



Prevalence of per- and polyfluoroalkyl substances (PFASs) in drinking and source water from two Asian countries

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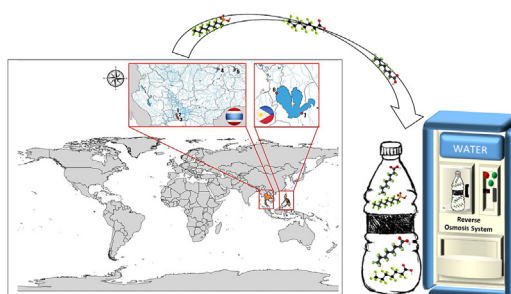
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HIGHLIGHTS

- PFASs targeted analysis and suspect screening were performed on water samples.
- Using targeted method, 12 PFASs were detected in drinking and 15 in source water.
- Σ PFASs ranged from 7.16 to 59.49 ng/L in drinking and 15.55–65.65 ng/L in source water.
- At least 4 different PFASs were detected in all commercial bottled waters tested.
- Three novel PFASs were detected in source water using suspect screening method.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 25 March 2020

Received in revised form

14 May 2020

Accepted 16 May 2020

Available online 19 May 2020

Handling Editor: Myrto Petreas

Keywords:

Asia waters

Suspect screening

EPA-PFAS Masterlist

Perfluorobutanoic acid (PFBA)

Perfluoropropionic acid (PFPrA)

Emerging PFASs

ABSTRACT

The present study focuses on the determination of the occurrence and levels of per- and polyfluoroalkyl substances (PFASs) in the drinking and source water from the Philippines and Thailand. A total of 46 samples (18 commercial bottled waters, 5 drinking water from vending machine (re-fill stations) and 23 source water) were analyzed using liquid chromatography with tandem high-resolution mass spectrometry. Using the targeted method, 12 different PFASs were detected in the drinking water samples with total quantifiable PFASs (Σ PFASs) levels ranging from 7.16 to 59.49 ng/L; 15 PFASs were detected in source water with Σ PFASs ranging from 15.55 to 65.65 ng/L. A 100% detection frequency was observed for perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), and perfluorosulfonic acid (PFOS) in all water samples. Six other PFASs, not included in the targeted analysis, were detected using the suspect screening approach. For the first time, the presence of 2-(N-methyl-perfluorooctanesulfonamido) acetic acid (N-MeFOSAA) in drinking water is reported, and 3 novel PFASs ($C_5H_5OF_8$, $C_6H_4O_2F_6$, and $C_9H_2O_2F_{16}$) were detected using suspect screening in source water. Combined results from target and suspect screening analysis showed that PFASs detected were predominantly (52%) short-chain (with fluorinated alkyl chain of ≤ 6) which could be explained by their high mobility in the environment. The detected PFASs levels in drinking water will not likely pose immediate health risk

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to consumers according to US EPA health advisory for PFOS and PFOA of 70 ng/L, but inclusion of bottled and drinking water from re-fill stations in monitoring programs is warranted.

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1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are a broad class of synthetic chemicals used in an array of industrial, commercial, and domestic applications (Buck et al., 2011; Rao and Baker, 1994). Releases of PFASs to the environment can occur next to chemical manufacturing locations, at industrial sites where PFASs are used, and at various stages of product use and disposal (Sunderland et al., 2019). Several studies have shown presence of PFASs in water, plants, wildlife, humans and food items (Buck et al., 2011; Domingo and Nadal, 2017; Perez et al., 2013; Barzen-Hanson et al., 2017; Martin et al., 2004; Ghisi et al., 2019). In humans, PFASs have been detected in blood and breastmilk (Jian et al., 2018); in important tissues such as lungs, liver, kidney, heart and brain (Perez et al., 2013); and in human embryonic and fetal organs (Mamsen et al., 2019). Routes of human exposure to PFASs include ingestion of contaminated drinking water, consumption of contaminated seafood, inhalation of indoor air, and contact with other contaminated media (Sunderland et al., 2019). In most countries with available information on the dietary intake of PFASs, food intake was established to be the most important source of exposure to these compounds, specifically consumption of fish and other seafood (Domingo and Nadal, 2017). However, for people living in a contaminated area (with nearby PFASs manufacturing facility or active military sites), drinking water is considered a substantial source of PFASs exposure (Banzhaf et al., 2017; Hu et al., 2016). PFASs in water are, for the most part, not removed by drinking water treatment such as coagulation, flocculation, sedimentation, filtration, biofiltration, oxidation (chlorination, ozonation, AOPs), UV irradiation, and low-pressure membranes (Rahman et al., 2014). Recent studies have shown presence of PFASs in commercial bottled water in several countries (Kabore et al., 2018; Schwanz et al., 2016; Llorca et al., 2012).

Several risk reduction approaches have been initiated to restrict and eliminate releases of long-chain PFASs and precursors, particularly in many high-income countries. The European Union started regulating perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and ammonium perfluorooctanoate (APFO), with specific restriction to PFOS for its use, production and export; C₁₁–C₁₄ perfluoroalkyl carboxylic acids (PFCAs) were also listed as substances of very high concern. In the United States (US), major manufacturers and processors of PFASs participated to work towards a phase-out of PFOA and related substances at the end of 2015 (OECD, 2015). Consequently, PFOS, PFOA and four other PFASs were included in the US Environmental Protection Agency (USEPA) third Unregulated Contaminant Monitoring Rule (UCMR3) (USEPA, 2012). A lifetime health advisory for a combined concentration of 70 ng/L for PFOS and PFOA in drinking water was also released (USEPA, 2016a, 2016b). In Asia, Japan has listed PFOS and its salt under Chemical Substance Control Law and PFOS was subjected to export restrictions. The Republic of Korea, listed PFOS, its salts and PFOS-F as restricted substances under the Persistent Organic Pollutants Control Act where manufacture, import, export and use of these substances are restricted except for specific exemptions and acceptable use in the Stockholm Convention. China started its regulatory and policy approach in 2008 with the issuance of the first batch of “High Pollution, High Environmental Risk Product

Catalogue” that includes high temperature melting membrane fluorine resin coating used on non-stick cookware, kitchenware, and food processing machinery (OECD, 2015).

