DISTRIBUTION OF PERFLUORINATED COMPOUND IN WATER, SEDIMENT AND BIOTA IN LANGAT RIVER WATER, MALAYSIA

Mohamad HDE [2], Ramli MR[3], Ahmad ED[1], Ali MM [2] Yoneda M[3]

[1]UBAT, Faculty of Medicine, University of Malaya, Kuala Lumpur, 50603, Malaysia, emmy85@um.edu.my
[2]SUCXeS, Faculty of Medicine, University of Malaya, Kuala Lumpur, 50603, Malaysia ; [3] Department of Environment Engineering, Kyoto University, KyotoDaigakuKatsura, Nishikyo-ku, Kyoto 615-8540, Japan

Introduction

The modern day environment is filled with thousands of synthetic chemicals and compounds used in everyday life. Some of these chemicals are useful and beneficial to the human body while there are also numerous global pollutants that are known to be toxic and can cause harm to human. Some of global pollutant that have undesirable effect to humans are Persistent Organic Pollutants (POPs)(1). PFCs, especially PFOS and PFOA, received special concern due to their persistence and the fact that the pollution is widely spread across a large geographical landscape (2).

Two known PFCs, perfluoro-n-octanoic acid (PFOA) and perfluoro-1-octanesulfonic acid (PFOS) are mostly used in firefighting foam, textiles, and electronic parts. Several countries are still producing PFOS and PFOA even though the uses of PFOS have been restricted worldwide (3). The toxicity of PFOA and PFOS have been extensively confirmed in several studies (4). Stockholm Convention has listed PFOS as one of the Persistent Organic Pollutant in Annex B (3).

Due to the highly resistant properties of PFCs to degradation processes and its tendency to bioaccumulate, these compounds will continue to persist in the environment in the near future. Furthermore, PFCs are mostly water soluble, thus making a conventional water treatment system ineffective in eliminating these compounds. PFCs have been found in surface and tap water in both developed and developing countries. Besides water environment, they were also found in animals and humans (5).

Under the UNU project, the widespread distribution of PFCs in the state of Selangor, Malaysia was investigated. Langat River Basin were chosen as the sampling location because these rivers receive effluents from industries and commercial activities, apart from that they are also used as the source for water treatment plants. The monitoring of 9 types of perfluorinated compounds were performed on surface water and sediment collected along Langat River during the wet season and the dry season in the year of 2016 until 2018.

Materials and methods

Locations and methods of sampling

A total of 25 locations along Langat River Basin were identified for sampling. Langat River is approximately 190 km long and covers an area of about 2423 km^2.

Sample preparation for water, sediment and biota

The same method used in water samples were also used for extraction in sediment and biota. However, there was a pre-treatment step for sample clean up prior to SPE. This is done through liquid-liquid extraction by using 20mL of 20% methanol-water. A total of 50µL of surrogate solution containing 100ng/mL was added into treated sample before it was loaded into SPE cartridge. Oasis WAX Plus (225 mg) cartridges (Waters Corp., Milford, MA) were conditioned with 3mL of 0.1% ammonia-methanol, water, methanol followed by 0.1 M acetic acid-sodium acetate buffer each at a flow rate of 10 mL/min. 500mL of water sample was loaded on to the preconditioned cartridges at a flow rate of 10 mL/min with a positive-pressure pump system. The remaining 500mL sample was stored in case additional analysis was required. The cartridges were then dried completely for 10 minutes. The target analytes were eluted from the cartridge with 4mL of 0.1% ammonia-methanol with flow rate 1 drop per second. The eluate was then reduced in volume to less than 1 mL by nitrogen gas. Methanol were then added to total volume of 1 mL.The eluant was then filtered using 0.2µm syringe filter and kept in -20ºC before analysis using LCMSMS.

Instrument analysis

In this research, the LC system consisted of an LC-20AD XR UFLC system with a SIL-HT automatic sample injector (Shimadzu, Kyoto Japan) was used. The Shimadzu LCMS-8040 was used to identify analytes based on their mass, fragmentation, and retention time. Chromatographic separation was performed on analytical column: Shim-pack XR-ODS II (2.0 mmI.D. x 100 mmL., 2.2 µm) and using delay column: ChromaNik Sunrise C28 (3.0 mmI.D. x 30 mmL., 3.0 µm). Column temperature was 40°C with total running time 15 min. Mobile phase used were 2 mmol/L of ammonium acetate in water (pump A) and methanol (pump B). The flow rate was set at 0.3 mL/min and a gradient elution was used at room temperature. The gradient program began with 20% B, then ramped to 100% B at 10.00 min, and held until 12.5 min. The gradient then returned to 20% B at 12.6 min and this condition was held for a further 15.00 min. Sample injection volume was 2 µL. The detection was performed in multiple reactions monitoring (MRM) mode using electrospray ionisation (ESI) ion source, in negative mode. In this analysis 9 perfluorinated compounds (PFBA, PFHxA, PFOA, PFNA, PFDA, PFUnDA, PFDoA, PFHxS and PFOS) were analyzed.

