



## Perfluoroalkyl acids (PFAAs) in the Pra and Kakum River basins and associated tap water in Ghana



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### HIGHLIGHTS

- PFCs are recalcitrant in many water treatment processes, making drinking water a potential source of human exposure.
- The study presents the first report on contamination from PFCs in river and drinking water in Ghana
- Five PFC congeners – PFOA, PFOS, PFHxA, PFDA and PFPeA – were commonly detected in river and tap water in Ghana
- The study revealed limitations of local tap water treatment in getting rid of these emerging pollutants

### ARTICLE INFO

#### Article history:

Received 20 August 2016

Received in revised form 20 October 2016

Accepted 6 November 2016

Available online 23 November 2016

Editor: D. Barcelo

#### Keywords:

Perfluorinated compounds

Pra River

Kakum River

Perfluorooctanoic acid

Perfluorooctane sulphonate

### ABSTRACT

Perfluoroalkyl acids (PFAAs) are persistent environmental pollutants that have been detected in various media including human serum. Due to concerns regarding their bioaccumulation and possible negative health effects, an understanding of routes of human exposure is necessary. PFAAs are recalcitrant in many water treatment processes, making drinking water a potential source of human exposure. This study presents the first report on contamination from PFAAs in river and drinking water in Ghana. The targeted PFAAs were perfluoroalkyl carboxylic acids (PFCAs) with C<sub>4–14</sub> carbon chain and perfluoroalkane sulphonic acids (PFSAs) with C<sub>6, 8, 10</sub>. Five PFAA congeners – PFOA, PFOS, PFHxA, PFDA and PFPeA – were commonly detected in river and tap water. The mean concentrations of  $\sum$  PFAAs in the Kakum and Pra Rivers were 281 and 398 ng/L, while tap water (supplied from the treatment of water from those rivers) contained concentrations of 197 and 200 ng/L, respectively. PFOA and PFOS constituted about 99% of the  $\sum$  PFAAs. The risk quotient (RQ) attributed to drinking of tap water was estimated at 1.01 and 1.74 for PFOA and PFOS, respectively. For a country that has not produced these compounds, the RQs were unexpectedly high, raising concerns particularly about contamination from such emerging pollutants in local water sources. The study revealed limitations of local tap water treatment in getting rid of these emerging pollutants.

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### 1. Introduction

Perfluoroalkyl acids (PFAAs) have received attention in recent years as environmental contaminants due to their occurrence in several environmental matrices and the adverse effects observed in animal toxicity studies (Giesy and Kannan, 2002; Kennedy et al., 2004; Lau et al., 2007; Zushi et al., 2011; Zushi et al., 2012). The two groups that have attracted the

most attention are the perfluoroalkane sulphonates (C<sub>n</sub>F<sub>2n+1</sub>SO<sub>3</sub><sup>-</sup>) and perfluoroalkyl carboxylic acids (C<sub>n</sub>F<sub>2n+1</sub>COOH) because they are often detected in environmental samples at levels relatively greater than the other congeners (Prevedouros et al., 2006; Paul et al., 2009). Studies have shown that perfluorooctanoic acid (PFOA) and perfluorooctane sulphonate (PFOS) accumulate in the hydrosphere (Boulanger et al., 2005; Yamashita et al., 2008), as well as the biosphere (Schultz et al., 2003; Calafat et al., 2006). They have also been found to persist in the environment for long periods of time with half-life of more than two thousand years (Lyons, 2007) and can equally bioaccumulate in humans (Johnson et al., 2009). Occupational exposure studies on workers have

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shown that the mean half-life of PFOA and PFOS in human serum is 3.8 and 5.4 years respectively (Olsen et al., 2007).

Evidence from scientific research has strongly shown that PFAAs contamination poses a serious health threat to humans and animals. Findings strongly associated PFOA to several cardiovascular risk factors. These include elevated uric acid levels linked to hypertension, higher serum cholesterol level associated with stroke and higher serum homocysteine level (Olsen et al., 2003; Costa et al., 2009; Steenland et al., 2010; Shankar et al., 2011; Min et al., 2012; Geiger et al., 2013; Fitz-Simon et al., 2013; Fisher et al., 2013). PFOA and PFOS contamination of the blood have been found to be associated with an increase in diabetes mortality, thyroid dysfunction and alteration of liver gene expression (Scott et al., 2006; Leonard et al., 2008; MacNeil et al., 2009). PFOA and PFOS have been strongly linked to a number of outcomes in animal studies particularly tumors and neonatal loss (USEPA, 2005; Lau et al., 2007). Epidemiological studies conducted in United States of America reported an association between PFOA exposure and kidney and testicular cancers in individuals who lived near and worked at plant that produced the chemical (Olsen et al., 2007).

