COMPARISON OF PERFLUORINATED SULFONAMIDES AND THEIR DEGRADATION PRODUCTS IN INDOOR DUSTS

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Introduction

Perfluorinated organics are widely used with many different applications.[1] Among them, the non-volatile perfluorooctane sulfonate (PFOS) and its acid, perfuorooctanoic acid (PFOA) have been found almost ubiquitously present in biological matrices and in human populations.[2-4] The presence of PFOS and PFOA in the environment, especially in remote areas such as Canadian Arctic are thought to be attributed to the use of perfluorooctane-sulfonyl fluoride (POSF)-based products including perfluorinated sulfonamides (PFASs) and fluorotelomer alcohols.[5,6] At least, the biotranformation of N-Ethyl perfluoro-octanesulfonamide to PFOS in Rainbow Trout has been confirmed.[7]

Only a few studies have investigated these chemicals in indoor environment which is suspected of being a major source to the enviornments. One example was the detection of PFOS and PFOA in Japanese homes where outdoor soil/dust was at minimum as Japanese do not carry their outdoor shoes into homes in general.[8] Recently, N-methylperfluorooctane sulfonamidoethanol (Me-FOSE) and N-ethylperfluorooctane sulfonamidoethanol (Et-FOSE), have been detected in indoor air and indoor dust in Canadian homes.[9] PFOS and PFOA were also found in the same dust samples.[10] The objective of this investigation is to study the relationship between levels of FOSEs, and PFOS and PFOA, in an attempt to better understand the sources of PFOS and PFOA.

Materials and Methods

Dust samples – The strategy of selecting representative residential homes, where the dust samples were collected, has been described elsewhere.[11] Dusts from 73 participating homes in the city of Ottawa, Canada, were collected between November 2002 and March 2003. Dust samples were sieved and fine dust of less than 150 µm were used for analysis.

Sample preparation and analysis – Detailed sample preparation and analysis of FOSEs and of PFOS and PFOA have been described elsewhere.[9,10] Briefly, for the analysis of FOSEs were extracted with Dichloromethane in a Soxhlet device and analysed by GC/MS in selective ion monitoring mode. PFOS and PFOA were extracted with acetonitrile, cleaned up using a C18- solid phase cartridge, and analyzed by LC/MS in negative ion mode using multiple reaction monitoring technique.

Statistical Analysis – The distribution of PFOS/PFOA and the FOSEs was investigated using the Anderson-Darling normality test. The original data and log-transformed data were found being not normally distributed and therefore further testing was conducted on the ranks of the data. Spearman rank-order correlation coefficient was used. The Spearman correlation coefficients were tested for significance. A *p*-value of less than 0.05 indicates a strong relationship between the two variables for which the Spearman correlation is being calculated.

Results and Discussion

The names and molecular formulae of four target chemicals are listed in Table 1. PFOS and PFOA are often considered as the degradation products of some perfluorinated chemicals. The structural connection between PFOS/PFOA, and the two FOSEs is clear: PFOS is formed when the S-N bond of the sulfonamide is broken. PFOA might be formed when the C-S bond on the other side of the sulfonate functional group ($-SO_2-$) is broken and C1 position carbon is oxidized to carboxylic group.

Table 1. Name and molecular formula of the PFCs

Compounds Acronym Molecular Formula

N-Methyl perfluorooctane sulfonamidoethanol Me-FOSE $C_8F_{17}SO_2N(CH_3)CH_2CH_2OH$

N-Ethyl perfluorooctane sulfonamidoethanol Et-FOSE $C_8F_{17}SO_2N(CH_2CH_3)CH_2CH_2OH$

Perfluorooctane sulfonate PFOS $C_8F_{17}SO_3H$

Perfuorooctanoic acid PFOA $C_7F_{15}COOH$

Due to limited quantity of sieved dust samples from some study homes and the need to perform various other analyses, only samples from 67 of the 73 homes were analyzed for PFOS and PFOA, and from 64 homes for FOSEs. Summary statistics (median, and mean) are reported in Table 2. Median values were five to ten times smaller than the mean values (Table 2) for both FOSEs and PFOS/PFOA, indicating that the distributions of the levels of these four chemicals were skewed. Concentration levels of PFOS/PFOA were several times lower than those of FOSEs. For example, the mean value of combined PFOS and PFOA concentrations (551 ng/g) was four times lower than that of combined Me-FOSE and Et-FOSE (2573 ng/g). The medians between these two groups were also different by a factor of 3.

