PER- AND POLYFLUORINATED CHEMICALS IN INDOOR SOURCES: LEVELS IN HOUSE DUST AND INDOOR AIR FROM CATALONIA, SPAIN

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Introduction

Poly- and perfluorinated compounds (PFCs) are widespread chemicals that have been used in numerous industrial and personal applications for more than 50 years. All over the world, people are exposed to these chemicals from various sources. Production and usage of PFCs have lead to their release to the environment but the elucidation of PFC exposure routes to humans is still underway. Direct sources of exposure are, among others, from the manufacture and use of PFOS and PFOA in commercial products. In addition, there exist some indirect exposure pathways, from precursor compounds, such as fluorotelomer alcohols (FTOHs) or perfluorooctane sulfonamides and sulfonamidoethanols (FOSA/Es), which are released to the environment or are present in commercial products[1,2]. Degradation occurs both in the atmosphere[3] and during biotransformation[4]. A number of compartments have been explored, suggesting food as the dominant pathway of PFC exposure[5]. Moreover, drinking water[6] and the indoor environment, including both air and dust, have been also pointed out as potentially important sources[7,8]. In earlier studies, the exposure to PFCs of people living in Catalonia (Spain) has been assessed by analyzing the human PFC levels in blood[9], human liver and milk[10]. It was concluded that food and drinking water may have some impact on the body burden of PFCs[11,12]. In this study, the human exposure in indoor environments was assessed by measuring both ionic (e.g., perfluorocarboxylic (PFCAs) and perfluorosulfonate (PFSAs) acids) and volatile (e.g., FTOH and FOSA/Es) in air as well as dust. Finally, a limited number of outdoor air samples were also included in the study.

Materials and methods

Perfluorochemicals, including PFCAs (C4-C14, C16, C18, $^{13}C_4$-labeled C4, C6, C8-C12, $^{13}C_8$-PFOA), PFSAs (C4, C6, C8, C10, $^{13}C_4$-labeled C6, C8, $^{13}C_8$-PFOS), FTOHs (both native and 13C 6:2, 8:2, 10:2) and FOSA/Es were obtained from Wellington Laboratories (Guelph, Ontario, Canada). Performance standard 7H-PFHpA (98 % in methanol) was purchased from ABCR (Karlsruhe, Germany). Methanol were of HPLC grade and was purchased from Fluka (Steinheim, Germany), Supelclean ENVI-carb (120/400 mesh) was purchased from Supleco (Bellafonte, PA, USA) and sodium acetate were purchased from E. Merck (Darmstadt, Germany). All water used was laboratory produced ultra pure water. Laboratory ware including filters were carefully rinsed with methanol before use. Sampling of air and dust was performed in December 2009. Duplicate samples of indoor air were collected in 10 households in the Catalan province of Tarragona, using precleaned SPE cartridges (Isolute ENV+, 1g, Biotage, Uppsala, Sweden) connected to AirChek 2000 personal pumps (SKC Inc., Eighty Four, PA, USA). Prior to sampling, 25 µL of internal standards ($^{13}C_4$-8:2 FTOH and $^{13}C_8$-PFOA) were injected to verify the sampling procedure. A flow rate of 2 mL/min and a sampling period of 24 h were used to collect 2820-3280 m^3 indoor air. Samples were kept at -20°C until analysis. Outdoor air sampling was performed for purposes of comparison and conducted following the air quality EU directive 1999/30/EC. A TE-1000 PUF high-volume sampling device (Tisch Environmental, Cleves, OH, USA) was used. Particles were collected on quartz microfiber filters, while the gas phase was retained in ORBO-2500 cartridges with PUF/XAD-2/PUF foams (Supelco, USA). Sampling times of approximately 48 hours resulted in air volumes between 606 and 678 m^3. After sampling, they were stored in air tight containers and kept at -20ºC until analysis. Dust samples were collected from household vacuum cleaner dust bags, cut open with clean scissors and fractionated using a sieve employing 1 g of dust <150 µM for further analysis.

Methanol was used as extraction solvent for both indoor and outdoor air adsorbents, and for extraction of seived dust. Repeated extractions with methanol was used for dust samples and ORBO outdoor air cartridges. Further clean up was performed using 25 mg of Supelclean EnviCarb (120/400 mesh from Supelco, Bellefonte, PA, USA) and extracts were filtered (2 µm nylon filter) before setting the final volume to 500 µL in methanol. Both air and dust extracts were split to analyze volatile PFCs (FTOHs and FOSA/Es) using a Waters Quattro Micro GC operating in the positive chemical ionization (PCI) mode for FTOHs and negative CI mode for FOSA/Es. The analysis was performed using multiple reaction monitoring (MRM) for the most abundant transitions. To the remaining extracts, 2 mM sodium acetate in water was added prior to UPLC-MSMS analysis (Waters Quattro Premier XP). Ionic PFCs, including PFCAs and PFSAs, were analysed looking at the two most abundant transitions in MRM. All data were acquired using MassLynx software with data processing performed using MassLynx with QuanLynx.

