

Chapter 1

A First Report of Perfluoroalkyl Substances (PFAS) in a Large West-Flowing River in Southern India



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1.1 Introduction

More than one-third of the accessible freshwater, which is renewable, is being utilized for industrial, agricultural and domestic purposes. These activities invariably contribute to water contamination due to a variety of synthetic compounds. The perfluoroalkyl substances (PFAS), found extensively in the ecosystem, are a major contributor of environmental contamination. The PFAS are used as water or oil repellents, foams for fighting fire, semiconductors used in electronics, plastic items, fabrics, pesticides and food packaging (3M 2000; Giesy and Kannan 2001). They are introduced into the environment through its manufacture, use, disposal or from biotic or abiotic precursors. The PFAS are raising environmental concerns because they can induce adverse health effects. They have a potential for long-range transport too. Traces of these deadly substances have been found in animals, human blood, breast milk and serum of patients with liver cancer (Giesy and Kannan 2001; Hansen et al. 2001). Studies conducted in the USA (Calafat et al. 2007) have presented a strong evidence that about 95% of the population have been exposed to PFAS and its derivatives. In 1999, National Health and Nutrition Examination Survey (NHANES) reported that at least 12 different PFAS were present in the blood samples of 12-year-old participants (Calafat et al. 2007). It is quite a disturbing trend considering how prevalent PFAS were even so far back as 1999. PFAS has been found to reduce the

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production of important hormones like testosterone in the human body (Joenson et al. 2013), making it extremely dangerous. PFAS is a group of per fluorinated compounds which contains an alkyl chain and a functional group at the end. The strong covalent C–F bond makes the PFAS resistant to degradation resulting in its persistence in nature. Long-chained PFAS ($C > 7$) are not degraded in ambient environmental conditions (Xiao et al. 2011). They can easily withstand high temperatures, alkaline and acid attacks (Woldegiorgis et al. 2006). PFOS and PFOA are the end products of degradation for several fluorochemicals (Martin et al. 2010). PFAS is also known as “forever chemical” in the popular media.

PFAS are also classified into perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs), depending on their functional group (Buck et al., 2010). PFAS with five or more carbons and PFCAs with seven or more carbons are long-chained PFAS (OECD 2002). The predominant compound in the PFASs (perfluorooctanoic acid (PFOA)—new POPs in the Stockholm convention, 2009) and perfluorooctane sulfonate (PFOS) in PFCAs are highly persistent and hazardous to organisms upon intake. PFAS are also the degradation product of other fluorochemicals. There are approximately 4700 products that degrade into PFAS, and the number is rapidly increasing.

In the Indian scenario, none of the PFASs are regulated despite being a member of the Stockholm convention in 2006 and the treaty that was later amended to its list of restricted products in 2009. A recent survey among mothers in India has revealed that in the cities of Chidambaram, Kolkata and Chennai, significant levels of PFAS and their derivatives were present (IPEN, Toxic links 2019). Dolphins in the River Ganges (Yeung et al. 2009), pigs living in open waste dumps, deep groundwater (> 100 m in depth), air and even Sundarbans mangrove wetland had been exposed to PFAS. It was found that transboundary movement of contaminants has contributed significantly to pollution in Western China as 70% of PFAS found in the snows were from the Indian monsoon (Wang et al. 2019).

Various research studies around the world are conducted to determine the concentration of PFAS in the aquatic environment (Giesy et al. 2001; Giesy et al. 2002; Loos et al. 2008; Yamashita et al. 2008; Zushi et al. 2008; Ahrens et al. 2010; Yamashita et al. 2013). Few studies have reported on the status of PFAS contamination in South Indian rivers. In the case of River Periyar, there are none. This study aimed to establish a baseline for the Periyar River. Further, this study aims to identify pollutant concentrations at various points, which will aid in tracking down the sources of contamination.

