



Indoor exposure to per- and polyfluoroalkyl substances (PFAS) in the childcare environment

Guomao Zheng^a, Brandon E. Boor^{b, c}, Erika Schreder^d, Amina Salamova^{a, *}

^a O'Neill School of Public and Environmental Affairs, Indiana University, Bloomington, IN 47405, United States

^b Lyles School of Civil Engineering, Purdue University, 550 Stadium Mall Drive, West Lafayette, IN 47907, United States

^c Ray W. Herrick Laboratories, Center for High Performance Buildings, Purdue University, 177 South Russell Street, West Lafayette, IN 47907, United States

^d Toxic Free Future, 4649, Sunnyside Ave N., Suite 540, Seattle, WA, 98103, United States

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ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are widely used in stain-resistant carpets, rugs, and upholstery, as well as in waxes and cleaners, and are potential contaminants in the childcare environment. However, limited knowledge exists on the occurrence of PFAS in indoor environments, apart from residential homes. Here, we determined the occurrence and distribution of 37 neutral and ionic PFAS, including perfluoroalkyl carboxylates (PFCAs) perfluoroalkyl sulfonates (PFSAs), fluorotelomer alcohols (FTOHs), fluorotelomer sulfonates (FTSs), perfluorooctane sulfonamides and perfluorooctane sulfonamidoethanols (FOSAs/FOSEs), and fluorotelomer acrylates and fluorotelomer methacrylates (FTACs/FTMACs) in the childcare environment and estimated children's exposure through dust ingestion and dermal absorption. We analyzed dust and nap mats, a commonly used item in many childcares, from eight facilities located in the United States. Twenty-eight PFAS were detected in dust with total PFAS concentrations (Σ PFAS) ranging from 8.1 to 3,700 ng/g and were dominated by the two neutral PFAS groups: Σ FTOH (n.d. – 3,100 ng/g) and Σ FOSA/FOSE (n.d. – 380 ng/g). The ionic PFAS were detected at lower concentrations and were dominated by 6:2 FTS and 8:2 FTS (median 12 and 5.8 ng/g, respectively). Σ PFAS concentrations in mats (1.6–600 ng/g) were generally an order of magnitude lower than in dust and were dominated by Σ FOSA/FOSE concentrations (n.d. – 220 ng/g). Daily intake of neutral PFAS in the childcare environment via dust ingestion was estimated at 0.20 ng/kg bw/day and accounted for 75% of the Σ PFAS intake. This higher exposure to neutral PFAS is concerning considering that many neutral PFAS are the precursors of toxic ionic PFAS, such as PFOA.

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1. Introduction

Per- and polyfluoroalkyl substances (PFAS) have been used in applications such as water- and grease-proof coatings, surfactants, lubricants in paper, textile coatings, polishes, food packaging, and fire-fighting foams for more than 60 years (Prevedouros et al., 2006). The PFAS family includes more than 4,700 different compounds (OECD, 2018) that can be divided into ionic and neutral chemical groups (Buck et al., 2011). Perfluoroalkyl sulfonates (PFSAs) and perfluoroalkyl carboxylates (PFCAs) are the two major categories of ionic PFAS and include the well-known perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA).

After the phase out of PFOS and PFOA (Buck et al., 2011; Wang et al., 2017), shorter carbon-chain ionic and neutral PFAS are now being increasingly used as their replacements (Field and Seow, 2017). Neutral PFAS are generally considered to be precursors of the ionic PFAS (Buck et al., 2011) and include fluorotelomer alcohols (FTOHs), perfluorooctane sulfonamides (FOSAs), perfluorooctane sulfonamidoethanols (FOSEs), fluorotelomer acrylates (FTACs), and fluorotelomer methacrylates (FTMACs) that degrade or metabolize to ionic PFAS (Ellis et al., 2004; Martin et al., 2005; Nabb et al., 2007; Seacat et al., 2003). PFAS have been widely detected in the environment, including air, water, and soil (Jian et al., 2017), as well as in wildlife and humans around the world (Delinsky et al., 2010; Field and Seow, 2017; Lee and Mabury, 2011; Zhang et al., 2010). Multiple studies have reported the adverse effects of PFAS on human health, including disrupting of the immune system, affecting the growth and learning abilities in children, and increasing the risk of cancer

* Corresponding author.

E-mail address: asalamov@indiana.edu (A. Salamova).

(Rappazzo et al., 2017; Sunderland et al., 2019).

Indoor environments are a major source of PFAS due to the presence of PFAS-containing consumer and commercial products, including stain- and water-resistant carpeting and rugs, clothing, upholstery, cleaning agents, food packaging, and kitchenware (Beesoon et al., 2012; Herzke et al., 2012; Prevedouros et al., 2006; Trier et al., 2011). PFAS evaporate from products, and partition to indoor air, dust, and surfaces (Eriksson and Kärman, 2015; Fraser et al., 2013; Karásková et al., 2016; Knobeloch et al., 2012; Shoeib et al., 2011; Strynar and Lindstrom, 2008; Tian et al., 2016; Yao et al., 2018). The majority of previous studies have focused on PFAS occurrence in the residential environment. However, it was suggested that other microenvironments, where people may spend a considerable amount of time, play a significant role in PFAS exposure assessments (Padilla-Sánchez et al., 2017).