The phase-out of PFOS and PFOA prompted the manufacture and use of short-chain homologues or other not fully fluorinated alternatives that have been called “emerging” PFASs (Wang et al., 2013) even though their safety information remains unclear. For example, GenX (2,3,3,3-tetrafluoro-2-((1,1,2,2,3,3,3-heptafluoropropoxy)-propanoate) was introduced as a safer alternative to PFOA, and 3H-perfluoro-3-((3-methoxy-propoxy) propanoic acid) ammonium salt (ADONA) replaced PFOA in fluoropolymer manufacturing (Renner, 2006). These alternatives are now being detected in the environment; GenX was detected in drinking water sources in North Carolina (Sun et al., 2016). A study on the worldwide occurrence and levels of PFASs in drinking water showed that short-chain PFASs, specifically perfluorobutanoic acid (PFBA), have the highest relative occurrence and level among other PFASs found in tap water and bottled water samples (Kabore et al., 2018). Several other fluorinated alternatives were also identified in the environment such as fluorinated ether acids and other classes of anionic, zwitterionic and cationic PFASs (McCord and Strynar, 2019; Barzen-Hanson et al., 2017).

In many high-income countries, studies focusing on PFASs identification utilizes suspect screening methods that take advantage of the accurate mass and fragmentation patterns derived from a high-resolution mass spectrometry (HRMS) (Barzen-Hanson et al., 2017; McCord and Strynar, 2019). Results of these studies prompt regulatory bodies to update requirement for PFASs monitoring and analysis. For example, in the US, the coverage of the USEPA method for determination of PFASs in drinking water is regularly updated (Shoemaker and Tetttenhorst, 2018), while Europe is gearing towards regulation of PFASs as a class and establishing a group limit value of 0.5 µg/L in drinking water under EU Drinking Water Directive (European Commission, 2017). While high-income countries have an organized approach to catch-up and deal with challenges brought up by the PFASs release in the environment, low and middle income countries (e.g. Philippines) have very limited data, if any, on PFASs. Instead, many Asian countries suffer from being a trash dump of other developed countries (Armas, 2019). Therefore, this work serves as the foundation for the PFASs data gathering to bring awareness on the presence of PFASs in the Philippine aquatic environment. On the other hand, Thailand, an upper-middle income country, became a party to the Stockholm Convention in 2005 and the treaty added PFOS to its 2009 global restriction list, this amendment went into legal force in 2010; however, other PFASs are not regulated (EARTH, 2019). Previous studies in Thailand were mainly focused on the analysis of legacy PFASs, hence, a more inclusive PFASs analysis would be useful to reinforce the need for a regulatory action. In this regard, we sampled bottled, tap, and vending machine drinking water and source water in the Philippines and Thailand. The occurrence and levels of legacy and emerging PFASs in the samples were analyzed using liquid chromatography with tandem high – resolution mass spectrometry (LC – HRMS) employing both targeted and suspect screening analysis for a more comprehensive PFASs detection. PFASs contamination of the drinking water linked to its source was also investigated.

2. Materials and methods

2.1. Chemicals

Reference standards of 33 PFASs were purchased from Wellington Laboratories (Guelph, ON, Canada) - perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUdA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTTrDA), perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA), perfluorooctadecanoic acid (PFODA); perfluoropropanesulfonic acid (PFPrS), perfluorobutanesulfonic acid (PFBS), perfluoropentanesulfonic acid (PFPeS), perfluorohexanesulfonic acid (PFHxS), perfluoroheptanesulfonic acid (PFHpS), perfluorooctanesulfonic acid (PFOS), perfluorononanesulfonic acid (PFNS), perfluorodecanesulfonic acid (PFDS), perfluorobutanesulfonamide (FBSA), perfluorooctanesulfonamide (FOSA), 2-(N-methylperfluorooctanesulfonamido) acetic acid (N-MeFOSAA), 2-(N-ethylperfluorooctanesulfonamido) acetic acid (N-EtFOSAA), 4:2 fluorotelomer sulfonic acid (4:2 FTS), 6:2 fluorotelomer sulfonic acid (6:2 FTS), and 8:2 fluorotelomer sulfonic acid (8:2 FTS), N-methylperfluoro-1-octanesulfonamide (N-MeFOSA), Hexafluoropropylene oxide dimer acid (HFPO-DA), 11-chloroeicosafuoro-3-oxaundecane-1-sulfonate (11Cl-PF3OUdS), 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate (9Cl-PF3ONS), Dodecafluoro-3H-4,8-dioxanonoate (ADONA). Isotopically labelled mix standard solution (MPFAC – 24 ES), composed of ten ^{13}C -labelled perfluoroalkyl acids (C_4 – C_{12} and C_{14}), three ^{13}C -labelled perfluoroalkyl sulfonates (C_4 , C_6 and C_8), three ^{13}C -labelled telomer sulfonates (4:2, 6:2 and 8:2), two ^2H -labelled perfluorooctanesulfonamidoacetic acids and perfluoro-1- $^{13}\text{C}_8$ octanesulfonamide and a solution of ^{13}C -labelled PFOA (MPFOA) were also purchased from Wellington Laboratories. Trifluoromethanesulfonic acid (TFMS) was purchased from Alfa Aescor and pentafluoropropionic acid (PFPrA) was purchased from Acros Organics. Ammonium acetate was purchased from J.T. Baker, methanol and LC-MS grade acetonitrile were purchased from MilliporeSigma.