Results and discussion

Dust samples

Monitoring of indoor dust samples revealed PFCA as the dominating compound class, with total PFCA concentrations ranging from 19 to 190 ng/g dust. The concentrations of PFSAs ranged from 2.5 to 20 ng/g dust. Individual PFCA/PFSA concentrations can be seen in Table 1. PFBA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFTrDA, PFHxS, and PFOS could be detected in all the analyzed samples. PFUnDA and PFDoDA was detected in 90%, PFPeA in 80%, and PFBS in 60% of the samples, while for the remaining compounds, only one (PFTDA and FTHUA) or no (PFOcDA, PFDS, 5:3 FTSA and FTDUA) ionic PFCs could be detected. The highest concentrations were observed for PFDA, PFNA, PFOA and PFBA (41, 37, 36 and 25 ng/g dust, respectively). For PFSAs, the greatest levels were obtained for PFOS (12 ng/g dust). The maximum concentration of PFTrDA (77 ng/g dust) was observed in one sample, but it could not be confirmed in the secondary trace monitored during LC-MSMS. This value should thus be treated with care. For ionic PFCs, the highest concentrations were detected in sample 3 and sample 9 but there is no additional information relating to these samples available.

Low levels of FTOHs and FOSA/Es were also measured in dust samples, with ranges of 0.008-1.8 and <0.073 to 2.1 ng/g, respectively. The individual concentrations of FTOHs and FOSA/Es measured in house dust are summarized in Table 2. For these volatile PFCs, maximum dust levels were 1.9 ng/g dust (EtFOSE) and 1.3 ng/g dust (8:2 FTOH). MeFOSA was measured in one sample at a concentration of 0.065 ng/g but could not be confirmed in the secondary transition when analyzed by GC-MSMS. The volatile compounds only accounts for 0.3 to 5 % of ionic PFCs in house dust samples.

When comparing dust results in the present study with those from microenvironments previously reported in the scientific literature ionic PFC concentrations from Spain were somewhat lower than what was reported for homes from Norway[13,14] and Belgium[15], and at least one order of magnitude lower than reported in other European countries[14,16,17], North America[7,17-20], Asia and Australia[17]. In general, carpets are not usual in Spanish homes and this could partially explain the difference in concentrations.

Air samples

For PFSAs and PFCAs in indoor air samples, only PFOS was observed in three samples at concentration of 6.1, 6.7 and 69 pg/m^3, while PFBA (62 pg/m^3) was detected in one sample. However, these values could not be confirmed in replicate samples. The major compound class in indoor air was telomer alcohols, with 6:2 and 8:2 FTOH detected in 100%, and 10:2 FTOH in 80% of the samples collected. Regarding FOSA/Es, MeFOSA was the main detected chemical in indoor air, being present in 65% of the samples. Remaining FOSA/Es could only be detected in 10-20% of the samples. The 8:2 FTOH was the dominant compound, with concentrations between 7.5 and 170 pg/m^3. Concentration ranges for 6:2 FTOH and 10:2 FTOH were 3.0 to 47 and <0.6 to 47 pg/m^3, respectively. MeFOSA ranged from <1.2 to 14 pg/m^3, while EtFOSA, EtFOSE and MeFOSE all ranged from non detected (<0.52 pg/m^3) to 6.1 pg/m^3. The total sum of FTOHs ranged from 13 to 234 pg/m^3, and FOSA/Es

levels were from non detect to 23 pg/m^3. In general terms, these levels are order of magnitudes lower than those previously reported in other countries[7,13].

Table 1: Levels of ionic PFCs (in ng/g) measured in ten house dust samples from Catalonia, Spain.