The objective of this study was to determine the occurrence of a wide range of ionic and neutral PFAS in the childcare environment. Children spend a significant amount of time (7 h/day on average) in childcare and it is important to elucidate early-life environmental exposures in this indoor environment (Capizzano, 2019; Stubbings et al., 2018). Previous studies have shown that exposure to brominated and organophosphate flame retardants in California childcare facilities is higher than in homes (Bradman et al., 2014). Dust ingestion and dermal absorption are important exposure pathways for toddlers due to their high hand-to-mouth activity and close proximity to the floor (Fraser et al., 2012; Karásková et al., 2016; Vestergren et al., 2015), resulting in higher PFAS intake for toddlers compared to adults (Eriksson and Kärman, 2015; Schlummer et al., 2013; Shoeib et al., 2011; Tian et al., 2016). In this study, we analyzed dust and nap mats, a commonly used item in many childcare facilities shown to contribute to chemical exposures in this microenvironment (Bradman et al., 2014; Stubbings et al., 2018), collected from eight childcare centers in the U.S. for thirty-seven PFAS chemicals in order to determine the occurrence and distribution of these compounds in childcares and estimate children's exposure through dust ingestion and dermal absorption.

2. Materials and methods

2.1. Sample collection

Seven childcare centers in Seattle, Washington ($n = 14$) and one childcare facility in West Lafayette, Indiana ($n = 6$ across six rooms) were recruited in this study. Recruited childcare facilities consisted of different building types, including multiple classrooms, a former church, and a former home. Dust samples were collected using a nylon collection sock inserted in a vacuum cleaner as reported previously (Stubbings et al., 2018). Because all centers were vacuumed and mopped daily, dust from elevated surfaces was collected along with floor dust (in the same sample) in order to obtain enough sample for laboratory analysis. Elevated surfaces consisted almost entirely of shelving and the tops of bookcases/storage cubbies. In addition, nap mat samples ($n = 26$) were collected from the seven Seattle centers, including polyurethane foam ($n = 20$) and vinyl cover ($n = 6$) samples.

2.2. Sample analysis

The details of the analytical method are provided in the Supporting Information, and only a brief description is included here. Approximately 100 mg of dust or finely cut mat foam or cover was placed in a 15 mL polypropylene tube, spiked with surrogate standards (M3PFBA, M3PFBS, MPFHxA, MPFHxS, MPFOA, MPFOS, MPFUdA and M2PFTeDA for ionic PFAS; M2FOET and d-MeFOSE for

neutral PFAS; Tables S1 and S2), and sonicated in 4 mL of methanol for 1 h. The mixture was centrifuged at 3000 rpm for 5 min, the supernatant was transferred to a clean tube, and the extraction was repeated twice with 4 mL of methanol. The supernatants were combined, and the resulting extract was concentrated to dryness, reconstituted in 500 μ L of methanol, filtered through a 0.2 μ m nylon syringe filter (Corning, NY) and spiked with internal standards (M3PFHxS, M7PFUdA, M8PFOA, M8PFOS and MPFBA for ionic PFAS; MFOET for neutral PFAS; Tables S1 and S2). All PFAS standards were purchased from Wellington Laboratories and all solvents were Optima grade.

Both dust and mat samples were analyzed using an ultra-performance liquid chromatograph coupled with a triple-quadrupole mass spectrometer (Agilent 1290 Infinity II UPLC – 6470 QQQ-MS) in the negative electrospray ionization (ESI-) mode for ionic PFAS and on an Agilent 7890 gas chromatograph (GC) coupled to an Agilent 5975C mass spectrometer (MS) in the electron capture positive ionization (PCI) mode for neutral PFAS. A total of 37 PFAS chemicals, including 8 perfluoroalkyl sulfonates (PFASs), 12 perfluoroalkyl carboxylates (PFCAs), 3 fluorotelomer sulfonates (FTSs), 4 fluorotelomer alcohols (FTOHs), 5 fluorotelomer acrylates and fluorotelomer methacrylates (FTACs/FTMACs), 5 perfluorooctane sulfonamides and perfluorooctane sulfonamidoethanols (FOSAs/FOSEs), were analyzed. The complete list of target analytes is given in Tables S1 and S2.

2.3. Quality assurance and quality control

Eight procedural blanks and eight matrix spike samples were included in the analysis. Absolute matrix spike recoveries ranged from 61 to 140% for all target analytes. Surrogate standard recoveries were $79 \pm 16\%$, $71 \pm 20\%$, $55 \pm 13\%$, $77 \pm 16\%$, $71 \pm 20\%$, $76 \pm 9\%$, $103 \pm 19\%$, $103 \pm 19\%$, $93 \pm 19\%$, and $131 \pm 27\%$ (mean \pm standard error) for M3PFBA, M3PFBS, MPFHxA, MPFHxS, MPFOA, MPFOS, MPFUdA, M2PFTeDA, M2FOET, and d-MeFOSE, respectively (Tables S1 and S2).

Blank levels constituted less than 1% of the levels in dust and mat samples. All results were blank corrected by subtracting average blank concentrations from the sample concentrations. Method detection limits (MDLs) were set as three times the standard deviation of the target analyte levels detected in the blanks. For compounds not detected in the blanks, MDLs were based on a signal-to-noise ratio of 3. MDLs and average analyte blank concentrations are given in Table S3.

