Home produced eggs: an important pathway of human exposure to perfluorobutanoic acid (PFBA) and perfluorooctanoic acid (PFOA) around a mega fluorochemical industrial park in China

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Highlights

- PFAAs were detected in eggs around a mega fluorochemical industrial park.
- PFAAs in home produced eggs were higher than those in commercially produced eggs.
- PFBA was firstly examined in eggs and found in all the samples.
- The estimated daily intakes of PFOA via home produced eggs posed health risks.

Abstract

Dietary intake is considered to be a major pathway of human exposure to perfluoroalkyl acids (PFAAs). Chicken eggs ~~is~~ can be an important contributor to the Chinese diet. In thise present study, PFAAs in home produced eggs (HPEs) and commercially produced eggs (CPEs) surrounding a mega fluorochemical industrial park (FIP) in China were investigated. PFAAs in HPEs decreased with increasing distance from the FIP. HPEs were much more contaminated than CPEs, with PFAAs in CPEs comparable to or lower than those in HPEs from 20 km away from the FIP. PFOA concentrations in HPEs were higher than the levels of PFOA in eggs from other studies reported so far. For the first time, PFBA was reported in eggs and detected ~~100%~~ in all egg samples. PFOA and PFBA were the predominant forms in HPEs, while PFOA, PFBA and PFOS dominated in CPEs. Comparison of PFAAs profiles between eggs and environmental matrices~~x~~ implied that bioaccumulation potential of PFBA, PFOA and PFOS were higher than other PFAAs in chicken eggs. For PFOA, estimated daily intakes (EDI) were 233 ng/kg.bw/day for adults and 657 ng/kg.bw/day for children who consume HPEs at households about 2 km away from the FIP. The EDI of PFOA via HPEs exceeded the provisional value of tolerable daily intake (100 ng/kg.bw/day) proposed by Drinking Water Commission of the German Ministry of Health.

Key words: PFOA, PFBA, home produced eggs, commercially produced eggs, Mega fluorochemical industrial park, health risk

1. Introduction

Perfluoroalkyl acids (PFAAs) represent a family of synthetic organic compounds characterized by a fully fluorinated linear carbon chain with a hydrophilic head (Lau et al. 2007; Fromme et al. 2009). Due to their hydrophobic and lipophobic nature, as well as their chemical and thermal stability, they have been widely used~~,~~ for over 60 years~~,~~ in a number of consumer and industrial applications (Ericson Jogsten et al. 2012). Among the PFAAs are perfluoroalkyl sulfonates (PFSAs) and perfluoroalkyl carboxylates (PFCAs), of which perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are most widely detected in the environment, wildlife and humans around the world (Giesy et al. 2001; Wang et al. 2014). These chemicals have attracted significant attention from scientists and regulators because of their persistence, bioaccumulation and toxicity, as well as their ability to be transported at great distances (insert REF). For the purpose of globally restricting the uses and production, PFOS, its salts, and perfluorooctane sulfonyl fluoride (POSF) were listed as persistent organic pollutants (POPs) in Annex B of the Stockholm Convention in May 2009 (UNEP 2009). Additionally, PFOA and its salt ammonium perfluorooctanoate (APFO) were added to the Candidate list of Substances of Very High Concern (SVHC) by the European Chemicals Agency (ECHA 2013). As a result of these regulations, the manufacture of PFAAs has shifted toward less regulated countries including China to meet increasing demands and toward un~~non~~regulated short-chain PFAAs homologues.

Epidemiologic research~~es~~ suggests that PFOS and PFOA levels may be associated with reduced birth weight (Fei et al. 2007; Stein et al. 2009), increased blood cholesterol concentrations (Nelson et al. 2010), kidney and testicular cancer (Barry et al. 2013), and hyperuricemia (Steenland et al. 2010; Geiger et al. 2013). Diet, drinking water, air inhalation, and dust ingestion have been identified as main human exposure routes for PFAAs (Fromme et al. 2009; D'Hollander et al. 2010). The ~~available~~ published investigations to date are mostly concerned with exposure of the general population, while a few studies~~y~~ have reported on exposure pathways for residents near hot spot areas, ~~like~~ such as manufacturing facilities~~y~~. Some of these residents ~~grow~~ manage their own livestock or grow vegetables for basic subsistence and may inadvertently ~~unconsciously~~ consume ~~large quantities of~~ contaminated food (Brambilla et al. 2015).

