View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by NERC Open Research Archive

NERC Open Research Archive
sharing our research

Centre for Ecology & Hydrology
NATURAL ENVIRONMENT RESEARCH COUNCIL

Article (refereed) - postprint

Su, Hongqiao; Lu, Yonglong; Wang, Pei; Shi, Yajuan; Li, Qifeng; Zhou, Yunqiao; Johnson, Andrew C.. 2016. **Perfluoroalkyl acids (PFAAs) in indoor and outdoor dusts around a mega fluorochemical industrial park in China: implications for human exposure.** *Environment International*, 94. 667-673. 10.1016/j.envint.2016.07.002

© 2016 Elsevier Ltd.

This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/

This version available http://nora.nerc.ac.uk/515654/

NERC has developed NORA to enable users to access research outputs wholly or partially funded by NERC. Copyright and other rights for material on this site are retained by the rights owners. Users should read the terms and conditions of use of this material at http://nora.nerc.ac.uk/policies.html#access

NOTICE: this is the author's version of a work that was accepted for publication in *Environment International*. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in *Environment International*, 94. 667-673 10.1016/j.envint.2016.07.002

www.elsevier.com/

Contact CEH NORA team at
noraceh@ceh.ac.uk

The NERC and CEH trademarks and logos ('the Trademarks') are registered trademarks of NERC in the UK and other countries, and may not be used without the prior written consent of the Trademark owner.

Perfluoroalkyl acids (PFAAs) in indoor and outdoor dusts around a mega fluorochemical industrial park in China: implications for human exposure

Hongqiao Su [a,b], Yonglong Lu [a,*], Pei Wang [a], Yajuan Shi [a], Qifeng Li [a,b], Yunqiao Zhou [a,b], Andrew C. Johnson [c]

[a] *State Key Laboratory of Urban and Regional Ecology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China*

[b] *University of Chinese Academy of Sciences, Beijing 100049, China*

[c] *Centre for Ecology & Hydrology, Maclean Building, Crowmarsh Gifford Wallingford, Oxon, OX 10 8BB, UK*

Corresponding author:
*Yonglong Lu
Tel: 86-10-62917903
Fax: 86-10-62918177
E-mail: yllu@rcees.ac.cn

Highlights

- 12 PFAAs were detected in dusts around a mega fluorochemical industrial park.
- PFOA was the predominant PFAAs followed by C4-C7 PFCAs.
- PFAAs congener patterns in outdoor dusts were similar to those in indoor dusts.
- PFAAs concentrations were higher in indoor dusts than in corresponding outdoor dusts at every site.
- High EDI of PFOA, though below the tolerable levels, is posing human health risk.

Abstract

The manufacture of fluorochemicals can lead to high levels of perfluoroalkyl acids (PFAAs) contaminating the surrounding environment and consequently elevated exposure to the local residents. In this study, measurements of PFAAs associated with indoor and outdoor dusts around a mega fluorochemical industrial park (FIP) were made. Perfluorooctanoic acid (PFOA) and short-chain perfluoroalkyl carboxylic acids (C4-C7 PFCAs) were the predominant forms in all samples. The signature of the PFAAs in dusts in the local area matched that found within the FIP complex. The contamination plume in the local area could be linked to the prevailing wind direction starting from the FIP. The dust concentrations decreased exponentially with distance from the FIP (noticeably in the first 5 km). PFAAs contamination could be detected at the furthest location, 20 km away from the FIP. The concentrations of PFAAs were higher in indoor dust (73-13,500 ng/g, median: 979 ng/g) than those in outdoor dust (5-9,495 ng/g, median: 62 ng/g) at every location. The highest estimated daily intake of PFOA via dust ingestion (26.0 ng/kg.bw/day) was for toddlers (2-5 yrs) living 2 km away from the FIP, which is posing human health risk, though exposure remains within the provisional tolerable daily intake values.

Keywords: PFOA; C4-C7 PFCAs; Indoor dust; Outdoor dust; Mega fluorochemical industrial park

1. Introduction

Perfluoroalkyl acids (PFAAs), including perfluorocarboxylates (PFCAs) and perfluorosulfonates (PFSAs), are synthesized chemicals which have high surface activity, thermal and acid resistance, and repellency of water and oil (Giesy and Kannan, 2002). These properties have led to their use in various commercial products and industrial processes, such as textile, food containers, upholstery, fire-fighting foams, metal plating and fluoropolymer manufacturing (OECD, 2002; Buck et al., 2011; Wang et al., 2014b). Their presence in so many products and non-biodegradability has led to their wide distribution in the environment. With a potential for bioaccumulation and potential adverse effects in biota and humans, they have attracted increasing scientific attention and enhanced awareness among regulators (Lindstrom et al., 2011). In 2009, perfluorooctane sulfonic acid (PFOS), its salts, and perfluorooctane sulfonyl fluoride (POSF) were listed as persistent organic pollutants (POPs) by the Stockholm Convention (UNEP, 2009). Perfluorooctanoic acid (PFOA), another highly investigated PFAA, is due to be phased out in the USA following agreements with industry in that country by 2015 (USEPA, 2006). There has been a trend for the manufacture of PFAAs and fluoro-polymers/-telomers to shift from North America and Europe to emerging economies, especially China (Wang et al., 2014a; Wang et al., 2016).

In humans, statistical associations between PFOS or PFOA levels and reduced birth weight (Stein et al., 2009), cholesterol (Nelson et al., 2010), uric acid (Steenland et al., 2010), sperm quality (Joensen et al., 2009), kidney and testicular cancer (Barry et al., 2013), and ulcerative colitis (Steenland et al., 2013) have been reported. The main routes for human exposure to PFAAs include ingestion of dust, food and drinking water consumption, and inhalation of PFAAs-contaminated air (Fromme et al., 2009; D'Hollander et al., 2010). A number of studies have reported that household dust contains PFAAs (Björklund et al., 2009; Goosey and Harrad, 2011; Fraser et al., 2013). Indoor dust is mixture of settled particles, human skin and fabric micro fibres, whereas outdoor dust is mostly made of microorgansisms, spores, traffic-related emissions and soil-derived particles. Humans can mitigate their exposure to contaminants in food or beverages by choosing different products, but this choice does not exist when the contaminant is present in their physical environment where they work, live and play. Given the association of PFAAs with dust, it is likely that young children who are often in close contact with floors and dusty surfaces and have a greater propensity to put their hands and objects in their mouths will be particularly exposed.

