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RESEARCH ARTICLE

Screening of textile finishing agents available on the Chinese market: An important source of per- and polyfluoroalkyl substances to the environment

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HIGHLIGHTS

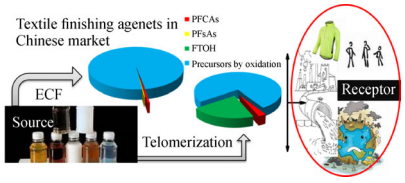
- Kendrick mass defect was used for PFASs screening in textile finishing agents (TFAs).
- Total oxidizable precursor assay provides insight into unknown precursors.
- Perfluorooctane sulfonate was found as impurity in short ECF technology based TFAs.
- Perfluorooctanoate was also detected in C6 telomerization based TFAs.
- Long chain precursors were also observed in both types of TFAs.

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ABSTRACT

Organofluorinated surfactants are widely employed in textile finishing agents (TFAs) to achieve oil, water, and stain repellency. This has been regarded as an important emission source of per-and polyfluoroalkyl substances (PFASs) to the environment. China is the biggest manufacturer of clothes, and thus TFA production is also a relevant industrial activity. Nevertheless, to date, no survey has been conducted on PFAS contents in commercially available TFAs. In the present study, TFA products were investigated by the Kendrick mass defect method. The quantification results demonstrated a significant presence of perfluorooctane sulfonate (0.37 mg/L) in TFAs manufactured by electrochemical fluorination technology. The products obtained by short-chain PFAS-based telomerization were dominated by perfluorooctanoic acid (mean concentration: 0.29 mg/L), whose values exceeded the limits stated in the European Chemical Agency guidelines (0.025 mg/L). Moreover, the total oxidizable precursor assay indicated high levels of indirectly quantified precursors with long alkyl chains (C7–C9). Together, these results suggest that there is currently a certain of environmental and health risks in China that originates from the utilization of TFAs, and a better manufacturing processes are required to reduce such risks.

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1 Introduction

Per- and polyfluoroalkyl substances (PFASs) have been commercialized since the 1950s and widely used in various applications related to the textile finishing, chrome plating, packaging, paper, and firefighting industries (Kissa, 2001; Lacasse and Baumann, 2004; Knepper and Lange, 2011; Trier et al., 2011). Particularly, companies have been reported to use PFASs as a surface active moiety in their products (outdoor apparel) to achieve repellency against oil, stains, and water (Kissa, 2001; Buck et al., 2011; Lacasse and Baumann, 2004). These finishes have a polymer backbone linked with the hydrophobic side. The non-polymer chain consists of PFAS moieties, and these attach with the fabric to make an umbrella-like structure that helps to achieve the repellency toward liquids (Holmquist et al., 2016). The active ingredients of textile finishing agents (TFAs) are normally copolymers having side-chain fluoropolymers (e.g., methyl acrylate or perfluoroalkyl acrylate) (Lacasse and Baumann, 2004; McKeen, 2015). Typical structures include fluorotelomer methyl acrylates, fluorotelomer acrylates, and perfluoroalkane sulfonamidoethanols. In aqueous phase, there can be unbound impurities and residues such as perfluoroalkyl carboxylates (PFCAs) and fluorotelomer alcohols (FTOHs) (Rao and Baker, 1994; McKeen, 2015) that are eventually released to the nearby media and can trigger

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several impacts on human's health and the environment (Buck et al., 2011; Washington and Jenkins, 2015). Therefore, the global presence of PFASs in environmental media, as well as related health issues, has drawn the attention of scientists (Wang et al., 2017; Ritscher et al., 2018; Xiao, 2017) particularly their use in outdoor apparel (Holmquist et al., 2016). Several regulations have been established and limits set in this regard [perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS): 1 $\mu g/m^2$] and in chemical formulations (PFOS: 10 mg/kg) (EU, 2006). Some long-chain PFASs (C9–C14) have also been listed as substances of high concern and recommended to be phased out from commercial products (Brendel et al., 2018). Furthermore, the launched PFOA stewardship program (2006−2015) has captured the attention of vendors, and regulations were passed to limit the concentration in commercial products (Lindstrom, 2011). Besides these concerns, recent studies have indicated that these PFASs are still widely applied to fabrics, with detected concentrations typically in the range of several $\mu g/m^2$ (Herzke et al., 2012; Liu et al., 2015a; Bečanová et al., 2016; Gremmel et al., 2016). Some reports about the indoor contaminated environment in the vicinity of a textile manufacturing plant are available in the literature (Heydebreck et al., 2016; Winkens et al., 2017), and a few reports regarding commercial products (Ye et al., 2015; Favreau et al., 2017), but TFAs have been largely neglected.