2.4. Data analysis

Estimated daily PFAS intakes (EDIs) via dust ingestion and dermal absorption were calculated based on the median and 95th percentile concentrations measured in dust using the average time spent in childcares (7 h), estimated children's dust ingestion rate (average and high ingestion scenarios), body surface area, the portion of dust adhered to skin, and the fraction of a contaminant absorbed by skin. Detailed information on EDI calculations is provided in the Supporting Information. Basic and descriptive statistics were calculated using IBM SPSS Statistics 24 and Microsoft Excel 2016. Plots were generated using Sigma Plot 13 (Systat Software Inc.) and R studio (R Core Team, 3.5.2, pheatmap). Statistical tests included the analyses of variance (ANOVA) using Minitab 13 and the significance level was set at $p < 0.05$.

3. Results and discussion

Table 1 shows detection frequencies, the minimum, maximum, median, and mean concentrations (with their standard errors) for

Table 1

Detection frequencies (DF, %), the minimum (Min), maximum (Max), median (Med) and mean (with their standard errors) concentrations of PFAS in dust and nap mats (ng/g) collected from the U.S. childcare centers. n.d.: not detected; SE: standard error.

Compound	Dust (n= 20)					Mats (n= 26)				
	DF	Mean ± SE	Med	Min	Max	DF	Mean ± SE	Med	Min	Max
PFBA	90	4.3 ± 0.77	3.2	n.d.	9.9	14	1.6 ± 0.4	0.67	n.d.	4.0
PFPeA	35	1.0 ± 0.29	0.32	n.d.	3.5	n.d.	n.d.			
PFHxA	100	1.5 ± 0.20	1.4	0.17	3.4	n.d.	n.d.			
PFHpA	100	0.64 ± 0.07	0.61	0.14	1.3	n.d.	n.d.			
PFOA	100	1.9 ± 0.28	2.0	0.34	5.1	23	0.34 ± 0.02	0.34	n.d.	0.50
PFNA	100	3.2 ± 0.83	1.7	0.11	13	36	0.19 ± 0.04	0.11	n.d.	0.65
PFDA	100	0.72 ± 0.10	0.59	0.22	2.4	18	0.36 ± 0.11	0.10	n.d.	1.2
PFUdA	100	0.89 ± 0.18	0.65	0.05	3.0	91	18 ± 14	0.29	n.d.	320
PFDoA	100	0.83 ± 0.15	0.58	0.26	3.1	86	16 ± 13	0.22	n.d.	280
PFTrDA	50	0.50 ± 0.14	0.31	n.d.	2.2	23	0.09 ± 0.003	0.08	n.d.	0.11
PFTeDA	85	0.63 ± 0.23	0.29	n.d.	4.4	64	0.14 ± 0.02	0.13	n.d.	0.31
PFHxDA	n.d.					82	1.1 ± 0.11	0.89	n.d.	2.9
ΣPFCA		15 ± 1.8	15	3.4	32		34 ± 26	1.7	n.d.	600
PFBS	90	0.34 ± 0.05	0.25	n.d.	0.86	5		0.04	n.d.	0.04
PFHxS	95	0.34 ± 0.05	0.25	n.d.	0.89	73	0.32 ± 0.03	0.30	n.d.	0.73
PFOS	100	1.5 ± 0.24	1.2	0.23	4.2	9	0.49 ± 0.07	0.49	n.d.	0.75
PFDS	75	6.7 ± 2.6	0.89	n.d.	34	14	0.20 ± 0.03	0.22	n.d.	0.34
ΣPFSA		7.2 ± 2.5	2.7	0.36	37		0.43 ± 0.05	0.33	n.d.	1.0
4:2 FTS	5		1.8	n.d.	1.8	n.d.				
6:2 FTS	70	18 ± 4.3	12	n.d.	63	n.d.				
8:2 FTS	40	11 ± 3.3	5.8	n.d.	46	n.d.				
ΣFTS		22 ± 5.8	12	n.d.	82					
6:2 FTOH	90	290 ± 130	130	n.d.	2500	31	11 ± 3.4	5.1	n.d.	52
8:2 FTOH	80	36 ± 8.0	20	n.d.	140	54	11 ± 0.51	11	n.d.	16
10:2 FTOH	90	69 ± 23	40	n.d.	460	8	6.9 ± 0.13	6.9	n.d.	7.3
ΣFTOH		390 ± 160	220	n.d.	3100		12 ± 2.1	11	n.d.	52
MeFOSE	40	33 ± 14	11	n.d.	190	31	79 ± 15	56	n.d.	220
EtFOSE	45	42 ± 14	15	n.d.	200	35	46 ± 7.9	27	n.d.	120
FOSA	35	0.07 ± 0.02	0.05	n.d.	0.30	32	0.26 ± 0.06	0.21	n.d.	0.91
MeFOSA	n.d.	n.d.				9	0.31 ± 0.03	0.31	n.d.	0.43
EtFOSA	n.d.	n.d.				5		0.15	n.d.	0.15
ΣFOSA/FOSE		65 ± 25	27	n.d.	380		81 ± 13	66	n.d.	220
6:2 FTAc	100	5.6 ± 1.9	2.9	0.07	37	n.d.				
ΣIonic PFAS		39 ± 8.0	26	3.9	140		34 ± 26	2.2	0.67	600
ΣNeutral PFAS		390 ± 170	200	3.6	3600		57 ± 13	25	7.2	220
ΣPFAS		430 ± 180	270	8.1	3700		78 ± 24	30	1.6	600

