Accumulation of Polycyclic Aromatic Hydrocarbons (PAHs) and Carbon Compositions in Lake Sediment Cores ofThaleNoi, Phatthalung

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***Abstract* - This research aims to study the accumulation of 15 PAHs (∑PAHs15) and to measure OC/EC in the sediment from ThaleNoi, Phatthalung, Thailand.By analyzing the relationships of elementsdeposited in the sediment through time at different depths, the sources of PAHs can be determined. The sediment extraction process was carried out by the soxhlet method using dichloromethane (DCM) as solvent, and then took to intensity measurement by GC/MS, before OC/EC analysis was conducted by thermaloptical method. The total concentration of PAHs)∑PAHs15 (in ThaleNoi sediment ranged from 169-1217, 20-169, and 19-167 ng/g (dry weight) for station core 1, 2 and 3 respectively.Itwas found that the accumulation of PAHs showed lower contaminationcompared to those found in many other lakes, and the intensity of TC, OC, and EC hasvalues of [632,590],[368,290], and [264,300] ng g^{-1}respectively. The diagnostic ratio plots Ind/Ind+B[g,h,i]P, B[a]A/B[a]A+Chry(, OC/EC,and Char-EC/Soot-EC indicated that most of the potential sources of PAHs may be originated from the incomplete combustion of petroleum products and biomass.**

Keywords: Polycyclic Aromatic Hydrocarbons (PAHs), OrganicCarbon (OC), Elemental Carbon (EC)

I. INTRODUTION

The combustion of fossil fuels,coupled with the burning of agricultural wastes, are the major causes of carbonaceous compositions emission, whichgreatly affect the global climate system,resulting in the increase of environmental contamination. During the past few decades, both positive and negativeeffects of organic carbon (OC), elemental carbon (EC), and polycyclic aromatic hydrocarbons (PAHs) have been consistently studied in various places [1], especially on health, environment, and the accumulation in human and animal food chains. In many studies of sediment cores, the OC, EC, and PAHs relationships display strong correlations with local socioeconomic factors, such as human industrial production, consumption, occupation, and population growth [2][3][4][5][6][7][8]. Eventually, these pollutants are accumulated as sediments in lakes through adsorption process. Therefore, the examination of the contamination history of OC, EC, and PAHs inor around the lakes, released from or related to anthropogenic sources and surface run-off erosion, can be used to infer past human activities that caused such pollution.