Our previous studies have found an important point source of PFAAs, a mega fluorochemical industrial park (FIP), in the Xiaoqing River basin in northern China (Wang et al., 2014a). PFAAs levels up to 1.06 mg/L, with a mass load of 174 kg/d, were identified at downstream of the FIP (Wang et al., 2016). The FIP is one of the largest production facilities of the fluorochemical industry in Asia. It was founded in 1987 and began to produce polytetrafluoroethylene (PTFE) in 2001, with a production capacity of 49,000 tons in 2013. This FIP also produces other fluoropolymers (FP) that involve PFOA as a processing aid (Wang et al., 2014a; Wang et al., 2016). Whilst PFOA is largely released via the production and use of Ammonium Perfluorooctanoate (APFO) (Wang et al., 2014b), the C4-C7 PFCAs mainly come from impurities of PFCAs in FP/fluoroelastomer (FE) products or degradation of FP precursors (Shi et al., 2015).

This study provides a detailed and systematic investigation on the concentration and distribution of PFAAs in indoor and outdoor dust samples from households around the FIP. The objective was to determine the influence of PFAAs emitted from the FIP and estimate the daily intake of dominant PFAAs present in dust. Such information is necessary for effective management of PFAAs production from the FIP and for human health risk assessment.

2. Materials and methods

2.1 Sampling design and collection

The sampling sites are shown in Fig. 1a. With the FIP in Huantai as the center, samples were taken with the radius of 2, 5, 10 and 20 km in four directions (East, E; South, S; West, W; North, N). 16 pairs of indoor and corresponding outdoor dusts samples were collected from randomly selected homes at each sampling site in October of 2014. An outdoor dust sample was also collected from a road in the FIP at the same time. At each site, dust samples were swept with a pre-cleaned brush from the inside and outside of the house, respectively. Individual samples were wrapped in aluminum foil and further sealed in polyethylene zip bags, and then they were transported to the laboratory and stored at -20 ℃ until analysis. Before chemical analysis, large debris and particles (visible hairs, fibers or grits etc.) were removed from the samples by using a methanol rinsed pair of tweezers.

2.2 Standards and reagents

A total of 12 native PFAAs, including perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), PFOS and 9 mass-labeled PFAAs, including $^{13}C_4$PFBA, $^{13}C_4$PFHxA, $^{13}C_4$PFOA, $^{13}C_4$PFNA, $^{13}C_4$PFDA, $^{13}C_4$PFUnDA, $^{13}C_2$PFDoA, $^{18}O_2$PFHxS and $^{13}C_4$PFOS were purchased from Wellington Laboratories with purities of >98% (Guelph, Ontario, Canada). Detailed information about standards and reagents is given in the Supplementary Information.

2.3 Sample extraction and instrumental analysis

Samples were extracted according to published methods (Wang et al., 2015) with some modifications. A sub-sample of 2 g dust was spiked with 5 ng mass-labeled internal standards, digested with 2 mL 100 mM NaOH in acetonitrile and ultrasonicated for 30 min. A 20 mL volume of acetonitrile was added into the mixture and then the samples were shaken at 250 rpm for 30 min. Subsequently, 0.1 mL 2 M HCl was added, followed by centrifugation at 3000 rpm for 15 min. The process of extraction of acetonitrile was repeated twice. The supernatants were combined together and concentrated under a gentle flow of high-purity nitrogen to 1 mL.

Clean-up was performed with solid phase extraction (SPE) using ENVI-Carb cartridges and Oasis-WAX cartridges. Supelco ENVI-Carb cartridges (250 mg, 3 mL, Sigma-Aldrich, St. Louis, USA) were conditioned with 1 mL methanol for three times, and then the extracts were loaded and collected. The cartridges were further washed with 1 mL methanol for three times and collected together with the extracts. All the extracts were diluted in 100 mL Milli-Q water and subjected to Oasis WAX-SPE cleanup. The Oasis WAX cartridges (6 cc, 150 mg, 30 μm, Waters, Milford, MA) were conditioned with 4 mL of 0.1% ammonium hydroxide in methanol, 4 mL methanol and 4 mL Milli-Q water successively. After loading the extracts, the cartridges were washed with 4 mL 25 mM ammonium acetate (pH 4) and air-dried. The analytes were eluted with 4 mL methanol, followed by 4 mL 0.1% ammonium hydroxide in methanol. The eluate was then evaporated under gentle flow of high-purity nitrogen to 1 mL, filtered through a 0.2 μm nylon filter, and transferred into a 1.5 mL PP snap top brown glass vial with polyethylene (PE) septa for HPLC analysis.

All PFAAs were analyzed via an Agilent 1290 Infinity HPLC System coupled to an Agilent 6460 Triple Quadrupole LC/MS System (Agilent Technologies, Palo Alto, CA). The instrument conditions are listed in Table S1, S2.

2.4 Quality control and quality assurance

To avoid contamination, PTFE and other fluoropolymer materials were not used in sample preparation. Field blanks and procedural blanks were prepared using anhydrous sodium sulfate as an alternative of dust to monitor contamination during sample collection and extraction. Solvent blanks using methanol were run for every 10 samples to check background interferences of the instrument. Matrix spike recovery was performed with 50 ng native PFAAs standards added into 2 g outdoor dust samples at site E4, S4, W4 and N4, respectively.

A 10-point internal quantification curves ranging from 0.01 to 1000 ng/mL were prepared for the quantification of individual PFAAs with coefficients of determination

(r^2) for all the target analytes higher than 0.99. Where samples had concentrations of PFAAs higher than 1000 ng/mL, we reduced the amount and extracted again to make sure the PFAAs concentrations in the extracts fell within the range of the calibration series. Concentrations of all target PFAAs in any of field and procedural blanks were less than the limit of detection (LOD), which was defined as 3 times of signal-to-noise ratio (S/N). The limit of quantification (LOQ) was set as 10 times of S/N. Matrix spike recoveries of PFAAs ranged from 73 to 118%. Detailed QA/QC measurements of PFAAs in dust are shown in Table S3.

2.5 Statistical analysis

Data analysis was performed with SPSS Statistics V20.0 (SPSS Inc, USA) and Origin Pro 9.0 (Northampton, USA). For the purposes of this analysis, where a detection was less than the LOD they were given a value by dividing the LOD by the square root of two, and those less than LOQ were set to half of the LOQ (Wang et al., 2014a). Spatial distributions of PFAAs were analyzed using ArcGIS V10.0 (ESRI)

3. Results and discussion

3.1 PFAAs in indoor dusts

Concentrations of total PFAAs (ΣPFAAs) measured in indoor dust samples ranged from 73 to 13,500 ng/g, with a median of 979 ng/g (Table S4). The frequency of detection for C4 to C10 PFCAs and PFBS, PFHxS and PFOS were 100%, and those of C11 and C12 PFCAs were 82% and 94%, respectively.

The mean concentrations of ΣPFAAs at 2, 5, 10 and 20 km sampling circles were 6402, 1568, 812 and 243 ng/g, respectively. The concentrations of ΣPFAAs decreased exponentially with the increase of distance from the source ($R^2 \geq 0.990$) (Fig. 2). The mean ΣPFAAs levels in indoor dusts from the 2, 5 and 10 km circles were at least one order of magnitude greater than the median levels in house dusts from more contaminated areas such as UK (350 ng/g), Germany (517 ng/g) and the US (619 ng/g), and they were also up to 2-3 orders of magnitude higher than those from slightly polluted areas like Egypt (1.7 ng/g) and Belgium (1.2 ng/g) (Shoeib et al., 2016).

