EVALUATION OF PERFLUOROALKYL ACIDS (PFAAs) IN WATER ENVIRONMENT, FOOD, AND HUMAN BODY IN KLANG VALLEY, MALAYSIA

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ABSTRACT

This thesis presents in-depth information on the level of PFAAs contamination in Malaysia, particularly in the Klang Valley area. The thesis was divided into 6 chapters with each of the chapter covers various part as followed:

Chapter 1 Introduction

This chapter briefly explained about the background and purpose of this research. The objectives, together with the scope of the studies were also covered in detail in this section.

Chapter 2 Literature review

Literature review mainly focused on the collection of literature on the topics relevant to the research that is being conducted. It starts with the introduction about Perfluoroalkyl Acids (PFAAs) such as characteristic, usage, and followed by the concern about PFAAs to the environmental and human health. Most of the previous studies done on the analysis of PFAAs in environmental media and human were also covered in this part. The literature about the pathway of human exposure to PFAAs was also collected and presented in this chapter.

Chapter 3 Level and Determinants of Serum Perfluoroalkyl Acids (PFAAs) In A Population In Klang Valley, Malaysia

This chapter focused on the level and exposure assessment of PFAAs in serum. The main objective of this article was to find out the significant determinants of PFAAs in the blood of the Malaysian population based on the self-report questionnaire to the level of PFAAs in serum. The types of determinants assessed were dietary intake, lifestyle, and socioeconomic. 219 participants from the Klang Valley area were selected for this study. The study showed that PFAAs concentrations up to 32.57ng/mL were detected in all serum samples. At least 7 PFAAs were detected in serum samples of 78% participant with Perfluorooctane sulfonate (PFOS) being the predominant PFAAs (median = 8.79ng/mL). Most PFAAs concentrations were higher in male and positively correlated

with age, while BMI and smoking were not significantly associated with serum PFAAs in the adjusted regression model. Taking into consideration the lifestyle variables, significant associations were found between nonstick cookware and perfluorononanoic acid, between dental floss and cosmetics and perfluorodecanoic acid (PFDA), and between leather sofa and perfluoroundecanoic acid (PFUnDA). In addition, consumption of beef was significantly associated with increased levels of serum PFUnDA, whereas consumption of lamb and chicken eggs was negatively associated with the serum levels of PFUnDA and PFDA, respectively.

Chapter 4 Perfluoroalkyl acids (PFAAs) in surface water and sediment of Selangor and Langat river basin: spatiotemporal, partitioning, and ecological risk assessment. This chapter focused on the analysis of PFAAs in both surface water and sediment collected from Selangor and Langat River basin during the sampling year in 2017. Spatiotemporal analysis together with the water-sediment partition was also assessed in this chapter. The presence of perfluoroalkyl acids in surface water and sediment of the Selangor and Langat River basins were quantified using LC-MS/MS. At least 3 and 1 PFAAs were detected in surface water and sediment samples, respectively. The total concentration of PFAAs (∑PFAAs) in surface water samples were in the range of 0.886 – 133.692 ng/L and 0.419 – 138.945 ng/L, while in the sediment the range of not detected to 249.7 pg/g dw and 18.7 – 465.6 pg/g dw were detected in Selangor and Langat River basin, respectively. PFOA and PFBA were found to be a dominants PFAAs in both water and sediment samples. The mean concentrations of PFAAs in sediments were higher than in surface water. Urbanization and industrialization were identified as potential sources of PFAAs contamination in the area of Klang Valley. Field-based Log K_D were in the range of 1.5 to 2.3, slightly different from the previously reported value due to the differences in the physicochemical properties of water and sediment among studies. None of the PFAAs levels exceeded the PNEC value, suggesting little to no potential risk to the aquatic organisms.

Chapter 5 Levels and source exposure assessment of perfluoroalkyl acids (PFAAs) in selected foods and drinking water collected from the market within Klang Valley, Malaysia.

This research revealed the first evidence of the contamination of PFAAs in selected food and drinking water samples from Malaysia, particularly in the Klang Valley. Nine PFAAs were analyzed in 56 foods samples from 19 different types and 36 drinking water samples from the tap and bottled water using LC-MS/MS. In this study, PFAAs were found above the detection limit in all food samples and some drinking water samples analyzed. The highest level of mean ∑PFAAs in food was found in chickens (5.78 ng/g ww), followed by beef (3.14 ng/g ww), and marine fish (0.93 ng/g ww). Overall, all marine food samples tested were the main contributor of long-chain PFAAs (C≥8), except for mollusk. Mollusk was the major contributor for PFOA while the other food samples were the major contributor for PFOS. Tap and bottled water samples showed a varied concentration of PFAAs, which is dependent on the sources of the raw water intake. Based on the dietary intake exposure assessment, frequent consumption of chicken may lead to the health risk associated with FPAS to the local population especially to all group assessed, due to the high presence of PFOS in chicken samples. Intake of other food and drinking water will not cause any immediate health risk to human. However, health quotient above unity were observed for consumption of marine fish for adolescent, after taking into account the combination hazard ratio of PFOA and PFOS.

Chapter 6 Conclusion and future recommendation

This chapter summarized the conclusion of the various findings and their implications, as well as the recommendations for further research.

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LIST OF ABBREVIATIONS

ESI	Electrospray Ionization
(-CO_2H)	Carboxylic Acid functional group
(-SO_3H)	Sulfonic Acid functional group
AF	Assessment Factor
AFFF	Aqueous Film Forming Foam
BW	Body Weight
CCC	Criterion Maximum Concentration
CMC	Criterion Continuous Concentration
DWTP	Drinking Water Treatment Plant
EC50	Half maximal Effective Concentration
EDI	Estimated Daily Intake
ESFA	European Food Safety Authority
EWI	Estimated Weekly Intake
FOSE	Perfluorooctane Sulfonamide Ethanol
FTOH	Fluorotelomer Alcohols
HA	Health Advisory
HR	Hazard Risk
IARC	International Agency for Research on Cancer
KD	Partition Coefficient
KOW	Octanol-Water partition coefficient
LC50	Median Lethal Dose
LC-MS/MS	Liquid Chromatography–Mass Spectrometry
LOD	Limit of Detection
LOQ	Limit of Quantification
MEC	Measured Concentration of Chemical
MRM	Multiple Reaction Monitoring
MTBE	Methyl Tert-Butyl Ether
MW	Molecular Weight
ND	Not Detected
NOAEL	No Observed Adverse Effect Level
NOEC	No Observed Effect Concentration
PFAAs	Perfluoroalkyl Acids
PFAS	Per- and Polyfluoroalkyl Substances
PFBA	Perfluorobutanoic Acid
PFBS	Perfluorobutane Sulfonic Acid
PFCA	Perfluoroalkyl Carboxylic Acid
PFDA	Perfluorodecanoic Acid
PFDoDA	Perfluorododecanoic Acid
PFDS	Perfluorodecane Sulfonic Acid
PFHpA	Perfluoroheptanoic Acid

PFHpS	Perfluoroheptane Sulfonic Acid
PFHxA	Perfluorohexanoic Acid
PFHxS	Perfluorohexane Sulfonic Acid
PFNA	Perfluorononanoic Acid
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctane Sulfonic Acid
PFOSA	Perfluorooctanesulfonamide
PFPE	Perfluoropolyether
PFPeA	Perfluoropentanoic Acid
PFSA	Perfluoroalkane Sulfonic Acids
PFTA	Perfluorotetradecanoic Acid
PFTrDA	Perfluorotridecanoic Acid
PFUnDA	Perfluoroundecanoic Acid
PNEC	Predicted No Effect Concentration
POP	Persistent Organic Pollutant
POSF	Perfluorooctanesulfonyl Fluoride
PTFE	Polytetrafluoroethylene
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
RfD	Reference Dose
RQ	Risk Quotient
SD	Standard Deviation
SPE	Solid Phase Extraction
sqrt	Square Root
SVHC	Substance of Very High Concern
TBA	Tert-Butyl Alcohol
TDI	Tolerable Daily Intake
TWI	Tolerable Weekly Intake
UHPLC	Ultra High Performance Liquid Chromatography
UNEP	United Nations Environment Program
USEPA	United States Environmental Protection Agency
WAX	Weak Anion Exchange

CHAPTER 1
INTRODUCTION

1.1 Research Background

In recent years there has been increasing concern regarding the effects of chemicals capable of causing the body harm. Many of these so-called perfluoroalkyl acids (PFAAs) are significant organic pollutants in the environment. PFAAs are a group of synthetic fluorinated organic chemicals and have been commonly used in industrial and commercial purposes as fire-fighting foams, grease-proof coating for food packaging, shampoo, stain repellent, and surface coating for carpets and outdoor apparels. However, PFAAs are bioaccumulative, highly stable, and resistance to degradation. Due to the relative ease of dispersion of many of these chemicals in the general environment and also their persistent characteristics, many PFAAs are also classified as persistent organic pollutants (POPs).

PFAAs are mostly water-soluble, thus making a conventional water treatment system ineffective in eliminating these compounds. Previous studies have documented that PFAAs were detected in the air (Liu et al., 2015; Rauert et al., 2018), waters (Wang et al., 2019; Zainuddin et al., 2012), soil and plant (Dalahmeh et al., 2018; Naile et al., 2010), sediment (Qi et al., 2016; Zhao et al., 2015), biota (Lam et al., 2017; Yeung et al., 2009), and food (Heo et al., 2014; Zhang et al., 2019). In addition, PFAAs were also found in human blood and urine (Kannan et al., 2004; Worley et al., 2017). Studies by White et al. (2011) and Olsen et al. (2007) found that PFAAs are resistant to human metabolism and long half-life (2.3 - 12 year), resulting in a very slow human excretion, thus increasing concentration over time in a human.

PFAAs exposure to human comes from various routes and sources. Multiple studies have reported that dietary intake (Domingo & Nadal, 2017; Ji et al., 2012), indoor dust and air inhalation (Cho et al., 2015; Liu et al., 2015), and dermal contacts (Bjerregaard-Olesen et al., 2016; Boronow et al., 2019) as a potential route of PFAAs exposure in human. Multiple studies have connected PFAAs to various diseases found in human such as liver disease (Bassler et al., 2019); (Nian et al., 2019), endocrine disorders such as altered fertility and puberty (Joensen et al., 2009; Lopez-Espinosa et al., 2011),

increased total cholesterol (Jain & Ducatman, 2018; Nelson et al., 2010), and immune suppression (DeWitt et al., 2009; Dong et al., 2013).

Besides human, growing evidence suggests that PFAAs can also induce a similar disruption to aquatic wildlife. The documented effects of PFAAs on wildlife also include inhibition of reproductive, antioxidant and neurological responses of *Daphnia Magna* fishes (Liang et al., 2017), delayed in early development for offspring of *zebrafish* (Jantzen et al., 2017), and also induced metabolism disturbance and multi-generational reproductive toxicity in *Oryziah latipes* fish (Lee et al., 2017). Concerns over the ubiquitous contamination of PFAAs on environmental effects and human health have led to the restrictions and bans of some PFAAs. For example, Perfluorooctane sulfonate (PFOS) and its salts, Perfluorooctanesulfonyl fluoride (POSF), were listed in Annex B of Persistent Organic Pollutants by the Stockholm Convention while perfluorooctanoic acid (PFOA) and related precursors are proposed as POP (UNEP, 2016). Furthermore, perfluorohexane sulfonic acid (PFHxS) and several long-chain PFCAs (C8-C14) are being included in the REACH candidate list as a substance of very high concern (SVHC) (European Chemicals Agency, 2017). Due to this restriction, a shorter chain PFAAs such as PFBA, PFHxA, and PFPeA are being widely manufactured as an alternative since it was believed that these alternatives may have less toxicity potency compared to the other long-chain PFAAs (Buhrke et al., 2013; Luz et al., 2019). Consequently, the presence of these short-chain PFAAs in the environment and biota (including human) have been found to be increasing (Hsu et al., 2013; Wu et al., 2017).

1.2 Problem Statement

Most of the previous studies on PFAAs contamination in the environment and human were focused on the developed and highly industrialized countries like USA, China, and Japan because these countries manufacture PFAAs and used these chemicals to produce or manufacture other products. However, with the advancement of logistic and openness of the trade borders, import and export industries of these products have resulted in the contamination of PFAAs worldwide. Because of that, PFAAs were also found in the environments and humans worldwide, even in poor and developing countries (Habibullah-Al-Mamun et al., 2017; Hemat et al., 2010; Lam et al., 2017; Zainuddin et al., 2012). Furthermore, due to its resistance to degradation characteristic, PFAAs are

prone to long-range transport and this process is responsible for a wide distribution of PFAAs across the globe. There is even a study that found the presence of PFAAs in the Arctic, Atlantic Ocean and Antarctic coast due to the long transport of these chemicals (Zhao et al., 2012). Thus, it is necessary to carry out more studies to determine the contamination level of PFAAs from these poor and developing countries, particularly in Asia and not just focusing on the developed countries.

Although some PFAAs such as PFOS and PFOSF were added into the annex B Stockholm Convention and are highly regulated around the world, Malaysia is still not a Party to the treaty. PFAAs are not yet regulated in Malaysia and thus no elimination or control plan is exacted in Malaysia. This is why there is a need to study the contamination level of PFAAs in Malaysia so that the severity of the situation can be assessed and controlled. The finding in this study in hope will provide a further understanding of the importance of PFAAs exposure assessment in Malaysia, but may also drive stakeholders to get involved in better control of these chemicals.

1.3 Research Objectives

This study was initiated and intended to provide baseline information on the level of PFAAs contamination in Malaysia, particularly Klang Valley. There are two main objectives in this study and elaborations are given as to the activities associated with each objective.

a) To assess the occurrence and level of PFAAs in various media in the Klang Valley by:

i. Monitoring the occurrence and distribution of PFAAs in Selangor and Langat river basin by a sampling of surface water and sediment.
ii. Measuring the concentration of PFAAs in commonly consumed food and drinking water by a collection of a sample from the wet market.
iii. Assessing the level of PFAAs in the blood serum collected from the volunteering residents.

b) To develop and assess the ecological and human health risk assessment based on the findings from the first objective.

1.4 Scope of the Study

This study focused on Perfluoroalkyl Acids (PFAAs). In addition, this study also focused on the population of Klang Valley, Malaysia. Klang Valley is the most densely populated area in Malaysia which is situated in between Selangor state and Kuala Lumpur. The region encompasses an area of 2,843.42 KM^2 with an estimated population of about 7.2 million. Klang Valley experiences the tropical climate and is a commercial region with a high volume of traffic, industries, and services.

There are seven river basins located in Klang Valley, which are Sungai Selangor, Sungai Langat, Sungai Klang, Sungai Buluh, Sungai Sepang, Sungai Bernam, and Sungai Tengi river basin. Among these river basins, Selangor river basin and Langat river basin were chosen as the area of research for this study because these two rivers were the major supply of raw water with 65.27% and 24.17% raw water supplied to the drinking water treatment plant in Klang Valley, respectively (JPBDSelangor, 2016). Further details on Langat and Selangor river basin will be explained in chapter 2.

1.5 Thesis Outline

This thesis is divided into 7 chapters with each of the chapters covers various part as followed:

A) Chapter 1 Introduction

This chapter briefly explained about the background and purpose of this research. The objectives, together with the scope of the studies were also covered in detail in this section.

B) Chapter 2 Literature Review

Literature review mainly focused on the collection of literature on the topics relevant to the research that is being conducted. It starts with the introduction about Perfluoroalkyl Acids (PFAAs) followed by the concern about PFAAs to the environmental and human health. Most of the previous studies done on the analysis of PFAAs in environmental media and human were covered in this part. The literature about the pathway of human exposure to PFAAs was also collected and presented in this chapter.

C) Chapter 3 PFAAs in human blood

This chapter focused on the level and exposure assessment of PFAAs in serum. The main objective of this chapter was to find out the significant determinants of PFAAs in the blood of the Malaysian population based on the self-report questionnaire to the level of PFAAs levels in serum. The types of determinants assessed were dietary intake, lifestyle, and socioeconomic. 219 participants from the Klang Valley area were selected for this study.

D) Chapter 4 PFAAs in surface water and sediment

Analysis of PFAAs in the surface water and sediment collected along Selangor and Langat river basin were included in this chapter. The source characterization, distribution, and ecological risk assessment were also assessed in this chapter.

E) Chapter 5 PFAAs in food and drinking water

Analysis of PFAAs in food and drinking water collected from the wet market around Klang Valley area was presented in this chapter. Various types of food under different food group were analyzed in order to determine the seriousness of the food contamination in Malaysia focusing on PFAAs. Health risk assessment of the consumption of these food and drinking water were also assessed and elaborated in this chapter.

F) Chapter 6 Conclusion and future recommendation

This chapter summarized the general discussion of the various findings and their implications, as well as conclusions and recommendations for further research.

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CHAPTER 2
LITERATURE REVIEW

2.1. Introduction

This chapter introduced information about Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) then focusing on Perfluoroalkyl Acids (PFAAs). This review also focused on the exposure pathway and presence of PFAAs throughout the world where it was identified in various media such as surface water, sediment, food and drinking water, and also human blood. The toxicological effect of PFAAs on a human also explained in detail in this chapter. This review concludes with a description of the study area (Klang Valley) then focusing on the major river basin locating within Klang Valley which is Selangor and Langat river basin.

2.2. Poly- and Perfluoroalkyl Substances (PFAS)

Poly- and perfluoroalkyl substances (PFAS) can be defined as a chemical compound that contains 1 or more carbon atoms with perfluoroalkyl moiety CnF_2n+1. However, not all fluorinated substance is PFAS, such as hexafluorobenzene or refrigerants. Specifically, PFAS is aliphatic substances where all the hydrogens that attached to the hydrocarbon backbones have been substituted with fluorine atoms (except for hydrogen that is associated with a functional group (Buck et al., 2011). PFAS is extremely stable and strong, thanks to its Carbon-Fluorine bond. PFAS have been widely used as a surfactant since the 1940s due to their high thermal and chemical stability, combines with its hydrophobic, lipophobic properties, and for its ability to repel grease, oil, and water (Herzke et al., 2012).

PFAS comprises of 2 categories which are a polymer and non-polymer groups. Polymer groups consist of fluoropolymer (e.g. Polytetrafluoroethylene (PTFE)), perfluoropolyethers (PFPEs), and side-chain–fluorinated polymers (e.g. Acrylate and methacrylate). A non-polymer group consists of perfluoroalkyl substances (e.g. Perfluoroalkyl acids (PFAAs)) and polyfluoroalkyl substances (e.g. Fluorotelomer such as 10:2 FTOH) (Buck et al., 2011). More focus has been given to non-polymer PFAS since these compounds are very persistent in the environment and have been commonly

used in industries and consumer products. Among non-polymer PFAS, special concern is given to perfluoroalkyl acids (PFAAs) not only because these compounds have been directly released into the environment, but also due to the possibility that these compounds could indirectly transform from the precursor compound (polyfluoroalkyl substances) from metabolism or degradation (Li et al., 2018). For example, fluorotelomer alcohol (8:2 FTOH), a polyfluoroalkyl substance can degrade or metabolize to PFAAs such as PFNA or PFOA (**Figure 2.1**) (N. Wang et al., 2009).

There are 2 major classes under PFAAs, which are perfluoro carboxylic acids (PFCAs) and perfluoroalkane sulfonic acid (PFSAs). PFCAs is a compound with a carboxylic acid functional group (-CO_2H), while PFSAs is a compound with a sulfonic acid functional group. (-SO_3H). Examples of PFCAs and PFSAs together with their physicochemical properties are shown in **Table 2.1**.

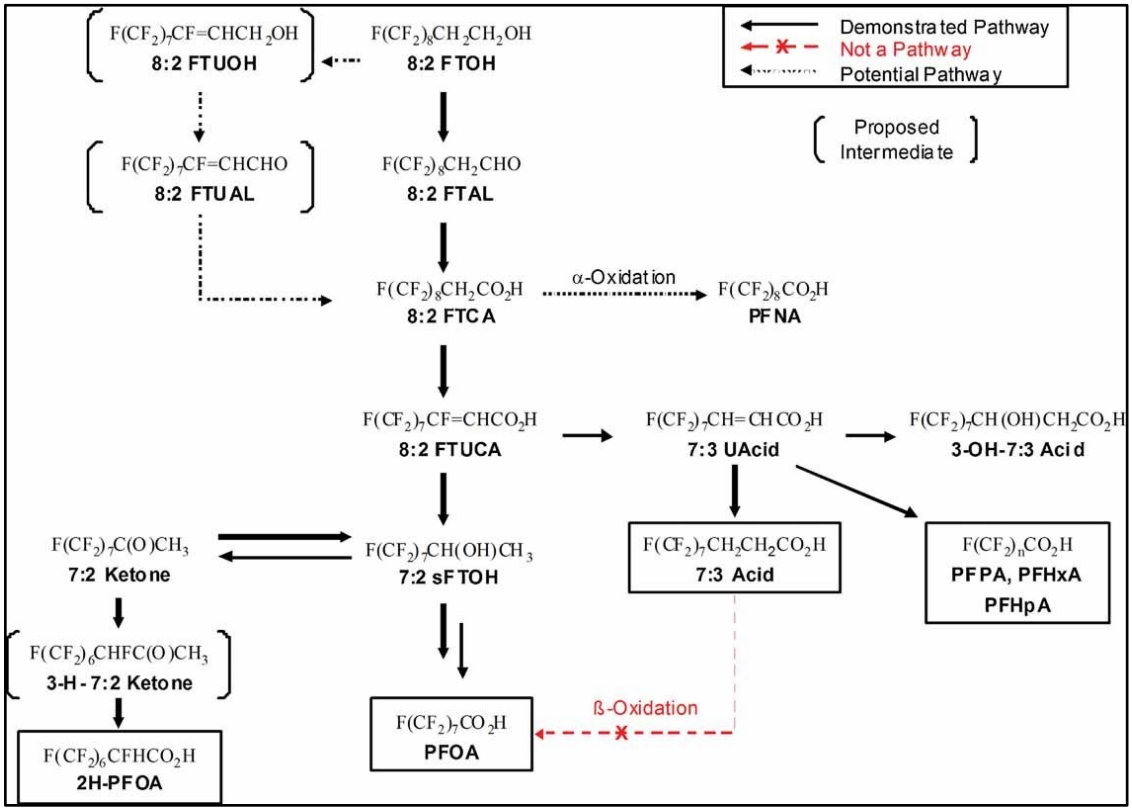
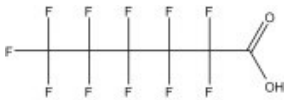
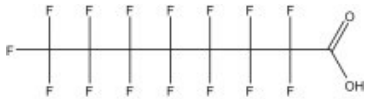
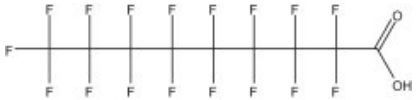
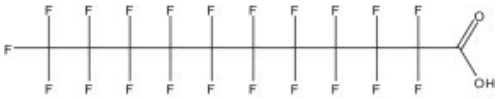
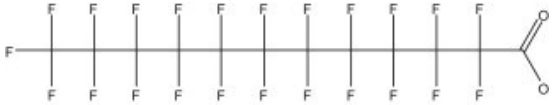
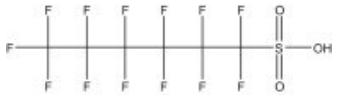
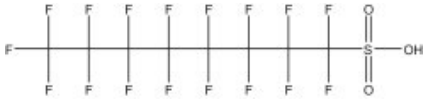


Figure 2.1. Transformation pathways of 8:2 fluorotelomer alcohol (8:2 FTOH) to perfluoroalkyl acids (PFAAs). Adapted from N. Wang et al. (2009).

Because fluorinated surfactants are very resistant to chemical damage such as acid, bases, and heat attack, they can be used in all kinds of media where a normal surfactant could not survive (Buck et al., 2011).

Table 2.1. Physicochemical properties of selected perfluoroalkyl acids (PFAAs). Adapted from CONCAWE (2016).

Name	Acronym	Chemical Structure	MW (g/Mol)	Log Kow	Vapor Pressure (Pa)	Water Solubility (g/L)
Perfluoroalkyl carboxylic acids (PFCAs)						
Perfluorobutanoic acid	PFBA		214.04	**2.82**	1307	Miscible
Perfluorohexanoic acid	PFHxA		314.05	**4.06**	**457**	**21.7**
Perfluorooctanoic acid	PFOA		414.07	**5.30**	4 - 1300	3.4 - 9.5
Perfluorononanoic acid	PFNA		464.08	**5.92**	1.3	9.50
Perfluorodecanoic acid	PFDA		514.09	**6.50**	0.2	9.50
Perfluoroundecanoic acid	PFUnDA		564.09	**7.15**	0.1	**0.004**
Perfluorododecanoic acid	PFDoDA		614.10	**7.77**	0.01	**0.0007**
Perfluoroalkyl sulfonic acids (PFSAs)						
Perfluorohexane sulfonic acid	PFHxS		400.11	**5.17**	**58.9**	**2.3**
Perfluorooctane sulfonic acid	PFOS		500.13	**6.43**	**6.7**	0.52 - 0.57

Bold font indicates value estimated with a published equation (Z. Wang et al., 2011). MW – Molecular Weight.

PFOA, one of the PFCA is used as aqueous dispersion agents for the production of a fluoropolymer such as a polytetrafluoroethylene (PTFE), which is an important polymer with very special properties which has been used in hundreds of industrial products. Water, grease, oil, and stain resistance properties of fluoropolymer make PFAAs a highly efficient surfactant. For example, PFAAs have been used to impart waterproof properties on clothes, non-stick properties on cookware, and stain-resistant properties of the carpet (Sunderland et al., 2019). PFAAs-based products can be used on either during the manufacturing process or aftermarket products such as water-resistant spray for shoes and clothes. PFAAs, particularly PFOS salts have also been used in aqueous film-forming foam (AFFF). AFFF is usually used in the area where the flammable liquid hazard is present, such as in airports and oil refineries due to its ability to extinguish even high-temperature fires (De Solla et al., 2012; Guelfo & Higgins, 2013; Sunderland et al., 2019).

2.2.1. Human exposure pathway to PFAAs

Human exposure pathways to PFAAs are not yet fully understood. A general outline of the PFAAs exposure pathway to humans is shown in **Figure 2.2**. PFAAs from industries can move through a different pathway before being ended up in humans. Most studies have suggested that oral exposure from consumption of food and drinking water as a major exposure pathway of PFAAs for humans (Sunderland et al., 2019). Consumption of PFAAs contaminated food and drinking water have been associated with the presence of PFAAs in humans (Averina et al., 2018; Halldorsson et al., 2008; Ingelido et al., 2018; Ji et al., 2012). Some of the studies also found that high level of PFAAs in food and drinking water, at which could pose adverse health effect to human in the long run (Heo et al., 2014; Liu et al., 2017; A. Zhang et al., 2019).

Blood samples collected from the population near the industries that manufacture or uses PFAAs has been known to contain PFAAs due to contamination of food and drinking water supplies from the releases of PFAAs from these industries (Boiteux et al., 2017; Steenland et al., 2009). However, the presence of PFAAs in human blood worldwide, even from the non-industrial area has suggested that another pathway of exposures may have been involved. For example, humans can also be exposed to PFAAs through inhalation of indoor or outdoor air and dust that are contaminated with PFAAs. Treated carpet and leather sofa have been found to contain PFAAs, and off-gassing of

PFAAs from these home accessories could contaminate an indoor air, which subsequently could end up in humans (Sunderland et al., 2019; T. Zhang et al., 2010). In addition, dermal contact with PFAAs containing items such as carpets, outdoor apparels, and textiles are also suspected as one of the human exposure pathway (Kotthoff et al., 2015). Furthermore, children are more vulnerable to PFAAs exposure from dermal contact and inhalation because they spent the most time in close contact with carpet from all the crawling and lying on top of a carpet. Thus, it is important to understanding the exposure pathway in order to determine the exposure risk of PFAAs to human.

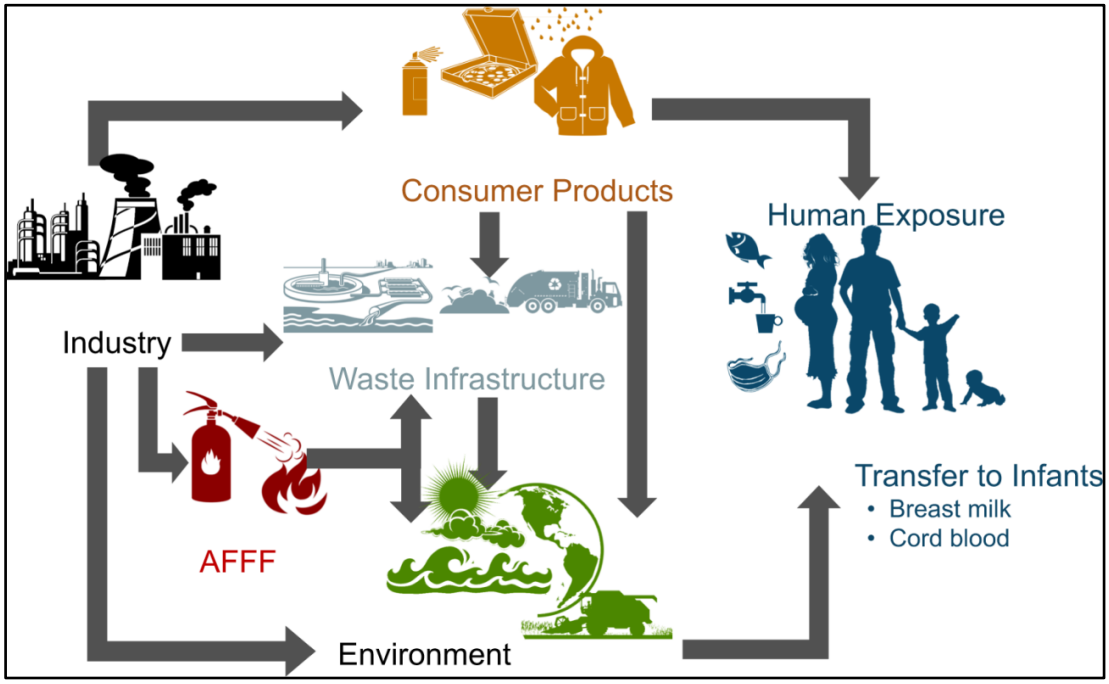


Figure 2.2. A general outline of the PFAAs exposure pathway to humans. Adapted from Sunderland et al. (2019).

2.2.2. Presence of PFAAs in the environment worldwide

PFAAs contamination worldwide was first reported in 2001. Analysis of tissue and blood samples of wildlife revealed the widespread distribution of PFAAs. The finding also suggests that PFAAs could bioaccumulate and that they could be persistent and toxic to organisms (Giesy & Kannan, 2001). Since then, thousands of studies have been conducted worldwide in order to find out PFAAs contamination in various environmental media such as surface waters, sediments, foods, and atmospheres. Various concentrations of PFAAs have been detected in surface waters, soils, and plants worldwide (Dalahmeh et al., 2018; Dong et al., 2018; Y. Wang et al., 2019; Zainuddin et al., 2012). High levels of PFAAs have been found particularly near PFAAs related

industries (Bao et al., 2011; Worley et al., 2017). Water bodies near airport and military bases at which AFFF have been used were also found to contain high levels of PFAAs, particularly PFOS (De Solla et al., 2012; Guelfo & Higgins, 2013). Furthermore, some studies have found a direct correlation between PFAAs levels in drinking water and raw water sources such as surface water (Boone et al., 2019; Rahman et al., 2014). PFAAs in sediment and biota also have been found to associate with the level of PFAAs in surface water (Campo et al., 2016; Lam et al., 2017). In addition, widespread contamination of PFAAs has also been found in human blood worldwide (Bjerregaard-Olesen et al., 2016; Kang et al., 2018). Occupationally exposed workers were notably shown a high concentration of PFAAs in their blood (Choi et al., 2017; Suja et al., 2009). Also, PFAAs were detected in animals and aquatic organism (Kumar et al., 2009; Senthilkumar et al., 2007). Consumption of PFAAs contaminated foods and drinking water have been suggested as a major exposure pathway to human (Babut et al., 2017; Domingo & Nadal, 2017). Residents of an area with PFAAs-polluted drinking water was shown to have high levels of PFAAs in their blood (Boiteux et al., 2017; Steenland et al., 2009). Furthermore, PFAAs has been found to resist human metabolism, with slow elimination and long half-life (2.3 - 12 year), resulting in a very slow PFAAs elimination in human, thus increasing concentration over time in humans (Olsen et al., 2007; White et al., 2011). The presence of PFAAs in some of the media worldwide is displayed in **Figure 2.3**.

Due to all the widespread distribution of PFAAs worldwide, combines with the concern on the adverse health effect of these PFAAs to humans, various organizations worldwide have restricted or controls the manufacturing, usage, and releases of PFAAs. For example, PFOS and its salts have been listed in Annex B of the Stockholm Convention on Persistent Organic Pollutants in the year 2009 which restrict the manufacturing and usage of these chemical (UNEP, 2016). In addition, perfluorohexane sulfonic acid (PFHxS) and several long-chain PFCAs (C8-C14) have been included in the REACH candidate list as a substance of very high concern (European Chemicals Agency, 2017). However, these regulations mostly focused on the developed or participating countries, which have resulted in the shifting of manufacturing and usage of PFAAs from one region to another. Thus, the more collaborated effort is necessaries in order to better control the contamination of PFAAs worldwide (Lindstrom et al., 2011).

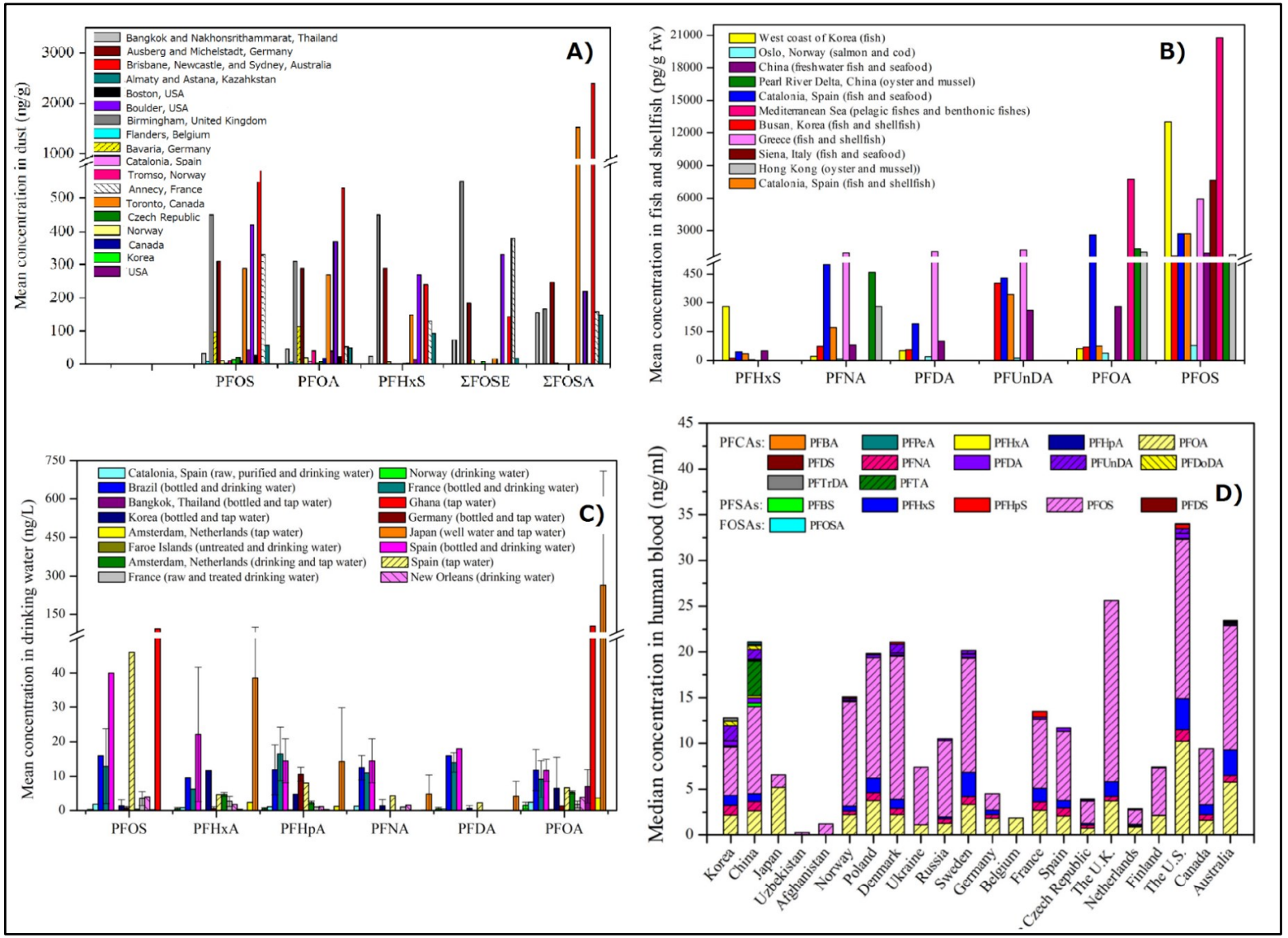


Figure 2.3. PFAAs distributions from selected studies worldwide in A) home dust; B) fish and seafood; C) tap and bottled water; and D) human blood. A, B, and C were adapted from Jian et al. (2017), while D was adapted from Jian et al. (2018). PFAAs acronyms are listed in the List of Abbreviations section.

2.2.3. Toxicological effects of PFAAs

Toxicological effects of PFAAs to human and animals have been conducted in the past few years to associate PFAAs exposure to various health effects like carcinogenicity, fertility, and immunology (Lau et al., 2007; Luz et al., 2019). Exposure studies on an occupationally exposed worker have associated PFOA with changes in birth weight, cholesterol, and thyroid disease in human (Barry et al., 2013; Darrow et al., 2013; Lopez-Espinosa et al., 2011; Steenland et al., 2013). A positive association between PFOA concentration and bladder, urinary tract, and kidney cancer were also found among the C8 Health Project's participants (Barry et al., 2013; Vieira et al., 2013). The mortality rate from disease in these organs was significantly higher than the mortality rate of the general population (Vieira et al., 2013). However, most of the positive results have been concluded as suggestive but not definitive (USEPA, 2016). In addition, studies of health effect on the general population did not show any correlation between PFAAs concentration and carcinogenicity (Eriksen et al., 2009; USEPA, 2016). Nevertheless, PFOA has been classified as a possible carcinogenic to humans (Group 2B) by the International Agency for Research on Cancer (IARC).

Although the studies on the health effect of PFAAs exposure on human are inconclusive, studies on animals are numerous with mounting evidence of adverse health effect. Carcinogenicity testing of PFOS on male and female rats showed a significant association with the incidence of hepatocellular adenoma (J. L. Butenhoff et al., 2004; USEPA, 2016). PFOA exposure in rats also showed a correlation with testicular Leydig cell adenomas and pancreatic acinar cell tumors (Biegel et al., 2001; John L. Butenhoff et al., 2012). However, it can be difficult to extrapolate the finding of these experiments to human health effects because of the differences in peroxisome proliferation expression, one of the mechanisms of PFAAs toxicity (Ghonem et al., 2014). In addition to carcinogenicity effect, chronic exposure of PFAAs has been shown to affect the liver, gastrointestinal tract, thyroid hormone levels and lipid metabolism in animals (Bassler et al., 2019).

2.3. Study Area

Klang Valley has been chosen as the study area. Klang Valley is the most populated area in Malaysia with an estimated 7.2 million populations living in this region (Department of Statistics Malaysia, 2014). Klang Valley typically refers to a region comprising of 4 highly developed districts that are located within the Selangor State (Petaling, Gombak, Klang, and Hulu Langat). However, Kuala Lumpur and Putrajaya State (former and new capital city of Malaysia, respectively) were also included as a study area due to its significant development and its close proximity to Klang Valley (**Figure 2.4**). Being the heart of Malaysia's industry and commerce, there are various industries, housing, businesses, and administrative area in Klang Valley, and this makes Klang Valley a very good study area for the assessment of PFAAs contamination in this country. There are four major river basins located within or near this region and these river basins provided raw water supply to the population of Klang Valley. Among these four, Selangor and Langat River are the most important river basins, which supplies over 90% of the raw water to the population. Brief description of Selangor and Langat River basin are given in the following section.

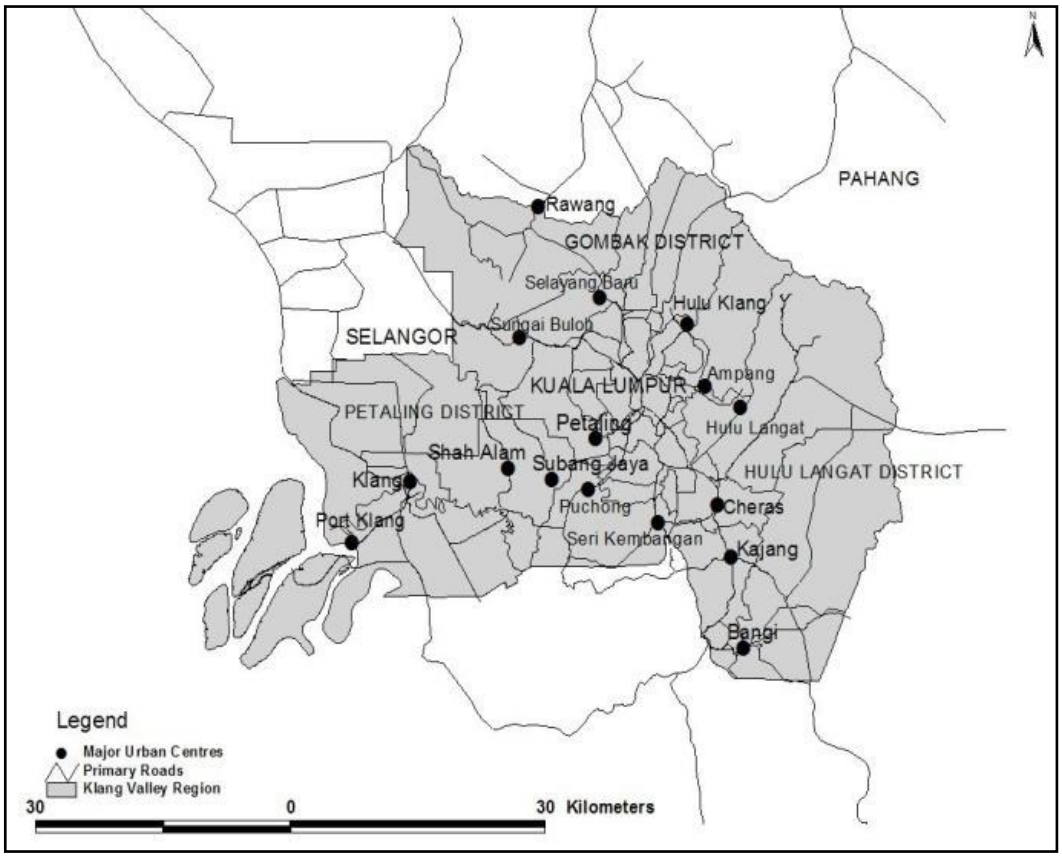


Figure 2.4. Map area of Klang Valley. Adapted from Dziauddin et al. (2013).

