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THE AIR THAT WE BREATHE: NEUTRAL PFAS IN INDOOR AND OUTDOOR AIR

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THE AIR THAT WE BREATHE: NEUTRAL PFAS IN
INDOOR AND OUTDOOR AIR

BY

MAYA ERIN MORALES-MCDEVITT

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OF

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ABSTRACT

Neutral, volatile perfluorinated alkyl substance (PFAS) precursors, such as fluorotelomer alcohols (FTOHs), perfluorooctane sulfonamides (FOSAs), perfluorooctane sulfonamide ethanol (FOSEs) are industrial (by)products that are commonly present in indoor environments, and have been found in urban, industrial, and even rural locations. They have also been detected in remote regions, such as the Arctic, suggesting that these compounds are transported long distances in the. However, measuring volatile and neutral PFAS in air and water has proven to be challenging. Therefore, in order to accurately measure these compounds in different indoor and outdoor environments from urban, rural, industrial and remote regions, we proposed the use of apolar polyethylene (PE) sheets as a passive detection tool for air and water.

The compounds of interest in this study included 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 8:2 FTAc, 10:2 FTAc, MeFOSA, MeFOSE, EtFOSA, and EtFOSE. Indoor sampling locations included classrooms, offices and laboratories from the University of Rhode Island, kindergarten classrooms and an outdoor clothing store in northern California, and classrooms, offices, laboratories and homes from the central valley of Jalisco, Mexico. Outdoor sampling of air and water included the North American Great Lakes, the Canadian Arctic, and Dhaka, Bangladesh. Studies were evaluated using two types of pre-cleaned PE passive samplers differentiated by thickness, and samples were analyzed by gas chromatography-mass spectrometry. These PE sheets were used to determine the partitioning coefficients (K_{PEa}) and uptake of the volatile PFAS by these samplers. Results from the kinetic study showed that after 14 days of exposure equilibrium of the compounds into the PE sheets had been reached. Passive samplers

were then paired with Radiello active samplers at an outdoor gear and clothing store to determine the K_{PEa} of each compound. Partitioning between both PE sheets suggests that interactions of the passive samplers with the volatile PFAS are occurring by absorption. Gas-phase concentrations were paired with concurrently analyzed dust samples taken at the same locations in Californian kindergartens, and indoor air concentrations were linked to carpet and dust concentrations and the ventilation rates of the indoor environments.

Results from all indoor studies indicated that volatile and neutral PFAS are ubiquitous in these environments, but that composition and concentration will vary depending on the contents of each location such as furniture, carpet, clothing, as well as ventilation rates. Volatile 6:2 FTOH was dominant in the U.S. indoor locations which was likely a reflection of the banning of longer chained PFAS and their precursors in North America. On the other hand, 10:2 FTOH was most abundant in the Mexican sites which pointed to the presence of older fluorinated products. Volatile PFAS from air, carpet and dust were closely related to each other which indicates that carpets and dust are major sources of FTOHs in air. Nonetheless, air poses the largest exposure risk of FTOH in children age 2 to 6 years old.

Outdoor air and water from the textile manufacturing industry in Dhaka, Bangladesh had FTOH concentrations comparable to those found indoors. The latter is significant because indoor air concentrations tend to be half as high as outdoor air concentrations. Thus, health concerns should be raised given the elevated concentrations found in ambient air and water. Concentration of FTOHs in the air from North American Great Lakes was higher than the Canadian Arctic. This suggested that

the amount of volatile and neutral PFAS present in air and water was in direct relationship with the size of its human settlements, and PFAS are ubiquitous and are capable of being transported atmospherically to remote regions.

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ACRONYM LIST

ACPH: air changes per hour

AFFF: aqueous fire-fighting foam

CS: Calibration standard

DWR: durable water resistance

ECF: electrochemical fluorination

EDI: estimated daily intake

FOSA: perfluorooctane sulfonamides

FOSE: perfluorooctane sulfonamide ethanol

FT: fluorotelomer

FTAc: fluorotelomer acrylates

FTOH: fluorotelomer alcohols

GC-MS: gas chromatography-mass spectrometry

HF: hydrogen fluoride

HOC: hydrophobic organic compounds

KG: kindergarten

K_{oa} : Octanol-air partitioning coefficients

K_{PEa} : PE-air partitioning coefficients

LOD: Limits of detection

MSD: Mass selective detector

OCS: Outdoor clothing store

PASF: perfluoroalkane sulfonyl fluoride

PE: polyethylene

PE: polyethylene

PFAA: perfluoroalkyl acids

PFAI: perfluoroalkyl iodide

PFAS: Per and polyfluorinated alkyl substances

PFC: poly and perfluorinated compounds

PFCA: perfluoroalkyl carboxylates

PFDS: Perfluorodecanesulfonic acid

PFHpA: Perfluoroheptanoic acid

PFHxA: Perfluorohexanoic acid

PFOA: perfluorooctanoic acid

PFOS: perfluorooctane sulfonic acid

PFPE: per- and polyfluoroalkyl ether

PFSA: perfluoroalkyl sulfonates

POPs: persistent organic pollutants

PRC: performance reference solution

PTFE: Fluoropolymers such as polytetrafluoroethylene

QA/QC: Quality assurance/Quality control

Rpm: revolutions per minute

SOP: Standard Operating Procedure

SPME: solid-phase microextraction

SVOC: Semi volatile compounds

TFE: tetrafluoroethylene

URI: University of Rhode Island

WS: Working standard

XAD: hydrophobic crosslinked polystyrene copolymer resin

Chapter 1

1.0 INTRODUCTION

High concentrations of persistent organic pollutants (POPs) have been detected in remote regions such as the Arctic (Lohmann *et al.*, 2007). In particular, elevated concentrations of per and polyfluorinated alkyl substances (PFAS) have been detected in pilot whales, seals and polar bears, as well as snow and water (Xie *et al.*, 2015; Giesy and Kannan 2001; Routti *et al.*, 2016). To this day, there is still debate on how ionic PFAS such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) end up in these regions. Latitudinal transport through ocean currents has been suggested as a potential pathway (Stock *et al.*, 2007). However, the strong partitioning preferences of ionic PFAS to proteins and sediments would limit the distances that these compounds can travel (Stock *et al.*, 2007; Armitage *et al.*, 2009; Dreyer *et al.*, 2009). Several studies have suggested that air currents are a more likely and faster transportation route (Ellis *et al.*, 2004b; Stock *et al.*, 2007). As such, it has been proposed that volatile, neutral, precursor PFAS such as fluorotelomer alcohols (FTOHs) that are quickly volatilized from their site of origin into the atmosphere and are transported long distances where they will eventually be oxidized into stable, ionic PFAS, which then partition to and accumulate in the snowpack, water, and biota (Stock *et al.*, 2007). The source point of these volatile precursor PFAS remains to be understood. It has been suggested that volatile PFAS from indoor environments are important sources of contamination to the environment and contribute significantly to concentrations found in remote regions (Shoeib *et al.*, 2004). However, few studies have been focused on the distribution of volatile PFAS within indoor environments, and their contribution to atmospheric contamination of PFAS. In addition, traditional

detection methods used for these indoor air studies are costly and time consuming (Lohmann, 2011). Passive sampling, and in particular polyethylene (PE) sheets, have proven to be effective and accurate detection tools for non-polar or weakly polar compounds, such as volatile and neutral PFAS (Adams *et al.*, 2007). What remains to be understood is how these compounds interact with the PE sheets.

The first hypothesis examined in this study is that volatile and neutral PFAS are ubiquitously found in indoor and outdoor environments from remote, rural, and urban locations. Thus, atmospheric transport can be inferred. Composition and concentration will differ between indoor and outdoor; and within indoor environments, composition will depend on the potential PFAS-use in each location.

The second hypothesis proposes that urban and developed regions in temperate regions have higher concentrations than rural underdeveloped regions in tropical regions due to the pricing and availability of many fluorinated products, and different ventilation systems related to climate.

Previous research has demonstrated that water-repellant and stain-proof carpets and clothing have high concentrations of PFAS to give such properties (Langer *et al.*, 2010; Gremmel *et al.*, 2016). Hence, the third and last hypothesis proposes that manufacturing sites and warehouses will be point-sources of volatile PFAS in indoor and outdoor environments.

2.0 REVIEW OF LITERATURE

2.1 Per- and polyfluorinated alkyl substances (PFAS)

Poly- and perfluorinated alkyl substances, hereafter referred to as PFAS, are a family of over 4,000 anthropogenic chemicals in which hydrocarbons of one or more C atoms have their H substituents partially or fully replaced by F (Buck *et al.*, 2011; Sunderland *et al.*, 2019). All PFAS contain the strongly electronegative perfluoro alkyl moiety ($C_nF_{2n+1}-$) and a hydrophilic end group that impart enhanced properties useful in a wide variety of industrial and commercial applications (Arvaniti and Stasinakis, 2015; Wang *et al.*, 2017). The C-F bond is strong, chemically and thermally stable, highly hydrophobic, lipophobic, and resistant to oxidation (Buck *et al.*, 2011; Arvaniti and Stasinakis, 2015).

According to the Organization for Economic Cooperation and Development (OECD, 2013) and as shown in Figure 1, PFAS can be categorized as non-polymeric or polymeric. Non-polymeric PFAS are comprised of four families (Figure 1), which mainly are 1) perfluoroalkyl acids (PFAAs) including but not limited to perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs); 2) compounds derived from perfluoroalkane sulfonyl fluoride (PASF); 3) fluorotelomer (FT)-based compounds; and 4) per- and polyfluoroalkyl ether (PFPE)-based compounds. Both PASF and FT derived or based products have the potential to degrade to PFSAs and PFCAs and as such are considered precursors.

Polymeric PFAS, on the other hand, are comprised of three groups (Figure 1): 1) Fluoropolymers such as polytetrafluoroethylene (PTFE), in which their C backbone is fully fluorinated; 2) side-chain fluorinated polymers which are composed of non-

fluorinated backbones with poly and perfluoroalkyl side chains; as such, they can also be considered precursors of PFSA and PFCAs; and 3) perfluoropolyethers which consist of backbones containing carbon and oxygen with fluorines directly attached to carbon (OECD, 2013).

Figure 1. PFAS classification. Figure and information obtained from OECD (2013).

2.2 History and uses of PFAS

The unique properties of PFAS have made them highly desirable in industrial and commercial applications (Wang *et al.*, 2017). In the late 1940's, the company 3M began the production of long-chain PFCAs using electrochemical fluorination with the purpose of non-stick coatings (Prevedouros *et al.*, 2006; ITRC, 2020). In the mid 1960's and up until the 1990's, PFAS were manufactured through electrochemical fluorination (ECF), and were applied in an increasing myriad of products such as surfactants for coatings, fluoropolymer manufacture, aqueous fire-fighting foam (AFFF), kitchen

appliances, paint, food containers and packaging, outdoor and recreational products, textiles, leather, rugs, paints, personal care products, cosmetics, among many others (Ahrens, 2011; Buck *et al.*, 2011; Venkatesan and Halden, 2013; Chen *et al.*, 2017; Eriksson *et al.*, 2017). After concerns were raised on the health effects that certain long-chain PFAS had on the health of workers manufacturing them in 1990's, 3M substituted ECF production of these compounds with a newer process called fluorotelomerization (ITCR, 2020).

Although both ECF and fluorotelomerization are registered methods for the manufacture of PFAS, their end products and byproducts are different. Therefore, it is important to define each method. ECF is a method in which a fluorinated raw material undergoes electrolysis in anhydrous HF where all the hydrogen atoms are replaced by fluoride (Buck *et al.*, 2011). This process results in a mixture of odd and even numbered C chains of ~70-80% linear ~20-30% and branched perfluorinated isomers and homologues of the parent material, in addition to salts, poly and perfluorinated compounds (PFCs) and other unintended byproducts (Buck *et al.*, 2011). Up until 2001, the most commercial compounds manufactured by 3M through ECF were perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) and their associated salts (Buck *et al.*, 2011). This company voluntarily phased out PFOA and PFOS from their production, however, these compounds were substituted with alternative products also manufactured through ECF (Buck *et al.*, 2011).

Fluorotelomerization was first developed in the 1970's and is the second most important manufacturing procedure for PFAS (ITRC, 2020). In contrast to ECF, it mainly yields even-number straight chain carbon isomers (Kissa, 2001). In this process,

a parent compound, perfluoroalkyl iodide (PFAI), reacts with tetrafluoroethylene (TFE) and yields long chained perfluoroalkyl iodides. Ethylene is later added to these mixtures, producing n:2 fluorotelomer alcohols (FTOHs) as a final product (Buck *et al.*, 2011). Historically, 8:2 FTOH is the most widely produced fluorotelomer alcohol; however, just as with PFOS and PFOA, it has now mostly been substituted with shorter chained compounds such as 6:2 FTOH (Buck *et al.*, 2011).

Concerns about the effects that PFAS have on humans and the environment have been raised since the 1990s. However, there were already studies in the 1970's that detected organic and inorganic fluoride in blood serum of exposed workers in the United States and China (Taves 1968; Ubel *et al.*, 1980; Berlisle 1981). By the 1980s, the application of PFAS to various products had significantly increased; and in 2001, PFOA and PFOS were first reported in 65 human sera samples (Hansen *et al.*, 2001). In addition, in 2001 the first report was made on the global distribution of PFOS in wildlife (Giesy and Kannan 2001). In this and other studies, tissues from bivalves, fish, birds, and marine mammals were collected from urban and remote regions across the globe (Kannan *et al.*, 2002, 2001; Giesy and Kannan 2001). The results demonstrated the widespread and global presence of PFOS in the environment. Later studies detected PFOA and other PFCAs in wildlife in remote regions such as the Arctic (De Silva and Mabury 2004; Ellis *et al.*, 2004; Routti *et al.*, 2016). By now, both PFOS and PFOA are known to be ubiquitously found in surface waters, sediments and soils, fish, birds, humans and other mammals (Venkatesan and Halden, 2013; Houtz *et al.*, 2016).

In an effort to regulate their emissions, PFOS, PFOA, and their salts were included in the Annex B of the Stockholm Convention in 2008 (Stockholm Convention,

2009). As a result of the 2010/2015 PFOA Stewardship program, eight fluorochemical manufacturers pledged to eliminate emissions and product contents of long-chain PFCAs and precursors by 2015 (EPA, 2006). Since then, PFOA and its homologues have been gradually phased out production in the U.S. and Europe (EPA, 2009; Wang *et al.*, 2014). Instead, companies have replaced these compounds with shorter perfluoroalkyl chains, including 6:2 fluorotelomer alcohol (6:2 FTOH) (Jahnke *et al.*, 2007a; Winkens *et al.*, 2017a).

By now, ionic PFAS are considered to be highly persistent, bioaccumulative, and toxic in the environment; and as such, have been nicknamed “forever chemicals” (Wang *et al.*, 2017). PFAS have also proven to have adverse effects for 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 (Buck *et al.*, 2011; Venkatesan and Halden, 2013; Arvaniti and Stasinakis, 2015). Precursors such as fluorotelomer alcohols (FTOHs), perfluorooctane sulfonamides (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).

2.3 Fate, transport and sources

The fate and transport of PFAS has not been fully understood, however, it is well established that these compounds will eventually enter the environment from direct sources such as emissions from production losses from their commercial products, or disposal of PFAS containing products (Arvaniti and Stasinakis, 2015). Ahrens *et al.* (2011) synthesized three main hypotheses for the global dissemination of

PFAS. The first one is the direct transport of these compounds in their ionic form through ocean currents. The second hypothesis proposes that PFSA and PFCA can be transported directly in the gas phase or by an aerosol-mediated pathway in the atmosphere. Lastly, neutral, volatile precursors, such as FTOHs, FOSAs and FOSEs, could undergo long-range atmospheric transport and be degraded by OH-initiated oxidation pathways, allowing these compounds to reach remote regions as PFCA and PFSA (Ellis *et al.*, 2004a; Ahrens *et al.*, 2011). However, little attention has been given to the possible sources of volatile PFAS into the atmosphere such as indoor environments and waste water treatment plants (Langer *et al.*, 2010). The pathways of volatile PFAS once they leave indoor environments are not yet fully understood.

Human exposure to PFAS and their precursors comes primarily from consumer and industrial products, many of which are readily available in people's homes (Prevedouros *et al.*, 2006; Shoeib *et al.*, 2005). For example, highest concentrations of volatile PFAS in indoor air have been found in the presence of durable water resistance (DWR) outdoor clothing, furniture and carpet, indicating that these groups are major sources of these compounds (Langer *et al.*, 2010; Gremmel *et al.*, 2016). Of these compounds, FTOHs are the dominant polyfluorinated compound in indoor air (Schlummer *et al.*, 2013). Furthermore, other studies have reported indoor air concentrations to be twice as high as outdoor levels and ~60% of detected PFAS were also associated with the particle phase (Shoeib *et al.*, 2005). Since most people spend more than 90% of their time indoors, (Shoeib *et al.*, 2005) it is unsurprising that food, drinking water, and indoor air and dust are important uptake pathways for human PFAS exposure (Ericson Jogsten *et al.*, 2012). Elevated concentrations of volatile precursors are generally observed in air masses coming from highly populated and/or

industrialized areas (Dreyer *et al.*, 2009); and within these regions, indoor air has been reported to have enhanced concentrations of selected PFAS (Jahnke *et al.*, 2007b).

2.4 Site Description for Outdoor locations

2.4.1 Bangladesh

Bangladesh has been traditionally 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 large 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 and 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 and Islam, 2015). Thus, Bangladesh's inland aquatic environments are recognized as some of the most polluted ecosystems in the world (Habibullah-Al-Mamun *et al.*, 2016).

It is important to note that 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 countries like the United States, Canada, and the European Union has shifted into developing countries making them important contamination hotspots (Li *et al.*, 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, and PFOA, PFOS, along with other PFAS remain unregulated PFAS (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). To the best of our knowledge only two other studies have reported PFAS in Bangladesh; although focused only in PFAAs in fish, surface water and sediments from around the Bay of Bengal (Habibullah-Al-Mamun *et al.*, 2016, 2017). Both studies reported the likelihood of the reported PFAS to come from the more industrialized region in Dhaka.

2.4.2 Canadian Arctic

The sampling locations from the Canadian Arctic from this study are located off Wellington Bay and Cornwallis Island. Wellington Bay in Victoria Island is located in the Kitikmeot Region in Nuwanut, Canada. It has a predominantly Inuit population and is in close proximity to Cambridge Bay which has the largest population of the Island (StatCan, 2021). Within this region, there are vessels dedicated to the industrial fishing of char, in addition to passenger and research vessels (DFO, 2021). The second sampling location was off of Cornwallis Island, next to Resolute Airport. Cornwallis Island is also located in Nuwanut, and is part of the Queen Elizabeth's Islands within the Arctic Archipelago in the Qikiqtaaluk Region. In 2016, the Island reported having a population of 198 people (StatCan, 2021). Resolute Airport, located on the southwestern boundary of the island, communicates all the central Arctic Islands of Nuwanut.

