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Perfluorooctane Sulfonic Acid (PFOS) in River Water and Groundwater along Bharathapuzha River Basin, India

Vivek Kanjiyangat ✉

Technical Support Office - Marine & Offshore, Lloyd's Register Marine and Inspection Services, Mumbai-400093, India

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ABSTRACT

Perfluorinated chemicals (PFCs) are widely used in industrial and commercial applications, leading to their release into the environment. The rapid industrialization and growing population in India make it a suitable case study to investigate PFOS contamination in environmental matrices. The purpose of this study is to investigate PFOS concentrations in river water and groundwater from several locations along the Bharathapuzha river basin and estimate PFOS intakes through drinking water. The highest PFOS level detected in the surface water is 1.3 ng/L and groundwater is 1.0 ng/L, which is significantly lower than the level of PFOS detected in major rivers of many developed countries. It is possible to attribute the low PFOS concentration to factors such as high annual precipitation, reduced industrial and municipal wastewater discharge, and relatively low emissions per capita in a region where agriculture is a major part of the economy. In addition, the daily intake of PFOS through drinking water in all age groups was below the safety threshold for cancer risk.

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INTRODUCTION

The production of Perfluoroalkyl substances (PFAS) and in particular perfluorocarboxylic acids (PFCAs) such as perfluorooctanoic acid (PFOA), perfluorosulfonates (PFSAs) like Perfluorooctane sulfonic acid (PFOS), and perfluorosulfonamides (PFOSAs) has started in the late 1950s but their industrial applications have increased all over the world in the last 25 years (Renner, 2001). Due to their wide industrial and commercial applications, Perfluorinated chemicals (PFCs) were released into the environment during their production and usage. The released PFCs were spread in various environmental matrices, viz water (Yamashita et al., 2005), sediments (Higgins & Luthy, 2006), air (Jahnke et al., 2007), wildlife (Wang et al., 2008; Beach et al., 2006) and humans (Kannan et al., 2004). As PFCs are persistent in the environment, where they can accumulate in tissues of humans and wildlife (Lindstrom et al., 2011) and can potentially have toxicological effects such as hepatotoxicity, developmental, reproductive and hormonal effects, and carcinogenic potency (Butenhoff, 2002; Lin et al., 2011) United States Environmental Protection Agency (EPA) has included both PFOA and PFOS among the list (Contaminant Candidate List 3 - CCL 3) of emerging contaminants.

There are no water standards in most countries for PFASs, despite PFASs being among major

*Corresponding Author Email: *iamvivekka@gmail.com*

environmental and health concerns worldwide. Following the conference of the parties, the Stockholm Convention on Persistent Organic Pollutants (POPs) listed PFOS, its salts, and PFOSF as POPs, and they were now regulated under EU POPs legislation. Since July 2020, PFOA has been banned under the POPs Regulation. Additionally, the EU chemicals legislation (REACH) is beginning to regulate some short-chain PFAS. A plan was announced recently by Norway to create a REACH restriction that covers all uses of the entire PFAS family. Also, the European Food Safety Authority (EFSA) has recommended limit for the four PFAS combined is 4.4 ng kg^{-1} body weight/week. In the USA currently, no Maximum Contaminant Levels (MCLs) on drinking water are established for PFAS. But an ongoing evaluation of the need for MCL is being carried out by EPA. An advisory value of $2x10^{-5}$mg/kg/day for PFOS and PFOA in drinking water was published by the EPA in March 2018. According to a Chinese health advisory, the recommended levels for PFOA and PFOS in drinking water are 85 ng/L and 47 ng/L, respectively, but most Chinese cities have crossed these limits. (Liu et al., 2021).

In 2006, India became a party to the Stockholm Convention however, India has refused to accept the modifications which added PFOS to its global list of restrictions in 2009. PFCs are not regulated in India, but studies demonstrate the concentrations of PFCs in breast milk from Vietnam, Cambodia, and India were 40-50% lower than the levels detected for America, Germany, and China. (Tao et al., 2008). The data also shows lowest concentration (39.4 pg/mL) of PFOS in breast milk was found in India among other Asian countries. (Tao et al., 2008). In 2020, the Bureau of Indian Standards (BIS) announced that the country will be adopting ISO benchmarks or setting domestic standards based on industrial sectors as a first step towards developing a framework for regulating PFAS. The Ganges river has significantly lower PFOS and PFOA concentrations than rivers in Europe and China, according to one study. (Sharma et al.,2015). In the same study, researchers confirmed that PFAS intake from drinking water posed no oral non-cancer risk to any age group. The PFAS contamination and emission status of the country are mostly unknown due to the limited number of studies conducted and insufficient amount of available data. There is an urgent need to assess PFAS emissions, contamination, and human exposure in the country. Some areas of India can be potential hotspots of PFAS contamination due to a low level of pollution control and waste management.