Perfluorooctane sulfonate production was voluntarily stopped by its primary producers in 2001/2002 (even though production by other manufacturers continued) and was added to the list of persistent organic pollutants (POPs) in the Stockholm Convention in 2009 (Stockholm Convention, 2013). Although PFOS-based products were phased out in 2002, their occurrence in the environment has still been observed in several countries in recent years (Boulanger et al., 2005; Sinclair et al., 2006; Guo et al., 2010; Shivakoti et al., 2010; Sun et al., 2012; Zhang et al., 2013). However, while some studies put it that PFOS concentration in tissues has decreased rapidly in human and wildlife species over the past decade (Butt et al., 2007; Hart et al., 2009; Olsen et al., 2012), others have shown an increase in the levels of PFOS even after the 2002 phase out (Reiner et al., 2011; Long et al., 2012).

Virtually no information is available on PFAAs and their precursors in environmental media in Ghana, despite the availability on the Ghanaian market of several consumer items known to contain such chemical products. Due to their unique properties, PFAAs have been used in various products e.g., upholstery, cookware, sports clothing, plastics, food handling equipment, medical equipment, motor oil additives, firefighting foams, paints and inks, making them available in the Ghanaian environment (Kissa, 2001; Dinglasan-Panlilio et al., 2004; Fiedler et al., 2010). PFAAs were reportedly also applied as emulsifiers and surfactants in mining and oil well drilling operations (Renner, 2001). Presumably, these are potential source factors that may introduce PFAAs into the Ghanaian environment.

As a class of POPs with comparatively high solubility in water (Vestergren and Cousins, 2009; D'Hollander et al., 2010), PFAAs at relatively low concentrations in drinking water can lead to elevated exposures in the general population. In the US for instance, the drinking water supplies for an estimated 6 million people reportedly exceeded the US EPA's lifetime health advisory of 70 ng/L for PFOS and PFOA (Hu et al., 2016). The situation in Africa is however largely unclear, given the scanty information available. While relatively low concentrations of PFOS (0.9–9.8 ng/L) and PFOA (1.3–28 ng/L) were reported in Lake Victoria in Kenya (Chirikona et al., 2015), the situation in South Africa was quite different. The levels of PFOA and PFOS in river water in South Africa (Mudumbi et al., 2014) were one to two orders greater than the reported levels in Kenya, and also surprisingly exceeding levels reported in the US. Thus, contamination from PFAAs in African countries deserves adequate scrutiny to ensure that residents were not unduly exposed to these pollutants. As a first report on PFAAs in environmental media in Ghana, the present study investigated contamination from PFAAs in some selected rivers in the country, as well as in tap water produced from those rivers. The potential exposure and risk considerations via drinking water was also evaluated.

## 2. Materials and methods

### 2.1. Study area

This study was conducted in Ghana. The selected sites were Kakum and Pra Rivers (Fig. 1), which feed the existing reservoirs at Brimsu and Daboase dams, respectively, for water treatment and subsequent distribution to the respective townships. These sites are respectively located in the Central and Western Regions of Ghana. The two rivers serve a population of >1,000,000 inhabitants of Cape Coast, Sekondi-Takoradi and their environs.

### 2.2. Sample collection

Water samples were collected from Pra and Kakum Rivers in Ghana between May and June 2015. This period fall within the rainy season in Ghana. Prior to sampling, the sampling areas (located around the Kakum and Daboase Water Treatment Dams) were divided systematically into nine sampling points along the Rivers. The first points were 100 m upstream from the Dams. Out of the nine sampling points, five points were randomly selected for each River (Fig. 1). Composite sample was collected at each sampling point. Each composite sample consisted of four samples collected randomly into a 1 L methanol-washed polypropylene sampling bottle. Collection of samples was done facing the direction of flow of the River into the Dam. At each sampling point, the sampling bottles were rinsed three times with the water before the collection of the samples. Each bottle was immersed at least 10 cm below the water surface. Community tap water samples were also collected into 1 L methanol-washed polypropylene sampling bottles. Sodium thiosulphate (3% w/v) was immediately added to the tap water samples to remove residual chlorine. Tap water samples ( $n = 5$  for each river basin) were collected from the vicinity where treated water from the River was supplied. The samples were placed in an ice chest and transported to the laboratory, where they were stored at 4 °C. In all, 10 river samples and 10 tap water samples were collected for analysis.

