

## Determination of PAHs in Selected Sampling Location in Langkawi Island, Malaysia

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Received date: December 10, 2013; Accepted date: February 4, 2014; Published date: February 11, 2014

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### Abstract

Surface seawater samples were collected from five selected sampling locations in the Langkawi Island during the northeast monsoon season in March 2013. Water samples were extracted by using two different solid phase microextraction (SPME) fibers followed by gas chromatography with flame ionization detector (GC-FID) analysis. Naphthalene compound (2-rings) indicated no significant different ( $p>0.05$ ) extracted by using 65  $\mu\text{m}$ -PDMS-DVB and anthracene compound (3-rings) extracted by using 85  $\mu\text{m}$ -PA fibers. The average spike recovery for PAHs ranged from 64.8 to 94.0%. Total PAH concentration ( $\Sigma 3$  PAHs) ranged from 10.79  $\mu\text{g/mL}$  to 369.28  $\mu\text{g/mL}$  which exceed the maximum admissible concentration of PAHs (0.0002  $\mu\text{g/mL}$ ) for the water standard of European Union. The result revealed that the surface seawater around the Langkawi Island was highly contaminated by PAHs. The high concentration of PAHs may be due to extensive port associated activities.

**Keywords:** Surface seawater; SPME; GC-FID; PAHs

### Introduction

The coast of Peninsular Malaysia is significant for recreational, tourism, fisheries, marine activities and maintaining the bio-diversity in the tropical region. However, the coast is now faced with constants threat of extensive environmental pollution [1]. Langkawi island situated in the straits of Malacca, North West of Peninsular Malaysia targeted for ecotourism faced with extensive marine pollution [2]. To cater with the boost in tourism-related activities which almost 3.06 million tourist visited Langkawi in 2012, the local population increased significantly from 40,000 in 1991 up to 150,000 in 2012 [3]. Numerous boating and shipping activities which directly discharge the petroleum-based products into the ocean would contribute towards the significant of organic pollutant especially polycyclic aromatic hydrocarbons (PAHs).

PAHs are hydrocarbon consisting of two or more fused benzene rings made up of carbon and hydrogen atoms [4]. Sixteen PAH compounds have been identified as priority pollutants by USEPA due to their toxic, mutagenic and carcinogenic characteristic [5].

They are classified as unique class of persistent organic pollutants (POPs) which can be divided into two groups based on their physicochemical properties [6]. Two- and three-rings PAHs such as naphthalenes, fluorenes, phenanthrenes and anthracenes are categorized as low-molecular weight (LMW), have significant acute toxicity to aquatic organisms while, four- to seven-rings starting from chrysenes to coronenes known as high-molecular weight (HMW) of PAHs, are carcinogenic [7]. Due to their low in water solubility and high lipophilicity, PAHs tends to rapidly absorbed by organism and be accumulated in aquatic organism. On the other hand, they are susceptible to adsorb on the surface of particles present in surface

waters in the form of suspended matter, get deposited in sediment and be passed onto the marine food chain.

PAHs are widely distributed in the environment due incomplete combustion of organic material, from both natural and anthropogenic activities. Sources of PAHs can be either petrogenic usually comes from the direct input of petroleum and its product or pyrogenic originated from the incomplete combustion of diesel fuel and engine oil [8]. Pyrogenic also resulted from the biomass burning, forest fires, internal combustion engines, industrial operations and garbage incineration [4]. In the marine environment, sources of PAHs can be resulted from the atmospheric deposition which tends to include combustion of fossil fuels, gasoline, refuse and wood that emitted to the atmosphere and return into aquatic system via the deposition and precipitation [9]. The most abundant sources of PAHs in surface water come from sea-based sources such as two-stroke vessel discharge, operational discharge, aircraft dumping and nontank vessel spills [10]. Research carried out on the surface seawater from seven locations in Langkawi showed that PAHs inputs mostly resulted from incomplete fuel combustion of boats and vehicle engines contribution from petrogenic sources [11].

Currently screening of semivolatile organic compounds in water matrices require a preconcentration step such as liquid-liquid extraction (LLE), solid phase extraction (SPE) and solid phase microextraction (SPME). LLE is a very useful classical technique, but it is laborious, time consuming and requires large amounts of frequently toxic organic solvent [12]. While, SPE consumes less solvent and time, but reproducibility and recovery are often problematic for complex matrix especially seawater [12]. Recently, a new solvent-free technique, SPME is useful for extraction of volatile and semi volatile samples such as polychlorinated biphenyls (PCBs), BTEX and other substituted benzene and PAHs from water samples [13,14]. SPME only requires only small amounts of samples for analysis and advantages in improving detection limits [12].

