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PFAS in air and water from Dhaka, Bangladesh

Poly- and Perfluorinated Alkyl Substances in Air and Water from Dhaka, Bangladesh

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Abstract: Bangladesh hosts extensive textile manufacturing, for some of which per- and polyfluorinated alkyl substances (PFAS) have been used to impart water and dirt repellency, among others. Textile waste emissions to the atmosphere and discharge into rivers and other bodies of water could present a significant concern for human and ecosystem health, but there is little information on PFAS in Bangladesh. To assess the presence of ionic PFAS and their precursors in air and water from Dhaka, Bangladesh, polyethylene (PE) sheets were deployed for 28 days as passive samplers for neutral PFAS in outdoor air and water, while ionic PFAS were measured from discrete water grabs.

Fluorotelomer alcohols (FTOHs) were detected almost all sites in air and water; the most frequently detected compound was 6:2 FTOH ranging from below instrumental detection limits (<IDL) to 70 ng m^{-3} in air, and from <IDL to- 19 ng L^{-1} in water. Of the ionic PFAS, perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorohexane sulfonic acid (PFHxS), and perfluorooctane sulfonic acid (PFOS) dominated in frequency of detection and magnitude with concentration ranging from 1.8 - 19.0 ng L^{-1} in surface waters. The prevalence of 6:2 FTOH and PFBA across sites probably reflect their use in textile manufacturing and could indicate the industry's switch to shorter chain PFAS alternatives.

Graphical Abstract
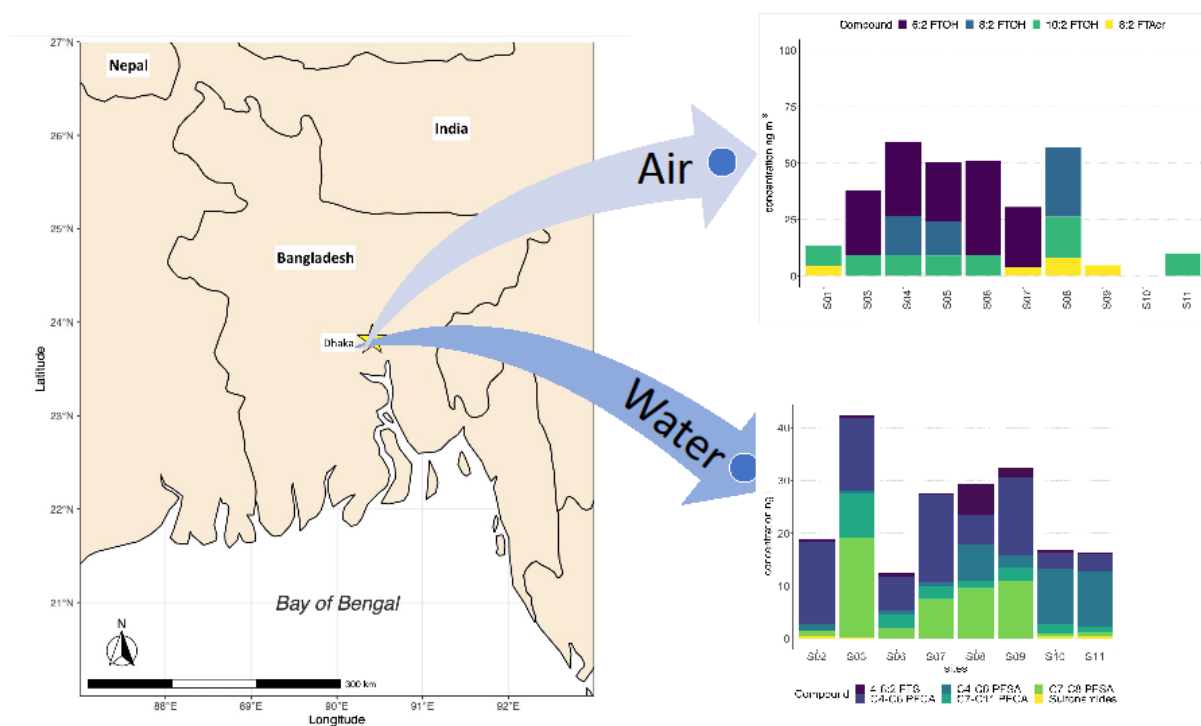
Keywords: FTOHs, PFAAs, outdoor air, surface water, textile industry, Dhaka

This article includes online-only Supporting Information.

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INTRODUCTION

Poly- and perfluorinated alkyl substances (PFAS) are a family of over 4,000 anthropogenic chemicals with at least one C-F bond in the molecule (Buck et al., 2011; Sunderland et al., 2019). All PFAS contain the strongly electronegative perfluoro alkyl moiety (C_nF_{2n+1}-) and a hydrophilic functional group that makes PFAS useful in a wide variety of industrial and commercial applications (Arvaniti & Stasinakis, 2015; Wang, DeWitt, Higgins, & Cousins, 2017). The PFAS are chemically and thermally stable, highly hydrophobic, lipophobic, and resistant to oxidation (Arvaniti & Stasinakis, 2015; Buck et al., 2011), which makes them highly persistent, at times bioaccumulative, and toxic in the environment (Wang et al., 2017). The mostly studied PFAS, perfluoroalkyl acids (PFAA), include perfluoroalkyl carboxylic acids (PFCA) and perfluoroalkane sulfonic acids (PFSA) (Buck et al., 2011). They may be either directly released into the environment during production, usage and disposal, or they can be abiotically or biologically transformed from their precursors (Hamid, Li, & Grace, 2017).

PFAA such as perfluorooctanoic acid (PFOA) and perflurooctanesulfonic acid (PFOS) are known to be ubiquitous in surface waters, sediments and soils, fish, birds, humans and other mammals (Houtz, Sutton, Park, & Sedlak, 2016; Venkatesan & Halden, 2013). In an effort to regulate their emissions, PFOS and their salts were included in the Annex B of the Stockholm Convention in 2008 (Stockholm Convention, 2009). Since then, long-chain PFAA and their precursors (such as perfluorooctane sulfonamide, FOSA) have been gradually phased out of production in the U.S. and

Europe (EPA, 2009; Wang, Cousins, Scheringer, Buck, & Hungerbühler, 2014). Instead, companies have replaced these compounds with shorter PFAA and their precursors, including 6:2 fluorotelomer alcohol (6:2 FTOH) (Jahnke, Ahrens, Ebinghaus, & Temme, 2007; Winkens et al., 2017).

PFAS have also proven to elicit adverse effects in flora and fauna, including humans, such as developmental toxicity, neurotoxicity, immunotoxicity, carcinogenicity, thyroid malfunction, low birthweight, infertility, early menopause, elevated cholesterol, and fatty liver disease (Arvaniti & Stasinakis, 2015; Buck et al., 2011; Venkatesan & Halden, 2013). Precursors such as FTOHs, FOSAs and perfluorooctane sulfonamide ethanol (FOSEs) have proven to have estrogenic effects in vitro and can be transformed to more stable compounds under environmental conditions (Fromme et al., 2015).

