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Ecological Risk Assessment of Poly Aromatic Hydrocarbons in the West Port, Malaysia

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Abstract. Sediment samples collected from the West Port, West Coastal water of Malaysia, were analyzed by GC–MS in order to determine the degree of hydrocarbon contamination, and identify the sources of poly aromatic hydrocarbon and PAHs. Concentrations of PAHs in the port sediments ranged from 98.28 to 3630.22 µg/kg dw. The highest concentration was observed in stations which is closed to the coastline, this locations affected by intensive shipping activities and industrial inputs and they were dominated by the high molecular weight PAHs (4–6- rings). Source identification showed that PAHs originated mostly from the pyrogenic source either from the combustion of fossil fuels, grass, wood and coal (majority of the samples) or from petroleum combustion (Port area). Regarding to risk index (HQ) estimation, only stations 13 (close to container terminal in West Port) is moderately polluted and the rest of stations were in rare or slight adverse biological effects with the PAHs exposure in surface sediment, suggesting PAHs are not considered as contaminants of concern in the West Port.

Keywords: PAHs, West Port, Ecological Risk

1. Introduction

Ecological risk assessment is a practical way to evaluate the health status in the marine environment which is widely used to quantify and qualify contaminates and their adverse effects in the environment. It is applied as tool to classify the toxicity level of contaminates based on the chemical assessment and individual bioassay (bioaccumulation and toxicity) [1].

In recent decades, among many chemistry assessments on environment contamination, petroleum pollution over time is of interest to many research institutions. An important category of petroleum pollution is groups of chemical compounds include of two or more fused benzene rings called polycyclic aromatic hydrocarbons (PAHs) that are carcinogenic, mutagenic and toxic [2, 3]. Numerous sources can impart their PAHs signature to the marine environment such as pyrogenic which includes combustion of fossil fuels and biomass burning (fireplaces, controlled burning) and petrogenic which includes unburned fossil fuels (crude oil and its refined products), primarily by street surface runoff, accidental spills and intentional discharge by ships. Thus, Source identification of petroleum contamination is essential to prevent pollution entry into the marine environment [1].The objectives of the present study are the following: to estimate concentration of Poly Aromatic Hydrocarbons (PAHs) in surface sediment to distinguish vulnerable stations and to evaluate ecologic risk to assess adverse biological effects. With regard to the importance of the West Port as an international shipping route, an industrial center and ecological habitat, it is necessary to do chemical research in order to evaluate environmental properties, control pollution occurrence and protect living organisms.

2. Material and Method

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2.1. Study Area and Sampling

West Port, is a new busiest port in west coast of Malaysia where constructed conjunction to development activities. In this present study area is restricted as narrow strait between mangrove forest and coastline, nine stations were selected from three transects parallel to the coastline with three different distances inside Port (see Fig 1 and Table 1), and one stations was selected 21 kilometer far from port as control points. Surface sediment samples were collected two times in year From November 2009 until October 2010. Peterson Grab sampler was used to collect samples from surface sediment and 10 cm sediment samples were chosen for laboratory analysis.

Fig. 1: Sampling location for PAHs in West Port

Table 1: Characterization of surface sediment in West Port

Station	*Description*	*Silt and clay (<64μm)%*	*Sand (%)*	*TOC* **(μg g^{-1}**
1	Coastline	53.57	46.42	10.24
2	Remote area	45.96	54.03	7.74
3	Mangrove	63.42	36.57	11.98
4	Coastline	56.33	43.66	9.14
5	Remote area	41.10	58.89	7.55
6	Mangrove	70.81	29.18	12.76
7	coastline	52.31	47.68	10.63
8	Remote area	50.69	49.30	10.15
9	Mangrove	70.36	29.63	15.49
10	Control Point	51.60	48.39	10.46

2.2. Experimental Analysis

Sediment grain size was determined using a multi-wavelength particle size analyzer (model LS 13 320), and results were divided into sand (>64 μm), silt (2 μm <size < 64 μm) and clay (<2 μm) fractions for the determination of heavy metals in the contaminated soil [4, 5]. Total organic carbon (TOC) was measured in surface sediment by using a Perkin-Elmer 2400 carbon–hydrogen–nitrogen–sulfur (CHNS) elemental analyzer at a 950°C combustion temperature [6].