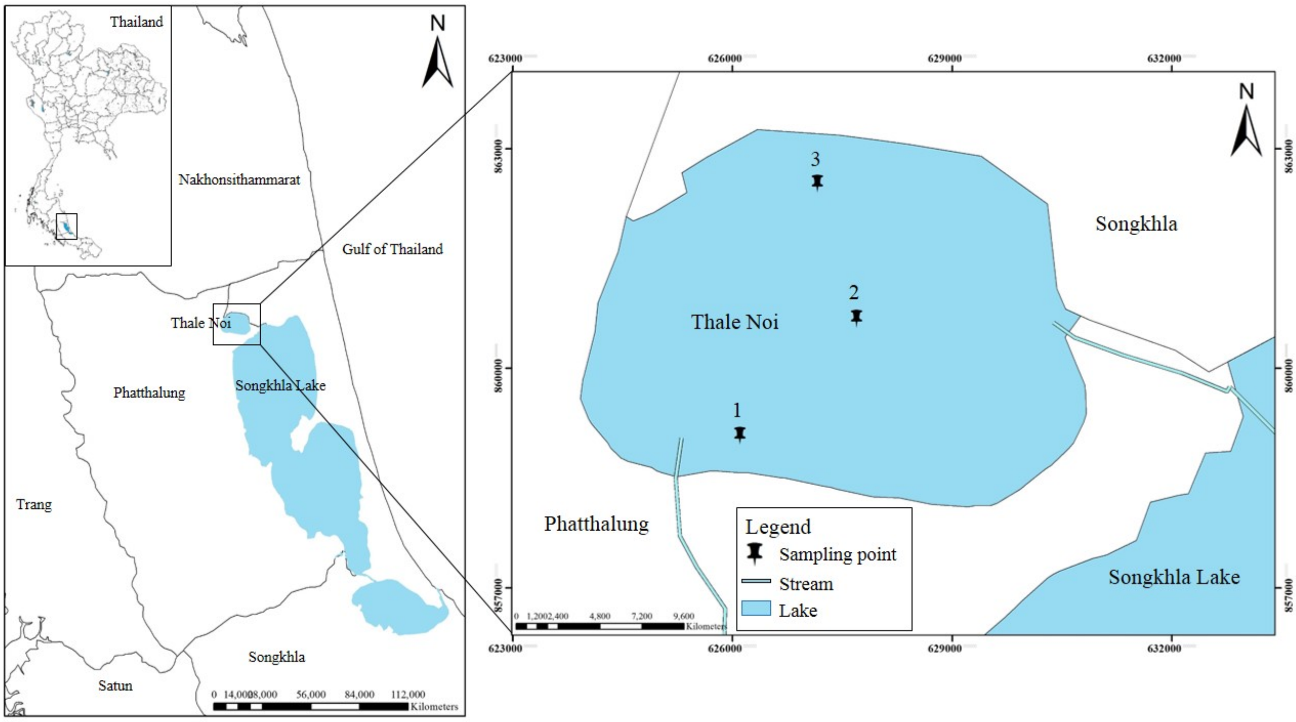


Fig. 1 Location of Studied Area

In this study, we examined the vertical profile of OC, EC and PAHs in sediment cores from ThaleNoiLake in Phatthalung province, Thailand to better understand activities that are anthropogenically-driven leading to environmental changes. The sources of the pollutants found would provide valuable information that leads to the better and sustainable management of the lake area.

II. MATERIALS AND METHODS

A. *Studied Sites and Sampling Methods*

ThaleNoi(Lat. 7°46’41.7520’’N, Long.100°7’ 22.0296’’E), located in Phatthalung, Thailand (Fig. 1), is a small and shallow eutrophic lake connected to the north of the larger Songkhla Lake. It has a surface area of 28 km^2,6 km long and 5 km wide,with an average depth of 1.5m .The sediment accumulated within the Quaternary period, with an age of about 1.8 million years,arising from the meeting of rivers and coastal waters. The line originates fromBanthadand Sankalakhiri Ranges.The totals of 73 samples, from 3 sediment core stations, werecollected on August, 12017 at depths using extractors with diameter of 10 cm and length of 150 cm. The core was cut longitudinally and divided into 2 cm pieces which were then preserved by freezing at around -20 °C in the aluminum foil.

B. *PAHs Analysis*

All solvents and reagents used were of HPLC grade for PAHs trace analysis obtained from Norwegian Standard. The 15 PAHs (∑PAHs15) includePhenanthrene (Phe), Anthracene (An), Fluoranthene(Fluo),11H-Benzo[a]Fluorene (11H-B[a]F), 11H-Benzo[b]Fluorene (11H-B[b]F), 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-c,d] 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 deuterated PAHs internal standard solutions [d12-Perylene (d12-Per) and d10-Fluorene (d10-Fl)].

The samples were prepared via soxhlet using dichloromethane by accelerated solvent extraction and 1 g of copper powder for 8 h. The extracts were concentrated with a rotary evaporator (Buchi R-100). The fractionation chromatography and the clean-up process followed the conventional method using solvent exchanged to hexane would yield low molecular weight PAHs, andhexane:toluene (1:0.6) would yield high molecular weight PAHs.

The extracts collected were purified by Colum Chromatography using silica gel. The elution was evaporated and concentrated to 100 µL under a gentle stream of nitrogen. More details of analytical methods were clearly explained in previous literature [9][10][11][12]. Analyses of PAHs were performed on a gas chromatography–mass spectrometry (GC-MS) using a Shimadzu GCMS-QP2010 Ultra.The GCMS system was operated in splitless liner mode of both the injection liner, and transfer line were maintained at 280 °C temperature. The mobile phase used helium (He) of 99.999% purity with 1.0 ml/min flow rate. The extracts were injected into an autosamplerusing a capillary column (30 m length x 0.25 mm i.d. 0.5 µm. film thickness). The splitless injection of 1.0 µl was held for about 48 min. [13][14].