According to the Köppen climate classification, Bangladesh has a tropical wet and dry climate where its wet season happens during the monsoon months of June to mid-October, and its dry season from November to May (Ahmed & Kim, 2003). Bangladesh has been a predominantly agricultural country that has undergone rapid industrialization, urbanization, and economic development (Habibullah-Al-Mamun et al., 2016). Environmental regulations have not been able to keep pace with the growth of the country and discharges of untreated and semi-treated domestic and municipal sewage enter most, if not all, rivers that eventually discharge into the Bay of Bengal (Dey & Islam, 2015; Habibullah-Al-Mamun et al., 2016). Along with sewage, heavy loads of organic and inorganic pollutants enter the water systems from large and small industries (Dey & Islam, 2015; A. Nargis et al., 2019; Aklima Nargis et al., 2021, 2018). In addition, Bangladesh is one of the most threatened countries by climate change; and

floodwater, caused by the retardation of river outflows by the rise of denser brackish or seawater at the mouth of the river, has continued to accumulate (Ali, 1999; Islam & van Amstel, 2018). Thus, Bangladesh's inland aquatic environments are recognized as some of the most polluted ecosystems in the world (Habibullah-Al-Mamun et al., 2016).

As awareness of the effects of PFAS has increased worldwide, consumer habits have become more sophisticated, and regulations in first world countries have become stricter. However, the enormous production of poorly managed waste, and the ongoing delocalization of fluorochemical industries from developed regions like the United States, Canada, and the European Union into developing countries making them important contamination hotspots (L Li, Zihan, Jianguo, & Jianxin, 2015; Sharma et al., 2016). Despite becoming a party to the Stockholm Convention in 2007, Bangladesh does not regulate PFAS and has not accepted the amendment listing; PFOA, PFOS, along with other PFAS remain unregulated (IPEN, 2019). Data on PFAS environmental concentrations and emissions, as well as information on human exposure in developing countries is scarce; however desperately needed (Sharma et al., 2016). Only two other studies have reported PFAS in Bangladesh; focusing on PFAA in fish, surface water and sediments from around the Bay of Bengal (Habibullah-Al-Mamun et al., 2017, 2016). Both studies reported the likelihood of the reported PFAS to come from the more industrialized region in Dhaka.

The use of passive sampling, which can measure the concentration of freely dissolved contaminants through time, has widely been accepted as an effective detection tool for trace organic compounds in atmosphere and water (Lohmann, 2011; Lohmann, Booij, Smedes, & Vrana, 2012). Single-phase polymers, such as polyethylene (PE)

sheets, have been able to accumulate a wide range of non-polar and moderately polar contaminants that are in the gas phase or dissolved in water (Dixon-Anderson & Lohmann, 2018; Morales-McDevitt et al., 2021). In addition, PE sheets are low cost, easy to handle, and can be easily transported and deployed (Lohmann et al., 2012). Recently, neutral PFAS were successfully measured in air and water using these devices (Dixon-Anderson & Lohmann, 2018).

To better understand the importance of industries manufacturing PFAS-containing textiles and clothing as source points of ionic and neutral PFAS and their precursors, outdoor air and water samples were taken in the vicinity of textile manufacturing sites in Dhaka, Bangladesh. Polyethylene sheets were used as passive samplers in air and water measuring the concentration of freely dissolved neutral PFAS; ionic PFAS in water were measured using traditional active sampling. The overall goals of the study were to (i) detect neutral PFAS in air and water, (ii) measure ionic PFAS in water, and (iii) assess whether legacy, long-chain PFAS, or rather their short-chain replacements dominate in Bangladesh.

MATERIALS AND METHODS

Precleaned PE sheets (for details see SI section 1.0) used as passive samplers (50 μm thickness, dimensions 4" x 15-1/2") were deployed for 28 day measurements in outdoor air and water of Dhaka, Bangladesh at 9 sites during January-March 2020. Eight water grab samples were collected in precleaned 500 mL high density polyethylene (HDPE) bottles. All samples were kept in a freezer at -20°C until their extraction. Further information on deployment locations, coordinates, collection times, and site characterization are available in the SI Table S11.

Polyethylene (PE) Sheet Extraction

Polyethylene sheets were wiped with paper fiber optic wipes to remove dust, mud, or biofouling. They were then individually inserted into 80 mL glass vials, spiked with surrogate standards and extracted overnight in ethyl acetate. In the case of the water PE sheets, ~ 0.5 g of sodium sulfate was added to each vial to absorb any residual water. Extracts were concentrated to an approximate final volume of 50 μL by heating the sample to 35 °C under a gentle stream of nitrogen. Prior to GC analysis, all samples were spiked with injection standard. After the extraction, all PE sheets were weighed for final concentration calculations.

Water Extraction

Water samples were well mixed and weighed before being spiked with a mass labeled surrogate standard. Extractions were done in accordance with a method previously developed in the Lohmann Lab based on EPA Method 533 for solid phase extraction for select perfluoroalkyl substances (Becanova et al. 2021). Approximately 500 mL of sample water was run through the weak anion exchange (WAX) SPE cartridges. Elution of the cartridges was completed with 0.5% ammonium hydroxide in methanol. Extracts were concentrated down to 0.5 mL by heating the sample to 35 C under a gentle stream of nitrogen.

Instrumental analysis

The PE extracts were analyzed for nine neutral PFAS on an Agilent 7890B gas chromatograph coupled to an Agilent 5977A mass selective (MS) detector operating in positive chemical ionization mode using selected ion monitoring. Additional details on the method can be found in the supplemental data section 1.2 and Table S2.

Water extracts were analyzed for 34 PFAS on a Shimadzu Prominence liquid chromatograph (UFLC) coupled to SCIEX TripleQuad 5500 MS/MS operating in a negative mode. Additional details on the method and operating parameters can be found in the supplemental data section 2.1 and Tables S3, S4, and S5.

Data interpretation

Results from a previous indoor kinetic study (Morales-McDevitt et al., 2021) showed that amounts of 6:2 FTOH and 8:2 FTOH reached equilibrium after 14 days. Given the higher flow rates outdoors, deployment times were hence prescribed as 28 days, with results representing the final 2 weeks of sampling.

The time averaged concentrations of neutral PFAS in air were derived using partitioning constants reported by Morales-McDevitt et al. (2021) and Dixon-Anderson & Lohmann (2018) and the concentration in the polyethylene sheets:

$$C_{air} = \frac{C_{PE}}{K_{PEair}} \quad (1),$$

where C_{air} is the time averaged gas-phase concentration (pg m^{-3}), C_{PE} is the concentration in PE sheets (pg m^{-3}), and K_{PEair} is the partitioning coefficient between the PE sheets and air. Concentrations of neutral PFAS in water were derived similarly and details are found in the supplemental data section 4.0 and Table S12.

According to the Bangladesh Meteorological Department, during the sampling period, from January 10th through March 10th, temperatures in Dhaka averaged 23°C ($\pm$ 5.5 °C). The temperature difference with the validation study from Morales-McDevitt et al. (2021) (25 °C) was deemed negligible, and thus temperature corrections were not performed.

QA/QC

PE sheet QA/QC

Passive sampling field blanks of air, matrix spikes, and field duplicate samples of air were included with each sample batch (for details, see SI section 3.0). Matrix spikes were prepared by spiking the known amount of the native and the mass labelled standard onto a new pre-cleaned sampler. Method detection limits (MDL) were calculated as the blank average plus three times the standard deviation; however, when a compound was not detected in the blanks, instrumental detection limits (IDL) were used (SI, Table S6). Recoveries of the matrix spikes ranged between 74% to 130% for all compounds (SI, Table S7).

