MONITORING POLY- AND PERFLUOROALKYL SUBSTANCES (PFASs) IN DRINKING WATER TREATMENT PLANT AND DISTRIBUTION SYSTEM IN CHANGZHOU, CHINA

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Introduction

Poly- and perfluoroalkyl substances (PFASs) are toxic, persistent, bioaccumulative and long-range migratory. It has been widely detected in various environmental media, as well as in drinking water. Based on this situation，the US EPA has developed a most stringent advisory for PFOS and PFOA in 2016, namely, the total concentration of PFOS and PFOA should not exceed 70 ng/L in drinking water [1].

In China, higher concentrations of PFOS and PFOA can be found in drinking water in many cities such as Shanghai (85.6 ng/L), Dalian (74.5 ng/L) and Shenzhen (60.7 ng/L), which has risk on human health. However, China still lacks corresponding water quality standards and studies on PFASs monitoring in drinking water treatment plants and distribution system.

In this study, a DWTP in Changzhou, taking water from Yangtze River, was selected to discuss the occurrence, removal and potential risks of PFASs in each unit process in this plant and public water supplies.

Materials and methods

Chemicals
Thirty-two PFASs were detected in this study, which are PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, NaDONA, OBS, 6:2 Cl-PFAES (F-53B), HFPO-DA, TrA, TeA, 4:2FTS, 6:2 FTS, 8:2 FTS, FOSA, MeFOSA, EtFOSA, MeFOSE and EtFOSE. Correspondingly, fifteen isotopically labeled internal standards and $^{13}C_2$-labeled L-PFOA were used as recovery and injection standard. All native and mass-labeled standards were produced by Wellington Laboratories Inc. (Guelph, ON, Canada), with purities over 98%.

Sample Collection
Water samples were collected in December 2017 from the largest drinking water treatment plant in Changzhou, Jiangsu Province, China. Raw water (Yangtze River), coagulation water, chlorine disinfected water, finished water and public supplies water were included in this study.
Grab sampling and continuous sampling were adopted simultaneously, in order to find out how PFASs fluctuate over time. Grab sampling was performed every two and half hours from 9:30 am to 5:30 pm. The portable samplers (Sigma SD900, HACH, US) were used for 8-hour continuous sampling.

Total Oxidizable Precursors (TOP) analysis
Total Oxidizable Precursors (TOP) analysis is a method to evaluate unknown precursors which have potential to form PFSAs and PFCAs[2]. There were two sample sets for TOP analysis: one is an oxidation set reacted with 60 Mm potassium persulfate and 150 mM NaOH; the other is a heated control sample set. Both persulfate-treated samples and thermolyzed control samples were bathed in water at 85 ℃ for 6 h.

Sample preparation
All samples before and after oxidation were placed in 1000 mL high-density polyethylene (HDPE) bottles and filtered by the glass microfiber filter (GF/F, 47 mm, Whatman, Kent, UK). 10 ng of recovery standards (50μL, 20μg/mL) were added in each sample. The PWAX cartridges (6 mL, 150 mg, Agela Technologies, China) were cleaned by 4 mL of 0.5% ammonium hydroxide in methanol, methanol and ultrapure water orderly, then were loaded with water samples at 5−10 mL/min for solid phase extraction (SPE). 3 ml of methanol and 0.5% ammonium hydroxide in methanol was used for elution. The resulting leacheate was concentrated into 0.25 ml under a gentle stream of nitrogen, added with 0.25 ml ultrapure water and 25 ng injection standard. Finally, the solution was filtered by 0.22 μm nylon filter.

Instrumental analysis

The injection volume was 5 μL. Eluents were analyzed on Agilent HPLC system coupled to an Agilent Triple Quadrupole 6460 mass spectrometer with negative electrospray ionization source operating in multiple reaction monitoring (MRM) mode. The chromatographic column is ZORBAX Eclipse XDB C18 column (5 μm×2.1 mm×150 mm, Agilent, CA) for separation. The column temperature was maintained at 30 ℃ and the flow rate was 0.3 mL/min. Methanol accounts for 60% of the initial mobile phase and 10 mM ammonium acetate accounts for 40%. Then methanol was ramped to 90% from 1 min to 15 min, held 90% to 27min, and restored to 40% and held for 8 min. MRM parameters for MS/MS detection were optimized, including precursor ion, product ion, fragment and CE.

QA/QC

Filed blanks were handled along with each sample set. One laboratory blank, one laboratory fortified blank and one laboratory fortified matrix were set for every extraction batch. More than 20% of the samples have three duplicates. There were 5 ways to ensure the QA and QC: calibration curves are liner with correlation coefficients over 0.99; filed, laboratory and instrument blanks are below the limit of quantification (LOQ); RSD (Relative standard deviation) of sample duplicates is below 30%; recoveries of internal standards range from 50% to 150%; recoveries of native standards in laboratory fortified blank and matrix samples range between 50% to 150%.