China is the largest apparel and textile exporter in the world, and the textile industry has expanded considerably in recent decades. China has the largest textile industry with the complete industrial chain and also the largest textile exporter in the world. (Lin et al., 2018). About 1800 workers have expertise in dyeing, weaving, and finishing of polyester fabric and manufacturing functional apparel for local and international brands (Heydebreck et al., 2016). According to a PFOS emissions inventory report, total PFOS emissions in China were 70 t/a, of which 35 t/a contributed by the textile treatment (i.e., 32% of selected metal plating, firefighting, and semiconductor industrial sectors) (Xie et al., 2013). Several significant studies are available regarding PFAS emissions to the environment from the textile sector (Heydebreck et al., 2016; Lu et al., 2017). However, until now, the main focus of the published literature has been on the quantification of PFASs from apparel and the textile industrial area. In contrast, the sources of these PFASs, particularly the TFAs, have received little attention. The furtive nature of the information related to such products and the related health effects is another issue (Wang et al., 2017). Furthermore, Chinese producers are also trying to adopt alternative (C6) approaches and shift toward replacements (production of perfluorohexane sulfonyl fluoride derivatives). The Ministry of Environmental Protection of China showed that in the next 5–10 years, alternative forms of production will reach 10,000 t/a (Huang et al., 2010). Concluding the discussion, details regarding the composition and trade percentages of PFASs in commercial TFAs are clandestine. It is also difficult to obtain details from vendors and labels on the products, necessitating a call for a survey of commercial TFAs available in China.

Hence, the present work was designed by considering the need to investigate the potential sources. First, TFAs were investigated, using the Kendrick mass defect (KMD) approach, to provide an overview of the occurrence of PFASs. Recently, this method has been used for the screening of PFASs from aqueous film-forming foam (AFFF) (Roach et al., 2011; Myers et al., 2014; Strynar et al., 2015). In the second stage, the main PFASs were quantified using the US Environmental Protection Agency (EPA) approach. However, this approach is limited to quantifying only 20–30 compounds (far from the number of commercially available PFASs), and thus the total oxidizable precursor (TOP) assay method was adopted to give rough estimates regarding perfluoroalkyl acid precursors. This method has been recommended as a monitoring tool for AFFF and its contaminated media (by Queensland, Australia) (Mumtaz et al., 2019) and successfully applied to water, soil and some commercial products particularly AFFF (Houtz et al., 2013; Houtz et al., 2016). The TOP assay method has also been used for the quantification of PFASs from fabric and paper (Robel et al., 2017). However, in the present study, the method was for the first time applied to commercial TFAs and several unknown precursors, along with PFCAs and perfluoroalkane sulfonates (PFSAs), which were quantified from electrochemical fluorination (ECF)- and telomerization-based TFAs. Additionally, a baseline data set is provided to highlight the PFASs in TFAs.

2 Materials and methods

2.1 TFA samples

The TFA samples were collected from both local and international brands (owing to confidentiality requirements, trade names are not shown). The main textile companies based in China were considered (Shanghai Lutong, Hubei Hengxin, and Wuhan Fengfan). The TFAs ($n = 5$) were purchased directly from the latter two, dealing locally and producing short-chained (C4 and C6) ECF-based TFAs. Whereas, in 2017, the alternative products ($n = 7$) from Shanghai Lutong (selling products based on telomerization technology but also providing some products of international brands) were obtained using an online trading platform. The details of the sample set are provided in Table S1.

2.2 Materials

The mass-labeled internal standards (IS) were obtained

from Wellington laboratories (Guelph, ON, Canada). HPLC grade methanol, acetone, and n-hexane were purchased from Duksan (Kyoungkido, Korea). The other materials included: sampling bottles (1L, PP), centrifuge tubes (15 mL and 50 mL), ultrapure water (UPW; 18 MΩ. cm, Millipore, MA, USA), acetic acid reagent (HPLC grade), ammonia solution (25% in H_2O), Oasis P-WAX cartridges (150 mg/6mL, Waters, MA), adjustable micro-pipettes (100–1000 µL, 20–200 µL) and microfiber filters (47 mm, Whatman, Kent, UK). Potassium persulfate ($K_2S_2O_8$) was used as an oxidant and sodium hydroxide was also used for pH adjustment. Further details about the materials are provided in the supporting information (SI, Text S1).

2.3 Screening, pretreatment and TOP assay for TFAs

The supernatant obtained after ultrasonic extraction (1 mL sample with 9 mL of methanol) was filtered (0.22 µm) prior to analysis for a quick overview of PFASs. The screening approach indicated the availability of certain PFASs, for which further quantification was conducted by following detailed pretreatment steps and an oxidation approach.

The pretreatment was conducted following two parallel approaches. For the first set of samples, PFASs were quantified directly. The semi-volatile compounds (FTOH) were measured by diluting the supernatant (10–500 times), passing it through a 0.22 µm filter, and directly analyzing via gas chromatography mass spectrometry (GC-MS). Ionic compounds (PFCAs, PFSAs) were extracted via the EPA-537 method using solid phase extraction (P-WAX cartridges) (EPA-537, 2009). The final extract was spiked with 50 µL of IS (M_2-PFOA) before analysis. For a detailed account of the pretreatment procedure, please refer to the SI (Text S1).

