

# Distribution Characteristics of Per- and Polyfluoroalkyl Substances (PFASs) in Human Urines of Acrylic Fiber Plant and Chemical Plant

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## Research Article

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# Abstract

Per- and polyfluoroalkyl substances (PFASs) are persistent and bio-accumulative substances that have many adverse effects on human bodies. This study investigated the PFASs distribution characteristics in urine samples of workers from an acrylic fiber plant and a chemical plant. It was found that perfluorobutanoic acid (PFBA) was the predominant PFASs both in urine samples from the chemical plant (detection frequency: 86.52%; median value: 39.01 ng/mL) and the acrylic fiber plant (detection frequency: 88.16%; median value: 44.36 ng/mL). Meanwhile, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) were detected with very low frequencies and low concentrations. Furthermore, the results showed that PFASs levels in urine samples of workers from different units of the plants were quite different. PFASs concentrations of urine samples in males were higher than those in females, especially for PFBA, PFHxA, and PFDoA. The age had limited effects on the PFASs distribution in urine samples in this study, as short-chain PFASs were the dominant compounds. The correlations between PFASs concentrations in urine and gender/ages of workers were finally analyzed by Person correlation. The overall results may indicate that short-chain PFASs (such as: PFBA and PFBS) were becoming dominant for human exposure, especially occupational workers.

## Introduction

Per- and polyfluoroalkyl substances (PFASs) are extensively used in a variety of consumer products and industrial applications owing to its unique properties, such as fire-fighting foams, non-stick coating materials, oil production, and fabrics (Boronow et al., 2019; Wu et al., 2019). Thus, they have been widely found in environmental samples and even in human tissues and organs (such as: serum, urine, hair, nails, lung, and liver) (Beesoon et al., 2012; Wang et al., 2018). Unfortunately, PFASs have multiple organ toxicities, such as reproductive toxicity, mutagenic toxicity, developmental toxicity, neurotoxicity, immunotoxicity (Lau et al., 2003; Mariussen, 2012; Morello-Frosch et al., 2016; Zhou et al., 2016). For example, it was reported that PFOA concentration in human serum has a negative relationship with birth weight (Apelberg et al., 2007), and even was associated with total cholesterol (CHOL), serum aspartate transaminase (AST), and thyroid-stimulating hormone (TSH) (Olsen and Zobel, 2007; Seo et al., 2018). Thus, regulators and manufacturers have taken a series of measures to phase out some long-carbon chain PFASs (e.g., PFOS and PFOA), which led to large productions of their substitutes. For example, major manufacturers choose shorter-chain (< C8) compounds, such as perfluorobutane sulfonic acid (PFBS) and PFBA to replace longer-chain PFASs (Wang et al., 2017).

For the general population, dietary intake is the most important route for chemical exposure (Zhang et al., 2010a), especially from seafood and fish. Several studies have found that a large amount of PFASs resides in drinking water (Wilhelm et al., 2010). In addition to dietary intake, respiratory intake and skin contact of pollutants are more severe to the occupational population. It was reported that PFASs could bind with serum protein *in vivo*, and then deposit in the liver, kidney, testis, and other organs after entering the human body. There are a lot of researches had been done on the distribution of PFASs in human samples, such as hair, nails, urine, blood, and feces (Beesoon et al., 2012; Li et al., 2013; Wang et al., 2018).

However, the levels of PFASs in hair, nails, and feces were far less than those in blood and urine (Beesoon et al., 2012; Li et al., 2013). Therefore, serum and urine samples are usually used to evaluate PFASs exposure levels to humans. A significant positive correlation of PFASs levels between serum and urine has been reported (Fu et al., 2016). Furthermore, urine was recommended to be the preferred and non-evaded matrix for short-chain PFASs biomonitoring than serum (Kato et al., 2018). It was reported that PFASs levels in occupational workers and general workers were quite different (Olsen et al., 2003; Zhang et al., 2015). For the non-occupational adults, the geometric mean concentration of PFOS and PFOA were determined to be 0.011 and 0.008 ng/mL (Zhang et al., 2015). However, PFOS and PFOA concentrations in occupational adults from the fluoride production plant could be as high as 92.03 µg/mL (Olsen et al., 2003). Wu et al. (Wu et al., 2019) gathered 58 indoor dust samples and 73 urine samples from saleswomen working in clothing shops, and a remarkable positive correlation between long-chain PFASs in dust and urine ( $p < 0.01$ ) was observed. Therefore, we should pay close attention to the exposure and health of the workers who are often exposed to PFASs.

