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## Fate and risk Assessment of Perfluoroalkyl substances (PFASs) in water treatment plants and tap water in Bangkok, Thailand

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### Abstract

Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs), especially Perfluorooctanoic acid (PFOA) and Perfluorooctanesulfonate (PFOS), were found to contaminate the natural water sources serving as a raw material in producing tap water. The main purpose of this study was to measure the quantities of PFASs in both conventional and advanced water treatment processes, and of the PFASs contaminated tap water in various forms, with comparison made between tap water and water passing through drinking devices. It was found from the investigation that the conventional treatment process using coagulation, sedimentation, filtration and chlorination was incapable of removing PFASs, and that the concentration of effluent increased more than 27% compared to the influent. On the contrary, advanced water treatment process using GAC filter and RO was able to remove more than 86% of PFASs. The tap water was found to contain PFASs at 0.58-1.15 ng/L. However, a comparison between the average of the water passing through drinking devices and direct faucet showed insignificant difference, but the concentration of PFASs decreased by a small amount when passing a filter-equipped device.

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**Keywords:** PFASs; PFOA ; PFOS; water treatment plants; tap water; drinking water

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**Nomenclature**

ACN	Acetonitrile	PFHxA	perfluorohexanoic acid
GAC	Granular activated carbon	PFHxS	perfluorohexane sulfonic acid
HPLC	High-performance liquid chromatography	PFNA	perfluorononanoic acid
MS	mass spectrometry	PFOA	perfluorooctanoic acid
PET	Polyethylene terephthalate	PFOS	perfluorooctane sulfonic acid
PFASs	perfluoroalkyl and polyfluoroalkyl substances	PFPA	Perfluoropentanoic acid
PFBA	perfluorobutanoic acid	PFUnA	Perfluorododecanoic acid
PFBS	perfluorobutane sulfonic acid	RO	reverse osmosis
PFDA	perfluorodecanoic acid	USEPA	United States environmental protection agency
PFHpA	perfluoroheptanoic acid	WHO	World Health Organization

**1. Introduction**

Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs), especially Perfluorooctanoic acid (PFOA) and Perfluorooctanesulfonate (PFOS), are substances used widely in several products. They are hydrophobic, lipophobic and do not attract dust. The substances are used for coating the surfaces of many products and are often included in stain repellents, surfactants, fire-fighting foams, corrosion inhibitors and photolithographic film<sup>1</sup>, but crucial problems of the substances are persistence and non-degradation. As a result, the substances will accumulate in the environment<sup>2</sup>, living areas and human bodies, negatively affecting health<sup>3,4</sup>. These substances can be introduced into the body in many ways. Tap water is one possibility as a potential source of contamination. Since industries and households use chemicals and products that contain PFOA and PFOS, wastewater discharge as well as runoff can flow into natural water sources, such as canals or rivers<sup>5,6</sup>, which could then be used for production of tap water. Several countries have set recommended limits for PFOA and PFOS in drinking water<sup>7,8</sup>. For example, the US Environmental Protection Agency (EPA) sets the recommended quantity of PFOA at 400 ng/L or less and PFOS at 200 ng/L or less. Germany sets the recommended quantities of both PFOA and PFOS at no more than 100 ng/L, while the US State of New Jersey sets the limit of PFOA at 40 ng/L or less<sup>9</sup>.

In Thailand, tap water quality (especially in Bangkok, Nonthaburi and SamutPrakan Provinces) is controlled by the drinking water guidelines of the World Health Organization (WHO)<sup>10</sup>, which has not yet set standard quantities for PFOA and PFOS. Moreover, the main raw water source for producing tap water is the Chao Phraya River, which was found to be contaminated with these substances. Up to 20-30 ng/L of PFOA was found in the Chao Phraya River and wastewater released into it was found to have quantities of PFOS up to 6,000 ng/L<sup>6,7</sup>. The primary process for water treatment in Thailand uses coagulation, sedimentation, filtration and disinfection by chlorine, which is conventional technology. Therefore, the objectives of this study were to identify the presence of PFASs in two main water treatment plants serving Bangkok that use conventional treatment processes and to compare the results with an advanced treatment plant in order to estimate the removal capability of PFASs. Additionally, aside from drinking tap water directly from household faucets, people in the community drink tap water from vending machines, water dispensers and water filtration systems. This equipment has filters installed to filter out harmful substances such as suspended solids, but it is not yet clear how much PFAS these filters can remove. Thus, another objective of this study was to examine the presence of PFASs in tap water as well as to assess their health risks.