Results and discussion:

Water samples analysis from year 2016 to 2018

The occurrence and concentrations of PFCs in samples collected from Langat River during wet season of 2016 are summarized in Table 1. Based on the results, most river water samples collected during wet season were tested positive for PFCs. From 9 compound analysed, 7 compounds were detected in water samples. All samples showed relatively high concentrations of all the PFCs monitored, and had a total PFCs (sum of all 9 compounds; PFC) concentration ranging between 1-307 ng/L. In Langat River, PFOA (mean=22 ng/L), PFBA (mean= 9 ng/L) and PFOS (mean= 9ng/L) were found to be the predominant PFCs and their concentrations in water ranged from 1 ng/L to 293 ng/L, from 1 ng/L to 42 ng/L and, 2 ng/L-26 ng/L respectively in wet season.

Meanwhile for year 2017, the summary concentrations of PFCs in river water along Langat River collected in March 2017 and July 2017 during wet and dry season are shown in Table 1. The mean ∑PFCs during wet season in the river water in Selangor area was approximately 16 ng/L and during dry season was approximately 8 ng/L. From 9 PFCs compound analysed, a total of 8 PFCs were detected in the water sample during wet season meanwhile only 4 PFCs were detected in dry season. Most samples showed relatively high concentrations of all of the PFCs monitored, and had a total PFCs (sum of all 9 compounds; PFC) concentration ranging between 1-139 ng/L and 1-41 ng/L for wet and dry season, respectively. PFNA, PFBA, PFOA and PFOS were the dominant PFCs found in samples during wet season with the mean values of 9 ng/L, 10 ng/L, 4 ng/L and 3ng /L respectively. Whereas PFHxA, PFBA, PFOA and PFOS were the dominant PFCs found in samples during dry season with the mean values of 2 ng/L, 4 ng/L, 5 ng/L and 1 ng/L respectively.

In 2018, sampling was only carried out at Langat River in February during the dry season and the summary concentrations of PFCs in river water along Langat River were shown in Table 1. The mean ∑PFCs during dry season in Langat River area was 8 ng/L. From 9 PFCs analysed, a total of 4 types PFCs were detected in the water samples during dry season meanwhile the other 5 types PFCs were either not detected or below the limit of quantitation. Most samples showed relatively great concentrations of all of the PFCs monitored, and had a total PFCs (sum of all 9 compounds; PFC) concentration ranging between 1- 43 ng/L. PFHxA, PFBA,PFOA and PFOS were the dominant PFCs found in samples with the mean values of 3 ng/L, 4 ng/L, 2 ng/L and 4 ng/L respectively.

Overall, PFBA, PFOS and PFOA are the types of PFCs commonly found in Langat River water. High concentrations of PFCs in water of this river may result from upstream transportation, tributaries of industrial discharges as well as local release of garbage and wastewater from human activities along the river. Many activities occur along the Langat River in which there are manufacturing activities, agriculture, fisheries and it is also a densely populated residential area (6). It was found that each year, the amount of PFCs content in the river water was not in specific trends in some locations. This may be due to several factors such as rainfall and uncertain weather in some areas causing uneven flow of rivers and poor water circulation.

Sediment samples analysis from year 2016 to 2018

As for sediment, the PFCs concentrations in Langat Rivers are summarized in Table 2. Concentrations of PFCs in sediments were generally less than the LOQ, and when detected, PFCs concentrations were generally less than those measured in water and biota. From the table, it was noted the most abundant PFCs found were PFOS and PFOA for sediment samples, the concentration was very minimum and most of the concentration was below the limit of quantification. Other PFCs such as PFUnA, PFNA, PFBA and PFDOA were also detected in several of the location with only small amount detected throughout the three-year period. Similar results were reported in other studies (7, 8). From year 2016 to 2018 it was found that only several sites contained PFC and most locations showed either not detected or below limit of quantification. In summary, only several sampling sites were tested positive with PFCs throughout the three-year period. The potential sources of the observed PFOS and other trace-level PFCs may be due to treatment of chemicals, piping materials, pumping facilities, or source contamination from the impact of waste streams (9). It appears that sediments collected along the Langat River contained only small amounts of PFCs and did not appear to be significant contributors to the levels of PFCs detected in biota samples.