The most important characteristic determining the performance of SPME is based on fiber selection which largely depends on their type and thickness of coating material. Non-polar coating such as polydimethylsiloxane- divinylbenzene (PDMS/DVB) are considered to be more efficient for analysis of non-polar compound PAH, whereas highly polar coatings of polyacrilate (PA) are more suited for extracting polar analytes [13,14]. The other parameters such as sample agitation, sampling type (immersion vs headspace), salting out and extraction temperature may also play important role for extracting PAHs [12-14].

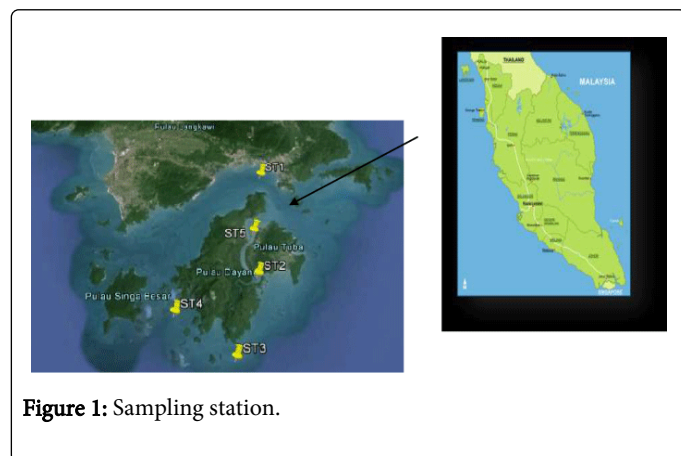
Therefore, the purpose of this study is to determine the efficiency of two fibers with different polarity for extracting low-molecular weight (LMW) of PAHs and its concentration in the Langkawi Island surface seawater.

## Methodology

### Study area

Sampling station was selected judgmentally based on the assumption about movement and distribution of PAHs sources with distance, time, fate and transport. Surface seawater were sampled from five stations as shown in Figure 1 and Table 1 show their coordinate, characteristic and observed anthropogenic activities take place in selected areas.

Sample preservation and storage was carried out by using Method 550.1 [15]. One litre (1L) surface seawater samples were collected directly by using pre-cleaned amber glass bottles or sealed with aluminium foil to avoid photooxidation. The pH of samples was adjusted to <2 with HCl and kept at 4°C in ice during transportation and cool at -4°C until analysed.



**Figure 1:** Sampling station.

Station(ST)	Coordinate	Characteristic/activities
ST1	06°18'26.43"N	Situated in front of Kuah jetty, served as the main pathway for boats and ferries.
	99°50'12.92"E	
ST2	06°13'2.9"N	Located in near to Dayang Bunting's Lake and several fishing boats observed.
	99°49'40.48"E	
ST3	06°09'24.09"N	Near to Ujung Buluh Island, located on the open sea where numerous shipping activities observed.
	99°48'34.13"E	

ST4	06°11'21.62"N	Situated on the open sea where port associated activities take place.
	99°46'09.74"E	
ST5	06°15'13.14"N	Located near to Tuba's Island Jetty and served as the main pathway for fishing boats
	99°49'38.16"E	

**Table 1:** Sampling coordinates and characteristic or activities.

### Reagent and Materials

The standard mixture of 3 PAHs such as naphthalene,fluorine and anthracene at a concentraion of 2000 µg/mL in methylene chloride-benzene (1:1 v/v) were prepared. These standards were stored at 4°C and were used for the preparation of working standards at 20 µg/mL in acetone. In general, PDMS/DVB and PA fibers with 65-µm and 85-µm thickness was used respectively. Both fibers were conditioned in the hot injector part of GC at 250-300°C before used.

The glassware used in this study was first washed with Decon detergent and with deionized water followed by placing them in cleaning solution overnight to remove all trace amounts of organics on the surface of glass bottles and vials. The glassware was then rinsed with deionized water and acetone and dried in the oven before use. For SPME, the vials were soaked overnight in a 10% (v/v) of dichlorodimethylsilane in toluene. Finally, the vials were rinsed with toluene and methanol before oven-dried.