C. Organic Carbon (OC) & Elemental Carbon (EC) Analysis

All sediment samples were analyzed for OC and EC using a Thermal/Optical Carbon Analyzer. The thermal/optical reflectance (TOR) protocol [15] was used for the carbon analysis. The sampleswere tested at various temperatures:OC1 (120 °C), OC2 (250 °C), OC3 (450 °C), OC4 (550 °C),EC1 (550 °C), EC2 (700 °C), and EC3 (800 °C). OC1-OC4 were texted in a non-oxidizing helium (He) atmosphere, while EC1-EC3 were tested in an oxidizing atmosphere of 2% oxygen in a balance of helium [16]. As oxygen was added to the system, the reflection of light was optically-detectedby pyrolyzed carbon (OP). Then,the ion was analyzedwith flame ionization detector at the absorbance of 663 nm [17].

III. RESULTS AND DISCUSSION

A.PAHs Analysis

The highest concentration of 15 PAHs ($\sum PAHs_{15}$) was found in core 1 which ranged from 169to 1,217 ng g^{-1}(dry weight), with the mean concentration value of 344.85±296.10 ng g^{-1}. The second highest was of core 2 which ranged from 20 to 169 ng g^{-1} with the mean concentration value of 85±61 ng g^{-1}. For core 3, the results ranged from 19 to 167 ng g^{-1} with the mean concentration value of 60±51 ng g^{-1}.Overall, the PAHs concentration levels in sediment of ThaleNoi Lake were found to be similar or lower than those of the other lake areas may be of activities that occur around different lake such as Kaohsiung Harbor in Taiwan (472 to 16,201 ng g^{-1})[18], Lake Baiyangdian in China (97 to 2,402 ng g^{-1}) [19], Lake Hongfengin southwestern China (2,934 to 5,282 ng g^{-1}) [20], and Lake Kitaura in Japan (380 to 520 ng g^{-1}) [21], as shown in Fig. 2.

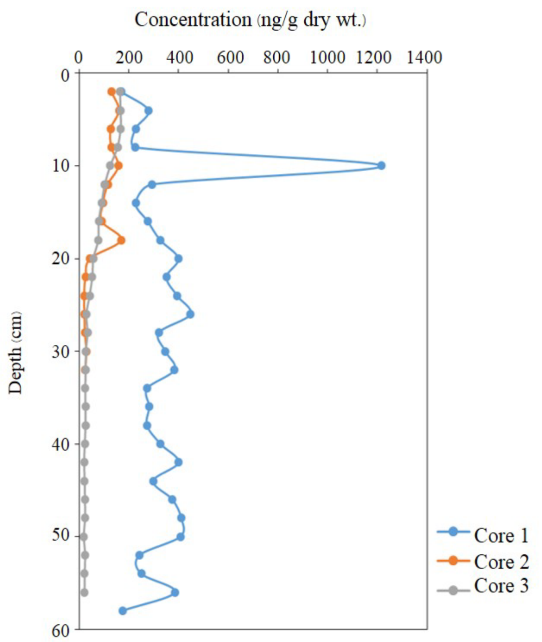


Fig. 2 Concentrations of $\sum PAHs_{15}$ in Sediment Cores: (A) Core 1, (B) Core 2, and (C) Core 3in ThaleNoi, Phatthalung

