

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES
JOURNAL OF
ENVIRONMENTAL
SCIENCES
www.jesc.ac.cn

The occurrence of per- and polyfluoroalkyl substances (PFASs) in fluoropolymer raw materials and products made in China

Lingyi Meng^{1,2}, Boyu Song³, Yao Lu^{1,2}, Kun Lv^{1,5}, Wei Gao¹,
Yawei Wang^{1,2,4,*}, Guibin Jiang^{1,2}

¹Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

²University of Chinese Academy of Sciences, Beijing 100049, China

³Foreign Environmental Cooperation Center, Ministry of Ecology and Environment of the China, Beijing 100035, China

⁴School of Environment, Hangzhou Institute for Advanced Study, University of Chinese Academy of Sciences, Hangzhou 310000, China

⁵Environment Research Institute, Shandong University, Qingdao 266237, China

ARTICLE INFO

Article history:

Received 20 November 2020

Revised 21 January 2021

Accepted 24 January 2021

Available online 12 February 2021

Keywords:

Fluoropolymer

Per- and polyfluoroalkyl substances (PFASs)

Perfluorooctanoic acid (PFOA)

Perfluoro-2,5-dimethyl-3,6-dioxanonanoic acid

(HFPO-TrA)

ABSTRACT

Perfluorooctanoic acid (PFOA), its salts, and related compounds were listed as new persistent organic pollutants by the Stockholm Convention in 2019. In this study, the occurrence of residues of PFOA and other per- and polyfluoroalkyl substances (PFASs) in raw materials and fluoropolymer products from the Chinese fluoropolymer industries are reported for the first time. The PFOA concentrations in raw materials and fluoropolymer products were in the range of 6.7 to 1.1×10^6 ng/g, and <MDL (method detection limit) to 5.3×10^3 ng/g, respectively. Generally, the levels of PFOA in raw materials were higher than in products, implying that PFOA in the emulsion/dispersion resin could be partly removed during the polymerization or post-processing steps. By tracking a company's polytetrafluoroethylene (PTFE) production line, it was found that over a 5 year period, the residual levels of PFOA in emulsion samples declined from 1.1×10^6 to 28.4 ng/g, indicating that the contamination of PFOA in fluoropolymer products from production source gradually decreased after its use had been discontinued. High concentrations of HFPO-TrA (2.7×10^5 to 8.2×10^5 ng/g) were detected in some emulsion samples indicating this alternative has been widely applied in fluoropolymer manufacturing in China.

© 2021 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Introduction

Per- and polyfluoroalkyl substances (PFASs) are produced for use in various industrial and consumer applications, in-

cluding surfactants, fire-fighting foam, non-stick cookware, food packaging, waterproofing, textiles, and metal plating (Brendel et al., 2018; Fromme et al., 2017; Liu et al., 2019; Mumtaz et al., 2019). PFASs have received widespread attention because of their ubiquitous presence throughout the

* Corresponding author.

E-mail: ywwang@rcees.ac.cn (Y. Wang).

environment, due to their high level of industrial use. PFASs have been detected in multiple environmental and human tissue samples to date, including soil, water, sediment, food, blood and placenta (Bangma et al., 2020; Cui et al., 2018; Gao et al., 2019; Gui et al., 2019; Jahnke et al., 2007; Lang et al., 2017; Sznajder-Katarzyńska et al., 2019; Washington et al., 2010; Zhang et al., 2019). Human exposure to PFASs is unavoidable, especially for some occupations such as firefighters, fluorinated ski wax production, fluoropolymer production and fluorine chemical production (Lu et al., 2019; Nilsson et al., 2013; Peaslee et al., 2020). Perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are two typical eight-carbon PFASs which were listed as persistent organic pollutants by the Stockholm Convention in 2009 and 2019, respectively, due to their toxicity, persistence, biomagnification and propensity for long-distance transmission (UNEP, 2019, 2009). The European Union imposed a ban on the manufacture and sale of PFOA from 4 July 2020. Furthermore, it was decided that the concentration of PFOA or any of its salts in substances, mixtures or articles should not surpass 25 ppb from 4 July 2020 (EU, 2020).

Fluoropolymers are an anthropogenic material with high thermostability, low flammability, hydrophobicity and corrosion resistance (Bruno, 2010; Demarteau et al., 2017). They are commonly used for applications such as aeronautics, fuel cell membranes and the automobile industry (Demarteau et al., 2017). Polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) are two of the most common fluoropolymers, representing 58% and 21% of all produced fluoropolymers by weight, respectively (Pladis et al., 2014). Perfluorinated acids or salts are commonly used as emulsifiers for the polymerization of fluoropolymers in the emulsion method (Puts et al., 2019), while the ammonium salts of PFOA (APFO) and perfluorononanoic acid (APFN) are typically used for the solubilization of fluoromonomers (Prevedouros et al., 2006). Roughly 80% of perfluoroalkyl carboxylic acids (PFCAs) in the environment originate from the fluoropolymer manufacturing industry (Kwiatkowski et al., 2020). The use of PFASs as emulsifying agents in fluoropolymer manufacturing was changed by recycling emulsifiers from waste or searching alternatives due to the management of PFOA in globe (Song et al., 2018). It has been reported that functionalized perfluoropolyethers (PFPEs) are the main alternatives to APFO including ammonium 4,8-dioxo-3H-perfluorononanoate (ADONA, CAS No. 958445-44-8), and hexafluoropropylene oxide dimer acid (HFPO-DA, GneX for trade name, CAS No. 62037-80-3) (Wang et al., 2013).

However, APFO continued to be used as an emulsifier in some fluoropolymer manufacturing in China as no limitations or restrictions were imposed on PFOA (Wang et al., 2014). The discharge of PFOA in China reached approximately 80 tonnes per year in 2013, with fluoropolymer manufacturing being the dominant source (Wang et al., 2016). Previous studies have mainly focused on the detection of PFASs in environmental media such as sediments or human tissues such as blood, to assess the level of exposure to PFASs (Codling et al., 2018; Jin et al., 2016; Yeung et al., 2013; Zhao et al., 2017). Fluoropolymer manufacturing is undoubtedly a major source of PFASs pollution (Wang et al., 2016). However, to the best of our knowledge, only one published study has previously quantified PFASs in the fluoropolymer samples (Rand and Mabury, 2011).

The manufacture and usage of fluoropolymer products continue to occur at a high level worldwide (Puts et al., 2019). China is one of the largest exporters of fluoropolymer products globally (Chen, 2019). However, little data is available on PFASs in fluoropolymer raw materials and products, especially in China.