Water extraction

13C-labeled or deuterated surrogate standards were added before sample extraction to both process blanks and water samples to correct the reported results for recoveries. A full list of analytes, native, and mass labeled standards can be found in the SI (Table S1). Method detection limits were calculated from instrumental detection limits and measurements of laboratory blanks consisting of 50 mL of LC-grade water (SI Table S6). Method detection limits were calculated as the greater value of the instrument detection limits or the sum of the median and 3-times standard deviation of the analyzed laboratory blank concentrations. Only compounds with mass labeled recoveries from 60-140% were reported in this publication (Table S8). Recoveries of surrogate standards, method detection limits, and matrix spike recoveries are all available in the SI (Table S6, S8, S9).

RESULTS AND DISCUSSION

Neutral PFAS

Neutral PFAS were analyzed in air at water at 9 locations in Dhaka, Bangladesh. Sampling locations are shown in Figure 1. The most frequently detected compound in air was 6:2 FTOH ranging from below limits of detection (<IDL) - 70 ng m^{-3} in air. 8:2 FTOH was detected only in Demra1 and Demra2 (17 ng m^{-3}and 14 ng m^{-3} respectively) and Gazipur air (30 ng m^{-3}). At seven out of ten sites, 10:2 FTOH was detected (Figure 2, SI Table S11) with concentrations ranging from <IDL - 18 ng m^{-3}. Of the fluorotelomer acrylates, only 8:2 FTAcr was detected at four sites in air by the PE sheets with concentrations ranging from <IDL - 8 ng m^{-3}.

In water, the most frequently detected compound was also 6:2 FTOH with concentrations ranging from 1.3 - 11 ng L^{-1}. (see Figure 2, and SI Table S11). Similarly, 8:2 FTOH was detected only in water from Balshi river in Savar Bank Town and Gazipur at <0.1 ng L^{-1}. Other neutral PFAS were below the MDL (EtFOSA MeFOSA, MeFOSE, and EtFOSE) (SI Table S6, S11).

As shown in Figure 2 and SI Table S11, in Bangladesh, neutral PFAS were detected at every location with the exception of Turag River site 1; concentrations in air and water were in the same order of magnitude as those reported in a Chinese wastewater treatment plant (Hongrui Chen, Peng, Yang, Hu, & Zhang, 2017) and higher than those reported in Chinese (Lai et al., 2016), Japanese, Western U.S. (Arkadiusz, Primbs, Field, Barofsy, & Simonich, 2007), and European air masses (Paragot et al., 2020). The elevated concentrations of FTOHs in select locations, while other sites had concentrations below detection limits, indicates that atmospheric concentrations are not homogenous in

Dhaka, and suggests the likelihood of point emissions, likely representing production sites. The latter is reinforced by the detection of neutral PFAS in water at some sites. Additionally, the presence of 8:2 FTAcr in multiple sites in Dhaka (Figure 2) implies that flourotelomer acrylates were being used in (textile) manufactured products(Wang et al., 2014). As stated previously, with stricter PFAS regulations being implemented in developed countries, the production of many fluorochemicals has been shifted to developing countries where environmental regulations are lax (L Li et al., 2015; Sharma et al., 2016). However, some of the most popular properties of PFAS such as water/oil/dust/ resistance and wrinkle-proof (Buck et al., 2011) are considered commodities. As such, the price of PFAS-treated products is higher and thus restrictive for communities living in extreme poverty or lack of disposable income (Holmquist, Jagers, Matti, Svanstr, & Peters, 2018). Therefore, outside of these suggested production sites, it is highly unlikely that fluorinated products are used and thus, concentrations below detection are unsurprising.

The low concentrations of the FOSAs in both air and water (Figure 2) could reflect their production phase-out in North America, Europe and Japan (Shoeib, Harner, Webster, & Lee, 2011). However, given that Bangladesh is one of the most important garment manufacturers in the world (Yunus & Yamagata, 2012), it more likely reflects that FTOHs were used in durable-water-resistant (DWR) clothing, and not FOSAs and FOSEs (Gremmel, Frömel, & Knepper, 2016). Although previously reported concentrations of ∑PFAS in surface water do not include any of the PFAA precursors, precursor concentrations were the same order of magnitude as the ∑PFAAs detected around Bay of Bengal previously (Habibullah-Al-Mamun et al., 2017).

Given that our samples were deployed and collected in February (i.e., dry season) (Ahmed & Kim, 2003), rain did not interfere with our samples. Fugacity ratios, shown in the SI Table S12, indicated that for the most part, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH with values close to 1 or 2, were close to equilibrium between the air and water phases.

Ionic PFAS in Surface Water

Of the 34 PFAS compounds targeted in this method, 16 were detected regularly and reported above the MDL in the surface waters around Dhaka, Bangladesh. PFBA, PFHxA, PFOA, PFHxS, and PFOS dominated in frequency of detection and magnitude with concentration ranging from 1.4 ng L^{-1} 19 ng L^{-1} in surface waters (Table S13). $\sum_{16}$PFAS ranged from 13 ng L^{-1} (Dhanmondi Lake) to 42 ng L^{-1} (Cannel Savar Denitex) in surface water samples as shown in Table 1 and SI Table S13. Individual concentrations were generally low, ranging from 1-5 ng L^{-1} for most compounds measured in Dhaka's surface waters.

As shown in Figure 3, the Cannel Savar (CS) site had the highest $\sum_{16}$PFAS concentration, suggesting a nearby textile mill could be responsible. Despite a lack of thorough regulation of PFAS in Bangladesh (Dey & Islam, 2015), the local prevalence of the 4 and 5 chain PFBA and PFPeA compounds at similar or higher concentrations than the longer chain PFAA (>C6) could indicate that local textile industries have been either importing shorter chain PFAS treatments or pre-treated textiles that contain these alternatives (Ateia, Maroli, Tharayil, & Karanfil, 2019). This abundance of shorter chain acids was evident at many sites, including the Gulshan (GL) and Hatirjheel (HL) lakes where PFBA was an order of magnitude higher than at other sites. Both Turag River sites

(TR1, TR2) also exhibited an increase in PFBS, the 4 chain sulfonate acid, in relation to the other sites investigated in this study.

Of the longer chain PFAS, PFOS and PFOA were found at relatively high concentrations of 19 ng L^{-1} and 7.5 ng L^{-1} respectively in the same Cannel Savar canal near the Denitrex mill; PFOS was also elevated in both the Gulshan and Hatirjheel lake sites. The Turag River sites (TR1, TR2), the Balshi River (BR), and Dhanmondi Lake (DL) all had similar concentrations of $\sum_{16}$PFAS, suggesting a consistent baseline of PFAS contamination, though follow up studies would need to evaluate these concentrations over diurnal and seasonal cycles. In addition to the CS site, next highest $\sum_{16}$PFAS were found at a site heavily influence by a nearby wastewater outlet (GMC) and the two aforementioned lakes with heavy influence from household wastewater and some nearby industry (GL, HL).

