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Perfluoroalkyl acids and their precursors in indoor air sampled in children’s bedrooms

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The contamination levels and patterns of perfluoroalkyl acids (PFAs) and their precursors in indoor air of children’s bedrooms in Finland, Northern Europe, were investigated. Our study is among the most comprehensive indoor air monitoring studies (n = 57) and to our knowledge the first one to analyse air in children’s bedrooms for PFASs (17 PFAs and 9 precursors, including two acrylates, 6:2 FTAC and 6:2 FTMAC). The most frequently detected compound was 8:2 fluorotelomer alcohol (8:2 FTOH) with the highest median concentration (3570 pg/m³). FTOH concentrations were generally similar to previous studies, indicating that in 2014/2015 the impact of the industrial transition had been minor on FTOH levels in indoor air. However, in contrast to earlier studies (with one exception), median concentrations of 6:2 FTOH were higher than 10:2 FTOH. The C8 PFAs are still the most abundant acids, even though they have now been phased out by major manufacturers. The mean concentrations of FOSE/As, especially MeFOSE (89.9 pg/m³), were at least an order of magnitude lower compared to previous studies. Collectively the comparison of FTOHs, PFAs and FOSE/FOSA with previous studies indicates that indoor air levels of PFASs display a time lag to changes in production of several years. This is the first indoor air study investigating 6:2 FTMAC, which was frequently detected (58%) and displayed some of the highest maximum concentrations (13 000 pg/m³). There were several statistically significant correlations between particular house and room characteristics and PFAS concentrations, most interestingly higher EtFOSE air concentrations in rooms with plastic floors compared to wood or laminate.

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1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are a structurally diverse group of >3000 anthropogenic chemicals (KEMI, 2015) that have been classified into various sub-families (Buck et al., 2011). Some sub-families of PFASs are moderately to strongly acidic (e.g. perfluoroalkyl acids (PFAAs)) and are usually in the anionic form in the environment, whereas other PFASs are uncharged. PFAs such as perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) are highly resistant to degradation and are the final transformation products of various neutral precursors. For example, fluorotelomer alcohols (FTOHs) can be abiotically or biotically transformed to PFCAs (Ellis et al., 2004; Butt et al., 2014), whereas perfluorooalkane sulfonamides (FASAs) and perfluorooalkane sulfonamidoethanols (FASEs) can be transformed to PFCAs and PFSAs (Martin et al., 2010). Neutral PFASs are volatile or semivolatile and are expected to be present in the gas and particle phases in air, whereas PFASs are expected to be mostly associated with particles in air due to the involatile nature of anions (Prevedouros et al., 2006).

Perfluoroalkyl acids (PFAs) are strong surfactants that have been used industrially, e.g. as processing aids in the production of fluoropolymers, but they are also present as residual impurities in a...
wide range of polymeric consumer products e.g. used to impart water and stain repellency in textiles, papers and boards (Prevedouros et al., 2006). While the high stability and combined hydro- and oleophobic properties make the perfluoroalkyl moiety useful in many applications, the stability also leads to high environmental persistence. Furthermore, long-chain PFAAs (C_f2n+1SO_2H, n ≥ 6, PFASs and C_f2n+1COOH, n ≥ 7, PFCAst (Buck et al., 2011)) bioaccumulate in humans as a result of slow elimination rates (e.g. Stahl et al., 2011; Lau et al., 2004; Kennedy et al., 2004; Vaughn et al., 2013) and have been shown to display an array of toxicological effects mostly in animal studies (e.g. Stahl et al., 2011; Lau et al., 2004; Kennedy et al., 2004; Vaughn et al., 2013; Johnson et al., 2014; Olsen et al., 2009). Long-chain PFAsas therefore fulfil the persistent, bioaccumulative and toxic criteria (i.e. they are PBT chemicals) and as a result several have been regulated internationally (e.g. PFOS and related substances have been added to Annex B of the Stockholm Convention on Persistent Organic Pollutants (POPs) (UNEP, 2009) and several long-chain PFCAst have been added to the Candidate List of Substances of Very High Concern (SVHC) of the European Chemicals Agency (ECHA, 2013, 2015)).

As a result of the industrial transition in PFAS production processes since the turn of the century, the composition of PFAs in products has changed and continues to change. Electrochemical fluorination (ECF) was historically the most important manufacturing process for PFAs between the 1950s and 2002 and this process results in products containing a mixture of branched and linear structural isomers of perfluoroalkyl chains (Prevedouros et al., 2006; Wang et al., 2014). However, between 2000 and 2002, the main global producer (3M Company) voluntarily phased out their C6, C8 and C10 products (US EPA, 2000) and started to manufacture C4-based PFAS products. Following this phase-out, telomerisation emerged as the dominant manufacturing process for long-chain PFAS-based products in the Western world with linear isomers of perfluoroalkyl chains only (Buck et al., 2011; Wang et al., 2014). More recently a group of eight fluorochemical manufacturers that have historically manufactured long-chain PFAS-based products by telomerisation have agreed to eliminate emissions and product contents of long-chain PFCAst and precursors by 2015 (2010/2015 PFOA Stewardship Program (US EPA, 2006)). These eight companies have replaced their long-chain PFAS-based products with alternatives, e.g. with PFAS-based products containing shorter perfluoroalkyl chains.

