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FATE AND DISTRIBUTION OF PERFLUOROALKYL SUBSTANCES (PFAS) IN WATER RESOURCES FROM GANGES RIVER BASIN: EMISSIONS AND HUMAN EXPOSURE

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1. Introduction

Perfluoroalkyl substances (PFAS) have been a matter of global concern due to their ubiquitous presence (underpinning exposure to humans and biota) and associated toxicological outcomes 1,2. These substances have been widely used in production process and daily-use products or may result from degradation of precursor compounds in products or the environment. India, with its developing industrialization and population moving from traditional to contemporary lifestyles, represents an interesting case study to investigate PFAS emission and exposure along steep environmental and socioeconomic gradients.

In this study, we focus on Northern India as one of the emerging industrial regions, for which data on PFAS environmental and human exposure are still very limited. This study presents a comprehensive assessment of fate and distribution of 21 PFAS in water resources of the Ganges River basin covering a transect of 2525 km (from pristine upper Himalayan region to highly industrialized and populated downstream region) and estimates direct emissions, specifically for PFOS and PFOA in sections of the river with contrasting socioeconomic conditions. An additional aim of this study was to assess exposure patterns of drinking water resources used by local populations and derive an assessment of human exposure through drinking water consumption.

2. Materials and methods

Grab bulk water sampling of river water and groundwater (used in this region as drinking water) using high density polyethylene (HDPE) bottles was performed so as to obtain information on possible co-variation of contamination of drinking water resources with surface water resources receiving domestic and industrial wastewater. Analysis of these collected samples Analysis was conducted in the RECETOX laboratory in Brno, Czech Republic.

Water samples were filtered through glass microfiber filters before extraction to remove suspended solids and were spiked with recovery standards. Samples were extracted using solid phase extraction. PFAS were eluted in falcon tubes and concentrated using a gentle stream of nitrogen. Each sample was cleaned-up using a syringe filter directly to the HPLC mini vial. Mass labeled internal standards were added to all samples, blanks, and calibration standards before analysis.

Separation and detection of all target compounds were performed by liquid chromatography equipped with a 50mm x 2 mm column coupled to a mass spectrometer and interfaced via an electrospray ionization source. The mass spectrometer was operated in negative ion mode using two MRM transition for each compound.

Recoveries ranged between 68% and 110%. Instrument quantification limits (IQLs) were calculated from the calibration curve as the concentrations giving peaks for which the signal-to-noise ratio was 9.

Method quantification limits (MLQs) were calculated from the sample noise and related to the matrix effect in individual samples.

3. Results and discussion

3.1. PFAS in the Ganges River water and direct emissions of PFOA and PFOS to river

Among the 21 analyzed PFAS, 15 compounds were detected in one or more locations (Figure 1). Total PFAS concentration in the Ganges River water samples ranged betwen 1.3 – 15.9 ng L-1. PFAS with C5 – C8 were detected more frequently than C9 – C14. Concentrations of PFOA and PFOS ranged between 0.1 – 1.2 ng L-1 and <MQL – 1.7 ng L-1, respectively. PFSAs concentrations in the Ganges were lower than concentrations reported in rivers from Japan, China, Italy, and North-East Spain; while they were in the same range as those detected in some rivers in Germany, Vietnam, and Brazil.

In the Ganges, due to the large river section, huge catchment and high dilution, atmospheric inputs of some PFAS may be important sources especially in areas of the catchment (such as in Himalayas) with a relatively low anthropogenic impact. In our study, concentrations of PFOA were lower than those of PFHxA, PFHpA, and PFPA by a factor 1.7 – 16 in all river sections and the spatial distribution of C5 – C8 PFCA concentrations in river water was strongly positively correlated, and had concentrations measured downstream of the major conurbations typically higher than those measured upstream. This indicates the prevalence of direct sources from the technosphere (e.g. direct discharge through waste water or leaching from poorly disposed solid waste) dominating PFAS inputs, especially in the most anthropic parts of the river. The prevalence of compounds with shorter alkyl chains is interpreted as a result of on-going substitution strategy adopted by industry. To our knowledge, this is the first experimental evidence of shorter chain PFCAs exceeding levels of PFOA in river water from a country with an emerging industrial economy.

The mean cumulative PFOA and PFOS discharges in the whole Ganges catchment were calculated to be in the order of 240 and 210 g day_1 respectively. Estimated emissions varied by up to 4 orders of magnitude in different subcatchments. Urban population displayed a strong positive correlation with PFOS emissions. Mean values of Estimated emission per urban resident ranged between 0.1 – 2.5 mg day-1person-1 for PFOS and 0.3 – 11 mg day-1person-1 for PFOA. Estimated emissions of PFOS and PFOA in the Ganges River were significantly lower than estimates from Europe 3.

Fig.1 Levels of PFAS in Ganges River water

3.2. PFAS in groundwater

This study is the first to analyze groundwater samples from the Ganges River basin in relation to exposure of surface water as receptors of wastewater inputs. Levels and patterns of PFAS were very similar to those observed in surface water (Figure 2). Out of 21 PFAS, 14 compounds were frequently detected. Similar to what was observed in Ganges River water, concentrations of PFOA in groundwater were lower than PFPA, PFHxA, and PFHpA concentrations. As described previously, this can be indicative of a shift in use to 6:2 fluorotelomer-based articles from 8:2 fluorotelomer-based articles.

