DETERMINATION OF PERFLUOROOCTANOIC ACID (PFOA) AND PERFLUOROOCTANE SULFONATE (PFOS) IN WATER SAMPLES OF LANGAT RIVER

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1. Introduction

Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are both perfluorinated compounds which contained 8 carbon atoms with fluorine molecule attached as a substitute of hydrogen. There are valuable properties of fire resistance, oil, stain and grease repellant. Their wide-range application as surfactants (So *et al*, 2004), food packaging (Moody *et al*, 2002), fire-fighting foams (Moody *et al*, 2002), leather (Tseng *et al*, 2006), surface coatings for carpets, furniture and paper products (Yamashita *et al*, 2005) as well as their characteristics which are persistence, bioaccumulative and toxic makes them an ubiquitous contaminants that are currently received worldwide attention.

Perfluorinated compounds (PFCs) have been found in many environmental matrixes such as in air (Martin *et al*, 2002) and biota (Tanisayu *et al*, 2005), surface water (Scott *et al*, 2006), wastewater (Boulanger *et al*, 2005), drinking water (Harada *et al*, 2003, seawater (Yamashita *et al*, 2004) and rainwater (Loewen *et al*, 2005). PFOA and PFOS are the most studied PFCs in most countries. However, to our knowledge there are no study concerning PFOA and PFOS in Malaysia. This is a pioneer work relative in studying PFCs in Malaysia.

This study is conducted as a baseline in analyzing PFOA and PFOS in Malaysia. This will provide a current scenario on the PFOA and PFOS contamination in Malaysian river water ecosystem. Methods used were combined and modified for feasibility and accessibility purposes. The methods modifications consist of during sample preparation, extraction and LC/MS/MS analysis.

2. Objectives

i) To optimize the method of analyzing PFOA and PFOS in river water samples.
ii) To identify the current concentrations of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) in Langat River.
iii) To determine the distribution of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) in water environments of Langat River.

3. Research Methodology

3.1. Sampling location

105 water samples were collected from 35 stations along Langat River in the west coast of Peninsular Malaysia in May 2009 (Figure 1). The samples were taken following against river flow which is from the downstream to upstream (S0 – S35). 3 replicates of

the water samples were taken from each of the station. Most of the samples taken were concentrated in the upper stretch. This is due to the domination of population and massive human activities in the upper stretch compare to the middle and lower stretches.