### 2.3. Chemical analysis

#### 2.3.1. Solid phase extraction

The water samples were filtered applying glass fiber filter (47 mm, pore diameter 1  $\mu\text{m}$ , Advantec Toyo Kaisha, Tokyo, Japan). One litre of each sample (at room temperature) was extracted using solid phase extraction method (Taniyasu et al., 2005). In brief, a weak anion exchange solid extraction octadecyl C18 cartridges (6 mL, 200 mg, Bond Elut, Analytichem, Harbour City, CA, USA) were preconditioned with 5 mL of 0.1%  $\text{NH}_4\text{OH}$  in methanol followed by double distilled water. One litre water samples were passed through C18 column cartridges via polypropylene tubing under vacuum at a flow rate of 5 mL per minute. After the extraction, cartridges were washed with deionised water to remove any inorganic ions. The cartridges were dried under vacuum for 15 min. The cartridges were then transported in dark, air-tight containers to the Laboratories of Yokohama National University in Japan for elution and analysis of PFAAs.

#### 2.3.2. Elution and spiking

Cartridges were eluted with 2 mL methanol and 2 mL 0.1%  $\text{NH}_4\text{OH}$  in methanol. Extracted samples were fortified with 20  $\mu\text{L}$  of 200  $\mu\text{g/L}$  of mixed internal standards, which included perfluoro- $n$ -[1,2- $^{13}\text{C}_2$ ] hexanoic acid ([ $^{13}\text{C}_2$ ]PFHxA), perfluoro- $n$ -[1,2,3,4- $^{13}\text{C}_4$ ] octanoic acid([ $^{13}\text{C}_4$ ]PFOA), perfluoro- $n$ -[1,2- $^{13}\text{C}_2$ ] dodecanoic acid([ $^{13}\text{C}_2$ ]PFDoDA) and perfluoro[1,2,3,4- $^{13}\text{C}_4$ ]octane sulphonic acid([ $^{13}\text{C}_4$ ]PFOS). Samples were mixed thoroughly with internal standards for 1 min using vortex. The spiked extracts were subjected to nitrogen evaporation until the final volume reached 400  $\mu\text{L}$ , filtered through