For fluorinated workers, although skin contact and accidental ingestion may contribute in part, the concentration of perfluorooctanoic acid ( $1\text{ }\mu\text{g}/\text{m}^3$ ) in the ambient air near the fluoropolymer production facility indicates that inhalation is the main exposure route (Barton et al., 2006; Olsen et al., 2003). Since workers spend most of their time indoors, the indoor air environment is a major source for PFASs exposure. Early studies have suggested that the concentration of PFASs in the air outside is one to two orders of magnitude lower than that in the air inside (Shoeib et al., 2005). Furthermore, there is a significant positive correlation of PFASs levels between indoor dust and human serum, urine, nails, and hair. Thus, some occupational workers (such as: acrylic fiber plant workers and chemical plant workers), who may exposure to PFASs-containing dust from fabrics, textile, or oil productions should be investigated (Harrad et al., 2010; Wu et al., 2019).

In this study, PFASs levels in the human urine of 307 workers from acrylic fiber plants and chemical plants were analyzed. Meanwhile, the distribution characteristics of PFASs in urine samples and the potential effect of gender, age, workplace were studied to gain a clear understanding of PFASs exposure to occupational workers from different industries.

## Materials And Methods

### Study chemicals and reagents

One mixture of internal standards (MPFAC-MAX), including MPFBA ( $^{13}\text{C}_4$ ), MPFHxA ( $^{13}\text{C}_2$ ), MPFOA ( $^{13}\text{C}_4$ ), MPFNA ( $^{13}\text{C}_5$ ), MPFDA ( $^{13}\text{C}_2$ ), MPFUdA ( $^{13}\text{C}_2$ ), MPFDoA ( $^{13}\text{C}_2$ ), MPFHxS ( $^{18}\text{O}_2$ ), MPFOS ( $^{13}\text{C}_4$ ), M2-6:2PAP ( $^{13}\text{C}_2$ ), M4-6:2diPAP ( $^{13}\text{C}_4$ ) and M8FOSA ( $^{13}\text{C}_8$ ), were purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada) with chemical purities of  $\geq 98\%$ . M8PFOS ( $^{13}\text{C}_8$ ), M8PFOA ( $^{13}\text{C}_8$ ), M2-8:2PAP ( $^{13}\text{C}_2$ ), and M4-8:2diPAP ( $^{13}\text{C}_4$ ) were used as recovery indicators and also supplied by Wellington Laboratories. High-performance liquid chromatography grade (HPLC) methanol (99.9%), acetone (99.6%), and acetonitrile (99.9%) were obtained from the Fisher Scientific (Geel, Belgium). Formic acid, ammonium hydroxide, and

acetate acid were also purchased from the Fisher Scientific (Geel, Belgium). The ultra-pure water used throughout the study was made by the Milli-Q purification system (Millipore, Germany).

### Sample collection and preparation

Morning urine samples were collected from 140 workers in the Chemical plant and 167 workers in the Acrylic fiber plant of the Daqing petrochemical Corp. in Heilongjiang Province, China. The acrylic fiber plant and chemical plant mainly use organic raw materials such as crude oil, light hydrocarbon, and natural gas to produce liquid chemical products and chemical fibers. The ages of workers were ranged from 27 to 58 with 77% male and 23% female, and some have even worked for more than 30 years. The summary of the demographic characteristics for workers is listed in Table S1. The sampling time was from May 8th to 25th, 2019. All samples were stored in a freezer at  $-20^{\circ}\text{C}$  until analysis. Participants in this study were informed on the purpose of the experiment and signed a consent form.

