PER- AND POLYFLUORINATED COMPOUNDS IN HOUSE DUST AND INDOOR AIR OF NORTHERN NORWAY

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Introduction

Per- and polyfluorinated compounds (PFCs) are extremely versatile and are used in a variety of consumer applications and products. In recent years, research has suggested that high levels of PFCs in indoor air and dust could act as sources to outdoor air contamination[1,2] as well as human exposure[3,4]. A number of different possible indoor sources of neutral and ionic PFCs have been identified. Fluorotelomer alcohols (4:2–12:2 FTOHs) have been measured as residuals left over from the manufacturing process in several commercially available and industrially applied polymeric and surfactant materials[5]. FTOHs and 10:2 Fluorotelomer olefin have been measured in waterproof jacket[6]. N-methyl-fluorooctane sulfonamidethanol (NMeFOSE) was detected in a commercially available carpet protector product[5] and the presence of perfluorooctanoate (PFOA) in carpet and textile samples has been demonstrated[7]. Recently it has been shown that FTOHs can be emitted from non-stick pans during their initial period of use and that PFOA was emitted in the gas phase during repeated use[8]. Although one study came to the conclusion that PFOA present in cookware does not contaminate food[9]. The presence of PFOA in food packaging was reported[7,10]. However, an exposure assessment and risk characterisation for PFOA in certain consumer articles, which included analysis of a number of carpets, textiles and garments, did not find levels that would provide a risk to users[11]. Exposure of humans to PFCs and the potential associated health risks at present is still unclear.

Material and Methods

Sampling

House dust samples were taken with an industrial vacuum cleaner (Nilfisk GM 80P) equipped with a special forensic nozzle with an one-way filter housing placed in front of the vacuum cleaner tube[12]. Twelve dust samples were collected in total: seven living rooms (L-room), one sleeping room (S-room), one sofa, one carpet and two rooms at work (office and archive).

Air samples were collected on polyuretan foam (PUF)-XAD-2-PUF tubes (SKC, 30mm/150mg/30mm) in duplicates with a flow of 4 mL/min per tube for 24 hours (SKC Leland Legacy sample pump). The top PUF slides were spiked with 20 µL of an internal standard mixture (ISTD,^{13}C-labelled 4:2 FTOH, 6:2 FTOH, 8:2 FTOH and d-labelled N-Et-FOSE/A and N-Me-FOSE, 500 pg/ µL) right before sampling. Nine air samples were collected at the same places as for dust sampling: six living rooms and three rooms at work (office, archive and lab).

Sample preparation

Dust samples were halved, spiked with ^{13}C-labelled PFOA, perfluorononanoate (PFNA) and perfluorooctane sulfonate (PFOS) and extracted with methanol for ionic PFCs according to Barber et al.[1] with some refinements. Extracts were concentrated by a RapidVap evaporator (Labconco Corp., Kansas City, MO) to a final volume of approximately 1 mL. After dispersive clean up with ENVI-Carb a volume of 500 µL was transferred to Chromacol vials and 5 ng of recovery standard (20 µL of 0.25 ng/ µL 3,5-BTPA) was added. Aliquots of 150 µL were pipetted to autosampler vials and 150 µL 2 mM aqueous ammonium acetate were added.

To prevent contamination from tube handling, PUF-XAD-2-PUF tubes were wiped with acetone and ethylacetate on the outer side. They were put in a 50 mL graduated cylinder with the small end on the bottom side and extracted with 2 x ~35 mL EtOAc, so that the top PUF slide was totally covered by the solvent. The sampling tubes were left to soak for one hour. After solvent change, the cylinders with the tubes were placed in

an ultrasonic bath for 30 min. Combined extracts were reduced in volume to approximately 1 mL in a TurboVap evaporator (Zymark, Hopkinton, MA, USA) after adding some drops of isooctane. Extracts were filtered into a tapered vial over prewashed cotton and 40 mg ENVI-Carb which was packed in a 150 mm pasteur pipette. Subsequently TurboVap concentration flasks were rinsed with a small amount of EtOAc as well as the prepared pasteur pipette. The volume was carefully reduced under a gentle stream of nitrogen to approximately 100 µL. 20 µL of a 3.6 ng/µL TCN in EtOAc solution was added as recovery standard. Blanks were extracted using the same procedure for quality control.

