

Source Apportionment of Polycyclic Aromatic Hydrocarbons (PAHs) in sediments from Chalong Bay, Phuket, Thailand

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Abstract

The potential sources of 16 PAHs in surface sediments from highly tourism activities of Chalong bay, Phuket province, Thailand were apportioned. Twenty-eight of sediment samples were collected by using van Veen grab Sampler from Chalong bay, Phuket. Quantitative analysis of the 16 PAHs which categorized according to the US-EPA was analyzed by Gas Chromatography-Mass Spectrometry (GC/MS). Moreover, the multi-technique such as diagnostic ratios and principle component analysis (PCA) were applied to apportion the potential source of PAHs in the study area. The results showed that total concentration of PAHs (Σ PAHs) of sediments in Chalong bay ranged from 0.391 to 138 ng/g dry weight, with an average of 56.2 \pm 49.2 ng/g dry weight. While, the Diagnostic ratios plot was used to identify the potential sources of PAHs that caused by the anthropogenic in the study area. It was found that 80% of PAHs in sediments have originated from pyrolytic sources whereas the rest is originated from petrogenic sources. The accumulation of PAHs in sediments at Chalong bay were influenced by various potential sources of PAHs such as petroleum spills, combustion of fossil fuels, automobile exhausts, wastewater discharge from the domestic community and street runoff. The multivariate statistical treatment implicated the same potential sources of PAHs that are agreed with PAHs Diagnostic ratios.

Keywords: Polycyclic Aromatic Hydrocarbon; Chemical fingerprinting; Thailand; Principal component analysis; Anthropogenic Coastal Sediment

1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are a pollutants of particular concern because of the mutagenic and carcinogenic properties of a number of the individual compounds (termed congeners). Consequently, the US Environmental Protection Agency has listed 16 PAHs as priority pollutants and categorised seven of them as carcinogenic chemicals (IARC, 1983). PAHs are formed both, naturally (by forest fires, volcanoes, plants, fungi and bacteria) and anthropogenic activities (through the incomplete combustion process) (Jiang *et al.*, 2009). They

are known to enter marine environments through petroleum spills, combustion of fossil fuels, automobile exhausts, and from non-point sources such as street runoff and atmospheric fall-out (Ahrens and Depree, 2010; Tolosa *et al.*, 2009). In addition, they are ubiquitous and can pose significant human and ecosystem health risk (Long *et al.*, 1995). PAHs are mainly from two sources: petrogenic source, which is composed by PAHs associated with crude and refined oil spills, and pyrogenic source, which includes compounds formed by fossil fuel combustion, waste incineration, biomass burning, and asphalt production. Petrogenic PAHs mainly consist of two or three rings, whereas pyrogenic PAHs are often characterized by four to six aromatic rings (Hong *et al.*, 2016). Moreover, the isomer ratios of PAHs anthracene/(anthracene + phenanthrene), benzo[a]anthracene/(benzo[a]anthracene + chrysene), and fluoranthene/(fluoranthene + pyrene) have been used widely to analyze the parent sources of PAHs (Yunker *et al.*, 1995; 2002; 2003). The ring numbers of PAHs were also used to identify sources of PAHs (Harrison *et al.*, 1996). The occurrence of PAHs in the marine ecosystem reflects the several of potential activities influence. Each activity or source emits PAHs with characteristic signatures, which can be used to trace its source (Malik *et al.*, 2011). Like many developed coastal tourist places, intensive economic-related activities including the steadily increasing number of houses, hotels, restaurants, rapid urbanization along the coast are major contributions for the significant accumulation of anthropogenic PAHs to the marine environment in the Phuket coastal area. Chalong bay is located at the east-central side of Phuket, Thailand where a combination of a port, residential areas, and shopping hub are the main activities of the region. It is a center for intense boating activities, especially the departure point for many surrounding islands trips in Phuket. Therefore, the potential sources of PAHs, such as domestic wastewater discharge, leakage of used oil, oil spills and incomplete combustion of fossil fuel, are typically diffuse sources of the anthropogenic PAHs (Brown and Peake 2006; Kose *et al.*, 2008) on this coastal area. The objectives of this study are to determine the distribution and concentration of the 16 EPA priority

PAHs in Chalong bay sediments and to identify the possible sources of PAHs by using PAH diagnostic ratios in combination with the multivariate descriptive statistical techniques to distinguish among different sources of PAHs.