1.2 Study Area

Since the 1990s, India underwent massive industrialization and economic development, which has inadvertently resulted in the increasing use of PFAS, thereby contributing to their ultimate presence in the environment. In the Indian context, there have been very few in-depth studies on river water quality. The Periyar River

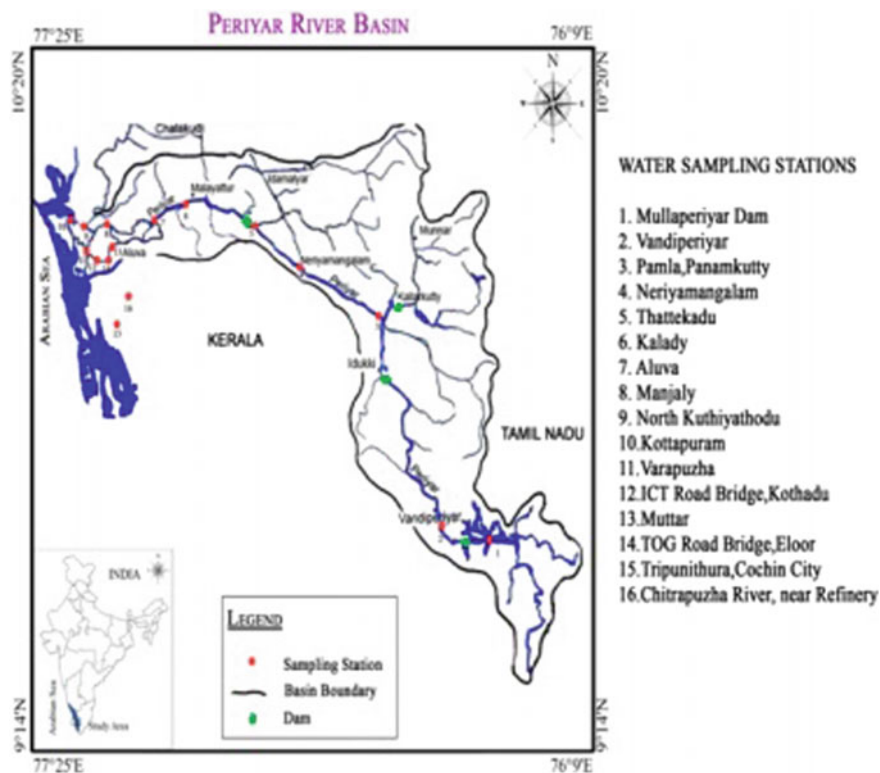


Fig. 1.1 Sampling locations—Periyar River, Kerala, India

was chosen as the study area because it is one of the major and most contaminated west-flowing river of Kerala (Fig. 1.1).

Periyar is the longest perennial river in Kerala with a length of 244 km. It is also called the “Lifeline of Kerala”. It originates in Sivagiri Hills of Western Ghats. It flows through Periyar National Park. It then flows into the Periyar Lake. This water then flows to the Vembanad Lake and discharges into the Arabian Sea. The major tributaries of this river are Mullayar, Muthirapuzha, Perinjankutti, Edamala and Cherutoni.

The Mullaperiyar dam is located on the point of convergence of Periyar and Mullayar rivers in the Idukki district of Kerala. The dam is operated and maintained by the state of Tamil Nadu. The Idukki dam is also situated on the Periyar River. Kerala’s electrical power is mainly generated in the Idukki dam.

Many economic activities take place along the Periyar River. Tourism is a major activity that generates wealth. Thekkady is a popular tourist destination with a large floating population of sightseers and tourists. Industries can also be found on the river Periyar’s downstream side. Pollutants from these industries can contaminate

river water. The upstream side of the river is generally less populated, and there is little industrial activity in the river.

1.3 Materials and Methods

1.3.1 Water Sampling

Water samples were collected between May 20 and 22, 2013, during pre-monsoon season, along the stretch of Periyar River ($n = 14$) and its main tributaries Tripunithura and Chitrapuzha rivers ($n = 2$). In order to compare, a few water samples were collected from Meenachil River ($n = 3$) and other contaminated sites ($n = 4$) like Mundakayam, Vaikom, Vaikom canal and Chempu, along with the Periyar River (sampling list shown in Tables 1.1 and 1.2). Grab samples were collected in 500 mL clean polypropylene bottles as per the protocol discussed elsewhere (Taniyasu et al. 2005; Yamashita et al. 2008). The collected samples were refrigerated at 4 °C in India and then transported to Advanced Industrial Science and Technology (AIST), Tsukuba, Japan, for further analysis, in cold condition using dry ice.