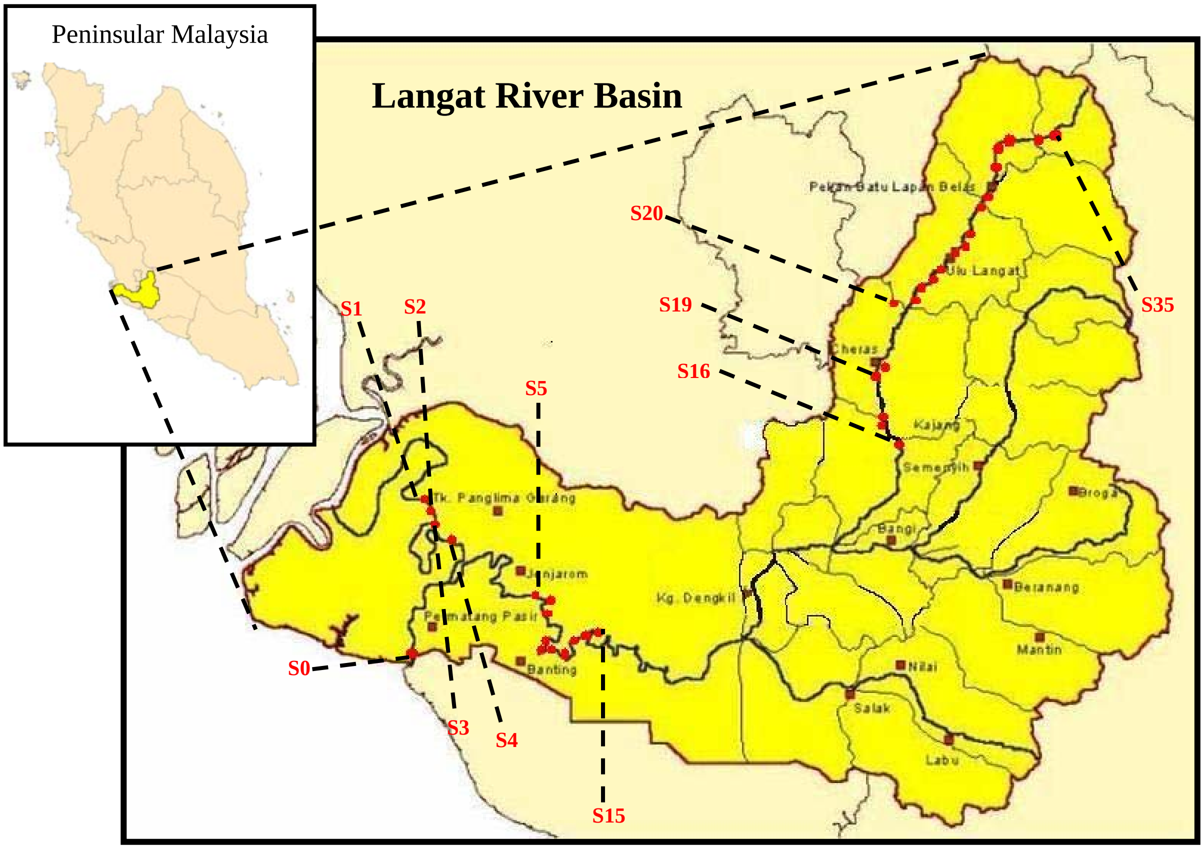

Figure 1. Map of the sampling sites in the Langat River.

Figure 1. Map of the sampling sites in the Langat River.

3 Liters of surface water were taken by using stainless steel bucket and stored individually in 1 Liter PP containers with screw caps. Each of the samples was sealed separately in zip-lock plastic bags and stored on ice in a cooler. Whenever possible, the samples were extracted within 24 hours or else they were refrigerated at ±4°C once they were returned to the laboratory.

Along with each sample collection, several field parameters were logged. The parameters were latitude and longitude by GPS, river flow, pH, conductivity, dissolved oxygen, water temperature, turbidity and general remarks about weather and site conditions.

In addition to the one hundred and five water samples, quality control (QC) samples were also collected. On the whole, ten matrix blanks were collected which were Mili-Q water filled in 1L PP bottle prior to sampling exposed to the same conditions as the samples and treated as the real sample.

