Perfluorinated Compounds in Archived House Dust Samples

Mark J. Strynar[1] and Andrew B. Lindstrom[1].

1.United States Environmental Protection Agency, Office of Research and Development/National Exposure Research Laboratory/Human Exposure and Atmospheric Sciences Division/Methods Development and Application Branch

Abstract

Perfluorinated compounds (PFCs) have come under recent scrutiny for their persistence, global distribution (environmental media, wildlife, humans) and animal toxicity. The majority of the scientific literature on PFCs suggests routes of exposure are largely unknown. Data gaps include both indoor and outdoor sources. A study was undertaken to develop methods to detect PFCs in house dust, and reduce uncertainty in indoor exposure. Archived EPA house dust samples (n=112) were sieved to 150 μm and analyzed for select PFCs. Telomer alcohols (6:2-FTOH, 8:2-FTOH, 10:2-FTOH) were analyzed by GC/MS after sonic extraction and SPE cleanup. Perfluorinated carboxylic acids (C_6-C_{12}) and sulfonates (PFOS, PFHS, and PFBS) were analyzed by LC-MS/MS. Recovery of spiked PFCs in house dust ranged from 39.5% (cv 0.10) for PFNA to 107.3% (cv 0.08) for PFUA. Mean concentrations were calculated for values above the lower limit of quantitation (LOQ). Mean concentrations for PFCs ranged from 0.357 μg/g (PFDA) to 11.23 μg/g (PFHS). Maximum concentrations ranged from 2.42 μg/g (6:2 FTOH) to 357.0 μg/g (PFHS). Data appear to be log-normally distributed with many samples at or below the limit of quantitation (LOQ) (~ 0.1 μg/g dust). PFOS, PFOA and 8:2 FTOH were below the LOQ in 5.4% , 3.6% and 46.4% of the samples respectively. Correlation coefficients suggest strong correlations between certain PFCs in house dust ($\alpha = 0.01$) and lack of correlation for others.

Introduction

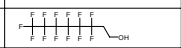
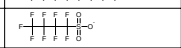
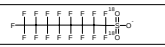
Perfluorinated compounds are widely used in a variety of consumer and industrial products. The C-F bond, gives perfluorinated compounds their unique properties, which include resistance to degradation, thermal stability, and persistence. Many recent studies have found global distribution of a handful of perfluorinated compounds in various environmental and biological media. In actuality, there may be many more compounds the scientific community is not yet aware of. To date, much of the published literature has focused on the toxicity and persistence of PFOS, PFOA and a select few other PFCs. The toxicity of precursors, and longer chain length PFCs has been largely ignored.

Some have hypothesized that human exposure to PFCs may come from stain-repellent treatments of carpet and upholstery. A recent study reported on concentrations of select PFCs in Japanese house-dust samples collected from 16 homes (Moriwaki et al., 2003). House dust may be an important indicator of what people are exposed to on a daily basis. Lewis et al., 1999, reported that house dust is a repository for pesticides and PAH. A study was undertaken to develop methods to assess PFCs in archived vacuum cleaner bag dusts collected as part of larger EPA study (Children's Total Exposure to Persistent Pesticides and Other Persistent Organic Pollutants – CTEPP).

Materials and Methods

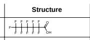
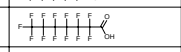
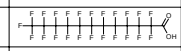
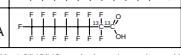
Archived house dust samples from the EPA's CTEPP study were acquired. Samples were collected between 7/2000 to 11/2001. Samples represented 112 homes located in Ohio (n=58) and North Carolina (n=54). Samples were sieved to 150 μm and stored in dark glass bottles at room temperature. Dust sub-samples were taken for analysis (102.5±6.7 mg). Replication of 10% of the samples was carried out for all analytes. Fluoro-telomer alcohols were extracted via shaking/sonication in hexane. Extracts were cleaned up by silica-SPE and elution with 5% diethyl-ether in hexane. Standard curves were made by spiking blank matrix with fluoro-telomer alcohols. Flouro-telomers were analyzed via negative EI GC/MS operating in SIM mode. Perfluorinated acids and sulfonates were extracted by shaking/sonication in acetonitrile. Sub-samples of extracts were taken with no further cleanup for ESI LC-MS/MS analysis. Perfluorinated acids and sulfonates standard curves were made by spiking tubes devoid of matrix with analytes . Analytes were quantitated by taking the area ratio (AR) (analyte/ internal standard) for unknowns compared to AR for standards. In all instances IS was added to all samples before extractions. See Tables 1 and 2 for analytes and internal standards used. Method blanks, matrix blanks and QC samples were analyzed with each set of samples to ensure quality control. LOQs were around 0.1 μg/g for all analytes (see Tables 1,2).

