SOURCE APPORTIONMENT OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN COASTAL SEDIMENTS OF PHANG NGA PROVINCE

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การจำแนกแหล่งกำเนิดของสารพอลิไซคลิกอะโรมาติกไฮโดรคาร์บอน (PAHs) ในตะกอนชายฝั่งทะเลจังหวัดพังงา

นายดนัย ทิพย์มณี

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
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Thesis Title	SOURCE APPORTIONMENT OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN COASTAL SEDIMENTS OF PHANG NGA PROVINCE
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ดนัย ทิพย์มณี : การจำแนกแหล่งกำเนิดของสารพอลิไซคลิกอะโรมาติกไฮโดรคาร์บอน (PAHs) ในตะกอนชายฝั่งทะเลจังหวัดพังงา. (SOURCE APPORTIONMENT OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN COASTAL SEDIMENTS OF PHANG NGA PROVINCE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร.เพ็ญใจ สมพงษ์ชัยกุล, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: รศ.ดร.กัลยา วัฒยากร, รศ.ดร.ศิวัช พงษ์เพียจันทร์, 157 หน้า.

สารพอลิไซคลิกไฮโดรคาร์บอน (PAHs) เหมาะสมที่จะประยุกต์ใช้เป็นตัวชี้วัดผลกระทบจากกิจกรรมของมนุษย์ในบริเวณพื้นที่ชายฝั่ง จังหวัดพังงา ผลการศึกษาความเข้มข้น องค์ประกอบ และการกระจายเชิงพื้นที่ของสาร PAHsในตะกอนชายฝั่ง พบว่าความเข้มข้นรวมของสาร PAHs 13 ชนิดมีค่าอยู่ในช่วง 11.9 ถึง 272.0 นาโนกรัมต่อกรัมน้ำหนักแห้ง ค่าเฉลี่ยเท่ากับ 57.1±35.7 นาโนกรัมต่อกรัมน้ำหนักแห้ง รูปแบบการกระจายของสาร PAHs ในบริเวณเกาะพระทอง ชี้ให้เห็นว่าแหล่งกำเนิดของสารพอลิไซคลิกไฮโดรคาร์บอนในบริเวณนี้มาจากการเผาไหม้ เนื่องจากพบการกระจายของสาร PAHs ที่มีน้ำหนักโมเลกุลสูง (วงแหวนเบนซีน 4-6 วง) ในพื้นที่ที่พบการปนเปื้อนของสาร PAHs สูง ได้แก่แหลมปะการัง พบการกระจายของสาร PAHs ที่มีน้ำหนักโมเลกุลสูง (วงแหวนเบนซีน 5-6 วง) ชี้ให้เห็นแหล่งกำเนิดหลักมีที่มาจากการเผาไหม้ของน้ำมันและฝุ่นถนนจากน้ำชะ ผลการศึกษาจากการใช้อัตราส่วนและรูปแบบองค์ประกอบของสาร PAHs ยืนยันแหล่งกำเนิดหลักมีที่มาจาก ฝุ่นถนน พื้นผิวถนนแอสฟัลท์ ชิ้นส่วนยางและการรั่วไหลของผลิตภัณฑ์ปิโตรเลียมจากกิจกรรมทางเรือ นอกจากนี้จากการประยุกต์ใช้สถิติขั้นสูง (HCA และ PCA)ในการจำแนกแหล่งกำเนิด ผลการศึกษายืนยันว่าแหล่งกำเนิดหลักจำนวนสามแหล่งกำเนิด คือ ฝุ่นถนน การเผาไหม้เชื้อเพลิง และการเผาไหม้ชีวมวล ตามลำดับ จากแหล่งกำเนิดของสาร PAHs ที่ได้มาชี้ให้เห็นว่าสภาพแวดล้อมบริเวณชายฝั่งทะเลจังหวัดพังงาได้รับผลกระทบจากกิจกรรมมนุษย์ค่อนข้างสูง อย่างไรก็ตามเมื่อเปรียบเทียบปริมาณการปนเปื้อนของสาร PAHs ในพื้นที่ศึกษากับค่ามาตรฐานตะกอนชายฝั่งของประเทศสหรัฐอเมริกา พบว่ามีค่าไม่เกินค่า ERM จึงไม่ก่อผลกระทบอย่างรุนแรงต่อสิ่งมีชีวิตในบริเวณชายฝั่งจังหวัดพังงา ทั้งนี้พบว่ามีเพียงสถานีเดียวที่มีค่าความเข้มข้นของ D[a,h]A สูงกว่าค่า ERL/TEL นอกจากนี้ผลการจากศึกษาสาร PAHs ยังบ่งชี้ว่าคลื่นสึนามิที่เกิดขึ้นในปี 2004 เป็นตัวการสำคัญในการชะเอาสาร PAHs จากชายฝั่งลงสู่พื้นท้องทะเลเป็นระยะทางไกลกว่า 25 กิโลเมตรจากชายฝั่ง

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต..............................
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ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม..............................
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KEYWORDS: PAHs / SOURCE APPORTIONMENT / ANTHROPOGENIC INFLUENCE INDICATOR / COASTAL SEDIMENT

DANAI TIPMANEE: SOURCE APPORTIONMENT OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN COASTAL SEDIMENTS OF PHANG NGA PROVINCE. ADVISOR: ASST. PROF. PENJAI SOMPONGCHAIYAKUL, Ph.D., CO-ADVISOR: ASSOC. PROF. GULLAYA WATTAYAKORN, Ph.D., ASSOC. PROF. SIWATT PONGPIACHAN, Ph.D., 157 pp.

Using PAHs as an environmental indicator is suitable for implications the anthropogenic influences on the Phang Nga coastal area. The concentration, composition and spatial distribution of PAHs were investigated in the study area. The total concentrations of the 13 PAHs were ranged from 11.9 to 272.0 ng g^{-1} dry weight, with an average of 57.1±35.7 ng g^{-1} dry weight. The distribution pattern of PAHs in the background group (Koh Phra Thong) can be characterized as pyrogenic in origin due to relatively higher contribution from HMW PAHs with 4~6 rings. In case of the hot spot group, the highest percentage of 5-6 ring PAHs was found at stations in front of Pakarang Cape, indicating fuel combustion or street run-off as the predominant sources. The diagnostic PAHs ratios and fingerprints indicated that the promising PAH sources might be originated from the traffic-related sources such as petroleum combustion, street dust, road paving asphalt, tires and leaking of petroleum used by shipping activities. In addition, application of the multivariate descriptive statistical techniques (e.g. HCA and PCA) also identified the three possible sources of PAHs to be road dust, fuel combustion and grass/wood combustion. As a consequence, all of the promising sources implied that this coastal marine have been impacted with high anthropogenic activities. However, the levels of PAHs in the study area did not exceed the ERM and should not cause acute biological damages, Although at one site D[a,h]A exceeded the ERL/TEL values only one station. Moreover, the PAHs results indicated that the 2004 Tsunami backwash played a key role in transporting anthropogenic PAHs to the sediment approximately 25 kilometers far away offshore.

Field of Study: Environmental Management Student's Signature
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CHAPTER I

INTRODUCTION

1.1 Motivations

Organic pollutions from anthropogenic sources (both point and non-point sources) to marine environments have been an area of great concern. Due to high hydrophobic property and relatively stable chemical structures, they have strong partitioning with particle surfaces and thus can be accumulated at high concentrations in coastal sediments (Cornelissen et al., 2006). Among the organic contaminants, polycyclic aromatic hydrocarbons (PAHs) have received much attention because of their ubiquitous distribution and toxic hazards associated in marine sediments (Boonyatumanond et al., 2006; Khairy et al., 2009; Liu et al., 2009; Leonardo et al., 2009; Tolosa et al., 2009). PAHs contaminated sediments appear to expose directly to benthic organisms and indirectly (via resuspension) to pelagic organisms. This will consequently have adverse impact natural ecosystems, especially for urban coastal regions where high anthropogenic influences and various contamination sources exist (Khairy et al., 2009; Liu et al., 2009; Leonardo et al., 2009; Tolosa et al., 2009).

Coastal sediments are considered as sinks of terrestrial derived materials. As a result, sediments loaded with anthropogenically derived materials, such as PAHs, which are mainly originated from incomplete fossil fuel, biomass burning and leakage of petroleum, may reflect the magnitude of anthropogenic activities. PAHs can be transported to the marine environment via two main pathways, i.e., riverine runoff (Wang et al., 2010) and long range atmospheric transport (Tsapakis et al., 2003).

The marine environment in Thailand has been degraded by various pollutants arising both from land-based sources and from heavy shipping traffic, together with the accompanying accidental oil spills (Wattayakorn, 2005, 2012). These pollutants are the typically diffuse sources of PAH contaminated in coastal sediments.

The assessment of the status of PAHs contamination in coastal and riverine environments in the Gulf of Thailand has previously carried out (Boonyatumanond, et al., 2006, 2007), but not in the other coastal zones. Thus, this study aims to assess the status of PAHs contamination in the Andaman coastal for the first time, especially on the Phang Nga coastal area. Even, the current status and source apportionment of PAHs contamination are needed in order to better understand environmental risks as well as to support decision-making for relevant management authorities. However, Thailand national guideline has not yet been established for managing PAHs contaminated sediment.

Like many newly 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 Phang Nga coastal zone. This area has also heavily affected by the Tsunami 2004 wave. Thus, severe damages occurred, including coastal shoreline erosion and destructive infrastructures such as buildings, road networks, bridges, fishing vessels, as well as the near-shore environment. As a consequence, the anthropogenic PAHs are expected to be transported from the potential sources on land and deposited into the near-shore seabed.

For decades, PAHs have been used to distinguish the anthropogenic source and biogenic source in marine sediment (Christensen et al., 1996; Tobiszewski and Namiésnik, 2012). They can be categorized as anthropogenic combustion sources (i.e. oil spill, automobile exhaust, and street runoff) and as natural combustion sources (i.e. forest fires) by using PAHs diagnostic ratios (Yunker et al., 2002, 2011; Yunker and Macdonald, 2003). PAHs of molecular mass 178, 202 and 258 are commonly used to distinguish between pyrogenic (combustion-derived) and petrogenic (unburned petroleum-derived) sources. In addition, Phenanthrene/Anthracene (m/z 178), Fluorantene/Pyrene (m/z 202) and Benz[a]Anthracene/Chrysene (m/z 258) have been previously used by some works (Wang et al., 2006; Khairy et al., 2009; Liu et al.,2009). Because of their usefulness in source identification, the use of PAHs as an anthropogenic indicator may be suitable for implications of anthropogenic influences on coastal marine environment.

By using PAH diagnostic ratios in combination with the multivariate descriptive statistical techniques, it should be possible to investigate that the PAHs contamination in the Phang Nga coastal sediment originated from what sources and whether the level of contamination and distribution in the recent deposits is an impact from 2004 Tsunami event or just simply terrestrial derived materials. The expected outcome information should lead to better understanding of the predominant PAH sources and their potential ecological impact, as well as an improved ability to design effective management and remediation strategies for degraded coastal ecosystems.

This study aims to use PAHs distribution for tracing the transport and distribution of land-derived materials and apportionment the dominant sources caused by human activities which have adverse effect on the study area. In addition, sediment quality guideline (SQGs) was applied to evaluate an occurrence of adverse ecological effects due to the levels of PAHs contaminated**.**

1.2 Objectives

1) To identify types and concentrations of each PAHs in the Phang Nga coastal soils and sediments.
2) To determine the current status of PAHs contamination in the Phang Nga coastal zone.
3) To apportion sources of PAHs in the Phang Nga coastal sediments.
4) To evaluate an occurrence of adverse ecological affects due to the levels of contamination with PAHs in the Phang Nga coastal sediments.

1.3 Scope of the Study

1) Sampling and chemical analysis of PAHs contamination in aerosols, soils and surface sediments were carried out to identify type and level of their contamination in the Phang Nga coastal zone.
2) Statistical treatment was performed to apportion the various sources of PAHs in the study area.
3) PAHs were used as a chemical proxy to indicate the 2004 Tsunami backwash which was predominant source for PAHs contamination in the study area.
4) Transport and distribution of anthropogenic PAHs was evaluated for proving the land to sea transportation in the study area.
5) Sediment quality guideline (SQGs) was applied to evaluate an occurrence of adverse ecological effects due to the levels of contamination with PAHs.

1.4 Expected Outcomes

1) To better understand the transport and distribution of anthropogenic PAHs in the Phang Nga coastal zone.
2) To assess the status of PAH contamination in the Andaman sea.
3) To achieve the potential sources of anthropogenic PAHs for designing the effective management and remediation strategies for degraded coastal ecosystems.
4) To assess an occurrence of adverse ecological effects due to the levels of contamination with PAHs.

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs), a class of organic compounds containing two or more benzene rings originated from incomplete combustion of organic matters, are introduced to the environment by both natural and anthropogenic emission sources. Forest fires and volcanic eruption are the major natural source of PAHs. On the other hand, anthropogenic sources mostly relate to combustion processes of fossil fuels such as vehicles, industrial and residential heating boilers, fireplaces, wood burnings, garbage burnings, waste incinerations, coke and asphalt productions, oil refining, aluminum productions, and other industrial activities (Banner et al., 1989; Heemken et al., 2000). Alternative potential sources are wastes from manufacturing that use coal tar, crude oil, creosote, roofing tar, and accidental spills of fuel oil, crude oil, and petroleum products (Simpson et al., 2002; Jiang et al., 2007).

There are hundreds of PAH compounds in the environment, but only 16 of them are included in the priority pollutants list of U.S. Environmental Protection Agency (US-EPA), as shown in Table 2.1. They are listed as priority pollutants by the US-EPA due to their toxic, mutagenic and carcinogenic effects (Table 2.2) (ATSDR, 1995). Currently, they have been recognized as priority pollutants in most countries, not only their toxicities, but also their high ongoing emission loadings (Yim et al., 2007; Khairy et al., 2009; Liu et al., 2009; Leonardo et al., 2009).

Table 2.1 Formula and chemical structure of 16 polycyclic aromatic hydrocarbons (PAHs) listed as priority pollutants by the U.S. Environmental Protection Agency (ATSDR, 1995).

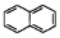
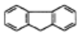
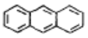
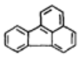
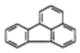
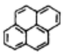
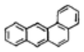
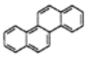
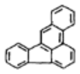
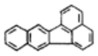
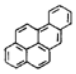
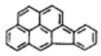
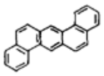
Name of Compound	Abbreviation	Formula	M.W.	Structure
Naphthalene	Nap	$C_{10}H_8$	128	
Acenaphthene	Ace	$C_{12}H_{10}$	152	
Acenaphthylene	Acy	$C_{12}H_8$	154	
Fluorene	Fl	$C_{13}H_{10}$	166	
Anthracene	An	$C_{14}H_{10}$	178	
Phenanthrene	Phe	$C_{14}H_{10}$	178	
Fluoranthene	Fluo	$C_{16}H_{10}$	202	
Pyrene	Py	$C_{16}H_{10}$	202	
Benzo[a] anthracene	B[a]A	$C_{18}H_{12}$	228	
Chrysene	Chry	$C_{18}H_{12}$	228	
Benzo[b]fluoranthene	B[b]F	$C_{20}H_{12}$	252	
Benzo[k]fluoranthene	B[k]F	$C_{20}H_{12}$	252	
Benzo[a]pyrene	B[a]P	$C_{20}H_{12}$	252	
Benzo[ghi]perylene	B[g,h,i]P	$C_{22}H_{12}$	276	
Indeno[1,2,3cd]pyrene	Ind	$C_{22}H_{12}$	276	
Dibenzo[a,h]anthracene	D[a,h]A	$C_{22}H_{14}$	278	

Table 2.2 Some physicochemical properties and carcinogenicity of PAHs (ATSDR, 1995).

PAHs	Vapor Pressure (Torr) at 20°C	Solubility (mg/L) at 20°C	K_{ow}[a]	Carcinogenicity (IARC[b]/US-EPA[c])
Nap	0.0492	32	23×10^{2}	2B
Ace	$10^{-3} – 10^{-2}$	3.4	21×10^{3}	no data
Acy	$10^{-3} – 10^{-2}$	3.93	12×10^{3}	no data
Flu	$10^{-3} – 10^{-2}$	1.9	15×10^{3}	3/D
An	2×10^{-4}	0.05 – 0.07	28×10^{3}	3/D
Phe	6.8×10^{-4}	1 – 1.3	29×10^{5}	3/D
Flu	$10^{-6} – 10^{-4}$	0.26	34×10^{4}	3/D
Py	6.9×10^{-9}	0.14	2×10^{5}	3/D
B[a]A	5×10^{-9}	0.01	4×10^{5}	2A/B2
Chry	$10^{-11} – 10^{-6}$	0.002	4×10^{5}	3/B2
B[b]F	$10^{-11} – 10^{-6}$	no data	4×10^{6}	2B/B2
B[k]F	9.6×10^{-7}	no data	7×10^{6}	2B/B2
B[a]P	$5 \times 10^{-}9$	0.0038	10^{6}	2A/B2
B[g,h,i]P	$\sim 10^{-10}$	0.00026	10^{7}	3/D
Ind	$\sim 10^{-10}$	no data	5×10^{7}	2A/B2
D[a,h]A	$\sim 10^{-10}$	0.0005	10^{6}	2A/B2

a *K_{ow} = octanol-water partition coefficient*
b *Classification by International Agency for Research on Cancer: IARC (1987)*
c *Office of Environmental Health Hazard Assessment: OEHHA (1993)*
2A *Probably carcinogenic to human (sufficient evidence for human cancer)*
2B *Possibly carcinogenic to human (sufficient evidence for animal cancer and possible evidence for human cancer)*
3 *Not classifiable as to human and animals (inadequate evidence for animal cancer and evidence for mutagenicity).*
B2 *Probably carcinogenic to human (inadequate evidence in human cancer and sufficient evidence in animal cancer)*
D *not classifiable as to human and animal (inadequate evidence in animal cancer)*

The fate of PAHs in the environment is largely determined by physiochemical properties, since vapour pressure and water solubility basically decrease with the increasing molecular weight, thus high mobility of low molecular weight PAH can be expected (Wild and Jones, 1995). On the other hand, PAHs are quite non-volatile, and have relatively low vapour pressure and resistance to chemical reactions. As a consequence, PAHs are persistent in the environment and demonstrate a tendency to accumulate in biota, soils, and sediments and they are also highly dispersed by the atmosphere (Maldonado et al., 1999).