The second approach was based on the TOP assay method. There can be several interferences in complex matrices, so the application of oxidative treatment is challenging. To ensure complete oxidation, samples were diluted (1000 times) in UPW. The final volume of the diluted sample was 50 mL. Before oxidative treatment, the pH was adjusted (10N sodium hydroxide; 150 mM; 0.75 mL), and $K_2S_2O_8$ (60 mM; 0.81 g) was added and thermalized at 85°C for 6 h (Houtz and Sedlak., 2012). As FTOHs are highly volatile, the sample was kept in a 50 mL centrifuge tube with a headspace volume of less than 1 mL, which was then tightened and wrapped with Parafilm®. After the oxidation samples were brought to room temperature, the pH was adjusted (5–7) and followed by the pretreatment step.

2.4 Instrumental analysis

Screening analysis was conducted on an UltiMate™ 3000 ultra-performance liquid chromatography (Dionex, USA) coupled with time-of-flight mass spectrometry (Bruker micro TOF-Q III, Bremen, Germany) (UPLC-TOF-MS). The TFAs were analyzed in negative electron spray ionization with multiple reaction monitoring mode. The spray voltage was adjusted to 3.5 kV. For the survey, the selected mass range was 100–1000. The temperature was maintained at 450°C with an ionization voltage of 4.5 kV. Further, the collision (argon), ion source gas 1 (nitrogen) and gas 2 (nitrogen) pressures were adjusted to 5 psi, 60 psi, and 40 psi, respectively.

Target PFASs were quantified by ultra-performance liquid chromatography (UPHLC, Dionex, USA) coupled with AB Sciex triple quadrupole mass spectrometry (API 3200; UPLC-MS/MS). 10 µL of prepared TFA sample was injected and target compounds were separated on a C18-XBridge, Waters column (3 × 150 mm, 3.5 µm). The corresponding mobile phase was 10 mM ammonium acetate solution (A) and methanol (B), with a flow rate of 0.3 mL/min. The following gradient program was used: Initially, B (40%) was consistent for 1 min, but was then increased to 90% within 26 min, maintained for 7 min, and finally reduced to 40% within 33.1 min and kept constant for 5 min.

The semi-volatile compounds (FTOH) were separated in negative ionization mode via GC-MS (QP-2010, Shimazu, Japan) by using a DB-WAX column (0.5 µm thickness, 30 m × 0.25 mm id; J&W Scientific). The GC system inlet, MS interface, and ion source temperature were maintained at 200°C, 230°C and 210°C, respectively. The following temperature program was followed for the GC column: for 1 min, the temperature was maintained at 60°C, before then being increased to 75°C at 5°C/min, and finally raised to 220°C through 20°C/min and held for 6 min. Helium was used as the carrier gas at a flow rate of 0.8 mL/min.

2.5 Corresponding quality assurance and quality control

Throughout the process from sampling to final analysis, quality assurance and quality control procedures were strictly followed. Glassware was completely avoided. Sampling bottles, centrifuge tubes, and all the equipment used for pretreatment were rinsed with acetone, n-hexane, methanol, and UPW, sequentially, and further air-dried to avoid contamination. The related IS stock solutions were prepared in HPLC grade methanol and stored at −18°C in polypropylene bottles. Calculated recoveries of the native standard were between 70% and 130%. The relative standard deviation of replicates was below 20%. The calculated limit of detection (LOD) was three times the signal-to-noise ratio, and the limit of quantification (LOQ) was 10 times (Table 1). For quantification, mass-labeled IS were used, and the calculated recoveries were 50%–150%. To avoid contamination, blanks were prepared, and the detected concentration was below the LOQ. A detailed description of the instrumental analysis and methodology can be found in the SI (Text S1, Table S2).

Table 1 Calculated recovery of PFASs, LOD and LOQ (ng/mL)

PFASs	Recovery[a] (%)	LOD[b] (ng/mL)	LOQ[c] (ng/mL)
PFBA	101±0.3	0.3	2.7
PFPeA	104±15.8	0.4	3.6
PFHxA	112±18.5	0.3	2.6
PFHpA	100±7.0	0.3	2.7
PFOA	115±17.5	0.2	2.3
PFNA	106±12.7	0.2	2.0
PFDA	133±13.6	0.2	2.4
PFUnDA	90±9.8	0.2	2.1
PFBS	100±7.4	0.3	3.2
PFPeS	115±9.5	0.2	2.0
PFHxS	98±10.5	0.4	3.6
PFHpS	85±6.1	0.3	2.9
PFOS	100±14.8	0.2	2.2
PFNS	84±3.2	0.1	1.33
PFDS	94±4	0.2	1.96
4:2FTOH	119±5.0	8.6	28.7
6:2FTOH	112±12.3	2.7	9.0
8:2FTOH	112±8.0	1.8	5.8
10:2FTOH	124±1.1	1.1	3.7

Notes: a) Mean±standard deviation, selected sample (n = 3) spiked at 200 ng/mL; b) Limit of detection; c) Limit of quantification.