Chicken eggs represent~~,~~ an important contributor to the Chinese diet~~, constitutes a good protein and vitamin source and~~ is therefore of economic importance (Iddamalgoda et al. 2001). ~~Nowadays~~Despite~~, there is~~ a general perception that free-range eggs are attributed a healthier nature and high nutritional qualities (Waegeneers et al. 2009) a number of ~~. Nevertheless, more and more~~ studies revealed in home produced eggs (HPEs) a high contamination levels of POPs, such as PFAAs (Zafeiraki et al. 2016), dioxins and polychlorinated biphenyls (Van Overmeire et al. 2009; Hoogenboom et al. 2016; Polder et al. 2016), and halogenated flame retardants (Zheng et al. 2012).

Our previous studies have investigated the transportation of PFAAs from a mega fluorochemical industrial park (FIP) to the surrounding environment and elevated PFOA and C4-C7 PFCAs levels were found in indoor and outdoor dusts (Su et al. 2016), surface and ground waters (Liu et al. 2016), and sediments (Wang et al. 2016). In this~~e~~ ~~present~~ study, ~~we examined~~a range of –PFAAs in HPEs have been reported in ~~and~~ commercially produced eggs (CPEs) from households surrounding the FIP. The main objectives of the study were: 1) to examine PFAAs in egg yolks, egg whites and pooled eggs separately for distribution of PFAAs in different parts of the egg ~~parts~~; 2) to investigate the levels and composition profiles of PFAAs in eggs; 3) to assess the human risks of PFAAs via consumption of these eggs ~~for~~ to the local residents.

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2. Materials and methods

2.1 Sampling design and collection

The selected FIP is located in Huantai county, Shandong province, in northern China. The FIP began to produce polytetrafluoroethylene (PTFE) in 2001, and the production has been expanded with an average annual growth rate of 25% since then (Wang et al. 2016). The capacity of PTFE production was expanded to over 49, 000 tons ~~at~~ by the end of 2013. Huantai county is densely populated with a population of about 0.5 million in 2013, of which 81% live in rural areas. A total of 16 egg samples were collected from households around the FIP in October of 2015 (Fig. 1). Some of the local residents rear chickens domestically (n=4, site 1-4), while the others buy eggs from nearby supermarkets (n=12, site 5-16). After ~~the~~ sampling~~,~~ the eggs were ~~brought~~ taken to laboratory and extracted within 1 week ~~after arrival in the lab~~. ~~Every~~Each sample consisted of 3 individual eggs.

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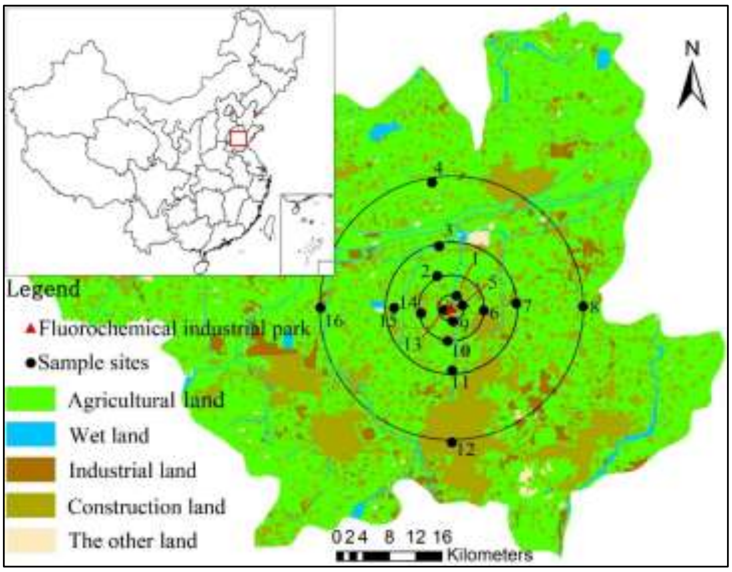

Fig. 1 Map of the study area and sampling sites.

