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Distribution of Polycyclic Aromatic Hydrocarbons in Sediments in Map Ta Phut Industrial Estate Area, Rayong Province, Thailand

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ABSTRACT

The distribution of polycyclic aromatic hydrocarbons (PAHs) and the natural characteristics of sediments were investigated in the Map Ta Phut industrial estate area, Rayong province, Thailand, from August 2010 to May 2011. Samples from 20 sites were analyzed using gas chromatography-flame ionization detection. The total concentration of PAHs ranged from 167.73 to 2,467.61 ng.g^{-1} dry weight with an average concentration of 1,527.07 ± 100.26 ng.g^{-1} dry weight. It was found that season change did not affect the distribution and accumulation of PAHs in sediments. Almost all sites showed high PAH pollution consisting of five major PAHs—fluoranthene, pyrene, chrysene, benzo(k)fluoranthene and benzo(a)pyrene. The patterns of PAHs in the sediment were dominated by four or five ring compounds estimated to be 85% of total PAHs and the total higher molecular weight PAHs showed higher amounts compared to the total lower molecular weight PAHs. The sources of PAHs were evaluated using composition pattern and molecular mass ratios, which indicated that the PAH input to the Map Ta Phut area came mainly from pyrogenic sources originating from incomplete combustion of fossil fuels and organic substances. However, the measured total PAH concentrations at all sites were below the sediment quality guideline values indicating non adverse effects to the biological environment.

Keywords: distribution, polycyclic aromatic hydrocarbons, sediment, Map Ta Phut, Rayong province

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds found widely in the marine environment and consist of two or more fused benzene rings in different arrangements (Moore and Ramamoorthy, 1984). PAHs are classified as contaminants in the environment as they are difficult to burn, slow to decay and persist in the environment for a long time and are highly toxic substances, carcinogens, which can cause genetic changes and act as mutagens (Sverdrup *et al.*, 2002). The physical and chemical properties of PAHs mean they are frequently found in the environment because they have high melting and boiling points (Agency for Toxic Substances and Disease Registry, 1995). Their dissolving abilities in water decrease when the boiling point and melting point increase according to the increase in their molecular weight and they are also soluble in lipids (Kennish, 1997). The lower molecular weight (LMW) PAHs are more

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soluble in water and are acutely toxic to humans and living organisms whereas higher molecular weight (HMW) PAHs are highly soluble in lipids and are more carcinogenic and mutagenic with more time period effects (Neff, 1979). PAHs can also cause abnormal embryos (teratogenicity) and have been reported in marine areas close to sources of contamination by oil with a higher incidence of cancer (Colombo *et al*., 2005). Those PAHs will affect marine ecosystems; human exposure to PAHs in large volumes will affect the function of various hormones associated with the system in the body and finally cause abnormal cells as a cause of cancer (Long *et al*., 1995; LaRocca *et al*., 1996). Some PAHs including benzo(a) pyrene, dibenz(a,h)anthracene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene and indeno(1,2,3-cd)pyrene are probably carcinogenic to humans (International Agency for Research on Cancer, 2010).

Sources of PAHs in the marine environment can be divided into two groups: Group one is from crude oil and petroleum products (petrogenic sources) mainly consisting of compounds such as alkyl-substituted aromatic hydrocarbons with 2-4 benzene rings which are substances with a low molecular weight. They originate from transport ships as transport oil following accidents on an oil tanker or cargo ship, from discharge ballast water from the hull and in wastewater from community and industry discharges, resulting in oil spills into the marine environment (Neff, 1979). The second source is from incomplete combustion (pyrogenic sources) consisting of unsubstituted aromatic hydrocarbons and heterocyclic aromatic hydrocarbons with a 3-5 benzene ring—substances with a high molecular weight originating from fuel combustion in automobile, engines, machines and industry (Budzinski *et al*., 1997a). These hydrocarbons contaminate the sea through the atmosphere, oil leaching and wastewater from community and industry that flows through canals and into rivers (Wells *et al*., 1993). There are many techniques to identify the sources of hydrocarbon pollution in the environment, such as isomer pair ratios (Yunker *et al*., 2002), individual compound ratios (Baumard *et al*., 1998; Zakaria *et al*., 2000) and biomarkers (Zakaria *et al*., 2002). The molecular weight based on the ratio of selected PAH concentrations in sediments can be used to assess the origin of PAHs, that is whether they are petrogenic or pyrogenic. The ratio of some isomers such as phenanthrene / anthracene, fluoranthrene / pyrene, anthracene / (anthracene + phenanthrene), fluoranthrene / (fluoranthrene + pyrene), Benzo(a) anthracene / chrysene and indeno (1,2,3-cd) pyrene / benzo(g,h,i) perylene have been widely used to distinguish PAHs from diverse origins (Budzinski *et al*., 1997a, 1997b; Baumard *et al*., 1998; Yunger *et al*., 2002; Jiang *et al*., 2009).

