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## PER- AND POLYFLUOROALKYL SUBSTANCES IN FINNISH INDOOR AIR

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### Introduction

Many household products are stain- and water-repellent. These properties can be achieved by adding or incorporating chemicals in the coating material e.g. per- and polyfluoroalkyl substances (PFASs). PFASs include perfluoroalkyl acids (PFAAs) and their precursors (i.e. substances that degrade to form PFAAs). The precursors include perfluorooctane sulfonamides (FOSAs), perfluorooctane sulfonamidoethanols (FOSEs), fluorotelomer alcohols (FTOHs), fluorotelomer acrylates (FTAC) and methacrylates (FTMAC). The precursors are often (semi-)volatile, whereas the PFAAs usually dissociate to persistent non-volatile anions in the environment. During the lifetime of a product, PFASs can outgas or be released in abraded material leading to their presence in dust and air samples in indoor environments (1-3).

The main global producer of perfluorooctane sulfonic acid (PFOS) and its precursors declared in 2000 that all their products containing long-chain PFASs would be phased out from production by 2002 (4). Phase-out actions were also taken for perfluorooctanoic acid (PFOA), and its long-chain fluorotelomer precursors as part of an industry stewardship program including 8 major producer (5). Since the 2000s, production shifted towards short-chain per- and polyfluorinated products and other fluorinated and non-fluorinated alternatives (6).

In 2014/15 we sampled indoor air in 57 Finnish homes by passive air samplers (PAS) and analysed the samples for 9 PFAS precursors and 16 PFAAs. The objectives of this study were i) to determine indoor air concentrations of PFASs for the first time in Finnish homes ii) to evaluate the effectiveness of regulatory action taken on fluorinated chemical production and usage (by comparing results with previous studies that were sampled  $\leq 8$  years after the phase-out).

### Material and methods

The passive air samplers consist of polyurethane foam disks impregnated with XAD-4 powder (SIP). The preparation of the SIP disks was carried out at Environment Canada following Shoeib et al. (7) with minor changes. The SIPs were shielded from dust by the sampler housing when deployed in children's bedrooms of 57 Finnish private homes in 2014/15. The sampling was approved by the Finnish Ethical Committee as an addition to case 48/2004, for a subgroup of a bigger cohort (LUKAS2). After three weeks, SIP disks were collected and stored in airtight glass jar in freezers until extraction. The SIP samples (incl. blanks) were spiked with mass labelled (ML) internal standards prior to accelerated solvent extraction (ASE 300, Dionex). Firstly, a mixture of petroleum ether and acetone (85:15) was applied to extract the precursor/volatile compounds (for extraction details see 8). The second extraction was carried out with acetonitrile for the PFAA containing fraction (8). The latter fraction has not been analysed yet. The extracts of the first (precursor) fraction were blown down to 1 mL and dried over 1 g sodium sulphate. The extracts were concentrated to 400  $\mu$ L and volumetric standard was added before analysis on a 30 m Supelcowax<sup>TM</sup>10 column (0.2 mm ID x 0.2  $\mu$ m film) in a trace GC ultra gas chromatograph coupled to a ISQ mass spectrometer operated in positive chemical ionization mode (both Thermo Scientific). Quantification of analytes (SIM mode for quantifier and qualifier ion) was carried against responses of their mass-labelled counterparts (added prior to extraction). The quantified amounts per sampler were converted to air concentrations based on sampling volumes of calibration studies (7, 8). The sampling volume for acrylates was assumed to be the same as for 6:2 FTOH.

## Results and discussion

The recoveries are in line with previous studies (9, 10), ranging in average from 43 to 175 %. 6:2 FTOH, 8:2 FTOH, 10:2 FTOH and Me-FOSE were detected in  $\geq 95$  % of the samples. MeFOSA, 6:2 FTAC and EtFOSA showed the lowest detection frequencies ( $\leq 33$  %).