2.2 Chemicals and regents

All samples were analyzed for 12 PFAAs, including 9 PFCAs with carbon lengths from C4 to C12 and 3 PFSAs (Table S1). All native and mass-labeled PFAAs standards were purchased from Wellington Laboratories with purities of >98% (Guelph, Canada). HPLC grade methyl tert-butyl ether (MTBE), methanol and acetonitrile (ACN) were purchased from J.T. Baker (Phillipsburg, USA). Tetrabutylammonium hydrogensulfate (TBAHS), sodium carbonate (Na_2CO_3), anhydrous sodium sulfate, and ammonium acetate were purchased from Sigma-Aldrich Co. (St. Louis, USA). Milli-Q water was obtained from a Milli-Q gradient A-10 (Millipore, Bedford, USA).

2.3 Sample extraction and instrumental analysis

The albumen of one egg was separated from the yolk and analyzed individually, while the other two eggs were homogenized. The albumen, yolks and pooled egg samples were all analyzed with the method below.

PFAAs were extracted using an ion pairing method described previously (Hansen et al. 2001) with some modifications. Approximately 1 g of the egg sample was spiked with 5 ng mass-labeled internal standard and mixed with 1mL of 0.5 M TBAHS and 2 mL of 0.25 M sodium carbonate buffer (pH 10). Subsequently, 5 mL of MTBE was added and shaken for 20 min. After centrifuging for 20 min at 3500 r/min, the supernatant MTBE was collected. The process of extraction was repeated twice. The supernatants were combined together, evaporated to near-dryness under a gentle flow of high-purity nitrogen, and then reconstituted in 1 mL of methanol.

Clean-up was performed by solid phase extraction (SPE) using ENVI-Carb cartridges and Oasis-WAX cartridges. Supelco ENVI-Carb cartridges (250mg, 3mL, 142 Sigma-Aldrich, St. Louis, USA) were preconditioned with 1 mL methanol for three times and then the sample extracts were loaded and collected. The samples were further eluted by passing 1 mL of methanol through three times. All the extracts were diluted in 100 mL of Milli-Q water and subjected to Oasis WAX cartridges for further

SPE cleanup. The Oasis WAX cartridges (6 cc, 150 mg, 30 μm, Waters, Milford, MA) were conditioned by passing through 4 mL of 0.1% ammonium hydroxide in methanol, followed by 4 mL of methanol and 4 mL of Milli-Q water successively. 100 mL of the samples were passed through the preconditioned cartridges. The cartridges were washed with 4 mL of 25 mM ammonium acetate (pH 4) and air-dried. The target analytes were then eluted with 4 mL of methanol, followed by 4 mL of 0.1% ammonium hydroxide in methanol. The final elution was concentrated to 1 mL under a gentle stream of high-purity nitrogen, filtered through a 0.2 μm nylon filter into a 1.5 mL auto-sampler vial fitted with polypropylene cap 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, no PTFE or other fluoropolymer materials were used during sample preparation. Procedural blanks and solvent blanks were ~~carried out~~included with each batch of 10 samples. Matrix spike recovery was performed with 5 ng native PFAAs standards added into the egg whites, egg yolks and pooled egg samples from the reference site, respectively. A 10-point standard calibration curve, from 0.01 ng/mL to 500 ng/mL, was prepared for the quantification of individual PFAAs. The correlation coefficients (r^2) were higher than 0.99 for all calibration curves. The Limit of Detection (LOD) and the Limit of Quantification (LOQ) were defined as the concentration that gave a signal to noise ratio of 3 and 10, respectively. Concentrations of all target PFAAs in any procedural and solvent blank were less than the LOD. Matrix spike recoveries of target compounds ranged from 68±1% to 134±7%. Detailed QA/QC measurements of PFAAs in egg samples are shown in Table S3.

3. Results and discussion

3.1 Occurrence of PFAAs in egg yolks

Concentrations of 12 PFAAs calculated on a wet weight (ww) basis detected in chicken egg yolks, egg whites and pooled egg samples are presented in Table 1 and Table 2. PFBS and PFHxS were not detected in any samples, ~~which~~ and ~~will~~so will not be discussed any ~~more in the following part~~further.

