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Analysis of perfluoroalkyl carboxylates in vacuum cleaner dust samples in Japan

Wanyang Liu, Shengying Chen, Kouji H. Harada, Akio Koizumi *

Department of Health and Environmental Sciences, Kyoto University Graduate School of Medicine, Yoshida Konoe, Sakyo, Kyoto 606-8501, Japan

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ABSTRACT

Perfluorooctanoic acid (PFOA) has long been an environmental contaminant of concern owing to its potential health risk. However, exposure to perfluorinated carboxylic acids (PFCAs) other than PFOA is not well understood. In this study, we investigated the concentrations of PFCAs in vacuum cleaner dust in Japan to measure the PFCAs contamination in an indoor environment. Most of the 77 samples contained PFCAs with 6–13 carbon atoms. The median concentration of perfluorononanoic acid (PFNA, 23.2 ng g^{-1}) was highest among PFCAs, followed by PFOA (20.8 ng g^{-1}) and perfluoroundecanoic acid (PFUnDA, 12.9 ng g^{-1}). The 90th percentile concentrations of PFNA, PFUnDA and perfluorotridecanoic acid (PFTrDA) were 948, 283 and 110 ng g^{-1}, respectively, and these were detected at greater concentrations than neighboring, even-numbered PFCAs. The proportion of long-chain PFCAs in vacuum cleaner dust from Japan was relatively higher than those reported for other countries. Factor analysis showed three independent factors. Odd-numbered long chain PFCAs (PFNA, PFUnDA and PFTrDA), which can correspond to factor 1, were major components of PFCAs in vacuum cleaner dust. Short chain PFCAs (factor 2) and even numbered long chain PFCAs (factor 3) were also statistically separated. These findings suggest that there are several sources of PFCAs with different origins in indoor environment. Further investigations into the origins of PFCAs are needed to evaluate indoor contamination with PFCAs.

1. Introduction

Perfluorinated alkyl acids such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have been detected in various media in the environment, including wildlife and humans (Houde et al., 2006). In 2002, a major manufacturer, 3M Company, phased out PFOS production (Renner, 2001). Since then, several studies have demonstrated that PFOS and PFOA induce developmental toxicities in animals and humans (Lau et al., 2007; Steenland et al., 2010). Although PFOA was a major component of perfluoroalkyl carboxylates (PFCAs) emission, long chain PFCAs (perfluorononanoic acid (PFNA), perfluoroundecanoic acid (PFUnDA) and perfluorotridecanoic acid (PFTrDA)) have also been detected in discernible concentrations in samples collected from wildlife (Prevedouros et al., 2006; Furdui et al., 2008).

In human biomonitoring studies, PFOS was the major perfluoroalkyl acids (PFAAs) found in human serum. In addition, PFOA was found to be the most prevalent component of serum PFCAs in western countries, followed by PFNA, perfluorodecanoic acid (PFDA) and PFUnDA (Kärrman et al., 2007; Haug et al., 2009; Kato et al., 2009b). Our previous study of Japanese, Korean and Vietnamese adults showed that PFNA and PFUnDA were found in serum at concentrations generally similar to PFOA, and that these levels have continued to increase, even after 2002 (Harada et al., 2011). Factor analysis of PFCAs also revealed two major factors composed of PFNA, PFUnDA and PFTrDA (factor 1) and PFOA and perfluoroheptanoic acid (PFHpA) (factor 2) (Harada et al., 2011). However, the origin of these factors is still not known.