The Map Ta Phut industrial estate has been the site of heavy and light industry including natural gas separation plants, petrochemical industry plants, chemical fertilizer industry sites and an oil refinery. It also has a high potential, deepwater port which is the largest port in the country with a high density of maritime activity because it is on the route of many cargo ships including those carrying crude oil and oil products (Pollution Control Department, 2010). As a result, there is ample opportunity for an oil leak into the sea caused by an accident such as ships colliding, ships running aground or hitting a reef, shipwreck and other maritime activities. Pollution Control Department (2010) has categorized this area into risk zones for oil spills which takes into account important tides and winds that could force oil onto the coastline as other nearby areas have fisheries and coastal aquaculture activities. Flowing through the industrial estate and adjacent communities, are various canals that serve as a reservoir of community and industrial wastewater before it is released to the sea as a source of large amounts of waste. Marine Water Division (2014) reported that the coastal area of the Map Ta Phut industrial estate area had levels of petroleum hydrocarbons in the seawater that exceeded the coastal water quality standards (not over 5 ug.L^{-1}), especially at the Ta Kuan canal mouth, the Chark Mark canal mouth, at Sai Thong beach and at Ao Pradu which receives wastewater directly from industrial plants in the Map Ta Phut industrial estate. These flows affect the activities and quality of the marine environment and result in the accumulation of organic matter in the sediment. PAHs are chemicals that have hydrophobic properties which provide the ability to be slightly soluble or insoluble in some substances (Long *et al*., 1995). Thus, when particles of PAHs penetrate the surface water, they capture particles and adhere to the suspension and drop as sedimentation to the sea floor. The contamination of PAHs in sediments from various natural sources will combine with small particles in the water. PAHs are degraded slowly and remain in the sediment for a long time, especially for PAHs with a high molecular weight (Kennish, 1997).

Thus, understanding the contributions of the various sources is essential for appropriately managing PAH levels in the environment, especially in sediments. Therefore, the present study aimed to investigate the natural characteristics of sediment and the distribution, composition and relative pollution levels of PAHs and to identify possible sources and the potential biological effects of PAHs in sediments in the Map Ta Phut industrial estate and nearby areas. This study provides valuable information as a reference for surveillance and planning for management of the PAH levels in this area.

MATERIALS AND METHODS

Sampling location and sample collection

Sediment samples from 20 sites in the Map Ta Phut industrial estate, Rayong province were divided into three groups: (1) 12 sites (M1–M12) from areas in the estate including coastal and offshore (3 and 5 km); (2) 5 sites (W1–W5) from the western side of the estate, and (3) 3 sites (E1–E3) from the east side of the estate (Figure 1). Sediment samples were collected twice—once in the wet season (August 2010) and then in the

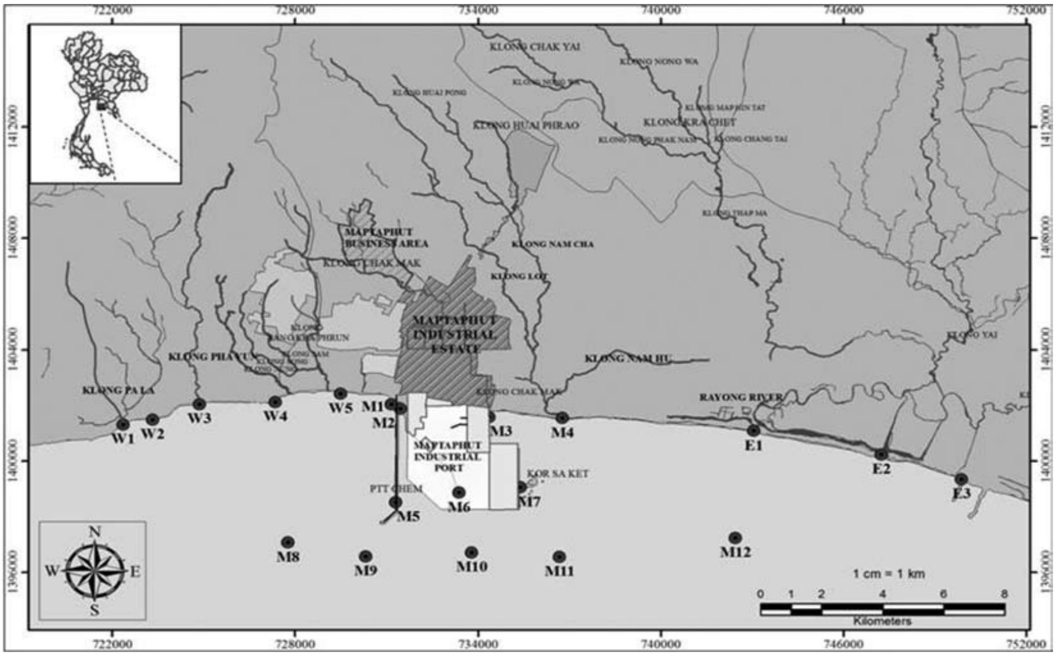

Figure 1 Sampling sites (E1–E3, M1–M12 and W1–W5) in Map Ta Phut industrial estate area, Thailand.

dry season (May 2011). The sediment samples were collected using an Ekman grab and were immediately transferred using a stainless steel scoop to hexane-rinsed, wide-mouthed, glass jars. The samples were kept in an ice box until returned to the laboratory and then were kept frozen at -20 ºC until analysis.