Table 1. Fluoro-telomer alcohol and perfluorinated sulfonate standards used

Analyte	Acronym	Structure	MW	Ions (*m/z*)*
2-(perfluorohexyl) ethanol	6:2 FTOH		364	363,344,314
2-(perfluorooctyl) ethanol	6:2 FTOH		464	463,444,405
2-(perfluorodecyl) ethanol	10:2 FTOH		564	563,544,505
3-(perfluorodecyl) propanol	Telomer I.S.		478	477,441,395
perfluorobutane sulfonate	PFBS		299	299 → 80
perfluorohexane sulfonate	PFHS		399	399 → 80
perfluorooctane sulfonate	PFOS		499	499 → 80
$^{18}O_2$-perfluoro-octane sulfonate	$^{18}O_2$-PFOS		503	503 → 84

* Fluoro-telomer alcohols analyzed by GC/MS operating in select ion monitoring (SIM) mode for specific *m/z*. Perfluorinated Acids and sulfonates analyzed by LC/MS/MS monitoring *m/z* → *m/z* transitions.

Table 2. Perfluorinated carboxylic acid standards used.

Analyte	Acronym	Structure	MW	Ions (*m/z*)*
perfluorohexanoic acid	PFHxA		314	313→ 269
perfluoroheptanoic acid	PFHpA		364	363 → 319
perfluorooctanoic acid	PFOA		414	413 → 369
perfluorononanoic acid	PFNA		464	463 → 419
perfluorodecanoic acid	PFDA		514	513 → 469
perfluoroundecanoic acid	PFUA		564	563 → 519
perfluorododecanoic acid	PFDoA		614	613 → 569
1,2-^{13}C perfluoro-octanoic acid	$^{13}C_2$-PFOA		416	415 → 370

* Perfluorinated acids and sulfonates analyzed by LC/MS/MS monitoring *m/z* → *m/z* transitions.

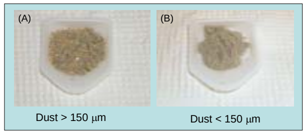


Figure 1. Vacuum cleaner dust samples retained (A) and passing (B) a 150 μm sieve.

Table 3. Recovery of perfluorinated compounds spiked into house-dust

	High Spike *		Low Spike*	
	% recovery	cv	% recovery	cv
6:2 FTOH	77.3	0.03	77.7	0.08
8:2 FTOH	85.2	0.03	82.1	0.06
10:2 FTOH	87.6	0.05	85.6	0.03
PFDoA	103.8	0.11	106.5	0.07
PFUA	101.5	0.09	107.3	0.08
PFDA	100.9	0.09	101.8	0.10
PFNA	39.5	0.10	47.9	0.04
PFOA	79	0.14	82.5	0.07
PFHpA	102.3	0.07	99.7	0.03
PFHxA	98.3	0.09	92.4	0.05
PFOS	103.5	0.07	103.2	0.09
PFHS	44.2	0.08	51.1	0.07
PFBS	95.1	0.05	98.9	0.05

•For fluoro-telomer alcohols high spike was 250 ng, low spike was 25 ng. For perfluorinated acids and sulfonates high spike was 1000 ng and low spike was 100 ng.

Table 4. Perfluorinated compounds in house-dust samples.