10 mL urine was taken from each sample into a 50 mL polypropylene tube (PP tube), and 15 mL of 0.1% formic acid and 5 ng internal standard or alternative standard (MPFAC-MAX) were added into each tube. The mixture was vortexed for 1–2 minutes and sonicated for 30 minutes under  $60^{\circ}\text{C}$ . Each sample was slowly pass through an Oasis HLB (60 mg, 6 mL) SPE (Solid Phase Extraction) cartridge. The SPE cartridge had been preconditioned with 4 mL of 0.1% ammonium hydroxide (in methanol), 4 mL of methanol, and 4 mL Millipore water at a rate of one drop/s. Cartridges were washed with 4 mL buffer solution (25 mM acetic acid/ammonium acetate, pH 4) and then air-dried with a vacuum (centrifuged for 10 min at 3,000 rpm) to remove the residual water. Target compounds were eluted with 4 mL of methanol and 4 mL of 0.1% ammonium hydroxide (in methanol). The resulting eluate was concentrated to 1 mL under nitrogen for injection. Finally, the liquid is transferred to an LC-MS vial for storage and ready for PFASs detection.

The approvals for human urine analysis were obtained from the Jinan University Review Board, Jinan University, China (2018-LSPK).

### Instrumental analysis

The determination of PFASs in all samples was carried out by an AB-Sciex 5500 triple quadrupole mass spectrometer (ESI-MS-MS; Applied Biosystems, Foster City, CA) coupled with a Shimadzu Nexera-XZ LC system (Shimadzu Corporation Inc. Kyoto). The electrospray negative ionization multiple-reaction monitoring (MRM) mode was adopted for the system. The samples were injected into a  $50 \cdot 21$  mm Waters BEH C18 column ( $1.7 \mu\text{m}$ ) with Milli-Q water (A) and gradient mobile phase of 2mM ammonium acetate in methanol (B) used for the LC system at a flow rate of 0.3 mL/min. The dual mobile-phase gradient started with 25% and held for 1.5min; gradually increased to 50 % B at 4 min, 75% B at 8 min, 100% B at 10 min and remained constant until 13 min; lastly returned to the original conditions at 14 min and then equilibrated for 4.1 min. The total run time of each sample was 18.1 min. Table S2 presents the details of optimized instrumental parameters.

### Quality control and quality assurance

All accessible polytetrafluoroethylene (PTFE) was removed from the experimental instrument and related equipment to reduce background contamination. Instruments used in the sample pretreatment (such as: syringes, filters, and the LC system) have been thoroughly washed with methanol before use. Three replicated samples were spiked with recovery standards before extraction and with isotope-labeled internal standards before LC/MS/MS analysis. Besides, a procedural blank was carried out after the determination of 10 samples to monitor the potential pollution of laboratory materials, instruments, and even the whole procedural. Solvent blank and matrix blank were also performed to evaluate the possible carryovers of target chemicals and monitor the potential contaminant of PFASs. The results indicate that no pollution higher than LOD was found in the container and blank tests. The detection limit (LOD) and quantification limit (LOQ) of the target PFASs are defined as 3:1 and 10:1 signal-to-noise ratio, respectively. The LOD and data related to calibration curves were all outlined in Table S3.

## Statistical analysis

Statistical analysis of the data was conducted by using the Social Science (SPSS) version 26.0 (SPSS Inc., Chicago, Illinois, USA). ANOVA and LSD tests were used to analyze PFASs concentrations in different variables (such as: age and gender groups), and the Pearson correlation test was used to investigate the statistically significant correlations between them with a significance level of  $p = 0.05$ . The sample level lower than LOD was set as  $LOD/\sqrt{2}$ , and the value higher than LOD and below the LOQ were set as LOQ for statistical analysis.

## Results And Discussion

### PFASs levels in urine samples

PFASs concentrations in urine samples from the acrylic fiber plant and chemical plant workers were outlined in Table 1. The major PFASs detected in urine samples were PFBA, perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoate (PFTeDA), perfluorohexanesulfonate (PFHxS) and PFBS (Fig. 1). PFBA was the predominant compound in urine samples of workers from the acrylic fiber plant (median = 44.36 ng/mL, detection frequency = 88.16%) and chemical plant (median = 39.01 ng/mL, detection frequency = 86.52%). Although the detection frequency of PFBS was high, its detection values (0.70 and 0.54 ng/mL, respectively) were far lower than that of PFBA (Table 1). As shown in Fig. 1, the concentration of perfluoroalkyl carboxylates (PFCAs) in the urine samples was significantly higher than that of perfluoroalkyl sulfonates (PFASs). It was found that the renal clearance efficiencies of some PFASs were much lower than those of PFCAs, and one PFCA was excreted more efficiently than one PFSA with the same carbon chain length. Similarly, it was reported that the concentrations of PFCAs (i.e., PFBA, PFHxA) in the urine samples from Spanish residents were obviously higher than PFASs (i.e., PFBS, PFHxS) (Perez et al., 2012).