Sample preparation

Samples of 25 g of freeze-dried sediments sieved at 500 µm were spiked with 1-chlorooctadecane and o-terphenyl (as the internal standard) and extracted with 180 mL of dichloromethane in a Soxtec apparatus (Universal Extraction System B-811; BÜCHI Labortechnik AG; Flawil, Switzerland) for 35 cycles (adapted from Maliszewska-Kordybach *et al.*, 2008) at heating level 9 for 8 hr. The extracts were then reduced to approximately 3 mL by rotary evaporation before being transferred to glass tubes and evaporated gently under a nitrogen stream with 1 mL of hexane added.

The extract was quantitatively transferred into a column chromatographer packed with activated silica gel, and then copper treatment was activated for elemental sulfur removal and finally sodium sulfate was added for water removal. Elution was performed using 20 mL of hexane for the first 5 mL of hexane fraction which was discarded (containing the aliphatic hydrocarbons), then the mixture of 30% dichloromethane in 40 mL hexane (Beg *et al.*, 2003) was passed through the column to yield the second fraction (containing the aromatic hydrocarbons-PAHs). The volumes of fractions were reduced by rotary evaporation and then blowing through a gentle nitrogen stream before adding 500 µL of toluene.

Analysis

The quantification of individual hydrocarbon compounds was analyzed using gas chromatography-flame ionize detection (6890GC; Agilent Technologies; Santa Clara, CA, USA) equipped with an Agilent 7683B injector. The capillary column was a HP-5MS (Hewlett-Packard Corp.; Palo Alto, CA, USA) coated with 5% phenyl-methylsiloxane 0.32 × 0.25 mm inner diameter × 0.25 µm film thickness. The injector and detector temperatures were 250 and 300 ºC, respectively. The oven temperature was programmed from 80 to 100 ºC (held for 0.5 min) at the rate of 10 ºC.min^{-1}, then increased to 140 ºC at the rate of 5 ºC.min^{-1}, then increased to 290 ºC at the rate of 5 ºC.min^{-1} and was then held at this temperature for 10 min. The carrier gas was helium at a constant flow rate of 1 mL.min^{-1}. The injection volume was 1.0 µL in the splitless mode.

The concentrations of total PAHs were determined by summing the concentrations of the 14 PAHs: acenaphthene (ACP), fluorene (FLR), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLU), pyrene (PYR), benz[a] anthracene (BaA), chrysene (CHR), benzo[b] fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DhA), Indeno[1,2,3-cd]pyrene (IcP) and benzo[ghi]perylene (BgP), which were among those listed as priority pollutants by the U.S. Environmental Protection Agency (Manoli and Samara, 1999).

Individual PAHs in the samples were identified using their respective standards and quantified based on peak areas with reference to the internal standard o-terphenyl. A quality control study was carried out by monitoring recovery of the surrogate standard. In this study, the recovery ranged from 59 to 95%. The acceptable range of recovery was between 40 and 120% (Mirza *et al.*, 2012). The sediment quality, water content, organic carbon content, organic matter and soil texture were also analyzed (adapted from Walkley and Black, 1934; Food and Agriculture Organization of the United Nations, 1970; Topp, 1993).

RESULTS AND DISCUSSION

Sediment characteristics

The sediment characteristics are presented in Table 1. Particle size analysis showed that the majority of the sediments consisted of a sand mixture, with the sea floor sediments in the Map Ta Phut area being mainly sand, sandy loam and loamy sand. The water content, organic matter and organic carbon in sediments were present in high quantities at sites located in the center of the industrial estate and the near-shore area and decreased with distance from the coast with M2 having the highest values of all sites, with averages of 43.31 ± 9.19, 1.95 ± 1.03 and 1.55 ± 1.13%, respectively, followed by site M1. These two sites were close to an industrial estate with drainage from a power plant and the soil texture was a loam so that the high resolution increased the accumulation of organic compounds.

Distribution and composition of polycyclic aromatic hydrocarbons

The average concentrations of PAHs in the sediment samples collected at different sites are given in Table 2. The total concentrations of PAHs (Σ14PAHs) detected in the Map Ta Phut area ranged from 167.73 to 2,467.61 ng.g^{-1} dry weight with an average of 1,527.07 ± 100.26 ng.g^{-1} dry weight. These results were compared with past studies of PAHs in sediments in Thailand around the ship-breaking industry area of Map Ta Phut, the coastal area of Rayong province and the Tha Chin estuary where similar values were in the ranges 60 to 1,870, traces to 1,660 and 220 to 1,520 ng.g^{-1}, respectively (Suthanaruk, 1991; Tappatat, 1995; Chaipuriwong, 2001). In addition, the results were lower than for other industrial areas such as an industrial port in the southern Kaohsiung harbor of Taiwan which was supposed to be extensively polluted by industrial waste water discharges and the Khowre-Musa system (Persian gulf) of Iran which had values varying from 4,425 to 51,261 and 4,518 to 28,334 ng.g^{-1} dry weight, respectively (Dong *et al.*, 2012; Shadi *et al.*, 2012). The results may have been due to the Map Ta Phut Industrial estate having a high quality, wastewater treatment system before discharge into the sea. In addition, the soil texture in this area is mostly sand which accumulated less PAHs than clay soil (Liao *et al.*, 2012).