In this study, we surveyed the occurrence of PFOS in surface water and groundwater at 26 locations across the Bharathapuzha river basin located in Southern India. The proposed location of this analytical work has very limited data availability on PFOS contamination which served as the basis of location selection. This study provides information on the concentration of PFOS in the Bharathapuzha river due to wastewater discharge from industries and domestic households. The study aimed to provide a framework for developing drinking water standards for PFOS in freshwater at the national level.

MATERIALS AND METHODS

Study area and sample collection

Bharathapuzha is the second-longest western-flowing river in Kerala with an annual discharge of 161 m^3/s. Also, with a basin size of 6,186 km^2, the Bharathapuzha basin is the largest among all the river basins in Kerala state and has a population of over 0.59 million in rural areas and 0.17 million in urban areas who consume untreated drinking water from the river daily. Five samples were collected near urbanized areas and industrial areas in the middle reach and four locations in the lower reach including the river inlet of Bharathapuzha.

A total of 26 samples of groundwater and 26 samples of river water were collected between April and June 2021 (Figure 1 shows the sites of the sampling). To identify if there is any possible correlation between the level of PFOS in drinking water and surface water receiving household and industrial effluents, river water and groundwater were simultaneously sampled. Samples of water were taken from each location with high-density polyethylene bottles that were

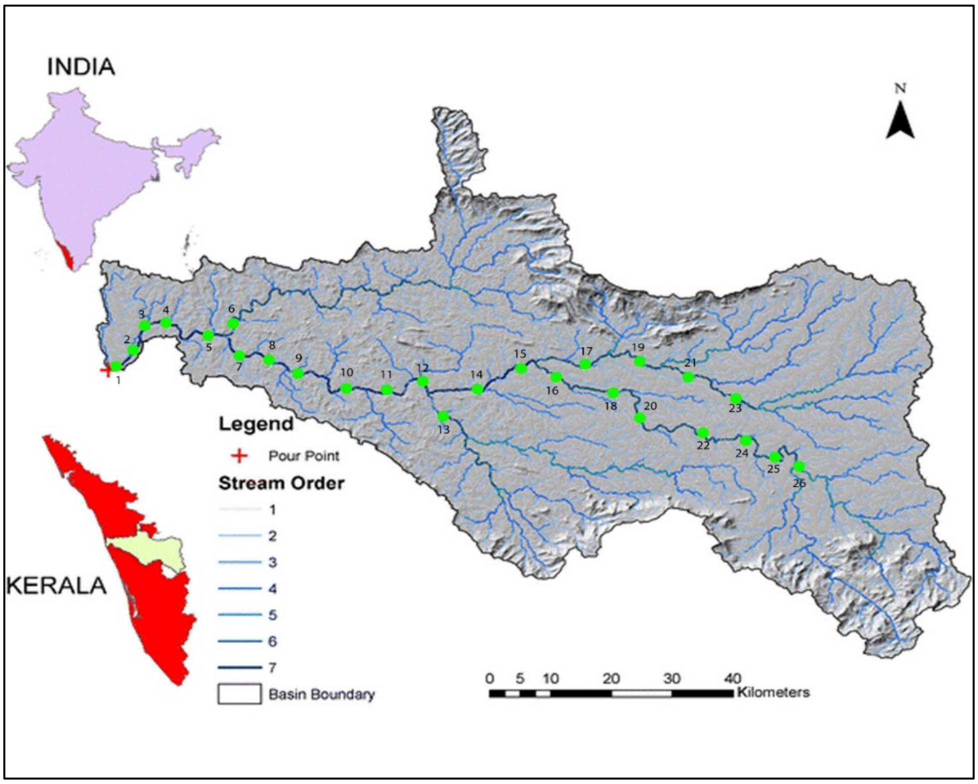

Fig. 1. Sampling locations in the Bharathapuzha river basin.

washed with methanol, Milli-Q water, and sampled water from the location. The samples were transported at -4 ±2° C to the Interlek Laboratories, Bangaluru, India for analysis.

Sample analysis and quality control.