2.2. Sample collection and solid phase extraction

In Thailand, source water samples were collected from the main river in central Thailand and multi-purpose dams in Northeastern Thailand (Fig. 1). The main river in the central Thailand, Chao Phraya River, flows through Bangkok and Greater Bangkok area, and then empties water to the South China Sea at the Gulf of Thailand. Source water samples were collected from three pumping stations located in Nonthaburi (the upper province), Bangkok (the capital of Thailand), and Samut Prakan (the lower province). Source water in Northeastern Thailand were collected from Ubol Ratana Dam and Lam Pao Dam. All are significant waterbody that are used for recreation, aquaculture farming, and source of drinking, domestic, and irrigation water. Drinking water samples were also collected from vending machines located in different districts in Bangkok. The general public in Bangkok heavily rely on drinking water from vending machines.

This work is the first study that investigates the occurrence of PFASs in Philippine aquatic environment and thus serves as a range-finding assessment for future work. Samples were collected from Laguna Lake, the largest inland body of fresh water in the Philippines. It serves as one of the major sources that provides raw water to Metro Manila (the capital) and surrounding provinces, and

is the main source of freshwater fish in the country (LLDA, 2016). The lake is surrounded by both rural and urban areas, thus to compare PFASs occurrence in both areas of the lake, samples were collected in Sucat, Paranaque (an urban area) and in Victoria, Laguna (a rural area) – Fig. 1. Data from these two different sites will inform the water industry of the potential contamination that may need to be addressed as more water is drawn from the lake to secure additional water supply for the rapidly growing population in Metro Manila. Three to four replicates were collected in each sampling locations. In addition, several brands of bottled drinking water from these sources were also analyzed.

A 1-L surface water samples were collected in polypropylene plastic bottles (pre-rinsed with methanol). Each bottle was rinsed with the water sample being collected at the sampling site before filling the bottle with water for actual analysis. Chilled surface water samples were transported to the laboratory and pH was adjusted to 2.5 ± 0.5 to reduce bacterial degradation, filtered using a 0.47 mm WhatmanTM GF/A glass microfiber filter and spiked with 25 μL of 1.0 $\mu\text{g}/\text{mL}$ MPFAC-24ES solution. Analytes of interest were extracted and pre-concentrated through solid phase extraction (SPE) using Oasis[®] HLB and Oasis[®] WAX cartridges in tandem, pre-conditioned with 10 mL of methanol, followed by 10 mL of NanopureTM water. The HLB-WAX tandem cartridge approach for sample preparation was done to capture all PFASs that are anionic, cationic and neutral. By passing the water through HLB first, neutral, cationic, and most of the longer-chain anionic PFASs and other organic contaminants will be captured. The shorter chain anionic PFASs that are not adsorbed in the HLB cartridge will be captured in WAX. Samples were loaded onto the cartridge at a flow rate of 3–5 mL/min, and cartridges were then completely dried under vacuum conditions at about 15 psi. Elution was done using 5 mL of 0.1% NH_4OH in methanol, followed by 5 mL of methanol and 5 mL of acetonitrile. Combined eluate was then evaporated to dryness under a stream of nitrogen, spiked with 25 μL of 1.0 $\mu\text{g}/\text{mL}$ MPFOA as internal standard and brought up to a final volume of 250 μL with water–acetonitrile (95:5, v/v) solution. The final solution was then vortexed and transferred to 2 - mL vials and 20 μL was injected to the instrument for analysis.

2.3. Liquid chromatography - high resolution mass spectrometry (LC-HRMS) analysis

LC-HRMS analysis of PFASs was performed using Thermo Scientific Q-Exactive FocusTM with Thermo Scientific UltiMate 3000 UHPLCTM, operated in the negative ion mode for electrospray ionization (-ESI). Chromatographic separation of 33 PFASs was obtained using Waters X-BridgeTM C18 column (3.5 μm particle size, 2.1 mm i.d., 150 mm length) and mobile phase consisting of water with 5 mM ammonium acetate (mobile phase A) and acetonitrile (mobile phase B) at a flow rate of 200 $\mu\text{L}/\text{min}$ operated in gradient mode. A full-scan with data-dependent MS^2 (full MS -dd MS^2) was used with a scan range set to 80–1200 m/z . Precursor ions for each target compounds were inputted in the inclusion list. The resolution for full scan was 70,000 and 17,500 for dd MS^2 . MS/MS fragmentation of PFASs were obtained using three collision energies: 10, 20 and 30 V. Summary of the precursor ions, chromatographic retention time and linear range for the 33 PFASs is presented in Table S1.

Quantification was performed using isotope dilution technique to account for any matrix effects and correct for losses during sample preparation and transport. Limit of detection (LOD) and limit of quantification (LOQ) were established according to the method validation guideline published by Eurachem (Magnusson and Örnemark, 2014). Result for the extraction recovery study,