1.3.2 PFSA Extraction

Unfiltered water samples were subjected to extraction with the solid phase extraction method (SPE) using the Oasis® WAX cartridges following the published methods (Taniyasu et al. 2005; Yamashita et al. 2008). The wax cartridges were preconditioned with 4 mL of 0.1% NH_4OH in methanol, followed by 4 mL of methanol and 4 mL of Milli-Q water. Water samples (500 mL) were passed through preconditioned cartridges at 1 drop sec^{-1} . After 2 min centrifugation at 3000 rpm, the cartridges were washed with 4 mL of ammonium acetate (25 mM) buffer at pH 4. The target analytes were eluted with 4 mL methanol, after which 4 mL of 0.1% NH_4OH in methanol was added. The eluates were finally concentrated to 1 mL under a gentle stream of nitrogen gas.

1.3.3 Instrumental Analysis

Analytes were separated using Agilent HP1100 LC (Agilent, Palo Alto, CA), and this system was integrated with Micromass Quattro Ultimata Pt mass spectrometer (Water Corp, Milford, MA) operated in the electrospray negative ionization mode. An aliquot of 10 μL of the extract was injected into a Keystone Betasil C18-column (2.1 mm i.d.*50 mm length, 5 μm , 100 Å pore size, endcapped) with ammonium

Table 1.1 Concentrations (ng/L) of PFAS compounds in the sampling stations (1–14 Periyar River; 18–20 Meenachil River; 17, 21–23 other stations)

Sampling locations		Latitude	Longitude	PFBS	PFHxS	PFOS	PFBA	PFOA	PFNA
LOQ				4 ppt	4 ppt	4 ppt	20 ppt	4 ppt	4 ppt
Native standard (PFC mix B recovery range)				83%	87%	85.50%	87.50%	87%	89.50%
<i>Periyar River sampling locations</i>									
1	Mullaperiyar	09.575653	77.179083	ND	ND	ND	610	49	44
2	Vandiperiyar	09.572560	77.091136	ND	12	ND	409	100	48
3	Panamkuttu Bridge, Kallarkutty	09.952121	76.981653	ND	ND	ND	900	106	62
4	Neriyamangalam	10.059007	76.776143	ND	ND	ND	324	22	20
5	Thattakadu	10.128544	76.686281	ND	ND	ND	439	53	22
6	Kalady	10.115223	76.358224	50	12	ND	58	34	28
7	Aluva	10.112169	76.347411	46	< 4	ND	176	58	42
8	Manjaly	10.152210	76.270829	ND	25	19	210	90	88
9	North Kuthiyathodu	10.162075	76.265811	ND	30	6	243	126	67
10	kottapuram	10.193857	76.201109	ND	ND	ND	299	102	51
11	Varapuzha	10.072906	76.281178	ND	ND	521	338	194	78
12	ICT Road Bridge, Kothadu	10.046312	76.267305	ND	37	124	214	168	44
13	Muttar	10.044168	76.300814	ND	127	156	578	190	109
14	Tog Road Bridge, Eloor	10.32832	76.182677	ND	103	140	656	118	123
15	Tripunithura	09.57074	76.20080	224	ND	1990	786	512	189

(continued)

Table 1.1 (continued)

Sampling locations		Latitude	Longitude	PFBS	PFHxS	PFOS	PFBA	PFOA	PFNA
LOQ				4 ppt	4 ppt	4 ppt	20 ppt	4 ppt	4 ppt
Native standard (PFC mix B recovery range)				83%	87%	85.50%	87.50%	87%	89.50%
16	Chitrapuzha River	09.59711	76.21141	1330	1860	12,958	2174	1503	705
<i>Other sampling locations</i>									
17	Mundakayam	09.53824	76.88795	ND	ND	ND	700	64	66
18	Erattupetta	09.69248	76.76991	ND	8	ND	200	24	32
19	Pala	09.69384	76.65719	ND	ND	36	ND	108	84
20	Kottayam	09.35836	76.31667	62	34	< 4	ND	106	34
21	Vaikom	09.44348	76.24382	ND	48	ND	866	194	102
22	Vaikom Canal	09.44005	76.23684	ND	ND	85	1240	176	89
23	Chempu	09.50758	76.23793	ND	ND	108	886	146	81