**2. Materials and Methods***2.1. Sampling Locations and Collection*

Water samples were collected from two conventional treatment plants in April 2014 and an advanced treatment plant in June 2014. The conventional treatment plants produce tap water for Bangkok and the surrounding areas. Another plant uses an advanced treatment process on recyclable water from treated wastewater for industrial estates. Water samples were collected in each stage of the process (A1-A4) and (B1-B6), as shown in Fig. 1.

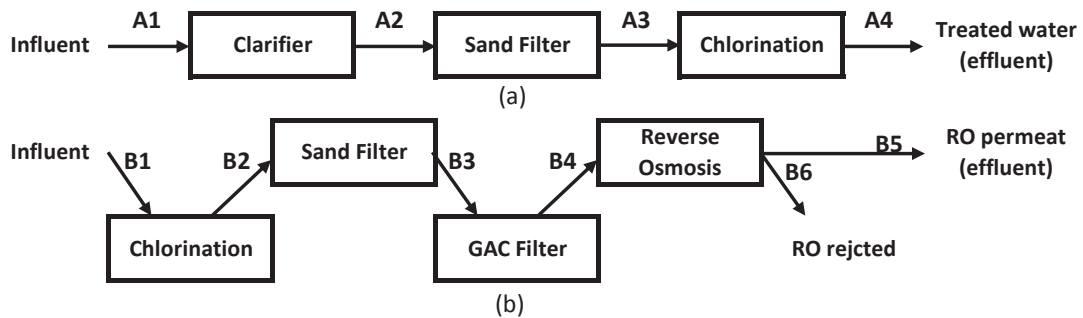


Fig. 1 Sampling Point for Water Treatment Processes (a) Conventional Water Treatment Process and (b) Advanced Water Treatment Process

## 2.2. Monitoring of Tap Water And Drinking Water

Water samples were collected from community areas in August 2014. There are six characteristics of tap water samples, including the “direct faucet”, “household water storage tank”, “vending machine”, “household water filter”, “water dispenser” and water samples from the “water supply pumping station” of this area, as shown in Fig.2.

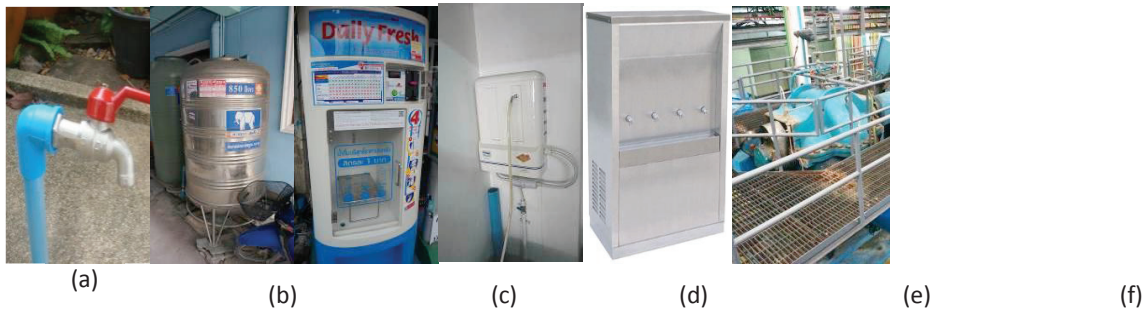


Fig.2 Tap Water and Drinking Water Monitoring from (a) Direct Faucet, (b) Household Water Storage Tank (c) Vending Machine (d) Household Water Filter (e) Water Dispenser (f) Water Supply Pumping Station

Samples were collected from the faucets. New 2L PET bottles were used as sampling containers, which were pre-washed with Milli-Q water and Methanol and then dried. The PET bottles were rinsed three times with the sample before collection.

