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Chemical characterization of polycyclic aromatic hydrocarbons (PAHs) in 2013 Rayong oil spill-affected coastal areas of Thailand☆

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ABSTRACTS

Among Southeast Asian countries, Thailand has gradually accustomed to extremely prompt urbanization, motorization, and industrialization. Chonburi and Rayong provinces are two provinces involved in "eastern seaboard" industrial zones, which is an emerging economic region that plays a key role in Thailand's economy. The 2013 Rayong oil spill did not only cause damages to the coastal and maritime environment, but also undermine trust in the overall safety system and negatively affect the investor confidence. In this study, 69 coastal soils collected around Koh Samed Island were chemically extracted and analyzed for 15 PAHs by using a Shimadzu GCMS-QP2010 Ultra system comprising a high-speed performance system with ASSP function. In this study, numerous diagnostic binary ratios were applied to identify potential sources of PAHs. Advanced statistical techniques such as hierarchical cluster analysis coupled with principal component analysis were also conducted for further investigations of source identifications.

1. Introduction

The coastal and marine ecosystems of the Gulf of Thailand (GoT) was critically threatened by the massive oil spill caused by a pipeline owned by PTT Global Chemical Public Company Limited (PTTGC) burst while oil was being transferred from undersea well to a tanker on July 27th, 2013. By the 28th of July 2013, ten vessels (i.e. five from PTTGC and the rest from the Royal Thai Nave and IRPC Plc.) coupled with C130 aircraft were included in the emergency response and recover operations were conducted in addition to continued application of dispersants (Dasic Slickgone NS and Super Dispersant 25). Based on the official report of PTTGC, approximately 50,000 L (310 bbl) of crude oil were spilled on the surface and deep waters of the northern GoT, reached the beach at Koh Samed Island (KSI)'s Coconut Bay (Ao Phrao) which is one of the most popular tourist attractions relatively adjacent to Bangkok. As a result, two beaches have been terminated due to unpredictability associated with water toxicity. There are two major categories of effects, which can be observed after the oil spill incidence. Firstly, the comparatively short-term of adverse economic impacts triggered by additional costs occurred by cleanup activities including the lost in both tourism and fishery revenue (Garza-Gil et al., 2006; Loureiro et al., 2009; Pan et al., 2015). It is crucial to note that the relatively more long-term impacts can take place in the case of public awareness of prolonged and wide-scale contamination exists long after the oil spill incident. Secondly, the oil spill incidents can inevitably provide the negative impacts on coastal and maritime ecosystems (Burns et al., 1993; Kingston, 2002; Peterson et al., 2003; Piatt et al., 1990).

Previous studies highligh the influences of oil spill incidents on the enrichment of polycyclic aromatic hydrocarbons (PAHs) in coastal and maritime sediments around the world (Allan et al., 2012; Bejarano and Michel, 2010; Franco et al., 2006; Peterson et al., 2003; Reddy et al., 2002). PAHs is well recognized as toxic organic compounds responsible for genotoxicity, metabolism,

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carcinogenicity and mutagenicity (Luch, 2005; Rosenkranz and Mermelstein, 1985; You et al., 1994). For these particular reasons, PAHs have been extensively investigated in various environmental compartments in the past few years (Pongpiachan, 2013a,b; 2015b; 2016; Pongpiachan et al., 2013a, 2016,b,c; 2015a,b). PAHs have numerous unique features which enable them relatively more persistent pollutants correlated to acid-leached heavy metals and/or water soluble ionic species because *i*) PAHs possess aromatic rings, whose structure is particularly not liable to undergo both chemical decomposition and photolysis making them persistence over the long-period (Beck et al., 1995; Wild et al., 1991; Wild and Jones, 1995), *ii*) PAHs are ubiquitous in dusts, terrestrial soils and coastal sediments (Pongpiachan, 2013a,b, 2015b, 2016; Pongpiachan et al., 2013a, 2016,b,c; 2015a,b), *iii*) PAHs are hydrophobic congeners, underlining that the precipitation may not adequately dissolve these persistent organic pollutants (Meador, 2008) and *iv*) PAHs have biomagnification and genotoxic possibility (Binková and Šrám, 2004; Gray, 2002; Luch, 2005). The major contributors of PAHs are vehicular emissions, factory exhausts, accidental oil spills, forest fires and agricultural waste burning (Allan et al., 2012; Bejarano and Michel, 2010; Franco et al., 2006; Kakareka and Kukharchyk, 2003; Kim et al., 2003; Peterson et al., 2003; Reddy et al., 2002; Slezakova et al., 2013; Yang et al., 1998). Without minimizing these fundamental source strengths, PAHs are apparently continue to exist in terrestrial soils, comprising the oil-spill contaminated coastal areas.

In spite of numerous studies that have consistently focusing on both spatial and temporal distributions of PAHs around the world, there are limited ecological studies focusing on the chemical characterization of PAHs in coastal area after major oil spill incident. Overall, the main objectives of this study are *i*) to determine the concentrations of 15 PAH congeners collected from 69 coastal soil samples around KSI, two years after the oil spill cleanup processes, *ii*) to compare the measured PAH contents from KSI with those of terrestrial soils around the world including oil spill contaminated sites, and *iii*) to conduct the source identification by using factor analysis coupled with diagnostic binary ratios.

2. Materials and methods

2.1. Study sites and sampling methods

KSI was carefully chosen as the study area, where was heavily contaminated with crude oil from oil spill incident during 27th-31st October 2013 (see Fig. S1). The study sties cover all of the beaches around KSI, where some parts was greatly polluted by crude oil especially Ao Prao Bay (AP) and Ao Noina Bay (ANN) as shown in Fig. S2. Sai Kaew Beach (SK), Ao Chor Bay (AC), and Ao Lungdum Bay (ALD) represents anthropogenic activities contaminated sites (e.g. leaking gasoline from speed boats) and Ao Pakarang Bay (APR) was selected as the control site of natural background. Soil sampling stations (69 stations) were collected during 14th-18th November 2015. Approximately a half kilogram of composite sample from 1 m^2 area of each station was collected by using the shovel with the depth of top 0–5 cm and then were kept in clean aluminum foil, placed in a glass bottle, and stored at−20 °C. After removing stones and shell residuals, they were freeze-dried and sieved to <0.076 mm (200 mesh), and then kept at −20 °C until analysis. In addition, more details of soil sampling protocol were previously mentioned in international standard methods (Barth and Mason, 1984; Ecology and Environment, Inc. 1990; Mason, 1983).

2.2. Chemicals and reagents

For the standard sample, all solvents are HPLC grade, purchased from Fisher Scientific. A cocktail of 15 PAHs Norwegian Standard (NS 9815: S-4008-100-T) (phenanthrene (Phe), anthracene (An), fluoranthene (Fluo), pyrene (Pyr), 11H-benzo[*a*]fluoranthene (11H-B[*a*]F), 11H-benzo[*b*]fluoranthene (11H-B[*b*]F), benz[*a*]anthracene (B[*a*]A), chrysene (Chry), benzo[*b*]fluoranthene (B[*b*]F), benzo[k]fluoranthene (B[k]F), benzo[e]pyrene (B[e]P), benzo[*a*]pyrene (B[*a*]P), indeno[1,2,3-*cd*]pyrene (Ind), dibenz[a,h]anthracene (D[a,h]A), benzo[g,h,i]perylene (B[g,h,i]P); each 100 μg mL^{-1} in toluene: unit: 1 × 1 mL) and a mix of recovery Internal Standard PAHs (d_{10}-fluorene; d_{10}-Fl, d_{12}-perylene; d_{12}-Per); each 100 μg mL^{-1} in xylene: unit: 1 × 1 mL) were supplied by Chiron AS (Stiklestadveine 1, N-7041 Trondheim, Norway). It is worth mentioning that Phe, An, Fluo, Pyr, 11H-B[*a*]F, 11H-B[*b*]F, B[*a*]A, and Chry can be catogorized as medium molecular weight (MMW) PAHs. Additionally, B[*b*]F, B[k]F, B[e]P, B[*a*]P, Ind, D[a,h]A, and B[g,h,i]P are widely acknowledged as high molecular weight (HMW) PAHs. Standard stock solutions of 4 μg mL^{-1} of deuterated PAHs (used as internal standard) and 100 μg mL^{-1} of native PAHs were prepared in nonane. Working solutions for quantifying instrumental detection limits (i.e. 1 ng μL^{-1}, 500 pg μL^{-1}, 100 pg μL^{-1}) were obtained by appropriate dilution in *n*-cyclohexane (see Table S1). All solutions were stored in amber coloured vials at −20 °C.