In yolks ~~of~~ from HPEs (site 1-4), detection frequency of C4 PFCA, C8-C12 PFCAs and PFOS ~~were~~ was 100%, and C5, C6 and C7 PFCAs were detected in 3, 2 and 1 out of 4 samples, respectively. The concentrations of ΣPFAAs (sum of 10 PFAAs except for PFBS and PFHxS) decreased with increasing distance from the FIP, being 482, 162, 63.7 and 8.99 ng/g for site 1, 2, 3 and 4, respectively. Concentrations of C9-C12 PFCAs and PFOS were similar for samples taken from these four sites. PFOA (5.11-368 ng/g) was the most abundant congener and contributed 69% of ΣPFAAs (Fig. 2). PFBA (1.75-110 ng/g) was the second most abundant congener in these samples with an average contribution of 22% of ΣPFAAs. PFOS (0.73-1.39 ng/g) contributed 3.6% of the total and the remaining seven PFCAs accounted for 5%. Both PFOA and PFBA concentrations declined with increasing distance from the FIP, which is consistent with ~~that in the~~ environmental media ~~like~~ such as surface water and dust in this area (Liu et al. 2016; Su et al. 2016). ~~To the contrary, u~~Unlike the environmental media, in which the concentrations and contributions to ΣPFAAs of PFPeA, PFHxA and PFHpA ~~are~~ were similar to PFBA (Liu et al. 2016; Su et al. 2016), the egg yolks contained much lower proportions of these three homologues than that of PFBA. This could be due to several reasons. Firstly, PFBA concentrations are higher than these three homologues in the ~~food~~ diet of the chickens, ~~like~~for example in maize from the farmland around the FIP (Krippner et al. 2014). Secondly, PFPeA,

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PFHxA and PFHpA are more prone to be excreted by chickens than PFBA (Insert Ref). Thirdly, precursors of short-chain (C<8) PFCAs are metabolized to PFBA in chicken rather than PFPeA, PFHxA and PFHpA (Insert Ref).

In yolks of CPEs (site 5-16), the detection frequency of PFBA, PFOA and PFOS was 100%, whereas other PFAAs were less frequently detected. PFHpA was not detected in any sample. ΣPFAAs concentrations ranged from 0.77 to 9.14 ng/g, which were similar with or much lower than that of HPE yolk sample from site 4, 20 km away from the FIP. Living environment and eating habits of the hens ~~might be the main reasons for~~may explain the difference between PFAAs levels in HPEs and CPEs (Brambilla et al. 2015; Zafeiraki et al. 2016). For example, laying hens in commercial farms usually eat processed or packaged food, while free foraging hens ~~always take~~consume soil~~s~~, earthworms, food ~~remains~~leftovers or weeds. In the yolks of CPEs, contributions of PFBA (27-62%, with a mean 39%), PFOA (6-51%, 38%) and PFOS (9-56%, 30%) to ΣPFAAs were comparable ~~to~~ with each other (Fig. 2). The contribution of the remaining PFCAs to ΣPFAAs was about 3%. PFOA concentrations ranged from 0.09 to 2.66 ng/g, which were lower than that of HPE yolk sample from site 4. The concentrations of PFBA (0.31-5.64 ng/g) were similar to that of the HPE yolk sample from site 4, while much lower than that of samples from sites 1-3. There was not much difference in PFOS concentrations between commercially produced and HPE yolks. For all yolks of CPEs, PFAAs levels were ~~irrelevant~~ unrelated to the distance of these samples from the FIP.

Compared with previous studies (Table S4), PFAAs levels in HPE from site 4 or in CPEs were similar with that in HPEs from Netherlands and Greece (Zafeiraki et al. 2016) or in CPEs from Sweden (Johansson et al. 2014; Gebbink et al. 2015), Norway (Haug et al. 2010) and China (Zhang et al. 2010). PFAAs in CPEs from several countries were ~~blow~~ below the LOQ, ~~like~~ such as from the U.S.A (Schecter et al. 2010), U.K (Clarke et al. 2010), and Italy (Guerranti et al. 2013). Different PFAAs congener patterns were found among regions. PFOS was the major component in eggs from European countries, while PFOA was found to be the most prevalent PFAAs in eggs from China.

