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OCCURRENCE AND DISTRIBUTION OF EMERGING POLLUTANTS PERFLUOROALKYL AND POLYFLUOROALKYL SUBSTANCES (PFASS) IN THE AQUATIC ECOSYSTEM OF INDIA

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ABSTRACT

Recent advancement in water quality assessment and remediation technologies has led to the identification of trace amounts of emerging contaminants of anthropogenic origin. The presence and toxicity of these compounds in each environmental niche (i.e. air, water, soil) has been identified as a major health concern throughout the world. Perfluoroalkyl and polyfluoroalkyl substances (PFASs) have been identified as one such class of ubiquitous, non-degradable, persistent organic pollutants (Kaboré et al., 2018). However, till date, India has no environmental quality standards and specific guidelines for the management of these compounds. Only limited studies on presence and toxic impact of these persistent organic pollutants have been carried out in India. There is an urgent need to conduct extensive and comprehensive studies for the detection of these emerging pollutants in the various environmental and biological matrices. This review paper summarizes the currently available literature on occurrence, distribution of Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in India.

KEY WORDS : Perfluoroalkyl and polyfluoroalkyl substances (PFASs), Pollutants, Water

INTRODUCTION

Non-biodegradable, accumulative and toxic Persistent Organic Pollutants (POPs) has always been a concern for scientists and policy makers. For efficient assessment and thereafter environmental management of POPs, Stockholm convention was adopted in 2001. Per and Polyfluorinated compounds (PFASs), were enlisted as a distinct class of emerging and persistent organic pollutants, at the fourth meeting of conference of parties to the convention (Weiss *et al.,* 2015).

PFASs belong to a complex family of anthropogenic fluoro-organic chemicals and have been manufactured and utilized for various industrial and household applications since the 1950s. These compounds exhibit excellent inert, water repellent and heat resistant properties that make them suitable for various industrial and household applications. They are used in paper and packaging industries, for surface treatment of textiles and leather compounds, in photography and semiconductor devices, as coating materials in various non-stick cook-wares, as surfactant in soap and shampoo and as surface tension lowering agents in firefighting foams (Hatton *et al.,* 2018).

Due to their exceptional physical and chemical stability, PFASs remain intact in the natural environment for a considerably long period of time, resisting any photolytic, chemical and biological degradation. High-water solubility, low volatility, and amphoteric chemical structure enable PFAS compounds to sustain easily in aquatic environments (Banzhaf *et al.,* 2017).

Albeit potentially hazardous nature of PFASs, only limited research is being carried out to

investigate the environmental and health impact of these compounds, probably due to their occurrence in only trace amounts (ng/L). In the year 2000, the global leader in PFASs compound producers, 3M, USA decided to phase out the use of PFASs citing their probable bioaccumulative and toxic potential towards the environment. Given the various environmental and biological hazards associated with the PFASs, eight major manufacturers of these compounds in the United States, agreed to stop the manufacturing and eliminate the usage of PFOAs in their products under PFOA Stewardship Program (Fact Sheet: 2010/2015 PFOA Stewardship Program).

A pioneer and preliminary study demonstrated the occurrence of perfluorooctane sulfonic acid in wildlife (Giesy *et al.,* 2006). Moreover, a study indicates presence of PFASs in trace amounts reported in various samples of blood across different countries, whereas global presence of PFASs has been witnessed in most environmental and biological systems (Houde *et al.,* 2011, 2005).

High concentration of PFAs in water, air, soil, marine and terrestrial biota has been reported by various research groups. An extensive study comprising the global production of PFASs, their direct and indirect sources, transport to environmental sinks like water, sediment and deep ocean has been reviewed in a holistic way by Prevedouros *et al.,* 2006. (Kim and Kannan, 2007) have reported presence of perfluorinated acids in urban lakes of Albany, USA. They measured relatively higher concentration of perfluorinated acids in different environmental components such as air (8.28 to 16.0 pg/m^3), surface runoff water (1.11 to 81.8 ng/l), lake water (9.49 to 35.9 ng/l). Recently, the presence of PFCAs, short-chain PFSAs as well as their precursors has been reported to show gradual increase from 2009 to 2018 in Arctic and North Atlantic Ocean region (Muir *et al.,* 2019).

Ecotoxicology associated with Perfluoroalkyl and polyfluoroalkyl substances (PFASs)

The presence of PFASs in surface and groundwater has been identified as a serious threat globally. The superlative chemical stability, higher water solubility and low volatility of PFASs compounds, make them ubiquitous to surface water, groundwater and oceans. Taniyasu *et al,* (2003) first reported the presence of PFASs in the surface and sea water collected from different locations in Japan (Taniyasu *et al.,* 2003).

Once introduced to surface water and groundwater, PFASs pose a serious threat to human health. Compounds such as PFOA and PFOS have an adverse impact on kidney, liver, immune system, thyroid gland and may also induce cancer. It has also been reported that after PFASs exposure they accumulate in liver and serum, causing serious hepatotoxicity and possibly adenomas in liver and thyroid tissue (Suja *et al.,* 2009). Several reports also highlight the induction of neoplasm of male reproductive system and bladder (Banzhaf *et al.,* 2017).

The presence of PFASs was also estimated in the blood samples of birds and fishes. High bioconcentration factor (274-41600) was reported based on the concentration of PFASs in water and fish liver. Research clearly demonstrates that the long chain PFASs have a tendency of biomagnification in animals including humans (Houde *et al.,* 2005; Norström *et al.,* 2015). A recently published research indicates the presence of PFASs (PFOS and PFOA) in human bone marrow and their possible impact on osteoblast cell differentiation (Koskela *et al.,* 2017). Exposure of compounds such as PFOS and PFOA to pregnant women may be associated with reduced birth weight of new born (Washino *et al.,* 2009). PFASs have been found in maternal serum and umbilical cord blood, suggesting their transfusion from mother to foetus through the placental barrier (Buck *et al.,* 2011; Manzano-Salgado *et al.,* 2017).

