rates, hydrogeological characteristics of the river, etc.

Table 1
Comparison of PFOS and PFOA concentration (ng/g) in river sediment with other studies

River	Location	Depth of sediment (cm)	PFOS range (mean) (ng/g)	PFOA range (mean) (ng/g)
The Hun river ^{a)}	China	0–10	0.13–0.37	< 0.08–0.17
The Taizi river ^{a)}		0–10	< 0.12–0.36	0.09–0.14
The Daliao river ^{a)}		0–10	0.14–0.28	0.10–0.13
The Zhujiang river ^{b)}	China	0–2	< 0.12–3.1 (0.58)	0.09–0.29 (0.21)
The Huangpu river ^{b)}	China	0–2	< 0.12–0.46 (0.11)	0.20–0.64 (0.43)
The Liao river ^{c)}	China		0.04–0.48 (0.11)	0.02–0.18 (0.08)
The Yellow river ^{d)}	China	0–10	75.48–456.98 (198.81)	-
The Yellow river ^{e)}	China	0–5	< LOD-3.69 (0.32)	0.14–0.93 (0.29)
The Hai river ^{e)}	China	0–5	< LOD-0.71 (0.30)	0.09–0.53 (0.23)
The Liao river ^{e)}	China	0–5	< LOD-0.10 (< LOD)	0.15–0.42 (0.24)
The Zhujiang river ^{e)}	China	0–5	0.27–1.28 (0.57)	0.31–0.68 (0.38)
The Dongjiang river ^{e)}	China	0–5	< LOD-1.48 (0.18)	0.13–0.92 (0.29)
L'Albufera Natural Park ^{f)}	Spain	0–30	0.10–4.80 (1.79)	0.03–10.9 (3.19)
The Nakdong river ^{g)}	Korea	1–5	0.04–0.27 (0.16)	0.04–0.08 (0.06)
The Yeongsan river ^{g)}		1–5	0.05–0.11 (0.07)	ND-0.05 (0.02)
The Nam river ^{g)}		1–5	0.02–0.12 (0.05)	0.03–0.09 (0.05)
The Bukhan river ^{g)}		1–5	0.01–0.07 (0.04)	ND-0.09 (0.04)
The Namhan river ^{g)}		1–5	0.02–0.048 (0.18)	0.03–0.28 (0.07)
Da Rang, Da Nong river ^{h)}	Vietnam	1–5	< 0.2	< 0.08–0.17
Cai, Quan Truong river ^{h)}		1–5	< 0.2	< 0.08
Dong Nai river ^{h)}		1–5	< 0.2	< 0.08
Sai Gon river ^{h)}		1–5	< 0.2	< 0.08
Mekong river ^{h)}		1–5	< 0.2	< 0.08
Cau river ⁱ⁾	Vietnam	0–5	1.19–4.73 (2.66)	0.17–1.78 (0.84)

^{a)} (Bao et al. 2009); ^{b)} (Bao et al. 2010); ^{c)} (Yang et al. 2011); ^{d)} (Wang et al. 2013); ^{e)} (Pan et al. 2015); ^{f)} (Pico et al. 2012); ^{g)} (Lam et al. 2014); ^{h)} (Lam et al. 2017); ⁱ⁾ This study.

River	Location	Depth of sediment (cm)	PFOS range (mean) (ng/g)	PFOA range (mean) (ng/g)
		5–10	1.55–4.54 (2.42)	0.37–1.98 (0.97)
		10–15	1.31–2.85 (2.79)	< 0.1–1.55 (0.55)
		15–20	1.21–2.35 (2.06)	< 0.1–1.56 (0.51)
		20–25	1.02–4.18 (1.42)	< 0.1–1.04 (0.25)
		25–30	0.51–1.88 (1.17)	< 0.1–0.60 (0.14)
a) (Bao et al. 2009); b) (Bao et al. 2010); c) (Yang et al. 2011); d) (Wang et al. 2013); e) (Pan et al. 2015); f) (Pico et al. 2012); g) (Lam et al. 2014); h) (Lam et al. 2017); i) This study.				