A wide range of PFAs have been detected in the indoor environment (Barber et al., 2007; Ericson Jogsten et al., 2012; Fromme et al., 2015; Huber et al., 2011; Kim et al., 2012; Langer et al., 2010; Haug et al., 2011; Liu et al., 2013; Shoeib et al., 2005, 2011). Analogously to other commonly used consumer chemicals, it can be expected that PFAs are transferred to the indoor environment from consumer products via different transport pathways depending on their physical-chemical properties (cf. for BFRs (Liagkouridis et al., 2014)). Volatile PFAs can directly outgas from products into indoor air or dust (Liu et al., 2015), whereas one would expect ionic PFAs to be abraded or leached from products and released to dust, if PFAs behave like other consumer chemicals. Humans spend more than 80% of their lifetime indoors (calculated for 18 to ~65 years (US EPA, 2011)) and indoor levels can be elevated compared to outdoor levels (Shoeib et al., 2005; Jahnke et al., 2007). Thus, indoor exposure pathways (especially dust ingestion) have been estimated to make an important contribution to human exposure for some PFAs (Nilsson et al., 2013; Vestergren et al., 2008), especially for some subgroups such as small children, due to their mouthing behaviour (Shoeib et al., 2011). However, the data for indoor air concentrations of PFAs remain quite limited with only a handful of studies from around the world reporting comprehensive data sets from a larger number of households (Haug et al., 2011; Liu et al., 2013; Shoeib et al., 2005, 2011).

This study aimed to investigate the current contamination levels and patterns of perfluoroalkyl acids (PFAAs) and their precursors in the air of children’s bedrooms. To achieve this aim, we sampled the indoor air in 57 Finnish households and analysed the sample extracts for 17 perfluoroalkyl acids and 9 precursors. The relatively large number of sampling sites (n = 57) provides a good average approximation of current PFAS indoor air concentrations in Finland, which might be representative of many other western industrial countries but particularly of Scandinavia. The dataset is used to determine a) if there are correlations between different PFASs measured, which may indicate common sources and production origins, b) to investigate differences in PFAS composition and levels in Finnish samples relative to previously published studies at other times and locations (Haug et al., 2011; Liu et al., 2013; Shoeib et al., 2005, 2011), and c) to investigate if there was any correlation between PFAS concentrations and recorded room and housing characteristics. We also investigate the presence of acrylates (6:2 FTAC and 6:2 FTMAC) in indoor air, which are not typically reported in literature.

2. Materials and methods

2.1. Standards, solvents and lab routines

2.2.3,4,4,5,6,6,7,8,8,8-penta decafluoro-1-octanol (7:1 FTOH), used as a volumetric standard for analysis of volatiles, was purchased from Sigma-Aldrich. The standards for acrylate analysis (2-perfluorohexyl ethyl acrylate (6:2 FTAC) and 2-perfluorohexyl ethyl methacrylate (6:2 FTMAC)) were received in bulk from Fluor ox Inc. (San Leandro, USA). All other native and mass-labelled (ML) standards were purchased from Wellington Laboratories. For the complete list of substances see Tables S1 and S3 in the Supplementary material.

Only solvents of the highest purity were used. For sorbent impregnated polyurethane (SIP) preparation these were petroleum ether, dichloromethane, methanol, acetone and acetonitrile (all OmniSolv®, EMD Chemicals Inc., USA), ethyl aceta te (≥99.8%, Caledon laboratory chemicals) and hexanes (non-UV, ≥99.5%, Caledon). Acetonitrile (CHROMASOLV®, Sigma-Aldrich), petroleum ether (for pesticide residue analysis low boiling point, Sigma-Aldrich), acetone and ethyl acetate (both SupraSolv®, Merck Millipore) were used for extraction and clean-up.

All glassware was baked at 450 °C for 5 h. All laboratory equipment contacting the samples was rinsed with the appropriate solvent before application.

2.2. SIP sampler preparation

The sorbent impregnated polyurethane (SIP) foam disks were prepared at Environment Canada, Toronto, based on the protocol of Shoeib et al. (2008) with minor adaptations. In brief, the polyurethane foam disks (PUF, 5 1/2” diameter times 1/2” thickness, Tisch Environmental) were washed with water, dried, then extracted via accelerated solvent extraction (ASE, ASE350, Dionex) with subsequently acetone, petroleum ether/acetone (75/25 v/v), petroleum ether and acetonitrile. The disks were dried (heat and nitrogen). The sorbent, XAD-4 (Amberlite® XAD-4, styrene-divinylbenzene, mesh 20–60, Sigma-Aldrich), was precleaned by sonication in methanol and subsequently dichloromethane. After drying, XAD-4 was ground in a Retsch planetary ball mill to approx. 0.75 μm particle size. The XAD-4 was transferred into thimbles and Soxhlet extracted with methanol, dichloromethane and hexane (each 6–8 h). Hexane was mixed with XAD-4 (approx. 6.4 g/L). Each
PUF was dipped three times (each time 1 min) into this slurry for saturated sorbent impregnation (previously for three times each 30 s (Shoeib et al., 2008)). Finally, they were placed on heating plates and flipped regularly. Following vacuum desiccation for complete drying, the SIPs were stored and shipped in airtight aluminium lined jars and kept at −21 °C until sampler deployment.