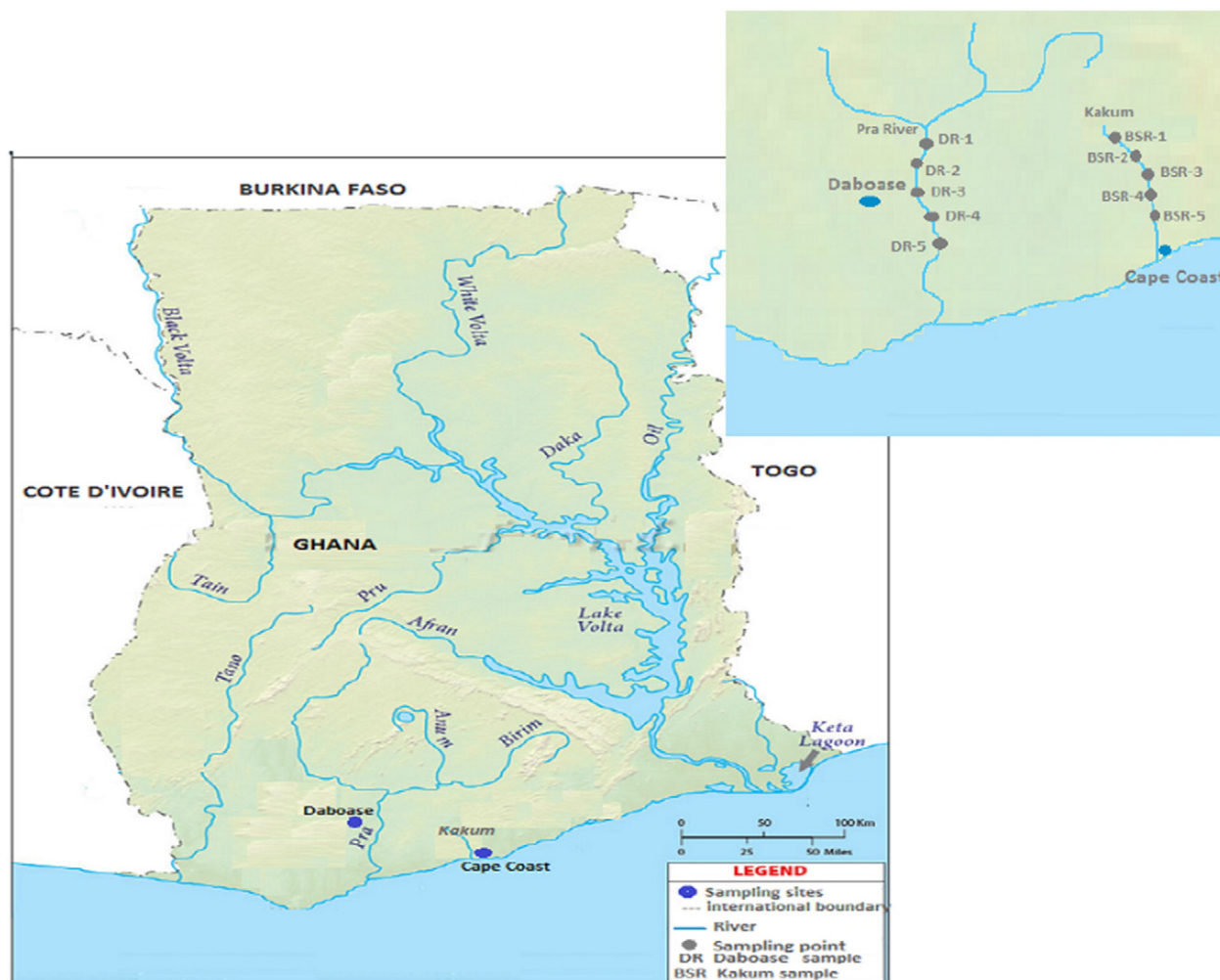


Fig. 1. Sampling sites located at the Southern parts of Ghana.

0.2  $\mu\text{m}$  nylon membrane and then transferred into auto sampler vials for liquid chromatography – mass spectrometry analysis.

### 2.3.3. Liquid chromatography–mass spectrometry analysis

The PFAAs were quantified using high performance liquid chromatograph–tandem mass spectrometry system (HPLC–MS/MS) that consisted of an HP 1100 HPLC system (Agilent Technologies) connected to a Micromass Quattro Ultima Pt mass spectrometer (Waters Corp., Milford, MA) operated in the electrospray negative ionization mode. A 10  $\mu\text{L}$  aliquot of extract was injected into C18 column (Zorbax XDB–C18) with 2.1 mm  $\times$  150 mm dimension packed with particle size of 5  $\mu\text{m}$ . The binary mobile phase consisted of 10 mM ammonium acetate in water (Solvent A) and methanol (Solvent B) at a flow rate of 0.2 mL/min. The column temperature was 40  $^{\circ}\text{C}$ . Chromatographic separation was achieved using gradient elution within 44.5 min. Argon was used as collision gas and the collision energy was optimized for each analyte.

### 2.3.4. Quality control/quality assurance

Linearity was evaluated in the 0.01–50  $\mu\text{g/L}$  concentration range. Six standard concentrations (0.01, 0.1, 5, 10, 30 and 50  $\mu\text{g/L}$ ) were prepared and used to construct a calibration curve (three replicates) to check the linearity of the instrument response and also for quantification. The regression coefficients ( $R^2$ ) of the calibration curve were calculated by plotting area ratio versus concentration. For most of the targeted compounds, regression coefficient was 0.99 indicating good linearity

(Table 1). Three blank samples were analysed and the average concentrations of each analyte in the blanks was used to correct the concentration of the corresponding analyte in the test samples. Recovery test was conducted by spiking a mixture of native standards (200  $\mu\text{g/L}$ ) into deionised water and then extracted following the same procedures used for the real samples. The average recoveries for the various PFC congeners ranged between 82% and 132% (Table 1). The intra-laboratory reproducibility of the method was determined by calculating the relative standard deviation (% RSD). Typically, a recovery within the range of 70–120% and reproducibility RSD  $\leq$  20% are preferable (Pihlström, 2011). The obtained recoveries and RSD values were largely satisfactory, indicating a fairly good precision for most of the analytes (Table 1). The limit of detection (LOD) (i.e. concentration that yielded signal to noise ratio of  $\geq$  3) and limit of quantification (LOQ) (i.e. concentration that yielded signal to noise ratio of  $\geq$  10) for the various analytes were determined for each sample. The median LOD and LOQ values were reported as the threshold values for each analyte (Table 1).

### 2.4. Risk assessment

The levels of risk associated with drinking PFAA-contaminated tap water were determined by considering the tolerable daily intake (TDI) and the risk quotients (RQs). The RQs of the major PFAA contaminants were each estimated by comparing the measured concentration in tap water samples with Drinking Water Health Advisory guidelines issued recently in May 2016 by the USEPA (USEPA, 2016a, 2016b). Risk

**Table 1**  
Limits of detection (LODs) and quantification (LOQs) in ng/L, correlation coefficients ( $R^2$ ), recoveries (%), and intra-laboratory reproducibility (RSD %) of the targeted PFAAs.