In this study, the concentrations of 20 PFASs including sixteen legacy PFASs and four emerging PFASs, reported to be used as substitutes in fluoropolymerization in fluoropolymer raw material and product samples from Chinese fluoropolymer manufacturing plants, were quantified. The residual concentrations of PFOA in raw materials and products were also compared. The objective of this study was to investigate and assess the level of PFOA and other PFASs residues in fluoropolymer manufacturing in China. Furthermore, the current situation and challenges for imposing PFOA restrictions in fluoropolymer manufacturing are also presented and discussed.

1. Materials and methods

1.1. Materials and reagents

The native standard mixture PFAC-MXB (2 µg/mL) including C4 – C14, C16 perfluoroalkyl carboxylic acids and C4, 6, 8, 10 perfluorosulfonic acids, single standard 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid (HFPO-DA, 50 µg/mL), single standard sodium dodecafluoro-3H-4,8-dioxanonoate (NaDONA, 50 µg/mL) and mass-labelled standard MPFAC-MXA (2 µg/mL) were purchased from Wellington Laboratories. Single standard 2,3,3,3-tetrafluoro-2-[1,1,2,3,3,3-hexafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propoxy]propanoic acid (HFPO-TrA, 1 g) was purchased from Fluorochem Pvt., Ltd. (UK) and 2,3,3,3-Tetrafluoro-2-[1,1,2,3,3,3-hexafluoro-2-[1,1,2,3,3,3-hexafluoro-2-(heptafluoropropoxy)propoxy]propoxy]propanamide (HFPO-TeA, 1 g) was obtained from Apollo Scientific Ltd. (UK). Detailed information on the standards used is provided in Appendix A Table S1. HPLC grade methanol and acetonitrile were obtained from J.T. Baker (Phillipsburg, NJ, USA). Ultra-pure water was prepared using the Milli-Q water purification system (Millipore, USA). Ammonium acetate (HPLC grade) was obtained from Dikma Technologies Inc. (USA).

A total of 23 samples of industrial raw materials (R1–10) and products (P1–13) were collected from seven fluoropolymer manufacturers in China in 2019. Detailed information on the samples is provided in Table 1.

1.2. Sample preparation and instrumental analysis

Prior to extraction, solid samples were ground into extremely fine fragments using shears. The samples in emulsion form were vortexed immediately prior to collection for analysis. The sample preparation method was similar to previously reported methods studies with some modifications (Bečánová et al., 2016; Choi et al., 2019). The detailed procedure was as follows: 0.2 g of sample was weighed into a 15 mL PP centrifuge tube and 0.8 ng internal standard (100 µL of 8 ng/mL MPFCA-MXA in methanol) was added. Then, 8 mL of 25 mmol/L ammonium acetate in methanol/acetonitrile (1:1) was added to

Table 1 – Physical traits and composition of samples obtained from fluoropolymer manufacturers.

Number	Name	Raw materials	Use of PFOA during production	Color
R1	PTFE coating emulsion	–	No (five years)	white
R2	PTFE impregnating emulsion	–	No (three years)	white
R3	PTFE impregnating emulsion	–	Yes	white
R4	PTFE impregnating emulsion	–	No	white
R5	PTFE impregnating emulsion	–	No	white
R6	PTFE impregnating emulsion	–	No	white
R7	PTFE impregnating emulsion	–	No	white
R8	PTFE dispersion resin for filament fiber	–	Yes	white
R9	PTFE dispersion resin for staple fiber	–	Yes	white
R10	PTFE dispersion resin for filament fiber	–	No	white
P1	Staple fiber	Dispersion resin	Yes	white
P2	Staple fiber	Dispersion resin	No	white
P3	Filament fiber	Dispersion resin	Yes	white
P4	Garment Film	Dispersion resin	Yes	white
P5	Packing	Emulsion	No	white
P6	Tetrafluoro line	Dispersion resin	No	white
P7	Extruded pipe	Dispersion resin	Yes	white
P8	Extruded pipe	Dispersion resin	Yes	white
P9	PVDF thin film	PVDF resin	Yes	white
P10	PTFE expansion plate	Dispersion resin	Yes	white
P11	PTFE wire cable	Dispersion resin	Yes	white
P12	PTFE linoleum	Emulsion	Yes	brown and yellow
P13	Thread sealing tape	Dispersion resin	Yes	white

Notes: To respect the privacy of manufacturers, A–G codes were used to distinguish different fluoropolymer manufacturers. R1–6 and P10–12 were collected from factory A; R7–10 were collected from factory B; P1–4 were collected from factory C; P5–6 was collected from factory D; P7–8 were collected from factory E; P9 was collected from factory F; P13 was collected from factory G.

the tube and the tube was immediately vortexed for one minute. The samples were ultrasonicated for 6 min at 60 °C and then shaken at 150 r/min for 10 hr. Following this, the tubes were centrifuged for 10 min at 4500 r/min and 4 mL of supernatant was collected and loaded on the ENVI CARB SPE cartridge (Supelco, 3cc, 100 mg) which had been previously conditioned using 3 mL methanol. The analytes remaining on the cartridge were eluted by 3 mL methanol. Seven mL of solvent was collected and the eluent was then concentrated to 0.2 mL using a gentle stream of high purity nitrogen. The concentrated sample was transferred to a 1.5 mL PP centrifuge tube and then centrifuged for 15 min at 4 °C at a speed of 10,000 r/min to remove particles. The supernatant was stored at 4 °C prior to instrumental analysis.

The analysis of PFASs was conducted using an Agilent 1290 Infinity Liquid Chromatography system coupled to an Agilent 6460 Triple Quadrupole Mass Spectrometer (Agilent Technologies, USA). The separation of target analytes was performed using a waters ACQUITY UPLC® BEH C18 column (2.1 × 100 mm, 1.7 μm) with a waters ACQUITY UPLC® Protein BEH C18 VanGuard™ Pre- column (2.1 × 5 mm, 1.7 μm). The column temperature was maintained at 40 °C during the analytical procedure. The sample injection volume was 10 μL and the mobile phase flow rate was 0.2 mL/min. Two kinds of mobile phase were used, including 2 mmol/L ammonium acetate in ultrapure water (A) and acetonitrile (B) with an initial proportion of A:B 95:5. These conditions were maintained for 0.5 min, then adjusted to A:B 5:95 over 9.5 min and maintained for 2 min, then returned to the initial conditions over 0.5 min and maintained for 0.5 min. Quadrupole Mass Spectrometry (Agilent Technologies, USA) was performed using an ion spray source operated in negative electrospray ionization

(ESI) mode. The analytes were qualified and quantified in multiple reaction monitoring (MRM) mode. The mass spectrometer parameters were as follows: gas temperature 250 °C, gas flow 5 L/min, nebulizer 50 psi, sheath gas temperature 250 °C, sheath gas flow 11 L/min and capillary –3500 V.