2.6 Non-target screening approach

KMD is considered a powerful tool for the screening of persistent pollutants (Fernando et al., 2014). Recently, KMD was used for screening PFASs from AFFF (Barzen-Hanson and Field, 2015; Barzen-Hanson et al., 2017). According to IUPAC (C = 12.0 Da), if the mass scale is converted to CF_2, then the same KMD can be calculated for homologous series of organic compounds. In PFASs, the head group is consistent but the fluorinated tail length is distinct, and the mass of PFAS compounds varies with a difference of 50 Da (Kendrick, 1963; Roach et al., 2011). Normally, the PFASs from the ECF process have a mass difference of 50 Da (CF_2); however, the telomerization-based substances have a mass difference of 100 Da (CF_2–CF_2). Theoretically, m/z could be calculated for 58 PFASs using Eqs. (1) and (2) (shown in Fig. S1). The computed mass defects were between 0.00013 and 0.1 (Roach et al., 2011; Place and Field, 2012; D'Agostino and Mabury, 2014; Barzen-Hanson and Field., 2015). The observed m/z from an instrument having a mass defect error less than 1 Da corresponds to PFASs and was selected for the current scenario. KMD was calculated using the following equations:

$$KM = exact\ mass \times 50/49.9968, \quad (1)$$

$$KMD = exact\ mass - nominal\ mass\ (rounded\ down) \times 50/49.9968. \quad (2)$$

3 Results and discussion

3.1 Overview of PFASs by KMD

Though TFAs are complex mixtures, the KMD approach is helpful in separating PFASs in homologs series having a defined mass defect (Roach et al., 2011). Data from UPLC-TOF-MS were used for the screening analysis. The total ion chromatogram was processed and the theoretically calculated m/z was compared with the observed m/z (Barzen-Hanson et al., 2017). The calculated KMD ranging between 0.8 and 1 corresponded to PFCAs and PFSAs (as shown across the y-axis in Fig. S1). Considering the ECF-based sample (FA10), PFCAs (C4–C7), PFSAs (C6, C8), N-Ethyl perfluorooctane sulfonamide (N-EtFOSA), N-Methyl perfluorooctane sulfonamide (N-MeFOSA), polyfluoroalkyl phosphates (6:2 PAP) and 6:2 fluorotelomer unsaturated carboxylic acid (6:2 FTUCA) were observed, as shown in Fig. 1. In this KMD plot, one identified homolog was helpful to locate the remaining homologs (Liu et al., 2015b; Dimzon et al., 2016).

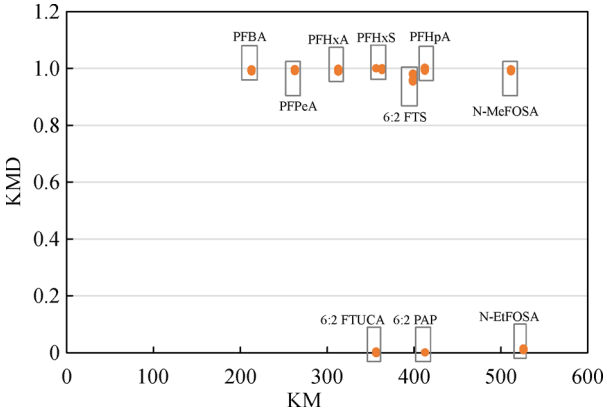


Fig. 1 KMD against KM plot for the entire mass in FA10, representing the overviewed PFASs among the selected list of 58 PFASs.

Regarding C6 telomerization-based formulation, long chains (PFOA and PFDA) were also observed (Fig. 2). Among all the tested TFAs, PFCAs (C4–C10) and PFSAs (C4–C10) were predominant. Several other precursors were also noticed, including fluorotelomer sulfonates (FTS), fluorotelomer carboxylic acids (n:2 FTCAs), fluorotelomer unsaturated carboxylic acids (n:2 FTUCAs), PAPs, perfluoroalkane sulfonamide acetic acids (FASAAs), and N-alkyl perfluoroalkane sulfonamides (MeFA-

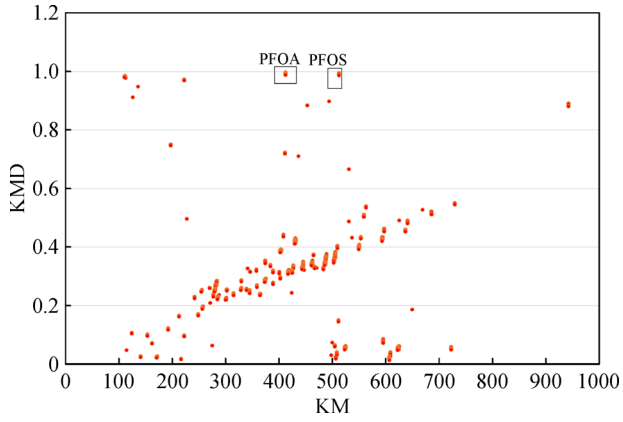


Fig. 2 KMD against KM plot for the entire mass spectrum in FA4, representing the overviewed PFASs among the selected list of 58 PFASs.

