POLYFLUOROALKYL CHEMICALS IN HOUSE DUST

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Introduction

Polyfluoroalkyl chemicals (PFCs), which owe many of their unique properties to the remarkable strength of the carbon-fluorine bond, have been used in a variety of commercial applications, including water, oil, soil and grease repellents for fabric, leather, rugs, carpets, stone, and tile; fire-fighting foams; alkaline cleaners; floor polish; as sizing agents (to resist the spreading and penetration of liquids) for packaging and paper products; and as leveling agents for coatings. Because of their manufacturing and their widespread uses, PFCs are found in the environment and ecosystem at concentrations in the low parts-per-billion in wildlife, humans, water, air, and soil around the world. Because of their stable structure, some PFCs resist hydrolysis, photolysis, and biodegradation in the environment and are of considerable concern as persistent organic pollutants.

The main source(s) and pathway(s) of exposure to PFCs in humans remain unclear. In addition, the association between human exposure to PFCs and adverse health effects in humans is uncertain. The fact that concentrations of some PFCs in children appear to be higher than in adults suggests that there might be different sources and routes of exposure to these compounds based on age. Dust has been used as indicator of indoor exposure to pesticides and could be a potential source of exposure to PFCs[1-3]. Young children may be more exposed to dust than adults, because children are in close contact with floors and dusty surfaces, and tend to put their hands in their mouth. In this study, we determined the concentrations of selected PFCs in house dust.

Material and Methods

Sample collection

Household dust samples were collected from the United Kingdom (N = 9), Austria (N = 10), Germany (N =10), and Atlanta, GA, United States (N = 20). Additional information, including the year the house was built, the number of electrical appliances in the house, and the presence of wall-to-wall carpeting in the house, was available for some samples.

Reagents

Methanol and acetonitrile were HPLC grade purchased from Caledon (Georgetown, Ont., Canada). Formic acid (99%) and acetic acid (glacial) were purchased from Sigma Aldrich Laboratories, Inc (St. Louis, MO). Ammonium hydroxide (30%) was purchased from J.T. Baker (Phillipsburg, NJ. Perfluorooctane sulfonamide (PFOSA), N-methyl-perfluorooctane sulfonamide (Me-PFOSA), N-ethyl-perfluorooctane sulfonamide (Et-PFOSA), 2-(N-methyl-perfluorooctane sulfonamido) ethanol (Me-PFOSA-EtOH), 2-(N-ethyl-perfluorooctane sulfonamido) ethanol (Et-PFOSA-EtOH), 2-(N-methyl-perfluorooctane sulfonamido) acetic acid (Me-PFOSA-AcOH), 2-(N-ethyl-perfluorooctane sulfonamido) acetic acid (Et-PFOSA-AcOH), perfluorobutane sulfonate potassium salt (PFBuS), perfluorohexane sulfonate potassium salt (PFHxS), perfluorooctane sulfonate potassium salt (PFOS), and perfluorooctanoic acid ammonium salt (PFOA) were provided by 3M Company (Saint Paul, MN). Perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDeA), perfluoroundecanoic acid (PFUA), and perfluorododecanoic acid (PFDoA) were purchased from Oakwood Products (West Columbia, SC). 1,2-^{13}C-perfluorooctanoic acid ($^{13}C_2$-PFOA) was provided by Dupont Company (Wilmington, DE). $^{18}O_2$-perfluorooctane sulfonate ammonium salt ($^{18}O_2$-PFOS) and $^{18}O_2$-perfluorooctane sulfonamide ($^{18}O_2$-PFOSA) were purchased from RTI Laboratories (RTP, NC). Perfluoro-n-[1,2,3,4,5-$^{13}C_5$] nonanoic acid ($^{13}C_5$-PFNA), 2-Perfluorooctyl [1,2-$^{13}C_{12}$]-ethanoic acid ($^{13}C_2$-PFDeA), N-methyl-d_3-perfluoro-1-octanesulfonamide (D_3-Me-PFOSA-AcOH), and N-ethyl-d_5-perfluoro-1-octanesulfonamide (D_5-Et-PFOSA-AcOH) were purchased form Wellington Laboratories (Guelph, ON, Canada). All chemicals and solvents were used without further purification.