PAHs are hazardous chemical pollutants because they have been described as mutagenic, carcinogenic and teratogenic (Neff et al., 2005). On the basis of hazardous properties, they have been included in the US EPA and the EU priority pollutant list (Tolosa et al., 2009). They have also been categorized as persistent organic pollutants (POPs) due to their widespread distribution in the environment and potential toxicity to organisms (Qiu et al., 2009).

In additions, PAHs distribution has been greater concerned due to its mutagenic and genotoxic potential in the environment, and their carcinogenic effects on natural ecosystems (Long et al., 1995). The bioavailabilities of sedimentary PAHs are readily enhanced in food webs by re-suspension or bioturbation of sediment into the water column (Jiang et al., 2009). Therefore, the study of PAHs in coastal sediments also relates to their bioaccumulation in shellfish and other benthic organisms, and possible entry to human food chains. However, Thailand national guideline for PAHs contaminated sediment has not been yet established.

PAHs exist in marine system in different forms including, free dissolved phase, dissolved organic matters (DOMs) associated phase, suspended particulate matters (SPMs) associated phase, and sediments associated phase. Distribution of PAHs among these phases is primarily controlled by their physical/chemical properties, such as solubility, vapor pressure, and sorption coefficient, as well as the characteristics of each phase (Zhou et al., 1999). Once PAHs enter into marine environment, they tend to be associated with particulate material and subsequently deposit in sediments (Maldonado et al., 1999; Shi et al., 2005; Sun, et al., 2009). In such a way, marine sediments act as temporary or long-term sink of natural and anthropogenic PAHs from land-based sources (Mostafa et al., 2009).

The status of PAHs contamination in coastal sediments from Gulf of Thailand has been intensively studied by some groups of researchers (Wongnapapan et al., 1997; Chumchuchan, et al. 1999; Wattayakorn, 2005, 2012). The results indicated that the levels of PAHs contamination was not much higher compared to other contaminated regions of the world, though some hot spots were found near port and harbor areas (as shown in Table 2.3). Recent assessment of the status of PAHs contamination in coastal and riverine environments in the Gulf of Thailand has carried out by Boonyatumanond et al. (2006, 2007). However, there are not many studies in the other coastal zones.

Table 2.3 Comparisons of PAHs concentrations in surface sediment collected from different coastal zones and bays (ng g^{-1} dry weight).

Location	Range	Mean	References
Gulf of Thailand			Wattayakorn (2005)
Coastal areas	11-1,992	506	
Offshore areas			
Upper Gulf	39-95	70	
Eastern Seaboard	11-324	79	
Lower Gulf	14-67	51	
Dalian Bay, China	32.7-3558	152.8	Liu et al. (2001)
Daya Bay, China	42.5-158.2	126.2	Yan et al. (2009)
Kyeonggi Bay, Korea	9.1-1400	120	Kim et al. (1999)
South China sea	24.7-275.4	146	Yang (2000)
Casco Bay, USA	16-20,748	2900	Kennicutt et al. (1999)
Northwestern Black sea	52.6-269	136	Maldonado et al. (1999)
Todos Santos Bay, Mexico	7.6-813	96	Macias-Zamora (2000)
Gulf of Aden, Yemen	2.2-604	82.4	Mostafa et al. (2009)

2.2 PAHs inputs in the coastal area

PAHs are known to enter marine environments through industrial discharges, petroleum spills, combustion of fossil fuels, forest fires, volcanic eruptions, automobile exhausts, and non-point sources such as urban runoff and atmospheric fall-out (Tolosa et al., 2009) as shown in Figure 2.1.

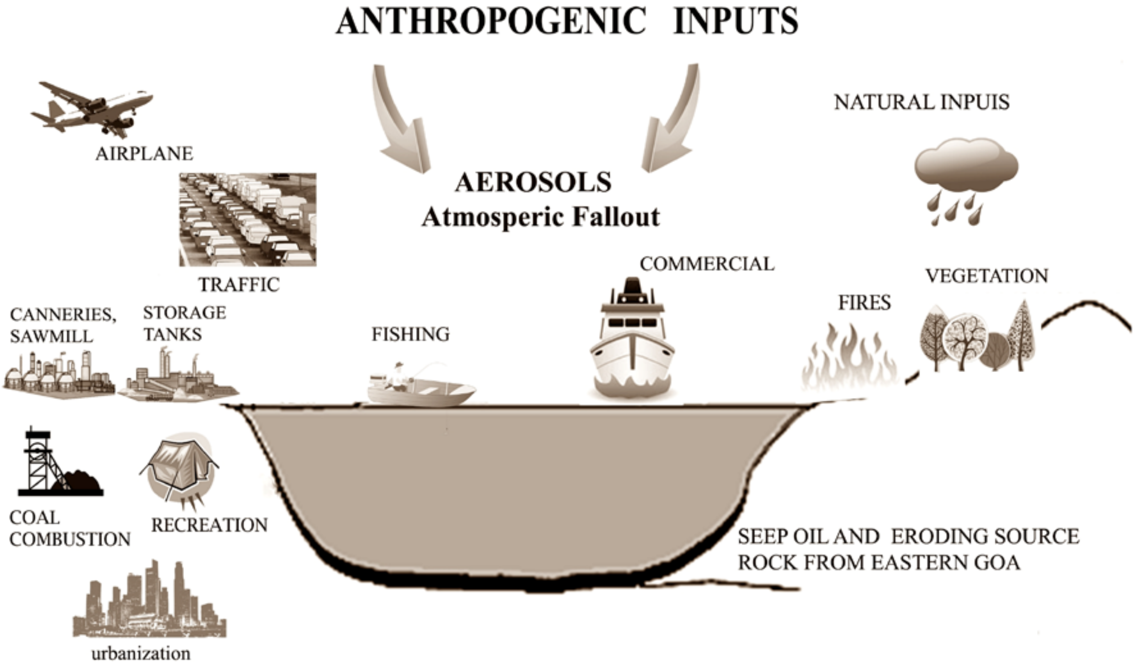


Figure 2.1 Types of PAHs inputs in the marine environment.

modified from http://www.bowdoin.edu/faculty/d/dpage/html/oilspill.shtml

Because of the several potential sources of PAHs contaminated in coastal sediment, sources of PAHs can be summarized into two distinct groups: pyrogenic and petrogenic sources. Pyrogenic sources are originated through incomplete combustion of coal, petroleum and wood. Pyrogenic sources include industrial and energy production using fossil fuels, waste incinerators, automobile exhausts by gasoline or diesel fuel, volcanic eruption and forest fires. Once, pyrogenic PAHs are emitted to the atmosphere, they are finally brought down to marine environments through direct atmospheric fallout and surface run-off (Eisler, 1987; Yim et al., 2007; Saha et al., 2009). Petrogenic sources include crude oil and petroleum products such as kerosene, gasoline, diesel fuel, lubricating oil, and asphalt. They are emitted directly to marine environment through oil spills and routine tanker operations (Boonyatumanond et al., 2006). Furthermore, petrogenic PAHs can be introduced to rivers and coastal zones through street dust run-off, which potentially contains petrogenic PAHs derived from leakage of used oil, vehicle tire and asphalt materials.

For Thailand coastal zone, the intensive economic, including the steadily increasing number of houses, vehicles, hotels, power plants and expanding communities along the coast and maritime activities, including major development projects, developments in shipping, oil and gas, a large and important fishery sector, intensive coastal aquaculture, and extensive tourism may be responsible for the accumulation of significant amounts of anthropogenic PAHs in the coastal sediments. In brief, the typically diffuse sources of PAH contaminated in coastal sediments of Thailand may be generated from both land-based sources and heavy shipping traffic, together with the accompanying accidental oil spills (Wattayakorn, 2005,2012). Wastes associated with such anthropogenic activities could also increase the inputs of contaminants, including PAHs (Boonyatumanond et al., 2006).

As Thailand is situated in the tropical zone, its coastal environment may heavily affect from the strong rain inherent to tropical Asia climate. As a consequence, the atmospheric fallout and surface run-off should be taken into consider to be accelerated trigger to transport the contaminated PAHs from land-base sources and sink down into the coastal sediments. The transporting mechanisms of PAHs during rainfall-runoff events have been rarely studied. Zheng et al. (2012) have studied the runoff pollution process on PAHs-contaminated soil, and found that soil organic matters, rather than clay particles, seem to be the main carrier of PAHs. The enrichment is highly conditioned on runoff and erosion processes, and its magnitude varies among PAH compounds.

Another promising source of PAHs is the long range atmospheric transport which originated from forest fire in Sumatra, Indonesia. Indonesia‘s forest fires have especially drawn the attention of the international community because of their environmental, social and economic consequences. They have large negative impacts on local and national development as they directly affect biodiversity, the livelihood and health of local people in the large area of the region as shown in figure 2.2. They emit a large amount of greenhouse gases and pyrogenic PAHs (Ostermann and Brauer, 2001; Radzi Bin Abas et al., 2004) as soot or gas to the atmosphere and are finally conveyed to coastal sediments through direct atmospheric fall-out.

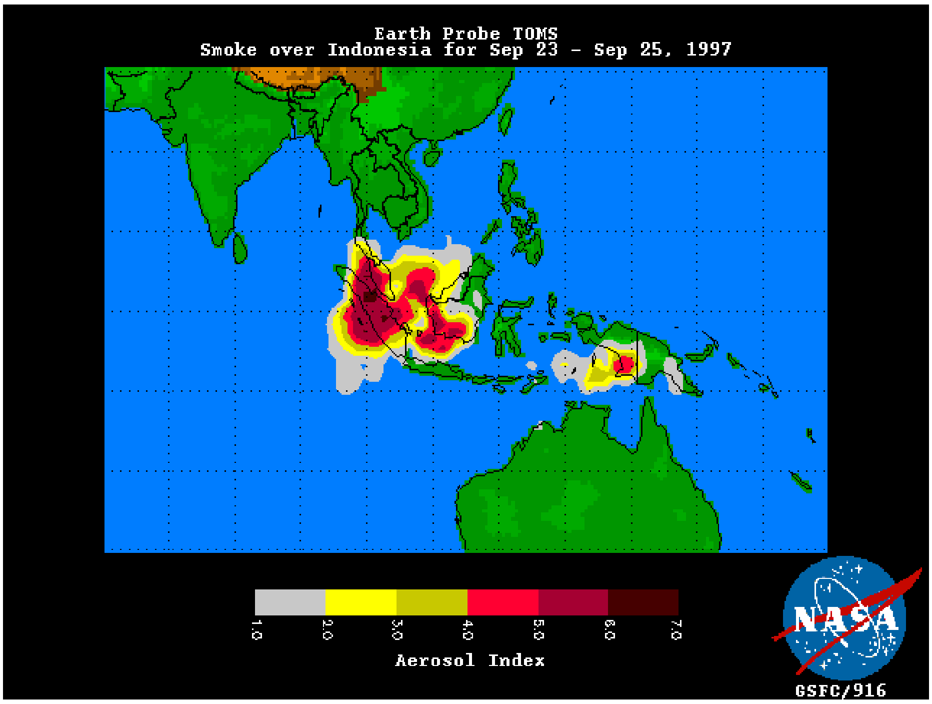


Figure 2.2 Long ranges atmospheric transport of PAHs was generated from the 1997/1998 fires in Sumatra and Kalimantan, Indonesia.

online at http://toms.gsfc.nasa.gov/aerosols/aerosols.html

Moreover, the tsunami event in 2004 at Phang Nga coastal zone severe damages including coastal shoreline erosion and destructive infrastructures such as buildings, road networks, bridges, fishing vessels, as well as the near-shore environment. As a consequence, the anthropogenic PAHs are expected to be transported from the potential sources on land and deposited into the near-shore seabed. The assessment of PAHs contamination after extreme events such as Tsunami has not been conducted yet. However, Mitra et al. (2009) has carried out the assessment of the impact of Hurricanes Katrina on seabed PAH dynamics in the Gulf of Mexico. They found that substantial amounts of PAH-laden particles may have been displaced from the seabed in shallow areas of water column caused by this event. It is scientific interest to further investigate the status of PAHs contamination in the coastal sediments after geo-hazard events such as the 2004 Indian Ocean Tsunami event.

The powerful nature of the 2004 Tsunami may have resulted in extensive resuspension followed by erosion and deposition of sediment throughout near-shore and offshore seabed in the Phang Nga coastal zone. The terrestrial derived materials contaminated with PAHs from land can be transported to accumulate in bottom sediment through the backwash current in the form of shoreline erosion (as shown in Figures 2.3). The transportation of contaminated PAHs may occur during street dust run-off from the normal transporting mechanisms such as those associated with the annual reversals of monsoons and hydro-meteorological extreme events or high precipitation in rainy season.

Figure 2.3 Evidence of the damage area which has been heavily destroyed by the tsunami 2004 in Khao Lak coastal zone.

online at http://www.gisthai.org/research/tsunamis/phangnga.html

Feldens et al. (2009) provide the strong evidence which can be confirmed the impact of Tsunami that carried the anthropogenically derived materials into the sediment in front of Pakarang Cape, Khao Lak area. They found that the impact was probably most effective during the backwash when stiff mud deposits containing grass, wood fragments and shells were transported by high density backwash flows. Moreover, several boulders, which might have been deposited during the tsunami backwash flow, were found in the channels in front of Pakarang Cape. Anthropogenic PAHs derived materials can be preserved in the channels through backwash current. The geophysical structure of seabed shows a promising evidence of terrestrial derived materials deposits in the study area. As shown in Figure 2.4, the resemblance between the backwash terrestrial derived materials plumes and the channels is clearly visible.

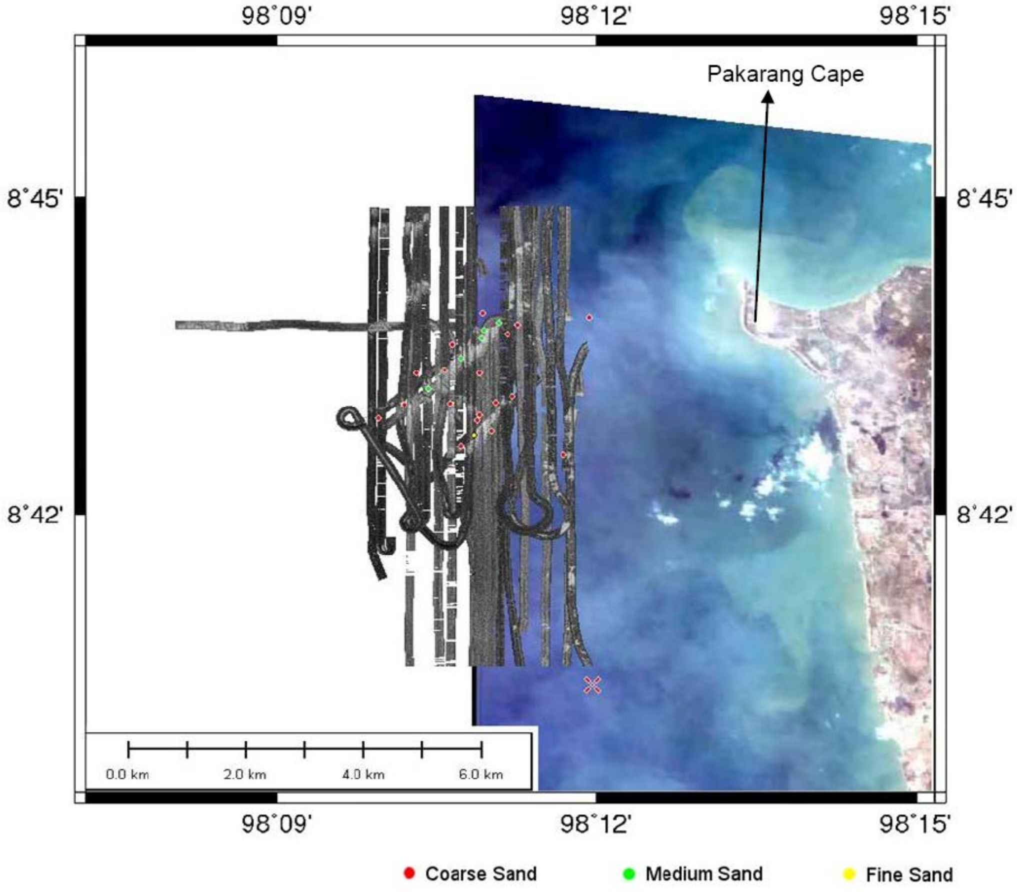


Figure 2.4 The resemblance between the satellite image of the Tsunami backwash terrestrial derived materials plumes combined with the Side Scan Sonar data.

Ikonos Satellite image taken on December, 29th 2004 (Feldens et al., 2009)

2.3 Source apportionment of PAHs

The distribution of PAHs in the environment typically exhibits large variations among different sites. Thus, the chemical composition (source fingerprint) of the major sources of anthropogenic PAHs has been intensively investigated by many researchers. Khalili et al. (1995) have determined the source fingerprint of the major sources of anthropogenic PAHs in the Chicago metropolitan area for the period 1990-1992. They found that two and three rings PAHs were responsible for 98%, 76%, 92% and 80% of the total concentrations of the measured 20 PAHs from coke evens, diesel engines, highway tunnels, gasoline engines and wood combustion samples, respectively (Table 2.4). Six rings PAHs such as Ind and B[g,h,i]P were only detected in the highway tunnel, diesel and gasoline engine samples.

Table 2.4 Source distribution of percentage PAHs to total mass. (Khalili et al., 1995)

PAH	Highway tunnel	Diesel engines	Gasoline engines	Coke oven	Wood combustion
2-ring	76	8.7	55	89	11
3-ring	16	56	18	8.9	69
4-ring	4.3	10	12	0.97	6.6
5-ring	3.1	18	13	0.22	13
6-ring	0.38	5.2	0.053	0.014	n.d.
7-ring	n.d.	0.18	0.082	n.d.	n.d.