The average concentrations of PAHs in sediments collected from each site in the study area are shown in Figure 2. The survey found that for both seasons (dry and rainy) in this area, site M8 (offshore 5 km) had the highest average concentration at 2,207.72 ± 138.88 ng.g^{-1} dry weight. This station was located in an area exposed to heavy maritime traffic on oil and cargo shipping routes. The second highest concentration was at site M4 (Naam-Hoo canal mouth) with an average of 2,199.18 ± 18.67 ng.g^{-1} dry weight. The Naam-Hoo canal flows through communities with fishing activities from which wastewater sources and various organic compounds are loaded before discharge into the sea. PAHs are organic compounds that are much less soluble and decay slowly; thus they accumulate and remain in the sediment for a long time (Breedveld and Karlsen, 2000). Site W4 (Naam-rin beach) had the lowest average concentration of PAHs at 209.13 ± 58.55 ng.g^{-1} dry weight because it was located in a sandy coastal area with major tourist activity compared to the maritime, shipping and recreational fishing activities which are more common sources of PAHs. The area in front of the Map Ta Phut industrial estate (sites M1–M12) had average concentrations

Table 1 Sediment characteristics (mean ± SD) of Map Ta Phut industrial estate area.

	% Sand	% Silt	% Clay	% Water	% Organic matter	% Organic carbon
Mean	84.80±18.21	6.90±10.72	8.30±8.26	23.44±3.29	0.52±0.31	0.30±0.18
Range	24–98	0–42	0–44	12.69–49.81	0.06–2.67	0.03–1.55

Table 2 Average concentrations of individual parent polycyclic aromatic hydrocarbons in sediments (ng.g^{-1} dry weight).

Compound	3-Ring				4-Ring				5-Ring				6-Ring		ΣLPAHs	ΣHPAHs	ΣPAHs	Level of
Stations	ACP	FLR	PHE	ANT	FLU	PYR	BaA	CHR	BbF	BkF	BaP	DhA	IcP	BgP				Pollution
W1	4.36	23.55	17.55	30.13	198.81	172.55	7.41	33.93	36.22	72.79	71.23	11.25	41.68	35.79	75.58	681.65	757.23	Moderate
W2	10.98	73.79	35.98	26.57	742.78	159.11	6.91	250.25	195.03	83.59	74.69	88.87	119.74	88.35	147.32	1,809.31	1,956.64	High
W3	19.03	15.90	30.44	49.59	796.37	189.94	136.20	108.57	133.90	90.94	53.29	122.08	58.57	41.35	114.96	1,731.21	1,846.16	High
W4	2.09	21.62	7.49	10.96	16.98	18.88	4.71	5.18	23.99	16.64	37.97	10.44	10.22	21.97	42.15	166.98	209.13	Moderate
W5	7.40	10.67	36.98	24.59	478.22	222.25	5.04	231.06	64.65	125.40	136.55	43.92	46.90	14.28	79.64	1,368.27	1,447.91	High
M1	14.25	25.78	28.09	25.64	498.39	62.65	74.64	158.98	120.65	101.77	38.34	66.89	69.15	85.56	93.76	1,277.01	1,370.78	High
M2	8.67	18.19	53.19	29.25	396.27	178.67	2.57	106.29	65.21	65.75	79.90	42.35	52.03	24.55	109.29	1,013.59	1,122.88	High
M3	16.15	56.43	27.31	21.86	658.05	104.82	127.52	64.29	97.21	181.97	96.89	107.46	55.84	86.86	121.74	1,580.90	1,702.64	High
M4	11.88	26.55	38.77	28.32	1,076.76	146.16	32.05	220.16	220.07	104.02	136.73	40.05	65.05	52.61	105.52	2,093.66	2,199.18	High
M5	16.19	20.23	36.34	15.49	494.04	156.34	10.89	184.65	79.84	161.53	133.82	74.97	146.49	25.57	88.24	1,468.12	1,556.37	High
M6	29.73	35.28	34.66	24.45	839.29	355.22	189.10	39.03	50.56	128.14	136.68	44.01	38.96	32.20	124.11	1,853.19	1,977.30	High
M7	8.39	36.62	30.65	23.56	681.40	151.64	23.31	252.26	52.59	155.81	196.91	85.63	84.05	62.64	99.21	1,746.24	1,845.45	High
M8	1.88	36.54	45.27	23.12	814.45	181.37	56.55	269.47	121.90	203.19	245.36	76.59	52.94	79.11	106.81	2,100.92	2,207.72	High
M9	4.85	25.32	29.99	21.78	596.30	253.10	50.92	40.71	64.67	133.42	163.64	55.91	42.88	44.72	81.94	1,446.27	1,528.21	High
M10	6.03	18.46	58.17	12.08	467.16	185.24	109.66	5.92	44.73	112.44	38.72	102.97	89.96	71.54	94.73	1,228.34	1,323.07	High
M11	5.03	140.20	56.60	17.38	954.23	141.16	35.51	127.54	74.07	80.32	111.63	84.92	82.32	117.74	219.21	1,809.44	2,028.65	High
M12	8.97	14.09	22.32	16.72	667.39	257.37	65.51	150.75	96.85	89.66	122.09	40.17	56.04	35.17	62.10	1,581.00	1643.10	High
E1	4.34	35.06	55.40	12.04	553.71	218.83	119.12	115.01	44.02	136.55	88.81	42.96	48.16	38.82	106.84	1,406.00	1,512.84	High
E2	6.52	8.91	30.75	24.51	746.64	206.53	74.25	134.55	47.90	114.50	136.81	39.72	28.33	19.54	70.69	1,548.79	1,619.48	High
E3	4.95	56.56	11.16	18.49	54.00	40.55	21.81	178.23	30.33	192.72	19.66	20.95	23.85	13.48	91.16	595.58	686.74	Moderate
Total	192	700	687	457	11,731	3,402	1,154	2,677	1,664	2,351	2,120	1,202	1,213	992	2,035	28,506	30,541	
Average	9.58	34.99	34.35	22.83	586.56	170.12	57.68	133.84	83.22	117.56	105.99	60.11	60.66	49.59	101.75	1,425.32	1,527.07	
ERL	16	19	240	85.3	600	665	261	384	-	-	430	63.4	-	-	552	1,700	4,022	
ERM	500	540	1,500	1,100	5,100	2,600	1,600	2,800	-	-	1,600	260	-	-	3,160	9,600	44,792	