1.3. Quality assurance and quality control

The method detection limit (MDL) and the method quantification limit (MQL) were determined as three-fold and ten-fold the signal/noise based on the matrix samples, respectively. One instrument blank and one procedural blank were analyzed in every ten samples to monitor the quality of analysis. A standard calibration curve was prepared using eight concentrations ranging from 0.1 to 500 ng/mL, which was then utilized for quantification, with the correlation coefficients (r^2) of all targeted PFASs being over 0.99. The matrix spiked recoveries of 20 analytical PFASs ranged from 64% to 124% for solid samples and 50% to 108% for liquid samples, respectively, while the method detection limits of 20 individual PFASs ranged from 0.03 to 0.5 ng/g. Other detailed information, including MDL, MQL and matrix spike recoveries of each targeted analytes is provided in Appendix A Table S3.

1.4. Calculation of annual PFOA consumption in PTFE products

The annual consumption (AC) of PFOA in PTFE products was calculated to estimate the total level of PFOA usage in fluoropolymer manufacturing in China. The AC can be calculated using the following Eq. (1)

$$AC_i = TC \times R_i \times C_i / 1000 \quad (1)$$

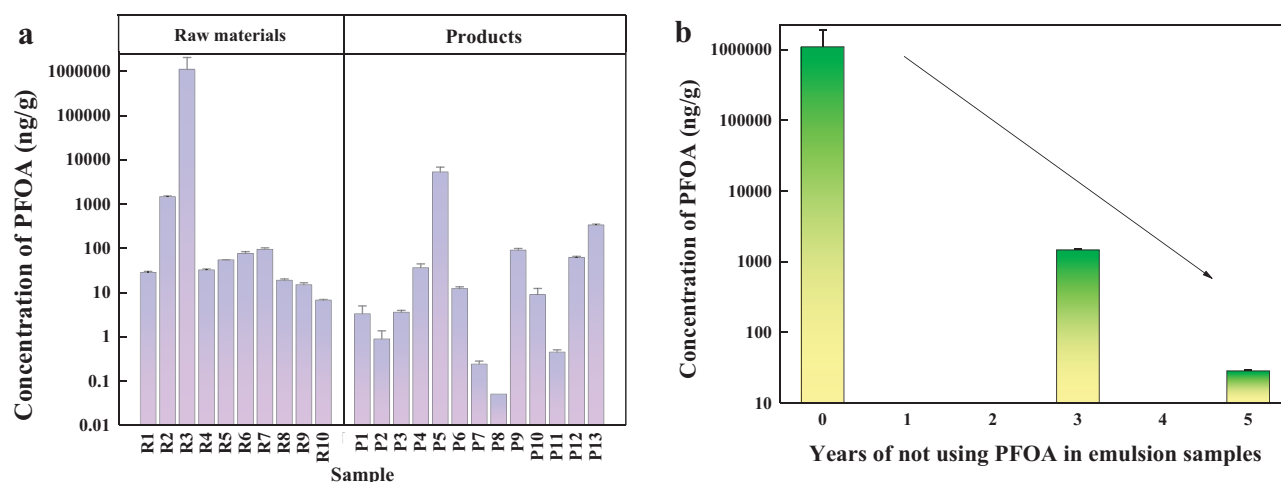


Fig. 1 – (a) Concentration of PFOA in samples of fluoropolymer raw materials ($n = 10$) and products ($n = 13$) collected from the fluoropolymer manufacturers and (b) concentration of PFOA in three emulsion samples collected from the same factory.

Where AC_i (g/year) is the annual consumption of PFOA in each PTFE product; TC (ton/year) is the total annual consumption of PTFE; R_i is the ratio of each PTFE product to total PTFE consumption; and C_i (ng/g) is the mean concentration of PFOA in each PTFE product.

1.5. Statistical analysis

Descriptive statistical analysis was performed using OriginPro V.v.0 (OriginLab Co.) and Microsoft Excel (2010) software. Principal component analysis (PCA) and hierarchical cluster analysis (HCA) were performed using IBM SPSS Statistics v.22 (SPSS Inc.) and OriginPro v.9.0 (OriginLab Co.), respectively. The concentrations of analytes below the MDL were reported as being <MDL.

2. Results and discussion

2.1. The concentration of PFOA in fluoropolymer raw material and product samples

Among the 23 samples, R1 to R10 were raw materials, while P1 to P13 were fluoropolymer products. The PFOA concentration ranged from <MDL to 1.1 mg/g in the 23 tested samples from fluoropolymer manufacturers (Fig. 1a). The concentration of PFOA in 12 of the samples (52%) did not exceed the limit value 25 ppb imposed by the European Union (EU, 2020). Fig. 1 shows that the concentrations of PFOA in raw materials (6.7 to 1.1×10^6 ng/g) were significantly higher than in products (<MDL to 5.3×10^3 ng/g) based on Mann-Whitney Test analysis at the 0.05 level. This reduction in concentration might occur because, in the later manufacturing procedures such as extrusion molding, PFOA either remains in an emulsion form or is volatilized at high temperatures (Prevedouros et al., 2006).

The highest concentration of PFOA appeared in a PTFE emulsion from sample R3 (1.1×10^6 ng/g), which was polymerized using PFOA as an emulsifier. Samples R1 and R2 were also

collected from the same manufacturing factory as R3. However, PFOA had not been used in the manufacturing of R1 and R2 in the previous 5 and 3 years, respectively (Table 1). Over the last 5 years since the use of PFOA in the polymerization of PTFE emulsions was stopped, the levels of PFOA were found to continually reduce in samples (Fig. 1b). The levels of PFOA declined from 1.1×10^6 ng/g to 1.5×10^3 ng/g over the first 3 years, declining further to 28.4 ng/g by 5 years. This indicates that after the use of PFOA in fluoropolymerization in China was stopped, PFOA contamination levels reduced significantly.

The samples R8–10 (6.7 to 18.9 ng/g) were all PTFE dispersion resins in which the concentrations of PFOA was significantly (at the 0.05 level) lower than in PTFE emulsion samples R1–7 (28.4 to 1.1×10^6 ng/g). The reason for this may be that the majority of PFOA salts (APFO) remained in the emulsion, with a small proportion transferred to the solid PTFE material after the dispersion process.

According to the information conveyed by fluoropolymer manufacturers, ten of the analyzed samples, including seven raw material samples R1, R2, R4, R5, R6, R7, R9, and three product samples P2, P5, P6, were all manufactured without PFOA (Table 1). However, PFOA was still detected in all of these samples at varying concentrations (from 0.9 to 1.5×10^4 ng/g), which may be due to the transfer of historical residues from tools, reactors and pipes used in polymerization, or from contact with other media during transportation. Therefore, to reduce the levels of PFOA contamination, fluoropolymer manufacturers should change either their production process or develop substitutes for PFOA, while old reactors and pipes which potentially contain high levels of PFOA residues should be replaced.