SAs/EtFASAs). The sulfonamides were prevalent in ECF-based formulations. Several formulations, such as FA8 and FA12, were claimed to be C6, but besides perfluorohexanoate (PFHxA) and perfluorohexane sulfonate (PFHxS), long-chains, particularly PFOS, were also observed in these short-chain ECF-based TFAs. Long chains (PFOS, PFOA, PFNA, and PFDA) were also overviewed in the C6 telomerization-based TFAs. Concluding the discussion, approximately 23 different PFASs and precursors were overviewed in the commercially available TFAs (Figs. S2–S8). A detailed structural analysis was beyond the scope of the present work.

3.2 PFASs and their homolog profile in the ECF-based TFAs

The present sampling set consisted of C4- and C6-based formulations. FA9 and FA12 were dominated by short chains — particularly C4. The quantification using the EPA method showed that short-chain perfluorobutane sulfonate (PFBS, with a detected mean concentration of 2.12 mg/L) and perfluorobutanoate (PFBA, with a mean concentration of 5.8 mg/L) were dominant, but the bioaccumulative perfluoroheptanoate (PFHpA) and PFOS (with mean concentrations of 0.02 and 0.83 mg/L, respectively) could not be neglected. The remaining TFAs (FA8, FA10, and FA11) were mainly C6. The homolog profile was consistent and, besides the dominant PFHxA (mean concentration: 5.77 mg/L), PFHxS (mean concentration: 2.52 mg/L) and PFOS (mean concentration: 0.08 mg/L) also existed.

Considering all of the representative ECF-based formulations, direct quantification revealed that the detected total concentrations of PFSAs were 0.57–6.05 mg/L (Fig. 3; details of the directly quantified PFAS concentrations presented in Table S3), with a major percentage contribution from PFHxS (mean concentration: 1.6 mg/L; 55%), followed by PFBS (mean concentration: 0.91 mg/L). PFOS was also detected, with a mean concentration of 0.37 mg/L. PFNS and PFDS were below the LOQ, and the percentage contribution was almost negligible. The total PFCA concentrations were 2.18–12.08 mg/L in all the ECF-based tested TFAs. The homolog profile (on the basis of mean concentration) showed that PFHxA (3.48 mg/L) was predominant, followed by some other short chains, such as PFBA (2.90 mg/L) and PFPeA (0.3 (for two DECIMALS 0.27 mg/L)). Some long chains, such as PFOA, PFNA and PFDA, were also detected but were below the LOQ. The analyzed TFAs were dominated by C6, but the detected concentrations of PFOS could not be neglected. Previous research has identified the presence of long-chain PFASs in a textile manufacturing plant, which

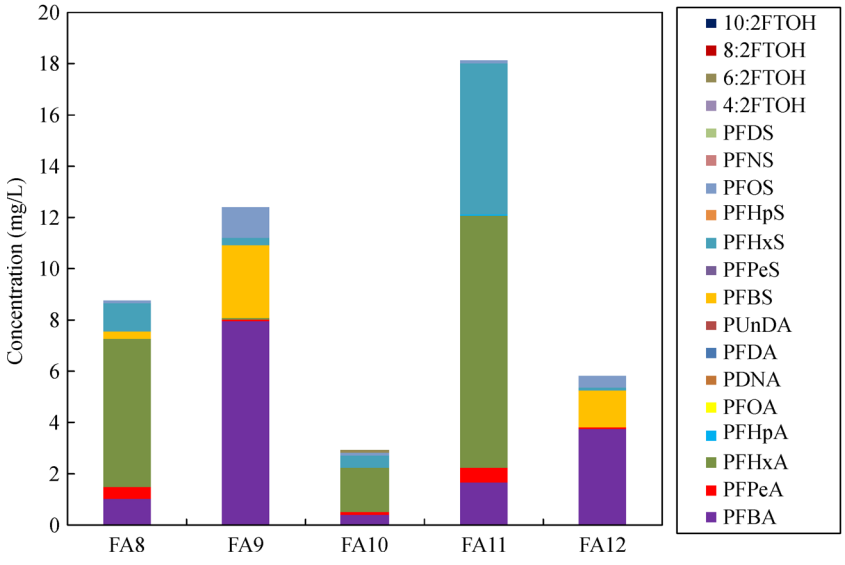


Fig. 3 Directly quantified PFASs in ECF-based TFAs.

validates the recent data of TFAs being the source of those PFASs (Heydebreck et al., 2016). Furthermore, the depicted KMD profile and confirmed PFASs highlighted that contradiction exists in labels and PFAS contents.