## 2.3. Sample Extraction and Analysis

Water samples were filtered through a glass fiber filter (WHATMAN, GF/B 1  $\mu$ m) to remove suspended solids. Filtered water was loaded into a Presep-C Agri cartridge at a flow rate of 10 mL/min using a concentration system (Sep – Pak Concentrator). Cartridges were dried under light vacuum and eluted by 4 mL methanol (HPLC grade), followed by 2 mL acetonitrile ( $\text{CH}_3\text{CN}$ ) into the vial. High-purity nitrogen gas was used to dry the solvent inside the vial at a temperature of 50°C for 1-2 hours. After the sample in the vial was dried completely, 30%  $\text{CH}_3\text{CN}$  was added to 0.5 mL reconstitute before being transferred to LC/MS vials. This analysis was performed using an Agilent 1200 SL high performance liquid chromatography (HPLC) interfaced to an Agilent 6400 triple quadrupole mass spectrometer (MS/MS). The mobile phase A was comprised of 10 mM ammonium acetate ( $\text{CH}_3\text{COONH}_4$ ) in ultrapure water and the mobile phase B was HPLC grade  $\text{CH}_3\text{CN}$  with a flow rate of 0.25 mL/min. The substances that were investigated in this study include PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFBS, PFHxS and PFOS.

## 2.4. Health Risk Assessment

The concentration of PFOA and PFOS in tap water can be used to calculate Daily Intake (DI), which is a measure of the amount of the substances in drinking water or food that can be ingested daily over a lifetime.

$$DI = \frac{C \times IR \times EF \times ED}{BW \times AT} \quad (1)$$

Where:

<i>DI</i>	= daily intake (mg kg <sup>-1</sup> day <sup>-1</sup> )
<i>C</i>	= concentration of PFOS and PFOA (mg/L)
<i>IR</i>	= amount of water for drinking per day (L/day)
<i>EF</i>	= exposure frequency (365 days/year)
<i>ED</i>	= exposure duration (years)
<i>BW</i>	= body weight (average 65 kg)
<i>AT</i>	= averaging time (for non-carcinogenic; AT = ED x 365 days)

From (1) setting quantity of water consumed per person at 2 liters a day (*IR*) for 1 year (*EF*) or 365 days. Average age (*ED*) is 70 years; average weight (*BW*) is 65 kg; average period of substance intake that does not cause cancer in the body (*AT*) is 365 x *ED* = 25,550 days. The health risks of PFOA and PFOS were assessed by hazard quotient (*HQ*), as shown in (2), for which the reference dose (*RfD*) of PFOA is 0.00002 mg/kg/day and PFOS is 0.00003 mg/kg/day. If a hazard quotient value is equal or less than 1, the risk is not considered significant to human health<sup>3,4</sup>.

$$HQ = \frac{\text{Daily Intake (mg/kg/day)}}{\text{Reference Dose (mg/kg/day)}} \quad (2)$$

Where

<i>HQ</i>	= hazard quotients
<i>DI</i>	= daily intake or exposure
<i>RfD</i>	= reference dose

## 3. Results and Discussion

### 3.1. Fate of PFASs during Treatment

The average PFASs concentrations for conventional water treatment are shown in Fig. 3(a), where the concentration of effluent (2.39 ng/L) is more than the concentration of influent (1.88 ng/L), which demonstrates that conventional treatment plants cannot efficiently remove PFASs. To assess removal ratios of PFASs, concentrations of each process (*C*) were divided by the concentrations in the influent (*C<sub>0</sub>*) and expressed as ratio *C/C<sub>0</sub>*. PFASs concentrations in the effluent were found to be over 27% higher than that in the influent. The results are consistent with several studies<sup>8,11</sup>, but different from the previous study conducted at the same site<sup>12</sup>. They reported that the conventional treatment process, especially the sand filter, could remove 50% more PFOA and PFOS. However, in this study, *C/C<sub>0</sub>* in sand filter effluent (A3) increased from the previous process (A2). The process that could remove the most contamination was the clarifier, which covered the coagulation, flocculation and sedimentation process in one unit. It could remove PFASs up to 20%, which is consistent with the work of Xiao et al<sup>13</sup>. They concluded that coagulation and flocculation could remove PFOA and PFOS, removing approximately 10-20% depending on coagulant dosage. Therefore, the results of this study conclude that conventional treatment processes cannot effectively remove PFASs, in which it is consistent with other researches<sup>8</sup>.