Previous research has reported the dominance of short chain PFAA such as PFBA and PFBS in surface waters in the proximity of a fluorochemical manufacturing plant and textile manufacturing sites (Chen et al., 2018; Kim, Ndabambi, Choi, & Oh, 2021). Additionally, the absence or low concentrations of long chain PFAAs such as PFNA, PFDA, PFUnA, and PFDoA was noted in the effluent water of two textile industries (Clara et al., 2008). Similar to our results, Yu, Liu, & Hua, (2022) reported the predominance of certain short chain PFAAS in surface water and suggests this to be an indication of short-chain PFAAS gradually replacing long-chain PFAS.

Environmental Implications

A recent study from 2016 on the occurrence of PFAA in the Bay of Bengal, along the Southern coast of Bangladesh, did not observe high concentrations of the shortest

chain PFBA or PFBS compounds (Habibullah-Al-Mamun et al., 2016). The $\sum_{16}$PFAS investigated in prior and this study were generally similar across seasonal measurements in the Bay of Bengal (Table 1). The relatively low concentrations of ionic PFAS in surface waters when compared to the high neutral PFAS measurements in air suggest that an atmospheric pathway may be the primary source to surface waters. The prevalence of shorter chain carboxylic acids compared to PFOA (C6 or <) has been proposed as an indicator for atmospheric sources of ionic PFAS in surface waters as part of the FTOH degradation process (Simcik & Dorweiler, 2005). The high FTOH measurements in the immediate Dhaka area could be a source of the 4, 5, and 6 chain carboxylic acids reported both locally in this study and farther away in the Bangladesh region. Future studies of the area should include broader sampling of surface waters farther away from Dhaka's industrial centers, where surface water PFCA measurements may be higher due to the increased impact of atmospheric transport away from the point sources.

Overall, the results of this study show increased concentrations of individual compounds and ∑PFAS compared to tropical latitude studies in the Caribbean portion of the Atlantic Ocean (Munoz et al., 2017), as should be expected based on the differences in the general population sizes, industrial footprint, and source dynamics. Compared to geographically closer tropical studies in a Singapore urban waterway, the samples analyzed from the Dhaka area display slightly lower PFAS concentrations, but a similar shift towards shorter chain chemistry as reflected by the abundance of 6:2 FTOH and PFBA in relation to longer chain acids (C. E. Chen, Zhang, Ying, & Jones, 2013). The dominance of 6:2 FTOH in both air and water is a clear indication of the textile industry shifting towards shorter chain compounds. Comparable ∑PFAS measurements and

abundance of shorter chain PFAS relative to the typical longer (>C6) were seen in the surface waters of two urban Northern Chinese cities and several sites along the Ganges River, India as well (Sharma et al., 2016; Yao et al., 2014) though the mean measurements reported for all sites in these studies are lower than the mean reported in this study (Table 1).

The water concentrations measured in the Dhaka area appear to be lower than expected for such an active textile area, where PFAS are likely part of DWR textiles. Further research is needed to understand the full scope of PFAS contamination. This study did not sample sediments, which have been identified as an important sink for PFAS in the environment (Codling et al., 2018; Habibullah-Al-Mamun et al., 2016; Mussabek, Ahrens, Persson, & Berndtsson, 2019). Suspect screening and other non-target analysis are suggested to investigate how novel chemistry and replacement compounds, specifically shorter chain PFAS, could be contaminating Dhaka's surface waters.

As previously stated, Bangladesh became a member of the Stockholm Convention in 2007; however it has not accepted the amendment list, and has refrained from reporting legacy and emerging PFAS (Bangladesh NIP, 2007). The source of these contaminants remains unclear since there are no documented PFAS manufacturers in the country (ESDO, 2019). Albeit, it is possible that PFAS could enter Bangladesh either as granulated PTFE mixtures that will be later applied to textiles, or the import of already PFAS-treated fabrics. The low ionic concentrations and high neutral concentrations are also supported by the results of the Environmental and Social Development Organizations 2019 report which states that textiles sold to Argentina from Bangladesh contained only 30 ug/kg ionic PFAS compared to ~7000 ug/kg volatile PFAS (ESDO,

2019). In any case, the presence of long-chain PFAS such as PFOA, PFOS, and PFHxS and their precursors that have already been phased-out of North America and Europe, suggest that their country of origin does not thoroughly comply with global standards.

CONCLUSION

The results presented here support the previous literature's suggestion that Dhaka could be a source of PFAAs to the surface waters of the Bay of Bengal (Habibullah-Al-Mamun et al., 2016). The most likely source of this PFAA contamination is the use of neutral FTOH compounds that degrade into shorter chain carboxylate PFAS (Simcik & Dorweiler, 2005) due to the relatively high ratios of shorter chain (C6 or shorter) PFCAs to PFOA. Overall, the surface water measurements displayed low concentrations, similar to most PFAAs measured in other urban rivers in the Asian continent as well as previously measured tropical latitudes (Hongrui Chen et al., 2017; Habibullah-Al-Mamun et al., 2016; Munoz et al., 2017; Sharma et al., 2016; Yao et al., 2014) though a more thorough study of sediments and non-target screening is needed. Generally, shorter chain (C6 or less) ionic compounds dominated in water, with the shortest of the neutral compounds, 6:2 FTOH, dominating in water and air as well. Measured concentrations of neutral PFAS in air were higher in comparison to established literature on Asian and US air masses (Arkadiusz et al., 2007), which points to the likely heavy use of FTOH's in Dhaka's bustling textile industry. The discrepancy between high concentrations of neutral PFAS and low concentrations of ionic PFAS could be indicative of local point sources emitting volatile PFAA precursors in large abundance. Previous studies and polymer degradation models have suggested that neutral PFAS can degrade in the atmosphere into ionic compounds such as the more commonly observed PFCA and PFSA (Ellis et al.,

2004; Li Li, Liu, Hu, & Wania, 2017; Shoemaker, Grimmett, & Boutin, 2009; Simcik & Dorweiler, 2005). The high concentrations of FTOH and FTAcr compounds measured in the Dhaka area, directly contrasts the expected theory that fluvial transport of high concentration ionic, legacy compounds is the primary pathway for PFAS contamination in Dhaka and Bangladesh.

Supporting Information—The Supporting information are available on the Wiley Online Library at DOI: 10.1002/etc.xxxx.

Disclaimer—The authors declare no competing financial interests.

Data availability—Data pertaining to this manuscript are deposited in the Open Science Framework at https://osf.io/32x9p/. All relevant data will also be available in the supplemental data. Data, associated metadata, and calculation tools are also available from the corresponding author (rlohmann@uri.edu).

Author contributions statement—Ashan Habib, PhD, finalized the sampling plan, deployed and retrieved passive samplers, and collected grab samples in the surrounding Dhaka area. Maya E. Morales-McDevitt and Matthew Dunn extracted and analyzed all samples, with verification of the methods and results provided by Jitka Becanova, PhD

and Simon Vojta, PhD. Jitka Becanova, PhD, Simon Vojta, PhD, and Rainer Lohmann, PhD provided supervision over the duration of the project. Maya E. Morales-McDevitt, MS took the lead in writing the manuscript with help from Matthew Dunn.

