PERFLUORINATED COMPOUNDS IN THE PHILIPPINE ENVIRONMENT FOCUSING ON MANILA BAY AND LAGUNA LAKE

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Introduction

The assessment on the presence of perfluorinated compounds (PFCs) in the Philippine environment is a component of the United Nations University Institute for the Advanced Study of Sustainability (UNU-IAS) project on monitoring and management of persistent organic pollutants in the Asian Region. Perfluorooctane sulfonic acid (PFOS), its salts, and perfluorooctane sulfonyl fluoride (PFOS-F) are listed as among the 16 new POPs in the Stockholm Convention (SC). In addition, perfluorooctanoic acid (PFOA) and perfluorohexane sulfonic acid (PFHxS) and their corresponding salts are also proposed for listing under the SC[1].

Manila Bay and Laguna Lake are among the economically and ecologically important water bodies in the Philippines. Both are valuable fishing grounds for marine and freshwater fishes, respectively. Lately, Laguna Lake has been tapped as additional source of drinking water to the rapidly growing population of the Greater Metropolitan Manila Area and the nearby provinces. However, both bodies of water are continuously impacted by increasing rates of industrialization and urbanization. This study may provide baseline information to Philippine regulatory agencies on the status of these POPs in these bodies of water. It may also contribute to the global monitoring plan for the assessment of the effectiveness of the SC on PFCs in the Asian region.

Materials and Methods

Nine PFCs, namely PFOA, PFOS, PFBA, PFHxA, PFHxS, PFNA, PFDA PFUnDA, PFDoDA were measured in the waters and sediments of selected tributary rivers of Manila Bay (n=5; MB1 to MB5) and Laguna Lake (n=3; LL1 to LL3) that were monitored from 2016 until 2018. Most of these rivers are suspected recipients of PFC pollution either from domestic and industrial sources, except for Laguna Lake, LL1 that has headwaters located in a forested area. Thus, LL1 may provide the baseline level of PFCs for an unpolluted site in the Philippines. To assess potential routes of human exposures, PFCs were also measured in commonly consumed fish species caught from Manila Bay (MBF), the mackerel species, *Rastrelliger kanagurta* (long-jawed) and *Rastrelliger brachysoma* (short) and from Laguna Lake (LLF), the freshwater species, *Chanos chanos* and the *Oreochromis niloticus*, and also in drinking water samples (DW3) sourced from treated water from Laguna Lake. PFCs were also determined in two other drinking water samples (DW1, DW2) supplied from a relatively pristine area. The sampling locations are shown in Fig. 1. Samples were collected twice a year to cover the two distinctive dry (November to May) and wet seasons (June to October) in the Philippines.

From each sampling site, 500 mL river water samples in duplicates were collected at the mid-section of the river using stainless steel bucket and stored in PE bottles. Sediment samples, approximately 1 kg were collected using an Ekman dredge and passed through a 2.0 mm sieve on site. Fish samples were brought from fishermen or market vendors in areas nearest to the selected sampling sites within the Bay and the Lake with the help of local government agencies. Drinking water samples were collected directly from the faucet into the PE bottles. All samples were immediately kept in the ice box during transport and stored at -20ºC until processing.

Samples were prepared using the UNU-IAS and Shimadzu Corporation developed analytical protocols[2] for water, sediment and fish. All extracts were analyzed for the PFCs using the Shimadzu HPLC/MS/MS 8040 and 8045. QA/QC protocols were implemented through the analysis of blank samples for every batch of 10 samples analyzed, evaluation of accuracy from the recoveries of matrix and mass-labeled mix surrogate (MPFAC-MXA, Wellington Laboratories) spiked samples, and precision from % RSD of duplicate analysis. Practical quantitation limits (PQLs) were determined as the value equivalent to 10x the SD of n=7 injections of the of 0.5 ng/mL of mix native PFCs calibration standard.

Results and Discussion

Water and Sediments in the Tributary Rivers of Manila Bay and Laguna Lake.