Table 1

The PFASs concentrations profile in urine of workers from the Chemical plant (n = 140) and the Acrylic fiber plant (n = 167)

	PFASs in the Chemical plant					PFASs in the Acrylic fiber plant				
	Mean	SD	Median	Max	%DF	Mean	SD	Median	Max	%DF
PFBA	50.47	50.73	39.01	309.24	87	64.77	73.56	44.36	449.90	88
PFPeA	3.23	8.23	0.86	66.58	72	11.06	41.84	1.17	290.88	76
PFHxA	0.30	0.21	0.25	1.32	84	0.34	0.29	0.27	1.60	80
PFHpA	BDL	BDL	BDL	BDL	0	ND	ND	ND	0.10	0
PFOA	BDL	BDL	BDL	BDL	0	ND	ND	ND	0.05	0
PFNA	BDL	BDL	BDL	BDL	0	BDL	BDL	BDL	0.75	1
PFDA	BDL	BDL	BDL	0.79	1	BDL	BDL	BDL	0.43	0
PFUdA	BDL	BDL	BDL	0.43	6	BDL	BDL	BDL	0.13	1
PFDoA	0.22	1.00	0.03	11.69	56	0.13	0.21	0.02	1.09	50
PFTrDA	0.56	3.18	0.02	37.07	52	0.27	0.51	0.09	4.20	60
PFTeDA	1.23	2.41	0.07	14.44	51	0.61	1.22	ND	8.49	43
PFODA	BDL	BDL	BDL	0.13	4	ND	ND	ND	0.07	1
PFBS	1.30	2.05	0.70	15.70	91	1.04	1.33	0.54	8.75	86
PFHxS	6.67	14.21	2.14	93.60	85	8.78	29.20	1.92	297.40	86
PFHpS	BDL	BDL	BDL	BDL	0	BDL	BDL	BDL	BDL	0
PFOS	BDL	BDL	BDL	0.12	2	BDL	BDL	BDL	BDL	11
PFDS	BDL	BDL	BDL	BDL	0	BDL	BDL	BDL	0.09	1

SD means standard deviation; %DF means detection frequency (%); BDL means below detection limit; ND means not detected, below the LOD.

However, long-chain PFASs were infrequently detected compare to the shorter ones in this study, and some PFASs were even lower than the detection limit (i.e., PFOA, perfluorononanoic acid (PFNA), and perfluorodecanoic acid (PFDA)). The detection frequencies of PFOS in urine samples of two factories were also quite low. The mean PFOS concentration (0.032 ng/mL) in the urine of workers in this study was similar to that of general adults in Tianjin City (0.023 ng/mL) and Shanxi Province (0.050 ng/mL)(Li et al., 2013; Zhang et al., 2015). Since manufacturers have gradually replaced the long-chain PFASs with short-chain PFASs in recent years(Yao et al., 2018), the workers had great exposure risks to short-chain PFASs from fabrics, textiles, or oil productions in the factories via inhalation or skin contact instead of longer

chain PFASs (such as: PFOS and PFOA). The findings are similar to those of urine samples from professional women like textile saleswomen, whose PFBS level was the highest among PFASs with a detection frequency of over 93%(Wu et al., 2019). Similarly, PFBA was the dominant PFASs in the urine samples collected from Spain, and the PFBA concentrations (ranged from 52.72 to 1495.68 ng/mL) were even significantly higher than those in this study(Perez et al., 2012). It was proposed that urine excretion was the main way to eliminate short-chain PFASs(Zhang et al., 2013), and fecal excretion may be conducive to the elimination of longer-chain PFASs (e.g., PFHxS and PFTTrDA)(Beesoon et al., 2012). Long-chain PFASs may be biodegraded to be PFBA and led to an increase of PFBA levels in urine(Lindstrom et al., 2011; Perez et al., 2012). Besides, the half-lives of short-chain PFASs in the human body are far less than those of longer ones. And a substance with a longer half-life usually indicates that it is more likely to accumulate in the organism and take a longer time to be removed from the body. It was estimated that the elimination half-lives of PFOS and PFOA in human bodies were 5.4 and 3.8, respectively(Zhang et al., 2013). In the contrast, short-chain PFCAs have higher aqueous solubilities, which are more water-soluble and easier to excrete(Bhhatarai and Gramatica, 2011; Inoue et al., 2012). It is found that the excretion of PFCAs with long-chains were more difficult than shorter ones due to the higher bonding affinities of longer chain PFASs towards organic anion transport proteins(Perez et al., 2012; Zhang et al., 2013).