The LOQ is measured in parts per trillion (ppt)

Table 1.2 Details of sample location

Sample code	Station	Details
P1	Mullaperiyar Dam	Upstream of Periyar River. Thekkady tourism spot (Tiger reserve, Dam Boating)
P2	Vandiperiyar	Domestic activities (domestic sewage, dumping of solid waste)
P3	Panamkuttu Bridge, Kallarkutty (Pamla Dam)	Dam site
P4	Neriyamangalam	Under Neriyamangalam bridge
P5	Thattekkad	Near Thattekkad bird sanctuary
P6	Kalady	Anthropogenic activities are observed
P7	Aluva (Manappuram)	Anthropogenic activities more, under Aluva bridge
P8	Manjaly	Under Manjaly bridge
P9	North Kuthiyathodu	Chalakkudy River joins to Periyar River
P10	Kottapuram	Downstream of Periyar River (Fishing site, heavy dilution, domestic and industrial activities)
P11	Varapuzha	Downstream, tributaries of Periyar join here
P12	Ict Road Bridge, Kothadu	Under bridge, domestic and industrial activities
P13	Muttar	Under bridge, domestic and industrial activities
P14	Tog Road Bridge, Eloor	Domestic and industrial activities
P15	Tripunithura	Domestic and industrial activities are high
P16	Chitrapuzha River	Industrial area (refineries, factories, etc.)

acetate and methanol (2 mM) as the mobile phase for quantifying C6-C18 PFAS. Also, the same extracts were injected into an ion-exchange column [RSpak JJ-50 2D (2.0 mm i.d.*150 mm length, 5 μ m; Shodex, Showa Denko K.K., Kawasaki, Japan)] with ammonium acetate and methanol solution (50 mM) for the quantification of C3-C5 PFAS. All samples were injected onto both RSpak JJ-50 2D and Keystone Betasil C18 column separately to confirm the accuracy of identification. The temperature and flow of the desolvation gas were kept at 450 °C and 610 L/h, respectively. The energies of collision, cone voltages and MS/MS parameters for the instrument were kept at an optimized value for individual analytes, as reported elsewhere (Taniyasu et al. 2005, 2013). Three major PFASs (PFBS—perfluorobutane sulfonate, PFHxS—perfluorohexane sulfonate and PFOS) and three major PFCAs (PFBA—perfluorobutanoic acid, PFOA and PFNA) were extracted and analyzed by

this method from the study area. The limit of quantification (LOQ) for each PFAS compound ranged differently in samples according to the property of the sample location and contamination level (Yamazaki et al. 2015; Taniyasu et al. 2013). The procedural recoveries ranged from 70 to 125% for most of the PFAS compounds.

1.3.4 Quality Control/Quality Assurance

The limits of quantification (LOQs) are defined as the smallest mass of the compound injected that can result in a reproducible measurement of peak areas, of which is within $\pm 20\%$ of the duplicate injection. LOQs are evaluated based on several criteria, which include (i) sample volume; (ii) the smallest concentration of standard on the calibration curve that could be accurately measured within $\pm 20\%$ of its theoretical value; (iii) concentration/dilution factor; and (iv) a signal-to-noise ratio of equal to or greater than 10. The standard calibration curve showed strong linearity (> 0.99). The linearity and repeatability of these calibration curves were found to confirm before each set of determinations. Procedural blanks were analyzed with every batch of samples. Analyte recoveries through the procedure were checked to determine the accuracy of the methods (Kwok et al. 2013). A known amount of target chemicals and ^{13}C -labeled standards were spiked into the test samples, and the recovery tests were performed to find out the recovery percentage of PFAS and the matrix spike recoveries (Table 1.1). The recoveries of PFAS ranged from 70 to 115%. The matrix spike recoveries ranged from 60 to 100% (Table 1.1).