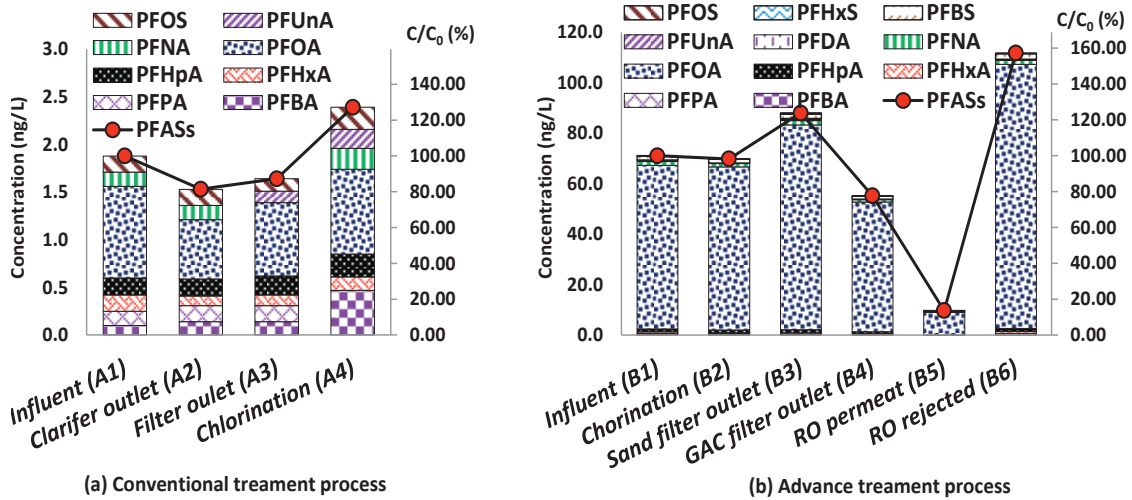


Fig. 3 PFASs Concentration in Water Treatment Process and Percentage of PFASs Concentration Compared with Influent (C/C<sub>0</sub>); (a) Conventional Treatment Plant and (b) Advanced Treatment Plant

The results of advanced treatment are shown in Fig. 3(b). The concentrations of PFASs were 71.07 ng/L for influent and 9.73 ng/L for effluent. Although PFASs concentrations were found to be higher in advanced treatment processes, because tap water was produced from treated industrial wastewater for recycling, advanced treatment was also demonstrated to be effective in the removal of PFASs. Particularly, a reverse osmosis unit could remove PFASs by more than 86%. However, the concentration of PFASs in RO rejected was much higher at 111.54 ng/L, which needs to be addressed. A method needs to be devised for how to handle it appropriately<sup>8</sup>.

The concentration of each substance is shown in Fig. 4. The substance detected the most was PFOA for both the conventional and advanced treatment processes. The highest concentration for a conventional treatment process was 0.96 ng/L, which was found in the influent. However, PFOA concentration in the effluent was found at 0.89 ng/L and had no significant difference with influent concentration. There is also another point to be noted: Almost all compounds in the effluent, especially PFBA, increased when compared to the previous process (sand filter). PFBA increased in the effluent (A4), though it was detected in very small quantities during the process. Further study about the variables affecting the increase of PFBA and other compounds should be conducted. The highest concentration