PFOA was detected in most samples except extrusion pipe samples P7 and P8. Among the two extrusion samples, P7 contained 0.24 ng/g PFOA (higher than MDL but below MQL), while P8 had a PFOA concentration below the MDL. This might result from the extrusion molding step after polymerization. At the start of polymerization, PFOA salts are added to the reactor as a surfactant and after polymerization, a large proportion of PFOA salts are transferred into the extrusion step

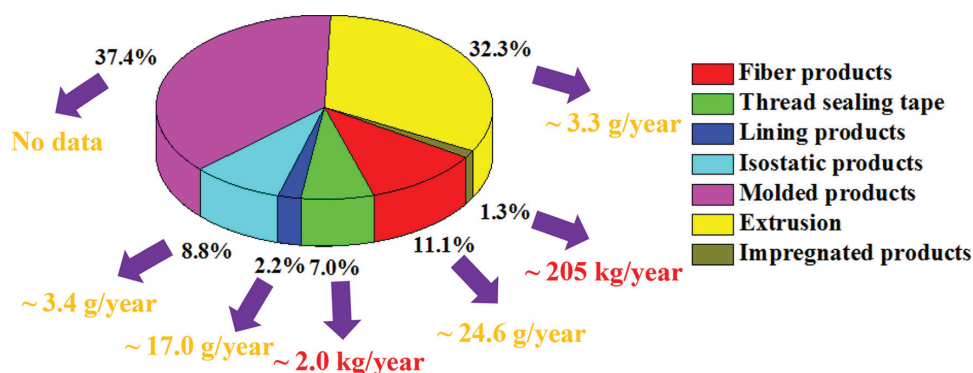


Fig. 2 – Composition of PTFE products and estimated amount of PFOA in different product types produced in China. The proportion of each product type is shown in black and the estimated amount of PFOA is shown in red or yellow.

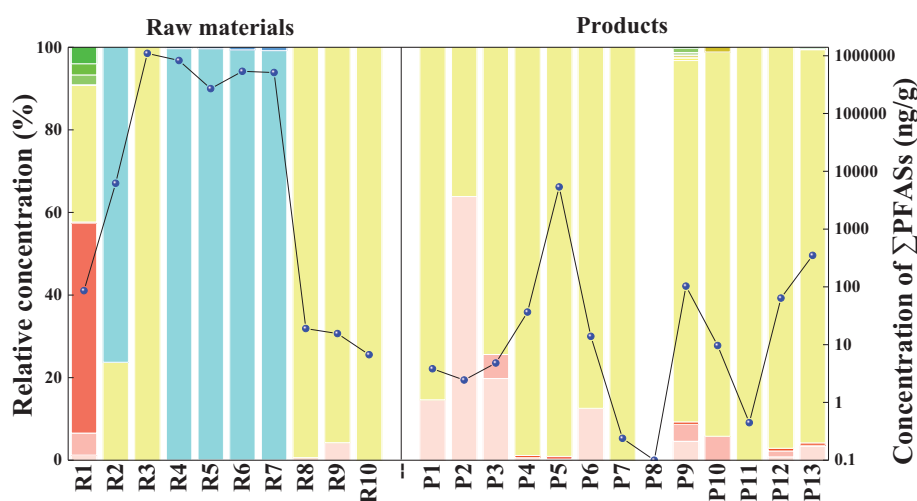


Fig. 3 – Individual PFASs composition (bar chart) and total PFASs concentration (line chart) of 23 raw material and product samples.

along with the emulsion. The extrusion molding step is usually performed under high pressure and high-temperature conditions. The boiling point of PFOA is 188 °C, which is lower than the extrusion temperature (generally above 200 °C) (UNEP, 2016). Under these severe conditions, PFOA can easily be vaporized/removed from the emulsion. Therefore, occupational exposure of workers to PFOA in fluoropolymer manufacturing plants requires urgent attention.

PTFE is the most widely produced and used fluoropolymer, with a wide range of applications (Pladis et al., 2014; Chen, 2019). Therefore, the annual amount of PFOA used in PTFE products was estimated. According to incomplete statistics from the Fluoroplastics Processing Subcommittee China Plastics Association (Chen, 2019), the consumption of PTFE was approximately 86,000 tonnes in 2018 (Chen, 2019). Fig. 3 shows the composition of PTFE products in China. The data was used to calculate the amount of PFOA consumed in these PTFE products. The highest amount of PFOA was used in impregnated products, reaching 205 kg/year, although it only accounted for 1.3% of the total PTFE consumption. The amount of PFOA contained in thread sealing tape was the second highest (~ 2.0 kg/year), at two- or three-orders of magnitude higher

than other products (except impregnated products). Thus, impregnated products and thread sealing tape require more attention due to their high PFOA load and the possible release of PFOA from these products to the environment.

2.2. Concentration of other PFASs in the samples and individual compounds composition

In this study, twenty targeted PFASs were analyzed in fluoropolymer raw material and product samples. Table 2 shows the concentrations and detection frequencies of all analytes. The total concentration of PFASs except PFOA in the fluoropolymer products samples ranged from < MDL (0.1 ng/g) to 50.3 ng/g. The predominant PFASs in fluoropolymer products were ranked in the order of: PFOA (over 99%) > PFHxA (0.62%) > PFBA (0.60%). PFOA was often associated with the presence of PFHxA and PFBA, which indicated that these two compounds might be the byproducts of PFOA. They are all perfluorocarboxylic acids with an even number of carbon atoms in higher concentrations than odd numbers, which can be attributed to the PFOA synthesis method. For raw materials, HFPO-TrA (65.8%) was the dominant compound followed by

Table 2 – Concentrations and detection frequencies (DF) of PFASs in samples collected from fluoropolymer manufacturers.