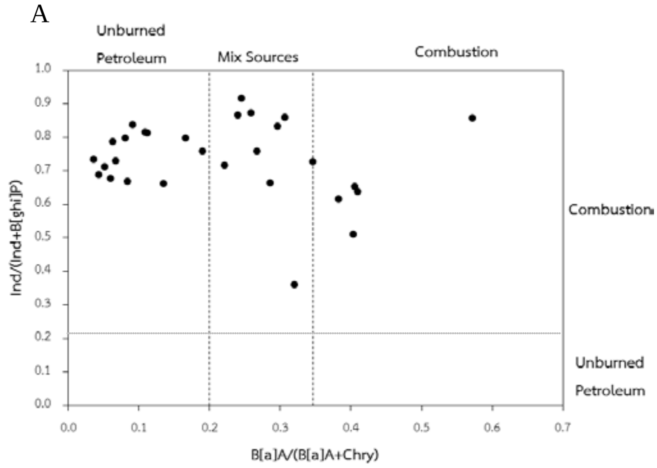
Considering the composition of the PAHs found in ThaleNoi Lake's sediments, the most common are B[a]P, Chry, Pyr, Fluo, and Ind, having 4-6predominant aromatic rings. This result suggested that the PAHs contamination in the sediment came from biomass and vehicle's fuel combustions [22][23][24][25].

B. Sources of PAHs

Sources of PAHs in the environment, including lake sediments, belong to two categories: petrogenic (from petrochemicals) and pyrogenic (from combustion). The feature of different PAHs and their possible sources are assessed by the diagnostic double/binary ratios plot of Ind/(Ind + B[g,h,i]P) and B[a]A/(B[a]A + Chry).If Ind/(Ind + B[g,h,i]P) is greater than to 0.2, the PAHs must have been originated from grass, wood, and coal combustion. If the diagnostic binary ratio is less than 0.2, the PAHs are most likely petrogenicin origin.In the case of B[a]A/(B[a]A + Chry), if the result is greater than to 0.35, the PAHs were originated from grass, wood, or coal ignitions. The interval between0.2-0.35 suggests that the PAHs are the product of petroleum combustion. If the ratio's result is less than 0.2, this indicated that the PAHs are of petrogenic sources [24].

PAH ratios were calculated for each sample shown in Fig.3. The results suggested that that lake sediment were contaminated by the incomplete combustion of petroleum product and biomass burning, which wereconsistent with human activities. There are many possible pyrogenic sourcesin the area such as agriculture and residence, combustion of biomass, open burning of agricultural wastes, forest fires, tourism activities, and fishery.However, the most possible sources may be from vehicles exhaust, oil spill, or discharge of lubricant oil.

A



to two categories: Char-EC (EC1-OP) and Soot-EC (EC2+EC3) by the ratio plot of Char-EC/Soot-EC.
The OC/EC ratio concentration value of 1.39, belonging to the interval of 1.0 to 4.0, suggested vehicular exhaust emission as the source [26]. The Char-EC/Soot-EC ratio concentration value of 26.20, belonging to the interval of 20.0 to 30.0, suggested biomass combustion as the source [27].

OC/EC and Char-EC/Soot-EC ratios were calculated for each sample. They all suggested that the lake sediments were contaminated by the incomplete combustion of vehicular exhaust emission and biomass combustion. These wereconsistent with the PAHs analysis.