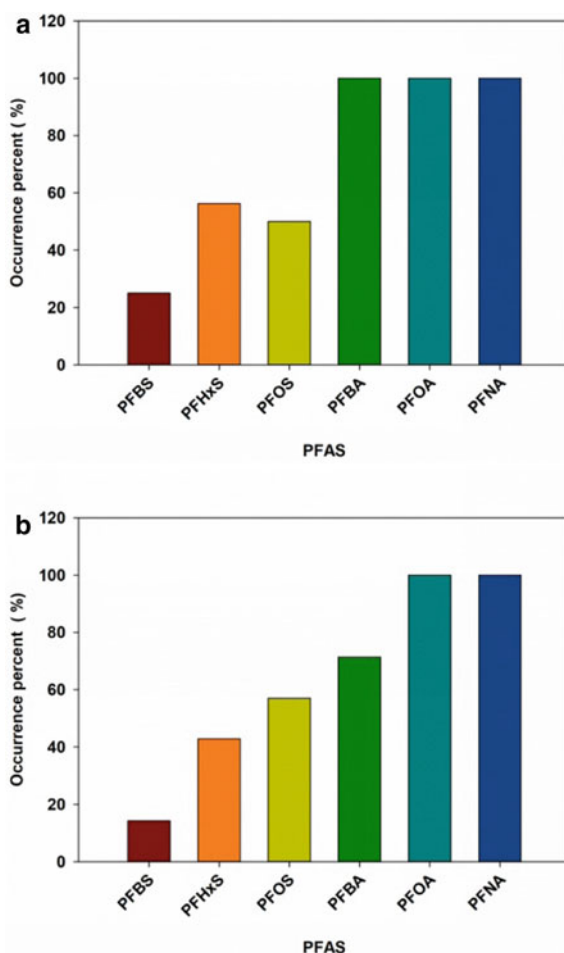
1.4 Results and Discussions

This is the first study in the southern part of India, which is aimed at detecting the presence of PFAS in river water samples. Out of 23 analyzed PFAS compounds, PFBS (C-4), PFHxS (C-6), PFOS (C-8), PFBA (C-4), PFOA (C-8) and PFNA (C-9) are found from the study area. The presence and concentration of these compounds were shown in Table 1.2. Various studies around the globe trace the concentration of two main and major long-chain compounds in the PFAS, i.e., perfluorooctane sulfonic acid (PFOS) and perfluorooctane acid (PFOA). Because of the high-water solubility's of these compounds, the aquatic environment is suggested to be the final sink for PFOS and PFOA. There have not been any studies related to PFAS in this river; hence, a baseline study is required to build a foundation for future works. The result shows that short-chain (C-4) compounds in PFCAs (PFBA) are measurable in 21 locations (Table 1.1). PFOA and PFOS concentrations are more significant in the estuary (Table 1.1). PFOS was found to be the most predominant.

The solubility in water for each compound differs with the length of the carbon chain. It is to be noted that short PFAS are more easily dissolved than long PFAS because of the larger hydrophobic moiety that arises with longer chains [PFOS

0.68 g/L solubility in freshwater (Jeon et al. 2011); PFOA 3.4–9.5 g/L solubility (Jensen et al. 2008)]. PFBA is a short-chain compound and that is present in all sampling stations of the study area. This may be because of the high solubility of short-chain compounds in water, and the highest concentration detected is 900 ng/L (station 3). PFAS have low volatility and do not substantially evaporate at normal temperatures while having a higher solubility than other hydrophobic contaminants (Jensen et al. 2008). The lack of volatility among the longer chain PFAS gives it even more reason to be persistent in river water bodies. The enhanced solubility in water is due to the functional groups, where both the hydroxyl groups and the carbonyl oxygen can bind to hydrogen in the water molecule. Table 1.1 summarizes all the analytical results, that is, the concentration of the target compounds, and Fig. 1.2a and b also shows the occurrence of the individual PFAS compounds, respectively.