2.3.1. Selangor River basin

The Selangor River is one of the major rivers in the State of Selangor. The river rises from a mountainous spine known as the Main Range of Malaysia (Banjaran Titiwangsa); the main channel of the Selangor River is ~110 km in length and it flows in a southwesterly direction before draining into the Straits of Malacca. Selangor River basin is located on the northern part of Klang Valley (**Figure 2.5**). Selangor River basin, which has an area of ~2,200 KM^2, covers nearly a quarter of the total area of the Selangor State. In the upper catchment, the Selangor River has three main tributaries, each of them comprising many other small tributaries connected in a dendritic pattern. The headwaters of the Selangor River originate from the hilly forest reserves, and flow westward and meeting at Rantau Panjang. In the lower catchment, the river mostly passes through rural areas including rubber and oil palm estates before draining into Malacca Straits. The lower catchment of the Selangor River has the total area size of about 500 km^2 (below Rantau Panjang); the river over this stretch is about 57 km in length and has no significant tributaries. This lower section of the river is flat with several meandering reaches. The settlements and townships are more developed in the lower catchment; the major town is Kuala Selangor.

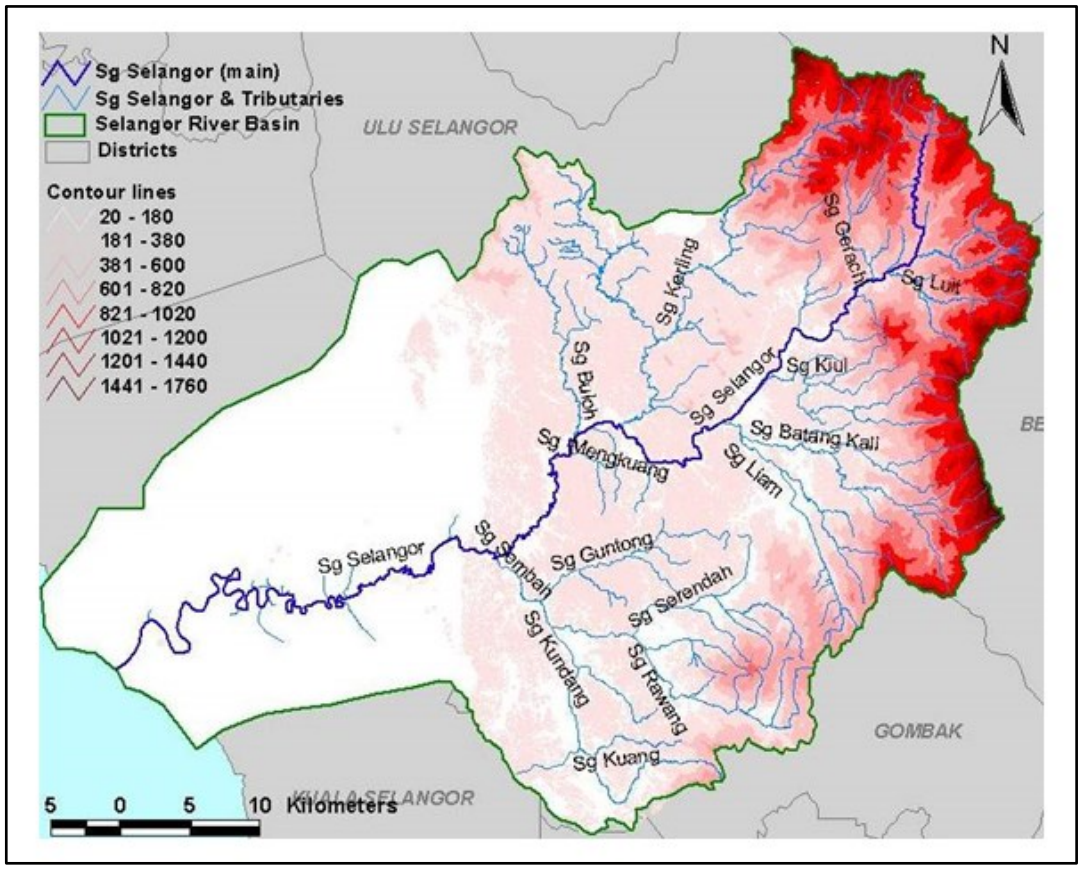


Figure 2.5. Selangor River and its main tributaries in Selangor River basin.

2.3.2. Langat River basin

The Langat River basin is the second biggest river basin in Selangor State with approximately 2,423 KM^2 of the water catchment area. Langat river basin starts from Nuang Mountain, which is located at the southern part of Klang Valley and flows through Kuala Lumpur, Selangor, and Putrajaya State and drains up at the Strait of Malacca, with a total length of 200 km (**Figure 2.6**). There has been rapid development and economic growth in this river basin for the past few years in order to fulfill housing, industrial and business demand in Selangor State. Except for the upstream area, the rest of the Langat River basin is much more developed with various infrastructure and industrial complex compared to the Selangor River basin. The biggest international airport in Malaysia is also located within this river basin. The rapid development in this river basin may have resulted in the deterioration of water quality due to pollution loading from domestic and industrial sources in this area, which possibly ends up in the main Langat River. Similar with Selangor River basin, sampling location for surface water and sediment samples in the Langat River basin were selected based on the accessibility of the sampling location, located near the populated and/or industrial area which also cover all tributaries that lead up to the main Langat River.

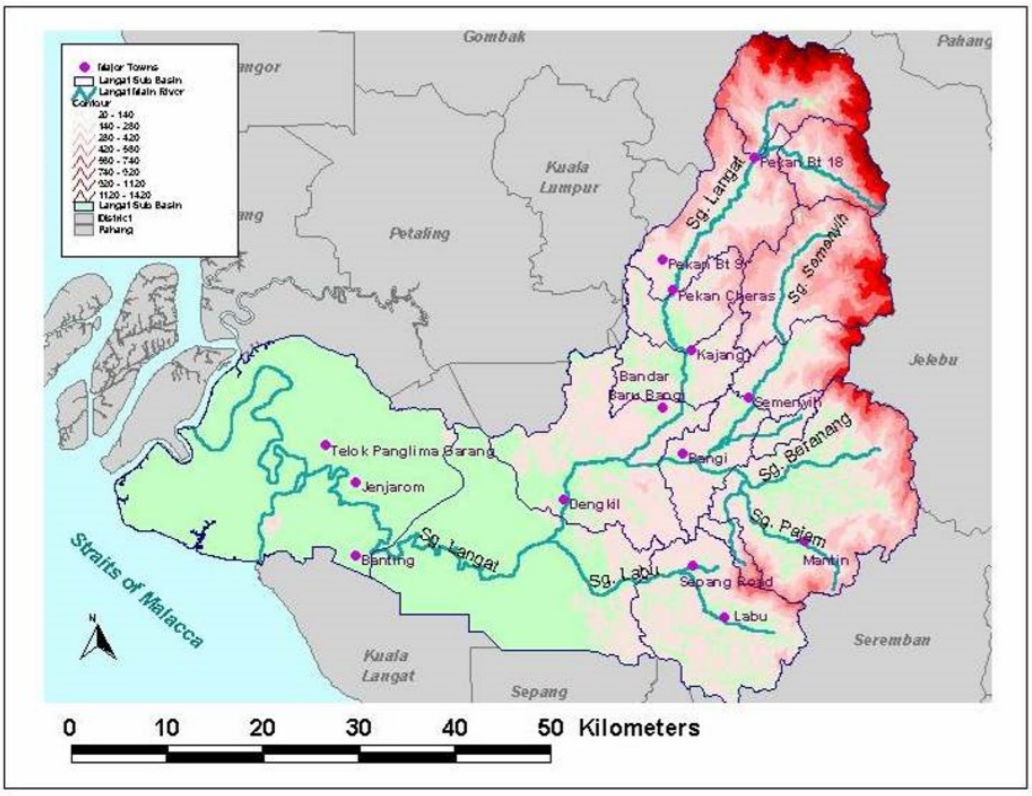


Figure 2.6. Langat River and its main tributaries in Langat River basin.

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CHAPTER 3
LEVEL AND DETERMINANTS OF SERUM PERFLUOROALKYL ACIDS (PFAAs) IN A POPULATION IN KLANG VALLEY, MALAYSIA

Abstract

For decades, perfluoroalkyl acids (PFAAs) have been commonly used for industrial and commercial purposes due to their water- and stain-resistant properties. Persistent pollutants that contain PFAAs have been associated with adverse health effects in humans, and many studies have documented dietary intake, indoor air inhalation, and dermal contact as the potential routes for human exposure to PFAAs. The aim of this study was to assess the level of PFAAs in the serum samples of a general population in a specific region in Malaysia. Using 219 serum samples collected from residents of Klang Valley, Malaysia, the levels of nine PFAAs were analyzed using liquid chromatography tandem mass spectrometry. In addition, questionnaire surveys on the dietary habits and lifestyles of the subjects were conducted. The results showed that PFAA concentrations of up to 32.57 ng/mL were detected in all serum samples. In 82.6% of the participants, at least seven PFAAs were detected in the serum samples, with perfluorooctanesulfonic acid being the predominant PFAA (median = 8.79 ng/mL). In the adjusted regression model, the concentrations of most PFAAs were higher in men than in women and positively correlated with age, although body mass index and smoking were not significantly associated with the serum PFAA concentrations. Taking into consideration the lifestyle variables, significant associations were found between nonstick cookware and perfluorononanoic acid, between dental floss and cosmetics and perfluorodecanoic acid (PFDA), and between leather sofa and perfluoroundecanoic acid (PFUnDA). In addition, consumption of beef was significantly associated with increased levels of serum PFUnDA, whereas consumption of lamb and chicken eggs was negatively associated with the serum levels of PFUnDA and PFDA, respectively.

3.1. Introduction

In recent years, great attention has been paid to perfluoroalkyl acids (PFAAs), such as perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs). PFAAs are a group of synthetic fluorinated organic chemicals that have been commonly used for industrial and commercial purposes, such as in fire-fighting foams, grease-proof coating for food packaging, shampoos, stain repellents, and surface coatings for carpets and outdoor apparels. Due to their widespread use and unique physicochemical properties, such as bioaccumulation, high stability, and resistance to

degradation, PFAAs are now being persistently used and occurring on a global scale. Previous studies have documented that PFAAs were detected in air, water, soil, plants, sediments, biota, and food (Domingo & Nadal, 2017; Xiao, 2017). In addition, PFAAs were also found in human blood and urine (Sunderland et al., 2019; Worley et al., 2017).

Many studies have reported the adverse effects of PFAAs on human health, including liver disease (Bassler et al., 2019; Nian et al., 2019); endocrine disorders, such as altered fertility and puberty (Joensen et al., 2009; Lopez-Espinosa et al., 2011); increased total cholesterol (Jain & Ducatman, 2018; Nelson et al., 2010); and immune suppression (DeWitt et al., 2009; Dong et al., 2013). Concerns over the ubiquitous environmental contamination with PFAAs and their effects on human health have led to the restrictions and banning of some PFAAs. For example, perfluorooctane sulfonate (PFOS) and its salts, such as perfluorooctane sulfonyl fluoride (PFOSF), were listed in the Annex B of Persistent Organic Pollutants by the Stockholm Convention, and perfluorooctanoic acid (PFOA) and its related precursors were proposed as persistent organic pollutants (UNEP, 2016). Furthermore, perfluorohexanesulfonic acid (PFHxS) and several long-chain PFCAs, such as C8-C14, were included in the REACH candidate list of substances that were of very high concern (European Chemicals Agency, 2017). Due to this restriction, shorter chain PFAAs, such as PFBA, PFHxA, and PFPeA, are being widely manufactured as alternatives that may have less toxicity, compared with the toxicity of long-chain PFAAs (Buhrke et al., 2013; Luz et al., 2019). Consequently, the presence of these short-chain PFAAs in the environment and biota, including humans, has been increasing (Ji et al., 2012; M. Wu et al., 2017). Human exposure to PFAAs comes from various routes and sources. Multiple studies have reported dietary intake (Domingo & Nadal, 2017; Ji et al., 2012), indoor dust and air inhalation (Cho et al., 2015; X. Liu et al., 2015), and dermal contact (Bjerregaard-Olesen et al., 2016) as potential routes of PFAA exposure in humans, but these findings were often inconsistent. For example, consumption of fish and seafood has been associated with an increased level of plasma PFAAs in South Korea and Norway (Averina et al., 2018; Kim et al., 2014), but no such association was found in the study by Eriksen et al. (2011) on Danish men. These differences can be attributed to the geographical differences in sources, pollution, and exposure.

Most of the previous studies on the PFAA level in humans focused on populations from developed countries (Eriksen et al., 2011; Gleason et al., 2015; Kärrman et al., 2009) or from nearby areas that were contaminated with PFAAs (Ingelido et al., 2018;

Steenland et al., 2013; Worley et al., 2017). Studies on populations from poor and developing countries, particularly in Southeast Asia, are limited. Furthermore, the contributions of specific food types and lifestyle to the PFAA level in human vary by geographical region and population characteristic (Muhammad et al., 2017). In 2004, Kannan et al. analyzed the level of PFAAs in human blood from populations of several countries and detected PFOS and PFHxS in the samples collected from a population in Malaysia. However, this study was limited in sample size and did not explore the exposure route of PFAAs to humans. Therefore, more studies need to be carried out, in order to determine the sources of exposure in such population. The present study was initiated for this purpose.

Specifically, the aim of this study was to assess the levels of nine PFAAs (seven PFCAs and two PFSAs) in the serum samples of the residents of Klang Valley, Malaysia. Klang Valley, which is strategically located at the heart of Selangor State and Kuala Lumpur, is the most densely populated area in Malaysia and has various industries and a high level of traffic. Based on the responses of the participants to a questionnaire, we aimed to investigate the association of PFAA concentrations and the possible significant determinants, such as dietary habits and lifestyle. The results of this study can provide further information on the contamination of polyfluoroalkyl substances (PFAAs), especially in developing countries, and subsequently assist the stakeholders in improving the control of these chemicals.

3.2. Materials and Methods

3.2.1. Collection of Serum Samples

In May 2016, a total of 219 blood samples were collected from the donors in Klang Valley. The demographic data of this population, as well as the number of cases per category of determinants, are shown in **Table 3.1**. A certified medical doctor drew approximately 8 mL of blood from the median cubital vein and placed this blood in a 10-mL red cap Vacutainer (Becton Dickinson, New Jersey, USA) without any additive. The blood was allowed to clot at room temperature and was centrifuged at 3000 rpm for 15 minutes before being transferred into a 2-mL Nalgene cryovial (Thermo Fisher Scientific, New York, USA) for storage at −80 °C until extraction. The serum samples were extracted within three months after collection. Ethics approval was obtained from the Medical Research Ethics Committee of the University of Malaya Medical Centre (MREC ID: 201512-1956).

Table 3.1. Characteristics of the participants.

Variable	N (%)	Variable	N (%)
Total Participants	219 (100%)	Car Use	
		Yes	41 (18.7%)
Gender		No	178 (81.3%)
Male	66 (30.1%)	Non-stick Cookware	
Female	153 (69.9%)	Yes	65 (29.7%)
		No	154 (70.3%)
Age		Camping Tents	
Less than 20 years	8 (3.7%)	Yes	20 (9.1%)
21-30 years	117 (53%)	No	199 (90.9%)
31-40 years	58 (26.9%)	Outdoor Clothes	
41-50 years	16 (7.3%)	Yes	63 (28.8%)
51 years and above	20 (9.1%)	No	156 (71.2%)
		Non-stain Carpet	
BMI		Yes	103 (47.0%)
Under weight	13 (6%)	No	116 (53.0%)
Normal weight	103 (47%)	Leather Sofa	
Overweight	58 (26.5%)	Yes	148 (67.6%)
Obese	45 (20.5%)	No	71 (32.4%)
		Dental Floss	
		Yes	86 (39.3%)
		No	133 (60.7%)
		Cosmetic	
		Yes	124 (56.6%)
		No	95 (43.4%)
		Smoking	
		Yes	11 (5%)
		No	208 (95%)

BMI - Body Mass Index (kg/m^2).
Underweight (BMI < 18.5), Normal weight (BMI 18.5 – 25),
Overweight (BMI 25 – 30), Obese (BMI > 30)

3.2.2. Chemical and Reagents

A mixture of native PFCAs and PFSAs (PFAC–MXB), together with a solution of mass-labeled PFCAs and PFSAs (MPFAC–MXA), were purchased from Wellington Laboratories (Guelph, Ontario, Canada). All standard and mass-labeled stock solutions were prepared in methanol hypergrade for LC-MS (Merck, Darmstadt, Germany) and were stored at −20 °C. High performance liquid chromatography-grade formic acid, methanol, and ammonium acetate were obtained from Fisher Scientific (Hampton, NH, USA). A solution with ≥25% of ammonium hydroxide was purchased from Merck. Ultrapure water was prepared using Milli-Q Direct (MilliporeSigma, Burlington, USA). All reagents were used as received.

3.2.3. Questionnaire Data

On the day of blood collection, a one-on-one interview was conducted by a trained investigator to gather sociodemographic (e.g., sex, weight, height, and age) and lifestyle (e.g., use of consumer products and smoking) information. Further information on dietary habits, such as frequency of food intake, and housing characteristics, such as use of products that may contain PFAAs, were asked. All donors were given a brief explanation of the study and were asked to sign a consent form prior to the interview session.

3.2.4. Analysis of PFAAs

The serum extraction procedure was slightly modified from the previous method reported elsewhere (Kärrman et al., 2005). Briefly, 0.5 mL of serum was transferred to a 15 mL centrifuge tube and 5ng surrogate (mix mass-labelled PFCAs and PFSAs) was added and mix thoroughly. Then, 3 mL formic acid/water (1:1 v:v) was added and subsequently sonicated for 10min and centrifuged at 8000 rpm for 30 min. Finally, the supernatant was extracted using WAX cartridge (Waters, Milford, MA, USA) that were preconditioned with 2% ammonium hydroxide in methanol, methanol, and water. After washing with 40% methanol in water, the cartridge was left to fully dry under vacuum suction. The PFAAs were then eluted from the cartridge with 2mL 1% ammonium hydroxide in methanol. The eluant was dried under a soft nitrogen stream and reconstitute with 250uL methanol. Prior to injection into the LCMS system, the extract was filtered through a 0.45µm cellulose membrane filter into a glass vial with 250uL polypropylene insert. Quantification was performed using UHPLC equipped with triple quadrupole mass spectrometry LCMS-8030 (SHIMADZU Corporation, Kyoto, Japan. PFAAs were separated on a 2.1×100 mm Zorbax Eclipse Plus C18 column (Agilent, Palo Alto, USA) and the column oven was kept at 40°C. Mobile phase constituted of 2mM ammonium acetate (A) and methanol (B) under gradient mode. The gradient with flow rate 0.3 mL/min was increased from 10% to 60% methanol in 6 mins and further increased to 100% methanol for another 2 mins. Methanol concentration was then rapidly reduced to 10% in 0.1min and reverted to re-equilibrium for 4mins. 10uL of analyte was injected and each analysis took 12mins to complete. MS analyses were carried out using multiple reaction monitoring (MRM) with negative ion mode. The electrospray ionization (ESI) were optimized at capillary voltage 2700V and nebulizer gas temperature 350°C. The precursors and product ions for each PFAAs are summarized in **Table 3.2**.

In order to check for possible contamination during extraction and instrument analysis, procedural blanks were extracted at an interval of ten samples, and solvent blanks containing methanol were injected after every fifteen samples. Calibration check standard (5ng/ mL) was injected after every twenty samples for accuracy and precision observation. Nine method blank samples spiked with 5ng PFAAs were extracted for repeatability test and all the percentage relative standard deviation (RSD %) were measured. Eight-point calibration curves ranging from 0.1 to 20 ng/ mL was prepared for every batch of analysis. The regression coefficients (r^2) of all the calibration curves were > 0.999. The limits of detection (LODs) and limits of quantification (LOQs) for each compound were defined as the smallest concentration giving a signal-to-noise ratio greater than 3, and 10, respectively. The LODs for all compounds were ranged from 0.08 to 0.22ng/ mL). The internal standard recoveries of nine PFAAs were ranged from 71 to 102%. More details on LODs, LOQs, and recoveries are given in **Table 3.2**.

Table 3.2. LC-MS/MS parameter and performance information for PFAAs.

Compound Name	Acronym	LODs (ng/mL)	LOQs (ng/mL)	%Recovery (±SD)	Internal Standard
Perfluoro-n-octanoic acid	PFOA	0.06	0.21	95 ± 9	MPFOA
Perfluoro-1-octanesulfonate	PFOS	0.02	0.08	88 ± 14	MPFOS
Perfluoro-n-butanoic acid	PFBA	0.10	0.34	73 ± 5	MPFBA
Perfluoro-n-hexanoic acid	PFHxA	0.05	0.15	94 ± 12	MPFHxA
Perfluoro-1-hexanesulfonate	PFHxS	0.06	0.20	89 ± 5	MPFHxS
Perfluoro-n-nonanoic acid	PFNA	0.05	0.16	83 ± 4	MPFNA
Perfluoro-n-decanoic acid	PFDA	0.04	0.12	101 ± 7	MPFDA
Perfluoro-n-undecanoic acid	PFUnDA	0.05	0.17	71 ± 3	MPFUnDA
Perfluoro-n-dodecanoic acid	PFDoDA	0.07	0.22	79 ± 13	MPFDoDA

LOD = Limit of detection.
LOQ = Limit of quantification.

3.2.5. Statistical Analysis

All statistical analyses were performed with SPSS Version 23.0 (IBM, New York, USA). For statistical analysis, the concentrations that were less than the LOD were replaced with the LOD/Sqrt(2). Only the PFAAs that were detected in more than 80% of the samples were used for statistical analysis. Natural log-transformation was performed on the PFAA levels in order to approximate a normal distribution. Spearman's rank correlation was performed to assess the relationship among PFAAs level in serum. The frequency of food intake was converted from a categorical format into a numerical value

of times of serving per week. For example, "Never," "1–3 times per week," "4–6 times per week," and "Once per day" were converted into values of 0, 2, 5, and 7, respectively.

To identify the potential determinants of serum PFAA levels, the unadjusted associations of each category (i.e., dietary habits and lifestyle) with the natural log-transformed serum PFAA levels were examined using multiple linear regression with backward elimination technique. The category of dietary habits included consumption of poultry, beef, pork, lamb/ mutton, fish, seafood, and eggs. For the lifestyle category, the variables chosen for this study included use of consumer products (i.e., car, nonstick cookware, camping tents, outdoor clothes, stain-resistant carpet, leather sofa, dental floss, and cosmetics) and smoking habits.

All the significant determinants ($p < 0.05$) in the unadjusted model analyses were examined in a mutually adjusted multiple regression model. Based on previous literature, the other possible determinants that were included in the mutually adjusted models were sex, body mass index (BMI; kg/m^2), and age in years. For all the statistical analyses conducted in this study, a p-value below 0.05 was used to indicate statistical significance. Using the equation $[(e^{\beta}-1) \times 100]$, the beta coefficients were back-transformed to observe the percent change in the serum PFAA levels for each determinant.

3.3. Results

3.3.1. Concentration of PFAAs in the Serum Samples

The median and interquartile range of the PFAAs in the serum samples are summarized in **Table 3.3**. Among the nine PFAAs analyzed, only seven compounds were detected in more than 86.6% of the serum samples; PFBA and PFDoDA were detected in only 12.8% and 8.2% of the samples, respectively. Moreover, the concentration of PFHxA in most of the samples was very low and was close to the LOD for PFHxA. Therefore, these three compounds were excluded from further statistical analyses. The predominant PFAA was PFOS (8.79 ng/mL), followed by PFOA (2.73 ng/mL) and PFNA (1.09 ng/mL). In general, PFOA and PFOS comprised >77% of the PFAAs detected in the serum samples of this population. All PFAAs had higher median serum concentrations in men than in women, except for PFNA and PFUnDA, which were slightly higher in women than in men (**Figure 3.1**). In addition, the concentration of PFAAs increased with older age. Similarly, the concentration of PFAAs, except PFDA, slightly increased with increasing BMI.

Table 3.3. PFAAs concentrations (ng/mL) in serum of the general population of Klang Valley.

Categories		PFOA	PFOS	PFBA	PFHxA	PFHxS	PFNA	PFDA	PFUnDA	PFDoDA
		Median (interquartile range) – ng/mL								
All samples	D.F. (%)	98.6	100	11.4	95.0	88.6	82.6	91.8	83.1	7.8
	Median	2.73 (1.93−3.88)	8.79 (5.44−12.08)	<LOD	0.32 (0.24−0.40)	0.9 (0.4−1.67)	1.09 (0.45−1.82)	0.47 (0.28−0.76)	0.6 (0.32−1.03)	<LOD
Gender	Male	3.86 (2.62−4.70)	11.0 (7.97−15.41)	<LOD	0.39 (0.28−0.48)	1.73 (1.07−2.68)	1.06 (0.69−2.04)	0.48 (0.32−0.75)	0.56 (0.15−0.97)	<LOD
	Female	2.44 (1.71−3.28)	8.42 (4.81−10.90)	<LOD	0.30 (0.23−0.37)	0.73 (0.33−1.21)	1.10 (0.41−1.61)	0.47 (0.28−0.80)	0.63 (0.37−1.16)	<LOD
Age group	<20	2.59 (1.97−3.07)	4.83 (3.38−6.62)	<LOD	0.34 (0.22−0.38)	0.75 (0.58−1.02)	1.00 (0.67−2.39)	0.35 (0.13−0.51)	0.18 (<LOD−0.5)	<LOD
	21−30	2.56 (1.83−3.72)	8.73 (4.83−11.36)	<LOD	0.30 (0.23−0.40)	0.83 (0.35−1.27)	0.99 (0.39−1.65)	0.46 (0.27−0.66)	0.57 (0.24−0.90)	<LOD
	31−40	2.98 (1.89−3.88)	9.41 (6.39−13.83)	<LOD	0.36 (0.24−0.44)	1.00 (0.49−2.18)	1.20 (0.63−1.74)	0.60 (0.3−0.92)	0.68 (0.40−1.22)	<LOD
	41−50	2.46 (1.81−3.76)	8.91 (5.07−13.33)	<LOD	0.31 (0.23−0.35)	1.10 (0.51−1.76)	1.09 (0.45−2.14)	0.51 (0.21−0.98)	0.87 (0.45−1.27)	<LOD
	>51	4.31 (2.80−6.22)	11.96 (7.62−19.1)	<LOD	0.33 (0.24−0.47)	2.07 (0.77−3.48)	1.34 (0.17−2.05)	0.72 (0.4−1.27)	0.71 (0.41−1.38)	<LOD
BMI	<18.4	2.46 (1.78−3.45)	8.74 (3.57−9.82)	<LOD	0.28 (0.09−0.41)	0.73 (<LOD−0.1)	1.19 (0.3−1.78)	0.71 (0.33−0.92)	<LOD	<LOD
	18.5−25	2.51 (1.76−3.76)	8.42 (5.47−11.31)	<LOD	0.29 (0.21−0.39)	0.88 (0.4−1.37)	1.16 (0.61−1.6)	0.44 (0.25−0.7)	0.61 (0.25−1.03)	<LOD
	25.1−30	3.04 (2.28−3.97)	10.40 (4.91−12.85)	<LOD	0.33 (0.26−0.41)	1.16 (0.4−2.19)	0.94 (0.07−1.83)	0.47 (0.29−0.86)	0.59 (0.4−1.21)	<LOD
	>30.1	3.16 (2.11−4.42)	9.96 (5.70−13.01)	<LOD	0.33 (0.27−0.46)	1.05 (0.48−1.71)	1.33 (0.07−2.13)	0.50 (0.32−0.77)	0.62 (0.4−1.04)	<LOD

LOD – Limit of Detection
Interquartile range was not calculated for samples with LOD below 25%.

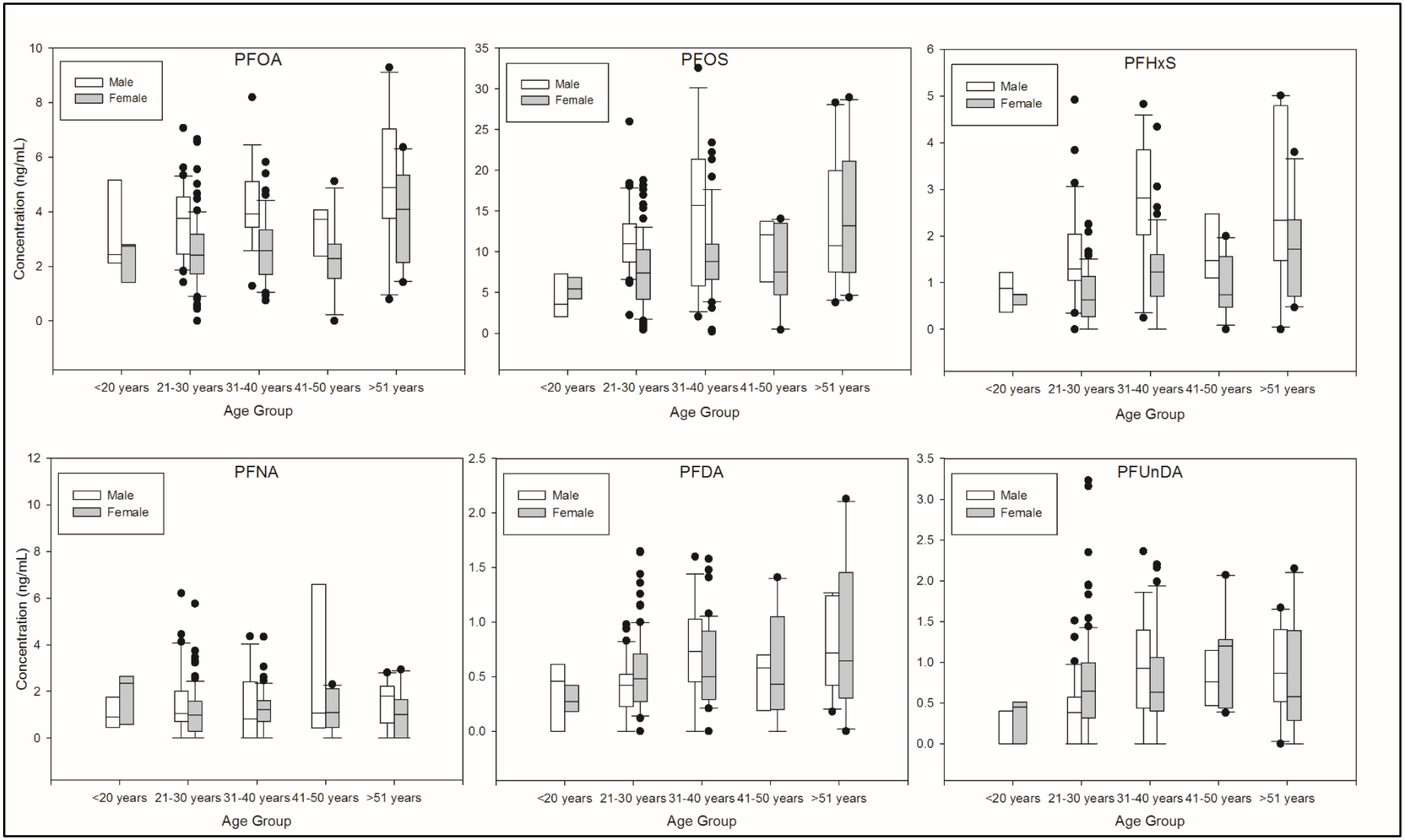

Figure 3.1. PFAAs concentrations grouped by age and gender. Box indicates the interquartile range showing the 25th and 75th percentile. Circle outside the whiskers denoted outlier.

3.3.2. Correlation among the serum PFAAs

The Spearman's rank correlation coefficients among the PFAAs in all samples are listed in **Table 3.4**. PFOA and PFOS were positively correlated ($p < 0.05$) with most of the PFAAs ($r = 0.142$ to 0.653). Furthermore, a highly significant positive correlation ($p < 0.01$) was found among long-chain PFAAs such as PFOA, PFOS, PFHxS, and PFDA ($r = 0.193$ to 0.653); the strongest correlation was between PFOA and PFHxS ($r = 0.653$), followed by that between PFOA and PFOS ($r = 0.528$). The high correlation among these compounds suggested common exposure sources, particularly for PFOS and PFHxS ($r = 0.453$), both of which were believed to be the endstage products of PFOSF degradation.

Table 3.4. Spearman's correlations coefficients among PFAAs measured

	PFOA	PFOS	PFHxS	PFNA	PFDA
PFOS	0.528**				
PFHxS	0.653**	0.453**			
PFNA	0.169*	0.200**	0.068		
PFDA	0.275**	0.527**	0.296**	0.005	
PFUnDA	0.142*	0.329**	0.030	-0.039	0.386**

**Correlation is significant at the 0.01 level (2-tailed).
*Correlation is significant at the 0.05 level (2-tailed).

3.3.3. Univariate analysis of the determinants of serum PFAA exposure levels

In this study population, consumption of some food was identified as a significant determinant for serum PFAAs (**Table 3.5**). Subjects with high consumption of beef tended to show high serum levels of PFDA ($p = 0.047$) and PFUnDA ($p = 0.025$), whereas high consumption of lamb/mutton was associated with low serum levels of PFUnDA ($p = 0.002$) and high consumption of chicken eggs was associated with low serum levels of PFDA ($p = 0.032$). Interestingly, consumption of chicken, fish, seafood, and pork was not associated with the serum PFAA levels in this study population. Note that food serving and portion size were not considered in this study and that all participants answered tap water as their source of drinking water.

Of the lifestyle determinants evaluated in this study (**Table 3.6**), use of nonstick cookware was significantly associated with high PFNA concentration, and use of outdoor clothes and leather sofa were significantly associated with high PFUnDA concentration. In contrast, participants who used camping tents showed significantly low concentrations

of PFNA and PFDA, whereas those who used dental floss and cosmetics had high concentration of PFDA. Smoking was found to be significantly associated with increased serum levels of some PFAAs. Compared with nonsmokers, smokers had higher concentrations of PFOA, PFOS, and PFHxS by 61.4%, 83.5%, and 112.9%, respectively. However, it is important to note that the small number of participants who smoked may have contributed to the large variances with the associations.

Table 3.5. Multiple linear regression[a] models of PFAAs levels in serum samples with dietary habit parameters.

PFAAs	**Food Type**	***% β***[b]	**95% CI**[c]	***p-value***
PFDA	Beef	12.7	(1.5, 28.9)	*0.047*
	Eggs	-11.4	(-21.4, -0.2)	*0.032*
PFUnDA	Beef	24.7	(2.8, 51.3)	*0.025*
	Eggs	-15.8	(-28.0, -1.4)	*0.033*
	Lamb	-22.7	(-34.5, -8.8)	*0.002*

[a] Backward elimination technique was used to screen variables
[b] beta coefficients were back-transformed by (eβ−1)*100
[c] 95% Confidence Interval

Table 3.6. Multiple linear regression[a] models of PFAAs levels in serum samples with lifestyle variables.

Variable	PFOA	PFOS	PFHxS	PFNA	PFDA	PFUnDA
	% β[b] (95% CI)[c]	*% β*[b] (95% CI)[c]	*% β*[b] (95% CI)[c]	*% β*[b] (95% CI)[c]	*% β*[b] (95% CI)[c]	*% β*[b] (95% CI)[c]
Consumer Product Use (Yes/No)[d]						
Car Use						
Non-stick Cookware		19.8 (-5.9, 52.6)		86.6 (19.4, 191.6)		
Camping Tents				-47.3 (-74.0, 7.0)	-37.0 (-60.1, -0.5)	
Outdoor Cloth						42.6 (-2.4, 108.4)
Non-stain Carpet						
Leather Sofa						42.4 (-1.3, 105.6)
Dental Floss	-16.8 (-31.4, 1.0)				32.3 (0.6, 73.9)	
Cosmetic					29.9 (-0.8, 70.0)	
Smoking (Yes/No)[d]	61.4 (4.6, 149.0)	83.5 (10.6, 204.6)	112.9 (0.0, 353.5)			
p-value	*0.019*	*0.014*	*0.046*	*0.009*	*0.018*	*0.020*

[a] Backward elimination technique was used to screen variables
[b] beta coefficients were back-transformed by ($e^{\beta}-1$)*100
[c] 95% Confidence Interval
[d] Reference group is “no” or “never”.

3.3.4. Determinants of serum PFAA exposure levels in the mutually adjusted regression models

In the mutually adjusted regression models for the associations of the significant determinants with the PFAAs in each category (**Table 3.7**), the R^2 for the different PFAAs ranged from 0.050 to 0.159, with all p-values < 0.05. Age was significantly associated with all the serum PFAA levels assessed, except PFOA and PFNA. In addition, PFOA, PFOS, and PFHxS were significantly associated with sex; in particular, the serum levels of those PFAAs were higher in men than in women. Meanwhile, BMI was not associated with any of the PFAAs assessed.

The following were the results after correcting for the other determinants in these models. The associations of nonstick cookware with PFNA, dental floss/cosmetics with PFDA, and leather sofa with PFUnDA remained significant. Compared with participants who did not use nonstick cookware, those who used nonstick cookware had higher concentrations of PFNA (89.6%). Moreover, the PFDA concentration was higher in participants who used dental floss (39.4%) and cosmetics (35.8%) than in those who did not. The concentration of PFUnDA was 44.1% higher in participants who had a leather sofa than in those who did not. For dietary intake, consumption of beef was associated with 29.3% higher levels of PFUnDA, but it was no longer significantly associated with PFDA level. We also found that smoking was no longer significantly associated with all the PFAAs; this suggested that smoking did not account for the high level of PFAAs in this study population.

Table 3.7. Mutually adjusted regressions analysis of determinants on natural log-transformed serum PFAAs concentration of Klang Valley general population.

Effect	PFOA	PFOS	PFHxS	PFNA	PFDA	PFUnDA
	% β[b] (95% CI)[c]	*% β*[b] (95% CI)[c]	*% β*[b] (95% CI)[c]	*% β*[b] (95% CI)[c]	*% β*[b] (95% CI)[c]	*% β*[b] (95% CI)[c]
Age (years)	0.5 (-0.4, 1.4)	**1.5 (0.4, 2.6)**	**2.0 (0.5, 3.6)**	0.9 (-1.2, 3.0)	**1.5 (0.2, 2.8)**	**1.9 (0.2, 3.6)**
Gender (ref=male)	**-39.3 (-50.9, -25.1)**	**-27.0 (-43.2, -6.4)**	**-60.6 (-71.9, -44.9)**	-17.9 (-47.4, 28.1)	0.2 (-26.7, 36.9)	36.4 (-5.2, 96.2)
BMI (kg/m^2)	0.4 (-1.3, 2.0)	-0.4 (-2.3, 1.5)	0.2 (-2.5, 3.1)	-0.1 (-3.7, 3.6)	0.2 (-2.1, 2.6)	2.8 (-0.3, 5.9)
Dietary Habits (serving/week)						
Lamb						**-18.6 (-30.8, -4.2)**
Beef					12.2 (-1.7, 28.1)	**29.3 (6.8, 56.6)**
Chicken Eggs					**-12.6 (-22.4, -1.4)**	-8.2 (-21.0, 6.8)
Consumer Product Uses (Yes/No)[a]						
Non-stick Pan		25.9 (-0.9, 59.9)		**89.6 (20.4, 198.5)**		
Camping Tents				-46.2 (-73.6, 9.5)	**-38.3 (-60.8, -2.7)**	
Outdoor Cloth						23.5 (-15.2, 79.9)
Leather Sofa						**44.1 (0.4, 109.2)**
Dental Floss	**-17.9 (-31.9, -1.1)**				**39.4 (6.3, 82.9)**	
Cosmetic					**35.8 (1.1, 82.3)**	
Smoking (Yes/No)[a]	9.0 (-30.0, 69.8)	37.8 (-18.7, 133.7)	-0.6 (-53.2, 111.3)			
R-Squared	0.136	0.101	0.159	0.050	0.105	0.136
p-value	<0.001	<0.001	<0.001	0.027	0.003	<0.001

[a] Reference group is "no" or "never".
[b] beta coefficients were back-transformed by ($e^{\beta}-1$)*100
[c] 95% Confidence Interval
Bold text indicated a statistically significant result ($p < 0.05$)

3.4. Discussion

The current levels of PFAA exposure in this study population were comparable with those reported in the studies in other countries, such as China (Li et al., 2011), Taiwan (Hsu et al., 2013), Korea (Cho et al., 2015), and USA (Worley et al., 2017; X. Wu et al., 2015), but were higher than those reported in the studies in other Asian countries, such as Singapore (Y. Liu et al., 2017), Vietnam (K. H. Harada et al., 2010), and China (Fu et al., 2014). However, other studies reported much higher serum concentrations of PFAAs (Kärrman et al., 2009; Lindh et al., 2012). Compared with the current study, the previous study by Kannan et al. (2004) on a Malaysian population (N = 23) showed a higher median serum concentration of PFOS in both men (13.1 ng/mL) and women (12.7 ng/mL). In addition, contrary to our findings, their results showed a higher concentration of PFHxS in women (2.3 ng/mL) than in men (1.4 ng/mL). However, PFOA was not detected in their study, probably due to a higher LOQ (10 ng/mL), compared with that in our study (0.21 ng/mL).