To better understand the distribution of PFOS and PFOA between water and sediment, the distribution coefficient (K_d) is estimated by the ratio between the concentration in the surface sediment (C_s) and the concentration in the liquid phase (C_w) followed the equation: $K_d = C_s / C_w$ and the organic carbon normalized partition coefficient (K_{oc}) was calculated by $K_{oc} = K_d / TOC$, where TOC is the sediment organic carbon fraction. The results are shown in Table 2. The results showed that the distribution coefficient K_d is relatively different for PFOS and PFOA, with $\log K_d$ values ranged from 1.31– 1.86 and 0.08 – 1.31 for PFOS and PFOA, respectively. The $\log K_{oc}$ value of PFOS (2.63 - 3.09) and PFOA (1.51- 2.54) in this study were similar to those in Tangxun Lake, China (3.7 ± 0.38 for PFOS and 2.3 ± 0.23 for PFOA) (Zhou et al. 2013). It can be seen that PFOS has a higher affinity to sediment than PFOA. This result is consistent with the hydrophobicity of the two compounds revealed by their K_{ow} values and solubility. The $\log K_{ow}$ value of PFOS (5.26) is higher than PFOA (4.59) which indicated that PFOS is more hydrophobic than PFOA. In addition, PFOS has very low water solubility (0.57 g/L) in contrast with PFOA that has a relatively high solubility (3.4 g/L). Even with the same length of the carbon chain PFOS has a significantly higher adsorption capacity in sediment than PFOA. It was explained that the dominant mechanism of the adsorption to the sediment of the PFCs is based on hydrophobic interactions and the greater hydrophobic properties of the sulfonate functional groups compared to the carboxylate functional groups (Christopher P. Higgins et al. 2006, Zhao et al. 2012, Du et al. 2014). It also elucidated the fate and bioavailability of PFCs in sediment. PFOS has a high adsorption affinity to sediments and they will prioritize distribution over sediments rather than in the aqueous phase. Meanwhile, PFOA has weak capacity adsorption, along with good water solubility, so it tends to be distributed in the liquid phase when exists in the aquatic environment.

Table 2
The distribution coefficient K_d between water and sediment in the Cau river

Site	PFOS						PFOA					
	C_s (ng/g)	C_w (ng/L) a)	Log K_d	Log K_{oc}	Log K_{ow} b)	Solubility (g/L) ^b	C_s (ng/g)	C_w (ng/L) a)	Log K_d	Log K_{oc}	Log K_{ow} b)	Solubility (g/L) ^b
M1	1.20	0.06	1.33	2.71	5.26	0.57	0.18	0.04	0.64	2.01	4.59	3.40
M2	3.77	0.18	1.31	2.64			1.78	0.89	0.30	1.62		
M3	4.73	0.07	1.86	3.10			1.71	0.08	1.31	2.54		
M4	1.52	0.06	1.38	2.70			0.54	0.05	1.01	2.33		
M5	1.57	0.07	1.33	2.75			0.26	0.19	0.08	1.51		

a) (Tran Hoai Le et al. 2019) b) (Deng et al. 2012)

3.2 Vertical distributions in core sediment of PFOS and PFOA

The core samples of Cau river sediment were collected to evaluate the distribution according to sediment depth of PFOS and PFOA. At each sampling site, the samples with a depth of 30 cm were collected and divided into six slices, each slice having a thickness of 5cm. The variation of concentration of PFOS and PFOA in each sediment layer at selected sites is shown in Fig. 2.

PFOS and PFOA exhibit a similar trend of the total concentration of all investigated depths in sampling sites along Cau river. The total concentration of all depth samples for PFOS and PFOA found highest at site M3 followed by M2. The lowest level for both compounds found at site M4. PFOS concentrations were higher than PFOA concentrations for all sample sites and at all different sediment depths. PFOS was detected in sediment samples at all depths ranging from 0-30cm. In contrast, PFOA was found only in all depths of 0–30 cm at M2 and M3 sites. With the remaining sites as M1, M4, and M5, PFOA was not detected or found at the very low level at the depth from 20 to 30 cm, in which < 0.1–1.04 ng/g (mean 0.25 ng/g) for depths of 20–25 cm, and < 0.1–0.60 ng/g (mean 0.14 ng/g) for depth of 25-30cm. These results suggest that the desorption from the sediment has occurred, and significant difference between PFOS and PFOA. This phenomenon often occurs in the surficial sediment, but it occurs in the deep layer in our research. The research results of Zhao et. al (Zhao et al. 2012) show that the desorption is one of the main processes to determine the existence of PFCs in sediments and is affected by the chain length and functional groups of PFC compounds, in which PFASs have the rate of desorption less than PFCAs with the same chain length. In their study, Zhao found that the desorption rate of PFOA was in the range of 77.6–87.3%, while PFOS was only 14.0-26.9%. This result is similar to the study of You et. al (You et al. 2010) confirming that the adsorption of PFOS to sediments is irreversible.