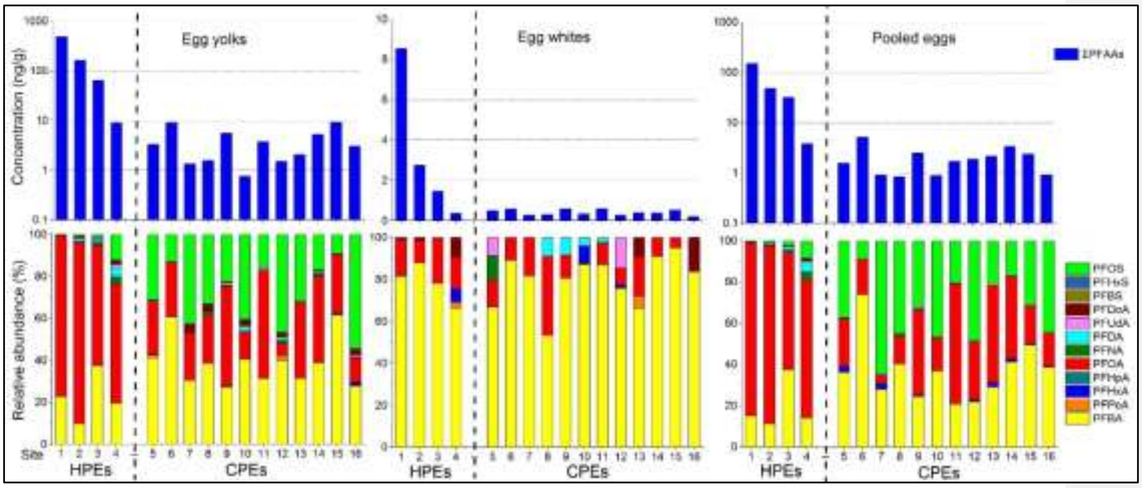

Fig. 2. PFAAs in egg yolks, egg whites and pooled eggs of home produced eggs (HPEs) and commercially produced eggs (CPEs) .

Table 1. PFAAs concentrations (ng/g) in home produced eggs (HPEs, n=4)

Site	Distance (km)	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA	PFBS	PFHxS	PFOS	ΣPFAAs
	Egg yolks													
1	2	110	0.57	0.20	0.29	368	0.87	0.73	0.13	0.20	< 0.02	< 0.02	1.39	482
2	5	16.0	0.11	< 0.02	< 0.03	140	0.97	1.83	1.26	0.78	< 0.02	< 0.02	1.37	162
3	10	23.8	0.17	0.08	< 0.03	36.4	0.94	0.93	0.50	0.22	< 0.02	< 0.02	0.73	63.7
4	20	1.75	< 0.05	< 0.02	< 0.03	5.11	0.30	0.39	0.15	0.17	< 0.02	< 0.02	1.11	8.99
	Egg whites													
1	2	6.97	< 0.05	0.02	< 0.03	1.46	0.01	< 0.02	< 0.04	0.08	< 0.02	< 0.02	< 0.02	8.54
2	5	1.15	< 0.05	< 0.02	< 0.03	0.32	< 0.01	< 0.02	< 0.04	< 0.02	< 0.02	< 0.02	< 0.02	1.47
3	10	2.43	< 0.05	< 0.02	< 0.03	0.29	< 0.01	< 0.02	< 0.04	0.05	< 0.02	< 0.02	< 0.02	2.76
4	20	0.24	< 0.05	0.02	< 0.03	0.05	< 0.01	< 0.02	< 0.04	0.03	< 0.02	< 0.02	< 0.02	0.35
	Pooled eggs													
1	2	22.5	0.22	0.04	< 0.03	125	0.19	0.26	0.08	0.10	< 0.02	< 0.02	0.86	149
2	5	5.40	< 0.05	< 0.02	< 0.03	41.5	0.15	0.40	0.13	< 0.02	< 0.02	< 0.02	0.45	48.1
3	10	12.0	0.07	< 0.02	< 0.03	18.0	0.33	0.48	0.12	0.12	< 0.02	< 0.02	0.71	31.9
4	20	0.54	< 0.05	< 0.02	< 0.03	2.54	0.14	0.17	< 0.04	0.05	< 0.02	< 0.02	0.32	3.75

Table 2. PFAAs concentrations (ng/g) in Commercially produced eggs (CPEs, n=12)

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA	PFBS	PFHxS	PFOS	ΣPFAAs
Egg yolks													