	Min (ng/g)	Median(ng/g)	Max (ng/g)	Mean (ng/g)	DF (%)
PFBA	<MDL	0.3	13.3	1.7	70
PFPeA	<MDL	<MDL	4.6	0.6	44
PFHxA	<MDL	<MDL	43.6	3.6	26
PFHpA	<MDL	<MDL	2.1	0.2	39
PFOA	<MDL	23.7	1.1×10^6	5.0×10^4	96
PFNA	<MDL	<MDL	0.5	0.0	9
PFDA	<MDL	<MDL	0.4	0.0	13
PFUdA	<MDL	<MDL	0.5	0.0	26
PFDoA	<MDL	<MDL	1.7	0.1	22
PFTTrDA	<MDL	<MDL	2.1	0.2	22
PFTeDA	<MDL	<MDL	2.3	0.1	17
PFHxDA	<MDL	<MDL	3.4	0.3	17
PFBS	<MDL	<MDL	<MDL	<MDL	0
PFHxS	<MDL	<MDL	<MDL	<MDL	0
PFOS	<MDL	<MDL	<MDL	<MDL	0
PFDS	<MDL	<MDL	<MDL	<MDL	0
HFPO-DA	<MDL	<MDL	168.2	26.1	17
HFPO-TrA	<MDL	<MDL	8.2×10^5	9.3×10^4	22
HFPO-TeA	<MDL	<MDL	4.2×10^3	487	17
NaDONA	<MDL	<MDL	<MDL	<MDL	0

PFOA (33.9%), HFPO-TeA (0.3%) and HFPO-DA (0.02%). The total concentration of PFASs (except PFOA) in the fluoropolymer raw material samples ranged from < MDL (0.1 ng/g) to 8.3×10^5 ng/g. HFPO-TrA, HFPO-TeA and HFPO-DA, hexafluoropropylene oxide (HFPO, C_3F_6O) oligomers, were typical alternatives to PFOA in fluoropolymer manufacturing and had been detected surrounding a major fluoropolymer manufacturing plant in China according to previous studies (Heydebreck et al., 2015; Pan et al., 2017; Song et al., 2018). The highest concentration of HFPO-TrA was observed in an emulsion sample R4 (8.3×10^5 ng/g), at a level close to the highest concentration of PFOA in (R3 1.1×10^6 ng/g) which indicates that HFPO-TrA had substituted for PFOA and been used heavily in the manufacturing of fluoropolymer emulsions in China.

The composition and total concentration of PFASs in fluoropolymer samples are shown in Fig. 3. PFOA was the dominant compound in most of the samples except P2, P8, R1, R2, R4, R5, R6 and R7. In sample P2, PFBA was dominant compound followed by PFOA. Although P1 and P2 were both staple fibers, they were polymerized with and without PFOA, respectively (Table 1). Therefore, the occurrence of PFOA in P2 indicates that PFOA residues gradually accumulated in the reactors or pipes. For P8, the concentrations of PFASs, including PFOA, were all below the MDL. PFHxA was the dominant compound in R1, followed by PFOA. The sample R1 was a type of coating emulsion that had been polymerized without PFOA for the past five years (Table 1). Other shorter-chain PFCAs, including PFPeA, and longer-chain PFCAs, including PFTeDA and PFTTrA accounted for a significant proportion of R1. The occurrence of these PFCAs in the products may be due to the fact that they are byproducts of PFOA which persist in the fluoropolymerization reactors. Samples R2 and R4–7 contained high levels of HFPO-TrA implying that this compound was the dominant emulsifier used in these emulsion samples. According to Appendix A Table S5, HFPO-DA and HFPO-TeA were also detected in emulsion samples R4–7, at levels three- and two-orders of magnitude lower than HFPO-TrA, respectively. This indicates

that oligomers of hexafluoropropylene oxide were major alternatives to PFOA in fluoropolymer manufacturing in China and that HFPO-TrA was the dominant monomer.

The concentrations of four perfluorosulfonic acids (PFSAs), including PFBS, PFHxS, PFOS and PFDS, were all below the MDL (0.03 ng/g) in the analyzed fluoropolymer raw material and product samples might due to that PFSAs are scarcely used in fluoropolymer polymerization. NaDONA was not detected in any samples, was might be because there has been minimal use of this compound in fluoropolymer manufacturing in China.

2.3. Statistical analysis of PFASs in fluoropolymer raw material and product samples

In order to further distinguish the composition of PFASs in fluoropolymer raw material and product samples, PCA was conducted to investigate the main PFAS monomer group profile characteristics (Fig. 3, Appendix A Table S8). PCA analysis results showed that the first, second and third principal components accounted for 33.7%, 20.6% and 18.9% of variance for PFASs. Component 1 was highly loaded with PFCAs including PFBA, PFPeA, PFHxA, PFHpA, PFNA, PFDA, PFUdA and PFTTrA. Component 2 was composed of medium-chains PFCAs with PFNA and PFDA being the most highly contributing monomer groups. Component 3 contained a high load of HFPO-DA, HFPO-TrA and HFPO-TeA. As shown in the score plot (Fig. 4a) all data was clustered into two groups. The distribution of fluoropolymer product samples varied in component 1 and 2, indicating that PFCAs monomers were the main influencing factors among products samples. For raw materials, component 3 had an important influence on the distribution of all ten samples, indicating that HFPO oligomers were the main differing components among raw materials.

Fig. 4b shows a dendrogram of the 23 samples obtained from HCA. Seven samples (R2–7 and P5) which were all emul-

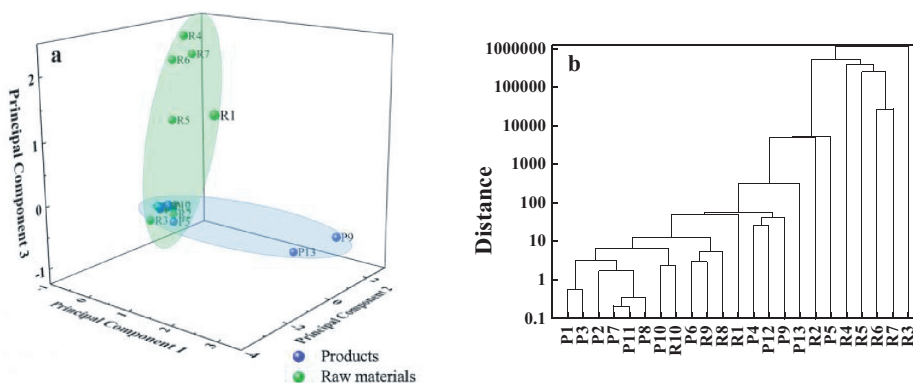


Fig. 4 – (a) Principal component analysis (PCA) score plot of PFASs in fluoropolymer raw materials ($n = 10$) and products ($n = 13$) and (b) a dendrogram showing the hierarchical cluster analysis (HCA) of fluoropolymer raw material and product samples.

sions or produced from emulsions, contained a high concentration of Σ PFASs (> 1000 ng/g). Samples R1, P4, P12, P9 and P13 contained a lower concentration of Σ PFASs (10 to 500 ng/g). The concentrations of Σ PFASs in the remaining eleven samples, which were made from or belong to dispersion resins, were less than 10 ng/g. These results showed that dispersion resin raw materials and products contained lower levels of PFASs than emulsion samples.