Results and discussion

Concentrations and composition profiles of PFASs in water source, DWTP and public water supplies

Out of the 32 targets, 11 PFASs were detected in raw water, DWTP and public water supplies samples. There is no pollution source around the raw water, so the occurrence of PFASs may be related to the production and use of the fluorine chemicals in the upper reaches of the Yangtze River.

The total concentrations of PFASs ranged from 36.6 ng/L to 39.7 ng/L and detection frequencies for 11 compounds were 100% across seven sites. The most prevalent compounds were PFBS and PFBA followed by PFOA, consistent with the increasing use of short-chain alternatives in recent years. PFBS was dominant contaminant, with a highest concentration 14.83 ng/L.

Along the treatment process of this plant, concentration of each compound fluctuated little, proving the coagulation and chlorination process has no removal on PFASs. It is a good indicator for residents living in high PFASs-contaminated regions since conventional water treatment processes are useless and advanced treatment processes should be introduced. Some studies have found that high-pressure membranes and GAC filtration were helpful for PFASs, with removal efficiencies up to 100%

#1, #2 and #3 public water supplies are located in the urban area, with the distance gradually increasing from DWTP. There was no change in concentration along the distribution line, demonstrating that PFAS are very stable in the supply system.

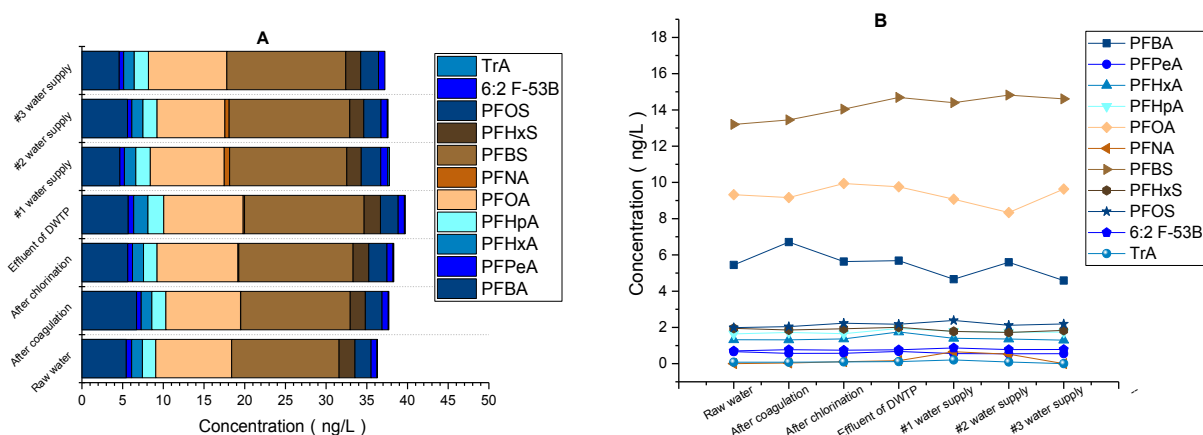The detected concentrations of PFASs are shown in Figure 1.

Fig. 1. Composition (A) and concentration (B) of PFASs in water samples

Daily fluctuation of PFASs

The relative standard deviation at four time points (1.1% - 20.5%) clearly indicates the PFASs fluctuate little within one day. At the same time, the results of the grab sampling and continuous sampling are almost same. Therefore, grab sampling and continuous sampling are all desirable sampling methods in this DWTP.

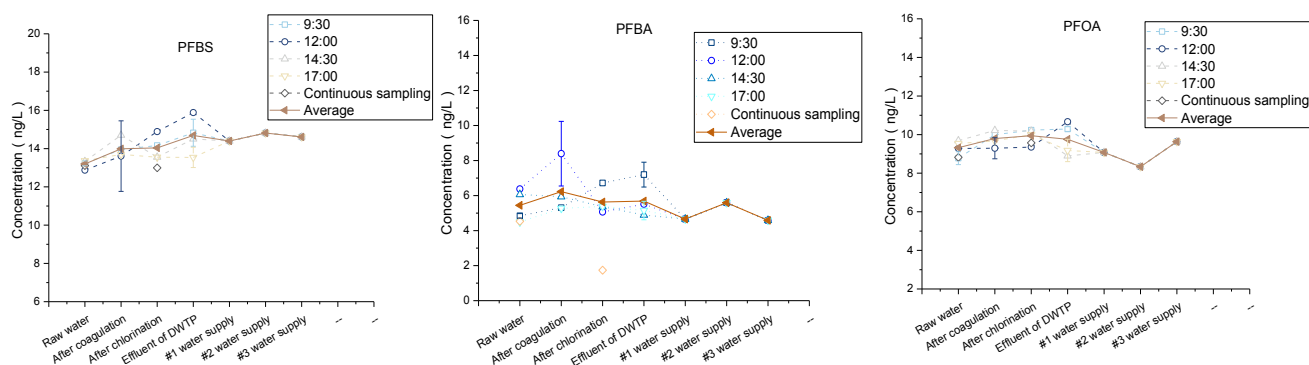The daily fluctuation of PFBS, PFBA and PFOA is shown in Figure 2.