Over the past 30 years, the emission of persistent organic pollutants (POPs) from urban, agricultural and industrial regions of various parts of the world, have

resulted in a substantial influx of pollutants to the Canadian Arctic (Cabrerizo *et al.*, 2018). From these emerging POPs, PFAS have been reported since the early 2000s in ringed seals, pilot whales, polar bears, seabirds, snow, water and air (Cabrerizo *et al.*, 2018; Xie *et al.*, 2015; Giesy and Kannan 2001; Routti *et al.*, 2016; Stock *et al.*, 2007). Long-range atmospheric transport has been suggested as the most likely pathway for these compounds to reach such remote regions (Stock *et al.*, 2007; Ellis *et al.*, 2004). In addition, global warming has increased the potential exposure of legacy and emerging POPs in the Arctic through permafrost degradation, erosion and summer rainfall (Cabrerizo *et al.*, 2018).

However, it is important to point out that Arctic regions such as Nuнавut have seen rapid population growth, and as a consequence local sources of pollution from industrial activity, tourism, and waste-water effluents has also increased in the region (Walker *et al.*, 2020; Back *et al.*, 2021). In particular, waste-water treatment in the Arctic has been proven to be less effective than in temperate regions due to harsh weather conditions such as polar darkness and freezing temperatures which deaccelerate sorbtion of POPs to soils (Back *et al.*, 2021).

2.4.3 Great Lakes

Sampling locations in the US-Canada Great Lakes basin are located in Lake Ontario, Lake Erie, and nearby towns Strathroy in Ontario, Canada and Barrington in New York, U.S. The Great Lakes greater area has been historically used as a waste disposal site and has been heavily polluted for the greater portion of the nineteenth century (Tremblay and Gilman, 1995). High concentrations of legacy compounds such as PCBs, dioxins, phosphorous have been linked to high incidence of cancer, birth

defects, and damage to the nervous and immune system in the area (Mcgoldrick and Murphy, 2015).

In the 1960's, Lake Erie, Ontario, and Michigan were considered the most polluted lakes, largely due to the heavy industrial activity, and unregulated farming and waste disposal (Mcgoldrick and Murphy, 2015). On 1971, the United States and Canada signed an agreement in which both countries pledged to protect and enhance the water quality of the lakes (Bilder, 1972). Onwards, constant environmental monitoring has shown that the concentration of many legacy compounds in water has significantly decreased (Tremblay and Gilman, 1995). Nonetheless, there is increasing evidence that demonstrates the accumulation of persistent compounds in sediments. In 2012, Lake Erie and Ontario still contained the highest concentration of contaminants such as organochloride pesticides, polychlorinated biphenyls, mercury and other metals (Codling *et al.*, 2014, 2018).

In the 2000's, PFAS were added to the list of monitored chemicals in the Great Lakes. Concentrations of perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUdA), perfluorobutyric acid (PFBA), perfluorotridecanoic acid (PFTrDA), perfluorodecanoic acid (PFDoA), perfluoro nonanoic acid (PFNA) and PFOS were all within the top 40 contaminants measured in Erie and Ontario based upon concentration and frequency of determination (Mcgoldrick and Murphy, 2015). Unsurprisingly, PFAS now represent a significant fraction of the total contaminants in fish, and Herring gull eggs in Lake Erie and Lake Ontario (Codling *et al.*, 2018).

2.5 Detection tools

Most environmental studies for volatile and neutral PFAS have used active sampling methods such as water and sediment grabs, or high volume air samplers (Jahnke *et al.*, 2007a; Liu *et al.*, 2012; Ahrens *et al.*, 2011). However, these methods require large volumes of air and water to detect minimal concentrations in the media, are costly and time consuming (Jahnke *et al.*, 2007b; Dixon-Anderson and Lohmann, 2018). Therefore, 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 *et al.*, 2012).

Traditionally, triolein-containing polyethylene (PE) tubes referred to as semipermeable membrane devices (SPMDs) and silica coated fibers contained in organic polymers referred to as solid-phase microextraction (SPME) have been used as passive detection tools for hydrophobic organic compounds (HOC) (Adams *et al.*, 2007). Although these tools have been proven to be useful, many sampling difficulties are associated with them. If SPMDs are torn, and some of the triolein is lost, the calculation of the HOCs becomes difficult (Petty *et al.*, 2000). In addition, cleanup and extraction of the sorbents and HOC is lengthy and requires additional steps, which makes it costly in time, solvents, and money (Petty *et al.*, 2000). On the other hand, even though SPMEs do not require solvents and their analysis is considerably simplified, they are quite fragile and their deployment in outdoor environments has been proven to be problematic (Adams *et al.*, 2007; De Fátima Alpendurada 2000).

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 (Booij *et al.*, 1998; Adams *et al.*, 2007). In addition, PEs are cheap, 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 and Lohmann, 2018). However, the partitioning of these compounds into or onto the PE sheets remains to be fully understood.

2.6 Objectives

In an effort to understand the pathways of volatile PFAS once they leave indoor environments, the main objective of this research **was to measure and compare the presence and abundance of volatile or neutral PFAS by using PEs sheets in different indoor and outdoor environments**. For this purpose, the following objectives have been proposed:

- 1) To accurately measure air concentrations of volatile PFAS, active and passive indoor sampling results were compared, and PE-air partitioning coefficients (K_{PE-a}) were derived.
- 2) To better understand the partitioning preferences of neutral and volatile PFAS to the PE sheets, two types of PEs differentiated by thickness were compared.
- 3) To assess the role that indoor environments have as a source of atmospheric contamination of fluorinated compounds, the volatile PFAS composition between different indoor environments were determined. Such environments are carpeted kindergarten classrooms, homes of different age and ventilation, and university offices, laboratories and classrooms.

- 4) To better understand the PFAS partitioning and exposure risk in carpeted classrooms, associations between the volatile PFAS in the gas phase with those in dust and carpet were determined. Measurements of PFAS in dust and carpet from the kindergartens have already been published by Wu *et al.* (2020).
- 5) To investigate the difference in volatile PFAS concentration and distribution between urban, developed regions in high latitudes and those in rural, underdeveloped settings in lower latitudes, results from indoor environments in California, Rhode Island, and Mexico were compared.
- 6) To better understand the importance of heavily fluorinated carpets and clothing as source points of volatile PFAS, first, indoor air measurements of these compounds were taken at an outdoor gear and apparel store in California, and a carpet warehouse in Rhode Island. Second, outdoor air and water measurements were taken next to, and in the vicinity of textile manufacturing sites in Dhaka, Bangladesh.
- 7) Lastly, in order to corroborate the presence of volatile PFAS in remote regions, air and water measurements were taken in the Canadian Arctic.

Chapter 3

3.0 METHODOLOGY

This study was divided in two sections and is summarized in Table 1: the first section was devoted to the development and validation for the use of PE sheets as effective and precise passive samplers; while the second section measured volatile and neutral PFAS in indoor air and outdoor air and water using PE sheets as passive samplers. The sampling sites for the second section were: 1) multiple carpeted kindergarten classrooms, residences, and an outdoor gear and apparel store in northern California; 2) university offices, classrooms and laboratories at URI-GSO, and a carpet store in southern Rhode Island; 3) residences, university offices, classrooms and laboratories in the valley region of Jalisco, Mexico; 4) the industrial area of Dhaka, Bangladesh; and 5) sites in the Canadian Arctic and North Atlantic.

Sampling of all locations was done between 2018 and 2020. For the kindergarten and outdoor clothing store studies, pilot studies were performed previously to determine the efficiency of the passive and active samplers in air and the partitioning of the volatile and neutral compounds to the samplers. As shown in Table 1, a total of 114 PE sheets were deployed in the indoor locations, in addition to 8 radiello samplers used as active samplers. A total of 20 PE sheets were used in Bangladeshi air, and 20 PE sheets for water. In the Great Lakes greater area and Canadian Arctic, 8 PE sheets were used to measure air and 7 were used for water.

Table 1. Detection tool inventory per site per sampling campaign

Detection tool	Kinetic Study	KG classrooms & residences	URI & Carpet Store	Pilot Study OCS**	Outdoor Clothing Store	Mexico	Bangladesh	Great Lakes & Canadian Arctic
PE (indoor air)	12	40	13	16**	8	25	NA	NA
Radiellos (indoor air)	NA	NA	NA	NA	8	NA	NA	NA
PE (outdoor air)	NA	NA	NA	NA	NA	NA	20	8
PE (water)	NA	NA	NA	NA	NA	NA	8	7
Days deployed	14	28	28	7	28	28	28	28

Sites with NA, refer to not applicable sampling. Total samples are considering Field Blanks. Laboratory Blanks are not considered.

**Outdoor gear and apparel store.

3.1 Chemicals and reagents

As shown in Table 2, nine individual neutral PFAS standards, one internal standard, and five individual isotopically-labeled internal standards were purchased from Wellington Laboratories (Table 2). Organic solvent ethyl acetate was purchased from Merck.

Table 2. Standard compound list

Compound name	Description	Molecular Formula	Manufacturer, origin, ordering info
FHET	2-Perfluorohexyl ethanol	C ₈ H ₅ F ₁₃ O	Wellington, FHET, Lot: FHET0318
FOET	2-Perfluorooctyl ethanol	C ₁₀ H ₅ F ₁₇ O	Wellington, FOET, Lot: FOET0317
FDET	2-Perfluorodecyl ethanol	C ₁₂ H ₅ F ₂₁ O	Wellington, FDET, Lot: FDET1116
N-MeFOSE-M	2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	C ₁₁ H ₈ F ₁₇ NO ₃ S	Wellington, N-MeFOSE-M, Lot: NMeFOSE0418M
N-EtFOSE-M	2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	C ₁₂ H ₁₀ F ₁₇ NO ₃ S	Wellington, N-EtFOSE-M, Lot: NEtFOSE0518M
N-MeFOSA-M	N-methylperfluoro-1-octanesulfonamide	C ₉ H ₄ F ₁₇ NO ₂ S	Wellington, N-MeFOSA-M, Lot: NMeFOSA0518M
N-EtFOSA-M	N-ethylperfluoro-1-octanesulfonamide	C ₁₀ H ₆ F ₁₇ NO ₂ S	Wellington, N-EtFOSA-M, Lot: NEtFOSA0518M
8:2FTAc	1H, 1H, 2H, 2H-Perfluorodecyl Acrylate	C ₁₃ H ₄ F ₁₇ O ₂	Wellington, 8:2FTAc, Lot: 82FTAc0318
10:2FTAc	1H, 1H, 2H, 2H-Perfluorododecyl Acrylate	C ₁₅ H ₇ F ₂₁ O ₂	Wellington, 10:2FTAc, Lot: 102FTAc0318
MFHET	2-Perfluorohexyl[1,1-2H ₂]-[1,2- ¹³ C ₂]ethanol	¹³ C ₂ C ₆ ² H ₂ H ₃ F ₁₃ O	Wellington, MFHET, Lot: MFHET1118
MFOET	2-Perfluorooctyl-[1,1-2H ₂]-[1,2- ¹³ C ₂]-ethanol	¹³ C ₂ C ₈ ² H ₂ H ₃ F ₁₃ O	Wellington, MFOET, Lot: MFOET0419
MFDET	2-Perfluorodecyl[1,1-2H ₂]-[1,2- ¹³ C ₂]ethanol	¹³ C ₂ C ₁₀ ² H ₂ H ₃ F ₁₃ O	Wellington, MFDET, Lot: FDET1215

d-N-MeFOSA-M	N-methyl-d3-perfluoro-1-octanesulfanamide	C ₉ H ₃ HF ₁₇ NO ₂ S	Wellington, N-MeFOSA-M, Lot: NMeFOSA0518M
d-N-MeFOSE-M	N-methyl-d7-perfluoro-1-sulfoamidoethanol	C ₁₁ H ₇ HF ₁₇ NO ₃ S	Wellington, N-MeFOSE-M, Lot: NMeFOSE0518M
7:1 FTOH	2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluoro-1-octanol	C ₉ H ₅ F ₁₇ O	Lohmann Lab prepared from granulated 7:1 FTOH

3.5.1. Standard Solution Preparation

3.5.1.1. QA/QC Standard Solution

The QA/QC standard solution had a concentration of 80 pg μL^{-1} which was a dilution in ethyl acetate of a 2000 pg μL^{-1} native compound working mixture. The working mixture was made by taking a 40 μL aliquot of the 50,000 pg μL^{-1} stocks of 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, N-MeFOSE, N-EtFOSE, N-MeFOSA, N-EtFOSA, 8:2 FTAc, 10:2 FTAc and 7:1 FTOH as PRC, and diluted with 600 μL of ethyl acetate.

3.5.1.2. Internal Standard Solution

The internal standard solution had a concentration of 80 pg μL^{-1} which was a dilution in ethyl acetate of a 2000 pg μL^{-1} working mixture. The working mixture was made by taking a 40 μL aliquot of the 50,000 pg μL^{-1} stocks of the mass labelled M4 6:2 FTOH, M4 8:2 FTOH, d7 MeFOSE, and d3 MeFOSA, and diluted with 840 μL of ethyl acetate.

3.5.1.3. Recovery Standard Solution

The recovery standard solution had a concentration of 400 pg μL^{-1} which was a dilution in ethyl acetate of a 2,000 pg μL^{-1} working mixture. The working mixture was

made by taking a 40 μL aliquot of the 50,000 $\text{pg } \mu\text{L}^{-1}$ stock of the mass labelled M4 10:2 FTOH and diluted with 940 μL of ethyl acetate.

3.5.1.4. Calibration Standard Solutions

Five calibration standard solutions were made with concentrations of 1000, 500, 100, 50, and 10 $\text{pg } \mu\text{L}^{-1}$ (CS5, CS4, CS3, CS2, CS1). These standards were made from two native compound working mixtures of 2000 and 100 $\text{pg } \mu\text{L}^{-1}$, and the 2000 $\text{pg } \mu\text{L}^{-1}$ internal and recovery working mixtures. The 2000 $\text{pg } \mu\text{L}^{-1}$ native compound working mixture (WS1) was made as explained in section 3.5.1.1., and the 100 $\text{pg } \mu\text{L}^{-1}$ (WS2) was a dilution in ethyl acetate of WS1. CS5, CS4, and CS3 were dilutions from WS1 while CS2 and CS1 were dilutions of WS2. Finally, 25 μL of both the internal and recovery working mixtures were added to all calibration standard solutions.

3.2 Sampler preparation

3.2.1 PE sheet preparation

Prior to deployment, PEs, were precleaned, dried, and stored according to validated SOPs from the Lohmann Laboratory. Both types of PE, 25 and 50 μm thickness, were cut using a cardboard template of dimensions 4 " x 15-1/2 ". Each batch consisted of 28 PEs which were stacked, rolled, and placed inside a previously baked 1/2 quart Mason jar. Every Mason jar was filled with acetone and allowed to soak overnight. The acetone was decanted and discarded, replaced with methanol, and then ethyl acetate.

Batches intended for outdoor sampling were impregnated with a performance reference solution (PRC) in order to determine if target compounds had reached equilibrium and adjust for any losses there may be within the PEs (Khairy and Lohmann, 2019). To prepare the PRC, a working solution was made by combining 3.2 L of LC grade methanol, 0.8 L of Milli-Q water, 30 mL of a previously prepared PRC solution spiked with 160 μL of a 50 $\text{pg } \mu\text{L}^{-1}$ 7:1 FTOH standard in an empty 4 L amber bottle. Of this working solution, ~300 ml was added to each Mason jar which, were then closed tightly and placed horizontally on a Lab Companion SK-71 shaker at 70 RPM for 30 days.

All PE sheets were wrapped individually in previously muffled aluminum sheets. Every batch of samplers was labelled and stored in a freezer until use. Three PEs were taken from each batch treated with PRC to test for recoveries.

3.2.2 Radiello preparation

Radiello tubes contained a hydrophobic crosslinked polystyrene copolymer resin referred to as XAD sorbent sandwiched between two cotton wool plugs; each layer filling one third of the sampler as shown in figure 2. Radiellos and cotton wool were precleaned in LC grade methanol and ethyl acetate. The XAD sorbent was cleaned with LC grade methanol and reagent ACS ethyl acetate, sonicating for 20 minutes three times for each solvent. All Radiellos were wrapped individually in previously muffled aluminum sheets. Every batch of samplers was labelled and stored in a freezer at -20°C until its use.

Figure 2. Illustration of a Radiello sampler packed with a cotton wool-XAD-cotton wool sandwich

3.3 Field work

3.3.1 Deployment and retrieval of Passive samplers for neutral PFAS

The number of samplers and deployment times are detailed in Table 1. For the indoor kinetic study, two types of PE passive samplers differentiated by thickness (25 μm and 50 μm) were deployed for 14 days and collected every other day to determine the uptake of the volatile PFAS. Samplers for the outdoor gear and apparel store (OCS) pilot study were deployed for 7 days. For the remainder campaigns, samplers were deployed for 28 days after which they were kept in a freezer at -20°C until their extraction.

Indoor air PEs were hung away from vents, windows and doors. No PRC was used for indoor experiments. No shielding was required since PEs were placed in dry and stable environments. PEs for outdoor air, except for those used in the Canadian Arctic and North Atlantic, were treated with a PRC prior to use and were shielded with a top and slightly smaller bottom aluminum bowls to protect them from the elements but still allowing air flow to go through as shown in figure 3.

Figure 3. Schematic of outdoor air PE passive sampler shielded with two aluminum bowls secured with nuts and screws, and elevated from the ground with a pot hanger.

For water passive sampling, the PEs were tied with plastic cable ties to a nylon rope attached to a floating device, keeping the sampler from sinking, and weighted down with ballasts as shown in figure 4.

Figure 4. Schematic of an outdoor water PE passive sampler tied to a nylon rope, and kept neutral buoyancy with the use of a floating device on the surface and a weight on the bottom

3.3.2 Air Active Sampling

Active sampling was performed on days 1, 7 and 14 of the sampling campaign at the outdoor gear and apparel store in northern California. Radiello samplers were attached to a QuickTake 30 SKC Pump and a flow meter using silicone tubing. The pump and the flow meter were placed upright on a flat surface. The tubing was secured to a clothes hanger so that the Radiellos could be kept upright and hung in the storage room. The flow was kept constant at 5 L min^{-1} using the flow meter for 240 minutes which was computed into the QuickTake 30 SKC Pump.

3.5 Laboratory work

3.5.2. Polyethylene (PE) Passive Sampler Extraction

Polyethylene sheets were wiped with Kim Wipes to remove dust, mud, or biofouling. They were then individually inserted into 80 mL glass vials, spiked with 50 μL of surrogate standards and extracted overnight in reagent ACS ethyl acetate. In the case of the water PE sheets, a small amount of sodium sulfate was added to each vial to absorb any residual water. Extracts were concentrated to a final volume of 200 μL using a gentle stream of Nitrogen. Prior to GC analysis, all samples were spiked with 10 μL of injection standard. All PE sheets were weighed for final concentration calculations.

3.5.3 Radiello Extraction

Each radiello was placed inside a falcon tube precleaned in ethyl acetate and spiked with 50 μL of surrogate standard. Enough reagent ACS ethyl acetate was added to cover each sample which were then capped, vortexed for 2 minutes, and left

extracting overnight. This extraction was repeated and the solvent from both extracts combined. Extracts were concentrated to a final volume of 500 μL using a gentle stream of Nitrogen, and then transferred to Eppendorf tubes where they were further concentrated to 250 μL . Samples were centrifuged at 1000 rpm and transferred to clean Eppendorf tubes. The samples were then concentrated to 30 μL and transferred to GC vials, rinsing each Eppendorf with ethyl acetate three times. All samples were spiked with 10 μL of injection standard.

