ANALYSIS OF PERFLUORINATED COMPOUNDS (PFCS) IN COMMERCIAL PRODUCTS

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Introduction

Perfluorinated compounds (PFCs) have been widely used since 1950s in various commercial products, such as car supplies, waterproof spray, insecticide, rust inhibitor and paint. However, they are persistent in the environment due to their chemical stability, and have been globally detected in aquatic and terrestrial habitats, wildlife, and humans since the end of 20th century. These chemicals are considered to pose health risk to humans as well as risk to the ecosystem.

Presently, commercial products (e.g. waterproof spray, carpet and insecticide) are considered to be one of the major source factors PFC pollution. However, detailed information regarding PFCs in commercial products are limited. In this study, we developed a method for analysis of PFCs in commercial products. Thirty two PFCs in 29 commercial products (25 from Japan, 3 from Britain, and 1 from Spain) were analyzed based on this method. Subsequently, the relationship between PFC pollution and commercial products containing PFCs, especially precursors of perfluorooctane sulfonates (PFOS) and perfluorocarboxylates (PFCAs) were investigated.

Materials and methods

Sample collection

Commercial products, which were considered to contain PFCs, such as Scotchgard™ series, were purchased from home centers and internet shops. Some products containing PFCs were donated from collaborators. The obtained samples were divided into 5 categories: car supplies, waterproof spray, insecticide, rust inhibitor and paint. The products, whose contents and feature were written in their label, such as "super endurance", "fluorine", "super water repellent", and "fluorine resin", were chosen as samples. Totally, 29 samples were collected and kept in polyethylene bag with zipper, and stored at room temperature in the dark until required for analysis.

Target compounds

Thirty two homologues (PFSAs: PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, PFHxDA, PFOcDA; PFSAs: PFBS, PFHxS, PFOS, PFDS; Precursor of PFCAs: 6:2 FTUCA, 8:2 FTUCA, 10:2 FTUCA, 6:2 FTCA, 8:2 FTCA, 10:2 FTCA; Precursor of PFOS: NMeFOSAA, NEtFOSAA, FOSAA, NEtFOSA, NMeFOSA, FOSA, NMeFOSE, NEtFOSE; THPFOS; PFHxPA) were analyzed (See Table 1)

Development of analytical method of PFCs in commercial products

The best method of sample preparation was evaluated after conducting three steps of extraction and cleanup procedures as follow:

• Liquid-phase extraction (Step 1)

PFC recoveries using six different solvent in extraction process were compared (methanol, ammonia methanol, ethanol, a mixture of methanol and ethanol (1:1), MTBE, ethyl acetate).

Table 1. target PFCs compounds

PFSAs	$CF_3(CF_2)_nSO_3^-$ (n=4,6,8,10)	Perfluoroalkyl sulfonate
Precursor of PFOS	$CF_3(CF_2)_7SO_2N(C_nH_5)CH_2CH_2OH$ (n=1,2)	Perfluoroalkyl amide alcohol
	$CF_3(CF_2)_7SO_2NHC_nH_3$ (n=0,1,2)	Perfluoroalkyl amide
	$CF_3(CF_2)_7SO_2N(CnH_3)CH_2COO^-$ (n=0,1,2)	Perfluoroalkyl amide acetate
PFCAs	$CF_3(CF_2)_nCOO^-$ (n=5~18)	Perfluoroalkyl carboxylic acid
Precursor of PFCAs	$CF_3(CF_2)_nCF=CHCOO^-$ (n=6,8,10)	Fluorotelomer unsaturated carboxylates
	$CF_3(CF_2)_nCH_2COO^-$ (n=5,7,9)	Fluorotelomer carboxylates
THPFOS	$CF_3(CF_2)_5CH_2CH_2 SO_3^-$	Fluorotelomer sulfonate
PFHxPA	$CF_3(CF_2)_5PO(OH)_2^-$	Perfluorohexane phosphonate

Samples were extracted with the solvents mentioned above by shaking and ultrasonication, and then centrifuged. The supernatant was collected. This procedure was repeated 3 times.

- Clean-up with K-solute® cartridge (Step 2)

    After reducing the volume of supernatant by evaporation under gentle stream of nitrogen, the supernatant was loaded on InertSep® K-solute cartridge (GL sciences Inc., Tokyo, Japan) to remove interfering factor such as emulsion. The effect of this clean-up procedure was compared with that of no clean-up.