The previous studies analyzing the variation of concentration of PFCs with depth for core sediment samples are shown a tendency of decrease of PFC concentrations with sediment depth increasing (Bao et al. 2009, Bao et al. 2010, Zushi et al. 2010, Wang et al. 2013). This trend is also clearly observed in the sediments of the Cau river. The highest total concentration in surface sediment (depth of 0-5cm) was recorded at 4.86 ng/g and 2.06 ng/g, respectively at M2 and M4. Meanwhile, all the highest recorded concentrations in sediments with a depth of 5–10 cm ranging from 2.63 ng/g to 6.52 ng/g at M1, M3, and M5. In the remaining sediment slices, with a depth from 10 to 30 cm, the total concentration of PFOS and PFOA at all sites tends to decrease gradually. Zushi et. al (Zushi et al. 2010) examined the trend in the use of PFCs by evaluating these compounds in core sediment samples in Tokyo Bay, Japan. Results show

the trend of consumption of PFOS products increased gradually from the 1970s, then gradually decreased from the 1990s, while the PFOA increased in the 1950s and 1960s and increased rapidly after 1990. This result is similar to studies by Codling et.al (Codling et al. 2014, Codling et al. 2018) in several US lakes which showed that total concentrations of PFCs peaked in the late 1990s and early 2000s, a slight increase in 2005, and then decreasing. The results of this study showed that a decreased trend of PFOS and PFOA pollution in the sediment in the Cau river in recent years.

3.3 The influences of sediment properties on the adsorption onto sediment

The review study of Du et. al suggests that the adsorption of PFOS and PFOA on the adsorbent materials is influenced by (1) chemistry solutions of liquid phase such as solution pH, inorganic ions, organic compounds; (2) properties of PFCs compounds such as chain length, functional groups, and (3) adsorbent properties like particle size, surface area, surface chemistry (Du et al. 2014). For some adsorbents containing organic components such as sediments and sludge, their adsorption properties are affected by the organic matter composition. Many studies have been conducted to investigate the effects of various sediment parameters such as surface area, the organic carbon content, ion exchange capacity, size of the particle, and sand content on PFC adsorption capacity on sediments, and the content of organic carbon was found to be decisive physicochemical properties of sediment affecting the adsorption of PFCs on sediment (Du et al. 2014).

In our study, the physicochemical properties of core sediment samples include total organic carbon (TOC) content, clay content, and particle size distribution in the sediments were also analyzed to evaluate the influence of these properties of sediment on the adsorption of the target compounds. Physicochemical properties of the Cau river sediment are summarized in Table 3. The TOC content ranges from 3.10 to 5.90%, of which the highest average concentration is recorded at the M3 site (mean 5.65%) corresponds to the receiving site of the Thai Nguyen wastewater treatment plant, and the lowest was recorded at the M1 site (mean 3.40%) is an upstream site of Cau river. The concentration of TOC in Cau river was lower than these values found in the sediments of Cedar and Ortega rivers (Florida, USA) with the concentration of TOC was ranged from 2.3–22.6% (Ouyang et al. 2006), but significantly higher than the values were explored in the sediments of the alluvial and estuarine in the Mahi river (India) with a range between 0.04 and 0.39% and 0.04 and 0.23%, respectively (Dinakaran et al. 2011). TOC concentrations in Cau river tend to more accumulate at the surface layers (0-10cm depth) than at the next layer (15-30cm). The percentages of gravel, sand, silt, and clay particles can be obtained from the particle-size distribution in which gravel (greater than 4.75 mm), sand (4.75 to 0.075 mm), and silt and clay (less than 0.075 mm). The results have shown that the majority of particles with a size larger than 0.6mm are mainly distributed in the surface layer (0-5cm), especially at M2 and M3 sites. These particles are mainly sands, sludges from the drainage system in these areas are deposited. With the next layers, the grain distribution is mainly particles smaller than 0.3 mm in diameter, especially at the M4 site (Thac Huong dam) where there is a strong deposition process. The clay content in all sediment samples is quite high, ranging from 30–90% (average 74.93%). In general, the Cau river sediments have relatively high TOC and clay content, especially at locations near the receiving points of domestic and industrial wastewater (M2 and M3 sites). The particle size distribution is different between the survey sites, but clearly shows the tendency of the proportion of small-sized particles to increase with the depth of the sediment. The above characteristics are predicted to be favorable factors for the adsorption of PFOS and PFOA on sediments.