3.3 PFASs and their homolog profile in the telomerization-based TFAs

The detected PFASs showed that FTOHs were dominant, with a total concentration of 1.67–1369.55 mg/L (Fig. 4; details of the directly quantified PFASs are given in Table S3). A similar trend was observed for consumer products, which have previously shown high detected concentrations of FTOH precursors (Vestergren et al., 2015). The total detected concentration of PFCAs was 0.02–1.69 mg/L. PFSAs (ND–0.16 mg/L) were also detected, with a 42% detection frequency. In telomer-based formulations, PFHxA, perfluoropentanoate (PFPeA) and PFBA were detected in all the tested formulations. The homolog profile (based on mean concentration) showed that, among PFCAs, PFOA (0.29 mg/L) was dominant, with a percentage contribution of 41.9%, followed by PFDA (0.15 mg/L; 21.7%), PFHxA (0.13 mg/L; 19%), PFHpA (0.04 mg/L; 5.3%), PFPeA (0.03 mg/L; 4.7%). The FTOH homolog profile showed that 8:2 FTOH (230.70 mg/L) was dominant, followed by 10:2 FTOH (203.23 mg/L) and 6:2 FTOH (77.78 mg/L). A similar trend was observed previously from a textile manufacturing facility in China, which had the highest concentration of 10:2 FTOH, followed by 8:2 FTOH (Heydebreck et al., 2016).

The information collected from vendors showed that the tested telomerization-based formulations (FA1–FA7) claimed to be C6. However, the current analysis of the PFAS profile disagreed with the available information, showing that only FA5 was purely C6 and no long chains were detected. In FA2, the long-chain PFCAs (C7–C10) were not detected, but 8:2 FTOH (0.82 mg/L) was quantified. The mean concentration profiles of the remaining TFAs (FA1, FA3, FA4, FA6, and FA7) again disagreed with the labels, depicting that PFOA (0.41 mg/L) was dominant, followed by PFHxA (0.17 mg/L). From this data set, it could be inferred that the Chinese scenario is different from elsewhere in the world insofar as long chains are still used in commercial products. Several studies have validated the presence of long-chain PFASs in textiles, which increases the severity of environmental problems in China (Greenpeace, 2011; Heydebreck et al., 2016).

3.4 Application of the TOP assay method and estimation of unidentified precursors

Besides FTOH, several other precursors were also overviewed through KMD plots. To estimate the total PFAS profile, an effort was made to apply the TOP assay method for the first time to TFAs. FTOHs are dominant precursors in the TFAs. In previous studies, the oxidation products of the FTOH precursors were not addressed (Houtz and Sedlak., 2012). Therefore, 25 ng/mL of 8:2 FTOH and 10:2 FTOH was spiked in UPW to ensure the application of the TOP assay method, and these samples were oxidized under similar specialized conditions as reported previously (Houtz and Sedlak, 2012). To avoid the volatilization of FTOH, the bottles were tightened and properly sealed. The TOP-assay-generated profile showed that 8:2 FTOH was converted into equimolar quantities of PFCAs (C4–C8). The equimolar quantities of PFCAs (C4–C9) were noticed by oxidizing 10:2 FTOH. The generated PFCA profile is shown in detail in Table S4.

Regarding TFAs, the concentration of PFCAs was significantly increased after oxidative treatment because precursors were transformed to equimolar quantities of

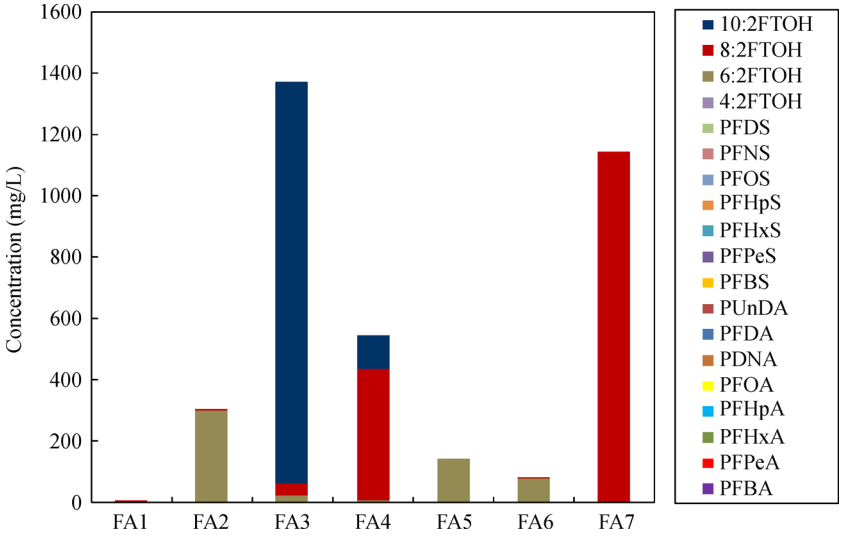


Fig. 4 Directly quantified PFASs in telomerization-based TFAs.