the 28 PFAS compounds detected in dust and nap mats. PFPrS, PFPeS, PFHpS, PFNS, 4:2 FTOH, 8:2 FTAc, 10:2 FTAc, 6:2 FTMAc, and 8:2 FTMAc were not detected in any dust or mat samples and are not included in the discussion. Fig. 1 shows analyte concentrations grouped as six PFAS classes, including perfluoroalkyl sulfonates (PFASs), perfluoroalkyl carboxylates (PFCA), fluorotelomer sulfonates (FTSs), fluorotelomer alcohols (FTOHs), perfluorooctane sulfonamides/perfluorooctane sulfonamidoethanols (FOSAs/FOSEs), in dust and in mats as box plots, and the letters in the plots represent the results of the one-way analysis of variance (ANOVA) performed using logarithmically transformed concentrations. Concentrations sharing the same letter are not significantly different at $p < 0.05$. Fig. 2 shows percent contributions of individual neutral and ionic PFAS to total concentrations.

3.1. Concentrations in dust

Of the 25 PFAS detected in dust samples, the majority were observed in more than 75% of samples, with the exception of PFPeA, 4:2 FTS, 8:2 FTS, MeFOSE, EtFOSE, and FOSA found in 45% of samples.

ΣPFAS concentrations (the sum of all 25 PFAS concentrations) ranged from 8.1 to 3,700 ng/g with a median concentration of 270 ng/g. Neutral PFAS (range 3.6–3,600 ng/g) dominated ΣPFAS dust concentrations and constituted 85% of ΣPFAS concentrations. FTOHs were the most abundant neutral PFAS with a median ΣFTOH concentration (the sum of 6:2, 8:2, and 10:2 FTOH concentrations)

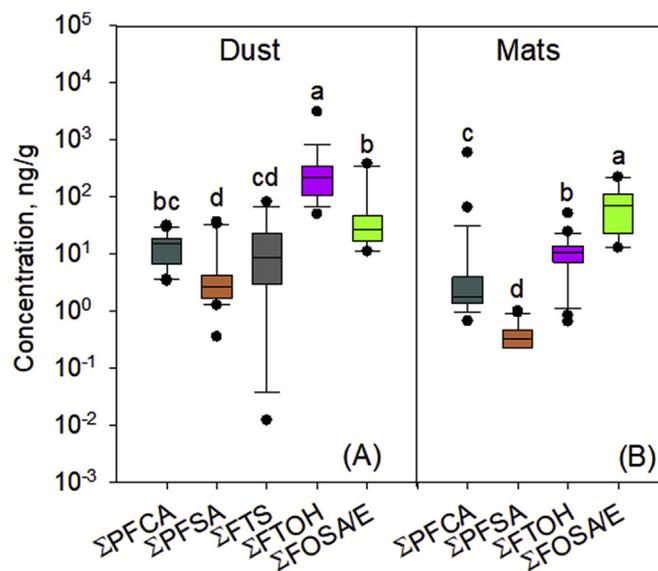


Fig. 1. ΣPFCA, ΣPFSA, ΣFTS, ΣFTOH, and ΣFOSA/FOSE concentrations in dust ($n = 20$) and nap mats ($n = 26$) collected from the U.S. childcares (ng/g). Concentrations are shown as boxplots, representing the 25th and 75th percentiles; black lines represent the median; and the whiskers represent the 10th and 90th percentiles. The letters represent the results of the one-way analysis of variance (ANOVA); the concentrations sharing the same letter are not statistically different at $p < 0.05$. The ANOVA was done separately for the concentrations included in plots A and B.