Correlation analysis between the concentration of PFOS and PFOA in sediment (Cs) and sediment characteristic parameters including TOC, clay content, and distribution of the size of sediment particles was conducted and shown in Fig. 3. The concentration in sediment and TOC have a signification positive correlation for both PFOS ($R^2 = 0.5286$, $n =$

30) and PFOA ($R^2 = 0.5699$, $n = 30$). This result reconfirms that the organic content is the determinant factor of adsorption affinity and hydrophobic interaction between the carbon chain and the organic matters is the driving force for the sorption of PFCs on sediment. This result is similar to published studies that show the content of TOC is the dominant parameter affecting the adsorption of PFOS and PFOA on sediment (Gobas et al. 2003, Christopher P. Higgins et al. 2006, Zareitalabad et al. 2013, Du et al. 2014, Cao et al. 2015). However, the biological activity of sludge was observed to be able to affect the PFC sorption, in which the sludges with high biological activity are higher sorption capacity than those with low biological activity. It suggests that the bio-properties of microorganisms in sludge also affect the PFC sorption (Du et al. 2014). There is a need for more in-depth studies on the effect of the organic composition from the microbiota in sediment on the adsorption of PFCs in the future.

The particle size of the adsorbent is considered to effecting on the adsorption capacity, Yu et.al found that the activated carbon particles with smaller sizes have a higher adsorption capacity even though they have the same specific surface area (Yu et al. 2009). Zhao et. al also examined the rate of sorption on the different sediment fractions and found that the majority of PFCs (above 90%) were distributed in these small-size fractions (smaller than $65 \mu\text{m}$) (Zhao et al. 2012). The tiny size and plate form of clay and mineral particles give a high surface area, which enhances the adsorption onto their surface. However, the influence of sediment particle size on the adsorption of sediment was not shown. Similarly, there was no significant correlation between Cs and clay content in the sediment in our study. Mussabek et al found that the sorption onto sediment of PFC also depends on the mineral contents in sediment such as metal ions. Their study explored that the correlation between PFCs concentration and sediment elemental content, in which a possitive correaltion was found between PFOS and lead, arsenic, iron contents, PFOA and lead, arsenic, titanium in sediment (Mussabek et al. 2020). It suggests that we need more detailed studies on the effecet of inorganic contents on the distribution of PFCs in sediment.

Table 3
Physicochemical properties of sediment in the Cau river

Sample		Total Organic Carbon (%)	Clay content (%)	Particles size distribution (%)				
				Larger than 1,18 mm	0.6–1.18 mm	0.3–0.6 mm	0.15–0.3 mm	Smaller than 0.15 mm
M1	0–5 cm	3.19	78.76	20.172	15.451	8.155	28.755	27.468
	5–10 cm	3.99	72.26	17.703	25.598	16.268	27.033	13.397
	10–15 cm	3.76	81.34	22.939	20.430	13.620	21.147	21.864
	15–20 cm	3.10	88.92	27.429	24.286	14.000	15.429	18.857
	20–25 cm	3.45	83.53	30.357	20.833	11.607	14.286	22.917
	25–30 cm	3.36	50.27	4.932	8.493	5.205	45.205	36.164
M2	0-5cm	4.76	87.87	31.527	20.690	15.271	17.241	15.271
	5–10 cm	4.81	89.89	28.272	27.225	16.230	17.277	10.995
	10-15cm	4.77	92.85	28.966	22.069	13.793	20.000	15.172
	15-20cm	4.42	73.83	34.247	20.091	11.416	12.329	21.918
	20-25cm	4.56	90.45	30.088	24.779	13.717	14.159	17.257
	25-30cm	4.26	63.18	31.839	22.422	12.556	13.453	19.731
M3	0-5cm	5.83	90.00	22.807	30.702	19.298	13.158	14.035
	5–10 cm	5.90	71.91	34.899	16.779	11.409	14.765	22.148
	10-15cm	5.06	91.35	35.989	20.321	10.160	17.647	15.882
	15-20cm	5.70	86.15	30.808	22.727	14.141	16.162	16.162
	20-25cm	5.42	88.65	39.554	25.478	12.102	13.567	9.299
	25-30cm	5.59	80.83	30.769	26.627	14.793	11.243	16.568
M4	0-5cm	3.78	64.20	33.034	13.034	12.360	27.978	13.596
	5–10 cm	3.95	46.35	33.443	5.902	4.918	40.328	15.410