Compound	Mean* (μg/g dust)	Mean** (μg/g dust)	Max. (μg/g dust)	Min. (μg/g dust)	% below LOQ	cv
6:2 FTOH	0.433	0.225	2.416	<LOQ (0.087)	56.3	0.023
8:2 FTOH	0.885	0.503	4.976	<LOQ (0.085)	46.4	0.055
10:2 FTOH	0.507	0.288	2.650	<LOQ (0.092)	49.1	0.064
PFHxA	1.202	1.174	12.45	<LOQ (0.100)	7.1	0.131
PFHpA	1.436	1.087	11.50	<LOQ (0.125)	25.9	0.171
PFOA	3.069	2.962	19.56	<LOQ (0.102)	3.6	0.249
PFNA	0.417	0.221	2.63	<LOQ (0.113)	57.1	0.083
PFDA	0.357	0.155	2.67	<LOQ (0.094)	69.6	0.095
PFUA	0.699	0.304	5.88	<LOQ (0.107)	63.4	0.119
PFDoA	0.624	0.180	5.20	<LOQ (0.110)	81.3	0.062
PFOS	8.040	7.612	121.24	<LOQ (0.089)	5.4	0.062
PFHS	11.230	8.743	357.03	<LOQ (0.125)	22.3	0.122
PFBS	1.078	0.417	11.46	<LOQ (0.129)	67.0	0.309

* Calculation of means include only values above the lower limit of quantitation (LOQ)
** Calculation of means include values below the LOQ as LOQ/sqrt(2)

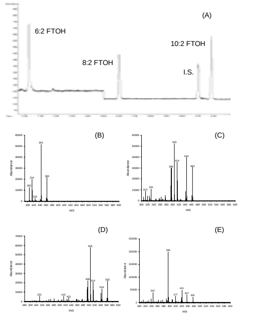


Figure 2. (A) GC/MS select ion monitoring (SIM) chromatogram showing analytes of interest, a 300-600 m/z scan for (B) 6:2 FTOH, (C) 8:2 FTOH, (D) 10:2 FTOH, and (E) FTOH IS.

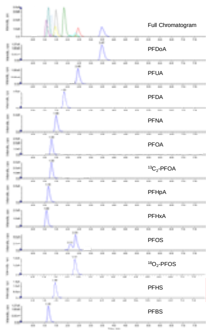


Figure 3. LC-MS/MS chromatogram of analytes of interest.

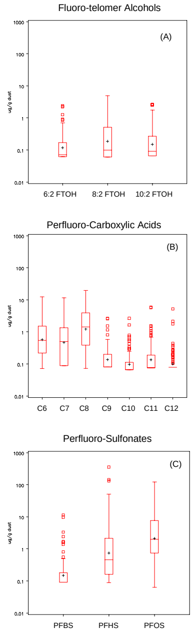


Figure 4. Distribution of fluoro-telomer alcohols (A), perfluorinated acids (B), and perfluorinated sulfonates (C) in house-dust samples.

Table 5. Perfluorinated compounds in Ohio versus North Carolina house-dust samples.

Compound	Mean* OH samples (μg/g dust)	n = (OH)	Mean* NC samples (μg/g dust)	n = (NC)	p** (α = 0.05)
6:2 FTOH	0.501	26	0.355	23	0.353
8:2 FTOH	1.043	28	0.747	32	0.309
10:2 FTOH	0.555	28	0.459	28	0.553
PFHxA	1.049	54	1.486	50	0.199
PFHpA	1.312	40	1.550	43	0.537
PFOA	3.155	56	2.977	52	0.815
PFNA	0.393	22	0.438	25	0.775
PFDA	0.291	17	0.423	17	0.489
PFUA	0.704	21	0.694	20	0.981
PFDoA	0.804	11	0.425	10	0.463
PFOS	8.353	56	7.688	50	0.846
PFHS	8.828	48	14.187	39	0.595
PFBS	1.560	20	0.510	17	0.225

* Calculation of means include only values above the lower limit of quantitation (LOQ)
** p (α=0.05) for t-Test for NC vs. OH populations assuming unequal variances.

Table 6. Spearman correlation coefficients for PFCs in house-dust samples. p-value below correlation coefficients.