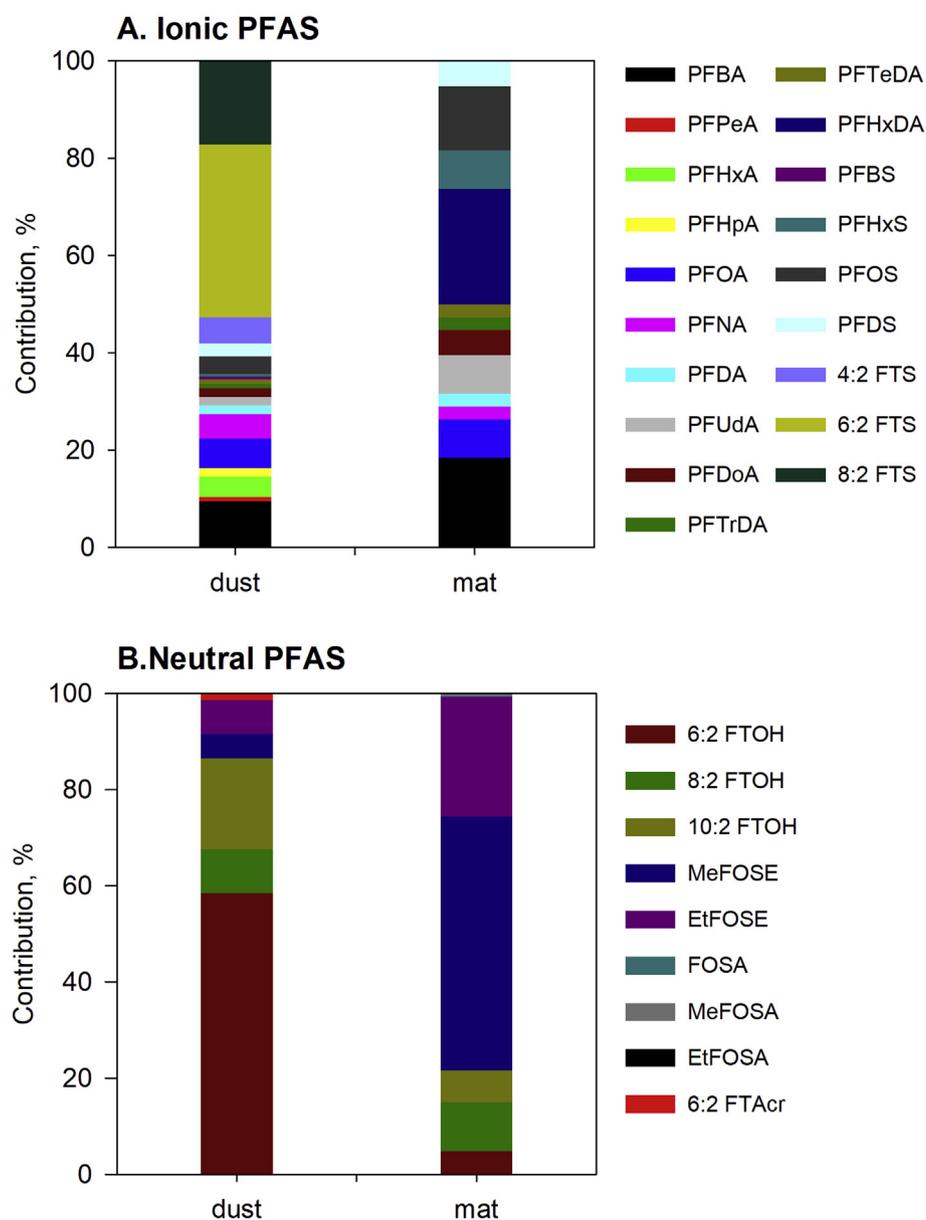


Fig. 2. Percent contributions (%) of individual ionic (A) and neutral (B) PFAS to Σ PFAS concentrations in dust and mats.

of 220 ng/g (range n.d. – 3,100 ng/g), followed by another neutral PFAS group, FOSA/FOSE with a median Σ FOSA/FOSE concentration (the sum of FOSA, MeFOSE, and EtFOSE concentrations) of 27 ng/g (range n.d. – 380 ng/g). Among neutral PFAS, 6:2 FTOH was the most abundant with a median of 130 ng/g (range n.d. – 2,500 ng/g) and contributed 67% to Σ Neutral PFAS concentrations (see Fig. 2). Following 6:2 FTOH, 10:2 and 8:2 FTOHs were the most abundant neutral PFAS with medians of 40 and 20 ng/g, respectively, and contributed up to ~20% of Σ Neutral PFAS concentrations. FTOHs are associated with polymeric surface coatings of stain-resistant products and carpets (Buck et al., 2011; Dinglasan-Panlilio and Mabury, 2006). It has been shown that FTOHs can off-gas from treated products in the indoor environment (Liu et al., 2015; Schlummer et al., 2013). FTOHs can degrade to PFCAs and indoor levels of FTOHs predict serum levels of PFOA (D'eon and Mabury, 2011; Fraser et al., 2012).

Sulfonamides, EtFOSE and MeFOSE, were also detected at relatively high concentrations (medians 15 and 11 ng/g, respectively)

and contributed up to 8% of Σ Neutral PFAS concentrations. FOSA was detected in only 35% of the dust samples at low concentrations (median 0.046 ng/g), and MeFOSA and EtFOSA were not detected in any of the samples. In addition, 6:2 FTAc, commonly used as a surfactant (Buck et al., 2011), was detected in all samples with concentrations ranging from 0.07 to 37 ng/g (median 2.9 ng/g) and contributed ~2% to Σ Neutral PFAS concentrations. To the best of our knowledge, this is the first report on the occurrence of 6:2 FTAc in dust.

FTOH concentrations found in this study were higher than those found in living room dust from Canada in 2007–2008 (median 150 ng/g) (Shoeib et al., 2011) and from the United States in 2000–2001 (87 ng/g) (Strynar and Lindstrom, 2008). Similarly, previous studies reported low detection of EtFOSE and MeFOSE in dust (Eriksson and Kärman, 2015; Karásková et al., 2016). Our Σ FOSA/FOSE concentrations were higher than those found in house dust from Indiana, United States, collected in 2013 (Karásková et al., 2016) and from Ottawa, Canada, collected in

2013–2014 (Eriksson and Kärrman, 2015).