3.5.4 Quality Assurance/Quality Control

Field blanks, matrix spikes, matrix blanks, and field duplicate samples were included with each sample batch. Field blanks were composed of PE sheets or Radiello from each corresponding batch. To prevent cross contamination, each sample was stored in its individual aluminum pouch. Matrix spikes were prepared by spiking 50 μL of the QA/QC standard solution and 50 μL of the Internal Standard into a clean (unused and never removed from the laboratory) sampler. Matrix blanks were prepared by spiking 50 μL of the Internal Standard into a clean sampler. All QA/QC samples were extracted and the same analytical steps were followed as with the rest of the samples. Duplicate samples were averaged to determine variability among them.

Field blanks were included in each campaign. Concentrations were then averaged and subtracted from field samples. Since field blanks were taken from various locations, variability was wide between locations and campaigns. Limits of detection were calculated as the blank average plus three times the standard deviation. Recoveries of the Matrix Spikes ranged between 75% to 97% for all compounds. Outdoor samples impregnated with PRC did not have measurable amounts of 7:1 FTOH

after analysis, so it was assumed that compounds had reached equilibrium in the PE sheets.

3.6. Instrumental analysis

3.6.1 Instrumental analysis for neutral and volatile PFAS

Samples for neutral and volatile compounds were analyzed using gas chromatography-mass spectrometry on an Agilent 7890B chromatograph coupled to an Agilent 5977A mass selective detector (MSD) device operating in positive chemical ionization mode using selected ion monitoring. The ion source was held at 300 °C, and the transfer line was held at 280 °C. Aliquots of 2 µL were injected via an autosampler. A splitless intake were held at 270 °C led into a polar Supelcowax 10 column of 60 m and an internal diameter of 10 µm. Gas flow of the helium carrier gas was held at 1.5 mL min⁻¹. The oven temperature is a modification of the Dixon-Anderson & Lohmann (2018) method and is as follows: 50 °C for 2 min, 3 °C min⁻¹ to 70 °C, 10 °C min⁻¹ to 130 °C, 20 °C min⁻¹ to 220 °C, 120 °C min⁻¹ to 270 °C, hold for 5 min, having a total run time of 34.58 minutes per sample. A five-point calibration check was performed prior to the analysis of each batch of samples. Samples were then analyzed through GC-MS. Concentrations were blank and weight corrected.

3.7 Analytical work

The partitioning of neutral PFAS between polyethylene and air or water ($K_{PE-matrix}$) shown in equation 1 were derived as the ratio of passive sampler concentrations (C_{PE}) to active sampling concentrations (C_{matrix}) sampled over the same time period (Dixon-Anderson and Lohmann, 2018):

$$K_{PE-matrix} = C_{PE} / C_{matrix} \quad (1)$$

Mean log values were then derived and compared to similar literature

Equation 2 was used to determine the liner uptake of the PFAS to the passive samplers during the kinetic study, and was first proposed by Vrana *et al.* (2001) and Bartkow *et al.* (2005) was used:

$$N_s = C_t \times K_{PE-matrix} \times m_s \times 1^{-R_s \times t / K_{PE-matrix} \times m_s} \quad (2)$$

where N_s is the amount of pollutant absorbed in pg; R_s is sampling rate given in L day⁻¹; t is exposure time (day); m_s is the passive sampler mass (kg); $K_{PE-matrix}$ is the polyethylene/air or water partitioning constant (L kg⁻¹); and C_t is the ambient concentration (pg L⁻¹).

Sampling rates (R_s), as shown in equation 3, were estimated using the 7:1 FTOH as PRC according to the method of Booij and Smedes (2010):

$$R_s = -\frac{\ln(N/N_0)}{t} * K_{PEa} m_{PE} \quad (3)$$

where N and N_0 are the 7:1 FTOH amounts at the end and beginning of exposure, K_{PEa} is the PE-air partitioning coefficient, m_{PE} is the PE mass (g), and t is the exposure time (days).

At equilibrium, the amount of neutral PFAS absorbed to the passive sampler is a function of ambient concentration and the equilibrium partitioning constant (Dixon-Anderson and Lohmann 2018) and is represented in equation 4:

$$N_s = C_{matrix} \times K_{PE-matrix} \times m_s \quad (4)$$

where C_{matrix} is the ambient dissolved or gas-phase concentrations in water (pg L^{-1}) or air (pg m^{-3}).

Active sampling was used in a single campaign only. Therefore, for the remainder of the campaigns, the concentrations of volatile PFAS in indoor and outdoor air from the PE sheets, gaseous concentrations (C_a , pg m^{-3}) were calculated from the PE sheets concentrations (C_{PE}) according to Khairy and Lohmann (2019) as shown in equation 5:

$$C_a = \frac{C_{PE}}{K_{PEa} * \left[1 - e^{-\frac{R_s * t}{K_{PEa} * m_{PE}}} \right]} \quad (5)$$

where C_{PE} is the concentration in the PE sheet (pg g^{-1} PE), R_s is the sampling rate ($\text{m}^3 \text{day}^{-1}$), t is the deployment period (days), m_{PE} is the mass of the PEs (g), and K_{PEa} is the PE-air partitioning coefficients.

Partitioning within the PE sheet, as shown in equation 6, will be derived as the ratio of the 25 μm passive sampler (C_{25}) to the 50 μm passive sampler (C_{50}) amounts at equilibrium sampled over the same time period and normalized to the mass of the PEs:

$$K_{25-50} = C_{25} / C_{50} \quad (6)$$

If absorption of the compounds of interest is governing the partitioning, the ratio should be equal or similar to 2; if adsorption is governing, the ratio should be equal or similar to 1.

The total estimated daily volatile and neutral PFAS intake via air inhalation and dust ingestion represented in equation 7 was based on the averaged levels of volatile PFAS measured in indoor air in kindergarten classrooms of California reported in this

study, those reported in dust by Wu *et al.*, 2020, and two other studies (USEPA 2008; Gebbink *et al.*, 2015). Exposure from non-dietary ingestion and air inhalation was calculated for children age 2 through 6. Indirect exposure to PFAAs via biotransformation of the precursors was included.:

$$Total\ EDI = \sum \left(\frac{C_{neutPFASair} \times q_{air} \times f_{time-in}}{mbw} \times F_{uptake} \right) + \sum \left(\frac{C_{neutPFASdust} \times q_{dust} \times f_{time-in}}{mbw} \times F_{uptake} \right) \quad (7)$$

where q_{air} and q_{dust} are the quantity of air inhaled ($m^3\ day^{-1}$) and of ingested dust ($g\ day^{-1}$); mbw is body weight (kg); $f_{time-in}$ is fraction of time spent indoors; F_{uptake} is gastrointestinal uptake fraction. The total estimated daily volatile and neutral PFAS intake equals the sum of direct intake of the neutral compounds in air and dust. To simulate three typical exposure scenarios, i.e., low-, intermediate-, and high-exposure, different values were applied. F_{uptake} were obtained from Gebbink *et al.* (2015).

Indoor air concentrations from the carpeted kindergarten classrooms were compared and associated with carpet and dust concentrations from the same locations published by (Wu *et al.*, 2020). Relevant associations were used to enhance estimated PFAS intake in indoor environments. Results between samplers, matrices, and sites were compared.

Chapter 4

4.0 Results on the validation of PE sheets

4.1. Validation of PE sheets

Results from the kinetic study (Figure 5) showed that amounts of 6:2 FTOH and 8:2 FTOH reached equilibrium after 14 days, possibly even after 8 days. All other compounds were below our detection limits (Appendix Table 9). Deployment times were hence prescribed as 14 days indoor, given higher flow rates outdoors, equilibrium should also be reached within 14 days for ambient deployments.

Figure 5. Weight-normalized, blank-corrected concentrations of 6:2 FTOH and 8:2 FTOH per gram of PE sheet. Note on the X axis that D refers to days, and PE25 and PE50 refers to the two types of PEs (25 and 50 μ m) used in this study

4.2. Partitioning constant coefficients of volatile and neutral PFAS into PE sheets

To derive air concentrations from the amounts of compounds accumulated in the PE sheets, it was necessary to evaluate their sampling rate and to derive the polyethylene/air partitioning (K_{PEa}) constants using the low volume active samplers described in the methods section (Appendix Table 10). Briefly, the calibration of the PE sheets was accomplished by deploying both the active and passive samplers in an outdoor clothing store in California for a period of 28 days. As shown in table 3, results indicated the log K_{PEa} values were approximately 4 -5 for the FTOHs, and closer to 5 for the 8:2 FTAc. The 10:2 FTAc was only detected by the 50 μ m PE sheets and none of the FOSAs and FOSEs were detected by the radiello active samplers. Thus, their K_{PEa} s were not derived from the outdoor clothing store deployments. The mean log K_{PEa} values from the FTOHs of this study were approximately two log units lower than those reported by Dixon-Anderson and Lohmann (2018) (Table 3), so it was assumed that such would be the case for the remainder of the targeted compounds.

Table 3. Estimated log polyethylene/air partitioning constant (K_{PEa}) values from the present study, and log polyethylene/air/water partitioning constants (K_{PEa}/K_{PEw}) estimated in an outdoor study

Compound	Mean log K_{PEa25} (this study)	Mean log K_{PEa50} (this study)	Mean log K_{PEa} (Dixon-Anderson and Lohmann, 2018)	Mean log K_{PEw} (Dixon-Anderson and Lohmann, 2018)
6:2 FTOH	4.35 $\pm$ 0.11	4.31 $\pm$ 0.04	7.6 $\pm$ 0.2	2.7 $\pm$ 0.1
8:2 FTOH	4.30 $\pm$ 0.05	4.52 $\pm$ 0.04	7.1 $\pm$ 0.2	4.3 $\pm$ 0.1
10:2 FTOH	4.99	4.99 $\pm$ 0.02	7.7 $\pm$ 0.4	4.5 $\pm$ 0.1
8:2 FTAc	4.86 $\pm$ 0.43	5.01 $\pm$ 0.19	N/A	4.3 $\pm$ 0.2
10:2 FTAc	7.1*	7.1*	9.1	4.7^
MeFOSA	N/A	N/A	N/A	3.5 $\pm$ 0.1

EtFOSA	6.8*	6.8*	8.8 ± 0.2	4.1 ± 0.1
MeFOSE	7*	7*	9.0 ± 0.1	3.0 ± 0.1
EtFOSE	6.9*	6.9*	8.9 ± 0.3	3.1 ± 0.1

N/A=not analyzed, ^KPEa/w from Dixon-Anderson and Lohmann (2018) for 10:2 FTAcr was estimated relative to 8:2 FTAcr with an increase of 0.5 log units, *KPEa from this study was estimated relative to those reported by Dixon-Anderson and Lohmann (2018) with a decrease of 2.0 log units

With respect to the partitioning coefficients of the FTOHs to the polyethylene sheets, there is a trend of increasing K_{PEa} with increasing molecular weight (Table 3). Similar trends were observed in the precursor log K_{PEws} , but not for the K_{PEas} (Dixon-Anderson and Lohmann, 2018). Measurements taken in this study were indoors while those in Dixon-Anderson and Lohmann (2018) were taken outdoors where environmental factors could be affecting the partitioning of the compounds. Discrepancies and challenges in determining descriptors for hydrophobic compounds have been previously reported and attributed to the difficulty in determining partition coefficients (Endo and Goss, 2014). Nonetheless, the minor differences in the 25 μ m and 50 μ m K_{PEa} result in similar air concentrations between samplers, as shown in Figure 6, and suggests that polyethylene sheets are in fact sensitive and effective detection tools for non-polar compounds.

Figure 6. Air concentration comparison between passive and active samplers. Error bars indicate variability among replicates.

4.4. Partitioning of volatile and neutral PFAS into PE sheets

The ratio of the partitioning coefficients normalized by the weight of the 50 μm and 25 μm polyethylene (PE) sheets used in the outdoor gear and apparel store are shown in Figure 7. Values of ~1 indicated that compounds were partitioning to the PEs by absorption, while values of ~2 indicated adsorption partitioning. The partitioning ratios of the FTOH species and 10:2 FTAc were ~1 (Figure 7) suggesting that they were being absorbed into the PEs. The wide variability of 8:2 FTAc (Figure 7) reflects the inconsistency of its detection in the 25 μm PE sheets indicating that further studies are needed to fully understand the interactions between the compounds and the passive samplers. However, the added thickness of the 50 μm PE sheets resulted in easier detection and arguably better results. The compound EtFOSE was consistently

adsorbed to the PEs (Figure 7), and thus suggests that the PEs worked as partitioning-by-adsorption devices.

Figure 7. Compound partitioning in indoor environments normalized by weight of the PEs. The single dot above 6:2 FTOH is an outlier. Error bars represent variability among replicates. Dotted lines indicate limits of absorption/adsorption.

Although temperatures were not taken, it is relevant to note that the sampling campaign in the clothing store campaign was done during the summer in northern California. A previous study performed in a controlled experimental glass chamber found that the steady-state concentration of pentachlorophenol, a known SVOC, increased with increased with increasing temperatures (Marchal *et al.*, 1998). Another study found that temperature also had an impact on the partitioning of compounds between water and PEs (Adams *et al.*, 2007). It is reasonable to assume that such would be the case in air and that it would also affect the sorption of certain compounds into the PEs. In addition, air turnover rates (ACPH, no. changes hr⁻¹) at the clothing store storage unit equaled 0.31. The latter, in addition to higher temperatures, would suggest

that the FTOH species remained for long periods of time in the clothing store storage unit and consequently, had more time to impregnate and equilibrate in the PEs.

Chapter 5

5.0 Results from Indoor Studies

5.1. Volatile and neutral PFAS in indoor air

Indoor air concentrations derived from the PEs are shown in Figure 8, as well as Appendix Tables 14, 15, 16 and 17. The indoor air studies were divided in four sections: 1) California Kindergarten classrooms (Appendix Table 15); 2) offices and classrooms at the University of Rhode Island, and a nearby carpet store (Appendix Table 16); 3) offices and classrooms at the Universidad de Guadalajara, and nearby homes in Jalisco, Mexico (Appendix Table 17); and 4) a storage unit at an outdoor clothing store in California (Appendix Table 14). Volatile and neutral PFAS were present at all locations, and from these compounds FTOHs were the most abundant and dominant group; confirming the observations reported by previous studies on the composition of PFAS in homes and other indoor environments (Schlummer *et al.*, 2013; Liu *et al.*, 2012; Shoeib *et al.*, 2011). Nonetheless, the composition and concentrations varied between locations and were most likely driven by the different PFAS-containing products used at each location.

Figure 8. Indoor air concentrations measured at California Kindergartens, URI classrooms, offices and laboratories, and a carpet store in southern Rhode Island, an outdoor clothing store, and classrooms, laboratories, and offices at UdG, and nearby homes in Jalisco, Mexico. Due to wide differences in concentration, y-axis scales are not constant.

In the case of the California kindergarten and homes, 6:2 FTOH was the most abundant compound, contributing 96 % to sum totals, followed by 8:2 FTOH with only 3 %. 6:2 FTOH had the overall highest concentrations ranging from 9 ng m⁻³ to 600 ng m⁻³ (Figure 8; Appendix Table 15). Only in KG2, KG3, and KG5 was the concentration of 8:2 FTOH higher (37 ng m⁻³, 159 ng m⁻³, and 33 ng m⁻³ respectively) than its 6:2 FTOH counterparts (20 ng m⁻³, 157 ng m⁻³, and 21 ng m⁻³, respectively). Both MeFOSA and EtFOSE were present at low concentrations, while EtFOSA was not detected and MeFOSE was below our detection limits (Figure 8; Appendix Table 15). Neither 8:2 FTAc nor 10:2 FTAc were detected in this campaign. It is important to point out that all kindergarten classrooms were carpeted (Appendix Table 15).

Similar to results from the kindergarten classrooms, we found that 6:2 FTOH, and 8:2 FTOH were the most abundant compounds in URI rooms, with 83%, and 17% contribution to sums total, respectively (Figure 8; Appendix Table 16). FTOHs were detected only in carpeted sites and one lab where these compounds are regularly analyzed by GC/MS (Appendix Table 16). Present in most carpeted environments was 6:2 FTOH, with the exception of two offices (Appendix Table 16). At the locations where 6:2 was detected, its concentrations ranged from 104 ng m⁻³ to 1911 ng m⁻³ in one laboratory and one office. The compound 8:2 FTOH was present only at one laboratory and one classroom, and in the carpet store. Nonetheless, at these sites, concentrations ranged from 160 ng m⁻³ to 270 ng m⁻³. The presence of 10:2 FTOH was only detected in one laboratory at 11 ng m⁻³, one office at 33 ng m⁻³ and at the carpet store with an average concentration of 18 ± 2 ng m⁻³ (Figure 8; Appendix Table 16). Neutral MeFOSA, EtFOSE, and MeFOSE were found at low concentrations or below our limits of detection at all sites. The presence of EtFOSA was detected at low concentrations only in one laboratory and one office. The FTAc were present at all locations but only in a second office did the concentrations of 10:2 FTAc exceed limits of detection (Appendix Table 16). It is important to note that the highest concentrations of the FTOHs were at an office and not the carpet store (Figure 8; Appendix Table 16).

Indoor air concentrations in the Mexico locations were also dominated by the FTOHs. 10:2 FTOH represented 97% of the total PFAS having concentrations over 50 ng m⁻³ at three locations and one site with concentrations over 40 ng m⁻³ (Figure 8; Appendix Table 17). However, 10:2 FTOH was not detected at any of the other sampling sites. Only 10:2 FTAc was detected at the same sites as 10:2 FTOH, albeit concentrations were lower by three orders of magnitude. Present in all locations was

8:2 FTOH with an average concentration of $0.5 \pm 0.07 \text{ ng m}^{-3}$. Both EtFOSA and EtFOSE were also present at all locations with average concentrations of $0.002 \pm 0.0003 \text{ ng m}^{-3}$ and $0.001 \pm 0.0002 \text{ ng m}^{-3}$ respectively. The low but constant concentration of 8:2 FTOH, EtFOSA, and EtFOSE suggests that these compounds are generic of everything found indoors in this region. MeFOSA (0.07 ng m^{-3}) and MeFOSE (2 ng m^{-3}) were only detected in the living room of one of the sampled homes (Figure 8; Appendix Table 16) suggesting that these compounds could come from specific products (Appendix Table 10).

Table 4. Comparison of neutral PFAS in indoor air environments from this study to other studies performed in various indoor locations. Blank values indicate compounds that were included in the study. ND refers to compounds not detected. LOD values are specified in corresponding appendix tables.

