



Cite this: *Environ. Sci.: Processes Impacts*, 2022, 24, 1060

A pilot study on extractable organofluorine and per- and polyfluoroalkyl substances (PFAS) in water from drinking water treatment plants around Taihu Lake, China: what is missed by target PFAS analysis?[†]

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Per- and polyfluoroalkyl substances (PFAS) have raised concerns due to their worldwide occurrence and adverse effects on both the environment and humans as well as posing challenges for monitoring. Further collection of information is required for a better understanding of their occurrence and the unknown fractions of the extractable organofluorine (EOF) not explained by commonly monitored target PFAS. In this study, eight pairs of raw and treated water were collected from drinking water treatment plants (DWTPs) around Taihu Lake in China and analyzed for EOF and 34 target PFAS. Mass balance analysis of organofluorine revealed that at least 68% of EOF could not be explained by target PFAS. Relatively higher total target concentrations were observed in 4 DWTPs (D1 to D4) when compared to other samples with the highest sum concentration up to 189 ng L⁻¹. PFOA, PFOS and PFHxS were the abundant compounds. Suspect screening analysis identified 10 emerging PFAS (e.g., H-PFAAs, H-PFESAs and OBS) in addition to target PFAS in raw or treated water. The ratios PFBA/PFOA and PFBS/PFOS between previous and current studies showed significant replacements of short-chain to long-chain PFAS. The ratios of the measured PFAS concentrations to the guideline values showed that some of the treated drinking water exceeds guideline values, appealing for efforts on drinking water safety guarantee.

Received 21st February 2022
Accepted 27th April 2022

DOI: 10.1039/d2em00073c

rsc.li/esp

Environmental significance

Per- and polyfluoroalkyl substances (PFAS) are man-made substances which have been manufactured and used extensively as additives in consumer products since the 1950s. Releases of PFAS have resulted in their detections in various environmental media, especially in drinking water which was identified as one of the major exposure pathways to humans. However, current monitoring of PFAS is far short of what is representative of the entire class of the thousands of compounds. Organofluorine mass balance analysis, therefore, was performed to investigate the extractable organofluorine (EOF) levels and to figure out the levels of unidentified components. This study describes a pilot study of EOF analysis in drinking water, and the results demonstrate a large percentage of unidentified EOF, indicating underestimation of the organofluorine pollution levels. This work also provides important information for drinking water safety assurance and the necessity to identify the unknown compounds.

Introduction

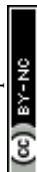
Per- and polyfluoroalkyl substances (PFAS) are a group of fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it)¹ according to the 2021 definition by the Organization for Economic Co-operation and Development (OECD)

and have been manufactured and used around the globe since the 1950s.² Their unique properties including high thermal stability and oil/water repellency³ have made them extensively used as additives in consumer products⁴ and have resulted in their prevalent presence in abiotic and biotic media.^{5–10} Some have raised environmental concerns, and among them, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) were listed in the Stockholm Convention, while perfluorohexane sulfonic acid (PFHxS) is now under review by the committee.¹¹ The regulations have led to the phase-out of these substances, and manufacturers have shifted to the compensatory production and usage of replacements such as some novel PFAS (mainly the substitutes of PFOA and PFOS) which already

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[†] Electronic supplementary information (ESI) available. See <https://doi.org/10.1039/d2em00073c>



showed ubiquitous occurrence.^{12,13} Besides, ultra-short PFAS (C2 and C3) also attract increasing attention due to their mobile properties, and among them, trifluoroacetate (TFA) has already been widely reported in surface water, rainwater, the atmosphere, and sediments.^{14–17}

According to OECD, there are nearly 5000 individual PFAS.¹⁸ Monitoring of all these registered PFAS, however, is challenging since they include a large number of structurally different chemicals.¹⁹ Occurrence of unknown PFAS, including transformation products, may result in increased environmental and human exposure.²⁰ The extractable organofluorine (EOF) has emerged to complement the current PFAS analysis²¹ and plays an important role in providing insight into the amount of unidentified organofluorines through an organofluorine mass balance approach.²² Suspect screening analysis performed by high-resolution mass spectrometry (HRMS) techniques (*e.g.*, quadrupole time-of-flight mass spectrometry (QTOF) and Orbitrap) allows better understanding of other emerging PFAS that are not regularly monitored. Recent studies have identified EOF and different classes of emerging PFAS in various environmental media.^{23–29} These techniques, however, were mostly applied to wastewater or biota samples. Studies focusing on drinking water are limited.

Humans are exposed to PFAS through contact with contaminated media; among them, drinking water consumption can be a major source of PFAS exposure.³ The US Environmental Protection Agency (EPA) and some other agencies or organizations^{30–32} have recommended guideline values for different PFAS in drinking water considering the human health. In China, the limit values of PFOA and PFOS are 80 and 40 ng L⁻¹, respectively. Other PFAS are not the candidate chemicals for regulatory monitoring, making it essential to understand the levels of PFAS in drinking water and to provide data support for further related standards.