Σ Ionic PFAS concentrations ranged from 3.9 to 140 ng/g and comprised of three PFAS groups, including Σ PFCA (median 15 ng/g), Σ FTS (median 12 ng/g), and Σ PFSA (median 2.7 ng/g). Overall, Σ Ionic PFAS concentrations were 8 times lower than Σ Neutral PFAS levels found in these dust samples. 6:2 FTS and 8:2 FTS were the most abundant among ionic PFAS with median concentrations of 12 and 5.8 ng/g, respectively. These two compounds contributed 35% and 17% to Σ Ionic PFAS concentrations, respectively. Among the PFCAs, PFBA was the most abundant (median 3.2 ng/g) with a contribution of 9% to Σ Ionic PFAS concentrations, followed by PFOA (median 2.0 ng/g; 6%), PFNA (median 1.7 ng/g; 5%), and PFHxA (median 1.4 ng/g; 4%). Among PFASs, PFOS was the most abundant compound (median 1.2 ng/g) with a contribution of ~4% to Σ Ionic PFAS concentrations.

Generally, Σ PFCA and Σ PFSA concentrations found in this study were up to 20 times lower than those found in earlier studies from North America (Σ PFCA: 39–110 ng/g; Σ PFSA: 14–70 ng/g) (Eriksson and Kärrman, 2015; Fraser et al., 2013; Knobeloch et al., 2012; Shoeib et al., 2011; Strynar and Lindstrom, 2008). This could be explained by the differences in sampled microenvironments (Yao et al., 2018), and perhaps by the substitution of PFOS and PFOA with other compounds (Buck et al., 2011). Only two studies have reported on the occurrence of FTSs indoors. 8:2 FTS was reported in house dust from Norway in 2008 (Haug et al., 2011) and Finland in 2014–2015 (Winkens et al., 2018) with median levels (3.1–5.3 ng/g) similar to those found in this study. 6:2 FTS was more frequently detected and found at higher concentrations in this study compared to homes in Norway (detected in 10% of the samples) (Haug et al., 2011) and Finland (detected in 2% of the samples) (Winkens et al., 2018). FTSs are considered PFOS replacements, and these findings may be related to the increased use of these chemicals since the phase out of PFOS (Fath et al., 2016; Wienand et al., 2013). Interestingly, only one of the childcares sampled here had carpeting, which has been recognized as a potential source of FTSs (Herzke et al., 2012), suggesting that other FTS sources are possibly present in the childcares, such as paints, waxes, and polishes (Field and Seow, 2017). Given the intense floor cleaning that takes place in most childcare settings, it seems likely that some of the childcares may be using floor cleaners or waxes that contain these compounds. These findings may have implications for other microenvironments, such as schools, hospitals, and senior care facilities that have intense cleaning protocols.

3.2. Concentrations in mats

Twenty-one out of 37 targeted PFAS were detected in up to 90% of the analyzed nap mats with Σ PFAS concentrations (the sum of 21 PFAS concentrations) ranging from 1.6 to 600 ng/g (median 30 ng/g). Similar to dust, neutral PFAS dominated PFAS concentrations in mats. FOSA/FOSE was the most abundant PFAS group (median Σ FOSA/FOSE concentration 66 ng/g). MeFOSE and EtFOSE were the most abundant chemicals in this group (medians 56 and 27 ng/g, respectively), contributing 53% and 25% to Σ Neutral PFAS concentrations, respectively (Fig. 2). FTOHs were less abundant than FOSA/FOSE (median 11 ng/g) with 8:2, 10:2, and 6:2 FTOHs contributing 10, 7, and 5% to Σ Neutral PFAS concentrations, respectively.

Ionic PFAS, PFCAs and PFASs, were found at lower levels (medians 1.7 ng/g and 0.33 ng/g, respectively), and FTSs were not detected in any samples. Long-chain ionic PFAS with 9–14 carbons, were frequently detected, including PFUdA (91%), PFDoA (86%), PFTeDA (64%), and PFHxS (73%). Overall, Σ Ionic PFAS concentrations (median 2.2 ng/g) were an order of magnitude lower than Σ Neutral PFAS concentrations. PFHxDA was the most abundant

ionic PFAS with a median concentration of 0.89 ng/g and contribution of 23% to Σ Ionic PFAS concentrations, followed by PFBA (median 0.67 ng/g; 17%), PFOS (0.49; 13%), and PFOA (median 0.34 ng/g; 9%).

Σ PFCA and Σ PFSA concentrations detected in nap mats were comparable to those reported in many consumer products, such as carpets, mats, and furniture textiles (Herzke et al., 2012; Vestergren et al., 2015), but were lower than those detected in popcorn bags and outdoor textiles (Robel et al., 2017; Yuan et al., 2016).

It is unclear whether PFAS have been intentionally added to mats, or are the result of cross-contamination during the manufacturing process or PFAS sorption from the air or dust onto the mats. Half of the analyzed mats in this study were purchased as new products and had not been used. When comparing the levels of PFAS in the new and used mats, there was no significant difference between Σ PFAS levels. In addition, Σ PFAS concentrations in the mat foam were similar to those in the mat cover. These results suggest that indoor air is not the major source of PFAS in mats, and that PFAS in mats could be the result of the manufacturing process.

The low detection frequencies of PFOA and PFOS in this study are possibly related to the phase-out of these two compounds (Land et al., 2018; Sunderland et al., 2019). High detection frequencies of 9–14 carbon PFCAs may be related to their use in imported consumer products (Vestergren et al., 2015). For example, China still manufactures long-chain PFAS (Wang et al., 2014). Σ FTOH concentrations in nap mats were generally higher than those in food contact materials (e.g., cupcake cups, paper cups, and paper boxes) from China (Yuan et al., 2016), but lower than those in furniture textiles, carpets, mats, and clothes (Herzke et al., 2012; Vestergren et al., 2015).