3.2 Analytical procedure of PFOA and PFOS

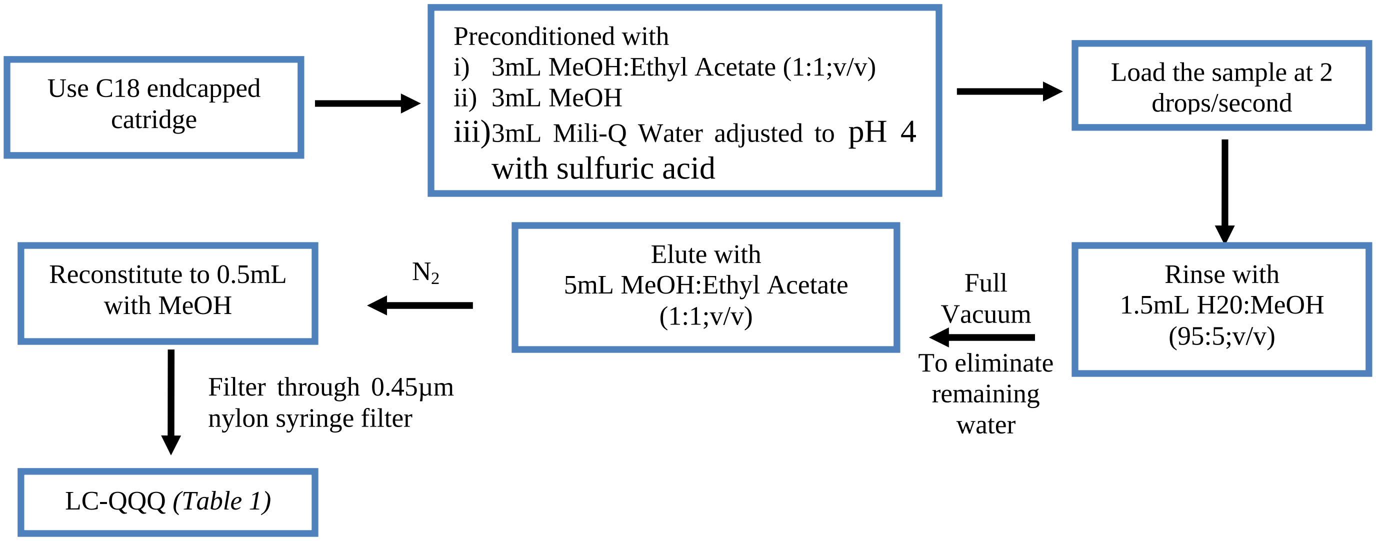

Table 1 Optimized LC/MS/MS Condition

HPLC	
Instrument	Agilent 1100 HPLC
Column	Agilent Eclipse Plus C-18
Guard column	2.1 mm x 12.5 mm, 5 µm C-18
Mobile phase	A: 10 mM CH_3COONH_4/H_2O; B:CH_3CN
Flow rate	0.2 mL/min
Column temperature	40°C
Injection volume	10 µL
MS	
Instrument	Agilent Triple Quadrupole Mass Spectrometer
Ionization	Electrospray Ionization (ESI)
Polarity mode	Negative (-ve)
Nebulizing gas	N_2 (90L/h)
Collison gas	N_2
Gas temperature	350°C
Scan type	Multiple Reaction Monitoring (MRM)
Total run-time	16 minutes

The mobile phase was a gradient prepared from 10 mM amonium acetate as component A and acetonitrile as component B. It started with 55% B for first 2 min, followed by linear gradient application to increase B to 95% during next 7 min, and finally changed back to 55% B during last 0.5 min.

Analyte identification is verified by comparison of chromatographic retention time, by mass spectral daughter characterization, and by selecting additional ion pair transitions. Retention times, monitored transitions for quantification and confirmation of the investigated PFCs, were listed in Table 2.

Table 2 Retention times, monitored transitions for quantification and confirmation of the investigated PFCs

Compound[a]	Molecular formula	t^R(min)	Precursor ion (m/z)	Product ion (m/z)	Collision Energy (eV)
PFOA	$C_7F_{15}CO_2H$	1.7	413.0	369.0	10
PFOS	$C_8F_{17}SO^{-3}$	2.7	499.0	130.0[b]	43
				230.0[c]	37
[$^{13}C_4$-PFOS]	$^{13}C_4C_4HF_{15}O_2$	1.7	417.0	372.0	10
[$^{13}C_2$-PFDA]	$^{13}C_2C_8HF_{19}O_2$	2.4	515.0	470.0	10

a Acronym
b Used for quantification
c Used for confirmation

3.3 TOC Analysis

The TOC analytical procedure used was performed with TOC Analyzer. Briefly, the samples were kept at 4°C or less in the refrigerator. Then, they were filtered with 45 µm glass microfiber filter (Whatman, England) before been loaded to the auto sampler.

3.4 Validation of analytical method

The validation procedures comprised determination of linearity, limit of detection (LODs), limit of quantification (LOQs), procedural blanks, surrogate recoveries, and the study of matrix effects. Perfluorooctanoic acid (PFOA, ammonium salt, >98%) and perfluorooctane sulfonate (PFOS, potassium salt, >98%) (Sigma Aldrich) were used to make standard solutions.

Both calibration curves of PFOS and PFOA range from 0.05 to 1 ng/ml and extraction standard curves showed linearity with high determination coefficients ($R^2 > 0.999$). PFOA and PFOS-spiked samples of Mili-Q water is analyzed according to the same procedure with environmental samples. Percentage recoveries ranged above 50% of the expected value (100%) for spiking concentrations of 10, 50 and 100 ng/L.