| Compound | LOD  | LOQ  | $R^2$ | Recovery (%) | RSD (%) |
|----------|------|------|-------|--------------|---------|
| PFBA     | 0.19 | 0.64 | 1.00  | 107          | 15      |
| PFHxA    | 0.01 | 0.02 | 1.00  | 121          | 8       |
| PFHpA    | 0.02 | 0.07 | 0.99  | 117          | 10      |
| PFOA     | 0.43 | 1.44 | 1.00  | 105          | 13      |
| PFNA     | 0.03 | 0.09 | 0.99  | 115          | 13      |
| PFDA     | 0.03 | 0.10 | 0.99  | 109          | 18      |
| PFUnDA   | 0.79 | 1.39 | 0.98  | 132          | 16      |
| PFDoDA   | 0.06 | 0.19 | 0.99  | 111          | 23      |
| PFTTrDA  | 0.01 | 0.06 | 0.98  | 125          | 19      |
| PFTeDA   | 0.05 | 0.11 | 0.96  | 110          | 12      |
| PFOS     | 0.39 | 1.31 | 1.00  | 107          | 14      |
| PFDS     | 0.11 | 0.36 | 0.99  | 106          | 26      |
| PFHxS    | 0.01 | 0.18 | 1.00  | 82           | 10      |
| PFPeA    | 0.01 | 0.03 | 0.99  | 105          | 13      |

quotients were used as indices to show the significance of PFAA contamination in water. If a RQ is greater than one, then this may indicate that drinking tap water could pose a risk to consumers.

### 2.5. Statistical analysis

The differences between means were evaluated using simple *t*-test. At 95% confidence interval (C.I.)  $p < 0.05$  was considered significant, while at 90% C.I.  $p < 0.10$  was considered significant.

## 3. Results and discussion

### 3.1. PFAAs congener composition

Water from the Pra and Kakum Rivers in Ghana, as well as community tap water sourced from those Rivers all contained detectable levels of PFAAs (Table 2). Out of the 15 PFAA congeners that were investigated, only 5 congeners were commonly detected at concentrations above their limits of detection (LOD). These were PFOA, PFOS, PFHxA, PFDA and PFPeA (Table 2). PFHpA was also detected at one sampling point (Table 2). Those not detected were PFBA, PFNA, PFDoDA, PFTTrDA, PFTeDA, PFUnDA, PFBS, PFHxS and PFDS. Thus, PFAA isomers with carbon chains below 5 and above 10 were not detected. The PFOA and PFOS concentrations were relatively very high, together constituting about 99% of total PFAAs at each site. PFPeA, PFHxA, PFHpA and PFDA were only present in relatively minute amounts. At each site, isomer profile was consistent between river and tap water (Fig. 2). For instance, the PFAA profiles at BSR-3 and BST-3, BSR-4 and BST-4, DR-1 and DT-1, and DR-2 and DT-2, just to indicate a few, were similar for each pair (river and tap water). It suggests that the PFAA contamination in the raw river water directly impacted PFAA profiles in the tap water.

The compositions of the major congeners (PFOA and PFOS) were compared to reported compositions in river or surface water and tap water from other parts of the world (Fig. 3). It emerged that the average profiles of PFOA and PFOS in river and tap water in Ghana were consistent with profiles reported for the Great Lakes (Lakes Erie and Ontario) (Boulanger et al., 2004) and in municipal drinking water from Catalonia, Spain (Ericson et al., 2009). The water samples from Ghana however differed in their composition of PFOA and PFOS profiles from reported profiles in surface and tap water in Asian countries (Rostkowski et al., 2006; Zushi et al., 2008; Kunacheva et al., 2010; Wang et al., 2012; Habibullah-Al-Mamun et al., 2016). The profile of river water from Kenya (Orata et al., 2009) was as well different from that of Ghana.

### 3.2. Concentrations of PFAAs in river and tap water

The mean  $\Sigma$  PFAAs concentrations of the Kakum and Pra Rivers were 280.80 and 397.63 ng/L, while tap water supplied from the