Considering the fact that the PFAAs were not manufactured in Malaysia, the reason for the higher PFAA concentrations in Malaysia than in the other countries is unclear. The presence of PFAAs in this study population might be attributed to the exposure to products that contained PFAAs or to the consumption of food and water contaminated with PFAAs. Unfortunately, literature regarding the PFAA concentrations in Malaysian food products and water is scarce. One study on fish collected from a Malaysian river detected PFAAs in snakehead (Murakami et al., 2011). In addition, in 2009, a study by Zainuddin et al. (2012) on the presence of PFAAs in Langat River, Malaysia detected PFOS and PFOA concentrations of up to 43.5 and 5.94 ng/mL, respectively. The Langat River is one of the main sources of tap water supply for over 27% of the residents in Klang Valley. Considering the fact that the conventional drinking water treatment system around the world was reported to be inefficient in removing PFAAs (Boiteux et al., 2017; Kucharzyk et al., 2017), some of the untreated PFOS and PFOA may end up being incorporated in the tap water supply and, subsequently, ingested by humans. Further studies that investigate the sources of PFAA exposure in a Malaysian population are needed.

In this study, the serum levels of PFAAs were found to be significantly associated with age. Similar observations were reported in other studies (Góralczyk et al., 2015; J. H. Lee et al., 2017; Sochorová et al., 2017). For example, a study on PFAAs in an adult population from South Korea showed a pattern of increasing concentrations of PFOS,

PFOA, PFNA, PFDA, and PFHxS with increasing age (J. H. Lee et al., 2017). The same pattern for PFOS and PFOA was found in Japan and California (K. H. Harada et al., 2010; X. Wu et al., 2015). The relatively high PFAA levels in older people have been attributed to the long biological half-life of PFAAs. White et al. (2011) and Olsen et al. (2007) found that PFAAs are resistant to human metabolism and have long half-lives of 2.3–12 years; this results in very slow excretion and increasing concentrations of PFAAs over time in humans. In addition, sustained and widespread lifetime exposure to PFAAs was reported to contribute to the increasing PFAA levels in humans (Calafat et al., 2006).

Similar to previous studies (Cho et al., 2015; Fu et al., 2014; Góralczyk et al., 2015), this present study showed an association between high PFAA levels and sex; in particular, the concentration of PFAAs was higher in men than in women. For example, in South Korea, the concentrations of PFOA, PFNA, PFHxS, and PFOSA in whole blood were reported to be higher in men than in women (Cho et al., 2015). A similar observation was found in a population from Henan, China, where the median concentrations of PFOA, PFNA, PFDA, and PFOS were higher in men than in women (Fu et al., 2014). K. Harada et al. (2005) hypothesized menstrual bleeding as a route for elimination of PFAAs in women. That study was supported by the study of J. Lee et al. (2008), who showed that PFAAs were detected in breast milk, maternal blood, and cord blood. These observations suggested that women could effectively eliminate PFAAs by lactation, menstruation, or during pregnancy, thereby resulting in lower serum concentrations of PFAAs in women than in men.

On the other hand, BMI was not significantly associated with any PFAAs in this study; a similar relationship was observed in a residential community in Alabama, USA (Worley et al., 2017). This observation was expected, based on a previous report, which showed that PFAAs were bound mainly to plasma proteins and not to adipose tissues (Sanchez-Garcia et al., 2018).

Various studies suggested dietary intake as one of the major exposure pathways for contamination with several PFAAs in humans (Averina et al., 2018; Papadopoulou et al., 2017). For example, Y. Liu et al. (2017) reported that fish, shellfish, red meat, and poultry were important food contributors to PFAA intake. In this study population, multiple linear regression analysis of the relationship between dietary habits and PFAA concentrations consistently identified consumption of beef as a significant determinant of PFUnDA level. Likewise, Halldorsson et al. (2008) observed an association between serum PFAA concentrations and consumption of beef in a Danish population, although

they classified beef as red meat, together with pork and lamb. In addition, PFAAs, including PFUnDA, have been detected in beef samples collected from Sweden and Taiwan (Chen et al., 2018; Vestergren et al., 2012).

Aside from dietary intake, another source of PFAA exposure is contact with consumer products. Kang et al. (2018) and X. Wu et al. (2015) reported outdoor equipment, such as waterproof clothes and camping tents, as positive significant predictors of the presence of PFAAs. In addition, similar to our study, the report by Fraser et al. (2012) showed significant associations between PFAA concentrations and some household and office items, such as leather sofas and stain-resistant carpets. The nonpolar perfluoroalkyl chain and polar end-group characteristics account for the excellent water- and stain-resistant properties of PFAAs in leather and carpet products. Indeed, PFAAs have been normally applied during the manufacturing process or to the finished products of carpet and leather; consequently, PFAAs have been frequently found in both these products (Herzke et al., 2012; Kotthoff et al., 2015). This association of PFAA level with the use of leather sofa implied that indoor air can be an important source of PFAA exposure (Fraser et al., 2013).

Intake of food prepared with a nonstick cookware was associated with relatively high levels of PFNA; this finding was strongly supported by other studies (Kang et al., 2018; J. H. Lee et al., 2017). PFAAs are used as emulsifiers in the production of polytetrafluoroethylene, which is commonly used as a coating for nonstick cookware (Ellis et al., 2001). An analysis by Herzke et al. (2012) showed that the nonstick layer removed from a nonstick pan contained several PFAAs. During cooking, these PFAAs could seep into food products or evaporate to indoor air and may subsequently end up in the bloodstream of humans.

The associations of the serum levels of PFAAs with cosmetic products and dental floss had been scarcely reported in previous literature. Our findings on the significantly increased serum level of PFDA with the use of dental floss were, to some extent, similar to the results of a study in the USA (Boronow et al., 2019). Begley et al. (2005) found the presence of fluorinated compounds in dental floss. Schultes et al. (2018) reported the presence of PFAS in various cosmetic products in Sweden. The Danish Environmental Protection Agency (EPA) found a total amount of PFAAs of up to 10,700 ng/g in concealers and that almost half of the cosmetic samples contained PFAAs above the 25 ng/g limit (Danish Environmental Protection Agency, 2018). Contact with these products may cause migration and exposure to PFAAs in humans. However, we could not find

any previous literature on a significant association between PFAAs and cosmetics to support our finding.

There were several limitations in this study. First, this study had a small number of participants (n = 219) and all the participants were from an urban area in Klang Valley. Therefore, the results may not be generalizable to the populations in the other regions in Malaysia. In addition, the very small ratios of smokers to nonsmokers and of users to nonusers of camping tents may have resulted in the broad 95% confidence interval estimates for these variables. Therefore, caution should be taken when comparing our results with those of other studies. Furthermore, our study used self-reported questionnaires. Therefore, the amount of food consumption may not have been accurately quantified because the information bias (i.e., over and under reporting) may have underestimated or overestimated the true associations. In addition, the lifestyle variables included in this study were limited. Because PFAAs are frequently detected in various kinds of media, further investigations on drinking water, cleaning products, food packaging, and cooking procedures, in addition to food groups, are also important.

3.5. Conclusions

In this study on a population of residents in Klang Valley, Malaysia, the levels of PFAAs in serum were associated with age, sex, and use of nonstick cookware, dental floss, cosmetics, and leather sofa but not with BMI and smoking. Moreover, the serum levels of some PFAAs were directly associated with the consumption of beef but inversely associated with the consumption of lamb and chicken eggs. The presence of PFAAs in dietary samples and environmental sources, such as air and water, needs to be further investigated to elucidate the exposure to PFAAs in the Malaysian population.

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CHAPTER 4

PERFLUOROALKYL ACIDS (PFAAs) IN SURFACE WATER AND SEDIMENT OF SELANGOR AND LANGAT RIVER BASIN: SPATIOTEMPORAL, PARTITIONING, AND ECOLOGICAL RISK ASSESSMENT

Abstract

The presence of perfluoroalkyl acids in surface water and sediment of the Selangor and Langat River basins were quantified using LC-MS/MS. At least 3 and 1 PFAAs were detected in surface water and sediment samples, respectively. The total concentration of PFAAs (∑PFAAs) in surface water samples were in the range of 0.886 – 133.692 mg/L and 0.419 – 138.945 mg/L, while in the sediment the range of not detected to 249.7 pg/g dw and 18.7 – 465.6 pg/g dw were detected in Selangor and Langat River basin, respectively. PFOA and PFBA were found to be a dominants PFAAs in both water and sediment samples. The mean concentration of PFAAs in sediments were higher than in surface water. Urbanization and industrialization were identified as potential sources of PFAAs contamination in the area of Klang Valley. Field-based Log K_D were in the range of 1.5 to 2.3, slightly different from the previously reported value due to the differences in the physicochemical properties of water and sediment among studies. None of the PFAAs levels exceeded the PNEC value, suggesting little to no potential risk to the aquatic organisms.

4.1. 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 human life while there are also numerous global pollutants that were known to be toxic and can cause harm to human. One of the organic pollutants that have various uses, especially in industries and consumer products, but have a significant undesirable effect of human are perfluoroalkyl acids (PFAAs) (Domingo & Nadal, 2017; Sunderland et al., 2019). PFAAs received special concern not only due to their negative impact on human health, but also due to their persistence, which widely spread globally in the environment (Krafft & Riess, 2015).

Two major PFAAs, 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 using PFOS and PFOA even though the uses of these chemicals have been restricted worldwide (Jensen & Brunn, 2008; Kotthoff et al., 2015). The toxicity of PFOA and PFOS has been extensively confirmed in several studies.

Stockholm Convention has listed PFOS as one of the Persistent Organic Pollutant in Annex B (UNEP, 2016). Epidemiological and medical risk assessment in human studies about PFAAs have been reported before. The health effect of PFAAs includes liver disease (Bassler et al., 2019; Nian et al., 2019), endocrine disorders such as altered fertility and puberty (Joensen et al., 2009; Lopez-Espinosa et al., 2011), increased total cholesterol (Jain & Ducatman, 2018; Nelson et al., 2010), and immune suppression (DeWitt et al., 2009; Dong et al., 2013).

Due to the highly resistant properties of PFAAs to degradation processes combined with the PFAAs tendency to bioaccumulate, these compounds will continue to persist in the environment even in the near future. Furthermore, PFAAs are mostly water-soluble, thus making conventional water and wastewater treatment system ineffective in eliminating these compounds (Arvaniti & Stasinakis, 2015; Kucharzyk et al., 2017). PFAAs have been found in surface water, sediment, and tap water worldwide (Chen et al., 2019; Lam et al., 2017). In addition, PFAAs were also detected in animals and humans globally (Lindh et al., 2012; Murakami et al., 2011).

The global sources of these compounds from manufacturing, use, and consumer products were estimated to be between 3200 and 7300 tonnes (Krafft & Riess, 2015). These pollutants will be accumulated in river and sea because factory production and domestic use will transfer chemical waste into it (Kucharzyk et al., 2017). Comprehensive studies of sediment, freshwaters, and coastal waters were conducted worldwide. The results were significant and caused major concern for the most part of the world (Dalahmeh et al., 2018; Masunaga & Zushi, 2016). To the best of our knowledge, Malaysia did not produce any PFAAs and also never regulated any PFAAs in the country. However, previous studies showed that PFAAs not only were detected in the Malaysian environment such as in surface water, but also in human blood and breast milk of its population (Kannan et al., 2004; Tao et al., 2008; Zainuddin et al., 2012). Thus, it is necessary to evaluate the widespread distribution of PFAAs in Malaysian river basins particularly in the Klang Valley. Klang Valley, which strategically located at the heart of Selangor State and Kuala Lumpur, is the most densely populated area in Malaysia with various industries and a high level of traffic.

The objective of this study was to investigate the levels of PFAAs in surface water and sediments of two major river basins in Klang Valley. Selangor and Langat River basins were selected as an area of focus because these rivers basins receive effluents from industries, commercial activities, and also are used as a water intake source for water treatment plants. These river basins supply 65.27% (Selangor River basin) and 24.17%

(Langat River basin) of raw water for the drinking water treatment plant for the population of Klang Valley (JPBDSelangor, 2016).

4.2. Materials and Methods

4.2.1. Chemicals and reagents

Both mixed PFAAs standards (PFAC-MXB), and mixed PFAAs surrogates (MPFAC-MXA) were purchased from Wellington Laboratories (Ontario, Canada). Liquid chromatography grade Methanol solvent used in both solid-phase extraction and analysis was purchased from MERCK (New Jersey, USA). Acetic acid glacial, ammonium solution (25%), and ammonium acetate were purchased from Fisher Chemical (Pennsylvania, USA). Weak anion exchange (WAX) Oasis Plus cartridges (225 mg, 60 μm) for solid-phase extraction (SPE) were purchased from Waters (Massachusetts, USA). Microfiber glass filter (GF/B) was purchased from Whatmann (Maidstone, United Kingdom). Deionized water used throughout the study was produced using Milli-Q Direct. (MilliporeSigma, Burlington, USA).

4.2.2. Site description and sample collection

A total of 44 sampling locations were selected which 19 sampling locations were from the Selangor River Basin while 25 sampling locations were from the Langat River basin (Figure 4.1). Information on sampling locations is summarized in Table 4.1. The sampling campaigns were conducted in March 2017 and July 2017. Surface water samples were collected on the bridge at the center of the river cross-section of each sampling point and stored in a 1L polypropylene (PP) bottles that were pre-rinsed with methanol, deionized water, and sample water. Sediment samples were collected at the same spot using Ekman grab sampler. Duplicate samples and field blank were also collected from selected sampling points. Water properties such as pH, temperature, conductivity, and dissolved oxygen were recorded at the sampling sites. Samples collected were kept in an icebox during sampling and then were stored in a cold room at 4°C. All samples were extracted within 3 days of storage. Apparatus made from glass or PTFE were avoided during the sample collection in order to avoid any potential contamination or loss of the target compound.

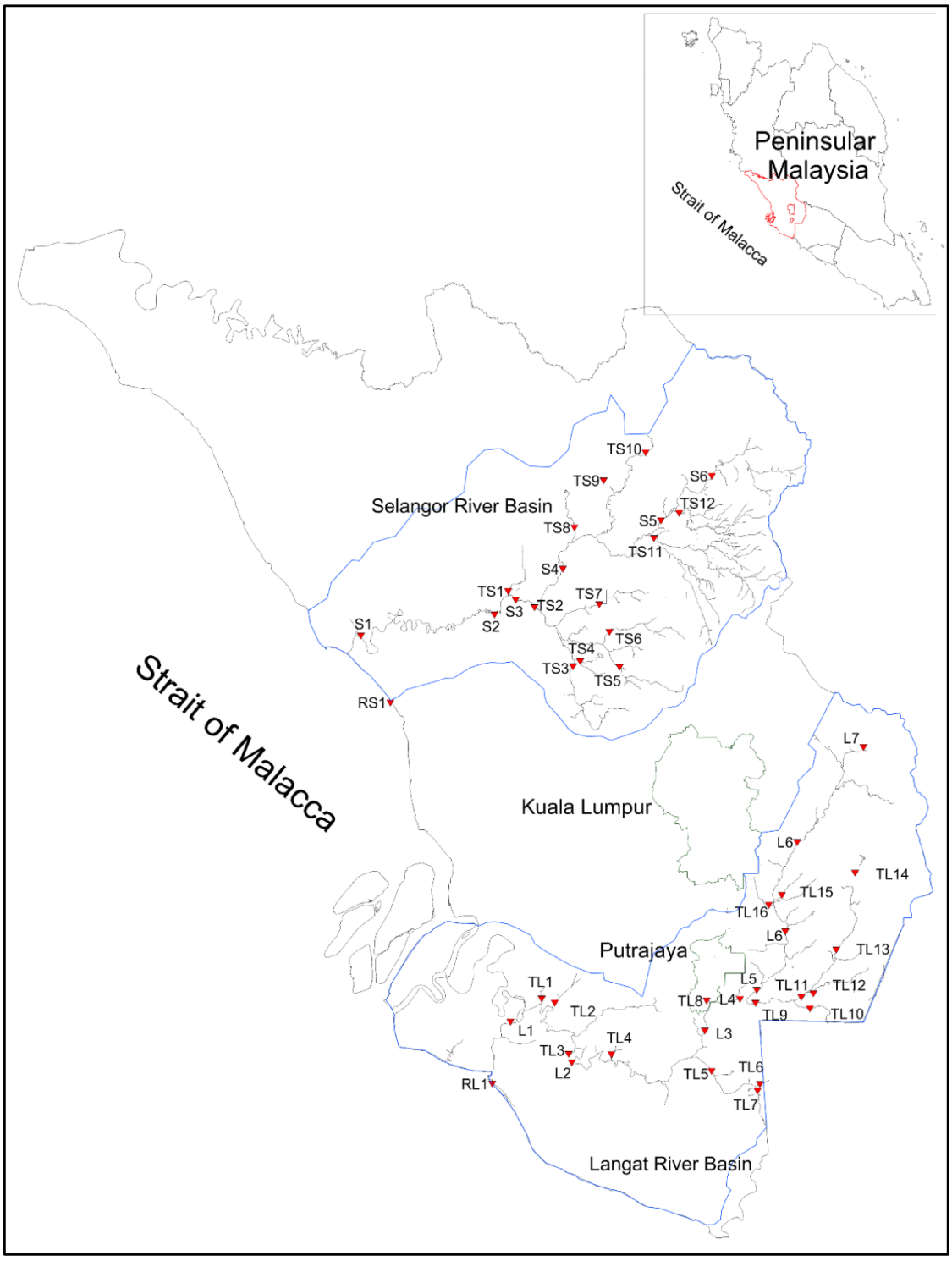

Figure 4.1. Location of sampling points in Selangor and Langat River basin

Table 4.1 Summarized information of the sampling sites in the Selangor river basin

Basin	Sites	Longitude	Latitude	Remarks
Selangor River Basin	RS1	101°18.3025	3°13.2186	Marine Coastal – Pantai Jeram
	S1	101°14.6370	3°21.3906	Sungai Selangor – Residental Area – Rural
	S2	101°24.8888	3°23.0202	Sungai Selangor – After WTP Water Intake (Rural)
	TS1	101°25.8921	3°24.4950	Sungai Selangor – Before WTP Water Intake (Rural)
	S3	101°26.4913	3°24.1097	Sungai Selangor
	TS2	101°27.9110	3°23.5557	Sungai Sembah – River Confluence (Rural)
	TS3	101°30.8670	3°19.1408	Sungai Kundang – Tributary (Residential and Industrial Area - Urban)
	TS4	101°31.5329	3°19.3901	Sungai Gong – Tributary (Residential Area – Rural)
	TS5	101°34.2744	3°19.0098	Sungai Rawang – Tributary (Residential and Industrial Area – Urban)
	TS6	101°33.6403	3°21.6505	Sungai Serendah (Residential and Industrial Area)
	TS7	101°31.4147	3°23.4901	Sungai Guntong – Tributary (Residential Area)
	S4	101°30.1560	3°26.4833	Sungai Selangor (Sand Mining Area)
	TS8	101°31.0488	3°29.6299	Sungai Tinggi - Tributary
	TS9	101°32.3931	3°33.8732	Sungai Beletak– Tributary (Residential Area – Rural)
	TS10	101°36.4117	3°35.2878	Sungai Kerling – Tributary (Residential Area)
	TS11	101°36.9381	3°29.0320	Sungai Batang Kali – Tributary (Industrial Area)
	S5	101°37.4767	3°29.9540	Sungai Selangor (Residential and Industrial Area)
	TS12	101°38.1932	3°30.5974	Sungai Rening – Tributary (Residential Area)
	S6	101°41.7094	3°34.3272	Selangor River Dam
Langat River Basin	RL1	101°24.6978	2°47.3715	Marine Coastal – Pantai Kelanang
	L1	101°26.3639	2°51.9341	Sungai Langat- Residential Area – Rural
	TL1	101°28.5124	2°53.5777	Teluk Panglima Garang (Industrial Area)
	TL2	101°29.3500	2°53.2666	Jenjarom Tributary (Residential Area – Urban)
	TL3	101°30.5091	2°49.5685	Banting Tributary (Residential Area – Urban)
	L2	101°30.6610	2°48.9430	Sungai Langat (Residential Area – Urban)
	TL4	101°33.7702	2°49.5759	Sungai Rambai (Agriculture Area – Urban)
	TL5	101°41.4472	2°48.3006	Sungai Batang Labu (Argricultural Area)
	TL6	101°45.0930	2°47.2413	Sungai Batang Labu (Residential Area - Rural)
	TL7	101°44.9847	2°46.8254	Sungai Chinchang (Argricultural Area)
	L3	101°40.8762	2°51.3564	Sungai Langat-Dengkil (Residential Area – Urban)
	TL8	101°41.0554	2°53.6735	Putrajaya Lake – Sungai Langat
	L4	101°43.5915	2°53.8306	Sungai Langat - Sepang (Residential Area – Rural)
	TL9	101°45.0110	2°53.5530	Sungai Semenyih (Residential Area – Urban)
	TL10	101°49.7372	2°53.3017	Kuala Pajam (Industrial Area – Urban)
	TL11	101°48.5536	2°54.2332	Sungai Semenyih - Rural
	TL12	101°48.6850	2°54.3060	Sungai Rinching (Residential Area – Rural)
	TL13	101°50.9308	2°57.5301	Sungai Semenyih - Rural
	TL14	101°52.3603	3°03.3652	Semenyih Dam
	L5	101°45.5241	2°55.1030	Sungai Langat-Bangi (Residential Area)
	L6	101°47.0886	2°59.6054	Sungai Langat – Hulu Langat (Residential Area)
	TL15	101°46.3592	3°01.3841	Sungai Sekamat (Residential Area – Urban)
	TL16	101°46.0612	3°00.8992	Sungai Langat-Balakong (Residential Area – Urban)
	L7	101°47.9293	3°05.7169	Sungai Langat – Hulu Langat (Residential Area)
	L8	101°53.0180	3°12.9355	Langat Dam

4.2.3. Sample preparation and extraction

Prior to the extraction of surface water samples, 10ng of PFAAs surrogate was injected into the 500mL of water samples. The samples were filtered through the 1µm glass microfiber filter to remove suspended solids. Next, PFAAs in the water samples were extracted using Water Oasis WAX cartridge (Milford, MA) that were pre-conditioned with 3 ml of 0.1% ammonium methanol, 3 ml of methanol, and 5ml of water at a flow-rate of 2 drops/sec. Then, the water sample was loaded onto the cartridges at a drop rate of 1 drop/sec. At the end of the sample loadings, the cartridges were washed with 5ml of 25mM acetate buffer solution and were left to fully dry under vacuum suction. Target compounds were eluted with 3mL 0.1% ammonium methanol and were slowly evaporated under a gentle stream of nitrogen to a volume of less than 1mL and then were reconstituted to an exact volume of 1mL. The eluants were filtered using a 0.2µm nylon syringe filter and transferred into a polypropylene vial prior to analysis using LC-MS/MS. The summary of the PFAAs extraction in surface water samples is displayed in Figure 4.2.

Water sample 500 mL
↓
Add surrogate 5 ng (100 ng/mL surrogate solution* x 50 uL)
Solid Phase Extraction (SPE, WAX cartridge)
· *Conditioning 3mL each (use 0.1% ammonia-methanol, methanol & water)*
· *Sample load (flow rate 1 drop/s), Washing (25mM acetate buffer)*
· *Drying (by vacuum pressure)*
· *Elution (use 3 mL 0.1% ammonia-methanol, flow rate 1 drop/s)*
Elute of PFCs *(3 mL)*
↓
Concentrate to less than 1 mL by nitrogen gas
Add methanol 1.0 mL
Filter (0.2µm nylon syringe filter) then transfer to the vial
Test sample for LC-MS/MS

Figure 4.2. The PFAAs extraction method in surface water samples using SPE.

The same method used in the extraction of PFAAs in water sample was also used for the extraction in sediment. However, there was an additional pre-treatment step to extract PFAAs from sediment samples prior to the solid phase extraction (SPE). This pre-treatment step started with the addition of 20mL of 20% methanol/water into the 50mL tube containing 5g of sediment samples. Then the samples were sonicated for 10 minutes and centrifuged at 2000rpm for another 10 minutes. The supernatant was collected and

transfer to the new tube and these whole steps were repeated twice for each sample. The summary of the PFAAs extraction in sediment is displayed in Figure 4.3.

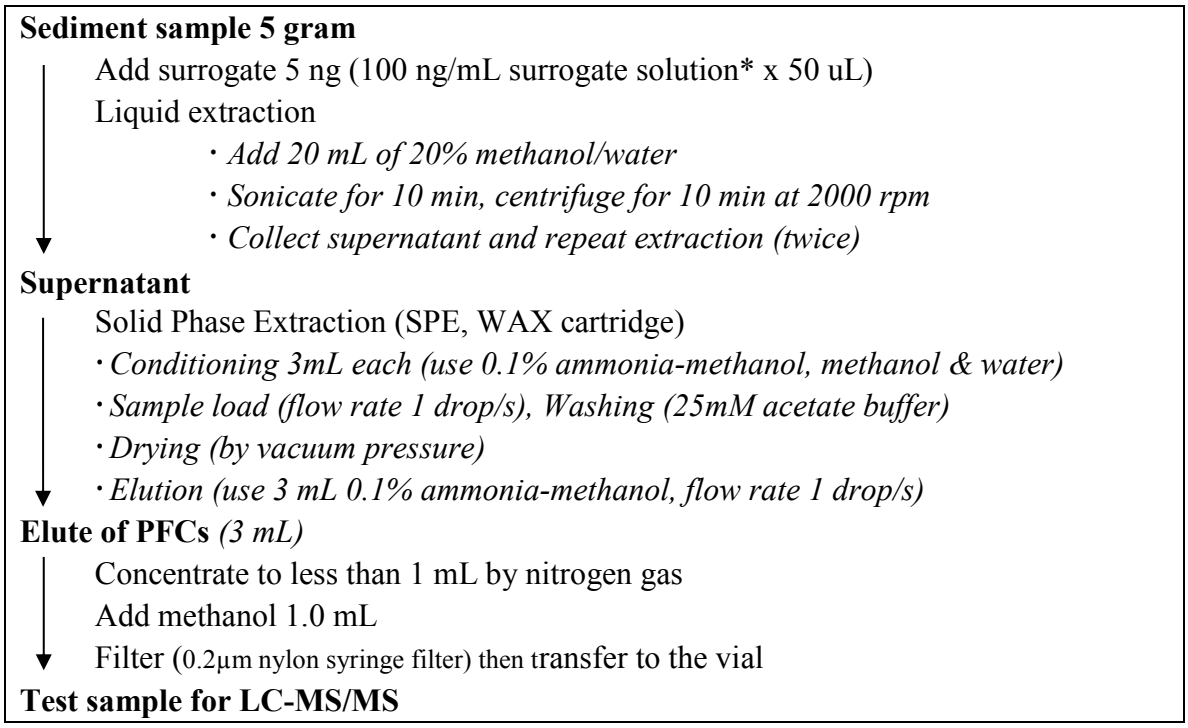

Figure 4.3. Summary of the PFAAs extraction method from sediment samples.

4.2.4. Instrumental analysis and quality control

The LC system consisted of an LC-20AD XR UHPLC system with a SIL-HT automatic sample injector (Shimadzu, Kyoto, Japan) was used for the analysis of PFAAs. The Shimadzu LCMS-8030 is used to identify analytes based on their mass, fragmentation, and retention time. Chromatographic separation is performed on an analytical column: Shim-pack XR-ODS II (2.0 mm I.D. x 100 mm L., 2.2 μm) with a delay column: ChromaNik Sunrise C28 (3.0 mm I.D. x 30 mm L., 3.0 μm). The oven temperature was kept at 40°C with a total running time 15 min. The mobile phase used was 2 mMol ammonium acetate/water in pump A and methanol in pump B. The flow rate was set at 0.3 mL/min and gradient elution was used. 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 until equilibrium was reached. Sample injection volume was 2 μL. The detections are performed in multiple reaction monitoring (MRM) mode using electrospray ionization (ESI) ion source, in negative mode.

Usages of any fluoropolymer plastic-based lab-ware were avoided to avoid contamination. Glassware also was avoided to prevent any possibility for loss of analytes during extraction and analysis. Method blanks (deionized water) were prepared in parallel with every 10 samples in order to rule out any contamination during the extraction procedure. In some cases where the analytes were detected in procedural blanks, concentrations of analyte found in the sample were corrected by subtracting with the average value of analyte detected in blanks. Instrumental blank (methanol) and 5ppb calibration standard were injected after every 10 analysis as to monitor the instrument stability and sensitivity. The lowest concentration of calibration standard (0.5ppb) was measured repeatedly (n=7) in order to calculate the standard deviation of the response (SD). From the SD value obtained, Limit of Detection (LOD) and Limit of Quantification (LOQ) were then determined as 3 times SD, and 10 times SD, respectively. Summary of the LOD, LOQ, and recoveries for the analysis is shown in Table 4.2. Recoveries were performed using matrix spike recovery method by spiking 5ng/mL standard and internal standard mixture into the selected sample's duplicate and extracted the same way like other samples.

Table 4.2. Parameter and performance information for the analysis of PFAAs in surface water and sediment.

PFAAs	Water (ng/L)			Sediment (pg/g)		
	LODs	LOQs	%Recovery (±SD)	LODs	LOQs	%Recovery (±SD)
PFBA	0.05	0.17	88 ± 1.3	10.15	33.84	103 ± 0.3
PFHxA	0.05	0.16	86 ± 0.7	9.79	32.65	89 ± 0.7
PFOA	0.08	0.28	97 ± 7.2	16.97	56.56	104 ± 1.2
PFNA	0.16	0.52	88 ± 0.4	31.38	104.60	96 ± 0.5
PFDA	0.14	0.48	88 ± 0.8	28.85	96.17	97 ± 0.9
PFUnDA	0.17	0.57	88 ± 1.8	33.96	113.21	97 ± 0.4
PFDoDA	0.14	0.46	85 ± 0.3	27.51	91.71	97 ± 0.9
PFHxS	0.17	0.57	89 ± 0.5	33.95	113.17	98 ± 0.5
PFOS	0.13	0.42	93 ± 1.0	25.44	84.80	99 ± 0.4

4.2.5. Statistical analysis

All statistical analyses were performed with SPSS Version 23.0 (IBM, New York, USA). For statistical analysis, concentrations that were less than LOQ but higher than LOD were replaced with the actual value detected from LC-MS/MS analysis, while concentrations that were less than LOD were substituted with the value of LOD/sqrt(2). Spearman's rank correlation was performed to assess the relationship among PFAAs for each sampling campaign and also the correlation between PFAAs concentration and water properties such as pH and temperature. Significant differences between the concentration of PFAAs and sampling period were performed using the Kruskal-Wallis test. The level of significance was set to $p \leq 0.05$.

4.3. Results and Discussion

4.3.1. Concentrations and composition profiles of PFAAs in surface water

A total of 88 samples collected were analyzed for the presence of PFAAs in surface water during two sampling campaigns, March and July 2017. The analysis covers two river basins which are Selangor River basin (n=38) and Langat River basin (n=50) and the summaries are shown in Table 4.3. The total concentration of PFAAs ranged from 0.886 to 133.692 ng/L for Selangor River basin, and 0.419 to 138.945 ng/L for Langat River basin. At least 3 PFAAs were detected in all surface water samples. Between the two river basins, Selangor River showed higher PFCA concentration (up to 126.953 ng/L) while the Langat River showed higher PFSA concentration (up to 8.791 ng/L). In Selangor River basin, the highest concentration of PFAAs were found for PFOA (126.9 ng/L), followed by PFBA (6.44 ng/L), PFOS (6.24 ng/L), PFHxA (2.73 ng/L), PFNA (2.31 ng/L), and PFDA (1.82 ng/L). A different pattern was observed for the Langat River basin where the highest concentration of PFAAs was found for PFBA (104.45 ng/L).

PFBA, PFHxA, PFOA, and PFNA were the predominant PFAAs in Selangor River basin with 100% detection frequencies while PFBA, PFHxA, and PFOA were the predominant PFAAs in Langat River basin with detection frequencies ranging from 84 to 100%. As for the sampling campaign period, the Selangor River basin showed a higher level of PFAAs for samples collected in July compared to samples collected in March. In contrast, an opposite observation was found in the Langat River basin, where higher PFAAs was detected in March compared to July, which suggests a different release pattern of PFAAs between these two river basins.

Table 4.3. Summarized levels (ng/L) and frequencies of detection (%) of PFAAs in surface water samples from Selangor and Langat River basins for two sampling campaigns (March and July 2017).

Basin	Month	Parameter	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS	PFOS	∑PFAAs
Selangor	March	D.F	100	100	100	100	32	6	37	5	0	–
	n= 19	Minimum	0.286	0.080	0.264	0.160	<LOD	<LOD	<LOD	<LOD	<LOD	0.886
		Mean	1.812	0.665	1.430	0.412	0.060	0.073	0.073	0.024	<LOD	4.575
		Median	1.176	0.496	0.911	0.246	<LOD	<LOD	<LOD	<LOD	<LOD	4.036
		Maximum	5.669	2.104	11.635	2.306	0.234	1.389	0.238	0.454	<LOD	12.852
	July	D.F	100	100	100	100	47	16	16	5	16	–
	n= 19	Minimum	1.334	0.088	0.312	0.202	<LOD	<LOD	<LOD	<LOD	<LOD	2.473
		Mean	2.121	1.099	14.326	0.440	0.216	0.026	0.034	0.025	0.415	18.713
		Median	1.657	0.859	6.809	0.343	<LOD	<LOD	<LOD	<LOD	<LOD	10.360
		Maximum	6.444	2.731	126.953	1.051	1.817	0.260	0.220	0.480	6.237	133.692
Langat	March	D.F	100	100	100	80	32	12	44	16	44	–
	n=25	Minimum	0.120	0.079	0.424	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.162
		Mean	7.827	1.271	2.854	0.927	0.103	0.155	0.250	0.103	0.751	14.257
		Median	3.110	1.157	1.471	0.305	<LOD	<LOD	<LOD	<LOD	<LOD	8.011
		Maximum	104.455	5.286	35.517	15.445	0.606	3.117	1.803	1.142	8.791	138.945
	July	D.F	84	100	100	60	24	0	24	4	24	–
	n=25	Minimum	<LOD	0.050	0.186	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.419
		Mean	1.811	0.633	2.283	0.197	0.065	<LOD	0.055	0.015	0.191	5.279
		Median	0.794	0.347	0.795	0.203	0.068	<LOD	<LOD	<LOD	<LOD	2.102
		Maximum	6.433	2.897	35.484	0.757	0.624	<LOD	0.420	0.370	1.339	42.381

D.F - Detection Frequency

The compositional profiles of individual PFAAs in surface water of both river basins during March and July sampling campaigns are displayed in Figure 4.4 and 4.5, respectively. In Selangor River basin, PFBA was the major PFAAs contributor during March sampling with an average contribution of 39.6% from the total PFAAs, followed by PFOA which contributed 31.3% and PFHxA with a 14.5 % average contribution. Conversely, major PFAAs for July sampling was PFOA, followed by PFBA, and PFHxA, accounting on average of 76.6%, 11.3%, and 5.9% from the total PFAAs, respectively. In addition, PFOS was only detected in samples collected from the Selangor River basin during the July sampling campaign. The other PFAAs contributed a minor percentage of the total PFAAs and were only found at a very low concentration.

Similar to the Selangor River basin, PFBA was the major PFAAs contributor for Langat River basin in March sampling with an average of 54.9% contribution of the total PFAAs, followed by PFOA with a 20 % average contribution and PFHxA with an 8.9 % average contribution. The same patterns with Selangor River basin during sampling in July were also observed in the Langat River basin during the July sampling campaign, which PFOA was the major contributor, followed by PFBA, and PFHxA, with a contribution to total PFAAs of 43.2, 34.3, and 12%, respectively. However, no PFUnDA were detected in July samples collected from the Langat River basin.

Among all PFAAs analyzed, short-chain PFCAs (PFBA and PFHxA) showed higher detection frequencies of detection (84 – 100%) compared to long-chain PFCAs (C>8) such as PFDA, PFUnDA, and PFDoDA (0 – 44%) in both river basins. In contrast, short-chain PFSAs (PFHxS) were only detected in 4 – 16% of samples. The same pattern was also reported by Pan et al. (2014) and Senthilkumar et al. (2007) where PFCAs were commonly detected in surface water compared to PFSAs and that a lower chain PFCA were predominant. However, the opposite pattern was also found where levels of PFSA were higher than PFCA (De Solla et al., 2012; Munoz et al., 2015). The differences in the type of industries and usage of PFAAs between different areas and countries worldwide may contribute to the differences in discharge trends of PFAAs in the aqueous environment. In addition, long-chain PFAAs have lower water solubility compared to short-chain PFAAs, resulting in a lower level of presence in surface water (Ahrens et al., 2016).

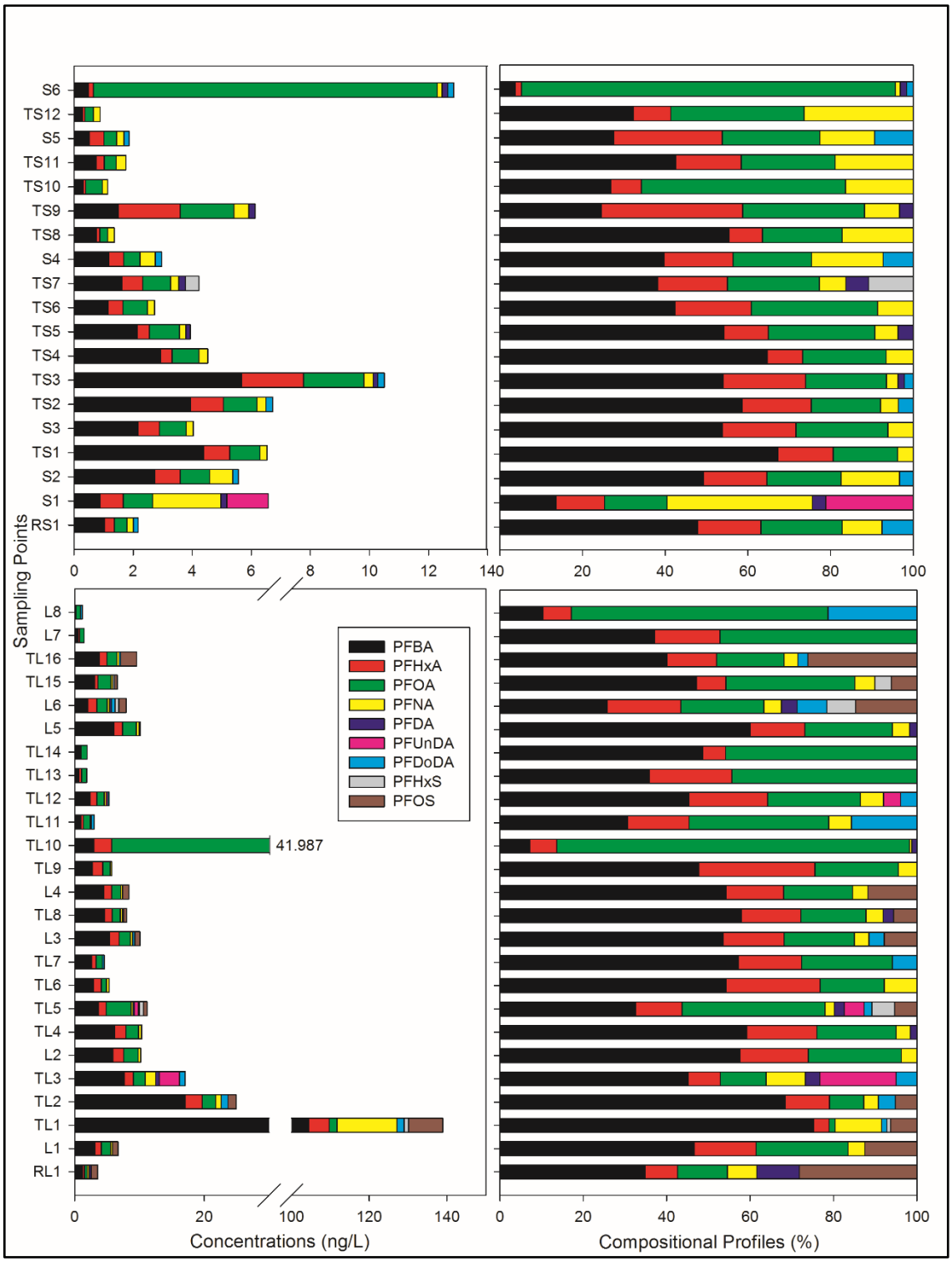

Figure 4.4. Levels and compositional profiles of individual PFAAs in surface water samples from Selangor and Langat River basin samples collected on *March 2017*. Top and bottom figures representing surface water samples collected from Selangor and Langat River basin, respectively.