2.4. Environmental implications, challenges faced by the development of PFOA substitutes and further perspectives

In this study, the occurrence of PFOA in fluoropolymer raw materials and products from manufacturers in China were assessed. PFOA was detected in high concentrations in industrial fluoropolymer raw materials and products, which can eventually be released into the environment and pose a potential threat to both natural ecosystems and humans. Moreover, the lower observed concentrations of PFOA in products, than in raw materials, implies that the manufacturing procedure might result in the elimination of PFOA due to either liquid-solid transformation or evaporation. The release of PFOA via evaporation during fluoropolymer manufacture presents an important occupational exposure pathway and deserves greater research attention. Moreover, the environment surrounding fluoropolymer production plants may suffer from a high risk due to the release of these compounds, particularly if there are no effective techniques or methods in place to recycle or remove PFOA and other PFASs (including substitutes) from effluent.

These results indicate that despite PFOA being restricted, fluoropolymers still contain high concentrations of PFOA. Therefore, PFOA continues to be a heavily used chemical in China's fluoropolymer industry. After the enactment of the Stockholm Convention restrictions on PFOA came into force, China, as one of the parties of the Stockholm Convention, had to restrict the production and consumption of PFOA and develop environmental-friendly substitutes for PFOA. As a result, some manufacturers are actively seeking suitable substitutes and adjusting the structural components of their products accordingly (Wang et al., 2013). However, due to the unique sur-

face tension produced by the carbon-fluorine bonds, currently available alternatives still exhibit similar molecular structures (Wang et al., 2013). Therefore, these alternatives are also likely to persist in the environment, while also presenting the risk of being transformed into persistent PFASs called "never-ending chemicals" (Wang et al., 2017). For example, some industries are utilizing structurally similar alternatives, including carbon homologues containing lower fluoride contents (short-chain PFASs) and other polyfluoroalkylether-based substances, with these short-chain PFASs considered to be less toxic and having lower levels of bioaccumulation (Brendel et al., 2018). However, research evidence indicated that short-chain PFASs also present a hazard to the natural environment and humans. For example, it has been demonstrated that PFHxA, a short-chain PFAS, has the potential to adversely affect the environment and biota (Gomis et al., 2018). Furthermore, some other alternatives have also been found to induce adverse environmental effects. For instance, HFPO-DA is one of the common alternatives to PFOA used in the polymerization of fluoropolymers (Wang et al., 2013) and was detected in some of the fluoropolymer samples assessed in the present study. However, the safety of HFPO-DA remains controversial as the environmental assessment data for this substance is not sufficient, with some studies reporting that HFPO-DA exhibits a similar toxic potential to PFOA (Blake et al., 2020; Gomis et al., 2018). High levels of HFPO-TrA and HFPO-TeA were also detected in the received samples, although few studies are available on the toxicity and risk assessment of HFPO-TrA and HFPO-TeA. Research indicates that incidences where substitute compounds have been used without adequate environmental impact assessment, has resulted in undesirable consequences (Liu et al., 2017; Pan et al., 2017; Shi et al., 2016). It is also likely that replacement compounds may be converted into toxic substances in the environment (Li et al., 2019; Shaw et al., 2018; Wang et al., 2015). Thus, evaluation of the product safety and environmental friendliness of novel alternatives is a major issue that needs to be addressed urgently. More measures should be implemented to develop the eco-friendly alternatives for PFOA for use in polymerization, or the currently used production methods require redevelopment.

Some previous research has suggested the implementation of a class-based method to more effectively eliminate the unnecessary use of PFASs and help develop safer alternatives (Kwiatkowski et al., 2020). However, some developers disagree with the management of perfluorinated compounds on a class basis as it is challenging to choose alternatives while managing perfluorinated compounds as a class. However, if a brand-new production line is established to produce fluorine-free options, a sharp increase in input costs will be incurred by manufacturers. Some studies have investigated new fluoropolymer polymerization methods without the use of surfactants, although these are still at an experimental stage (Jaye and Sletten, 2019; Pan et al., 2014).

China is one of the largest global producers and exporters of fluoropolymer products. Proper risk management of PFASs is essential for fluorine chemical production and consumption worldwide. As China is one of the parties of the Stockholm Convention, it is necessary to urgently improve the management and control of PFOA using domestic legislation and to strengthen the environmental monitoring of PFASs. Furthermore, safe, environment-friendly and economical PFASs substitutes and alternative technologies should be systematically developed using multidisciplinary projects, combining industry and scientific research. The environmental safety and toxicity of PFASs substitutes and alternative technologies should be considered during development, promoting cleaner production, while also developing a recycling-based economy in China.

Moreover, active international cooperation among countries, organizations, corporations and consumers should be encouraged during the development of PFASs substitutes. As a result, advances in the safe substitutes for PFASs and relevant technologies can be shared, helping to effectively control their production and consumption, while also minimizing the environmental hazard they present.

4. Conclusions

This study assesses the occurrence of PFASs in fluoropolymer raw material and product samples made in China. PFOA was the predominant compound in industrial fluoropolymer raw materials and products, which can eventually be released into the environment, posing a potential threat to the environment and humans. Results show that the concentration of PFOA in products was lower than in raw materials, implying that the manufacturing procedure might lead to the elimination of PFOA by either liquid-solid transformation or evaporation. The release of PFOA via evaporation during fluoropolymer manufacturing is of concern and deserves greater research attention. Furthermore, the detection of HFPO-DA, HFPO-TrA and HFPO-TeA in some of fluoropolymer samples demonstrates that oligomers of hexafluoropropylene oxides have been used in fluoropolymer manufacturing in China as a substitute for PFOA. The management and environmental monitoring of PFOA and other PFASs using domestic legislation are necessary in China.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 21625702).

Appendix A. Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2021.01.027.