For all indoor dust samples, PFOA (56-8,873 ng/g) was found to be the dominant PFAA, contributing 80.4% of ΣPFAAs, followed by short chain PFCAs, including PFPeA (2.90-3,362 ng/g, 6.3%), PFBA (5.82-220 ng/g, 5.0%), PFHpA (1.34-662 ng/g, 3.9%), PFHxA (4.75-424 ng/g, 3.8%) (Fig. 1c). For the other long chain PFCAs and all PFSAs (2.16-18.5 ng/g), the contribution to the total was less than 1%. The congener pattern of PFAAs in dusts was consistent with that in surface water and sediment in this area, in which PFOA and short chain PFCAs dominated as well (Wang et al., 2016). Like the congener pattern in the present study, PFOA was found to be the predominant PFCA in many other countries, such as Canada, Sweden, Spain or Australia (Eriksson and Kärrman, 2015). The median concentration of PFOA (852 ng/g) in house dust here was 1-2 orders of magnitude higher than that in house dusts from these countries (9-21 ng/g) (Eriksson and Kärrman, 2015) and was also 4 times higher than the mean PFOA concentration (205 ng/g) in indoor dusts from ordinary houses without a nearby point source in China (Zhang et al., 2010).

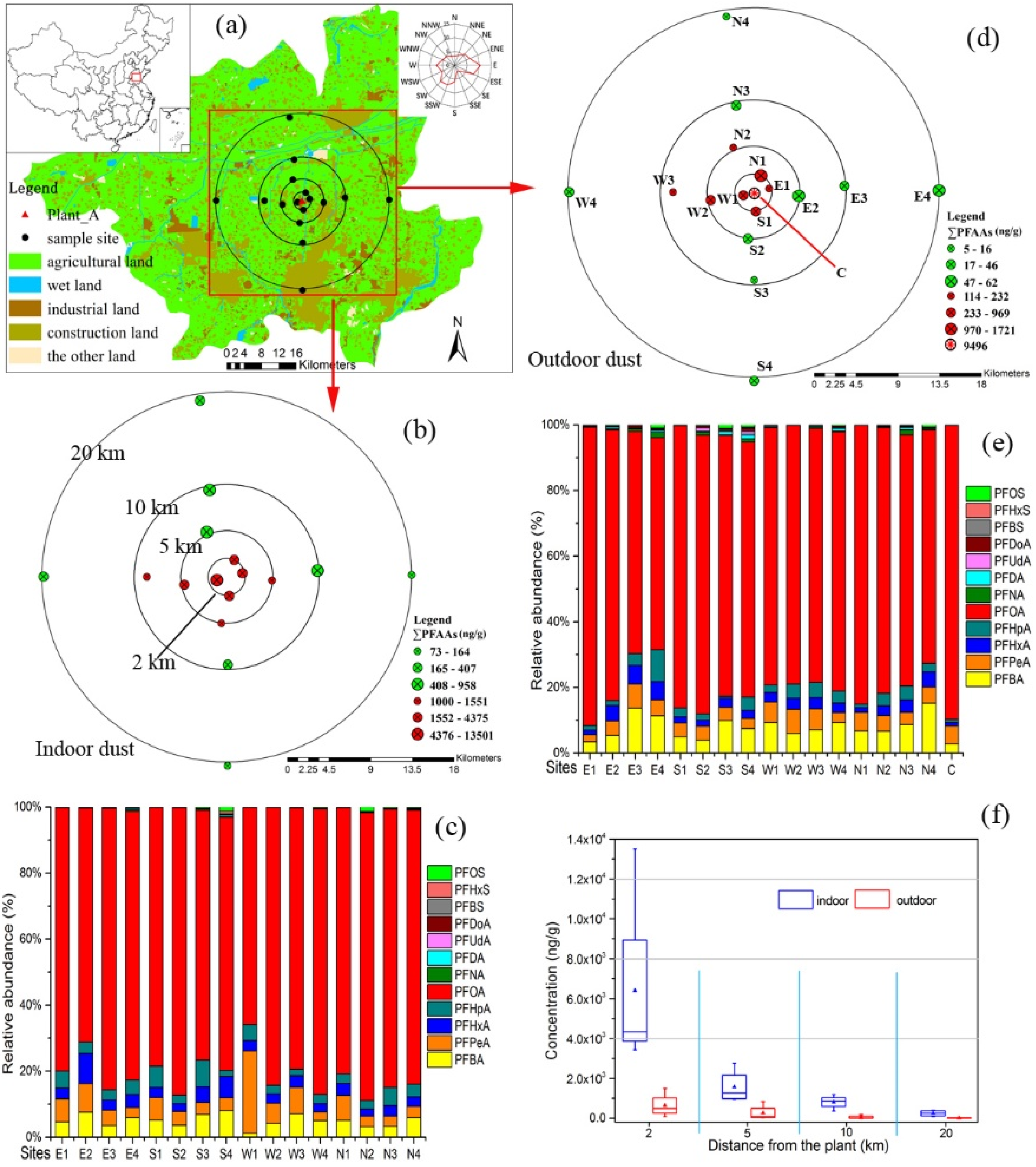

Fig. 1. (a) Map of the study area and sampling sites; (b) Spatial distribution of PFAAs in indoor dusts; (c) Relative abundance of individual PFAA in indoor dusts; (d)Spatial distribution of PFAAs in outdoor dusts; (e) Relative abundance of individual PFAA in outdoor dusts; (f) Comparison of PFAAs concentration in indoor dust and outdoor dust.

The lower and upper ends of the box are the 25th and 75th percentiles of the data. The horizontal solid line within the box is the median value and the symbol ▲ represents the arithmetic mean value.