**Table 2**  
Concentrations (ng/L) of PFAAs in river and tap water samples from Kakum and Daboase areas in Ghana.

| Sampling points   | PFHxA  | PFHpA | PFOA              | PFDA | PFOS | PFPeA | $\Sigma$ PFAAs |
|---|--------|-------|-------------------|------|------|-------|----------------|
| <b>Kakum River Water</b>  |        |       |                   |      |      |       |                |
| BSR-2   | BDL    | BDL   | 1.78 <sup>a</sup> | BDL  | 101  | 0.02  |                |
| BSR-3   | BDL    | BDL   | 115               | BDL  | 112  | 0.07  |                |
| BSR-4   | 0.02   | BDL   | 301               | 0.04 | 77.2 | 0.08  |                |
| BSR-5   | 0.01   | BDL   | 86.4              | BDL  | 163  | 0.02  |                |
| Average   | 0.0075 | –     | 167.4             | 0.01 | 113  | 0.05  | 281            |
| <b>Tap Water from Kakum Area</b>                                |        |       |                   |      |      |       |                |
| BST-1   | BDL    | 0.06  | 83.7              | BDL  | 168  | BDL   |                |
| BST-2   | BDL    | BDL   | 190               | BDL  | 79.8 | 0.08  |                |
| BST-3   | BDL    | BDL   | 85.5              | BDL  | 94.4 | 0.06  |                |
| BST-4   | BDL    | BDL   | 68.1              | BDL  | 16.2 | 0.04  |                |
| Average   | –      | 0.02  | 107               | –    | 89.7 | 0.05  | 197            |
| <b>Pra River Water</b>  |        |       |                   |      |      |       |                |
| DR-1  | 0.02   | BDL   | 296               | 0.06 | 277  | 0.09  |                |
| DR-2  | 0.06   | BDL   | 86.2              | BDL  | 95.4 | 0.02  |                |
| DR-3  | 0.02   | BDL   | 116               | BDL  | 108  | 0.11  |                |
| DR-4  | 0.03   | BDL   | 321               | 0.05 | 210  | 0.16  |                |
| DR-5  | 0.04   | BDL   | 205               | 0.04 | 275  | 0.09  |                |
| Average   | 0.03   | –     | 205               | 0.03 | 193  | 0.09  | 398            |
| <b>Tap Water from Daboase Area (in the Pra River Watershed)</b> |        |       |                   |      |      |       |                |
| DT-1  | 0.07   | BDL   | 156               | 0.07 | 99.8 | 0.03  |                |
| DT-2  | 0.01   | BDL   | 66                | BDL  | 74.8 | 0.03  |                |
| DT-3  | 0.08   | BDL   | 77.2              | 0.05 | 118  | 0.09  |                |
| DT-4  | 0.01   | BDL   | 102               | BDL  | 94.6 | 0.05  |                |
| DT-5  | 0.05   | BDL   | 112               | 0.08 | 98.7 | 0.07  |                |
| Average   | 0.04   | –     | 103               | 0.04 | 97.5 | 0.05  | 200            |
| <b>Blanks</b>   |        |       |                   |      |      |       |                |
| Blank 1   | 0.06   | 0.10  | <LOD              | 0.06 | <LOD | <LOD  |                |
| Blank 2   | 0.04   | <LOD  | <LOD              | <LOD | <LOD | <LOD  |                |
| Blank 3   | <LOD   | 0.16  | <LOD              | <LOD | <LOD | <LOD  |                |
| Average   | 0.03   | 0.09  | <LOD              | 0.02 | <LOD | <LOD  |                |

BDL – Below Detection Limit. Samples BSR-1 and BST-5 were lost, hence, not analysed.

<sup>a</sup> Outlier (not included in average).

treatment of those rivers contained concentrations of 196.57 and 200.29 ng/L, respectively (Table 2). Both the river and tap water contained very minimal amounts of PFHxA, PFDA and PFPeA (Table 2). Respectively, their concentrations ranged from below detection limit (BDL)–0.02, BDL–0.04, and 0.02–0.08 ng/L in the Kakum River water. Both PFHxA and PFDA were below detection limit in the tap water (sourced from the Kakum River), while PFPeA was ranged 0.02–0.08 ng/L. The concentrations of PFHxA, PFDA and PFPeA in the Pra River water were 0.02–0.06, BDL–0.05, and 0.02–0.11 ng/L; and in tap water (sourced from the Pra River) 0.01–0.08, BDL–0.07, and 0.03–0.09 ng/L, respectively.

The average concentrations of PFOA and PFOS in River Pra were 204.7 ng/L (range: 86.2–321.1 ng/L) and 192.8 ng/L (range: 95.4–276.6 ng/L), respectively. The respective levels of PFOA and PFOS in the Kakum river were 167.4 ng/L (range: 86.4–301.2) and 113.3 ng/L (range: 77.2–163.1). Compared to the few reported issues in Africa, these levels are quite high. For instance, rivers draining into Lake Victoria in Kenya contained PFOA (0.4–96.4 ng/L) and PFOS (0.4–13.2 ng/L), which were higher levels than in the Lake itself (PFOA, 0.4–11.7 ng/L and PFOS, 0.4–2.5 ng/L) (Orata et al., 2009). Chirikona et al. (2015) also reported PFOA 1.3–28 ng/L and PFOS 0.9–9.8 ng/L in Lake Victoria in Kenya, suggesting that the respective pollutants have increased in concentration in the Lake following the initial report in 2009. In South Africa, levels of PFOA up to 390 ng/L and PFOS up to 182 ng/L were measured in various river water (Mudumbi et al., 2014). Thus, the concentrations of PFOA and PFOS in river water in Ghana were comparable to those reported in rivers in South Africa but greater than the respective concentrations in Lake Victoria in Kenya (Orata et al., 2009; Chirikona et al., 2015). Compared to global levels, PFOA concentrations in the Pra and Kakum Rivers in Ghana were greater