2.3. Indoor air sample collection

The indoor passive air samples (PAS) were taken in 57 private households in the area of Kuopio, Eastern Finland during 2014/15. These households are part of a Finnish population based birth cohort, LUKAS2 (Karvonen et al., 2009), in which all pregnant women with estimated delivery at Kuopio University Hospital between May 2004 and May 2005 were invited to the study at 32 weeks of gestation. The majority of the children lived in detached single-family houses (78%) and 12 lived in semi-detached or terraced houses (22%; information available for 54 out of 57 children). Only one house was located in the city centre of Kuopio, the biggest city in Eastern Finland with approx. 113 000 inhabitants. The other houses were located within 110 km distance of Kuopio in several smaller towns (all <20 000 inhabitants), suburban areas or villages. Housing and room parameters were recorded as discussed in the results and discussion subchapter 3.4. Influence of house and room characteristics. The samplers were deployed in children’s bedrooms with one exception, where the child slept in the living room. Children’s bedrooms were investigated because this air sampling campaign was part of a larger study on environmental exposure to children. Sampling and analysis was approved by the Ethical Committee of the Kuopio University Hospital as an amendment to case number 48/2004.

In the lab, the sampler housings were thoroughly cleaned, rinsed with solvents and then transported sealed to the households. For sampler deployment, the SIPs were transferred from the airtight jars into their sampler housings and placed on shelves, cupboards or other suitable horizontal surfaces where they would not be disturbed (on average 1.36 m above the floor). Exposure of the sampler to possible draughts and direct sunlight was avoided. The housing’s roof prevented dust from settling onto the SIP and the triangular wire below served as bearing surface allowing an unhindered airflow through the SIP. After 21 days of sampling, the SIPs were taken down, stored airtight and shipped cooled to Stockholm. They were then stored in a freezer at −21 °C until extraction.

2.4. Sample extraction, analysis and data evaluation

Each SIP was squeezed with tweezeers into a cleaned ASE cell and spiked with mass-labelled (ML) internal standards in methanol (50 µL approx. 0.5 ng ML-PFASs/PFCAs, 100 µL approx. 30 ng ML-FTOHs, 19 ng ML-Et/MeFOSA and 6.4 ng ML-Et/MeFOSA, the latter both in 50 µL). Volatile and ionic PFASs were extracted from the SIPs sequentially. The first extraction was done with petroleum ether/acetone (85/15 v/v) for the volatile PFAS fraction (i.e. PFPA precursors: FTAC, FTMAC, FTOHs, FOSAs and FOSEs). For the second ionic PFAS fraction (i.e. PFAs and PFCAs), the collection bottles were changed and the SIPs were extracted with acetonitrile. Both extractions were run in two cycles on an ASE300 instrument ( Dionex) according to settings by Ahrens et al. (2013) and by Shoeib et al. (2008) for 6.2 FTOH. It was assumed that sampling for each compound was performed at 22 °C indoor air temperature for 21 days (see Table S4 for the list of air volumes). The SIPs were not calibrated for 6.2 FTAC, 6.2 FTMAC and PFHxP for any branched PFPA isomers. However, the calculated sampled air volumes were in a narrow range for the different compounds (cf. Table S4). For quantification, the acrylates were related to the internal standard with the closest retention time (ML-6.2 FTOH) and the corresponding 65 m3 sampled air volume for 6.2 FTOH for three weeks was applied for the acrylates, neglecting different volatility. PFHxA was related to the average sampled air volume for PFHxA and PFOA. The sum-branched PFHxS, PFOS and PFOA isomers were quantified against the respective linear standard (see example chromatogram for sum-br-
PFOS in Fig. S1) and the branched acids were assumed to have the same sampling volume as for the corresponding linear isomer. For these reasons, sum-branched isomer, as well as 6:2 FTAC, 6:2 FTMAC and PFHpA results should be considered as semi-quantitative.

2.5. Quality assurance and quality control

Five SIPs were kept within the sampler housings only for 1 min, before they were put back into the sealed jars. These SIPs served as field blanks. Additionally, ten SIPs served as procedural blanks and were not removed from the jars until analysis. However, all blanks were shipped, stored, spiked and extracted identically to the SIPs used for sampling. For data evaluation, the field and procedural blanks were considered as one group as they were similar in their results.