The sediments and biota were removed from water samples by filtering them through 0.22 mm fibreglass membranes. In the first step of preconditioning, 10 mL of methanol and 10 mL of 1% acetic acid were applied sequentially to the SPE cartridge (GracePure SPE C-18-MAX, 6 mL). Distilled water was fed through preconditioned cartridges at a frequency of one drop every second and then rinsing with Milli-Q water was done, followed by drying under vacuum for at least two hours. Five mL of methanol were eluted at a rate of one drop every second and collected in a 10 mL PP tube washed with a 1:1 (v/v) methanol/acetone solution. Using a high purity stream, the eluant was dried, and then methanol was added to fix it to a volume of 5 mL or 2 mL. Prior to PFOS analysis, every prepared solution is maintained at 2°C. The recovered solution was transferred to a 100 μL polypropylene insert with polymer feet in 2-mL HPLC/GC autosampler vial. By using HPLC and quadrupole/time-of-flight (Q-ToFMS) mass spectroscopy, the concentrations of PFOS in the solution were determined.

Spike and recovery tests were carried out to verify the precision and accuracy of the extraction and analytical techniques. PFOS concentrations were all below the detection limit in a procedure blank test, indicating that the test procedure was error-free. A method recovery test was conducted with a standard solution and the recovery rates were 96.2–97.3%, indicating no PFOS was lost during the extraction process. The standard addition experiment resulted by adding 2–50 ng/L standard PFOS to the samples resulting in a method recovery rate ranging from 96.22% to 113.63%, and a relative standard deviation ranging from 0.43% to 10.21%. The LOQ (signal to noise ratio = 14.83) for river water was 0.50 ng/L. The LOD of the instrument used was 0.2 μg/L for the standard PFOS solution and 0.5 μg/L for water samples.

RESULTS AND DISCUSSION

The concentration of PFOS in river water

The presence of PFOS was found in 21 of the 26 samples examined. Fig. 2 shows the concentration of PFOS measured in water samples. Total PFOS concentration in the collected samples from the study area ranged from 0.1 – 1.3 ng/L. The sample collected at location 2 contained the highest levels of PFOS (1.3 ng/L). Samples from location 1 also had a similar concentration of PFOS (1.2 ng/L). PFOS concentrations in the Bharathapuzha were found to be reasonably lower than concentrations reported in the river Ganges. Also, PFOS concentration in the Bharathapuzha river is lesser than levels reported in rivers from Asia and Europe. (Chimeddulam & Wu, 2013)

The concentration of PFOS in groundwater

There is little available data on the concentrations of PFOS in Indian groundwater. The Ganges river basin was a subject of one such study (Sharma et al., 2016), but given the size and population of the nation, the information on the concentration of PFOS in groundwater is still insufficient. Since groundwater is used for both irrigation and drinking, this study is the first to examine the PFOS contamination in groundwater samples from the Bharathapuzha river basin. This result is used to assess daily PFOS exposure for different exposure scenarios. The concentration of PFOS in groundwater is shown in Fig. 2. The contamination levels were very similar to those observed in surface water. The presence of PFOS was found in 17 of the 26 samples examined. Groundwater concentrations of PFOS were lower than those observed in river water, similar to what was found in Ganges river water. The highest concentration of PFOS was found at location 3 (1.0 ng/L). Additionally, PFOS concentration was close to the sample from location 2 (0.9 ng/L). Total PFOS concentration in the collected samples from the study area ranged from 0.1 – 1.0 ng/L. Locations 2 and 3 were in a river estuary and received a sizable volume of industrial and municipal waste from the nearby towns. These local contaminations may be the cause of the observed high value of PFOS in these locations.