Spearman Correlation Coefficients, N = 112
Prob > |r| under H0: Rho=0

	6:2 FTOH	8:2 FTOH	10:2 FTOH	C12 Acid	C11 Acid	C10 Acid	C9 Acid	C8 Acid	C7 Acid	C6 Acid	PFOS	PFHxS	PFBS
6:2 FTOH	1	0.88937 <.0001	0.87057 <.0001	0.42439 <.0001	0.50289 <.0001	0.54976 <.0001	0.47593 <.0001	0.35627 0.0001	0.39449 <.0001	0.40375 <.0001	0.30934 0.0009	0.34386 0.0002	0.04224 0.6584
8:2 FTOH	0.88937 <.0001	1	0.96378 <.0001	0.40613 <.0001	0.53112 <.0001	0.57934 <.0001	0.52044 <.0001	0.39319 <.0001	0.46671 <.0001	0.47922 <.0001	0.32952 0.0004	0.33015 0.0004	0.07146 0.454
10:2 FTOH	0.87057 <.0001	0.96378 <.0001	1	0.40102 <.0001	0.53771 <.0001	0.57011 <.0001	0.54484 <.0001	0.4336 <.0001	0.50846 <.0001	0.51648 <.0001	0.37435 <.0001	0.38386 <.0001	0.10699 0.2615
C12 Acid	0.42439 <.0001	0.40613 <.0001	0.40102 <.0001	1	0.66528 <.0001	0.72555 <.0001	0.58537 <.0001	0.32327 0.0005	0.37022 <.0001	0.35839 0.0001	0.2785 0.0029	0.2864 0.0022	0.10394 0.2755
C11 Acid	0.50289 <.0001	0.53112 <.0001	0.53771 <.0001	0.66528 <.0001	1	0.87886 <.0001	0.82538 <.0001	0.45134 <.0001	0.52583 <.0001	0.54188 <.0001	0.4277 <.0001	0.36842 <.0001	0.2104 0.026
C10 Acid	0.54976 <.0001	0.57934 <.0001	0.57011 <.0001	0.72555 <.0001	0.87886 <.0001	1	0.79429 <.0001	0.39854 <.0001	0.45208 <.0001	0.4925 <.0001	0.3661 <.0001	0.32999 0.0004	0.11122 0.243
C9 Acid	0.47593 <.0001	0.52044 <.0001	0.54484 <.0001	0.58537 <.0001	0.82538 <.0001	0.79429 <.0001	1	0.61067 <.0001	0.68324 <.0001	0.66994 <.0001	0.53214 <.0001	0.42119 <.0001	0.25109 0.0076
C8 Acid	0.35627 0.0001	0.39319 <.0001	0.4336 <.0001	0.32327 0.0005	0.45134 <.0001	0.39854 <.0001	0.61067 <.0001	1	0.95115 <.0001	0.93501 <.0001	0.86464 <.0001	0.58784 <.0001	0.33566 0.0003
C7 Acid	0.39449 <.0001	0.46671 <.0001	0.50846 <.0001	0.37022 <.0001	0.52583 <.0001	0.45208 <.0001	0.68324 <.0001	0.95115 <.0001	1	0.96003 <.0001	0.82475 <.0001	0.57195 <.0001	0.33097 0.0004
C6 Acid	0.40375 <.0001	0.47922 <.0001	0.51648 <.0001	0.35839 0.0001	0.54188 <.0001	0.4925 <.0001	0.66994 <.0001	0.93501 <.0001	0.96003 <.0001	1	0.87856 <.0001	0.66045 <.0001	0.34255 0.0002
PFOS	0.30934 0.0009	0.32952 0.0004	0.37435 <.0001	0.2785 0.0029	0.4277 <.0001	0.3661 <.0001	0.53214 <.0001	0.86464 <.0001	0.82475 <.0001	0.87856 <.0001	1	0.83672 <.0001	0.33067 0.0004
PFHxS	0.34386 0.0002	0.33015 0.0004	0.38386 <.0001	0.2864 0.0022	0.36842 <.0001	0.32999 0.0004	0.42119 <.0001	0.58784 <.0001	0.57195 <.0001	0.66045 <.0001	0.83672 <.0001	1	0.24859 0.0082
PFBS	0.04224 0.6584	0.07146 0.454	0.10699 0.2615	0.10394 0.2755	0.2104 0.026	0.11122 0.243	0.25109 0.0076	0.33566 0.0003	0.33097 0.0004	0.34255 0.0002	0.33067 0.0004	0.24859 0.0082	1