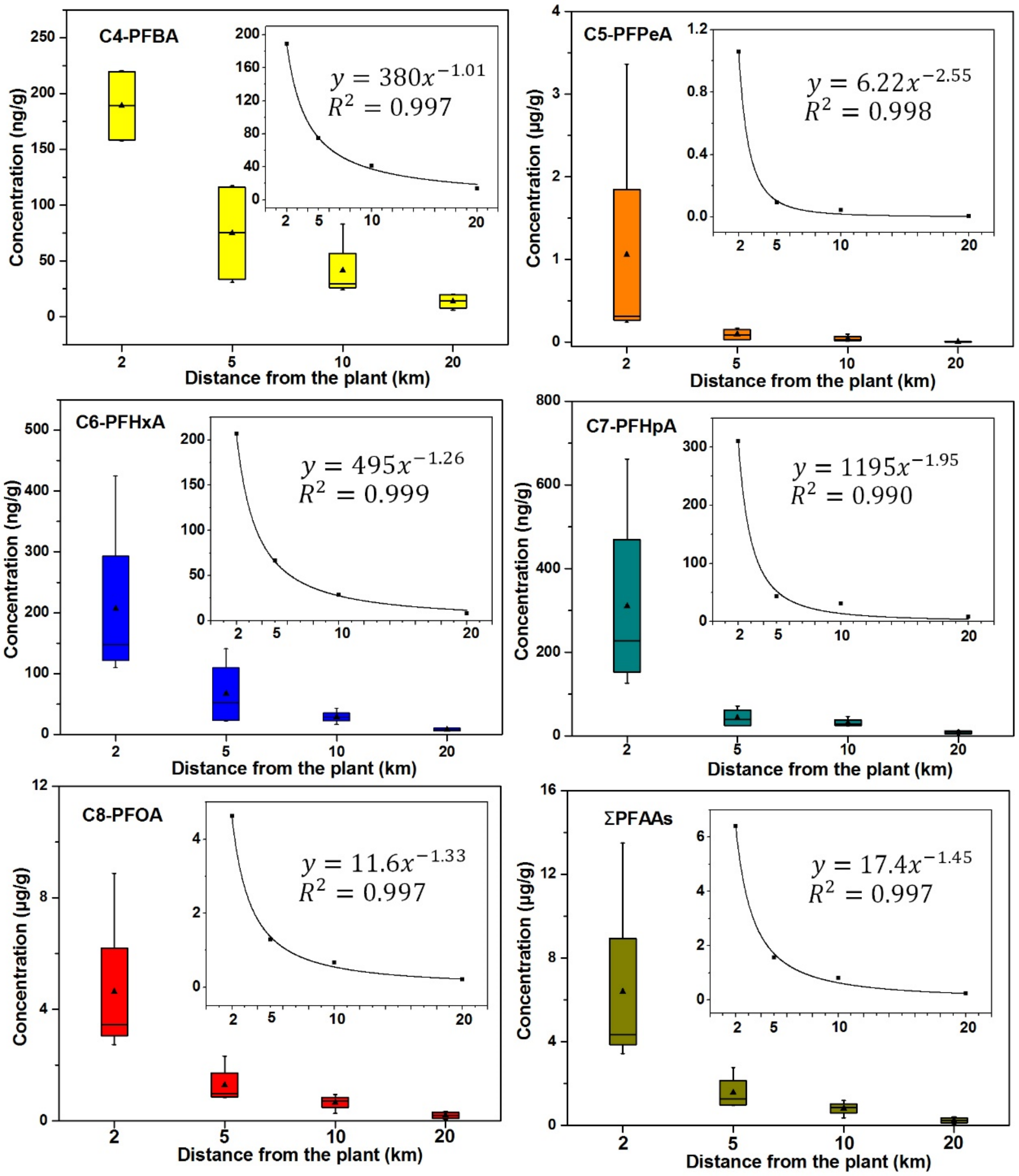

Fig. 2. Decline in C4-C8 PFCAs and ΣPFAAs concentrations in indoor dust samples with the distance from the FIP. The decline curve was based on the arithmetic mean concentration. The lower and upper ends of the box are the 25th and 75th percentiles of the data. The horizontal solid line within the box is the median value and the symbol

▲ represents the arithmetic mean value.

3.2 PFAAs in outdoor dusts

The concentrations of ΣPFAAs in outdoor dusts ranged from 5 to 9,495 ng/g (median: 62 ng/g) (Table S5). The highest ΣPFAAs concentration was found in the dust collected from the road located in the FIP. Detection frequency of C4 to C9 and C12 PFCAs were 100% and that of C10 and C11 PFCAs were 94%, while the detection rate of PFBS and PFOS was 88% and that of PFHxS was 41%. With the increase in distance from the FIP, the concentrations of PFAAs in outdoor dusts decreased (Fig. 1d). Mean concentrations of ΣPFAAs for 2, 5, 10 and 20 km from the FIP were 747, 319, 77.6 and 34.7 ng/g, which were about 13-274 times lower than that in dusts from the FIP. The relative contributions of individual PFAAs for indoor and outdoor dusts were similar (Fig. 1c, 1e). PFOA (4.29-8,511 ng/g) was the dominant PFAA and contributed 79.5% of ΣPFAAs, followed by PFBA (0.53-255 ng/g, 7.7%), PFPeA (0.22-521 ng/g, 4.8%), PFHxA (0.15-108 ng/g, 3.1%), PFHpA (0.03-82.2 ng/g, 3.1%) (Fig. 1e). Concentrations of C9-C12 PFCAs and all PFSAs ranged from 0.17 to 16.6 ng/g.

Studies on PFAAs in outdoor dust are rare, although these dusts play an important role in the global transportation of PFAAs (Yao et al., 2016). PFOA levels ranged from 1.2 to 11 ng/g in street dust including residential area and heavy traffic area in Japan (Murakami et al., 2008), which were lower than PFOA concentrations (11-36 ng/g) in outdoor dusts from 20 km away from the FIP. As for outdoor dust nationwide in China (Yao et al., 2016), C4-C12 PFCAs as a whole accounted for 89% of the PFAAs, among which PFOA was the predominant form as well. In their study, the highest PFOA concentrations (65-100 ng/g) occurred in outdoor dusts from Shanghai, one of the most urbanized cities in China (Yao et al., 2016), which were more than 2-6 times lower than the mean concentrations of PFOA in dust samples from the 2 km (627 ng/g) and 5 km (254 ng/g) circles, and higher than those from 10 km (59 ng/g) and 20 km (25 ng/g) circles in our study.

For each site, the concentrations of PFAAs measured in indoor dust exceeded that measured in outdoor dust (Fig. 1f). The same phenomenon has also been observed in other organic contaminants, like Fipronil (Mahler et al., 2009), PBDEs (Yu et al., 2012), or PCBs (Wang et al., 2013). Indoor dust particles have different properties from outdoor such as in particle size, or organic content, potentially making them more attractive sorbents fort PFAAs. Meanwhile, house dust is not subject to the same environmental conditions as outdoor dust (e.g., wind and rain dispersal, runoff, moisture, sunlight). Therefore, elimination or degradation of contaminants associated with dust is assumed to be slower indoors than outdoors (Vorhees et al., 1999; Mahler et al., 2009).

3.3 Source identification of PFAAs in dust

Associations among different PFAAs concentrations in dusts were explored using Spearman Rank Correlations (Table S6, S7). PFCAs from C4 (PFBA) to C8 (PFOA) were highly correlated ($p < 0.01$, correlation coefficients > 0.85) with each other. Furthermore, a significant correlation ($p < 0.05$) was observed among the remaining PFCAs, while associations within PFSAs as well as between PFCAs and PFSAs were less significant. The associations among individual PFAAs indicated that these congeners share similar origins or fate. A significant PFOA and PFOS correlation in house dust which has been reported in many studies (Kato et al., 2009; Haug et al., 2011a; Fraser et al., 2013) was not observed here. This might be due to different dust PFAAs origins.