Long chain PFCAs have not been detected in food duplicate samples in Japan at concentrations greater than method detection limits (MDL: 0.1 ng g^{-1} for PFNA, 0.5 ng g^{-1} for PFDA and PFUnDA, respectively) (Kärrman et al., 2009). In addition, the predominance of odd numbered PFCAs has not been reported in aquatic systems in Japan (Murakami et al., 2008, 2009; Zushi et al., 2008; Raj Shivakoti et al., 2011). Fluorotelomer alcohols (FTOHs) are considered to be precursors of long chain PFCAs and have been detected in Japan and Western countries (Martin et al., 2002; Jahnke et al., 2007; Oono et al., 2008a,b; Mahmoud et al., 2009). Although atmospheric degradation of 8:2 FTOH has shown comparable yields of PFOA and PFNA (Ellis et al., 2004), the dominance of odd number PFCAs

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Abbreviations: PFCAs, perfluorinated carboxylic acids; PFOS, perfluorooctane sulfonate; PFOA, perfluorooctanoic acid; PFHxA, perfluorohexanoic acid; PFHpA, perfluoroheptanoic acid; PFNA, perfluorononanoic acid; PFDA, perfluorodecanoic acid; PFUnDA, perfluoroundecanoic acid; PFDoDA, perfluorododecanoic acid; PFTrDA, perfluorotridecanoic acid; PFTeDA, perfluorotetradecanoic acid; PFAAs, perfluoroalkyl acids; IDLs, instrumental detection limits; LOD, limit of detection; MDLs, method detection limits; RSD, relative standard deviation; SD, standard deviation; GM, geometric mean; GSD, geometric standard deviation.

* Corresponding author. Tel.: +81 75 753 4456; fax: +81 75 753 4458.
E-mail address: koizumi.akio.5v@kyoto-u.ac.jp (A. Koizumi).

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in human serum has been observed only in East Asian countries (Harada et al., 2011). A review by Prevedouros et al. (2006) indicated that odd numbered PFCAs have been applied to fluoropolymer manufacturing aids and surfactants that were manufactured *via* oxidation of fluorotelomer olefins. Their application to commercial products might be an exposure source of long chain PFCAs in human serum. Given the indoor use of those products, a portion of them likely disperses and contaminates indoor dusts.

The primary goal of the present study was to investigate PFCAs in house dust. To achieve this goal, we investigated vacuum cleaner dust concentrations of PFCAs in Japan. To evaluate the potential factors influencing the PFCAs level, questionnaires regarding housing conditions and articles were collected. In addition, we conducted factor analysis to elucidate the potential compositions of PFCAs in indoor dust.

2. Materials and methods

2.1. Sample collection

To evaluate geographical differences in PFCAs in vacuum cleaner dust in Japan, we recruited 77 homes from Osaka, Kyoto, Wakayama and Toyama, Japan and conducted sampling from October to December, 2010. Osaka was selected to evaluate the effects of a local industrial source of PFOA (Saito et al., 2004; Morikawa et al., 2006; Niisoe et al., 2010). Vacuum cleaner dust samples were collected from the used bag of the household vacuum cleaner into a sealable polyethylene bag. Samples were shipped via an overnight delivery service to Kyoto University.

A 500 mg cleaner dust sample was taken out from the sealable polyethylene bag and hairs and plastic garbage were removed from the samples using forceps and a loupe. Samples were then sieved to remove materials greater than 150 μm in diameter and stored at −4 °C until analysis in the Kyoto University Human Specimen Bank (Koizumi et al., 2005, 2009). Information regarding the home condition, articles use and life habits was then collected by questionnaire (Table 1 and Supplemental Table 1). The research protocol for the present study was reviewed and approved by the Ethics Committee of the Kyoto University Graduate School of Medicine on 13 October 2010 (E960). Written informed consent was obtained from all participants.

2.2. Reagents

Methanol (LC–MS grade) and water (distilled LC–MS grade) were obtained from Kanto Chemicals (Tokyo, Japan). Ammonium hydroxide (25% in water) was purchased from Merck (Darmstadt, Germany). Benzyl bromide was purchased from Wako pure chemicals (Osaka, Japan). A mixture of $^{13}C_2$-labeled perfluorohexanoic acid (PFHxA), $^{13}C_2$-labeled PFOA, $^{13}C_4$-labeled PFOA, $^{13}C_5$-labeled PFNA, $^{13}C_2$-labeled PFDA, $^{13}C_2$-labeled PFUnDA and $^{13}C_2$-labeled perfluorododecanoic acid (PFDoDA) was obtained from Wellington Laboratories (Guelph, Ontario, Canada) and Perkin Elmer (Boston, MA).