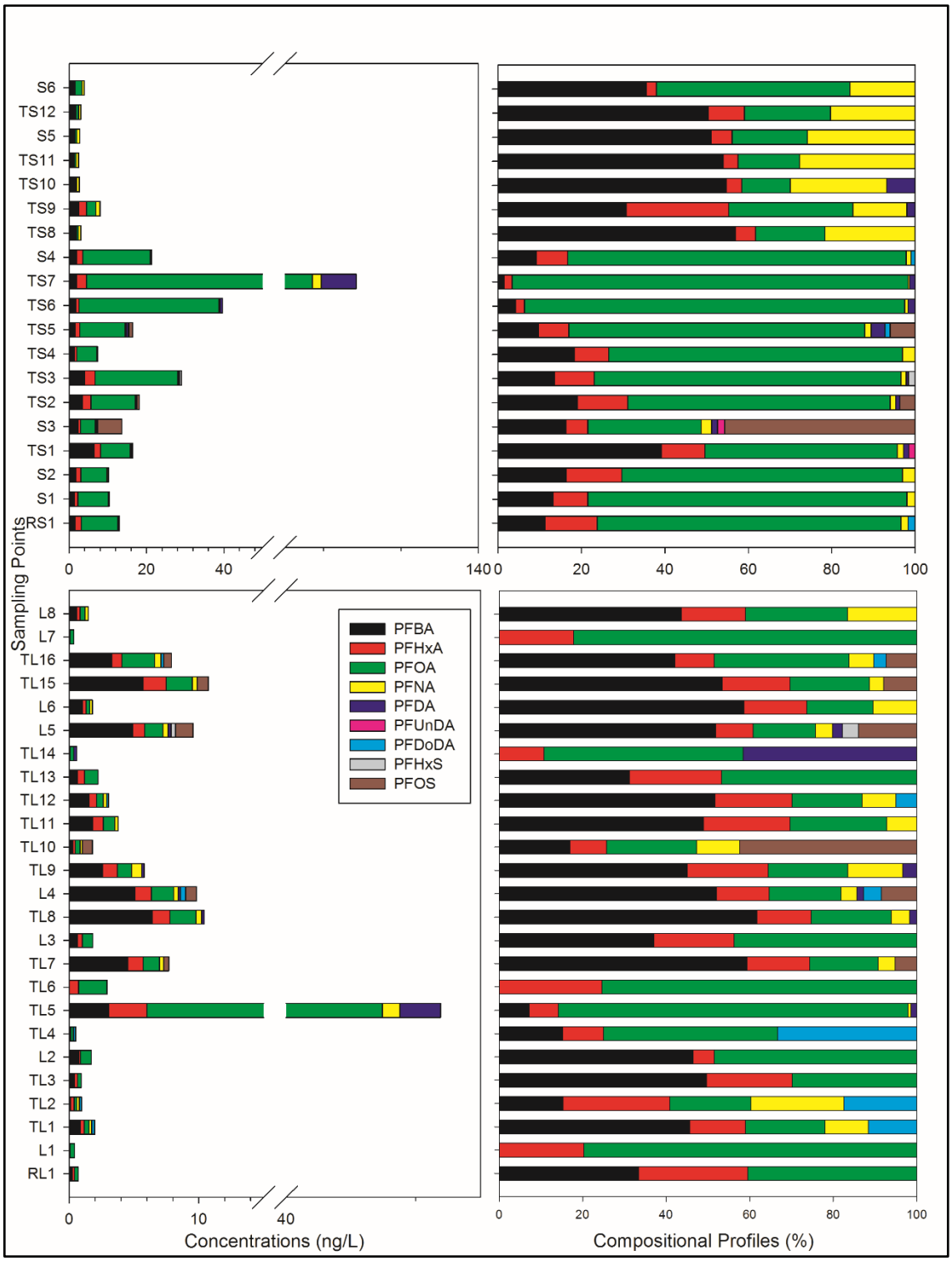

Figure 4.5. Levels and compositional profiles of individual PFAAs in surface water samples from Selangor and Langat River basin samples collected on *July 2017*. Top and bottom figures representing surface water samples collected from Selangor and Langat River basin, respectively.

Comparisons on the levels of PFAAs in Langat and Selangor River basins with selected previous studies on surface water worldwide are tabulated in Table 4.4. In general, levels of PFAAs detected in this study were similar to levels of PFAAs found in rivers around Kyoto, Japan (Senthilkumar et al., 2007) and major rivers in France (Munoz et al., 2015), but lower than levels of PFAAs detected in Hanjiang River in China (B. Wang et al., 2013) and in the Llobregat River in Spain (Campo et al., 2015). However, levels of PFAAs detected in this study were higher than the levels of PFAAs found in other Asia countries like Vietnamese rivers (Lam et al., 2017), Korean river (Lam et al., 2014), and Ganges River, India (Yeung et al., 2009).

Among all PFAAs, PFOA and PFOS were the two of the most discussed PFAAs with extensive toxicology studies and proven effects on human and environment (Sunderland et al., 2019). PFOA and PFOS levels in this study were higher than the levels of PFAAs found in Orge River, France (Labadie & Chevreuil, 2011) and Yangtze River, China (Pan et al., 2014). Nevertheless, the concentration of PFOA and PFOS in Langat and Selangor River basins was considerably lower compared to the PFOA and PFOS detected in the Jucar River basin, Spain (Campo et al., 2016), in PFAAs manufacturing industries along Daling River, China (Zhu et al., 2015), and also in major river within Beijing, China (Y. Wang et al., 2019). All of the findings of PFAAs in Selangor and Langat River basin indicate that PFAAs contamination exists in the Klang Valley area.

Table 4.4. Comparisons of PFAAs levels in surface water samples among different water bodies worldwide.

Location	Year	Concentration (ng/L)									References
		PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS	PFOS	
Llobregat River, Spain	2010	0.07–111	0.63–25.2	0.07–146	0.77–52.4	0.07–4.25	0.09–0.09	ND	14.2–33.2	0.01–2710	Campo et al., 2015
Yangtze river, China	2013	0.35−8.38	<LOD−2.59	0.52−18.0	<LOD−0.86	<LOD–0.33	<LOD	–	<LOD−4.50	<LOD−3.39	Pan et al., 2014
Vietnam rivers	2013–2015	–	<0.07–4.26	<0.13–53.5	<0.06–4.81	<0.03–1.37	<0.03–0.33	<0.03–0.03	<0.07–5.98	<0.03–40.2	Lam et al., 2017
Korean rivers	2010−2012	–	ND–7.94	ND–8.34	ND–4.49	ND–4.80	ND–1.13	ND–0.33	ND–3.97	ND–15.07	Lam et al., 2014
Hanjiang River, China	2010	–	–	<LOD−256	<LOD−73.6	–	<LOD−76.7	2.48−33.3	–	<LOD−88.9	Wang et al., 2013
Beijing, China	2013−2014	<LOQ−75.75	<LOQ−30.0	<LOQ−69.0	<LOQ−7.65	<LOQ−13.43	<LOQ−1.92	ND	<LOQ−4.90	<LOQ−50.75	Wang et al., 2019
Northern Europe	2013	0.47–3.7	0.51–4.2	0.21–4.2	0.090–5.8	0.024–4.4	0.018–1.8	0.016–0.82	0.051–18	0.040–6.9	Nguyen et al., 2017
French Nationwide	2012	<0.17–11	<0.10–86	<0.08–36	<0.04–30	<0.07–10	<0.05–1.3	<0.07–0.94	<0.02–217	<0.06–173	Munoz et al., 2015
Orge River, nearby France	2010	–	11.3 ± 1.0	9.4 ± 0.6	1.3 ± 0.1	1.1 ± 0.1	0.10 ± 0.02	0.10 ± 0.01	13.6 ± 1.7	17.4 ± 2.2	Labadie & Chevreuil, 2011
Ganges River	2008	–	<0.092−2.29	<0.04−0.201	<0.04−0.176	<LOQ	–	–	–	<0.04−1.81	Yeung et al., 2009
Daling River, China	2013	<LOD−1570	<LOD−603	<LOD−2280	<LOD−20.1	<LOD−15.5	<LOD−0.44	–	<LOD−4.34	0.16−483	Zhu et al., 2015
Singapore water bodies	2013−2014	3.5−22.5	2.5−9.5	4.8−12.9	2.8−40.2	2.25−4.8	0.04−0.44	0.15−1.45	1.3−3.9	4.9−9.8	Chen et al., 2017
Jucar River basin, Spain	2010	5.21−644	1.44−18.7	0.07−52.2	0.85−19.8	0.09−213	0.62−0.62	ND	12.07−36.7	0.01−128	Campo et al., 2016
Welland river, Canada	2008& 2010	–	0.1−25.6	5.3−62.4	0.5−17.3	2.8−51.9	–	–	–	6.1−458	De Solla et al., 2012
Kyoto rivers, Japan	2005	–	–	7.9−110	–	–	–	<LOQ	<LOQ	<LOQ−10	Senthilkumar et al., 2007
Langat River, Malaysia	2009	–	–	200−5940	–	–	–	–	–	710−43500	Zainuddin et al., 2012
Langat River Basin, Malaysia	2017	<LOD−104.46	0.05−5.29	0.19−35.48	<LOD−15.45	<LOD−0.62	<LOD−3.12	<LOD−1.80	<LOD−1.14	<LOD−8.791	This study

ND – Not Detected, LOD – Limit of Detection, LOQ – Limit of Quantification.

4.3.2. Concentrations and composition profiles of PFAAs in sediment

Unlike the concentration of PFAAs in surface water, levels of PFAAs in sediment found in this study were higher (pg/g or ng/kg level). From all of the sediment samples analyzed (n=82), only two samples (*D.F.* = 2%) that did not contain any PFAAs above the detection limits. PFHxS and PFUnDA were found in only one sediment samples, while PFNA, PDFA, PFDoDA, and PFOS were found in 5 to 10 samples out of a total of 82 samples analyzed. At least 1 PFAAs were detected in sediment samples (except for the two samples that showed no presence of PFAAs). There were six sampling locations that did not have sediment samples due to the difficulty in collecting sediment samples during sampling campaign (either due to very fast river water flow or only sedimentary rock were present at the sampling site). The summaries of analysis results for the presence of PFAAs in sediment are tabulated in Table 4.5.

The total concentration of PFAAs ranged from <LOD to 249.7 pg/g dry weight (dw) for the Selangor River basin, and 18.7 to 465.6 pg/g dw for the Langat River basin. Overall, sediment contamination levels in the Langat River basin were higher compared to the Selangor River Basin. Compared to surface water where PFCAs were higher in the Selangor River basin while PFSA were higher in the Langat River basin, sediment showed higher PFCA levels in both river basins and that PFOA was the most frequent PFAAs detected in sediment samples, just like in surface water (*D.F* = 74 – 89%; a mean concentration of 36.98 pg/g dw and D.F. = 100%; 36.18 pg/g dw for Selangor River basin and Langat River basin respectively). PFHxA was the second most frequently detected PFAAs in Langat River basin, being present in 74 – 80% samples, followed by PFBA with 0 – 74% frequencies. In contrast, PFBA was the second most frequently detected PFAAs in the Selangor River basin with detection frequencies between 16 to 53%, followed by PFHxA with 21 – 32% frequencies. The other PFAAs such as PFDA, PFUnDA, PFDoDA, PFHxS, and PFOS were detected in less than 13% for both river basins. Differentiating the PFAAs levels by sampling campaign period, Selangor River basin showed a higher level of mean ∑PFAAs in sediment collected in March compared to July period (96.9 pg/g dw vs. 44.2 pg/g dw), which is in contrast to the finding on surface water. Similar to Selangor river basin, mean levels of ∑PFAAs in sediment in Langat River basin also were higher in samples collected in March compared to July (93.9 pg/g dw vs. 82.3 pg/g dw).

Table 4.5. Summarized levels (pg/g dw) and frequencies of detection (%) of PFAAs in sediment samples collected from Selangor and Langat River basins during March and July 2017 sampling campaigns.

Basin	Month	Parameter	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS	PFOS	∑PFAAs
Selangor	March	D.F	53	32	89	5	5	0	5	0	5	–
	n= 17	Minimum	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	20.300
		Mean	27.311	6.763	36.979	1.579	1.505	0.000	1.063	0.000	11.511	96.912
		Median	21.200	0.000	26.900	0.000	0.000	0.000	0.000	0.000	0.000	56.400
		Maximum	114.500	44.000	106.400	30.000	28.600	0.000	20.200	0.000	218.700	249.700
	July	D.F	16	21	74	0	10	0	10	0	5	–
	n= 17	Minimum	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		Mean	3.821	2.089	20.032	0.000	5.453	0.000	6.326	0.000	1.837	44.212
		Median	0.000	0.000	25.300	0.000	0.000	0.000	0.000	0.000	0.000	26.300
		Maximum	27.800	11.100	41.700	0.000	70.400	0.000	63.000	0.000	34.900	123.200
Langat	March	D.F	74	74	100	26	13	4	4	0	4	–
	n=23	Minimum	0.000	0.000	18.300	0.000	0.000	0.000	0.000	0.000	0.000	20.700
		Mean	33.048	15.974	30.313	5.470	3.574	1.183	1.330	0.000	2.983	93.874
		Median	28.100	14.800	28.100	0.000	0.000	0.000	0.000	0.000	0.000	80.700
		Maximum	98.000	52.000	95.800	24.100	42.800	27.200	30.600	0.000	68.600	233.800
	July	D.F	0	80	100	12	4	0	4	4	12	–
	n=25	Minimum	0.000	0.000	18.700	0.000	0.000	0.000	0.000	0.000	0.000	18.700
		Mean	0.000	10.888	36.176	6.140	1.568	0.000	2.476	2.400	22.660	82.308
		Median	0.000	9.200	26.200	0.000	0.000	0.000	0.000	0.000	0.000	39.300
		Maximum	0.000	76.000	232.400	94.900	39.200	0.000	61.900	60.000	283.700	465.600

D.F - Detection Frequency

The compositional profiles of individual PFAAs in the sediment of both river basins during March and July sampling campaigns are displayed in Figure 4.6 and 4.7, respectively. Different from the surface water compositional profiles where PFBA was the major contributor in March sampling, compositional profiles of sediment showed that PFOA was predominant with 32.3 – 38.2% and 44 – 45.3% average contribution from the total PFAAs with levels from <LOD to 106.4 pg/g dw and <LOD to 232.4 pg/g dw for both March and July sampling, respectively. In fact, the contribution of PFBA in sediment compared to surface water differed significantly where 11.3 – 34.3% average contribution was detected in surface waters while only 0 – 8.64% average contribution of total PFAAs was detected in sediment samples collected in July. In addition, PFBA was not detected in the Langat River basin in July sampling.

Comparisons on the levels of PFAAs in Langat and Selangor River basins with selected previous studies in sediments worldwide are tabulated in Table 4.6. In general, levels of PFAAs detected in sediments were comparable, or slightly lower than the levels of PFAAs found in Savannah River, USA (Kumar et al., 2009), Korean major rivers (Lam et al., 2014), Singapore's urban catchment (Chen et al., 2019), and Yangtze River, China (Pan et al., 2014). However, levels of PFAAs in previous studies such as in Llobregat River in Spain (0.09 – 11.4 ng/g dw) (Campo et al., 2015), major rivers in French (0.01 – 17 ng/g dw) (Munoz et al., 2015), and Ebro River, Spain (<LOD – 22.6 ng/g dw) (Pignotti et al., 2017) were significantly higher compared to the findings in sediment found in Klang Valley (<LOD – 0.28 ng/g dw). Focusing on the two major PFAAs, which are PFOA and PFOS, the concentration found in sediments in Selangor and Langat River basin were among the lowest compared to previous studies worldwide. For examples, levels of PFOS and PFOA in Czech rivers (0.09 – 11.4 ng/g dw) (Hloušková et al., 2014), Kyoto's rivers (0.09 – 11.4 ng/g dw) (Senthilkumar et al., 2007), Haihe River, China (0.09 – 11.4 ng/g dw) (Li et al., 2011), and Jucar River basin (0.09 – 11.4 ng/g dw) (Campo et al., 2016) were much higher compared to levels of PFOA and PFOS in Selangor and Langat River basins. No PFOA was detected in Vietnamese rivers and Orge River compared to Klang Valley (<LOD – 0.23 ng/g dw) (Labadie & Chevreuil, 2011; Lam et al., 2017). However, the concentration of PFOS in the same rivers (<LOD-6.72 for Vietnamese rivers and <LOD – 9.83 for Orge River) were much higher compared to Klang Valley (<LOD – 0.28 ng/g dw). Just like observation in surface waters, the differences in the type of industries and usage of PFAAs between different areas and countries worldwide may contribute to the differences in PFAAs levels in sediments.

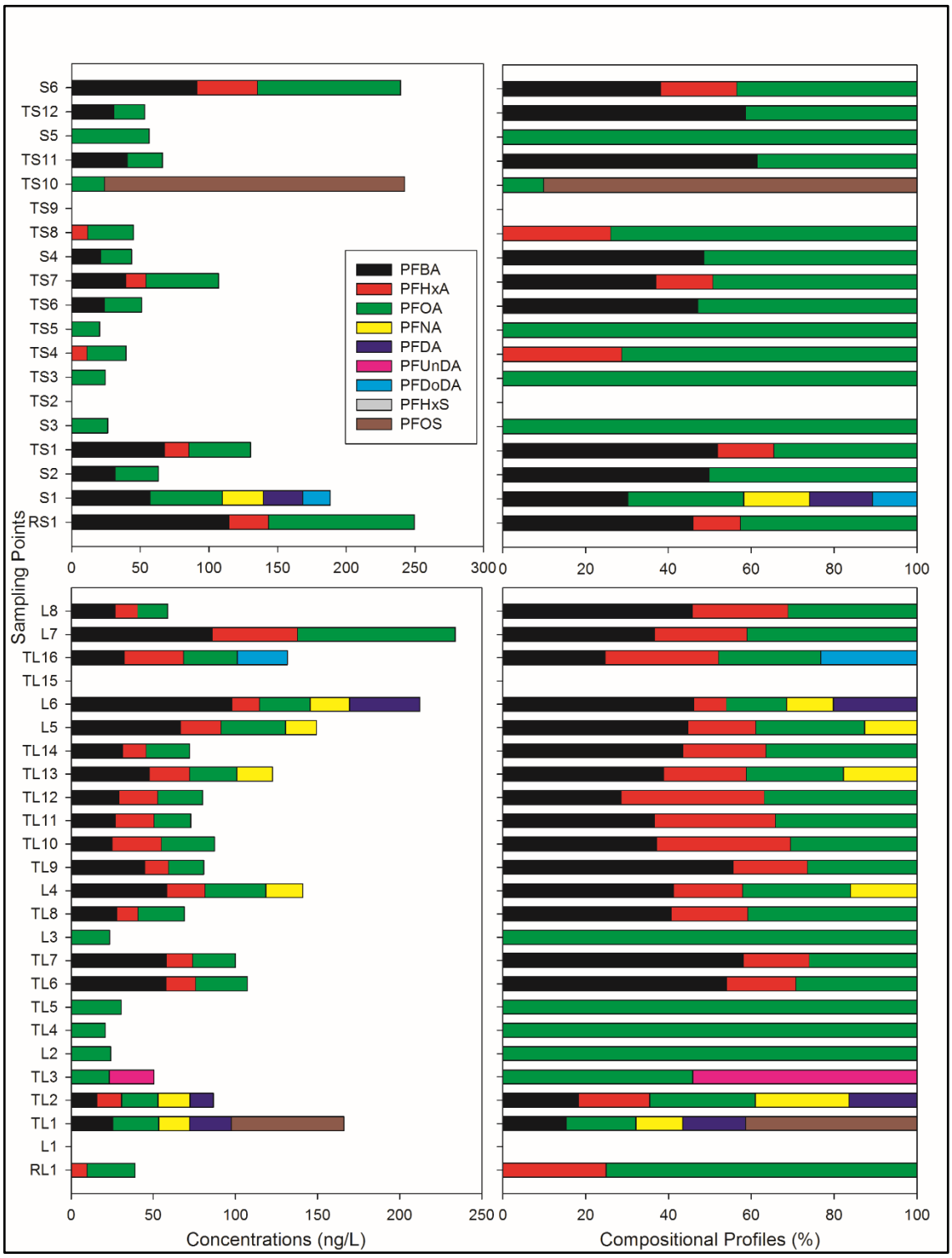

Figure 4.6. Levels and compositional profiles of individual PFAAs in sediment samples from Selangor and Langat River basin samples collected on *March 2017*. Top part of the figures representing sediment samples collected from Selangor and Langat River basin, respectively.

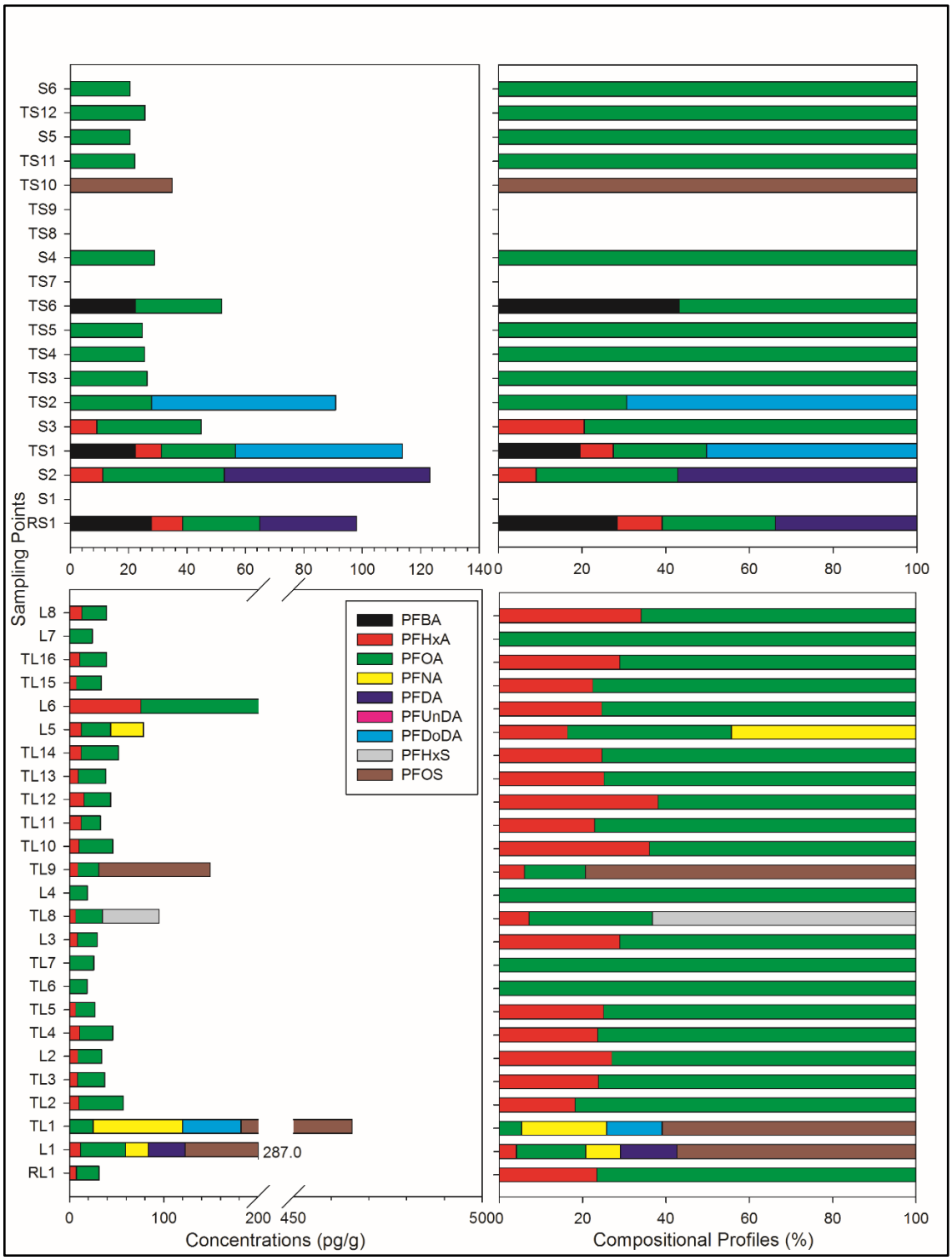

Figure 4.7. Levels and compositional profiles of individual PFAAs in sediment samples from Selangor and Langat River basin samples collected on *July 2017*. Top and bottom figures representing sediment samples collected from Selangor and Langat River basin, respectively.

Table 4.6. Comparisons of PFAAs levels in sediment samples among different water bodies worldwide.

Location	Year	Concentration (ng/L)									References
		PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS	PFOS	
Llobregat River Basin, Spain	2010	0.61–12.9		0.36–1.52	3.87–3.87	0.09–0.55	0.12–0.41	0.11–0.22	0.03–0.29	0.15–11.4	Campo et al., 2015
Yangtze river, China	2013	–	<LOD–0.32	0.03–0.72	<LOD–0.06	<LOD–0.06	<LOD–0.10		<LOD	<LOD–0.59	Pan et al., 2014
Vietnam rivers	2013–2015	–	<LOD	<LOD	<LOD	<LOD-0.17	<LOD-0.24	<LOD-0.16	<LOD-18.3	<LOD-6.72	Lam et al., 2017
Korean rivers	2010-2012	–	ND–0.05	ND–0.28	ND–0.15	ND–0.08	ND–0.09	0.01–0.13	ND–0.01	0.01–0.48	Lam et al., 2014
Orge River, nearby France	2010	–	0.06 ± 0.01	<LOD	0.05 ± 0.01	0.30 ± 0.02	0.29 ± 0.01	1.7 ± 0.0	0.10 ± 0.02	4.3 ± 0.3	Labadie & Chevreuil, 2011
Jucar River basin, Spain	2010	2.7-10.7	ND	<LOD-6.69	<LOD-3.63	<LOD-1.65	ND	ND	ND	<LOD-9.83	Campo et al., 2016
Savannah River, Georgia, USA	2007	–	ND-0.6	ND-0.2	ND-0.1	–	ND-0.2	ND-0.1	ND-0.3	0.3–0.8	Kumar et al., 2009
Haihe River, Tianjin, China	2010	–	0.2-3.0	1.0-3.5	<0.1-0.2	0.2-1.0	–	–	–	2.0-9.0	Li et al., 2011
French Nationwide	2012	–		<0.11–1.1	<0.04–0.97	<0.05–2.4	<0.01–2.6	<0.06–1.9	<0.02–0.63	<0.01–17	Munoz et al., 2015
Singapore urban catchment	2014-2015	–	1.23–2.85	0.02–0.09	<0.02–0.2	<0.08–0.2	0.09–0.4	0.45–1.53	<0.02–0.27	0.07–0.38	Chen et al., 2019
Kyoto rivers, Japan	2005	–	–	<LOQ-3.9	–	–	–	<LOQ	<LOQ	<LOQ-11	Senthilkumar et al., 2007
Ebro River, Spain	2015-2016	–	<LOQ-3.7	<LOQ-12.0	<LOQ-4.2	<LOQ	<LOQ	<LOQ-4.0	<LOQ-1.5	<LOQ-22.6	Pignotti et al., 2017
Czech rivers	2010	<LOQ	<LOQ	0.365–2.25	0.487–0.607	0.420–5.01	0.399–5.08	0.395–2.65	0.263–0.966	0.160–17.7	Hloušková et al., 2014
Langat River Basin, Malaysia	2017	<LOD-0.10	<LOD-0.08	0.02-0.23	<LOD-0.09	<LOD-0.04	ND	<LOD-0.06	<LOD-0.06	<LOD-0.28	This study
Selangor River Basin, Malaysia	2017	<LOD-0.11	<LOD-0.04	<LOD-0.11	<LOD-0.03	<LOD-0.07	ND	<LOD-0.06	ND	<LOD-0.22	This study

ND – Not Detected, LOD – Limit of Detection, LOQ – Limit of Quantification.

4.3.3. Spatial and temporal distribution of PFAAs in surface water of Selangor and Langat River basin.

The spatial and temporal distribution of PFAAs in surface waters of Selangor and Langat River basin during both sampling campaigns are shown in Figure 4.8 and Figure 4.9, respectively. For Selangor River basin, total PFAAs in surface water were varied between the tributaries and showed a different pattern between March and July samplings. Note that samplings were conducted after no rain was observed for at least 72 hours. PFBA, PFHxA, and PFOA were detected in all samples collected in the Selangor River basin during both sampling campaigns. Significant differences were observed for PFOA where concentrations were higher during July sampling compared to March sampling and this was further confirmed by the significant value of Kruskal-Wallis test ($p < 0.004$) between sampling campaigns (Table 4.7). On the upper part of the Selangor River basin, PFOA was detected at a concentration higher than 1 ng/L at S6 and TS9 without any significant variation between 2 sampling periods for the whole upstream. However, high level of PFOA was noticed at S6 during March sampling (11.635 ng/L vs. 1.818 ng/L for March and July sampling, respectively), which is contrary to the other sampling location where PFOA levels were higher during July sampling compared to March sampling. This location was situated nearby to the downstream of the Selangor River Dam. Because the average monthly rainfall during February and March that year were the lowest compared to the other months, and that Selangor River Dam water level was the lowest, an only small volume of water was released from the dam into the river, resulting in low water flow and volume. However, the fact that PFOA was detected at a high level right after Selangor River dam outlet (1 km distance apart), and that area is only covered in forest, should raise a concern about the quality of treated water supply originated from the Selangor River dam.

Compared to the upstream, PFOA was detected at a very high level in the surface water at the middle stream section. The middle section particularly tributaries TS3 to TS7 are located in the Rawang city and these tributaries are flowing through the most industrialized town in the Selangor River basin with various industries such as electronics, automotive, cement, and plastic manufacturing industries. PFOA detected in the middle section in July sampling were significantly higher compared to samples collected in March. These observations can be attributed to the differences in water level, flow, dry and wet deposition, and water quality of that time (Xiao, 2017). Although no rain was observed within 72 hours prior to sampling for both periods, a visual observation

confirmed that the water level and flow of TS7 were significantly lower during July sampling compared to March sampling. This proved that dilution effects were significant for March sampling at this location, which diluted the PFAAs level considerably. However, at sampling location TS7, PFOA levels in July were 126 times higher in July compared to March (126.953 ng/L vs. 0.943 ng/L). There were other significant factors that may contribute to the significant differences in the detection pattern such as one-time release or due to periodical discharge from related industries.

Compared with the other long-chain PFAAs, PFNA was detected in surface water of all sampling locations during both sampling campaigns. However, PFNA was most dominant in the upper part of the river basin and that higher levels were detected during July sampling compared to March sampling. Except for S5 where there is a small industrial area, all of the other sampling locations upstream is located in the rural population area. Therefore, it was suggested that PFNA may have occurred mainly from the population area which then distributed towards the estuary. PFBA and PFHxA were also detected in all samples but were most dominant in the middle part, similar to the pattern of PFOA. The high and significant correlation observed between PFOA, PFBA, and PFHxA ($r>0.576$ and $p<0.01$) for both sampling campaigns showed that these compounds possibly originate from the same sources.

PFOS was only detected in surface water during July sampling in the middle section of the Selangor River basin. PFOS was detected starting from the sampling point TS5 (0.986 ng/L), which then flowed into tributary TS2 (0.668 ng/L) downstream before entering Selangor River main stream S3 (6.237 ng/L). TS5 sampling point is located in the middle of Rawang city, a highly populated urban area. In addition, this tributary is flowing through the most industrialized town in the Selangor River basin with various industries such as electronics, cement, and plastic manufacturing industries. Since PFOS were only detected in this tributary before converging into the main Selangor River, it was suggested that PFOS may have originated from the industries and populated town located in this section, similar to the pattern of PFOA. However, a significant increase of PFOS at further downstream at S3 compared to tributaries at TS5 and TS2 is currently unknown. From S4 to S3, Selangor River only flows through an agricultural and forested area with a very small population area. In addition, S3 has a large water flow compared to the tributaries TS5 and TS2, which makes the dilution effect not applicable in this situation. The fact that PFOS was only detected during July sampling, and that no PFOS was detected in sediments around these sampling locations suggests that PFOS was

recently released into the river (either from new industry or from existing industry but with periodical discharge). Further analysis is warranted in order to elucidate the sources. Another complex observation can also be observed in sampling location T10. There were no PFOS detected in surface water at this location for both sampling campaigns. However, analysis of PFAAs of sediment collected at this sampling location showed the presence of PFOS in both periods. One possible reason was that PFOS usage was terminated prior to the sampling session or was replaced with another alternative of PFOS such as PFBA and PFHxA and PFHxS after the usage and production of PFOS were restricted. PFOS that were possibly present during that period were then distributed onto sediment due to its affinity to sorption to sediment which serves as an internal reservoir for PFOS (Habibullah-Al-Mamun et al., 2017; Pan et al., 2014). The decrease level of PFOS in sediment over time (from March to July) supported the observation.

In March sampling, PFDoDA were detected at low levels (up to 0.214 ng/L) in the main Selangor River where the detection started from the most upstream part (S6) and continue flowing downstream into the estuary. PFDoDA were also detected at TS3 tributary (0.221 ng/L) which then flowed downstream to TS2 where PFDoDA were also detected (0.238 ng/L) before converging with Selangor River. However, PFDoDA were not detected on the upstream part during July sampling and were only detected in the middle part of the river basin (Rawang city). PFDoDA may have been present in the upper stream, but due to the low concentration of PFDoDA detected (slightly above LOD, but well below LOQ), accurate assessment of the source is quite difficult to prove. The same can be said for PFUnDA (except S1, 1.389 ng/L), PFNA (except TS9, 1.051 ng/L), and PFDA (except TS7, 1.817 ng/L) where all the concentration detected were slightly above LOD but below LOQ level. Even when detected at above LOQ levels for some sampling locations, a different pattern was not observed for their counterpart during the sampling period. For example, PFUnDA were detected at S1 downstream (1.389 ng/L) but were not detected during July sampling. Furthermore, PFDA that were detected above LOQ (1.817 ng/L) at TS7 during July sampling were detected at a low level during March sampling (0.234 ng/L). It is noteworthy to mention that PFDA were only detected in the middle stream (except TS4 where no PFDA detected) and that the concentrations were higher during July sampling compared to March sampling.

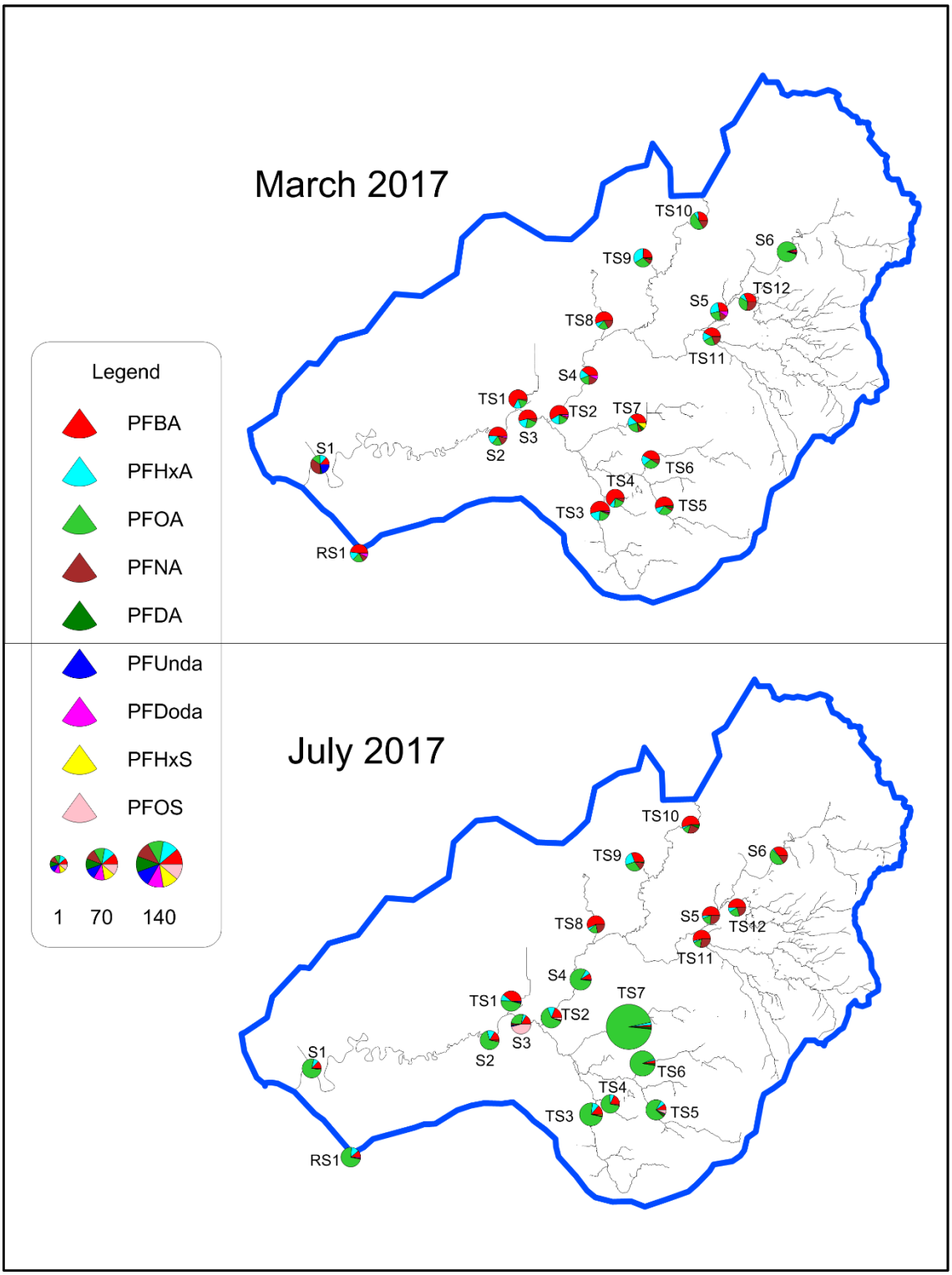

Figure 4.8. Spatial distribution and temporal variation of PFAAs in surface water samples collected from the Selangor River Basin.

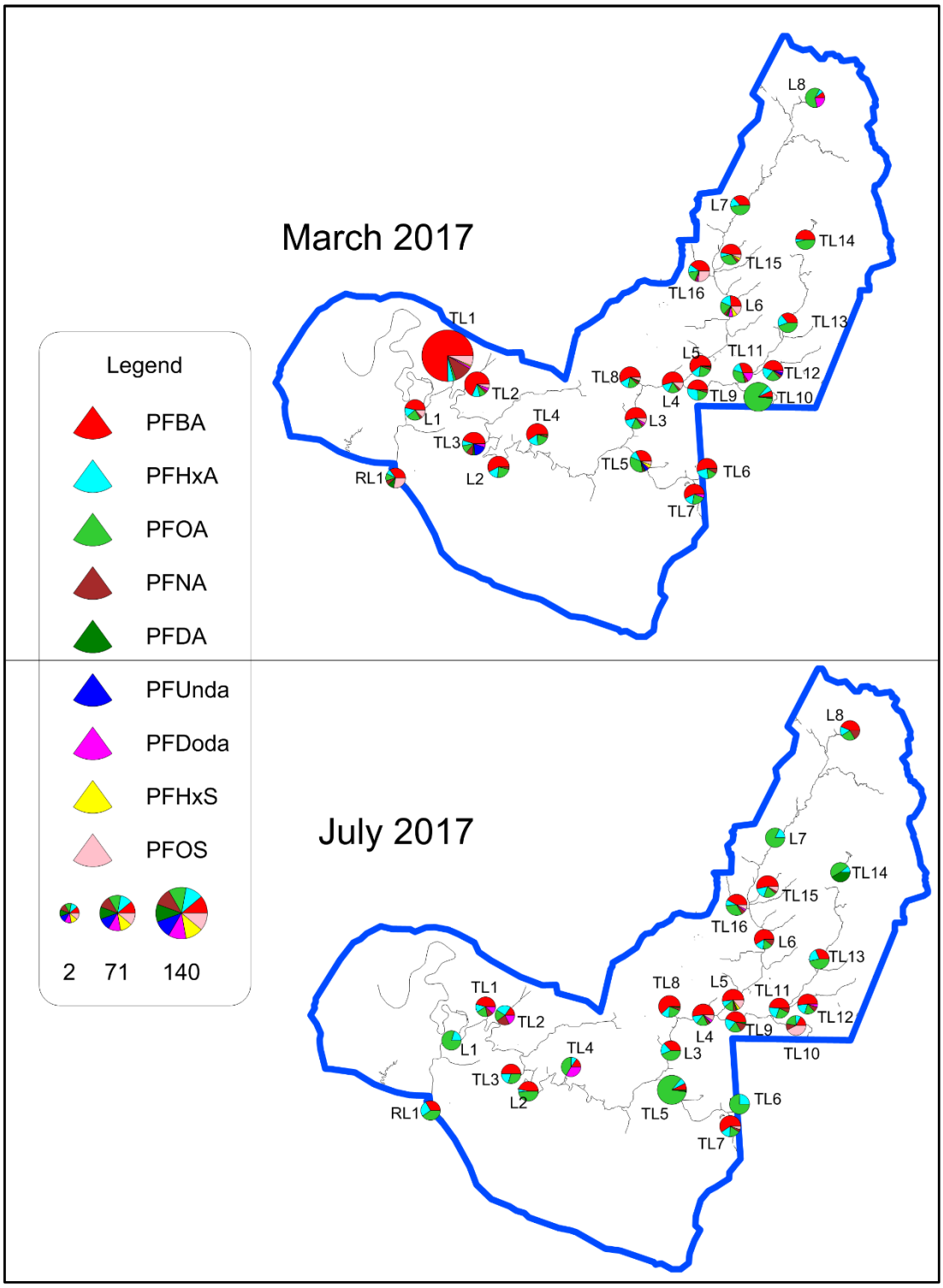

Figure 4.9. Spatial distribution and temporal variation of PFAAs in surface water samples collected from the Langat River Basin.

Table 4.7. Mann-Whitney test for comparison of individual PFAAs level between different sampling period for both Selangor and Langat River basin. Bold text indicates significant value ($p < 0.05$)

Variable	*p-value*	
	Selangor	**Langat**
PFBA	0.138	**0.004**
PFHxA	0.181	**0.005**
PFOA	**0.004**	**0.007**
PFNA	0.116	0.073
PFDA	0.370	0.834
PFUnDA	0.977	**0.039**
PFDoDA	0.212	0.055
PFHxS	1.000	0.151
PFOS	0.418	0.100

Similar to the Selangor River basin, the total PFAAs in surface water of the Langat River basin varied among sampling location and that different patterns were observed between March and July samplings (Figure 4.9). PFOA was detected in all samples during both March and July samplings, but were significantly higher during March sampling. On the upper part of the river basin, PFOA was detected above 1 ng/L at tributaries TL15 and TL16 during both sampling campaigns. Similar observations were also found for PFOS. TL15 and TL16 are located in the most populated area in Langat River basin. There are also a few small industrial areas situated within this region. PFOA may have come from these industries or from the housing area, just like what was observed in other studies in Kotthoff et al. (2015) and Arvaniti and Stasinakis (2015) where PFOA was released from industrial and housing area. The highest PFOA in Langat River basin was detected at TL10 during March sampling (35.5 ng/L) but no PFOS was detected at the same location. However, only a low concentration of PFOA and PFOS were detected at the same location during July sampling (0.38 ng/L and 0.756 ng/L, respectively). This can either due to the larger volume of water during July sampling, which resulted in dilution of PFOA and PFOS or due to the one-time significant release of PFOA in March. There are 2 tributaries with multiple drain outlets that connected prior to this location. One of these tributaries only flows through the rural residential area while the other tributaries flow through Nilai industrial area and rural residential area. Just like in location TL15 and TL16, PFOA may have also come from these areas. In contrast, the concentration of PFOA was the highest at location TL5 during July sampling. This

location is close to the Kuala Lumpur International Airport. There were various studies that found a high concentration of PFAAs such as PFOA and PFOS, which originated from the airport due to the usage of AFFF (De Solla et al., 2012; Moody et al., 2002). It was suggested that a high concentration of PFOA detected at this location came from the AFFF that were used during training. The periodical training period may have resulted in the different concentration of PFOA detected at this location.