### Solid phase microextraction (SPME) procedure

The extraction of seawater samples was performed according to Doong et al. [13]. SPME were performed by placing samples in 10-mL amber vials capped with PTFE-coated septa and then spiking the working standards at final concentration 10 µg/mL. Magnetic stirrer with 1-cm long was used to agitate the solution at 800 rpm at 80% of the maximum speed of the stirrer.The SPME equilibrium was conducted by immersing the fiber into aqueous phase (direct SPME) with stirring at room temperature for 30 minutes to allow analytes sorb on the stationary phase of the fibers. After extraction, the fibers were thermally desorbed for 5minutes in the GC injector port at 270°C (PDMS/DVB) and at 320°C (PA).

### Apparatus and analysis

Analysis of PAHs was carried out by using Agilent Technologies 6890N gas chromatography-flame ionization detector (GC- FID) with split-splitless injection port. The carrier gas was nitrogen at a flow rates of 3 mL/min. The detector flow-rates were 350 mL/min for air, 35 mL/min for hydrogen and 30 mL/min for nitrogen (makeup gas). The gas chromatograph was operated in the splitless mode with splitless time 5 minutes. The column was held at 40°C for 5 minutes, increased to 180°C at a rate of 20°C/min and again ramped to 250°C at a rate of 4°C/min, then increased the Temperature to 270°C at a rate 2°C/min and finally ramped to 320°C at a rate of 10°C/min and then held for 2 minutes.

## Result and Discussion

### Spike recovery

Spike recovery for all surface seawater samples ranged from 64.8% to 94.0%. Naphthalene showed the highest spike recovery with 65 µm-

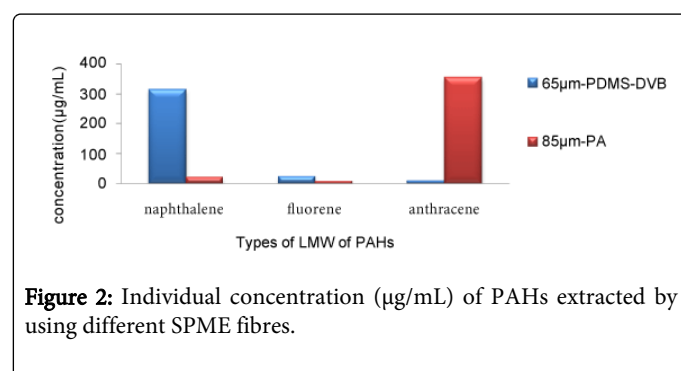
PDMS-DVB while, anthracene showed the most abundant using 85  $\mu\text{m}$ -PA fiber. Thus, PDMS-DVB fiber can be considered too has high efficiency for extracting naphthalene and PA fiber has high efficiency for anthracene. This indicates that, the data obtained in this study were considered to be remarkably reasonable and SPME can be used as an effective technique in extracting 2-3 rings of PAHs.

### Fiber selection

Two types of fibers with different polarity were employed in this experiment to compare their efficiencies for extracting LMW of PAHs such as 2-rings naphthalene, 3-rings fluorene and anthracene in aqueous phase. The individual concentration ( $\mu\text{g/mL}$ ) of PAHs extracted by using different SPME fibers is shown in Table 2 and Figure 2. Overall result indicated that the LMW of PAHs with different number of rings showed different physicochemical properties. For example, naphthalene fall into the non-polar class with relatively high-octanol-water partition coefficients showed the most abundant when extracting by using PDMS-DVB fiber which approximately 313.14  $\mu\text{g/mL}$ . Essentially, statistical analysis by T-test gave no significant difference ( $p>0.05$ ) of naphthalene with this fibre. This showed that the DVB coating used showed a good sorption of non-polar 2-rings PAHs compound. Thus, this analyte would be expected to partition readily into a more non- polar fiber coating rather than a polar one. Comparable to fluorene (2-rings) and anthracene (3-rings) indicated the significant difference ( $p<0.05$ ) when extracting by using this non- polar coating fiber. They recorded lower concentration of 24.39 and 9.40  $\mu\text{g/mL}$ , respectively. The result showed that as the number of rings and polarity increases, the extraction efficiency of PDMS-DVB fibre tends to decrease. This result was corresponding as was proposed by Doong et al. [13].