Reference	Location	Sampler*	Unit	6:2 FTOH	8:2 FTOH	10:2 FTOH	MeFOSA	EtFOSA	MeFOSE	EtFOSE
This study	California KG, US	PE	ng m ⁻³	126	32	7	0.01	ND	<LOD	0.08
This study	Rhode Island, US	PE	ng m ⁻³	280	56	<LOD	0.1	ND	0.1	0.03
This study	Jalisco, MX	PE	ng m ⁻³	ND	0.5	21	0.01	0.002	0.2	0.002
This study	California OCS, US	PE	ng m ⁻³	70	60	13	0.07	0.02	<LOD	0.1
Fraser et al (2011)	Boston, US	GFF/PUF-XAD-PUF	ng m ⁻³	<LOD-11	0.2-70	0.1-13	0.005-0.1	<LOD-0.1	0.05-4	<LOD-0.2
Schlummer et al (2013)	Germany	ISOLUTE ENV + SPE	ng m ⁻³	0.1- 46	0.2-285	0.1-57	-	-	-	-
Winkens et al (2017)	Finland	SIP disks	ng m ⁻³	<LOD-8	1.3-13	0.2-9	-	-	<LOD-0.4	<LOD-0.1
Shoeib et al (2005)	Canada	SIP disks	ng m ⁻³	-	-	-	0.01-0.1	-	0.3-8	0.2-7
Shoeib et al (2011)	Canada	SIP disks	ng m ⁻³	<LOD-22	0.6-16	0.2-8	<LOD-0.8	-	0.05-9	<LOD-1
Haug et al (2011)	Norway	PUF-XAD-PUF	ng m ⁻³	0.06-9	0.9-25	0.3-29	0.0-0.07	0.0-0.09	0.06-1	0.0-0.3
Huber et al (2011)	Norway	PUF-XAD-PUF	ng m ⁻³	0.02-9	3-11	1-6	0.01-0.2	0.002-0.1	0.2-1.2	0.05-0.3
Fromme et al (2015)	Germany	PUF-XAD-PUF	ng m ⁻³	0.2-5	4-21	1-4	0.05-0.1	0.05-0.1	0.3-3	0.02-0.1
Langer et al (2010)	Germany	PUF-XAD-PUF	ng m ⁻³	1-3	8-17	2-5	1-1.2	1.2-1.6	2.7-3	2.1-2.1
Liu et al (2013)	Japan	ACF	ng m ⁻³	0.5-12	0.3-60	0.7-13	-	-	-	-

*Acronyms definition: PE: Polyethylene; GFF: glass fiber filter, PUF: Polyurethane foam; XAD: hydrophobic copolymer of styrene-divinylbenzene resin; ISOLUTE ENV+: hyper crosslinked hydroxylated polystyrene-divinylbenzene copolymer, with very high surface area; SIP disks: sorbent impregnated polyurethane disks; ACF: activated carbon filter felts

Fraser et al. (2011) reported concentrations of FTOHs ranging from below limits of detection (<LOD) to 11 ng m⁻³ for 6:2 FTOH, 0.3 ng m⁻³ to 70 ng m⁻³ for 8:2 FTOH, and 0.138 ng m⁻³ to 12 ng m⁻³ for 10:2 FTOH in multiple office spaces in Boston, Massachusetts. These concentrations were in the same order of magnitude as those previously reported for homes and other indoor environments (Table 4) (Shoeib *et al.*, 2011; Schlummer *et al.*, 2013). Thus, the FTOH concentrations in indoor air, even the higher values in URI offices reported here (Figure 8), fell within the range of those previously reported. It is important to note that locations at Rhode Island with higher concentrations of FTOHs were a carpeted classroom and office, and a carpet store (Appendix Table 16). However, concentrations in one URI office were higher than at the carpet store, suggesting that in this office space, these compounds were outgassing from other sources such as durable-water-resistant (DWR) outdoor clothing or furniture (Langer *et al.*, 2010) in addition to the carpet (Appendix Table 10, 16).

By now, longer-chain PFAS, such as 10:2 FTOH have been phased out of the industry (Buck *et al.*, 2011), so it is unsurprising that this compound was detected at such low concentrations in California and Rhode Island, especially when compared to studies performed in previous years as shown in Table 4. In contrast to the locations in U.S., however, in the locations in Mexico where 10:2 FTOH was detected, the concentrations were one to two orders of magnitude higher than those in Rhode Island and California, but similar to those reported in previous years (Table 4). This could be a reflection on the lack of regulations regarding PFAS in Mexico (Arrieta-Cortéz, 2015), or merely the presence of items and products manufactured and imported into the country prior to restrictions imposed by the U.S. and the E.U.

Although low in concentration, 10:2 FTAc was only detected at sites in Mexico where 10:2 FTOH was present (Appendix Table 17). Residual fluorotelomer acrylates from the production of commercial fluorotelomer-based polymer products have been reported to enter the environment in a similar manner as FTOHs (Joyce *et al.*, 2006; Russell *et al.*, 2008). Thus, it is not surprising that they would be found paired in indoor environments.

A study in Ottawa, Canada, in 2005 reported concentrations of MeFOSE, EtFOSE and EtFOSA in indoor air of approximately 7 ng m⁻³, 2 ng m⁻³ and 0.1 ng m⁻³ respectively (Shoeib *et al.*, 2005). In 2011, MeFOSE, EtFOSE, MeFOSA, and EtFOSA were detected at 0.4 ng m⁻³, 0.06 ng m⁻³, 0.03 ng m⁻³, and 0.02 ng m⁻³ respectively in Vancouver, Canada (Shoeib *et al.*, 2011). In the present study, although present in many locations, FOSEs rarely exceeded concentrations over 0.001 ng m⁻³ (Table 4). Exception to this was the living room sampled in Mexico with a concentration of 0.02 ng m⁻³ of MeFOSE (Appendix Table 17). FOSAs were detected even fewer times. The difference in concentrations of the FOSAs and FOSEs in different locations across North America could be a reflection of geographic differences in indoor sources (Shoeib *et al.*, 2011), as well as differences between urban and rural regions (Martin *et al.*, 2002). Additionally, these difference in concentrations between locations also point towards a decreasing temporal trend of the compounds that could be a consequence of their ban in North America (Shoeib *et al.*, 2011).

The differences between our urban and rural sampling sites are important to note because not only are the indoor locations at different geographies, but they also belong to different countries with different regulations and access to certain products.

All indoor environments measured in the U.S. were urban or suburban regions, with an average income ranging from \$40,5990 to \$80,912 per year, and most jobs are behind desks (U.S. Census Bureau, 2021). Sampling sites in Mexico were all located in the rural central valley of the state of Jalisco where, in 2019, the average income was \$4,800 per year, and the main economic activity was agriculture (INEGI, 2021). A study lead by Martin *et al.* (2002) found a stark difference in concentration between urban and rural sites in Canada, which was also observed in this study.

Regardless, indoor air concentrations taken in the U.S. and Mexico (Table 4) were consistently higher than those taken outdoors, which will be detailed in chapter 6. These findings are consistent with results by Shoeib *et al.*, (2005) who reported concentrations of volatile PFAS to be up to 20 times greater in indoor environments than outdoor concentrations. Given that most people spend more than 90% of their time indoors, drinking water, diet, indoor air, and dust are the main pathways of human exposure to PFAS (Ericson Jogsten *et al.*, 2012; Wu *et al.*, 2020; Shoeib *et al.*, 2011). Thus, estimations of daily intake and correlations between air and dust are important.

5.2 Volatile and neutral PFAS in indoor dust and carpets

Concentrations of volatile and neutral PFAS in dust and carpet were measured by Wu *et al.* (2020) and are shown in Figure 9 and Appendix Table 19. Volatile and neutral PFAS were detected in dust and carpet at all sampling sites; however, their composition varied from air. FTOHs were the most dominant group and from these, 6:2 FTOH was found most frequently (Figure 9) and at highest concentrations ranging from 21 ng g⁻¹ to 571 ng g⁻¹ in dust and 7 ng g⁻¹ to 581 ng g⁻¹ in carpet (Appendix Table 19). Despite having lower concentrations, 8:2 FTOH was also detected at all locations

ranging from 13 ng g⁻¹ to 297 ng g⁻¹ in dust, and 12 ng g⁻¹ to 231 ng g⁻¹ in carpets. 10:2 FTOH was detected in all sites as well, usually with the lowest concentrations of the analyzed FTOHs ranging from <LOD to 326 ng/g in dust and <LOD to 200 ng g⁻¹ in carpet (Figure 9; Appendix Table 19). Only 8:2 FTAc was detected in a dust sample of KG2 at almost 1 ng g⁻¹ and a carpet sample of KG7 at 1 ng g⁻¹. The compound 10:2 FTAc was not detected at any of the classrooms (Appendix Table 19). Neutral MeFOSA was detected only in carpet of KG3 at 0.2 ng g⁻¹, and dust and carpet from KG7 at 0.7 ng g⁻¹ and 0.2 ng g⁻¹ respectively. At most sites FOSEs were below detection limits (Appendix Table 19). Neutral MeFOSE ranged from <LOD to 123 ng g⁻¹ of dust, and <LOD to 122 ng g⁻¹ of carpet; while EtFOSE ranged from <LOD to 8 ng g⁻¹ of dust, and <LOD to 67 ng g⁻¹ of carpet (Figure 9; Appendix Table 19).

Figure 9. Volatile and neutral PFAS concentrations in dust and carpet from California kindergartens. Data was obtained from Wu et al. (2020)

The FTOHs have been reported to be used in carpet protection products and in the manufacture of carpets and rugs (Joyce *et al.*, 2006; Liu *et al.*, 2015). Thus, the dominance of these compounds is expected. The distribution pattern of the volatile and neutral PFAS in dust and carpet was similar, but not identical, to what was observed in the air concentrations in the California kindergartens (Figure 8, 9). Similar observations were reported by Shoeib *et al.* (2011); however, in their study, 8:2 FTOH was the dominant neutral PFAS in dust as it was in air. A more recent study reported concentrations trends of 6:2 FTOH > 8:2 FTOH > 10:2 FTOH in daycare dust (Giovanoulis *et al.*, 2019), which were in close agreement to this study. The recent dominance of 6:2 FTOH was probably a reflection of carpet industries shifting from longer chain compounds to shorter ones (Wu *et al.*, 2020). Nonetheless, 8:2 FTOH was still present at all sites (Figure 9).

Similar to Shoeib *et al.* (2011), the relative abundance of the FOSEs in dust and carpet was different from what was detected in air. The higher concentrations in dust and carpet of EtFOSE and MeFOSE, and their absence or low concentration in air (Figure 8, 9), could be a reflection of their lower volatilization and vapor pressures, and higher K_{oa} values compared to the FTOHs (Dreyer *et al.*, 2009). The fact that FOSAs and FOSEs were only detected at a handful of sites (Figure 9), suggests that they were not added to the carpet during their manufacture. In fact, FOSAs and FOSEs are commonly used as active surfactants for impregnation treatment of furniture and floors, as well as consumer products such as water/stain-proofing agents (Haug *et al.*, 2011). In products such as carpets, FTOHs have been detected consistently at higher concentrations than the FOSAs and FOSEs (Haug *et al.*, 2011), which is in accordance with the distribution patterns of this study.

5.2.1. Correlations

Air-dust partitioning of PFAS is a useful tool to evaluate their environmental fate and potential exposure risk to humans via inhalation of air and dust (Shoeib *et al.*, 2005). Octanol-air partitioning (K_{OA}) based models have been problematic since they greatly underpredict the extent to which MeFOSE and EtFOSE are associated with particles (Shoeib *et al.*, 2005). Instead, associations between the volatile and neutral PFAS in indoor air, dust, and carpet from the kindergarten rooms in California were explored applying r-squared correlations and t-tests to a fitted regression line as shown in Figure 9, Table 5, and Appendix Table 20. Significant correlations ($RSQ > 0.7$, $P > 0.05$) were observed among the FTOHs of air-dust, air-carpet, and dust-carpet (Table 5). Only 6:2 FTOH in air-carpet showed no significant correlations. With the exception of MeFOSE in carpet-dust, no significant correlations were observed between the FOSEs in air, dust or carpet.

Figure 10. Linear fitted regression between air, dust, and carpet. Dust and carpet values were provided by Wu *et al.* (2020). Linear fitted regression lines evaluate the relationship between components.

Table 5. RSQ correlations and *P* values between air, dust, and carpet. RSQ > 0.7 and *P* > 0.05 were considered significant.

Compound	RSQ _{air-dust}	<i>P</i> air-dust	RSQ _{air-carpet}	<i>P</i> air-dust	RSQ _{carpet-dust}	<i>P</i> dust-carpet
6:2 FTOH	0.76	0.78	0.58	0.63	0.83	0.83
8:2 FTOH	0.89	0.41	0.87	0.63	0.88	0.70
10:2 FTOH	0.74	0.17	0.90	0.31	0.95	0.41

Distribution of PFASs between indoor air and floor dust were reported to be controlled by partitioning between the gas phase PFASs in the air and the PFASs sorbed to the organic phases in the dust (Winkens *et al.*, 2018). Our results corroborated that volatile PFAS, presumably from carpets, were found in the air and partitioned to dust. It has been demonstrated that FTOHs, FOSAs, and FOSEs are likely to degrade in the atmosphere into more stable PFCAs (Ellis *et al.*, 2004a; Haug *et al.*, 2011). Previous

studies had reported significant associations between 6:2 FTOH and PFHxA ($q = 1$, $r^2 = 0.91$), PFHpA ($q = 0.943$, $r^2 = 0.76$) and PFOA ($q = 0.829$, $r^2 = 0.77$), indicating that the precursor were being degraded in indoor air (Huber *et al.*, 2011). Similarly, significant associations were observed between FOSAs/FOSEs in air and PFOS and PFDS in house dust (Haug *et al.*, 2011). There were no significant associations between the FOSAs/FOSEs in air, dust and carpet from this study suggesting that the FOSAs/FOSEs detected in air could be generic of everything else in the rooms. Previous studies did not find significant correlations between the FOSEs in kindergartens either, but did however find strong associations in offices (Goosey and Harrad, 2012), implying that there were common sources of these sulfonamidoethanols in items associated with office spaces that perhaps were not usually found in kindergartens.

5.5.2. Estimated daily ingestion of volatile PFAS through air and dust

To assess the relevance of volatile and neutral PFAS in indoor air for children aged two to six years old the estimated daily intake (EDI) were calculate (see Table 6 and Appendix Table 21) for three exposure estimates: 1) "low", where air inhaled was assumed to be contaminated at the 5th percentile concentrations; (2) "intermediate", where median concentrations were assumed to be inhaled; and (3) "high", where volatile PFAS concentrations inhaled were assumed to be at the 95th percentile (Goosey and Harrad, 2012; Wu *et al.*, 2020). To do so, it was assumed that for a child aged 2-6 years old and average bodyweight (m_{bw}) of 17.50 kg , the daily inhalation of air (q) was 5.49 m³, 7.60 m³, and 9.71 m³ and daily ingestion of 60 mg, 60 mg, and 100 mg of dust for each scenario (USEPA 2008; Winkens et al. 2018). In addition, it was assumed

that the fraction of time spent indoors ($f_{\text{time_in}}$) was 90% (USEPA, 2008). Gastrointestinal uptake factors (F_{uptake}) were obtained from Gebbink *et al.* (2015).

The total EDI (Table 6) in the low exposure scenario was $1.53 \text{ ng kg}^{-1} \text{ bw day}^{-1}$, the intermediate exposure scenario was $14.00 \text{ ng kg}^{-1} \text{ bw day}^{-1}$, and the high exposure scenario was $153.53 \text{ ng kg}^{-1} \text{ bw day}^{-1}$. Compounds that were regularly detected in both air and dust were 6:2 FTOH, 8:2 FTOH, and, to a lesser extent, 10:2 FTOH; while MeFOSE and EtFOSE appeared to have significantly larger contributions in dust than air as shown in Figure 11 and Table 6. Results from this study and Wu *et al.* (2020), as shown in Table 7, indicate that volatile and neutral PFAS measured in air contributed 4.93-61.19 % to $\sum \text{PFAA}$ intake, while ionic PFAS measured in dust contributed 34.25-95.02 % to $\sum \text{PFAA}$ intake. These results are in agreement with Vestergren *et al.* (2008) who reported that precursors contributed 41–68 % to $\sum \text{PFOS}$ uptake via all investigated exposure pathways. Similarly, Winkens *et al.* (2017; 2018) found that PFAA precursors contributed 90 % to the $\sum \text{PFOS}$ intake in air at the intermediate scenario. Nonetheless, comparisons between the EDI_{air} and EDI_{dust} , suggest that air inhalation was a major exposure pathway for FTOHs, while dust ingestion was dominant for FOSEs in children age 2 to 6 years old. Similar findings were reported by Goosey and Harrad (2012). Adults have been reported to have even higher EDIs via inhalation at any given risk scenario (Shoeib *et al.*, 2005, 2011).

Table 6. Estimated daily volatile and neutral PFAS intake ($\text{ng kg}^{-1} \text{ bw day}^{-1}$) by children at ages 2 to 6 years via air inhalation and dust ingestion. *Dust values were provided by Wu *et al.* (2020). Total estimated contributions were calculated from both air and water.

Compound	Estimated daily precursor air intake (ng/kg bw/day)			Estimated contribution by air intake (%)			Estimated contribution of gas intake to total uptake by dust and air for total precursors (%)			Fraction gas of total intake per compound (%)		
	L	M	H	L	M	H	L	M	H	L	M	H
6:2 FTOH	1.06	10.28	116.20	71.26	74.36	77.31	69.22	73.46	75.69	97.60	99.02	98.81

8:2 FTOH	0.25	2.67	29.26	17.08	19.27	19.47	16.59	19.04	19.06	95.74	98.74	97.98
10:2 FTOH	0.16	0.85	4.75	11.05	6.18	3.16	10.74	6.10	3.10	96.23	96.40	86.03
MeFOSE	0.01	0.01	0.01	0.35	0.06	0.01	0.34	0.06	0.01	99.99	99.99	2.91
EtFOSE	0.00	0.02	0.08	0.26	0.13	0.05	0.26	0.13	0.05	99.98	100.00	69.45
Compound	Estimated daily precursor dust ingestion (ng/kg bw/day)			Estimated contribution by dust ingestion (%)			Estimated contribution of dust intake to total uptake by dust and air for total precursors (%)			Fraction dust of total intake per compound (%)		
	L	M	H	L	M	H	L	M	H	L	M	H
6:2 FTOH	0.03	0.10	1.39	59.47	60.72	43.24	1.70	0.73	0.91	2.40	0.98	1.19
8:2 FTOH	0.01	0.03	0.60	25.82	20.29	18.71	0.74	0.24	0.39	4.26	1.26	2.02
10:2 FTOH	0.01	0.03	0.77	14.70	19.00	23.95	0.42	0.23	0.50	3.77	3.60	13.97
MeFOSE	0.00	0.00	0.42	0.00	0.00	13.07	0.00	0.00	0.27	0.01	0.01	97.09
EtFOSE	0.00	0.00	0.03	0.00	0.00	1.03	0.00	0.00	0.02	0.02	0.00	30.55

Figure 11. Percent of volatile and neutral PFAS intake via air inhalation and dust ingestion by children at ages 2 through 6

Given the potential for precursors to be biotransformed into more stable PFAAs, estimations of PFAA indirect exposure were also calculated and are shown in Table 7. These values were 1.17 ng kg⁻¹ bw day⁻¹, 75.11 ng kg⁻¹ bw day⁻¹, 2774.45 ng kg⁻¹ bw

day⁻¹ for the low, intermediate, and high exposure scenario respectively. The major contributors of indirect PFAA were from 6:2 FTOH and 8:2 FTOH in air, and MeFOSE, in dust.

The total estimated exposure of PFAA intake via dust were 22.15, 89.41, and 1637.72 pg kg⁻¹ bw day⁻¹ for the low, intermediate, and high exposure scenarios. Estimated daily direct PFAA intake via dust was provided by Wu *et al.* (2020). Compounds with significant contributions were PFBA, PFHxA, PFOA, PFOS, PFNA, and PFBS (Table 7). This data indicates that short-chain PFCAs are important contributors to children's exposure to PFAS. Volatile and neutral PFAS represent a smaller fraction of exposure to dust; however, they are major contributors in air (Table 7).