2.3. Analytical methods

All the freeze-drying, chemical extraction, and the fractionation/clean up processes of PAHs were conducted according to the procedure. PAH extraction via Soxhlet with dicloromethane was performed by applying to the soil sample a known amount of internal standard (d_{10}-Fl (used to quantify Phe, An, Fluo, Pyr, B[*a*]A, Chry, 11H-B[*a*]F, 11H-B[*b*]F); d_{12}-Per (used to quantify B[*b*]F, B[k]F, B[e]P, B[*a*]P, Ind, D[a,h]A, and B[g,h,i]P) and 1 g of copper powder for 8 h. The fractionation/cleanup process followed the conventional method using the difference in solvent polarity. After the Soxhlet extraction, the DCM eluent was decreased to incipient dryness by using both rotary evaporation and blowing under a gentle nitrogen stream. More details of analytical methods were clearly explained in previous literature and will not be mentioned here (Pongpiachan, 2013a,b, 2015b, 2016; Pongpiachan et al., 2013a, 2016,b,c; 2015a,b). All injections (1 μL) were conducted using a universal injector in the splitless mode, and the standards were introduced using a 10 μL Hamilton syringe. The GC oven temperature was set as follows: 1 min at 40 °C, heated at 8 °C min^{-1} to 300 °C and held for 45 min using a Shimadzu GCMS-QP2010 Ultra system comprising a high-speed performance system with ASSP function (i.e. achieving maximum scan speed of 20,000 u sec^{-1}) and an ultra-fast data acquisition speed for comprehensive two-dimensional gas chromatography (GC × GC) with GC capillary column (DB-5, 30 m × 0.25 mm). More comprehensive GC/MS method was given in earlier references and will not be discussed here (Pongpiachan et al., 2009, 2011). Standard reference material (SRM-NIST1941b-Marine Sediment) was used to perform both quality control and quality assurance of analytical results. Mean recovery (based on extraction of matrix-matched certified reference materials SRM-NIST1941b-Marine Sediment, ($n = 8$) was in range of 78–107%. The precision of the procedure, calculated as relative standard deviation on the duplicate samples, was less than 15%.

3. Results and discussion

Table 1 was arranged according to the columns: firstly, samples corresponding to control site APR, later the ones corresponding to other human activities ALD, AC, SK and the ones greatly polluted by oil spill: ANN and AP. It is important to note that the samples of

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Table 1
Statistical descriptions of Paths collected at coastal soils of KSI.

Conc. (ng g^{-1})	APR ($n = 4$)		ALD ($n = 4$)		AC (n = 4)		SK (n = 4)		ANN ($n = 4$)		AP ($n = 49$)		KSI ($n = 65$)	
	Aver	Stdesv	Aver	Stdev	Aver	Stdev	Aver	Stdev	Aver	Stdev	Aver	Stdev	Aver	Stdev
Phe	1.19	2.38	0.793	0.921	1.33	2.66	1.33	2.67	0.740	1.48	0.665	1.12	0.808	1.41
An	1.15	1.78	0.114	0.229	N.D.	N.D.	N.D.	N.D.	0.397	0.793	0.329	0.881	0.339	0.890
Fluo	0.121	0.242	0.480	0.405	0.236	0.472	0.343	0.449	0.084	0.169	0.269	0.597	0.272	0.542
Pyr	0.147	0.294	1.12	1.16	0.0736	0.147	0.892	1.17	0.764	0.931	0.422	0.683	0.487	0.748
11H-B[*a*]F	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.00724	0.0371	0.005	0.032
11H-B[*b*]F	N.D.	N.D.	0.422	0.615	N.D.	N.D.	N.D.	N.D.	0.863	1.73	0.0406	0.230	0.106	0.487
B[*a*]A	0.0408	0.0816	1.59	1.74	N.D.	N.D.	1.56	2.96	1.31	2.62	0.533	1.93	0.658	1.93
Chry	0.784	1.45	0.332	0.594	1.86	3.71	1.90	3.69	N.D.	N.D.	0.249	0.896	0.473	1.49
B[*b*]F	3.57	6.35	11.9	23.6	5.21	7.47	5.23	10.5	11.8	23.6	3.65	8.26	4.77	10.8
B[k]F	1.66	2.95	8.15	16.2	3.30	5.17	2.43	4.87	8.08	16.2	1.99	4.64	2.79	6.78
B[e]P	1.19	2.37	0.406	0.813	0.846	1.69	2.83	5.66	N.D.	N.D.	1.54	4.65	1.41	4.23
B[*a*]P	0.900	1.47	5.21	10.3	1.24	2.48	0.749	1.50	6.10	9.84	1.26	3.30	1.77	4.44
Ind	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.0155	0.0992	0.0113	0.0849
D[a,h]A	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.00632	0.0443	0.00462	0.0379
B[g,h,i]P	21.3	28.4	23.3	43.2	22.4	26.1	23.0	26.9	3.47	6.95	21.0	69.7	20.4	61.0
ΣPAHs15[a]	32.0	29.5	53.9	53.0	36.5	28.1	40.2	30.4	33.6	31.2	32.0	70.6	34.3	62.7
ΣPAHs12[b]	30.8	29.4	53.0	53.0	35.7	28.1	37.4	29.8	32.7	31.2	30.4	70.5	32.8	62.6
ΣPAHs(3,4)[c]	3.43	3.33	4.84	2.48	3.50	4.59	6.03	5.58	4.16	3.68	2.51	2.73	3.15	3.14
ΣPAHs(5,6)[d]	28.6	29.3	49.0	52.9	33.0	27.8	34.2	29.8	29.4	31.0	29.5	70.6	31.1	62.7

[a] Sum of 15 PAH congeners namely Phe, An, Fluo, Pyr, 11H-B[*a*]F, 11H-B[*b*]F, B[*a*]A, Chry, B[*b*]F, B[k]F, B[e]P, B[*a*]P, Ind, D[a,h]A, and B[g,h,i]P.

[b] Sum of 12 PAH congeners namely Phe, An, Fluo, Pyr, B[*a*]A, Chry, B[*b*]F, B[k]F, B[*a*]P, Ind, D[a,h]A, and B[g,h,i]P.

[c] Sum of 3 and 4 ring PAH congeners namely Phe, An, Fluo, Pyr, 11H-B[*a*]F, 11H-B[*b*]F, B[*a*]A, and Chry.

[d] Sum of 5 and 6 ring PAH congeners namely B[*b*]F, B[k]F, B[*a*]P, Ind, D[a,h]A, and B[g,h,i]P.

control site APR were not included in the column KSI. The study of statistical differences among samples sites could also provide important information associated with contamination sources. The average total contents of twelve probably carcinogenic PAHs in KSI ranged from 30.4 ± 70.5 ng g^{-1} (AP) to 37.4 ± 29.8 ng g^{-1} (SK). In this investigation, the $\sum_{12}$PAHs indicates the sum of detected Phe, An, Fluo, Pyr, B[*a*]A, Chry, B[b+k]F, B[*a*]P, Ind, D[a,h]A and B[g,h,i]P. In this study, ANOVA test was conducted to investigate the effect of sampling locations on individual PAH contents. Although no significant differences ($p < 0.05$, $F_{\text{Critical Value}} = 2.361$) were observed in all PAH congeners collected from seven different sampling groups (i.e. APR, ALD, AC, SK, ANN, AP, and KSI), there are some major differences associated with *F*-values. The observed sequence in decreasing order of *F*-values was Chry ($F = 1.934$)>B[*a*]P ($F = 1.549$) >Pyr ($F = 1.461$)>B[k]F ($F = 1.201$)>An ($F = 0.967$)>B[*b*]F ($F = 0.818$) >B[*a*]A ($F = 0.666$)>Phe ($F = 0.367$)>Fluo ($F = 0.281$)>B[e]P ($F = 0.243$)>B[g,h,i]P ($F = 0.0638$). This can be attributed to the fact that PAH concentrations represent a comparatively homogeneous distribution. In other words, a site specific emission can be considered as a minor of importance. The average $\sum_{12}$PAHs in KSI (32.8 ± 62.6 ng g^{-1}) was 1654 times, 581 times, 382 times, and 276 times lower than those values reported in the harbor sediment of Boston (54,253 ng g^{-1}), marine sediment of Northern Irish Sea (19,061 ng g^{-1}), riverine sediment of Guangzhou Channel (12,525 ng g^{-1}), and marine sediment of Bayou St. John, New Orleans (9037 ng g^{-1}), respectively (Bixian et al., 2001; Guinan et al., 2001; Mielke et al., 2001; Wang et al., 2001). It is also interesting to note that the average $\sum_{12}$PAHs in KSI was still 19 times and 2.4 times lower than those marine sediments in oil spilled area of Persian Gulf, Iran (628 ± 281 ng g^{-1}) and Guan River Estuary, China (78 ± 231 ng g^{-1}), respectively (Aghadadashi et al., 2017; He et al., 2014).

3.1. *Spatial distribution characteristics of PAHs*

The average Σ_{12}PAHs in KSI (32.5 ± 61.7 ng g^{-1}) was 116 times, 663 times, 21 times, and 188 times lower than those values of ERL (*Effects Range Low*), ERM (*Effects Range Median*), TEL (*Threshold Effect Levels*), and PEL (*Probable Effect Levels*) indicated low probability of causing adverse biological effects (<ERL 3759 ng g^{-1}; <ERM 21,560 ng g^{-1}; <TEL 677 ng g^{-1}; <PEL 6118 ng g^{-1}; see Table 2). It is well known in environmental toxicology that ERL and ERM can be used as indicators of evaluating toxicity in marine sediment. While ERL shows the content below which toxic effects are barely detected, ERM highlights that above which effects are frequently detected (Long et al., 1995). ERL and ERM can be employed as a category of sediment "benchmark". According to the US-EPA, soil/sediment samples have been identified as "good" for zero ERL exceedances, "intermediate" if there are ERL exceedances but zero ERM exceedances, and "poor" for any ERM exceedance (US-EPA, 2012). Average values of ERL, ERM, and 11 PAH congeners obtained from this study were 342 ng g^{-1}, 1960 ng g^{-1}, and 2.96 ng g^{-1}, respectively. Since the average value of 11 PAH congeners is 116 times and 663 times lower than those of ERL and ERM, respectively, it appears reasonable to conclude that KSI soil samples can be categorized as "good".

In spite of the fact that the average Σ_{12}PAHs contents was lower

Table 2
Comparison of the sediment PAHs from coastal areas of Koh Samed Island with standard pollution criteria (ng g^{-1} dw).