Fibers	PDMS-DVB	PA
PAH		
Napthalene	313.14	21.57
Fluorene	24.39	8.65
Anthracene	9.4	353.62

**Table 2:** Individual concentration ( $\mu\text{g/mL}$ ) of PAHs extracted by using different SPME fibers



**Figure 2:** Individual concentration ( $\mu\text{g/mL}$ ) of PAHs extracted by using different SPME fibres.

On the contrary, PA fiber showed an increase in signal response to anthracene relative to the PDMS fiber with approximately 353.62  $\mu\text{g/mL}$  same as proposed by Doong et al. [13]. The T-test analysis indicated no significant difference ( $p>0.05$ ) of anthracene and there is

significant difference ( $p<0.05$ ) for naphthalene and fluorene with this PA fibre. The polarity of PAHs compound tends to increase with the increase in the number of rings, thus causing the polar analyte especially anthracene to partition readily into the polar coating fiber. In addition to that, thickness of PA fiber also acts as a contributing factor that improves the extraction efficiencies of LMW of PAHs. In other words, the high amount of PAHs compound can be extracted with increasing of coating thickness same as stated by Doong et al. [13].

As a conclusion, PDMS-DVB fiber showed to has high affinity of extracting 2-rings naphthalene compared to PA fiber which demonstrating to has high sorption of 3-rings anthracene.

### Concentration of PAHs in surface seawater

The surface seawater samples were collected during the northeast monsoon on March 2013 in selected sampling location in Langkawi Island and analysed by GC-FID. The distributions of individual and total mean concentration of PAHs in surface seawater at different stations are presented in Table 3. The mean concentration of individual PAHs in all samples ranged from 2.17 to 275.23  $\mu\text{g/mL}$ . These are higher than the Annual Average Environmental Quality Standards of European (AA-EQS) Water Framework Directive (WFD) for individual PAHs stated at the safe range of  $2.0 \times 10^{-5}$  to  $2.4 \times 10^{-3}$   $\mu\text{g/mL}$  [16].

Stations	ST1	ST2	ST3	ST4	ST5
PAHs					
Naphthalene	7.91	46.25	258.98	ND	21.57
Fluorene	2.88	5.48	22.51	2.17	ND
Anthracene	ND	ND	87.79	275.23	ND
Total PAHs	10.79	51.73	369.28	277.4	21.57

**Table 3:** Individual and total mean concentrations ( $\mu\text{g/mL}$ ) of PAHs in surface seawater at different sampling stations. \*ND: non-detected

This is may be due to physicochemical properties of low molecular weight of PAHs in which their solubility decreases with increasing in the number of rings [7]. Thus, it is served as the reason of most frequently detected individual PAHs in Langkawi was naphthalene due to its high solubility in water compared to the other two which is fluorene and anthracene. The individual concentration of PAHs for naphthalene and fluorene are also higher than that stated by Government of British Columbia (1993) at 0.001 and 0.012  $\mu\text{g/mL}$ , respectively [17].

Besides that, the total PAHs concentration in March from all the sampling station ranged from 10.79 to 369.28  $\mu\text{g/mL}$ . The highest total concentration of PAHs approximately 369.28  $\mu\text{g/mL}$  was found in ST3 which located in the open sea near to the Teluk Nangka. In this station, the major sources of PAHs may contribute from the extensive shipping activities and deposition of fuel combustion of boats observed. The higher concentration of 277.4  $\mu\text{g/mL}$  also showed by ST4 which also located in the open sea where it serves as the main pathway for the shipping activities. The operational shipping activities such as deballasting, tank cleaning, cargo loading and unloading may contribute towards the present of these hydrocarbons in both station as proposed by Wattayakorn [18]. Whereas, the lower concentration

was showed by the others three station due to their geographical location that situated in closed straits. Based on these three stations, the total concentration at ST1 was expected to be the highest due to its unique location situated in front of Kuah Jetty where it serves as the main route for the ferries and boats with two stroke engine. However, the lowest concentration shown by this station may be due to the photodegradation of PAHs that can converted into humic substance which serve to absorb a lot of radiation energy in the UV range as proposed by Bertilsson [19]. In addition to that, Uthe [20] stated that two and three-ringed PAHs potentially to be biodegraded faster by PAH-degrading organism. Notably, ST5 and ST2 showed the lower concentration were situated near to Tuba Island's fish farm and Dayang Bunting Lake. The main sources at both stations may come from the direct discharge of effluent water from the residential area and fewer boating activities as supported by McIntosh et al. [21]. The total average concentration of LMW of PAHs observed for all sampling station are significantly higher than the maximum admissible concentration of the European Union and the Environmental Quality Criteria of the United States which is 0.0002 and 0.00003 µg/mL, respectively [22]. Both the admissible concentration is applicable for the protection of human consumers of aquatic life. In addition to that, water with total PAHs concentration greater than 0.01 µg/mL can be ranked as heavily contaminated by PAHs pollutants [23]. In as much as all the sampling stations recorded the total concentration of PAHs are more than 0.01 µg/mL which showed that they are highly polluted by LMW of PAHs. Thus, it may cause certain organism especially fish in this area which serves as the main food chain to the human are likely to have been exposed to rather high levels of PAHs during their life time.