8:2 FTOH was quantified with the highest arithmetic mean concentration of 4,250 pg/m<sup>3</sup> (Fig. 1), which is in accordance with earlier studies from Northern Europe, Japan and North America (2, 10, 11). The 6:2 FTMAC arithmetic mean concentration (285 pg/m<sup>3</sup>) exceeded all FOSA/Es' arithmetic mean values, but was influenced by one extreme value (12,978 pg/m<sup>3</sup>). Among the FOSA/Es, MeFOSE was most frequently detected and with the highest arithmetic mean concentration (90 pg/m<sup>3</sup>).

In summary, the air concentrations of FTOHs are in the same range or slightly lower compared to data reported 7-8 years earlier (e.g. 2, 10). In contrast, Me-FOSE concentrations were approx. one order of magnitude lower than the majority of previous measurements (2, 10), or even two orders in comparison to a study sampling in 2002/3 (3). This could be an indication of the phase-out of PFOS precursors, which led to lower concentrations in households, whereas the substitution of long-chain fluorotelomer precursors has not yet have an impact on indoor environments. Possible explanations for the apparent lag time to changes in product formulations could be: a) the replacement cycle of products or furniture and renovation routines in private households is long i.e. old furniture still degassing; b) replaced household products still contain PFASs (intentionally or as impurities); c) that the building and furnishings materials absorbed previously outgassing PFASs now act as a secondary source. However, given that previous studies have been performed in various countries inferences to temporal trends of PFASs in the indoor environment should be interpreted with caution.

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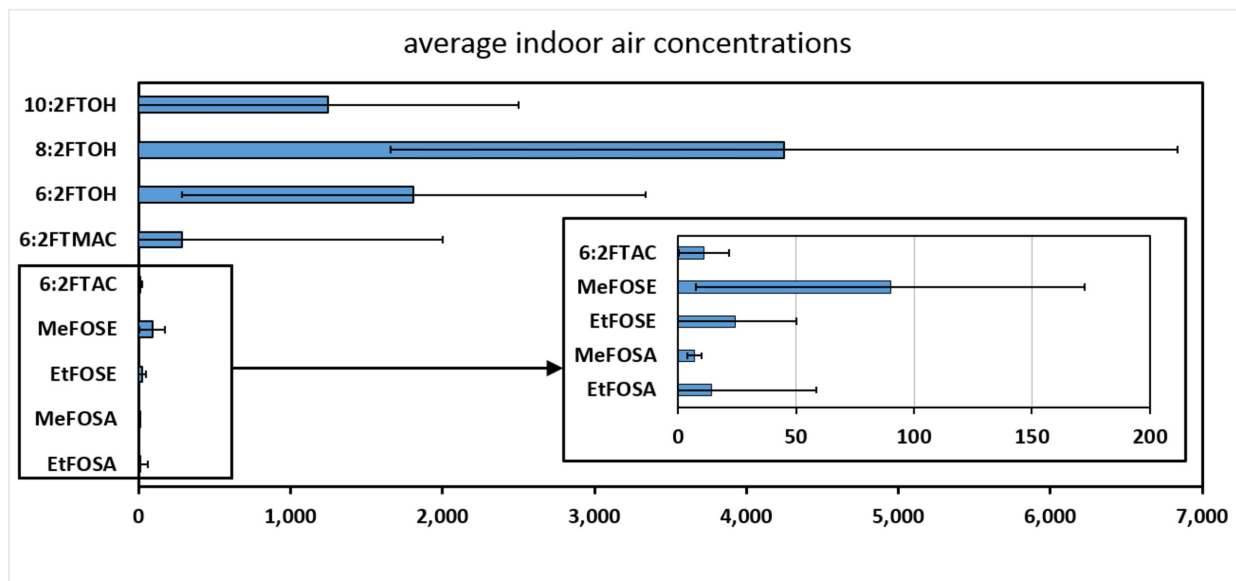


Fig.1: Arithmetic mean PFAS indoor air concentrations of 57 Finnish homes with standard deviations. Measurements below the method detection limit were included in the calculation in form of MDL divided by the square root of 2.