Therefore, the present study was conducted to analyze PFAS in water samples collected from eight drinking water treatment plants (DWTPs) around the Taihu Lake Basin, which serves as a major drinking water source in one of the most populous and economically developed regions of China.³³ The objectives of this study were: (i) to conduct extractable organofluorine analysis in drinking water around Taihu Lake; (ii) to investigate the removal efficiency under current DWTP processes in China; (iii) to identify any emerging PFAS in water samples using suspect screening analysis; and (iv) to evaluate the PFAS levels with reference to the guideline values.

Methods and materials

Chemicals and reagents

Extractable organofluorine (EOF) and 34 target PFAS were studied (Table S1†). Native standards of PFCAs (C4–C14, C16, and C18), PFSAs (C2, C4–C10, and C12), fluorotelomer sulfonic acid (FTSAs), novel compounds (hexafluoropropylene oxide dimer acid (HFPO-DA), 6 : 2 chlorinated polyfluorinated ether sulfonate (6 : 2 Cl-PFESA), 8 : 2 chlorinated polyfluorinated ether sulfonate (8 : 2 Cl-PFESA), 3*H*-perfluoro-3-[(3-methoxypropoxy) propanoic acid] (ADONA), and perfluoro-4-

ethylcyclohexanesulfonate (PFECHS)), isotope-labeled PFCAs (C4–C12, C14, and C16), PFSAs (C4, C6, and C8) and isotope-labeled HFPO-DA were all purchased from Wellington Laboratories (Guelph, ON, Canada). TFA and perfluoropropanoic acid (PFPrA) were purchased from Sigma Aldrich (Darmstadt, Germany), and perfluoroethane sulfonic acid (PFETs) was purchased from Kanto Chemical Co. Inc (Tokyo, Japan). All standard solutions were prepared in HPLC grade methanol. For EOF analysis, a PFOS standard from Sigma-Aldrich was used.

Sample collection and pretreatment

The investigated DWTPs are located in 5 cities around the Taihu Lake Basin, China (Fig. 1). River and river network water were used as water sources in D5 and D8, while the water sources of the other 6 DWTPs were lake water. The overall treatment process includes pre-ozonation, coagulation, sedimentation, sand filtration, post-ozonation, bio-activated carbon and disinfection, although there are some differences between DWTPs. Both raw and treated water samples were collected in August 2019. In each sampling site, two water samples including raw and the corresponding treated water (each approximately 2 L) were collected. All samples were collected in pre-cleaned polypropylene bottles, shipped to the laboratory, and kept in the cooling room (4 °C) until analysis.

The water sample (500 mL) was first filtered by using a 0.47 μm membrane. Then the membrane was sonicated for 10 min in MeOH, and the MeOH was poured into the water sample. After this, 2 ng internal standard was spiked into the water samples. The solid phase extraction (SPE) method with Oasis WAX cartridges (Waters 150 mg, 6 mL, and 30 mm) was used for extraction. In brief, the cartridges were pre-conditioned with 4 mL 0.1% NH₄OH/methanol, 4 mL methanol and 4 mL Milli-Q water. After loading the samples, the cartridges were washed with 4 mL of MilliQ-water, 4 mL of an ammonium acetate buffer solution (pH = 4) and then dried under vacuum for 30 min. Eluted with 4 mL 0.1% NH₄OH/methanol, the anionic fraction was then evaporated under nitrogen gas to a final volume of 200 μL. Then, aliquots of the samples were taken and mixed with different volumes of the aqueous mobile phase to obtain different compositions of the organic solvent of 80% (ultrashort PFAS analysis) and 40% (remaining PFAS analysis) in the vial with the addition of 2 ng recovery standard for PFAS analysis.



Fig. 1 Sampling sites around the Taihu Lake Basin showing eight DWTPs (D1 to D8).



Sample pretreatment of the extractable organofluorine

The pretreatment of EOF was similar to the method mentioned above, except that both the internal standard and recovery standard were not added. In addition, a more extensive wash was used after loading the samples; cartridges were washed with 20 mL 0.01% NH₄OH/water (to remove inorganic fluoride), 10 mL MilliQ three times, followed by 4 mL ammonium acetate buffer and 4 mL 20% methanol/water. Aliquots of the samples were subjected to PFAS analysis as described above, to enable calculation of the EOF mass balance, and 100 μL of the aliquot was subjected to EOF analysis.

Instrumental analysis

Separation of the ultra-short analytes was performed using an Acquity Ultra Performance Convergence Chromatography (UPC²) system coupled with a tandem mass spectrometer (Waters Corporation, Milford, USA) that was operated in the electrospray negative ionization mode with the source temperature at 150 °C. The extracts were injected into a Torous™ DIOL column (3 mm × 150 mm, 1.7 μm; Waters Corporation, Milford, USA) with supercritical CO₂ (A) and 0.1% ammonium hydroxide in methanol (B) as the mobile phase. Details of the method are provided elsewhere.³⁴

