

## Assessment of contamination levels and exposure risk of perfluoroalkyl substances (PFOS and PFOA) in Vietnamese fish

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### Abstract

Contamination levels of two typical perfluoroalkyl substances (PFASs) including perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) were evaluated in Vietnamese fish samples by using our monitoring results and database reported in previous studies. In freshwater fish taken from West and Yen So Lakes (Hanoi), PFOS and PFOA concentrations ranged from < 0.030 to 0.48 (mean 0.12) ng/g, and from < 0.010 to 0.19 (mean 0.058) ng/g, respectively. These levels were comparable to those measured in fish samples from other areas in Vietnam, but were generally lower than values documented for fish samples from other countries. PFOS and PFOA daily intake doses via fish consumption ranged from 0.015 to 0.48 (mean 0.12) and from 0.005 to 0.20 (mean 0.065) ng/kg/day. In general, these intake doses were lower than the reference dose of 20 ng/kg/day, suggesting acceptable levels of risk.

**Keywords:** PFOS, PFOA, fish, dietary exposure, Vietnam.

### 1. INTRODUCTION

Perfluoroalkyl substances (PFASs) such as perfluorocarboxylic acid (PFCAs) and perfluoroalkyl sulfonic acid (PFSAs) are persistent organic pollutants (POPs) with critical properties such as persistent in the environment, bioaccumulative, and toxic [1]. Among PFASs, perfluorooctane sulfonic acid (PFOS) and related compounds were restricted by the Stockholm Convention on POPs in 2009. Perfluorooctanoic acid (PFOA) and related compounds were listed as eliminated chemicals by the Stockholm Convention in 2019.

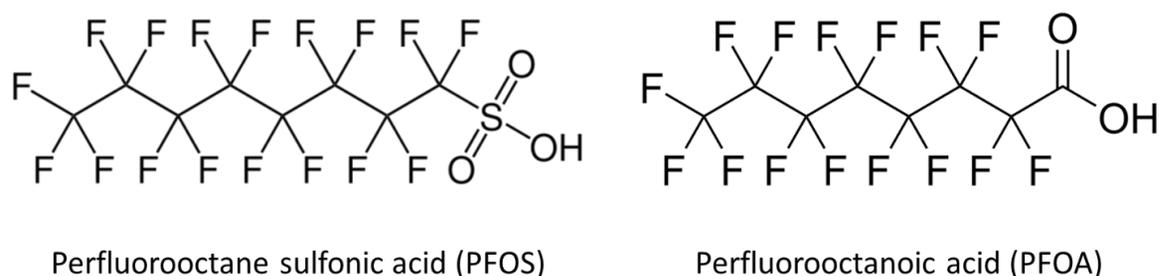
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Structural formulas of PFOS and PFOA are shown in Figure 1. These substances are persistent with excellent surface characteristics. Therefore, they are popularly used in industries as additives in coating materials, paints, surfactants, textiles, foams, and emulsifiers [2]. The contamination of PFASs in the environment and their occurrence in humans and animals have been reported since the 2000s [3-4]. Because of PFAS abundance in water environment, many studies on the accumulation of PFASs in aquatic animals have been conducted for pollution monitoring and risk assessment purposes [5].



**Figure 1.** Structural formulas of PFOS and PFOA

Little is known about the contamination and impacts of PFASs in Vietnam. PFOS and PFOA were found for the first time in some water samples collected from Nhue River, Hanoi in 2006 at levels smaller than 1 and 10 ng/L [6]. Since then, PFASs have been detected in different sample matrices such as water, sediment, biota, human blood, breast milk, etc. [7-9]. Studies on PFAS in Vietnamese fish samples are scarce. [7, 9]. Moreover, these studies did not focus on evaluating PFAS exposure risks through fish consumption. To assess contamination degree, human exposure, and health risks related to PFOS and PFOA, freshwater fish samples from West and Yen So Lakes (Hanoi) were examined for PFOS and PFOA concentrations in muscle tissues. The results of this study were analyzed and compared with previous studies to provide comprehensive and updated information about PFOS and PFOA in Vietnamese fish. Exposure levels and potential effects of these two compounds in fish were estimated through daily intake doses in the comparison with reference doses.