ACP = Acenaphthene, FLR = Fluorene, PHE = Phenanthrene, ANT = Anthracene, FLU = Fluoranthene, PYR = Pyrene, BaA = Benz(a)anthracene, CHR = Chrysene, BbF = Benzo(b)fluoranthene, BkF = Benzo(k)fluoranthene, BaP = Benzo(a)pyrene, IcP = Indeno(1,2,3-cd)pyrene, DhA = Dibenzo(a,h)anthracene, BgP = Benzo(g,h,i)perylene

ΣLPAHs = Sum of ACP, FLR, PHE and ANT; ΣHPAHs = Sum of FLU, PYR, BaA, CHR, BbF, BkF, BaP, DhA, IcP and BgP; ΣPAHs = Sum of 14PAHs.

ERL = Effects Range Low; ERM = Effects Range Median (Long *et al.*, 1995).

at 1,708.78 ± 452.78 ng.g^{-1}, followed by the east side (sites E1–E3) and west side (W1–W5) of the Map Ta Phut industrial Estate, with highest averages of 1,273.02 ± 647.94 and 1,243.41 ± 728.30 ng.g^{-1}, respectively. Seawards from the shoreline, offshore 3 km (M5-M7) had a highest average concentration of 1,793.04±370.56 ng.g^{-1}, followed by the offshore 5 km and shoreline sites which averaged 1,746.15 ± 406.70 and 1,598.87 ± 583.92 ng.g^{-1}, respectively. These results are associated with the fact that the Map Ta Phut area has been reclaimed for construction industries and the Map Ta Phut port has been extended by a reclamation area that is 3 km offshore and is occupied by a group of petrochemical plants with the storage of raw materials and petrochemical products and coal power plants that ferry coal and have coal piles along the shore. Furthermore, there is a large amount of combustion of fuel from industry and from the many ships passing through the port. Thus, there was a greater accumulation of PAHs in this area than in other areas.

The pollutant level classification of PAHs suggested by Baumard *et al*. (1998) has four ranges: (a) low, 0–100 ng.g^{-1}; (b) moderate, > 100 to 1,000 ng.g^{-1}; (c) high, > 1,000 to 5,000 ng.g^{-1}; and (d) very high, > 5,000 ng.g^{-1}. Sediments from this study area can be characterized as having high PAH levels of pollution because this area has industrial activities with tanker traffic and untreated wastewater discharged from municipal wastewater.

The percentage of average concentration of each PAH compound in this study is shown in Figure 3. Fluoranthene (38%) was present as the fraction of PAHs with the highest concentration in the study area, followed by pyrene (11%), chrysene (9%), benzo(k)fluoranthene (8%) and benzo(a) pyrene (7%), respectively. Many other PAH compounds were present at low concentration. The fact that fluoranthene was found in many sediment samples was an indicator that this area was characterized by lower-temperature, incomplete combustion.

The molecular structure of specific PAH compounds in the environment can be used for classification. Low molecular weight (LMW) PAHs are categorized by two to three benzene rings while four to six rings are known as high molecular weight (HMW) PAHs. In this study, ΣHMW PAHs was higher than ΣLMW PAHs in the sediment samples collected from all sampling