Conc. (ng g^{-1})	ERL[a]	ERM[a]	TEL[b]	PEL[b]	This Study	
					Aver	Stdev
Phe	240	1500	86.7	544	0.784	1.40
An	85.3	1100	46.9	245	0.330	0.879
Fluo	600	5100	113	1494	0.264	0.536
Pyr	665	2500	153	1398	0.473	0.741
B[*a*]A	261	1600	74.8	693	0.639	1.90
Chry	384	2800	108	846	0.459	1.47
B[*b*]F	320	1880	–	–	4.77	10.6
B[k]F	280	1620	–	–	2.78	6.69
B[*a*]P	430	1600	88.8	763	1.72	4.39
D[a,h]A	430	1600	6.22	135	0.00449	0.0373
B[g,h,i]P	63.4	260	–	–	20.3	60.2
Σ_{11}PAHs[c]	3759	21,560	677	6118	32.5	61.7

[a] Effect range-low and effects range-median values (data from Long et al., 1995).

[b] Threshold effect levels and probable effect levels (data from Macdonald et al., 1996).

[c] The sum of Phe, An, Fluo, Pyr, B[*a*]A, Chry, B[*b*]F, B[k]F, B[*a*]P, D[a,h]A, B[g,h,i]P.

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than the international guideline values, the spatial distribution of the $\Sigma_{3\text{-}4\ \text{Rings}}$ PAHs and $\Sigma_{5\text{-}6\ \text{Rings}}$ PAHs clearly demonstrates the impacts of comparatively higher contribution of HMW PAHs, particularly in coastal soils of Ao Prao (see Fig. 1 and Fig. 2). While the diagnostic binary ratios of An/Σ178, Fluo/Σ202, and B[*a*]A/Σ228 obtained from this study were comparable to those of other world sediment samples, ΣPAHs(3,4)/ΣPAHs(5,6) of KSI samples showed the lowest value of 0.0986 (see Table 3). This finding again highlights the importance of HMW PAHs as the main composition of carcinogenic compounds in the oil spilled area of KSI. Numerous factors migh have been responsible for this phenomenon. According to a previous study, photooxidation rate constants of 2–3 ring and 4–5 ring PAHs in Light Louisiana Sweet crude oil were 0.08–0.09 day^{-1} and 0.01–0.07 day^{-1}, respectively (Bacosa et al., 2015). As a consequence, the comparatively high contribution of HMW PAHs observed in this study can be explained by its relatively low photooxidation rate constants. It is alwo worth mentioning that sunlight can inhibit biodegradation of pristine and phytane (Bacosa et al., 2015) and thus complicate the ecotoxicological risk assessment associated with crude oil contaminations in tropical coastal zones. Although biodegradation can play a crucial role in changing PAH profiles, photooxidation induced by ultraviolet (UV) is considered as one of the most significant processes of long-term weathering particularly for crude oil (Shankar et al., 2015).

Since HMW PAHs may retain some carcinogenic properties for decades (Sammarco et al., 2013), the oil spill incidence has the potential of serious adverse health effects through long-term bioaccumulation and biomagnification of $\Sigma_{5\text{-}6\ \text{Rings}}$ PAHs (D'adamo et al., 1997; Nfon et al., 2008; Wang et al., 2012). On the contrary, it is revealed that the dominant congeners of spilled crude oil and world oil spilled area are $\Sigma_{3\text{-}4\ \text{Rings}}$ PAHs (see Fig. 3). This literature review is consistent with previous studies based on the chemical analysis of PAHs in 48 different crude oils around the world, which was found that naphthalene (Naph) existed in the highest content in crude oil (427 mg kg^{-1}) followed by Phe (146 mg kg^{-1}) and Fl (70.3 mg kg^{-1}) (Kerr et al., 1999). It is also worth mentioning that $\Sigma_{3\text{-}4\ \text{Rings}}$ PAHs are the major congeners from vehicle emissions (Khillare et al., 2005; Lim et al., 2015; Rogge et al., 1993). Although several factors may responsible for this discrepancy, it seems rationale to ascribe the comparatively high contribution of HMW PAHs observed in KSI coastal soils as a unique profiling of PAHs in Rayong crude oil. In spite of numerous inconsistencies, the fact that HMW PAHs is the dominant congener in KSI soils cannot be explained by considering only the PAH concentrations. As a consequence, more sophisticated statistical techniques are essentially required to elucidate the potential sources of PAHs in KSI coastal soils.

3.2. *Diagnostig binary ratios of PAHs*

The classification of PAH emission sources needs a comprehensive investigation. The identification process relies on several

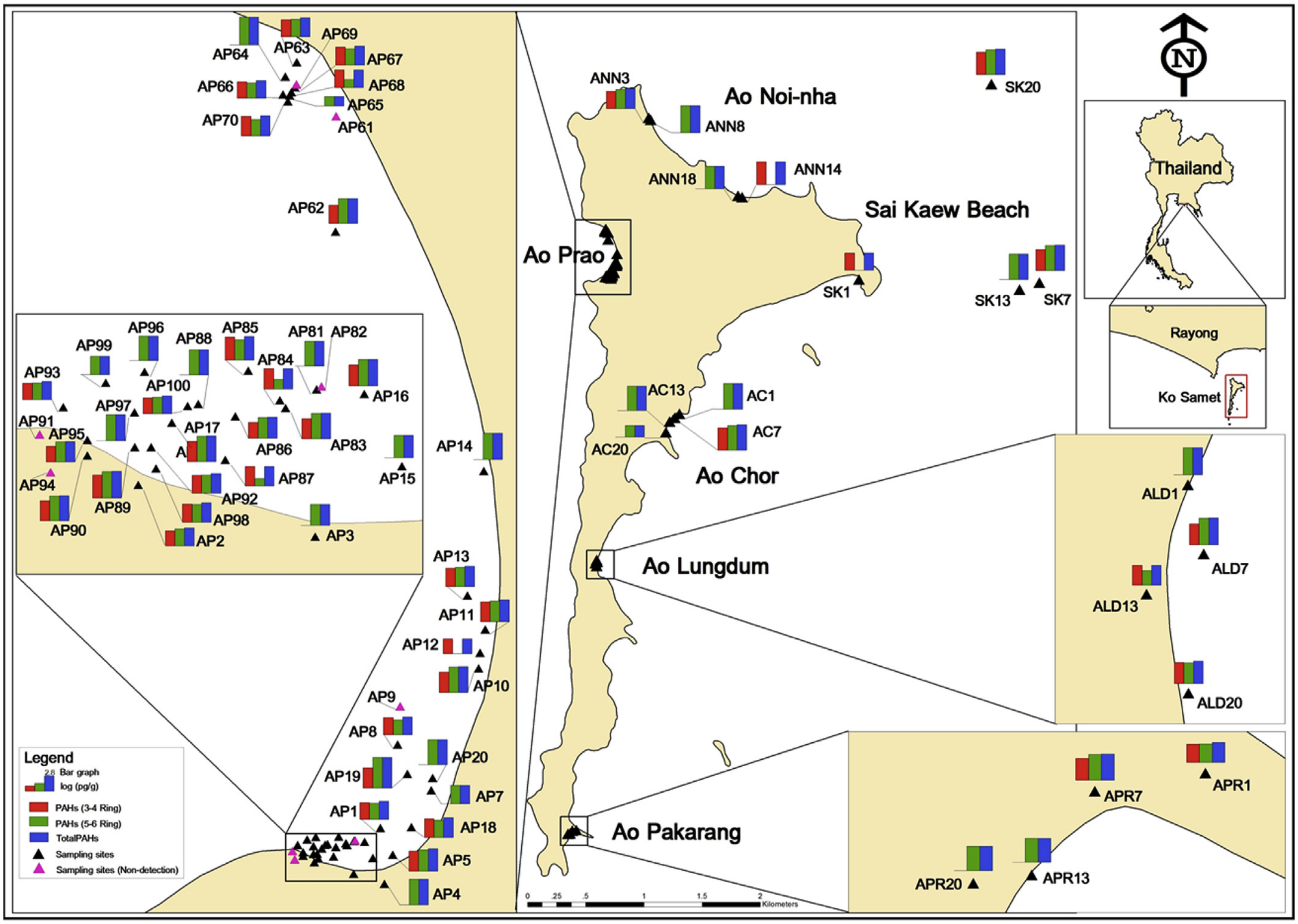

Fig. 1. Logarithmic scales of 3–4 ring, 5–6 ring, and total PAH concentrations collected at coastal soils of KSI.