	10-15cm	3.14	36.17	24.255	9.362	14.255	39.574	12.553
	15-20cm	3.45	31.57	15.774	8.924	16.824	32.257	26.220
	20-25cm	3.87	54.13	11.610	8.989	5.243	26.592	47.566
	25-30cm	3.24	73.66	9.877	18.107	10.700	28.807	32.510
M5	0-5cm	4.77	79.08	33.766	18.182	12.987	16.883	18.182
	5-10cm	4.53	87.70	12.451	25.681	18.677	34.241	8.949
	10-15cm	4.13	74.76	18.696	20.773	17.391	36.377	6.763
	15-20cm	4.11	77.97	31.463	19.919	12.602	19.756	16.260
	20-25cm	4.01	80.70	19.298	20.175	12.281	19.298	28.947
	25-30cm	4.58	79.36	17.727	24.545	14.545	19.091	24.091

Conclusions

This is the first study on the occurrence of PFOS and PFOA in sediment from the Cau river, Vietnam. The results show that PFOS and PFOA are present in the surface sediment of the Cau river with the range of concentration of PFOS and PFOA being 0.19–4.73 ng/g, and 0.17–1.78 ng/g, respectively. The highest concentrations were observed near the highly populated and industrial areas, which indicated that the potential pollution sources of PFCs were untreated municipal and industrial wastewater. The depth-related concentration in sediment tended to decrease with increasing depth. Concentrations in the surface sediments (0-5cm) are lower than the second layer (5-10cm), which suggested a downward trend in the contamination of these compounds in recent years. The water-sediment distribution coefficient (log K_d) result is relatively different for PFOS and PFOA in the range of 1.31–1.86 and 0.08–1.31 for PFOS and PFOA, respectively, and suggested that PFOS has a higher affinity to sediment than PFOA. It elucidated the fate and bioavailability of PFCs in sediment, in which PFOS will prioritize distribution over sediments rather than in the aqueous phase, PFOA tends to be distributed in the liquid phase when exists in the aquatic environment. This study also confirmed that the content of total organic carbon is the physiochemical property that has the main influence on the adsorption to sediments of PFOS and PFOA. The results of this study provide an overview of PFOS and PFOA contamination in sediment in the Cau river, which helps to build a general picture of the current state of PFC pollution in Vietnam.

Declarations

5. ACKNOWLEDGEMENTS

This research is funded by the National University of Civil Engineering (NUCE) under grant number 09-2020/KHXD-TD.

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Availability of data and materials

All data generated or analyzed during this study are included in this published article.

Competing interests

The authors declare that they have no competing interests.

Funding

The authors acknowledge financial support from the National University of Civil Engineering (NUCE) under the grant number 09-2020/KHXD-TD.

Authors' contributions

Hoai Le Tran: conceptualization, sampling, analysis, data analysis, writing original draft, writing - review and editing.

Dieu Anh Van: conceptualization, analysis, data collecting, writing - review and editing. **Trung Hai Huynh:** conceptualization, data analysis, supervision, writing - review and editing. **Duc Thao Vu:** conceptualization, supervision, writing - review and editing.