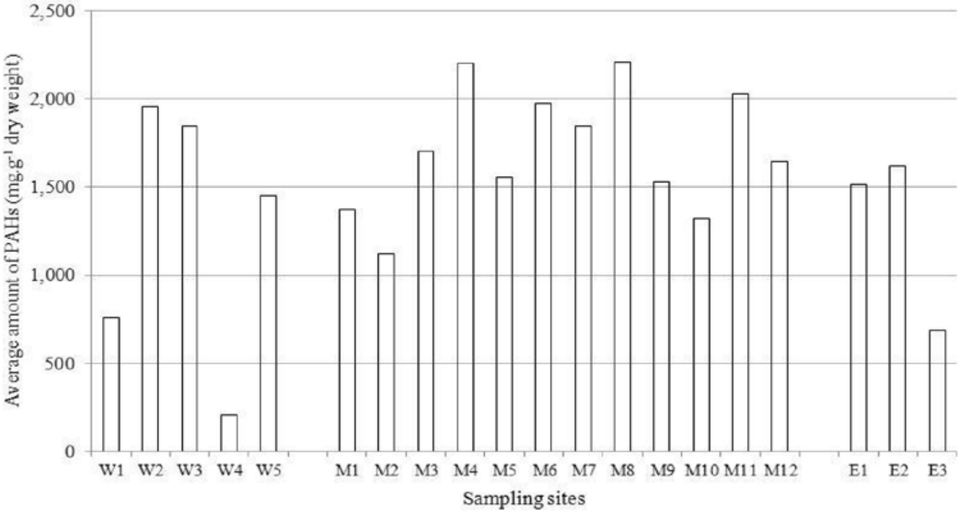

Figure 2 Average concentration of polycyclic aromatic hydrocarbons (PAHs) in sediments collected from each sampling site.

sites (Table 2). The predominance of HMW PAHs reflects the presence of significant combustion products from sources of pyrogenic processes. The PAHs originated mainly from the incomplete combustion of organic matter, fossil fuel and oil or coal. In general, HMW PAHs are more abundant than LMW PAHs in the sediments from river, lacustrine and marine environments (Khalid *et al*., 2007; Yan *et al*., 2009). The distribution of PAHs is associated with their ability to dissolve and their degradation. Therefore, HMW PAHs have a high boiling point and low vapor pressure which restricts the levels of degradation and chemical structural changes in LMW PAHs. For these reasons, HMW PAHs can accumulate in the sediment and the environment to greater levels than LMW PAHs (Yamada *et al*., 2003).

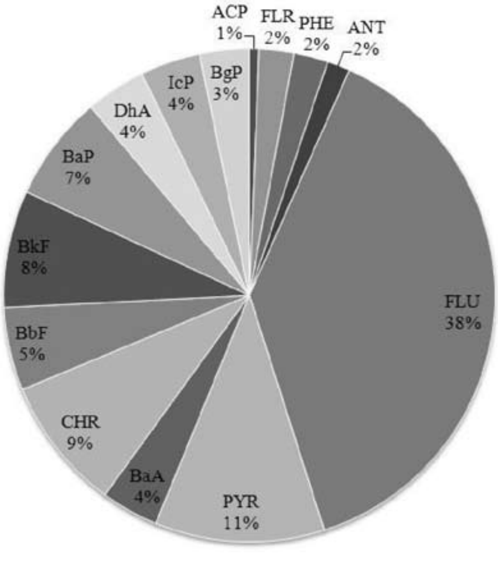

Figure 3 Percentage of average concentration of the polycyclic aromatic hydrocarbons compounds identified in the study area (ACP = Acenaphthene, FLR = Fluorene, PHE = Phenanthrene, ANT = Anthracene, FLU = Fluoranthene, PYR = Pyrene, BaA = Benz(a) anthracene, CHR = Chrysene, BbF = Benzo(b)fluoranthene, BkF = Benzo(k) fluoranthene, BaP = Benzo(a)pyrene, DhA = Dibenzo(a,h)anthracene, IcP = Indeno(1,2,3-cd)pyrene, BgP = Benzo(g,h,i)perylene).

The 14PAHs were divided into four groups based on their benzene ring structure—3-ring, 4-ring, 5-ring and 6-ring PAHs. The PAH distribution pattern by the number of aromatic rings is shown in Figure 4. The 4-ring PAHs were predominant in the sediments from the Map Ta Phut industrial estate, ranging from 21.88 to 71.95% with an average of 59.38%, followed by the 5-ring, 3-ring and 6-ring PAHs with averages of 25.52, 7.59 and 7.51%, respectively, except for the sediment from site W4 (Naam-rin beach), where the 5-ring PAHs dominated (42.47%). These results were consistent with studies in sediments from San Francisco Bay and Daya Bay (Pereira *et al*., 1996; Khalid *et al*., 2007).

Diagnostic ratios of polycyclic aromatic hydrocarbons

The identification of different sources of PAHs has been based on the PAH isomeric ratios. In this study, ANT / (ANT+PHE) and FLU / (FLU+PYR) were chosen to determine sources of PAHs in sediments from Map Ta Phut industrial estate since their different physicochemical properties meant they could behave differently in the environment and lead to different ratios (Cardellicchio *et al*., 1997). Ratios of ANT / (ANT + PHE) < 0.1 and FLU / (FLU + PYR) < 0.4 usually imply contamination by PAHs from a petrogenic source with petroleum-derived input, while ratios of ANT / (ANT + PHE) > 0.1 and FLU / (FLU + PYR) > 0.5 imply these pyrogenic PAHs are derived from biomass combustion (grass, wood or coal combustion) and if the FLU / (FLU + PYR) ratio is between 0.4 and 0.5, this indicates petroleum combustion. (Yunger *et al*., 2002; Fang *et al*., 2007).