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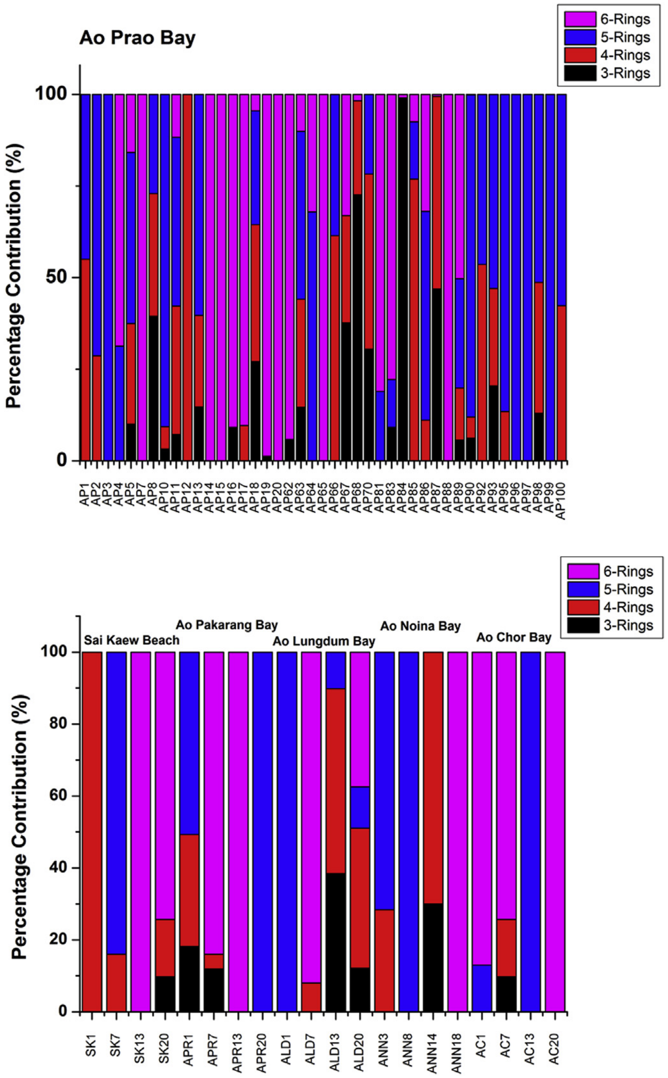

Fig. 2. Percentage contribution of 3, 4, 5, and 6-ring PAHs collected from coastal soils of Ao Prao Bay, Sai Kaew Beach, Ao Pakarang Bay, Ao Lungdum Bay, Ao Noina Bay, and Ao Chor Bay.

statistical applications including diagnostic binary ratios, hierarchical cluster analysis and factor analysis (Pongpiachan, 2013a,b; Pongpiachan et al., 2013a, 2015a,b; 2016). Since several factors such as physicochemical parameters (e.g. particle size of soil and sediment samples, pH, conductivity) and meteorological conditions (e.g. temperature, relative humidity, solar radiation coupled with both heterogeneous and homogeneous reaction with trace gaseous species) can dramtically alter PAH contents, the application of diagnostic binary ratios should be conducted with great caution (Pongpiachan, 2015a). It is also important to note that PAH diagnostic binary ratios show both substantial intrasource variability and intersource similarity (Galarneau, 2008). These complications are especially crirical for coal combustion categories, which are problematic to distinguish in the case of applying B[*a*]A/(B[*a*]A + Chry) ratio (Yunker et al., 2002). However, these constraints can be considered negligible since the major contributor of PAHs in KSI is obviously oil spill contamination. Secondly, it is crucial to underline that relative PAH contents are not conserved in the atmospheric environment (Galarneau, 2008). For purposes of simplicity, it is hypothesized that physicochemical parameters coupled with meteorological condition effects only play a minor role on alteration of PAH diagnostic binary ratios as a result of relatively stable weather conditions during the sample preservation period.

In this study, Ind/(Ind + B[g,h,i]P), Fluo/(Fluo + Pyr), An/(An + Phe), and B[*a*]A/(B[*a*]A + Chry) were used to distinguish between petrogenic and pyrolytic potential sources (Zhang et al., 2006). It is well known that Fluo/(Fluo + Pyr) and An/(An + Phe) can be applied to identify potential sources of PAHs. If An/(An + Phe) is greater than or equal to 0.1, this highlighted grass, wood and coal combustion sources, whilst a diagnostic binary ratio is smaller than 0.1 indicated petrogenic source. In the case of Fluo/(Fluo + Pyr) is in the interval between 0.4 and 0.5, this revealed petroleum combustion, when a diagnostic binary ratio is greater than 0.5 suggested grass, wood and coal ignitions (Yunker et al., 2002). In the case of Ind/(Ind + B[g,h,i]P) is greater than 0.5, it underlined the impacts of biomass and coal combustions while the ratio is in the range between 0.2 and 0.5 highlighting the influence of petroleum combustions such as traffic emissions and crude oil combustions (Yunker et al., 2002).

As illustrated in Fig. 4a, the diagnostic binary ratios of Fluo/(Fluo + Pyr), An/(An + Phe), Ind/(Ind + B[g,h,i]P), and B[*a*]A/(B[*a*]A + Chry) in marine sediments collected from oil spilled around the world were plotted in two dimensions and compared with those of KSI coastal soils. Here, the ratios of Fluo/(Fluo + Pyr) and An/(An + Phe) from oil spilled sediments almost entirely positioned in the zones of petrogenic source. Similarly, the combination of Fluo/(Fluo + Pyr) and Ind/(Ind + B[g,h,i]P) showed the two dimensional plots of oil spilled samples situated in petroleum combustion zone. While Fluo/(Fluo + Pyr) and B[*a*]A/(B[*a*]A + Chry) characterized oil spilled sediments as mixed of petrogenic and pyrogenic sources. Interestingly, the ratios of Fluo/(Fluo + Pyr), An/(An + Phe), and Ind/(Ind + B[g,h,i]P) emphasized that most of KSI coastal soils were considerably affected by oil spill accidents. It is also important to note that the some of KSI coastal soils plot were also situated in the zone of pyrogenic combustion category. This underlines the contributions of vehicular exhausts plausibly shipping emissions traffic emissions even in the middle of oil spill episode. Further attempts were also made by using average diagnostic binary ratios of An/(An + Phe), B[*a*]A/(B[*a*]A + Chry), and Fluo/(Fluo + Pyr) obtained from six different sampling locations (i.e. AP, SK, APR, ALD, ANN, and AC) as illustrated in Fig. 4b. It is obvious that SK and AC were most likely contaminated by oil spill. On the contrary, it appears reasonable to interpret that APR, AP, ALD, and ANN were influenced by several sources such as grass, wood, and coal combustion coupled with oil spill. In addition, it seems rationale to conclude that oil spill is not the only source of PAHs in KSI coastal soils but also other pyrogenic combustion categories, underlining complexity of emission source strengths in the study area.

3.3. Hierarchical cluster analysis (HCA)

Unlike "*K-means Cluster Analysis*" and "*Two-Step Cluster Analysis*", HCA can be applied for categorize comparatively smaller sample numbers (e.g. $n < 200$) without any data pre-treatment such as specifying the number of clusters in advance (Dachs et al., 1999). Additionally these two clustering methods need an extremely large scale of data set (e.g. $n > 1000$) and are not suitable for this study. Therefore, clusterization of PAH congeners according to profile similarity was carried out with the application of HCA (see Fig. 5). Theoretically, if the main contributor of PAH congeners is oil contamination, HCA should reveal the relatively high level of close proximity between KSI soil samples and other world oil-spilled sediments. In order to test this hypothesis, HCA had been performed on the 11 PAH congeners collected from oil-spilled sediments, crude oil samples, and terrestrial coastal soils as clearly described in Fig. 5.

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Table 3
Comparisons of diagnostic binary ratios of the sediment PAHs between this study and other world sediment samples.

Sample type	Location		Country	Ref	ΣPAHs(3,4)/ΣPAHs(5,6)	An/Σ178	Fluo/Σ202	B[*a*]A/Σ228
Coastal Soil	KSI	Koh Samed Island	Thailand	This Study	0.0986	0.296	0.358	0.582
Harbor Sediment	Bayou St. John	New Orleans	USA	Mielke et al., 2001	1.59	0.283	0.226	0.705
Harbor Sediment	San Diego Harbor	California	USA	Deshmukh et al., 2001	0.513	0.205	0.908	0.179
Marine Sediment	Northern Irish Sea	Northern Irland	UK	Guinan et al., 2001	1.72	0.139	0.515	0.377
Harbor Sediment	Mystic River	Boston	USA	Wang et al., 2001	1.73	0.380	0.350	0.413
	Island End River	Boston	USA		3.14	0.561	0.524	0.557
Marine Sediment	Mangrove	Sai Keng	Hong Kong	Tam et al., 2001	1.75	0.130	0.172	N.D.
		Tolo			2.44	0.0691	0.443	N.D.
		Ho Chung			1.15	0.102	0.737	N.D.
		Mai Po			2.91	0.117	0.158	N.D.
Riverine Sediment	Pearl River	Guangzhou Channel	China	Bixian et al., 2001	0.933	0.233	0.551	0.448
		Shiziyang Channel			1.67	0.121	0.448	0.500
		Lingding Bay			1.68	0.0840	0.567	0.267
Marine Sediment	Northern Adriatic	Sea (GT2-1.25 cm)	Italy	Notar, 2001	1.64	0.145	0.483	0.465
Coastal Sediment	Coastal area	Cotonou (Benin)	Africa	Soclo et al., 2000	2.22	0.122	0.474	0.468
		Aquitaine	France		2.18	0.196	0.495	0.602
Coastal Sediment	Coastal area	Mediterranean	France	Baumard et al., 1998	0.899	0.0946	0.517	0.350
					1.16	0.196	0.544	0.350
					1.92	0.220	0.541	0.483
Coastal Sediment	Coastal area	Mediterranean	Spain	Baumard et al., 1998	8.64	0.0530	0.533	0.519
					1.31	0.132	0.558	0.429
					1.97	0.128	0.541	0.403
Coastal Sediment	Coastal area	Mediterranean	Brazil	Medeiros and Bicego, 2004	15.8	0.156	0.642	0.280
					5.67	0.346	0.576	0.284
					4.11	0.433	0.547	0.409
					7.12	0.375	0.489	0.312
Coastal Sediment	Coastal area	Guba Pechenga	Russia	Savinov et al., 2003	5.06	0.409	0.615	0.471