Table 7. Estimated daily indirect PFAA intake via air inhalation and dust ingestion. Due to low concentrations, values are shown in pg/kg bw/day. Values of <0.01 were considered insignificant. Direct and indirect PFAA intake via dust was obtained from Wu *et al* (2020). Percentages indicate the contribution on the total.

Estimated daily direct PFAA intake via dust (pg kg ⁻¹ bw day ⁻¹)				Estimated daily indirect PFAA intake via air (pg kg ⁻¹ bw day ⁻¹)			
Compounds	L	M	H	Compounds	L	M	H
PFBA	3.12	11.2	272	6:2 FTOH	0.21	51.41	1975.42
PFPeA	0.91	3.40	21.6	8:2 FTOH	0.05	13.33	497.38
PFHxA	3.10	11.3	113	10:2 FTOH	0.03	4.27	80.83
PFHpA	1.13	5.10	61.8	MeFOSE	0.49	1.74	4.04
PFOA	3.41	12.1	109	EtFOSE	0.37	3.52	24.16
PFNA	1.90	7.87	60.6	Estimated daily indirect PFAA intake via dust (pg kg ⁻¹ bw day ⁻¹)			
PFDA	0.42	2.65	64.3	Compounds	L	M	H
PFUnDA	1.87	5.44	40.2	6:2 FTOH	0.01	0.51	23.71
PFDoDA	0.55	3.22	50.3	8:2 FTOH	<0.01	0.17	10.26
PFTTrDA	0.90	2.46	21.2	10:2 FTOH	<0.01	0.16	13.13
PFTeDA	1.27	4.01	48.5	MeFOSE	<0.01	<0.01	134.90
PFBS	0.42	1.31	268	EtFOSE	<0.01	<0.01	10.63
PFPeS	0.10	0.15	2.12		L	M	H

PFHxS	1.26	3.34	20.0	ΣDirect PFAA intake via dust	22.14 (95.02%)	88.57 (54.11%)	1445.09 (34.25%)
PFHpS	0.09	0.19	1.47	ΣIndirect PFAA intake via dust	0.01 (0.04%)	0.84 (0.51%)	192.63 (4.57%)
PFOS	1.56	11.5	127	ΣIndirect PFAA intake via air	1.15 (4.94%)	74.27 (45.38%)	2581.83 (61.19%)
PFDS	0.13	3.33	164	Total PFAA intake	23.30	163.68	4219.55

Chapter 6

6.0 Findings in Outdoor Studies

6.1 Volatile and neutral PFAS in outdoor air and water in Dhaka, Bangladesh

Figure 12. Sampling locations in the textile manufacturing region of Dhaka, Bangladesh.

Sampling locations are shown in Figure 12. The most frequently detected compound was 6:2 FTOH ranging from ND to 70.00 ng m^{-3} in air, and from ND to 19.00 ng L^{-1} in water as shown in Figure 13, and Appendix Table 16. 8:2 FTOH was detected only in Demra and Gazipur air. It recorded its highest concentration in Demra at 46.00 ng m^{-3} . Similarly, 8:2 FTOH was detected only in water from Balshi river in Savar Bank Town and Gazipur with an average concentration of 0.02 ng L^{-1} . At most sites, 10:2 FTOH was detected with the exception of Turag River, Gulshan Lake, and Hatirjheel (Figure 13, Appendix Table 16). Concentrations of this compound ranged from ND to 19.00 ng m^{-3} . Volatile 8:2 FTAc was detected in four sites by the 50 μm PE sheets with concentrations ranging from ND to 8.00 ng L^{-1} . In neither air or water at any of the sites was 10:2 FTAc detected. Neutral MeFOSE was only detected by the

25 μm PE sheets in Gazipur and Balshi River with concentrations 0.10 and 0.20 ng m^{-3} in air, and 0.50 and 0.60 ng L^{-1} in water. Below the limits of detection were EtFOSA, MeFOSA, and EtFOSE.

Figure 13. Volatile and neutral PFAS concentration in outdoor air and water of Dhaka, Bangladesh.

As shown in Figure 12, 13 and Appendix Table 22, in Bangladesh, volatile and neutral PFAS were detected at every location and concentrations in air and water were at least one order of magnitude higher than those detected around the North American Great Lakes and the Canadian Arctic (Figure 14). However, concentrations in Bangladeshi air were in the same order of magnitude as those reported for indoor air in this study and others reported elsewhere (Figure 8, Table 4). The elevated and constant presence of 8:2 FTAc in these industrialized sites (Figure 13; Appendix Table 22) suggests that residual flourotelomer acrylates were being used during the production of

commercial fluorotelomer-based products (Joyce *et al.*, 2006; Russell *et al.*, 2008) or that they were being directly applied to manufactured products.

The low concentrations of the FOSAs/FOSEs in both air and water (Figure 13; Appendix Table 22) could be a consequence of their ban in North America (Shoeib *et al.*, 2011). However, given that Bangladesh is one of the most important garment manufacturers in the world (Yunus and Yamagata, 2012), it more likely reflects that FTOHs were used in DWR clothing, and not FOSAs and FOSEs (Gremmel *et al.*, 2016). The latter is in agreement with the dominant composition of FTOHs detected at the outdoor clothing store (Figure 13).

Although previously reported concentrations of Σ PFAS in surface water do not include any of the precursors, our results are in the same order of magnitude as the Σ PFAs detected around Bay of Bengal (Habibullah-Al-Mamun *et al.*, 2016). Overall concentrations in water at all locations were at least two orders of magnitude higher than those detected in the Arctic.

Bangladesh is located in the tropics and according to the Köppen climate classification, it has a tropical wet and dry climate (Ahmed and Kim, 2003). Its wet season is during the monsoon months of June to mid-October, and its dry season is from November to May (Ahmed and Kim, 2003). Therefore, given that our samples were deployed and collected in February, rain did not interfere with our samples. Fugacity ratios, shown in Table 8, 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.

Table 8. Fugacity of volatile and neutral PFAS between air and water in Dhaka, Bangladesh. NA values indicate that not enough data was available to determine the fugacity of the compounds.

PE μm	Location	6:2 FTOH	8:2 FTAcr	8:2 FTOH	10:2 FTOH
25	Gazipur Metropolitan City	1.15	NA	<0.01	1.14
25	Balshi river, Savar Bank Town	<0.01	<0.01	<0.01	0.79
25	Dhanmondi Lake, Dhaka	NA	NA	NA	NA
25	Hatirjheel Lake, Dhaka	<0.01	NA	<0.01	NA
50	Gazipur Metropolitan City	2.05	NA	1.95	1.95
50	Balshi river, Savar Bank Town	0.10	<0.01	<0.01	0.83
50	Dhanmondi Lake, Dhaka	<0.01	NA	NA	NA
50	Hatirjheel Lake, Dhaka	<0.01	NA	NA	1.04

6.2 Volatile PFAS in rural and remote areas

Volatile FTOHs were detected at all Canadian Arctic Sites, at three out of seven sites in the Great Lakes locations in both air and water, and at one site in Barrington, NY as shown in Figure 14 and 15 (see also Appendix Table 23). Neutral FOSAs and FOSEs were also detected but were below detection limits (Appendix Table 23). In the Great Lakes area, concentrations in air ranged between 20.00 ng m⁻³ to 30.00 ng m⁻³ of 6:2 FTOH, and 16.00 ng m⁻³ to 17.00 ng m⁻³ of 8:2 FTOH. Only one site in the Canadian Arctic had measurable concentrations of 10:2 FTOH (6.00 ng m⁻³ in Wellington Bay) (Figure 15).

In water, 6:2 FTOH was detected once in Lake Erie and twice in the Canadian Arctic at 1 ng L⁻¹, 8:2 FTOH was detected once in the Canadian Arctic at 0.02 ng L⁻¹, as well as for 10:2 FTOH detected at 0.02 ng L⁻¹ (Figure 14; Appendix Table 23). The dominant FTOH was dependent on sampling location; however, 6:2 FTOH was the most abundant in both air and water (Figure 14). This likely was a reflection of industries phasing out of PFOS and PFOA, including their precursors (Buck *et al.*,

2011) and the increase in alternative compounds such as 6:2 FTOH (Brendel *et al.*, 2018). Nevertheless, 8:2 FTOH and 10:2 FTOH were detected at both the Canadian Arctic and Great Lakes region (Figure 14).

Figure 14. Sampling locations at the Canadian Arctic and Great Lakes

Only one air sample was recovered from the Canadian Arctic (Appendix Table 23), so definitive conclusions other than the presence of 10:2 FTOH at Wellington Bay are not possible. However, the concentration of 10:2 FTOH at this site was of 6.00 ng m⁻³ of air (Figure 14) which is three orders of magnitude higher than those of Butt *et al* (2010) who reported a range of 1.90 to 17.00 pg m⁻³ of this compound in Arctic air concentrations. It is important to note that local inputs may be an important source of PFAS into the arctic regions (Butt *et al.*, 2010). This particular site is located off of the Kitikmeot Region in Nuwanut with a predominantly Inuit population close by (StanCan, 2021) that could be exposed or is the source to these compounds. Vessels dedicated to

the commercial fishing of char in Wellington Bay (DFO, 2021), could be the source of these compounds.

Figure 15. Volatile and neutral PFAS concentrations in outdoor air and water from the Canadian Arctic and Great Lakes. Note the difference in scale on the y-axes for air and water.

Airborne concentrations of FTOHs were higher among rural locations, such as Barrington NY, than the Canadian Arctic (Figure 14). However, water concentrations were similar between locations with positive measurements (Figure 14). The presence of FTOHs in air of rural and remote regions is further evidence that these compounds are widely distributed throughout the North American troposphere (Stock *et al.*, 2004). The somewhat uniform concentrations of these compounds in the Great Lakes region (Figure 14) suggests that point sources are found elsewhere. The latter is based on research that has found atmospheric plumes with higher concentrations of volatile PFAS in the vicinity of fluorochemical manufacturing industries than those reported in

remote regions (Jahnke *et al.*, 2007). Furthermore, it is consistent with the hypothesis proposed by Stock *et al.* (2007) that precursor chemicals such as FTOHs undergo long-range atmospheric transport to remote regions and subsequent degradation by biotic or abiotic means to PFSA and PFCA.

The remainder of the Arctic sampling sites were water measurements and were taken off the coast of Cornwallis Island at relatively close proximity to the Resolute Airport (Figure 13). They all have considerably uniform concentrations of approximately 1 ng L⁻¹ (Figure 13). Given the high volatility and partitioning preferences of FTOHs, it seems plausible that they could have the same origin, it being the Resolute Airport or the local settlements on the Island. Similar findings were reported by Stock *et al.* (2007) who attributed the elevated concentrations of PFAS such as PFOS and PFOA to the AFFF contamination and sewage runoff from the aforementioned airport.

Chapter 7

7.0 Conclusion

Throughout this work, PE sheets proved to be an accurate and reliable passive detection tool for volatile and neutral PFAS, not only in indoor air, but also outdoor air and water. This signifies that PE sheets are cost efficient alternatives to other detection tools, and can and should regularly be used in environmental monitoring.

Although not all compounds of interest were detected in our partitioning studies, it can be concluded that FTOHs and FTAc partition into the PE sheets. Future studies are needed to determine the K_{PEa} of FOSAs/FOSEs, and additional studies to corroborate the K_{PE} in water. This research determined that 14 days is sufficient time for compounds to reach equilibrium in the PE sheets. Lastly, given the small differences between the K_{PE25a} and K_{PE50a} , it can be concluded that either sampler will derive similar concentrations in air as an active sampler. However, the findings in this study indicated that the 50 μ m PE sheets provide less variability within replicates, and therefore, should be given priority if choosing between them.

Volatile and neutral PFAS were present in most indoor environments, especially in carpeted and/or poorly ventilated locations. Composition and abundance of the compounds varied amongst indoor locations, indicating that the presence of volatile and neutral PFAS is mostly regulated by the PFAS-containing products at each location. The dominance of 6:2 FTOH in indoor locations in the U.S. was likely a reflection of the banning of longer chained PFAS and their precursors in North America. On the other hand, the dominance of longer chained compounds, such as 10:2

FTOH, in Mexican locations, spoke of the lack of regulation of fluorinated substances in that country, as well as the presence of "older" fluorinated products. Nonetheless, the higher concentrations in urban and suburban sites in the U.S. pointed to the higher abundance or access to fluorinated products compared to rural sites in Mexico.

Carpeted environments and associated dust were major sources of FTOHs in air. Low correlations of FOSAs/FOSEs between air and dust, and air and carpet, suggested that these compounds do not volatilize as easily as lower molecular weight compounds. This study indicated that it was air that pose the largest exposure risk of FTOHs in children of age 2 to 6 years old; while dust, given the hand-to-mouth habits of young children, was the major exposure pathway of FOSAs/FOSEs.

Unsurprisingly, in this study, the carpet store location showed some of the highest concentrations in air, while some of the lowest values were detected in locations with older carpets or no carpets whatsoever. This implies that new carpets that have been recently manufactured will outgas more compounds and their composition will reflect the carpet industry shifting away from longer chain compounds. In this study, it was found that indoor air concentrations of the sum of volatile and neutral PFAS in carpeted locations were lower than in the outdoor clothing store. Exceptions were two kindergarten classrooms in California and a classroom and office at URI-GSO. The latter suggested that within indoor environments there were multiple sources of contamination that added up to the total concentration of PFAS.

To the best of our knowledge, this is the first report to find volatile and neutral PFAS in Bangladesh, and the first to report PFAS of any kind in its capital, Dhaka.

Volatile and neutral PFAS were detected at all sites in Dhaka, Bangladesh in both air and water. The dominance and abundance of 6:2 FTOH was likely a reflection of their wide use in textiles. Human and environmental health concerns should thus be raised given that these compounds can and will be degraded into more stable PFAAs. Two reports by Habibullah-Al-Mamun reported elevated concentrations of PFAA in water, sediments and fish from the Bay of Bengal region, and it is likely that at least a fraction of these PFAA are degraded products from their precursors and that most of these compounds come from the textile-industry region in Dhaka. Therefore, it is important to continue doing research in this region in order to provide scientific tools that will hopefully aid the regulation of PFAS in Bangladesh.

Air in the Great Lakes region appeared to be higher than the Canadian Arctic. This suggested that the amount of volatile and neutral PFAS present in air and water was in direct relationship with the size of its human settlements or the lack thereof. In addition, these findings implied that volatile and neutral PFAS were ubiquitous, and capable of being transported by some pathway to remote regions such as the Arctic. The constant presence of these compounds in air suggested that this pathway is atmospheric.

Chapter 8

8.0 Appendices

Table 9. Volatile and neutral PFAS analyzed by GC/MS under positive chemical ionization (PCI) mode

Abbr.	Compound Name	CAS # ^a	Formula	Mol. Wt.	Retention time (min)	Quantifier	Qualifier
6:2 FTOH	2-Perfluorohexyl ethanol (6:2)	647-42-7	C ₈ H ₅ F ₁₃ O	364.10	16.17	365	327
8:2 FTOH	2-Perfluorooctyl ethanol (8:2)	678-39-7	C ₁₀ H ₅ F ₁₇ O	464.12	17.26	465	427
10:2 FTOH	2-Perfluorodecyl ethanol (10:2)	865-86-1	C ₁₂ H ₅ F ₂₁ O	564.13	18.31	565	527
8:2 FTAcr	1H,1H,2H,2H-Perfluorodecyl acrylate	27905-45-9	C ₁₃ H ₇ F ₁₇ O ₂	518.17	16.54	519	499
10:2FTAcr	1H,1H,2H,2H-Perfluorododecyl acrylate	17741-60-5	C ₁₅ H ₇ F ₂₁ O ₂	618.18	17.86	619	599
MeFOSA	N-methyl perfluorooctane sulfonamide	754-91	C ₈ H ₂ F ₁₇ NO ₂ S	527.2	22.28	514	515
EtFOSA	N-ethyl perfluorooctane sulfonamide	4151-50-2	C ₈ F ₁₇ SO ₂ NHC ₂ H ₅	513.17	21.83	528	529
MeFOSE	N-methyl perfluorooctane sulfonamidoethanol	24448-09-7	C ₁₁ H ₈ F ₁₇ NO ₃ S	557.22	22.84	558	540
EtFOSE	N-ethyl perfluorooctane sulfonamidoethanol	1691-99-2	C ₁₂ H ₁₀ F ₁₇ NO ₃	539.19	22.90	572	554
M4-6:2 FTOH	2-Perfluorohexyl-[1,1,2,2- ² H ₄]-ethanol(6:2)		C ₈ H ₅ F ₁₃ O+D ₄	368.12	16.30	369	331
M4-8:2 FTOH	2-Perfluorooctyl-[1,1,2,2- ² H ₄]-ethanol(8:2)		C ₁₀ H ₅ F ₁₇ O + D ₄	468.12	17.67	469	431
M4-10:2 FTOH	2-Perfluorodecyl-[1,1,2,2- ² H ₄]-ethanol(8:2)		C ₁₂ H ₅ F ₂₁ O+D ₄	568.12	18.62	569	431

d7MeFOSE (SS)	2-(N-methyl-d ₃ -perfluoro-1-octanesulfonamido)ethan- d ₄ -ol		C ₁₁ H ₁ F ₁₇ NO ₃ S + D ₇	564.22	23.04	517	
d3MeFOSA	2-Perfluorooctyl-[1,1- ² H ₂]-[1,2- ¹³ C ₂]-ethanol(8:2)		C ₈ H ₃ F ₁₇ O + ¹³ C ₂ D ₂	468.12	22.58	565	

Table 10. Physico-chemical properties of volatile and neutral PFAS. Common uses the compounds are included

Compound	log Kow	log Koa	log Kaw	Boiling Point (°C)	Melting Point (°C)	Vapor Pressure (Pa)	Water Solubility (g L ⁻¹)	Henry's Law Constant (Pa m ³ mol ⁻¹)	Enthalpy of vaporization (kJ mol ⁻¹)	Uses
6:2 FTOH	5.6 ^a	4.812 ^a	0.788 ^a	172 ^b	-33 ^b	18.2 ^b	0.02 ^b	5726 ^b	47.8 ^a	Inks, paints, coatings, polymers, adhesives, waxes, polishes, caulks, cleaning agents ^{b,d}
8:2 FTOH	7.53 ^a	5.301 ^a	2.229 ^a	114 ^b	45 ^b	3.98 ^b	0.001 ^b	5039 ^b	49.4 ^a	
10:2 FTOH	6.63 ^b	5.7	NA	222.4 ^b	NA	0.2 ^b	0.00001 ^b	7776 ^b	NA	
8:2 FTAc	NA	NA	NA	NA	NA	NA	NA	NA	NA	Used in the manufacture of all fluorotelomer based polymers, stain repellency ^e
10:2 FTAc	NA	NA	NA	NA	NA	NA	NA	NA	NA	
MeFOA	6.07 ^b	6.3 ^c	NA	NA	NA	0.3 ^b	0.0002 ^b	NA	NA	Pesticides, insecticides ^b
EtFOA	6.71 ^b	6.6 ^c	NA	NA	NA	0.12 ^b	0.0001 ^b	NA	NA	
MeFOE	6 ^b	6.4 ^c	NA	NA	NA	0.0004 ^b	0.0003 ^b	NA	NA	Carpet treatment ^d
EtFOE	6.52 ^b	6.7 ^c	NA	NA	NA	0.002 ^b	0.0001 ^b	NA	NA	