REFERENCES

- Bangma, J., Eaves, L.A., Oldenburg, K.S., Reiner, J., Manuck, T., Fry, R.C., 2020. Identifying risk factors for levels of per- and polyfluoroalkyl substances (PFAS) in the placenta in a high-risk pregnancy cohort in North Carolina. *Env. Sci. Technol.* 54 (13), 8158–8166.
- Bečanová, J., Melymuk, L., Vojta, Š., Komprdová, K., Klánová, J., 2016. Screening for perfluoroalkyl acids in consumer products, building materials and wastes. *Chemosphere* 164, 322–329.
- Blake, B.E., Cope, H.A., Hall, S.M., Keys, R.D., Mahler, B.W., McCord, J., et al., 2020. Evaluation of maternal, embryo, and placental effects in CD-1 mice following gestational exposure to perfluorooctanoic acid (PFOA) or hexafluoropropylene oxide dimer acid (HFPO-DA or GenX). *Environ. Health Perspect.* 128 (2), 027006.
- Brendel, S., Fetter, E., Staude, C., Vierke, L., Biegel-Engler, A., 2018. Short-chain perfluoroalkyl acids: environmental concerns and a regulatory strategy under REACH. *Env. Sci. Eur.* 30, 9.
- Bruno, A., 2010. Controlled radical (Co)polymerization of fluoromonomers. *Macromolecules* 43 (24), 10163–10184.
- Chen, S., 2019. Development and change of China fluoroplastics market. In: china international forum on development of fluoroplastics processing. Guilin, China. Nov 5–6.
- Choi, Y.J., Lazcano, R.K., Yousefi, P., Trim, H., Lee, L.S., 2019. Perfluoroalkyl acid characterization in U.S. Municipal organic solid waste composts. *Environ. Sci. Technol. Lett.* 6 (6), 372–377.
- Codling, G., Hosseini, S., Corcoran, M.B., Bonina, S., Lin, T., Li, A., et al., 2018. Current and historical concentrations of poly and perfluorinated compounds in sediments of the northern Great Lakes – Superior, Huron, and Michigan. *Environ. Pollut.* 236, 373–381.
- Cui, Q.Q., Pan, Y.T., Zhang, H.X., Sheng, N., Wang, J.S., 2018. Occurrence and tissue distribution of novel perfluoroether carboxylic and sulfonic acids and legacy per/polyfluoroalkyl substances in black-spotted frog (*pelophylax nigromaculatus*). *Environ. Sci. Technol.* 52 (3), 982–990.
- Demarteau, J., Améduri, B., Ladmiral, V., Mees, M.A., Hoogenboom, R., Debuigne, A., et al., 2017. Controlled synthesis of fluorinated copolymers via cobalt-mediated radical copolymerization of perfluorohexylethylene and vinyl acetate. *Macromolecules* 50 (10), 3750–3760.
- EU (European Union), 2020. Commission regulation (EU) 2020/784 of 8 April 2020. Available: <https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32020R0784&qid=1609204057764&from=EN>. Accessed January 3, 2021.
- Fromme, H., Wockner, M., Roscher, E., Volkel, W., 2017. ADONA and perfluoroalkylated substances in plasma samples of German blood donors living in South Germany. *Int. J. Hyg. Env. Heal.* 220 (2), 455–460.
- Gao, K., Zhuang, T.F., Liu, X., Fu, J.J., Zhang, J.X., Fu, J., et al., 2019. Prenatal exposure to per- and polyfluoroalkyl substances (PFASs) and association between the placental transfer efficiencies and dissociation constant of serum proteins-PFAS complexes. *Env. Sci. Technol.* 53 (11), 6529–6538.
- Gomis, M.I., Vestergren, R., Borg, D., Cousins, I.T., 2018. Comparing the toxic potency in vivo of long-chain perfluoroalkyl acids and fluorinated alternatives. *Environ. Int.* 113, 1–9.