## 2. MATERIALS AND METHODS

### 2.1. Sample information

Fish samples were collected by using nets in Yen So and West Lakes on June 2016. In each lake, 6 individual samples of 4 species were selected for PFOS and PFOA analysis (total n = 24). Investigated species include bighead carp (*Hypophthalmichthys nobilis*), common carp (*Cyprinus carpio*), rohu (*Labeo rohita*), and tilapia (*Tilapia* spp.). Data on PFOS and PFOA concentrations in fish samples from previous studies were also included to facilitate comparison. Murakami et al. (2011) reported PFOS and PFOA levels in 4 snakehead samples collected from Bac Ninh and Hung Yen Provinces in 2007 [7]. Lam et

al. (2017) analyzed PFOS and PFOA in 5 species including tilapia (*Oreochromis niloticus*,  $n = 10$ ), snakehead (*Chana striata*,  $n = 3$ ), dusky sleeper (*Eleotris fusca*,  $n = 3$ ), shark catfish (*Pangasius elongatus*,  $n = 10$ ), and flying barb (*Esomus danricus*,  $n = 5$ ) collected between 2013 and 2015 from Da Rang (Phu Yen Province), Dong Nai River and Me Kong River [8].

## 2.2. Analytical methods

The analytical method for PFOS and PFOA in fish samples was referred to previous studies [4, 8]. The fish samples were stored at  $-22\text{ }^{\circ}\text{C}$  until analysis. About 1 g of muscle tissue was transferred to a 50-mL tube and homogenized with 5 mL pure water by a T-25 Digital ULTRA-TURRAX® equipment (IKA, Germany). Then, one portion of homogenate (1 mL) was transferred into a new tube with surrogate standard, 0.5 M tetrabutylammonium hydrogen sulfate solution (1 mL), and 0.25 M sodium carbonate buffer solution (2 mL). The extraction process was conducted twice with  $2 \times 5\text{ mL}$  methyl tert-butyl ether on a KS 501 Digital shaker (IKA, Germany). Extract portions were pooled, evaporated, and redissolved in methanol (1 mL) before analysis. The analytical standard (PFAC-MXB) containing PFOS and PFOA, and surrogate standard (MPFAC-MXA) containing  $^{13}\text{C}_4$ -PFOA and  $^{13}\text{C}_4$ -PFOS, were purchased from Wellington Laboratories. The standard solutions were prepared in methanol. One hundred microliters of the surrogate standard ( $^{13}\text{C}_4$ -PFOA and  $^{13}\text{C}_4$ -PFOS) at a concentration of 10 ng/mL each compound was spiked into each sample. The standard solutions for the calibration curve were prepared with PFOA and PFOS concentrations ranging from 0.1 to 20 ng/mL, with  $^{13}\text{C}_4$ -PFOA and  $^{13}\text{C}_4$ -PFOS as 10 ng/mL.

PFOS and PFOA were analyzed by using a liquid chromatography-mass spectrometry system (LCMS-8040, Shimadzu Corporation, Japan). The separation column and guard column were Poroshell 120 EC-C18 (inner diameter 2.1 mm, particle size 2.7  $\mu\text{m}$ , length 150 mm and 5 mm). The oven temperature was  $40\text{ }^{\circ}\text{C}$ . Mobile phase comprised of channel A (methanol/ammonium acetate 2 mmol/L, 1 : 9, v/v), channel B (methanol), ratio of channel B: 50% (2.01 min), 95% (18 min), 95% (22 min), 50% (22.1 to 25 min). The flow rate of mobile phase was 0.25 mL/min. Negative electron spray ionization (ESI<sup>-</sup>) and multi-reaction monitoring (MRM) modes were applied. The MS parameters for PFOS were:  $m/z = 498.8 \rightarrow 98.9$ ;  $Q1 = 18\text{ V}$ ;  $CE = 44\text{ eV}$ ;  $Q3 = 17\text{ V}$ . The MS parameters for PFOA were:  $m/z = 412.8 \rightarrow 368.8$ ;  $Q1 = 15\text{ V}$ ;  $CE = 11\text{ eV}$ ;  $Q3 = 24\text{ V}$ . Concentrations of PFOS and PFOA in fish samples were calculated by internal standard/isotope dilution method and expressed in ng/g wet weight (w/w).