Biota samples analysis

Detectable concentrations of some PFCs were observed in biota, including sea bass (n = 2) and mackerel (n = 5). Sea bass contained the greatest concentrations of PFCs, ranging from mean 0.8 to 2 ng/g compared to Mackerel ranging from mean 0.11-0.82 ng/g with PFHxA being the dominant analyte in mackerel while PFDA is the dominant analyte in sea bass (Table 3). Ironically, PFBA was found in sea bass, which could be due to the exposure to PFBA in the river water. The various PFCs concentrations in sea bass may be caused by habitat differences.

Conclusion

Selangor is a highly developed state in Malaysia that is home to millions of people and is vital for both manufacturing and tourism industry. In these studies we found relatively great PFCs concentrations in Selangor river water but little was known about their sources, distribution and transport that is known to have used PFCs extensively. Langat River has been chosen as major river site because the Langat River basin is unique in that it passes through three distinct administrative regions such as the federal territory of Putrajaya and Cyberjaya, the state of Selangor, and the state of Negeri Sembilan (10). The Langat River currently plays a crucial role not only in supplying drinking water, but also for waste disposal industry, agriculture, and manufacturing industry. However, the river's catchment area has been subject to deforestation, intensification of agriculture, soil erosion, urbanization, and industrialization; as a result, water pollution and water shortages have now become a severe problem (3), drawing attention from the public and the government.

As part of an ongoing study to determine the current status and extent of PFC concentrations, as well as potential for detrimental environmental effects in Langat River, the present study determined overall concentrations of PFCs in various environmental samples along Langat River in Malaysia. In general, it appears that water samples in Langat River contain more amounts of PFCs compared to sediment samples. In addition, some sampling locations in the lower reaches of the river with a reduced flow rate might serve as a final sink for contaminants from the upstream river runoffs. Generally, PFBA and PFOA were the dominant PFCs found in samples from the river water and sediment respectively which shows that these compound are commonly used in industries which could be due to its unique properties, such as they contains both hydrophobic and hydrophilic properties. In summary, we found that PFCs were widely distributed in the water, sediments and biotic organisms in Langat River. This is because the areas around Langat River are more developed and densely populated with industrial sites. Overall, the detection of PFCs in various environmental matrixes from this region of Malaysia suggests that further studies characterizing PFCs and their potential risk to both humans and wildlife are needed since there is some of the unusual PFC detected in biota and sediment sample.

Table 1: Summary of water samples in Langat River from 2016 to 2018

LANGAT RIVER (ng/L)

Analyte	2016 wet		2017 wet		2017 dry		2018 dry	
	n>LOQ	n=17	n>LOQ	n=25	n>LOQ	n=25	n>LOQ	n=25
PFHxA	6	ND-9.95 (3.36)	16	ND-5.29 (1.76)	6	ND-2.90 (1.58)	17	ND-14.30 (2.56)
PFDOA	0	ND	2	ND-1.80 (1.42)	0	ND- <LOQ	0	ND
PFUnA	0	ND	1	ND-3.12 (3.12)	0	ND	0	ND-<LOQ
PFDA	2	ND-3.82 (2.45)	0	ND- <LOQ	0	ND- <LOQ	1	<LOQ-1.10 (1.10)
PFNA	0	ND-1.11 (1.11)	2	ND-15.45 (8.52)	0	ND- <LOQ	0	<LOQ
PFBA	17	1-41.68(8.66)	20	ND-104.46 (9.62)	11	ND-6.43 (3.67)	25	1.04-13.75 (4.40)
PFOA	16	ND-293.34(21.60)	18	<LOQ-35.52 (3.67)	10	ND-35.48 (5.08)	13	<LOQ-1.04 (1.75)
PFHxS	0	ND-<LOQ	1	ND-1.14 (1.14)	0	ND- <LOQ	0	ND
PFOS	8	ND-26.21(8.85)	5	ND-8.79 (2.95)	1	ND-1.34 (1.34)	2	ND-10.52 (4.31)

Table 2: Summary of sediment samples in Langat River from 2016 to 2018

LANGAT RIVER (ng/g)