Fig. 1.2 a Occurrence percentage of PFAS compounds in Periyar River. b Occurrence percentage of PFAS compounds in other selected stations



The most frequently detected compounds in the Periyar River were perfluoroalkyl carboxylates, named as PFBA, PFOA and PFNA (occurrence 100%), followed by perfluoroalkyl sulfonates, i.e., PFHxS (50%), PFOS (50%), which were calculated according to the percentage of detection. The compound which was detected at the lowest was PFBS (25%), but that was never detected above the limit of detection or the LOQ shown in Table 1.1. The upstream part of the study area is less populated compared to the lower regions as it flows through the forest (stations 1–6). In these locations, relatively less concentration of individual PFAS compounds was detected, and according to the point source of contamination, the concentration of such substances varied. Mullaperiyar dam (Station1) should be the reference point for the least contamination of study area; however, PFCA compounds are present here, which could be due to effects of polishing substance used in tourist boats or from the anthropogenic activities of tourists.

The stretch between Angamaly and Kochi is an industrialized zone in the Periyar River basin. At Aluva (station 7), the river splits into the Marthandavarma and the Mangalapuzha branches, of which Mangalapuzha branch joins Chalakkudy River (station 9) and empties into the Lakshadweep Sea at Munambam-(kottapuram, i.e., station 10), and the flux has been calculated for this region. The Marthandavarma branch flows southward through the Udhyogamandal area and then joins the Cochin backwater system at Varapuzha. The Eloor-Edayar region of Cochin estuary presents a typical example of industrial contamination. Five PFAS compounds were detected in three stations along the entire stretch of the Marthandavarma branch. PFNA and PFOA were detected in 23 locations. According to the point source of contamination, other compounds like PFHxS and PFNA were detected below 200 ng/L except at Cochin Refinery station.

Between 2000 and 2002, global manufacturers stopped producing PFOS and related compounds and PFOA and completely restricted their usage (Buck 2011a, b). 3M phased out production of PFOS and its derivatives by 2003. However, there is no regulation for the manufacture, use and disposal of PFAS compounds in India, as discussed earlier. Therefore, this study is more significant as a baseline study to know the present status of the target compounds. The sampling stations near to downstream part of Periyar River are highly populated, and water from Periyar River is used for many purposes, including drinking. The concentrations in these locations showed a gradual increase in C-8 compounds, i.e., PFOS and PFOA, which might be because of the industrial or domestic discharge of target compounds into the aquatic environment.

In 2009, the survey of perfluorochemicals (PFCs) in surface water from the Ganges River and other water bodies in India showed the profiles of PFCs in the Indian rivers are dominated by PFOS followed by PFOA (Yeung 2009). The present study is also supporting this observation in the Periyar River. However, there is a different trend observed elsewhere in Japan, USA, Korea, where PFOA was the predominant compound in waters.

This issue is prevalent in other parts of the world and is not limited to South India. A study has conducted to create a concentration profile of 40 different PFAS in surface water along the Rhine River; it was found that perfluorobutane sulfonate

(PFBS) and perfluorobutanoic acid (PFBA) were found in high concentration (181 and 335 ng/L) (Nakayama et al. 2010). In a similar study conducted in Upper Mississippi to understand the environmental distribution of PFAS, it was found that PFBA, PFOA, perfluorohexanoic acid (PFHxA) and perfluoroheptanoic acid were found in large quantities above 60% of the LOQ (Moller et al. 2010). These studies all point toward a large industrial emission coming from a point source located in the proximity of the sampling location. The second study also indicated that the local wastewater treatment systems also contributed to the PFAS emissions to the river water in upper Mississippi. This finding is completely similar with our study where a sampling location close to the industrial area recorded, PFAS concentrations on the higher side. The sampling location at Chitrapuzha (P16) and Tripunithura (P15) recorded the highest PFAS concentrations among all points for all compounds (Table 1.2).

1.4.1 Levels of PFAS in Other Stations

At the time of sample collection from all stations in the pre-monsoon time, water flow in station 15 and 16 was stagnant. The maximum concentrations of PFOS reached 12,958 ng/L near to Cochin Refinery (station 16). However, other locations showed less concentration compared to this station (i.e., 2000 ng/L and below). Extensive sampling is needed to confirm the presence and check the sources which are discharging PFAS into these stations. PFAS concentrations showed similar trends at Meenachil River (station 18–20), Periyar River and other selected contaminated sites. PFAS concentrations in all locations are summarized in Fig. 1.3a and b.