Authentic standard for 16 PAHs was selected for this research includs naphthalene (Naph), acenaphthylene (Acy), acenaphthene(Ace), fluorine (Fluo), phenanthrene (Phen), anthracene(Ant), fluoranthene (Flt), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chry), benzo[*b*] fluoranthene (BbF), benzo[*k*]fluoranthene(BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*] pyrene (IcdP), dibenzo[*a*,*h*]anthracene (DahA) and benzo[*ghi*]perylene (BghiP). In addition, anthracene-d10 was applied prior to GC-MS injection as an internal standard to estimate possible variations of the instrument. Organic solvents such as hexane and dichloromethane SupraSoly were provided from the Merck Company, and the specific cartridges for the solid phase extraction (SPE) alumina (5 g, 25 ml) were purchased from International Sorbent Technology. The extraction and fractionated of the samples using the Soxhlet method was based on the SW-846 test methods. Quantification and qualification of 16 USEPA priority PAHs were performed based on the modified method of USEPA 8270 by a capillary gas chromatograph (GC; Varian CP-3800) [7]. The integrated peak area was used to quantify the PAH compound based on the comparison between the peak area of the selected ion and the peak area of the IISTD (a known standard), and the concentration of PAHs was calibrated according to the standard calibration curve. Some sediment samples were polluted to sulfur; thus, copper powder was used for desulphurization. HCL (1N) was used to activate the copper powder, which was then washed with acetone, hexane, and water. The applied method of extraction and clean up was

checked based on the sediment reference material IAEA-417. The result of recovery was ranged from 78% to 95%. Detection limit (MDL) was ranged from 0.095 until 1.018 for sediment.

PAH isomer ratios have been used as distinct chemical tracers to infer possible anthropogenic sources of PAH from the natural source. Based on the PAH isomer pair ratio measurements compiled by Yunker in 2002: Flu/(Flu + Pyr) < 0.4 implies petroleum, 0.4–0.5 implies petroleum combustion, and >0.5 implies combustion of coal and biomass; Ant/(Ant + Phe) ratio <0.10 are seen in petroleum input or diagenetic sources, whereas values >0.1 are characteristic of combustion processes [1].

2.3. Ecological Risk Assessment Based on the Sediment Quality Guidelines

The sediment quality guidelines (SQGs) that are applied to assess toxicity risk [8]. This method indicates that the relationship between the concentrations of contaminants in sediment samples and adverse biological effects is based on the specific values of effect range low (TEL) and effect range medium (PEL).The overall toxicity of heavy metals and PAHs was estimated by PEL quotients (PELq's).The PELq factor is the average of the ratios between the heavy metal concentration in the sediment sample and the related PEL value [9, 10]. This factor describes the sediment toxicity range as non-toxic (PELq < 0.1), slightly toxic (0.1< PELq > 0.5), moderately toxic (0.5< PELq > 1.5) and heavily toxic (PELq > 1.5) [11]. Statistical analyses were performed using Microsoft Excel and SPSS 17 software to estimate statistical tests on monitoring and bioassays data.

3. Results and Dissections

3.1. Spatial Distribution of Pahs in Sediments

Table 2: concentration of PAHs (µg/kg dw) in surface sediments of West Port

Station code	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*Mean*	*SD*	*TEL*	*PEL*
Nap	1.26	5.70	1.20	0.80	0.72	2.04	16.10	2.96	2.20	1.78	3.48	4.5	34.6	391
Acy	ND	ND	ND	ND	ND	ND	645.28	ND	ND	ND	64.53	198.6	5.87	128
Ace	ND	1.04	ND	ND	0.66	0.98	14.84	0.49	ND	ND	1.80	4.4	6.71	88.9
Flr	27.6	39.0	7.68	23.6	48.76	39.7	620.80	33.78	8.72	12.4	86.23	183.3	21.2	144
Phn	127	6.78	5.12	5.04	15.60	24.8	225.00	75.78	9.60	1.70	49.70	71.8	86.7	544
Ant	267	71.4	8.16	10.1	37.80	233.	308.00	181.30	3.78	4.10	112.6	118.83	46.9	245
Fla	10.3	13.5	ND	ND	17.65	21.5	166.50	15.80	0.00	0.00	24.53	49.23	113	1494
Pyr	12.7	15.7	28.1	236.5	25.10	341.	243.75	14.03	0.00	0.00	91.75	125.6	153	1398
BaA	204	50.5	191	278.8	29.50	774.	390.90	146.30	78.3	56.8	220.1	219.7	74.8	693
Chy	ND	ND	198.	ND	ND	ND	ND	ND	ND	ND	19.80	60.94	108	846
BbF	ND	ND	ND	ND	ND	ND	11.60	11.32	12.8	23.4	5.91	8.91	-	-
BkF	47.6	ND	ND	ND	367.56	1.34	28.56	ND	ND	ND	44.51	111.6	-	-
BaP	ND	122	ND	ND	ND	0.96	825.20	59.90	ND	ND	100.8	252.18	88.8	763
DibA	ND	ND	67.8	ND	ND	7.26	ND	ND	130.	ND	20.53	42.7	-	-
Bghip	ND	64.2	ND	ND	ND	ND	49.40	ND	ND	ND	11.36	23.6	6.22	135
Inp	ND	77.4	ND	68.74	ND	ND	ND	31.80	348.	ND	52.63	105.9	-	-
∑PAHs	698	467	507	623.7	543.35	1448	3545.9	573.46	594.	100.	910.3	958.8	1684	1677
$\sum PAH_{Combust}$	274	343.	485	584.1	439.8	1046	1715.9	279.2	569.	80.3	646.5	233.2	-	-
$\sum PAHs_{toxic}$	251	250	457.	347.6	397.1	784.	1256.3	249.3	560.	79.6	515.9	213.9	-	-
Ant/Ant+Phn	0.6	0.91	0.61	0.67	0.71	0.9	0.58	0.71	0.28	0.71	0.75	0.22	-	-
Fla/Fla+Pyr	0.45	0.46	ND	ND	0.41	0.08	0.41	0.53	ND	ND	0.26	0.28	-	-