2-ring: naphthalene

3-ring: acenaphthene, acenaphthylene, fluorine, phenanthrene, anthracene and retene;

4-ring: fluoranthene, pyrene, benzo[a] anthracene, chrysene and triphenylene;

5-ring: cyclopenta[c,d]pyrene, benzo[b/k]fluoranthene, benzo[a/e]pyrene and dibenzo[a,h]anthracene;

6-ring: indeno[1,2,3c,d]pyrene and benzo[g,h,i]perylene;

7-ring: coronene

n.d. not detected

Boonyatumanond et al. (2006) have also been investigated the source fingerprint of the major sources of anthropogenic PAHs in various sample types collected in coastal and riverine environments in the Gulf of Thailand (Figure 2.5). They concluded that street dust is one of the major sources of the petrogenic PAHs in soil and sediment samples.

In general, naphthalene, fluorene, Phe, Fluo, Py, B[a]A, Chry, B[b]F and B[a]P are the dominant PAHs found in the sediments. The three typical pyrogenic PAHs, Py, Chry and B[a]P (Pereira et al., 1999) are generally found at high concentrations in sediments. Other studies have shown that petroleum derived low molecular weight PAHs are degraded more rapidly in sediments (Jones et al., 1986), while PAHs with three and four rings are more refractory in natural environments (Sauer and Boehm, 1991).

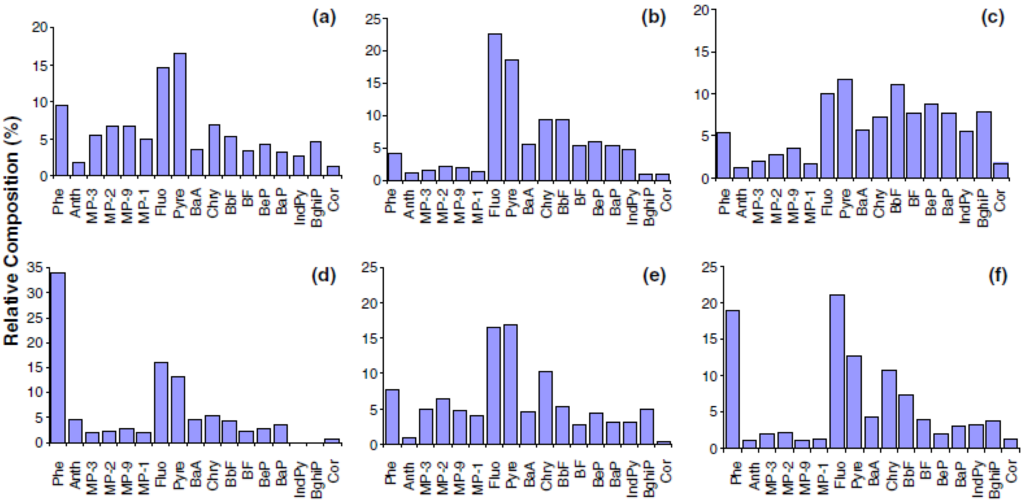


Figure 2.5 PAH profiles of sediment, street dust, and soil: (a) canal sediment (b) river sediment (c) estuarine sediment (d) coastal sediment (e) street dust and (f) soil (Boonyatumanond et al., 2006).

Phe: phenanthrene; An: anthracene; MP: methylphenanthrenes (substitution position: 3, 2, 9, 1 in the order of elution); Fluo: fluoranthene; Pyre: pyrene; BaA: benz[a]anthracene; Chry: chrysene; BbF: benzo[b] fluoranthene; BF: benzo[j]fluoranthene and/or benzo[k]fluoranthene BeP: benzo[e]pyrene; BaP: benzo[a] pyrene; Pery: perylene; IndPy: indeno[1,2,3-cd]pyrene; BghiP: benzo[ghi]perylene; Cor:coronene.

For decades, PAHs have been used as a “tracer” to distinguish the anthropogenic source and biogenic source (Yunker et al., 1995, 2002; Christensen and Karls, 1996; Cantwell et al., 2007; Fang et al., 2009). They can be categorized as anthropogenic combustion sources (i.e. traffic emissions, industrial activities, incinerators etc.) from natural combustion sources (i.e. forest fires, volcano activities, re-evaporization, etc.) by using binary diagnostic ratios (Yunker et al., 2002; Yunker and Macdonald, 2003).

Sources of PAHs can be divided into two distinct groups, including pyrogenic and petrogenic sources, based on their characteristic fingerprints. Pyrogenic sources are combustion of organic matter (coal, petroleum, and wood), anthropogenic industrial activity, or natural fires. These sources give rise to complex mixtures of PAHs characterized by a high abundance of parent PAHs and a low proportion of alkylated PAHs. Petrogenic sources are petroleum hydrocarbons from petroleum transportation, off-shore exploitation, oil spills or natural oil seeps. The composition of petroleum hydrocarbon is very complex and is characterized by a high abundance of alkylated PAHs (Yunker et al., 2002).

Because of their usefulness in source identification, the using of PAHs as an anthropogenic impact tracer in coastal sediments provides a better understanding of their land to sea transportation, and also gives an integrated picture of their transport in the marine environment (Fang et al., 2009). Because of PAHs have both natural sources and anthropogenic sources, in case of the PAH compositions of the two sources overlap, the significance of anthropogenic PAHs in the environment must be evaluated against a dynamic background of natural PAHs.

2.3.1 Diagnostic ratios of PAHs

The PAH emission profile for the specific source depends on the processes producing the PAHs (Yunker et al., 1995). During low temperature processes (e.g. wood burning), low molecular weight PAHs are usually formed, whereas high temperature processes, such as the combustion of fuels in engines, emit higher molecular weight PAH compounds (Yunker et al., 2002). At high temperatures organic compounds are cracked to reactive radicals, which react to form stable PAHs during pyrosynthesis. These PAHs are less alkylated and their molecules contain more aromatic rings than petrogenic PAHs (Hwang et al., 2003).

Most studies have been applied PAH diagnostic ratios as indicators to distinguish between the contamination arising from different sources (Yunker et al., 2002; Boonyatumanond et al., 2006; Wang et al., 2006; Li et al., 2006a; Mostafa et al., 2009; Khairy et al., 2009; Liu et al., 2009; Sun et al., 2009). Yunker et al. (2002) noted that using PAH ratios for source identification in sediments requires an understanding of the relative discrimination ability (relative thermodynamic stability) of different parent PAHs, the characteristics of different PAH sources and the changes in PAH composition between source and sediment (the relative stability of different PAH isomers and PAHs from different sources).

PAH diagnostic ratios show intrasource variability but intersource similarity (Galarneau, 2008). The search for PAH emission sources using diagnostic ratios should proceed with the determination of the ratios for each emission source present in the area investigated. The PAH ratios calculated for each hypothetical source are not definitive. Table 2.5 lists typical diagnostic ratios taken from the literature (Tobiszewski and Namieśnik, 2012).

Table 2.5 Diagnostic ratios used with their typically reported values for particular processes.

PAH ratio	Value range	Source	Reference
ΣLMW/ΣHMW	<1	Pyrogenic	Zhang et al., 2008
	>1	Petrogenic	
ΣCOMB/ΣPAHs	~1	Combustion	Ravindra et al., 2008[a]
Fluo/(Fluo + Py)	<0.5	Petrol emissions	Ravindra et al., 2008[b]
	>0.5	Diesel emissions	
An/(An + Phe)	<0.1	Petrogenic	Pies et al., 2008
	>0.1	Pyrogenic	
Fluo/(Fluo + Py)	<0.4	Petrogenic	De La Torre-Roche et al., 2009
	0.4-0.5	Fossil fuel combustion	
	>0.5	Grass, wood, coal combustion	
B[a]A/(B[a]A + Chry)	0.2-0.35	Coal combustion	Akyüz and Çabuk, 2010
	>0.35	Vehicular emissions	Yunker et al., 2002
	<0.2	Petrogenic	
	>0.35	Combustion	
B[a[P/(B[a[P + B[e]P)	~0.5	Fresh particles	Oliveira et al., 2011
	<0.5	Photolysis (ageing of particles)	
Ind/(Ind + B[g,h,i,]P)	<0.2	Petrogenic	Yunker et al., 2002
	0.2-0.5	Petroleum combustion	
	>0.5	Grass, wood and coal combustion	
Ret/(Ret + Chry)	~1	Wood burning	Yan et al., 2005
2-methylnaphthalene /Phe	<1	Combustion	Opuene et al., 2009
	2-6	Fossil fuels	
ΣMePhe/Phe	<1	Gasoline combustion	Callen et al., 2011
	>1	Diesel combustion	
B[b]F/B[k]F	2.5-2.9	Aluminium smelter emissions	
B[a]P/B[g,h,i]P	<0.6	Non-traffic emissions	Katsoyiannis et al., 2007
	>0.6	Traffic emissions	

ΣCOMB: (Flu, Py, B[a]A, Chry, B[k]F, B[b]F, B[a]P, Ind and B[g,h,i]P); ΣPAHs: sum of total non-alkylated PAHs; ΣLMW: sum of two and three-ring PAHs; ΣHMW: sum of four and five ring PAHs.

Parent PAHs with a large range of thermodynamic stability amongst isomers particularly molecular mass 178, 202 and 276 allow us to go beyond distinguishing petroleum from combustion and permit the refinement of distinguishing the combustion sources themselves. Applied B[a]A/(B[a]A+Chry) and Ind/(Ind+B[g,h,i]P) plus the less common PAHs (e.g. acephenanthrylene and pentaphene) to corroborate the identification of combustion sources would be particularly useful in urban areas where mixed combustion sources tend to predominate (Budzinski et al., 1997).

PAHs with molecular mass 178 and 202 are commonly used to distinguish between pyrogenic and petrogenic sources. Ratio values such as Phe/An (m/z 178) and Fluo/Py (m/z 202) have–been used by previous workers (Yunker et al., 2002; Boonyatumanond et al., 2006; Wang et al., 2006; Li et al., 2006a; Mostafa et al., 2009; Sun et al., 2009; Khairy et al., 2009; Liu et al., 2009). Petroleum often contains more Phe relative to An, which is a more thermodynamically stable tricyclic aromatic isomer, so that the Phe / An ratio is observed to be very high in the case of petrogenic pollution with PAHs but low in pyrolytic contamination cases. Budzinski and coworker (1997) found that sediments with Phe/An > 10.0 were mainly contaminated by petrogenic inputs and Phe/An < 10.0 was typical of pyrolytic sources. In addition to the Phe/An ratio, Fluo/Py ratio also indicated the origin of PAHs. Sicre and coworker (1987) found that a Fluo/Py < 1.00 was attributed to petrogenic sources and values greater than 1.00 were obviously related to a pyrolytic origin.

In remote areas the main source of PAHs in sediments is atmospheric deposition followed by sedimentation (Tsapakis et al., 2003). The diagnostic ratios are therefore similar to those reflecting biomass burning, particle ageing and atmospheric PAH background ratios.

Fang et al. (2006) compared several diagnostic ratios for assessing the pyrogenic and petrogenic group of PAHs in sediments. The Fluo/(Fluo+Py) ratio was found to be a poor indicator of pyrogenic and petrogenic activities, whereas B[a]A/(B[a]A+Chry) was a good indicator of pyrogenic pollution emission sources. The usefulness of PAH diagnostic ratios for source identification in southwest Taiwan sediments was also assessed on the basis of the correlations of each ratio with the sum of petrogenic or pyrogenic PAHs (Jiang et al., 2009). The An/(An +Phe) ratio was useful for identifying petrogenic sources, whereas Fluo/(Fluo+Py), B[a]A/(B[a]A+Chry) and Ind/Ind+B [g,h,i]P were better for identifying pyrogenic sources.

Wagener et al. (2010) identified biomass burning and petroleum combustion activities as the main sources of PAHs in tropical bay sediments. However, they question the sole use of diagnostic ratios for source identification in tropical areas, owing to the rapid weathering of petrogenic hydrocarbons there.

PAHs originating from asphalt pavements shift the ratios towards pyrogenic regions (Arens and Depree, 2010). The PAH content in coal tar is extremely high, as much as 10%, so even minimal contamination of sediments with pavement material may lead to a significant input of PAHs to the aquatic environment, especially in urban areas (Yang et al., 2010).

The characteristics of PAH patterns in the coastal sediments are subject to different emission patterns from various sources, and thus a single ratio may not be enough to identify sources. Instead of using a single ratio, the combinations of two or more indicators provide more information for source identifications (Khairy et al., 2009; Mostafa et al. 2009; Sun et al., 2009; Yan et al., 2009; Sojinu et al., 2010). Liu and co-worker (2010) have been applied the binary diagnostic ratio for investigation of PAHs contamination in urban soil which correlated with the Beijing’s urbanization history. It can be obviously discriminated the possible sources from different land used in study area as shown in Figure 2.6.

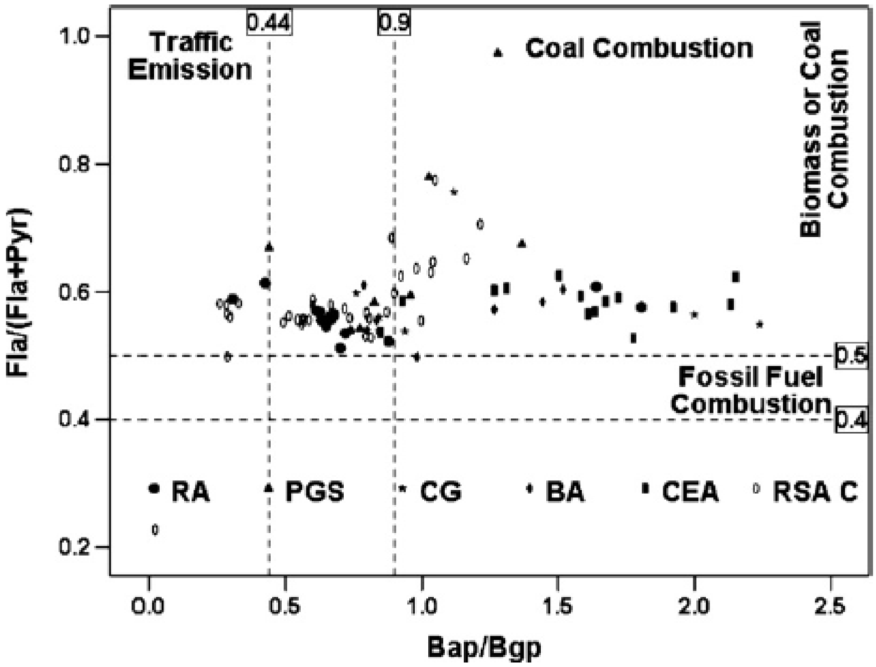


Figure 2.6 Plot of PAH binary diagnostic ratios in different land uses urban soils of Beijing (Liu et al., 2010).

The goal of source apportionment is to determine the percent contribution of different PAH sources. The using of diagnostic ratios, cluster analysis and PCA can provide the reliability major sources of sedimentary PAHs in the Phang Nga coastal sediments which should be a valuable reference data set for environment managers.

2.3.2 Statistical treatment

While diagnostic ratios of PAHs have been widely applied to identify sources in various environments, their use is limited due to a lack of reliability. More sophisticated statistical approaches have been demonstrated, including cluster analysis and PCA, which can provide information on source contributions, has been performed to identity and apportion PAH sources in the soil, and sediment in many cities (Li et al., 2006b; Zuo et al., 2007).

2.3.2.1 Principal Components Analysis (PCA)

PCA is a multivariate statistical technique that can be used to simplify large data sets and convert data into a graphical form, allowing similarities and differences between data sets to be visualized more readily (Simpson et al., 1996). PCA has been applied to identify PAH sources in other studies as well (Yim et al., 2005; Xu et al., 2007; Liu et al., 2009; Men et al., 2009).

In PCA, all variables are expressed in standardized form with a mean of 0 and a standard deviation of 1. The total variance therefore equals the total number of variables, and the variance of each factor expressed as a fraction of the total variance is referred to as the eigenvalue. If a factor has a low eigenvalue, then it is contributing little to the explanation of variances in the variables and may be ignored. PCA seeks a linear combination of variables such that the maximum variance is extracted from the variables. It then removes this variance and seeks a second linear combination that explains the maximum proportion of the remaining variance, and so on. This is called the principal axis method and results in orthogonal (uncorrelated) factors. Thus, the largest combination, accounting for most of the variance, becomes principal component 1 (PC1), the second largest accounts for the next largest amount of variances and becomes principal component 2 (PC2), and so on.

In general, the first component (*P1*) for observed variables *X1, X2, ………, Xp* can be expressed as:

$$P_1 = a_{(1)1} X_1 + a_{(1)2} X_2 + \dots\dots + a_{(1)p} X_p \qquad (3\text{-}1)$$

Where the $a_{(1)1}, a_{(1)2}, \dots\dots, a_{(1)p}$ are the weights chosen to maximize the ratio of the variance of *P1* to the total variation, subject to the constraint that

$$\sum_{i=1}^{p} a_{(1)i}^2 = a_{(1)}^t a_{(1)} = 1 \qquad (3\text{-}2)$$

The second principal component (*P2*) is the combination of the observed variables, which is uncorrelated with the first linear combination and which accounts for the maximum amount of the remaining total variance not already accounted for by *P1*. Assume that the data set has *n* samples for *p* variables. The basic (*n x p*) data matrix can be written as:

$$\underset{(n\times p)}{X} = \begin{bmatrix} X_{11} & X_{12} & \dots & \dots & X_{1p} \\ X_{21} & X_{22} & \dots & \dots & X_{2p} \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ X_{n1} & X_{n2} & \dots & \dots & X_{np} \end{bmatrix} \qquad (3\text{-}3)$$

Where *Xij* is the value of variable *j* obtained for sample *i*. When the matrix *X* is used, *P* can be rewritten as:

$$P = (X - M)A \qquad (3\text{-}4)$$

Where *M* is the mean matrix given by:

$$\underset{(n\times p)}{M} = \begin{bmatrix} \overline{X_1} & \overline{X_2} & \dots & \dots & \overline{X_p} \\ \overline{X_1} & \overline{X_2} & \dots & \dots & \overline{X_p} \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \overline{X_1} & \overline{X_2} & \dots & \dots & \overline{X_p} \end{bmatrix} \qquad (3\text{-}5)$$

Where Equation 3-5 is the mean for variable *j*.

$$\overline{X_j} = \left(\frac{1}{n}\right)\sum_{i=1}^{n} X_{ij} \qquad (3\text{-}6)$$

The matrix of standardised loadings, A, is a (p x p) matrix such that $A^T A = I$. The scores matrix, P, is a (n x p) matrix such that $P^T P$ is a diagonal matrix. Equation 3-3 becomes

$$X = M + PA^T \qquad (3\text{-}7)$$

2.3.2.2 Hierarchical Cluster Analysis (HCA)

HCA can be a suitable statistical tool for identification the homogeneous groups of individual PAHs (Liu et al., 2009). HCA can distinguish the individual PAHs into a few groups which should be the representative of various sources of PAHs in the Andaman sea sediments such as biomass burning group, petroleum combustion group or diesel emission group.