### Comparison study

The comparative of present study in PAHs concentration in surface seawater collected from Langkawi island waters were compared with several previous studies as demonstrated in Table 4. The present study of PAHs concentration in the surface seawater of Langkawi Island ranged from  $10.79 \times 10^3$  to  $369.28 \times 10^3$  µg/L. In general concentration of PAHs in the present study was one to two orders higher than the previous study in different locations and up to three orders higher than the study conducted by Nasher et al. [11]. The high concentration of PAHs showed by present study may be due to extensive boating activities for tourism during the peak season where Langkawi Island act as a host for LIMA's event last March. The numerous associated port activities such as shipping activities that take place in the open sea near to this island may also contribute the sources of PAHs during the operational activities as proposed by Nasher et al. [11]. It also contributed from the direct discharge of petroleum products as well as the dry and wet deposition of fuel combustion. Since Langkawi was situated on the Straits of Malacca, the sources may not only comes from the island itself but also from the others location nearby such as Indonesia and Gulf of Thailand [4,18,26]. There is an increasing trend of distribution of PAHs from oil spills over the last two decades. It was reported over 200 oil spill incidents from seven oil refineries in Thailand occurred along oil transport routes at the mouth of the main entrance to the Bangkok Port as reported by Wattayakorn [18].

Besides, Jakarta Bay that was affected by both petrogenic and pyrogenic sources due to extensive growth of industry and motor vehicles as stated by Rinawati et al. [4] also may contributed the pathway of PAHs to this island. Moreover, inland and offshore oil-fields in Sumatra Island and extensive deballasting that take place in the South China Sea also may contributed the oil pollution in Straits of

Mallaca and passed to Langkawi Island [1,18]. According to the Malaysia Environmental Quality Report (2006) by Department of Environment, Langkawi Island was ranked as the third highly polluted areas by oil and grease among the fifteen monitoring station in Peninsular Malaysia that exceeded about 80% of water quality standard, thus can serve as the main reason of its high in concentration comparable to the other locations [3].

Reference	Locations	Concentration (µg/L)
Tronczynski et al.[24]	Bay of Biscay,France	$3.4 \times 10^1$ - $1.1 \times 10^3$
Zrafi-Nouira et al. [25]	Mediterranean sea	$2.8 \times 10^3$ - $7.6 \times 10^3$
Wang et al. [26]	Yellow river delta, china	$6.6 \times 10^1$ - $6.8 \times 10^2$
Nasher et al. [12]	Langkawi Island, Malaysia	$6.1$ - $4.6 \times 10^1$
Present study	Langkawi Island, Malaysia	$1.08 \times 10^4$ - $3.69 \times 10^5$

**Table 4:** PAHs concentration (µg/L) reported in the surface seawater in different areas of the world.

### Conclusion

This study has provided important data about PAHs concentration, distribution and sources in seawater of the Langkawi Island, Malaysia. Total PAHs concentration varied from 10.79 to 369.28 µg/mL in surface seawater. The levels of PAHs in seawater were comparable to those found in many other marine systems from different areas. The PAHs group profile demonstrating that the predominance 2-3 rings of PAHs in which naphthalene showed the most significant when using PDMS-DVB fibers while anthracene extracted most abundance by using PA fiber. All low molecular weight (LMW) of PAH detected is significantly higher than the maximum admissible concentration of the protection of human consumers of aquatic life.