Table 2. Statistics of concentrations (ng/g) in indoor dust

	PFOA	**PFOS**	**PFOA +PFOS**		**Me-FOSE**	**Et-FOSE**	**Me + Et FOSE**
Sample size (n)	67	67	67		64	64	64
Mean	106	444	551		393	2181	2573
Median	20	38	78		98	86	230

Although PFOS and PFOA could be formed through the degradation of the FOSEs, it is also reported that PFOS and PFOA have been used directly in various products.[1] Some insight can be obtained by examining the correlation of the two groups of chemicals in the same dust samples. Spearman's rank-order correlation coefficients among the four target chemicals and their groups are reported in Table 3. The Spearman's correlation coefficient values were in the range of 0.4 to 0.8. PFOA, PFOS, Me-FOSE and Et-FOSE were all significantly and positively correlated. As well, the combined PFOA and PFOS level was significantly and positively correlated with the combined Me-FOSE and Et-FOSE. The correlations indicate that increasing levels of the FOSEs are coupled with increased levels of PFOS/PFOA.

Table 3. Spearman Correlation coefficient of target chemicals detected in house dust (*p*-values are provided in parentheses)

	PFOS	Me-FOSE	Et-FOSE	PFOA + PFOS	Me+Et FOSE
PFOA	0.753 (<0.0001)	0.543 (<0.0001)	0.502 (<0.0001)	0.856 (<0.0001)	0.609 (<0.0001)
PFOS		0.442 (0.0003)	0.350 (0.0049)	0.968 (<0.0001)	0.473 (<0.0001)
Me-FOSE			0.517 (<0.0001)	0.504 (<0.0001)	0.775 (<0.0001)
Et-FOSE				0.410 (0.0008)	0.868 (<0.0001)
PFOA + PFOS					0.538

		(<0.0001)

Among the information collected during field sampling through a questionnaire, percentage of carpet that covered house floors and the age of the house were selected to be tested for their correlation with the levels of target chemicals in house dust. Again, Spearman's correlation coefficient was used to investigate these relationships (Table 4). PFOA and PFOS had significant negative correlation with the age of house and significant positive correlation with the percentage of carpet coverage on the house floors. Older homes have lower levels of PFOS and PFOA, and homes with more carpeting on the floors have higher levels of PFOS and PFOA. It is also interesting to note that age of house and percentage of house covered by carpets were significantly and negatively correlated. Older houses tend to have less carpeting and hence lower levels of PFOA and PFOS in their house dust. On the other hand, as indicated by the Spearman's correlation coefficient, Me-FOSE and Et-FOSE had no significant relationships with either the age of house or the percentage of carpeting in the house (Table 4).

In conclusion, significant correlations between PFOS/PFOA and FOSEs in house dust show that the presence of these two groups of chemicals in indoor environment are related, either through the application of these chemicals in products, and/or the degradation of FOSEs in the environments and in the dust. However, the impact of age of the vacuum dust, which could be somewhere between several weeks to several months, should be taken into consideration when interpret these results as the degradation of FOSEs in the dust overtime could not be ruled out. The fact that the levels of PFOS and PFOA in house dust were related to the use of carpets in the house indicated that, in addition to be the possible end degradation products, PFOS-related chemicals and fluoropolymers manufactured using PFOA salts, might be used directly in carpets. The identification of sources of these chemicals is an important issue that requires for further investigation. It will help to resolve questions regarding the sources of PFOS and PFOA, and help to answer the question of why PFOS are so ubiquitously present in the environment.

Table 4. Spearman Correlation coefficient of perfluorinated chemical concentrations in dust and selected house characters (*p*-values are provided in parentheses)

	PFOA	PFOS	PFOA + PFOS	Me-FOSE	Et-FOSE	Me + Et FOSE
Age of house	-0.335 (0.0055)	-0.340 (0.0049)	-0.351 (0.0036)	-0.192 (0.1294)	-0.120 (0.3434)	-0.179 (0.1572)
% Carpeting in homes	0.347 (0.0044)	0.368 (0.0024)	0.378 (0.0018)	0.197 (0.1221)	0.093 (0.4676)	0.162 (0.2056)

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