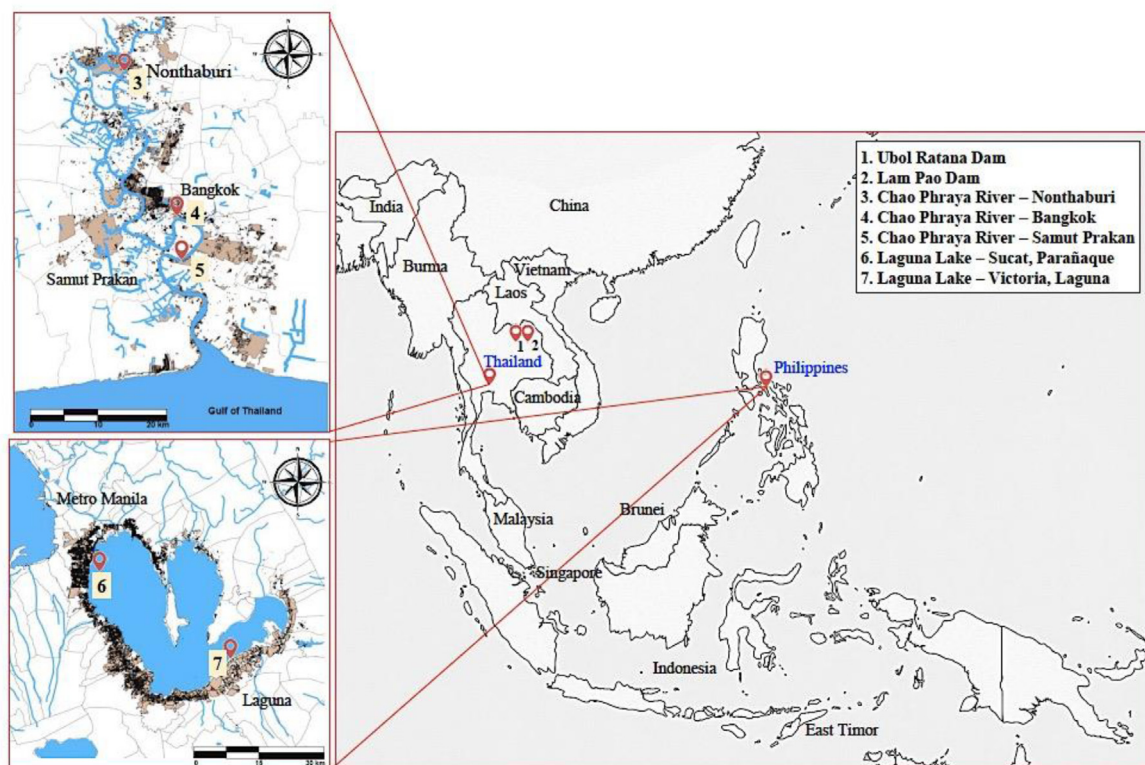


Fig. 1. Sampling sites for collecting source water samples investigated in this study. Locations 1 and 2 are Dams located Northeast of Bangkok, the capital of Thailand. Inset on the top left shows the sampling locations along Chao Phraya River (3–5) in Thailand, and inset on bottom left shows sampling locations in Laguna Lake (6–7), Philippines.

and the method LOD and LOQ are summarized in the supplementary information (Table S3).

2.4. Suspect screening for other PFASs not included in targeted analysis

Suspect screening for other PFASs that are not included in the targeted analysis was also performed. The list of PFASs was taken from the EPA PFAS Masterlist (USEPA, 2020) that contained 6792 fluorinated compounds with Chemical Abstract Service (CAS) of different PFASs classes (carboxylates, sulfonates, telomers, etc.) Due to the lack of MS² library for these compounds, the first step in screening only relied on the precursor ions within 5 ppm mass error and isotopic match of at least 80% using TraceFinder™ software. Peaks that were also found in the blank and standard mix were disregarded. After which, molecular formula and MS² fragmentation were inputted in MetFrag (MetFrag), to assess which is the most probable molecular structure that corresponds to the experimental data. Characteristics PFAS fragments such as $m/z = 118.9925$ which corresponds to CF_3CF_2^- and $m/z = 79.9573$ corresponding to SO_3^- , and fragmentation patterns such as neutral loss of CO_2 which is common for PFCAs, and neutral loss of HF which is common to polyfluorinated alkyl substances were also inspected if observed in the MS² spectra. Lastly, MS² fragmentation were manually annotated and probable structure is proposed.

3. Results and discussion

3.1. PFASs occurrence and levels

A summary of the frequency of detection of PFAS in drinking and surface water from Philippines and Thailand based on targeted

analysis is presented in Table 1 and detailed results showing actual PFASs concentrations detected in all samples are listed in Table S3.

Philippines. Out of 33 PFASs in the targeted analysis, 15 were detected in the Philippines source water samples, 11 of which were also detected in the drinking water samples. A 100% detection for PFBA, PFHxA, PFHpA, PFOA, PFNA and PFOS in both drinking and source water samples was observed and at least 43% detection frequency was observed for other PFASs determined (Table 1). The maximum concentration obtained for all PFASs ($\sum_{15}\text{PFASs}$) in the Philippines source water was 35.73 ng/L and 11.63 ng/L in drinking water. Suspect screening resulted in the detection of 4 additional PFASs that were not included in the targeted analysis (Table 2) in the source water, of which 2 were also detected in the drinking water. PFASs determined from suspect screening are classified according to confidence reporting proposed by Schymanski and co-workers (Schymanski et al., 2014). Two ultra-short chain PFASs (TFMS and PFPrA) that were detected in at least 70% of the samples were confirmed with a standard (confidence level 1, based on Schymanski category (Schymanski et al., 2014). Semi-quantitative analysis was performed and the concentration ranges found in source water are 6.21–22.09 ng/L (TFMS) and 2.38–4.20 ng/L (PFPrA). In drinking water, ranges are 0.10–0.84 ng/L and 0.95–8.59 ng/L for TFMS and PFPrA, respectively (Table S3).

Other PFASs in Table 2 were reported with confidence level 2a if the corresponding fragments in MS² spectra matched the spectra found in the literature, or if the compound has been previously reported in the environment; confidence level 2b is designated if fragment ions in MS² spectra provide diagnostic evidence of the structure, and confidence level 3 if at least one fragment corresponds to the possible structure proposed. MS² spectra and ion assignment for the observed experimental fragment for suspected PFASs with confidence levels 2a and 3 (Schymanski et al., 2014) are

Table 1

Summary of PFASs occurrence (% frequency of detection) in drinking and source water from Philippines and Thailand.