The remaining target compounds were analyzed by using the Acquity UPLC system coupled with the Xevo TQ-S tandem mass spectrometer (Waters Corporation, Milford, USA) that was operated in the electrospray negative ionization mode. The chromatographic separation was accomplished by using an Acquity BEH C18 column (2.1 mm × 100 mm, 1.7 μm) (Waters Corporation Milford, USA). A gradient mobile phase of (A) 2 mM ammonium acetate (in 30 : 70, methanol: MilliQ) with 5 mM 1-methyl piperidine and (B) 2 mM ammonium acetate (in MeOH) with 5 mM 1-methyl piperidine at a flow rate of 0.30 mL min⁻¹ was used. Details of the LC and MS conditions are provided elsewhere.³⁵

The EOF were analyzed by combustion ion chromatography (CIC) (Metrohm, Switzerland), consisting of a combustion module, a 920 absorbent module and a 930 compact IC flex. In brief, the sample was placed in a quartz boat, and all fluorine was converted to hydrogen fluoride and absorbed into the water after combustion at 1000–1050 °C. The dissolved fluoride was then analyzed by using the ion chromatograph. Separation of anions was completed by using an ion exchange column (Metrosep A Supp5, 4 mm × 150 mm) with 64 mM sodium carbonate and 20 mM sodium bicarbonate in water as the eluent solution. Details of the method are provided elsewhere.³⁶

Suspect screening analysis was performed by using an Acquity UPLC system coupled with a quadrupole time-of-flight mass spectrometer (QTOF) (G2-XS, Waters Corporation, Milford, USA) in the electrospray negative ionization mode.³⁷ The separation of the compounds was performed by using an Acquity BEH C18 column (2.1 mm × 100 mm; 1.7 μm; Waters Corporation, Milford, USA) with the mobile phase (A) 2 mM ammonium acetate (in 30 : 70, methanol: MilliQ) and (B) 2 mM ammonium acetate (in MeOH). A data independent acquisition mode (MS^E) was used to obtain the precursor and fragment

ions. Details about the parameters are provided in Table S2† and elsewhere.³⁷

Quality control and quality assurance

To avoid interference of background contamination, poly tetrafluoroethylene (PTFE) and fluoropolymer materials from the instruments and other possible sources were removed.

For UPLC-MS/MS and UPC²-MS/MS analyses, recovery samples for each batch of sample analysis were prepared using Milli-Q water to monitor contamination or loss during the whole extraction. Native and internal standards (2 ng) were added to the recovery samples in the same way as for the samples. For blanks, internal standards (2 ng) were spiked into Milli-Q water which was prepared in the lab. For blank spikes, native standards (2 ng) were spiked into the bottle containing Milli-Q water in addition to internal standards. All blanks and recovery samples were extracted and stored in the same way as for the real samples. The recoveries of internal standards for blanks all ranged from 71% to 111%. The native compounds in the recovery samples ranged from 73% to 102% (Table S2 and S3†). Matrix spike recovery tests were also carried out using tap water. Two ng each of all of the target analytes was spiked into 500 mL of tap water. Except for long-chain PFAS (PFUnDA and PFDoDA), all other PFASs showed acceptable recoveries, ranging from 75% to 103%. Although each target compound was analyzed using the isotope-labelled standards as internal standards, establishing exact matching internal standards for some compounds was not possible due to the lack of the isotope-labelled standards. Therefore, the internal standards with the closest retention time under the same analytical method were selected. For example, TFA and PFPrA were corrected using 13C-PFBA. TFMS, PFEtS and PFPrS were corrected using 13C-PFBS. PFTrDA was corrected using 13C-PFDoDA. PFOcDA was corrected using 13C-PFHxDA. PFPeS was corrected using 13C-PFHxS. PFHpS, PFDS, PFNS and PFDoDS were corrected using 13C-PFOS. F-53B was corrected using 13C-PFOS. 4 : 2 FTSA and 8 : 2 FTSA were corrected using 6 : 2 FTSA. Except for these compounds, all the other compounds used their corresponding isotope-labelled standards as internal standards.

Quantification of PFAS was based on an internal calibration method using corresponding isotope-labelled internal standards. The method detection limit (MDL) of PFAS was determined as average concentrations in procedural blanks plus three times the standard deviation. The method quantification limit (MQL) was determined as average concentrations in procedure blanks plus ten times the standard deviation. The lowest point of the calibration curve was used if the analyte was not found in the blanks (Table S5†).

Quantification of EOF was based on external calibration using PFOS as the standard that was combusted in the same way as the samples. Since the background fluoride signal was detected when an empty quartz boat was combusted, real sample analysis was conducted when variation of the level of the combustion blank (combustion of the empty quartz boat) was below 10%. Quantification of EOF in the blanks and samples was done after subtracting the combustion blanks injected



before and after the sample. For EOF analysis, the MDL was $50 \text{ ng L}^{-1} \text{ F}^{-1}$. The sample concentrations were corrected for the blank level and were reported when their levels were at least two times higher than the MDL.

For suspect screening analysis, extraction blanks were also analyzed together with the samples. The identified emerging PFAS (target PFAS excluded) were not found in blanks. Considering the lack of standards for the PFAS identified through suspect screening, semi-quantification was performed using surrogate native standards^{24,26} (Table S8†). Mass errors for all of the classes were set to 5 ppm.