Injection blanks were performed with each batch of samples and were free of any measurable contamination (signal/noise-ratio $S/N < 3$). Method detection limits (MDL) are listed in Table S5. In case at least one field/procedural blank SIP showed a contamination ($S/N \geq 3$), MDLs were calculated as the mean of the blank SIPs plus three times their standard deviation (for the other blank SIPs noise was integrated). The lowest concentration point of the standard curve with a $S/N \geq 3$ was taken as the MDL for compounds without any contamination. In both cases, the total amount was divided by the air volume for the different analytes to obtain pg/m$^3$. For the acids, the recoveries ranged from an arithmetic mean of 75% (MPFNA) to 100% (MPFOS) and displayed small variations. There was no difference between blank and sample mean of 75% (MPFNA) to 100% (MPFOS) and displayed small variations in recoveries were observed in previous studies (cf. Table S7). All in all, the matrix effects and the wide span in recoveries support again the crucial role of mass-labelled standard addition for accurate quantification in each sample and for each analyte of interest (Shoeib et al., 2011).

3. Results and discussion

3.1. Frequency of detection and concentrations of precursors in indoor air

FTOH homologues were detected in nearly all samples (98% 6:2 FTOH, 100% 8:2 FTOH and 100% 10:2 FTOH), whereas the FOSA/Es were less frequently detected (cf. Table S8). Among FOSA/Es, the FOSAs had a higher frequency of detection (95% MeFOSA and 68% EtFOSA) than the FOSAs (33% EtFOSA and 21% MeFOSA). The detection frequency was comparable to previous studies for FTOHs (Haug et al., 2011; Shoeib et al., 2011), but lower in our study for FOSAs and EtFOSA (Shoeib et al., 2011). This could be partly explained by higher MDLs and possibly lower concentrations in the current study. 6:2 FTMAC was detected in more than half of the indoor air samples (58%) and 6:2 FTAC in 28%, which is in contrast to Fromme et al. (2015), who detected 6:2 FTAC in none of 13 German homes and in 2 out of 14 schools. Similar frequencies were reported for Japanese homes ($n = 84$) for 8:2 FTMAC and 8:2 FTAC though (40% and 87% (Liu et al., 2013)) and 100% 8:2 FTAC in Fromme et al. (2015).

FTOHs were observed at the highest concentrations among the measured precursors with concentrations approximately two orders of magnitude higher than for FOSA/Es and FT(M)ACs (cf. Fig. 1, 2 and 3).
Table S8). Median concentrations were 928 pg/m$^3$, 1310 pg/m$^3$ and 3570 pg/m$^3$, respectively, for 10:2 FTOH, 6:2 FTOH and 8:2 FTOH.

Among the sulfonamides, MeFOSE was present at the highest concentrations (56.0 pg/m$^3$, median), followed by EtFOSE (16.9 pg/m$^3$, cf. Fig. 1). MeFOSE is used in textiles, which is probably more present in sleeping rooms than paper and packaging, which is known to contain EtFOSE (Olson et al., 2005). 6:2 FTMAC had higher median concentrations than EtFOSE (20.6 pg/m$^3$; 6:2 FTMAC). The presence of volatile precursors in the indoor environment may primarily be due to unreacted residual monomers in various side-chain fluorinated polymers (Russell et al., 2008), which at the time of sampling were likely dominated by the market-leading fluorotelomer-acrylate polymers (Prevedouros et al., 2006). It is not possible to quantify the potential degradation of side-chain fluorinated polymers (Butt et al., 2014; Russell et al., 2008; Washington et al., 2009), but cleavage of side chains could be a potential additional source of precursors. It has to be considered that the quantification of the acrylates using ML-6.2 FTOH as internal standard might lead to a systematic over- or underestimation of the concentration. Nonetheless, the presence and detection frequency observed here suggest that an air sampler calibration for acrylates should be performed in future studies (even for other chain lengths, such as 8:2 and 10:2 see Fromme et al., 2015; Langer et al., 2010; Liu et al., 2013)). In addition, mass-labelled standards should be made commercially available for accurate quantification.

There was a large variability in concentrations between the different homes, e.g. 1290 to 13 500 pg/m$^3$ for 8:2 FTOH and below MDL (<11.4 pg/m$^3$) to 13 000 pg/m$^3$ for 6:2 FTMAC (cf. Fig. 1 and Table S7, Figs. S1 and S2 for data on individual homes). The highest measured indoor air concentration of all compounds and homes was 13 500 pg/m$^3$ for 8:2 FTOH sampled in a bedroom, followed by an outlying 6:2 FTMAC concentration of 13 000 pg/m$^3$. These two data points originated from different homes (Figs. S1 and S2).

3.2. Frequency of detection and concentrations of PFCA and PFSA in indoor air

Among the acids, the PFCA containing eight (PFOA) to twelve carbons (PFDoDA) were most frequently detected (>96% of the samples, cf. Table S9). Among the PFSA, PFOS was the most frequently detected (linear isomer: 88%; branched isomers: 93%) followed by PFBS (47%).