Figure 1. showed that the  $\sum$ PFASs concentration in the urine of workers in the acrylic fiber plant (87 ng/mL) is higher than that in the chemical plant (63.98 ng/mL). Such results may indicate that the acrylic fiber workers may exposure more PFASs than the chemical workers. The acrylic fiber production process requires two main steps: raw material preparation and production. PFASs are widely used as additives in fiber processing to protect textiles from water, stains, and oil penetration(Heydebreck et al., 2016). Thus, the workers from the acrylic fiber plant may contact the PFASs-containing materials directly. In addition to direct contact, respiration is also an important exposure route to short-chain PFASs (e.g., PFBS and PFBA) easily evaporated into the indoor air(Zhang et al., 2020). Furthermore, the use of different types of PFASs raw materials may lead to different PFASs distribution characteristics in the urine of workers in different plants. Fu et al.(Fu et al., 2016) and Gao et al.(Gao et al., 2015) found that PFHxS, PFOS, and PFOA were the main PFASs species in urine samples of occupational workers in a fluorochemical manufacturing plant. However, the major exposure of raw materials was short-chain PFASs such as PFBA and PFBS in our study, which accounted for more than 75% of  $\sum$ PFASs concentration.

#### Gender, working-age and workshop effect in urine

There are six main units in the acrylic fiber plant named Spinning Workshop (SW, N = 85), Polymerization Workshop (POW, N = 26), Pilot Workshop (PIW, N = 11), Recycling Workshop (RCW, N = 18), Repair Workshop (RPW, N = 10) and Instrument Workshop (IW, N = 12). Figure 2 showed that PFASs levels in urine samples collected from different workshops were quite different. The PFBA concentration in urine samples collected from the IW was much higher than those in other workshops and the PFPeA level in urine samples of PIW workers was higher than those in workers of RCW, POW, RPW, IW, and SW. Such results may indicate that short-chain PFASs-based products (especially PFBA and PFPeA) were used as raw materials in this plant. Some long-chain PFASs with carbon atom over 10 (such as: PFDoA, PFTTrDA,

PFTeDA) has an extremely low content in all samples. The total PFASs concentration of IW workers was the highest among all workshop workers, which may be due to the stronger release of PFASs during the treatment of PFASs-containing raw materials by instruments in IW.

Gender and age are important factors influencing the distribution of PFASs in samples of human bodies(Wang et al., 2018; Zhang et al., 2015). The median concentration of PFASs in urine samples of 167 workers in the acrylic fiber plant and 140 workers in the chemical plant stratified by gender and working-age are given in Table 2. In general, PFASs concentrations of urine samples in males were higher than those in females, especially for PFBA, PFHxA, and PFDoA. Such a result is consistent with the previous study of Li et al.(Li et al., 2013), which indicated that the PFASs concentration of urine in men was higher than that in women. In the acrylic fiber plant, the concentrations of PFPeA and PFHxS in males were two times higher than those in females, but their concentrations in females were slightly higher than those in males in the chemical plant. The different PFASs levels between sexes may be due to the specific excretion pathways of females (such as: latex and menstruation). Moreover, it was reported that half-lives of PFASs in females are shorter than males(Zhang et al., 2013).

Table 2

Median concentrations of PFASs in workers from the Acrylic fiber plant and Chemical plant for gender and age groups.