For PFOS, the highest concentration during March sampling was detected at TL1. In fact, all other PFAAs have also been the highest at this location compared to another location in the Langat River basin, except for PFDA and PFUnDA which were not detected. TL1 is a major free industrial zone in this river basin with various kinds of industries such as the manufacturer of food, plastic, chemical, semiconductor, and furniture. There are also palm oil refineries situated near this sampling point. Similar to PFOA, PFOS may have originated from these industries. However, only low concentrations of PFAAs were detected at this location during July sampling compared to March sampling and the reason is unknown. Further analyses of PFAAs at this location in another sampling period are warranted in order to clarify the reason.

The previous study on the analysis of PFOA and PFOS in Langat River in the year 2009 found a very high concentration (up to 5,940 ng/L and 47,190 ng/L of PFOA and PFOS, respectively) along the river (Zainuddin et al., 2012). However, the current study found that the concentration of PFOA and PFOS in Langat River has decreased significantly (more than 1000 – 10000 folds) compared to last time. In addition, detection frequencies of PFOS along the Langat River have dropped significantly from 100% to just 24 – 44% detection frequencies. One of the reasons may be due to the use of PFOS alternative such as PFBA and PFHxA, where after the production and usage of PFOS and its salts were phased-out and restricted after these compounds were included in Annex B of the Stockholm Convention on persistent organic pollutants (UNEP, 2016). For example, PFOS and PFOA were the predominantly PFAAs detected in Daling River, China from an analysis conducted in 2004 (Bao et al., 2010). However, the same analysis conducted a few years later in 2013 found that PFBA and PFBS was the major contributor compared to last time (Zhu et al., 2015). This suggests that the production and usage of long-chain PFAAs were replaced by short-chain PFAAs such as PFBA, PFBS, and PFHxA. High detection frequencies of PFBA and PFHxA in surface water of the Langat River confirmed the opinion. Furthermore, high detection frequencies were also observed for PFNA (60 – 80% D.F.; <LOD – 15.45 ng/L) and PFDA (40 – 56% D.F.; <LOD –

0.62 ng/L), suggesting the uses of other alternatives to PFOA and PFOS in Klang Valley. However, since PFAAs were not regulated in Malaysia, and that currently only a few or no information on the production, usage, and volumes of PFAAs in Malaysia, conclusion on the specific sources of PFAAs in Malaysia particularly in Klang Valley area still remain to be elucidated.

PFHxS in the Langat river basin may have originated from TL15 where it was detected at a low level and detected further downstream at L6. TL5 and TL1 also showed the presence of PFHxS although at a low level. However, during July sampling, PFHxS was only detected at L5 compared to L6 which were detected in March. Since both concentrations were detected at a very low level, dilution of PFHxS due to the large volume of water may have resulted in detection below the LOD level. For long-chain PFAAs such as PFDA, PFNA, PFUnDA, and PFDoDA, low frequencies of detection combined with a very low concentration detected (slightly above LOD, but well below LOQ) may have hindered an accurate distribution analysis of these compounds in the Langat River basin, except for TL1 which was discussed earlier and TL3 where high concentration of PFNA (1.59 ng/L) and PFUnDA (3.12 ng/L) were detected. TL3 is a suburban residential area with no specific area for industries, thus suggesting that PFNA and PFUnDA in this location might have only originated from the residential area.

No obvious pattern was observed for PFHxA since the PFHxA distribution between sampling points are irregular even though PFHxA were detected in all samples. However, significant differences were observed between concentration detected in March compared to July ($p<0.05$), where PFHxA were higher in March samples compared to July. In addition, a high correlation between PFOA and PFHxA ($r = 0.757 – 0.821$, $p<0.01$) indicates that these compounds may have originated from the same sources. A similar observation was also observed for PFBA which no obvious pattern was found beside that PFBA were detected in all samples. Except for sampling location TL1 during March sampling, which showed a very high concentration of PFBA (104.45 ng/L), high and significant correlation were also observed between PFBA, PFHxA, and PFOA. However, high contribution of PFBA (28.2% to 35.2%) in sediment collected during March sampling compared to July sampling were observed, although slightly lower than the contribution of PFOA. The reason for the differences in PFBA behavior between March and July sampling are unknown. Various factors such as rainfall volume and riverbank soil erosion could play a role in such behavior and thus requires further analysis. Soil from riverbank that was free from any PFAAs may have been settled into

sediment due to the effect of rainfall or riverbank soil erosion (Habibullah-Al-Mamun et al., 2017). A physicochemical property of each individual PFAAs such as adsorption potential and solubility also affects the distribution of each PFAAs. A study by Higgins and Luthy (2006) observed that long-chain PFAAs showed higher sorption potential compared to short-chain PFAAs and by increasing chain length of PFAAs, the adsorption potential would also increase. Long-chain PFAAs is also prone to partition onto the sediment phase due to the low solubility properties compared to short-chain PFAAs with high solubility (Ahrens et al., 2016; Ahrens et al., 2011). The finding of this study was consistent with the physicochemical observation where the PFOA showed a higher sorption ability compared to PFBA, and that the concentrations of long-chain PFAAs such as PFNA, PFDA, PFUnDA, and PFDoDA in sediment were higher compared to its levels in surface waters.

4.3.4. Pattern analysis of PFAAs composition

To estimate the potential sources of individual PFAAs in Selangor and Langat River basin, Spearman's rank correlation was performed on the concentration of each individual PFAAs obtained for both sampling campaigns, and the results are shown in Table 4.8 and 4.9 for Selangor and Langat River basin, respectively. In Selangor River basin, a significant correlation was found between PFBA, PFHxA, and PFOA ($r>0.576$ and $p<0.01$) and between PFOA and PFDA ($r=0.601$, $p<0.01$) for March sampling, which may indicate the common source of contamination for these PFAAs. In addition, the same significant correlations were also observed in July sampling, suggesting the consistent source of these PFAAs pollutions in both March and July samplings. Furthermore, since PFOS were only detected in the Selangor River basin in July sampling, but not in March sampling, it is safe to assume that the PFOA may have a different source of pollution than PFOS in this river basin. This observation was also found by other studies such as in the Yangtze River and Jiulong River in China, where these studies also found no correlation between PFOA and PFOS (Cai et al., 2018; Pan et al., 2014). In addition, except for PFDA/PFOS in July sampling, no significant correlation was found between PFSAs (PFOS and PFHxS) to any other PFCAs during both sampling periods, which further support the assumption that PFOA and PFOS have different contamination source in the Selangor River basin.

Similar to the Selangor River basin, short-chain PFCAs such as PFBA, PFHxA, and PFOA were also significantly correlated ($r>0.745$, $p<0.01$) between each other in the

Langat River basin. In addition, PFNA was also significantly correlated with these PFCAs ($r>0.578$, $p<0.01$) which may also indicate a common source of contamination for these PFAAs. However, based on the concentration of PFAAs collected in the Langat River basin collected in July, all PFAAs were significantly correlated among each other ($p<0.05$), except for PFDoDA and PFHxS. Different from the source profiles in the Selangor River basin, PFSA (PFOS and PFHxS) were significantly correlated with each other ($r=0.464$, $p<0.05$) in the Langat River basin in March samples. Samples collected in July also showed the same behavior, suggesting the consistent source of these PFAAs pollutions in both March and July samplings.

The ratios between individual PFAAs were also considered in this study. For examples, PFOA/PFOS ratios of 9 and 4.4 have been associated with the precipitation and surface runoff, respectively (Kim & Kannan, 2007). Ratio ~0.001 between PFOA/PFOS also was associated with the release of fire-fighting foams (Moody et al., 2002) while the typical surface waters have a ratio above 1.1 (V. T. Nguyen et al., 2011). Since PFOS was not detected in samples collected in the Selangor River basin in March sampling and low detection frequencies in samples collected in July sampling, the PFOA/PFOS ratio could only be calculated for S3 (0.6), TS2 (17.1), and TS5 (11.8). The ratio indicates that precipitation may be a significant contributor for PFAAs in location TS2 and TS5. In contrast, none of the ratios in the Langat River basin exceeded the value of 9, which suggests that precipitation may not be a significant contributor for this river basin. PFOA/PFOS ratio between 3 and 6.5, which were close to ratio 4.4 was also observed for some sampling location, indicating that surface runoff may be an important contributor to these locations.

Beside PFOA/PFOS ratio, PFNA/PFOA ratio also has been proposed as an estimation of atmospheric deposition when the ratio value is less than 1.0 (Simcik & Dorweiler, 2005; Sun et al., 2017). In this study, most of the ratios were lower than 1.0 except for sampling point TL1 (7.6) and TL2 (1.1) in the Langat River basin and sampling point S5 (1.4), TS11 (1.9), and TS10 (2.0) in the Selangor River basin. This indicates that PFNA contamination may have originated within these areas which were then deposited into the surface water at these sampling locations.

Table 4.8. Spearman rank correlation coefficient among individual PFAAs in surface water of *Selangor* River basin. Top and bottom table representing March and July samples, respectively. Dash symbol (-) indicates no correlation found due to no detection.

	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS
PFHxA	**0.765****							
PFOA	**0.576****	**0.673****						
PFNA	0.402	**0.633****	0.200					
PFDA	0.066	0.327	**0.601****	0.181				
PFUnDA	-0.129	0.172	0.108	0.388	0.417			
PFDoDA	0.221	0.267	0.326	0.155	-0.054	-0.174		
PFHxS	0.086	0.086	0.043	0.043	**0.469***	-0.056	-0.174	
PFOS	-	-	-	-	-	-	-	-

	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS
PFHxA	**0.719****							
PFOA	**0.456***	**0.777****						
PFNA	-0.002	-0.381	-0.619					
PFDA	**0.576****	0.448	**0.486***	-0.046				
PFUnDA	0.444	0.105	-0.026	-0.099	0.374			
PFDoDA	-0.024	0.217	0.366	-0.481	-0.091	-0.148		
PFHxS	0.344	0.387	0.301	0.043	0.047	-0.081	-0.102	
PFOS	0.283	0.133	0.167	-0.222	**0.457***	0.342	0.165	-0.102

** - p<0.01, * - p < 0.05

Table 4.9. Spearman rank correlations coefficient among individual PFAAs in surface water of *Langat* River basin. Top and bottom table representing March and July samples, respectively. Dash symbol (-) indicates no correlation found due to no detection.

	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS
PFHxA	**0.768****							
PFOA	**0.745****	**0.757****						
PFNA	**0.856****	**0.716****	**0.578****					
PFDA	0.194	0.255	0.322	0.182				
PFUnDA	0.140	0.042	0.214	0.136	0.355			
PFDoDA	0.222	0.234	0.173	0.298	-0.012	0.293		
PFHxS	0.147	0.226	0.395	0.227	0.163	0.187	0.338	
PFOS	0.368	0.232	0.230	0.368	0.036	-0.131	0.359	**0.464***

	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS
PFHxA	**0.850****							
PFOA	**0.685****	**0.821****						
PFNA	**0.848****	**0.788****	**0.603****					
PFDA	0.362	**0.398***	0.369	**0.425***				
PFUnDA	-	-	-	-	-			
PFDoDA	0.121	0.008	-0.055	0.231	-0.103	-		
PFHxS	0.255	0.170	0.170	0.263	0.378	-	-0.113	
PFOS	**0.531****	**0.412***	**0.466***	**0.525****	0.137	-	0.170	**0.453***

** - p<0.01, * - p < 0.05

4.3.5. Partitioning behavior of PFAAs between surface water and sediment

The transport mechanism of PFAAs in the aquatic environment could be further evaluated by the use of the partition coefficient. Partition coefficient can be described as to how a solute is distributed between two media. In the aquatic environment, partition coefficient, K_D is used to determine the partition between surface water and sediments, which involves the removal of the chemical from surface water onto the sediment by a mechanism such as flushing or sedimentation.

The partition coefficients, K_D, of PFAAs were calculated using the ratio between concentrations of PFAAs in sediment to the concentration of PFAAs in surface water. The ratios were calculated only when individual PFAAs were detected in both sediment and surface water samples at the same sampling location. The calculation of the partition coefficient is summarized as follows:

$$\text{Partition coefficient, } K_D \text{ (L/Kg)} = Cs/Cw \quad (1)$$

where *Cs* is the measured concentration of individual PFAAs in sediment samples (ng/Kg) and *Cw* is the measured concentration of individual PFAAs in surface water samples (ng/L).

The mean Log K_D value of PFAAs in this study were all above 1.5 (1.5 to 2.3), except for PFUnDA (0.94) and PFOS (0.89) where these compounds were detected in both sediment and surface water at only 1 sampling point, respectively (Table 4.10). Except for PFOS and PFUnDA, some of the log K_D values for PFAAs in this study were in agreement with previous reported field-based K_D value (Guo et al., 2015; Labadie & Chevreuil, 2011; Munoz et al., 2015). Note that no pair of PFHxS was detected in sediment and water.

However, the log K_D value of PFOA was significantly lower compared to the value calculated from Jucar River, Spain (Campo et al., 2016) but significantly higher compared to the value calculated from Lake Taihu, China (Guo et al., 2015). These differences in log K_D were to be expected because of the differences in physicochemical characteristics of the water and sediment in this region compared to the other regions.

The plot of $LogK_D$ versus PFAAs chain length showed that the average $LogK_D$ was significantly correlated to the carbon number of PFAAs (Figure 4.10). The $LogK_D$ increases as the carbon number increases. Higher hydrophobicity properties from the increasing chain-length of PFAAs would, therefore, increase the sorption potential of

PFAAs onto sediment. These observations were supported by other studies which mentioned the importance of van der Waals interaction with hydrophobicity mechanism (Higgins & Luthy, 2006; Joerss et al., 2019; Kwadijk et al., 2010; Yan et al., 2015).

However, PFBA did not follow the trend discussed before, PFBA, with only 4 carbon atoms, have similar $LogK_D$ value compared to PFHxA and PFOA, which have 6 and 8 carbon atoms, respectively. The same findings were also observed in lab-based sorption experiments (Higgins & Luthy, 2006) and field-based analysis (Habibullah-Al-Mamun et al., 2017; Joerss et al., 2019). It was previously hypothesized that the van der Waals interaction may not be the only significant mechanism in PFAAs sorption. Another mechanism such as ion exchange or the interaction with a sorptive site which may not present in longer-chain compound due to steric hindrance may also play an important role for shorter-chain PFAAs (Guelfo & Higgins, 2013).

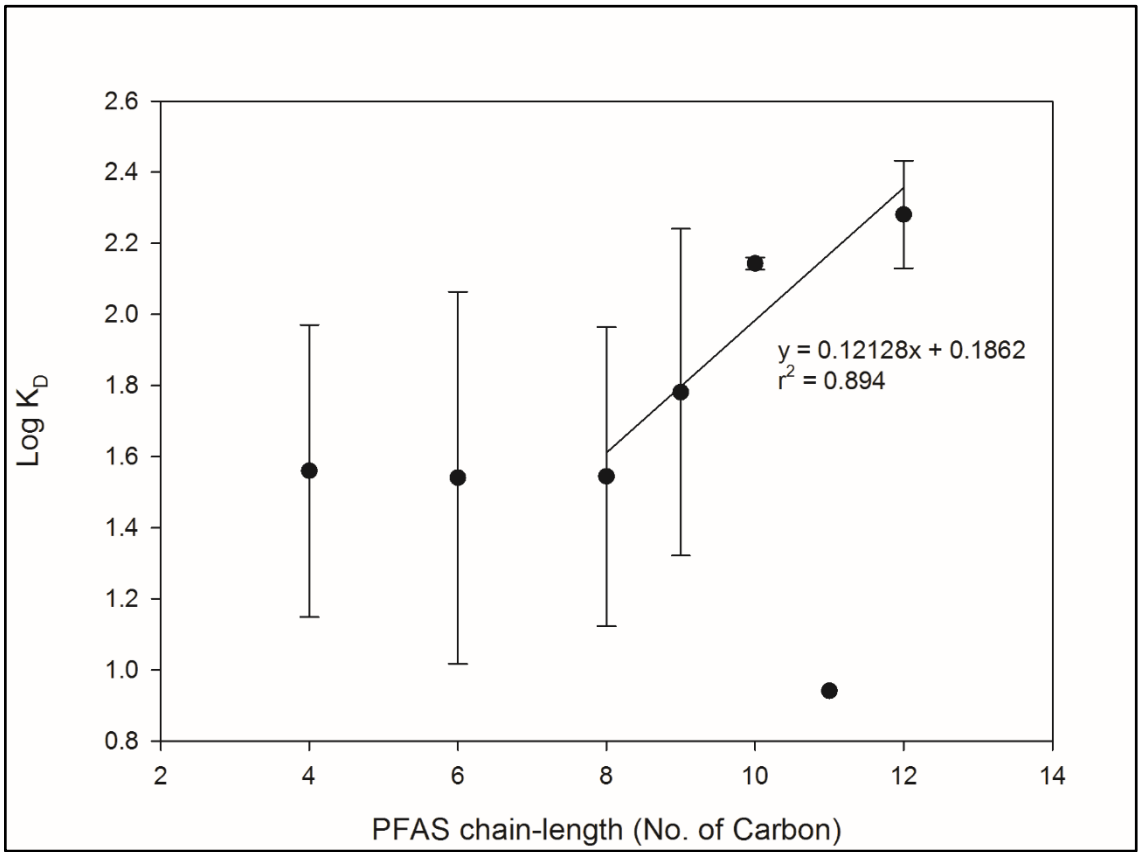

Figure 4.10. Correlation between PFAAs chain length (n carbon atoms) and log K_D.

Table 4.10. Comparison of mean Log K_D of PFAAs between this study and selected literature.

Location	PFAAs									References
	PFBA	**PFHxA**	**PFOA**	**PFNA**	**PFDA**	**PFUnDA**	**PFDoDA**	**PFHxS**	**PFOS**	
Langat & Selangor River basin	1.56 ± 0.41	1.54 ± 0.52	1.54 ± 0.42	1.78 ± 0.46	2.14 ± 0.02	0.94	2.28 ± 0.15	–	0.89	This study
Orge River, France	–	0.8	–	1.5 ± 0.1	2.4 ± 0.2	3.4 ± 0.1	4.3 ± 0.2	0.9 ± 0.0	2.4 ± 0.2	Labadie, 2011
Jucar River, Spain	2.4	–	3.36	–	–	–	–	1.68	2.45	Campo,2016
Llobregat River, Spain	2.33	–	2	–	2.51	1.3	–	–	–	Campo, 2015
Lake Taihu, China	1.64 ± 0.24	0.86 ± 0.34	0.65 ± 0.30	1.88 ± 0.44	2.16 ± 0.31	2.47 ± 0.41	2.49 ± 0.13	1.82 ± 0.36	2.24 ± 0.61	Guo, 2015
French freshwater ecosystems	–	–	1.9 ± 0.6	2.5 ± 0.5	2.6 ± 0.6	3.0 ± 0.6	2.7 ± 0.6	1.8 ± 0.6	2.3 ± 0.8	Munoz, 2015

4.3.6. Ecological risk assessment

Several studies have reported that PFAAs may pose potential hazards to aquatic organisms (Suja et al., 2009; Xiao, 2017). However, most works were limited to either PFOS or PFOA. Recently, a shorter chain PFAAs such as PFBA, PFHxA, and PFPeA are being widely manufactured as an alternative since it was believed that these alternatives may have less toxicity potency compared to the other PFAAs (Buhrke et al., 2013; Luz et al., 2019). Therefore, it is necessary to assess their risks to the aquatic environment. There is no standard method to assess the risk of chemical to aquatic and human. Various approaches were used to estimate the risk characterization. The most commonly used methods use risk quotients (RQs) to evaluate the environmental hazard to aquatic organisms (Amiard & Amiard-Triquet, 2015). RQs are described as the ratio between measured concentrations of chemicals in the environment (MEC) to the chronic toxicity of the same chemicals, which typically expresses as Predicted Non-Effect Concentration (PNEC). The calculation of RQs was summarized as follows:

$$\text{Risk Quotients, RQs} = \frac{MEC}{PNEC\ or\ NOEC} \quad (3)$$

However, when no values of PNEC are available, the PNEC values can be derived by dividing toxicological dose descriptors (EC50, LC50, NOEC) with an assessment factor (Amiard & Amiard-Triquet, 2015). These values were defined from the study on the exposure of these chemicals to aquatic organisms and can be calculated using this equation:

$$\text{Predicted Non-Effect Concentration, PNEC} = \frac{EC50\ or\ LC50\ or\ NOEC}{Assessment\ Factor\ (AF)} \quad (4)$$

where the assessment factor was assigned as 1000 based on the Technical Guidance Document on Risk Assessment (European Chemicals Agency, 2003).

However, except for PFOA and PFOS, epidemiology and toxicology data for other PFAAs are very limited. Thus, in the absence of comprehensive toxicity data, model operation by ECOSAR™ was applied to predict the aquatic toxicity value (EC50 or LC50) of PFAAs (Campo et al., 2016). The value adopted from Campo et al. (2016) was then summarized in Table 4.11.

Table 4.11. Modeled (ECOSAR) acute toxicity values of PFAAs in different trophic levels (algae, Daphnia sp. and fish) (Campo et al., 2016).

Compound	ECOSAR Acute toxicity- EC50 (mg/L)		
	Green Algae	Daphnia sp.	Fish
PFBA	597.14	760.59	1322.59
PFHxA	103.82	79.34	127.93
PFOA	16.22	7.44	10.10
PFNA	6.26	2.22	2.84
PFDA	2.39	0.66	0.79
PFUnDA	0.90	0.19	0.22
PFDoDA	0.34	0.06	0.06
PFHxS	220.42	190.35	301.32
PFOS	32.65	16.92	23.66

According to the results of RQs obtained in this study using a mean concentration of PFAAs in surface water of both Selangor River and Langat River basin (Table 4.12), PFAAs exhibited a very low risk to the three different trophic levels (green algae, Daphnia sp. and fish). However, when using maximum measured concentration value, PFOA and PFUnDA may slightly pose a potential risk to Daphnia sp. and fish (RQs > 0.01) in both Selangor and Langat River basin. In addition, a high concentration of PFDoDA in Langat River basin may also pose a potential risk to Daphnia sp. and fish (RQs > 0.03). Note that the other adverse effect of PFAAs that could lead to higher toxicity risk, such as biomagnification and bioaccumulation is not assessed in this risk assessment and should be further investigated in the future.

Table 4.12. Risk quotient (RQ) of PFAAs in surface water of Selangor and Langat River basin for both sampling periods calculated using mean and max levels of PFAAs.

		RQ_{March}			RQ_{July}		
	PFAAs	**Green Algae**	**Daphnia sp.**	**Fish**	**Green Algae**	**Daphnia sp.**	**Fish**
				Mean			
Selangor	PFBA	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	PFHxA	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	PFOA	0.0001	0.0002	0.0001	0.0009	0.0019	0.0014
	PFNA	0.0001	0.0002	0.0001	0.0001	0.0002	0.0002
	PFDA	0.0000	0.0001	0.0001	0.0001	0.0003	0.0003
	PFUnDA	0.0001	0.0005	0.0004	0.0000	0.0002	0.0002
	PFDoDA	0.0002	0.0014	0.0014	0.0001	0.0006	0.0006
	PFHxS	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	PFOS	–	–	–	0.0000	0.0000	0.0000
Langat	PFBA	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	PFHxA	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	PFOA	0.0002	0.0004	0.0003	0.0001	0.0003	0.0002
	PFNA	0.0001	0.0004	0.0003	0.0000	0.0001	0.0001
	PFDA	0.0000	0.0002	0.0001	0.0000	0.0001	0.0001
	PFUnDA	0.0002	0.0009	0.0007	–	–	–
	PFDoDA	0.0007	0.0042	0.0042	0.0002	0.0009	0.0009
	PFHxS	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	PFOS	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
				Max			
Selangor	PFBA	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	PFHxA	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	PFOA	0.0007	0.0016	0.0012	0.0078	0.0171	0.0126
	PFNA	0.0004	0.0010	0.0008	0.0002	0.0005	0.0004
	PFDA	0.0001	0.0004	0.0003	0.0008	0.0028	0.0023
	PFUnDA	0.0015	0.0073	0.0063	0.0003	0.0014	0.0012
	PFDoDA	0.0007	0.0040	0.0040	0.0006	0.0037	0.0037
	PFHxS	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	PFOS	–	–	–	0.0002	0.0004	0.0003
Langat	PFBA	0.0002	0.0001	0.0001	0.0000	0.0000	0.0000
	PFHxA	0.0001	0.0001	0.0000	0.0000	0.0000	0.0000
	PFOA	0.0022	0.0048	0.0035	0.0022	0.0048	0.0035
	PFNA	0.0025	0.0070	0.0054	0.0001	0.0003	0.0003
	PFDA	0.0003	0.0009	0.0008	0.0003	0.0009	0.0008
	PFUnDA	0.0035	0.0164	0.0142	–	–	–
	PFDoDA	0.0053	0.0301	0.0301	0.0012	0.0070	0.0070
	PFHxS	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	PFOS	0.0003	0.0005	0.0004	0.0000	0.0001	0.0001

In addition, Giesy et al. (2010) and Yang et al. (2014) have developed a criteria maximum concentration (CMC) and criteria continuous concentration (CCC) of PFOA and PFOS in water for the protection of aquatic organism in North America and China, respectively. All the concentrations detected were below those criteria, suggesting that the PFAAs were unlikely to cause harm to the aquatic organism in the Selangor river basin. Furthermore, if the analyzed surface water was used as a drinking water source, maximum concentration of PFOA (site TS7) would exceed the updated US EPA lifetime health advisory level of 70 ng/L for a combination of PFOS and PFOA in drinking water (Boone et al., 2019), whereas mean concentrations of PFOA and PFOS did not exceed the health advisory level.

4.4. Conclusion

The presence of perfluoroalkyl acids (PFAAs) in the surface waters and sediments of Selangor and Langat River basin were analyzed in this study. All 9 target PFAAs were present in both media with different detection frequencies and compositional patterns. The total concentration of PFAAs (∑PFAAs) in surface water samples were in the range of 0.886 – 133.692 ng/L and 0.419 – 138.945 ng/L, while in the sediment the range of not detected to 249.7 pg/g dw and 18.7 – 465.6 pg/g dw were detected in Selangor and Langat River basin, respectively. PFOA was found to be the predominant PFAAs in water and sediment with a mean of 1.43 – 14.33 ng/L and 20.0 – 36.98 pg/g dw, respectively. Levels of PFAAs detected in this study were similar to levels of PFAAs found in rivers around Japan, France, but lower than levels of PFAAs detected in China and Spain. Urbanization and industrialization were identified as potential sources of PFAAs contamination in the area of Klang Valley. Ecological risk assessment indicates that none of the PFAAs levels exceeded the PNEC value, suggesting little to no potential risk to the aquatic organisms. However, biomagnification and bioaccumulation effects could lead to higher toxicity risk and should be further investigated in the future. The presence of PFAAs in surface waters and sediments in Selangor and Langat River basin indicates the widespread distribution of PFAAs in the area of Klang Valley, which should not be ignored.

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CHAPTER 5

LEVELS AND SOURCE EXPOSURE ASSESSMENT OF PERFLUOROALKYL ACIDS (PFAAs) IN SELECTED FOODS AND DRINKING WATER COLLECTED FROM WET MARKETS WITHIN KLANG VALLEY, MALAYSIA

Abstract

Previous analysis of the blood of Klang Valley's residents showed the presence of PFAAs. Since dietary intake is one of the major PFAAs routes of exposure to human, it is deemed necessary to conduct an analysis of the presence of PFAAs in food and drinking water. This research revealed the first evidence of the contamination of PFAAs in selected food and drinking water samples from Malaysia, particularly in the Klang Valley. Nine PFAAs were analyzed in 56 samples from 19 different types of foods and 36 drinking water samples from the tap and bottled water using LC-MS/MS. In this study, PFAAs were found above the detection limit in all food samples and some drinking water samples analyzed. The highest level of mean ∑PFAAs in food was found in chickens (5.78 ng/g ww), followed by beef (3.14 ng/g ww), and marine fish (0.93 ng/g ww). Overall, all marine food samples tested were the main contributor of long-chain PFAAs (C≥8), except for mollusks. Mollusk was the major contributor for PFOA while the other food samples were the major contributor for PFOS. Tap and bottled water samples showed a varied concentration of PFAAs, which is dependent on the sources of the raw water intake. Based on the preliminary dietary intake exposure assessment, frequent consumption of chicken may lead to the health risk associated with FPAS to the local population assessed, due to the high presence of PFOS in chicken samples. Intake of other food and drinking water will not cause any immediate health risk to human. However, health quotient above unity was observed for consumption of marine fish for adolescent, after taking into account the combination hazard ratio of PFOA and PFOS.

5.1. Introduction

Polyfluoroalkyl substances (PFAAs) are a group of synthetic fluorinated chemical that has been manufactured to be used in industrial and commercial products such as stain and water repellent, cosmetics, and fire-fighting foams (Fiedler et al., 2010; Krafft & Riess, 2015). Due to its widespread usage, combined with its difficulty to degrade and hydrolyze, PFAAs have been detected in human blood and urine (D.-H. Kim et al., 2014; Worley et al., 2017), surface water and sediment (W. Dong et al., 2018; Joerss et al., 2019; Suja et al., 2009), soil and biota (Campo et al., 2016; Dalahmeh et al., 2018), and foods and drinking waters (Boone et al., 2019; Domingo & Nadal, 2017; Ingelido et al., 2018).

PFOA and PFOS, two of the most commonly described PFAAs, have been associated with various health effects on human and animal such as an increase in bladder

cancer mortality (Lau et al., 2007; Steenland et al., 2009), altered puberty and fertility (Joensen et al., 2009; Lopez-Espinosa et al., 2011), positively associated with increase of total cholesterol (Nelson Jessica et al., 2010; Steenlanan increasecrease009), and immune suppression (DeWitt et al., 2009; G.-H. Dong et al., 2013). Because of these adverse health effects, various organizations around the world have banned or restricts the usage and production of certain PFAAs (EFSA, 2008; Sunderland et al., 2019; USEPA, 2016c). In addition, PFOS and its salts have been listed in Annex B of Persistent Organic Pollutants by the Stockholm Convention, which enforces the restriction of PFOS manufacturing toward full elimination by the year 2020 (UNEP, 2016).

Although PFAAs route of exposure to humans has not been fully characterized yet, various studies have suggested that dietary intake as one of the major routes of exposure of PFAAs in human (Post et al., 2012; Sunderland et al., 2019). Among dietary intake, fish and seafood have been positively associated with long-chain PFAAs (Habibullah-Al-Mamun et al., 2017; Yang et al., 2012). However, some studies also noted that nonaquatic organisms such as animal-derived foods were more contaminated compared to the aquatic organism (Chen et al., 2018; Heo et al., 2014). In addition, there are also some studies that correlated the consumption of drinking water with an increased level of PFAAs in human blood (Domingo et al., 2012; Ingelido et al., 2018). Due to the widespread of PFAAs in food and drinking water worldwide, it is necessary to also assess the risk of exposure from the consumption of these food and drinking water towards humans.

Recently we conducted for the first time the analysis of PFAAs in the blood of population in Klang Valley, Malaysia and we found that all PFAAs were detected in the serum of participants (Chapter 3). Thus, we believe it is important to identify the sources of PFAAs exposure in the population from the consumption of food and drinking water. To the best of our knowledge, no analysis of PFAAs in foods and drinking water has been done before in Malaysia and therefore, this study was initiated in order to investigate the presence of PFAAs in selected food and drinking water samples in the region of Klang Valley, Malaysia. Based on the data obtained from the analysis, we estimated the mean daily intake of PFAAs from consumption of food and drinking water by Malaysian adults and adolescent and subsequently assessed the human health risk due to the intake of PFOA and PFOS.

5.2. Materials and Methods

5.2.1. Sample collection

A total of 56 food samples was collected from 3 major wet markets around Klang Valley in March 2019. The food samples were of 19 different food types and were classified into 4 food categories, which are fish (freshwater and marine fish), meat (beef and chicken), seafood (mollusk, squid, prawn), and other (chicken egg). Types of food samples collected were based on a common type of food eaten by Malaysian based on the survey by the Malaysian Government (Institut Kesihatan Umum, 2014).

In addition, a total of 36 water samples (tap and bottled water) was also collected within an area of Klang Valley during the same period in order to assess the PFAAs intake of Klang Valley population from drinking water. Information on all the samples, including the numbers of samples collected, are summarized in Table 5.1, while the location of tap water samples collected and wet markets are summarized in Figure 5.1.

Table 5.1. Selected foods and information on consumption per capita of the population in Malaysia (Year 2014).

Category	Item	n	Mean Daily Intake (ng/day or L/day)			Remark
			Adult[a]		Adolescent[b]	
			Male	Female		
Fish	Freshwater fish	6	22.56	20.65	11.39	Snakehead fish, silver carp, and red snapper.
	Marine fish	27	51.7	48.4	45.56	Threadfin breams, skipjack tuna, torpedo scad, Barramundi, yellow tail scad, mackerel, black and white Pomfret, and four-finger threadfin.
Meat	Beef	2	14.17	8.32	5.91	Beef
	Chicken	3	39.87	29.47	25.63	Chicken
Shellfish	Mollusk	5	37.38	23.94	15.38	Mussel and cockles
	Squid	7	6.42	5.42	2.76	Squid
	Prawn	3	3.29	3.46	4.33	Prawn
Other	Egg	3	3.58	3.3	5.12	Egg
Drinking Water	Water	36	2.30	2.00	1.5	Tap water and bottled water

[a]Institut Kesihatan Umum (2014)
[b]Institut Kesihatan Umum (2017)

5.2.2. Target PFAAs compounds

Samples were analyzed for 9 PFAAs, which are perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorononanoic

acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorohexane sulfonate (PFHxS), and perfluorooctane sulfonate (PFOS). Description of the PFAAs is displayed in Table 2.1 (Chapter 2).

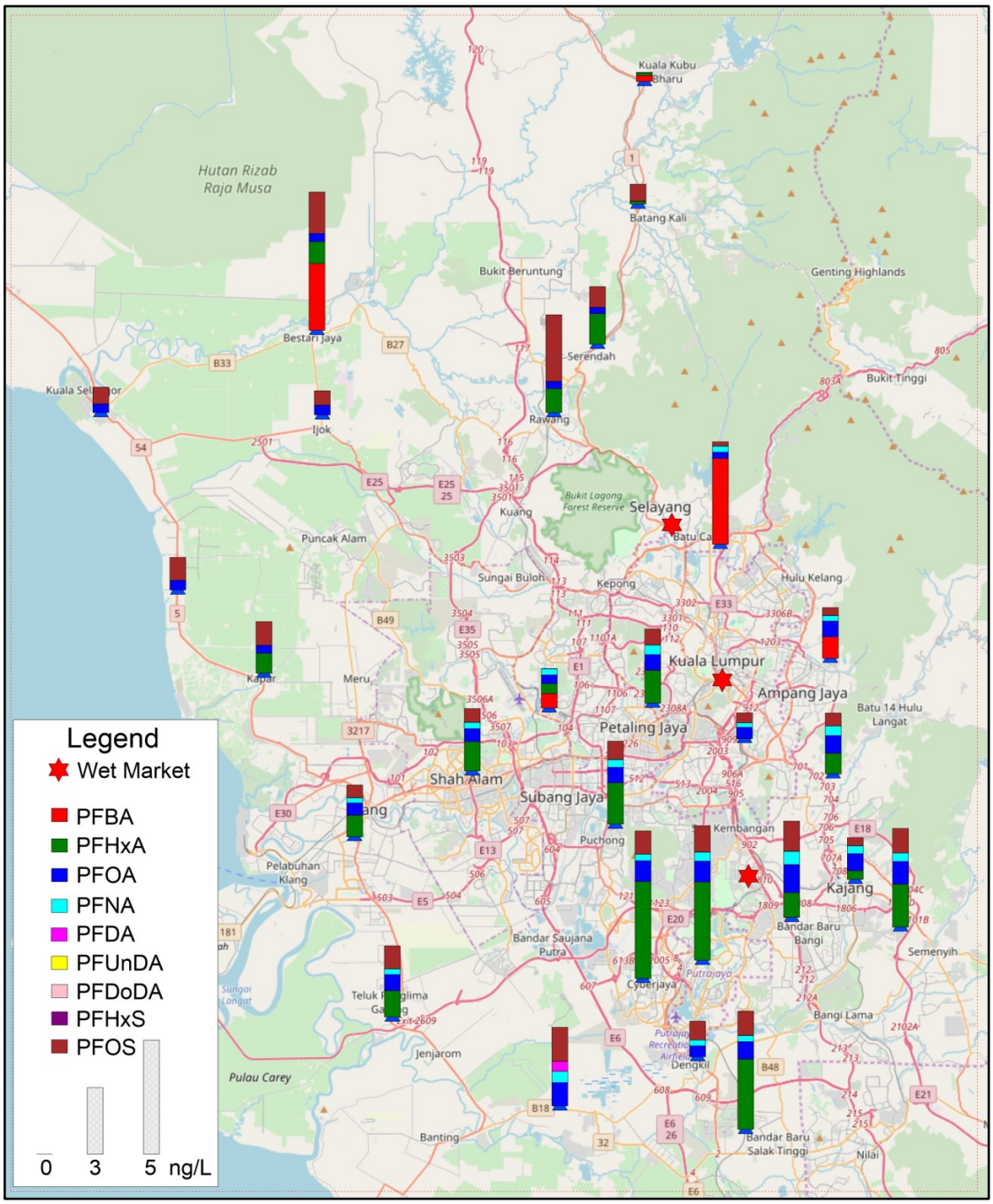

Figure 5.1. Location of the wet market and the PFAAs distribution in tap water collected within the Klang Valley region.

5.2.3. Sample extraction and clean-up

Extraction of food samples was adopted from the analysis conducted by Heo et al. (2014) and Bossi et al. (2005) using ion-pairing method. Briefly, 5 ng of PFAAs internal standard (MPFAC-MXA) containing 9 isotope PFAAs were added into approximately 10gram of homogenized food samples in 50 mL methanol-rinsed centrifuge tube. After that, 2 mL of 0.5 M tert-butyl alcohol (TBA), 4 mL of 0.25 M sodium carbonate, and 5 mL of ultrapure water were added into the food samples and the samples were subjected to vortex mixer for 30 seconds. Then, 5 mL methyl tert-butyl ether (MTBE) was added and the mixture was shaken for 30 minutes using a shaker and finally was centrifuged at 10,000 rpm for another 30 minutes. The supernatant was collected (approximately 4 mL) and transferred to a new 15 mL methanol-rinsed centrifuge tube. Another 5 mL of MTBE was added into the food samples and the process was repeated. Approximately 8 mL of supernatant collected was dried fully under a soft nitrogen stream and were reconstituted in 1 mL of methanol and filtered using 0.2 um nylon membrane filter prior to transfer into the vial.

For tap and bottled water samples, solid-phase extraction method was employed. Briefly, the same 5 ng internal standard used in the extraction of food sample earlier were injected into 500 mL of water samples. Then, the samples were filtered through a 1 µm glass microfiber filter (GF/B Whatmann). The filtered samples were then extracted using WAX SPE cartridge (Waters) that were pre-conditioned with 3 ml of 0.1% ammonium/methanol, 3 ml of methanol, and 5ml of water. The samples were loaded at a rate of 1 drop/sec under vacuum pressure. Then, the SPE cartridge was dried completely under vacuum suction. The elution of PFAAs in SPE cartridge started by adding 3 mL of 0.1% ammonium/methanol into the cartridge and the eluant were left to dry under a soft nitrogen stream. The dried eluant was then reconstituted using 1 mL methanol and filtered by 0.2 um nylon membrane filter before being transferred into polypropylene vial for subsequent analysis.

5.2.4. Instrumental analysis and quality assurance/quality control (QA/QC)

The extracted PFAAs were quantified using Shimadzu UHPLC Prominence (SHIMADZU, Kyoto, Japan) equipped with QTRAP 5500 triple quadrupole mass spectrometry (AB Sciex, California, USA). PFAAs were separated on a 2.1×100 mm Zorbax Eclipse Plus C18 column (Agilent, Palo Alto, USA) where the column oven was kept at 40°C throughout the analysis. 2mM Ammonium acetate/water and hypergrade

methanol were used as mobile phase under gradient mode. The gradient mode begins at 20% Methanol at a flow rate of 0.3 mL/min and increased to 100% for 6 minutes before being re-equilibrated to 20% at 8 minutes. The detections are performed in multiple reaction monitoring (MRM) mode using electrospray ionization (ESI) ion source, in negative mode.

To eliminate or reduce any possibility of cross-contamination or loss of analyte, usage of any fluoropolymer plastic and glass apparatus were avoided. A concentration gradient of 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, and 20.0 ng/mL were prepared as calibration curves and strong regression coefficients ($r^2 > 0.999$) were achieved for all PFAAs. Procedural blanks were extracted for every ten food and drinking water samples in order to assess and correct any contamination that may have been present during the extraction processes. Methanol (instrumental blank) and calibration check standard (5 ng/mL of PFAAs mixture) were injected for every 10 sample injections in order to monitor the instrument stability and sensitivity. PFAAs recoveries were measured based on the percentage recovery of surrogates for every sample. Limit of detection (LOD) and limit of quantification (LOQ) for each PFAAs were calculated based on the standard deviation (SD) from repeated analysis (n=7) of the lowest calibration standard (0.1 ng/mL) using the following formula:

$$\text{Limit of Detection} = SD \times t_{0.99} \quad (5\text{-}1)$$

where $t_{0.99}$ is student's t-distribution for 99% confidence level, which in this case is 3.143 (n=7). Information about LOD, LOQ, and recoveries of PFAAs in food and drinking water samples are shown in Table 5.2.