- Solid-phase extraction (Step 3)

    Reversed-phase sorbent cartridge (Oasis® HLB, Waters Corp., Milford, MA, USA) and anion exchange sorbent cartridge (Oasis® WAX, Waters Corp., Milford, MA, USA) was used for extraction and clean-up with different procedures described below, and their recovery rates were compared.

    Target retain method:

    A method retains target PFCs in the cartridge by their affinity to cartridge packing materials and then elutes target PFCs after the impurities are removed from the cartridge by solvents that have low affinity to the target PFCs. And we call this method "Target retain method"

    Target flow-through method:

    A method keeps impurities in the cartridge and passes the PFCs through the cartridge with solvents that have high affinity to the target PFCs. And we call this method "Target flow-through method"

Analysis of PFCs in commercial products

- Procedure

    Small amount of sample (0.05 g) was taken from the product, because same commercial products containing high concentrations of PFCs. For the spray cans, their contents were sprayed into polyethylene bags and 0.05 g of the samples was collected from the bags. The collected samples were spiked with carbon labeled internal standards (^{13}C-PFC), dissolved in methanol, shook (20 min), ultrasonicated (20 min) then centrifuged (20 min). The supernatant was collected and the procedure repeated three times. The volume of the collected solvent was reduced to 1 ml by gentle stream of nitrogen. The concentrate was loaded onto HLB cartridge (pre-washed with 5 ml methanol). After the solid-phase extraction, the sample was concentrated to 1mL by gentle stream of nitrogen, then analyzed for the target compounds using LC-MS/MS high-performance liquid chromatograph (HPLC; Agilent 1100LC, Agilent Technologies, Palo Alto, CA, USA) interfaced with a tandem mass spectrometer (MS/MS; Micromass Quattro, Waters, Milford, MA, USA).

- Quality Assurance and Quality Control

    The samples with high concentration of target PFCs (> 2000 ng /g) were diluted appropriately. Duplicated analyses were conducted to make sure that their diluted concentrations were in the range of calibration curves. The calculated concentrations were reported when their recoveries were between 50 and 120%.

    Procedural blank samples (*n*=3) were prepared and analyzed. The average procedural blank value was subtracted from the measured concentration.

Results and discussions

Development of the analytical method of PFCs in commercial products

After the comparison of those analytical methods, the method which has the best recovery rates obtained in this study for the 32 target PFCs was selected. The selected method is a combination of methanol as extraction solvent and reversed-phase sorbent cartridge with target flow-through method.

Analysis of PFCs in commercial products

The total PFC concentraion in 8 samples were higher than 1,000 ng /g among the 29 samples analyzed. And among these 8 samples, 2 samples were higher than 100,000 ng /g (Figure 1).

- Relationship between usage and concentration of PFCs in commercial products

    No remarkable relationship between total PFCs levels in products and their usage was observed. The precursors of PFOS and Precursors of PFCAs (fluorotelomer alcohol) constitute a greater proportion of PFCs in the 29 samples. Precursors of PFOS were mainly detected from the samples of "fabric textiles use", and PFCAs were detected from almost all the samples.

- Relationship between purchase date and concentration of PFCs in commercial products