Instrumental analyses and quantification

Ionic PFCs were analysed by liquid chromatography quadrupole-time-of-flight mass-spectrometry (LC-Q-TOF-MS). Analysis was performed using a Waters binary pump 1525µ with a Waters 2777 Sample Manager coupled to a Micromass Q-TOF-MS (QTOF micro). Separation was achieved on an ACE C18-coloumn (150 x 2.1 mm, 3 µm) by the gradient program described elsewhere[13] in ESI^--mode. Mass spectra were recorded in full scan mode and extracted high resolution chromatograms were used for quantification.

Neutral PFCs were analysed by gas chromatography mass-spectrometry (GC-MS) in selected ion monitoring (SIM) -mode. An Agilent Agilent 7890A GC with split/splitless injector coupled to an HP 5975 C MS (Agilent, Böblingen, Germany) was used with helium as carrier gas and methane as reagent gas in positive chemical ionisation (PCI) mode for quantification and in negative chemical ionisation (NCI) mode for signal conformation. For analyses during optimisation of the extraction and the clean up step, for breakthrough and blank experiments, and for the three samples from the working area, a Varian CP-Wax 57 CB capillary column for glycols and alcohols (25 m x 0.25 mm x 0.2 µm) was used. Constant injector temperature was set to 200 °C in splitless mode, the GC temperature program with a constant carrier gas flow of 0.8 mL/min is described elsewhere[1]. For house sample analyses, separation was achieved on a Supelcowax 10 column (60 m x 0.25 mm x 0.25 µm)[14] with temperature program as follows: 50 °C (held 1 min), ramped at 3 °C/min to 70 °C, ramped at 10 °C/min to 130 °C, ramped at 20 °C/min to 220 °C, then ramped at 120 °C/min to 275 °C (held 5 min) and a carrier gas flow of 1.5 mL/min. Transferline temperature was set to 250 °C, ion source temperature to 250 °C in PCI and to 150°C in NCI.

Results and Discussion:

Method optimisation and testing for neutral PFCs:

Recoveries found in the testing of extraction and clean up step ranged between 67% (^{13}C 4:2 FTOH) and 115% (d N-Et-FOSA), with no significant signal enhancement observed. For each breakthrough experiment two columns were put in series, where both columns were spiked with 20 µL of the ISTD-mixture. The front columns were additionally spiked with native standards in two different concentrations, 25 ng and 0.5 ng, in order to check the retention capacity of the adsorbent. Recoveries of the labelled ISTDs ranged between 36 % (^{13}C 4:2 FTOH) and 263 % (d N-Me-FOSE). The signal enhancement for FOSA/Es is related to the extracts of the front columns, which were spiked and subsequently air was collected. Columns only spiked with ISTD and blanks showed better recoveries with 158 % for d N-Me-FOSE as the highest reported recovery. No breakthrough could be observed in the low concentration experiment, except for the native 4:2 FTOH where a 152 % absolute recovery was obtained using both columns and 62 % of the absolute recovery was collected on the second column as breakthrough. In the high concentrated spike experiment recovery levels ranged from 18 % (^{13}C 4:2 FTOH) to 101 % (d N-Me-FOSA). Breakthroughs for all analysed native FTOHs were observed.

Sampling tubes appear to be useful for low to moderate concentration levels for indoor air sampling. However, a loss of 4:2 FTOH is expected, but correct concentrations can be estimated by using mass labelled internal standards. Due to the small sampling volume of 5.76 m^3/tube no dramatic breakthrough or loss of analytes is expected.

Ionic PFCs in dust:

Sum concentrations of ionic PFCs in dust are shown in figure 1. Carboxylates and Sulfonates were detected in each sample. The archive sample shows the highest concentrations with > 2 µg/g for Σ-Telomers and Σ-Carboxylates and 32.5 µg/g for Σ-Sulfonates. For the sulfonates, perfluoropentane sulfonate (PFPS) is dominating with a concentration of 17.8 µg/g, followed by PFOS at 7 µg/g and 6:2 fluorotelomer sulfonate (6:2 FTS) at 2.3 µg/g. Perfluoroundecanoate (PFUnA) is the most prominent compound in the carboxylate-group

from the archive sample with a concentration of 614 ng/g. It could be verified in almost all samples, except living room 1-3, and surprisingly often in quite higher amounts than PFOA (living room 4-7, sleeping room and carpet). As expected, PFOA and PFOS were recorded on all places; PFOA was detected in levels from 2.2 ng/g (carpet) to 500 ng/g (archive), whereas PFOS concentration ranged from 3.1 ng/g (carpet) to 23.7 ng/g (living room 5) in the houses and 147.7 ng/g in the office. PFPS and perfluorononane sulfonate (PFNS) could not be detected in any households, but they were present in the office and archive samples. Furthermore some neutral compounds in the methanol extract were analysed by LC-MS as well, but were under the detection limits with only low amounts of N-Me-FOSE/A and N-Et-FOSE detected at some places.
As displayed in figure 1, no direct correlation can be shown between the distribution pattern of the carpet and sofa and their related living rooms L4 and L7 respectively.