MIN	0.31	< 0.05	< 0.02	< 0.03	0.09	< 0.01	< 0.02	< 0.04	< 0.02	< 0.02	< 0.02	0.31	0.77
MAX	5.64	0.05	0.07	< 0.03	2.66	0.08	0.04	0.07	0.09	< 0.02	< 0.02	1.68	9.14
Mean*	1.72	0.05	0.04	< 0.03	1.20	0.03	0.03	0.06	0.04	< 0.02	< 0.02	0.85	3.85
Median	1.02	< 0.05	< 0.02	< 0.03	0.78	< 0.01	< 0.02	< 0.04	0.04	< 0.02	< 0.02	0.78	3.15
n>LOD (%)	12 (100)	1 (8)	3 (25)	0 (0)	12 (100)	5 (42)	4 (33)	2 (17)	9 (75)	0 (0)	0 (0)	12 (100)	
Egg whites													
MIN	0.16	< 0.05	< 0.02	< 0.03	< 0.01	< 0.01	< 0.02	< 0.04	< 0.02	< 0.02	< 0.02	< 0.02	0.19
MAX	0.52	< 0.05	0.03	< 0.03	0.12	0.06	0.05	0.04	0.04	< 0.02	< 0.02	< 0.02	0.59
Mean*	0.33	< 0.05	0.03	< 0.03	0.06	0.06	0.04	0.04	0.03	< 0.02	< 0.02	< 0.02	0.41
Median	0.31	< 0.05	< 0.02	< 0.03	0.06	< 0.01	< 0.02	< 0.04	< 0.02	< 0.02	< 0.02	< 0.02	0.37
n>LOD (%)	12 (100)	0 (0)	1 (8)	0 (0)	10 (83)	1 (8)	2 (17)	2 (17)	2 (17)	0 (0)	0 (0)	0 (0)	
Pooled eggs													
MIN	0.25	< 0.05	< 0.02	< 0.03	0.04	< 0.01	< 0.02	< 0.04	< 0.02	< 0.02	< 0.02	0.35	0.83
MAX	3.82	< 0.05	0.05	< 0.03	1.34	0.02	< 0.02	< 0.04	< 0.02	< 0.02	< 0.02	0.91	5.16
Mean*	0.85	< 0.05	0.03	< 0.03	0.59	0.02	< 0.02	< 0.04	< 0.02	< 0.02	< 0.02	0.55	2.01
Median	0.49	< 0.05	0.04	< 0.03	0.49	< 0.01	< 0.02	< 0.04	< 0.02	< 0.02	< 0.02	0.51	1.78
n>LOD (%)	12 (100)	0 (0)	6 (50)	0 (0)	12 (100)	1 (8)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	12 (100)	

*: Mean value is calculated based only on the concentrations above LOQ.

3.2 Occurrence of PFAAs in egg whites, pooled eggs and distribution pattern of PFAAs in eggs

In all 16 egg whites, PFBA and PFOA were detected in 16 and 14 samples, respectively. The remaining PFCAs and PFOS were detected at low frequency or not detected. Unlike PFAAs congener pattern in egg yolks, PFBA was the predominant form in egg whites, contributing 77% of ΣPFAAs, followed by PFOA (17%) (Fig. 2). Concentrations of PFBA (0.24-6.97 ng/g) and PFOA (0.05-1.46 ng/g) in whites of HPEs declined with increasing distance from the FIP. PFBA and PFOA concentrations in whites of CPEs, in the range of 0.16 to 0.52 ng/g and $<$0.01 to 0.12 ng/g, resemble those in home produced samples from site 4, the most distant location.

Distribution patterns of the three mostly detected PFAAs in egg yolk and egg white parts was examined (Fig. 3). In agreement with previous studies (Wang et al. 2008; Zafeiraki et al. 2016), approximately 100% of PFOS and more than 90% of PFOA were found in the egg yolks ~~here~~. PFBA was firstly examined in eggs, and showed a little difference from the other PFAAs. The proportion of PFBA in egg whites ranged from 6% to 48%, with an average of 20%. This distribution pattern might be attributed to the different affinity between individual PFAA and the proteins in egg yolk and egg white parts.