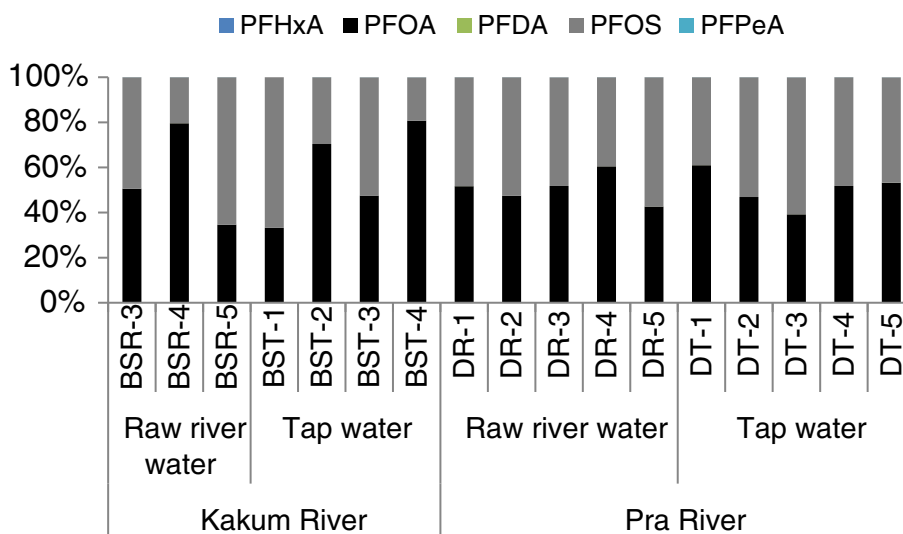


Fig. 2. PFAA congener composition of river and tap water in Ghana.

than those reported for some water bodies in Canada (15–70 ng/L) (Boulanger et al., 2004) and South Korea (0.9–62 ng/L) (Rostkowski et al., 2006), but largely within of range of values reported in Japan (4.2–2600 ng/L) (Lein et al., 2008), China (2.0–260 ng/L) (So et al., 2006), USA (140–598 ng/L) (Hansen et al., 2002) and Italy (60–1300) (Loos et al., 2008). The PFOS concentrations in the Ghanaian rivers were also largely within the range of values reported for some surface waters in Japan (0.7–157) (Saito et al., 2003) and South Korea (2.2–651) (Rostkowski et al., 2006). Thus, although PFAAs have not been manufactured in Ghana, an appreciable level of contamination existed in surface waters in the country. A wide range of PFAA-containing products such as upholstery, cookware, sports clothing, plastics, food handling equipment, medical equipment, motor oil additives, firefighting foams and paints are imported for local use in Ghana. Waste materials ensuing from these products are poorly disposed of and have been found to contaminate open drainages and water bodies. This might have contributed to the unexpected level of PFAA contamination in Ghana (Kissa, 2001; Dinglasan-Panlilio et al., 2004; Fiedler et al., 2010).

The difference in contamination from PFOA between the Pra and Kakum Rivers was not statistically significant ( $p = 0.34$ ). PFOS in water samples from the Pra River was however significantly greater (at 90% confidence interval) than the levels in the Kakum River ( $p = 0.07$ ). The Pra River was experiencing pollution from mine wastes, especially, effluents from illicit small-scale gold mining activities (Donkor

et al., 2006). It is unclear if this has partly contributed to the elevated concentration PFOS in the Pra River. Aside mining which impacted the Pra River sampling sites, both the Pra and Kakum Rivers were impacted by agricultural activities in the respective watersheds.

The Pra and Kakum Rivers have both been dammed for drinking water treatment and supply of tap water to adjoining communities. Tap water, sourced from the Pra and Kakum Rivers, were sampled at local communities, Daboase and Kakum, respectively, and analysed for PFAAs. PFOA and PFOS also predominated in the tap water (Table 2). The average concentrations of PFOA and PFOS in tap water sourced from the Pra River were 102.6 ng/L (range: 66–156 ng/L) and 97.5 ng/L (range: 74.8–119.7 ng/L), and in tap water sourced from the Kakum River were 106.8 ng/L (range: 68.1–190 ng/L) and 89.7 ng/L (range: 16.2–168.3 ng/L), respectively. The concentrations of PFOA, as well as PFOS, averagely did not vary in tap water, irrespective of the community of sampling. The average concentrations of both pollutants in the tap water were however above the USEPA guideline of 70 ng/L; that is, the threshold above which it is anticipated that lifetime exposure to PFOA and PFOS may trigger adverse health effects (USEPA, 2016a, 2016b). Indeed, the levels of these pollutants in tap water in Ghana were above what have been reported in drinking water in many industrialized countries (Takagi et al., 2008; Quinones and Snyder, 2009; Wilhem et al., 2010; Thompson et al., 2011), possibly due to more rigorous water treatment processes in these countries. Nevertheless, it is worth noting that compared to the river water, PFOA concentration in