Among the nine PFCs measured, five PFCs, i.e., PFOS, PFOA, PFBA, PFHxA and PFHxS were consistently detected in most of the water samples collected from the selected tributary rivers of Manila Bay and Laguna Lake in 2016 to 2018 particularly during the wet season, except in the background site (LL1: Pangil River) where the concentrations of all the PFCs were either not detected or below the PQL values (Fig. 2). The concentrations of the remaining four PFCs, i.e., PFNA, PFDA, PFUnDA and PFDoDA were generally low

Manila Bay Tributary Rivers | Laguna Lake Tributary Rivers (LL1 – Background Site)
Drinking Water Sampling | Fish Sampling

Fig. 1. Map of sampling sites for monitoring PFCs in the Philippines in 2016 to 2017.

except for the water samples obtained from LL3 (San Cristobal River) where relatively higher concentrations of PFNA were measured throughout the three-year monitoring period, ranging from 11 ng/L (2017 wet season) to 16 ng/L (2016 wet season). Several industrial areas are located in the vicinity of the river which may be the potential source of PFNA.

The frequency of occurrence of the PFCs in most of the river water samples were generally in the order PFBA>PFOA>PFHxA>PFHxS>PFOS. Generally higher concentrations of the PFCs were measured during the wet season as compared to the dry season (Fig. 3). PFCs may have been flushed into the rivers by the rains. The concentrations of PFBA are relatively higher than that of PFOS which is listed as POPs and also that of PFOA and PFHxS which are considered for listing as well. This may indicate that PFBA is used as substitute for these POPs PFCs.

Most of the PFCs in the sediments were generally not detected in all the tributary rivers, both during the dry and wet season samplings throughout the three-year monitoring period. There were sporadic detections of the POPs PFCs, i.e., PFOS and the candidates PFOA and PFHxS as well as PFNA and PFUnDA; however, the concentrations were generally low at less than the PQL values of the PFCs in the sediments. As these are polar compounds, PFCs may not be preferentially accumulated in the sediments.

Drinking Water

The concentrations of the PFCs that were detected in the drinking waters samples during the three-year monitoring period are presented in Table 1. Aside from PFOS, PFOA and PFHxS, PFBA was also detected at relatively higher concentrations. Among the drinking waters samples, higher concentrations of the detected PFCs were obtained in DW3 which is sourced from treated Laguna Lake water.

Fish in Manila Bay and in Laguna Lake

In the wet season sampling in 2018, the concentrations of PFOS and PFOA in the freshwater fish samples collected from Laguna Lake were relatively higher than those found in the marine fish samples from Manila Bay (Table 2). The PFOS concentrations in the fish samples from Laguna Lake were comparable to those found in the U.S. Great Lakes (Minnesota)[3], higher than those reported in Lake Vättern, Sweden[4]. The PFOA concentrations in the fish samples from both Laguna Lake and Manila Bay were relatively lower than the concentrations reported elsewhere[3,4,5].

