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ORIGINAL ARTICLE

Analysis Detection of Perfluorooctanoic Acid (PFOA) Prevalence in Rajang River, Sibu

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ABSTRACT - Perfluorooctanoic acid (PFOA) is an emerging contaminant due to its persistence and toxicity to human and environment. It has been widely used in industry and disposed without proper regulations in past years. Many countries enforced elimination of PFOA since year 2016 due to potential adverse human health effects from human exposure. In year 2022, United States Environmental Protection Agency (USEPA) has regulated the health advisory value of 0.004 ng/L in drinking water to reduce human health risk. This study aimed to detect the presence of PFOA from Rajang River in Sibu to solve the possible risk faced from PFOA persistent. Samples are collected at 6 sampling stations by polyethylene (PET) bottle from upstream at Jalan Kong Yit Khim to downstream at Jalan Tanjung Batang of Rajang River, Sibu. All of the samples are collected from the surface of river at normal river flow in sunny weather. High performance liquid chromatography (HPLC) is used as analytical instrument to detect the prevalence of PFOA in river water. Result of river water samples from Rajang River indicated PFOA can be found in the river at the concentration of 0.525 ng/L, 0.576 ng/L, 0.992 ng/L, 1.000 ng/L, 1.041 ng/L and 1.052 ng/L. This had exceeded the USEPA health advisory value of 0.004 ng/L, which may bring long term health effects to human that required concerns from the community. Therefore, further study of PFOA could provide larger view of current PFOA contamination as a reference of water quality assessment in Sarawak.

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INTRODUCTION

Perfluorooctanoic acid (PFOA) is a highly fluorinated surfactant considered as emerging contaminants from the class of perfluorinated compounds (PFCs) that threatens human health. PFOA is a water and lipid repellent compounds that are applied in wide range of industrial product that are released to the environment during the manufacturing process [1]. Previous research has established that PFOA are the most concerned among the PFCs due to their toxicity, persistence and bioaccumulation [2]. They can be found in water, grease and stains resistant materials such as fabrics, textiles, furniture, food wares and paper packaging [3]. In addition, it is also used in variety of products such as firefighting foams, coating additives and cleaning products [4]. Furthermore, usage of PFOA containing products also leached PFOA into the environment. Human are exposed to PFOA in daily life through drinking water and usage of PFOA containing product. According to [5], the researcher proved that washing of fabrics migrated PFOA into water as a source to the environment and human.

Research has consistently shown that PFOA is resistant to biodegradation process such as direct photolysis, hydrolysis and atmospheric photooxidation. This is shown that in PFOA compound is an emerging and persistent contaminant in the environment [6]. PFOA has a long half-life that leads to

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longer breakdown time in the environment that can threatens human health. To date, researchers finding shown that current conventional water treatments are analyzed and proven that they have weakness in removing PFCs compound from water [7]–[11]. This seems to be a problem since human is in the risk of exposure to PFOA from drinking water in daily life.

According to [12], research shows that there is detection of PFCs concentrations in human bloods and urine. Previous studies also shown that human body resists to break down PFCs due to its biological resistance [13]. Exposure to PFOA in drinking water could lead to human health disorders such as cancer, infertility, kidney disease, immune disorders, thyroid dysfunction and cholesterol changes [14]–[20]. Furthermore, it was reported that PFCs accumulates and stays in human body over time [12]. In order to solve the issue, novel treatment approaches are therefore needed to manage PFCs exists in water to protect human and environmental health [21]. According to United States Environmental Protection Agency (USEPA) regulation in 2016, human is in high exposure rate to PFOA manufacturing products. In 2022, public webinar of USEPA released the updated health advisory value of PFOA with 0.004 ng/L in water [22]. Lower value of PFOA can reduce the risk of human health. In table 1, prior research proved that PFOA existed in mean concentration of 0.20 ng/L to 17.8 ng/L in Malaysia surface rivers located at Kota Kinabalu, Johor and Selangor [23]–[25]. This seems to be an issue because PFOA impact are not reported yet in in Malaysia federal and Sarawak state guidelines.

Table 1. Concentration of PFOA in Malaysia surface waters

Location	Concentration of PFOA (ng/L)	Year
Kota Kinabalu	0.20 - 3.20	2006
Johor	2.4 - 17.8	2011
Selangor	0.20 - 5.94	2012

Additional studies in Malaysia are required to understand more completely about PFOA prevalence in the surface waters. Recent evidence reported in year 2020 by the Department of Environment Malaysia is that most of the rivers in Sarawak are clean, while some rivers are slightly polluted. Rajang river remains as a clean in year 2020 with water quality index of 85 and categorized as class II, which required conventional treatment for water supply. However, PFOA are less consistent on water quality assessment in Malaysia [26]. This seems to be a problem since global elimination of PFOA have been enforced in most countries. According to New Straits Times Malaysia Newspaper on November 2020, the environmental and water ministry requires to enforce the law and regulations to restrict PFOA pollutants in drinking water [27]. Hence, this study is carried out to determine the existence of PFOA in surface water of Rajang River, Sibu in Sarawak to create awareness to community and related Department of Environment (DOE) in Sarawak.