In contrast to PCA, cluster analysis does not reduce the number of characters, but stepwise reduces the number of objects by placing them into groups. An agglomerative clustering method starts with as many clusters as there are objects (each cluster thus contains a single object), and then sequentially joins objects (or clusters), on the basis of their similarity, to form new clusters. This process continues until one big cluster is obtained that contains all objects. The result of this process is usually depicted as a dendrogram, in which the sequential union of clusters, together with the similarity value leading to this union, is depicted. A dendrogram, therefore, does not define one partitioning of the data set, but contains many different classifications. A particular classification is obtained by “cutting” the dendrogram at some optimal value (defined relative to the dendrogram). In order to interpret the pattern(s) revealed by the cluster analysis, it is studied for its relation with several characteristics of the objects, including characteristics that were not part of the data set proper, so-called label information, e.g. epidemic sites of origin of strains, dates of sampling, etc.

After selecting the hierarchical cluster methods, it is important to select the clustering algorithm (i.e. the rules which govern between which point distances are measured to determine cluster membership). The examples of algorithms are listed such as,

1) Average linkage cluster is defined as the dissimilarity between clusters and calculated using cluster average valves. The most common method to calculate an average is UPGMA (Un-weight Pair-Groups Method Average).

2) Complete linkage cluster is defined as the dissimilarity between 2 groups is equal to the greatest dissimilarity between a member of cluster *i* and a member of cluster *j*. This method tends to produce very tight clusters of similar cases.

3) Single linkage cluster is defined as the dissimilarity between 2 clusters is the minimum dissimilarity between members of two clusters. This method has been widely applied in numerical taxonomy.

4) Within groups cluster is similar to UPGMA except cluster is fused so that within cluster variances is minimized. This tends to produce tighter cluster than the UPGMA method.

5) Ward's method is calculated the total sum of squared deviations from the mean of a cluster. The criterion for fusion is that it should produce the smallest possible increase in the error sum of squares.

2.4 Environmental risk assessment

To conduct an environmental risk assessment for evaluation the possibility of occurrence of adverse ecological effects to benthic species due to the exposure to PAHs concentrated in the sediments, the various types of SQGs have been applied to assess the aquatic sediment with a ranking of low to high impact values (Long et al., 1995, 1998; Swartz, 1999; Xu et al., 2007; Mostafa et al., 2009). Recently, many researchers have compared SQGs and found that in many cases there is a large degree of similarity that allows for the development of "consensus" guidelines. Swartz (1999) has developed consensus guidelines for the sum of PAHs, since they almost always occur as mixtures. These guidelines were the geometric means of guidelines, such as ERLs, TELs, SLCs, ERMs, and PELs (Table 2.6). It is also useful to determine the magnitude of exceedances of multiple SQGs by using a hazard quotient approach (Long et al. 1998).

Table 2.6 Sediment quality guideline for PAHs in coastal sediment (ng g^{-1})

PAHs	NOAA TEL marine [a]	TEL [b]	ERL [b]	SLC [b]	NOAA PEL marine [a]	PEL [b]	ERM [b]
Phe	86.68	90	240	270	86.68	540	1500
An	46.85	50	90	160	543.53	240	1100
LMW PAHs	311.7				1442		
Fluo	112.82	110	600	640	1493.54	1490	5100
Pyr	152.66	150	660	660	1397.6	1400	2600
B[a]A	74.83	70	260	260	692.53	690	1600
Chry	107.77	110	380	380	845.98	850	2800
B[b]F		70	320	320		710	1880
B[k]F		60	280	280		610	1620
B[e]P							
B[a]P	88.81	90	430	400	763.22	760	1600
Ind							
D[a,h]A	62.2		63.4		134.61		260
B[g,h,i]P							
HMW PAHs	655.34		1700		6676.14		9600
Total PAHs	1684.6	870	3500	4090	16770.4	8040	23580

CHAPTER III

MATETIALS AND METHODS

There are 3 main experimental processes in this study consisting of sample collection, PAHs determination, and data analysis/interpretation as shown in Table 3.1. For sample collection, it consists of the criteria used for choosing the study area, sampling locations and sampling procedures. Then, PAHs analysis was carried out starting from sample pretreatment, PAHs extraction, PAHs clean-up, PAHs qualification and quantification using GC-MS and finally checking the method's reliable using QA/QC process. Finally, data analysis was conducted using various types of interpretation and statistical techniques which consist of GIS for spatial distribution, PAHs diagnostic ratios, source fingerprint, HCA, PCA and sediment quality guidelines (SQGs) to apportion the potential source, transport and fate of anthropogenic PAHs and risk assessment in the study area.

Table 3.1 Overall study procedures.

Sample collection	PAHs determination	Data analysis/interpretation
1) Criteria for choosing the study area 2) Sampling locations 3) Sampling procedures - Coastal sediment - Coastal soil - Aerosol	1) Sample pretreatment - Freeze drying and sieving - CHN analyzer 2) PAHs extraction - Sohxlet extraction 3) PAHs clean-up - Column chromatography 4) PAHs qualification and quantification - GC-MS 5) QC/QA	1) GIS for spatial distribution pattern 2) PAHs diagnostic ratios 3) PAHs source fingerprint 4) HCA 5) PCA 6) SQGs

3.1 Criteria for choosing the study area

3.1.1 Geological setting

Located on the east of the Andaman Sea, the Phang Nga coastal zone, Phang Nga Province, Thailand was chosen as a study area. It covers approximately 1,000 km^2 between Thup Lamu and Koh Phra Thong. This coastal area is dominated by rocky cliffs altering with sandy lowlands and pocket beaches. The region is characterized as tropical climate zone with seasonal heavy rains during southwest monsoon from May to September while the northeast monsoon dominates during December to February (Khokiattiwong et al., 1991). The influence of storms and typhoons on this part of Thailand's coastline is low (Jankaew et al., 2008).

Along the coastal marine bottoms of Phang Nga Province, the local and northern rivers and tidal channels are likely a natural source of sediment, but sediment loading is increased by land and offshore tin mining started in 1970. The Andaman marine current is generally controlled by the tropical monsoonal regime and by coastal morphology, flowing to the south and southwest from June to February caused the loading of sediment from the coast. Most parts of the suspension river sediment and the re-suspension by waves and storms during the southwest monsoon season should be dispersed far away at the Andaman continental shelf. Nevertheless, a large amount of sediment, after trespassing the rocky shoal line through the numerous submerged channels is trapped just after in a relatively quiet zone off bounded by the open sea Andaman current (Di Geronimo et al., 2009).

3.1.2 Human activities

The rapid development of Thailand's Andaman Coast over a few decades has coincided with a strong increase in the anthropogenic impacts to the coastal sediment in this area. Like most tourism places, tourism has become the largest and most lucrative industry in the Khao Lak, for example, attracting 321,938 visitors in 2004 when the destination was at the height of its popularity (TAT, 2004). Other fundamental activities for local livelihoods include rubber, fruit and palm oil plantations, construction, and fishing. Tourism development has steadily expanded to Bang Niang in 1999 and then stretched further northward to Pakarang Cape, Pakweep beach and Bang Sak beach. The classification of different types of land use in Phang Nga coastal shows in Figure 3.1. The intensive human activities are in the Khao Lak area and expand along the main highway route.

Moreover, there are 2 ports for daily boat to the Similan Island and fishery community at Thup Lamu and Nam Khem villages. The Phang Nga Naval Base is also located in the Thup Lamu area. The shipping activities are crowed for logistic, fishery and tourism industries (Figure 3.2).

Accelerated by exceptionally booming tourism, the number of vehicles tends to increase along with the increasing number of the visitors. The main highway route is along the shoreline of Phang Nga coastal and the sub-road is far from shoreline only a few hundred meters (Figure 3.3). Thus, the street run-off may be one of the predominant sources of the accumulation of anthropogenic PAHs in the coastal area particularly during the rainy season.

In addition, this area was heavily affected by the 2004 Indian Ocean tsunami which inundated the coastal plain from a few hundred meters up to more than one kilometer inland. The tsunami run-up height at the maximum inundation limit varied from < 3 m at Kho Khao Island to almost 10 m at the Nam Khem and the Pakarang Cape (Szczucińnski, 2012). The tsunami wave height was reaching over 15 m at the Nam Khem (Tsuji et al., 2006) and the Pakarang Cape (Siripong, 2006). During the Tsunami backwash, the anthropogenic PAHs are expected to be fast and widely transported from the potential sources on land and deposited into the near-shore seabed as well.

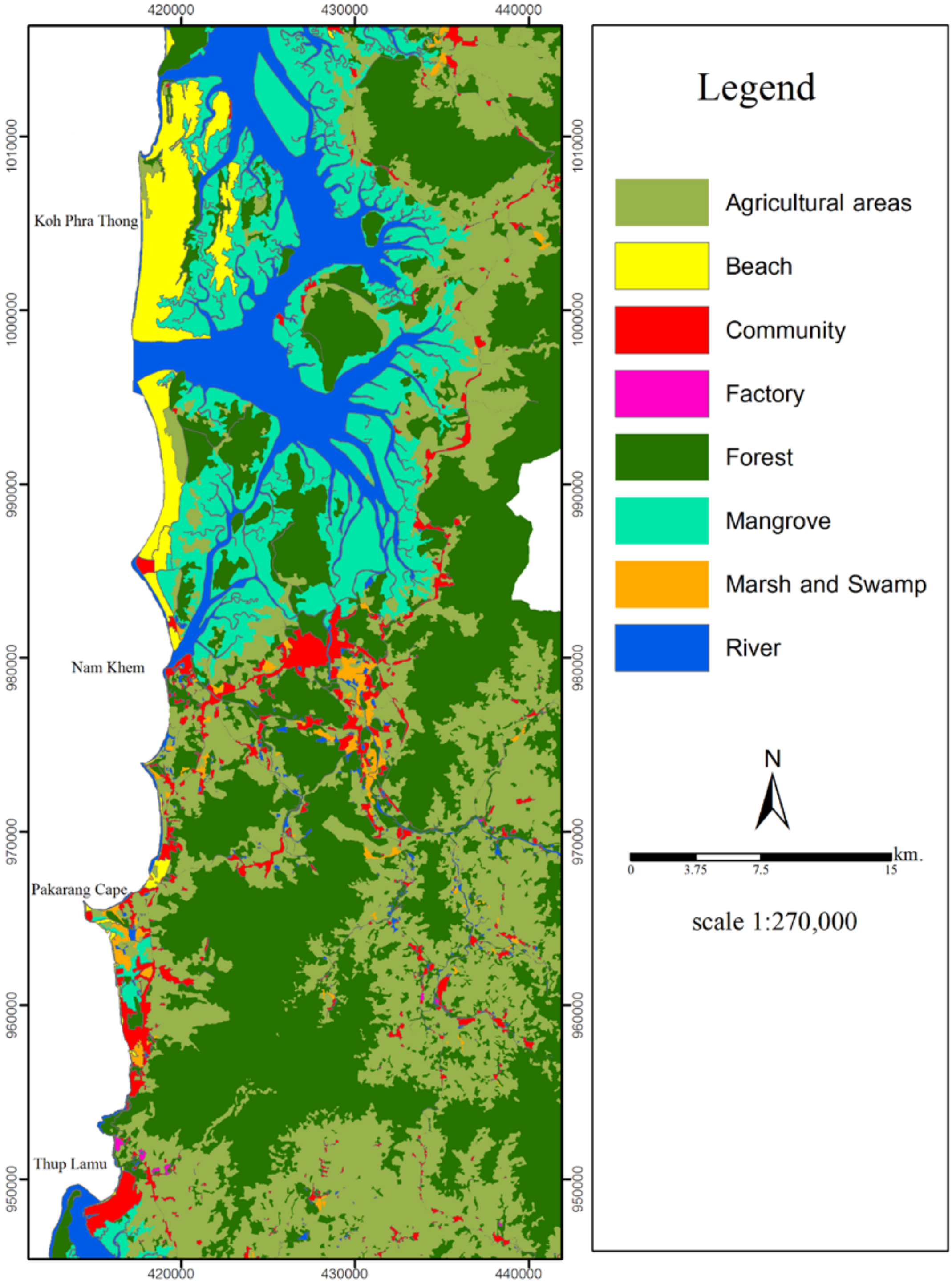


Figure 3.1 The land use classification of the Phang Nga coastal area.

http://www.ldd.go.th/gisweb/landuse/main_landuse.html

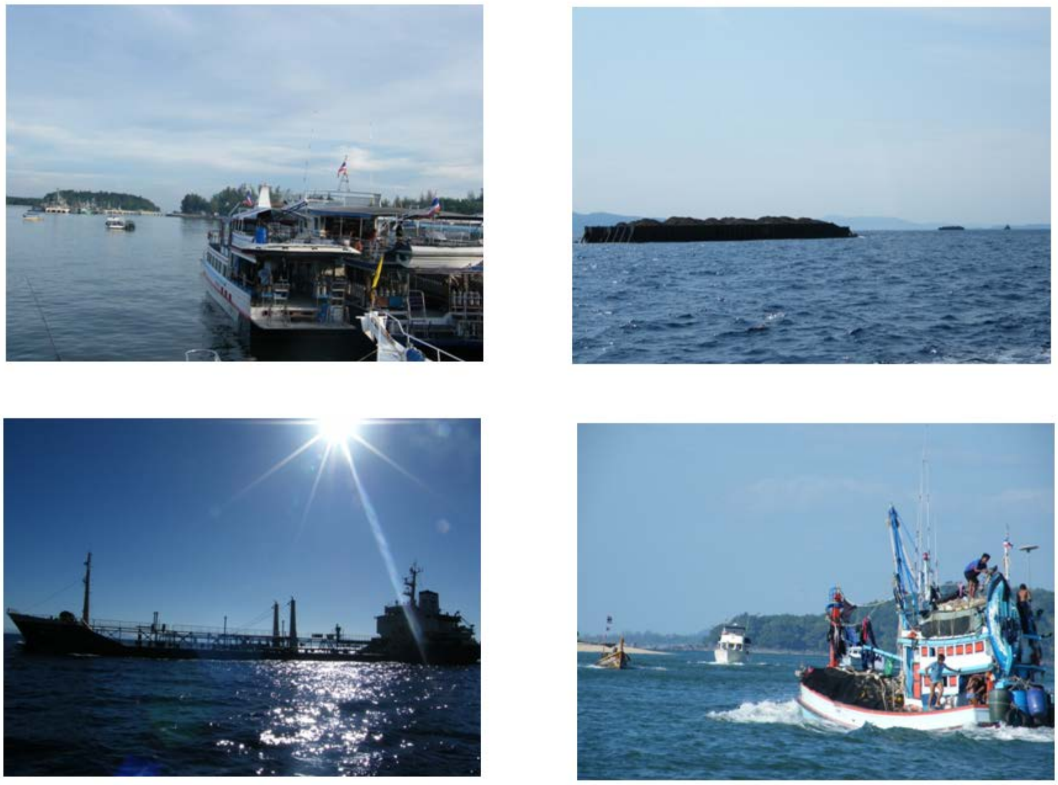


Figure 3.2 The intensive shipping activities in the study area.

Given the above-mentioned facts, the Phang Nga coastal zone was selected as a study site to identify the accumulation of anthropogenic PAHs in the coastal sediment and further describe the potential ecological impact of contaminants. This knowledge will help to improve ability to design effective management and remediation strategies for degraded coastal ecosystems.

All of samples including surface sediments and soil were collected in the study area covering approximately 1,000 km^2 (east-west extension: 25 km, north-south extension: 40 km) as shown in Figure 3.3.