Extractable organofluorine analysis

The amount of EOF in the samples was assessed by CIC ($\text{ng L}^{-1} \text{ F}^{-1}$). To evaluate the extent of unidentified organofluorine, the target PFAS concentrations were first converted to fluoride through eqn (1).

$$c_{\text{F,target PFAS}} = n_{\text{F}} \times \text{MW}_{\text{F}} \times c_{\text{PFAS}} / \text{MW}_{\text{PFAS}} \quad (1)$$

where $c_{\text{F,target PFAS}}$ is the fluoride concentration converted from target PFAS, $\text{ng L}^{-1} \text{ F}^{-1}$; n_{F} is the number of fluorine atoms in the PFAS molecule; c_{PFAS} is the concentration of the target PFAS which was measured by UPLC-MS/MS and UPC²-MS/MS, ng L ; MW_{F} and MW_{PFAS} are the molecular weight of fluorine and target PFAS, respectively. The amount of unidentified organofluorine was calculated as the difference between EOF and the target PFAS concentration after conversion into the fluoride equivalent.

Results and discussion

Extractable organofluorine analysis in raw and treated water

Relatively high EOF concentrations were observed for four DWTPs (D3, D4, D5 and D8) as shown in Fig. 2. The EOF concentrations in raw water from D3, D4, D5 and D8 were 400, 378, 187 and 81.2 ng of F/L , respectively, while in treated water, the concentrations were 409, 340, 125 and 130 ng of F/L , respectively. The higher concentrations observed in D3 and D4 might be related to the industries (*e.g.*, the textile industry

and chemical industry) around these areas. In both raw and treated water samples from D3 and D4, the largest known contributors to EOF were PFCAs (8% and 13%, respectively), and PFSAs (11% and 13%, respectively). The novel PFAS and ultrashort PFAS only accounted for around 1% of EOF. In the samples from D5 and D8, the largest contributors to EOF were PFCAs (ranging from 4% to 25% of EOF). The PFSAs and novel PFAS made up less than 4% and 2% of EOF, respectively, with ultra-short PFAS accounting for less than 2%. The percentage of target PFAS to EOF ranged from 8% to 32%, indicating a large portion of unidentified origin.

Observable differences (>20%) in EOF after treatment were noted in D8 (increase), and the opposite phenomenon was observed in D5 (Table S6†); no observable changes were noted in D3 (2%) and D4 (-9.8%). It was hypothesized that any increase or decrease in EOF after treatment might be reflected in changes in target PFAS concentrations after treatment. However, no clear trends were concluded from the target PFAS results. As shown in D5, the decrease in EOF (33%) and the inconsistent increase or decrease for different classes of PFAS was observed after treatment, and a similar situation was observed in D8. It is not possible to speculate what types of unknown PFAS were removed or produced during the treatment processes. As discussed before, the overall treatment processes were quite similar between DWTPs. However, an additional biofilter technology was included in D5 which might help explain the decrease of EOF. Further investigation for the use of the biofilter technology is needed.

Likewise, some other researchers have also discovered that unidentified organofluorine in water matrices accounted for a large proportion of EOF.^{22,29,38,39} Precursor compounds might make a significant contribution to the unknown portion of EOF due to their incomplete transformation. Instead of fully converting to common perfluoroalkyl acids (PFAAs), they may also form some unknown intermediates under the treatment process which might also result in better binding abilities of the transformation products to WAX cartridges, explaining the increase of EOF levels in D8. Besides, fluorine-containing drugs could also contribute to EOF.⁴⁰ Many fluorinated

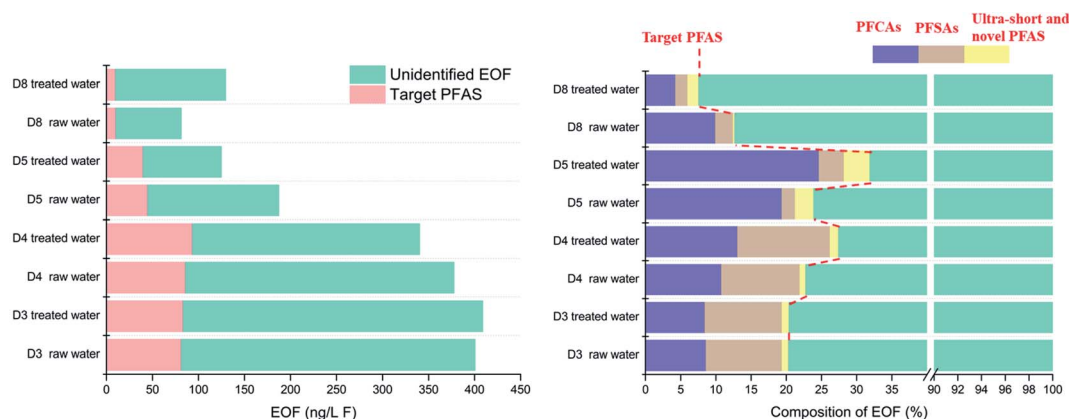


Fig. 2 EOF concentrations ($\text{ng L}^{-1} \text{ F}^{-1}$) (left) and composition of EOF by converting the target PFAS concentration to fluorine equivalents (right) in four DWTPs (D3, D4, D5 and D8).



pharmaceuticals are included in the updated definition of PFASs. More efforts, therefore, are needed to understand what the unknowns are and how to improve the quality of water sources.