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Figures

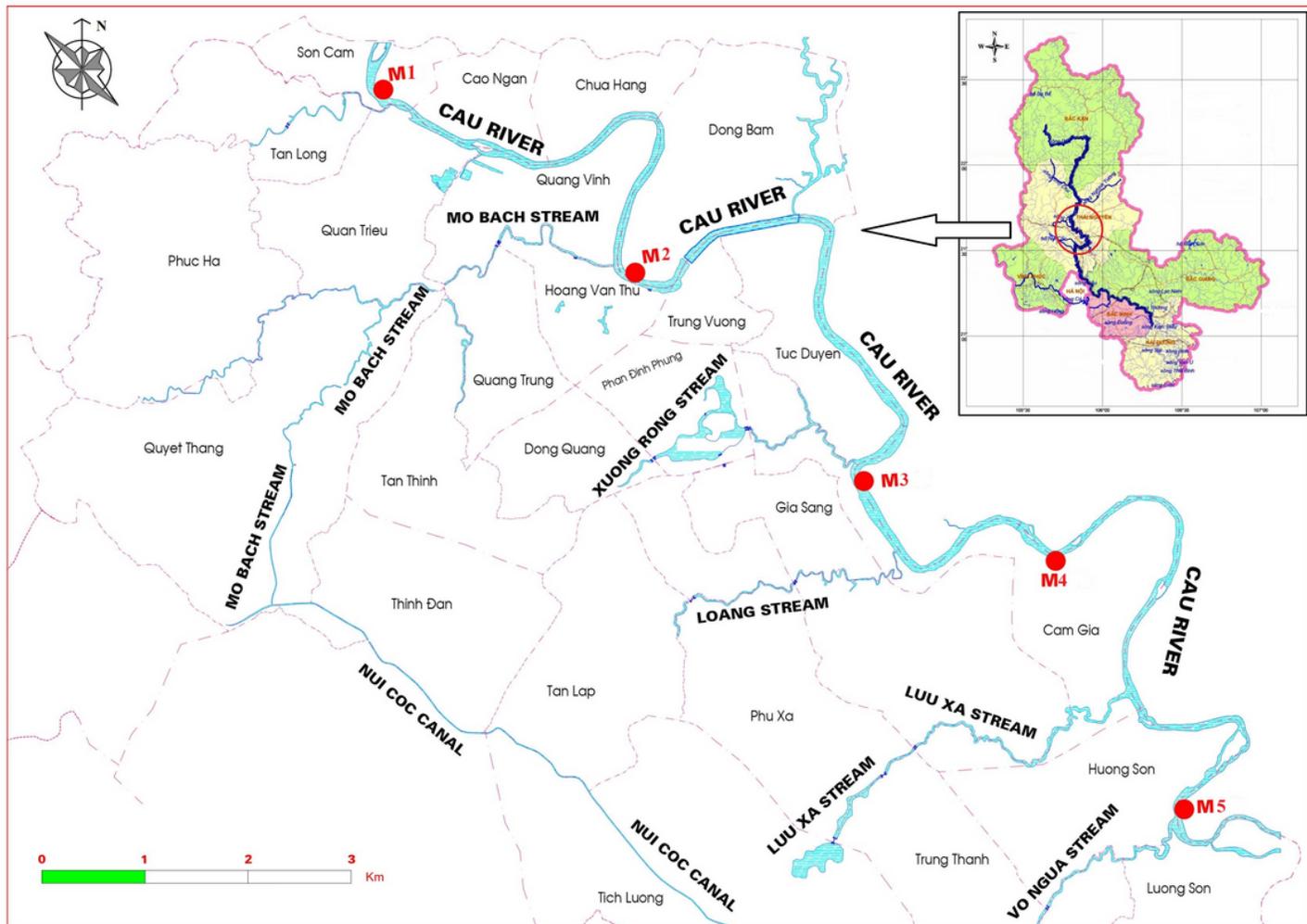


Figure 1

Map of sampling sites in Cau river, Thai Nguyen city Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