Products of Scotchgard™ series purchased in the 1990s showed the highest concentrations. These were obviously higher as compared to the other samples. However as a whole, no time trend in concentration of PFCs was observed for the 29 samples analyzed.
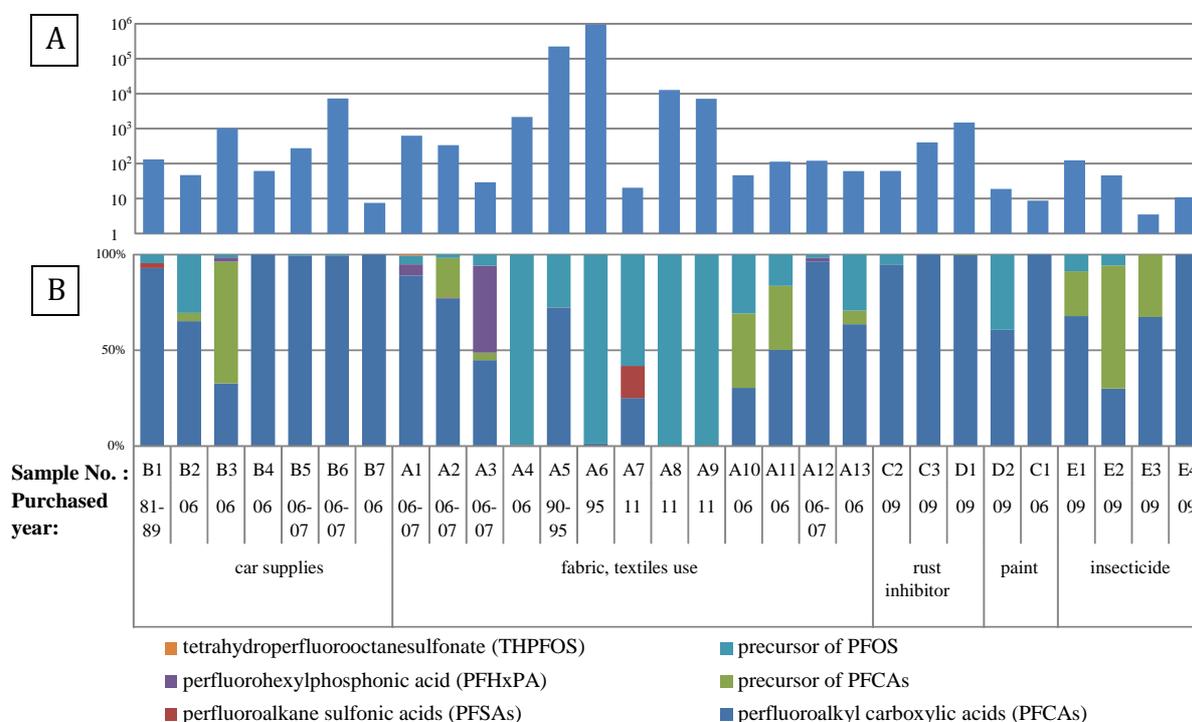

Fig. 1. Total PFC concentration (ng /g) (A) and homologue profiles (%) (B) in commercial products of different purchase year and usage

• PFCAs

PFCAs were detected in almost all the samples with proportions more than 50% among the target PFCs. The order of PFCA concentrations in 29 products were: PFOA(C8) > PFHxA(C6) > PFHpA(C7) > PFNA(C9). The samples purchased before 2000 were observed to contain relatively higher levels of PFOA(C8), PFHxA(C6) and PFHpA(C7) (> 30,000 ng /g) as compared with the samples purchased after 2006. On the other hand, PFNA(C9) values were relatively higher (> 6,000 ng /g) on the products purchased after 2006. These showed a decreasing trend of PFOA(C8), PFHxA(C6) and PFHpA(C7) use and an increasing trend of PFNA(C9) use in commercial products. Similar trends were reported in the studies of Tokyo bay basin, wastewater and street runoff in Kanto region[2, 3]. Both studies showed similar PFC profile with our results, suggesting correlation between PFCs in commercial products and that in aquatic environment.

• Precursors of PFCAs (FTCAs, FTUCAs)

Concentrations of FTCAs and FTUCAs were detected in less than half of the samples, which had been purchased mainly after the year 2006. The rank order of concentration level in 29 products was: 10:2 FTCA > 10:2 FTUCA > 8:2 FTCA > 6:2 FTUCA. Relatively high FTCAs and FTUCAs concentrations (> 300 ng /g) were observed in the products, compared to their reported concentration in Tokyo bay basin (< 0.09 ng /L)[2]. More information is required for precursors of PFCAs to explain the relationship between the PFCs in commercial products and in Tokyo bay basin.

• PFSAs

PFSAs were detected with less than half of the samples, and the concentrations were low (<300 ng /g). The rank order of concentration level among PFSAs in the 29 products was: PFOS > PFHxS > PFBS > PFDS. PFSAs were mainly detected from the Scotchgard™ series products purchased before 2000.

• Precursors of PFOS

Precursors of PFOS were detected with high concentration from products for fabric and textiles. The order of concentration level of PFOS precursors in 29 products was NMeFOSE > NEtFOSE > NMeFOSA > FOSA. NMeFOSE contributed more than half of total concentration of PFOS precursors in all the samples. It is remarkable that methyl type (NMeFOSA, NMeFOSE) was observed in the Scotchgard™ series products from Britain, Spain and Japan while ethyl type was only detected in the Scotchgard™ series products from Japan. This observation was consistent with the PFC profiles in the sediment collected form Tokyo bay[1]. The result indicated that ethyl type based products are mainly used in Japan among the 3 countries, and suggested the correlation between products containing PFCs and PFC pollution in aquatic environment.

Considering the relationship between PFC profile in commercial products and that in aquatic environment, the use of commercial products which contain PFCs were considered to be one of the important sources of aquatic PFC pollution.

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