2. Materials and Methods

2.1 Study area and sampling methods

Chalong bay, Phuket, Thailand located in the eastern of Andaman Sea was chosen as a study area due to the maritime intensive activities. Chalong bay has an influence by many activities that loaded the PAHs into the sediments. All of the activities of ports, residential areas, hotels, restaurants and shopping hub could be the potential sources of PAHs in the study area. The sediment samples were collected from the study area covering the bay area of approximately 80 km² (east-west extension: 8 km, north-south extension: 10 km). Twenty eight surface sediment samples were collected along the Chalong bay in order to analyze the distribution of 16 individual PAHs using the van-Veen Grab sampler during 22th-23th September 2015. The sampling stations are shown in Figure 1. Sediment samples were then wrapped in clean aluminum foil, placed in a glass bottle, and kept frozen at -20 °C. They were ground and sieved to homogenize the samples, and kept in the refrigerator at -4 °C until analysis.

2.2 PAHs analysis

All solvents were HPLC grade, purchased from Fisher Scientific. A mix standard solution of 16 PAHs [Sigma Aldrich 36991: Naphthalene (Nap), acenaphthene, (Ace), acenaphthylene (Acy), phenanthrene (Phe), anthracene (An), fluoranthene (Fluo), pyrene (Pyr), benz[a]anthracene (B[a]A), chrysene (Chry), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), benzo[e]pyrene (B[e]P), indeno[1,2,3-cd]pyrene (Ind), dibenz[a,h]anthracene (D[a,h]A), and benzo[g,h,i] perylene (B[g,h,i]P)] and a mix of recovery internal standard (IS) PAHs [d₁₂-perylene (d₁₂-Per) and d₁₀-fluorene (d₁₀-Fl)] were purchased from Chiron AS (Stiklestadveine 1, N-7041 Trondheim, Norway). Standard stock solutions of deuterated and native PAHs were prepared in nonane. Working solutions were obtained by appropriate dilution in n-cyclohexane. Approximately 5 grams of dried sediment samples were extracted by Soxhlet extractor for 8 hours using dichloromethane as a solvent. Known amount of d₁₀-Fl and d₁₂-Per were spiked as internal standard. Fractionation/clean-up process was carried out following the method of Gogou *et al.* (1997). The extractant was passed through silica gel column using 4:6 (v/v) toluene:hexane as an eluant. The eluate was then purged with nitrogen to almost dryness. The solvent was then changed to cyclohexane and purged with nitrogen again until the final volume was 100 µl. A 1 µl volume of the aliquot was further analyzed by using a LECO Pegasus GC Time-of-Flight Mass Spectrometer (TOFMS) in the selective ion monitoring mode which was equipped with an Agilent J&W DB-5MS GC column (30 m x 0.25 mm i.d. capillary column, 0.25 µm thick films of 5%-phenyl-95%-methyl silicon). The GC oven temperature was programmed as follows: 1 min at 40 °C, ramped at 10 °C min⁻¹ to 300 °C, and held constant for 20 min. A LECO Pegasus TOFMS mass-selected detector was operated at 70 eV electron energy with a source temperature at 280 °C.

The instrument was tuned daily with perfluorotributyl amine (PFTBA) introduced via the calibration gas valve. Data were collected by a ChromaTOF work station Software. Accuracy was evaluated using the standard SRM 1941b. Mean recovery (based on extraction of matrix-matched certified reference materials, (n=8) was in range of 77–119%. The precision of the procedure, calculated as relative standard deviation on the duplicate samples, was less than 15%. All sample concentrations were calculated using standardized relative response factors run with each batch.

2.3 Statistical analysis

Data prepared for multivariate statistical analysis were arranged in matrix, where columns correspond to PAH compositions and rows represent sampling stations. The normalized data matrix was then analyzed by Principal Component Analysis (PCA). PCA as a multivariate analytical tool was used to reduce the set of original observed variables (PAH compositions in sediment samples) and to extract a small number of the dominant principal components to explain the relationships among the observed variables (Larsen and Baker, 2003). To obtain more clear features, Varimax rotation method with Kaiser Normalization was used.