Suspect screening analysis

A total of 10 emerging PFAS of five classes were identified in the raw and treated water samples at different confidence levels based on the scale proposed by another study,⁴¹ which included hydro substituted PFCAs (H-PFCAs), hydro substituted PFSAs (H-PFSAs), chlorine substituted perfluoroalkyl ether sulfonates (Cl-PFESAs), hydro substituted perfluoroalkyl ether sulfonates (H-PFESAs) and *p*-perfluorooxynonanesulfonate (OBS) (Table S8†). By comparing the HRMS spectral information with the database from other literature studies,^{24,27} six PFAS were identified at a confidence level of 2, while others were at a confidence level of 3. The semi-quantified concentrations and composition together with the detailed information of these emerging PFAS are presented in Table S8 and Fig. S1.†

For H-PFCAs, C5, C8 and C9 were identified in this class. H-PFPeA showed the highest detection frequency of 50%, followed by H-PFOA (13%). H-PFNA was only identified in one sample (treated water from D3). The total concentrations of H-PFCAs ranged from 0.100 to 0.703 ng L⁻¹, which further explained the EOF increase from 0.02% to 0.10%. No observable differences in concentrations for H-PFCAs were noted between raw and treated water (<20%). For H-PFSAs, H-PFBS and H-PFOS were identified, and increases were observed after the treatment processes (>20%). For Cl-PFESAs, 5 : 2 Cl-PFESA was identified. For H-PFESAs, 2 : 2 H-PFESA, 4 : 2 H-PFESA and 6 : 2 H-PFESA were identified with a detection frequency higher than 63%. 6 : 2 H-PFESA was the most predominant compound among H-PFESAs, which was not unexpected as it has been found to be the transformation product of 6 : 2 Cl-PFESA.⁴² The semi-quantified concentrations of 6 : 2 H-PFESA (0.008–0.439 ng L⁻¹) were lower than those of 6 : 2 Cl-PFESA, which was found to be consistent with the results from another study on surface water.⁴² OBS was identified in 11 out of the 16 samples; this compound was widely used in fire-fighting foam and oil production.⁴³ The identified 10 emerging PFAS contributed to a further 0.01% to 0.28% of EOF. These identified emerging PFAS, therefore, raised concerns about their high presence in drinking water and potential health risk for humans.

Concentrations and profiles of target PFAS in raw and treated water

Out of the 34 target compounds, 22 PFAS were detected at levels above the MQLs in the raw ($n = 8$) and treated water samples ($n = 8$) collected from the 8 DWTPs. The results are presented in Fig. 3, 4 and Table S7.† PFCAs (C4–C6 and C8–C10) and PFSAs (C4, C6 and C8) were the most frequently detected compounds with a detection frequency of 100%, followed by F-53B (94% of total samples), PFHpA (88%) and PFPeS (88%). Ultra-short PFAS were detected at frequencies of 56% or higher. Lower frequencies of detection were observed for some long-chain PFAS.

Total concentrations (\sum PFAS) ranged from 25.8 to 187 ng L⁻¹ in the raw water and 29.4 to 188 ng L⁻¹ in the treated water. The concentrations of PFAS showed little differences between raw and treated water, indicating limited removal efficiency although activated carbon was already in use in these DWTPs.⁴⁴ Among all target PFAS, 5 ultra-short PFAS (TFA, PFPrA, TFMS, PFETS and PFPrS) were detected with the sum concentrations ranging from 7.53 to 78.7 ng L⁻¹ contributing to 6% to 89% of \sum PFAS, which highlights the importance of these compounds. PFPrA and TFMS displayed generally high levels, accounting for 55% of \sum ultra-short PFAS or higher. F-53B, a substitute of PFOS produced in China, was also observed in 8 DWTPs (median: 2.70 ng L⁻¹). Although 6 : 2 FTSA and HFPO-DA were also widely detected, the sum concentrations of these two compounds were at lower levels (less than 1.6 ng L⁻¹), only accounting for 2% or lower of the total PFAS. For the sum of PFCAs and PFSAs, the concentrations ranged from 2.95 to 157 ng L⁻¹ in the raw water and 3.21 to 170 ng L⁻¹ in the treated water. Among the PFCAs and PFSAs, PFBA was at higher levels compared to the PFSAs with the same carbon chain length (PFBS), and PFOA (range: 1.36–49.0 ng L⁻¹) was also abundant with its concentration generally higher than that of PFOS (range: 0.193–15.4 ng L⁻¹), which might be due to the higher production and usage of PFOA, PFBA and their precursors.⁴⁵ PFHxS was also one of the abundant compounds, ranging from 0.03 to 61.4 ng L⁻¹. The ratios of PFBA to PFOA and PFBS to PFOS were calculated to reflect the extent to which PFOA and PFOS were replaced. The ratios of PFBS to PFOS showed an observable increase, ranging from 0.31 in tap water collected from Shanghai in 2008³ to 1.63 in the treated water in this study. PFBA/PFOA also increased from 0.05 in tap water collected from Shanghai in 2008³ to 0.42 in this study. Another study also found a high ratio of PFBA to PFOA in tap water collected from Shanghai in 2017⁴⁶ with a value up to 11.4, indicating the increasing usage of shorter chain alternatives.