		PFBA	PFPeA	PFHxA	PFDoA	PFTTrDA	PFTeDA	PFBS	PFHxS
Acrylic fiber plant	male	48.37	1.19	0.28	0.03	0.09	0.00	0.45	2.39
	female	31.01	0.42	0.26	0.00	0.12	0.00	0.90	0.92
	≤ 10 <sup>a</sup>	39.25	1.41	0.39	0.02	0.00	0.00	0.79	4.42
	11–20	29.20	0.60	0.29	0.08	0.26	0.63	0.93	2.81
	21–30	50.43	0.99	0.28	0.01	0.08	0.00	0.61	1.91
	≥ 31	41.75	1.23	0.18	0.02	0.14	0.00	0.34	1.74
Chemical plant	male	39.07	0.85	0.26	0.04	0.04	0.10	0.63	2.11
	female	38.36	0.92	0.20	0.02	0.00	0.07	1.20	2.54
	≤ 40 <sup>b</sup>	54.08	0.93	0.28	0.01	0.01	0.30	0.79	2.21
	41–50	38.36	0.95	0.22	0.06	0.05	0.07	0.66	2.75
	≥ 51	37.06	0.58	0.31	0.03	0.01	0.00	0.69	1.88
<sup>a</sup> This figure represents the total working age of the workers									
<sup>b</sup> This number represents the age of the workers									

Previous studies showed that correlations between age and PFASs concentration were different within different studies (Haug et al., 2009; Zhang et al., 2010a; Guo et al., 2011). In the current study, it can be observed that PFASs concentrations slightly decreased with the increase of age, especially for the short-chain PFASs. For instance, the PFHxS level in urine samples of workers (4.42 ng/mL) with working-age less than 10 years was two times higher than that of workers (1.74 ng/mL) over 30 years. Zhou et al. (Zhou et al., 2014) reported that longer chain PFASs (such as: PFOS and PFDA) levels increased with the increase of age, but shorter chain PFASs had no such trend. Such a result may be attributed to different elimination rates of PFASs with different chain lengths. As end-products of long-chain PFASs, half-lives of short-chain PFASs are shorter than long-chain and more soluble in urine, thus, the PFASs concentration in urine is just a reflection of recent exposure and associated with the metabolism state of workers during the exposure time (Kim et al., 2014; Jian et al., 2018).

### Correlation analysis

The correlations between PFASs concentrations in urine and gender/ages of workers were further analyzed by Person correlation. The PFASs levels between female and male groups don't exist significant statistical differences both in the acrylic fiber plant and chemical plant. Significant differences in PFASs concentrations of serums between male and female groups ( $p < 0.01$ ) were usually reported (Guo et al., 2011; Olsen et al., 2012), but such differences in urine cannot be observed (Zhang et al., 2015). It was found that there was a correlation between working-age and some PFASs in urine samples in the acrylic fiber plant. PFHxA ( $p = 0.01$ ), PFBS ( $p = 0.04$ ) and PFHxS ( $p = 0.01$ ) were inversely correlated with working-age. As short-chains PFASs are easily excreted from the urine, the detection of PFASs may be recent exposure concentrations, and the slow metabolism in the elderly may lead to their lower PFASs concentrations. And no statistical difference was observed between PFASs concentrations in urines and ages of workers in the chemical plant. PFASs concentration in the human body is not only related to the accumulation of age but also the differences in metabolic rate, lifestyle, and eating habits between young and old people. A similar result has been reported that the PFASs concentrations increased with working-age in saleswomen under 40 years old in urine (Wu et al., 2019). We also examined the PFASs concentration in the chemical plant workers of different ages, but no significant correlation was observed. Hence, the PFASs concentration had some association with age, but the correlation is limited.

Additionally, the significant correlations ( $p < 0.01$ ) among PFBS, PFHxS, PFHxA, PFTTrDA, PFTTeDA, and PFDoA were further analyzed (Table 3); The results showed that PFTTeDA, PFTTrDA, PFDoA in urine samples of workers from the chemical plant were significantly correlated (Table 4), with the Pearson correlation coefficient ranged from 0.30 to 0.99 ( $p < 0.01$ ). These associations suggested that these PFASs probably had a common exposure source. For PFDoA and PFTTrDA, the correlation between them was strongly significant ( $r = 0.99$ ,  $p < 0.01$ ), indicating that the PFDoA level could be used to predict PFTTrDA concentrations in the urine of workers from the Acrylic fiber plant workers. Similar relationships between PFTTrDA and PFDoA were also reported by Wu et al. (Wu et al., 2019), who found that PFDoA was significantly correlated with PFTTrDA in saleswomen's urine. This correlated phenomenon might be

explained by the degradation of fluorotelomer alcohols (FTOHs) in humans, and it indicated that humans may have common exposure pathways to these long-chain PFCAs(Zhang et al., 2010b).