The observed consistent contamination profile and spatial trends of PFCAs and PFOS indicates that the occurrence of PFAS in groundwater has similar drivers compared to that in surface water in that particular location.

Possible sources of PFAS contamination to groundwater can include leaching and runoff from unpaved surfaces (including leaching of contaminated atmospheric depositions) as well as leaks from municipal and industrial wastewater drains and landfills. Abstraction of polluted river water for irrigation and leaching from agricultural soils may also contribute to aquifer contamination of that particular subsurface location with PFAS emitted through wastewater directly to the river.

The observed trends with higher concentrations in groundwater compared to river water for the more soluble substances and decreasing CGW/CRW ratio at increasing KOC suggests that groundwater may be preferentially contaminated by direct sources through processes that are mediated by partitioning with soil and/or sediment. In principle, these include all the processes mentioned above (i.e. leaching from contaminated ground, leaks from the sewage and exchange with riverwater by infiltration through the river sediment bank). Concentrations of PFOS in groundwater and river water had a similar spatial trends.

Fig.2 Levels of PFAS in groundwater in Ganges River basin

3.3. Estimation of human exposure to PFAS

In this study, low-exposure, intermediate-exposure and high-exposure scenarios to PFAS for children, adults, and senior citizens through contaminated drinking water were estimated by the approach presented by Gebbink et al., 4. Daily exposure intakes for PFAS via drinking water consumption (Edw) were calculated (Figure 3). These intakes were 2 – 3 times lower than those calculated for the adult population of Catalonia in Spain and children from Taiwan 5, 6. Health risks based on exposure to PFAS through contaminated water consumption were also assessed. The oral non-cancer risk, expressed as a Hazard Index (HI), was determined by comparing oral exposure dose (through water intake) with a Reference Dose (Rf) for each PFAS. For all PFAS and age groups, the exposure intake did not exceed the Rf under any of the exposure scenarios. The estimated HI values, therefore, were below 1, implying no considerable risks from drinking water consumption.

Figure 3. Estimated exposure intake of general population to different PFAS in Ganges River basin (logarithmic scale, base 10). (HES: high exposure scenario, IES: intermediate exposure scenario, LES: low exposure scenario).

4. Conclusions

This study provided a first regional overview on PFAS occurrence in, and emissions to the water resources in the Ganges River basin along with a preliminary first assessment of human exposure through drinking water in this region. The enormous availability of renewable water resources controlling dilution of wastewater effluents in the large Ganges River, relatively low per-capita emissions in a region with an economy that is still largely based on agriculture and a large part of the population still living a traditional lifestyle, resulted in limited environmental and human exposure to PFAS. But this is expected to change with higher aspiration of the merging middle class in India which is a huge number. This recommends to periodic monitoring and surveillance of PFAS in India. Ground/drinking water had a similar contamination pattern (both at regional and local scale) as waste water-receiving river water, suggesting that these compartments are sensitive to the same diffuse and/or local sources of PFAS. Presence of PFAS in groundwater can be interpreted as a consequence of river water infiltration, spills from sewage, or leaching from contaminated surface water (possibly including the use of contaminated river water for irrigation and subsequent leaching).

5. References

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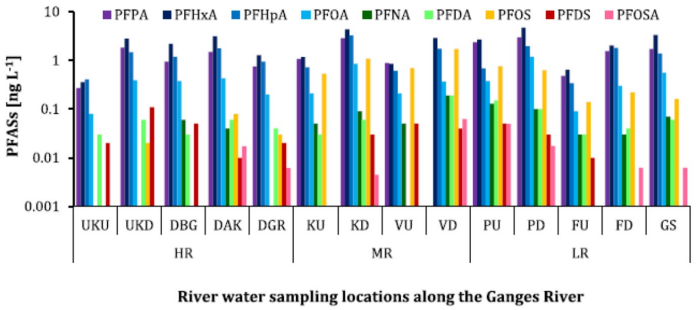


Fig.1 Levels of PFAS in Ganges River water

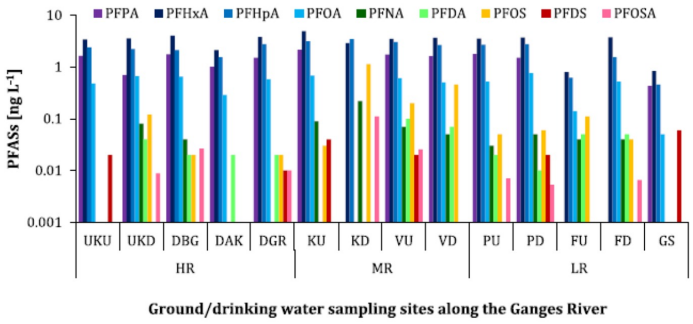
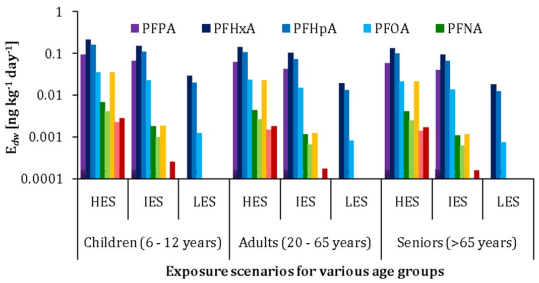


Fig.2 Levels of PFAS in groundwater in Ganges River basin



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