Supporting information

Investigation on per- and polyfluorinated compounds in paired samples of house dust and indoor air from Norwegian homes

Line S. Haug[*1], *Sandra Huber*[2], *Martin Schlabach*[3], *Georg Becher*[1,4], *Cathrine Thomsen*[1],

[1]Norwegian Institute of Public Health, P.O. Box 4404 Nydalen, NO-0403 Oslo, Norway

[2]Norwegian Institute for Air Research (NILU), The Polar Environmental Centre, Hjalmar Johansens gate 14, NO-9296 Tromsø, Norway

[3]Norwegian Institute for Air Research (NILU), Instituttveien 18, NO-2007 Kjeller, Norway

[4]Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, NO-0315 Oslo, Norway

[*]**Corresponding author:**

Line Småstuen Haug

Tel: +47 21076549

Fax: +47 21076686

E-mail: line.smastuen.haug@fhi.no

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Determination of PFCs in house dust and indoor air

The method used for determination of PFCs in house dust and indoor air is described in detail elsewhere (1).

Chemicals

All solvents and reagents used in this work were of Suprasolv or Lichrosolv grade, and were purchased from Merck-Schuchardt (Hohenbrunn, Germany), with the exception of acetone, ethylacetate and methanol which were of Pestiscan grade from LabScan (Dublin, Ireland). All chemicals and standards used are described by Huber et al. (1).

Sample preparation

The samples and calibration standards were prepared according to the method described by Huber et al. (1), with the exception that internal standards for the air samples were added after sampling, but prior to the sample preparation in the present study.

In brief, air sampling tubes were put in a graduated cylinder, added internal standards (^{13}C-labelled 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, NMeFOSE, NEtFOSE and NMeFOSA) and extracted with 2 x ~35 mL ethylacetate using an ultrasonic bath. Solvent from both extraction steps and the two parallel sampling tubes were combined and reduced in volume. Extracts were filtered over prewashed cotton and ENVI-Carb material. The volume was carefully reduced and 1,2,3,4-tetrachloronaphthalene (TCN) was added as recovery standard.

Prior to the sample preparation, dust samples were visually inspected and non-dust material like hairs, cotton fibers, glass or plastic pieces etc., were removed. The filter containing the dust was put in a reagent tube, spiked with internal standards (^{13}C-labelled PFOA, PFNA and PFOS) and extracted with methanol in an ultrasonic bath according to Barber et al. (2). The focus during the method development and optimization was to establish fast and simple

methods with low consumption of solvents. Accelerated solvent extraction (ASE) was considered, but since parts of the ASE unit consisted of Teflon®, it was not chosen due to the possibility of contamination. Ultrasonic extraction has been applied successfully by others e.g. by Björklund et al. (3), and was thus tested (1). The extract was concentrated, cleaned up using dispersive ENVI-Carb with glacial acetic acid, reduced in volume and added 3,5-bis(trifluoromethyl)phenyl acetic acid as a recovery standard. Prior to analysis, aliquots of 150 µL were transferred to an autosampler vials and added 150 µL of 2 mM aqueous ammonium acetate.

Analyses

The analyses of the dust samples were carried out using liquid chromatography time-of-flight mass-spectrometry (LC-TOF-MS) (4). An 50 µl aliquot of the sample was injected. The PFCs were separated on an ACE C_{18}-column (150 x 2.1 mm, 3 µm, ACE) column and detected on the TOF-MS using negative electrospray ionization.

Air samples were analyzed by gas chromatography-mass spectrometry (GC-MS) in selected ion monitoring mode as described by Huber et al. (1). The extract was injected (1µL) on a split/splitless injector, helium was used as carrier gas and methane as reagent gas in positive chemical ionisation mode for quantification and in negative chemical ionisation mode for signal confirmation. Separation of PFCs was achieved using a Supelcowax 10 column (60 m x 0.25 mm x 0.25 µm).

Blanks

Field blanks (n=8), procedural blanks (n=4) and solvent blanks (n =8) were analyzed simultaneously to the air and dust samples. Field blanks were taken by carrying a filter compartment and two PUF-XAD_2-PUF-tubes onsite, which had been wrapped in alumina foil

and put in a sealed plastic bag. The field blanks were stored, extracted and analyzed equally to the real samples. Procedural blanks were prepared similar to the field blanks except that filters and PUF-XAD_2-PUF were left out. Solvent blanks, solvents added to an autosampler vial, were analyzed equally to the other samples.