Correlation analysis of PFAA congeners between the central FIP (C) and the other dust sampling sites (Table S8, S9) showed that they were similar in the signature profiles ($p < 0.01$，correlation coefficients > 0.76). Based on our previous examination of the area (Wang et al., 2014a), the FIP was the only point source in the study area, which generated the PFAAs contaminants in dust samples. The FIP is a self-sufficient manufacturer, so the PFCAs could be generated and released through their direct production, the production of fluoropolymers or the production of many intermediates (Wang et al., 2016). Global source inventories have also demonstrated that emissions of PFCAs can be largely attributed to these processes (Wang et al., 2014b).

Spatially, PFAAs concentrations of dust samples in the west were higher than that in other three directions, which were comparable to each other (Fig. 1b, 1d). Wind rose plot for local area shows that the E (east) wind and the ESE (east-south-east) wind are the primary wind directions in the study area (Fig. 1a, S1). Hence, the downwind location may be the main reason for higher concentrations of PFAAs at the sites in the west. So air transport and deposition was the most likely pathway for PFAAs from the FIP to the households in the surrounding areas, which is similar to the APFO transportation in environmental media near a fluorochemical manufacturing facility (Davis et al., 2007).

Correlations of PFAAs in indoor and outdoor dusts at each sample site were also investigated (Table S10). The total PFAAs in the indoor dust samples correlated well with that in the corresponding outdoor dust samples ($p < 0.01$, correlation coefficients > 0.74), which implies similar sources. It is possible that outdoor dust is walked into the houses by the residents (Mahler et al., 2012). Indoor air and outdoor to indoor air transport may contribute to the organic contaminants in indoor dust as well (Mercier et al., 2011). The clothing and skin of workers who live close to the FIP is possibly another source of PFAAs in dusts (Fu et al., 2015). These sources of PFAAs in dusts around the FIP (Fig. 3) are different from those in ordinary homes where the source is use, wear and abrasion of consumer products inside the home (Moriwaki et al., 2003; Shoeib et al., 2005).

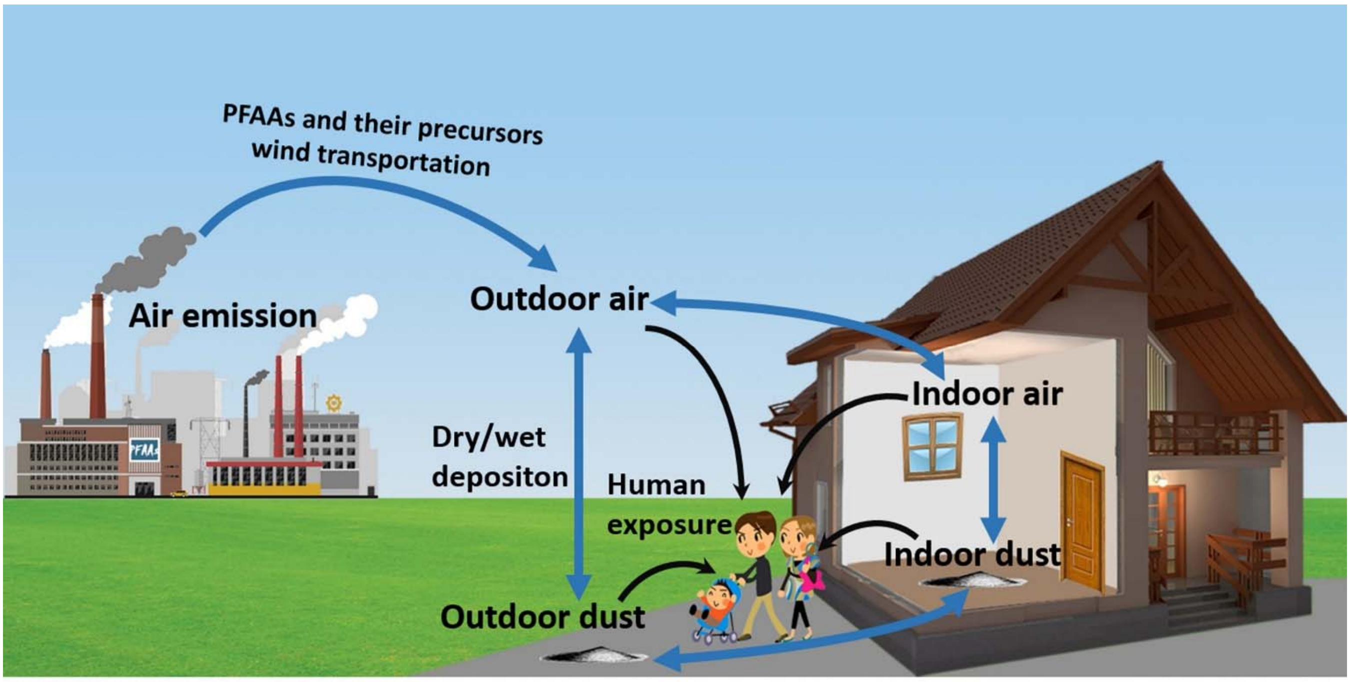

Fig. 3. Schematic diagram of sources of PFAAs in dust around the FIP.

3.4 Human exposure to PFAAs via dust ingestion and dermal absorption

Humans can be exposed to PFAAs in dust via ingestion and dermal absorption. The estimated daily intake (EDI, ng/kg.bw/day) of PFAAs through dust ingestion and dermal absorption can be calculated by averaging the intake dose over body weight, with equations and exposure/ingestion factors recommended by the Environmental Protection Agency of the United States (USEPA, 2011) and Zhang et al (2010, 2015). Considering that body weights and consumption rates vary by age, we estimated the EDI of PFAAs for five age groups: infants (0-1 yrs), toddlers (2-5 yrs), children (6-10 yrs), teenagers (11-17 yrs), and adults (≥18 yrs). The details of the calculation and data sources are shown in Table S11 and Table S12. As for the EDI calculation of each sampling circle, arithmetic mean concentrations of PFAAs were used.