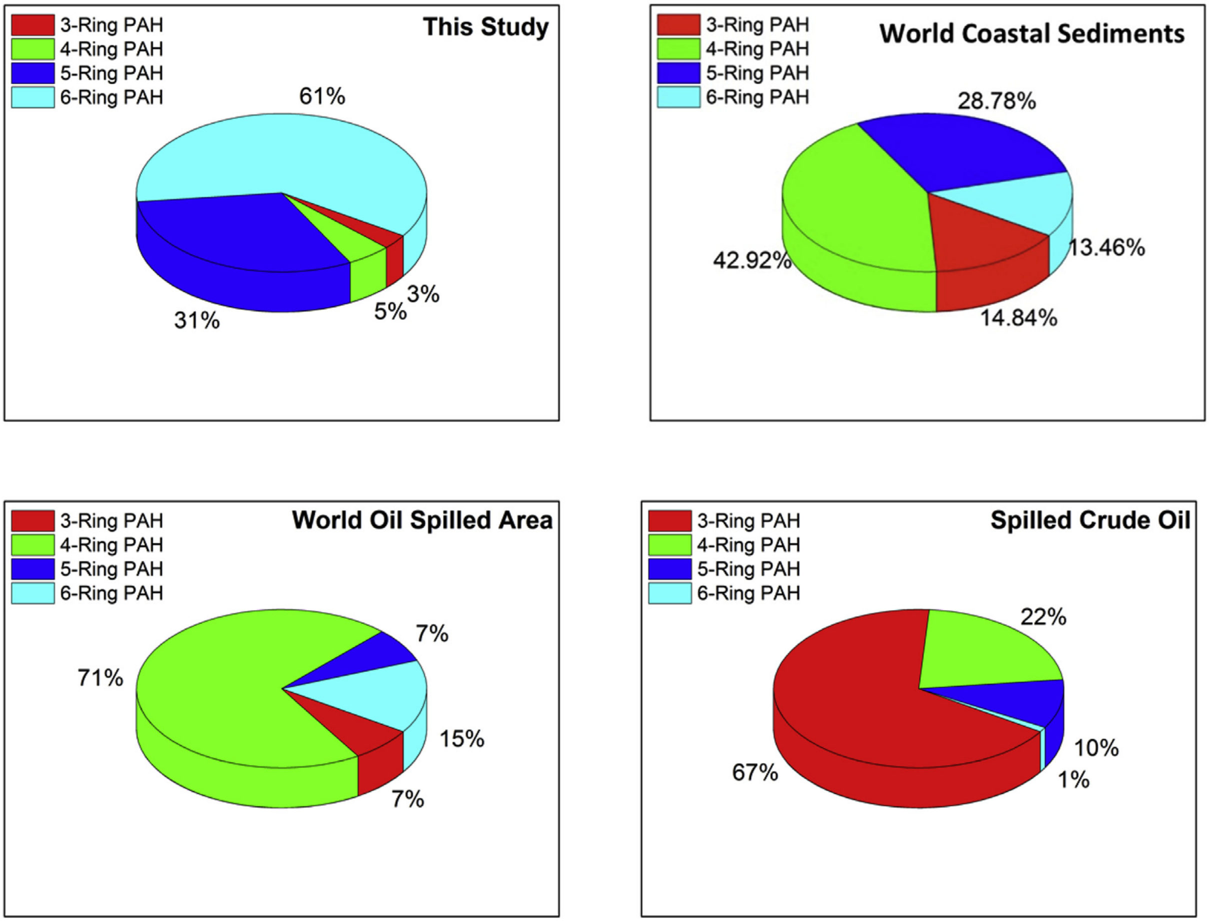

Fig. 3. Percentage contribution of 3, 4, 5, and 6-ring PAHs collected from this study in comparison with those of world oil spilled area, world coastal sediments and spilled crude oil.

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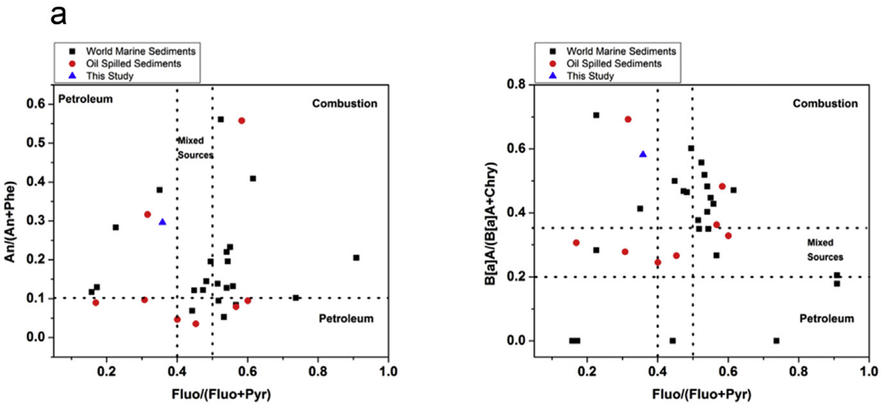
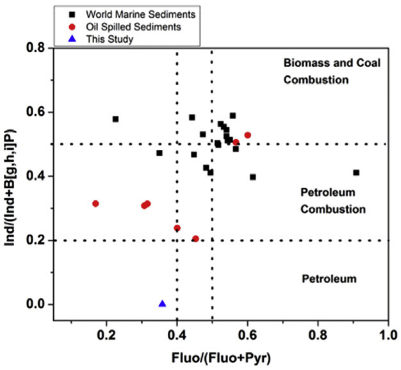
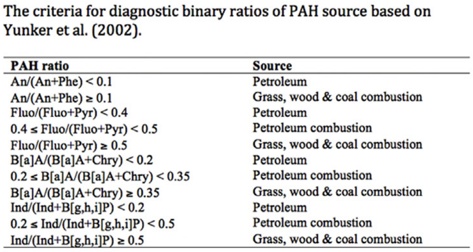





The criteria for diagnostic binary ratios of PAH source based on Yunker et al. (2002).

PAH ratio	Source
An/(An+Phe) < 0.1	Petroleum
An/(An+Phe) ≥ 0.1	Grass, wood & coal combustion
Fluo/(Fluo+Pyr) < 0.4	Petroleum
0.4 ≤ Fluo/(Fluo+Pyr) < 0.5	Petroleum combustion
Fluo/(Fluo+Pyr) ≥ 0.5	Grass, wood & coal combustion
B[a]A/(B[a]A+Chry) < 0.2	Petroleum
0.2 ≤ B[a]A/(B[a]A+Chry) < 0.35	Petroleum combustion
B[a]A/(B[a]A+Chry) ≥ 0.35	Grass, wood & coal combustion
Ind/(Ind+B[g,h,i]P) < 0.2	Petroleum
0.2 ≤ Ind/(Ind+B[g,h,i]P) < 0.5	Petroleum combustion
Ind/(Ind+B[g,h,i]P) ≥ 0.5	Grass, wood & coal combustion

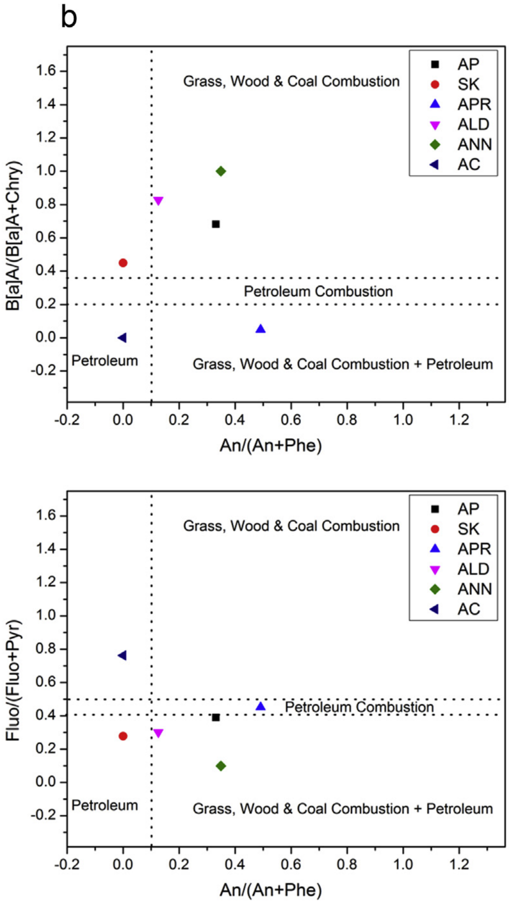
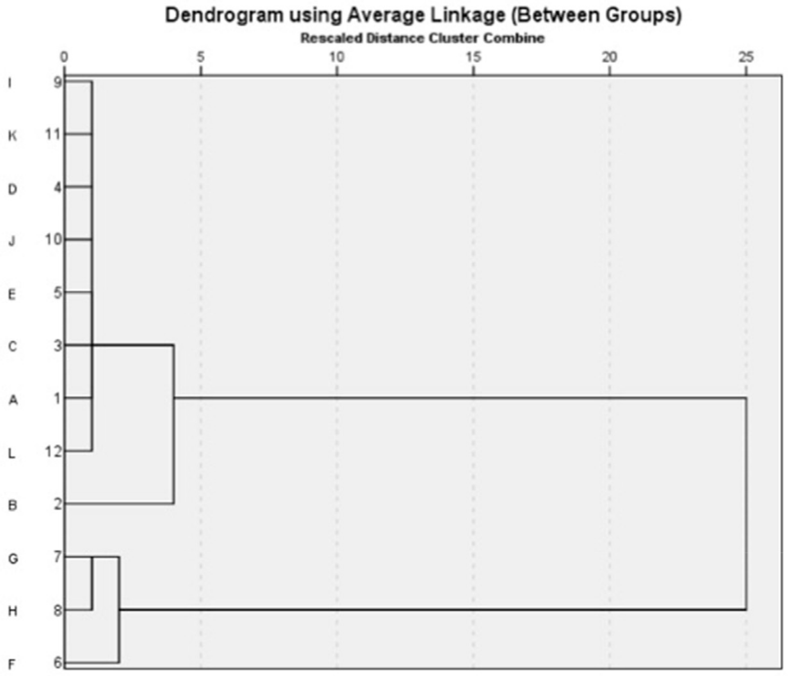


Fig. 4. a. Diagnostic binary ratios of PAHs obtained from this study in comparison with those of world marine sediments (Baumard et al., 1998; Bixian et al., 2001; Deshmukh et al., 2001; Guinan et al., 2001; Medeiros and Bicego, 2004; Mielke et al., 2001; Notar, 2001; Savinov et al., 2003; Soclo et al., 2000; Tam et al., 2001; Wang et al., 2001) and oil spilled sediments (Aghadadashi et al., 2017; Armenta-Arteaga and Elizalde-González, 2003; He et al., 2014; Li et al., 2015; Yim et al., 2002). b. Diagnostic binary ratios of PAHs obtained from six different sampling sites.