In general, the profiles in 7 DWTPs (except D7) were all dominated by PFCAs and PFSAs. PFBA, PFOA, PFHxS and PFOS were the main compounds, and the sum of the four substances accounted for 31% or higher of the total PFAS. It was notable that the concentration of PFHxS was at higher levels in this study, probably due to the increasing production and use of PFHxS in recent years, which was similar to another study that also found that PFHxS was predominant in Taihu Lake (45.9–351 ng L⁻¹).⁴⁷ In D7, however, ultra-short PFAS accounted for a larger proportion, reaching up to 89%, and PFPrA was the dominant substance (17.9 and 14.3 ng L⁻¹ for raw and treated water, respectively). TFA and PFPrA can be the breakdown products of hydrofluorocarbons (HFCs) which are used mainly as refrigerants.⁴⁸ The different profile in D7, therefore, might be explained in that there is a fluorine industry producing fluorine-containing refrigerants in its nearby cities. Besides, F-53B was prevalent, which was not surprising due to its extensive application in China. Compared to the raw water, the concentrations of PFAS in treated water showed a insignificant decrease and may even increase due to the transformation of some precursor compounds.⁴⁹



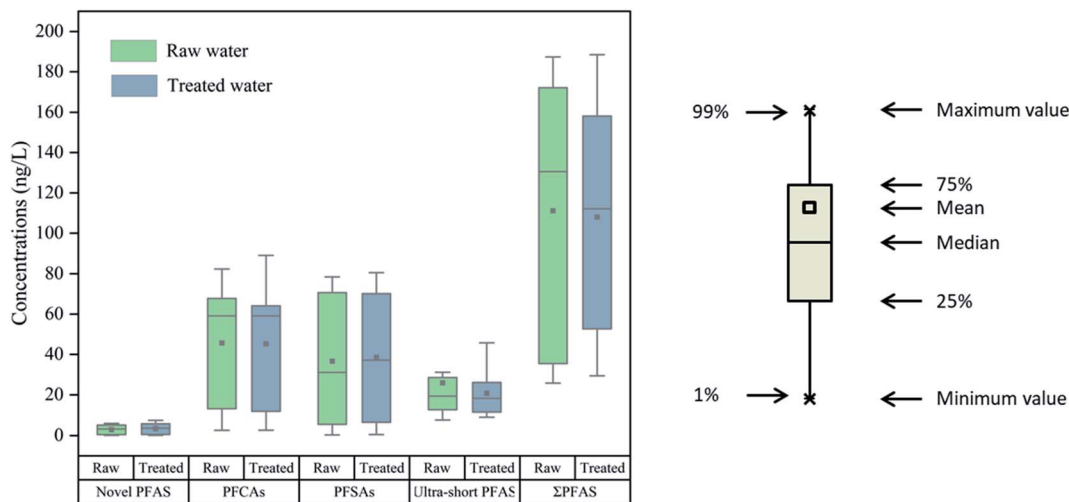


Fig. 3 Σ 22 PFAS concentrations (ng L^{-1}) in raw and treated water from 8 DWTPs.

The comparison of EOF levels between the present study and other studies

Recent publications have revealed the ubiquitous presence of unknown organofluorine substances by analyzing EOF. However, the knowledge of EOF in drinking water is scarce. With regard to EOF in water, the highest EOF concentration in the present study was around $400 \text{ ng L}^{-1} \text{ F}^{-1}$ which was comparable to the EOF concentration in surface water collected at two sites in Sweden (320 and $408 \text{ ng L}^{-1} \text{ F}^{-1}$, respectively), but much lower than that from other two sampling sites in Sweden (1110 to $3930 \text{ ng L}^{-1} \text{ F}^{-1}$, respectively).³⁶ A high level of EOF was also found in surface water from Norway (up to $4030 \text{ ng L}^{-1} \text{ F}^{-1}$).²⁹ Another study investigated the mass balance in wastewater in Nordic countries and found EOF ranging from 183 to $1460 \text{ ng L}^{-1} \text{ F}^{-1}$.⁵⁰ However, target compounds can only explain at most 32% of EOF in this study. In other studies related to surface water and wastewater, they also discovered that a large percentage of EOF couldn't be explained by the monitored PFAS (>45%).