Results

Developed methods appear to indicate that PFCs can be analyzed for in a repeatable fashion with sufficient sensitivity. Recoveries for all PFCs ranged from 39.5% (PFNA high spike) to 107.3% (PFUA low spike) (Table 3). Though recovery was low in some instances, coefficients of variation (cv) indicate the method is repeatable, even at a 10-fold spike difference, with the worst cv being 0.14 for PFOA (Table 3). GC/MS operating in negative EI with SIM of unique high m/z showed adequate sensitivity (LOQ ~0.09 μg/g dust) (Figure 2). LC-MS/MS operating in ESI was sufficient to separate and detect 12 unique PFCs in an 8 minute run with comparable sensitivity (LOQ ~0.1mg/g dust) (Figure 3).

Concentrations of PFCs in the dust samples were quite variable. Concentrations ranged from < LOQ for all compounds to 357 μg/g of dust for PFHS (Table 4.) Mean concentrations were calculated for only samples above the LOQ (Mean*) and with those below the LOQ taken as LOQ/sqrt(2) (Mean **) (Table 4). As expected, as percent below LOQ increases, these two means differ. PFOA had the fewest samples below the LOQ (3.6%) while PFDoA had the most samples below the LOQ (81.3%) (Table 4). Coefficients of variation from repeat measurements ranged from 0.309 (PFBS) to 0.023 (6:2 FTOH) (Table 4). Means (only >LOQ) ranged from 0.357 μg/g (PFDA) to 11.23 μg/g (PFHS) (Table 4).

Distributions plotted on a log scale indicate that PFCs are log-normally distributed (Figure 4). Comparison of means of samples from North Carolina and Ohio (>LOQ) indicate the populations do not differ ($\alpha = 0.05$) (Table 5).

Spearman ranked correlation coefficients indicate a high degree of correlation among the PFCs analyzed for (Table 6). Though the correlation coefficients are quite variable, the majority of the analyzed for PFCs are significantly correlated ($\alpha = 0.0001$) with many p-values <0.0001 (Table 6).

Discussion

The one published report on PFCs in Japanese house dust (Moriwaki et al., 2003) found significantly less PFOS (mean 0.2 μg/g) and PFOA (mean 0.38 μg/g) compared to this study. Though the sample size was smaller (n=16) Moriwaki et al. found maximum concentrations (PFOS) 2.5 μg/g and (PFOA) 3.7 μg/g more comparable to mean concentrations in this study (8.0 μg/g and 3.1 μg/g) PFOS and PFOA respectively. There was a strong correlation between PFOS and PFOA (r^2= 0.99) in the Moriwaki et al. data, however the correlation drops when the one outlier is removed (r^2=0.345). The correlation between PFOS and PFOA in this study (n=112) was found to be 0.865 (p <0.0001), a strong correlation (Table 6). Unfortunately lack of other published reports does not allow for further comparisons.

It is apparent that PFCs are present in house dust samples at appreciable concentrations. These data may help to reduce uncertainty in risk assessment of PFCs for indoor exposure.

Conclusions

Perfluorinated compounds are present in house dust samples as high as 357 μg/g dust (PFHS) (Table 4). The data appear to be log-normally distributed in nature (Figure 4). There does not appear to be a regional bias for PFC concentrations based on sample locations represented in this study (Table 5). Future studies will be needed on contemporary dust samples to assess PFC concentrations on a national scale.

Acknowledgements

Dr. Peter Egeghy for his help with statistical analysis of the data.

Dr. Marsha Morgan for providing the CTEPP samples for analysis.

References

Moriwaki et al., 2003. Concentrations of perfluorooctane sulfonates (PFOS) and perfluorooctanoic acid (PFOA) in vacuum cleaner dust collected in Japanese homes. J. Environ. Monit., (5) 753-757.

Lewis et al., 1999. Distribution of pesticides and PAHs in house dust as a function of particle size. EHP 107 (9) 721-726.

Future Plans

EPA in cooperation with HUD is conducting the American Healthy Homes Survey. As part of this endeavor, vacuum-cleaner house-dust samples are being collected. Assessment of the dust samples for PFCs will provide additional data on PFC levels in house dust.