Table 5.2. Parameter and performance information for the analysis of PFAAs in food and drinking water samples.

PFAAs	Food (ng/g)			Drinking Water (ng/L)		
	LODs (ng/L)	LOQs (ng/mL)	%Recovery (±SD)	LODs (ng/L)	LOQs (ng/mL)	%Recovery (±SD)
PFBA	0.05	0.17	23 ± 4	0.21	0.69	101 ± 17
PFHxA	0.05	0.16	27 ± 7	0.10	0.34	100 ± 15
PFOA	0.08	0.28	41 ± 16	0.15	0.50	85 ± 7
PFNA	0.16	0.52	56 ± 24	0.17	0.57	79 ± 4
PFDA	0.14	0.48	47 ± 18	0.25	0.83	102 ± 6
PFUnDA	0.17	0.57	75 ± 29	0.12	0.38	80 ± 4
PFDoDA	0.14	0.46	63 ± 25	0.17	0.57	89 ± 3
PFHxS	0.17	0.57	62 ± 21	0.20	0.68	73 ± 7
PFOS	0.13	0.42	63 ± 25	0.08	0.25	101 ± 7

LOD – Limit of Detection
LOD – Limit of Quantification
SD – Standard Deviation

5.3. Results and discussion

5.3.1. PFAAs concentrations in food samples

PFAAs concentrations that were detected in food samples are summarized in Table 5.3. At least one PFAAs were detected in all samples, except for the egg. The concentration ranged from not detected (ND) to 9.54 ng/g wet weight (ww). Chicken samples showed the highest mean concentration of total PFAAs (5.78 ng/g), followed by beef (3.14 ng/g), marine fish (0.93 ng/g), squid (0.71 ng/g), freshwater fish (0.69 ng/g), prawn (0.39 ng/g), and mollusk (0.14 ng/g). However, PFAAs were not detected in any of the egg samples. Note that all PFAAs concentration below LODs were assumed as 0 when calculating for mean PFAAs concentration. The concentration of PFAAs in chicken samples were significantly high, approximately 6 times higher compared to other food samples. Similar to the chicken sample, beef samples also contained 3 magnitudes greater PFAAs than other food samples. These results were similar to the results obtained from other studies where high concentrations of PFAAs were detected in meat (Tittlemier et al., 2007; Wang et al., 2018; T. Zhang et al., 2010).

PFAAs detected in livestock such as cow and chicken may have come from the consumption of contaminated feed and water. Tap water, which was found to be

contaminated in this study may have been used as a water feed for the livestock. This is assuming that the poultry farm where the meat samples were originated from was located within the Klang Valley region. In addition, livestock that ingested contaminated feed or grazing on fields where contaminated biosolids were applied also has the possibility to accumulate PFAAs into its meat (Blaine et al., 2014; Lupton et al., 2014). A few studies have found the presence of PFAAs in biosolid-amended soils, which are commonly applied to crops for livestock feed (Navarro et al., 2017; Wen et al., 2014). In addition, a study by Kowalczyk et al. (2012) on two sheep which have been fed PFAAs contaminated corn silage for a period of 21 days has shown a continuously increasing level of PFAAs in its plasma, which was then transferred into milk and meat.

Among the species under marine fish categories, yellowtail scad contained the highest level of mean total PFAAs, three times higher than other fish in the same categories (Figure 5.2). A similar observation was also found in snakehead fish under freshwater fish categories in which 4 times higher mean total concentration of PFAAs was observed compared to the other fish in the same group.

From all the PFAAs analyzed, only 3 PFAAs (PFOA, PFUnDA, and PFOS) were detected in more than 50% of the food samples while PFNA, PFDA, and PFDoDA were detected in 23, 36, and 45% of the samples, respectively. In contrast, all short-chain PFAAs (PFBA, PFHxA, and PFHxS) were only detected in less than 11% samples. PFOA and PFOS, the legacy PFAAs have been frequently found in food samples worldwide (Domingo & Nadal, 2017; Sunderland et al., 2019). In our study, PFOS has been the most frequently detected in all food samples, except for squid and mollusk where PFOA has been the most frequently detected. In addition to PFOA and PFOS, there were other PFAAs that were detected at high frequencies in food samples in our study, especially for long-chain PFAAs. For example, PFUnDA (C-11) were detected in all freshwater fish and squid, while PFDoDA were detected in all squid and prawn samples. In general, all long-chain PFAAs (C>8) have been detected at high frequencies for most samples. High detection frequencies of long-chain PFAAs have also been found in other studies (Heo et al., 2014; A. Zhang et al., 2019). These observations can be attributed to a higher bioaccumulation factor of long-chain PFAAs where the bioaccumulation potential of PFAAs increases with the increasing number of fluorinated carbons (Conder et al., 2008).

The compositional profiles of individual PFAAs in food samples are shown in Figure 5.3. A different pattern was observed between food categories. PFSAs (PFHxS and PFOS) were found to be predominant PFAAs in food, except for mollusk. For mollusk, PFCAs (PFBA, PFOA, and PFUnDA) was predominant PFAAs. This finding suggests that PFCAs tend to bioaccumulate more into the mollusk compared to PFSAs. Another possible explanation can be attributed to the different fraction of PFAAs at bottom sediment. Mollusk, being a benthic organism tends to dwell at the bottom aquatic zone close to sediment, and the concentration of PFAAs in sediment tends to have an effect on the bioaccumulation of PFAAs in mollusk (D'Hollander et al., 2010). The higher presence of PFCAs in sediment compared to PFSAs may have resulted in higher PFCA in a mollusk.

Marine organism (marine fish, mollusk, prawn, and squid) showed the presence of most PFAAs. However, the opposite compositional profile was observed for freshwater fish where only PFOS and PFUnDA were detected in all freshwater fish samples and only one sample showed the presence of PFOA. Various factors such as the compositional pattern of PFAAs in water, the different bioaccumulation potential between species in the aquatic organism, environmental conditions, and properties of PFAAs could be a factor that resulted in the variation of PFAAs detected in the aquatic organism (Habibullah-Al-Mamun et al., 2017; Hong et al., 2015). Since the concentration of PFAAs in the aquatic organism is highly dependent on the concentration of PFAAs in the water, the different compositional profile of PFAAs between freshwater (rivers) and marine (sea or ocean) could have resulted in different compositional profiles between these two aquatic organisms (Ahrens & Bundschuh, 2014). In this case, a higher concentration of all PFAAs in the marine environment compared to a freshwater environment may have resulted in multiple PFAAs detected in marine samples.

For non-aquatic food samples (beef and chicken), only PFOS and low level of PFOA were found in chicken, while only PFOS and low level of PFDA were detected in beef. Although all chicken samples were collected from three different wet markets, PFAAs distribution between chicken samples (Appendix C-1) revealed that two of the chicken samples shared similar compositional profiles, which suggests that these two chickens may have originated from the same poultry farm. Further analysis of additional chicken samples, preferably from the other local poultry farm is needed in order to compare the PFAAs compositional profiles of each poultry farm so that the PFAAs contamination in chicken can be identified and thus eliminated.

Table 5.3. PFAAs concentrations in each food group (Unit: ng/g).

Category	Parameter	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDa	PFDoDA	PFHxS	PFOS	∑PFAAs
All Food Samples	DF	4	5	68	23	36	50	45	11	84	
n=56	Mean	0.0025	0.0022	0.0202	0.0058	0.0187	0.0238	0.0134	0.0047	0.9754	1.0668
	Max	0.1340	0.0618	0.1960	0.0452	0.3700	0.1310	0.1010	0.0731	9.5412	
Freshwater fish	DF	0	0	17	0	0	100	0	0	100	
n=6	Mean	<LOD	<LOD	0.0011	<LOD	<LOD	0.0143	<LOD	<LOD	0.6778	0.6932
	Max	<LOD	<LOD	0.0068	<LOD	<LOD	0.0388	<LOD	<LOD	2.2400	
Marine Fish	DF	4	11	82	26	37	52	52	4	100	
n=27	Mean	0.0002	0.0045	0.0126	0.0056	0.0155	0.0255	0.0166	0.0027	0.8469	0.9300
	Max	0.0043	0.0618	0.0397	0.0408	0.0919	0.1290	0.1010	0.0731	3.6576	
Beef	DF	0	0	0	0	50	0	0	0	100	
n=2	Mean	<LOD	<LOD	<LOD	<LOD	0.1850	<LOD	<LOD	<LOD	2.9580	3.1430
	Max	<LOD	<LOD	<LOD	<LOD	0.3700	<LOD	<LOD	<LOD	3.6100	
Chicken	DF	0	0	67	0	0	0	0	0	100	
n=3	Mean	<LOD	<LOD	0.0295	<LOD	<LOD	<LOD	<LOD	<LOD	5.7531	5.7826
	Max	<LOD	<LOD	0.0494	<LOD	<LOD	<LOD	<LOD	<LOD	9.5412	
Egg	DF	0	0	0	0	0	0	0	0	0	
n=3	Mean	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0000
	Max	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	
Mollusk	DF	20	0	80	0	0	0	20	20	20	
n=5	Mean	0.0268	<LOD	0.0754	<LOD	<LOD	<LOD	0.0058	0.0102	0.0232	0.1415
	Max	0.1340	<LOD	0.1960	<LOD	<LOD	<LOD	0.0292	0.0511	0.1160	
Squid	DF	0	0	100	100	86	100	100	57	71	
n=7	Mean	<LOD	<LOD	0.0430	0.0250	0.0282	0.0614	0.0282	0.0201	0.5030	0.7089
	Max	<LOD	<LOD	0.0636	0.0452	0.0464	0.1130	0.0397	0.0476	1.3500	
Prawn	DF	0	0	67	0	100	33	100	0	100	
n=3	Mean	<LOD	<LOD	0.0064	<LOD	0.0209	0.0437	0.0260	<LOD	0.2927	0.3897
	Max	<LOD	<LOD	0.0142	<LOD	0.0242	0.1310	0.0328	<LOD	0.3840	

<LOD – Limit of detection

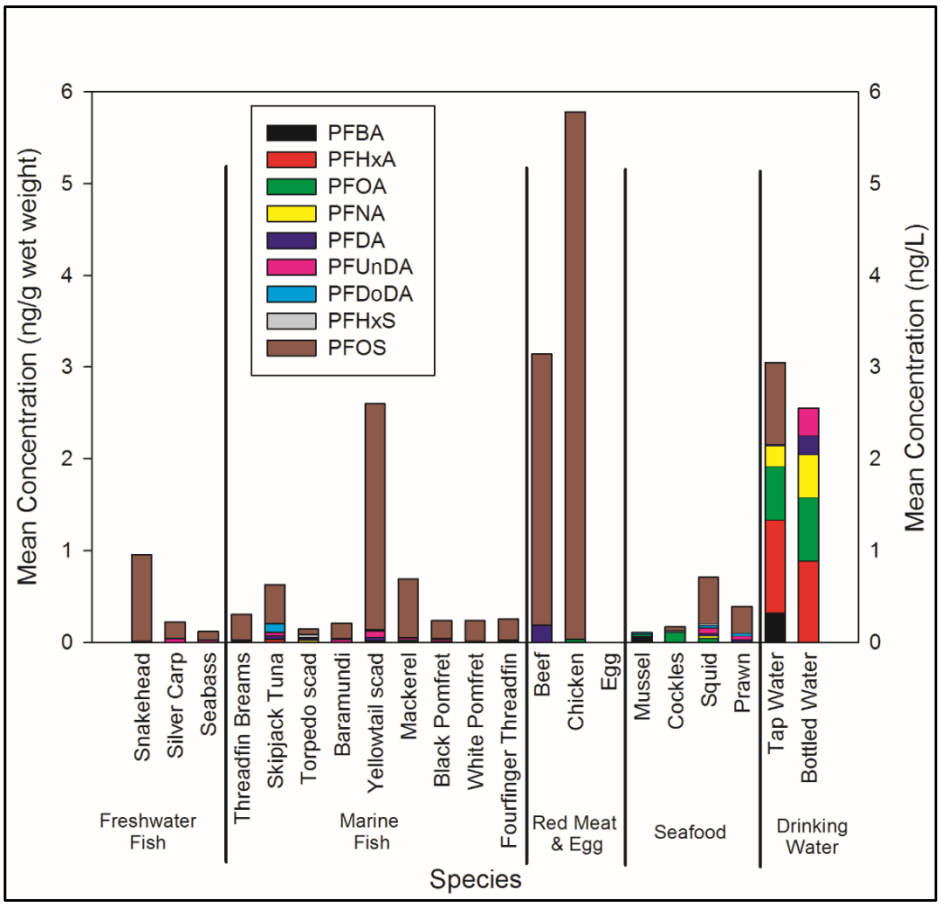

Figure 5.2. PFAAs concentrations in each food group analyzed.

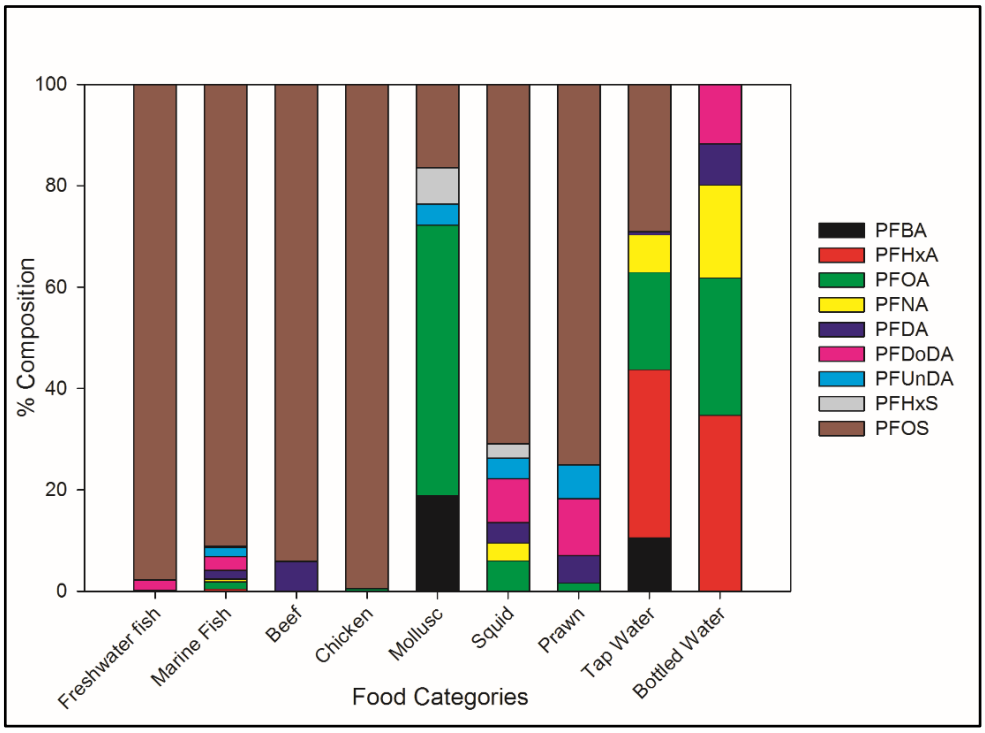

Figure 5.3. Compositional profiles of PFAAs in each of the food group analyzed.

5.3.2. PFAAs concentrations in drinking water samples

PFAAs concentrations that were detected in drinking water (tap and bottled water) samples are summarized in Table 5.4. At least two PFAAs were detected in tap water samples, while one bottled water sample did not show any presence of PFAAs. The individual PFAAs concentration ranged from not detected (ND) to 4.36 ng/L. From all the PFAAs analyzed in tap water samples, PFOA and PFOS have been the most frequently detected with 93% detection frequencies, followed by PFHxA, PFNA, PFBA, and PFDA with 70, 67, 19, and 4% detection frequencies, respectively. PFUnDA, PFDoDA, and PFHxS were not detected in any of the tap water samples. In contrast, PFOA and PFNA were the most frequently detected PFAAs in bottled water samples with 56% detection frequencies, followed by PFHxA and PFUnDA with 33% detection frequencies, and PFDA with 22% detection frequencies. None of the PFSA (PFHxS and PFOS), PFDoDA, and PFBA were detected in bottled water samples. Presence of PFAAs in tap and bottled water were also observed in other studies, and that concentrations of PFAAs were higher in tap water compared to bottled water (Ericson, Nadal, et al., 2008; Heo et al., 2014).

Although PFOA has been the most frequently detected in all drinking water samples, the highest mean concentration of PFAAs was actually PFHxA with 1.01 ng/L and 0.866 ng/L of PFHxA compared to 0.59 ng/L and 0.69 ng/L of PFOA, in tap and bottled water samples, respectively. Mean concentration of PFOS were also higher than PFOA in tap water samples (0.887 ng/L vs. 0.59 ng/L). These observations were due to the high PFHxA and PFOS levels in some of the samples, resulting in higher overall mean concentration.

The spatial distribution of PFAAs in tap water collected within the Klang Valley is displayed in Figure 5.1. It can be observed that PFOS were predominant in the upper middle part of Klang Valley, while PFHxA were predominant in the lower middle part of the Klang Valley. Most of the tap water in the Klang Valley region was treated in water treatment plants that received its raw water intake from Selangor River basin (65.27%), while only 24.17% of treated water in Klang Valley comes from raw water of the Langat River basin. The differences in raw water sources of treated water may have resulted in the different pattern of PFAAs distribution in Klang Valley. For example, the highest PFOS concentration in the Selangor River basin was detected in S3 (Chapter 4) in July 2017. Sampling point S3 is located right before the raw water intake of Sungai Selangor Water Treatment Plant, a major water treatment plant in Klang Valley which

supplies 59% of treated water in the Klang Valley region (JPBDSelangor, 2016). Considering the fact that conventional drinking water treatment system around the world did not efficiently remove PFAAs, some of the untreated PFAAs could end up into the tap water supply (Boone et al., 2019; Rahman et al., 2014).

Table 5.4. PFAAs concentrations in drinking water (Unit: ng/L).

Category	All Drinking Water (n=36)			Tap Water (n=27)			Bottled Water (n=9)		
Parameter	D.F	Mean	Max	D.F	Mean	Max	D.F	Mean	Max
PFBA	14	0.2429	3.86	19	0.3239	3.86	0	<LOD	<LOD
PFHxA	61	0.9791	6.33	70	1.0101	4.36	33	0.886	6.33
PFOA	83	0.6126	4.28	93	0.5859	1.27	56	0.693	4.28
PFNA	64	0.2849	1.692	67	0.2246	0.6	56	0.4661	1.69
PFDA	8	0.0646	1.248	4	0.0169	0.46	22	0.2076	1.25
PFUnDa	8	0.0746	0.95	0	<LOD	<LOD	33	0.2983	0.95
PFDoDA	0	<LOD	<LOD	0	<LOD	<LOD	0	<LOD	<LOD
PFHxS	0	<LOD	<LOD	0	<LOD	<LOD	0	<LOD	<LOD
PFOS	69	0.6654	3	93	0.8871	3	0	<LOD	<LOD
∑PFAAs		2.9241			3.0484			2.551	

D.F - Detection Frequency (%)

The different PFAAs pattern was observed among bottled water samples as shown in Figure 5.4. Compared to tap water, PFHxS, PFOS, PFDoDA, and PFBA were not detected in any of the bottled water samples. This is similar to previous studies where only PFOA, PFNA, and PFHxA were detected in bottled water samples (Endirlik et al., 2019; Ericson, Nadal, et al., 2008). The abundance of these compounds in raw water may have contributed to their presence in bottled water. In general, the concentration of PFAAs in bottled water were lower compared to tap water. However, one bottled water sample showed a very high concentration of PFHxA (6.33 ng/L), and other bottled water samples showed a high level of PFOA (4.28 ng/L), which resulted in higher mean concentration of these PFAAs in bottled water.

Three of the bottled water samples showed the presence of PFOA. However, PFUnDA were observed in bottled water samples that did not contain PFOA. Both of these compounds were not present in the same samples. This is probably due to the differences in material or impurities used in the production of the plastic bottle. Previous studies have hypothesized that PFAAs may have leached from a plastic container into a drinking water (Llorca et al., 2012; Schwanz et al., 2016). Improper storage of bottled

drinking water may also have resulted in leaching of the bottle plastic material onto the water (Schwanz et al., 2016). In addition, PFAAs in bottled drinking water may also come from the water sources itself. For example, a similar pattern of PFAAs was found in 2 bottled water samples (BW1 and BW2). Although these 2 bottled water came from a different manufacturer, further investigation revealed that these bottled water samples came from the same water source, which implies that PFAAs may have been present in the water itself prior to being bottled.

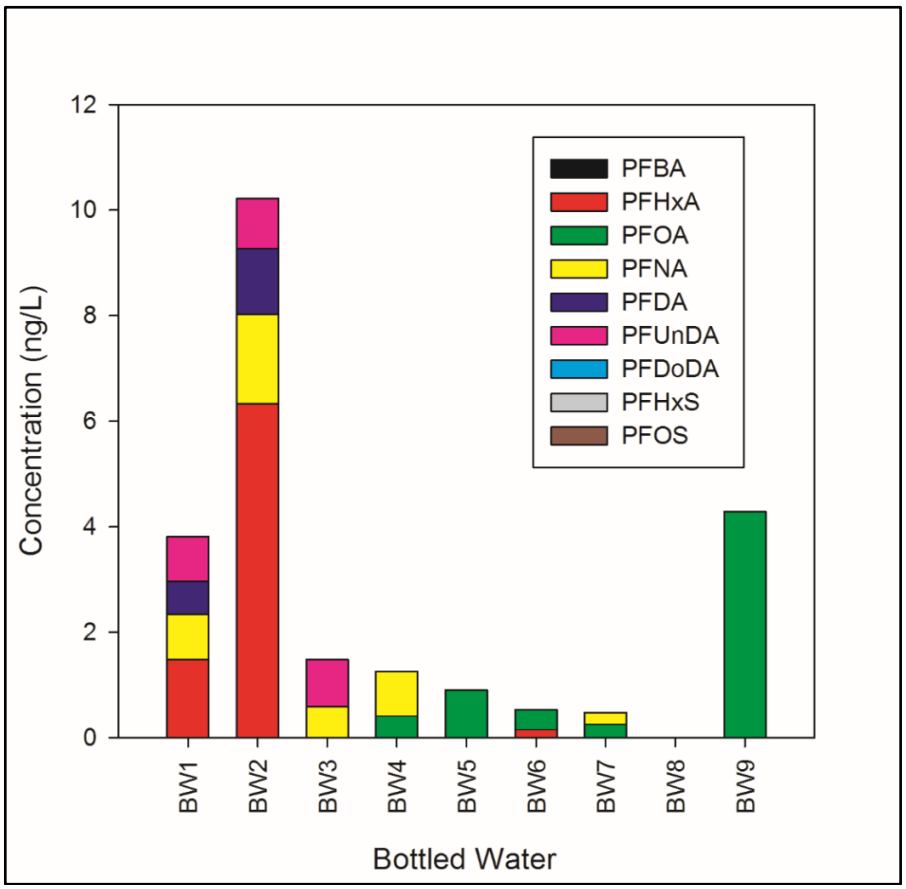

Figure 5.4. PFAAs concentrations in bottled water samples (Unit: ng/L).

5.3.3. Comparison of foods and drinking water data with previous studies globally

PFAAs contamination in foods and drinking waters in this study were compared with the previous literature (Table 5.5). The accurate comparison was not possible due to the differences in types of species and sampling region that were analyzed between studies. However, a general comparison between foods under the same categories revealed that PFAAs levels in fishes (marine and freshwater) and seafood in Malaysia were comparable or slightly lower than other studies (Table 5.5).

Compared to other studies, high concentration of PFAAs in fishes and seafood samples were found in Pearl River Delta, China (Pan et al., 2014) and Mississippi river, USA (Ye et al., 2008), which can be attributed to the higher level of PFAAs in the environment where the samples were taken. Labadie and Chevreuil (2011) and Ahrens et al. (2016) found a significant correlation between the concentration of PFAAs in surface water and the concentration of PFAAs in fishes that were caught in the same location. A higher degree of PFAAs tends to accumulate in fishes when the concentration of PFAAs in the surface water is high. Similar to this study, it can be observed that PFOS showed the highest levels of PFAAs contamination in these food group samples worldwide compared to other PFAAs. This can also be attributed due to the high level of PFOS in the environment, combined with the bioaccumulation potential of PFOS in aquatic organism compared to other PFAAs (Babut et al., 2017).

PFOS detected in meat samples collected from the Klang Valley's wet market was among the highest compared to other studies, but similar to the result found in meat from Korea (Heo et al., 2014). However, the concentration of other PFAAs detected in meat from this study is significantly lower compared to PFOS. Similar findings were also reported in most studies (Noorlander et al., 2011; Vestergren et al., 2012). However, meat in Taiwan showed a higher level of PFOA compared to PFOS, which is contrary to most studies found (Chen et al., 2018). The authors suggested that the discrepancy may be due to the differences in local contamination of PFAAs and also from the reduced production and use of PFOS after it was added in Annex B list of Persistent Organic Pollutant Stockholm Convention in 2009 (Chen et al., 2018).

As for the drinking water, levels of PFAAs in drinking water from Klang Valley, Malaysia were also comparable and lower than most of the studies worldwide (Table 5.5). However, significantly higher concentrations of PFAAs were found in treated drinking water from the United States, which was 10 to 20 times higher compared to the concentration found in drinking water in Klang Valley (Boone et al., 2019). High PFAAs concentration detected, particularly in drinking water treatment plant (DWTP) 22 and 23 were due to the high concentration of PFAAs in raw water sources. Low water treatment efficiencies, especially for PFAAs at this drinking water treatment plant, have resulted in a very high concentration of PFAAs in drinking water samples.

Table 5.5. Comparison of PFAAs (ng/L) range concentrations in foods and drinking water samples in this study with other countries worldwide.

Categories	Location	Concentration (ng/g ww) or (ng/L)									References
		PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS	PFOS	
Marine Fish	Korea	<LOD–1.19	<LOD–1.0	<LOD–1.7	<LOD–2.15	<LOD–0.626	<LOD–4.26	<LOD–1.01	<LOD–0.712	<LOD–16	Heo et al. (2014)
	Oslo, Norway	–	<LOD–0.011	0.03–0.046	0.006–0.01	0.013–0.026	0.005–0.021	<LOD	0.003–0.006	0.055–0.1	Haug et al. (2010)
	Greece	<LOD	<LOD	<LOD	<LOD–0.60	<LOD–0.65	<LOD–1.50	<LOD–1.86	<LOD	<LOD–20.37	Vassiliadou et al. (2010)
	Bengal Bay, Bangladesh	<LOD–0.72	<LOD–0.73	<LOD–0.40	<LOD–1.56	<LOD–1.20	<LOD–0.88	<LOD–2.01	<LOD–0.69	0.10–3.86	Habibullah-Al-Mamun et al. (2017)
	Catalonia, Spain	–	<LOD	<LOD–0.091	0.075–0.51	<LOD	0.32–0.71	<LOD–0.24	<LOD–0.037	0.54–8.32	Domingo et al. (2012)
	Bohai Bay, China[b]	–	–	0.29–1.67	<LOD–0.26	<LOD–3.39	<LOD–0.35	<LOD–0.01	<LOD–0.17	2.54–11.9	Yang et al. (2012)
	Klang Valley, Malaysia	<LOD–0.004	<LOD–0.062	<LOD–0.04	<LOD–0.041	<LOD–0.092	<LOD–0.129	<LOD–0.101	<LOD–0.073	0.018–3.658	This study
Freshwater Fish	Rhône River, France	–	–	<LOD–0.12	0.7–17	0.45–3.5	35–348	0.86–13	<LOD–0.1	2.61–14	Babut et al. (2017)
	Pearl River Delta, China	<LOD	<LOD	<LOD	<LOD–0.15	<LOD–5.1	<LOD–2.4	<LOD–0.81	<LOD	<LOQ–79	Pan et al. (2014)
	Lake Vättern, Sweden	–	–	<LOD–0.25	<LOD–0.71	0.13–0.81	0.09–0.89	<LOD–0.53	<LOD–0.8	0.97–23.1	Berger et al. (2009)
	Hanjiang river, China	0.43–3.1	0.13–0.49	<0.10–5.55	0.18–4.54	0.18–5.71	0.27–13.3	0.17–12.8	–	0.45–15.9	He et al. (2015)
	Mississippi river, USA	–	<4.00–18.4	<0.20–2.1	<0.20–5.89	<0.20–9.01	<0.40–48	<0.20–4.13	<0.20–8.14	<10.0–1250	Ye et al. (2008)
	Korea	–	<0.16-0.34	<0.11-0.18	<0.11-3.70	<0.14-33.7	<0.14-12.4	<0.11-6.14	<0.28-1.19	<0.11-71.7	Hung et al. (2018)
	Klang Valley, Malaysia	<LOD	<LOD	<LOQ–0.007	<LOD	<LOD	0.007–0.039	<LOD	<LOD	0.09–2.24	This study
Seafood	Greece	<LOD	<LOD	<LOD	<LOD–1.27	<LOD–1.73	<LOD–2.76	<LOD–1.36	<LOD	<LOD–5.15	Vassiliadou et al. (2010)
	Catalonia, Spain	<LOD	<LOD	<LOD–0.098	0.03–0.17	<LOD	<LOD–0.22	<LOD–0.2	<LOD	<LOD–0.48	Domingo et al. (2012)
	Taiwan[a]	–	0.87–1.2	5.6–8.23	–	7.05–10.5	0.66–1.39	3.07–9.93	0.08–0.26	0.06–1.06	Chen et al. (2018)
	Bohai Bay, China[b]	–	–	<LOD–4.37	<LOD	<LOD–0.27	<LOD	<LOD	<LOD	<LOD–10.2	Yang et al. (2012)
	China	–	<0.25–0.29	<0.25–1.67	<0.25–0.61	<0.25–0.30	0.27–0.93	<0.25	0.33–13.9	–	Gulkowska et al. (2006)
	Klang Valley, Malaysia	<LOD–0.134	<LOD	<LOD–0.196	<LOD–0.045	<LOD–0.046	<LOD–0.131	<LOD–0.04	<LOD–0.051	<LOD–1.35	This study

– : Not analyzed
<LOD : Limit of detection
[a] : range of median value between foods under the same categories
[b] : concentration were reported as dry weight (ng/g dw)

Table 5.5. continued

Categories	Location	Concentration (ng/g ww) or (ng/L)									References
		PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS	PFOS	
Meat	Oslo, Norway	<LOD–0.001	<LOD	0.012–0.052	0.006–0.015	<LOD–0.023	<LOD–0.013	<LOD	<LOD–0.001	0.017–0.06	Haug et al. (2010)
	Korea	<LOD–0.539	<LOD–4.38	ND	ND	<LOD–1.45	<LOD–2.01	<LOD–2.11	ND	<LOD–5.96	Heo et al. (2014)
	Netherland	<LOD	<LOD	<LOD–0.015	0.001–0.004	<LOD–0.006	<LOD–0.002	<LOD	<LOD–0.003	<LOD–0.82	Noorlander et al. (2011)
	Sweden	–	<LOD	0.012–0.024	0.006–0.009	0.005–0.006	0.002–0.008	0.002–0.002	0.005–0.009	0.003–0.19	Vestergren et al. (2012)
	Taiwan[a]	–	1.02–1.21	5.91–8.27	–	3.35–3.70	0.18–0.3	1.3–1.68	0.09–0.15	0.11–0.28	Chen et al. (2018)
	Klang Valley, Malaysia	<LOD	<LOD	<LOD–0.049	<LOD	<LOD–0.37	<LOD	<LOD	<LOD	<LOD–9.541	This study
Drinking Water (Tap and bottled water)	Oslo, Norway	–	<LOD–0.78	0.65–2.5	<LOD	0.22–1.0	0.065–0.35	<LOD–0.43	0.045–0.15	0.071–0.31	Haug et al. (2010)
	Korea	<LOD–23.1	<LOD–16.7	<LOD–20.7	<LOD–4.29	<LOD–2.46	<LOD–0.435	<LOD–0.501	<LOD–1.29	<LOD–10.1	Heo et al. (2014)
	United States	0.661–104	0.088–60.8	0.713–104	0.116–38.6	0.113–24.7	0.105–1.85	0.092–0.092	0.105–38.4	0.184–36.9	Boone et al. (2019)
	Catalonia, Spain	<LOD–4.4	<LOD–3.6	<LOD–9.6	<LOD–9.6	<LOD–3.8	<LOD–3.2	<LOD–0.16	<LOD–1.6	<LOD–6.6	Domingo et al. (2012),
	Faroe Islands	0.57–0.82	<LOD–0.08	0.23–0.25	0.16–0.17	0.027–0.032	0.03–0.056	–	0.028–0.047	0.17–0.61	Eriksson et al. (2013)
	China	–	<LOD–0.12	0.44–5.3	<LOD	<LOD	<LOD	<LOD	<LOD	0.24–0.35	T. Zhang et al. (2011)
	Catalonia, Spain[c]	–	<LOD	<LOD–0.67	<LOD–0.2	<LOD	<LOD	<LOD	<LOD	<LOD	Ericson, Nadal, et al. (2008)
	Turkey	0.27–1.93	0.08–2.90	0.1–2.37	0.07–0.44	0.08–0.41	–	–	0.1–2.18	0.09–2.04	Endirlik et al. (2019)
	Brazil[c]	–	<LOD	3.4–12	10–10	<LOD	<LOD	<LOD	<LOD	<LOD	Schwanz et al. (2016)
	Klang Valley, Malaysia	<LOD–3.86	<LOD–6.33	<LOD–4.28	<LOD–1.692	<LOD–1.248	<LOD–0.95	<LOD	<LOD	<LOD–3.0	This study

– : Not analyzed

<LOD : Limit of detection

[a] : range of median value between foods under the same categories

c : bottled water only

5.3.4. Dietary exposure to PFAAs and risk assessment

Various researches have reported that dietary intake (food and drinking water consumption) was significantly associated with human exposure to PFAAs (Averina et al., 2018; Domingo & Nadal, 2017; Papadopoulou et al., 2017; A. Zhang et al., 2019). For example, Liu et al. (2017) reported that fish, shellfish, meat and poultry were significant food contributors to PFAAs intake in humans. Thus, it is deemed necessary to assess for the potential PFAAs exposure from the consumption of food and drinking water collected from the local area and for that, risk assessment was conducted. Hazard ratio (HR) for risk assessment was calculated based on the comparison between PFAAs exposure from dietary intake and tolerable daily intake (TDI) or a reference dose (RfD) for non-cancer effects and the calculation can be summarized as (5-2) below (European Chemicals Agency, 2003);

$$\text{Hazard Ratio (HR)} = \text{EDI} / \text{TDI or RfD} \quad (5\text{-}2)$$

where EDI is the estimated daily intake (ng/kg/day)

Hazard ratio (HR) that is higher than the value of 1 (unity) implies that the exposure level of individual PFAAs from food and drinking water consumption exceeds the tolerable daily intake of that PFAAs. This implies a higher possibility for PFAAs to pose risks to human health. Until today, no official TDI or RfD values for PFAAs have been established yet by any government worldwide. However, provisional TDIs have been proposed based on human and animal carcinogenicity and a multigenerational study by several critical organizations (EFSA et al., 2018; USEPA, 2016a).

For example, US EPA proposed RfD of 0.02 µg/kg bw per day for both PFOS and PFOA based on a decreased neonatal rat body weight and reduced ossification and accelerated puberty effects in mice (USEPA, 2016b, 2016c). In addition, the US EPA also proposed a lifetime drinking water Health Advisory (HA) of 70 ng/L for the summation of both PFOS and PFOA when these two chemicals are present simultaneously in drinking water (USEPA, 2016a). In 2008, EFSA has also proposed provisional TDI of 150 ng/kg per bw per day for PFOS based on the lowest no-observed-adverse-effect-level (NOAEL) of 0.03 mg/kg bw per day derived from a sub-chronic study on cynomolgus monkey. For PFOA, a TDI value of 1.5 µg/kg bw per day was proposed based on a benchmark dose of 10% increase in liver weight of 0.3 mg/kg bw

per day in mice and rats (EFSA, 2008). However, after examining new human epidemiological evidence, EFSA has proposed to revise the TDI value to 1.8 ng/kg bw per day for PFOS and 0.8 ng/kg bw per day for PFOS (EFSA et al., 2018). In order to take into account the long half-life of both PFOA and PFOS, EFSA also proposed to use Tolerable Weekly Intake (TWI) of 6 ng/kg bw per day for PFOS and 13 ng/kg bw per day for PFOA, instead of TDI.

Thus, the most recent TWI values of 6 ng/kg bw per day for PFOS and 13 ng/kg bw per day for PFOA proposed by EFSA for food intake and 70 ng/L total value of PFOA and PFOS from drinking water consumption were used for the risk assessment for food intake in this study, because these values are more conservative compared to other proposed provisional TDI or RfD values. However, no other provisional RfD or TDI was found for other PFAAs. As for EDI, the value from the consumption of food and drinking water can be calculated using the following formula (European Chemicals Agency, 2003);

$$\text{Estimated Daily Intake (EDI)} = C \times IR / BW \quad (5\text{-}3)$$

where C is the average concentration of individual PFAAs in food and drinking water samples in this study (ng/g ww), IR is the average intake rate of food and drinking water daily (g/day ww), and BW is the average body weight.

The average food intake rate of Malaysian adult and adolescent were obtained from National Health and Mobility Survey 2014 and 2017 by the Ministry of Health, Malaysian Government and the mean intake rate are displayed in Table 5.1 (Institut Kesihatan Umum, 2014, 2017). The average body weight for a Malaysian adult are 66.56 kg, 58.44 kg, and 46.04 kg for male, female, and adolescent, respectively (Baharudin et al., 2014; Y Azmi et al., 2009). However, since TWI value was used for the risk assessment in this study, EDIs values were converted to EWIs by multiplying the mean daily food intake rate by 7. The EWIs value of PFAAs calculated from food consumption of adults (male and female) and adolescent of the population in Klang Valley is shown in Table 5.6 and 5.7, respectively.

Large variations of EWIs can be observed among different food categories. In general, EWIs of total PFAAs from food consumption ranged between 0.096 to 24.247 ng/kg bw per week, 0.092 to 20.412 ng/kg bw per week, and 0.059 to 22.534 ng/kg per

week, for male, female and adolescent, respectively. It can be observed that PFOS was the primary PFAAs contributor in food, followed by PFOA. A higher EWIs of PFOA and PFOS in all groups were observed for chicken consumptions, which were about 2 to 5 times higher compared to the consumption of 2nd highest EWI, marine fishes, respectively. This suggests that chicken was the major contributor of PFOA and PFOS levels in the population of the Klang Valley region. However, marine fish were found to be the highest contributor of PFHxA, PFNA, PFUnDA, PFDoDA, and PFHxS in humans, whereas beef was a major contributor for PFDA.

Meanwhile, EWIs of PFAAs from beef consumptions were lower than marine fish, even though the total mean concentration of PFAAs in beef samples was higher than marine fish samples. This can be attributed to the Malaysian preference in eating marine fish compared to beef (Institut Kesihatan Umum, 2014). In addition, although the mean weekly consumption of these foods was higher in adults compared to adolescent, EWIs of adults for marine fish were slightly lower compared to adolescent. The higher EWIs of the adolescent was due to the relatively lower mean body weight of adolescent compared to adults, since EWIs value was dependent on the mean body weight. In addition, the adolescent was found to be more exposed to PFNA, PFUnDA, PFDoDA, and PFHxS compared to adults. This is mostly related to the higher level of PFNA, PFUnDA, PFDoDA, and PFHxS in prawn and squid, which the consumption was higher for adolescent compared to other groups.

Figure 5.5 showed a comparison of PFAAs consumption between tap and bottled water. Slight differences were found for the consumption of total PFAAs between tap water and bottled water. Slightly higher total PFOA consumption for all three groups was found for bottled water compared to consumption of tap water. The discrepancy was mostly due to the different level of PFOA found in bottled water compared to tap water. A similar pattern could also be found in other PFAAs compounds (Appendix C-3). For example, EWI for PFOS was higher for tap water consumption due to the higher mean concentration of PFOS in tap water compared to bottled water.

Table 5.6. Estimated daily intake (EDI) between male and female in Klang Valley based on the concentration of PFAAs in food samples analyzed.

Categories	EWI (ng/kg bw per week)									
	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS	PFOS	∑PFAAs
					Male					
Freshwater fish	0	0	0.003	0	0	0.034	0	0	1.608	1.645
Marine Fish	0.001	0.024	0.068	0.030	0.084	0.138	0.090	0.015	4.605	5.057
Beef	0	0	0	0	0.276	0	0	0	4.408	4.684
Chicken	0	0	0.124	0	0	0	0	0	24.123	24.247
Egg	0	0	0	0	0	0	0	0	0.000	0
Shellfish	0.018	0	0.051	0	0	0	0.004	0.007	0.016	0.096
Squid	0	0	0.015	0.009	0.010	0.021	0.010	0.007	0.174	0.245
Prawn	0	0	0.002	0	0.008	0.016	0.010	0	0.110	0.147
TOTAL	0.019	0.024	0.263	0.039	0.378	0.210	0.114	0.029	35.044	36.119
					Female					
Freshwater fish	0	0	0.003	0	0	0.035	0.000	0	1.676	1.715
Marine Fish	0.001	0.026	0.073	0.032	0.090	0.148	0.096	0.016	4.910	5.391
Beef	0	0	0	0	0.184	0	0	0	2.948	3.132
Chicken	0	0	0.104	0	0	0	0	0	20.308	20.412
Egg	0	0	0	0	0	0	0	0	0	0
Shellfish	0.017	0	0.049	0	0	0	0.004	0.007	0.015	0.092
Squid	0	0	0.018	0.010	0.012	0.025	0.012	0.008	0.208	0.294
Prawn	0	0	0.003	0	0.008	0.017	0.010	0	0.116	0.154
TOTAL	0.018	0.026	0.249	0.043	0.294	0.226	0.122	0.031	30.182	31.190

Table 5.7. Estimated daily intake (EDI) of the adolescent in Klang Valley based on the concentration of PFAAs in food samples analyzed.