In the West Port, Concentration of PAHs was ranged from 98.28 to 3630.2 µg/kg dw with an average concentration of 910.3 µg/kg dw (Table 2). PAHs with higher concentration mostly observed in the stations close to coastline such as station 7 in front of the container terminal, station 1 in front of cement outlets. PAHs concentration was generally lower in others remotes station except stations 6, which had an elevated

concentration of PAHs (1448.8 µg/kg dw). PAHs concentration showed an insignificant correlation with percentage of TOC and fine grained ($p< 0.05$, $r = 0.17$ and $r = 0.20$) sediment in surface sediment of West Port. Kruskal Wallis analysis (nonparametric test) showed that there are the significant differences ($p< 0.05$, df= 8, sig=0.003) between concentration of PAHs at all of stations, and PAHs concentration of stations 10 (control stations), 7, 4 are not homogenous to others stations.

Concentration of high molecular weight PAHs (Fla, Pyr , BaA, Chy, BbF, BkF , BaP, InP, DibA , BghiP) are typically estimated to assess combustion value [1]. Concentration of high molecular weight PAHs ranged from 39.34% to 95.8% of the total PAHs concentration with mean value of 74.02% (Table 2). Concentration of some high molecular weight PAHs such as BaA, Chy, BbF, BkF , BaP, InP and DibA are known as toxic PAHs because of their mutagenic and carcinogenic effect on human being health and biological communities[12]. Concentrations of toxic PAHs included 56.67% of the total PAHs concentration and ranged from35.42 to 95.83%. These concentrations represented the highest values in the stations 6 and 7.

3.2. Origin of Pahs in the West Port

Pyrogenic and petrogenic sources are typically distinguished based on the mixed ratios of PAHs. This result presented a mixed pattern of combustion and petroleum sources in some of stations (1, 2, 4 and 6). At same time combustion fingerprints were completely estimated in stations 7 also other stations (3, 5, 8, 9 and 10) have mainly originated from combustion, while petroleum-derived contamination cannot be ignored (Table 2). In general, the results showed that anthropogenic sources of PAHs are derived by a mixed sources of pyrogenic and petrogenic pollution in all stations with high frequent from combustion of fossil flues and biomass burning which can be originated from industry discharge such as cement, Food and oil factories. Minor amounts of PAHs derived from petrogenic source can be related to the runoff, oil spill and ship discharges.

3.3. Ecological Risk Assessment

The comparison of contamination levels with sediment quality guidelines revealed that concentrations of Nap, Ace, Phn, Fla, Pyr, Chy and total PAHs were below their respective values TEL values, indicating that rarely adverse biological effects are probably to occur for these compounds at all stations. Concentration of Ace, Flr, Ant, BaA, BaP and Bghip showed the occasionally adverse biological effects (≥TEL and < PEL). Some individual PAHs such as benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[g,h,i]perylene and indeno[1,2,3-c,d]pyrene were estimated at some stations which can cause mild toxic effects but will not cause serious biological effects in the sedimentary environment in this port .