For the target PFAS, an early study has reported PFOA and PFOS in 21 major cities from China; Shenzhen was found to have

the highest concentration of PFOA (45.9 ng L^{-1}) and PFOS (14.8 ng L^{-1}) in tap water,⁵¹ which was similar to the highest PFOA (49.0 ng L^{-1}) and PFOS (15.4 ng L^{-1}) levels in the present study. PFHxS (max: 61.4 ng L^{-1}) was also one of the predominant substances in this study. This compound was also found at high levels in nearby surface water (Taihu Lake) with the maximum concentration up to 292 ng L^{-1} .¹² Subsequent research studies were later conducted to investigate the PFAS contamination (mainly PFCAs and PFSAs) in different Chinese cities, showing the total concentration reaching up to 130 and 175 ng L^{-1} , respectively.^{3,52} Similar total levels were detected in the present study, with the maximum sum concentrations of 188 ng L^{-1} . Besides, the changes of the levels in DWTPs were also studied, and the limited removal efficiency of PFAS in each treatment process except for the activated carbon step was observed.⁵³ Compared to other foreign studies, one study was conducted in several European countries, and predominant contaminants in the investigation of tap water in Amsterdam were PFBS (18.8 ng L^{-1}) and PFOA (8.6 ng L^{-1}), while PFOS (8.8 ng L^{-1}) was the substance with the highest concentration in Sweden.⁵⁴

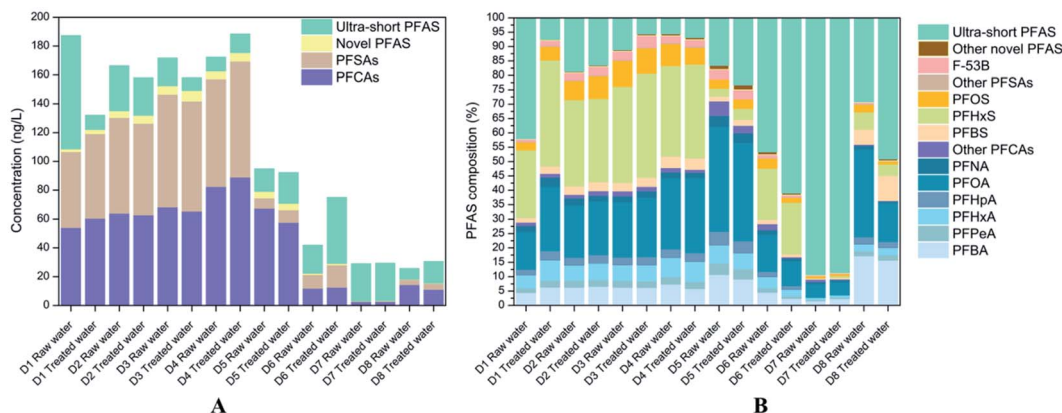


Fig. 4 Profiles of the major PFAS classes (A), and the individual PFAS composition (B) in raw and treated water from 8 DWTPs.



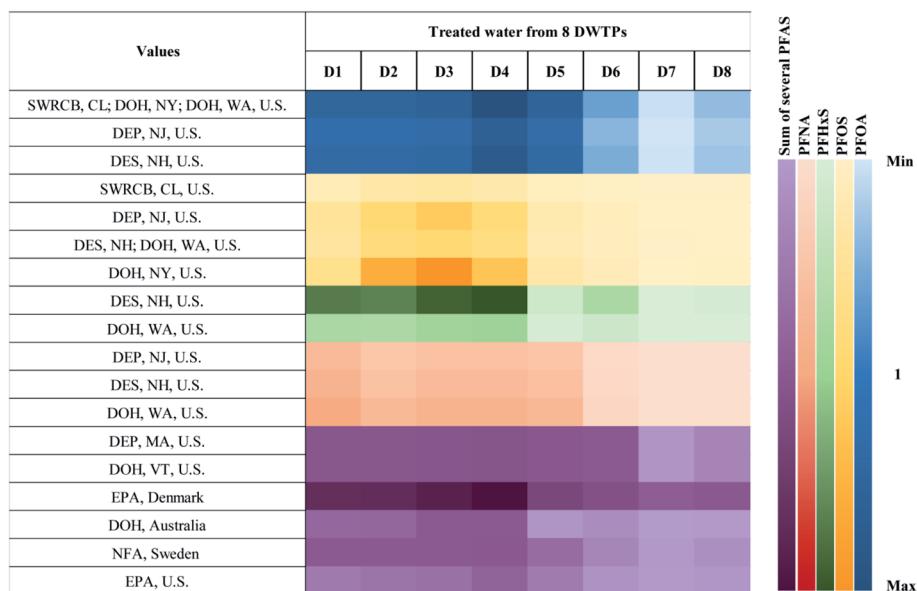


Fig. 5 Ratios of measured PFAS concentrations in treated water and the standard and guideline values issued by agencies.