A: World Coastal Soils (Pongpiachan et al., 2013c)
B: This Study
C: Persian Gulf, Iran (Aghadadashi et al., 2017)
D: Guan River Estuary, China (He et al., 2014)
E: Bohai Sea, China (Li et al., 2015)
F: Spilled Crude Oil, Arabian Light (Yim et al., 2002)
G: Spilled Crude Oil, Arabian Medium (Yim et al., 2002)
H: Spilled Crude Oil, Khafji (Yim et al., 2002)
I: S5-Sori Island (Yim et al., 2002)
J: S6-Sori Island (Yim et al., 2002)
K: S7-Sori Island (Yim et al., 2002)
L: Mecoacan Lake, Mexico (Armenta-Arteaga and Elizalde-Gonzalez, 2003)

Fig. 5. Hierarchical cluster analysis of PAH congeners obtained from this study in comparison with those of other oil-spilled sediments.

It is crucial to underline that average values of PAH congeners collected at Persian Gulf (i.e. C; $n = 17$), Guan River Estuary (i.e. D; $n = 13$), world coastal soils (i.e. A; $n = 19$), and KSI soil samples obtained from this study (i.e. B; $n = 69$) were considered to carry out both HCA and PCA. Only one sample was considered for E, F, G, H, I, J, K, and L. The HCA can be distinguished in two major clusters: I (Sori Island), K (Sori Island), D (Guan River Estuary), J (Sori Island), E (Bohai Sea), C (Persian Gulf), A (World Coastal Soils), L (Mecoacan Lake), B (This Study) and G (Arabian Medium), H (Khafji), F (Arabian Light). Into the first cluster, two sub-clusters can be considered: I, K, D, J, E, C, A, L and the other one which is B. B samples cannot be considered similar to the ones of Arabian Light, Arabian Medium and Khafji because It will be depending on the linkage distance which is quite different. B samples would be different to the marine sediments and to the spilled crude oil. Into the second cluster, two sub-clusters can be also distinguished: G, H and F. Based on the findings appeared in dendrogram, the members exist in the first subgroup can be considered to be a mixture of “oil-spilled deposits” and “terrestrial components” with the percentage contribution of 58% ($n = 7$) to all samples ($n = 12$). The second main cluster (i.e. G, H, and F) is another key-feature in dendrogram, which displays the close proximity of crude oil products namely Arabian Light, Arabian Medium, and Khafji. Since these three members represent the crude oil components, it appears reasonable to assume that HCA successfully categorized Arabian oil spill groups from other marine sediments. In addition, the comparatively close proximity of B (i.e. KSI soil samples) with L (i.e. oil-spilled Mecoacan Lake samples) and A (i.e. world coastal soils) can be ascribed as a consequence of oil spilled incidence occurred on July 27, 2013, in GoT coupled with pyrogenic combustions as previously mentioned in Section 3.2.

3.4. Principal component analysis (PCA)

Principal component analysis (PCA) was conducted to assess the influences of oil-spilled incidence on chemical characteristics of 12 PAH congeners collected from KSI in comparison with those of crude oil products, oil contaminated deposits, and world coastal soils. As illustrated in Fig. 6, the principal component patterns for Varimax rotated components of 12 PAH congeners composed of three components, which account for 49.7%, 19.3% and 17.9% for the

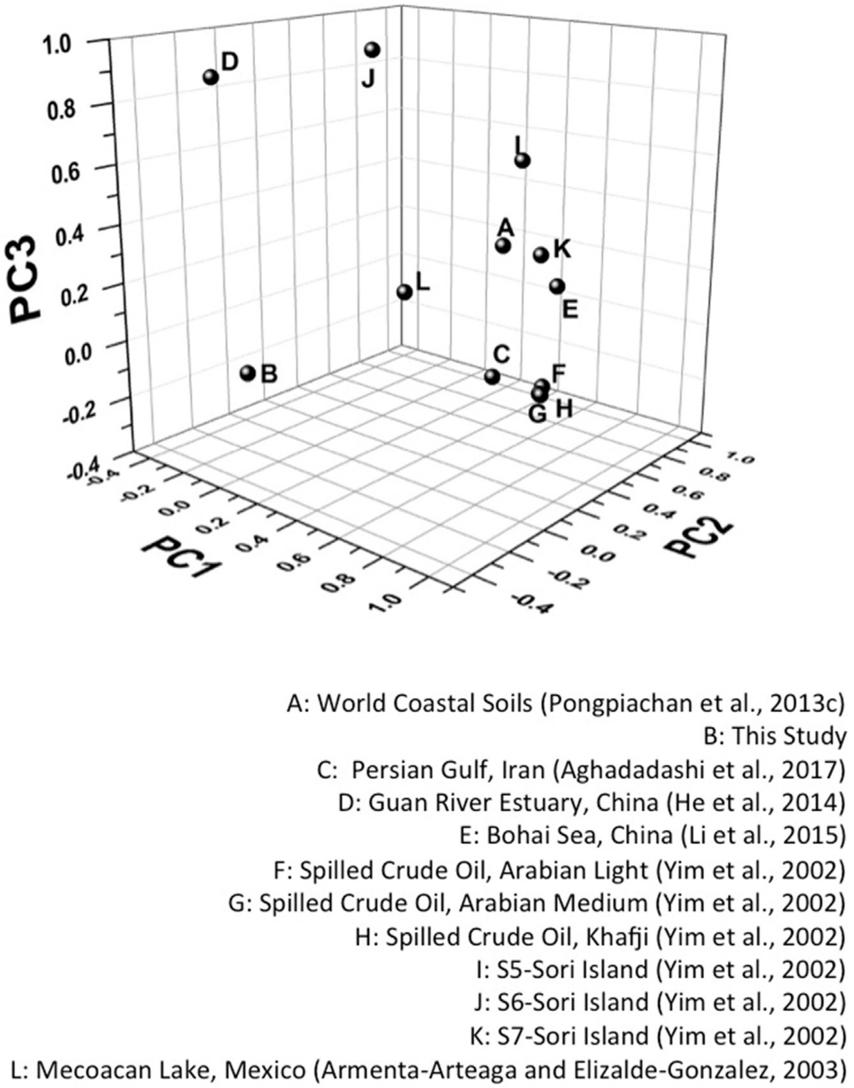


Fig. 6. Three dimensional plots of PC1, PC2, and PC3 of PAH congeners obtained from this study in comparison with those of other oil-spilled sediments.

total of variances of PC1, PC2 and PC3 respectively, which together explained 86.9% of total variance. The contribution of PC1 and PC2 explains 69% of total variance, and furthermore PC1 (49.7% of variation) is approximately 2.6 times and 2.8 times higher than PC2 and PC3, respectively. The most obvious features in all categories (see Fig. 6) can be described as follows: (*i*) 3D plots of D, J, and I deviate significantly from those of other oil-spilled samples with relatively high dispersion of three-deminsional (3D) plots attributed to greater complexities of PAH profiles contaminated in riverine sediments of Guan River Estuary and marine deposits of Sori Island; (*ii*) there are extremely explicit similar sources in crude oil samples of Arabian Light, Arabian Medium, and Khafji (i.e. F, G, H); (*iii*) A 3D plot of Persian Gulf sediment (i.e. C) located adjacent to those of F, G, and H suggesting that oil-spilled incidence might be significant sources of PAHs in this area; and (*iv*) A 3D plot of KSI samples (i.e. B) highly deviated from those of other samples. This can be explained due to several reasons. Firstly, a substantial dissimilarity in 3D plot of KSI samples was plausibly due to a comparatively unique PAH profile of crude oil contaminated in GoT. As previously discussed in Section 3.1, $\Sigma_{5\text{-}6\ \mathrm{Rings}}$ PAHs is the main composition of PAH congeners observed in KSI while $\Sigma_{3\text{-}4\ \mathrm{Rings}}$ PAHs is widely acknowledged as the major component of aromatic compounds at oil-spilled sites around the world. Secondly, PAH profiles can greatly altered across a broad spectrum by the different magnitudes of heterogeneous reactions with trace gaseous species (e.g. OH radicals, NO_3 radicals and O_3) coupled with various photolysis rates. Thirdly, the environmental fate of PAHs is fundamentally governed by their gas/particle (g/p) partitioning mechanisms namely *ab*sorption into organic layer and *ad*sorption onto soot phase. Since meteorological parameters can greatly affect the g/p partitioning of PAH congeners, it appears reasonable to interprete the relatively high deviation of a 3D plot of KSI samples as a consequence of tropical weather conditions in Thailand. Fourthly, biodegradation rates of LMW PAHs might have surpassed those of HMW PAHs. As a consequence, KSI samples are dominated by HMW PAHs after more than two years of oil spill incident.