corresponding PFCAs (Houtz and Sedlak, 2012). The total detected concentration of PFCAs by the TOP assay method was 58.83–3361.67 mg/L and 380.47–3156.07 mg/L, in ECF- and telomerization-based TFAs respectively (Table S5). The significant change was observed in oxidized TFAs (Fig. 5). Concerning telomerization-based samples, the mean ΔPFHxA was 700.91 mg/L, followed by ΔPFOA (324.40 mg/L), ΔPFPeA (258.08 mg/L), ΔPFHpA (254.49 mg/L), and ΔPFBA (115.05 mg/L). In ECF-based TFAs, the observed change was in the following order: Δ PFHxA (711.32 mg/L), ΔPFBA (157.82 mg/L), ΔPFPeA (143.86 mg/L), and ΔPFOA (0.002 mg/L).

In the current situation, the increase in concentration cannot be related to measured precursors only. The TOP assay showed that several unidentified precursors, with concentrations of 16.74–3352.95 mg/L (corresponding to PFCAs generated after oxidative treatment and could not be related to measured precursors; details provided in the SI), also existed in the TFAs, and a major portion of the total PFAS concentration upon oxidation (sum of the concentrations of directly quantified PFCAs, PFSAs, measured and unidentified precursors) was related to unidentified precursors (64%$_{\mu M}$) (Fig. 6). This observed increase in concentration may be related to FTS or sulfonamides containing precursors (Rao and Baker, 1994). Through the KMD plots, some precursors (PAPs) were noticed, which could also be a reason for the observed changes. Furthermore, the perceived increase in

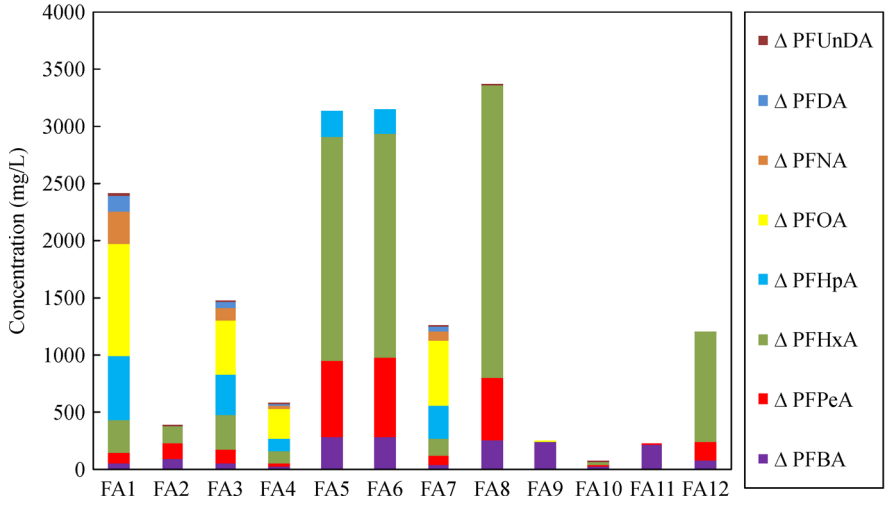
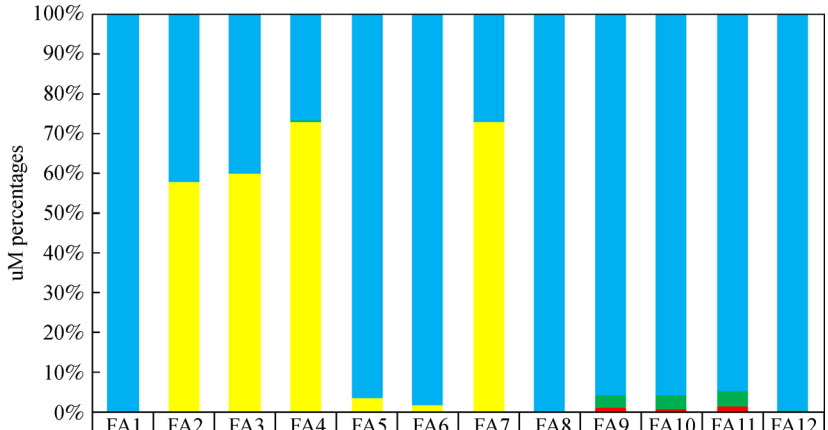


Fig. 5 Observed increase in the concentration (mg/L) of PFCAs after oxidative treatment.