Method detection limits (MDL) of PFOA and PFOS were 0.01 and 0.03 ng/g, respectively, which were estimated as the average blank level plus three times of blank standard deviation. Method quantification limits (MQL) of PFOA and PFOS were 0.03 and 0.09 ng/g, respectively. Calibration curves of PFOA and PFOS had correlation coefficients over 0.999, showing good linearity over the concentration range of 0.1 to 20 ng/mL. Recoveries of PFOA and PFOS in matrix-spike samples ( $n = 3$ ) at a spiking level of 1 ng/g were  $108 \pm 7\%$  and  $97 \pm 12\%$  (RSD < 20%), indicating good accuracy and precision of our analytical method.

### 2.3. Risk assessment

Exposure levels to PFOS and PFOA from fish were estimated by daily intake doses (ID, ng/kg/day):  $ID = C \times R / BW$ . Where: C is PFOS or PFOA concentration in fish (ng/g, w/w), R is fish consumption rate (g/day), and BW is body weight (kg). According to the National Nutrition Survey in 2009 - 2010, the fish consumption rate was 59.7 g/day [10]. The average body weight was 60 kg. The ID values of PFOS and PFOA were directly compared with the reference dose  $RfD = 20$  ng/kg/day by the US Environmental Protection Agency (US EPA).

## 3. RESULTS AND DISCUSSION

### 3.1. Concentrations of PFOS and PFOA in Vietnamese fish

PFOS and PFOA have been detected in Vietnamese fish samples, suggesting their widespread occurrence in the environment of this country. PFOS and PFOA concentrations in fish samples were presented in Table 1.

*Table 1. Concentrations of PFOS and PFOA (mean, ng/g w/w) in Vietnamese fish*

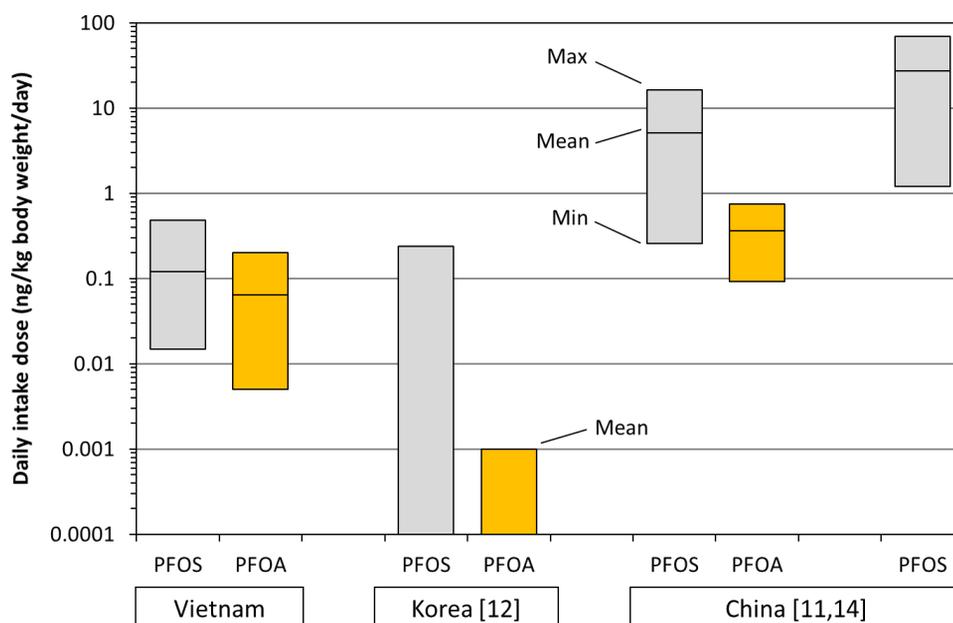
<i>Species (sample size)</i>	<i>Location (year)</i>	<i>PFOS</i>	<i>PFOA</i>	<i>Reference</i>
<i>Bighead carp (n = 6)</i>	West and Yen So Lake (2016)	0.092	0.033	This study
<i>Common carp (n = 6)</i>	West and Yen So Lake (2016)	0.27	0.030	This study
<i>Rohu (n = 6)</i>	West and Yen So Lake (2016)	0.079	0.12	This study
<i>Tilapia (n = 6)</i>	West and Yen So Lake (2016)	0.040	0.048	This study
<i>Snakehead (n = 4)</i>	Bac Ninh, Hung Yen (2007)	0.13	< 0.070	[7]
<i>Tilapia (n = 10)</i>	Da Rang River (2013 - 15)	0.020	< 0.20	[8]
<i>Snakehead (n = 3)</i>	Dong Nai River (2013 - 15)	0.16	< 0.20	[8]
<i>Dusky sleeper (n = 3)</i>	Dong Nai River (2013 -15)	0.050	< 0.20	[8]
<i>Shark catfish (n = 10)</i>	Me Kong River (2013 -15)	< 0.080	0.20	[8]
<i>Flying barb (n = 5)</i>	Me Kong River (2013 - 15)	< 0.080	< 0.20	[8]