Several epidemiological studies show the positive co- relationship between exposure of PFASs and thyroid disorders, enzyme level alteration, high level cholesterol and cancer induction (Agency for Toxic Substances and Disease Registry, 2016). The World Health Organization's International Agency for Research on Cancer has found that PFOA is possibly carcinogenic to humans (Group 2B) (Chiu *et al.,* 2015)

PFASs have already been enlisted as a "Substance of Very High Concern" by the European Chemicals Agency, under Annex XVII, entry 53, of REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) (Vierke *et al.,* 2012). Hence, regulatory and government agencies such as the US Environmental Protection Agency (EPA), European Chemical Agency (ECHA), and others are looking to limit their presence in the environment.

Solid Phase Extraction (SPE) methods are normally implied to extract the PFASs compound from environmental matrices followed by the Liquid

Chromatography- tandem mass spectrometry (LC/MS) mediated identification (EPA 537.1) of these compounds in lower concentration units (ng/L). In 2019, the US EPA released a new method, EPA 533, to analyze 25 PFAS compounds. The method includes analysis of shorter chains (C-chain <6) and some newer or emerging PFASs in drinking water, using SPE and LC/MS/MS (Shoemaker and Tettenhorst, 2020).

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in India

Rapid industrialization followed by the uncontrolled and unmindful urbanization has been a serious threat in the environmental matrix (air, water, and soil). India has emerged as a global manufacturing hub for textile goods, metallurgy and machinery items. A large amount of Per- and polyfluoro alkyl substances are extensively used in the different industrial processes.

Although, these fluorinated compounds have been phased out by the global manufacturers such as 3M and DuPont. However, recent reports clearly indicate the usage of PFASs compounds has increased in countries like India, China, and Russia (OECD, 2015).

Kannan *et al.,* (2004), has firstly reported the presence of PFASs compounds in human serum and blood. He reported presence of Perfluoroalkyl and polyfluoroalkyl substances in 473 human blood/serum/plasma samples collected from various countries across the globe such as Belgium, Brazil, Colombia, India, Italy, Malaysia, Poland, South Korea and the United States. Surprisingly a very low amount of PFAS compounds was observed in the Indian population (< 3ng/L) as compared to the US population (>30ng/L) (Kannan *et al.,* 2004).

Tao *et al.,* (2008), have reported the presence of PFASs in human breast milk samples from several asian countries including India with concentration of 39.4 pg/mL (Tao *et al.,* 2008). Yeung *et al.,* (2009) conducted a study to investigate the presence of perfluorinated compounds in surface water and aquatic biota including dolphins of Ganges River in India. Samples were taken from surface water including Ganga River water and its associated biota such as shrimp, fish, and dolphins. Out of all PFASs compounds, PFOS was dominated in concentration. The concentration of PFOS in the surface water was observed (0.04–3.91 ng/L). However, the average concentration of PFOS in biota was found to be 0.248–27.9 ng/g (Yeung *et al.,* 2009).

Quantitative analysis of PFASs compounds was conducted in various lakes of Tamil Nadu by Sunantha and Vasudevan (2016). The average concentration of PFOA was observed ranging 4 to 93 ng/l while the concentration of PFOS was observed 3 to 29 ng/l. Study clearly identified textile dyeing wastewater and domestic water as a potential source of PFOS and PFOA compounds (Sunantha and Vasudevan, 2016). Sharma *et al.,* (2016) have conducted a comprehensive study to evaluate the concentration of PFASs in river and groundwater from different locations of Ganga river basin. Samples were collected at Uttarkashi, Devprayag, Kanpur, Varanasi, Patna, Farakka, and Gangasagar. Total PFASs concentration in the Ganges River water samples ranges from 1.3 to 15.9 ng/l. Concentrations of PFOA and PFOS ranged between 0.1 and 1.2 ng/l, less than their threshold value. PFSAs concentrations in the Ganges were lower than concentrations reported in rivers of other continents (Sharma *et al.,* 2016).

CONCLUSION

Due to non-biodegradability and biomagnification properties, the probability of finding these fluorinated compounds in biological and environmental systems is quite high. Their presence and concentration in trace amounts (in ng/l) in aquatic systems make them difficult to be detected. Limited studies have been conducted to estimate the presence of these compounds in surface water/ground water of Indian subcontinents. Due to a paucity of sufficient scientific data, in India, no specific guideline or Environmental Quality Standard (EQS) for PFASs compounds exist. As these compounds are non-biodegradable and ubiquitous, the biomagnification of these compounds in flora and fauna is inevitable. The rapid industrialization and consequent urbanization of the country rely on the consumption of more materials and related products. So, an effective management plan for these critical compounds required an estimation and quantification of PFASs. Assessment of spatio- temporal variability of the occurrence of these compounds in surface water bodies (river, lakes, ponds, sewage water) is desired to create baseline information about the physicochemical association of perflourinated compounds with the seasonal/environmental variabilities. Source apportionment studies utilizing multiple factor analysis and hierarchical clustered

analysis considering numerical and categorical variable such as different land use type, seasons, type of industry etc. is required to give a first-hand information about the effective pollution potential of a specific source of Per and polyfluorinated compounds (PFOS and PFOA).

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