### References

1. Zakaria MP, Okuda T, Takada H (2001) Polycyclic Aromatic Hydrocarbon (PAHs) and hopanes in stranded tar-balls on the Coast of Peninsular Malaysia: Application of Biomarkers for Identifying Sources of Oil Pollution. Mar Pollut Bull 42: 1357-1366.
2. DOE, Malaysia Environmental Quality Report, 2005, 2006.
3. Samat N (2010) Assessing land use land cover changes in Langkawi island: towards sustainable urban living. Malaysian J Environ Manag 11: 48-57.
4. Rinawati, Koike T, Koike H, Kurumisawa R, Ito M et al. (2012) Distribution, sources identification and historical trends of organic micropollutants in coastal sediment in Jakarta Bay, Indonesia. J Hazard Mater 208-216.
5. Gao Guanfa, Hou Yizhuang, Wang Zhong (1999) The development of enrichment technology of trace polycyclic aromatic hydrocarbons in water. Environ Shandong (in Chinese) 3: 30-31
6. Martinez E, Gros M, Lacorte S, Barceló D (2004) Simplified procedures for the analysis of polycyclic aromatic hydrocarbons in water, sediment and mussels. J Chromatogr A 1047: 181-188.
7. Neff JM (1979) Polycyclic aromatic hydrocarbons in the aquatic environment: sources, fates and biological effects. Applied Science Publishers, London, UK.
8. Szewczynska M, Posniak M, Dobrzynska E (2013) Study on individual PAHs content in ultrafine particles from solid fractions of biodiesel exhaust fumes.



9. Latimer JS, Zheng J (2003) PAHs: an ecotoxicological perspective. The sources, transport and fate of PAHs in the marine environment. PAHs: An Ecotoxicological Perspective.
10. Oil in the sea III: Inputs, Fates and Effects (2003) National Academic Press, Washington, DC, USA.
11. Nasher E, Heng LY, Zakaria Z, Surif S (2013) Concentrations and sources of PAHs in the Seawater around Langkawi Island, Malaysia.
12. Li Q, Xu X, Sen-Chun LF, Wang X (2006) Determination of trace PAHs in seawater and sediment pore-water by SPME coupled with GC/MS. *Sci China Chem* 49: 481-491.
13. Doong RA, Chang SM, Sun YC (2000) Solid-phase microextraction for determining the distribution of sixteen US Environmental Protection Agency polycyclic aromatic hydrocarbons in water samples. *J Chromatogr A* 879: 177-88.
14. Coelho E, Ferreira C, Almeida CMM (2008) Analysis of PAHs by SPME-GC-FID in environmental and tap waters. *J Braz Chem Soc* 19: 1084-1097.
15. Determination of Polycyclic Aromatic Hydrocarbons in Drinking Water by Liquid-Solid Extraction and HPLC with UV and Fluorescence Detection (1990) USEPA, United States Environmental Protection Agency.
16. Werres F, Balsaa P, Schmidt TC (2009) Total concentration analysis of polycyclic aromatic hydrocarbons in aqueous samples with high suspended particulate matter content. *J Chromatogr A* 1216: 2235-2240.
17. Ambient Water Quality Criteria for Polycyclic Aromatic Hydrocarbons (PAHs) (1993) Environmental Protection Division.
18. Wattayakorn G (2012) Petroleum pollution in the Gulf of Thailand: A historical review. *Coast Mar Sci* 35: 234-245.
19. Bertilson S, Widenfalk A (2002) Photochemical degradation of PAHs in freshwater and their impact on bacterial growth- influence of water chemistry. *Hydrobiologia* 469: 23-32.
20. Uthe JF (1991) Polycyclic aromatic hydrocarbons in the environment. *Can Chem News* 43: 25-27.
21. McIntosh AD, Webster L, Hayes PJ, Moffat CF (2002) The source and fate of polycyclic aromatic hydrocarbons (PAHs) in sediment and water from Loch Leven. FRS Marine Laboratory. Aberdeen Report.
22. National Recommended Water Quality Criteria (2009) United States Environmental Protection Agency.
23. Tronczyński J, Munschy C, Héas-Moisan K, Guiot N, Truquet I, et al. (2004) Contamination of the Bay of Biscay by PAHs following the T/V Erika oil spill. *Aquat. Living Resour* 17: 243-259.
24. Zrafi Noura I, Khedir-Ghenim Z, Bahri R, Cheraief I, Rouabhia M, et al. (2009) Hydrocarbons in seawater and water extract of Jarzouna-Bizerte coastal of Tunisia (Mediterranean Sea): petroleum origin investigation around refinery rejection place. *Water Air Soil Pollut* 202: 19-31.
25. Law AT, Hii YS (2006) Status, impacts and mitigation of hydrocarbon pollution in the Malaysian seas. *Aquat Ecosyst Health Manag* 9: 147-158.
26. Malaysian Marine Department (1998) Malaysian Ministry of Transport Occasional Publication.