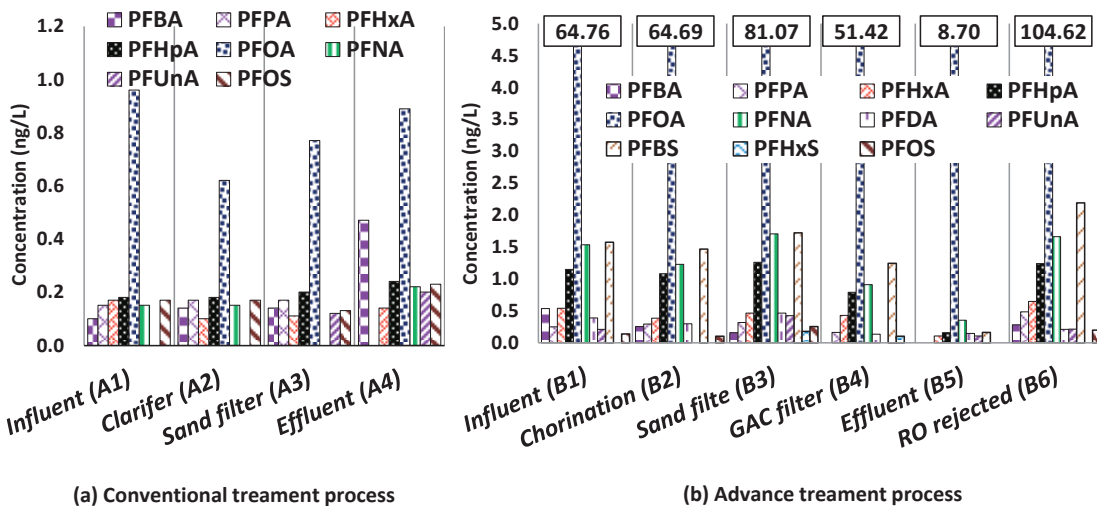


Fig. 4 Concentration of PFASs by the Concentration of Individual Compounds

for an advanced treatment process was PFOA at 104.62 ng/L in RO rejected, which is water that did not pass through the membrane. When compared with the concentration of the influent (64.76 ng/L), the quantity of RO rejected concentration was found to be quite different. Even though the rate of drainage of RO rejected is a very small quantity when compared to the capacity of the process, PFOA is a non-degradable compound. Thus, there is an increasing risk for accumulation in the environment. PFHpA, PFNA and PFBS were detected by more than 1.0 ng/L during the process of advanced treatment, except the RO permeate plant, which was different in a conventional treatment plant and was found to be the least of all processes.

Although the concentration of PFOA was detected at the highest concentration among other PFASs effluent for both processes, the concentration was not high when compared with the concentration based on the drinking water guidelines (40 ng/L)<sup>8</sup> of the New Jersey Department of Environmental Protection. However, if the contamination of water sources increased, conventional treatment would not be sufficient for PFASs removal. Therefore, advanced water treatment processes should be considered.

### 3.2. Fate of PFASs in Tap Water

From Table 1, there is little difference between the average concentration of PFASs in tap water from the community at 0.88 mg/L and in water at the water supply pumping station (1.09 mg/L). The substance detected in the largest quantity was PFBA. The highest concentration of PFBA was found in tap water from direct faucets, in which it was detected at 0.50 ng/L or around 50% of total PFASs. The second highest concentration was in the water from the storage tank at 0.46 ng/L or around 40% of total PFASs, as shown in Fig. 5. PFOS was detected in the household storage tank and vending machine at 0.12 ng/L and 0.10 ng/L, respectively. There is the possibility that both devices had some materials that were contaminated with PFOS, or used PFOS as component elements. However, there may be other factors that require further study.

Table 1 PFASs Concentration in Tap Water and Drinking Water

Sites		PFBA	PFPA	PFHxA	PFOA	PFUnA	PFOS	PFASs	Avg.
Water supply pumping station		0.40	0.18	0.12	0.24	0.15	ND	1.09	1.09
Community area	Direct faucet	0.50	0.18	ND	0.18	0.13	ND	1.07	0.88
	Vending machine	0.17	0.15	0.11	0.23	ND	0.10	0.74	
	Household water storage tank	0.46	0.24	0.11	0.19	0.11	0.12	1.15	
	Water dispenser	0.19	0.15	ND	0.31	0.16	ND	0.83	
	Household water filter	0.13	0.13	ND	0.15	0.13	ND	0.58	

Note: ND = Non-Detect; Unit :ng/L

The tap water, which was detected in the minimum quantity of PFASs, was water through the household water filter system with a concentration of 0.58 ng/L. When compared to the tap water from a direct faucet, PFASs concentration of water through the household water filter decreased by more than 40%. The water dispenser and vending machine used carbon filters and membrane filters as filter elements, which are the same as a household water filter. The PFASs concentrations in the water dispenser and vending machine were less than the water from a direct faucet at 0.83 ng/L and 0.74 ng/L respectively. However, since the amount used for both devices is higher than a household water filter because it is equipment used by the public at large, PFASs removal efficiency may be less than the household water filter. The pathways of the water supply for consumers could affect the results. Thus, further sampling may be required to reveal the variation of PFAS concentrations in tap water.