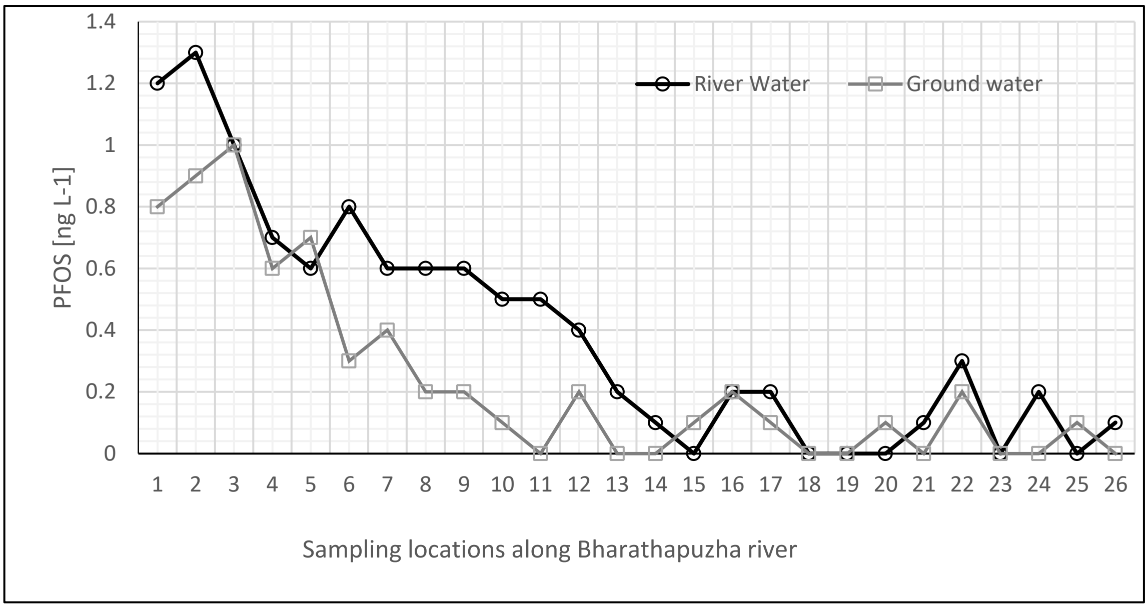

Fig. 2. The concentration of PFOS in river and groundwater samples along the Bharathapuzha river at different sampling sites

Table 1. Estimate daily PFOS exposure for different exposure scenarios

	Daily PFOS exposure					
	Children		Adult		Elderly	
	50th Percentile	95th Percentile	50th Percentile	95th Percentile	50th Percentile	95th Percentile
Low Exposure Scenario (0.66)	0.004	0.034	0.002	0.023	0.002	0.021
Intermediate Exposure Scenario (0.8)	0.004	0.042	0.003	0.028	0.003	0.026
High Exposure Scenario (0.91)	0.005	0.048	0.003	0.031	0.003	0.029

Calculation of PFOS Human Exposure

Although humans are exposed to PFOS through multiple pathways, drinking water has been the most significant route of exposure (Trudel et al., 2008). To calculate exposure from drinking water, scenario-based risk assessment (SceBRA) is adopted. PFOS exposure for children, adults, and senior citizens from drinking water is assessed under three exposure levels: low, intermediate, and high (Gebbink et al., 2015). According to the below equation, daily exposure to PFOS via drinking water consumption (P_w) was determined:

$$Pw = (Cw \times Qw \times Fuptake)/m \qquad (1)$$

Where, C_w is the concentration of PFOS in drinking water (ng/L), Q_w is the quantity of drinking water consumed (L/day) and m is body weight (kg). F_{uptake} is the gastrointestinal uptake fraction which is 66%, 80%, and 91% in the low-exposure, intermediate, and high-exposure scenarios (Trudel et al., 2008). Children consume an average of 1.3 L of water per day, while adults and elderly individuals consume 2.5 and 2 L/day, respectively (EFSA., 2010). Children, adults, and elderly individuals weigh an average of 24, 70, and 60 kg, respectively.

Daily PFOS exposure is calculated using groundwater contamination data for the 50th, and 95th percentile of concentrations from all locations as presented in Table 1. Children consumed the highest amount of PFOS per kilogram of body weight (0.048 ng/kg/day) among different scenarios. In all three-exposure scenarios, seniors receive the least PFOS exposure. In contrast to the adult population of Catalonia and the children of Taiwan, these exposure levels were 3-4 times lower (Domingo et al., 2012). Based on PFOS exposure through drinking water and the Reference Dose (R_F) (75 ng/kg/day/), a Hazard Index (HI) is calculated. The daily exposure value for PFOS in scenarios did not exceed the R_F. Accordingly, drinking water consumption did not pose significant health risks, with HI values below 1. Comparing HI values from this study to Taiwanese River water, the results of this study were 2-3 orders of magnitude lower.

CONCLUSIONS

This study gave a preliminary regional overview of PFOS and its occurrence in the Bharathapuzha river basin. Low river water and groundwater levels of PFOS can be attributed to factors like high annual precipitation, reduced domestic and industrial wastewater discharge, relatively low per-capita emissions in a region where the economy is still largely based on agriculture, and a sizable portion of the population still follows the traditional way of living. River water and groundwater both had comparable patterns of contamination, indicating that they can be both susceptible to the same PFOS local contamination sources. The presence of PFOS in groundwater can also be attributed to infiltration from the river, sewage spills, or leaching from tainted surface water. Furthermore, using the current concentration levels, the potential health risks and daily human exposure do not pose any health risks. Conducting thorough toxicity studies for all PFASs is necessary to lessen the uncertainty in health risks and to find potential PFAS contamination hotspots in the country. Further research on the potential toxicity of PFASs is necessary given the incomplete knowledge of their toxicological mechanisms.