3. Results and Discussion

3.1 PAHs contamination in Chalong bay sediment

On the basis of sediment analysis, the total PAHs concentration (Σ PAHs) is defined as the sum of Nap, Acy, Ace, Fl, 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]. Σ PAHs in the study area were in a range of 0.390 to 138 ng/g dry weight, with an average of 56.2 ± 49.2 ng/g dry weight. It was found that the hot spot areas where highly contaminated PAHs in the sediments are along the coastal line as shown in figure 1. These implied that the potential sources of sedimentary PAHs should be originated from combustion of fossil fuels, automobile exhausts, and from non-point sources such as street runoff, river input and atmospheric fall-out. The highest PAHs concentrations were found at the C1, C2, C5, C7, and C8 where they are located at the outflow of discharge wastewater from domestic communities and canal mouth. Figure 1 shows the spatial distributions of sedimentary PAHs in Chalong bay. The petrogenic PAHs mainly consist of two or three rings, whereas pyrogenic PAHs are often characterized by four to six aromatic rings, therefore the spatial distribution of low molecular weight and high molecular weight PAHs provided that the hot spot points implicate the different pattern between the petrogenic and pyrogenic PAHs in the study area. For petrogenic sources, the hot spots are located at the commercial ports, the location where one day trip vessels throw out the anchor (Center of Chalong bay) and the outflow of discharge wastewater from domestic communities and canal mouth (Figure 1). The potential source of petrogenic PAHs are mainly originated from leakage of used oil, oil spills, ship activities, and domestic wastewater discharge from community. Otherwise, the hotspot points of high molecular weight PAHs are along the coastal line which could be originated from automobile exhausts and street runoff.

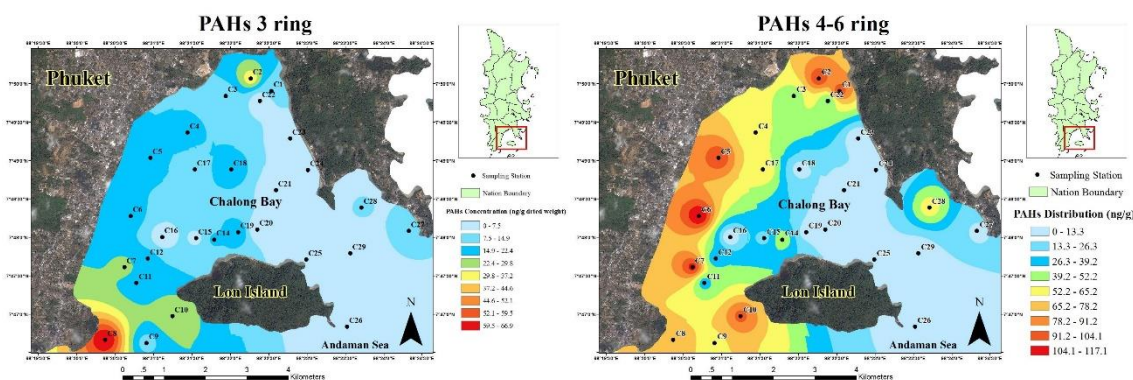


Figure 1. The spatial distribution of sedimentary low (3 ring) and high molecular weight (4-6 ring) PAHs in Chalong bay.

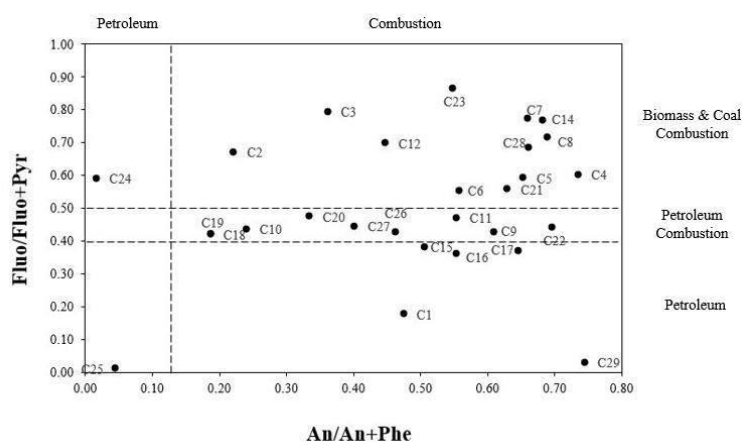


Figure 2. Cross-plot between ratios $An/(An + Phe)$ and $Flou/(Flou + Pyr)$.