	FA1	FA2	FA3	FA4	FA5	FA6	FA7	FA8	FA9	FA10	FA11	FA12
Unidentified	6299	596	1653	415	10298	10568	906	11371	1106	213	976	4031
PFCAs	4.0	3.4	1.2	1.3	6.7	3.7	2.3	24.7	37.5	7.6	41.2	17.6
PFSAs	0.3	0.0	0.0	0.0	0.0	0.2	0.1	3.9	12.5	1.4	15.1	5.9
Precursors FTOH	4	821	2463	1136	390	214	2468	0.0	0.0	0.4	0.0	0.0

Fig. 6 Percentage contribution by unidentified precursors [PFCAs generated upon oxidation that could not be related to measured precursors, and calculated by the difference between the oxidation products (i.e., all PFCAs) and the identified precursors (i.e., FTOH)].

the concentration of long-chain PFCAs (C8–C11) could be related to the presence of long-chain precursors in the TFAs (Houtz and Sedlak, 2012). This rise in the PFCA profile upon the TOP assay is similar to previously published results regarding AFFF (Houtz et al., 2013; Houtz et al., 2016), and showed that complex formulations are dominated by several unknowns. On the other hand, though providing conservative estimates, the TOP assay method can be used for complex formulations other than AFFF.

3.5 Total PFAS profile compliance with regulations and potential environmental implications

The total PFAS concentration was the sum of the directly quantified PFCAs, PFSAs, FTOHs and PFCAs observed via the TOP assay method (Fig. S9). The total quantified PFASs were 58.83–3361.67 mg/L and 380.47–3156.07 mg/L in the ECF- and telomerization-based commercially available TFAs, respectively. Comparison with the related guidelines showed that the detected PFOS in ECF-based TFAs were within the limits (10 mg/L) suggested for commercial products. PFOA was not detected in short-chain ECF-based TFAs. However, the precursor profile (>1 mg/L) showed that these ECF-based products used locally for textile treatment are not safe (ECHA, 2016). Regarding telomerization-based TFAs (by Shanghai Lutong, which also included products of some international brands), the comparison with the limits for PFOA (0.025 mg/L) recommended by the European Chemical Agency (ECHA) showed that these so-called C6 finishing agents are not safe. The TOP-assay-generated precursor profile (C7–C10) in telomerization-based TFAs also exceeded the ECHA guidelines (1 mg/L) and needs to be addressed carefully (ECHA, 2016). Another important point is that the quantified PFASs with seven or more perfluorinated carbon chains are contaminants of concern that are prone to persisting and bio-accumulating in the surrounding environment (Giesy and Kannan, 2001; Moody et al., 2002; Houde et al., 2006). Particularly, the high detected concentration of 8:2 FTOH and 10:2 FTOH (>1 mg/L) in telomerization-based TFAs is alarming. These are the precursors of PFOA in the environment that can persist for a long time (Butt et al., 2014). Recently, a survey report mentioned the transport of fluorotelomers over long distances, ultimately causing soil contamination (Rankin et al., 2016).

Besides contamination of the local environment, China is a major exporter of textiles, and a study from Norway previously showed that imported products from China were contributing to the PFOA (1.5%) and 8:2 FTOH (0.3%) emissions in the Norwegian environment (Vestergren et al., 2015). Also, the occurrence of these long chains needs to be addressed because these PFASs may enter the environment through textile treatment or through the washing of treated fabric (Greenpeace, 2011; Heydebreck et al., 2016). Humans may also be exposed through direct contact with clothes, and children, in particular, are at high risk (Liu et al., 2015a; Favreau et al., 2017). In the present work, only PFAS concentrations were estimated, and very little is known about the structures, intermediate metabolites and biological effects of unidentified precursors. Furthermore, the observed complexity, diversity of TFAs (ultimate PFAS source), and limited data set showed that it would be challenging to assess the exposure, risk, and release to the environment. The paucity of available information and mounting concerns highlight the need to explore the sources of PFASs to understand the likely future trends in the environment and effects on human.

4 Conclusions

Based on the current data set, it can be concluded that the target screening (EPA method) is limited insofar as it can only quantify a small portion (>30%) of all PFASs. On the other hand, the TOP assay method is more successful for TFAs and can conservatively quantify precursors (64% on a molar basis). The dominant compound among all TFAs was found to be PFHxA, but the detected concentration of PFOA — particularly in telomer-based TFAs — cannot be neglected. The high detected concentration of FTOH precursors (8:2 FTOH, 10:2 FTOH) is another concern and indicates that TFAs sold commercially in the Chinese market for local and global applications may inadvertently affect human health and the environment. Non-fluorinated alternatives could be an option, but the oil repellency is still questionable. Furthermore, it is also uncertain to what extent vendors are willing to pay for alternatives. The short-chain substitute is a comparatively safe option that can be adopted by Chinese producers, but this needs to be addressed further in the future. Furthermore, the present data can be used as a baseline for detailed structural analysis and quantification of precursors. This is recommended with respect to commercial textile products in order to assess the emissions status of the industry and the ultimate effects on receptors.

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