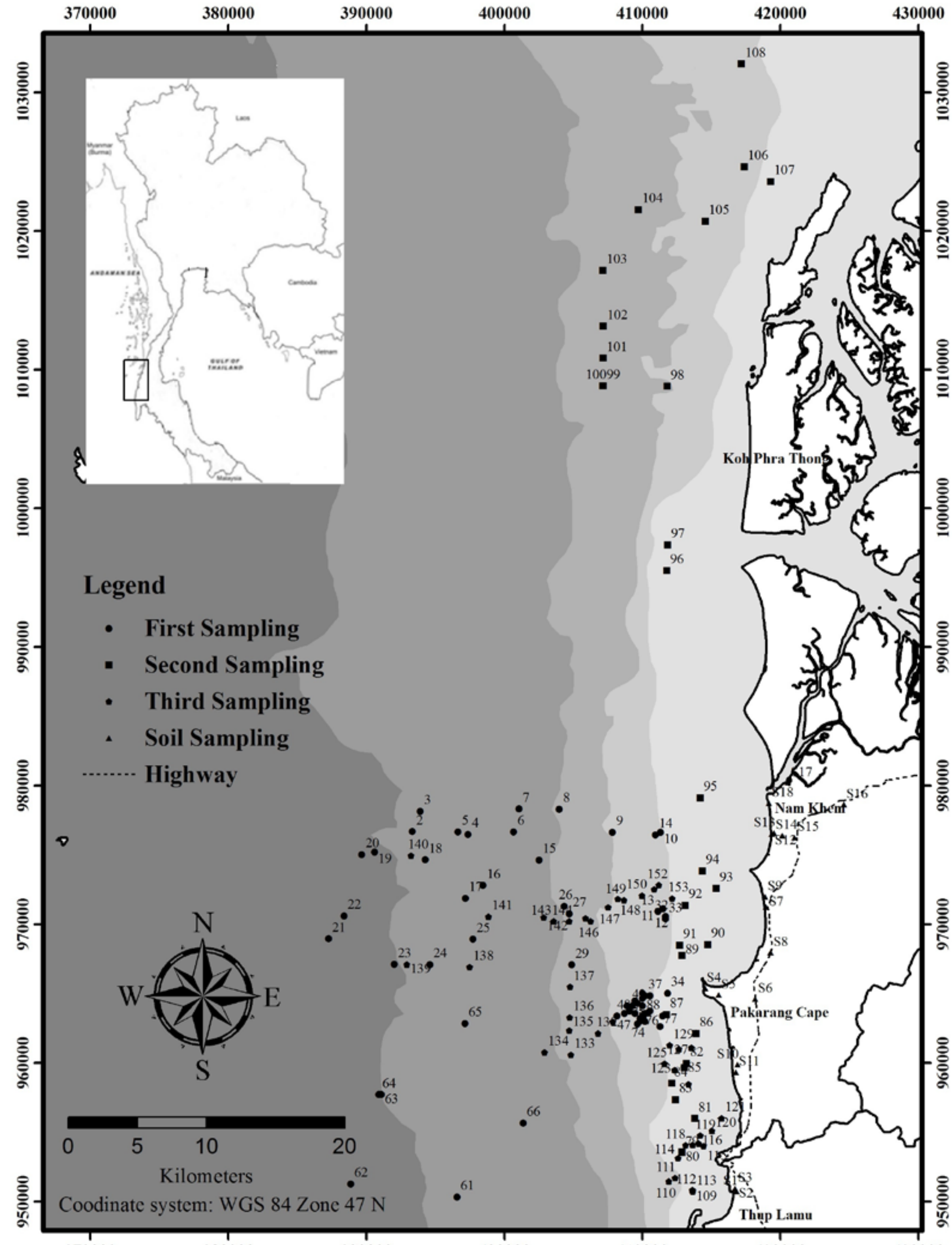


Figure 3.3 Sampling locations of coastal soil and sediment samples in Phang Nga coastal area.

3.2 Sampling locations

3.2.1 Coastal sediment

The 145 of coastal sediment samples were collected in December 2007, 2008 and March 2010, respectively. The sampling locations are shown in Table 3.2.

3.2.2 Coastal Soil

The 18 of coastal soil samples were collected during 18-22 July 2009. The sampling locations are shown in Table 3.3.

3.2.3 Aerosol

The 8 of ship-board aerosol samples were collected during 18-24 March 2008.

Sample information of coastal sediments and soils samples are shown in Table 3.4.

Table 3.2 Sampling locations of coastal sediment samples collected in Phang Nga coastal area (UTM system).

Station	Date	Location (UTM)		Station	Date	Location (UTM)	
		X	Y			X	Y
2	1/12/2007	393345	976672	40	5/12/2007	409446	964472
3	1/12/2007	393899	978145	41	5/12/2007	409629	964287
4	1/12/2007	397377	976478	42	5/12/2007	409995	964102
5	1/12/2007	396644	976664	43	5/12/2007	409262	964104
6	1/12/2007	400676	976654	44	5/12/2007	408895	964105
7	1/12/2007	401047	978311	45	5/12/2007	409078	963736
8	1/12/2007	403979	978304	46	5/12/2007	409444	963551
9	1/12/2007	407823	976637	47	5/12/2007	408711	963552
10	1/12/2007	411305	976629	48	5/12/2007	408160	963369
11	2/12/2007	411110	970918	49	7/12/2007	388299	940015
12	2/12/2007	411110	970918	50	7/12/2007	389595	944619
13	2/12/2007	411110	970918	51	7/12/2007	389046	944989
14	2/12/2007	410939	976446	52	7/12/2007	389047	945357
15	2/12/2007	402504	974622	53	7/12/2007	387030	945915
16	2/12/2007	398467	972789	55	7/12/2007	391618	946640
17	2/12/2007	397182	971871	56	7/12/2007	397482	944783
18	2/12/2007	394256	974643	58	7/12/2007	397665	944783
19	2/12/2007	390592	975205	57	7/12/2007	398211	942939
20	2/12/2007	389675	975023	61	7/12/2007	396579	950313
21	3/12/2007	387276	968949	62	7/12/2007	388879	951254
22	3/12/2007	388380	970604	63	7/12/2007	391096	957698
23	3/12/2007	392037	967093	64	7/12/2007	390913	957698
24	3/12/2007	394604	967087	65	7/12/2007	397159	962842
25	3/12/2007	397724	968922	66	7/12/2007	401359	955646
26	3/12/2007	404329	971301	68	8/12/2007	410371	963579
27	3/12/2007	404694	970748	69	8/12/2007	410544	963733
29	3/12/2007	404869	967062	70	8/12/2007	410177	963549
31	5/12/2007	411477	971101	71	8/12/2007	409994	963365
32	5/12/2007	411659	970548	72	8/12/2007	409810	963181
33	5/12/2007	411659	970364	73	8/12/2007	410176	962996
34	5/12/2007	411830	965020	74	8/12/2007	409810	962997
35	5/12/2007	410547	964838	75	8/12/2007	409626	962813
36	5/12/2007	409997	965024	76	8/12/2007	411460	963362
37	5/12/2007	410180	964839	77	8/12/2007	411275	962625
39	5/12/2007	409996	964655	78	8/12/2007	409993	963181

Table 3.2 Sampling locations of coastal sediment samples collected in Phang Nga coastal area (cont.).

Station	Date	Location (UTM)		Station	Date	Location (UTM)	
		X	Y			X	Y
79	6/12/2008	412850	953523	117	3/3/2010	413651	954064
80	6/12/2008	412864	953576	118	3/3/2010	413126	954037
81	6/12/2008	413787	955970	119	3/3/2010	414180	954723
82	6/12/2008	413183	959964	120	3/3/2010	415045	955057
83	6/12/2008	412383	957355	121	3/3/2010	415723	955991
84	6/12/2008	412110	958522	122	3/3/2010	413343	958427
85	6/12/2008	413029	959657	123	3/3/2010	412337	959472
86	6/12/2008	413890	962112	124	3/3/2010	413011	959651
87	6/12/2008	411723	963468	125	3/3/2010	411623	959914
88	6/12/2008	410021	963367	126	3/3/2010	412629	960995
89	6/12/2008	412850	967733	127	3/3/2010	413537	961063
90	6/12/2008	414719	968540	128	3/3/2010	413879	962129
91	6/12/2008	412691	968482	129	3/3/2010	411961	961263
92	6/12/2008	413099	971358	130	3/3/2010	407848	962948
93	6/12/2008	415340	972581	131	4/3/2010	407848	962948
94	6/12/2008	414340	973841	132	4/3/2010	406783	962107
95	6/12/2008	414184	979122	133	4/3/2010	404832	960570
96	10/12/2008	411763	995514	134	4/3/2010	402913	960746
97	10/12/2008	411810	997362	135	4/3/2010	404691	962301
98	10/12/2008	411790	1008809	136	4/3/2010	404741	963265
99	10/12/2008	407140	1008837	137	4/3/2010	404770	965459
100	10/12/2008	407137	1008830	138	4/3/2010	397489	966905
101	10/12/2008	407146	1010830	139	4/3/2010	392922	967066
102	10/12/2008	407157	1013143	140	4/3/2010	393229	974936
103	10/12/2008	407134	1017177	141	4/3/2010	398858	970534
104	10/12/2008	409709	1021557	142	4/3/2010	402840	970454
105	10/12/2008	414540	1020705	143	5/3/2010	403585	970193
106	10/12/2008	417366	1024649	144	5/3/2010	404689	970183
107	10/12/2008	419267	1023576	145	5/3/2010	405888	970401
108	10/12/2008	417167	1032059	146	5/3/2010	406236	970194
109	3/3/2010	413652	950782	147	5/3/2010	407527	971183
110	3/3/2010	411919	951418	148	5/3/2010	408212	971813
111	3/3/2010	412365	951663	149	5/3/2010	408658	971718
112	3/3/2010	413600	950782	150	5/3/2010	409971	972053
113	3/3/2010	413652	950700	151	5/3/2010	410843	972497
114	3/3/2010	412564	953114	152	5/3/2010	411195	972796
115	3/3/2010	414423	953989	153	5/3/2010	412156	971847
116	3/3/2010	414061	954159				

Table 3.3 Sampling locations of coastal soil samples collected in Phang Nga coastal area (UTM system).

Station	Date	Location (UTM)		Station	Date	Location (UTM)	
		X	Y			X	Y
S1	18/7/2009	416780	950720	S10	20/7/2009	416883	959852
S2	18/7/2009	416783	950767	S11	20/7/2009	416764	959323
S3	18/7/2009	416710	950928	S12	20/7/2009	419381	976499
S4	19/7/2009	414557	965353	S13	20/7/2009	419529	976547
S5	19/7/2009	415513	964886	S14	20/7/2009	420128	976390
S6	19/7/2009	418160	964593	S15	20/7/2009	420995	976231
S7	19/7/2009	418952	971228	S16	20/7/2009	424569	978616
S8	19/7/2009	419280	967944	S17	20/7/2009	420518	980185
S9	19/7/2009	418871	971963	S18	20/7/2009	419160	978725

Table 3.4 Sample information of coastal sediments and soils samples.

Sampling code	Sampling date	Sampling description
Soil		
S1	July-18-2009	Canal bank
S2	July-18-2009	Tsunami deposit layer
S3	July-18-2009	Rubber Plantation
S4	July-19-2009	Beach
S5	July-19-2009	Shrimp pond
S6	July-19-2009	Road side
S7	July-19-2009	Tsunami deposit layer
S8	July-19-2009	Rubber Plantation
S9	July-19-2009	Tsunami deposit layer
S10	July-20-2009	Canal bank
S11	July-20-2009	Canal bank
S12	July-20-2009	Tsunami deposit layer
S13	July-20-2009	Pond
S14	July-20-2009	Rubber Plantation
S15	July-20-2009	Palm Plantation
S16	July-20-2009	Pond
S17	July-20-2009	Nam Khem port
S18	July-20-2009	Mangrove
Sediment		
2,3,4,5,6,7,8,9,10	December-1-2007	Pakarang Cape sediment
11,12,13,14,15,16,17,18,19,20	December-2-2007	Pakarang Cape sediment
21,22,23,24,25,26,27,29	December-3-2007	Tsunami affected sediment
31,32,33,34,35,36,37,39,40,41,42,43,44,45,46,47,48	December-5-2007	Tsunami affected sediment
49,50,51,52,53,55,56,57,58,61,62,63,64,65,66	December-7-2007	Thup Lamu Sediment

Table 3.4 Sample information of coastal sediments and soils samples (cont.).

Sampling code	Sampling date	Sampling description
68,69,70,71,72,73,74,75,76,77,78	December-8-2007	Tsunami affected sediment
109,110,111,112,113,114,115,116, 117,118,119,120,121,122,123,124, 125,126,127,128,129,130	March-3-2010	Khao Lak near shore sediment
131,132,133,134,135,136,137,138, 139,140,141,142	March-4-2010	Pakarang Cape sediment
143,144,145,146,147,148,149,150, 151,152,153	March-5-2010	Pakarang Cape sediment
96,97,98,99,100,101,102,103,104, 105,106,107,108	December-6-2008	Koh Phra Thong sediment
79,80,81,82,83,84,85,86,87,88,89, 90,91,92,93,94,95	December-10-2008	Nam Khem sediment

3.3 Sampling procedures

All samples were collected along the Phang Nga coastal area, in order to investigate the distribution of 13 individual PAHs, including Phe, An, Fluo, Pyr, B[a]A, Chry, B[b]F, B[k]F, B[a]P, B[e]P, B[g,h,i]P, D[a,h]A and Ind. List of 13 PAHs compounds is shown in Table 3.5. In this study concentrated only 13 PAHs because the aliphatic fraction was taken as discard fraction. As a consequence, most of low molecular weight PAHs (Naphthalene, Acenaphthene and Fluorene) did not taken into consideration for PAHs analysis.

Table 3.5 List of 13 PAHs compounds, their abbreviation and number of rings in this study.

PAHs Compounds	Abbreviation	Number of rings
Phenanthrene	Phe	3
Anthracene	An	3
Fluoranthene	Fluo	4
Pyrene	Py	4
Benz[a]anthracene	B[a]A	4
Chrysene	Chry	4
Benzo[b]fluoranthene	B[b]F	5
Benzo[k]fluoranthene	B[k]F	5
Benzo[a]pyrene	B[a]P	5
Benzo[e]pyrene	B[e]P	5
Dibenz[a,h]anthracene	D[a,h]A	5
Indeno[1,2,3-cd]pyrene	Ind	6
Benzo[g,h,i]perylene	B[g,h,i]P	6

3.3.1 Coastal sediment

The sampling stations were selected on the basis of the basic data acquired from hydroacoustic mapping using equipment which consisted of Multi-beam, Side Scan Sonar and Boomer system to investigate the sedimentary deposition on near-shore seabed (Feldens, 2011). These supporting data provided the geophysical structure of seabed which was a promising evidence of terrestrial deposits in the study area as shown in Figure 3.4. Van Veen Grab Sampler was used to collect the 145 surface sediment samples (as shown in Figure 3.5). Sediment samples were wrapped in clean aluminum foil, placed in a glass bottle, and kept frozen at – 20 ºC.

3.3.2 Coastal soil

Soil sampling stations were selected by considering the areas which have affected by the 2004 Tsunami (Szczuciński et al., 2005). In addition, the locations of soil sampling stations were also in the transect line of the surface sediment sampling stations. They were collected during 18-22 July 2009. The surface layer was collected (about the first ten cm.) by using the clean shovel. About half kilogram of composite samples from 2 m^2 area of each station was taken following the procedure of Badin et al. (2008). They were wrapped in clean aluminum foil, placed in a glass bottle, and kept frozen at - 20ºC

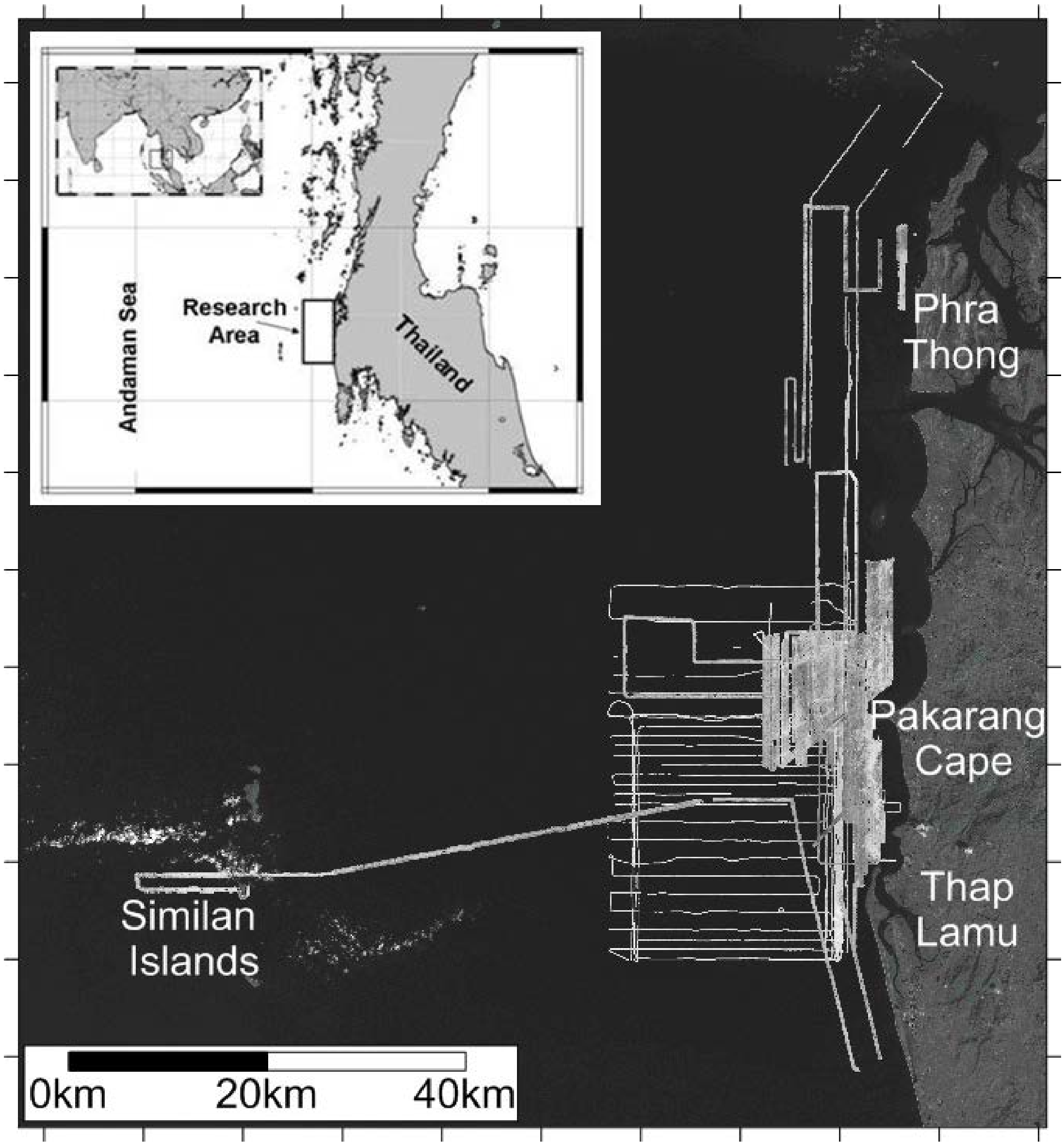


Figure 3.4 Seafloor mapping using Side Scan Sonar for selecting the surface sediment sampling locations (Felden, 2011)

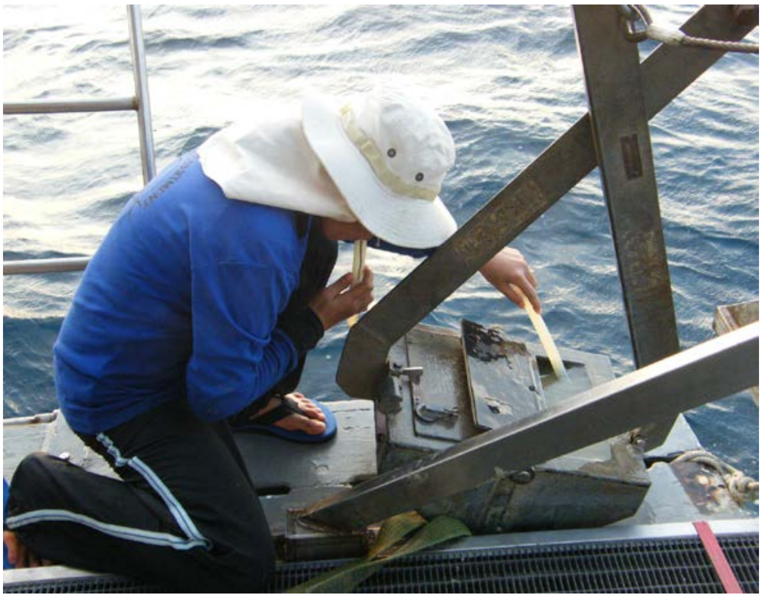


Figure 3.5 Surface sediment sampling using Van Veen grab sampler.