Results estimated from the ecological risk assessment of PAHs in surface sediments of the West Port are summarized in Table 3. Most of the PAHs such as Nap, Ace, phy, Fla, Pyr, Chy, BbF, BkF, DibA and Bghip showed rare risk (HQ <1) in all stations and others PAHs (Acy, Flu, Phy, Aut, BeA and BaP) were significantly more than one (HQ> 1) in some stations such as,1,6 and 7 which are highlighted in table 3. In general, the results of risk assessment revealed that total PAHs likely cause to slight adverse effect on biological communities in stations 1 and 6, because these stations varied between 0.1 and 0.5. Moderately adverse biological effect are observed in station 7 (0.5 <HQ<1.5), but the rest of stations showed rare adverse ecological effects with the PAHs exposure in surface sediment (HQ< 0.1). Cluster analysis showed the better view of PAHs contaminations, it classified the stations into three groups, stations 7 completely separate from other stations and stations 1 and 6 are arranged in same groups (Fig 2). According to the above discussion, it may be concluded that PAHs, are not main pollutants of potential concern in the West Port and only station 7 can be considered as vulnerable station.

During 2000 to 2007, more researches recorded significant decline of PAHs discharges around West coastal water of Malaysia. The high value was estimated 1700 ng/g d. w in near shore sediment samples during 1976 to 1999 with predominant input of petroleum products because of the development activities in marine transportation, urbanization, industrialization and motorizations along during this period in west coastal water of Malaysia. Several reasons cause to decline of the petroleum hydrocarbon during 2000-2007 such as integrated management programme, Metrological condition and weathering [13].

Table 3: Ecologic risk value in different stations

Stations	*Nap*	*Acy*	*Ace*	*Flu*	*Phy*	*Aut*	*Fla*	*Pyr*	*BeA*	*Chy*	*BbF*	*BkF*	*BaP*	*DibA*	*Bghip*	*risk*
1	ND	ND	ND	0.19	0.23	1.09	0.01	0.01	0.29	ND	ND	0.03	ND	ND	ND	0.12
2	0.01	ND	0.01	0.27	0.01	0.29	0.01	0.01	0.07	ND	ND	ND	0.16	ND	0.04	0.06
3	ND	ND	ND	0.05	0.01	0.03	ND	0.02	0.28	0.23	ND	ND	ND	0.50	ND	0.08
4	ND	ND	ND	0.16	0.01	0.04	ND	0.17	0.40	ND	ND	ND	ND	ND	ND	0.05
5	ND	ND	0.01	0.34	0.03	0.15	0.01	0.02	0.04	ND	ND	0.23	ND	ND	ND	0.06
6	0.01	ND	0.01	0.28	0.05	0.95	0.01	0.24	1.12	ND	ND	ND	ND	0.05	ND	0.18
7	0.04	7.26	0.12	4.31	0.41	1.26	0.11	0.17	0.56	ND	0.01	0.02	1.08	ND	0.03	1.03
8	0.01	ND	ND	0.23	0.14	0.74	0.01	0.01	0.21	ND	0.01	ND	0.08	ND	ND	0.10
9	0.01	ND	ND	0.06	0.02	0.02	ND	ND	0.11	ND	0.01	ND	ND	0.96	ND	0.08
10	ND	ND	ND	0.09	ND	0.02	ND	ND	0.08	ND	0.01	ND	ND	ND	ND	0.01

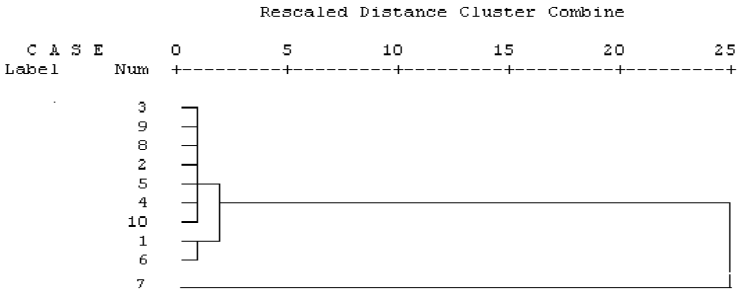

Fig. 2: Cluster analyses to classify the different stations based on ecological risk

4. Conclusion

Ecological assessment of PAHs compounds in this study at Highlighted via two main problems: the first problem was related to the scarcity of information on the PAHs concentrations in sediments of port, and therefore no background and updated database was available. The second problem was related to the biological effects and guidelines, as no SQGs were available to coastal water of Malaysia. In spite of these limitations, the adopted approach in the present study highlighted that no adverse biological effects are associated with the exposure to PAHs levels in the West Port and only areas around terminal container (station 7) are moderately polluted. Source analysis showed that PAHs are derived with high frequent from combustion of fossil fuels/petroleum (gasoline, crude oil, and coal) and biomass (wood and grasses), with minor amounts of PAHs derived from direct petroleum input. Pyrolytic input appears be a main source of PAHs in West Port sediment and petrogenic sources are also apparent for PAHs, from oil spill, urban runoff, tanker operation and shipping activities.

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