3.3. Concentration correlations

To further investigate the sources of PFAS in dust, heatmaps and cluster analyses were conducted using Pearson correlation coefficients of logarithmically transformed concentration correlations for compounds detected in more than half of the dust samples (Fig. 3). These analyses resulted in two clusters: one included most of the PFCAs, PFASs, and FTOHs clustered in the largest group, and the second smaller cluster included 6:2 FTAc, PFBA, PFTrDA, and PFTeDA. Particularly, the concentrations of 6:2, 8:2, and 10:2 FTOHs were strongly correlated (r : 0.76–0.99; p < 0.001), which was consistent with findings in previous studies and their presence as mixtures in products (Dinglasan-Panlilio and Mabury, 2006; Eriksson and Kärrman, 2015; Winkens et al., 2018). Additionally, FTOH concentrations were strongly correlated with those of most PFCAs (r : 0.31–0.64; p < 0.001), probably because FTOHs degrade to PFCAs in the environment (Butt et al., 2014; Ellis et al., 2004). PFOA concentrations were highly correlated with those of both short-chain (e.g., PFHxA and PFHpA) and long-chain PFAS (e.g., PFNA, PFDA, PFDoA, and PFUdA) (r : 0.54–0.82; p < 0.001). Similar findings were reported for PFAS concentrations in dust from Europe and the United States (Karásková et al., 2016). These results may be explained by the common occurrence of PFOA, PFDA, and PFDoA in fluorotelomer-based products, where long-chain PFCAs are found as impurities (Karásková et al., 2016). Most PFCA and PFSA concentrations were highly correlated, consistent with previous studies in different microenvironments (Björklund et al., 2009; D'Hollander et al., 2010; Fraser et al., 2013; Haug et al., 2011; Karásková et al., 2016; Moriwaki et al., 2003; Shoeib et al., 2011), suggesting potential common sources for these chemicals. Concentrations of two long-chain PFCAs, PFTrDA (13 carbons) and PFTeDA (14 carbons), while correlated with each other, also correlated with short-chain PFCAs, suggesting common sources for the

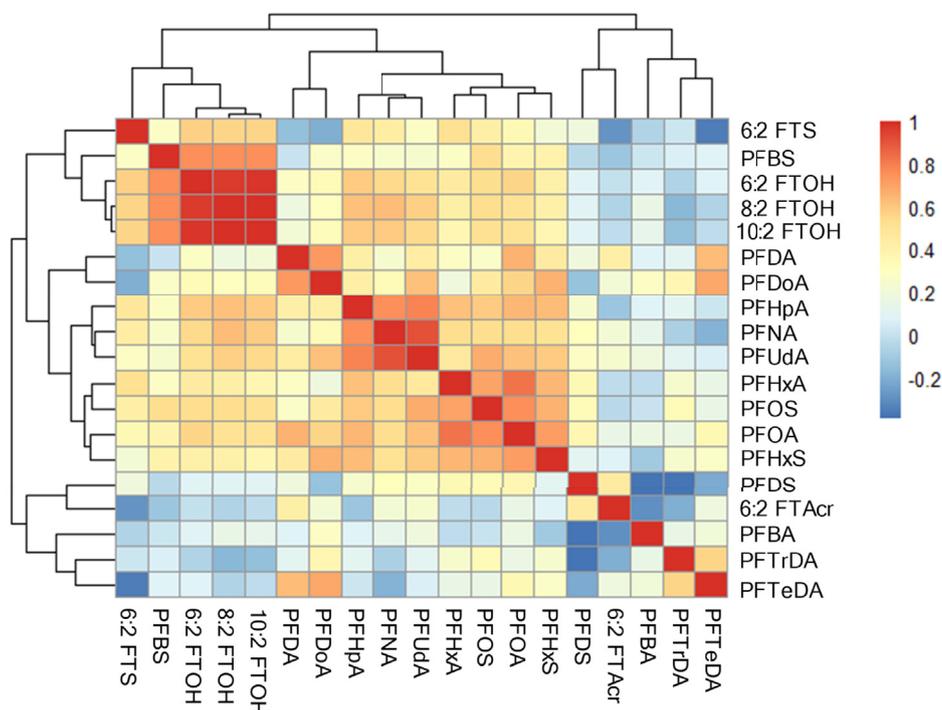


Fig. 3. Correlation heatmaps and hierarchical clustering of individual PFAS homologues based on their Pearson correlation coefficients.

phased out and current-use PFAS (Buck et al., 2011).