1.5 Conclusions

The aim and scope of this study was to detect, analyze and quantify major PFAS in the River Periyar. It was found the concentration of PFAS was maximum near the Periyar estuary (12,958 ng/L for PFOS). This can be attributed to the industrial emissions from nearby industrial areas. It was also found that out of six major PFAS analyzed, three perfluoroalkyl sulfonates (PFASs) and three perfluoroalkyl carboxylic acids (PFCAs) were detected in the study area, and the concentrations varied according to point source of contamination. PFBA, PFOA and PFNA were found in all the sampling locations, which include the entire stretch of the river and its tributaries. The findings indicate that there is a high level of PFAS in the estuary of the river. For the first time in the Periyar River, a study of this magnitude and scope has established a baseline for emissions.

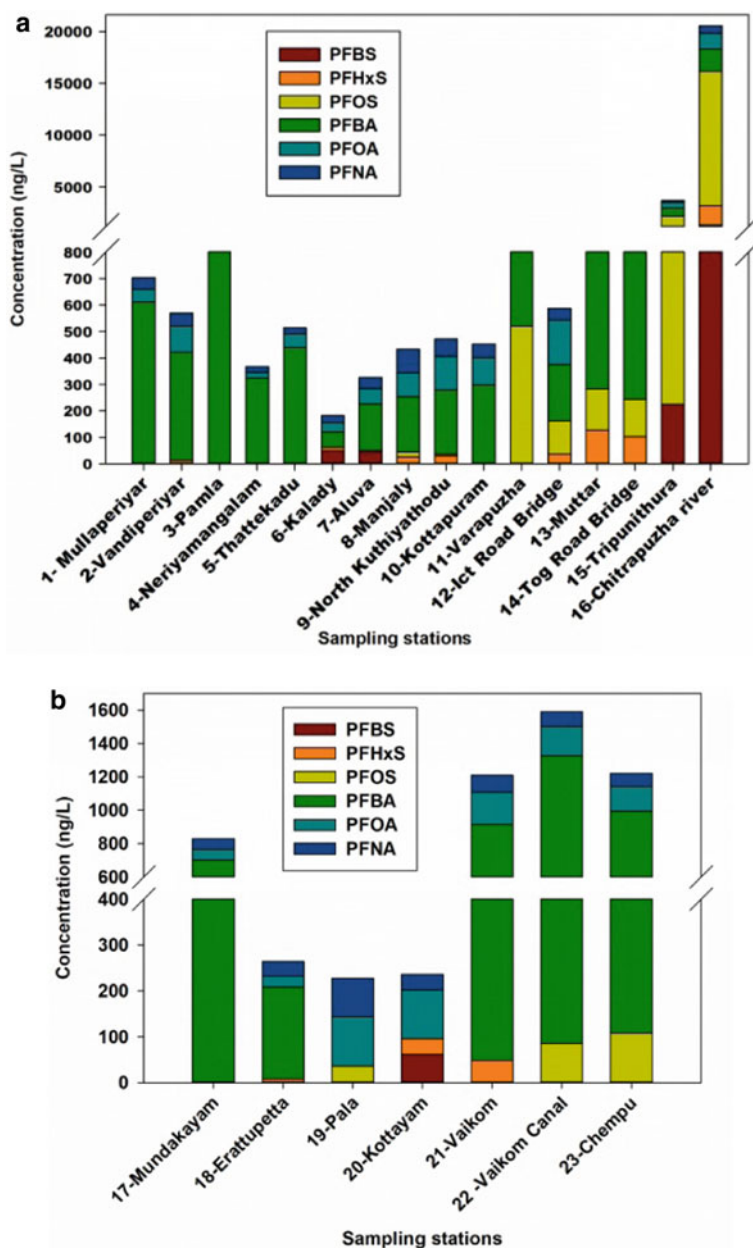


Fig. 1.3 **a** Concentration of selected PFAS in River Periyar, Meenachil and other contaminated sites. **b** Concentration of selected PFAS in River Periyar, Meenachil and other contaminated sites

Acknowledgements This study was supported by the Japan Society for the Promotion of Science (JSPS), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan, and Manipal Academy of Higher Education.

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