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DECLARATION OF CONFLICTING INTERESTS

The author(s) declare that there is not any conflict of interest regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the author(s).

LIFE SCIENCE REPORTING

No life science threat was practiced in this research

REFERENCES

Beach, S., Newsted, J., Coady, K. and Giesy, J. (2006). Ecotoxicological Evaluation of Perfluorooctanesulfonate (PFOS). *Reviews Of Environmental Contamination And Toxicology*, 133-174.

Butenhoff, J. (2002). Toxicity of Ammonium Perfluorooctanoate in Male Cynomolgus Monkeys after Oral Dosing for 6 Months. *Toxicological Sciences*, *69*(1), 244-257.

Chimeddulam, D. and Wu, K. (2013). River water contaminated with perfluorinated compounds potentially posing the greatest risk to young children. Chemosphere, 90(5), 1617-1624.

Domingo, J., Ericson-Jogsten, I., Perelló, G., Nadal, M., Van Bavel, B. and Kärrman, A. (2012). Human Exposure to Perfluorinated Compounds in Catalonia, Spain: Contribution of Drinking Water and Fish and Shellfish. *Journal Of Agricultural And Food Chemistry*, *60*(17), 4408-4415.

Gebbink, W., Berger, U. and Cousins, I. (2015). Estimating human exposure to PFOS isomers and PFCA homologues: The relative importance of direct and indirect (precursor) exposure. *Environment International*, *74*, 160-169.

Higgins, C. and Luthy, R. (2006). Sorption of Perfluorinated Surfactants on Sediments. *Environmental Science &Amp; Technology*, *40*(23), 7251-7256.

Jahnke, A., Berger, U., Ebinghaus, R. and Temme, C. (2007). Latitudinal Gradient of Airborne Polyfluorinated Alkyl Substances in the Marine Atmosphere between Germany and South Africa (53° N−33° S). *Environmental Science &Amp; Technology*, *41*(9), 3055-3061.

Kannan, K., Corsolini, S., Falandysz, J., Fillmann, G., Kumar, K. and Loganathan, B. et al. (2004). Perfluorooctanesulfonate and Related Fluorochemicals in Human Blood from Several Countries. *Environmental Science &Amp; Technology*, *38*(17), 4489-4495.

Lin, C., Wen, L., Lin, L., Wen, T., Lien, G. and Chen, C. et al. (2011). Associations between Levels of Serum Perfluorinated Chemicals and Adiponectin in a Young Hypertension Cohort in Taiwan. *Environmental Science &Amp; Technology*, *45*(24), 10691-10698.

Lindstrom, A., Strynar, M. and Libelo, E. (2011). Polyfluorinated Compounds: Past, Present, and Future. *Environmental Science &Amp; Technology*, *45*(19), 7954-7961.

Liu, L., Qu, Y., Huang, J. and Weber, R. (2021). Per- and polyfluoroalkyl substances (PFASs) in Chinese drinking water: risk assessment and geographical distribution. *Environmental Sciences Europe*, *33*(1).

Renner, R. (2001). Growing Concern Over Perfluorinated Chemicals. *Environmental Science &Amp; Technology*, *35*(7), 154A-160A.

Scientific Opinion on Dietary Reference Values for water. (2010). *EFSA Journal*, *8*(3).

Sharma, B., Bharat, G., Tayal, S., Larssen, T., Bečanová, J. and Karásková, P. et al. (2016). Perfluoroalkyl substances (PFAS) in river and ground/drinking water of the Ganges River basin: Emissions and implications for human exposure. *Environmental Pollution*, *208*, 704-713.

Tao, L., Ma, J., Kunisue, T., Libelo, E., Tanabe, S. and Kannan, K. (2008). Perfluorinated Compounds in Human Breast Milk from Several Asian Countries, and in Infant Formula and Dairy Milk from the United States. *Environmental Science &Amp; Technology*, *42*(22), 8597-8602.

Trudel, D., Horowitz, L., Wormuth, M., Scheringer, M., Cousins, I. and Hungerbühler, K. (2008). Estimating Consumer Exposure to PFOS and PFOA. *Risk Analysis*, *28*(2), 251-269.

Wang, I., Hsieh, W., Chen, C., Fletcher, T., Lien, G. and Chiang, H. et al. (2011). The effect of prenatal perfluorinated chemicals exposures on pediatric atopy. *Environmental Research*, *111*(6), 785-791.

Yamashita, N., Kannan, K., Taniyasu, S., Horii, Y., Petrick, G. and Gamo, T. (2005). A global survey of perfluorinated acids in oceans. *Marine Pollution Bulletin*, *51*(8-12), 658-668.