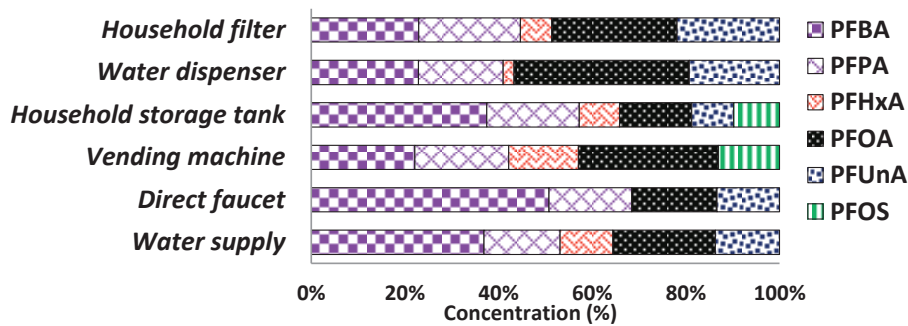


Fig. 5 Ratio of PFASs Concentration in Different Water's Characteristics

### 3.3. Health Risk Assessment

PFOA and PFOS contaminations were used to assess health risks by hazard quotient ( $HQ$ ). Daily intake was calculated with a maximum concentration of PFOA and PFOS, and the results of  $DI$  were  $9.54 \times 10^{-9}$  mg/kg/day and  $3.69 \times 10^{-9}$  mg/kg/day, respectively. Subsequently, health risks were assessed by referring to U.S. EPA reference doses, which are 0.00002 mg/kg/day for PFOA<sup>3</sup> and 0.00003 mg/kg/day for PFOS<sup>4</sup>. The results of the hazard quotient ( $HQ$ ) for PFOA and PFOS were 0.00048 and 0.00012, respectively, which are less than 1. That meant there were no health risks for consumers. However, if PFOA and PFOS levels in raw water sources are higher in the future, it will affect higher contamination of PFOA and PFOS in the tap water distributed to the public. The results obtained from this study can provide awareness and a starting point for further study of other emerging contaminants contained in the public water supply, which can be used in planning and decision-making for water management projects in the future.

### 4. Conclusion

Contamination of PFASs in water treatment processes, tap water and drinking water especially PFOA and PFOS, can be concluded as follows:

1) PFASs were detected in all water treatment processes, tap water and drinking water samples. PFBA and PFOA were detected in most samples, while the other nine PFASs (PFPA, PFHxA, PFHpA, PFNA, PFDA, PFUnA, PFBS, PFHxS and PFOS) were detected in very low concentrations.

2) PFASs concentrations of influent and treated water for conventional treatment processes were found to be 1.88 ng/L and 2.39 ng/L, respectively. PFASs concentrations of influent and treated water for advanced treatment processes were found to be 71.07 ng/L and 9.73 ng/L, respectively. The results also demonstrated that an advanced treatment process is more effective than a conventional treatment process for removing PFASs, especially a reverse osmosis process.

3) PFASs concentrations in tap water directly from the faucet, household water storage tank, vending machine, household water filter and water dispenser were 1.07 ng/L, 1.15 ng/L, 0.74 ng/L, 0.58 ng/L and 0.83 ng/L, respectively. The results also showed that devices with filter elements could reduce some PFASs contamination in tap water.

4) The current concentrations of PFASs, especially PFOA and PFOS in raw water sources, in treated water and tap water, were not high when compared to the concentration based on the drinking water guidelines of the New Jersey Department of Environmental Protection (PFOA < 40 ng/L), and their hazard quotients were less than 1. However, if there are no laws in the future to regulate PFOA and PFOS contaminants in wastewater or surface water, it is likely to result in raw water sources with higher levels of contamination. That will affect higher contamination of PFOA and PFOS in the tap water that is distributed to the public, since water treatment plants currently use conventional water treatment processes.

Based on the conclusion above, despite the advanced treatment process capability to remove more than 80% of PFASs, particularly the reverse osmosis, the concentration of PFASs in the influent is high, giving a high chance of being able to remove PFASs. The study of advanced treatment with low concentration of PFASs in the influent should be subsequently furthered. This study involved only a certain period of time, whereas studies conducted in such other times as other seasons may give varied results. Studies in wider periods are essential for further studies in the future. In addition, the flow rate of the water in a water treatment process is also important since the amounts of time of the water flowing through individual treatment stage are different. Therefore, if there is any additional study in the future, the flow rate and individual amounts of water flowing time should be taken into account.

For water supply and drinking water, although the results showed that a filter-equipped device was able to partially remove PFASs, the study did not differentiate the types of filters for different types of devices in detail. Even the same type of device might use different filter element. A detailed study to determine the extent to which various kinds of filter elements are able to remove PFASs would be helpful in getting to know the varied mechanisms of individual filter elements.

## Acknowledgments

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