The cross plots of ANT / (ANT + PHE) and FLU / (FLU + PYR) ratios in the wet and dry season are shown in Figure 5. The ratios of ANT / (ANT + PHE) > 0.1 and FLU / (FLU +

PYR) > 0.5 in the two seasons indicated that most sediment samples involved combustion of grass, wood and coal as possible contributions to the PAHs. However, surface sediments from site M6 in the wet season had a ratio of ANT / (ANT + PHE) and FLU / (FLU + PYR) higher than 0.1 and between 0.4 and 0.5, respectively, indicating that petroleum combustion could be the possible source of these PAHs. In the dry season, M11, W1, W4 and E3 had ratios of ANT / (ANT + PHE) < 0.1 and FLU / (FLU + PYR) < 0.4 which usually implies contamination by PAHs from a petrogenic source with petroleum-derived input. The ratio calculations suggest that the input of the PAHs to the Map Ta Phut area mainly came from pyrogenic sources due to incomplete combustion as this area was the site of a large industrial estate and deep-water port with many industries, in particular petrochemical plants and coal power plants with coal transport and coal banks on land reclaimed from the sea. Thus, the main source of the PAHs that had accumulated in the sediments in the Map Ta Phut area could be expected to have been derived from coal combustion, combustion in the oil industry, fuel consumption by ship traffic into and out of the Map Ta Phut port, emissions from cars, ships and industrial plants leaching into the sediments contaminated with PAHs, including the discharge of wastewater contaminated with oil from domestic and industrial sources and waste oil from ship maintenance disposed of directly into the sea.

Potential biological effects

The PAH levels in the sediment samples were assessed for possible hazards to the marine benthic community using a comparison with effect-based sediment quality guideline values. Effects-range low (ERL) and effects-range median (ERM) were calculated from the lowest 10th percentile and the 50th percentile of biological effects concentrations, respectively. These two values defined three concentration ranges for each particular chemical that were: (1) rarely (< ERL), (2) occasionally (≥ ERL, < ERM) or (3) frequently (≥ ERM) associated with the adverse effects on benthic marine organisms from Long *et al*. (1995). The measured concentrations of PAH

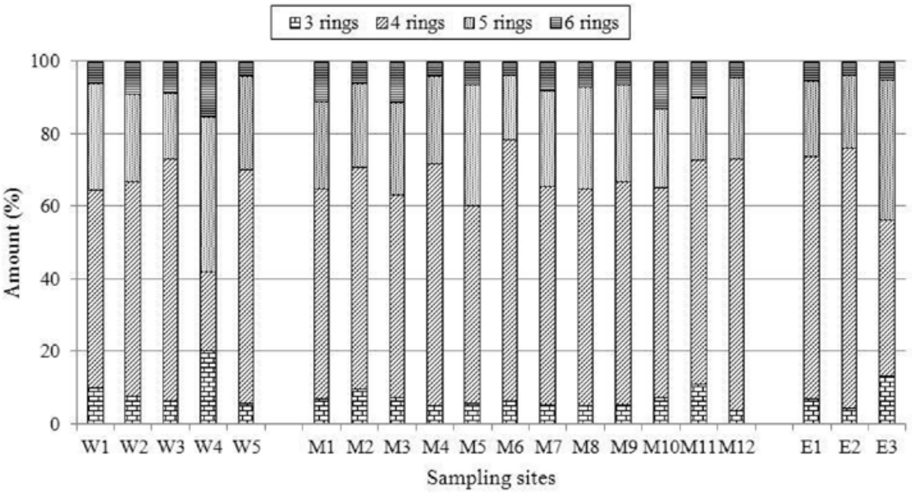

Figure 4 Distribution patterns of polycyclic aromatic hydrocarbons in sediments from the sampling sites based on the number of benzene rings, where: 3 rings = acenaphthene, fluorene, phenanthrene, anthracene; 4 rings = fluoranthene, pyrene, benz(a)anthracene, chrysene; 5 rings = benzo(b) fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene); 6 rings = indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene.