PFAS	LOD, ng/L	LOQ, ng/L	Philippines						Thailand					
			drinking water (n = 7)			source water (n = 8)			drinking water (n = 16)			source water (n = 15)		
			%DF	%QF	max, ng/L	%DF	%QF	max, ng/L	%DF	%QF	max, ng/L	%DF	%QF	max, ng/L
PFBA	0.03	0.06	100	100	1.12	100	100	5.15	94	94	1.65	100	100	6.52
PFPeA	0.03	0.06	71	0	0.05	100	100	1.57	25	19	0.72	80	80	30.26
PFHxA	0.03	0.06	100	85	0.26	100	100	2.08	88	88	1.08	100	100	2.86
PFHpA	0.02	0.03	100	100	6.19	100	100	5.94	100	100	50.48	100	100	95.17
PFOA	0.02	0.03	100	100	3.01	100	100	8.43	100	100	7.89	100	100	10.70
PFNA	0.02	0.03	100	100	0.43	100	100	1.54	100	100	2.73	100	100	1.82
PFUdA	0.03	0.06	0	0	—	63	63	0.99	31	31	2.02	0	0	—
PFBS	0.02	0.03	85	43	0.05	100	100	1.24	81	56	0.16	100	100	2.73
PFPeS	0.02	0.03	0	0	0.02	50	50	0.10	0	0	—	0	0	—
PFHxS	0.02	0.03	43	0	0.02	100	100	0.90	25	5	0.04	100	67	0.73
PFHpS	0.02	0.03	0	0	—	50	0	0.03	0	0	—	0	0	—
PFOS	0.02	0.03	100	100	0.39	100	100	2.85	100	100	0.33	100	100	1.30
6_2FTS	0.03	0.06	57	0	0.04	71	14	0.11	0	0	—	60	40	0.90
FBSA	0.02	0.03	0	0	—	100	100	2.63	13	0	—	100	100	9.59
N-MeFOSAA	0.06	0.13	71	71	4.88	100	100	6.23	88	75	11.01	20	13	3.24
Number of PFASs detected			11			15			12			12		
Range of the sum of quantifiable PFAS (Σ_{15} PFASs), ng/L			9.08–11.63			15.55–35.73			7.16–59.49			22.18–65.65		

LOD – Limit of detection; LOQ – Limit of quantification; %DF – %frequency of detection in samples containing PFAS concentration above LOD (% samples \geq LOD); %QF – % frequency of detection at concentrations above the LOQ (% samples \geq LOQ); Max – maximum concentration observed in the sample (ng/L).

Table 2

PFASs detected in the Philippines and Thailand water samples based on suspect screening approach using LC-HRMS.

PFAS	Formula	m/z observed	mass error, ppm	retention time, min	confidence level	CAS Number	% Detection Frequency			
							Philippines		Thailand	
							drinking water (n = 7)	source water (n = 8)	drinking water (n = 16)	source water (n = 15)
Trifluoromethanesulfonic acid (TFMS) ^a	CHO ₃ SF ₃	148.9533	4.9	3.65	1	1493-13-6	71	100	87	100
Pentafluoropropionic acid (PFPrA) ^a	C ₃ HO ₂ F ₅	162.9832	4.9	5.03	1	422-64-0	100	100	87	100
Trifluoroacetic acid (TFA)	C ₂ HO ₂ F ₃	112.9860	3.7	2.42	2a	75-05-1	0	100	38	100
1-Perfluoropropylethanol	C ₅ H ₅ OF ₈	213.0156	0.5	10.49	2b	375-14-4	0	0	13	40
3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-2-(trifluoromethyl) octanoic acid	C ₉ H ₂ O ₂ F ₁₆	444.9718	−1.8	16.48	2b	—	0	0	0	60
—	C ₆ H ₄ O ₂ F ₆	221.0030	−4.9	12.1	3	—	0	100	0	100

^a Confirmed with a reference standard; semi-quantitative results summarized in Table S3.

shown in supplementary information part IV, Figures a–d.

Thailand. Using targeted analysis, 12 PFASs were detected in the source water samples, all of which were also detected in drinking water samples. A 100% detection frequency for PFHpA, PFOA, PFNA and PFOS in both drinking and source water samples was observed and at least 13% detection frequency was observed for other PFASs determined (Table 1). The maximum concentration observed for Σ_{15} PFASs above LOQ in the source water was 65.65 ng/L, and 59.49 ng/L in drinking water. Suspect screening resulted in the detection of 6 PFASs that were not included in the targeted analysis method, 4 of which were also detected in drinking water (Table 2). Semi-quantitative concentration obtained for TFMS and PFPrA were 3.32–30.72 ng/L and 1.57–7.23 ng/L in source water, respectively; and TFMS and PFPrA were 0.06–5.91 ng/L and 0.21–2.40 ng/L in drinking water, respectively (Table S3).

3.2. Implication of result

3.2.1. Types of PFASs detected

PFASs can be classified based on the head group (e.g.

carboxylates, sulfonates) and on the length of alkyl chain. A fluorinated alkyl chain of six-carbon or less is considered short-chain and a fluorinated alkyl chain with at least seven carbon is considered long-chain (Buck et al., 2011). Considering results from both targeted analysis and suspect screening for all samples from both countries, 10 out of 21 detected PFASs were carboxylates, 6 out of 21 were sulfonates, and 5 out of 21 belong to other classes (telomer sulfonic acid, sulfonamide and telomer alcohol). Overall, 11 out of 21 (52%) detected were short-chain PFASs. Because there is no known fluorochemical manufacturing facility nor an active military site near the sampling locations, it can be assumed that contamination in the Philippines and Thailand is due to PFASs release from various consumer products that contain PFASs, and effluents from wastewater treatment plants. Unlike in studies from industrialized countries where direct inputs from a fluorochemical company or from an active military site have been identified (McCord and Strynar, 2019; Barzen-Hanson et al., 2017; Sun et al., 2016), these types of sources do not exist near the sampling sites used in this current study. Short-chain PFASs have higher mobility in the environment, and hence can be detected in water samples (Gellrich

et al., 2012). Specific regulation on PFOS and PFOA did not affect the production and use of unbranched and uneven chain PFASs such as PFBS, PFHxS, PFBA, PFHxA, PFHpA and PFNA (Kotthoff and Bucking, 2018). Therefore, it is not surprising that these PFASs were detected at 100% frequency in surface water samples from both countries. Ultra-short-chain PFASs (C_4 and shorter) such as TFMS, TFA and PFPrA were also detected in both countries; TFA and PFPrA have been previously detected in rainwater samples from Japan (Taniyasu et al., 2008) and in surface and groundwater in Germany (Janda et al., 2019). In a recent study focusing on the ultra-short-chain PFASs in Sweden, TFMS, TFA, PFPrA and other ultra-short-chain PFASs were found to constitute a large fraction of the total concentrations of PFASs in water (Bjornsdotter et al., 2019), hence detection of the ultra-short-chain PFASs is warranted. Previous studies have demonstrated that short-chain PFASs are primarily linked to releases from consumer products such as plastic materials, electronics, foam and textiles, wooden boards, carpets, food contact materials and in metal plating (Becanova et al., 2016; Kotthoff et al., 2015; Wang et al., 2013). The observed dominance of short-chain PFASs in this work could be linked to the presence of manufacturing industries near the sampling sites. For example, there is an industrial zone near Laguna Lake where several plastics, electronics, and metal manufacturers are located. Similarly, within Bangkok metropolis and Samut Prakan Province there are textile, electronics and wood/furniture factories; in Northeastern Thailand where Ubol Ratana Dam and Lam Pao Dam are located, textile, plastic/nylon-based consumer products, and pulp and paper manufacturing plants are also situated.