In the present study, ultra-short PFAS were also detected. However, there is limited published data about their levels in drinking water. TFA was found to display an increase from not detected (2002) to 155 ng L^{-1} (2012) in tap water from Beijing,⁵⁵ and PFPrA was also present in addition to the commonly investigated PFAS (max: $0.011 \mu\text{g L}^{-1}$) in tap water in Germany.⁵⁶ They were even detected in bottled water with the maximum concentrations of 6.52 and 0.18 ng L^{-1} for PFPrA and PFPrS, respectively.⁵⁷

However, it should be noted that many adverse effects of the novel substitutes (*e.g.*, F-53B) have already been observed.^{58,59} Therefore, in view of the phase-out of some PFAS in China together with the known or unknown toxicity of some

replacements, the substitutes (*e.g.*, novel PFAS and ultra-short PFAS) have already become a new concern.⁴⁴

PFAS levels with reference to some guideline values

Exposure through drinking water has become a concern that needs to be emphasized since it was reported that low levels of PFAS in drinking water could increase their levels in serum, indicating health effects for humans.⁶⁰

In China, the limit values of PFOA and PFOS are 80 and 40 ng L^{-1} , respectively. The concentrations of these two substances in the treated water did not exceed the limits of 80 and 40 ng L^{-1} . Therefore, a ratio between the measured concentrations in the water and the values proposed by other

Table 1 The standards and advisory guideline values for PFAS in drinking water

No.	Location and agencies	Finalized into law	Values (ng L^{-1})	References
1	U.S. United States environmental protection agency (EPA)	—	PFOA and PFOS (individual or combination) (70)	30
2	The state water resources control board (SWRCB), California (CA)	Yes	PFOA (10), PFOS (40), and PFBS (5000)	61 and 62
3	Department of environmental protection (DEP), Massachusetts (MA)	Yes	Individual or sum of 6 PFAS (PFOA, PFOS, PFNA, PFHxS, PFHpA, and PFDA) (20)	63
4	DEP, New Jersey (NJ)	Yes	PFOA (14), PFOS (13), and PFNA (13)	64
5	Department of health (DOH), Vermont (VT)	Yes	PFOA + PFOS + PFHxS + PFHpA + PFNA (20)	65
6	Department of environmental services (DES), New Hampshire (NH)	Yes	PFOA (12), PFOS (15), PFNA (11), and PFHxS (18)	31
7	DOH, New York (NY)	Yes	PFOA (10) and PFOS (10)	66
8	DOH, Washington (WA)	Yes	PFOA (10), PFOS (15), PFNA (9), PFBS (345), and PFHxS (65)	67
9	EPA, Denmark	—	PFOA + PFOS + PFNA + PFHxS (2)	68
10	DOH, Australia	—	PFOA (560) and PFOS + PFHxS (individual or combination) (70)	69
11	National food agency (NFA), Sweden	—	$\Sigma 11\text{PFAS}$ (90)	70



different government agencies were calculated (Fig. 5); the values proposed by different agencies are presented in Table 1.

The calculated ratios of all treated water for PFBS were far below 1 and are not presented in Fig. 5. For other individual PFAS, PFNA showed acceptable levels with the ratios of all the treated water below 1. However, when evaluating individual PFAS using the limit values from the U.S., it could be seen that ratios of PFAS (PFOA and PFHxS) in a majority of treated water samples were higher than 1 (up to 4.9 and 3.4, respectively), showing safety concerns. Treated water from 3 out of the 8 DWTPs showed excessive concentrations of PFOS when compared to the maximum contaminant level in New York. The ratios became much higher when considering the sum of PFAS. For the values issued by other agencies such as the Department of Health in Vermont, the Swedish action guideline and Danish EPA, the calculated ratios of the sum of several PFAS were much higher than 1, reaching up to 62.5 when compared with the health-based values in Denmark. Mixtures, therefore, might need more attention since they may interact synergistically,³ and the health effects are difficult to investigate. Besides, the unknown risk of ultra-short PFAS and other novel PFAS remains a concern. Measures, therefore, should be implemented to protect drinking water safety.

Conclusions

The occurrence of PFAS in water samples from China was investigated; PFOA, PFOS and PFHxS were the abundant compounds among the target PFAS. Higher total concentrations, ranging from 132 to 189 ng L⁻¹, were observed in the samples from D1 to D4. No observable differences in PFAS concentrations were noted between raw water and its corresponding treated water, which indicated insignificant removal efficiency under the current treatment process. Apart from commonly monitored PFAS, EOF was also uncovered, and the contributions of target compounds to EOF ranged from 10% to 33%. The results from suspect screening analysis identified 10 emerging PFAS in raw and treated water. H-PFPeA, H-PFESAs and OBS showed higher presence, which contributed to a further 0.01% to 0.26% of the EOF. The ratios between the measured PFAS concentrations and the values proposed by different agencies showed that some of the treated drinking water exceeds guideline values, indicating potential health concerns.

Data availability

All data used in this study are included in the main text and the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The project was financially supported by the Major Science and Technology Program for Water Pollution Control and

Treatment (2017ZX07201005) and the National Key Research and Development Project of China (2021YFC3200801). The authors from ORU acknowledge the funding from the Knowledge Foundation (KKS) within the Enforce Research Profile (20160019), Sweden, and Swedish Research Council FORMAS (2020-02032). Authors also acknowledged scholarship (Ref: ORU 2019/03505) from Örebro University for promoting internationalization.

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