Neutral PFCs in air:
Analytes of interest could be detected in all collected air samples (see figure 2). 8:2 FTOH is the most prominent compound in almost each sample and is observed in concentration levels from 470 pg/m^3 (lab) to 11.1 ng/ m^3 (living room 4). In the living rooms much higher concentrations were found compared to the working areas with the archive as an exception. Within these samples 6:2 FTOH was found at 9 830 pg/m^3. In living room 5 all analysed FTOHs (4:2 – 10:2) could be determined in levels from 23.8 pg/m^3 (4:2 FTOH) to 10 945 pg/m^3 (8:2 FTOH). Compared to previous studies, higher concentrations of FTOHs are recorded[1,2]. N-Et-FOSA shows concentrations from 17.1 to 147.4 pg/m^3 and is detected in all samples except living room 6. No signal enhancement for FOSA/Es could be observed by using the Supelcowax 10 column for the house samples; recoveries between 54 % (d N-Et-FOSA) and 97 % (d N-Me-FOSE) could be achieved. Distribution pattern of the FOSA/Es in air samples looks different compared to the dust samples. Only in living room 3, N-Me-FOSE was detected in both, air and dust samples, and in the archive, N-Me-FOSA was found in both as well. Further investigation with larger sample quantity and additional analyses of neutral PFC in dust by GC-MS is recommended.

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Figure 1: Comparison of sum-concentrations and chemical distribution patters of ionic PFCs and FOSA/Es in dust samples; archive sample: Σ-Telomers 2 342 ng/g, Σ-Sulfonates 32 515 ng/g, Σ-Carboxylates 2 112 ng/g; office sample: Σ-Sulfonates 601 ng/g;

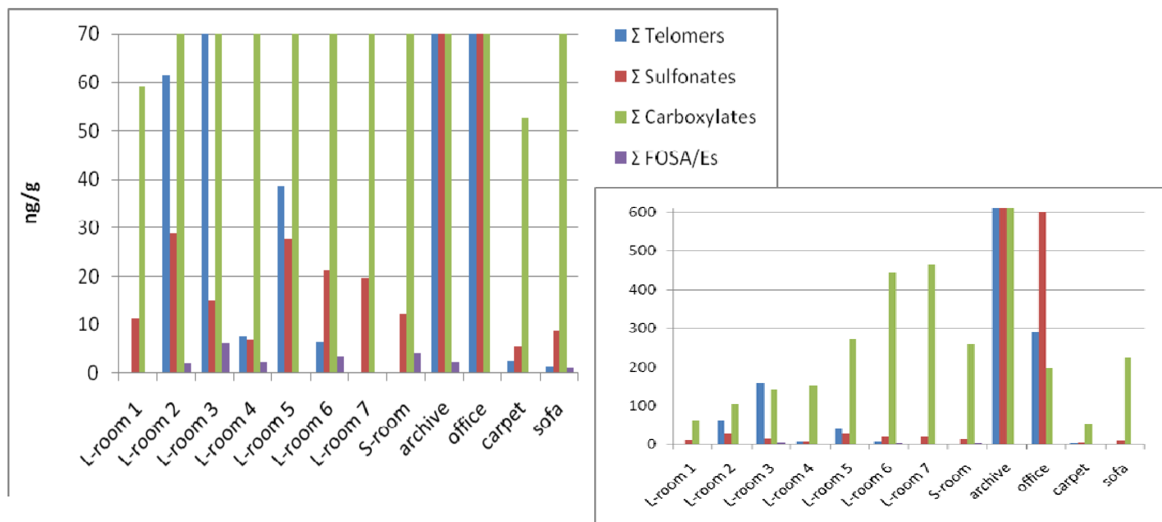

Figure 2: Comparison of concentrations and chemical distribution patters of neutral PFCs in air samples;