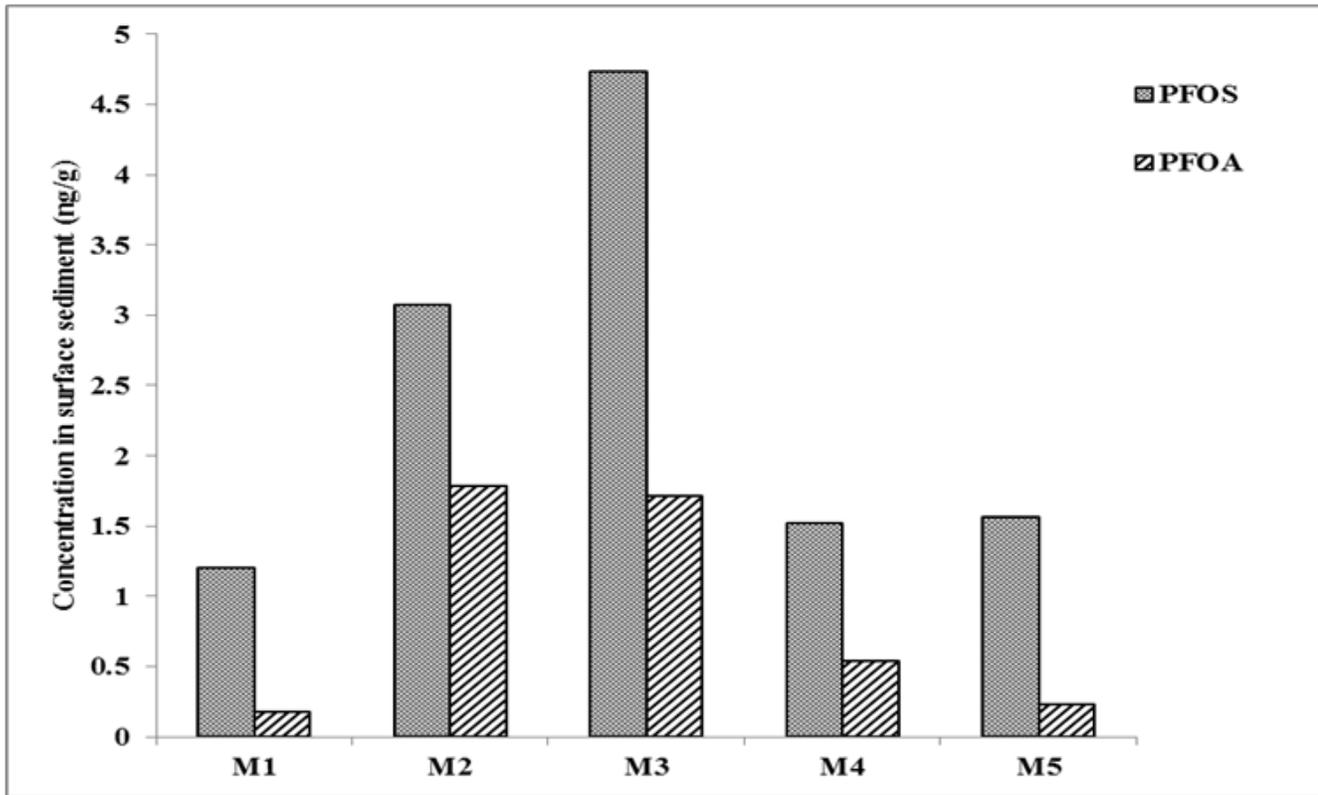


Figure 2

Concentration (ng/g) of PFOS and PFOA in surface sediment

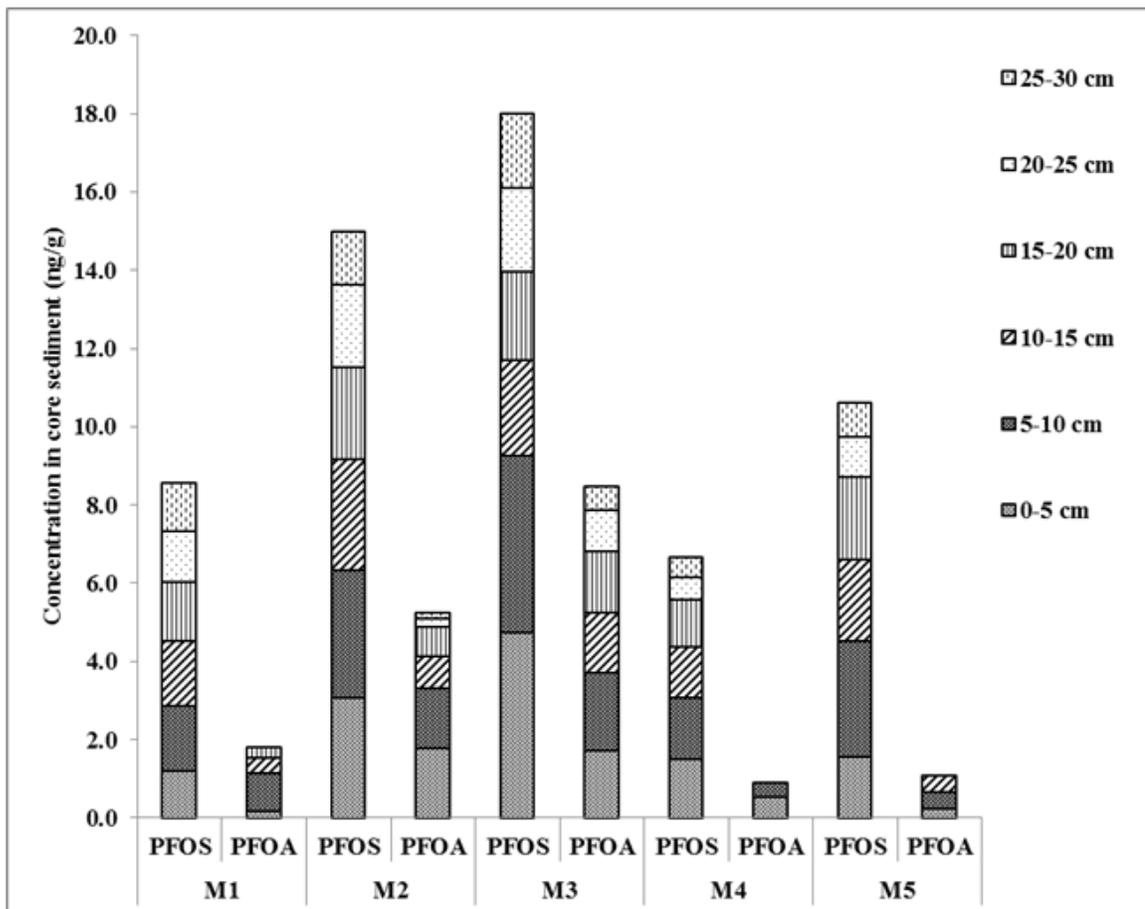


Figure 3

Concentrations of PFOS and PFOA in the core sediment