Other PFASs detected (6:2 FTS, FBSA, N-MeFOSAA) are either a PFOS alternative or a perfluoroalkyl acids precursors (Buck et al., 2011). For example, 6:2 FTS which is considered both as precursor and as PFOS alternative is used in metal decorative plating in Europe (UNEP, 2012) and as a main component in aqueous film forming foam formulations (Kleiner and Jho, 2009). FBSA, on the other hand is considered as a metabolite of a fluorinated compound that contain N-methyl-perfluorobutanesulfonyl chemical moiety ($C_4F_9SO_2N(CH_3)^-$), which is an active component of post-2002 Scotchguard™ fabric protector (Chu and Letcher, 2014). The 3 novel PFASs ($C_5H_5OF_8$, $C_9H_2O_2F_{16}$, $C_6H_4O_2F_6$) detected from suspect screening have not been previously reported in any environmental samples; two of which were listed in online databases - EPA PFAS Masterlist ($C_5H_5OF_8$ - 1-Perfluoropropylethanol) and in Pubchem ($C_9H_2O_2F_{16}$ - 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-2-(trifluoromethyl) octanoic acid), while $C_6H_4O_2F_6$ was proposed based on the analysis of precursor ion and MS² fragmentation.

3.2.2. PFASs in source water

Surface water samples from both countries were collected from a multi-purpose river, lake and dams that are used as drinking water source, aquaculture sites and other important activities that have a direct impact to human health. Based on individual detection of compounds, it was observed that all the PFASs detected in surface water were also detected in the drinking water samples; higher detection frequency was observed in drinking water for PFASs that have a 100% detection frequency in surface water samples. For example, the compounds with the highest detection frequency (>80%) in drinking water (TFMS and PFPrA) are also the same compounds detected at highest frequency (100%) in source water. PFASs concentration levels between source and drinking water are also correlated; PFASs that are found to have higher levels in source water also have higher levels in drinking water such as PFHpA and PFOA; whereas, PFHpS which was below LOQ in source water samples was not detected in any drinking water sample. This observation suggests that the PFASs in drinking water is primarily coming from the contamination of the source water. Similar

findings were observed in a previous study (Boone et al., 2019; Kim et al., 2011) which reported correlation between the occurrence and levels of PFASs in drinking water and its source.

Philippines. Two of the identified causes of PFASs influx in aquatic environment are discharges from wastewater treatment plants (Arvaniti and Stasinakis, 2015) and discharges by urban runoff contaminated by non-point sources (Murakami et al., 2009; Zushi and Masunaga, 2009). Results from this study suggest that these two sources are the main culprit, based on the comparison of the Σ_{15} PFASs levels of the different surface water sampling locations in the Philippines. As shown in Fig. 2, two sampling points were compared in Laguna Lake - Victoria, Laguna (VL) which is surrounded by agricultural farms and residential area and Sucat, Parañaque (SP) - a more urbanized area, and receives discharges from wastewater treatment plants and flows from Pasig River and Manila Bay (two main waterways within Metro Manila - the capital of the Philippines). Σ_{15} PFASs in samples collected from Laguna is lower compared to samples collected from Parañaque at 95% confidence level ($p = 0.003$) suggesting that urban activities contribute to PFASs contamination of drinking water sources (Fig. 2).

Thailand. Among the different sampling locations for the source water analyzed, only Chao Phraya River had a previous data on PFASs occurrence and levels. In the 2008 study that determined the concentration of 10 PFASs ($C_5 - C_{12}$ PFCAs, PFHxS and PFOS) in the river, a maximum total concentration (Σ_{10} PFASs) of 10.3 ng/L was reported (Kunacheva et al., 2011). In this current study, among the 10 PFASs considered in the previous study, two long chain PFCAs (C_{11} (PFUdA) and C_{12} (PFDoA)) were not detected; however, the maximum concentration obtained for the other 8 PFASs ($C_5 - C_{10}$ PFCAs, PFHxS and PFOS) was 57.90 ng/L which is about ten times higher from the previous work. The significant increase in concentration could be attributed to the continuous use of PFASs in several consumer products that can be released once the product abrades. Chao Phraya River passes through the urban area and receives wastewater from both industrial and domestic activities. Three sampling points were compared within the Chao Phraya

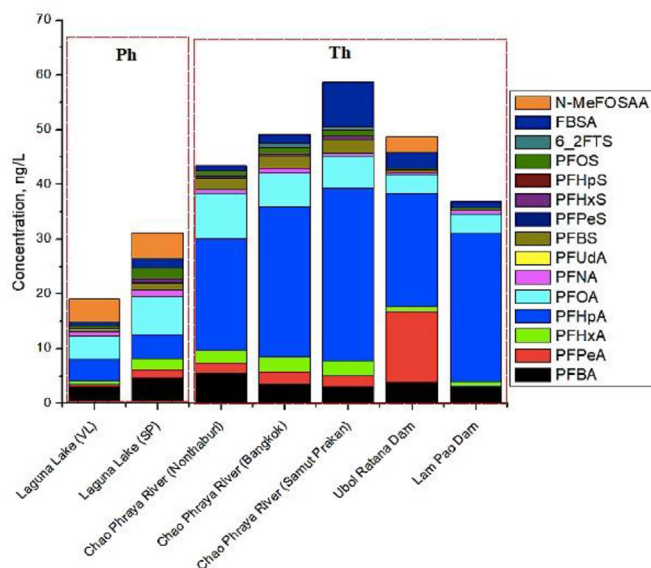


Fig. 2. Comparison of PFASs occurrence and levels in the different source water considered in this study. In the Philippines, two sampling locations were compared around Laguna Lake: Victoria, Laguna (VL) and in Sucat, Parañaque (SP). In Thailand, samples were collected along Chao Phraya River (Nonthaburi, Bangkok, Samut Prakan) and in two multi-purpose dams in Northeastern Thailand - Ubol Ratana Dam and Lam Pao Dam (concentrations are average values of replicates ($n = 3$ or 4) for each sampling location).