MATERIALS AND METHODOLOGY

Chemicals and Standards

All of the chemicals of PFOA (95% purity), HPLC grade acetonitrile (CH3CN), HPLC grade methanol (MeOH), were purchased from Sigma Aldrich, Co.. All chemicals are reagent grade that are used without further purification. Distilled water is used to prepare the aqueous solutions. Standard solution of concentration of 1000 mg/L were prepared by weighing the powder standard and dissolved in methanol. The working standards concentrations of 0.05 ng/L to 10ng/L were prepared by successive dilutions.

Sampling Location

River water is collected in a 5 L methanol disinfected polyethylene (PET) bottles. PET bottle is rinsed with methanol and pure water prior sampling collection to reduce contaminations. All of the samples are collected in the evening at a sunny weather. Table 2 shows the sampling location in Rajang River. Samples are collected from 6 stations along upstream to downstream as illustrated in figure 1 along Rajang River. Samples are sent to lab within 24 hours and kept in cool room at 4°C to avoid microorganism growth until PFOA analysis.

Table 2. Sampling station and location

STATION	LOCATION
S1	Jln Kong Yit Khim, 96000 Sibu.
S2	Lorong Then Kung Suk 4, 96000 Sibu.
S3	Jalan Khoo Peng Loong, 96000 Sibu.
S4	Jalan Ding Lik Kong, 96000 Sibu.
S5	Lorong Wawasan 28D1, 96000 Sibu.
S6	Rh Jalak, Jalan Tanjung Batang, 96000 Sibu.

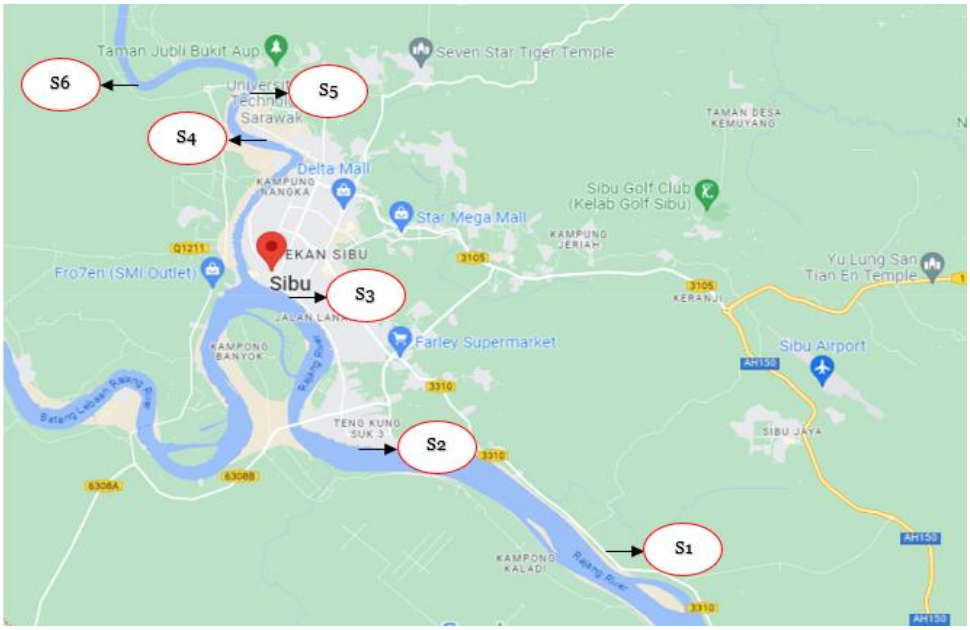

Figure 1. Sampling location in Rajang River, Sibu

Sampling Preparation

Samples were centrifuged at 12,000 rpm for 40 mins by Thermo Scientific Megafuge 8R centrifuge. Then, the samples are filtered by 0.45 µm nylon filters before HPLC analysis to prevent clogging in the column. Agilent 1220 Infinity HPLC system, reverse phase Zorbax C-18 column (2.1 × 50 mm, 3.5 µm), mobile phase of 5 mM ammonium acetate (CH_3COONH_4) as (A) and methanol (MeOH) as (B) are used in chromatographic separation of samples. 2 mL of sample is injected into HPLC vial by 0.22 µm nylon filter attached syringe.