Limit of quantification (LOQ)

Individual LOQs were calculated automatically for all analytes in all samples using the quantification software. The LOQ was set as the concentration corresponding to S/N = 3 divided by the related dust amount or air volume of each sample. Where blank contamination was detected, LOQs were estimated as three times the highest blank. If the LOQ calculated from the blank contamination was higher as the individual LOQ of the sample, LOQ calculated based on blank sample was used. The LOQ ranges are given in Table 1.

Quality assurance

The solvent blanks did not contain any PFCs above the limit of quantification (LOQ). In all blanks determined along with the dust samples, the concentration of the PFCs were less than 5% of the lowest sample concentration, except for PFDoDA which was observed in 7 of 8 blanks, with a mean blank concentration of 17% of the mean concentration in the samples. The measured concentrations of PFDoDA in the dust samples were thus corrected by subtracting the mean blank concentration. For the blanks analyzed simultaneously to the air samples, the only two compounds observed in concentrations higher than 5% of the lowest sample concentration were MeFOSE and EtFOSE, showing mean concentrations in the blanks of 6.2% and 13% of the sample concentrations, respectively. All samples of indoor air were thus corrected by subtracting the mean blank concentrations of MeFOSE and EtFOSE. For the dust samples the absolute recovery of the ^{13}C internal standards were in the range 35-110%,

except for one sample where the recovery of ^{13}C PFOA was 23%. The recoveries of the internal standards used for the air samples were in general between 50-130%, however eight samples had recoveries of one or two of the 13C internal standards below 50%. For samples of dust 78% or the recoveries were above 50%. The low recoveries varied between analytes and samples, i.e. no general trend was seen. Due to use of the internal standard method for quantification, the recoveries do not influence the determined concentrations considerably as long as the recoveries are acceptable (e.g. above 20-30%). The recoveries of ^{13}C 8:2 FTOH were often above 130% due to matrix effects, however this does not affect the quantification of 8:2 FTOH as the native compound is influenced by the matrix the same way as the internal standard. Matrix effects in samples of air have previously been reported. For instance Jahnke et al. (5) reported recoveries up to 300%. As reported by Dreyer et al.(6) enhancement of signals could also occur due to use of small amounts of acetic acid in the ethylacetate used for extraction. Some of our blank samples showed enhancement for 8:2 FTOH as well, supporting the explanation by Dreyer et al (6). It would have been advantageous to analyse samples of SRM together with the real samples of house dust. However, use of the internal standard method for quantification, will compensate for possible losses during extraction. One of the indoor air samples was rejected due to inappropriate sample preparation.

References

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Table S1: Factors that are likely to influence the indoor atmosphere, which were tested for possible bivariate correlations to concentrations of PFCs in indoor air or house dust.

Indoor parameters	Unit (range)
Presently residing in an apartment (as opposed to a house)	yes/no
Number of years the residence has been occupied by the participant	years (0.5-19)
Age of the residence	years (3-128)
Total floor space of the residence	m^2 (60-256)
Floor space of the living room	m^2 (12-70)
Volume of the living room	m^3 (41-180)
Forced ventilation in the residence	yes/no
Central heating of the residence	yes/no
Electric furnaces of the residence	yes/no
Wood stove/fireplace heating of the residence	yes/no
Lives near a high-traffic road (< 500m)	yes/no
Distance from the residence to a high-traffic road	m (3-500)
Daily airing of living room	yes/no
Daily airing of bedroom	yes/no
Has a rug in the living room	yes/no
Has a synthetic rug in the living room	yes/no
Has a wool/cotton rug in the living room	yes/no
Living room rug is newer than one year	yes/no
Living room rug is between one and five years old	yes/no
Living room rug is older than five years	yes/no
Owns Gore-tex® or similar clothing	yes/no
Number of Gore-tex® or similar clothing items owned	number (0-12)
Pairs of Gore-tex® or similar shoes owned	number (0-10)
Total number of Gore-tex® or similar items owned	number (0-20)
Has kitchen utensils of non-stick material	yes/no
Typically buy new car	yes/no
Typically buy new furniture	yes/no
Typically buy new children's clothes	yes/no
Furniture always bought new	yes/no
Number of times living room is vacuumed per month	number (2-20)
Number of times the living room is vacuumed/washed per month	number (3-28)

The following parameters were not considered due to too few answers (<5) in one of the categories: current smokers, owns a cat or a dog, owns Gore-tex® or similar shoes, typically buy new TV/stereo, typically buy new white goods, use polish agents.