In the fish samples collected from Hanoi lakes, PFOS and PFOA concentrations ranged from < 0.030 to 0.48 (mean 0.12) ng/g and from < 0.010 to 0.19 (mean 0.058) ng/g, respectively. PFOS concentrations in common carp (mean 0.27; range < 0.030 - 0.48 ng/g) were somewhat higher than those measured in other species (mean 0.12; range 0.067 - 0.19 ng/g). Meanwhile, concentrations of PFOA in rohu (mean 0.037; range 0.067 - 0.19 ng/g)

were generally higher than in the remaining samples (mean 0.037; range < 0.010 - 0.15 ng/g). However, the difference in PFOS and PFOA levels between species and between lakes was not statistically significant due to large variation and small sample size. PFOS and PFOA concentrations in fish samples from Hanoi lakes were comparable with those found in some locations in northern Vietnam like Bac Ninh and Hung Yen Provinces (PFOS < 0.10 - 0.30 ng/g; PFOA < 0.070 ng/g) [7], and rivers in central and southern Vietnam (PFOS < 0.080 - 0.16 ng/g; PFOA < 0.20 - 0.20 ng/g) [8]. PFOS and PFOA levels in Vietnamese fish were generally lower than concentrations reported for some fish from other locations in China [11, 14], South Korea [12], and the US [13].

### 3.2. PFOS and PFOA daily intake doses via fish consumption

Based on available data on fish concentrations of PFOS and PFOA (levels <MDL were assigned as one-half of MDL), concentration ranges of these two compounds in Vietnamese fish were 0.015 to 0.48 (mean 0.12) and 0.005 to 0.20 (mean 0.065) ng/g, respectively. The PFOS and PFOA daily intake doses ranged from 0.015 to 0.48 (mean 0.12) and from 0.005 to 0.20 (mean 0.065) ng/kg/day, respectively. These intake doses were comparable to or lower than values reported by a study in South Korea (mean 0.24 and 0.001 ng/kg/day for PFOS and PFOA, respectively) [12]. Because of the markedly higher contamination degree, PFOS and PFOA daily intake doses estimated for Chinese fish were much higher [11,14]. Daily intake doses of PFOS in fish collected from Taihu Lake and Pearl River Delta ranged from 0.26 to 16.4 [11] and from 1.2 to 69 ng/kg body weight/day [14], respectively. A comparison of PFOS and PFOA daily intake doses via consumption of fish in Vietnam and other countries was presented in Figure 2.