3.3.3 Aerosol

Ship-board aerosol samples were collected along the transect of the cruise from Phuket province to Phang Nga province (as shown in Figure 3.6). Samples were generally collected with flow rate of 1,140 – 1,698 m^3min^{-1}; with an average 1,419 m^3min^{-1} using the high volume (Peak roof inlet). The air sampler was placed windward on the uppermost deck of the ship; about 10 m above sea level as show in Figure 3.7, to minimize contamination from emissions from the ship's exhausts following the procedure of Foday et al. (2004). Aerosal (< 100 µm) was trapped on a quartz fibre filter (QFF). After sampling, the QFFs were kept in solvent rinsed aluminum foil and stored at -20 ºC until analysis.

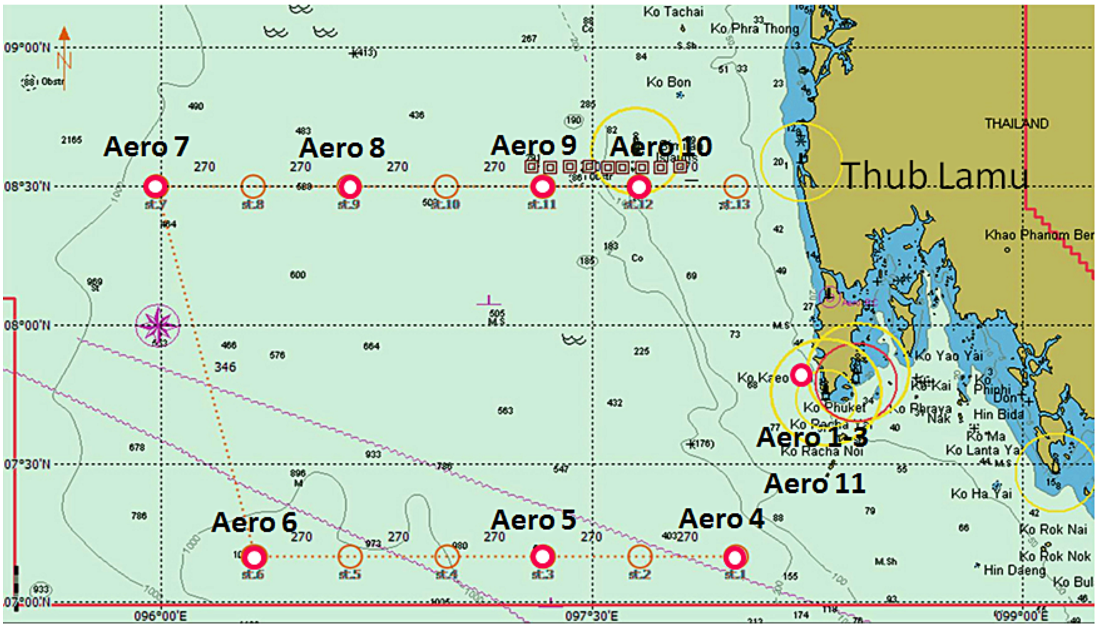


Figure 3.6 Sampling locations of ship-board aerosol collected during the cruise from Phang Nga to Phuket.

Figure 3.7 The high volume air sampler (Peak roof inlet) for collecting the ship-board aerosol.

3.4 PAHs analysis

3.4.1 Chemical

Chemical products and standards used in this study were as follows:

1) Mix standard solution of 15 native PAHs [Norwegian Standard (NS 9815: S-4008-100-T)] (Chiron AS).
2) Mix of recovery internal standard (IS) PAHs [N-7041 Trondheim, d_{12}-perylene (d_{12}-Per) and d_{10}-fluorene (d_{10}-Fl)] (Chiron AS).
3) Sediment Standard Reference Material SRM 1941b, (Organic in Marine Sediment; NIST).
4) Dichloromethane, CH_2Cl_2 (LAB-SCAN, 99.9 % HPLC grade).
5) n-Hexane, $CH_3(CH_2)_4CH_3$ (LAB-SCAN, 99.9 % HPLC grade).
6) Cyclohexane, C_6H_{12} (LAB-SCAN, 99.9 % HPLC grade).
7) Toluene, $C_6H_5CH_3$ (LAB-SCAN, 99.9 % HPLC grade).
8) Methanol: CH_3OH (LAB-SCAN, 99.9% HPLC grade).
9) Silica Gel, $SiO_2$70-230 mesh ASTM (Merck).
10) Cu powder, 0.04 mm (Riedel-deHaën, 99.5%).
11) Hydrochloric acid, HCl (Carlo Erba Reagents, 37%).

3.4.2 Sample pretreatment

Surface sediment and soil samples were freeze-dried and sieved to <0.076 mm (200 mesh) after removing stones and shell residuals, and then stored at -20 ºC until analysis.

3.4.3 Measurement of total organic carbon

An aliquot (~5 g) of each sample was treated with 10% HCl to remove inorganic carbon, and dried at 60 ºC in an oven to obtain a constant weight. An elemental analyzer (2400 Series II CHNS/O Analyzer, USA) was used to determine total organic carbon (TOC) contents.

3.4.4 PAHs extraction

Approximately 5 grams of dried samples (both of soil and surface sediment sample) was placed in a prewashed cellulose thimble and inserted into a 100 ml Soxhlet extractor. Before the extraction, dried samples were spiked with known amount of d_{10}-Fl and d_{12}-Per as internal standards. The apparatus was fitted with a 200 ml flask containing 150 ml of dichloromethane that was boiled with a heating mantle and refluxed for 8 hours with 5–6 cycles/hours (Figure 3.8). The extractant was reduced to exactly 2 ml by using rotary evaporator and then concentrated by nitrogen blow-down at ambient temperature to 1 ml. It was finally changed to hexane and purged with nitrogen again until the final volume was 2 ml prior to the clean-up process. For aerosol samples, they were no needed to use the cellulose thimble for extraction.

Figure 3.8 Sohxlet Extraction of coastal sediment samples.

3.4.5 PAHs clean-up

Fractionation process was carried out following the procedure of Gogou et al. (1997). An open column (25 cm x 1.4 cm *i.d.*) was plugged with clean glass wool. The column was filled with approximately 5 g of activated silica gel and topped with 1 cm of activated copper powder to remove sulfur (as shown in Figure 3.9). Ten milliliter of hexane was used to prewash the column and allowed to drain to bed level. The extractant was transferred quantitatively to the column. The column was eluted with 15 ml of hexane. The PAH fraction was then eluted with 15 ml of 4:6 (*v/v*) toluene:hexane into a calibrated centrifuge tube. The eluate was purged with nitrogen to almost dryness, then changed to cyclohexane and purged with nitrogen again until the final volume was 100 µl prior to GC/MS analysis. The summary of overall procedure for PAHs analysis is shown in Figure 3.10.

Figure 3.9 Fractionation process using silica gel chromatography column.

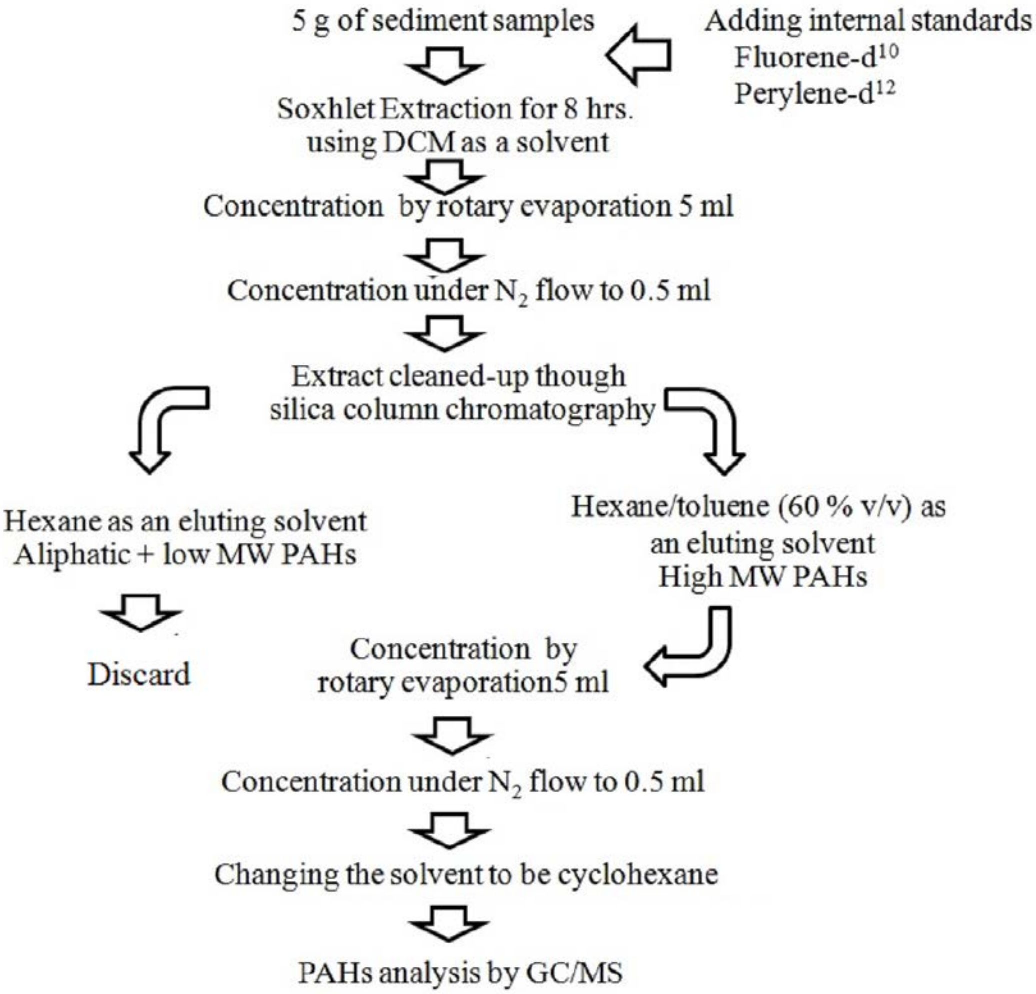


Figure 3.10 The summary of overall procedure for PAHs analysis.

3.4.6 PAHs analysis by GC/MS

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 ºC, ramped at 10 ºC min^{-1} to 300 ºC, 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 ºC. The GC-MS optimum conditions are shown in Table 3.6. The instrument was tuned daily with perfluorotributyl amine (PFTBA) introduced via the calibration gas valve. Data were collected by a ChromaTOF work station Software.

Table 3.6 Optimum conditions of GC-MS.

GC	Column type	Agilent J&W DB-5MS GC column (30 m x 0.25 mm i.d. capillary column, 0.25 µm film thickness)
	Mobile phase	99.999% He gas at flow rate 1.0 mL/min
	Injector temperature	250 ºC
	Transfer line temperature	280 ºC
	Injection mode	Splitless mode (injection volume 1 µL)
MS	Mass analyzer type	Time of flight (TOF)
	Ionization mode	Electron ionization
	Ionization energy	70 eV
	Collected ion data mode	SIM (Selected Ion Monitoring)

3.4.7 Quality assurance/quality control

Extraction thimbles and silica used for the cleanup and fractionation were pre-extracted with dichloromethane prior to extract. Blank in sampling media, trip, reagent, method, and instrument were investigated to check for interference and across contamination. Accuracy test was evaluated using the sediment SRM 1941b. Mean recovery (based on extraction of matrix-matched certified reference materials, (n=8) was investigated. The precision of the procedure, calculated as relative standard deviation on the duplicate samples, was less than 15%. Quantity analysis was calculated using relative response factors run in between each batch.

3.4.8 Quantity analysis of PAHs using Internal Standard

Assume that the detector response is linear over the entire concentration range.

$$\frac{W_{Nat}}{W_{Deut}} = \frac{A_{Nat}}{A_{Deut}} \qquad (3\text{-}1)$$

where A_{Nat} = Peak area of native PAHs in sample

A_{Deut} = Peak area of deuterated PAHs in sample

W_{Nat} = Weight of native PAHs in sample

W_{Deut} = Weight of deuterated PAHs in sample

From equation 3-1, the ratio of peak area of Native PAHs in sample and peak area of deuterated PAHs in sample is assumed to equal to the ratio of weight of native-PAHs in sample weight of native deuterated PAHs in sample.

$$C_{Nat} = \frac{A_{Nat}}{A_{Deut}} x W_{Deut} \, x \frac{1}{RRF} \, x \frac{1}{V} \qquad (3\text{-}2)$$

where C_{Nat} = Concentration of native PAHs in sample (ng/g)
A_{Nat} = Peak area of native PAHs in sample
A_{Deut} = Peak area of deuterated PAHs in sample
W_{Deut} = Weight of deuterated PAHs in sample
RRF = Relative response factor
V = Weight of sample (g)

A relative response factor (RRF) for each native PAH was determined. This is used for quantification, as the relative response between the internal standard (IS) and the native analyte should remain constant. It is a convenient method because recovery losses of the compound during extraction and analysis are assumed to match those of the IS. It is calculated using the following equation.

$$RRF = \frac{A_{Nat}}{A_{Deut}} x \frac{C_{Deut}}{C_{Nat}} \tag{3-3}$$

Where A_{Nat} = Peak area of the native PAHs in the standard
C_{Nat} = Concentration of native PAHs in the standard
A_{Deut} = Peak area of deuterated PAHs in the standard
C_{Deut} = Concentration of deuterated PAHs in the standard

The RRF used for quantifying samples are the mean of those calculated for the two quantification standards run on the same day.

$$\% \mathrm{Re}\,\mathrm{cov}\,ery = \left(\frac{(A_{Deut})_S / (A_{Deut})_{STD}}{(C_{Deut})_S / (C_{Deut})_{STD}} \right) x100\% \tag{3.4}$$

Where $(A_{Deut})_S$ = Peak area of the deuterated PAHs in the sample

$(A_{Deut})_{STD}$ = Peak area of the deuterated PAHs in the standard

$(C_{Deu})_S$ = Concentration of deuterated PAHs in the sample

$(C_{Deu})_{STD}$ = Concentration of deuterated PAHs in the standard

Recoveries of deuterated PAHs were used as an indication of the analyte losses during extraction, pre-concentration, clean-up/fractionation and blow down stages.

3.4.9 Data analysis and interpretation

Arc View Geographic Information System (GIS) software version 9.0 was used for visualizing the spatial distribution of the level of PAHs contamination in Phang Nga coastal zone. Sources of PAHs in sediment are apportioned using the combinations of several diagnostic ratios following the Tobiszewski and Namieśnik's work (2012). They were plotted to distinguish the sources of PAHs.

To obtain more clear explanation of the sources of PAH, HCA was used to group the stations by relative contents of PAH compounds in sediment samples. Distances of similarity between objects were measured as squared Euclidean distances (Fang et al., 2007). Ward's method was used for amalgamation of clusters (Savinov et al., 2000). Moreover, 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). The statistical analysis was performed using Statistical Package for Social Sciences (SPSS) software (version 16, SPSS, Inc, Chicago, IL, USA). The three dimensional plot was performed using OriginPro 8.5.0 software (OriginLab Corporation, Northampton, MA, USA).

Before performing statistical analysis using PCA and HCA, data were subjected to the logarithmic transformation (y = log(x+1)). This technique is the most common approach for transforming environmental data, as it is robust to non-normal data distribution (Field et al., 1982). The significance level, Kaiser-Meyer-Olkin (KMO) and Bartlett's test of sphericity were performed to test the adaptability of PCA (Wang et al., 2010). Data prepared for multivariate statistical analysis were arranged in the matrix, where columns correspond to PAH compositions and rows represent sampling stations. The normalized data matrix was then analyzed by PCA and HCA. To obtain more clear features, the Varimax rotation method with Kaiser Normalization was used.

3.4.10 Assessment of the adverse ecological affects due to the levels of contamination with PAHs

To conduct an environmental risk assessment for evaluation the possibility of occurrence of adverse ecological effects to benthic species due to the exposure to PAHs concentrated in the sediments, the various types of SQGs have been applied to assess the aquatic sediment with a ranking of low to high impact values such as ERLs, TELs, SLCs, ERMs, and PELs.