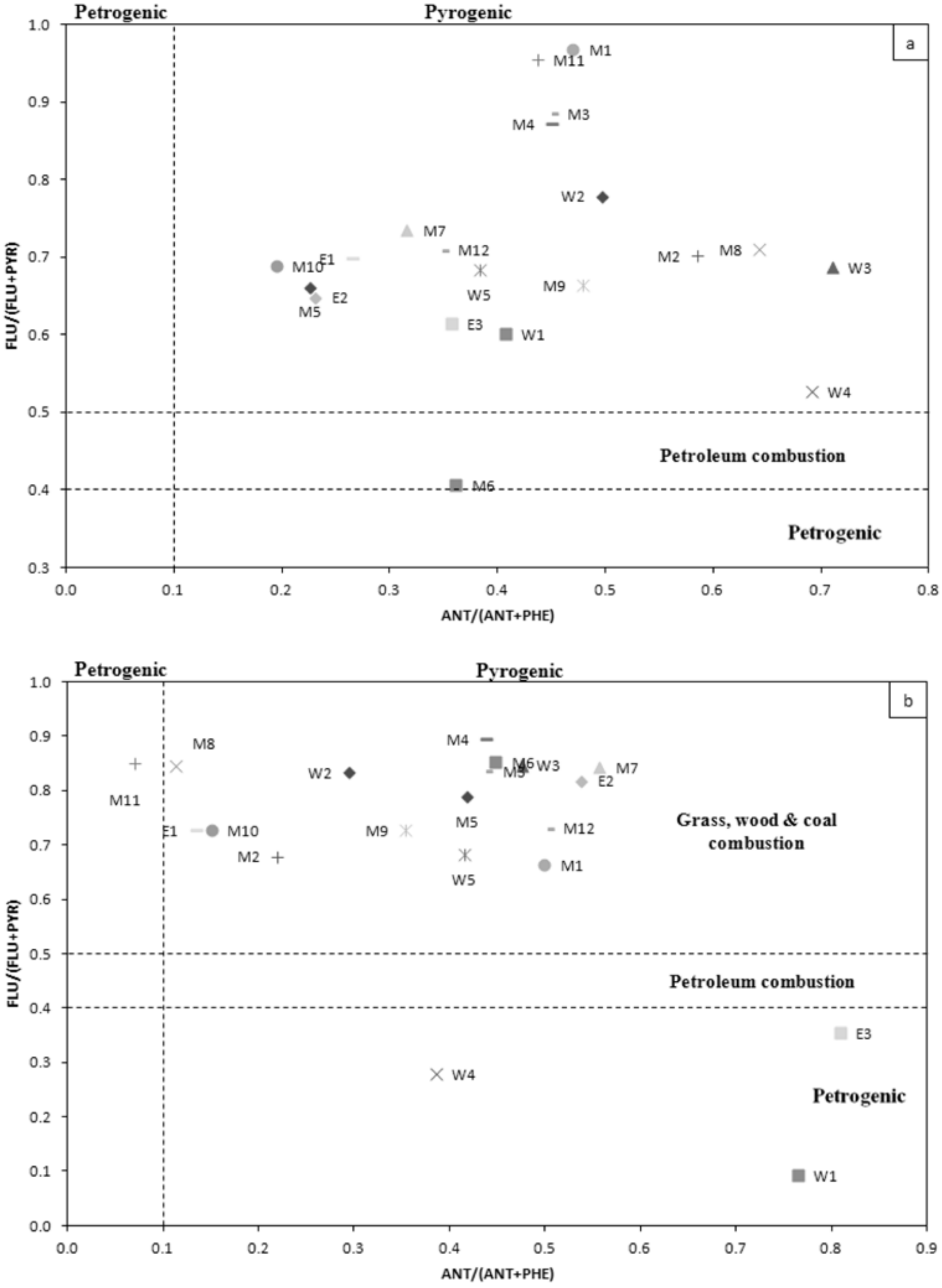

Figure 5 Cross plots of isomeric anthracene (ANT) / (ANT + phenanthrene (PHE)) and fluoranthene (FLU / (FLU + pyrene (PYR)) ratios in sediments from sample points in the Map Ta Phut area during: (a) Wet season; (b) Dry season.

compounds based on ERL and ERM values are shown in Table 2. The total PAH concentrations (ΣPAHs) and ΣLPAHs for all sites were below ERL, which indicated that adverse biological effects should be rare. The ΣHPAHs were below ERL at 13 sites and between ERL and ERM at 7 sites. All individual PAHs, such as phenanthrene, anthracene, pyrene, benz(a)anthracene, chrysene and benzo(a)pyrene, at all sites were below ERL. Furthermore, acenaphthene, fluorene, fluoranthene and dibenz(a,h)anthracene were between ERL and ERM in 4, 14, 10 and 9 sites, respectively, which indicated that biological effects at those sites would occur occasionally.

CONCLUSION

This paper reported substantial data on the natural characteristics of sediment and on the distribution, possible sources and potential biological effects of PAHs in sediments of the Map Ta Phut industrial estate area, Rayong province, Thailand. The results showed that sea floor sediments in the Map Ta Phut industrial estate area were mostly sand, sandy loam and loamy sand. The water content, organic matter and organic carbon in sediments averaged 23.44 ± 3.29, 0.52 ± 0.31 and 0.30 ± 0.18 %, respectively. The total concentration of PAHs ranged from 167.73 to 2,467.61 ng.g^{-1} dry weight with an average concentration of 1,527.07 ± 100.26 ng.g^{-1} dry weight. The season did not affect the distribution and accumulation of PAHs in sediments. The sediment samples from this study area indicated that most of the sites have high pollution of PAHs, except for three sites which have moderate pollution levels of PAHs. Fluoranthene, pyrene, chrysene, benzo(k)fluoranthene and benz(a)pyrene represented the top five PAHs in surface sediment samples. The 4-ring and 5-ring PAHs were the most abundant compounds which accounted for 85% of total PAHs. The amount of ΣHMW PAHs was higher than for ΣLMW PAHs in sediment samples collected from all sampling sites. The study identified the possible sources of PAHs that occur from incomplete combustion (pyrogenic sources) or petroleum products (petrogenic sources). The results showed that PAHs in the Map Ta Phut area mainly came from pyrogenic sources resulting from the incomplete combustion of fossil fuels and organic substances. Compared with effect-based sediment quality guideline values, the concentrations of total PAHs for all sites were below ERL, which indicated that biological effects would occur rarely. The results should be useful in the planning and management for environmental protection of the Map Ta Phut area.

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