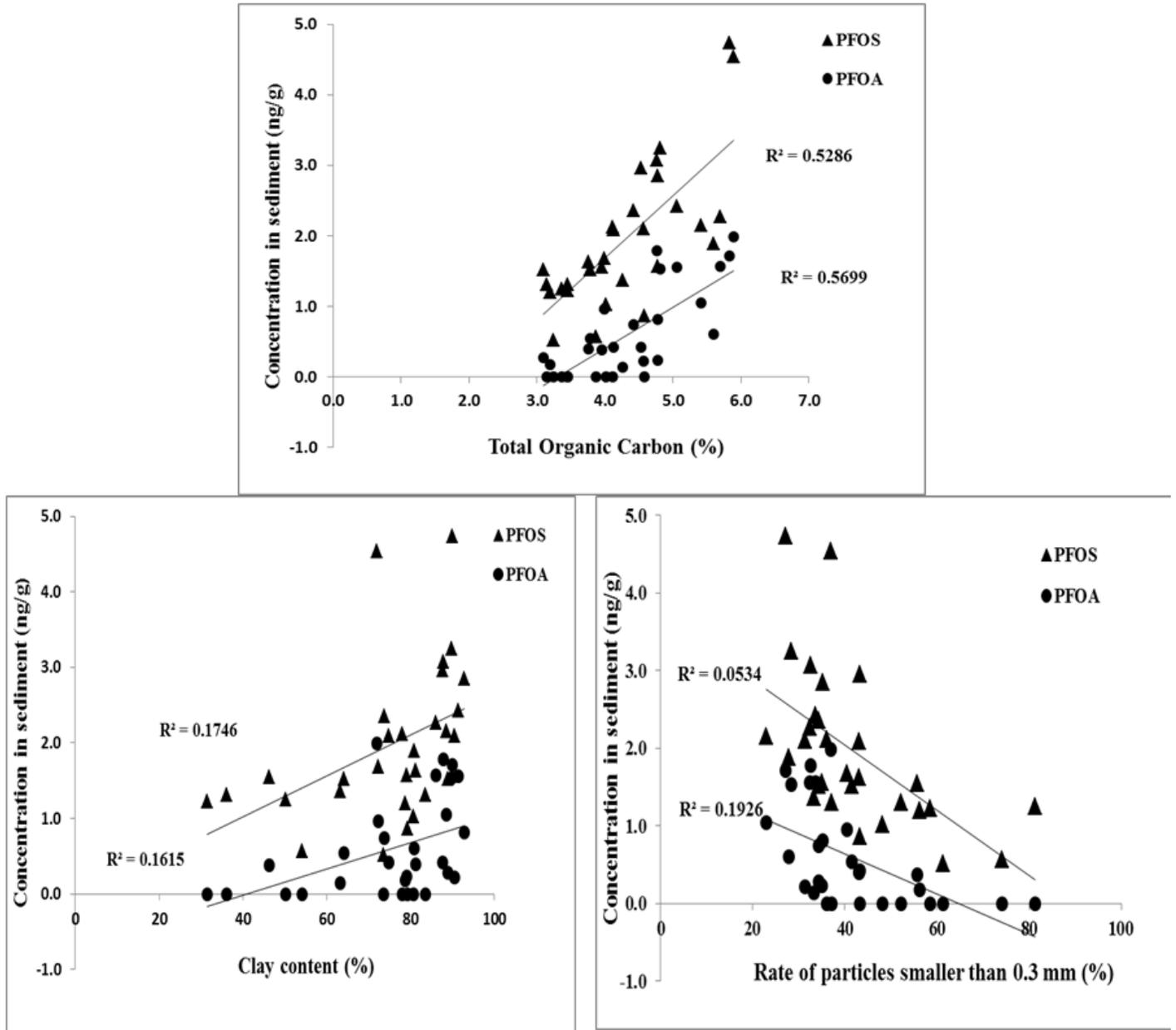


Figure 4

Correlation between concentration of PFOS and PFOA in sediment and physicochemical properties of sediment of the Cau river