CHAPTER IV

RESULTS AND DISCUSSION

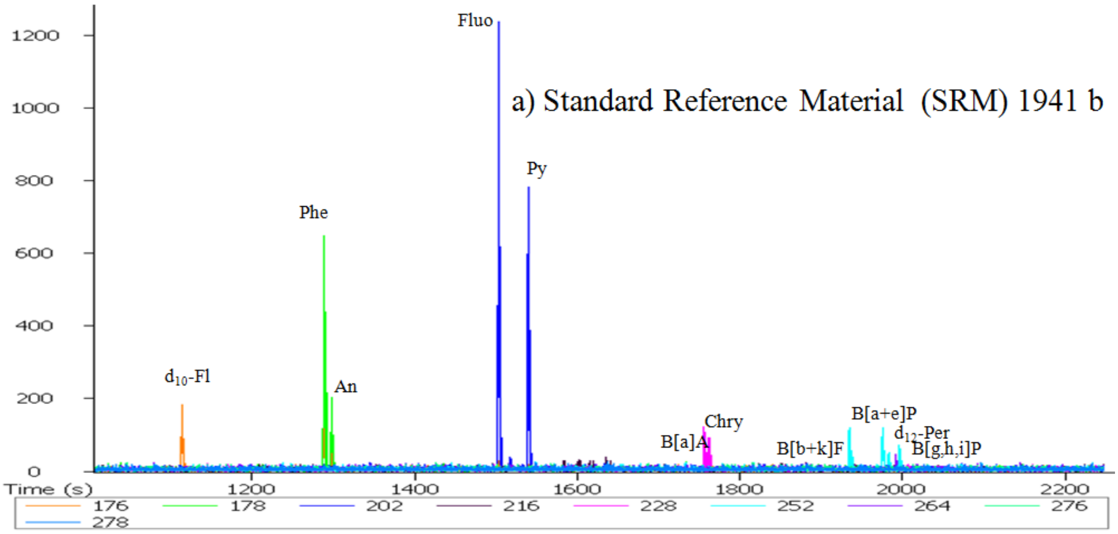
All results and discussion are divided into five main parts as follows: 1) The status of PAHs contamination; 2) Source apportionment of PAHs in Phang Nga coastal sediments; 3) Transport and distribution of PAHs in Khao Lak coastal area; 4) Assessment of an occurrence of adverse ecological effects due to the levels of contamination with PAH; and 5) Using PAHs as a chemical proxy for tracing the 2004 Tsunami. The content in each part is shown in Table 4.1 for the ease in tracking the steps of the study.

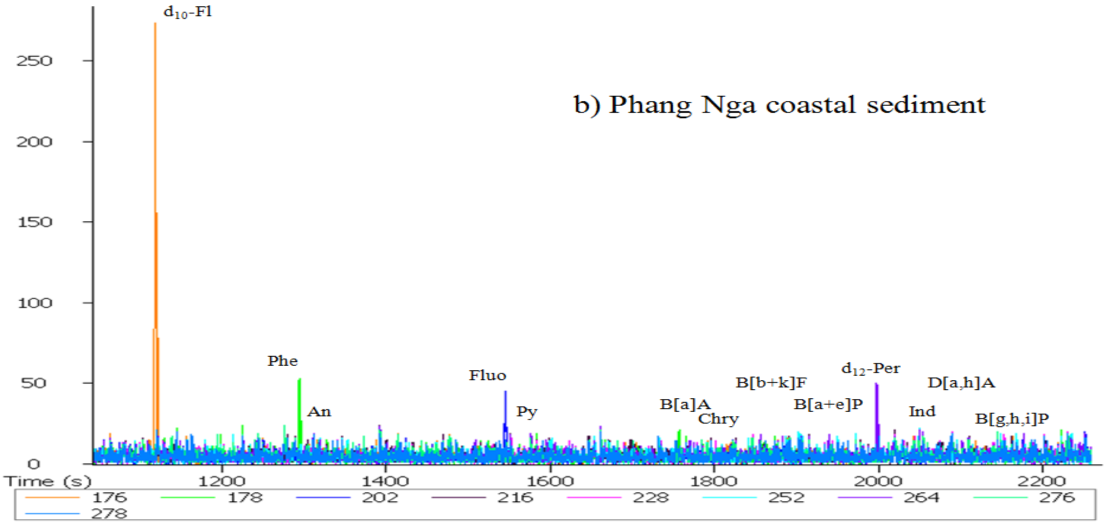
Table 4.1 Contents of the experimental results and discussion.

1) The status of PAHs contamination	
Objective To identify types and concentrations of each PAHs in aerosol, soils and sediments of Phang Nga coastal	**Methodology** - Qualitative and quantitative of PAHs analysis - Spatial Distribution - Distribution pattern of number of PAHs ring
2) Source apportionment of PAHs in Phang Nga coastal sediments	
Objective To apportion sources of PAHs in the Phang Nga coastal sediments.	**Methodology** - Diagnostic PAHs ratios - PAHs source fingerprints - HCA - PCA
3) Transport and distribution of PAHs in Khao Lak coastal area	
Objective To evaluate the fate and transport of anthropogenic PAHs in the study area.	**Methodology** - Spatial distribution - Diagnostic PAHs ratios - HCA - PCA
4) Assessment of an occurrence of adverse ecological effects due to the levels of contamination with PAH	
Objective To evaluate an occurrence of adverse ecological affects due to the levels of contamination with PAHs in the Phang Nga coastal sediments	**Methodology** - SQGs
5) Using PAHs as a chemical proxy for tracing the 2004 Tsunami	
Objective To use PAHs as a chemical proxy to indicate the 2004 Tsunami backwash	**Methodology** - Spatial distribution - Diagnostic PAHs ratios - HCA - PCA

4.1 The status of PAHs contamination

PAHs in Phang Nga coastal sediments, soils and aerosol samples were identified for both of qualitative and quantitative analysis using GC-MS technique. Selected ion monitoring chromatograms of PAHs in Standard Reference Material 1941 b, Phang Nga coastal sediment and Phang Nga coastal soil are shown in the Figure 4.1.





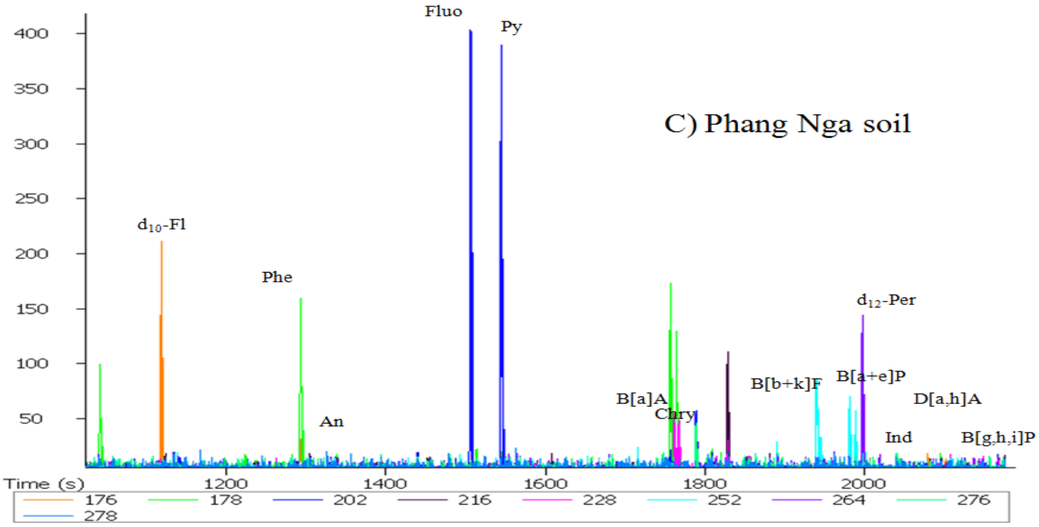


Figure 4.1 Selected ion monitoring chromatograms of PAHs in a) SRM 1941b; b) Representative Phang Nga coastal sediment and c) Representative Phang Nga coastal soil.

d_{10}-Fl, d_{10}-fluorene Phe, phenanthrene; An, anthracene; Fluo, fluoranthene; Py, pyrene; BaA, benz[a]anthracene; Chry, chrysene; B(b+K)F, benzo[b+k]fluoranthenes; B[a+e]P, benzo[a+e]pyrene; d_{12}-Per, d_{12}-perylene; Ind, indeno[1,2,3-cd]pyrene; B[g,h,I,]P, benzo[ghi]perylene; D[a,h]A, Dibenz[a,h]anthracene

4.1.1 Coastal sediment

On the basis of sediment analysis, the total concentration of PAHs (ΣPAHs) is defined as the sum of Phe, An, Fluo, Pyr, 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. The level of each PAH and ΣPAHs contamination for coastal sediments are shown in Figure 4.2. ΣPAHs in 145 of Phang Nga coastal sediments were in the range of 11.9 to 272.0 ng g^{-1} dry weight, with an average of 57.1±35.7 ng g^{-1} dry weight.

In general, ΣPAHs range from low in the offshore areas (except that off the Pakarang Cape where PAH concentrations were highest) and pristine coastal area (north of Phang Nga coastal area: Koh Phra Thong) to high in the vicinity of urban/tourist centers (Khao Lak beach) and river outflows areas. Highly contaminated sediments coincide to the near-shore areas with significant anthropogenic inputs of PAHs. Since the study area is sparsely inhabited and not industrialized, the high anthropogenic inputs could be attributed to be from the street run-off of terrestrial derived PAHs from the near-by highways.

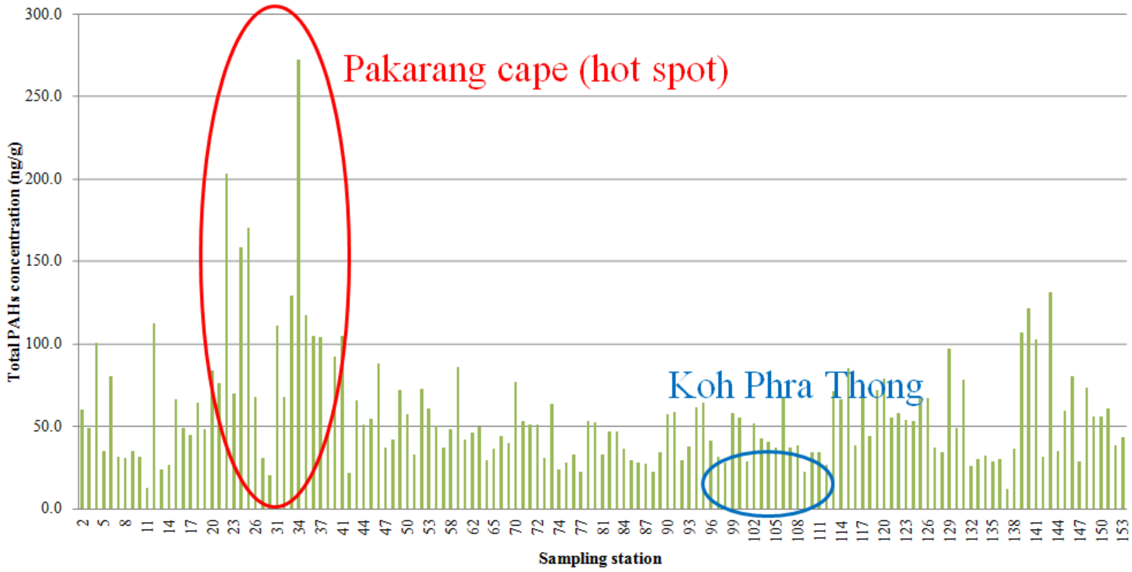


Figure 4.2 Level of PAHs concentration in Phang Nga coastal sediment.

Comparison between the quantitative across reported PAH data is difficult because of variances in the number and type of individual PAH species in each study, their sediment fraction, and analytical methods. According to Baumard et al. (1998), the level of PAH contamination can be characterized as low, moderate, high and very high when ΣPAH concentrations are in the range of 0–100, 100–1000, 1000–5000 and >5000 ng g^{-1}, respectively. PAHs values lower than 100 ng g^{-1} are indicative of low pollution area, whereas values higher than 1000 ng g^{-1} correspond to chronically pollute industrialized areas and harbors.

The PAHs concentrations detected in the Phang Nga coastal sediments are comparable with those contaminations found previously in some coastal areas and bays (Table 4.2). However, they were much lower than some coastal and harbor hot spots that are highly under an influence of human activities such as Dalian Bay, Casco

Bay and Kyeonggi Bay. On the basis of classification adopted by Baumard et al. (1998), the Phang Nga coastal sediments can be classified as low to moderate contaminated with PAHs (11.9 - 272.0 ng g^{-1}), whereas soil samples are considered to be low to high (22.0 - 2083.8 ng g^{-1}) contaminated with PAHs.

Table 4.2 Comparisons of ∑PAHs in surface sediment collected from different coastal areas and bays (ng g^{-1} dry weight).

Location	Range	Mean	Reference
Phang Nga Coastal	11.9 - 272.0	57.1	This study
Gulf of Thailand			
Coastal areas	11-1,992	506	
Offshore areas			Wattayakorn, 2005
Upper Gulf	39-95	70	
Eastern Seaboard	11-324	79	
Lower Gulf	14-67	51	
Dalian Bay, China	32.7-3558	152.08	Liu et al., 2001
Daya Bay, China	42.5-158.2	126.2	Yan et al., 2009
Kyeonggi Bay, Korea	9.1-1400	120	Kim et al., 1999
Malaysian riverine and coastal	4-924	139.5	Zakaria et al., 2002
Casco Bay, USA	16-20,748	2900	Kennicutt et al., 1999
Northwestern Black sea	52.6-269	136	Maldonado et al., 1999
Todos Santos Bay, Mexico	7.6-813	96	Macías–Zamora et al., 2000
Gulf of Aden, Yemen	2.2-604	82.4	Mostafa et al., 2009

The spatial distribution of ΣPAHs contamination in coastal sediment of Phang Nga coastal zone is shown in Figure 4.3. From the contour scale, the distinctive high concentration patterns are obviously seen in sediments offshore of the Pakarang Cape. Sediments collected from the northern section of the coastal zone (*i.e.* Koh Phra Thong) show PAH concentrations that were generally much lower than those observed in Khao Lak area. Evidently, the contamination levels are lower for the sites far from the pollution sources. On the other hand, the stations which are influenced by human activities have shown the higher concentrations of ΣPAHs.

Human activities in the study area (as mentioned in Chapter 3) supported the hypothesis that the anthropogenic PAHs originated from the intensive activities in the urban area as in Khao Lak coastal. From the Figure 4.3, the prominent feature of sediments exported from the Pakarang Cape can be observed. This evidence can be expected that the tsunami backwash may play an important role in transporting anthropogenic PAHs to the nearby coastal area far from the shoreline up to approximately 25 km. The intensive discussion will be done later in the next Section.

When arrange the top 20 highest ΣPAHs contaminated stations in coastal sediments, the result is shown in Figure 4.4. All of sampling station are in front of the Pakarang Cape, thus it should be transported from land to sea during the 2004 Tsunami event. The source apportionment and land to sea transportation will be investigated in the next Section.

Table 4.3 Classification of PAH contamination levels in coastal sediment of Phang Nga coastal zone.

Sampling code	Sampling description
4,12,22,24,25,31,33,34,35,36,37,40,41,46,57, 129, 139, 140, 141, 143	Hot spot (top 20 highest PAHs contaminated stations)
96,97,98,99,100,101,102,103,104,105,106,107, 108	Background (Koh Phra Tong sediment)
79,80,81,82,83,84,85,86,87,88,89,90,91,92,93,94 95	Mixed sources (Nam Khem sediment)

In Table 4.3, the sampling stations are categorized into 3 groups to simplify the distribution patterns of number of rings PAHs in coastal sediments. They consist of the hot spot stations (top 20 highest PAHs contaminated stations), background (Koh Phra Thong) and mixed source (Nam Khem). In Figure 4.5, the result provides that the different of distribution pattern are obviously seen between the hot spot and background group.

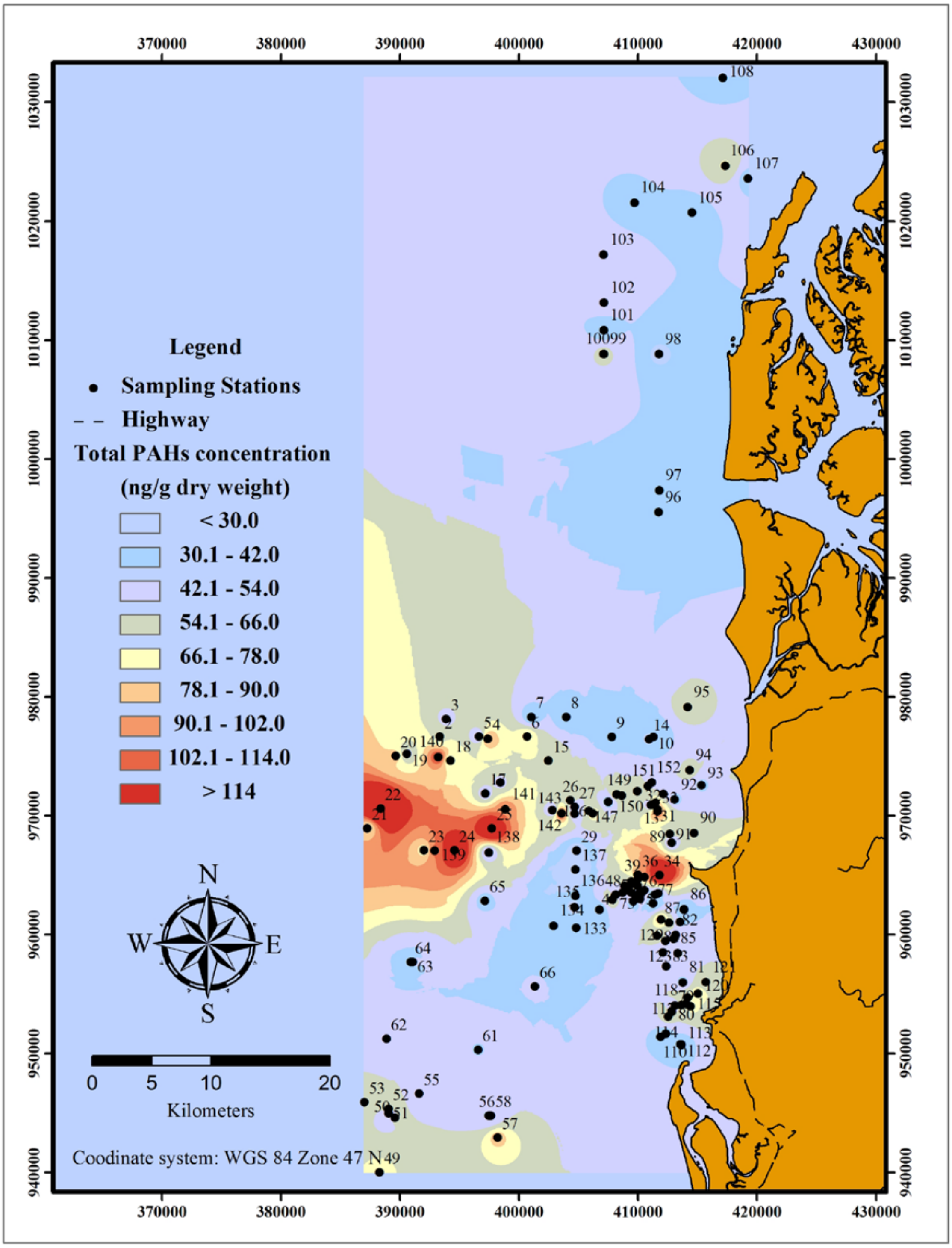


Figure 4.3 The spatial distribution of PAHs contamination in coastal sediments of Phang Nga coastal zone.