Analyte	2016 wet		2017 wet		2017 dry		2018 dry	
	n>LOQ	n=17	n>LOQ	n=25	n>LOQ	n=25	n>LOQ	n=25
PFHxA	0	ND	0	ND-<LOQ	0	ND-<LOQ	0	ND-<LOQ
PFDOA	0	ND	1	ND-0.41 (0.41)	0	ND-<LOQ	0	ND
PFUnA	1	ND-0.13 (0.13)	0	ND	0	ND	0	ND-<LOQ
PFDA	0	ND-<LOQ	0	ND-<LOQ	0	ND-<LOQ	0	ND-<LOQ
PFNA	6	ND-0.20 (0.13)	0	ND	0	ND-<LOQ	0	ND-<LOQ
PFBA	0	ND	1	ND-0.10 (0.10)	0	ND	0	ND
PFOA	0	ND-<LOQ	1	ND-0.10 (0.10)	1	ND-0.23 (0.23)	0	ND-<LOQ
PFHxS	0	ND	0	ND	1	ND-<LOQ	0	ND
PFOS	1	ND-0.31 (0.31)	0	ND-<LOQ	3	ND-0.28 (0.19)	1	ND-0.14 (0.13)

Table 3: Summary of Biota samples

BIOTA (ng/g)

Analyte	Sea Bass (*Lates calcarife*)		Mackerel *(R. kanagurta)*	
	n>LOQ	n=2	n>LOQ	n=5
PFHxA	1	ND-1.57(1.57)	1	ND-0.85 (0.82)
PFDOA	1	ND-0.80 (0.80)	0	ND
PFUnA	1	<LOQ-1.31 (1.31)	0	<LOQ
PFDA	1	ND-2.19 (2.19)	0	ND
PFNA	1	ND-2.01 (2.01)	2	ND-0.11 (0.11)
PFBA	2	0.58-1.46 (1.02)	0	ND-<LOQ
PFOA	2	0.20-2.15 (1.18)	0	ND
PFHxS	1	ND-0.96 (0.96)	0	ND
PFOS	0	ND	0	ND

Acknowledgements:
Special thanks are given to United Nation University-Institute for the Advanced Study of Sustainability and Shimadzu Co. Ltd for their long-term contribution to this project including funding resources and supporting analysis.

References:

1. Codling, G., Hosseini, S., Corcoran, M. B., Bonina, S., Lin, T., Li, A., ... & Giesy, J. P. (2018). Current and historical concentrations of poly and perfluorinated compounds in sediments of the northern Great Lakes–Superior, Huron, and Michigan. *Environmental pollution*, *236*, 373-381.
2. Fenton, S. E., Reiner, J. L., Nakayama, S. F., Delinsky, A. D., Stanko, J. P., Hines, E. P., ... & Petropoulou, S. S. E. (2009). Analysis of PFOA in dosed CD-1 mice. Part 2: Disposition of PFOA in tissues and fluids from pregnant and lactating mice and their pups. *Reproductive Toxicology*, *27*(3-4), 365-372.
3. Gore AC, Crews D, Doan LL, Merrill ML, Patisaul H, Zota A. Introduction to endocrine disrupting chemicals (Edcs). *Endocrine Society:76*.
4. Kunacheva, C., Tanaka, S., Fujii, S., Boontanon, S. K., Musirat, C., & Wongwattana, T. (2011). Determination of perfluorinated compounds (PFCs) in solid and liquid phase river water samples in Chao Phraya River, Thailand. *Water Science and Technology*, *64*(3), 684-692.
5. Li, X., Gao, Y., Wang, Y., & Pan, Y. (2014). Emerging persistent organic pollutants in Chinese Bohai Sea and its coastal regions. *The Scientific World Journal*, *2014*.
6. Ma, R., & Shih, K. (2010). Perfluorochemicals in wastewater treatment plants and sediments in Hong Kong. *Environmental Pollution*, *158*(5), 1354-1362.
7. Nordin, M. J., & Azrina, L. A. (1998). Training and research for measuring and monitoring ecosystem health of a large-scale ecosystem: The Langat Basin, Selangor, Malaysia. *Ecosystem Health*, *4*(3), 188-190.
8. (2013) Stockholm Convention on Persistent Organic Pollutants (POPs). In: Idowu S.O., Capaldi N., Zu L., Gupta A.D. (eds) *Encyclopedia of Corporate Social Responsibility. Springer*, Berlin, Heidelberg
9. Zainuddin, K., Zakaria, M. P., Al-Odaini, N. A., Bakhtiari, A. R., & Latif, P. A. (2012). Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) in surface water from the Langat River, Peninsular Malaysia. *Environmental Forensics*, *13*(1), 82-92.
10. Zhu, Z., Wang, T., Wang, P., Lu, Y., & Giesy, J. P. (2014). Perfluoroalkyl and polyfluoroalkyl substances in sediments from South Bohai coastal watersheds, China. *Marine pollution bulletin*, *85*(2), 619-627.