^a <http://www.chemspider.com>^b (Smith *et al.*, 2016)^c (Dreyer, Langer and Ebinghaus, 2009)^d (Stock *et al.*, 2004)^e (Butt, Muir and Mabury, 2010)

Table 11. Amounts of volatile PFAS in PE sheets of two different thicknesses for the kinetic study in California kindergartens with a sampling period of 21 days

Time (days)	Deployed	Collected	PE sheet Thickness (um)	Environ	Sample	Unit	6:2 FTOH	8:2 FTOH	8:2 FTAcr	10:2 FTOH	10:2 FTAcr	EtFOSA	MeFOSA	MeFOSE	EtFOSE
1	10/25/18	10/26/18	50	Indoor Air	190-02	g (PE sheet)	<LOD	<LOD	999.099911	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
2	10/25/18	10/27/18	50	Indoor Air	190-03	g (PE sheet)	1543.49108	<LOD	1791.29148	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
4	10/25/18	10/29/18	50	Indoor Air	190-04	g (PE sheet)	922.956665	270.51379	1921.81465	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8	10/25/18	11/2/18	50	Indoor Air	190-05	g (PE sheet)	4909.74499	215.515691	2556.08193	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
15	10/25/18	11/9/18	50	Indoor Air	190-06	g (PE sheet)	6589.8624	300.974629	3429.79138	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
21	10/25/18	11/15/18	50	Indoor Air	190-07	g (PE sheet)	6275.11485	281.486214	3568.74582	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
1	10/25/18	10/26/18	25	Indoor Air	191-02	g (PE sheet)	<LOD	<LOD	6500.1562	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
2	10/25/18	10/27/18	25	Indoor Air	191-03	g (PE sheet)	887.350713	<LOD	4167.41399	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
4	10/25/18	10/29/18	25	Indoor Air	191-04	g (PE sheet)	4521.06751	<LOD	5059.42502	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8	10/25/18	11/2/18	25	Indoor Air	191-05	g (PE sheet)	16262.1966	481.165197	3690.47837	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
15	10/25/18	11/9/18	25	Indoor Air	191-06	g (PE sheet)	14917.8577	487.910792	6027.39653	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Table 12. Estimated polyethylene/air partitioning values

Amount of compound per volume of sampler							Estimated polyethylene/air partitioning values					Estimated logpolyethylene/air partitioning values			
Name	Sampler	Unit	6:2 FTOH	8:2 FTAc	8:2 FTOH	10:2 FTOH	KPE25a	6:2 FTOH	8:2 FTAc	8:2 FTOH	10:2 FTOH	6:2 FTOH	8:2 FTAc	8:2 FTOH	10:2 FTOH
AS_01	Radiello	pg mL ⁻¹	0.076582	0.001233	0.062563	0.026833	198/Radiello	18821	0	19294	0	log KPE25a	4.27	0.00	4.29 NA
AS_07	Radiello	pg mL ⁻¹	0.098432	0.001582	0.083329	0.023992	198/Radiello	23722	35957	20275	0	log KPE25a	4.38	4.56	4.31 NA
AS_14	Radiello	pg mL ⁻¹	0.033919	0.000884	0.050312	0.022949	198/Radiello	25635	147858	22323	0	log KPE25a	4.41	5.17	4.35 NA
198-09	PE25	pg mL ⁻¹	1311	0	1262	0	198/Radiello	32653	0	0	0	log KPE25a	4.51	0.00	0.00 NA
198-10	PE25	pg mL ⁻¹	1652	44	1326	0	198/Radiello	19186	0	21130	0	log KPE25a	4.28	0.00	4.32 NA
198-11	PE25	pg mL ⁻¹	1785	182	1460	0	198/Radiello	17021	0	16642	0	log KPE25a	4.23	0.00	4.22 NA
198-12	PE25	pg mL ⁻¹	2274	0	0	0	Estimated polyethylene/air partitioning values					Estimated logpolyethylene/air partitioning values			
198-14	PE25	pg mL ⁻¹	1336	0	1382	0									
198-15	PE25	pg mL ⁻¹	1185	0	1088	0	KPE50a	6:2 FTOH	8:2 FTAc	8:2 FTOH	10:2 FTOH	6:2 FTOH	8:2 FTAc	8:2 FTOH	10:2 FTOH
199-09	PE50	pg mL ⁻¹	1609	75	2602	2410	199/Radiello	23110	60950	39790	98002	log KPE50a	4.36	4.78	4.60 4.99
199-10	PE50	pg mL ⁻¹	1570	188	1965	2525	199/Radiello	22546	152335	30046	102671	log KPE50a	4.35	5.18	4.48 5.01
199-11	PE50	pg mL ⁻¹	1400	65	2197	2298	199/Radiello	20103	52818	33589	93438	log KPE50a	4.30	4.72	4.53 4.97
199-12	PE50	pg mL ⁻¹	1265	135	2072	2355	199/Radiello	18159	109117	31685	95784	log KPE50a	4.26	5.04	4.50 4.98
199-13	PE50	pg mL ⁻¹	1351	148	2217	2512	199/Radiello	19396	120279	33902	102161	log KPE50a	4.29	5.08	4.53 5.01
199-14	PE50	pg mL ⁻¹	1367	135	2086	2223	199/Radiello	19623	109148	31896	90380	log KPE50a	4.29	5.04	4.50 4.96
199-15	PE50	pg mL ⁻¹	1323	212	2015	2347	199/Radiello	18999	172271	30814	95437	log KPE50a	4.28	5.24	4.49 4.98

Table 13. *t*-Test: Two-Sample Assuming Unequal Variances between KPE25a and KPE50a

t-Test: Two-Sample Assuming Unequal Variances	6:2 FTOH		8:2FTAc		8:2 FTOH		10:2 FTOH	
	Variable 1	Variable 2	Variable 1	Variable 2	Variable 1	Variable 2	Variable 1	Variable 2
Mean	22840	20276	30636	110988	16611	33103	0	96839
Variance	33648065	3421163	3504712220	1907660609	69919815	10608404	0	20009629
Observations	6	7	6	7	6	7	6	7
Hypothesized Mean Difference	0		0		0		0	
df	6		9		6		6	
t Stat	1.04		-2.75		-4.54		-57.28	
P(T<=t) one-tail	0.17		0.01		0.00		0.00	
t Critical one-tail	1.94		1.83		1.94		1.94	
P(T<=t) two-tail	0.34		0.02		0.00		0.00	
t Critical two-tail	2.45		2.26		2.45		2.45	

Table 14. Concentration of volatile and neutral PFAS in air from an outdoor clothing store

Name	PE thickness (uM)	Days Deployed	Unit	6:2 FTOH	8:2 FTAc	8:2 FTOH	10:2 FTAc	10:2 FTOH	EtFOSA	MeFOSA	MeFOSE	EtFOSE
198-09	25	28	ng m ⁻³	63.64	0.00	68.74	0.02	ND	0.03	0.10	0.18	0.15
198-10	25	28	ng m ⁻³	80.21	0.67	72.24	0.02	ND	0.03	0.11	0.18	0.15
198-11	25	28	ng m ⁻³	86.68	2.73	79.53	0.02	ND	0.03	0.10	0.18	0.14
198-12	25	28	ng m ⁻³	110.41	ND	ND	0.00	ND	0.03	0.05	0.18	0.16
198-13	25	28	ng m ⁻³	ND	ND	ND	0.00	ND	0.02	0.05	0.18	0.14
198-14	25	28	ng m ⁻³	64.88	ND	75.28	0.02	ND	0.04	0.13	0.18	0.17
198-15	25	28	ng m ⁻³	57.55	ND	59.29	0.01	ND	0.02	0.09	0.18	0.12
199-09	50	28	ng m ⁻³	85.68	0.80	85.42	0.02	26.81	ND	0.05	0.18	0.07
199-10	50	28	ng m ⁻³	83.59	1.99	64.50	0.02	28.08	ND	0.05	0.18	0.08
199-11	50	28	ng m ⁻³	74.53	0.69	72.11	0.02	25.56	ND	0.05	0.18	0.08
199-12	50	28	ng m ⁻³	67.33	1.43	68.02	0.02	26.20	ND	0.05	0.18	0.08
199-13	50	28	ng m ⁻³	71.91	1.57	72.78	0.02	27.94	0.01	0.05	0.18	0.07
199-14	50	28	ng m ⁻³	72.75	1.43	68.48	0.02	24.72	0.01	0.05	0.18	0.08
199-15	50	28	ng m ⁻³	70.44	2.26	66.15	0.02	26.10	0.01	0.05	0.18	0.07

<LOD values noted in red. ND refer to not detected. NA refers to information not available.

Table 15. Concentration of volatile and neutral PFAS in air from California kindergarten classrooms

Name	Sample	Unit	Days deployed	Description	6:2 FTOH	8:2 FTAc	8:2 FTOH	10:2 FTAc	10:2 FTOH	EtFOSA	MeFOSA	MeFOSE	EtFOSE
191-09	air	ng m ⁻³	28	KG1	607.9	ND	19.3	ND	5.2	ND	ND	0.03	0.05
191-11	air	ng m ⁻³	28	KG2	20.2	ND	37.6	ND	7.1	ND	ND	0.03	0.07
191-13	air	ng m ⁻³	28	KG3	157.6	ND	159.4	ND	24.1	ND	ND	0.03	0.24
191-14	air	ng m ⁻³	28	KG4	19.0	ND	10.5	ND	5.1	ND	ND	0.03	0.05
191-16	air	ng m ⁻³	28	KG5	21.9	ND	33.5	ND	8.4	ND	ND	0.03	0.08
191-18	air	ng m ⁻³	28	KG6	9.8	ND	2.2	ND	0.0	ND	0.012	0.03	ND
191-19	air	ng m ⁻³	28	KG7	106.0	ND	16.9	ND	6.0	ND	ND	0.03	0.06
191-22	air	ng m ⁻³	28	KG8	180.4	ND	19.0	ND	6.1	ND	ND	0.03	0.06
191-24	air	ng m ⁻³	28	KG9	101.5	ND	4.7	ND	4.8	ND	0.001	0.03	0.05
191-26	air	ng m ⁻³	28	H1	37.0	ND	14.5	ND	5.5	ND	ND	0.03	0.05

<LOD values noted in red. ND refer to not detected. NA refers to information not available

Table 16. Concentration of volatile and neutral PFAS in air from classrooms, offices, and laboratories from the University of Rhode Island, and a carpet store from southern Rhode Island

Location	Sample ID	Sample	Unit	Days Deployed	Observations	6:2 FTOH	8:2 FTAc	8:2 FTOH	10:2 FTAc	10:2 FTOH	MeFOSA	MeFOSE	EtFOSE
Horn 126	194-01	Air	ng m ⁻³	28	Laboratory space with two exhaust hoods	ND	ND	ND	<LOD	ND	ND	0.67	0.23
Horn 120	194-02	Air	ng m ⁻³	28	No carpet, old building, old furniture, no new paint, no open windows, no AC, entrance door open	ND	ND	ND	<LOD	<LOD	0.28	<LOD	<LOD
OSEC elevator	194-03	Air	ng m ⁻³	28	New carpet recently installed, high transit	175	ND	ND	<LOD	ND	0.41	0.36	<LOD
OSEC 115	194-04	Air	ng m ⁻³	28	New carpet and furniture recently installed. No open windows, A/C functioning properly, high transit	229	ND	162	<LOD	<LOD	0.06	<LOD	<LOD
CACS 301	194-05	Air	ng m ⁻³	28	Instrumental analysis space with one exhaust hood. Lab space is dedicated to the analysis of volatile PFAS, along with other emerging contaminants through GC/MS	105	ND	ND	<LOD	11	0.13	<LOD	<LOD
Horn 124	194-06	Air	ng m ⁻³	28	No carpet, old building, old furniture, no new paint, no open windows, no AC, entrance door open	ND	ND	ND	0.08	ND	0.17	<LOD	ND
Watkins 317	194-07	Air	ng m ⁻³	28	Old building, carpet of unknown age, poor ventilation, no A/C	1911	ND	274	ND	34	ND	<LOD	ND
OSEC 118	194-08	Air	ng m ⁻³	28	Small carpeted office space, new furniture, A/C functioning properly, air purifier in corner	ND	ND	ND	<LOD	ND	ND	ND	ND
CI 234	194-09	Air	ng m ⁻³	28	Carpeted office space, unknown age of carpet, no new paint, no open windows, A/C,	ND	ND	ND	<LOD	ND	<LOD	ND	<LOD
RM1	194-10	Air	ng m ⁻³	28	Storage room in OSEC building	ND	ND	ND	0.07	ND	<LOD	0.72	<LOD
Carpet Store	194-11	Air	ng m ⁻³	28	Large storage facility, A/C	703	ND	183	ND	17	ND	<LOD	0.16
Carpet Store dup	194-12	Air	ng m ⁻³	28	Large storage facility, A/C	768	ND	211	<LOD	20	0.16	0.43	0.22

<LOD values noted in red. ND refer to not detected. NA refers to information not available

Table 17. Concentration of volatile and neutral PFAS in air from classrooms, offices and laboratories from the Universidad de Guadalajara-Campus Valles, and nearby homes in Jalisco, Mexico

Sample ID	Sample	Location	Observations	Days deployed	Unit	6:2 FTOH	8:2 FTACr	8:2 FTOH	10:2 FTACr	10:2 FTOH	EtFOSA	MeFOSA	MeFOSE	EtFOSE
192-01	air	Office	Small office, no A/C, cluttered with agricultural instruments, pesticides and fertilizer present, entrance door regularly open	28	ng m ⁻³	ND	ND	0.65	ND	ND	0.00	ND	ND	0.00
192-05	air			28	ng m ⁻³	ND	ND	0.41	ND	ND	0.00	ND	ND	0.00
192-06	air	Auditorium	Carpeted Auditorium, age of carpet and upholstery less than 5 yr, painted less than 1 yr ago, well ventilated	28	ng m ⁻³	ND	ND	0.48	0.03	79.27	0.00	ND	ND	0.00
192-11	air	Lab & class	No carpet, new equipment, well ventilated, open windows, open doors, no A/C	28	ng m ⁻³	ND	ND	0.53	ND	ND	0.00	ND	ND	0.00
192-13	air			28	ng m ⁻³	ND	ND	0.43	ND	ND	0.00	ND	ND	0.00
192-18	air	Home 1	Bedroom, no carpet,	30	ng m ⁻³	ND	ND	0.57	ND	ND	0.00	ND	ND	0.00
192-19	air	Home 2	Bedroom, no carpet, new paint, poor ventilation, windows and door opened rarely	30	ng m ⁻³	ND	ND	0.51	0.02	47.67	0.00	ND	ND	0.00
192-20	air	Home 3	Bedroom, cleaned frequently	30	ng m ⁻³	ND	ND	0.49	ND	ND	0.00	ND	ND	0.00
192-21	air	Home 4	Bedroom next to beauty station, painted wood furniture, cleaned frequently	30	ng m ⁻³	ND	ND	0.52	0.05	56.68	0.00	ND	ND	0.00
192-23	air	Home 5	Guest Bedroom, cleaned frequently, well ventilated. Entrance door usually open	30	ng m ⁻³	ND	ND	0.51	ND	ND	0.00	ND	ND	0.00
192-25	air	Home 6	Living room, no carpet, cleaned frequently, well ventilated. Next to kitchen	30	ng m ⁻³	ND	ND	0.64	0.03	55.55	0.00	0.07	2.04	0.00

<LOD values noted in red. ND refer to not detected. NA refers to information not available

Table 18. Kindergarten classrooms description. Information was gathered and published by Wu et al. (2020)

Sample ID from air sampler project	Room Number	Location of sample	Type of floor covering	Type of hard floor	Sample taken from	Carpets worn or soiled?	Area rugs soiled?	Upholstered furniture present?	Visible dust?	Notes
190/191-02 to -08,	Room 2	Childcare room	Hard + Area rug(s)	Other: Marmoleum	Air/Area rug	NA	No	Yes	No	Tan looped carpet
190/191-14 and -15	Preschool Room	Childcare room (big preschool room)	Wall to wall carpet	NA	Air/Carpet	No	No	Yes	No	Tan and brown low pile tile carpet.
190/191-12 and -13	Children's Room	Childcare room (living room)	Wall to wall carpet	Wood	Air/Carpet	No	No	No	No	Dark Green Plush Carpet.
	Children's Room	Childcare room (play room)	Hard + Area rug(s)	Wood	Air/Area rug	NA	No	No	No	Blue area rug; plush fibers
190/191-19, -20, and -21	Front Door Area	Childcare room (front room, 1st floor)	Wall to wall carpet + area rug(s)	Tile	Air/Carpet	Yes	No	No	No	Low pile, gray looped carpet
	Children's Room	Childcare room (back room, 1st floor)	Wall to wall carpet + area rug(s)	NA	Air/Area rug	No	No	No	No	Circular rainbow yarn rug
	Children's Room	Childcare room (class room, 1st floor)	Wall to wall carpet + area rug(s)	Tile	Air/Area rug	NA	No	No	No	Low pile rug, blue and green
190/191-01 and -09	Red Room	Childcare room (front play room0	Wall to wall carpet	Vinyl (in other rooms)	Air/Carpet	No	No	No	Yes	Low pile gray carpet
190/191-19, -20, and -21	Children's Room (Downstairs)	Childcare room (downstairs classroom)	Wall to wall carpet	Tile (in half of room)	Air/Carpet	No	No	Yes	Yes	Low pile dark gray carpet
	Children's Room (Downstairs)	Childcare room (class room #2)	Wall to wall carpet + area rug(s)	Tile (in half of room)	Air/Area rug	No	No	Yes	No	Circular rainbow yarn rug
190/191-16, -17, & -18	Beluga classroom (Preschool)	Childcare room (back class room)	Hard + Area rug(s)	Marmoleum	Air/Area rug	NA	Yes	Yes	Yes	Plush blue rug
	Downstairs playroom	Childcare room (play room #2 central0	Hard + Area rug(s)	Minoleum	Air/Area rug	NA	No	No	No	Plush gray area rug
	Upstairs Playroom	Childcare room (play room upstairs0	Hard + Area rug(s)	Marmoleum	Air/Area rug	NA	Yes	No	Yes	Blue lady bug plush rug
190/191-10 and -11	Preschool Room	Childcare room (class room)	Wall to wall carpet	NA	Air/Carpet	No	NA	Yes	No	Low pile purple and blue carpet.
190/191-22 and -23	Front Door Area	Other: Front room	Hard + Area rug(s)	Wood	Air/Area rug	NA	No	No	No	Blue and brown low pile plush carpet
	Childcare Room	Childcare room	Hard	Wood	Air/Area rug	NA	No	Yes	No	Light blue and white patterned low pile plush carpet
190/191-24 and -25	Childcare Room	Childcare room to left as you walk in	Hard + Area rug(s)	Vinyl	Air/Area rug	no	No	Yes	Yes	Tan, grey, black shaggy area rug