The EDIs of several main PFAAs in the study area via dust ingestion and dermal absorption varied, depending on the age group and the distance of the residents from the FIP (Table S13). The EDI of PFAAs through dust ingestion was approximately 4-14 times higher than that through dermal absorption. The total exposure of PFBA, PFPeA, PFHxA, PFHpA, PFOA, and ΣPFAAs via dust were 0.184, 0.997, 0.196, 0.293, 4.42 and 6.09 ng/kg.bw/day for adults who reside about 2 km away from the FIP, and corresponding exposures were 1.10, 5.81, 1.14, 1.70, 26.0 and 35.9 ng/kg.bw/day for toddlers, respectively (Table 1). As expected, the EDI for toddlers was higher than those for other age groups in each sample circle (Fig. 4) due to more frequent hand-to-mouth contact, indicating that the dust imposes more potential health risk on this age group. Tolerable daily intake (TDI) values are only available for PFOS and PFOA. Compared to current recommended TDI values of 100 to 1,500 ng/kg.bw/day for PFOA proposed by several countries (Fig.4, Table S14), the EDI of PFOA via dust for residents in the study area are less than these limits. However, it is important to note that there is an ongoing discussion about the relevance of these TDIs. Some argue that these values are insufficiently protective and may be several hundred fold too high (Grandjean and Budtz-Jørgensen, 2013; Grandjean and Clapp, 2015). PTFE production has been expanded in the FIP with an average annual growth rate of 25% since 2001, and without suitable substitutes for PFOA in the production of most fluoropolymers (Wang et al., 2016), high exposure is likely to continue for the local residents.

The EDIs of PFAAs via dust ingestion have been reported in the previous studies. Zhang et al (2010) estimated PFOA intake via indoor dust collected from four cities in China to be 0.87 ng/kg.bw/day for toddlers, about 3 times higher than that for children and teenagers and adults, and a little lower than the EDI of PFOA for toddlers living about 20 km away from the FIP. The EDI of PFOA was 0.43 ng/kg.bw/day for adults and 5.3 ng/kg.bw/day for children in Birmingham, UK (Goosey and Harrad, 2011) and was 0.20 ng/kg.bw/day for adult women in Norway (Haug et al., 2011b). The estimated intake of PFAAs (PFOA) via dust ingestion by 2 years' children was between 2.5 (0.06) and 7.0 (0.11) ng/kg.bw/day in Australia, Canada, the Faroe Islands and Japan, 0.3-0.8 (0.04-0.06) ng/kg.bw/day in Greece, Spain, and Sweden, and 0.02 (0) ng/kg.bw/day in Nepal (Eriksson and Kärrman, 2015). Overall, the estimated intakes of PFOA/PFAAs by residents about 2 km and 5 km from the FIP in our study were highest compared with the values previously reported.

Table 1 Estimated Daily Intake (EDI) of PFAAs via dust (ng/kg.bw/day) for various age groups

Distance (km)	**objectives**	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**∑PFAAs**

2	Infants	0.53	2.86	0.56	0.84	12.6	17.4
	Toddlers	1.10	5.81	1.14	1.70	26.0	35.9
	Children	0.45	2.35	0.46	0.69	10.5	14.5
	Teenagers	0.23	1.24	0.25	0.37	5.52	7.62
	Adults	0.18	1.00	0.20	0.29	4.42	6.09
5	Infants	0.21	0.26	0.18	0.12	3.54	4.33
	Toddlers	0.44	0.54	0.38	0.25	7.34	8.99
	Children	0.18	0.22	0.15	0.10	2.97	3.64
	Teenagers	0.09	0.11	0.08	0.05	1.54	1.89
	Adults	0.07	0.09	0.06	0.04	1.23	1.51
10	Infants	0.11	0.12	0.08	0.09	1.80	2.21
	Toddlers	0.24	0.25	0.16	0.17	3.69	4.53
	Children	0.10	0.10	0.06	0.07	1.49	1.83
	Teenagers	0.05	0.05	0.03	0.04	0.79	0.97
	Adults	0.04	0.04	0.03	0.03	0.63	0.77
20	Infants	0.04	0.02	0.02	0.02	0.56	0.67
	Toddlers	0.08	0.04	0.05	0.05	1.14	1.37
	Children	0.03	0.02	0.02	0.02	0.46	0.56
	Teenagers	0.02	0.01	0.01	0.01	0.24	0.29
	Adults	0.01	0.01	0.01	0.01	0.19	0.23

Note: Infants (0-1 yrs); Toddlers (2-5 yrs); Children (6-10 yrs); Teenagers (11-17 yrs); Adults (≥18 yrs)

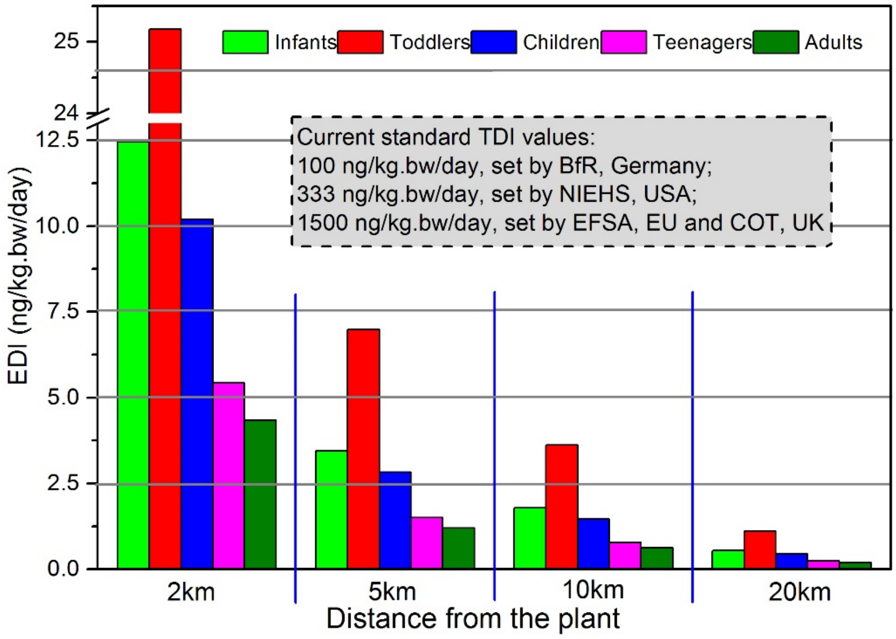

Fig. 4. Estimated daily intake (EDI, ng/kg.bw/day) of PFOA via indoor dust for residents around the FIP. Current standard Total Daily Intake (TDI, ng/kg.bw/day) values are reported in Thayer and Houlihan, 2002; BfR, 2006; Benford et al., 2008; COT, 2009

4 Conclusion

PFAAs in indoor and outdoor dusts were investigated around a mega fluorochemical industrial park (FIP). PFAAs generated from the FIP have diffused into the surrounding households and resulted in a zone of PFAAs contamination, at least 20 km in radius. The signature of the PFAAs in indoor and outdoor dust within this zone matches that within the FIP facility. The plume shape is consistent with air transport from the prevailing easterly winds from the FIP. PFOA and C4-C7 PFCAs were the predominant PFAAs in all dust samples with average contributions over 79% and 19%, respectively. The levels of PFAAs were significantly higher in indoor dusts than in outdoor dust. The entry of PFAAs contaminated dusts into resident's houses is most likely associated with entry via the window together with dusts being walked in.