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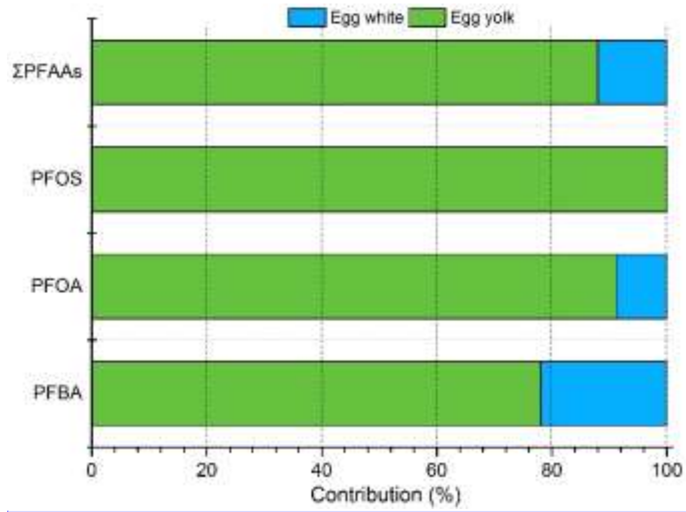

Fig. 3. Distribution pattern of PFBA, PFOA, PFOS and ΣPFAAs in egg yolk and egg white parts.

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In all pooled egg samples, PFAAs concentrations were 2-8 times lower than that in corresponding egg yolk samples, while the congener patterns were similar (Fig. 2). Egg samples were prepared in different ways for analysis of PFAAs in previous studies. Some mixed the whole eggs (Clarke et al. 2010; Zhang et al. 2010; D'Hollander et al. 2011), whilst others homogenized the yolks only because the PFAAs they analyzed predominantly partition into the yolks (Johansson et al. 2014; Zafeiraki et al. 2016). Results of this study and a former study (Wang et al. 2008) showed that PFAAs concentrations in mixed whole eggs were diluted in comparison to that in egg yolks. Analysis of PFAAs in yolks ~~solely~~ would underestimate the health risk on account of the relatively higher proportion of PFBA in egg white. As a result, only analysis of yolks was recommended when studying the PFSAs in eggs, while yolks and albumen should be analyzed separately when examining the PFCAs.

3.3 Human exposure to PFAAs via egg consumption

The uptake of PFAAs from HPEs was identified as an important exposure pathway ~~of exposure~~ for the residents near a manufacturing facility (Wang et al. 2010;

D'Hollander et al. 2011). According to Shandong Statistic Year Book, the average egg consumption in the studied area was 37.5 g/day/person (SDSB 2015). Applying an average body weight (bw) of 59.4 kg for adults and 21.1 kg for children (Zhang et al. 2010), daily intakes of several main PFAAs and ΣPFAAs via HPEs and CPEs consumption were estimated. Estimated Daily Intake (EDI) of PFAAs were calculated by EDI (ng/kg.bw/day) = egg consumption (g/day) × PFAAs' concentration (ng/g) / body weight (kg). PFAAs' concentration referred to the sum of PFAAs in egg yolks and that in egg whites. As for EDI calculation of CPEs, arithmetic mean concentrations of PFAAs were used.

The provisional tolerable daily intake (TDI) value proposed by the German Drinking Water Commission (TWK) is 100 ng/kg.bw/day for both PFOS and PFOA for the whole population, including infants and pregnant women (TWK 2006). The EDIs of PFOS through all HPEs (0.46-3.01 ng/kg.bw/day) and CPEs (0.54-1.52 ng/kg.bw/day) were comparable, accounting for only 0.46-3.01% of the provisional TDI. It is alarming that the EDI of PFOA via HPEs from site 1 was 233 and 657 ng/kg.bw/day for adults and children, which exceeded more than 2 times the provisional TDI for adults and more than 6 times for children. Due to low concentrations of PFAAs found in eggs, reports on EDI via eggs are scarce. The highest EDI of PFOA in the present study were at least 2 orders of magnitude higher than the average values estimated in HPEs ~~the~~ from Netherlands and Greece ~~HPEs~~ (0.34-2.7 ng/kg.bw/day) (Zafeiraki et al. 2016) and CPEs from Sweden (0.012 ng/kg.bw/day) (Gebbink et al. 2015). A recent study reported total dietary intake of PFOA was 11.95 ng/kg.bw/day for general population in China (Shan et al. 2016), being 20 times lower than the EDI via HPEs from site 1. Elevated PFAAs' EDI values via consumption of HPEs were also found in nearby communities of a fluorochemical