	Dust 1	Dust 2	Dust 3	Dust 4	Dust 5	Dust 6	Dust 7	Dust 8	Dust 9	Dust 10	LOD[b]
PFBS	<0.001	<0.001	1.9	0.58	*0.35*	<0.001	*0.38*	*0.57*	6.5	<0.001	0.001
PFHxS	0.29	0.36	0.17	0.53	0.53	5.3	0.20	0.35	2.0	1.0	0.003
PFOS	2.2	3.8	2.2	3.0	4.3	1.1	2.7	1.9	12	1.9	0.13
PFDS	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.002
PFBA	*7.4*[a]	*7.9*	*20.7*	*10.2*	*19.8*	*7.2*	*18.3*	*24.7*	*23.5*	*22.6*	0.06
PFPeA	0.47	0.54	0.43	<0.013	0.93	*0.25*	*0.10*	*0.30*	0.65	<0.013	0.013
PFHxA	1.9	1.3	2.2	0.64	2.7	*0.54*	0.53	0.40	2.9	*0.7*	0.019
PFHpA	1.4	1.6	3.4	0.51	4.0	0.79	0.54	0.46	2.6	1.0	0.13
PFOA	7.6	5.4	21	3.0	13.9	1.5	2.8	2.0	36	1.9	0.16
PFNA	1.0	0.74	18	1.8	6.9	0.58	0.61	0.66	37	0.4	0.038
PFDA	3.4	1.5	41	1.4	12	1.1	1.1	1.2	*33.9*	0.75	0.067
PFUnDA	0.43	0.47	15	0.73	6.7	<0.061	0.35	0.75	9.0	0.30	0.061
PFDoDA	0.66	1.2	11	0.61	6.7	<0.010	0.56	0.53	17	1.4	0.010
PFTrDA	0.057	0.10	4.6	*0.047*	1.9	*77.1*	*0.062*	*0.10*	25	0.22	0.035
PFTDA	<0.29	<0.29	*6.7*	<0.29	<0.29	<0.29	<0.29	<0.29	<0.29	<0.29	0.29
PFOcDA	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	<0.46	0.46
5:3 FTSA	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	2.0
FTDUA	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	0.006
FTHUA	0.02	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.002

[a] Not confirmed in secondary trace during LC-MSMS analysis. [b] Based on a signal to noise ratio of three or three times the blank level when detected. LOD: Limit of detection

Table 2: Levels of volatile PFCs (in ng/g) measured in ten house dust samples from Catalonia, Spain.

	Dust 1	Dust 2	Dust 3	Dust 4	Dust 5	Dust 6	Dust 7	Dust 8	Dust 9	Dust 10	LOD[b]
	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g
6:2 FTOH	0.038	0.008	0.018	0.012	0.009	0.060	0.046	0.034	0.023	0.047	0.004
8:2 FTOH	0.15	<0.050	0.46	0.25	0.15	0.23	0.46	0.59	1.3	0.45	0.050
10:2 FTOH	<0.036	<0.036	<0.036	<0.036	<0.036	<0.036	0.15	0.22	0.39	<0.036	0.036
MeFOSA	<0.054	<0.054	<0.054	<0.054	*0.065*[a]	<0.054	<0.054	<0.054	<0.054	<0.054	0.054
EtFOSA	<0.062	<0.062	<0.062	<0.062	<0.062	<0.062	<0.062	<0.062	<0.062	<0.062	0.062
MeFOSE	<0.12	<0.12	<0.12	<0.12	0.16	0.22	0.51	<0.12	0.17	0.13	0.1242
EtFOSE	0.26	0.20	<0.073	<0.073	1.9	0.13	0.11	0.078	0.16	0.40	0.073

[a] Not confirmed by secondary trace during GC-MSMS analysis. [b] Based on a signal to noise ratio of three or three times the blank level when detected. LOD: Limit of detection. Recoveries for labelled compounds during GC-MSMS analysis was 34-98 % for $^{13}C_4$-8:2 FTOH and 48-118 for deuterated FOSA/Es.

For outdoor air comparison, only a limited number of samples were collected, and hence the results are only indicative for the Spanish outdoor air environment. PFOA was the only ionic PFC detected in outdoor samples, ranging from 6.0 to 20 pg/m^3. No other PFCAs or PFSAs could be detected. This concentration is higher than

those of volatile PFCs measured in outdoor air where FTOHs were detected in the concentration range of 0.34 to 8.6 pg/m^3, while FOSA/Es ranged from below limit of detection to 0.025 pg/m^3 although FOSA/Es could not be confirmed in secondary traces during GC-MSMS analysis. Maximum concentration for volatile PFCs were detected for the 6:2 FTOH with a concentration range of 0.07 to 8.1 pg/m^3. The 8:2 FTOH ranged from 0.21 to 1.7 pg/m^3, and the 10:2 FTOH levels were from <0.082 to 0.76 pg/m^3.

This study shows the presence of a wide range of PFCs in the indoor home environment in Catalonia, Spain. Both per- and polyfluorinated compounds are found in house dust and indoor air samples at lower levels compared to concentrations available for other countries. Also total PFC levels in outdoor air are lower than indoor air samples. Concentrations presented herein can be used for calculating the human exposure of PFCs of people from the Catalan region of Tarragona, Spain, through inhalation and ingestion of PFCs via these exposure routes in comparison with available results on other sources.

Acknowledgements

Department of Health, Generalitat de Catalunya, is acknowledged for providing financial support.

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