

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

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Abstract—The pollution of sediments sampled from the North Port by polycyclic aromatic hydrocarbons (PAHs) was investigated. Concentrations of PAHs estimated in the port sediments ranged from 199 to 2851.2 $\mu\text{g}/\text{kg dw}$. The highest concentration was found which is closed to the Berth line, this locations affected by intensive shipping activities and Land based runoff 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). Ecological Risk Assessment on the port sediments presented that slightly adverse ecological effects to biological community are expected to occur at the vicinity of the stations 1 and 4. Thus PAHs are not considered as pollutants of concern in the North Port.

Keywords—PAHs, North Port, Ecological Risk, sediment

I. INTRODUCTION

IN recent years, many researchers have focused on Ecological risk assessment to understand and predict the relationship between stressors and ecological effects in a way that is useful for environmental decision making. This assessment includes chemical, physical and biological monitoring in water and sediment (U.S. EPA, 1992a). More studies have been done on ecological risk assessment according to chemical analysis to evaluate health status and sensitivity of the marine environment which is practical to quantify and qualify contaminates and their adverse effects in the environment. In general, it is applied as tool to classify the toxicity level of contaminates based on the chemical assessment and individual bioassay (bioaccumulation and toxicity)[1] [2].

In recent decades, among many risk assessments on marine and coastal contamination, petroleum pollution over time is of interest to many research institutions. Petroleum compounds are classified into three main categories which including aliphatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs) and biomarkers[3, 4]. 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.

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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 [2]. Northport is busiest port in the West Coast of Peninsular Malaysia where constructed conjunction to development activities. Now, ocean-going ships enter into this port from Far East and Middle East to upload and download of goods. The main objectives of this research are; 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 Northport as an international shipping route, and ecological habitat, it is necessary to evaluate environmental properties in order to control pollution occurrence and protect living organisms.

II. MATERIAL AND METHODS

A. Study area

This port is well developed along mangrove forest and Klang Strait. In this research 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 in this project [5] (see Fig 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 Location of stations in the North Port

B. Sampling and Experimental analysis

Sediment grain size was determined using a multi-wavelength particle size analyzer (model LS 13 320), and results were divided into sand ($>64 \mu\text{m}$), silt ($2 \mu\text{m} < \text{size} < 64 \mu\text{m}$) and clay ($<2 \mu\text{m}$) fractions for the determination of heavy metals in the contaminated soil [6, 7]. 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 [8] [9].

Authentic standard 16 PAHs 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). These standards were purchased from Supelco at a concentration $2,000 \mu\text{g/L}$ in hexane (Bellefonte, PA, USA). 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 SupraSolv were provided from the Merck Company, and the specific cartridges for the solid phase extraction (SPE) alumina (5 g, 25 ml) were 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) [10].

C. Source identification and ecological risk assessment

PAH isomer ratios, such as anthracene/anthracene+phenanthrene ($\text{Ant}/(\text{Ant} + \text{Phy})$) and fluoranthene/fluoranthene + pyrene ($\text{Flu}/(\text{Flu} + \text{Pyr})$), have been used as distinct chemical tracers to infer possible anthropogenic sources of PAH from the natural source [2, 11]. Based on the PAH isomer pair ratio measurements compiled by Yunker in 2002: $\text{Flu}/(\text{Flu} + \text{Pyr}) < 0.4$ implies petroleum, $0.4-0.5$ implies petroleum combustion, and >0.5 implies combustion of coal and biomass; $\text{Ant}/(\text{Ant} + \text{Phe})$ ratio <0.10 are seen in petroleum input or diagenetic sources, whereas values >0.1 are characteristic of combustion processes. The sediment quality guidelines (SQGs) that are applied to assess toxicity risk [12]. 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 TEL value has been estimated as the concentration of contaminants with a relatively low effect on biological communities, and PEL is a concentration of contaminants with high toxic effects. Occasional toxic effects are expected to occur from contaminates Concentrations between TEL and PEL occasional toxin effect are expected [13-16].

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 [17, 18].