Limit of detection was set at signal-to-noise ratio of 3:1 whereas the limit of quantification (LOQ) was defined by signal-to-noise ratio of above 10. Measurement of Mili-Q water is always conducted, as the blank control, following the same procedure as for environmental samples.

3.5 Statistical Analysis

Least significant difference (LSD) test and analysis of variance (ANOVA) were performed to determine any significant differences in PFOA and PFOS concentrations in the water samples. When the p values were lower than 0.05, the differences were considered significant. Prior to the analysis the data was inspected for homogeneity of variance (Levene test). A correlation between means of PFOA, means of PFOS concentrations in water samples and TOC was tested. A hierarchical cluster analysis based on PFOA and PFOS concentrations was tested to determine the sources of PFOA and PFOS. All statistical calculations were carried out by using Statistic 5.0 for Windows.

4. Results

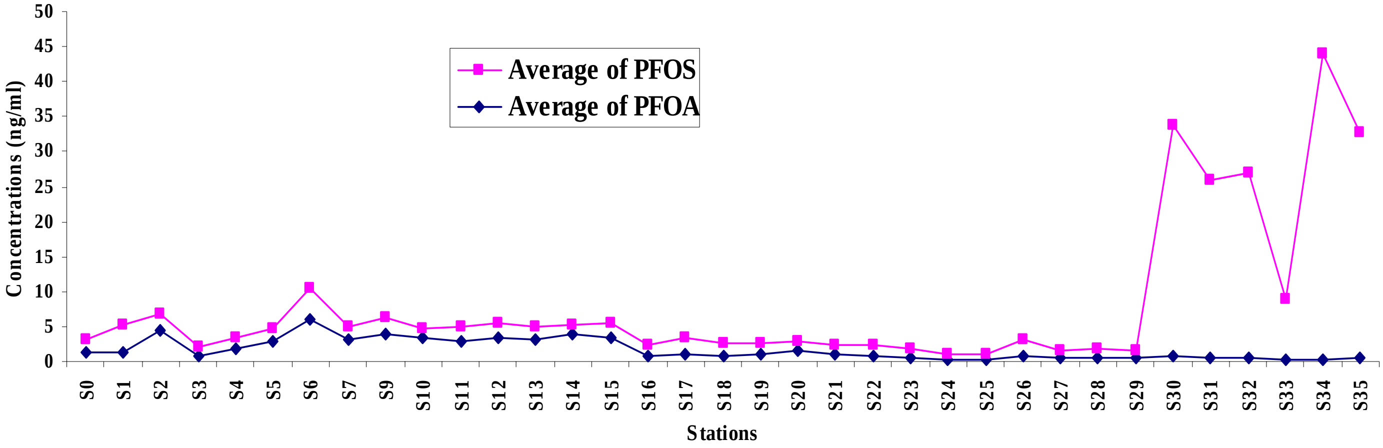

Figure 2. Average PFOA and PFOS concentrations (ng/ml) in Langat River waters

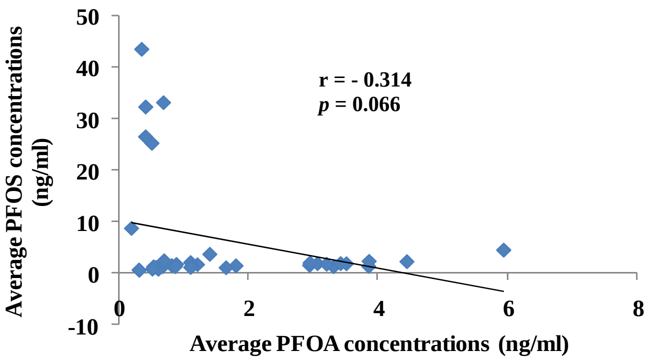

Figure 3. Correlation between average PFOA and PFOS concentrations in the water samples from Langat River.