Compared to the FTOHs, the individual acid concentrations in air (Fig. 2) were approximately three orders of magnitude lower (compare Tables S8 and S9). The substantially lower concentrations of the acids compared to the precursors may be mainly caused by their lower volatility (Prevedouros et al., 2006), but also possibly by the lower levels of residuals in consumer products (Vestergren et al., 2015). The highest concentration among the acids was detected for PFOA (median 15.2 pg/m$^3$); branched PFOA was only detected in 5% of the samples. The lack of branched PFOA indicates that the PFOA primarily originated from telomer-based products. However, these isomer profiles should be interpreted with caution as they may have been influenced by low branched PFCA concentrations, which fell below the MDL. The PFCA were observed in higher concentrations than the PFSA. The order of PFCA concentrations was PFOA > PFHxA > PFDA > PFNA (Table S9, Fig. 2). This indicates, that the C8 homologue still dominates the PFCA pattern in indoor air and that the US EPA 2010/2015 PFOA Stewardship Program has had little effect by the time of sampling in 2014/2015 (US EPA, 2006). PFOA has also been found to be abundant in coated fabrics (Herzke et al., 2012), which are likely to be important consumer products in bedrooms. In general, PFCA concentrations decreased with increasing chain length (cf. Fig. 2).

Among the sulfonic acids, PFDS was not detected in any sample above the detection limit (MDL = 0.05 pg/m$^3$) and is therefore excluded from any further data treatment. PFOS had the highest median concentration (1.24 pg/m$^3$), followed by PFBS (0.69 pg/m$^3$, Table S9), even though PFOS was phased out more than a decade ago by the main producer (3M). PFOS has been shown to be present in consumer products after the phase-out. For example, it was the dominant PFSA in paints in a survey conducted in 2009 by Herzke et al. (2012). Paints, however, were most likely not the major PFOS/PFSA source. We expect that residual impurities in POSF-based polymeric products used to provide stain and water repellency to textiles and paper packaging are the most relevant indoor sources (Paul et al., 2009). PFHxS was hardly detected (frequency 16%). The fraction of sum-branched PFOS was 35% (branched 0.67 vs. linear 1.24 pg/m$^3$, median), which is in line with ECF-based product formulations typically containing approx. 30% sum-branched isomers. For more information on the variability of the different PFAA homologues among different homes consult Fig. S3.

In addition to the transfer of PFAA residuals from consumer products, degradation of volatile precursors may also be a source of PFAAs to the indoor environment. It is widely accepted that sulfonamides (Martin et al., 2006) and telomer alcohols (Ellis et al., 2004) can be transformed to PFAAs via atmospheric oxidation. However, to what extent these reactions occur in the indoor environment is poorly understood. Microbial biodegradation of FTOHs is reported for anaerobic and aerobic conditions (Liu et al., 2010; Dinglasan et al., 2004; Zhang et al., 2013), but not studied in the indoor environment.

3.3. Correlations between compounds

Strongly positive correlations between measured concentrations of two or more analytes in the dataset can point towards a) a common origin of the compounds (including precursors and their
corresponding acids, e.g., 6:2 FTOH and PFHxA/PFHpA) from the same consumer products or b) compounds that originate from different products but have similar release and subsequently similar uptake mechanisms by the SIPs. In some instances, PFASs may have a common source (case a), but may lack similar release mechanisms and indoor fate processes (needed for b to be true) and thus these PFASs may not be correlated.

The 8:2 FTOH and 10:2 FTOH were strongly positively correlated with each other \( (r = 0.91, p < 0.001, \text{Fig. 3}) \) and this is in accordance with the correlation coefficient of 0.94 \( (p < 0.001) \) reported by Shoeb et al. (2008). The correlations between 6:2 FTOH and 8:2 FTOH \( (p = 0.63) \), as well as between 6:2 FTOH and 10:2 FTOH \( (0.61) \), were slightly weaker, but still highly significant \( (p < 0.001) \). Similar positive correlations were also reported by Liu et al. (2013) for indoor air levels of Japanese homes. Since long-chain telomer-based products are known to contain impurities of varying chain lengths (Wang et al., 2014), the observed correlations probably reflect common sources for these homologues. Additionally, the chemical release and uptake processes by the SIP among the FTOHs are similar due to their structural relationship resulting in strong and highly significant relationships especially for 8:2 and 10:2 FTOH. The slightly weaker correlation between 6:2 and the longer chain FTOHs may indicate additional sources of short-chain FTOHs, which do not contribute to the concentrations of longer chain FTOHs.

MeFOSE and EtFOSE correlated positively with each other \( (p = 0.74; p < 0.001) \). EtFOSE is applied as a starting material for paper and packaging treatment, whereas MeFOSE is used as a building block in textile treatment with fluorinated chemicals (Olsen et al., 2005). Therefore hypothesis a) “same primary products” can be rejected and hypothesis b) “same fate” is the probable reason for their correlation. Additionally, the FOSEs are weakly positively correlated with 8:2 and 10:2 FTOH \( (p = 0.32, p < 0.05 \text{ and } p = 0.37, p < 0.01) \) and it is likely that they are derived from the same products (Buck et al., 2011). The acrylates are in polymeric products, which make up more than 75% of the global production market of fluorotelomer-based products (Prevedouros et al., 2006). Up to 0.1–0.5 wt% FTOHs have been found as residuals in fluoroacrylate polymer formulations along with acrylate monomers (Prevedouros et al., 2006; Russell et al., 2008). The production of acrylate monomers is a separate production pathway from any other fluorinated monomer class but the FTOHs (Buck et al., 2011). Both of these facts could explain why 6:2 FTMAC is solely correlated to the FTOHs.