- Gui, D., Zhang, M., Zhang, T., Zhang, B., Lin, W.Z., Sun, X., et al., 2019. Bioaccumulation behavior and spatiotemporal trends of per- and polyfluoroalkyl substances in Indo-Pacific humpback dolphins from the Pearl River Estuary, China. *Sci. Total Environ.* 658, 1029–1038.
- Heydebreck, F., Tang, J.H., Xie, Z.Y., Ebinghaus, R., 2015. Alternative and legacy perfluoroalkyl substances: differences between European and Chinese river/estuary systems. *Env. Sci. Technol.* 49 (14), 8386–8395.
- Jahnke, A., Berger, U., Ebinghaus, R., Temme, C., 2007. Latitudinal gradient of airborne polyfluorinated alkyl substances in the marine atmosphere between Germany and South Africa (53 degrees N–33 degrees S). *Environ. Sci. Technol.* 41 (9), 3055–3061.
- Jaye, J.A., Sletten, E.M., 2019. Modular and processable fluoropolymers prepared via a safe, mild, iodo-ene polymerization. *ACS Cent. Sci.* 5, 982–991.
- Jin, H.B., Zhang, Y.F., Jiang, W.W., Zhu, L.Y., Martin, J.W., 2016. Isomer-specific distribution of perfluoroalkyl substances in blood. *Environ. Sci. Technol.* 50 (14), 7808–7815.
- Kwiatkowski, C.F., Andrews, D.Q., Birnbaum, L.S., Bruton, T.A., DeWitt, J.C., Knappe, D.R.U., et al., 2020. Scientific basis for managing PFAS as a chemical class. *Environ. Sci. Technol. Lett.* 7 (8), 532–543.
- Lang, J.R., Allred, M.K., Field, J.A., Levis, J.W., Barlaz, M.A., 2017. National estimate of per- and polyfluoroalkyl substance (PFAS) release to U.S. Municipal landfill leachate. *Environ. Sci. Technol.* 51 (4), 2197–2205.
- Li, R., Munoz, G., Liu, Y.N., Sauvé, S., Ghoshal, S., Liu, J.X., 2019. Transformation of novel polyfluoroalkyl substances (PFASs) as co-contaminants during biopile remediation of petroleum hydrocarbons. *J. Hazard. Mater.* 362, 140–147.
- Liu, Y.W., Ruan, T., Lin, Y.F., Liu, A.F., Yu, M., Liu, R.Z., et al., 2017. Chlorinated polyfluoroalkyl ether sulfonic acids in marine organisms from Bohai Sea, China: occurrence, temporal variations, and trophic transfer behavior. *Environ. Sci. Technol.* 51 (8), 4407–4414.
- Liu, Y.Q., Zhang, Y., Li, J.F., Wu, N., Li, W.P., Niu, Z.G., 2019. Distribution, partitioning behavior and positive matrix factorization-based source analysis of legacy and emerging polyfluorinated alkyl substances in the dissolved phase, surface sediment and suspended particulate matter around coastal areas of Bohai Bay. *Env. Pollut.* 246, 34–44.
- Lu, Y., Gao, K., Li, X.N., Tang, Z., Xiang, L., Zhao, H.Z., et al., 2019. Mass spectrometry-based metabolomics reveals occupational exposure to per- and polyfluoroalkyl substances relates to oxidative stress, fatty acid β -oxidation disorder, and kidney injury in a manufactory in China. *Env. Sci. Technol.* 53 (16), 9800–9809.
- Mumtaz, M., Bao, Y.X., Liu, L.Q., Huang, J., Cagnetta, G., Yu, G., 2019. Per- and polyfluoroalkyl substances in representative fluorocarbon surfactants used in Chinese film-forming foams: levels, profile shift, and environmental implications. *Environ. Sci. Technol. Lett.* 6 (5), 259–264.
- Nilsson, H., Kärrman, A., Rotander, A., van Bavel, B., Lindström, G., Westberg, H., 2013. Professional ski waxers' exposure to PFAS and aerosol concentrations in gas phase and different particle size fractions. *Environ. Sci. Process. Impacts* 15, 814–822.
- Pan, M.W., Yang, L.Y., Wang, J.C., Tang, S., Zhong, G.J., Su, R., et al., 2014. Composite poly(vinylidene fluoride)/polystyrene latex particles for confined crystallization in 180nm nanospheres via emulsifier-free batch seeded emulsion polymerization. *Macromolecules* 47 (8), 2632–2644.
- Pan, Y.T., Zhang, H.X., Cui, Q.Q., Sheng, N., Yeung, L.W.Y., Guo, Y., et al., 2017. First report on the occurrence and bioaccumulation of hexafluoropropylene oxide trimer acid: an emerging concern. *Env. Sci. Technol.* 51 (17), 9553–9560.
- Peaslee, G.F., Wilkinson, J.T., McGuinness, S.R., Tighe, M., Caterisano, N., Lee, S., et al., 2020. Another pathway for firefighter exposure to per- and polyfluoroalkyl substances: firefighter textiles. *Environ. Sci. Technol. Lett.* 7 (8), 594–599.
- Pladis, P., Alexopoulos, A.H., Kiparissides, C., 2014. Mathematical modeling and simulation of vinylidene fluoride emulsion polymerization. *Ind. Eng. Chem. Res.* 53 (18), 7352–7364.
- Prevedouros, K., Cousins, I.T., Buck, R.C., Korzeniowski, S.H., 2006. Sources, fate and transport of perfluorocarboxylates. *Env. Sci. Technol.* 40 (1), 32–44.
- Puts, G.J., Crouse, P., Ameduri, B.M., 2019. Polytetrafluoroethylene: synthesis and characterization of the original extreme polymer. *Chem. Rev.* 119 (3), 1763–1805.
- Rand, A.A., Mabury, S.A., 2011. Perfluorinated carboxylic acids in directly fluorinated high-density polyethylene material. *Env. Sci. Technol.* 45 (19), 8053–8059.
- Shaw, D.M.J., Gabriel, M., Bottos, E.M., Vo, D.S., Sébastien, S., Jinxia, L., et al., 2018. Degradation and defluorination of 6:2 fluorotelomer sulfonamidoalkyl betaine and 6:2 fluorotelomer sulfonate by *Gordonia* sp. strain NB4-1Y under sulfur-limiting conditions. *Sci. Total Environ.* 647 (10), 690–698.
- Shi, Y.L., Vestergren, R., Xu, L., Zhou, Z., Li, C.X., Liang, Y., et al., 2016. Human exposure and elimination kinetics of chlorinated polyfluoroalkyl ether sulfonic acids (Cl-PFESAs). *Environ. Sci. Technol.* 50 (5), 2396–2404.
- Song, X.W., Vestergren, R., Shi, Y.L., Huang, J., Cai, Y., 2018. Emissions, transport, and fate of emerging per- and polyfluoroalkyl substances from one of the major fluoropolymer manufacturing facilities in China. *Env. Sci. Technol.* 52 (17), 9694–9703.
- Sznajder-Katarzyńska, K., Surma, M., Wiczowski, W., Cieřlik, E., 2019. The perfluoroalkyl substance (PFAS) contamination level in milk and milk products in Poland. *Int. Dairy J.* 96, 73–84.
- UNEP (United Nations Environment Programme), 2019. Listing of perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds. Available: <http://chm.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx>. Accessed June 8, 2020.
- UNEP (United Nations Environment Programme), 2016. Pentadecafluorooctanoic acid (PFOA, Perfluorooctanoic acid), its salts and PFOA-related compounds. Available: <http://chm.pops.int/TheConvention/ThePOPs/AllPOPs/tabid/2509/Default.aspx>:2016. Accessed June 16, 2020.
- UNEP (United Nations Environment Programme), 2009. Listing of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonfyl fluoride. Available: <http://chm.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx>. Accessed June 8, 2020.
- Wang, T., Vestergren, R., Herzke, D., Yu, J.C., Cousins, I.T., 2016. Levels, isomer profiles, and estimated riverine mass discharges of perfluoroalkyl acids and fluorinated alternatives at the mouths of Chinese rivers. *Env. Sci. Technol.* 50 (21), 11584–11592.
- Wang, Z.Y., Cousins, I.T., Scheringer, M., Buck, R.C., Hungerbühler, K., 2014. Global emission inventories for C4–C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, part II: the remaining pieces of the puzzle. *Environ. Int.* 69, 166–176.
- Wang, Z.Y., Cousins, I.T., Scheringer, M., Hungerbuehler, K., 2015. Hazard assessment of fluorinated alternatives to long-chain perfluoroalkyl acids (PFAAs) and their precursors: status quo, ongoing challenges and possible solutions. *Environ. Int.* 75, 172–179.
- Wang, Z.Y., Cousins, I.T., Scheringer, M., Hungerbühler, K., 2013. Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFASAs) and their potential precursors. *Environ. Int.* 60, 242–248.

- Wang, Z.Y., DeWitt, J.C., Higgins, C.P., Cousins, I.T., 2017. A never-ending story of per- and polyfluoroalkyl substances (PFASs)? *Env. Sci. Technol.* 51 (5), 2508–2518.
- Washington, J.W., Yoo, H., Ellington, J.I., Jenkins, T.M., Libelo, E.L., 2010. Concentrations, distribution, and persistence of perfluoroalkylates in sludge-applied soils near Decatur, Alabama, USA. *Env. Sci. Technol.* 44 (22), 8390–8396.
- Yeung, L.W.Y., De Silva, A.O., Loi, E.I.H., Marvin, C.H., Taniyasu, S., Yamashita, N., et al., 2013. Perfluoroalkyl substances and extractable organic fluorine in surface sediments and cores from Lake Ontario. *Environ. Int.* 59, 389–397.
- Zhang, X.M., Lohmann, R., Sunderland, E.M., 2019. Poly- and Perfluoroalkyl Substances (PFAS) in Seawater and Plankton from the Northwestern Atlantic Margin. *Environ. Sci. Technol.* 53 (21), 12348–12356.
- Zhao, L.X., Zhang, Y.F., Zhu, L.Y., Ma, X.X., Wang, Y., Sun, H.W., et al., 2017. Isomer-specific transplacental efficiencies of perfluoroalkyl substances in human whole blood. *Environ. Sci. Technol. Lett.* 4 (10), 391–398.