River: (1) Nonthaburi which is about 40 km north of Bangkok – the capital of Thailand, (2) central Bangkok (highly urbanized area) and (3) Samut Prakan which is about 10 km south of Bangkok. An increasing \sum_{15} PFASs concentration was observed in Nonthaburi to Samut Prakan (Fig. 2). Because PFASs are stable in the environment, contamination in Chao Phraya river could result to PFASs contamination in Gulf of Thailand, which is an important fish breeding and nursery grounds. PFASs detection in two multi-purpose dams (Ubol Ratana Dam and Lam Pao Dam) in Northeastern Thailand (Fig. 2) is also an important finding since both dams are primarily used for drinking water source, irrigation and aquaculture farming. For populations that relies heavily on fish as a major part of their diet, people from the Philippines and Thailand, may have significant human PFASs exposure through diet (Domingo and Nadal, 2017).

3.2.3. PFASs in drinking water

Philippines. A total of 13 different PFASs (11 based on targeted

analysis, 2 from suspect screening) were confirmed in the drinking water samples from the Philippines, of which 62% was short-chain. Prevalent PFASs were PFPrA, PFBA, PFHpA, PFOA, PFNA and PFOS (Tables 1 and 2) which all have 100% detection frequency in the drinking water samples. While this is the first study documenting the presence of PFASs in the Philippine drinking water, the profile of the PFASs detected is similar to what is commonly observed in several countries (Fig. 3).

Thailand. Except for PFHpS, the other 12 PFAS observed in the Philippines were also observed in Thailand, of which 64% is short-chain PFASs; and 100% detection frequency was observed for PFHpA, PFOA, PFNA and PFOS (Table 1). Despite of the worldwide effort to restrict PFOS and PFOA, their prevalence in the environment is still evident, with PFOA present at higher concentrations (2.19–7.89 ng/L) compared to PFOS (0.08–0.63 ng/L) (Table S3).

In both countries, PFHpA was found to be the most abundant

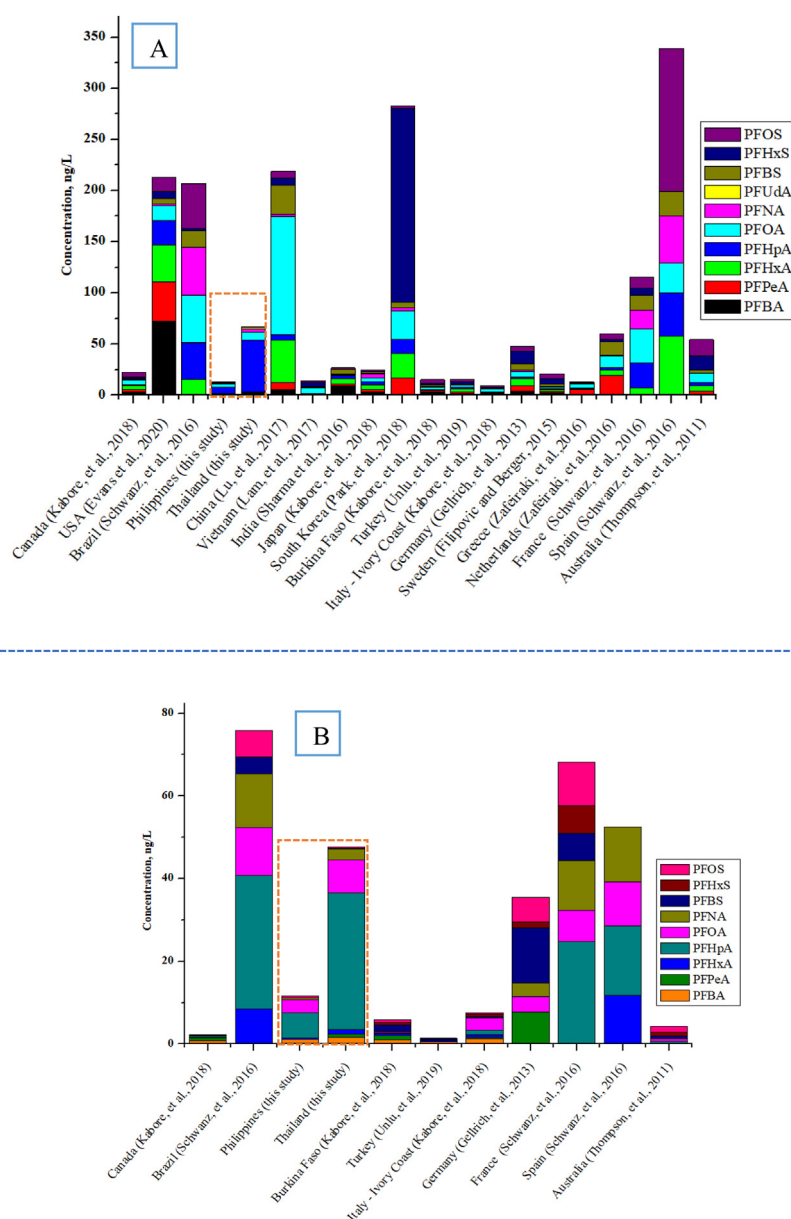


Fig. 3. Comparison of PFASs levels in drinking water from Philippines and Thailand (boxed area) to international data; A – All types of drinking water (bottled and vending machine water); B – bottled water only.