3.2 Source identification by diagnostic PAH isomer ratios

The characteristics of PAH patterns in the coastal sediments are subjected to the different emission sources. Isomer ratios of PAHs have been used to identify PAH sources ranging from urban to marine environments (Yunker *et al.*, 2002). Pyrogenic and petrogenic are the primary sources of PAHs commonly found in coastal marine sediments (LaFlamme and Hites, 1978). Cross-plot between ratios of $An/(An + Phe)$ and $Flou/(Flou + Pyr)$ were applied to identify the potential sources of sedimentary PAHs in study area. The results indicated that most of sediment samples have originated from the mixed pyrogenic sources as a results of the incomplete combustion, pyrolysis of fuel, biomass burning and non-point sources such as street run-off and automobile exhausts (both of vehicles and vessels) (Figure 2). However, the petrogenic PAHs at the sampling stations of C1, C9, C15, C16, C17, C25, and C29 are located at the position of the vessels throw out the anchor (Figure 1). 3.3 Source identification by PCA

In this study, concentrations of 16 PAHs and the 28 sediment samples were selected as active variables and subjects, respectively. The majority of the variance (75.0%) of the scaled data was explained by three eigenvectors—principal components (PC). The first principal component (PC1) explained 43% of the total

variance, the second (PC2) explained 19% of the total variance, the third (PC3) explained 13% of the total variance, respectively as shown in Figure 3. According to the results, the PC1 is heavily weighted in Phe, An, Flou, Pyr, and B[a]A. This group is usually originated from the using of petroleum product and oil combustion. Fang *et al.* (2006) reported that high loadings of Pyr and Flou indicate incomplete combustion, pyrolysis of fuel and oil burning. This factor is believed to be the oil burning source of PAHs. In contrast, the PC2 is predominately composed of B[b]F, B[k]F, B[a]P, Ind, D[a,h]A and B[g,h,i]P which are the high molecular weight PAHs with 5–6 rings. This group usually originates from automobile exhaust, road dust, and biomass burning (Jiang *et al.*, 2009). Moreover, the PC3 is heavily weighted in low molecular weight PAHs that composed of Acy, Ace, and Fl which generally originated from leakage of used oil, oil spills, and ship activities in the study area (Liu *et al.*, 2009; Mostafa *et al.* 2009).

4. Conclusion

By analyzing the compositions of sedimentary PAHs in combination with the application of the multivariate descriptive statistical techniques, the potential sources of 16 PAHs in surface sediments from highly tourism activities of Chalong bay, Phuket province, Thailand were apportioned.

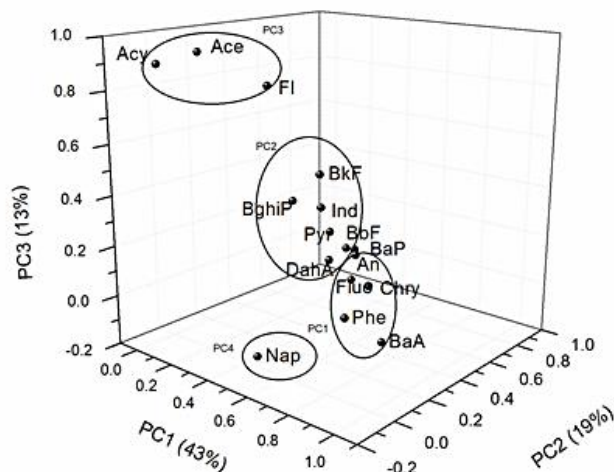


Figure 3. The 3-dimension loading plot of sedimentary PAHs in Chalong bay.

The results indicated that most of sediment samples have originated from the mixed pyrogenic sources as originated from incomplete combustion, pyrolysis of fuel, biomass burning and non-point sources such as street run-off, and automobile exhausts (both of vehicles and vessels). However, the petrogenic PAHs found at the sampling stations where located at the position of the vessels throw out the anchor and the outflow of discharge wastewater from domestic community and canal mouth. This PAHs should be originated from leakage of used oil, oil spills and ship activities in the study area

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