Comment [AS8]: Need to explain why you selected this organization

Comment [AS9]: Need to be careful as this represents only 1 sample plant in Wuhan, China (Wang et al. 2010) and in Zwijndrecht, Belgium (D'Hollander et al. 2011). The EDIs of PFOA in their study were not determined due to low concentrations of PFOA in eggs. However, the EDIs of PFOS were 1.0-1.6 times of the reference dose (25 ng/kg.bw/day) and up to 496 ng/kg.bw/day in the location of China and Belgium, respectively. These values were much higher than that in the present study. This difference could most likely be attributed to different production pattern among the plants.

The EDI of PFBA via egg consumption ranged from 1.26 to 73.6 ng/kg.bw/day for adults and 3.54 to 207 ng/kg.bw/day for children, respectively. There are few Sstudies on human exposure and toxicology effect of PFBA were very few, which might be due to shorter serum elimination half-lives of PFBA, -(3- to 4 days) in human (Chang et al. 2008). However, a recent study on PFAAs in autopsy tissues from the general population in Catalonia, Spain revealed high levels of short-chain PFAAs, especially PFBA (median values: 807 and 263 ng/g in lung and kidney, respectively) (Pérez et al. 2013). This implies that PFBA may accumulate in these human tissues other rather than be excreted from the body. As an important short-chain alternative, PFBA was has been detected across the world widelyglobe in the environmental samples (Wang et al. 2015; Lorenzo et al. 2016). Thus, human exposure pathways of PFBA is worthy of attention and health effects of PFBA exposure to local residents around the FIP via egg consumptions need urgent further investigation.

Table 3. Estimated Daily Intake (EDI) (ng/kg.bw/day) of PFAA via home produced eggs (HPEs) and commercially produced eggs (CPEs) consumption

	Site	Distance (km)	PFBA	PFOA	PFOS	ΣPFAAs
			HPEs (n=4)			
Adults	1	2	**73.6**	**233**	1.07	**310**
	2	5	10.8	**88.4**	0.86	**103**

	3	10	16.5	23.1	0.46	41.9
	4	20	1.26	3.26	0.70	5.92
Child	1	2	**207**	**657**	3.01	**873**
	2	5	30.4	**249**	2.43	**291**
	3	10	46.5	**65.1**	1.30	**118**
	4	20	3.54	9.19	1.97	16.7
			CPEs (n=12)			
Adults	mean		1.30	0.79	0.54	2.69
Child	mean		3.66	2.23	1.52	7.58

4. Conclusions

The present study investigated PFAAs in home and commercially produced eggs surrounding a mega fluorochemical industrial park in China. Egg yolks, egg whites and pooled eggs were analyzed separately. PFAAs were much more contaminated in HPEs than in CPEs, with the levels of PFAAs in CPEs comparable to or lower than that in HPE from site 4, 20 km away from the FIP. About 100% of the C4-C12 PFCAs and PFOS were detected in HPEs, while only PFBA, PFOA and PFOS were detected 100% in CPEs. Concentrations of PFOA (5.11-368 ng/g) and PFBA (1.75-110 ng/g) in HPEs decreased with increasing distance from the FIP. Concentrations of PFOA in HPEs except from site 4 were higher than those reported in previous studies across the world. To the best of our knowledge, the is the first study that measured PFBA was firstly examined in eggs and showed high concentrations and high detection frequency in our study. Comparison of PFAAs patterns between eggs and environmental matricesx implied that bioaccumulation potential of PFBA, PFOA and PFOS were higher than other PFAAs in chicken eggs. Most of PFAAs distributed in egg yolks, while an average of 20% of PFBA found in egg white need requires particular attention. Health risks of PFAAs via consumption of HPEs are of great concern for the local residents near the FIP. The EDIs of PFOA via HPE from site 1 were up to 233 and 657 ng/kg.bw/day for adults and children, which exceeded the provisional TDI (100 ng/kg.bw/day) proposed by the German Drinking Water Commission. Accordingly, CPEs are more recommended to consume for residents around the FIP.

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