**Figure 2.** Comparison of daily intake doses PFOS and PFOA via fish consumption in Vietnam, Korea, and China

### 3.3. Risk assessment of PFOS and PFOA

To evaluate health risk of PFOS and PFOA, the daily intake doses are usually compared with reference doses (RfD) proposed by environmental and health protection authorities or by previous studies. Besides, hazard ratios (HR) were also estimated as ratio of daily intake doses and respective reference doses. The US EPA proposed a RfD value of 20 ng/kg body weight/day for both PFOS and PFOA based on toxicological studies on laboratory animals [15-16]. The PFOS and PFOA daily intake doses from Vietnamese fish were significantly smaller than the RfD of 20 ng/kg body weight/day, corresponding to HR values from  $7.5 \times 10^{-4}$  to  $2.4 \times 10^{-2}$  for PFOS and from  $2.5 \times 10^{-4}$  to  $1.0 \times 10^{-2}$  for PFOA. These results indicate that fish consumption in Vietnam is not responsible for health problems related to PFOS and PFOA exposure. More comprehensive risk assessment studies should be conducted to cover multiple exposure pathways of PFOS and PFOA such as other food types, drinking water, personal care products, and indoor environments.

## 4. CONCLUSION

This study investigated PFOS and PFOA concentrations in selected freshwater fish species in West Lake and Yen So Lake (Hanoi), together with published data on these two compounds in fish from different locations in Vietnam. In general, PFOS and PFOA levels in Vietnamese fish samples were low (less than 1 ng/g, w/w) and in a lower range as compared to other countries in the world. Consumption of PFOS- and PFOA-contaminated fish is a considerable exposure source in humans. Based on available data on PFOS and PFOA in fish and risk assessment methodology, daily intake doses and hazard ratios were estimated. Our results indicate that contamination levels of PFOS and PFOA in Vietnamese fish were relatively low, and daily intake doses and hazard ratios were also low and reflect acceptable levels of risk. However, more detailed and comprehensive studies should be conducted for other PFASs and multiple exposure pathways.

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## **Nghiên cứu mức độ ô nhiễm và đánh giá rủi ro phơi nhiễm các hợp chất perfluoroalkyl (PFOS và PFOA) trong cá ở Việt Nam**

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### **Tóm tắt**

Mức độ ô nhiễm của hai hợp chất perfluoroalkyl (PFASs) điển hình là perfluorooctane sulfonic acid (PFOS) và perfluorooctanoic acid (PFOA) được đánh giá trong các mẫu cá tại Việt Nam, dựa trên số liệu đo đạc thực tế và cơ sở dữ liệu đã được công bố trước đây. Trong các mẫu cá thu thập tại Hồ Tây và Hồ Yên Sở ở Hà Nội, hàm lượng PFOS dao động từ < 0,030 đến 0,48 ng/g (trung bình 0,12 ng/g), hàm lượng PFOA dao động từ < 0,010 đến 0,19 ng/g (trung bình 0,058 ng/g). Mức hàm lượng này tương đương so với các kết quả nghiên cứu trước đây trên mẫu cá lấy tại một số tỉnh thành trên cả nước và nằm trong khoảng giá trị tương đối thấp khi so sánh với các quốc gia khác trên thế giới. Liều lượng hấp thụ hàng ngày của PFOS và PFOA từ cá dao động tương ứng từ 0,015 đến 0,48 ng/kg (trung bình 0,12 ng/kg) và từ 0,005 đến 0,20 ng/kg (trung bình 0,065 ng/kg) thể trọng/ngày. Nhìn chung, liều lượng này thấp hơn so với liều tham chiếu (20 ng/kg thể trọng/ngày), cho thấy mức độ rủi ro tương đối thấp.

**Từ khóa:** PFOS, PFOA, cá, phơi nhiễm từ thực phẩm, Việt Nam.