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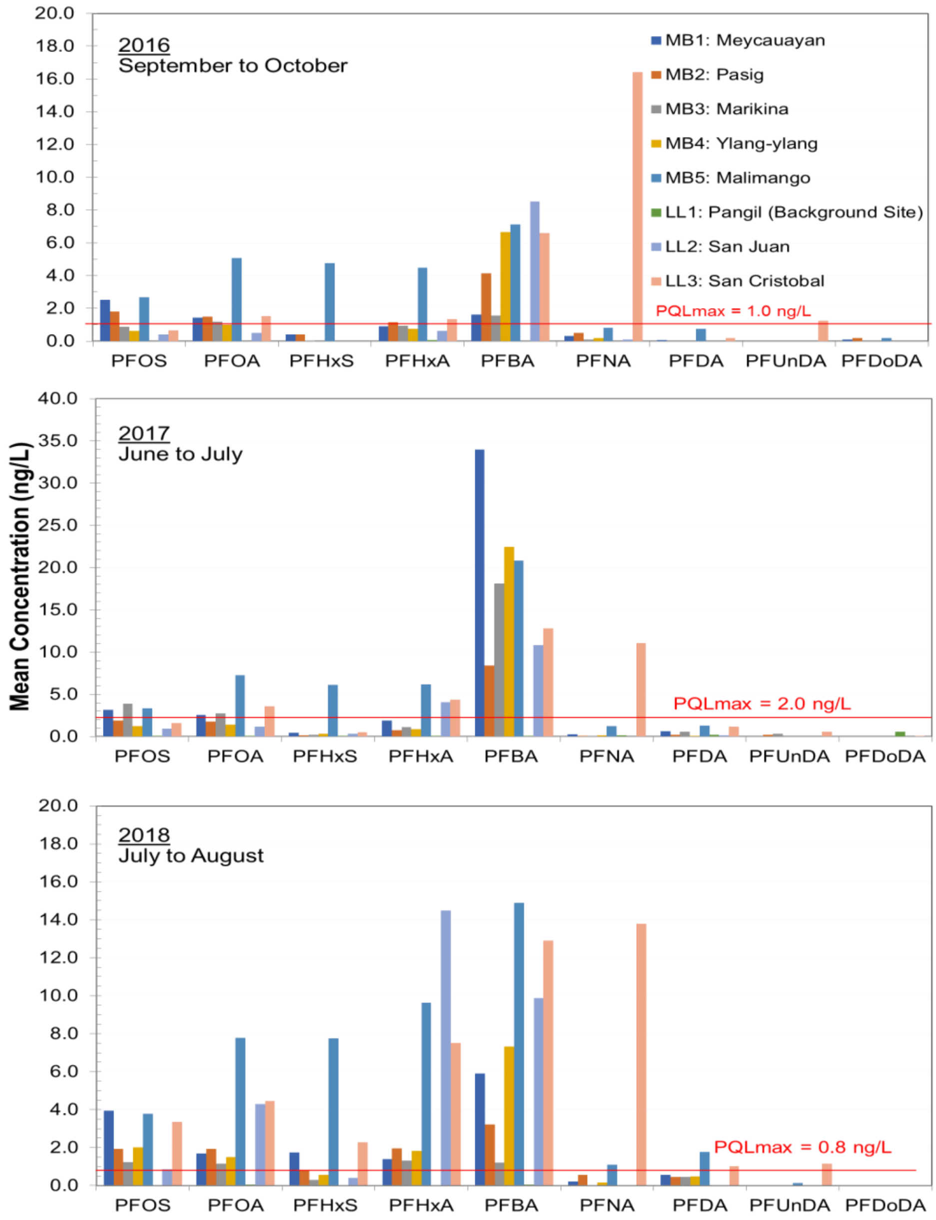

Fig. 2. Profiles of the PFCs in the water samples collected from the tributary rivers of Manila Bay and Laguna Lake during the wet season in 2016 to 2018.

Table 1. Concentrations of PFCs in samples of drinking water for the Greater Metropolitan Manila Area collected during the wet season in 2016 to 2018.

PFC	Concentration, ng/L								
	DW1			DW2			DW3		
	Year I	Year II	Year III	Year I	Year II	Year III	Year I	Year II	Year III
PFOS	<PQL(0.6)	ND	<PQL(0.4)	ND	ND	ND	<PQL(0.6)	<PQL(2)	1.6
PFOA	<PQL(0.6)	<PQL(2)	ND	<PQL(0.6)	ND	ND	0.9	<PQL(2)	2.9
PFHxS	ND	<PQL(2)	ND	ND	ND	ND	<PQL(1)	<PQL(2)	1.1
PFBA	6.39	5.62	0.44	1.88	0.97	<PQL(0.2)	2.68	5.64	6.17