Categories	EWI (ng/kg bw per week)									
	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS	PFOS	∑PFAAs
					Adolescent					
Freshwater fish	0	0	0.002	0	0.000	0.025	0	0	1.174	1.200
Marine Fish	0.001	0.031	0.087	0.038	0.107	0.176	0.115	0.019	5.867	6.442
Beef	0	0	0	0	0.166	0	0	0	2.658	2.824
Chicken	0	0	0.115	0	0	0	0	0	22.419	22.534
Egg	0	0	0	0	0	0	0	0	0	0.000
Shellfish	0.011	0	0.032	0	0	0	0.002	0.004	0.010	0.059
Squid	0	0	0.028	0.016	0.019	0.040	0.019	0.013	0.331	0.467
Prawn	0	0	0.005	0	0.016	0.034	0.020	0	0.228	0.303
TOTAL	0.012	0.031	0.269	0.055	0.309	0.276	0.156	0.036	32.686	33.830

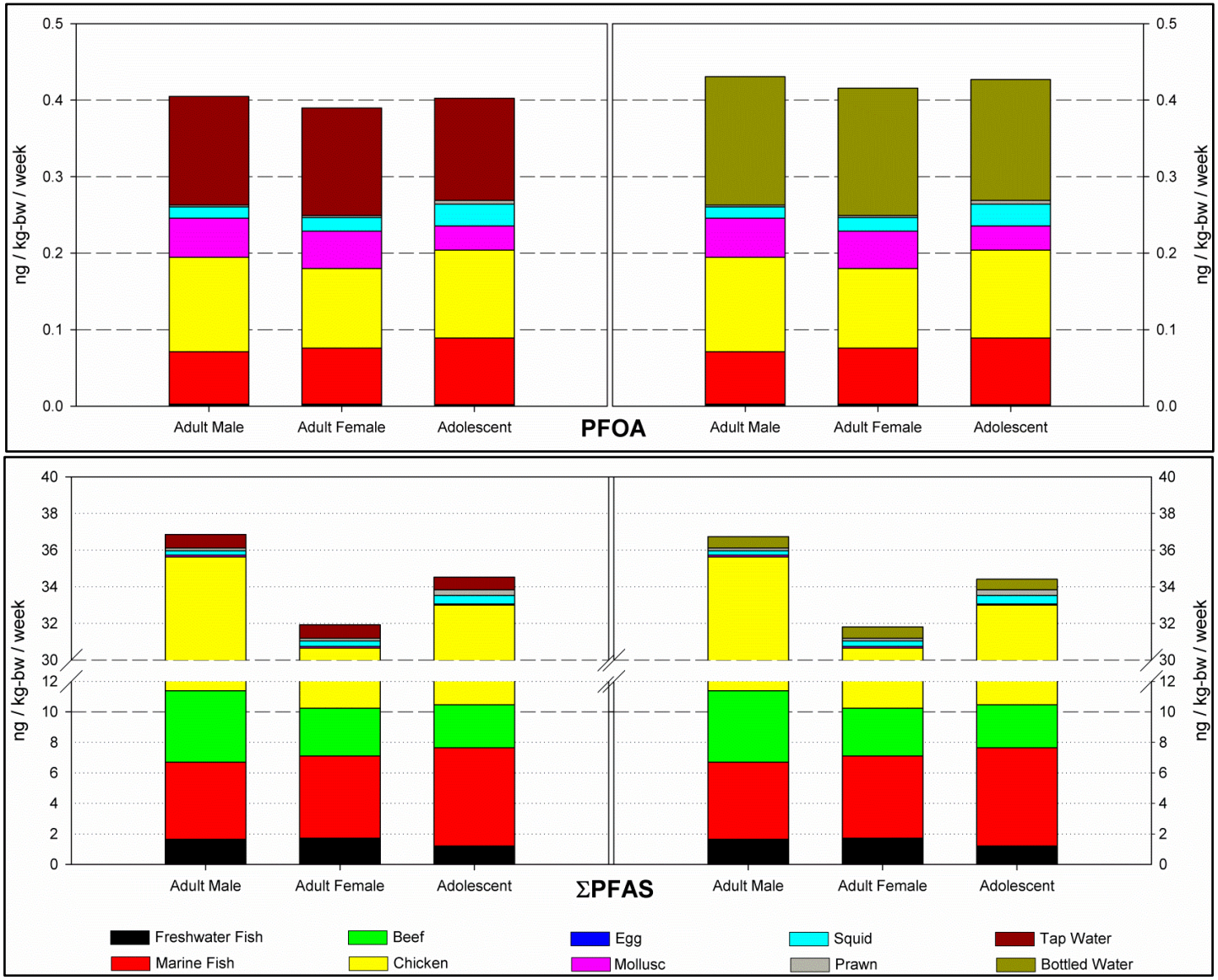

Figure 5.5 Comparison of EWI among the population in Klang Valley in two scenarios. Scenario1 (left figure) – foods and tap water consumption; Scenario2 (right figure) – foods and bottled water consumption. Top figure and bottom figure represent PFOA and ∑PFAAs, respectively.

Figure 5.6 showed the pattern of dietary intake of PFOA and PFOS for adult male for the population in Klang Valley (without consumption of drinking water). In this study, the average male consumed approximately 2332.55 ng/week or 333.22 ng/day of PFOS and 17.5 ng/week or 2.5 ng/day for PFOA. A study by Tittlemier et al. (2007) on the dietary exposure of PFAAs by Canadian from the consumption of fish, seafood, meat and fast food was estimated to be 110 ng/day for PFOS and 70 ng/day for PFOA, which was 3 times lower than the total intake of PFOS in this study but 28 higher than the total intake of PFOS. In addition, dietary exposure of PFOS to population near Catalan Market (Spain) from consumption of meat, fish, canned food, cheese, milk, vegetables, and other commonly consumed food was estimated to be 62.5 ng/day (non-detected was assumed as 0), which was significantly lower compared to this study (5 times lower) (Ericson, Martí-Cid, et al., 2008). In general, PFOS dietary intake in this study [333.22 ng/day] were higher compared to studies in Germany [123.4 ng/day] (Fromme et al., 2009), Japan [86.8 ng/day] (Kärrman et al., 2009), Taiwan [30.3 ng/day] (Chen et al., 2018), and Norway [105 ng/day] (Haug et al., 2010).

In contrast, PFOA dietary intake in this study [2.5 ng/day] were significantly lower compared to Norway [42 ng/day] (Haug et al., 2010), Taiwan [5534 ng/day] (Chen et al., 2018), Germany [269.4 ng/day] (Fromme et al., 2009), and Japan [58.6 ng/day] (Kärrman et al., 2009). The differences in a number of food categories and concentration found in different food samples may have resulted in significant variation of total intake of PFOA and PFOS between these studies.

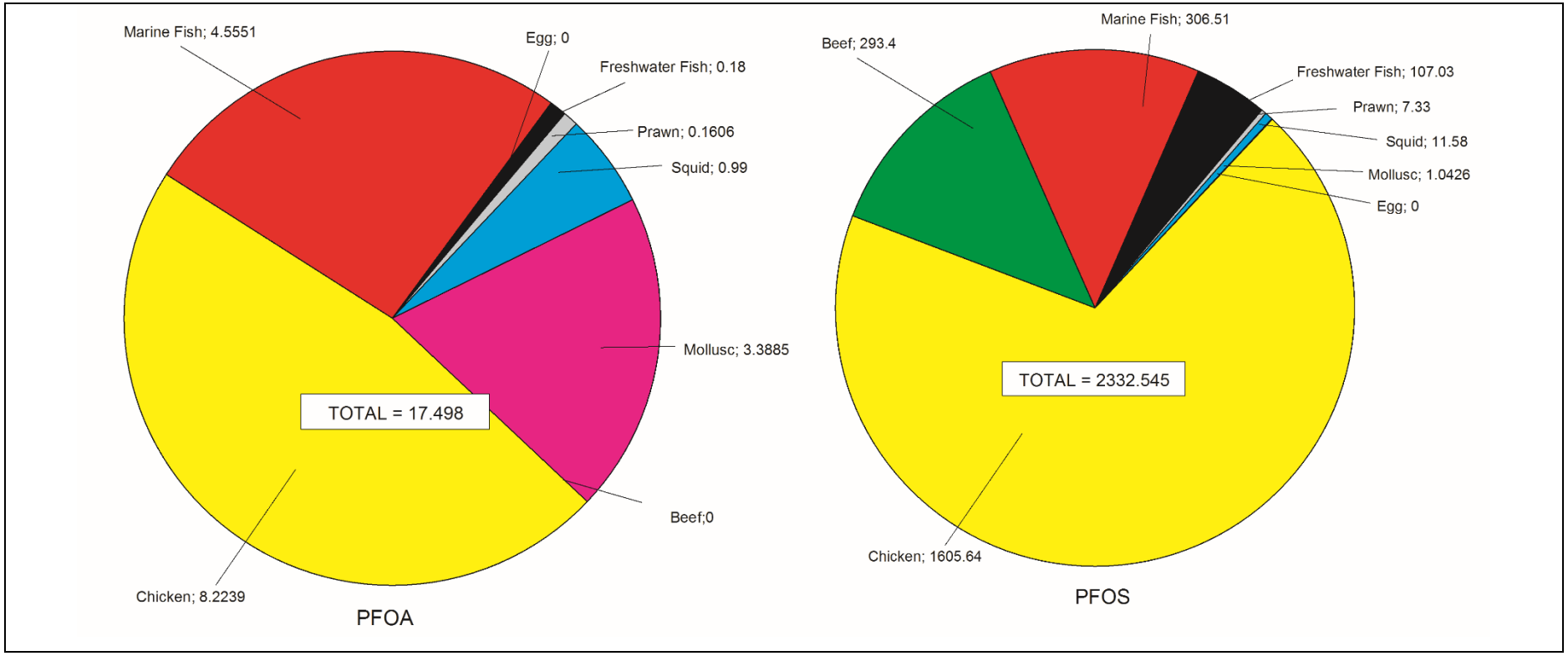

Figure 5.6. Dietary intake estimation (ng/week) of PFOA and PFOS for each food category of an adult man (66.56 kg of bw).

Since there is no RfD or TDI for PFAAs compound except for PFOA and PFOS, HRs can only be calculated for PFOA and PFOS. Most of the calculated HRs were less than unity (HRs < 1), except for PFOS in chicken where the HR were 1.855 and 1.562 for male and female, respectively (Figure 5.7). This suggests that chicken consumption is likely to cause immediate harm to the Klang Valley population. Much higher HRs were observed when dietary intakes of PFOS and PFOA for all food samples were combined. Furthermore, since these HRs values were only calculated using average daily intake, population with higher dietary intake might exhibit significantly higher HRs. In addition, considering that human can be exposed to PFAAs from various other routes beside dietary intake, a higher level of health risk is to be expected in this population.

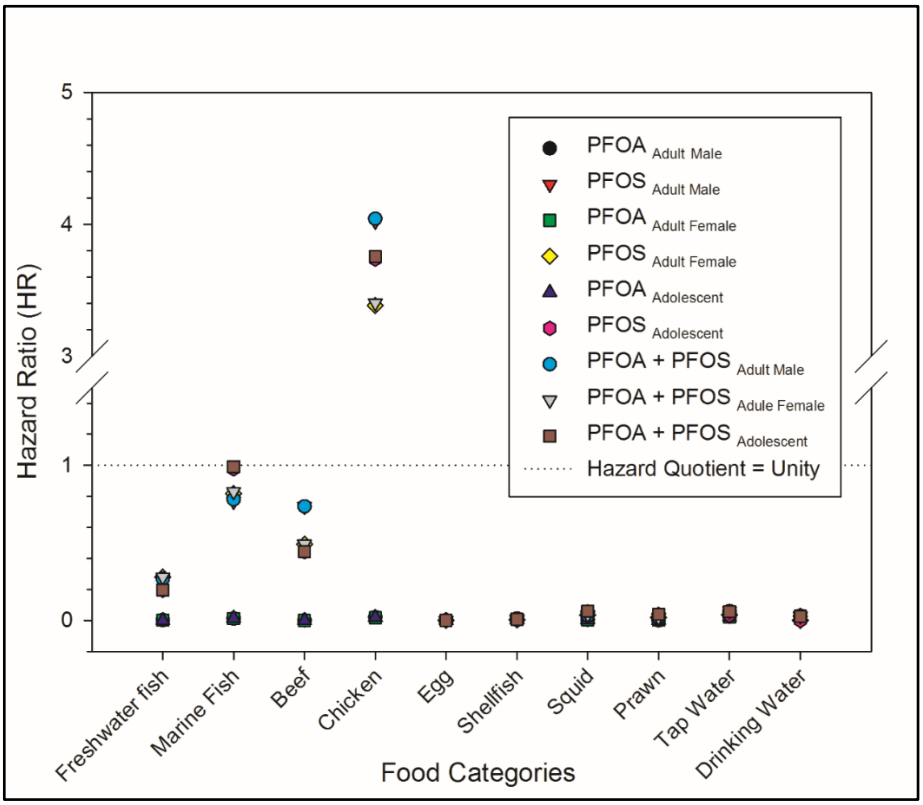

Figure 5.7. Hazard ratios (HRs) from food consumption of different food group.

5.3.5. Association between PFAAs serum levels and estimated dietary intakes.

PFOA and PFOS levels in foods detected in this study were used for the calculation of dietary intake of PFOA and PFOS based on the questionnaire feedback in Chapter 3. The estimated dietary intakes in this study were compared with the concentration of PFAAs in serum samples collected from the residents of Klang Valley (Chapter 3). A very weak but significant correlation was found between the PFAAs levels

in serum and estimated dietary intakes of the participants (Figure 5.8). This observation supports the finding in Chapter 3 where consumption of some food items could be a significant contributor to PFAAs in the population of Klang Valley. Note that other commonly consumed food that we did not analyze in this study such as rice, vegetable, and fruit, in which may also contain PFAAs were not included in the correlation analysis.

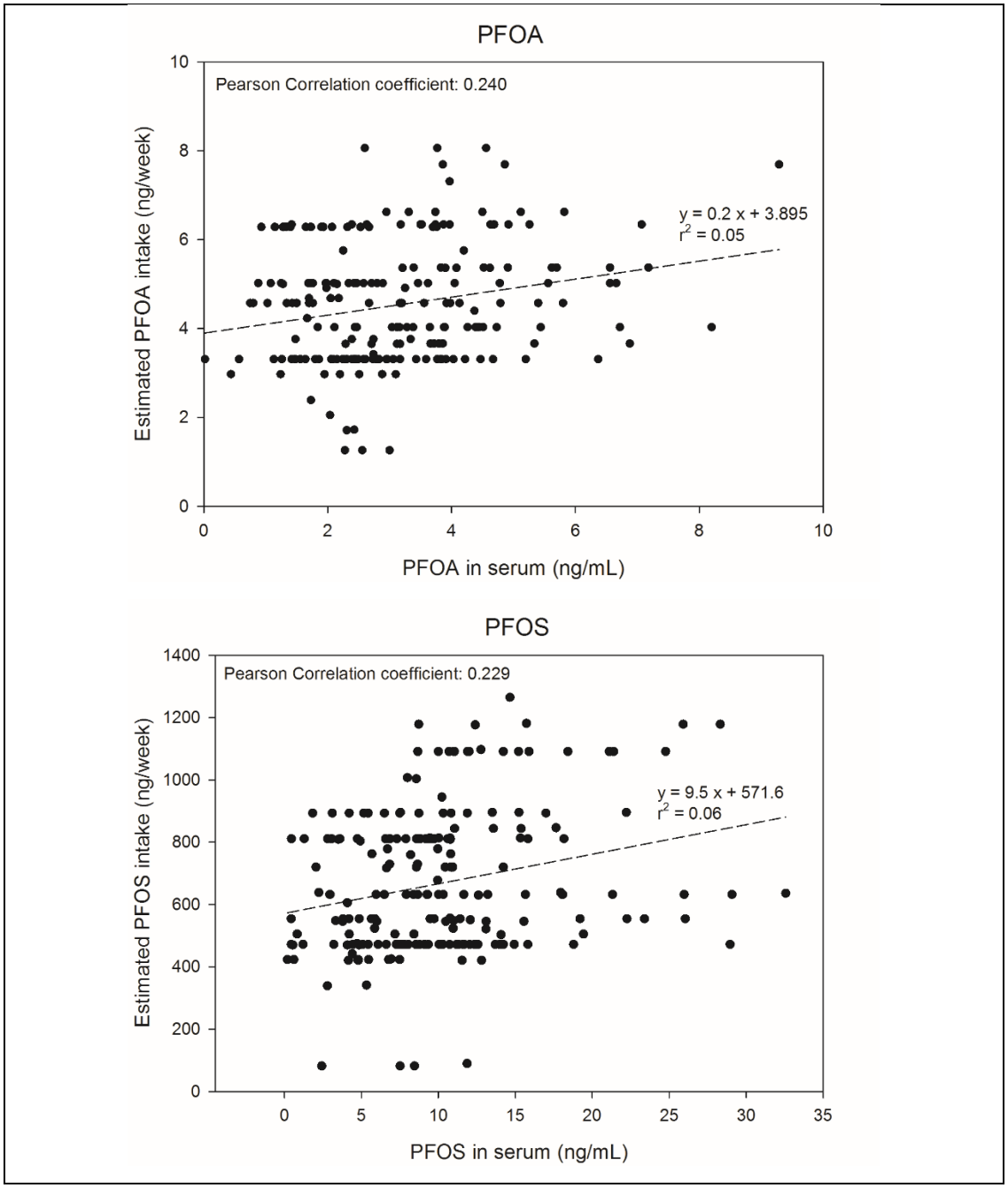

Figure 5.8. The association between PFOA and PFOS estimated dietary intakes (ng/week) and their levels in serum of participant (ng/L).

However, opposite findings were found in other studies by Kärrman et al. (2009), H.-Y. Kim et al. (2014), and Fromme et al. (2007), in which no significant association was found between PFAAs serum levels and estimated dietary intakes. Variation in PFAAs concentration in food consumed by each individual over their lifetime has been suggested as the reason for the non-significant association (Kärrman et al., 2009). In addition, changes in dietary habits of individuals due to various reasons such as changes in income level and lifestyles may also contribute to the variation in PFAAs intake over their lifetime.

5.4. Conclusion

This study revealed the first evidence of the contamination of PFAAs in selected food and drinking water samples from Malaysia, particularly in the Klang Valley. In this study, PFAAs were found above the detection limit in all food samples and some drinking water samples analyzed, which indicates wide contamination of PFAAs in food and drinking water in Malaysia. The levels of PFAAs in food and drinking water samples tested were comparable to those of the previous study globally. Concentration and compositional profiles of PFAAs varied among food samples tested, which might be dependent on the level of PFAAs in the habitat environment where the samples were originally taken from. Highest level of mean ∑PFAAs in food was found in chicken (5.78 ng/g ww), followed by beef (3.14 ng/g ww), and marine fish (0.93 ng/g ww). Overall, all marine food samples tested were the main contributor of long-chain PFAAs (C≥8), except for mollusk. Mollusk was the major contributor for PFOA while the other food samples were the major contributor for PFOS. Tap and bottled water samples showed a varied concentration of PFAAs, which is dependent on the sources of the raw water intake. Based on the preliminary dietary intake exposure assessment, frequent consumption of chicken may lead to the health risk associated with FPAS to the local population especially to all groups assessed. Intake of other foods and drinking water will not cause any immediate health risk to human. However, health quotient above unity was observed for consumption of marine fish for adolescent, after taking into account the combination HQ of PFOA and PFOS. Given the widespread presence of PFAAs in food samples tested, it is thus important to further analyze other commonly consumed food in order to accurately assess the exposure level of PFAAs among the Malaysian population.

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CHAPTER 6
GENERAL CONCLUSION AND FUTURE RECOMMENDATION

6.1 General Conclusion

Polyfluoroalkyl substances (PFAAs) are a group of synthetic fluorinated chemicals that have been manufactured to be used in industrial and consumer products. PFAAs have been detected in multiple mediums worldwide and have been shown to cause adverse health effect in humans and animals. This thesis examined the levels of PFAAs in the surface waters, sediments, commonly consumed food, drinking water, and in human blood, focusing on the region of Klang Valley, Malaysia.

For analysis of PFAAs in human, blood samples of 231 participants were collected and analyzed for the presence of PFAAs. However, only 219 participants successfully managed to complete all the questionnaire given by the interview and thus only those 219 samples were chosen for further exposure assessment. Based on the results obtained, levels of PFAAs in the blood of resident in the Klang Valley were similar and comparable to the level of PFAAs in the blood of non-exposed population in other countries such as China, Korea, and the USA. However, PFAAs level in the Klang Valley population was higher compared to other Southeast Asian countries like Vietnam and Singapore, although the reason was currently unknown since Malaysia and these countries are not a manufacturer for PFAAs. Spearman's rank correlation coefficient revealed that most PFAAs in the serum of residents of Klang Valley were significantly correlated, which suggest that most of these PFAAs may have come from the same sources of exposure. In addition, this study found that PFAAs levels in male were significantly higher compared to female. Menstruation, lactation, and pregnancy have been suggested as the possible elimination rate for female, thus resulted in lower PFAAs levels in blood of female compared to male. Exposure assessment through contact with consumer products revealed that leather sofa, use of non-stick cookware, dental floss, and cosmetic as a significant contributor of some PFAAs in this population. In addition, consumption of beef was significantly associated with increased levels of serum PFAAs in serum. However, note that other commonly consumed foods of Malaysian such as rice, vegetable, and fruits that may also contain PFAAs were not included in the assessment.

Smokers also showed significantly higher PFOA, PFOS, and PFHxS level in the blood compared to nonsmokers. Some studies found the same associations, but there were also other studies that did not show any significant association between smoking and PFAAs level in blood. Further assessment may be required in order to find out the association for other types of foods and smoking habit with the level of PFAAs in blood.

For analysis of PFAAs in surface water and sediment, the samples were collected from Langat and Selangor River basin in two sampling periods, which are March and July 2017. In general, concentrations of PFAAs found in the Langat River basin were higher compared to the Selangor River basin. This is due to the high population density and a higher number of industries in the Langat River basin compared to the Selangor River basin. However, temporal analysis revealed different patterns of PFAAs between these two river basins. PFAAs levels in the Langat River basin were found to be significantly higher during March sampling compared to July sampling. However, an opposite observation was found in the Selangor River basin where PFAAs level was higher during July sampling compared to March sampling, although the difference was only significant for PFOA. Compositional profiles suggest PFOA was dominant for both river basins while PFOS was only dominant for the Langat River basin. In addition, pattern analysis showed that PFAAs may have originated from industries and populated area and that Selangor and Langat River basin have different sources of contamination. The transport mechanism between surface water and sediment was further explained by the partition coefficient, K_D between these two mediums. Higher partition coefficient means that PFAAs tends to partition into sediment from water, and vice versa. Calculation of Log K_D for each PFAAs showed that Log K_D increases as PFAAs chain-length increases. This is due to the increasing hydrophobicity properties (van der Waals interaction) of PFAAs, which would increase the sorption potential of PFAAs into sediment. However, PFBA, a short-chain PFAAs, did not follow this trend and this observation was also supported by other studies. Besides van der Waals interaction, ion exchange or interaction between PFBA (small molecules) and sorptive site may also involve in the transport mechanism of PFAAs between these two mediums. Ecological risk assessment of PFAAs in surface water to three different trophic levels (green algae, daphnia sp., and fish) showed that PFAAs in both Selangor and Langat River basin did not pose any significant risk toward these aquatic organisms. Although surface water in both river basins was not used as a direct drinking water, PFOA level in one of the sampling locations in Selangor River basin (site TS7) exceeded the US EPA lifetime

health advisory level of 70 ng/L for PFOA in drinking water, which may prove hazardous if the surface water was to be used as drinking water.

For analysis of PFAAs in foods and drinking water, 56 food samples under 4 food groups were purchased from three major wet markets located in the Klang Valley region. 26 tap water samples were also collected in every major populated area in Klang Valley. Levels of PFAAs in food samples were comparable or lower compared to other studies, except for chicken. In this study, chicken was revealed as the most contaminated due to the high presence of PFOS, followed by beef, and marine fish. PFOS was found to be predominant PFAAs in all food samples, except for mollusk where PFOA was the predominant PFAAs. Mollusk, being a benthic organism, may have been exposed to different fractions of PFAAs compared to pelagic organism. In addition, long-chain PFAAs such as PFUnDA and PFDoDA can only be found in marine organism, which can be attributed to the presence of these PFAAs in marine environment compared to other media. The differences in bioaccumulation potential between marine species compared to other species, combined with higher salinity in the marine environment may also affect bioaccumulation of PFAAs in organism. Compositional profiles of PFAAs in tap water was different compared to bottled water where PFOS and PFBA were not detected in any bottled water samples compared to tap water samples. PFHxA was predominant PFAAs in both drinking water samples, followed by PFOA for bottled water and PFOS for tap water samples. It was suggested that concentration of PFAAs in both tap and bottled water were closely related to the level of PFAAs in their respective raw water sources. Based on the dietary intake exposure assessment, frequent consumption of chicken may lead to the health risk associated with FPAS with studied population. However, health quotient above unity was also observed for consumption of marine fish for adolescent, after taking into account the combination HQs of PFOA and PFOS.

The assessment of the presence of PFAAs in various multimedia and humans in this study should be able to provide information on the widespread contamination of PFAAs in Malaysia, particularly in the Klang Valley and subsequently assist stakeholders in controlling or eliminating these PFAAs for the safety of the population.

6.2 Future Recommendations

A) Since the serum samples were limited, the assessment can only cover the region of Klang Valley. Furthermore, Klang Valley is categorized as an urban city. To cover the general population of Malaysia such as in rural areas, more samples which cover various region and states need to be collected and assessed. In addition, since Malaysian consist of different types of races such as Malay, Chinese, and Indian, blood sample collected should be more diverse and covers all races. Races and culture played an important role in the type of exposure of these chemicals to human. For example, due to religious reason, the Malay population would not consume pork or drink alcohol compared to Chinese and Indian. For the same reason, some Indian also would not consume beef compared to Malay and Chinese. The different culture and religious practice such as this warrant further look during the assessment of the chemical.

B) The analysis of surface water and sediment in both Selangor and Langat River basin revealed the presence of the PFAAs. However, some sampling locations revealed the presence of some PFAAs during one of the sampling period but not on the other sampling period. This observation may be either due to the one-time release or periodical release of PFAAs from existing or new industries into the surface water. Additional analysis of PFAAs is necessary in order to elucidate further the temporal variation of PFAAs in surface water and sediment of Selangor and Langat River basin. This way, confirmation whether PFAAs concentration increases or decreases over time can be achieved.

C) In addition, there was a lack of observation of the presence of PFAAs in aquatic organism within these river basins. As various studies have proven that PFAAs indeed bioaccumulate in these organisms such as fish and shellfish, it is then necessary to measure the level of PFAAs in the organism that particularly exists in these aquatic regions. In addition, due to the differences in type of species that living in these regions compared to other countries around the world, it is also necessary to assess the risk that specifically focused on the species that present in these regions.

D) Although foods that were analyzed in this study focused on the commonly consumed food for the population of Malaysia, the type of food analyzed in

this study was limited. To thoroughly assess the risk of PFAAs from the consumption of food, more diverse sample is needed to be analyzed. For example, rice is the most consumed food for Malaysian, followed by bread. Although the Klang Valley region neither has paddy field, nor wheat field, presence of PFAAs in these products also needs to be assessed.

E) Although samples were collected from three different wet markets, all chicken samples showed a high presence of PFOS. In addition, compositional profiles of two of the chicken samples were similar, which suggest that the chickens may have come from the same poultry. Additional chicken samples, preferably from other local poultry may be needed in order to compare the PFAAs compositional profiles of each poultry so that the PFAAs contamination in chicken can be identified and reduced.

F) Currently, the Malaysian Government did not regulate the usage and manufacturing of PFAAs in Malaysia. In addition, Malaysia is also not yet a treaty to the Stockholm Convention after PFOS were added into the list of Persistent Organic Pollutants by the Convention in 2009. From the best of our knowledge, no regulation or elimination plan of PFAAs is currently in motion. Therefore, we believed that regulation and intervention from the government are necessary so that PFAAs exposure risk of Malaysian population can be controlled and prevented.

APPENDIX
SUPPORTING INFORMATION

APPENDIX A

Appendix A-1: Concentration of PFAAs in serum of participants (ng/mL).

	PFOA	PFOS	PFBA	PFHxA	PFHxS	PFNA	PFDA	PFUnDA	PFDoDA	∑PFAAs
S101	2.11	10.32	0.46	0.5	<LOD	<LOD	0.43	0.55	<LOD	14.37
S102	4.52	10.93	0.15	0.31	3.87	2.16	<LOD	1.02	1.27	24.23
S103	3.89	8.66	0.56	0.37	4.83	2.78	<LOD	0.38	<LOD	21.47
S104	2.47	18.08	0.5	0.52	2.19	1.68	0.98	<LOD	<LOD	26.42
S105	2.8	6.57	2.45	0.46	0.84	0.61	0.4	0.94	<LOD	15.07
S106	5.56	10.78	0.44	0.66	2.26	2.02	0.58	0.78	<LOD	23.08
S107	1.43	5.65	<LOD	0.27	<LOD	0.98	0.37	<LOD	<LOD	8.7
S108	0.44	4.09	0.45	0.17	0.26	0.57	0.25	0.44	<LOD	6.67
S109	2.42	6.62	0.59	0.49	2.14	1.71	0.46	0.5	<LOD	14.93
S110	0.51	2.66	0.6	0.17	0.3	<LOD	0.22	<LOD	<LOD	4.46
S111	3.31	10.23	0.6	0.43	2.09	1.43	0.71	0.8	<LOD	19.6
S113	2.07	11.89	0.42	0.31	0.83	1.3	0.61	<LOD	<LOD	17.43
S114	1.31	8.61	0.62	0.22	0.39	0.77	0.9	1.3	<LOD	14.12
S115	3.87	21.11	0.64	0.41	3.62	<LOD	0.74	1.35	<LOD	31.74
S117	3.17	8.42	0.59	0.34	<LOD	0.6	0.5	1.03	<LOD	14.65
S119	1.73	16.99	0.55	0.36	1.67	0.38	1.36	2.35	<LOD	25.39
S120	2.32	13.58	0.46	0.4	1.36	1.2	1.36	2.07	<LOD	22.75
S121	3.38	29.08	<LOD	0.6	3.2	1.84	1.06	<LOD	<LOD	39.16
S122	2.44	13.7	0.73	0.46	0.87	0.54	0.85	1.31	<LOD	20.9
S124	1.25	6.87	<LOD	0.29	0.83	1.3	0.61	1.25	<LOD	12.4
S125	4.05	18.16	1.6	0.53	2.25	1.19	1.64	3.16	2.22	34.8
S126	3.83	7.82	1.43	0.42	0.69	1.42	0.73	1.04	<LOD	17.38
S127	4.68	21.39	0.49	0.68	4.08	2.61	1.08	1.37	<LOD	36.38
S128	8.2	21.32	<LOD	0.72	2.57	0.83	1.6	2.36	<LOD	37.6
S129	4.5	17.65	0.36	<LOD	<LOD	1.9	<LOD	1.24	<LOD	25.65
S130	1.47	11.31	0.67	0.3	0.31	1.38	<LOD	1.95	<LOD	17.39
S131	1.93	8.74	0.45	0.28	0.73	0.56	0.52	<LOD	<LOD	13.21
S132	1.28	5.16	<LOD	<LOD	0.52	2.62	<LOD	1	<LOD	10.58
S133	2.73	13.1	0.48	0.36	1.44	1.12	0.97	1.94	1.91	24.05
S134	1.7	8.2	<LOD	0.32	0.96	1.6	0.4	0.75	<LOD	13.93
S135	1.08	5.69	<LOD	0.22	<LOD	2.47	0.3	<LOD	<LOD	9.76
S136	4.69	10	<LOD	0.5	0.35	1.44	0.24	0.58	3.12	20.92
S137	2.29	10.96	<LOD	0.28	0.66	2.03	0.62	<LOD	<LOD	16.84
S138	5.4	23.4	2.21	0.65	0.98	4.34	<LOD	1.74	<LOD	38.72
S139	4.24	15.36	<LOD	0.55	1.96	4.45	0.42	<LOD	1.93	28.91
S140	4.79	22.26	<LOD	0.54	1.57	1.69	1.36	1.63	1.83	35.67
S141	1.56	10.29	<LOD	0.29	<LOD	1.96	<LOD	1.28	<LOD	15.38
S142	3.86	15.56	1.1	0.47	1.48	3.57	<LOD	1.51	<LOD	27.55
S143	7.07	15.22	0.45	0.64	4.92	6.21	0.37	0.42	2.27	37.57
S144	3.77	12.58	0.56	0.41	2.09	0.48	0.5	<LOD	<LOD	20.39
S145	4.86	28.32	<LOD	0.48	4.4	<LOD	1.23	1.35	<LOD	40.64
S146	5.26	24.77	0.64	0.63	3.27	1.32	<LOD	1.64	<LOD	37.53
S147	3.77	12.77	0.6	0.44	1.97	<LOD	<LOD	0.6	<LOD	20.15
S148	4.78	8.59	<LOD	0.53	1.66	3.06	0.69	0.9	<LOD	20.21
S149	2.67	11.06	0.46	0.37	<LOD	1.68	0.59	<LOD	<LOD	16.83
S150	1.97	8.83	<LOD	0.48	0.53	2.35	0.49	0.88	2	17.53
S151	5.8	26.05	0.59	0.34	2.31	2.94	1.26	<LOD	<LOD	39.29
S152	3.56	9.73	0.66	0.46	3.08	1.25	0.35	<LOD	<LOD	19.09
S153	1.28	8.57	<LOD	0.33	0.4	0.82	0.68	0.97	1.58	14.63
S201	0.93	10.83	1.15	0.22	0.54	1.55	0.5	<LOD	<LOD	15.72
S202	2.39	11.9	0.43	0.5	1.14	2.03	<LOD	<LOD	<LOD	18.39
S203	1.69	4.74	<LOD	0.33	<LOD	1	0.48	1.19	<LOD	9.43
S204	2.74	9.96	0.5	0.44	1.26	1.78	0.47	0.74	<LOD	17.89
S205	2.31	2.79	<LOD	0.26	0.56	2.03	0.15	0.31	<LOD	8.41
S206	4.67	18.79	0.36	0.4	0.68	1.23	1.26	1.54	<LOD	28.93
S207	2.47	9.19	0.83	0.44	<LOD	3.3	0.86	<LOD	<LOD	17.09
S208	3.76	15.38	1.45	0.26	1.48	0.96	1.15	1.83	<LOD	26.27
S209	3.17	5.87	0.77	0.28	1.13	1.29	0.95	1.38	1.91	16.75
S210	2.88	4.8	0.66	0.31	<LOD	1.92	0.27	0.5	3.02	14.36
S211	4.2	17.95	0.96	0.57	5.01	1.03	1.27	1.39	<LOD	32.38

S212	4.39	11	1.21	0.37	0.51	1.94	0.44	0.92	1.46	22.24
S214	3.97	14.22	1.29	0.49	3.14	4.13	0.42	0.62	<LOD	28.28
S215	1.57	5.71	0.96	0.21	<LOD	0.7	<LOD	0.07	<LOD	9.22
S216	1.95	11.54	3.4	0.24	0.39	2.65	<LOD	<LOD	<LOD	20.17
S217	3.12	15.66	0.85	0.46	0.25	1.82	0.42	0.61	<LOD	23.19
S220	6.56	15.82	<LOD	0.45	0.93	3.29	1	1.4	<LOD	29.45
S221	1.33	3.11	<LOD	0.21	0.53	1.36	0.29	0.4	<LOD	7.23
S222	2.61	7.66	0.34	0.37	<LOD	1.06	0.26	0.51	<LOD	12.81
S226	1.64	5.1	0.44	0.35	0.69	1.61	0.28	0.62	<LOD	10.73
S227	2.09	12.35	1.52	0.19	<LOD	1.08	0.94	1.99	<LOD	20.16
S228	4.47	11.6	0.41	0.3	1.27	3.74	0.8	1.13	<LOD	23.72
S229	3.17	14.23	0.43	0.51	<LOD	<LOD	0.93	1.06	<LOD	20.33
S230	3.1	12.81	0.86	0.4	0.86	1.83	0.65	0.9	<LOD	21.41
S231	5.82	22.22	<LOD	0.41	2.52	0.93	1.48	1.74	<LOD	35.12
S301	0.6	2.07	0.5	0.17	0.31	3.23	<LOD	0.26	<LOD	7.14
S303	1.81	12.64	0.31	0.4	2.14	<LOD	0.53	0.51	1.59	19.93
S304	1.65	1.84	0.4	0.29	<LOD	1.23	0.16	0.25	1.59	7.41
S306	3.34	9.97	0.76	0.29	0.88	1.02	0.67	0.89	<LOD	17.82
S308	0.75	3.81	0.53	<LOD	<LOD	0.94	0.23	0.48	<LOD	6.74
S309	2.31	8.57	0.32	0.18	0.84	1.53	0.25	0.41	<LOD	14.41
S310	1.86	7.47	0.42	0.26	1.13	1.16	0.58	1.19	<LOD	14.07
S311	1.9	5.44	0.37	0.34	0.29	2.16	0.28	0.56	<LOD	11.34
S312	4.56	15.73	0.47	0.39	2	0.65	0.9	1.4	<LOD	26.1
S313	3.97	12.4	0.78	0.37	4.49	0.77	0.72	0.82	<LOD	24.32
S314	3.5	10.7	0.28	0.39	1.22	1.49	0.5	0.61	<LOD	18.69
S315	9.29	25.91	0.34	0.5	4.94	1.82	1.27	1.44	<LOD	45.51
S316	3.84	4.76	0.35	0.36	1.56	0.45	0.43	0.48	<LOD	12.23
S317	3.72	6	0.36	0.22	2.99	1.08	0.64	0.33	<LOD	15.34
S319	3.66	13.11	0.43	0.46	2.37	0.95	0.46	0.55	<LOD	21.99
S320	3.88	6.49	<LOD	0.28	1.72	3.07	0.18	0.32	<LOD	15.94
S321	6.72	7.92	0.28	1.64	4.74	2.61	0.67	0.59	<LOD	25.17
S322	6.37	12.04	0.89	0.39	2.4	2.44	0.44	0.55	<LOD	25.52
S324	5.34	10.48	0.52	0.4	3.84	0.72	<LOD	0.35	<LOD	21.65
S325	4.13	19.21	0.69	0.43	1.49	1.1	1.41	1.94	<LOD	30.4
S326	1.8	6.77	0.34	0.37	0.57	3.47	0.52	0.83	<LOD	14.67
S327	1.72	2.81	0.32	0.48	<LOD	1.37	0.16	0.35	<LOD	7.21
S401	2.71	7.89	0.51	0.33	0.87	0.39	0.31	0.49	<LOD	13.5
S403	4.63	12	0.61	0.34	1.18	2.3	0.38	0.51	<LOD	21.95
S407	2.74	6.84	0.59	0.31	0.53	2.65	0.18	0.45	<LOD	14.29
S411	7.18	8.58	1.31	0.36	1.37	0.9	0.7	0.61	<LOD	21.01
S412	2.06	11.68	0.49	0.36	0.52	0.41	0.75	1.35	<LOD	17.62
S413	2.63	11.01	0.66	0.17	0.36	0.98	0.46	1.31	<LOD	17.58
S414	1.76	4.86	1.06	0.46	0.31	0.92	0.29	0.4	<LOD	10.06
S415	4.45	8.39	0.88	0.51	1.74	0.72	0.13	0.22	<LOD	17.04
S416	5.2	28.96	0.7	0.53	3.8	1.34	2.13	2.15	<LOD	44.81
S417	3.18	11.04	1.24	0.23	1.04	1.4	0.43	0.57	<LOD	19.13
S418	2.89	7.3	1.12	0.32	1.3	0.25	0.34	0.53	<LOD	14.05
S419	2.53	6.5	0.63	0.28	0.35	0.55	0.24	0.53	<LOD	11.61
S420	1.73	4.41	0.88	0.24	0.47	1.33	0.19	0.38	<LOD	9.63
S421	2.24	7.52	0.94	0.27	1.83	0.46	0.2	0.44	<LOD	13.9
S422	5.62	10.83	1.13	0.29	1.44	1.1	0.27	0.43	<LOD	21.11
S423	4.13	7.18	0.94	0.34	0.73	1.38	0.41	0.61	<LOD	15.72
S424	6.88	3.79	0.71	0.24	2.53	<LOD0.170	0.18	0.29	<LOD	14.62
S501	2.15	6.64	0.65	0.4	0.85	0.88	0.38	0.97	<LOD	12.92
S503	0.88	3.07	0.73	0.19	<LOD	0.49	0.2	0.47	<LOD	6.03
S505	3.86	8.73	0.61	0.38	1.36	0.7	0.14	0.34	<LOD	16.12
S506	3.18	6.19	0.68	0.33	0.96	1.43	0.3	0.53	<LOD	13.6
S510	3.06	5.47	0.39	0.25	0.83	1.51	0.48	0.64	<LOD	12.63
S511	6.66	10.8	0.81	0.32	0.48	0.67	0.85	0.71	<LOD	21.3
S512	2.04	5.34	1.15	0.35	<LOD	<LOD	0.35	0.76	1.59	11.58
S513	2.51	4.16	0.35	0.37	0.74	0.64	0.33	0.42	<LOD	9.52
S514	2.56	2.43	0.53	0.25	0.66	1.48	<LOD	0.25	<LOD	8.16
S515	2.61	4.8	0.9	0.26	0.34	1.02	0.12	0.44	<LOD	10.49
S516	1.73	3.61	0.22	0.28	0.4	0.63	<LOD	0.32	<LOD	7.19