The long-chain PFCAs were all highly positively correlated with each other \( (r = 0.72–0.96; p < 0.001) \). PFHxA was less strongly correlated to the long-chain PFCAs \( (r = 0.44–0.60, p < 0.001) \). The weaker correlation of PFHxA with the longer chain PFCAs may reflect the transition to new short-chain fluorotelomer products. The hypothesis that PFHxA partly originates from more recent telomerisation production is supported by the positive, highly significant correlation of PFHxA with exclusively 6:2 FTOH among

Fig. 3. Spearman rank correlation matrix of precursors and acids (confidence interval 0.95), indicating the correlation coefficients. Correlations with \( p > 0.05 \) treated as not significant (n.s.). Significance levels indicated by asterisk: *\( <0.05 \), **\( <0.01 \), ***\( <0.001 \). Only substances with >50% detection frequency are included in the correlation analysis; lin – linear, br – sum-branched.
the precursors ($p = 0.44, p < 0.001$). 6:2 FTOH and PFHxA are most likely co-occurring residual impurities in fluorotelomer-based products. Additionally, PFHxS was not significantly correlated with the PFOS isomers, in contrast to the C8-C12 PFCAs ($p = 0.30–0.53$, $p < 0.05$). Long-chain PFCAs from C8 to at least C12 were significantly positively correlated with all precursors except for 6:2 FTMAC (cf. Fig. 3), which has a separate production pathway (Buck et al., 2011). This indicates that long-chain PFCAs originate from both telomerisation and ECF production processes (correlation range long-chain PFCAs–FTOH/FOSEs: $\rho = 0.27–0.46$, $p < 0.05$, cf. Fig. 3 and Wang et al. (2014)).

The lin-PFOS isomer was strongly positively correlated with the sum of br-PFOS ($\rho = 0.90$, $p < 0.001$, cf. Fig. 3) and median percentage of sum-br-PFOS (35%) was generally in line with historical 3M products synthesized by ECF (30.0–37.7% br-PFOS (Arsenault et al., 2008)). The PFOS isomers were not correlated with any FOSE/FOSA precursors. There was a weak, but significant correlation between sum-branch­ed and linear PFOS and C8–C12 PFCAs ($\rho = 0.30–0.49$, $p < 0.05$). This could be due to both similar indoor fate processes and shared production using ECF.

### 3.4. Influence of house and room characteristics

In this section, the influence of several room and housing characteristics on measured PFAS levels was examined, which might explain partly the variances among the homes (Figs. S1, S2, S3). The house area was on average 135 m², the bedroom size 13.2 m² and the room volume 31.9 m³. The room size could be hypothesised to influence the air concentration, because a small room has a lower air volume, which could lead to SIPs reaching saturation faster or even to depletion of chemicals in the air. However, this is unlikely due to ventilation systems, which are commonly installed in every room of Scandinavian households to exchange indoor with outdoor air. Secondly, there was neither a correlation between the sleeping room volume (m³) and the individual PFASs’ concentrations, nor for the sleeping room or house living area (m²) (Spearman rank correlation).

We observed a positive correlation for 8:2 FTOH ($\rho = 0.32$, $p < 0.05$) and 10:2 FTOH ($\rho = 0.41, p < 0.01$) indoor air concentrations with the distance of the house to Kuopio city centre, whereas a weakly negative correlation was found for sum-br-PFOS ($\rho = –0.27, p < 0.05$) and linear PFOS ($\rho = –0.27, p < 0.05$). The distance to a city centre could hypothetically have an influence on lifestyle, consumer behaviour and furniture or products in the house. However, this is very speculative and could also be a chance finding. Additionally, the distance from Kuopio may represent a biased parameter for remoteness, as there were several smaller towns within the sampled area.

For our study purposes, we sampled children’s bedrooms, which is not common in the literature; mostly living rooms are sampled (Fromme et al., 2015; Huber et al., 2011; Haug et al., 2011). One study by Shoeb et al. (2011) analysed bedroom air as well and Liu et al. (2013) sampled in several rooms of the same homes. In the Liu et al. study, PFAS concentrations in different rooms correlated significantly and positively with levels in the living room ($p > 0.65$) for 8:2 FTAC, 6:2, 8:2 and 10:2 FTOH. This could have been due to air exchange between the rooms. Sleeping rooms had higher 8:2 FTOH air concentrations in comparison to other rooms in the study by Liu et al. (2013); different consumer products in living rooms (e.g. more electronics and carpeting) in comparison to children’s bedrooms (e.g. more clothes) might influence the PFAS concentrations and patterns.