The estimated daily ingestion dose of PFAAs for this area in China via contaminated dusts was higher than any previously recorded around the world, and the dusts impose more potential health risk on toddlers than any other age groups. Until new replacement products emerge, this high local exposure of residents to PFAAs via dust is likely to continue. In order to mitigate human exposure to fugitive gases and dusts heavily contaminated with PFOA and other PFAAs released from the FIP, scrubbers are suggested to be applied in smokestacks to capture smoke and toxic gases as well as fine particulates, and health risk awareness for the people (especially children) living in close proximity to the FIP should be enhanced to prevent them from exposures. This study identified primarily the sources of dust PFAAs and the possible transport pathways of PFAAs from the FIP to surrounding areas. Further investigation is needed for health risk assessment and management.

Acknowledgements

This study was supported by the International Scientific Cooperation Program with Grant No. 2012DFA91150, National Natural Science Foundation of China under Grant No. 414201040045 and No. 41371488, and the Key Project of the Chinese Academy of Sciences under Grant No. KZZD-EW-TZ-12.

References

Barry, V., Winquist, A., Steenland, K., 2013. Perfluorooctanoic acid (PFOA) exposures and incident cancers among adults living near a chemical plant. Environ. Health. Perspect. 121, 1313-1318.

Benford, D., Boer, J., Carere, A., Domenico, A., Johansson, N., Schrenk, D., Schoeters, G., Voogt, P., Dellatte, E., 2008. Opinion of the scientific panel on contaminants in the food chain on perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and their salts. EFSA J. 653, 1-131.

BfR (Bundesinstitut für Risikobewertung, German Federal Institut for Risk Assessment), 2006. High levels of perfluorinated organic surfactants in fish are likely to be harmful to human health. http://www.bfr.bund.de/en/press_information/2006/21/high_levels_of_perfluorinated_organic_surfactants_in_fish_are_likely_to_be_harmful_to_human_health-8172.html.

Björklund, J. A., Thuresson, K., de Wit, C. A., 2009. Perfluoroalkyl Compounds (PFCs) in Indoor Dust: Concentrations, Human Exposure Estimates, and Sources. Environ. Sci. Technol. 43, 2276-2281.

Buck, R. C., Franklin, J., Berger, U., Conder, J. M., Cousins, I. T., de Voogt, P., Jensen, A. A., Kannan, K., Mabury, S. A., van Leeuwen, S. P., 2011. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. Integr. Environ. Assess. Manag. 7, 513-541.

COT (Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment), 2009. COT statement on the tolerable daily intake for perfluorooctanoic acid. http://cot.food.gov.uk/cotstatements/cotstatementsyrs/cotstatements2009/cot200902#sthash.Jcv7t56q.dpuf.

D'Hollander, W., de Voogt, P., De Coen, W., Bervoets, L., 2010. Perfluorinated substances in human food and other sources of human exposure. Rev. Environ. Contam. Toxicol. 208, 179-215.

Davis, K. L., Aucoin, M. D., Larsen, B. S., Kaiser, M. A., Hartten, A. S., 2007. Transport of ammonium perfluorooctanoate in environmental media near a fluoropolymer manufacturing facility. Chemosphere. 67, 2011-2019.

Eriksson, U., Kärrman, A., 2015. World-Wide Indoor Exposure to Polyfluoroalkyl Phosphate Esters (PAPs) and other PFASs in Household Dust. Environ. Sci. Technol. 49, 14503-14511.

Fraser, A. J., Webster, T. F., Watkins, D. J., Strynar, M. J., Kato, K., Calafat, A. M., Vieira, V. M., McClean, M. D., 2013. Polyfluorinated compounds in dust from homes, offices, and vehicles as predictors of concentrations in office workers' serum. Environ. Int. 60, 128-136.

Fromme, H., Tittlemier, S. A., Völkel, W., Wilhelm, M., Twardella, D., 2009. Perfluorinated compounds exposure assessment for the general population in Western countries. Int J Hyg Environ. Health. 212, 239-270.

Fu, J., Gao, Y., Wang, T., Liang, Y., Zhang, A., Wang, Y., Jiang, G., 2015. Elevated levels of perfluoroalkyl acids in family members of occupationally exposed workers: the importance of dust transfer. Sci. Rep. 5, 9313

Giesy, J. P., Kannan, K., 2002. Peer reviewed: perfluorochemical surfactants in the environment. Environ. Sci. Technol. 36, 147A-152A.

Goosey, E., Harrad, S., 2011. Perfluoroalkyl compounds in dust from Asian, Australian, European, and North American homes and UK cars, classrooms, and offices. Environ. Int. 37, 86-92.

Grandjean, P., Budtz-Jørgensen, E., 2013. Immunotoxicity of perfluorinated alkylates: calculation of benchmark doses based on serum concentrations in children. Environ. Health. 12, 35.

Grandjean, P., Clapp, R., 2015. Perfluorinated Alkyl Substances Emerging Insights Into Health Risks. New Solut. 25, 147-163.

Haug, L. S., Huber, S., Becher, G., Thomsen, C., 2011a. Characterisation of human exposure pathways to perfluorinated compounds comparing exposure estimates with biomarkers of exposure. Environ. Int. 37, 687-693.

Haug, L. S., Huber, S., Schlabach, M., Becher, G., Thomsen, C., 2011b. Investigation on Per- and Polyfluorinated Compounds in Paired Samples of House Dust and Indoor Air from Norwegian Homes. Environ. Sci. Technol. 45, 7991-7998.

Heydebreck, F., Tang, J., Xie, Z., Ebinghaus, R., 2015. Alternative and legacy perfluoroalkyl substances: differences between European and Chinese River/Estuary systems. Environ. Sci. Technol. 49, 8386-8395.

Joensen, U. N., Bossi, R., Leffers, H., Jensen, A. A., Skakkebæk, N. E., Jørgensen, N., 2009. Do perfluoroalkyl compounds impair human semen quality? Environ. Health. Perspect. 117, 923.

Kato, K., Calafat, A. M., Needham, L. L., 2009. Polyfluoroalkyl chemicals in house dust. Environ. Res. 109, 518-523.

Lindstrom, A. B., Strynar, M. J., Libelo, E. L., Field, J. A., 2011. Guest Comment: Perfluoroalkyl Acid Focus Issue. Environ. Sci. Technol. 45, 7951-7953.

Mahler, B. J., Van Metre, P. C., Wilson, J. T., Musgrove, M., Zaugg, S. D., Burkhardt, M. R., 2009. Fipronil and its degradates in indoor and outdoor dust. Environ. Sci. Technol. 43, 5665-5670.