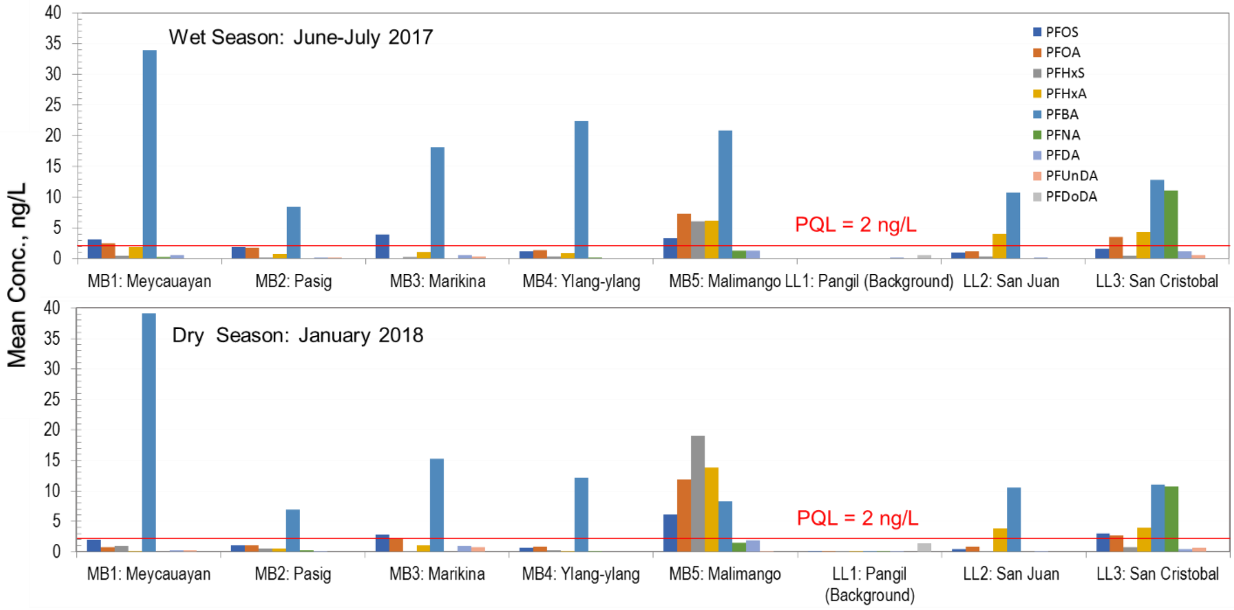

Fig. 3. Seasonal variation of PFCs in the selected tributary rivers of Manila Bay and Laguna in 2017-2018.

Table 2. Concentrations of PFOS and PFOA in selected fish species collected from Manila Bay and Laguna Lake during the wet season sampling in 2018.

Fish Sample	Location	Concentration, ng/g (wet wt.)		Reference
		PFOS	PFOA	
Mackerel, *Rastrelliger kanagurta*	Manila Bay, Philippines	ND	ND	This Study
Mackerel, *Rastrelliger brachysoma*	Manila Bay, Philippines	0.09-0.2	ND-<PQL(0.02)	This Study
Milkfish, *Chanos chanos*	Laguna Lake, Philippines	0.55-1.1	<PQL-0.04	This Study
Nile tilapia, *Oreochromis niloticus*	Laguna Lake, Philippines	ND-0.8	ND-0.02	This Study
Blue gills, black crappie, pumpkinsee	U.S. Great Lakes-Minnesota	1.08-52.4		Delinsky et al. (2010)
Salmon	Lake Vättern, Sweden	<0.1-0.13	6.86-10.1	Berger et al. (2009)
Japanese mackerel	Guangzhou, China		2.18	Gulkowska et al. (2016)

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References:

1. http://chm.pops.int/Implementation/NewPOPs/The9newPOPs/tabid/672/language/en-US/Default.aspx. Accessed 30 November 2018.
2. UNU-IAS Shimadzu Training Manuals: Monitoring and Management of POPs in Asia Training Workshops, July 2016.
3. Delinsky, AD, Strynar MJ, McCann PJ, et al. (2010) *Environ. Sci. Technol.* 4(7):2549-2554.
4. Berger U, Glynn A, Holmstrom KE, Berglund M, et al. (2009) *Chemosphere* 76(6):799–804.
5. Gulkowska A, Jiang Q, So MK, et al. (2006) *Environ. Sci. Technol* 40(12):3736–3741.