REFERENCES

Ahmed, R., & Kim, I. (2003). Patterns of Daily Rainfall in Bangladesh During the Summer Monsoon Season: Case Studies at Three Stations. *Physical Geography*, *24*(4), 295–318. https://doi.org/10.2747/0272-3646.24.4.295

Ali, A. (1999). Climate change impacts and adaptation assessment in Bangladesh. *Climate Research*, *12*(2-3 SPEC. ISS. 6), 109–116. https://doi.org/10.3354/cr012109

Arkadiusz, P., Primbs, T., Field, J., Barofsy, D., & Simonich, S. (2007). Semivolatile Fluorinated Organic Compounds in Asian and Western U.S. Air Masses. *Environ. Sci. Technol*, *41*, 8248–8255. https://doi.org/10.1021/es0713678

Arvaniti, O. S., & Stasinakis, A. S. (2015, August 5). Review on the occurrence, fate and removal of perfluorinated compounds during wastewater treatment. *Science of the Total Environment*. Elsevier. https://doi.org/10.1016/j.scitotenv.2015.04.023

Ateia, M., Maroli, A., Tharayil, N., & Karanfil, T. (2019). The overlooked short- and ultrashort-chain poly- and perfluorinated substances: A review. *Chemosphere*, *220*, 866–882. https://doi.org/10.1016/j.chemosphere.2018.12.186

Bangladesh NIP. (2007). *Bangladesh National Implementation Plan (NIP): For Management of Persistent Organic Pollutants (POPs)*. Dhaka, Bangladesh.

Buck, R. C., Franklin, J., Berger, U., Conder, J. M., Cousins, I. T., Voogt, P. De, … van Leeuwen, S. P. J. (2011). Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integrated Environmental*

Assessment and Management, *7*(4), 513–541. https://doi.org/10.1002/ieam.258

Chen, C. E., Zhang, H., Ying, G. G., & Jones, K. C. (2013). Evidence and recommendations to support the use of a novel passive water sampler to quantify antibiotics in wastewaters. *Environmental Science and Technology*, *47*(23), 13587–13593. https://doi.org/10.1021/es402662g

Chen, H., Yao, Y., Zhao, Z., Wang, Y., Wang, Q., Ren, C., … Kannan, K. (2018). Multimedia Distribution and Transfer of Per-and Polyfluoroalkyl Substances (PFASs) Surrounding Two Fluorochemical Manufacturing Facilities in Fuxin, China. *Environ Sci Technol*, (52), 8263–0271. https://doi.org/10.1021/acs.est.8b00544

Chen, Hongrui, Peng, H., Yang, M., Hu, J., & Zhang, Y. (2017). Detection, Occurrence, and Fate of Fluorotelomer Alcohols in Municipal Wastewater Treatment Plants. *Environmental Science and Technology*, *51*(16), 8953–8961. https://doi.org/10.1021/acs.est.7b00315

Clara, M., Scheffknecht, C., Scharf, S., Weiss, S., Gans, O., & Clara, A. M. (2008). Emissions of perfluorinated alkylated substances (PFAS) from point sources-identification of relevant branches. *Water Science & Technology*, *58*(1), 59–66. https://doi.org/10.2166/wst.2008.641

Codling, G., Hosseini, S., Corcoran, M. B., Bonina, S., Lin, T., Li, A., … Giesy, J. P. (2018). Current and historical concentrations of poly and perfluorinated compounds in sediments of the northern Great Lakes – Superior, Huron, and Michigan. *Environmental Pollution*, *236*, 373–381. https://doi.org/10.1016/j.envpol.2018.01.065

Dey, S., & Islam, A. (2015). A Review on Textile Wastewater Characterization in Bangladesh. *Resources and Environment*, *5*(1), 15–44. https://doi.org/10.5923/j.re.20150501.03

Dixon-Anderson, E., & Lohmann, R. (2018). Field-testing polyethylene passive samplers for the detection of neutral polyfluorinated alkyl substances in air and water. *Environmental Toxicology and Chemistry*, *37*(12), 3002–2010. https://doi.org/10.1002/etc.4264

Ellis, D. A., Martin, J. W., De Silva, A. O., Mabury, S. A., Hurley, M. D., Sulbaek Andersen, M. P., & Wallington, T. J. (2004). Degradation of Fluorotelomer Alcohols: A Likely Atmospheric Source of Perfluorinated Carboxylic Acids. *Environmental Science & Technology*, *38*(12), 3316–3321. https://doi.org/10.1021/es049860w

EPA. (2009). *Long-Chain Perfluorinated Chemicals (PFCs) Action Plan*. USEPA.

ESDO. (2019). *PFAS: Bangladesh Situation Report PFAS: Bangladesh Situation Report*. Dhaka, Bangladesh.

Fromme, H., Dreyer, A., Dietrich, S., Fembacher, L., Lahrz, T., & Völkel, W. (2015). Neutral polyfluorinated compounds in indoor air in Germany - " The LUPE 4 study. *Chemosphere*, *139*, 572–578. https://doi.org/10.1016/j.chemosphere.2015.07.024

Gardiner, C., Robuck, A., Becanova, J., Cantwell, M., Kaserzon, S., Katz, D., … Lohmann, R. (2021). Field validation and application of a novel passive sampler to determine sources and sinks of PFAS in an urbanized estuary. *Environ. Sci. Technol, In prep*.

Gremmel, C., Frömel, T., & Knepper, T. P. (2016). Systematic determination of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in outdoor jackets. *Chemosphere*, *160*, 173–180. https://doi.org/10.1016/j.chemosphere.2016.06.043

Habibullah-Al-Mamun, M., Ahmed, M. K., Raknuzzaman, M., Ali, M., Tokumura, M., & Masunaga, S. (2017). Occurrence and assessment of perfluoroalkyl acids (PFAAs) in commonly consumed seafood from the coastal area of Bangladesh. *Marine Pollution Bulletin*, *124*, 775–785. https://doi.org/10.1016/j.marpolbul.2017.02.053

Habibullah-Al-Mamun, M., Ahmed, M. K., Raknuzzaman, M., Islam, M. S., Negishi, J., Nakamichi, S., … Masunaga, S. (2016). Occurrence and distribution of perfluoroalkyl acids (PFAAs) in surface water and sediment of a tropical coastal area (Bay of Bengal coast, Bangladesh). *Science of the Total Environment*, *571*, 1089–1104. https://doi.org/10.1016/j.scitotenv.2016.07.104

Hamid, H., Li, L. Y., & Grace, J. R. (2017). Review of the fate and transformation of per-and polyfluoroalkyl substances (PFASs) in landfills *. *Environmental Pollution*, *235*, 74–84. https://doi.org/10.1016/j.envpol.2017.12.030

Holmquist, H., Jagers, S. C., Matti, S., Svanstr, M., & Peters, G. M. (2018). How information about hazardous fluorinated substances increases willingness-to-pay for alternative outdoor garments: A Swedish survey experiment. *Journal of Cleaner Production*, *202*, 130–138. https://doi.org/10.1016/j.jclepro.2018.07.215

Houtz, E. F., Sutton, R., Park, J. S., & Sedlak, M. (2016). Poly- and perfluoroalkyl substances in wastewater: Significance of unknown precursors, manufacturing shifts, and likely AFFF impacts. *Water Research*, *95*, 142–149. https://doi.org/10.1016/j.watres.2016.02.055

IPEN. (2019). *PFAS POLLUTION ACROSS THE MIDDLE EAST AND ASIA*. IPEN's Middle East & North Africa (MENA). Retrieved from https://ipen.org/documents/pfas-pollution-across-middle-east-and-asia

Islam, N., & van Amstel, A. (2018). *Bangladesh I: Climate Change Impacts, Mitigation and Adaptation in Developing Countries*. (N. Islam & A. van Amstel, Eds.) (1st ed.). Switzerland: Springer.