3.4. Exposure assessment

Table 2 summarizes PFAS estimated daily intakes (EDIs) for toddlers via dust ingestion using average and high dust ingestion scenarios (100 $\mu\text{g}/\text{day}$ for average intake and 200 $\mu\text{g}/\text{day}$ for high intake) (EPA, 2011) and dermal dust absorption. Dermal exposure from nap mats was not included since sheets or other covers are generally used, so the children are not in direct contact with mats during nap time. PFAS uptake through dust ingestion was generally 2 orders of magnitude higher than through dermal absorption. Median ΣPFAS EDIs were 0.26 and 0.85 ng/kg body weight (bw)/day for the average and high dust ingestion scenarios, respectively. Although children spend only a part of the day in childcare (here we estimated time in childcare as 7 h/day), uptake of ΣPFAS via dust ingestion was 4.6 ng/kg bw/d when considering the 95th percentile ΣPFAS concentrations in dust and high dust ingestion rate, comparable to 24-h exposure estimated for homes in the United States (7.9 ng/kg bw/d) (Karásková et al., 2016) and Canada (3.2 ng/kg bw/d) (Eriksson and Kärrman, 2015). Intake of neutral PFAS constituted up to 75% of ΣPFAS EDI, similar to what was reported previously for other indoor environments, such as children's bedrooms, houses, and clothing stores (Eriksson and Kärrman, 2015; Winkens et al., 2018; Yao et al., 2018). This higher exposure to neutral PFAS is concerning considering that many neutral PFAS are the precursors of toxic ionic PFAS, such as PFOA (Rand and Mabury, 2017).

EDIs for ionic PFAS and neutral PFAS using the average dust ingestion rate were 0.07 and 0.20 ng/kg bw/d, respectively, which were generally lower than previously reported (Karásková et al., 2016; Shoeib et al., 2011; Winkens et al., 2018). EDIs via dust ingestion estimated for PFOA (0.004 and 0.03 ng/kg bw/d for average and high exposure scenarios, respectively) and PFOS (0.002 and 0.02 ng/kg bw/d for average and high exposure scenarios, respectively) were below established tolerable daily intake rates

Table 2

Estimated daily intakes (EDIs) for PFAS via average and high dust ingestion scenarios and dermal dust absorption (ng/kg bw/d) for toddlers in the U.S. childcare environment.

Compound	Dust ingestion EDI (ng/kg bw/d)				Dermal absorption EDI (ng/kg bw/d)	
	Average		High			
	Med.	95 th perc.	Med.	95 th perc.	Med.	95 th perc.
PFBA	0.01	0.02	0.04	0.13	0.004	0.01
PFPeA	0.001	0.01	0.004	0.04	0.001	0.004
PFHxA	0.003	0.01	0.02	0.04	0.002	0.004
PFHpA	0.001	0.002	0.01	0.02	0.001	0.001
PFOA	0.004	0.01	0.03	0.05	0.002	0.004
PFNA	0.003	0.02	0.02	0.16	0.002	0.01
PFDA	0.001	0.002	0.01	0.02	0.001	0.001
PFUdA	0.001	0.01	0.01	0.04	0.001	0.003
PFDoA	0.001	0.004	0.01	0.03	0.001	0.002
PFTrDA	0.001	0.003	0.004	0.02	0.001	0.002
PFTeDA	0.001	0.004	0.004	0.02	0.001	0.002
PFBS	0.001	0.001	0.003	0.01	0.001	0.001
PFHxS	0.001	0.002	0.003	0.01	0.001	0.001
PFOS	0.002	0.01	0.02	0.04	0.001	0.004
PFDS	0.002	0.06	0.01	0.42	0.001	0.04
4:2 FTS	0.004	0.004	0.02	0.02	0.002	0.002
6:2 FTS	0.02	0.11	0.16	0.73	0.01	0.07
8:2 FTS	0.01	0.07	0.08	0.46	0.01	0.04
$\Sigma\text{Ionic PFAS}$	0.07	0.33	0.45	2.3	0.04	0.20
6:2 FTOH	0.12	0.67	0.23	1.33	0.15	0.86
8:2 FTOH	0.02	0.09	0.04	0.18	0.02	0.12
10:2 FTOH	0.04	0.14	0.07	0.28	0.05	0.18
FOSA	0.001	0.001	0.001	0.001	0.001	0.001
MeFOSE	0.01	0.12	0.02	0.23	0.01	0.15
EtFOSE	0.01	0.14	0.03	0.28	0.02	0.18
6:2 FTAc	0.003	0.02	0.01	0.04	0.004	0.02
$\Sigma\text{Neutral PFAS}$	0.20	1.2	0.40	2.3	0.26	1.5
ΣPFAS	0.26	1.5	0.85	4.6	0.004	0.01

established in Europe (0.86 and 1.9 ng/kg bw/d for PFOA and PFOS, respectively) (Knutson et al., 2018). However, considering high intake rates estimated here and in other studies for neutral PFAS,

the precursors of PFOA and PFOS in humans, actual exposure to these chemicals could be much higher (Eriksson and Kärman, 2015). Future assessment of PFAS exposure warrants inclusion of PFAS precursors in the estimates of daily PFAS intake.

This study has several limitations. The sample size was small and covered a limited geographical area, which restricted the ability to evaluate variations among childcare facilities and the relationship between PFAS exposure and building characteristics and chemical products used in facilities. In addition, air sampling was not conducted. Nonetheless, these findings indicate that PFAS are abundantly found in the U.S. childcare environment, sometimes at levels similar to those in homes, leading to significant early-life exposures. Our finding that FTSs were the most abundant PFCAs suggests that use patterns in the childcare environment differ from those in homes. Further, they indicate that the impact of the use of PFAS-containing floor treatments on exposures in schools, hospitals, and other workplaces and institutional environments needs to be better understood.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2019.113714>.

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