Different variables of recorded housing or room characteristics were statistically tested for variance for each PFAS’s concentration by ANOVA in JMP® 12.0.1. In cases where the variance was significantly bigger than it would be for data belonging to the same category ($p < 0.05$), the Tukey-Kramer HSD ($\alpha = 0.05$) post-hoc-test was chosen. Only for the house type (two categories: detached single-family houses and semi-detached or terraced houses), even a t-test (confidence interval = 0.95) was performed. Both tests showed that the house type had no influence on PFAS concentrations.

The bedroom was located on the ground floor for 30 children (54%), on the first floor for 22 (39%), on the second floor for 3 children and in the basement for 1 child (information on 56 out of 57 homes). There was a statistically significant difference ($p < 0.001$, Tukey-Kramer HSD) for PFHxS and the floor level of the room within the house (between second and first, as well as second and ground level). The correlation could just be chance, because only 3 bedrooms were located on the second floor and any outlier has a huge effect on the data distribution.

Among the children, 33 had their own bedroom (59%, case 1), 20 shared with sibling(s) (36%, case 2), two slept in their mother’s (case 3) and one in his/her parents’ bedroom (case 4) (information on 56 out of 57 homes). The air concentration was found to be different between case 1 and case 3 for PFNA ($p < 0.01$), PFUnDA ($p < 0.001$) and PFDaDa as well as MeFOSE ($p < 0.05$, Tukey-Kramer HSD). For PFUnDa there was also a difference between sharing with the mother and parents (case 3 and 4, $p < 0.05$) or sibling(s) (case 3 and 2, $p < 0.001$). The bedroom was shared with one person by 20 of the children and with two other persons by 3 children. The number of people sleeping in the same bedroom seemed to effect the air concentrations significantly ($p < 0.05$) for lin-PFOA, PFDA, PFDaDa and PFTeDa (MeFOSE only ANOVA significant $p < 0.05$, not post-hoc test), if 1 person or 3 persons were sleeping in the same room. The age and the number of people could have influenced the type and quantity of consumer products in the bedroom, which could explain the difference. Furthermore the number of people sleeping in a room can influence the air turbulence and movement, which could possibly have had an effect on the sampling. However, this is very speculative and the significance can also be chance findings as the majority of the children slept alone.

The last recorded parameter was the floor material, which was either laminate (44%), wood (33%), plastic (19%), cork (1 bedroom) or tiles (1 bedroom). EtFOSE was the only compound with a statistical difference between plastic and laminate as well as between plastic and wood ($p < 0.05$, Tukey-Kramer HSD). The significance increased when excluding the two singly occurring floor materials, cork and tiles, from the analysis ($p < 0.01$ plastic-laminate). The mean EtFOSE air concentrations were 18.0 pg/m³ for laminated and 20.3 pg/m³ for wooden floor, which was less than half of the mean air concentration in rooms with plastic floor material (47.6 pg/m³, see Fig. S5 for EtFOSE plotted against floor material). The finding could be due to different ingredients of the floor materials, their surface treatment products or the capacity of different floor materials to act as a secondary source of PFASs.

### 3.5. Comparison to previous studies

Many different methods and sampler types have been applied for indoor air sampling of organic contaminants (Harner et al., 2006). Analytical methods also varied between studies. Quantitative comparison of indoor air measurements is therefore challenging. Furthermore, the extend of the sample number was rather small (2–13 homes) for the majority of the publications on PFASs in air (Barber et al., 2007; Ericson Jogsten et al., 2012; Fromme et al., 2015; Huber et al., 2011; Kim et al., 2012; Langer et al., 2010). Here, we focus on the comparison of our results with the four larger studies from Norway, Japan, and Canada (two separate studies in Vancouver and Ottawa), in order to compare studies with similarly
large sample sizes (n ≥ 40 homes) (Haug et al., 2011; Liu et al., 2013; Shoeib et al., 2005, 2011). In 2002/2003, FOSA/E indoor air levels have been measured for the first time (Shoeib et al., 2005). The remaining three studies sampled in 2008 and analysed for more compounds (Haug et al., 2011; Liu et al., 2013; Shoeib et al., 2011).

Only three studies have previously measured PFASs in residential indoor air and none investigated branched isomers (Barber et al., 2007; Ericson Jogsten et al., 2012; Shoeib et al., 2011). The few detects in the studies of Barber et al. (2007) and Ericson Jogsten et al. (2012) were mostly for C6, C8 PFASs and C6, C8-C10 PFCAs, which also had the highest levels in our study (cf. Table S9 and Fig. 2). Shoeib et al. (2011) also reported a dominance of PFHxS, PFPeA, PFNA and PFDA in their indoor air samples. Listed median concentrations in the Shoeib et al. study and our study were of the same order of magnitude; for PFHxS they were identical, whereas for PFOA and PFDA they were 2–4 times lower in our study (compare Table S9 to Shoeib et al., 2011).