Jahnke, A., Ahrens, L., Ebinghaus, R., & Temme, C. (2007). Urban versus remote air

concentrations of fluorotelomer alcohols and other polyfluorinated alkyl substances in Germany. *Environmental Science and Technology*, *41*(3), 745–752. https://doi.org/10.1021/es0619861

Kim, K. Y., Ndabambi, M., Choi, S., & Oh, J. E. (2021). Legacy and novel perfluoroalkyl and polyfluoroalkyl substances in industrial wastewater and the receiving river water: Temporal changes in relative abundances of regulated compounds and alternatives. *Water Research*, *191*, 116830. https://doi.org/10.1016/J.WATRES.2021.116830

Lai, S., Song, J., Song, T., Huang, Z., Zhang, Y., Zhao, Y., … Xie, Z. (2016). Neutral polyfluoroalkyl substances in the atmosphere over the northern South China Sea *. *Environmental Pollution*, *214*, 449–455. https://doi.org/10.1016/j.envpol.2016.04.047

Li, L, Zihan, Z., Jianguo, L., & Jianxin, H. (2015). Estimating industrial and domestic environmental releases of perfluorooctanoic acid and its salts in China from 2004 to 2012. *Chemosphere*, *129*, 100–109. https://doi.org/10.1016/j.chemosphere.2014.11.049

Li, Li, Liu, J., Hu, J., & Wania, F. (2017). Degradation of Fluorotelomer-Based Polymers Contributes to the Global Occurrence of Fluorotelomer Alcohol and Perfluoroalkyl Carboxylates: A Combined Dynamic Substance Flow and Environmental Fate Modeling Analysis. *Environ Sci Technol*, (51), 4461–4470. https://doi.org/10.1021/acs.est.6b04021

Lohmann, R. (2011). Critical Review of Low-Density Polyethylene's Partitioning and Diffusion Coefficients for Trace Organic Contaminants and Implications for Its Use As a Passive Sampler. *Environ. Sci. Technol*, *46*, 606–618. https://doi.org/10.1021/es202702y

Lohmann, R., Booij, K., Smedes, F., & Vrana, B. (2012). POPs Workshop, ten years after the signature of the Stockholm Convention. Use of passive sampling devices for monitoring and compliance checking of POP concentrations in water. *Environmental Science and*

Pollution Research, (19), 1885–1895. https://doi.org/10.1007/s11356-012-0748-9

Morales-McDevitt, M. E., Becanova, J., Blum, A., Bruton, T. A., Vojta, S., Woodward, M., & Lohmann, R. (2021). The Air That We Breathe: Neutral and Volatile PFAS in Indoor Air. *Environ. Sci. Technol. Lett*, *8*, 902. https://doi.org/10.1021/acs.estlett.1c00481

Munoz, G., Labadie, P., Botta, F., Lestremau, F., Lopez, B., Geneste, E., … Budzinski, H. (2017). Occurrence survey and spatial distribution of perfluoroalkyl and polyfluoroalkyl surfactants in groundwater, surface water, and sediments from tropical environments. *Science of the Total Environment*, *607–608*, 243–252. https://doi.org/10.1016/j.scitotenv.2017.06.146

Mussabek, D., Ahrens, L., Persson, K. M., & Berndtsson, R. (2019). Temporal trends and sedimentewater partitioning of per-and polyfluoroalkyl substances (PFAS) in lake sediment. *Chemosphere*, *227*, 624–629. https://doi.org/10.1016/j.chemosphere.2019.04.074

Nargis, A., Sultana, S., Raihan, M. J., Haque, M. E., Sadique, A. B. M. R., Sarkar, M. S. I., … Habib, A. (2019). Multielement analysis in sediments of the River Buriganga (Bangladesh): potential ecological risk assessment. *International Journal of Environmental Science and Technology*, *16*(3), 1663–1676. https://doi.org/10.1007/s13762-018-1822-8

Nargis, Aklima, Habib, A., Harun-Or-Rashid, Harun, H. B., Islam Sarker, M. S., Jin, R., … Cai, M. (2021). Status of multielement in water of the river Buriganga, Bangladesh: Aquatic chemistry of metal ions in polluted river water. *Emerging Contaminants*, *7*, 99– 115. https://doi.org/10.1016/j.emcon.2021.03.001

Nargis, Aklima, Harun-Or-Rashid, Khanam Jhumur, A., Haque, M. E., Islam, M. N., Habib,

A., & Cai, M. (2018). Human health risk assessment of toxic elements in fish species collected from the river Buriganga, Bangladesh. *Human and Ecological Risk Assessment*, *26*(1), 120–146. https://doi.org/10.1080/10807039.2018.1496397

Paragot, N., Be Canov, J., Kar Askov, P., Proke, R., Kl, J., Lammel, G., & Degrendele, E. (2020). Multi-year atmospheric concentrations of per-and polyfluoroalkyl substances (PFASs) at a background site in central Europe *. *Environmental Pollution*, *265*(114851). https://doi.org/10.1016/j.envpol.2020.114851

Sharma, B., Bharat, G., Tayal, S., Larssen, T., Becanova, J., Karaskova, P., … Nizzetto, L. (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. https://doi.org/10.1016/j.envpol.2015.10.050

Shoeib, M., Harner, T., Webster, G. M., & Lee, S. C. (2011). Indoor Sources of Poly-and Perfluorinated Compounds (PFCS) in Vancouver, Canada: Implications for Human Exposure. *Environ. Sci. Technol*, *45*, 7999–8005. https://doi.org/10.1021/es103562v

Shoemaker, J. A., Grimmett, P. E., & Boutin, B. K. (2009). Method 537. Determination of selected perfluorinated alkyl acids in drinking water by solid phase extraction and liquid chromatography/tandem mass spectrometry (LC/MS/MS). *EPA*, 1–50.

Simcik, M. F., & Dorweiler, K. J. (2005). Ratio of perfluorochemical concentrations as a tracer of atmospheric deposition to surface waters. *Environmental Science and Technology*, *39*(22), 8678–8683. https://doi.org/10.1021/es0511218

Stockholm Convention. (2009). *C.N.524.2009.TREATIES-4 (Depositary Notification)*.