Table 19. Concentration of volatile and neutral PFAS in dust and carpet from California kindergarten classrooms. Values were obtained and provided by Wu et al. (2020)

Site	Matrix	Unit	6:2 FTOH	8:2 FTOH	10:2 FTOH	8:2 FTAc	10:2 FTAc	MeFOSA	MeFOSE	EtFOSE
KG1	Dust	ng g ⁻¹	571	78.4	105	ND	ND	ND	0.00027788	5.4
KG2	Dust	ng g ⁻¹	110	29.1	6.42	0.97	ND	ND	0.00027788	0.00033415
KG3	Dust	ng g ⁻¹	354	297	356	ND	ND	ND	0.00027788	0.00033415
KG4	Dust	ng g ⁻¹	21.6	13.6	0.00591602	ND	ND	ND	0.00027788	0.00033415
KG5	Dust	ng g ⁻¹	109	13.6	10.2	ND	ND	ND	0.00027788	0.00033415
KG6	Dust	ng g ⁻¹	81.7	31.7	34.5	ND	ND	ND	4.42	7.78
KG7	Dust	ng g ⁻¹	45.9	29	31.1	ND	ND	0.72	123	6.07
KG8	Dust	ng g ⁻¹	87.1	53	23.4	ND	ND	ND	40.7	4.18
KG9	Dust	ng g ⁻¹	63.4	21.6	14.7	ND	ND	ND	0.00027788	0.00033415
KG2	Carpet	ng g ⁻¹	69	13.6	7.9	ND	ND	ND	0.00027788	0.00033415
KG3	Carpet	ng g ⁻¹	317	231	200	ND	ND	0.17	0.00027788	0.00033415
KG4	Carpet	ng g ⁻¹	7.78	12.5	5.17	ND	ND	ND	0.00027788	0.00033415
KG5	Carpet	ng g ⁻¹	322	18.7	0.00591602	ND	ND	ND	0.00027788	67.1
KG6	Carpet	ng g ⁻¹	146	20.6	9.41	ND	ND	ND	0.00027788	0.00033415
KG7	Carpet	ng g ⁻¹	64.4	75.1	35.2	1.11	ND	0.16	122	0.00033415
KG8	Carpet	ng g ⁻¹	72.5	20	0.00591602	ND	ND	ND	8.33	0.00033415
KG9	Carpet	ng g ⁻¹	38.7	14.6	5.34	ND	ND	ND	0.00027788	0.00033415

<LOD values noted in red. ND refer to not detected. NA refers to information not available

Table 20. *t*-Test of air, dust, and carpet from Kindergarten Classrooms

t-Test: Two-Sample Assuming Unequal Variances	air-dust						air-carpet						dust-carpet					
	6:2 FTOH		8:2 FTOH		10:2 FTOH		6:2 FTOH		8:2 FTOH		10:2 FTOH		6:2 FTOH		8:2 FTOH		10:2 FTOH	
	Variable 1	Variable 2	Variable 1	Variable 2	Variable 1	Variable 2	Variable 1	Variable 2	Variable 1	Variable 2	Variable 1	Variable 2	Variable 1	Variable 2	Variable 1	Variable 2	Variable 1	Variable 2
	Variable 1	Variable 2	Variable 1	Variable 2	Variable 1	Variable 2	Variable 1	Variable 2	Variable 1	Variable 2	Variable 1	Variable 2	Variable 1	Variable 2	Variable 1	Variable 2	Variable 1	Variable 2
Mean	136	160	33	63	7	64	136	179	33	47	8	31	160	179	63	47	72	31
Variance	35410	33075	2362	8121	44	12909	35410	35969	2362	5100	41	4111	33075	35969	8121	5100	14083	4111
Observations	9	9	9	9	9	9	9	9	9	9	8	9	9	9	9	9	8	9
Hypothesized Mean Difference	0		0		0		0		0		0		0		0		0	
df	16		12		8		16		14		8		16		15		10	
t Stat	-0.3		-0.9		-1.5		-0.5		-0.5		-1.1		-0.2		0.4		0.9	
P(T<=t) one-tail	0.4		0.2		0.1		0.3		0.3		0.1		0.4		0.3		0.2	
t Critical one-tail	1.7		1.8		1.9		1.7		1.8		1.9		1.7		1.7		1.8	
P(T<=t) two-tail	0.8		0.4		0.2		0.6		0.6		0.3		0.8		0.7		0.4	
t Critical two-tail	2.1		2.2		2.3		2.1		2.1		2.3		2.1		2.1		2.2	

Table 21. . Parameters assigned to individual volatile and neutral PFAS for the estimation of daily PFAA intake by children age 2-6 via air inhalation and dust ingestion.

	C _{air} (ng/m ³)			q _{air} (m ³ /day, Children age 2- <5)			f _{time_in}	m _{bw} (kg)	F _{uptake}			F _{biotransf.}		
	L	M	H	L	M	H			L	M	H	L	M	H
6:2 FTOH	13.92	69.23	415.53	5.49	7.60	9.71	0.90	17.50	0.27	0.38	0.56	0.00	0.01	0.02
8:2 FTOH	3.34	17.95	104.62	5.49	7.60	9.71	0.90	17.50	0.27	0.38	0.56	0.00	0.01	0.02
10:2 FTOH	2.16	5.75	17.00	5.49	7.60	9.71	0.90	17.50	0.27	0.38	0.56	0.00	0.01	0.02
MeFOSE	0.03	0.03	0.03	5.49	7.60	9.71	0.90	17.50	0.66	0.80	0.91	0.10	0.20	0.32
EtFOSE	0.02	0.06	0.17	5.49	7.60	9.71	0.90	17.50	0.66	0.80	0.91	0.10	0.20	0.32
	C _{dust} (ng/g)			q _{dust} (g/day, Children age 2- <5)			f _{time_in}	m _{bw} (kg)	F _{uptake}			F _{biotransf.}		
	L	M	H	L	M	H			L	M	H	L	M	H
6:2 FTOH	31.32	87.10	484.20	0.06	0.06	0.10	0.90	17.50	0.27	0.38	0.56	0.00	0.01	0.02
8:2 FTOH	13.60	29.10	209.56	0.06	0.06	0.10	0.90	17.50	0.27	0.38	0.56	0.00	0.01	0.02
10:2 FTOH	7.74	27.25	268.15	0.06	0.06	0.10	0.90	17.50	0.27	0.38	0.56	0.00	0.01	0.02
MeFOSE	0.00	0.00	90.08	0.06	0.06	0.10	0.90	17.50	0.66	0.80	0.91	0.10	0.20	0.32
EtFOSE	0.00	0.00	7.10	0.06	0.06	0.10	0.90	17.50	0.66	0.80	0.91	0.10	0.20	0.32

The 5th percentile, median, and 95th percentile air and dust concentrations (C_{air}, C_{dust}) were applied for low (L), intermediate (M)

and high (H) exposure scenarios. Dust concentrations were obtained from the work of Wu et al (2020). Quantity (q) of air inhaled,

dust ingested, fraction of time spent indoors (f_{timein}), and body weight (m_{bw}) of children age 2-6 were based on USEPA (2008)

and Winkens et al (2018). The gastrointestinal uptake factor (F_{uptake}) and the biotransformation (F_{biotransformation}) of the volatile

PFAS were provided by Gebbink et al (2015).

Table 22. Concentration of volatile and neutral PFAS in outdoor air and water at different locations around Dhaka, Bangladesh

Location	Latitude	Longitude	Deployed	Retrieved	Notes	PE sheet	Type	Unit	6:2 FTOH	8:2 FTAc	8:2 FTOH	10:2 FTAc	10:2 FTOH	EtFOSA	MeFOSA	MeFOSE	EtFOSE
Gazipur Metropolitan City	23.981129	90.337443	24-Jan-20	28-Feb-20	Wastewater outlet of Gazipur metropolitan city. There are many textile and sweater industries here	25 um	air	ng m ⁻³	53	ND	ND	ND	18	<LOD	<LOD	0.24	<LOD
Balshi river, Savar Bank Town	23.817976	90.257421	30-Jan-20	3-Mar-20	Heavily textile, dyeing and other industries wastewater direct discharge	25 um	air	ng m ⁻³	ND	ND	ND	ND	14	<LOD	<LOD	0.12	<LOD
Turag river_1	23.884597	90.392615	31-Jan-20	3-Mar-20	One of the most polluted rivers by many industries in Bangladesh	25 um	air	ng m ⁻³	ND	ND	ND	ND	ND	<LOD	<LOD	<LOD	<LOD
Dhanmondi Lake, Dhaka	23.743232	90.377405	1-Feb-20	3-Mar-20	Household and some unknown industries here	25 um	air	ng m ⁻³	55	ND	ND	ND	20	<LOD	<LOD	<LOD	<LOD
Gulshan Lake, Dhaka	23.794233	90.421494	8-Feb-20	10-Mar-20	Mainly Household wastewater	25 um	air	ng m ⁻³	57	ND	ND	ND	ND	<LOD	<LOD	<LOD	<LOD
Hatirjheel Lake, Dhaka	23.775457	90.419685	8-Feb-20	10-Mar-20	Household and some heavy industries here	25 um	air	ng m ⁻³	ND	ND	ND	ND	ND	<LOD	<LOD	<LOD	<LOD
Demra-1	23.7196881	90.4485566	1-Feb-20	3-Mar-20	Municipal solid waste dumping site	25 um	air	ng m ⁻³	50	ND	47	ND	ND	<LOD	<LOD	<LOD	<LOD
Demra-2	23.7173201	90.4490118	1-Feb-20	3-Mar-20	Medical waste incineration plant	25 um	air	ng m ⁻³	44	ND	47	ND	17	<LOD	<LOD	<LOD	<LOD
Amin Bazar, Dhaka	23.793963	90.299432	30-Jan-20	28-Feb-20	Municipal solid waste dumping site	25 um	air	ng m ⁻³	ND	ND	ND	ND	17	<LOD	<LOD	<LOD	<LOD
Gazipur Metropolitan City	23.981129	90.337443	24-Jan-20	28-Feb-20	Wastewater outlet of Gazipur metropolitan city. There are many textile and sweater industries here	50 um	air	ng m ⁻³	71	8	31	ND	18	<LOD	<LOD	<LOD	<LOD
Balshi river, Savar Bank Town	23.817976	90.257421	30-Jan-20	3-Mar-20	Heavily textile, dyeing and other industries wastewater direct discharge	50 um	air	ng m ⁻³	29	ND	ND	ND	9	<LOD	<LOD	<LOD	<LOD
Turag river_1	23.884597	90.392615	31-Jan-20	3-Mar-20	One of the most polluted rivers by many industries in Bangladesh	50 um	air	ng m ⁻³	ND	ND	ND	ND	ND	<LOD	<LOD	<LOD	<LOD
Turag river_2	23.881722	90.406183	31-Jan-20	3-Mar-20	One of the most polluted rivers by many industries in Bangladesh	50 um	air	ng m ⁻³	ND	ND	ND	ND	10	<LOD	<LOD	<LOD	<LOD

Dhanmondi Lake, Dhaka	23.743232	90.377405	1-Feb-20	3-Mar-20	Household and some unknown industries here	50 um	air	ng m ⁻³	42	ND	ND	ND	9	<LOD	<LOD	<LOD	<LOD
Gulshan Lake, Dhaka	23.794233	90.421494	8-Feb-20	10-Mar-20	Mainly Household wastewater	50 um	air	ng m ⁻³	27	4	ND	ND	ND	<LOD	<LOD	<LOD	<LOD
Hatirjheel Lake, Dhaka	23.775457	90.419685	8-Feb-20	10-Mar-20	Household and some heavy industries here	50 um	air	ng m ⁻³	ND	5	ND	ND	ND	<LOD	<LOD	<LOD	<LOD
Demra-1	23.7196881	90.4485566	1-Feb-20	3-Mar-20	Municipal solid waste dumping site	50 um	air	ng m ⁻³	33	ND	17	ND	10	<LOD	<LOD	<LOD	<LOD
Demra-2	23.7173201	90.4490118	1-Feb-20	3-Mar-20	Medical waste incineration plant	50 um	air	ng m ⁻³	27	ND	15	ND	9	<LOD	<LOD	<LOD	<LOD
Amin Bazar, Dhaka	23.793963	90.299432	30-Jan-20	28-Feb-20	Municipal solid waste dumping site	50 um	air	ng m ⁻³	ND	4	ND	ND	9	<LOD	<LOD	<LOD	<LOD
Gazipur Metropolitan City	23.981129	90.337443	24-Jan-20	28-Feb-20	Wastewater outlet of Gazipur metropolitan city. There are many textile and sweater industries here	25 um	water	ng L ⁻¹	2	ND	0.05	ND	0.05	<LOD	<LOD	<LOD	<LOD
Balshi river, Savar Bank Town	23.817976	90.257421	30-Jan-20	3-Mar-20	Heavily textile, dyeing and other industries wastewater direct discharge	25 um	water	ng L ⁻¹	20	ND	0.06	ND	0.06	<LOD	<LOD	<LOD	<LOD
Dhanmondi Lake, Dhaka	23.743232	90.377405	1-Feb-20	3-Mar-20	Household and some unknown industries here	25 um	water	ng L ⁻¹	ND	ND	ND	ND	ND	<LOD	<LOD	<LOD	<LOD
Hatirjheel Lake, Dhaka	23.775457	90.419685	8-Feb-20	10-Mar-20	Household and some heavy industries here	25 um	water	ng L ⁻¹	ND	ND	ND	ND	ND	<LOD	<LOD	<LOD	<LOD
Gazipur Metropolitan City	23.981129	90.337443	24-Jan-20	28-Feb-20	Wastewater outlet of Gazipur metropolitan city. There are many textile and sweater industries here	50 u	water	ng L ⁻¹	1	ND	0.03	ND	0.03	<LOD	<LOD	<LOD	<LOD
Balshi river, Savar Bank Town	23.817976	90.257421	30-Jan-20	3-Mar-20	Heavily textile, dyeing and other industries wastewater direct discharge	50 um	water	ng L ⁻¹	11	ND	0.03	ND	0.03	<LOD	<LOD	<LOD	<LOD
Dhanmondi Lake, Dhaka	23.743232	90.377405	1-Feb-20	3-Mar-20	Household and some unknown industries here	50 um	water	ng L ⁻¹	1	ND	ND	ND	ND	<LOD	<LOD	<LOD	<LOD
Hatirjheel Lake, Dhaka	23.775457	90.419685	8-Feb-20	10-Mar-20	Household and some heavy industries here	50 um	water	ng L ⁻¹	1	ND	ND	ND	0.03	<LOD	<LOD	<LOD	<LOD

<LOD values noted in red. ND refer to not detected. NA refers to information not available

Table 23. Concentration of volatile and neutral PFAS in outdoor air and water from the Canadian Arctic, and from and around the Great Lakes

Latitude	Longitude	Location	Deployment (dd/mm/yyyy)	Recovery (dd/mm/yyyy)	Water °C	Air °C	Notes	Unit	Matrix	6:2 FTOH	8:2 FTAc	8:2 FTOH	10:2 FTAc	10:2 FTOH
N69.2368167	W-106.4468167	Arctic, Wellington Bay	04/082018	43563	NA	5		ng m ⁻³	air	ND	ND	ND	ND	6
N42°35'56"	W79°55'18"	Lake Erie 1	15/04/2019	28/10/2019	NA	NA	depth of deployment met buoy arm	ng m ⁻³	air	23	ND	ND	ND	ND
N42°56'14"	W81°38'58"	Strathroy, ON, CAN	NA	20/10/2019	NA	NA		ng m ⁻³	air	ND	ND	ND	ND	ND
N41°48'52"	W82°59'15"	Lake Erie 3	NA	19/10/2020	NA	NA		ng m ⁻³	air	29	ND	16	ND	ND
N43°15'32"	W79°32'19"	Lake Ontario	16/04/2019	19/11/2019	3.8	5		ng m ⁻³	air	ND	ND	ND	ND	ND
N42°30'37"	W77°05'07"	Barrington, NY, USA	16/04/2019	43688	1.5	5		ng m ⁻³	air	31	ND	17	ND	ND
N43°20'22"	W79°39'46"	Lake Erie 4	18/04/2019	43688	2	10		ng m ⁻³	air	ND	ND	ND	ND	ND
N74°41'21.9"	W95°05'38.3"	Arctic, Marks' Point	43231	43621	0	-15		ng L ⁻¹	water	ND	ND	ND	ND	ND
N74°41'21.9"	W95°05'38.3"	Arctic, Marks' Point	43231	43621	0	-15		ng L ⁻¹	water	ND	ND	ND	ND	0.02
N41°56'12"	W81°38'42"	Lake Erie 2	NA	20/10/2019	NA	NA		ng L ⁻¹	water	ND	ND	ND	ND	ND
N41°48'54"	W82°59'23"	Lake Erie 3	NA	19/10/2019	NA	NA	Depth of deployment 5 m	ng L ⁻¹	water	ND	ND	ND	ND	ND
N43°20'22"	W79°39'46"	Lake Erie 4	15/04/2019	28/10/2019	1.6	2		ng L ⁻¹	water	1	ND	ND	ND	ND
N74°37'06"	W94°44'09"	Arctic, First PS	43529	16/06/2019	0	-11	ice sheet of 1.42 cm, then PE at 2 m below ice, vertical	ng L ⁻¹	water	1	ND	ND	ND	ND
N74°37'06"	W94°44'10"	Arctic, First PS	43530	16/06/2019	0	-11	ice sheet of 1.42 cm, then PE at 2 m below ice, vertical	ng L ⁻¹	ice	1	ND	0.02	ND	ND

<LOD values noted in red. ND refer to not detected. NA refers to information not available

Chapter 9

9.0 Bibliography

- Adams, R. *et al.* (2007) 'Polyethylene Devices: Passive Samplers for Measuring Dissolved Hydrophobic Organic Compounds in Aquatic Environments', *Environ. Sci. Technol.* doi: 10.1021/es0621593.
- Ahmed, R. and Kim, I. (2003) 'Patterns of Daily Rainfall in Bangladesh During the Summer Monsoon Season: Case Studies at Three Stations', *Physical Geography*. doi: 10.2747/0272-3646.24.4.295.
- Ahrens, L., Shoeib, M., Harner, T., *et al.* (2011) 'Comparison of Annular Diffusion Denuder and High Volume Air Samplers for Measuring Per- and Polyfluoroalkyl Substances in the Atmosphere', *Anal. Chem*, 83, pp. 9622–9628. doi: 10.1021/ac202414w.
- Ahrens, L. (2011) 'Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate', *J. Environ. Monit.* The Royal Society of Chemistry, 13(1), pp. 20–31. doi: 10.1039/C0EM00373E.
- Ahrens, L., Shoeib, M., Del Vento, S., *et al.* (2011) 'Polyfluoroalkyl compounds in the Canadian Arctic atmosphere', *Environmental Chemistry*, 8(4), pp. 399–406. doi: 10.1071/EN10131.
- Armitage, J., Macleod, M. and Cousins, I. (2009) 'Comparative assessment of the global fate and transport pathways of long-chain perfluorocarboxylic acids (PFCAs) and perfluorocarboxylates (PFCs) emitted from direct sources', *Environmental Science and Technology*, 43(15), pp. 5830–5836. doi: 10.1021/es900753y.
- Arvaniti, O. S. and Stasinakis, A. S. (2015) 'Review on the occurrence, fate

- and removal of perfluorinated compounds during wastewater treatment’, *Science of the Total Environment*. Elsevier, pp. 81–92. doi: 10.1016/j.scitotenv.2015.04.023.
- Back, D. Y. *et al.* (2021) ‘On the impact of wastewater effluent on phytoplankton in the Arctic coastal zone: A case study in the Kitikmeot Sea of the Canadian Arctic’, *Science of the Total Environment*. Elsevier B.V., 764. doi: 10.1016/j.scitotenv.2020.143861.
 - Bartkow, M. E. *et al.* (2005) ‘Passive air sampling theory for semivolatile organic compounds’, *Chemosphere*. Pergamon, 60(2), pp. 170–176. doi: 10.1016/J.CHEMOSPHERE.2004.12.033.
 - Bilder, R. B. (1972) *Controlling Great Lakes Pollution: A Study in United States-Canadian Environmental Cooperation*, Source: *Michigan Law Review*.
 - Booij, K., Sleiderink, H. M. and Smedes, F. (1998) ‘Calibrating the uptake kinetics of semipermeable membrane devices using exposure standards’, *Environmental Toxicology and Chemistry*, 17(7), pp. 1236–1245. doi: 10.1897/1551-5028(1998)017<1236:CTUKOS>2.3.CO;2.
 - Booij, K. and Smedes, F. (2010) ‘An improved method for estimating in situ sampling rates of nonpolar passive samplers’, *Environmental Science and Technology*. American Chemical Society, 44(17), pp. 6789–6794. doi: 10.1021/es101321v.
 - Brendel, S. *et al.* (2018) ‘Short-chain perfluoroalkyl acids: environmental concerns and a regulatory strategy under REACH’, *Environmental Sciences Europe*. Springer Verlag, 30(1). doi: 10.1186/s12302-018-0134-4.
 - Buck, R. C. *et al.* (2011) ‘Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins’, *Integrated*

Environmental Assessment and Management. doi: 10.1002/ieam.258.