This factor describes the sediment toxicity range as non-toxic ($\text{PELq} < 0.1$), slightly toxic ($0.1 < \text{PELq} < 0.5$), moderately toxic ($0.5 < \text{PELq} < 1.5$) and heavily toxic ($\text{PELq} > 1.5$) [19]. Statistical analyses were performed using Microsoft Excel and SPSS 17 software to estimate statistical tests on monitoring and bioassays data.

III. RESULT AND DISCUSSION

A. Spatial distribution of PAHs in sediments

In the North Port, Concentration of PAHs was ranged from 199 to $2851.2 \mu\text{g/kg dw}$ with an average concentration of $897.7 \mu\text{g/kg dw}$ (Table.I). The highest concentration of PAHs was estimated in station 4 and lowest concentration was observed in station 2. PAHs with higher concentration mostly observed in the stations close to coastline such as station 1 and 4 in front of the container terminal. PAHs concentration was generally lower in others remotes station. 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 North Port. Kruskal Wallis analysis (nonparametric test) showed that there are the significant differences ($p < 0.05$, $df = 5$, $\text{sig} = 0.003$) between concentration of PAHs at all of stations, and PAHs concentration of stations 1 and 4 are not homogenous to others stations.

High temperature combustion process is main sources to emit the high molecular weight PAHs (HMWPAH) with 4 or more rings in natural resources. Thus, concentration of high molecular weight PAHs (Fla, Pyr, BaA, Chy, BbF, BkF, BaP, InP, DibA, BghiP) are typically estimated to assess combustion value [2]. Concentration of high molecular weight PAHs represented from 27.5% to 97.04% of the total PAHs concentration with a mean value of 87.59% (Table 2). Moreover, the combustion PAHs showed a significant portion of the total PAHs concentrations in stations 4 (in front of container terminal) and 1 which can reflect recent input of PAHs in these stations. 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 [20]. Concentrations of toxic PAHs included 67.3% of the total PAHs concentration and ranged from 0% to 96.23%. These concentrations represented the highest values in the station 4 whereas station 3 was significantly observed in the lowest concentration of toxic PAHs.

TABLE I
 CONCENTRATION OF PAHS ($\mu\text{G/KG DW}$) IN SURFACE SEDIMENTS OF WEST PORT

Station code	1	2	3	4	5	6
Nap	ND	1.3	1.7	0.4	0.82	4
Acy	ND	ND	ND	ND	ND	ND
Ace	2.1	ND	8.1	ND	0.33	0.43
Flr	34.2	9.7	118.	1.1	16.8	57.3
Phn	47.5	13.3	89	10	12.6	36.2
Ant	100	12.7	58.8	59.8	12.5	37.9
Fla	ND	ND	42.7	12.5	10	26
Pyr	482	131	62.9	12	195.	31.8
BeA	613	31.5	ND	66.7	ND	179.
Chy	ND	ND	ND	50	ND	ND
BbF	ND	ND	ND	852.8	11	ND

BkF	47.6	ND	ND	ND	ND	47.6
BaP	ND	ND	ND	1495.8	ND	ND
DibA	ND	ND	ND	190.2	ND	ND
Bghip	ND	ND	ND	ND	ND	ND
Inp	ND	77.4	ND	99.8	ND	42.3
∑PAHs	128	199	381.4	2851.2	259.2	415.
∑PAH _{Combust}	1195.8	162.8	105.6	2767.8	206.6	279.
∑ PAHs _{toxic}	613	31.5	ND	2755	11	221.
Ant/Ant+Phn	0.68	0.49	0.4	0.86	0.49	0.51
Fla/Fla+Pyr	ND	ND	0.4	0.51	0.05	0.45
TOC (%)	12.49	10.13	17.04	11.41	10.08	14.7

ND= below the method detection limit; Nap = naphthalene; Acy = acenaphthylene; Ace = acenaphthene; Flr = fluorene; Phn = phenanthrene; Ant = anthracene; Fla = fluoranthene; Pyr = pyrene; BaA = benzo(a)anthracene; Chy = chrysene; BbF = benzo(b)fluoranthene; BkF = benzo(k)fluoranthene; BaP=benzo(a)pyrene; InP=indeno[1,2,3-(c,d)]pyrene; DibA=dibenzo(a,h)anthracene; BghiP= benzo(g,h,i)perylene

B. Origin of PAHs in the North 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 all of stations. At same stations 4 have mainly originated from combustion, while petroleum-derived contamination cannot be ignored (Table.I). 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 Land based runoff combustion of fossil fuels. Minor amounts of PAHs derived from petrogenic source can be related to oil spill and ship discharges.