PFAS, with maximum concentration of 6.19 ng/L observed in tap water from the Philippines, and 50.48 ng/L found in vending machine water from Thailand. PFHpA is also the most abundant PFASs in all source water samples collected from Thailand (Fig. 2). Conventional and advanced drinking water treatment processes in Thailand (Tabtong et al., 2015) and other countries (Takagi et al., 2011) such as coagulation, sedimentation, chlorination and ozonation were found to be ineffective in removing PFASs; while activated carbon can efficiently remove PFOS and PFOA only when used for less than a year. In a previous study that determined the distribution and concentration of PFASs from consumer products, building materials and wastes, it was found that PFHpA was predominantly a breakdown product of coatings on carpets and textiles (Becanova et al., 2016). Textile and garments industries are one of the primary industries in Thailand and have a significant contribution to Thailand's economic development (Facts and Details, 2019). Prevalence of PFHpA in drinking water were also observed in samples collected from Brazil, France and Spain (Schwanz et al., 2016). N-MeFOSAA was found to be the second most abundant PFASs in the drinking water samples with highest concentration of 11.02 ng/L detected from locally produced bottled water in Bangkok. Although, N-MeFOSAA has not been previously reported in drinking water samples, it has been detected in Marina Bay, an urban watershed in Singapore (Nguyen et al., 2011).

PFASs detected in drinking water were compared to international data obtained from the literature ((Kabore et al., 2018; Evans et al., 2020; Schwanz et al., 2016; Lu et al., 2017; Lam et al., 2017; Sharma et al., 2016; Park et al., 2018; Ünlü - Endirlik et al., 2019; Gellrich et al., 2013; Filipovic and Berger, 2015; Zafeiraki et al., 2015; Thompson et al., 2011), comparison was limited to the commonly analyzed and detected PFASs (PFCAs and PFASs (perfluoroalkyl sulfonic acids)) in the previous studies (Fig. 3). Fig. 3A shows the comparison of all types of drinking water and Fig. 3B for commercial bottled water; both figures illustrate the prevalence of PFASs in drinking water across the globe even after bottled water treatment processes. Although generally, the levels are lower in bottled water sample, majority of the PFASs are still detected. Based on the USEPA health advisory of 70 ng/L for the combined concentration of PFOS and PFOA, the PFASs levels in the drinking water analyzed in this work will not likely pose immediate health risk to consumers. Nevertheless, a recent study found that exposure to low-level PFASs in drinking water (<20 ng/L) is a significant determinant of PFASs levels in serum for 5th grade children in Sweden (Glynn et al., 2020). Moreover, in an immunotoxicity study that determined the benchmark dose levels (BMDL) for the association of PFOS and PFOA to immune system suppression, the results suggest that the current US EPA limits for PFOS and PFOA in drinking water is too high. BMDL for PFOS was calculated to be 1.3 ng/mL and 0.3 ng/mL for PFOA, based on serum - PFAS level of 5-yr old children and serum antibody concentration against tetanus and diphtheria toxoids measured at 7 years old (Grandjean and Budtz-Jørgensen, 2013). In this regard, the levels of PFASs detected in drinking water from Philippines and Thailand may potentially pose risk to new-born babies and children. In particular, the brands of the bottled water samples from the Philippines are the preferred brands used for preparing formula milk for new-born babies and for their drinking water. In the US, several States have implemented stricter health guidelines or maximum contaminant levels (MCLs) for PFASs. For example, New York recommended MCL of 10 ng/L each for PFOS and PFOA; Vermont and Rhode Island are recommending a combined level of 20 ng/L for 5 PFASs (PFOS, PFOA, PFHpA, PFHxS, PFNA) and Massachusetts is recommending 70 ng/L for these 5 PFAS (Kindschuh and Lee, 2019).

4. Conclusion

A total of 21 legacy and emerging PFASs were detected in water samples collected from the Philippines and Thailand using targeted analysis and suspect screening. Although there were more types of PFASs detected in the Philippines water samples, PFASs concentrations were considerably higher in Thailand water samples. The PFASs profile and levels in source water and drinking water were found to be related, such that the frequently detected PFASs with high levels in source water were also detected in drinking water samples. Prevalence of short-chain PFASs in the water samples was also observed, suggesting the need to include short-chain PFASs in monitoring efforts. Despite the worldwide effort to regulate PFOS and PFOA, their environmental persistence remains problematic and result in their prevalence at levels above method LOQ. Overall, PFASs concentrations found in drinking water samples from the Philippines and Thailand were comparable to those found in other countries and do not exceed the US EPA health advisory for PFOS and PFOA. However, since data on the human health effects of short-chain PFASs currently do not exist, the inclusion of bottled water and drinking water re-fill stations in PFASs monitoring programs is warranted.

Declaration of competing interest

None.

CRediT authorship contribution statement

Mary Grace E. Guardian: Conceptualization, Methodology, Investigation, Writing - original draft. **Edison G. Boongaling:** Methodology, Investigation, Writing - review & editing. **Valeree Ross R. Bernardo-Boongaling:** Methodology, Investigation, Writing - review & editing. **Jirasak Gamonchuang:** Methodology, Investigation, Writing - review & editing. **Tittaya Boontongto:** Methodology, Investigation, Writing - review & editing. **Rodjana Burakham:** Methodology, Investigation, Writing - review & editing, Supervision. **Prapha Arnnok:** Methodology, Investigation, Writing - review & editing. **Diana S. Aga:** Conceptualization, Writing - original draft, Supervision, Funding acquisition.

Acknowledgements

The authors acknowledge National Science Foundation (Award #1905274 to DSA). MGEg acknowledge Nila T. Gnam Research Fund from the University at Buffalo for the support of this research.

The authors also acknowledge Shyrill Mae Mariano (Marine Science Institute, University of the Philippines – Diliman) and Patrick L. Fernandez (University at Buffalo) for the geographical maps and sample collection preparation.

Any opinions, findings, conclusions, or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the view of the NSF.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2020.127115>.

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