Extraction procedure and sample preparation

We transferred approximately 300 mg of dust to a 15 mL polypropylene tube, added 2 mL of 0.1 M formic acid and 2 mL of methanol. The dust suspension was mixed well by use of a vortex mixer and ultrasonic bath for 10 min. Then, the samples were left to pass by gravity through an empty (i.e., without sorbent) SPE cartridge (3mL, Varian) fitted with two consecutive frits (20 μm polyethylene/ diameter 3/8 in), and the filtrate was collected in a polypropylene tube. We transferred 100 μL of the filtered sample solution to a polypropylene autosampler vial, to which we also added 25 μL of solution containing the isotope labeled internal standards and 300 μL of 0.1M formic acid. The contents of the autosampler vial were mixed well by use of a vortex mixer.

On-line SPE-HPLC-MS/MS

The on-line SPE-HPLC-MS/MS system was built using a ThermoFinnigan Surveyor liquid chromatograph (ThermoFinnigan, San Jose, CA, USA) coupled with a ThermoFinnigan TSQ Quantum Ultra triple-quadrupole mass spectrometer equipped with a heated electrospray ionization interface (HESI), a ThermoFinnigan Surveyor LC pump, and a six-port switching valve (Rheodyne MX7960, Rohnert Park, CA, USA). The operation of the liquid chromatograph, including the switching valve and LC pump, was controlled by the ThermoFinnigan Xcalibur software.

The PFCs in the dust solution were preconcentrated on a Betasil C8 guard column (3.0 X 10 mm, 5 μM, Thermo Electron Corporation, Bellefonte, PA). After injection (425 μL), the analytes were loaded on the Betasil C8 column using 0.1% formic acid at 1000 μL/min for 1.5min, then the column was washed with 15 % methanol / 85% 0.1% formic acid at 500 μL for 1.5 min, followed by 0.2 % NH_4OH at 500 μL for 1 min. After 4 min, the switching valve changed position, and the analytes were eluted from the column by the HPLC pump. The HPLC pump operated at a 300 μL/ min flow rate with 20 mM ammonium acetate (pH 4) in water as mobile phase A and acetonitrile as mobile phase B. A Betasil C8 HPLC analytical column (2.1 X 50 mm, 3μm) was used for the chromatographic separation of the analytes. The HPLC gradient program (17 min) was as follows: started at 15 % B (4 min), B content changed to 20% and increased to 90% (4 to 16 min), and then B content decreased to 15 % (16 to 17 min).

We used HESI in the negative ion mode to form negatively charged analyte ions at the interface under the following fixed instrument settings: spray ion voltage, –3000 V; HESI vaporizer temperature, 200°C; sheath gas (N_2) pressure, 50 arbitrary units; auxiliary gas (N_2) pressure, 4 arbitrary units; Ion sweep gas (N_2), 26 arbitrary units; capillary temperature, 285°C; collision gas (Ar) pressure, 1.5 mTorr. Ionization parameters and collision cell parameters were optimized for each analyte. Unit resolution was used for both Q1 and Q3 quadrupoles. The mass spectrometer was set in selective reaction monitoring mode. The precursor/product ion combinations (one for quantification and one for confirmation for some analytes) were monitored for each analyte; one precursor/product ion combination for quantification was monitored for the isotope-labeled analytes.

Results and Discussion:

Of the seventeen analytes measured, six of them PFBuS, Et-PFOSA, Me-PFOSA-EtOH, PFHxS, PFOS, and PFOA had detection frequencies >70% (Table1). We detected PFOS, PFOA, and PFHxS at the highest median concentration (i.e., 1-2 μg/g), followed by PFBuS, PFHpA and PFHxA. Except for the ethanol derivatives, the ethyl sulfonamides (which were primarily used in paper and packaging protectant applications) were detected more frequently and at higher median concentrations that the corresponding methyl sufonamides (which were used primarily in surface (e.g., textile, carpets) treatment applications).

Statistically significant correlations ($p < 0.001$) existed between the concentrations of PFOS and PFOA (Pearson correlation coefficient r=0.725) and PFHxS (r=0.938); between PFOA and PFHxS (r=0.565); and between Me-PFOSA-EtOH and PFOS (r=0.852) and PFOA (r=0.885). These results suggest that these PFCs may share similar sources or routes of exposure.

Figure1 shows the median concentrations of selected PFCs in this convenience sampling of household dust from the four countries. Dust samples collected in Atlanta, USA, in general, had the highest median concentrations of most PFCs.