Sunderland, E. M., Hu, X. C., Dassuncao, C., Tokranov, A. K., Wagner, C. C., & Allen, J. G. (2019). A review of the pathways of human exposure to poly- and perfluoroalkyl

substances (PFASs) and present understanding of health effects. *Journal of Exposure Science and Environmental Epidemiology*, *29*(2), 131–147. https://doi.org/10.1038/s41370-018-0094-1

Venkatesan, A. K., & Halden, R. U. (2013). National inventory of perfluoroalkyl substances in archived U.S. biosolids from the 2001 EPA National Sewage Sludge Survey. *Journal of Hazardous Materials*, *252–253*, 413–418. https://doi.org/10.1016/j.jhazmat.2013.03.016

Wang, Z., Cousins, I. T., Scheringer, M., Buck, R. C., & Hungerbühler, K. (2014, September 1). Global emission inventories for C4-C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: Production and emissions from quantifiable sources. *Environment International*. Elsevier Ltd. https://doi.org/10.1016/j.envint.2014.04.013

Wang, Z., DeWitt, J. C., Higgins, C. P., & Cousins, I. T. (2017). A Never-Ending Story of Per-and Polyfluoroalkyl Substances (PFASs)? *Environ Sci Technol*, (51), 2508–2518. https://doi.org/DOI: 10.1021/acs.est.6b04806

Winkens, K., Koponen, J., Schuster, J., Shoeib, M., Vestergren, R., Berger, U., … Cousins, I. T. (2017). Perfluoroalkyl acids and their precursors in indoor air sampled in children's bedrooms. *Environmental Pollution*, *222*, 423–432. https://doi.org/10.1016/j.envpol.2016.12.010

Yao, Y., Zhu, H., Li, B., Hu, H., Zhang, T., Yamazaki, E., … Sun, H. (2014). Distribution and primary source analysis of per- and poly-fluoroalkyl substances with different chain lengths in surface and groundwater in two cities, North China. *Ecotoxicology and Environmental Safety*, *108*, 318–328. https://doi.org/10.1016/j.ecoenv.2014.07.021

Yu, L., Liu, X., & Hua, Z. (2022). Occurrence, distribution, and risk assessment of

perfluoroalkyl acids in drinking water sources from the lower Yangtze River.

*Chemosphere*, *287*(132064). https://doi.org/10.1016/j.chemosphere.2021.132064

Yunus, M., & Yamagata, T. (2012). The Garment Industry in Bangladesh. In Fukunishi (Ed.),

The Dynamics of the Garment Industry in Low-Income Countries: Experience of Asia and

Africa (p. 28). Chousakenkyo Houkokusho: IDE-JETRO.

FIGURE CAPTIONS
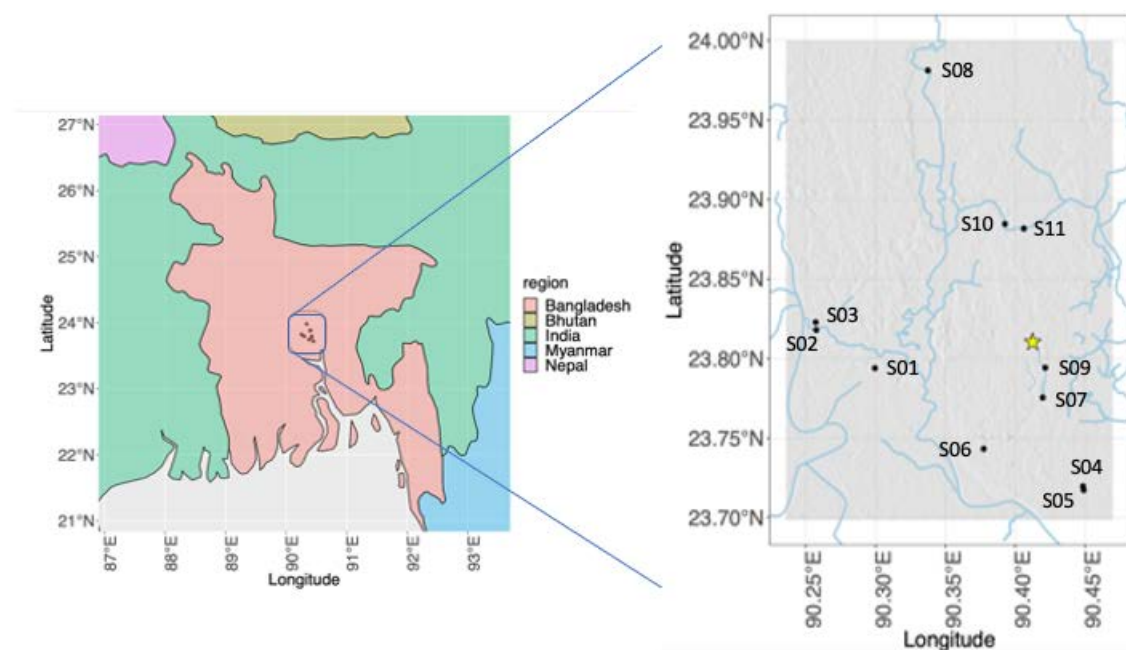
Figure 1. Sampling locations in the textile manufacturing region of Dhaka, Bangladesh. The

star symbol indicates the city of Dhaka. Sampling locations are indicated by dots and the

following abbreviations: S01: Amin Bazar in Dhaka, S02: Balshi River in Savar Bank

Town, S03: Cannel Savar at Denitex textile industry, S04: Demra Site 1, S05: Demra Site

2, S06: Dhanmondi Lake in Dhaka, S07: Gulshan Lake in Dhaka, S08: Gazipur

Metropolitan City, S09: Hatirjheel Lake in Dhaka, S10: Turag River Site 1, S11: Turag

River Site 2. PEair samples were retrieved from all sites except S03; PEwater samples

were retrieved from S02, S06, S08, S09; water grabs were collected from S02, S03, S06,