2.3. Determination of PFCAs in vacuum cleaner dust

PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA and perfluorotetradecanoic acid (PFTeDA) were analyzed by gas chromatography/mass spectrometry (Agilent 6890GC/5973MSD, Agilent Technologies Japan, Ltd., Tokyo, Japan). Perfluorooctane sulfonamides were not included because main purpose in this study was to elucidate a pattern of PFCAs exposure in indoor environment. Vacuum cleaner dust samples were subjected to a clean-up procedure consisting of a weak anion exchange, solid-phase extraction. Briefly, approximately 500 mg of vacuum cleaner dust sample and internal standards (10 ng mixture of $^{13}C_2$-labeled PFHxA, $^{13}C_4$-labeled PFOA, $^{13}C_5$-labeled PFNA, $^{13}C_2$-labeled PFDA, $^{13}C_2$-labeled PFUnDA, and $^{13}C_2$-labeled PFDoDA) were put into a 50 mL polypropylene (PP) centrifugation tube and 20 mL of methanol were added. The samples were then vortexed and shaken on a vertical shaker for 30 min, after which they were placed in an ultrasonic bath for 15 min. Next, the samples were centrifuged (11 000*g*, 15 min), and the supernatant was then reduced to approximately 5 mL by rotary evaporation. Approximately 15 mL of water were subsequently added to the sample, and the solution was put through a WAX solid phase cartridge (6 cc, 150 mg 30 mm, Waters, Milford, MA, USA) that had been previously conditioned with 4 mL methanol and 4 mL water. Subsequent loading of the sample was followed by washing the sorbent with 4 mL 40% (v/v) methanol in water and a second wash using 8 mL methanol. The perfluorinated compounds were then eluted into a tube using 2 mL 2% (v/v) ammonium hydroxide in methanol. The solution was then dried under N_2, after which 0.25 mL of 100 mM benzyl bromide acetone and the performance standard $^{13}C_2$-PFOA were added. Next, the solution was transferred to an autosampler vial and heated for 1 h at 80 °C. Extracts were subsequently analyzed by GC/MS in electron impact ionization mode using single ion monitoring. PFCA benzyl esters were separated on a DB-5MS column (30 m length, 0.25 mm i.d., 1 μm film thickness) with a helium carrier gas. Splitless injections (0.5 μL) were performed with the injector set to 220 °C, and the split was opened after 1.5 min. The initial oven temperature was 70 °C for 2 min, after which it was increased to 100 °C at 20 °C min^{-1}, and then to 280 °C at 30 °C min^{-1}. Ion fragments ($[M]^+$) were monitored and used for quantification (Supplemental Table 2).

Instrumental detection limits (IDL) were defined as the mass of the analyte producing a peak with a signal-to-noise ratio of 3, and ranged from 2 pg (PFTeDA) to 0.5 pg (other PFCAs) (Supplemental Table 2). All samples were quantified using a seven-point calibration curve (range: 0.5–50 000 ng mL^{-1} in methanol). Limit of detection (LOD) was defined as the lowest concentration with a relative standard deviation (RSD) of the relative response factors <15% ($n = 3$ for each concentration). The method detection limit (MDL) was defined as the blank response +3 standard deviations in procedural blank samples. The procedural blank levels using 0.5 mL distilled water were evaluated in every 11 samples. Since blank samples (0.5 mL distilled water) contained no detectable concentrations, MDL was considered to be equal to the LOD

Table 1
Study area and population.

Sampling site	Population density ($\times10^3$ km^{-2})	*n*	Building age[a] (yr)	House type		Building Construction	
				Houses	Apartments	Timber	Concrete
Osaka	11.7	21	31.0 ± 27.3	10	11	7	14
Kyoto	1.7	20	30.3 ± 21.2	13	7	11	9
Wakayama	0.50	16	18.1 ± 14.2	14	2	13	3
Toyama	0.86	20	20.8 ± 9.7	19	1	15	5

[a] Data are presented as the mean ± standard deviation.