HPLC detector is set with wavelength of 254nm and purge valve is on for 5 min with flow rate of 1 mL/min for 10 min to equilibrate C-18 column. Mobile phases are operated in isocratic condition where 100% of (A) is hold for 5 min, then operate to 100 % (B) for 20 min. Calibration of HPLC is carried out with standard at the concentration of 1.0 ng/L and 10.0 ng/L. After calibration, samples are infused to C-18 column at flow rate of 0.2 mL/min for separation. Area of curve from the HPLC chromatographic curve are calculated to obtain the concentration of PFOA in the samples.

RESULTS AND DISCUSSION

According to HPLC result in figure 2, retention time of standard solution for PFOA calibration occurred at 6.693 minutes. Peak of standard solution of 1.0 ng/L has the area of 14.765 mAU*s at 6.693 min. Table 2 shows concentration of PFOA of 6 different locations in Rajang River. PFOA is detected from the samples with different concentration depending on the location with retention time at 6.689min, 6.690 min, 6.698 min, 6.696 min, 6.692min and 6.687 min. Area of peak is obtained from HPLC chromatographic curve to calculate the concentration of PFOA in the samples.

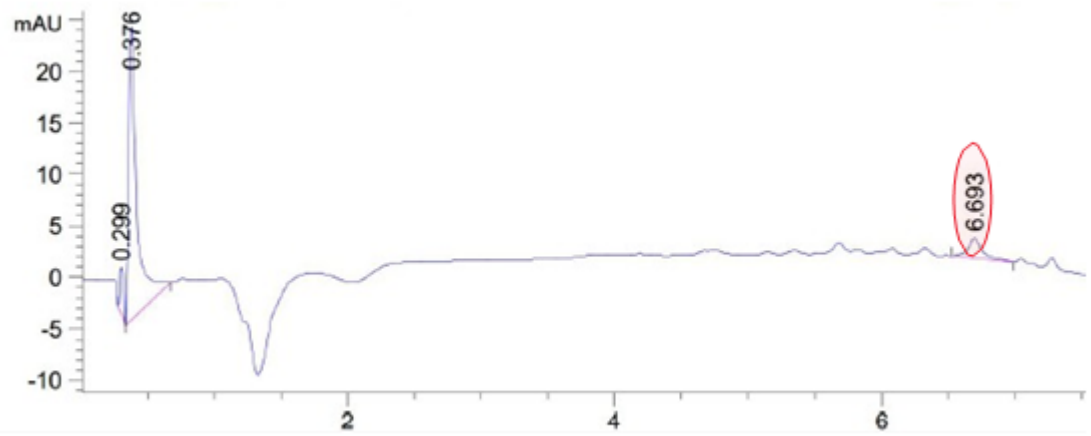

Figure 2. Retention time of 1.0 ng/L PFOA standard calibration by HPLC analysis

Table 3. Retention time and concentration of PFOA in HPLC analysis

Station	Retention time (min)	Area (mAU*s)	Concentration of PFOA (ng/L)
S1	6.689	7.754	0.525
S2	6.690	8.499	0.576
S3	6.698	14.647	0.992
S4	6.696	14.771	1.000
S5	6.692	15.379	1.041
S6	6.687	15.060	1.052

Concentration of PFOA detected increasingly from 0.525 ng/L at upstream to 1.020 ng/L at downstream. Concentration of PFOA is increasing from upstream to downstream along the water flow. Station S1 is located nearby Sibu Water Board raw water intake which is less developed area. Station S2 is located at industrial area, where the concentration slightly increased. Samples from S3 located along developed area where the concentration of PFOA concentration significantly increased due to surrounding activities of Pulau Babi Wharf, Sibu. Along the water flow, PFOA concentration increased from the samples at station S4 and S5 where they are collected beside industrial facilities such as shipyard. Sample from S6 slightly increased due to lesser activities at the surrounding of longhouse Rh Jalak, Jalan Tanjung Batang, Sibu.

All of the concentrations from samples collected in Rajang River, Sibu exceeded the USEPA health advisory values of concentration of PFOA in 0.004 ng/L. This study shows PFOA is detected in Rajang River, Sibu which could be released from the consequences of industrial, agriculture and usage of products containing PFOA. PFOA has long half time which it requires long duration to break down in the environment where contamination risk extend over time. Drinking water is a source of human exposure to PFOA which leads to potential side effects on human health. Source of drinking water in Sibu is from this Rajang River, where the conventional water treatment has proven with decrease efficiency in breaking down PFOA. Further action such as treatment of PFOA should be considered in water treatment to reduce the risk of human exposure to PFOA.

CONCLUSION

This study shown PFOA is prevalence at rivers in Sarawak. Household and industrial effluent are the possible contributors for PFOA contamination in Rajang River, Sibu. As a result, sample collected from industrial area has higher concentration of PFOA compared to less developed area. More works should be done to confirm the source of contributors of PFOA to the water environment in Rajang River, Sibu. Further study is required to determine the larger view of PFOA contamination in Sarawak aquatic environments as a reference for water quality monitoring in order to reduce the risk of human health.

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