S07, S07, S08, S09, S10, S11.
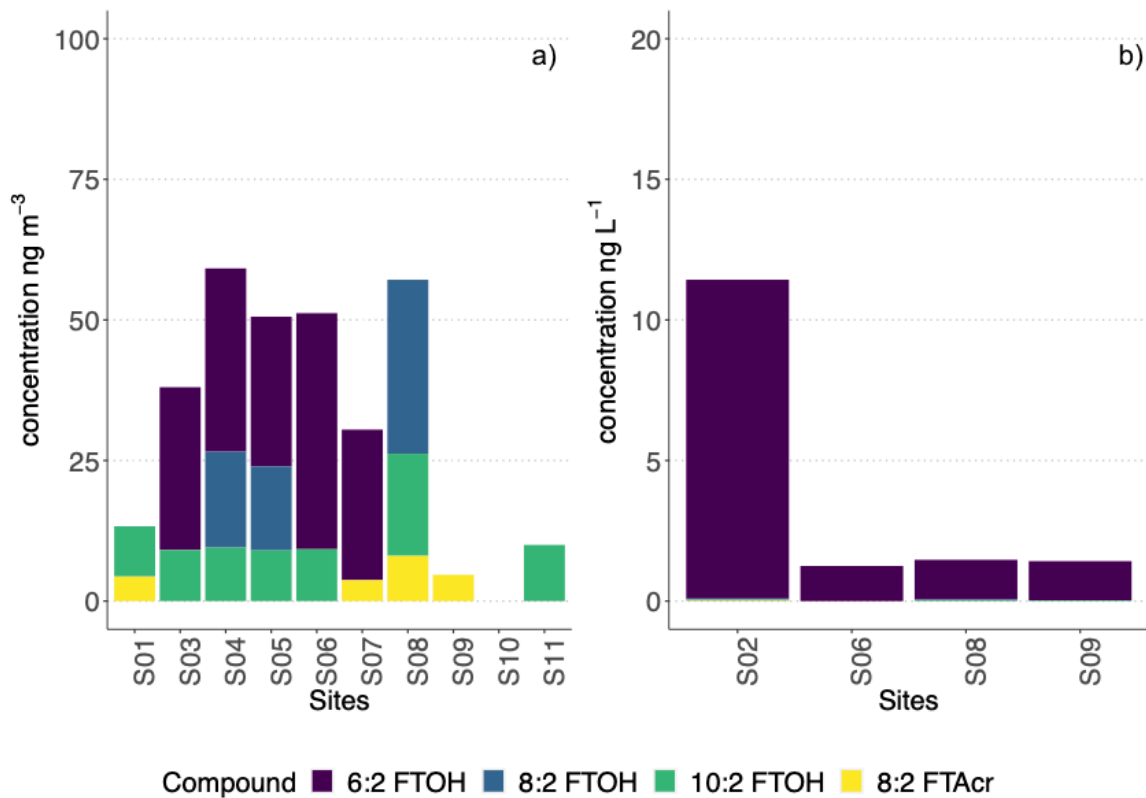
Figure 2. Neutral PFAS concentration in outdoor air and water of Dhaka, Bangladesh. Figure 2a shows concentrations in air; Figure 2b shows concentrations in water. S01: Amin Bazar in Dhaka, S02: Balshi River in Savar Bank Town, S03: Cannel Savar at Denitex textile industry, S04: Demra Site 1, S05: Demra Site 2, S06: Dhanmondi Lake in Dhaka, S07: Gulshan Lake in Dhaka, S08: Gazipur Metropolitan City, S09: Hatirjheel Lake in Dhaka, S10: Turag River Site 1, S11: Turag River Site 2. Compounds stand as follows: 6:2 Fluorotelomer alcohol; 8:2 Fluorotelomer alcohol; 10:2 Fluorotelomer alcohol; 8:2 Fluorotelomer acrylate.
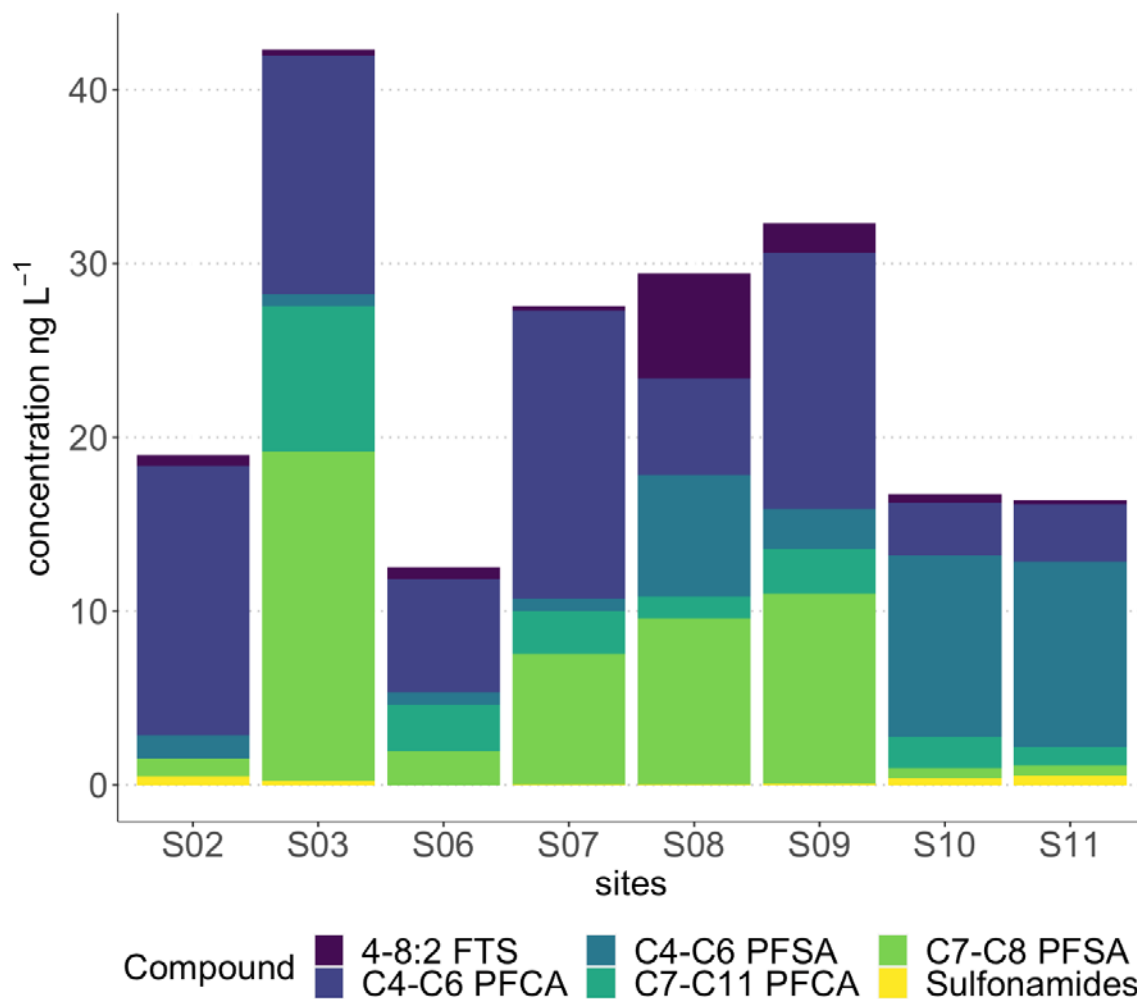
Figure 3. Relative concentrations for 16 PFAS compounds divided into 6 sub-groups based on their chemistry. Perfluoro alkyl acids are split into C6 or smaller for both Sulfonates and Carboxylates, as well as >C6 chain lengths. Three common fluorotelomer sulfonates (4:2, 6:2, and 8:2), and sulfonamide precursors (FBSA, FHxSA) are also grouped accordingly. S02: Balshi River in Savar Bank Town, S03: Cannel Savar at Denitex textile industry, S06: Dhanmondi Lake in Dhaka, S07: Gulshan Lake in Dhaka, S08: Gazipur Metropolitan City, S09: Hatirjheel Lake in Dhaka, S10: Turag River Site 1, S11: Turag River Site 2. Compounds stand as follows: 4-8:2 Fluorotelomer Sulfonate; C4-C6 Perfluoro Sulfonic Acid; C7-C8 Perfluoro Sulfonic Acid; C4-C6 Perfluoro Carboxylic

Acid; C7-C11 Perfluoro Carboxylic Acid; Sulfonamides.

Table 1. A comparison of the 6 dominant PFAS concentrations measured in surface waters from urban rivers and tropical regions reported in literature. Mean measurements in ng L^{-1} are reported when given and reported ranges (minimum and maximum) were used when mean or median were not available in the cited literature or supporting information. [1.] (Habibullah-Al-Mamun et al., 2016); [2.] (Munoz et al., 2017); [3.] (Sharma et al., 2016); [4.] (Chen et al., 2017); [5.] (Yao et al., 2014)

ng L^{-1}	Dhaka (mean, range)	Bay of Bengal (mean)[1]	Atlantic Tropics (mean)[2.]	Ganges River (mean)[3.]	Urban Catchment (range)[4.]	Northern Chinese Rivers (range)
No. of PFAS Compounds Reported	16	15	22	9	17	2
Sum PFAS	25 (13-42)	22	7.0	8.9	31-190	15-25
PFBA	6.8 (1.6-15)	0.48	0.8	<MQL	3.2-23	
PFHxA	3.5 (1.8-8.1)	0.67	0.83	2.3	2.5-9.5	
PFOA	2.3 (1.0-7.5)	12	0.71	0.4	4.8-13	10-18
PFBS	1.8 (0.1-4.0)	0.85	0.66	5.6	2.1-42	