**Table 3** Pearson correlation matrix among PFASs in urine samples of the Acrylic fiber plant

	PFBA	PFPeA	PFHxA	PFDoA	PFTTrDA	PFTeDA	PFBS	PFHxS
PFBA	1	0.04	-0.04	0.09	0.05	0.13	0.03	-0.08
PFPeA		1	0.08	-0.12	-0.07	-0.12	-0.07	0.03
PFHxA			1	0.00	-0.02	-0.12	0.40**	0.33**
PFDoA				1	0.65**	0.52**	-0.09	-0.02
PFTTrDA					1	0.48**	-0.09	-0.56
PFTeDA						1	-0.08	-0.07
PFBS							1	0.07
PFHxS								1
** Correlation was significant at the level of p = 0.01 (two tailed)								

**Table 4** Pearson correlation matrix among PFASs in urine samples of the Chemical plant

	PFBA	PFPeA	PFHxA	PFDoA	PFTTrDA	PFTeDA	PFBS	PFHxS
PFBA	1	-0.02	-0.07	0.05	0.07	0.07	-0.10	0.04
PFPeA		1	0.01	-0.06	-0.05	-0.11	-0.08	-0.04
PFHxA			1	-0.07	-0.05	0.07	0.16	-0.05
PFDoA				1	0.99**	0.33**	0.11	0.30**
PFTTrDA					1	0.30**	0.14	0.30**
PFTeDA						1	0.05	-0.06
PFBS							1	0.02
PFHxS								1
** Correlation was significant at the level of p = 0.01 (two tailed)								

## Conclusions

The distribution characteristics of PFASs in workers' urines of acrylic fiber plant and chemical plant were analyzed in the present study. The results indicate that occupational workers are exposed to different PFASs sources, and no significant differences were found between workshop or gender and PFASs levels. Some short-chain PFASs (i.e., PFBA, PFHxA, and PFHxS) have significantly correlated relationships with working-ages, as the excretion rates of PFASs with different chain lengths are affected by aging. Besides, the results demonstrate that concentrations of short-chain PFASs (i.e., PFBA and PFHxS) were higher than longer PFASs (i.e., PFOA and PFOS) owing to the international regulatory action for long-chain PFASs. And PFBA was the predominant PFASs in all urine samples of the acrylic fiber and chemical plant workers. Therefore, the bioaccumulation and toxic effects of short-chain PFASs on human bodies should be studied systemically.

## **Declarations**

### **Ethics approval and consent to participate**

The approvals for human urine analysis were obtained from the Jinan University Review Board, Jinan University, China (2018-LSPK).

### **Consent for publication**

Not applicable

### **Availability of data and materials**

All data of this study can be obtained from the corresponding authors according to reasonable requirements.

### **Competing interests**

The authors declare no competing interests.

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### **Authors' contributions**

Wang Xu, Qinghuai Zeng, Yao Cheng, and Yingjie Zhang performed sampling of human urine and analysis. Lin Peng was a major contributor in writing the manuscript. Ying Guo, Da Chen, Chao Jiang, and Fei Wang was responsible for revision of the manuscript. These authors contributed equally to this work. All authors read and approved the final manuscript.