As also observed in our study, FTOHs were the dominant PFASs in all previous studies. Our 8:2 FTOH levels (median 3570 pg/m³) agree well with previous studies (median range: 2720–5840 pg/m³ (Haug et al., 2011; Liu et al., 2013; Shoeib et al., 2011)). The order of median concentrations in these studies was as follows: 8:2 FTOH > 10:2 FTOH > 10:2 FTAC (Haug et al., 2011; Liu et al., 2013), which was even the case for some studies with a lower sample number (Fromme et al., 2015; Huber et al., 2011). In contrast to previous studies, 6:2 FTOH surpassed 10:2 FTOH concentrations (median 6:2 FTOH 1310 pg/m³ > 10:2 FTOH 928 pg/m³) in our measurements (cf. Table S8). A plausible cause for 6:2 FTOH concentrations exceeding 10:2 FTOH in our more recent study could be the production shift from long to short-chain fluorinated chemicals (Ritter, 2010; Renner, 2006). A consumer product analysis (n = 54) purchasing products in 2011 and 2013 also showed that 6:2 FTOH was more abundant than 10:2 FTOHs and had even higher maximum levels than 8:2 and 10:2 FTOH (Liu et al., 2015). Shoeib et al. (also sampling sleeping rooms) showed the same trend, but even more subtle than in our study (median 6:2 FTOH 1040 pg/m³ > 10:2 FTOH 980 pg/m³ (Shoeib et al., 2011)). Therefore, 6:2 FTOH concentrations could also be higher in sleeping rooms than living rooms due to different consumer products and furnishings. More studies should investigate the current air levels to corroborate if there is a true shift towards short-chain FTOHs or if the subtle differences are due to the different sampled rooms. At the same time it should be mentioned that 8:2 FTOH concentrations measured in our study are in a similar range as indoor air samples collected prior to the completion of the US EPA stewardship program (US EPA, 2006). Possible explanations for the apparent time lag in reduction of FTOH levels following recent regulatory measures and voluntary actions by industry could be: a) the replacement cycle of products or furniture and renovation routines in private households is long; b) replaced household products still contain PFASs (intentionally or as impurities). However, given that previous studies have been performed in various countries, different homes, different rooms and that sampling and analytical methods were variable, inferences to temporal trends of PFASs in the indoor environment should be interpreted with caution.

In contrast to FTOHs, the concentrations of MeFOSE in particular, vary greatly between previous studies and the present study. The concentration order of FOSA/Es, however, is the same: MeFOE > EtFOE > Et/MeFOSA (Haug et al., 2011; Liu et al., 2013; Shoeib et al., 2005, 2011). The earliest measurements of MeFOSE reported 8:2 FTOH >6:2 FTOH (Haug et al., 2011; Liu et al., 2013), whereas measurements six and five years later in 2008 and 2007 resulted in concentrations of 265 and 320 pg/m³ (Haug et al., 2011; Shoeib et al., 2011). The homes in our studies were sampled another six to seven years later (2014–2015) and again the levels were five-fold lower (56.0 pg MeFOSE/m³). The cause for this apparent decrease in concentrations with the sampling year is most likely linked to the production phase out of POSF chemicals, which was completed in 2002. The lack of an observable trend for the FOSAs and EtFOSE could be caused by the already comparably low starting levels in 2002/2003. A general downward trend in airborne Et/MeFOSA/E was also shown by outdoor air measurements at identical locations between 2006 and 2011 within the global atmospheric passive sampling (GAPS) program (Gawor et al., 2014). Even though venting of residences releases PFASs into the environment, a direct evidence of correlating indoor and outdoor air levels is missing until now, therefore the outdoor trend can just be taken as a vague evidence to support the indoor differences. Again, the decline in environmental levels is expected to be gradual due to long lifetime of many products containing ECF-based chemistries.

As far as we know, there are no indoor air measurements for 6:2 FTMAC reported in the literature. Even though the quantification of any acrylate has to be treated with caution due to a lack of mass labelled standards, comparing our 6:2 FTMAC levels (median 20.6 pg/m³) to 8:2 FTMAC measured in Japanese homes (<20 pg/m³ (Liu et al., 2013)), the median concentrations seem similar. The detection frequency of (meth)acrylates varies greatly between studies, which might also be caused by the partly small sample numbers (Fromme et al., 2015; Langer et al., 2010; Liu et al., 2013). Acrylates are more often investigated than methacrylates, especially the 8:2 FTAC was already investigated in three previous studies (Fromme et al., 2015; Langer et al., 2010; Liu et al., 2013). Median values of 8:2 FTAC varied among the studies (90 pg/m³ (Liu et al., 2013), 271 pg/m³ (Fromme et al., 2015)) and within the Langer et al. study with two residences (200 and 1500 pg/m³ (Langer et al., 2010)). 10:2 FTAC was also detected in homes (median 123 pg/m³ in Fromme et al. (2015) as well as 700 and 1100 pg/m³ for the homes investigated by Langer et al. (2010)). The variability between studies and single homes seems to be high, as supported by our study as well (Fig. S3). The frequent detection and the concentration exceedance of typically sampled precursors (FOSAs and EtFOSE) show that methacrylates and acrylates should be regularly investigated in future studies.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.12.010.

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