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Disclaimer
The findings and conclusions in this report are those of the authors and do not necessarily represent the views of the Centers for Disease Control and Prevention.

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Table 1 PFCs Concentrations (ng/g) at selected percentiles and their frequency of detections.

	Selected percentiles			Frequency of detection (%)
abbreviation	25th	50th	75th	
PFHxS	46.8	266.7	1028.0	77.6
PFBuS	87.4	325.6	769.2	93.9
PFHpA	54.7	140.9	850.5	18.4
PFOA	< LOQ	318.0	1150.5	71.3
PFHxA	< LOQ	74.3	820.9	55.1
PFNA	< LOQ	< LOQ	86.8	38.8
PFDeA	< LOQ	< LOQ	112.7	49.0
PFOS	< LOQ	479.6	1907.1	71.3
PFUA	< LOQ	< LOQ	79.4	34.7
Me-PFOSA-AcOH	< LOQ	< LOQ	130.4	26.5
PFDoA	< LOQ	16.7	114.4	51.0
Et-PFOSA-AcOH	86.2	200.7	424.6	51.0
PFOSA	< LOQ	< LOQ	39.8	30.6
Me-PFOSA-EtOH	70.9	218.6	46.9	79.6
Me-PFOSA	< LOQ	< LOQ	< LOQ	14.3
Et-PFOSA-EtOH	< LOQ	155.2	587.8	59.2
Et-PFOSA	86.2	200.7	424.6	87.8

LOQ : 2.6 ng/g, except PFHpA, Me-PFOSA-EtOH, Et-PFOSA-EtOH : 4.0 ng/g

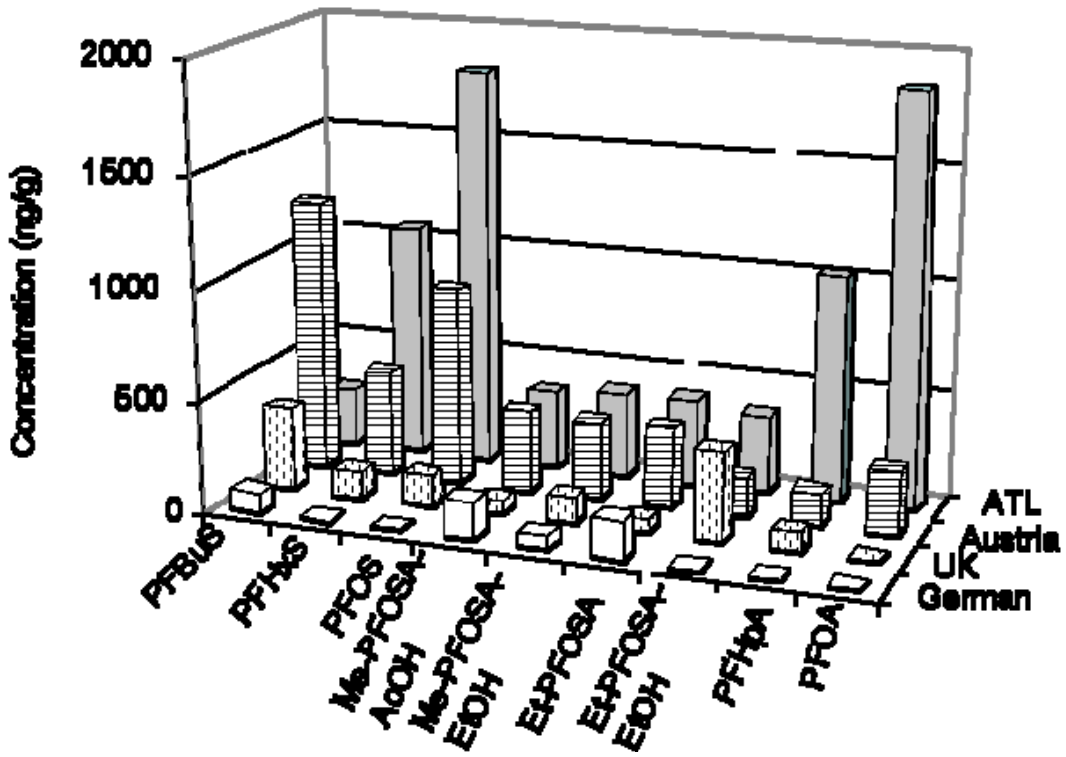

Figure1. Median concentrations (ng/g) of selected PFCs among four countries.