S517	1.15	7.5	<LOD	0.25	0.48	0.66	0.64	2.04	<LOD	12.72
S518	4.22	12.43	<LOD	0.27	1.7	0.68	0.85	1.29	<LOD	21.44
S519	2.34	8.67	0.29	0.38	0.66	<LOD	0.3	0.5	<LOD	13.14
S520	2.15	0.45	0.42	0.18	<LOD	<LOD	0.28	<LOD	<LOD	3.48
S521	2.96	10.05	0.27	0.31	0.57	0.91	0.6	0.91	<LOD	16.58
S522	1.98	4.09	0.52	0.27	<LOD	1.11	0.24	0.69	<LOD	8.9
S523	0.8	4.21	0.87	0.2	0.23	2.29	0.19	0.63	<LOD	9.42
S525	4.37	12.08	1.29	0.32	1.48	2.64	0.76	0.76	<LOD	23.7
S601	3.12	6.94	0.37	0.23	1.58	0.39	0.36	0.68	<LOD	13.67
S602	1.83	3.53	0.95	0.29	<LOD	2.4	<LOD	<LOD	<LOD	9
S603	0.79	9.37	0.44	0.24	<LOD	0.88	0.77	1.67	<LOD	14.16
S606	2.95	7.54	0.79	0.35	<LOD	<LOD	0.38	0.98	<LOD	12.99
S607	<LOD	7.78	1.36	0.17	<LOD	<LOD	0.4	0.67	1.27	11.65
S608	3.39	2.05	0.3	0.4	2.48	<LOD	0.7	1.03	<LOD	10.35
S609	3.74	15.24	0.25	0.48	3.1	1.23	0.97	0.99	<LOD	26
S610	3.52	15.89	0.36	0.52	1.1	<LOD	0.92	1.43	<LOD	23.74
S611	2.6	14.66	0.85	0.21	1.35	10.56	0.58	1.32	<LOD	32.13
S614	2.1	0.46	0.47	0.19	0.83	<LOD	0.33	0.69	<LOD	5.07
S616	2.39	8.79	0.3	0.32	1.79	<LOD	<LOD	<LOD	<LOD	13.59
S617	3.59	9.09	0.38	0.31	1.27	1.82	0.54	0.62	<LOD	17.62
S618	4.51	11.65	0.21	0.28	1.1	<LOD	0.49	0.59	<LOD	18.83
S619	3.28	13.21	0.58	0.31	0.35	<LOD	0.94	1.01	3.15	22.83
S620	3.91	10.23	0.54	0.36	1.18	<LOD	0.46	0.66	<LOD	17.34
S621	2.06	8.55	0.43	0.25	1.22	<LOD	0.48	0.61	<LOD	13.6
S622	4.43	2.97	0.57	0.36	2.11	<LOD	0.56	0.88	<LOD	11.88
S623	5.44	2.95	0.54	0.26	2.31	4.36	0.37	0.61	<LOD	16.84
S624	3.83	4.93	1.19	0.4	3.92	<LOD	0.79	<LOD	1.59	16.65
S625	2.39	6.7	0.26	0.17	0.4	<LOD	0.26	0.36	<LOD	10.54
S626	4.91	10.45	0.59	0.21	1.79	2.81	0.4	0.6	<LOD	21.76
S627	1.24	4.85	0.62	0.19	0.43	<LOD	0.33	0.66	<LOD	8.32
S628	2.28	7.52	0.55	0.18	0.89	<LOD	0.34	0.5	<LOD	12.26
S629	1.34	4.2	0.4	0.17	0.31	<LOD	0.27	0.7	<LOD	7.39
S630	4.62	10.76	0.41	0.18	1.75	<LOD	0.65	0.51	<LOD	18.88
S703	7.54	6.46	0.9	0.16	1.98	2.08	0.43	0.8	<LOD	20.35
S704	4.03	13.98	0.87	0.31	2.33	0.42	1.31	1.69	<LOD	24.94
S705	3.21	10.03	0.63	0.33	0.67	0.96	0.75	1.44	<LOD	18.02
S706	1.26	6.09	0.47	0.19	<LOD	1.74	0.44	0.79	<LOD	10.98
S707	1.42	14.94	<LOD	0.26	0.63	<LOD	1.89	0.99	<LOD	20.13
S708	3.65	18.05	0.87	0.26	2.45	0.71	1.24	1.72	<LOD	28.95
S709	1.48	8.65	<LOD	0.28	0.52	0.82	0.81	1.34	<LOD	13.9
S710	4.08	15.34	0.83	0.41	1.01	1.43	0.74	0.85	<LOD	24.69
S711	6.56	14.22	0.41	0.3	2.62	1.58	0.37	0.44	<LOD	26.5
S712	1.01	3.94	0.48	0.21	0.25	1.37	0.22	0.72	<LOD	8.2
S714	5.12	13.51	0.56	0.32	2	2.3	1.05	1.23	<LOD	26.09
S715	1.67	14.08	0.41	0.25	<LOD	0.99	1.65	3.23	<LOD	22.28
S716	2.59	15.82	<LOD	0.32	1.14	0.95	1.16	1.94	1.27	25.19
S717	1.5	5.88	0.72	0.27	<LOD	5.76	0.52	0.95	<LOD	15.6
S718	4.66	13.79	0.28	0.36	1.7	0.71	0.98	1.39	<LOD	23.87
S719	2.58	10.74	0.48	0.23	0.29	0.71	0.92	2.16	<LOD	18.11
S720	3	8.45	0.32	0.27	<LOD	1.25	0.8	1.37	<LOD	15.46
S721	2.81	11.19	0.53	0.33	0.45	2.15	1.41	1.25	<LOD	20.12
S722	2.28	14.07	0.59	0.3	0.49	<LOD	1.05	1.2	<LOD	19.98
S723	1.8	8.05	0.77	0.2	<LOD	1.32	0.89	1.42	<LOD	14.45
S724	1.18	9.66	0.36	0.16	0.61	0.92	0.92	1.57	<LOD	15.38
S725	0.57	3.21	0.54	0.23	0.48	<LOD	<LOD	<LOD	<LOD	5.03
S802	2.83	8.57	0.37	0.38	1.01	0.89	0.54	0.73	<LOD	15.32
S803	2.79	5.44	<LOD	0.36	0.74	2.35	0.27	0.51	<LOD	12.46
S804	3.7	10.32	0.36	0.3	1.66	2.38	0.68	0.65	<LOD	20.05
S805	1.13	4.45	0.61	0.17	0.4	0.76	0.27	0.6	<LOD	8.39
S806	1.7	0.83	0.36	0.17	0.57	<LOD	<LOD	0.42	<LOD	4.05
S807	<LOD	0.43	0.41	0.18	0.74	2.11	0.31	0.55	<LOD	4.73
S808	1.98	10.61	0.62	0.24	0.88	<LOD	1.01	<LOD	<LOD	15.34
S809	3.2	10.75	0.33	0.25	1.09	1.88	0.45	0.63	<LOD	18.58
S810	2.18	3.51	0.49	0.3	0.34	0.4	0.28	0.34	<LOD	7.84

S812	<LOD	0.62	0.38	0.45	0.73	<LOD	1.44	1.28	<LOD	4.9
S813	1.54	7.87	<LOD	0.17	1.02	1.44	0.35	0.63	<LOD	13.02
S814	3.62	9.74	<LOD	0.32	1.93	<LOD	0.35	0.59	<LOD	16.55
S815	2.49	1.21	0.45	0.32	1.35	<LOD	0.38	0.44	<LOD	6.64
S816	3.25	10.76	0.85	0.29	1.18	<LOD	0.63	1.27	<LOD	18.23
S817	<LOD	0.98	0.37	0.29	0.61	<LOD	0.3	0.65	<LOD	3.2
S818	2.58	1.29	0.69	0.2	0.27	<LOD	0.4	0.48	<LOD	5.91
S819	2.43	7.49	0.23	0.33	<LOD	1.45	0.41	0.34	<LOD	12.68
S820	2.2	0.55	0.24	0.27	1.4	<LOD	0.52	1.19	<LOD	6.37
S821	3.92	19.43	0.91	0.24	1.74	<LOD	<LOD	<LOD	<LOD	26.24
S822	2.95	0.2	1.15	0.18	0.39	<LOD	0.42	<LOD	<LOD	5.29
S823	0.92	4.81	0.34	0.17	0.7	<LOD	0.26	0.57	<LOD	7.77
S824	4.73	25.97	2.42	0.4	2.04	<LOD	<LOD	<LOD	<LOD	35.56
S825	2.4	0.78	0.31	0.19	0.74	<LOD	<LOD	0.19	<LOD	4.61
S827	2.71	4.73	<LOD	0.32	0.79	1.1	0.25	0.38	<LOD	10.28
S828	3.41	21.34	0.32	0.21	2.27	<LOD	1.58	2.2	<LOD	31.33
S829	1.03	0.44	0.26	0.23	0.32	0.56	0.21	0.58	1.91	5.54
S830	1.76	6.82	0.26	0.31	1.62	2.56	0.46	0.63	<LOD	14.42
S831	5.02	1.56	0.61	0.51	1.14	<LOD	0.58	0.84	<LOD	10.26
S832	3.98	11.41	0.29	0.26	1.48	<LOD	0.64	0.79	<LOD	18.85
S902	2.25	2.24	0.68	<LOD	1.05	0.58	0.32	<LOD	<LOD	7.12
S903	5.7	32.57	0.63	0.38	3.05	3.91	1.37	<LOD	<LOD	47.61
S904	1.48	9.35	2.03	0.38	0.68	1.31	1.08	<LOD	<LOD	16.31
S905	2.67	9.47	0.43	<LOD	0.92	1.33	1	<LOD	<LOD	15.82
S906	3.74	8.67	0.53	0.42	1.11	1	0.55	<LOD	<LOD	16.02
S908	2.06	7.99	1.17	<LOD	1.09	0.84	0.37	<LOD	<LOD	13.52
S909	3.46	9.57	1.28	<LOD	0.87	1.45	0.94	<LOD	<LOD	17.57
S910	4.92	18.42	0.53	<LOD	2.04	2	0.83	<LOD	<LOD	28.74
S911	2.44	3.33	0.21	<LOD	0.88	0.91	0.53	<LOD	<LOD	8.3
S912	4.26	10.02	0.99	0.48	1.84	1.44	0.67	<LOD	<LOD	19.7
S913	3.04	9.26	<LOD	<LOD	1.63	1.5	0.66	<LOD	<LOD	16.09
S914	3.43	9.13	0.44	<LOD	0.96	1.56	0.71	<LOD	<LOD	16.23
S915	3.9	9.45	0.58	0.46	1.04	1.84	0.9	<LOD	<LOD	18.17
S916	2.05	10.78	0.5	<LOD	0.9	1.61	0.99	<LOD	<LOD	16.83
S917	2.78	7.27	0.61	0.37	0.95	1.33	0.71	<LOD	<LOD	14.02
S918	1.42	7.99	0.46	<LOD	0.87	0.94	0.55	<LOD	<LOD	12.23
S919	2.43	11.87	0.99	0.45	2.15	1.78	0.81	<LOD	<LOD	20.48
S920	2.43	9.34	1.31	<LOD	1.19	1.26	0.73	<LOD	<LOD	16.26
S921	1.4	4.21	0.76	0.39	0.75	0.59	0.42	<LOD	<LOD	8.52
S922	3.8	12.61	0.51	<LOD	1.13	1.35	0.74	<LOD	<LOD	20.14
S923	3.16	5.96	0.84	0.38	1.07	1.09	0.46	<LOD	<LOD	12.96
S924	2.46	10.06	0.47	0.37	1.03	1.31	0.54	<LOD	<LOD	16.24
S925	1.84	9.3	0.41	0.4	1.48	0.86	0.52	<LOD	<LOD	14.81

APPENDIX B

Appendix B-1: Concentration of PFAAs in surface water of Selangor and Langat River Basin during March sampling (ng/L).

March	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUna	PFDoa	PFHxS	PFOS	∑PFAAS
RL1	1.236	0.274	0.424	0.252	0.362	<LOD	<LOD	<LOD	0.998	3.546
L1	3.112	0.989	1.471	0.272	<LOD	<LOD	<LOD	<LOD	0.83	6.674
TL1	104.455	5.286	2.023	15.445	<LOD	<LOD	1.803	1.142	8.791	138.945
TL2	17.06	2.645	2.057	0.872	<LOD	<LOD	1.034	<LOD	1.273	24.941
TL3	7.705	1.318	1.869	1.591	0.606	3.117	0.846	<LOD	<LOD	17.052
L2	5.873	1.666	2.277	0.375	<LOD	<LOD	<LOD	<LOD	<LOD	10.191
TL4	6.154	1.743	1.985	0.349	0.162	<LOD	<LOD	<LOD	<LOD	10.393
TL5	3.635	1.242	3.832	0.26	0.262	0.535	0.206	0.614	0.589	11.175
TL6	2.897	1.203	0.819	0.42	<LOD	<LOD	<LOD	<LOD	<LOD	5.339
TL7	2.597	0.691	0.993	<LOD	<LOD	<LOD	0.265	<LOD	<LOD	4.546
L3	5.393	1.48	1.702	0.35	<LOD	<LOD	0.363	<LOD	0.792	10.08
TL8	4.634	1.145	1.254	0.331	0.199	<LOD	<LOD	<LOD	0.448	8.011
L4	4.534	1.157	1.389	0.305	<LOD	<LOD	<LOD	<LOD	0.981	8.366
TL9	2.731	1.598	1.143	0.255	<LOD	<LOD	<LOD	<LOD	<LOD	5.727
TL10	0.929	0.45	1.016	0.166	<LOD	<LOD	0.476	<LOD	<LOD	3.037
TL11	2.397	1.007	1.176	0.295	<LOD	0.217	0.204	<LOD	<LOD	5.296
TL12	2.988	2.748	35.517	0.23	0.504	<LOD	<LOD	<LOD	<LOD	41.987
TL13	0.67	0.369	0.829	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.868
TL14	0.927	0.104	0.872	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.903
L5	6.078	1.333	2.126	0.42	0.173	<LOD	<LOD	<LOD	<LOD	10.13
TL15	2.05	1.404	1.587	0.337	0.296	0.169	0.57	0.549	1.165	8.127
TL16	3.11	0.462	2.038	0.315	<LOD	<LOD	<LOD	0.262	0.401	6.588
TL17	3.842	1.146	1.546	0.323	0.145	<LOD	0.227	<LOD	2.505	9.734
L6	0.544	0.23	0.692	<LOD	0.144	<LOD	<LOD	<LOD	<LOD	1.61
L7	0.12	0.079	0.715	<LOD	<LOD	<LOD	0.248	<LOD	<LOD	1.162
RS1	1.036	0.331	0.425	0.21	<LOD	<LOD	0.162	<LOD	<LOD	2.164
S1	0.89	0.772	0.996	2.306	0.214	1.389	<LOD	<LOD	<LOD	6.567
S2	2.739	0.851	0.996	0.79	<LOD	<LOD	0.182	<LOD	<LOD	5.558
TS1	4.388	0.881	1.019	0.243	<LOD	<LOD	<LOD	<LOD	<LOD	6.531
S3	2.172	0.718	0.902	0.244	<LOD	<LOD	<LOD	<LOD	<LOD	4.036
TS2	3.941	1.123	1.131	0.293	<LOD	<LOD	0.238	<LOD	<LOD	6.726
TS3	5.669	2.102	2.046	0.302	0.158	<LOD	0.221	<LOD	<LOD	10.498
TS4	2.929	0.388	0.911	0.298	<LOD	0.174	<LOD	<LOD	<LOD	4.7
TS5	2.134	0.421	1.016	0.218	0.144	<LOD	<LOD	<LOD	<LOD	3.933
TS6	1.152	0.502	0.83	0.235	<LOD	<LOD	<LOD	<LOD	<LOD	2.719
TS7	1.614	0.713	0.943	0.271	0.234	<LOD	<LOD	0.454	<LOD	4.229
S4	1.176	0.496	0.563	0.515	<LOD	<LOD	0.214	<LOD	<LOD	2.964
TS8	0.757	0.111	0.264	0.234	<LOD	<LOD	<LOD	<LOD	<LOD	1.366
TS9	1.497	2.104	1.804	0.515	0.204	<LOD	<LOD	<LOD	<LOD	6.124
TS10	0.306	0.085	0.563	0.187	<LOD	<LOD	<LOD	<LOD	<LOD	1.141
TS11	0.746	0.277	0.399	0.331	<LOD	0.173	0.15	<LOD	<LOD	2.076
S5	0.514	0.487	0.441	0.246	<LOD	<LOD	0.174	<LOD	<LOD	1.862
TS12	0.286	0.08	0.286	0.234	<LOD	<LOD	<LOD	<LOD	<LOD	0.886
S6	0.475	0.187	11.635	0.16	0.191	<LOD	0.204	<LOD	<LOD	12.852

LOD - Limit of Detection

Appendix B-2: Concentration of PFAAs in surface water of Selangor and Langat River Basin during July sampling (ng/L)

July	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUna	PFDoa	PFHxS	PFOS	TOTAL
RL1	0.233	0.183	0.282	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.698
L1	<LOD	0.085	0.334	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.419
TL1	0.901	0.26	0.376	0.203	0.133	<LOD	0.229	<LOD	<LOD	2.102
TL2	0.148	0.244	0.186	0.213	<LOD	<LOD	0.168	<LOD	<LOD	0.959
TL3	0.463	0.19	0.277	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.93
L2	0.794	0.085	0.827	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.706
TL4	0.079	0.05	0.216	<LOD	<LOD	<LOD	0.172	<LOD	<LOD	0.517
TL5	3.104	2.897	35.484	0.272	0.624	<LOD	<LOD	<LOD	<LOD	42.381
TL6	<LOD	0.718	2.199	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	2.917
TL7	4.573	1.146	1.258	0.311	0.073	<LOD	<LOD	<LOD	0.4	7.761
L3	0.676	0.347	0.795	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.818
TL8	6.433	1.348	2.003	0.449	0.179	<LOD	<LOD	<LOD	<LOD	10.412
L4	5.126	1.228	1.699	0.362	0.158	<LOD	0.42	<LOD	0.836	9.829
TL9	2.608	1.118	1.103	0.757	0.196	<LOD	<LOD	<LOD	<LOD	5.782
TL10	1.858	0.782	0.873	0.275	0.068	<LOD	<LOD	<LOD	<LOD	3.856
TL11	0.697	0.489	1.043	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	2.229
TL12	0.305	0.155	0.384	0.185	0.107	<LOD	<LOD	<LOD	0.756	1.892
TL13	1.569	0.553	0.508	0.245	0.068	<LOD	0.151	<LOD	<LOD	3.094
TL14	<LOD	0.064	0.284	<LOD	0.248	<LOD	<LOD	<LOD	<LOD	0.596
L5	4.959	0.859	1.424	0.387	0.222	<LOD	<LOD	0.37	1.339	9.56
TL15	1.048	0.267	0.284	0.187	<LOD	<LOD	<LOD	<LOD	<LOD	1.786
TL16	5.749	1.734	2.033	0.362	0.051	<LOD	<LOD	<LOD	0.858	10.787
TL17	<LOD	0.065	0.3	<LOD	0.12	<LOD	<LOD	<LOD	<LOD	0.485
L6	3.323	0.735	2.546	0.469	0.112	<LOD	0.231	<LOD	0.579	7.995
L7	0.639	0.223	0.357	0.243	<LOD	<LOD	<LOD	<LOD	<LOD	1.462
RS1	1.461	1.635	9.462	0.229	<LOD	<LOD	0.22	<LOD	<LOD	13.007
S1	1.372	0.859	7.927	0.202	<LOD	<LOD	<LOD	<LOD	<LOD	10.36
S2	1.657	1.342	6.809	0.313	<LOD	0.174	<LOD	<LOD	<LOD	10.295
TS1	6.444	1.724	7.595	0.256	0.192	0.26	<LOD	<LOD	<LOD	16.471
S3	2.221	0.715	3.709	0.343	0.191	0.234	<LOD	<LOD	6.237	13.65
TS2	3.455	2.185	11.419	0.237	0.186	<LOD	<LOD	<LOD	0.668	18.15
TS3	3.952	2.731	21.386	0.357	0.149	<LOD	<LOD	0.48	<LOD	29.055
TS4	1.353	0.617	5.213	0.231	<LOD	<LOD	<LOD	<LOD	<LOD	7.414
TS5	1.577	1.204	11.662	0.251	0.542	<LOD	0.202	<LOD	0.986	16.424
TS6	1.669	0.844	36.176	0.305	0.691	<LOD	<LOD	<LOD	<LOD	39.685
TS7	1.858	2.617	126.953	0.447	1.817	<LOD	<LOD	<LOD	<LOD	133.692
S4	1.966	1.597	17.37	0.234	<LOD	<LOD	0.22	<LOD	<LOD	21.387
TS8	1.711	0.145	0.499	0.651	<LOD	<LOD	<LOD	<LOD	<LOD	3.006
TS9	2.481	1.984	2.405	1.051	0.158	<LOD	<LOD	<LOD	<LOD	8.079
TS10	1.465	0.101	0.312	0.62	0.182	<LOD	<LOD	<LOD	<LOD	2.68
TS11	1.334	0.088	0.364	0.687	<LOD	<LOD	<LOD	<LOD	<LOD	2.473
S5	1.391	0.136	0.49	0.704	<LOD	<LOD	<LOD	<LOD	<LOD	2.721
TS12	1.547	0.264	0.633	0.625	<LOD	<LOD	<LOD	<LOD	<LOD	3.069
S6	1.394	0.097	1.818	0.616	<LOD	<LOD	<LOD	<LOD	<LOD	3.925

LOD - Limit of Detection

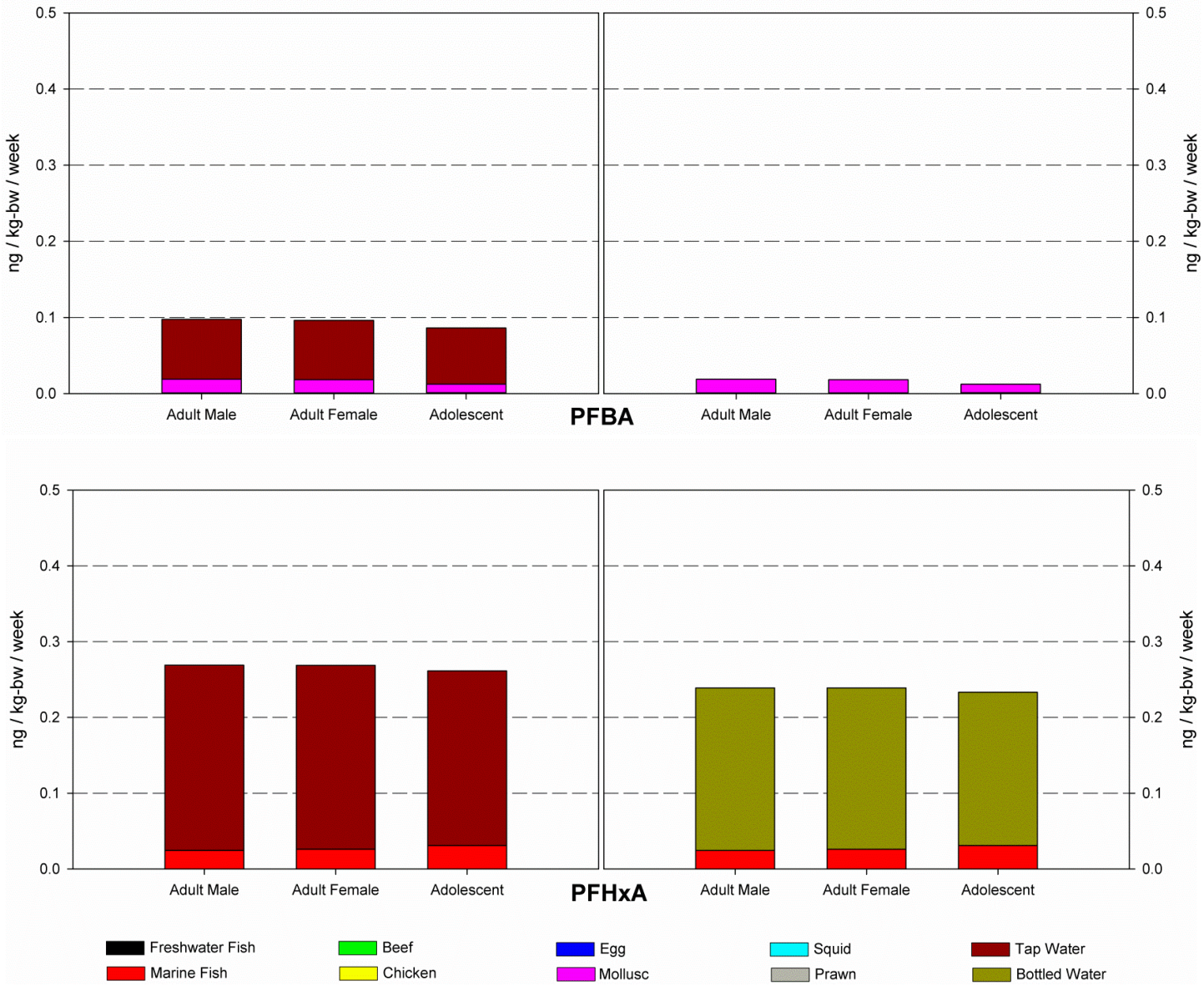
APPENDIX C

Appendix C-1: Concentration of PFAAs in food samples.

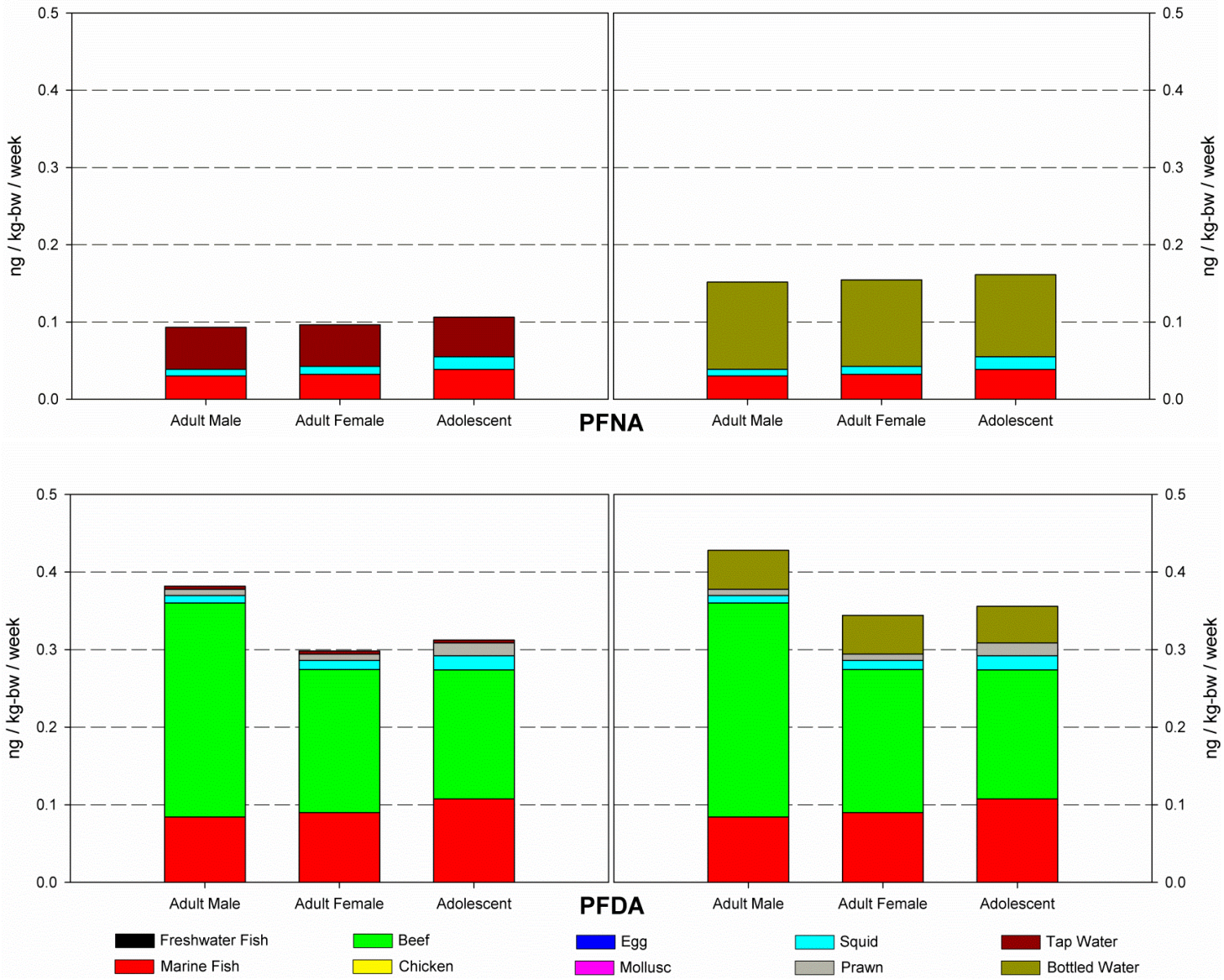
Categories	Samples	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS	PFOS	∑PFAAs
Freshwater fish	FS1	<LOD	<LOD	<LOD	<LOD	<LOD	0.011	<LOD	<LOD	2.240	2.251
	FS2	<LOD	<LOD	<LOD	<LOD	<LOD	0.007	<LOD	<LOD	0.622	0.629
	FS3	<LOD	<LOD	<LOD	<LOD	<LOD	0.007	<LOD	<LOD	0.575	0.582
	FS4	<LOD	<LOD	<LOD	<LOD	<LOD	0.007	<LOD	<LOD	0.354	0.361
	FS5	<LOD	<LOD	<LOD	<LOD	<LOD	0.039	<LOD	<LOD	0.181	0.220
	FS6	<LOD	<LOD	0.007	<LOD	<LOD	0.015	<LOD	<LOD	0.095	0.116
Marine Fish	MF1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.739	0.739
	MF2	<LOD	<LOD	0.019	0.004	<LOD	<LOD	0.028	<LOD	0.089	0.139
	MF3	<LOD	<LOD	0.005	<LOD	<LOD	<LOD	<LOD	<LOD	0.018	0.023
	MF4	<LOD	<LOD	0.014	<LOD	0.037	0.063	0.101	<LOD	0.415	0.630
	MF5	<LOD	0.062	<LOD	<LOD	0.036	<LOD	0.087	<LOD	0.439	0.623
	MF6	<LOD	<LOD	0.040	0.041	0.061	<LOD	0.049	0.073	0.629	0.893
	MF7	<LOD	<LOD	0.023	0.016	0.092	<LOD	0.073	<LOD	0.750	0.954
	MF8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.072	0.072
	MF9	<LOD	<LOD	0.015	<LOD	<LOD	0.047	0.011	<LOD	0.265	0.338
	MF10	<LOD	<LOD	0.010	<LOD	0.024	0.039	<LOD	<LOD	0.981	1.054
	MF11	<LOD	<LOD	0.011	<LOD	0.026	0.034	<LOD	<LOD	3.658	3.729
	MF12	<LOD	<LOD	0.018	0.019	0.038	0.058	0.022	<LOD	1.652	1.808
	MF13	<LOD	<LOD	0.017	0.019	0.032	0.045	0.009	<LOD	3.331	3.454
	MF14	<LOD	<LOD	0.017	<LOD	0.027	0.079	0.014	<LOD	2.297	2.434
	MF15	<LOD	<LOD	0.020	0.018	0.046	0.129	0.018	<LOD	2.880	3.111
	MF16	<LOD	0.050	0.013	<LOD	<LOD	0.034	<LOD	<LOD	0.787	0.883
	MF17	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.713	0.713
	MF18	<LOD	<LOD	0.007	<LOD	<LOD	<LOD	<LOD	<LOD	0.604	0.611
	MF19	<LOD	<LOD	0.026	<LOD	<LOD	<LOD	<LOD	<LOD	0.645	0.671
	MF20	0.004	<LOD	0.017	0.033	<LOD	0.052	0.012	<LOD	0.448	0.565
	MF21	<LOD	<LOD	0.005	<LOD	<LOD	0.055	0.010	<LOD	0.404	0.474
	MF22	<LOD	<LOD	0.007	<LOD	<LOD	0.008	<LOD	<LOD	0.077	0.091
	MF23	<LOD	<LOD	0.015	<LOD	<LOD	<LOD	<LOD	<LOD	0.221	0.236
	MF24	<LOD	<LOD	0.009	<LOD	<LOD	0.030	0.011	<LOD	0.254	0.304
	MF25	<LOD	0.009	0.023	<LOD	<LOD	<LOD	<LOD	<LOD	0.042	0.074
	MF26	<LOD	<LOD	0.010	<LOD	<LOD	<LOD	<LOD	<LOD	0.224	0.234
	MF27	<LOD	<LOD	<LOD	<LOD	<LOD	0.016	0.001	<LOD	0.235	0.252
Beef	B1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	3.610	3.610
	B2	<LOD	<LOD	<LOD	<LOD	0.370	<LOD	<LOD	<LOD	2.306	2.676
Chicken	C1	<LOD	<LOD	0.039	<LOD	<LOD	<LOD	<LOD	<LOD	9.541	9.580
	C2	<LOD	<LOD	0.049	<LOD	<LOD	<LOD	<LOD	<LOD	5.698	5.748
	C3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	2.020	2.020
Egg	E1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.000
	E2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.000
	E3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.000
Mollusk	M1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.029	<LOD	<LOD	0.029
	M2	<LOD	<LOD	0.196	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.196
	M3	0.134	<LOD	0.045	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.179
	M4	<LOD	<LOD	0.079	<LOD	<LOD	<LOD	<LOD	0.051	<LOD	0.131
	M5	<LOD	<LOD	0.057	<LOD	<LOD	<LOD	<LOD	<LOD	0.116	0.173
Squid	S1	<LOD	<LOD	0.014	<LOD	<LOD	0.034	0.012	<LOD	0.170	0.230
	S2	<LOD	<LOD	0.017	0.010	0.012	0.028	0.015	<LOD	0.201	0.283
	S3	<LOD	<LOD	0.064	0.031	0.040	0.074	0.040	0.048	<LOD	0.295
	S4	<LOD	<LOD	0.056	0.045	0.046	0.113	0.038	<LOD	1.350	1.648
	S5	<LOD	<LOD	0.047	0.020	0.031	0.056	0.034	0.029	0.770	0.988
	S6	<LOD	<LOD	0.059	0.040	0.042	0.079	0.037	0.031	1.030	1.319
	S7	<LOD	<LOD	0.045	0.029	0.027	0.046	0.022	0.033	<LOD	0.201
Prawn	P1	<LOD	<LOD	0.005	<LOD	0.017	<LOD	0.013	<LOD	0.297	0.332
	P2	<LOD	<LOD	<LOD	<LOD	0.022	<LOD	0.032	<LOD	0.384	0.438
	P3	<LOD	<LOD	0.014	<LOD	0.024	0.131	0.033	<LOD	0.197	0.399

Appendix C-2: Concentration of PFAAs in bottled and tap water samples.

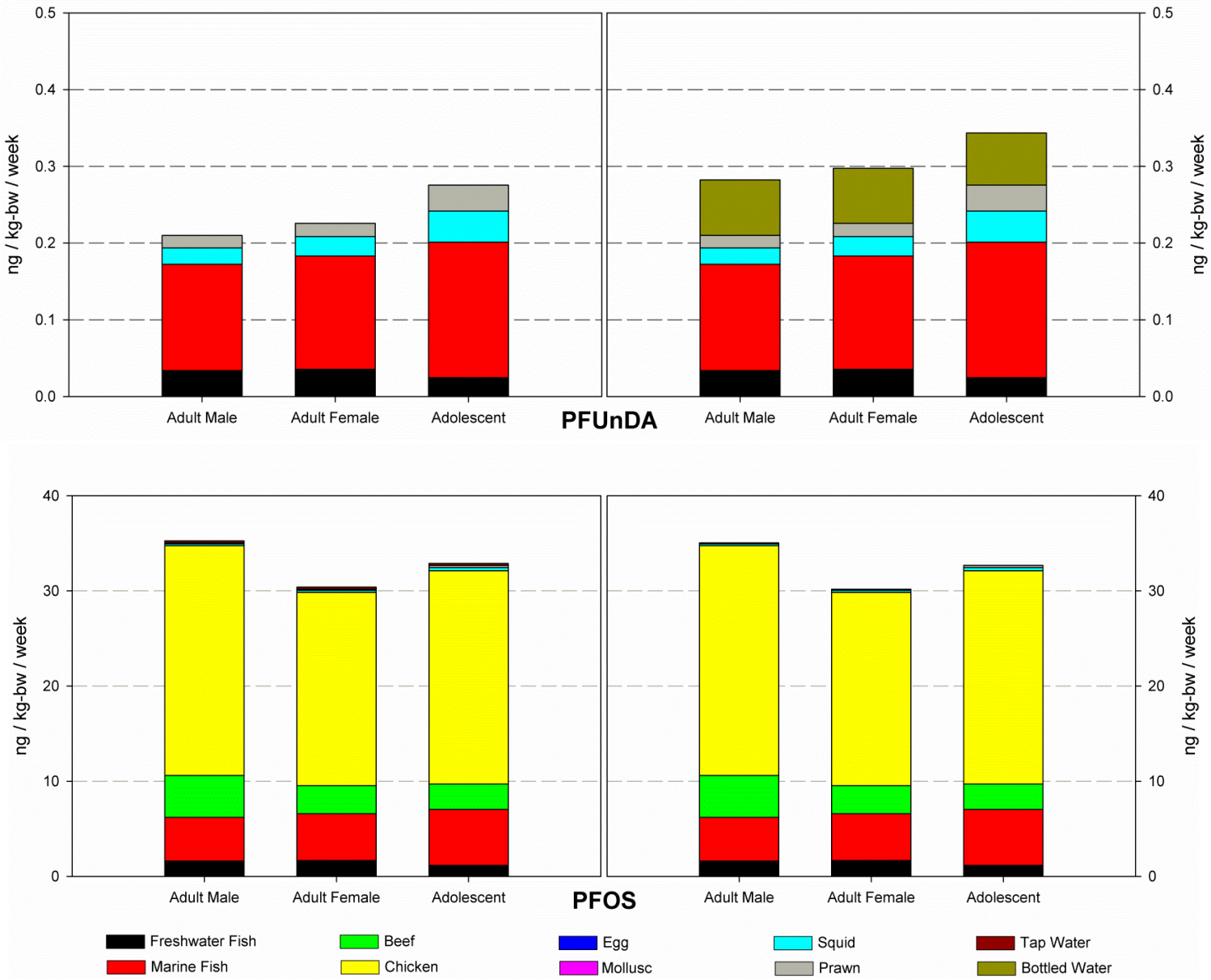
No.	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS	PFOS	∑PFAAs
TW1	<LOD	1.38	0.274	<LOD	<LOD	<LOD	<LOD	<LOD	0.938	2.592
TW2	<LOD	0.1402	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.756	0.8962
TW3	0.268	0.1354	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.4034
TW4	<LOD	1.07	0.33	<LOD	<LOD	<LOD	<LOD	<LOD	3	4.4
TW5	<LOD	<LOD	0.436	<LOD	<LOD	<LOD	<LOD	<LOD	0.652	1.088
TW6	3	0.992	0.364	<LOD	<LOD	<LOD	<LOD	<LOD	1.868	6.224
TW7	<LOD	<LOD	0.384	<LOD	<LOD	<LOD	<LOD	<LOD	0.76	1.144
TW8	<LOD	<LOD	0.436	<LOD	<LOD	<LOD	<LOD	<LOD	1.03	1.466
TW9	<LOD	0.898	0.358	<LOD	<LOD	<LOD	<LOD	<LOD	1.068	2.324
TW10	<LOD	0.968	0.552	0.236	<LOD	<LOD	<LOD	<LOD	0.572	2.328
TW11	<LOD	1.1858	0.726	0.254	<LOD	<LOD	<LOD	<LOD	1.036	3.2018
TW12	<LOD	<LOD	1.054	0.5	0.456	<LOD	<LOD	<LOD	1.53	3.54
TW13	<LOD	3.16	0.792	0.284	<LOD	<LOD	<LOD	<LOD	1.088	5.324
TW14	<LOD	<LOD	0.494	0.258	<LOD	<LOD	<LOD	<LOD	0.85	1.602
TW15	<LOD	4.36	0.938	0.294	<LOD	<LOD	<LOD	<LOD	1.044	6.636
TW16	<LOD	3.52	0.946	0.41	<LOD	<LOD	<LOD	<LOD	1.19	6.066
TW17	<LOD	1.1098	1.268	0.598	<LOD	<LOD	<LOD	<LOD	1.354	4.3298
TW18	<LOD	0.3898	0.764	0.358	<LOD	<LOD	<LOD	<LOD	0.362	1.8738
TW19	<LOD	1.932	1.022	0.374	<LOD	<LOD	<LOD	<LOD	1.11	4.438
TW20	<LOD	0.922	0.8	0.426	<LOD	<LOD	<LOD	<LOD	0.584	2.732
TW21	<LOD	<LOD	0.502	0.202	<LOD	<LOD	<LOD	<LOD	0.452	1.156
TW22	<LOD	1.86	0.698	0.348	<LOD	<LOD	<LOD	<LOD	0.824	3.73
TW23	<LOD	1.32	0.582	0.284	<LOD	<LOD	<LOD	<LOD	0.618	2.804
TW24	0.97	<LOD	0.704	0.254	<LOD	<LOD	<LOD	<LOD	0.358	2.286
TW25	3.86	<LOD	0.292	0.274	<LOD	<LOD	<LOD	<LOD	0.1888	4.6148
TW26	<LOD	1.48	0.706	0.436	<LOD	<LOD	<LOD	<LOD	0.72	3.342
TW27	0.647	0.45	0.396	0.273	<LOD	<LOD	<LOD	<LOD	<LOD	1.766
BW1	<LOD	6.33	<LOD	1.692	1.248	0.95	<LOD	<LOD	<LOD	10.22
BW2	<LOD	1.482	<LOD	0.857	0.62	0.845	<LOD	<LOD	<LOD	3.804
BW3	<LOD	<LOD	<LOD	0.592	<LOD	0.89	<LOD	<LOD	<LOD	1.482
BW4	<LOD	<LOD	0.423	0.836	<LOD	<LOD	<LOD	<LOD	<LOD	1.259
BW5	<LOD	<LOD	0.902	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.902
BW6	<LOD	0.162	0.373	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.535
BW7	<LOD	<LOD	0.259	0.218	<LOD	<LOD	<LOD	<LOD	<LOD	0.477
BW8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
BW9	<LOD	<LOD	4.28	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	4.28



Appendix C-3: Comparison of EWI among the population in Klang Valley in two scenarios. Scenario1 (left figure) – foods and tap water consumption; Scenario2 (right figure) – foods and bottled water consumption



Appendix C-3: continued



Appendix C-3: continued.