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## Figures

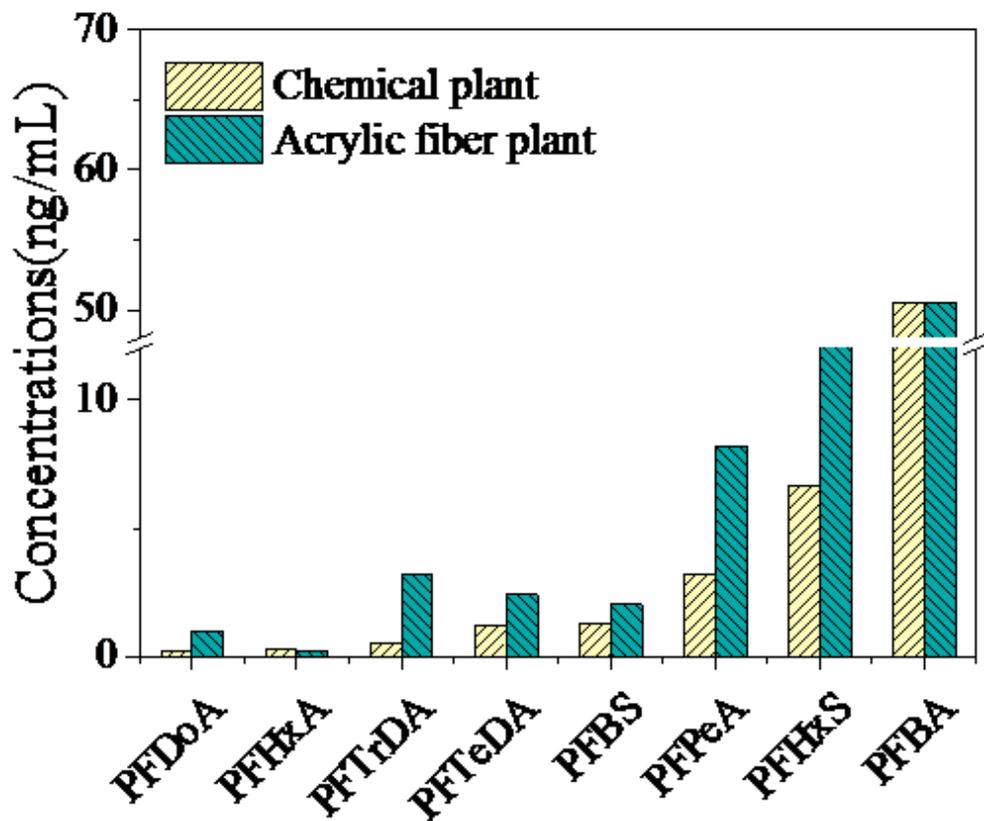


Figure 1

Concentration profiles of eight PFASs in human urine from the Acrylic fiber plant and Chemical plant

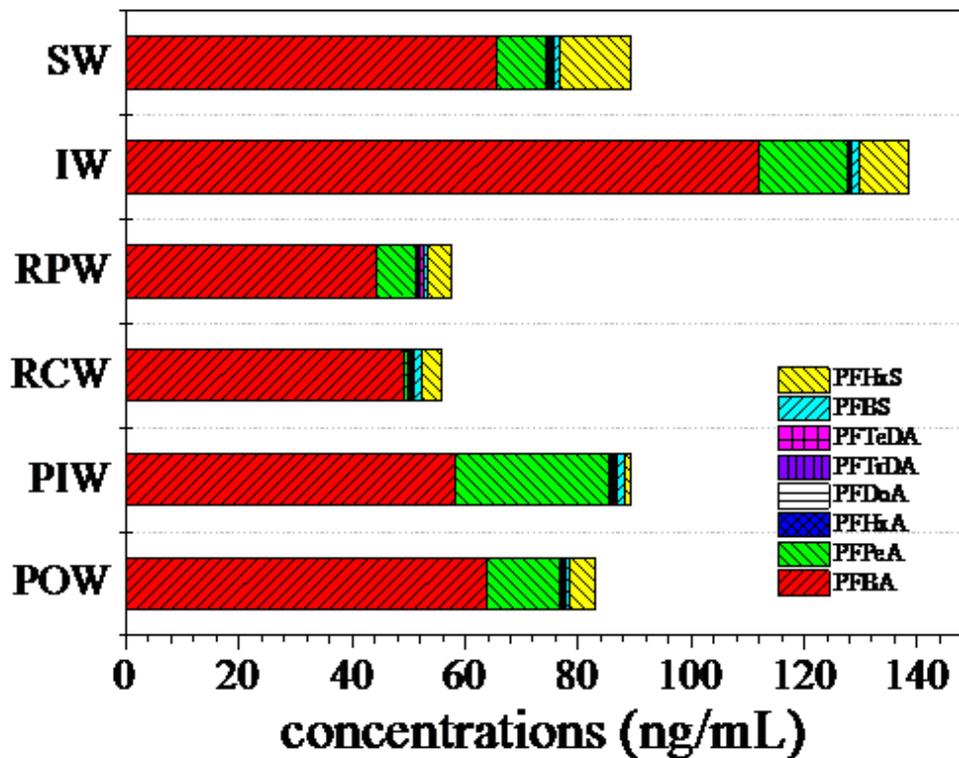


Figure 2

PFASs concentration profiles in human urine from six workshops of the Acrylic fiber plant

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