- Butt, C. M., Muir, D. C. G. and Mabury, S. A. (2010) 'Biotransformation of the 8:2 fluorotelomer acrylate in rainbow trout. 1. In vivo dietary exposure', *Environmental Toxicology and Chemistry*, 29(12), pp. 2726–2735. doi: 10.1002/etc.349.
- Cabrerizo, A. *et al.* (2018) 'Legacy and Emerging Persistent Organic Pollutants (POPs) in Terrestrial Compartments in the High Arctic: Sorption and Secondary Sources'. doi: 10.1021/acs.est.8b05011.
- Chen, H. *et al.* (2017) 'Detection, Occurrence, and Fate of Fluorotelomer Alcohols in Municipal Wastewater Treatment Plants'. doi: 10.1021/acs.est.7b00315.
- Codling, G. *et al.* (2014) 'Historical trends of inorganic and organic fluorine in sediments of Lake Michigan', *Chemosphere*. Elsevier Ltd, 114, pp. 203–209. doi: 10.1016/j.chemosphere.2014.03.080.
- Codling, G. *et al.* (2018) 'Spatial and temporal trends in poly- and per-fluorinated compounds in the Laurentian Great Lakes Erie, Ontario and St. Clair', *Environmental Pollution*. Elsevier Ltd, 237, pp. 396–405. doi: 10.1016/j.envpol.2018.02.013.
- Dey, S. and Islam, A. (2015) 'A Review on Textile Wastewater Characterization in Bangladesh', *Resources and Environment*, 5(1), pp. 15–44. doi: 10.5923/j.re.20150501.03.
- Dixon-Anderson, E. and Lohmann, R. (2018) 'Field-testing polyethylene passive samplers for the detection of neutral polyfluorinated alkyl substances in air and water', *Environmental Toxicology and Chemistry*. doi: 10.1002/etc.4264.

- Dreyer, A. *et al.* (2009) ‘Polyfluorinated compounds in the atmosphere of the Atlantic and Southern Oceans: Evidence for a global distribution’, *Environmental Science and Technology*. American Chemical Society, 43(17), pp. 6507–6514. doi: 10.1021/es9010465.
- Dreyer, A., Langer, V. and Ebinghaus, R. (2009) ‘Determination of Octanol-Air Partition Coefficients (K_{OA}) of Fluorotelomer Acrylates, Perfluoroalkyl Sulfonamids, and Perfluoroalkylsulfonamido Ethanols’, *Journal of Chemical Engineering*, pp. 3022–3025. doi: 10.1021/je900082g.
- Ellis, D. A. *et al.* (2004a) ‘Degradation of Fluorotelomer Alcohols: A Likely Atmospheric Source of Perfluorinated Carboxylic Acids’, *Environmental Science & Technology*, 38(12), pp. 3316–3321. doi: 10.1021/es049860w.
- Endo, S. and Goss, K.-U. (2014) ‘Applications of Polyparameter Linear Free Energy Relationships in Environmental Chemistry’. doi: 10.1021/es503369t.
- EPA (2009) *Long-Chain Perfluorinated Chemicals (PFCs) Action Plan*. Available at: <http://www.epa.gov/pbt/>. (Accessed: 20 March 2020).
- EPA, U. (2006) *Invitation Letter to 2010/2015 PFOA Stewardship Program of Former Administrator Stephen L. Johnson*. Available at: <https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/letter-inviting-participation-pfoa-stewardship-program> (Accessed: 18 June 2020).
- Ericson Jogsten, I. *et al.* (2012) ‘Per- and polyfluorinated compounds (PFCs) in house dust and indoor air in Catalonia, Spain: Implications for human exposure’, *Environment International*, 39, pp. 172–180. doi: 10.1016/j.envint.2011.09.004.
- Eriksson, U., Haglund, P. and Kärman, A. (2017) ‘Contribution of precursor compounds to the release of per- and polyfluoroalkyl substances (PFASs) from

waste water treatment plants (WWTPs)’. doi: 10.1016/j.jes.2017.05.004.

- De Fátima Alpendurada, M. (2000) ‘Solid-phase microextraction: A promising technique for sample preparation in environmental analysis’, in *Journal of Chromatography A*. Elsevier, pp. 3–14. doi: 10.1016/S0021-9673(00)00453-2.
- Fraser, A. J. *et al.* (2011) ‘Polyfluorinated Compounds in Serum Linked to Indoor Air in Office Environments’. doi: 10.1021/es2038257.
- Fromme, H. *et al.* (2015) ‘Neutral polyfluorinated compounds in indoor air in Germany - “ The LUPE 4 study’’, *Chemosphere*. doi: 10.1016/j.chemosphere.2015.07.024.
- Gebbink, W., Berger, U. and Cousins, I. (2015) ‘Estimating human exposure to PFOS isomers and PFCA homologues: The relative importance of direct and indirect (precursor) exposure’, *Environment International*. Elsevier Ltd, 74, pp. 160–169. doi: 10.1016/j.envint.2014.10.013.
- Giesy, John P. and Kannan, K. (2001) ‘Global distribution of perfluorooctane sulfonate in wildlife’, *Environmental Science and Technology*. American Chemical Society , 35(7), pp. 1339–1342. doi: 10.1021/es001834k.
- Giovanoulis, G. *et al.* (2019) ‘Reduction of hazardous chemicals in Swedish preschool dust through article substitution actions’, *Environment International*. Elsevier, 130(May), p. 104921. doi: 10.1016/j.envint.2019.104921.
- Goosey, E. and Harrad, S. (2012) ‘Perfluoroalkyl substances in UK indoor and outdoor air: Spatial and seasonal variation, and implications for human exposure’, *Environment International*. Elsevier Ltd, 45(1), pp. 86–90. doi: 10.1016/j.envint.2012.04.007.

- Gremmel, C. *et al.* (2016) ‘Systematic determination of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in outdoor jackets’. doi: 10.1016/j.chemosphere.2016.06.043.
- Habibullah-Al-Mamun, M. *et al.* (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*. Elsevier B.V., 571, pp. 1089–1104. doi: 10.1016/j.scitotenv.2016.07.104.
- Habibullah-Al-Mamun, M. *et al.* (2017) ‘Occurrence and assessment of perfluoroalkyl acids (PFAAs) in commonly consumed seafood from the coastal area of Bangladesh’. doi: 10.1016/j.marpolbul.2017.02.053.
- Hansen, K. J. *et al.* (2001) ‘Compound-Specific, Quantitative Characterization of Organic Fluorochemicals in Biological Matrices’, *Environ. Sci. Technol.* doi: 10.1021/es001489z.
- Haug, L. *et al.* (2011) ‘Investigation on Per-and Polyfluorinated Compounds in Paired Samples of House Dust and Indoor Air from Norwegian Homes’, *Environ. Sci. Technol.*, 45, pp. 7991–7998. doi: 10.1021/es103456h.
- Houtz, E. F. *et al.* (2016) ‘Poly- and perfluoroalkyl substances in wastewater: Significance of unknown precursors, manufacturing shifts, and likely AFFF impacts’, *Water Research*. Elsevier Ltd, 95, pp. 142–149. doi: 10.1016/j.watres.2016.02.055.
- Huber, S., Haug, L. and Schlabach, M. (2011) ‘Per-and polyfluorinated compounds in house dust and indoor air from northern Norway-A pilot study’. doi: 10.1016/j.chemosphere.2011.04.075.
- IPEN (2019) *PFAS POLLUTION ACROSS THE MIDDLE EAST AND ASIA*.

- ITRC (2020) *History and Use of Per-and Polyfluoroalkyl Substances (PFAS)*. Available at: https://pfas-1.itrcweb.org/fact_sheets_page/PFAS_Fact_Sheet_History_and_Use_April2020 (Accessed: 30 December 2020).
- Jahnke, A., Huber, S., *et al.* (2007a) ‘Development and application of a simplified sampling method for volatile polyfluorinated alkyl substances in indoor and environmental air’, *Journal of Chromatography A*, 1164, pp. 1–9. doi: 10.1016/j.chroma.2007.06.068.
- Jahnke, A., Ahrens, L., *et al.* (2007) ‘Urban versus remote air concentrations of fluorotelomer alcohols and other polyfluorinated alkyl substances in Germany’, *Environmental Science and Technology*, 41(3), pp. 745–752. doi: 10.1021/es0619861.
- Joyce, M., Dinglasan-Panlilio, A. and Mabury, S. (2006) ‘Significant Residual Fluorinated Alcohols Present in Various Fluorinated Materials’. American Chemical Society. doi: 10.1021/es051619.
- Kannan, K. *et al.* (2001) ‘Research Perfluorooctane Sulfonate in Fish-Eating Water Birds Including Bald Eagles and Albatrosses’. doi: 10.1021/es001935i.
- Kannan, K. *et al.* (2002) ‘Perfluorooctane Sulfonate in Oysters, *Crassostrea virginica*, from the Gulf of Mexico and the Chesapeake Bay, USA’. doi: 10.1007/s00244-001-0003-8.
- Khairy, M. A. and Lohmann, R. (2019) ‘Organophosphate flame retardants in the indoor and outdoor dust and gas-phase of Alexandria, Egypt’, *Chemosphere*. Elsevier Ltd, 220, pp. 275–285. doi: 10.1016/j.chemosphere.2018.12.140.
- Langer, V., Dreyer, A. and Ebinghaus, R. (2010) ‘Polyfluorinated Compounds

in Residential and Nonresidential Indoor Air', *Environmental Science and Technology*. doi: 10.1021/es102384z.

- Li, L. *et al.* (2015) 'Estimating industrial and domestic environmental releases of perfluorooctanoic acid and its salts in China from 2004 to 2012', *Chemosphere*. doi: 10.1016/j.chemosphere.2014.11.049.
- Liu, W. *et al.* (2012) 'Polyfluorinated telomers in indoor air of Japanese houses'. doi: 10.1016/j.chemosphere.2012.09.062.
- Liu, X. *et al.* (2015) 'Determination of fluorotelomer alcohols in selected consumer products and preliminary investigation of their fate in the indoor environment', *Chemosphere*. Elsevier Ltd, 129, pp. 81–86. doi: 10.1016/j.chemosphere.2014.06.012.
- Lohmann, R. *et al.* (2007) 'Global fate of POPs: Current and future research directions', *Environmental Pollution*. Elsevier, 150(1), pp. 150–165. doi: 10.1016/j.envpol.2007.06.051.
- 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'. doi: 10.1021/es202702y.
- Lohmann, R. *et al.* (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*. doi: 10.1007/s11356-012-0748-9.
- Marchal, P., Ozanne, G. and Vasseur, P. (1998) *Glass Test Chamber Model to Evaluate Pesticide Air Emissions from Treated Wood Key Words Wood preservative Fungicide Pentachlorophenol PCP PCPNa*.

- Martin, J. W. *et al.* (2002) ‘Collection of Airborne Fluorinated Organics and Analysis by Gas Chromatography/Chemical Ionization Mass Spectrometry’. doi: 10.1021/ac015630d.
- McGoldrick, D. J. and Murphy, E. W. (2015) ‘Concentration and distribution of contaminants in lake trout and walleye from the Laurentian Great Lakes (2008e2012) *’. doi: 10.1016/j.envpol.2015.12.019.
- Petty, J. D. *et al.* (2000) ‘Considerations involved with the use of semipermeable membrane devices for monitoring environmental contaminants’, in *Journal of Chromatography A*. Elsevier, pp. 83–95. doi: 10.1016/S0021-9673(00)00315-0.
- Prevedouros, K. *et al.* (2006) ‘Critical Review Sources, Fate and Transport of Perfluorocarboxylates’, *Environmental Science & Technology*. doi: 10.1021/es0512475.
- Routti, H. *et al.* (2016) ‘Spatial and temporal trends in perfluoroalkyl substances (PFASs) in ringed seals (*Pusa hispida*) from Svalbard *’. doi: 10.1016/j.envpol.2016.04.016.
- Russell, M. *et al.* (2008) ‘Investigation of the Biodegradation Potential of a Fluoroacrylate Polymer Product in Aerobic Soils’, *Environ. Sci. Technol.*, (42), pp. 800–807. doi: 10.1021/es0710499.
- Schlummer, M. *et al.* (2013) ‘Detection of fluorotelomer alcohols in indoor environments and their relevance for human exposure’, *Environment International*, 57–58, pp. 42–49. doi: 10.1016/j.envint.2013.03.010.
- Sharma, B. *et al.* (2016) ‘Perfluoroalkyl substances (PFAS) in river and ground/drinking water of the Ganges River basin: Emissions and implications for human exposure’, *Environmental Pollution*. doi:

10.1016/j.envpol.2015.10.050.

- Shoeib, M. *et al.* (2004) 'Indoor and Outdoor Air Concentrations and Phase Partitioning of Perfluoroalkyl Sulfonamides and Polybrominated Diphenyl Ethers', *Environmental Science & Technology*. doi: 10.1021/es0305555.
- Shoeib, M. *et al.* (2005) 'Perfluorinated Sulfonamides in Indoor and Outdoor Air and Indoor Dust: Occurrence, Partitioning, and Human Exposure', *Environmental Science & Technology*. doi: 10.1021/es048340y.
- Shoeib, M. *et al.* (2011) 'Indoor Sources of Poly-and Perfluorinated Compounds (PFCS) in Vancouver, Canada: Implications for Human Exposure', *Environ. Sci. Technol*, 45, pp. 7999–8005. doi: 10.1021/es103562v.
- De Silva, A. O. and A. Mabury, S. (2004) 'Isolating Isomers of Perfluorocarboxylates in Polar Bears (*Ursus maritimus*) from Two Geographical Locations', *Environmental Science & Technology*. doi: 10.1021/es049296p.
- Smith, J. *et al.* (2016) *Environmental fate and effects of poly-and perfluoroalkyl substances (PFAS) Prepared for the Concauwe Soil and Groundwater Taskforce (STF/33)*. Available at: <https://www.concauwe.eu/publication/environmental-fate-and-effects-of-poly-and-perfluoroalkyl-substances-pfas-report-no-816/> (Accessed: 11 January 2021).
- Stock, N. *et al.* (2004) 'Polyfluorinated Telomer Alcohols and Sulfonamides in the North American Troposphere', *Environmental Science and Technology*. doi: 10.1021/es034644t.
- Stock, N. *et al.* (2007) 'Perfluoroalkyl Contaminants in the Canadian Arctic:

Evidence of Atmospheric Transport and Local Contamination’, *Environ. Sci. Technol*, (41). doi: 10.1021/es062709x.

- Stockholm Convention (2009) *C.N.524.2009.TREATIES-4 (Depositary Notification)*.
- Sunderland, E. M. *et al.* (2019) ‘A Review of the Pathways of Human Exposure to Poly-and Perfluoroalkyl Substances (PFASs) and Present Understanding of Health Effects HHS Public Access’, *J Expo Sci Environ Epidemiol*, 29(2), pp. 131–147. doi: 10.1038/s41370-018-0094-1.
- Tremblay, N. W. and Gilman, A. R. (1995) *Human Health, the Great Lakes, and Environmental Pollution: A 1994 Perspective, Environ Health Perspect.*
- USEPA (2008) *Exposure Factors Handbook (EFH)*, *Epa/600/C-90/001*.
- Venkatesan, A. K. and 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*. Elsevier, 252–253, pp. 413–418. doi: 10.1016/j.jhazmat.2013.03.016.
- Vestergren, R. *et al.* (2008) ‘Estimating the contribution of precursor compounds in consumer exposure to PFOS and PFOA’, *Chemosphere*, 73, pp. 1617–1624. doi: 10.1016/j.chemosphere.2008.08.011.
- Vrana, B. *et al.* (2001) ‘Membrane-enclosed sorptive coating. An integrative passive sampler for monitoring organic contaminants in water’, *Analytical Chemistry*. American Chemical Society , 73(21), pp. 5191–5200. doi: 10.1021/ac010630z.
- Walker, V. K. *et al.* (2020) ‘Identification of Arctic Food Fish Species for Anthropogenic Contaminant Testing Using Geography and Genetics’, *Foods*, 9(12), p. 1824. doi: 10.3390/foods9121824.

- Wang, Z. *et al.* (2014) ‘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, pp. 62–75. doi: 10.1016/j.envint.2014.04.013.
- Wang, Z. *et al.* (2017) ‘A Never-Ending Story of Per-and Polyfluoroalkyl Substances (PFASs)?’ doi: 10.1021/acs.est.6b04806.
- Winkens, K. *et al.* (2017a) ‘Perfluoroalkyl acids and their precursors in indoor air sampled in children’s bedrooms’, *Environmental Pollution*. Elsevier Ltd, 222, pp. 423–432. doi: 10.1016/j.envpol.2016.12.010.
- Winkens, K. *et al.* (2018) ‘Perfluoroalkyl acids and their precursors in floor dust of children’s bedrooms – Implications for indoor exposure’, *Environment International*. Elsevier, 119(June), pp. 493–502. doi: 10.1016/j.envint.2018.06.009.
- Wu, Y. *et al.* (2020) ‘Per-and polyfluoroalkyl substances in paired dust and carpets from childcare centers’, *Chemosphere*. doi: 10.1016/j.chemosphere.2020.126771.
- Xie, Z. *et al.* (2015) ‘Neutral Poly-/perfluoroalkyl Substances in Air and Snow from the Arctic’, *Scientific Reports*, 5, pp. 1–6. doi: 10.1038/srep08912.
- Yunus, M. and 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*. Chousakenkyo Houkokusho: IDE-JETRO.