Fig. 2. Daily fluctuation of PFBS, PFBA and PFOA

PFASs precursors indicated by oxidation

After oxidized by potassium persulfate, the amount of perfluorinated carboxylic acids (PFCAs) has a significant increase, while perfluoroalkyl sulfonic acids (PFSAs) and others remains unchanged. The total concentration of PFCAs with 4-9 membered perfluoroalkyl chains increased between 6.7 and 12.8 ng/L (median concentration increase = 10.1 ng/L). A maximum increase occurred on PFBA (5.3-8.1 ng/L), follow by PFPeA (1.3-2.5 ng/L) and PFHxA (0.9-8.1 ng/L).

Common PFASs precursors (4:2FTS, 6:2 FTS, 8:2 FTS, FOSA, MeFOSA, EtFOSA, MeFOSE and EtFOSE) were not found in samples before oxidation. Therefore, the increase in total PFASs is due to unknown precursors that can be converted into PFCAs in water.

Over 3000 PFASs have been on the global market and precursors are an important component of them. Since not all substances can be included in the HPLC/MS-MS measurement, Top analysis provides a means to quantify unknown precursors through oxidation and evaluate potential risks in water.

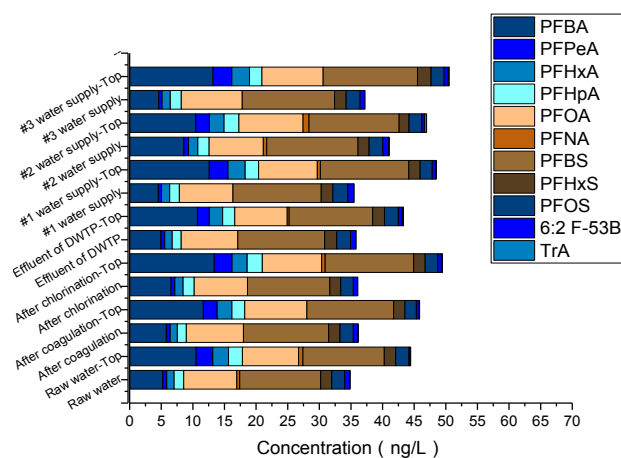The concentrations of PFASs before and after oxidation are shown in Figure 3.

Fig. 3. PFASs concentrations before and after oxidation in water samples

Risk assessment

There is neither drinking water nor environmental water quality standard for PFASs in China. Compared with the standards in other countries, PFASs in drinking water in Changzhou are not above the limits in most areas, such as the US (i.e. US EPA, PFOS+PFOS<70 ng/L; Vermont, PFOS+PFOS<20 ng/L; New Jersey, PFOA<40 ng/L, PFON<10 ng/L), the UK (PFOA<300 ng/L, PFOS<300 ng/L) and Canada (PFOA<600 ng/L)[3]. However, PFASs is not compliant with the EU Environmental Quality Standards (PFOA<1 ng/L).

For sensitive groups like children, studies based on immunotoxicity experiments suggested the total amount of PFOS and PFOA in drinking water was not above 1 ng/L. But in this study, concentration of PFOS and PFOA was as high as 11.8 ng/L in regular samples and 12.2 ng/L in oxidized samples, far exceeding the recommended values.

The standard values for PFASs in different regions are shown in Table 1.

Table 1 Standard values for PFASs in different regions (unit: ng/L)

Regions		Water quality standard for PFASs					
		PFOS	PFOA	PFBS	PFBA	PFNA	PFOS+PFOA
European Union		1					
US	US EPA	70	70				70
	Vermont						20
	New Jersey		40			10	
	Minnesota	300	300	700	700		
	North Carolina		2000				
Italy		30	500				500
UK		300	300				
Germany							100
Canada		600					
Suggestive limit for children							1

References
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3. Hu, X. C., Andrews, D. Q., Lindstrom, A. B., Bruton, T. A., Schaider, L. A., Grandjean, P., ... & Higgins, C. P. (2016) *Environmental science & technology letters* 3(10), 344-350.