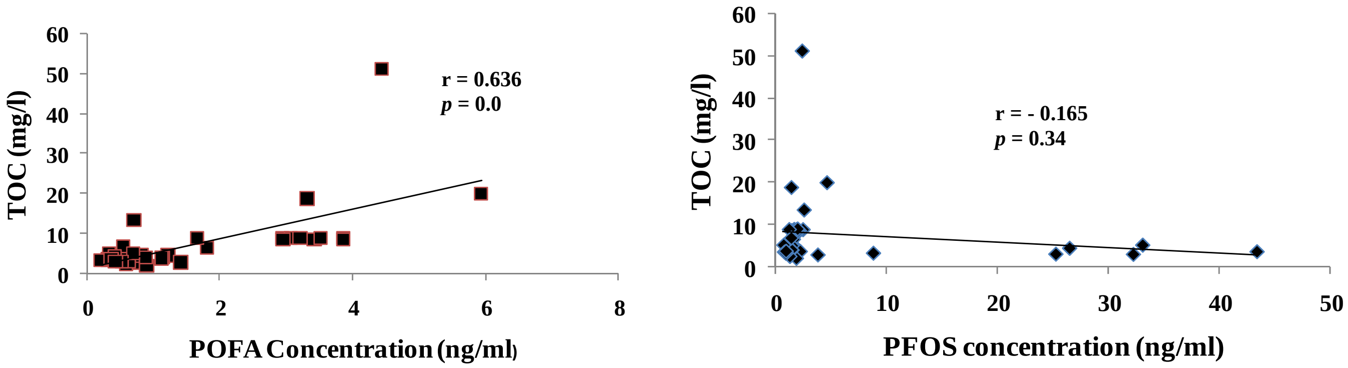

Figure 4. Correlation between average PFOS and PFOA concentrations and average TOC concentrations in the water samples from Langat River.

PFOA concentration (ng/ml)

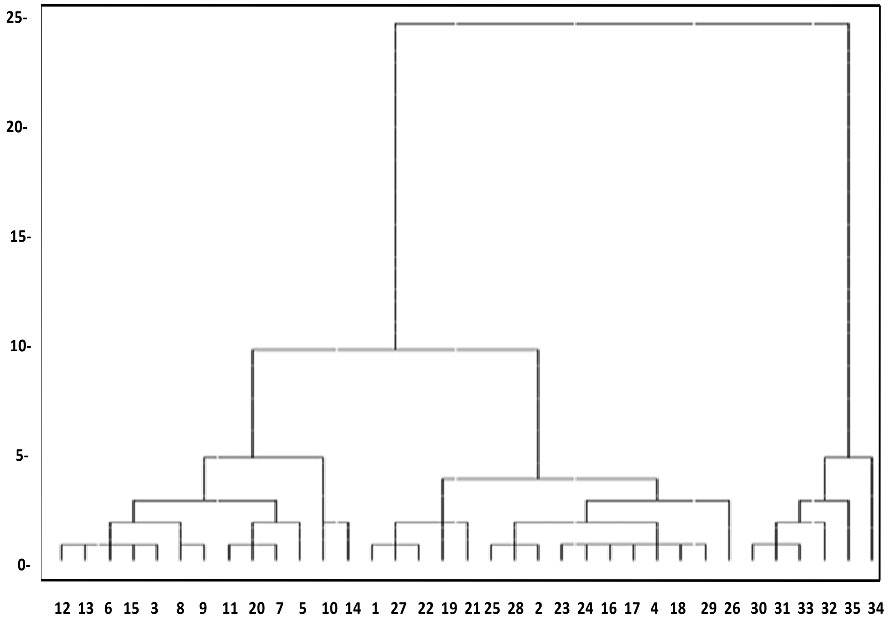

Figure 5. Dendrogram for water samples from the stations 1-35, according to their average PFOA and PFOS concentrations after hierarchical cluster analysis. Numbers indicate the stations (1-35)

5. Significance of Findings

In this study, method of analyzing PFOA and PFOS in Malaysian river water sample was optimized. This will provide feasibility and accessibility in analyzing the emerging contaminants and identifying the current concentrations in the study area. Samples were collected along Langat River concentrating in more dense area providing the contribution of the populated area in polluting the river ecosystem.

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