4. Conclusions

After two years of 2013 Rayong oil-spilled incidence, 69 coastal soil samples around KSI were carefully analyzed and statistically investigated. The average Σ_{12}PAHs in KSI (32.5 ± 61.7 ng g^{-1}) was much lower than those values of international guidelines suggested low probability of causing adverse biological effects. In spite of the

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comparatively low PAH contents observed in this study, some serious concerns still remain with respect to adverse health effects through long-term bioaccumulation and biomagnification of $\Sigma_{5\text{-}6\ \text{Rings}}$ PAHs. Although the diagnostic binary ratio underlined that the majority of KSI coastal soils were appreciably influenced by oil spill accidents, it is also crucial to mention that the impacts of pyrogenic combustion category were not negligible. The close proximity between KSI samples and oil spill samples of Mecoacan Lake observed in HCA dendrogram also highlighted the contributions of oil-spilled incidence as a major source of PAH congeners. According to Fig. 6, KSI samples seem to be not related to the other ones. Because KSI samples are mainly constituted by HMW PAHs and after more than two years of the oil spill (i.e. biodegradation will take place), the contribution of other anthropogenic sources is affecting these PAHs concentrations. Perhaps shipping emissions are contributing to these HMW PAHs. The application of dispersants used after the oil spill could also affect PAHs concentrations. Additionally, the highly deviated KSI sample appeared in PCA 3D plots can be explained by both the unique PAH profile originally presents in crude oil and tropical climate conditions that can dramatically alter chemical compositions of PAHs.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2017.09.096.

References

Aghadadashi, V., Mehdinia, A., Molaei, S., 2017. Origin, toxicological and narcotic potential of sedimentary PAHs and remarkable even/odd n-alkane predominance in Bushehr Peninsula, the Persian Gulf. Mar. Pollut. Bull. 114 (1), 494–504.

Allan, S.E., Smith, B.W., Anderson, K.A., 2012. Impact of the Deepwater Horizon oil spill on bioavailable polycyclic aromatic hydrocarbons in Gulf of Mexico coastal waters. Environ. Sci. Technol. 46 (4), 2033–2039.

Armenta-Arteaga, G., Elizalde-González, M.P., 2003. Contamination by PAHs, PCBs, PCPs and heavy metals in the mecoácfin lake estuarine water and sediments after oil spilling. J. Soils Sediments 3 (1), 35–40.

Bacosa, H.P., Erdner, D.L., Liu, Z., 2015. Differentiating the roles of photooxidation and biodegradation in the weathering of Light Louisiana Sweet crude oil in surface water from the Deepwater Horizon site. Mar. Pollut. Bull. 95 (1), 265–272.

Barth, D.S., Mason, B.J., 1984. Soil Sampling Quality Assurance User's Guide. EPA-600/4-84-043.

Baumard, P., Budzinski, H., Garrigues, P., Sorbe, J.C., Burgeot, T., Bellocq, J., 1998. Concentrations of PAHs (polycyclic aromatic hydrocarbons) in various marine organisms in relation to those in sediment and to trophic level. Mar. Pollut. Bull. 36, 951–960.

Beck, J.A., Alcock, E.R., Wilson, C.S., Wang, J.M., Wild, R.S., Sewart, P.A., Jones, C.K., 1995. Long-term persistence of organic chemicals in sewage sludge-amended agricultural land. Adv. Agron. 55, 345–391.

Bejarano, A.C., Michel, J., 2010. Large-scale risk assessment of polycyclic aromatic hydrocarbons in shoreline sediments from Saudi Arabia: environmental legacy after twelve years of the Gulf war oil spill. Environ. Pollut. 158 (5), 1561–1569.

Binková, B., Šrám, R.J., 2004. The genotoxic effect of carcinogenic PAHs, their artificial and environmental mixtures (EOM) on human diploid lung fibroblasts. Mutat. Research/Fundamental Mol. Mech. Mutagen. 547 (1), 109–121.

Bixian, M., Jiamo, F., Gan, Z., Zheng, L., Yushun, M., Guoying, S., Xingmin, W., 2001. Polycyclic aromatic hydrocarbons in sediments from the Pearl river and estuary, China: spatial and temporal distribution and sources. Appl. Geochem 16, 1429–1445.

Burns, K.A., Garrity, S.D., Levings, S.C., 1993. How many years until mangrove ecosystems recover from catastrophic oil spills? Mar. Pollut. Bull. 26 (5), 239–248.

Dachs, J., Bayona, J.M., Fillaux, J., Saliot, A., Albaigés, J., 1999. Evaluation of anthropogenic and biogenic inputs into the western Mediterranean using molecular markers. Mar. Chem. 65 (3), 195–210.

D'adamo, R., Pelosi, S., Trotta, P., Sansone, G., 1997. Bioaccumulation and biomagnification of polycyclic aromatic hydrocarbons in aquatic organisms. Mar. Chem. 56 (1–2), 45–49.

Deshmukh, P.A., Chefetz, B., Hatcher, G.P., 2001. Characterization of organic matter in pristine and contaminated coastal marine sediments using solid-state 13C NMR, pyrolytic and thermochemolytic methods: a case study in the San Diego harbor area. Chemosphere 45 (6–7), 1007–1022.

Ecology and Environment, Inc, 1990. Standard Operating Procedures: “Equipment Decontamination,” and “Sample Packaging and Shipping.”.

Franco, M.A., Viñas, L., Soriano, J.A., De Armas, D., González, J.J., Beiras, R., Albaigés, J., 2006. Spatial distribution and ecotoxicity of petroleum hydrocarbons in sediments from the Galicia continental shelf (NW Spain) after the Prestige oil spill. Mar. Pollut. Bull. 53 (5), 260–271.

Galarneau, E., 2008. Source specificity and atmospheric processing of airborne PAHs: implications for source apportionment. Atmos. Environ. 42, 8139–8149.

Garza-Gil, M.D., Prada-Blanco, A., Vázquez-Rodríguez, M.X., 2006. Estimating the short-term economic damages from the Prestige oil spill in the Galician fisheries and tourism. Ecol. Econ. 58 (4), 842–849.

Gray, J.S., 2002. Biomagnification in marine systems: the perspective of an ecologist. Mar. Pollut. Bull. 45 (1), 46–52.

Guinan, J., Charlesworth, M., Service, M., Oliver, T., 2001. Sources and geochemical constraints of polycyclic aromatic hydrocarbons (PAHs) in sediments and mussels of two Northern Irish sea-loughs. Mar. Pollut. Bull. 42 (11), 1073–1081.

He, X., Pang, Y., Song, X., Chen, B., Feng, Z., Ma, Y., 2014. Distribution, sources and ecological risk assessment of PAHs in surface sediments from Guan River Estuary, China. Mar. Pollut. Bull. 80 (1), 52–58.

Kakareka, S.V., Kukharchyk, T.I., 2003. PAH emission from the open burning of agricultural debris. Sci. Total. Environ. 308 (1), 257–261.

Kerr, J.M., Melton, H.R., Mc Millen, S.J., Magaw, R.I., Naughton, G., Little, G.N., 1999. Polyaromatic hydrocarbon content in crude oils around the world. In: Conference Paper from the 1999 SPE/EPA Exploration and Production Environmental Conference Held in Austin, Texas, USA, 28 February-3 March.

Khillare, P.S., Balachandran, S., Hoque, R.R., 2005. Profile of PAH in the exhaust of gasoline driven vehicles in Delhi. Environ. Monit. Assess. 110 (1), 217–225.

Kim, E.J., Oh, J.E., Chang, Y.S., 2003. Effects of forest fire on the level and distribution of PCDD/Fs and PAHs in soil. Sci. Total. Environ. 311 (1), 177–189.

Kingston, P.F., 2002. Long-term environmental impact of oil spills. Spill Sci. Technol. Bull. 7 (1), 53–61.

Li, S., Zhang, S., Dong, H., Zhao, Q., Cao, C., 2015. Presence of aliphatic and polycyclic aromatic hydrocarbons in near-surface sediments of an oil spill area in Bohai Sea. Mar. Pollut. Bull. 100, 169–175.

Lim, J., Lim, C., Kim, S., Hong, J., 2015. Characterizations of organic compounds in diesel exhaust particulates. J. Environ. Sci. 34, 171–183.

Long, E.R., Macdonald, D.D., Smith, S.L., Calder, F.D., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ. Manag. 19, 81–97.

Loureiro, M.L., Loomis, J.B., Vázquez, M.X., 2009. Economic valuation of environmental damages due to the Prestige oil spill in Spain. Environ. Resour. Econ. 44 (4), 537–553.

Luch, A., 2005. The Carcinogenic Effects of Polycyclic Aromatic Hydrocarbons. World Scientific.

Mason, B.J., 1983. Preparation of Soil Sampling Protocol: Technique and Strategies. EPA- 600/4-83-020.

Macdonald, D.D., Carr, R.S., Calder, F.D., Long, E.R., Ingersoll, C.G., 1996. Development and evaluation of sediment quality guidelines for Florida coastal waters. Ecotoxicol 5, 253–278.

Meador, P.J., 2008. Polycyclic aromatic hydrocarbons. Encycl. Ecol. 2881–2891.

Medeiros, M.P., Bicego, C.M., 2004. Investigation of natural and anthropogenic hydrocarbon inputs in sediments using geochemical markers. I. Santos, SP——Brazil. Mar. Pollut. Bull. 49 (9–10), 761–769.