Mahler, B.J., Metre, P.C.V., Crane, J.L., Watts, A.W., Scoggins, M., Williams, E.S., 2012. Coal-

Tar-Based Pavement Sealcoat and PAHs: Implications for the Environment, Human Health, and Stormwater Management. Environ. Sci. Technol. 46, 3039-3045.

Mercier, F., Glorennec, P., Thomas, O., Bot, B. L., 2011. Organic Contamination of Settled House Dust, A Review for Exposure Assessment Purposes. Environ. Sci. Technol. 45, 6716-6727.

Moriwaki, H., Takata, Y., Arakawa, R., 2003. Concentrations of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in vacuum cleaner dust collected in Japanese homes. J. Environ. Monitor. 5, 753-757.

Murakami, M., Takada, H., Yao, Y., Sun, H., Gan, Z., Hu, H., Zhao, Y., Chang, S., Zhou, Q.-X., 2008. Perfluorinated surfactants (PFSs) in size-fractionated street dust in Tokyo. Chemosphere. 73, 1172-1177.

Nelson, J.W., Hatch, E.E., Webster, T.F., 2010. Exposure to polyfluoroalkyl chemicals and cholesterol, body weight, and insulin resistance in the general US population. Environ. Health. Perspect. 118, 197-202.

OECD (Organization for Economic Co-operation and Development), 2002. Hazard assessment of perfluorooctane sulfonate and its salts. ENV/JM/RD (2002) 17/FINAL.

Shi, Y., Vestergren, R., Xu, L., Song, X., Niu, X., Zhang, C., Cai, Y., 2015. Characterizing direct emissions of perfluoroalkyl substances from ongoing fluoropolymer production sources: A spatial trend study of Xiaoqing River, China. Environ. Pollut. 206, 104-112.

Shoeib, M., Harner, T., Wilford, B. H., Jones, K. C., Zhu, J., 2005. Perfluorinated sulfonamides in indoor and outdoor air and indoor dust: occurrence, partitioning, and human exposure. Environ. Sci. Technol. 39, 6599-6606.

Shoeib, T., Hassan, Y., Rauert, C., Harner, T., 2016. Poly-and perfluoroalkyl substances (PFASs) in indoor dust and food packaging materials in Egypt: Trends in developed and developing countries. Chemosphere. 144, 1573-1581.

Stein, C.R., Savitz, D.A., Dougan, M., 2009. Serum levels of perfluorooctanoic acid and perfluorooctane sulfonate and pregnancy outcome. Am. J. Epidemiol. 170, 837-846.

Steenland, K., Tinker, S., Shankar, A., Ducatman, A., 2010. Association of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) with Uric Acid among Adults with Elevated Community Exposure to PFOA. Environ. Health. Perspect. 118, 229-233.

Steenland, K., Zhao, L., Winquist, A., Parks, C., 2013. Ulcerative colitis and perfluorooctanoic acid (PFOA) in a highly exposed population of community residents and workers in the mid-Ohio valley. Environ. Health. Perspect. 121, 900-905.

Thayer, K., Houlihan, J., 2002. Perfluorinated chemicals: Justification for inclusion of this chemical class in the national report on human exposure to environmental chemicals. Environmental Working Group, Washington, DC.

UNEP (United Nations Environment Programme), 2009. Report of the conference of the parties of the Stockholm convention on persistent organic pollutants on the work of its fourth meeting. http://chm.pops.int/TheConvention/ConferenceoftheParties/ReportsandDecisions/tabid/208/Default.aspx.

USEPA (United States Environmental Protection Agency), 2006. 2010/2015 PFOA Stewardship Program. https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/20102015-pfoa-stewardship-program.

USEPA, 2011. Exposure Factors Handbook 2011 Edition (Final). U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-09/052F, 2011.

Vorhees, D. J., Cullen, A. C., Altshul, L. M., 1999. Polychlorinated Biphenyls in House Dust and Yard Soil near a Superfund Site. Environ. Sci. Technol. 33, 2151-2156.

Wang, P., Lu, Y., Wang, T., Fu, Y., Zhu, Z., Liu, S., Xie, S., Xiao, Y., Giesy, J. P., 2014a. Occurrence and transport of 17 perfluoroalkyl acids in 12 coastal rivers in south Bohai coastal region of China with concentrated fluoropolymer facilities. Environ. Pollut. 190, 115-122.

Wang, P., Lu, Y., Wang, T., Meng, J., Li, Q., Zhu, Z., Sun, Y., Wang, R., Giesy, J. P., 2016. Shifts in production of perfluoroalkyl acids affect emissions and concentrations in the environment of the Xiaoqing River Basin, China. J. Hazard. Mater. 307, 55-63.

Wang, P., Lu, Y., Wang, T., Zhu, Z., Li, Q., Zhang, Y., Fu, Y., Xiao, Y., Giesy, J. P., 2015. Transport of short-chain perfluoroalkyl acids from concentrated fluoropolymer facilities to the Daling River estuary, China. Environ. Sci. Pollut. Res. 22, 9626-9636.

Wang, W., Huang, M.-J., Zheng, J.-S., Cheung, K. C., Wong, M. H., 2013. Exposure assessment and distribution of polychlorinated biphenyls (PCBs) contained in indoor and outdoor dusts and the impacts of particle size and bioaccessibility. Sci. Total Environ. 463-464, 1201-1209.

Wang, Z., Cousins, I. T., Scheringer, M., Buck, R. C., Hungerbühler, K., 2014b. Global emission inventories for C4 C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: production and emissions from quantifiable sources. Environ. Int. 70, 62-75.

Yao, Y., Sun, H., Gan, Z., Hu, H., Zhao, Y., Chang, S., Zhou, Q., 2016. A Nationwide Distribution of Per-and Polyfluoroalkyl Substances (PFASs) in Outdoor Dust in Mainland China From Eastern to Western Areas. Environ. Sci. Technol. 50, 3676-3685.

Yu, Y.-X., Pang, Y.-P., Li, C., Li, J.-L., Zhang, X.-Y., Yu, Z.-Q., Feng, J.-L., Wu, M.-H., Sheng, G.-Y., Fu, J.-M., 2012. Concentrations and seasonal variations of polybrominated diphenyl ethers (PBDEs) in in- and out-house dust and human daily intake via dust ingestion corrected with bioaccessibility of PBDEs. Environ. Int. 42, 124-131.

Zhang, T., Chen, X., Wang, D., Li, R., Ma, Y., Mo, W., Sun, H., Kannan, K., 2015. Perchlorate in Indoor Dust and Human Urine in China: Contribution of Indoor Dust to Total Daily Intake. Environ. Sci. Technol. 49, 2443-2450.

Zhang, T., Sun, H. W., Wu, Q., Zhang, X. Z., Yun, S. H., Kannan, K., 2010. Perfluorochemicals in meat, eggs and indoor dust in China: assessment of sources and pathways of human exposure to perfluorochemicals. Environ. Sci. Technol. 44, 3572-3579.