C. Ecological risk assessment

The comparison of contamination levels with sediment quality guidelines revealed that concentrations of NAP, Ace, Acy, Phn, Fla, Chy, Bghip 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 Flr (in stations 1,3 and 6), Ant(stations 1,3, and 4), Pyr (in stations 1 and 5) and BeA (1 and 6) showed the occasionally adverse biological effects (\geq TEL and $<$ PEL) at same time, only Bap was higher PEL value in stations 4 (Table II).

Apart from this, the lowest safety value do not defined for some PAHs with high molecular weight such as indeno benzo[k]fluoranthene, [1,2,3-c,d]pyrene, benzo[b]fluoranthene and benzo[g,h,i]perylene that is to mean, the exits of these PAHs will cause toxic effects to marine environment [16]. In North Port, 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 .

TABLE II
COMPARISON OF MEAN CONCENTRATION OF PAHS WITH SPECIFIC VALUE IN SEDIMENT QUALITY GUIDELINE

Individual PAHs	Mean of individual PAHs in this study	TEL	PEL
Nap	1.37	34.6	391
Acy	0	5.87	128
Ace	1.82	6.71	88.9
Flr	39.6	21.2	144
Phn	34.76	86.7	544
Ant	46.95	46.9	245
Fla	15.2	113	1494
Pyr	152.5	153	1398
BeA	148.4	74.8	693
Chy	8.33	108	846
BbF	143.9	-	-
BkF	15.86	-	-
BaP	249.3	88.8	763
DibA	31.7	-	-
Bghip	0	6.22	135
Inp	36.58	-	-

Results estimated from the ecological risk assessment of PAHs in surface sediments of the North Port are summarized in table 3. These results were arranged based on the concentration of fifteen PAHs determined in ten stations. Most of the PAHs except of BaP and DibA showed HQ $<$ 1 in all stations while BaP and DibA significantly showed HQ $>$ 1 in at station 4 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 4, because these stations showed 0.1 $<$ HQ $<$ 0.5 and the rest of stations showed rare adverse ecological effects with the PAHs exposure in surface sediment (HQ $<$ 0.1) (Table III). According to the above discussion, it may be concluded that PAHs, are not main pollutants of potential concern in the North Port and only station 1and 4 can be considered as vulnerable station.

TABLE III
ECOLOGIC RISK VALUE

Stations	Nap	Acy	Ace	Flu	Phy	Aut	Fla	Pyr	BeA	Chy	BbF	BkF	BaP	DibA	Bghip	risk
1	ND	ND	0.02	0.23	0.08	0.36	ND	0.41	0.8	ND	ND	ND	ND	ND	ND	0.11
2	ND	ND	ND	0.07	0.02	0.05	ND	0.09	0.05	ND	ND	ND	ND	ND	ND	0.02
3	ND	ND	0.06	0.82	0.16	0.24	0.03	0.04	0.00	ND	ND	ND	ND	ND	ND	0.09
4	ND	ND	ND	0.01	0.02	0.24	0.01	0.01	0.10	0.06	0.45	ND	1.96	1.41	ND	0.28
5	ND	ND	ND	0.12	0.02	0.05	0.01	0.14	ND	ND	0.01	ND	ND	ND	ND	0.02
6	0.01	ND	ND	0.40	0.07	0.15	0.02	0.02	0.26	ND	ND	ND	ND	ND	ND	0.06

IV. 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 North Port and only areas around terminal container (station 4) are moderately polluted. Source analysis showed that PAHs are derived with high frequent from combustion of fossil fuels/petroleum (gasoline, crude oil, and coal) with minor amounts of PAHs derived from direct petroleum input. Pyrolytic input appears be a main source of PAHs in North Port sediment and petrogenic sources are also apparent for PAHs, from oil spill, tanker operation and shipping activities.

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