Mielke, W.H., Wang, G., Gonzales, R.C., Le, B., Quach, N.V., Mielke, W.P., 2001. PAH and metal mixtures in New Orleans soils and sediments. Sci. Total. Environ. 281 (1–3), 217–227.

Nfon, E., Cousins, I.T., Broman, D., 2008. Biomagnification of organic pollutants in benthic and pelagic marine food chains from the. Balt. Sea. Sci. Total. Environ. 397 (1), 190–204.

Notar, M., Leskovsek, H., Faganeli, J., 2001. Composition, distribution and sources of polycyclic aromatic hydrocarbons in sediments of the Gulf of Trieste, Northern Adriatic Sea. Mar. Pollut. Bull. 42 (1), 36–44.

Pan, G., Qiu, S., Liu, X., Hu, X., 2015. Estimating the economic damages from the Penglai 19-3 oil spill to the Yantai fisheries in the Bohai Sea of northeast China. Mar. Policy 62, 18–24.

Peterson, C.H., Rice, S.D., Short, J.W., Esler, D., Bodkin, J.L., Ballachey, B.E., Irons, D.B., 2003. Long-term ecosystem response to the Exxon Valdez oil spill. Science 302 (5653), 2082–2086.

Piatt, J.F., Lensink, C.J., Butler, W., Kendziorek, M., Nysewander, D.R., 1990. Immediate impact of the'Exxon Valdez'oil spill on marine birds. Auk 387–397.

Pongpiachan, S., Bualert, S., Sompongchaiyakul, P., Kositanont, C., 2009. Factors affecting sensitivity and stability of polycyclic aromatic hydrocarbons. Anal. Lett. 42 (13), 2106–2130.

Pongpiachan, S., Hirunyatrakul, P., Kittikoon, I., Khumsup, C., 2011. Parameters Influencing on Sensitivities of Polycyclic Aromatic Hydrocarbons Measured by Shimadzu GCMS-QP2010 Ultra. Gas Chromatography/Book 3. Intech Open

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Access Publisher, ISBN 978-953-51-0298-4. https://doi.org/10.5772/32234.

Pongpiachan, S., 2013a. Vertical distribution and potential risk of particulate polycyclic aromatic hydrocarbons in high buildings of Bangkok, Thailand. Asian Pac. J. Cancer Prev. 14 (3), 1865–1877.

Pongpiachan, S., 2013b. Diurnal variation, vertical distribution and source apportionment of carcinogenic polycyclic aromatic hydrocarbons (PAHs) in chiang-mai, Thailand. Asian Pac. J. Cancer Prev. 14 (3), 1851–1863.

Pongpiachan, S., Choochuay, C., Hattayanone, M., Kositanont, C., 2013a. Temporal and spatial distribution of particulate carcinogens and mutagens in Bangkok, Thailand. Asian Pac. J. Cancer Prev. 14 (3), 1879–1887.

Pongpiachan, S., Ho, K.F., Cao, J., 2013b. Estimation of gas-particle partitioning coefficients (kp) of carcinogenic polycyclic aromatic hydrocarbons by carbonaceous aerosols collected at chiang-mai, bangkok and hat-yai, Thailand. Asian Pac. J. Cancer Prev. 14 (4), 3369–3384.

Pongpiachan, S., Tipmanee, D., Deelaman, W., Muprasit, J., Feldens, P., Schwarzer, K., 2013c. Risk assessment of the presence of polycyclic aromatic hydrocarbons (PAHs) in coastal areas of Thailand affected by the 2004 tsunami. Mar. Pollut. Bull. 76, 370–378.

Pongpiachan, S., 2015a. Assessment of reliability when using diagnostic binary ratios of polycyclic aromatic hydrocarbons in ambient air PM10. Asian Pac. J. Cancer Prev. 16 (18), 8605–8611.

Pongpiachan, S., 2015b. A preliminary study of using polycyclic aromatic hydrocarbons as chemical tracers for traceability in soybean products. Food control. 47, 392–400.

Pongpiachan, S., Tipmanee, D., Khumsup, C., Kittikoon, I., Hirunyatrakul, P., 2015a. Assessing risks to adults and preschool children posed by PM2.5-bound polycyclic aromatic hydrocarbons (PAHs) during a biomass burning episode in Northern Thailand. Sci. Total. Environ. 508, 435–444.

Pongpiachan, S., Hattayanone, M., Choochuay, C., Mekmok, R., Wuttijak, N., Ketratanakul, A., 2015b. Enhanced PM_{10} bounded PAHs from shipping emissions. Atmos. Environ. 108, 13–19.

Pongpiachan, S., 2016. Incremental lifetime cancer risk of PM2. 5 bound polycyclic aromatic hydrocarbons (PAHs) before and after the wildland fire episode. Aerosol. Air Qual. Res. 16, 2907–2919.

Pongpiachan, S., Hattayanone, M., Pinyakong, O., Viyakarn, V., Chavanich, S.A., Bo, C., Khumsup, I., Kittikoon, I., Hirunyatrakul, P., 2016. Quantitative ecological risk assessment of inhabitants exposed to polycyclic aromatic hydrocarbons in terrestrial soils of King George Island. Antarct. Polar Sci. (in press).

Reddy, C.M., Eglinton, T.I., Hounshell, A., White, H.K., Xu, L., Gaines, R.B., Frysinger, G.S., 2002. The West Falmouth oil spill after thirty years: the persistence of petroleum hydrocarbons in marsh sediments. Environ. Sci. Technol. 36 (22), 4754–4760.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R., 1993. Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. Environ. Sci. Technol. 27, 636–636.

Rosenkranz, H.S., Mermelstein, R., 1985. The genotoxicity, metabolism and carcinogenicity of nitrated polycyclic aromatic hydrocarbons. J. Environ. Sci. Health. C. 3 (2), 221–272.

Sammarco, P.W., Kolian, S.R., Warby, R.A.F., Bouldin, J.L., Subra, W.A., Porter, S.A., 2013. Distribution and concentrations of petroleum hydrocarbons associated with the BP/Deepwater Horizon oil spill, Gulf of Mexico. Mar. Pollut. Bull. 73, 129–143.

Savinov, M.V., Savinova, N.T., Matishov, G.G., Dahle, S., Næs, K., 2003. Polycyclic aromatic hydrocarbons (PAHs) and organochlorines (OCs) in bottom sediments of the Guba Pechenga, Barents Sea, Russia. Sci. Total. Environ. 306 (1–3), 39–56.

Slezakova, K., Castro, D., Delerue–Matos, C., da Conceição Alvim–Ferraz, M., Morais, S., do Carmo Pereira, M., 2013. Impact of vehicular traffic emissions on particulate-bound PAHs: levels and associated health risks. Atmos. Res. 127, 141–147.

Shankar, R., Shim, W.J., An, J.G., Yim, U.H., 2015. A practical review on photooxidation of crude oil: laboratory lamp setup and factors affecting it. Water. Res. 68, 304–315.

Soclo, H.H., Garrigues, P., Ewald, M., 2000. Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas. Mar. Pollut. Bull. 40 (5), 387–396.

Tam, N.F.Y., Ke, L., Wang, X.H., Wong, Y.S., 2001. Contamination of polycyclic aromatic hydrocarbons in surface sediments of mangrove swamps. Environ. Pollut. 114, 255–263.

US-EPA, 2012. Sediment contamination. Accessed: May 24, 2012. http://www.epa.gov/emap/maia/html/docs/Est5.pdf.

Wang, C.X., Zhang, X.Y., Chen, F.R., 2001. Distribution and partitioning of polycyclic aromatic hydrocarbons (PAHs) in different size fractions in sediments from Boston Harbor, United States. Mar. Pollut. Bull. 42 (11), 1139–1149.

Wang, D.Q., Yu, Y.X., Zhang, X.Y., Zhang, S.H., Pang, Y.P., Zhang, X.L., Fu, J.M., 2012. Polycyclic aromatic hydrocarbons and organochlorine pesticides in fish from Taihu Lake: their levels, sources, and biomagnification. Ecotoxicol. Environ. Saf. 82, 63–70.

Wild, R.S., Obbard, P.J., Munn, I.C., Berrow, L.M., Jones, C.K., 1991. The long-term persistence of polynuclear aromatic hydrocarbons (PAHs) in an agricultural soil amended with metal-contaminated sewage sludges. Sci. Tot. Environ. 101 (3), 235–253.

Wild, R.S., Jones, C.K., 1995. Polynuclear aromatic hydrocarbons in the United Kingdom environment: a preliminary source inventory and budget. Environ. Pollut 88 (1), 91–108.

Yang, H.H., Lee, W.J., Chen, S.J., Lai, S.O., 1998. PAH emission from various industrial stacks. J. Hazard. Mat. 60 (2), 159–174.

Yim, U.H., Oh, J.R., Hong, S.H., Lee, S.H., Shim, W.J., 2002. Identification of PAHs sources in bivalves and sediments 5 Years after the *sea prince* oil spill in korea. Environ. Forensics. 3, 357–366.

You, J.H., Chiang, P.C., Chang, K.T., Chang, S.C., 1994. Polycyclic aromatic hydrocarbons (PAHs) and mutagenicity of soot particulates in air emissions from two-stage incineration of polystyrene. J. Hazard. Mat. 36 (1), 1–17.

Yunker, B.M., Macdonald, W.R., Vingarzan, R., Mitchell, H.R., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org. Geochem 33, 489–515.

Zhang, H.B., Luo, Y.M., Wong, M.H., Zhao, Q.G., Zhang, G.L., 2006. Distributions and concentrations of PAHs in Hong Kong soils. Environ. Pollut. 141, 107–114.

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