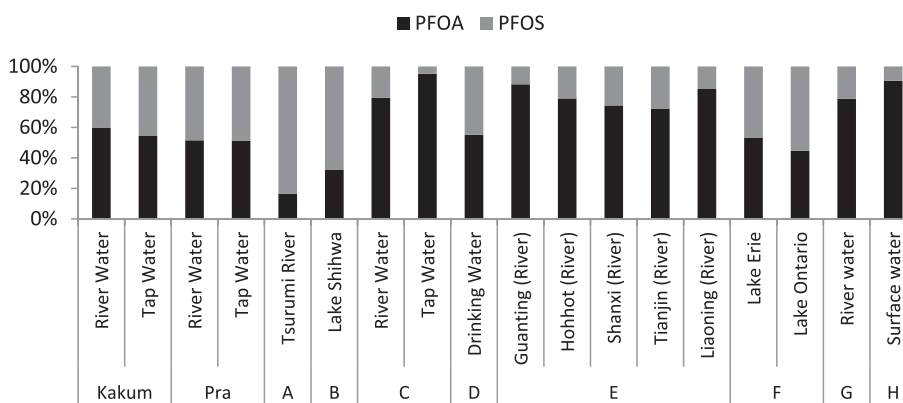


Fig. 3. Average PFOA/PFOS profile in river and tap water in Ghana compared to reported profiles from other parts of the world. A: Japan (Zushi et al., 2008); B: South Korea (Rostkowski et al., 2006); C: Thailand (Kunacheva et al., 2010); D: Spain (Ericson et al., 2009); E: China (Wang et al., 2012); F: Great Lakes (Boulanger et al., 2004); G: Kenya (Orata et al., 2009); H: Bangladesh (Habibullah-Al-Mamun et al., 2016).

tap water was reduced by 50% and 36%, and PFOS concentration by 49% and 21%, in the Pra and Kakum basins, respectively. Thus, the water treatment process in Ghana could only remove up to half the amount PFOA and PFOS in local river water.

### 3.3. Potential exposure and risk considerations

Potential exposure and risk were evaluated for the major PFAA contaminants – PFOA and PFOS. The average tolerable daily intake (TDI) including all potential routes is reportedly 1.6 ng/kg body weight for PFOS and 2.9 ng/kg body weight for PFOA in adults (Fromme et al., 2009). It therefore suggests that for an adult of average weight 70 kg, the total daily exposure to PFOS and PFOA should not exceed 112 ng (i.e.  $1.6 \times 70$  ng) and 203 ng (i.e.  $2.9 \times 70$  ng), respectively. The average amount of PFOS in tap water in Ghana was 97.5 ng/L. Assuming that an adult of body weight 70 kg consumes 2 L of tap water per day for drinking purposes (Gadgil, 1998), he/she would be exposed to  $2 \times 97.5$  ng = 195 ng of PFOS on daily basis. Similarly, considering that tap water in Ghana contained about 102.6 ng/L PFOA, exposure to PFOA from drinking 2 L of tap water could be estimated at  $2 \times 102.6$  ng = 205.2 ng. With these exposure estimates, the RQ for the respective pollutants was derived applying the formula  $RQ = PEC/PNEC$ , where PEC = Predicted Environmental Concentration (i.e. exposure) and PNEC = Predicted No-Effect Concentration.

$$RQ_{PFOS} = 195 \text{ ng} / 112 \text{ ng} = 1.74.$$

$$RQ_{PFOA} = 205.2 \text{ ng} / 203 \text{ ng} = 1.01.$$

The RQ of PFOS ( $>1$ ) and PFOA ( $\approx 1$ ) both suggest significant risk concerns associated with the contamination from the respective pollutants in Ghana; particularly so, considering that only drinking water (tap water) has contributed to these levels of exposure burden. The present study underscored limitations in the tap water treatment process in getting rid of these emerging pollutants in community tap water supplies in Ghana. The fact that treatment of river water reduced the levels of PFAAs in tap water supplies by almost half the initial contamination that existed in the river water is encouraging. Nevertheless, to sufficiently reduce the risk burden, PFAAs should be specifically targeted for removal in tap water treatment. PFOS and PFOA exposure assessment via all other routes such as food and air are needed to fully comprehend the total risk burden associated with these pollutants in Ghana.

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