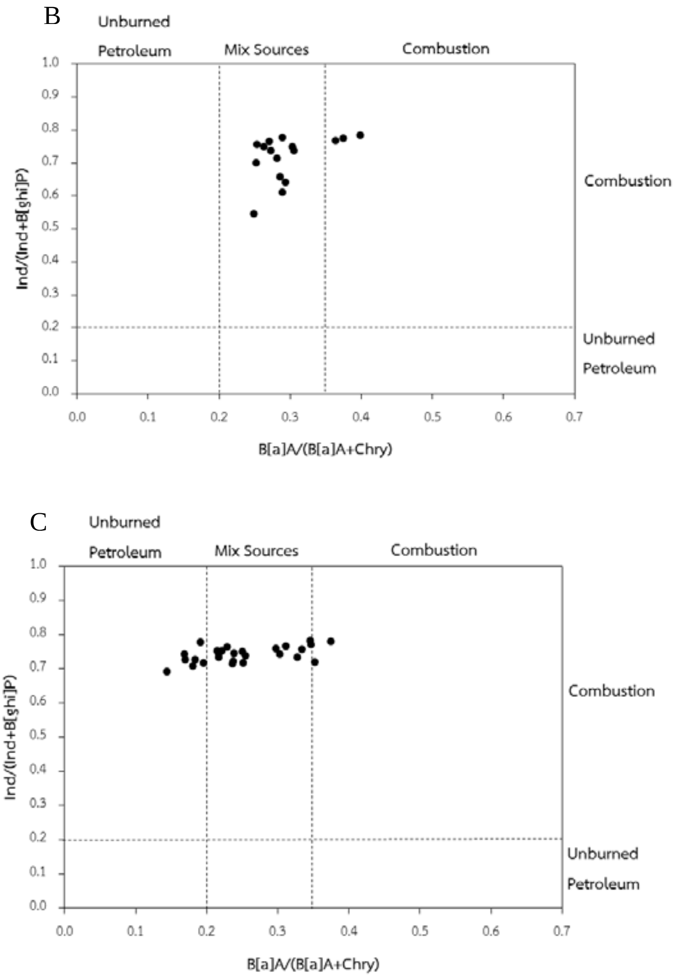


Fig. 3. Diagnostic ratios Ind/(Ind + B[g,h,i]P) versus B[a]A/(B[a]A + Chry) identifying sources of PAHs in sediments from (A) Core 1 (B) Core 2 and(C) Core 3 in ThaleNoi, Phatthalung

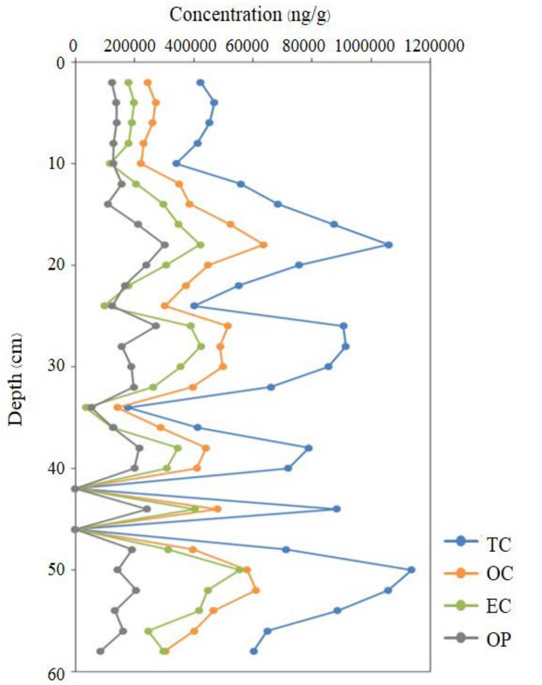


Fig. 4 Concentrations of Total Carbon (TC), Organic Carbon (OC), and Elemental Carbon (EC) in Sediment Cores from ThaleNoi, Phatthalung

C. OC/EC Analysis

The carbon composition in sediment consists of total carbon (TC), organic carbon (OC), and elemental carbon (EC). The analysis yielded that average concentrations of TC, OC, and EC values of [632-590],[290-368], and [264-300] ng g^{-1} respectively, as shown in Fig. 4.Of all the 8 types of carbon concentration (OC1, OC2, OC3, OC4, EC1, EC2, EC3, and OP) in of sediments collected from the lake, the most common were EC1, OC3, and OP, withvalues of [230-349],[190-810], and [162-760] ng g^{-1} respectively.This suggested vehicular exhaust emission from all types,incomplete combustion of fossil fuels and biomass fuels, as the sources [17].

D.Sources of OC/EC

Sources of OC/EC in the environment in the lake sediments were assessed by the ratio plot of OC/EC. Inaddition, the EC could explain the origin of different burning periods belonging

IV. CONCLUSION

The concentrations of total PAHs in the studied sediment samples were substantially lower than those found in many other lakes, consistentwith the OC/EC ratios. For the PAHs found in lake, the most common/predominant had 4-6 aromatic rings.This study also provided information on the source apportionment of lake sediments with the application of different methods. The main sources of PAHs found in this study werefrom hydrocarbons derived by incomplete combustion of petroleum products, forest fires, or biomass combustion. These included oil spill, vehicle’s exhaust, discharge of lubricant oil, and other waste discharge that had adversely affected the study area.

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