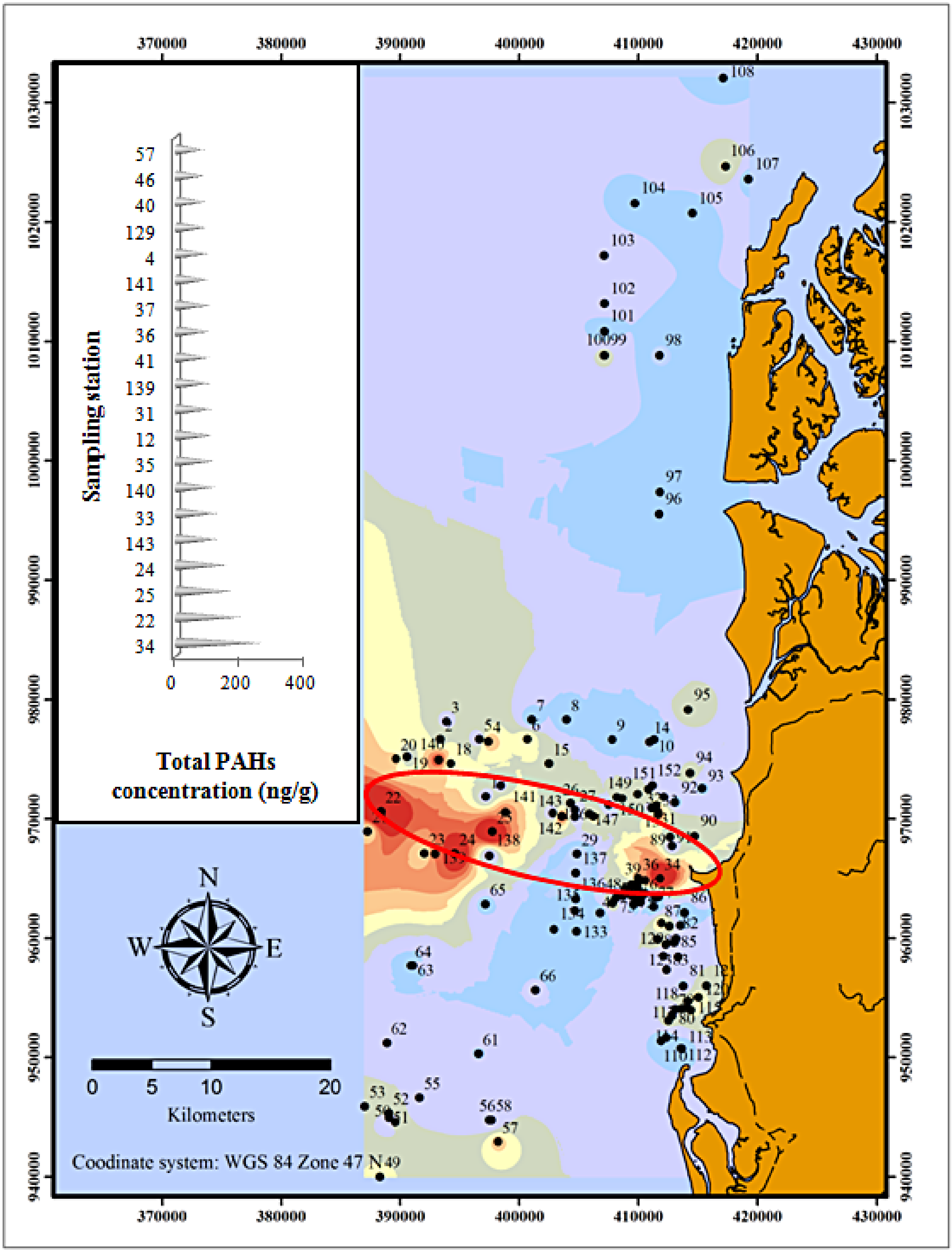


Figure 4.4 Top 20 of highest ΣPAHs contamination are located in front of Pakarang cape.

Tsapakis et al., (2003) noted that the main source of PAHs in sediments is atmospheric deposition followed by sedimentation in the remote area of the Eastern Mediterranean. In this study, the background level of PAHs in marine sediment station group should be originated from the atmospheric deposition (pyrogenic origin). The distribution pattern of PAHs in the background group can be characterized as pyrogenic in origin due to relatively higher contribution from HMW PAHs with 4~6 rings because of no petrogenic point sources from mainland in that area (Koh Phra Thong). In case of the hot spot group, the result can be indicated the totally different of its distribution pattern (Figure 4.5). The hot spot area have higher contribution from the 5-6 ring PAHS in most of stations. The highest percentage of 5-6 ring PAHs was found at stations in front of Pakarang Cape, indicating fuel combustion or street run-off as the predominant sources (Larsen and Baker, 2003). For more supporting information, coastal soil samples were collected and investigated to clarify the intensive influence of human activities on the study area.

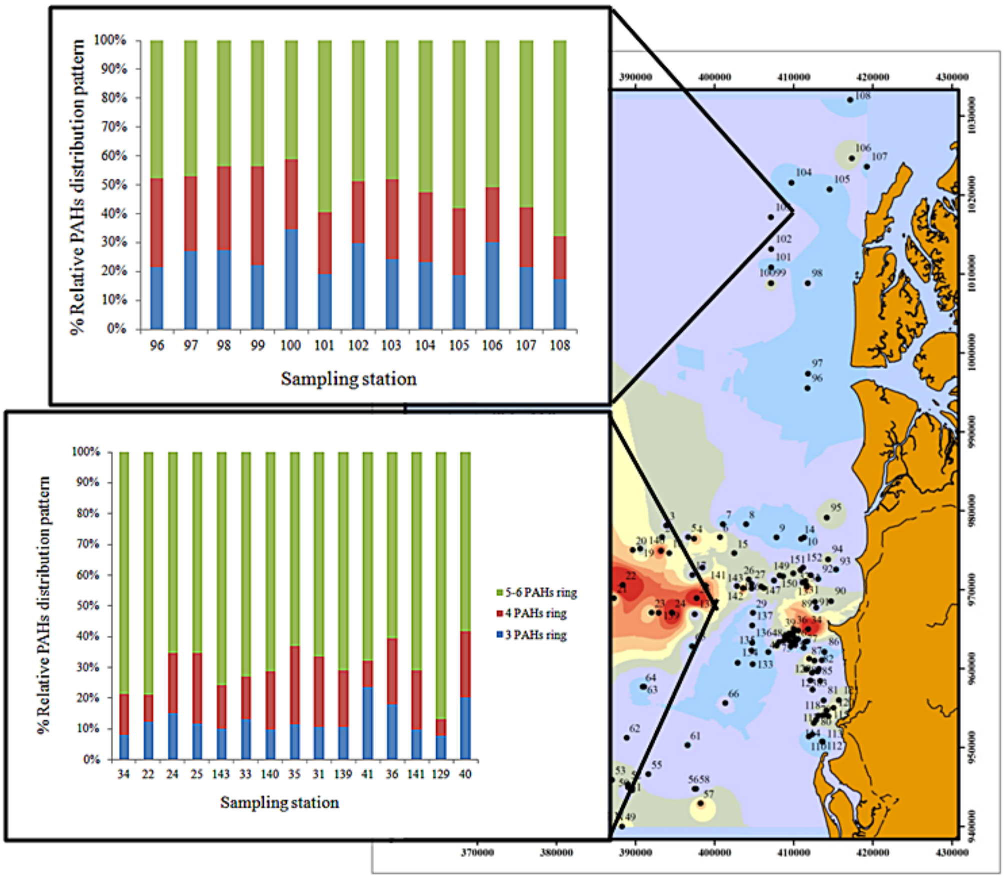


Figure 4.5 Distribution pattern (%) of 3-6 ring PAHs in coastal sediment.

4.1.2 Soils

Analysis of 18 of coastal soil samples indicating that ΣPAHs varies from 22.0 to 2083.8 ng g^{-1} dry weight, with an average of 54.1 ± 44.6 ng g^{-1} dry weight (except S17 station ΣPAHs = 2083.8 ng g^{-1} dry weight). The level of each of PAHs and ΣPAHs contamination of soil samples are shown in Figure 4.6. The hot spot stations showed in Figure 4.7, they are mostly act as a sink of PAHs contaminated soil in the study area *e.g.*, S16 (pond in the middle of Nam Khem village), S17 (Nam Khem port), S13 (natural pond located in between highway road and shoreline) and S5 (shrimp farm). During the rainy season and the Tsunami 2004 event, the anthropogenic PAHs are expected to transport from the potential source in the form of street run-off to accumulate into the potential sinks here. As a consequence, the high levels of PAHs contaminations were accumulated in all of these hotspot stations. Thus, in the next section, the land to sea transportation will be proven by investigating the correlation between soil and sediment samples along the coastal zone.

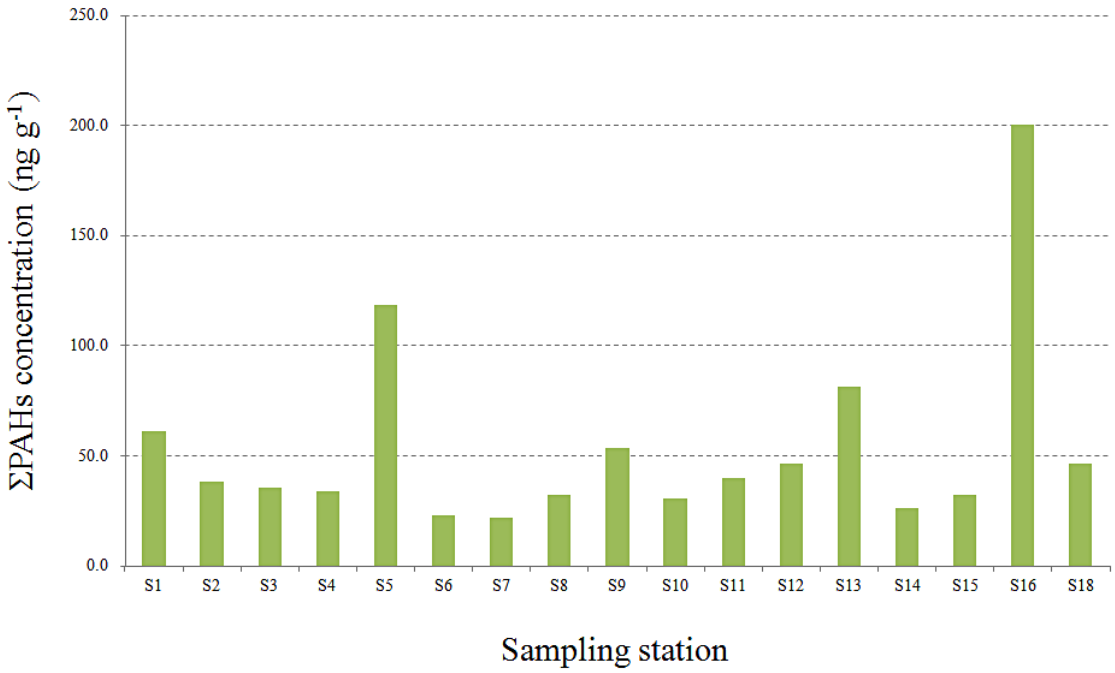


Figure 4.6 ΣPAHs contamination in contaminated Phang Nga coastal soil. (except S17 station ΣPAHs = 2083.8 ng g^{-1} dry weight)

S16

S17

S13

S5

Figure 4.7 Hot spot stations in coastal soil.

4.1.3 Aerosol

For 8 of ship-board aerosol samples, ΣPAHs varies from 174 to 376 pg m^{-3}, (aero 1, aero 2 and aero 3 are located in Phuket port). Level of each of PAHs and total PAHs (ΣPAHs) contamination in aerosol samples is shown in Figure 4.8. The assessment of the status of PAHs contamination in atmospheric environments in the Andaman Sea, as well as in the Gulf of Thailand, does not exist yet even in the Gulf of Thailand. Thus, this study aims to assess the status of atmospheric PAHs contamination in the open sea (Andaman Sea) for the first time. By using the fingerprint of atmospheric PAHs, it can be used for implication of the influence of human activities on the Phang Nga coastal zone. The pyrogenic PAHs are considered as the background level of PAHs concentration in the sediments.

The ship-board ΣPAHs concentrations detected in the Andaman Sea were much lower than the study by Foday et al. (2004) in the Atlantic Sea (190-680 pg m^{-3}).

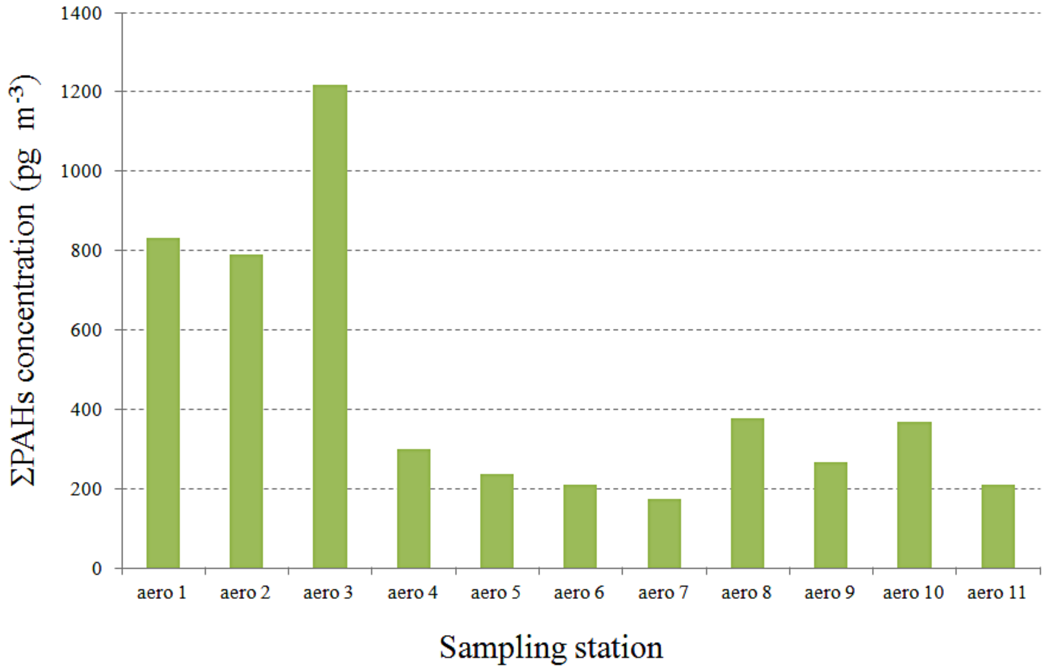


Figure 4.8 ΣPAHs contamination in aerosol samples.

4.2 Source apportionment of PAHs in the Phang Nga coastal sediments

To manage the risk of PAHs to environment and human health, it requires an ability to identify and control the dominant sources of PAH contamination. The challenge for environmental managers has to concentrate that PAHs are often derived from a multitude of sources, both present and past. The goal of source apportionment is needed to simplify the dominant sources for improved ability to design effective management and remediation strategies for degraded coastal ecosystems.

The previous information on the relative inputs is often lacking and confined to very general classifications, such as pyrogenic and petrogenic origins. Normally, in the urban area, PAHs typically come from a variety of combustion sources, including vehicle, industrial and domestic atmospheric emissions (Brown and Peake, 2006; Kim et al., 2008). For the Phang Nga coastal area, the input of PAHs is unique over other coastal area due to the strong coastal erosion by the 2004 Tsunami. Therefore, the identification of the dominant sources is needed to assess the unusual PAHs accumulation in these coastal sediments.

The spatial distribution of ΣPAHs contamination in the sediments of the Phang Nga coastal zone has already been discussed in the Section 4.1. One of the standing-out features from the overlaying contour plot is the distinctive high ΣPAHs contamination obviously seen in front of the Pakarang Cape. In sediments collected from the northern sectors of the coastal zone (Koh Phra Thong), the PAHs concentrations were generally much lower than those observed in Khao lak area (as shown in Figure 4.2). The contamination levels were also lower for the sites far from the pollution source (Koh Phra Thong). On the other hand, the stations which are influenced by human activities showed the higher concentrations of ΣPAHs.

4.2.1 Source identification by diagnostic PAH isomer ratios

Due to the characteristics of PAH patterns in the coastal sediments are subject to different emission sources. Pyrogenic and petrogenic are the primary sources of PAHs commonly found in coastal marine sediments (LaFlamme and Hites, 1978). The usefulness of isomer ratios of PAHs is able to identify PAHs sources, ranging from urban to marine environment (Yunker et al., 2002) that is suitable for the variety of the human activities such as in the Phang Nga coastal zone.

Binary cross plots between the ratios of An/An+Phe and Fluo/Fluo+Pyr, B[a]A/B[a]A+Chry and the ratios of Ind/Ind+B[g,h,i]P were applied to identify the potential sources of PAHs contamination in coastal sediment in the study area. Each of binary PAHs ratios provides the difference in possible pollution sources as shown in Figure 4.9 and 4.10.

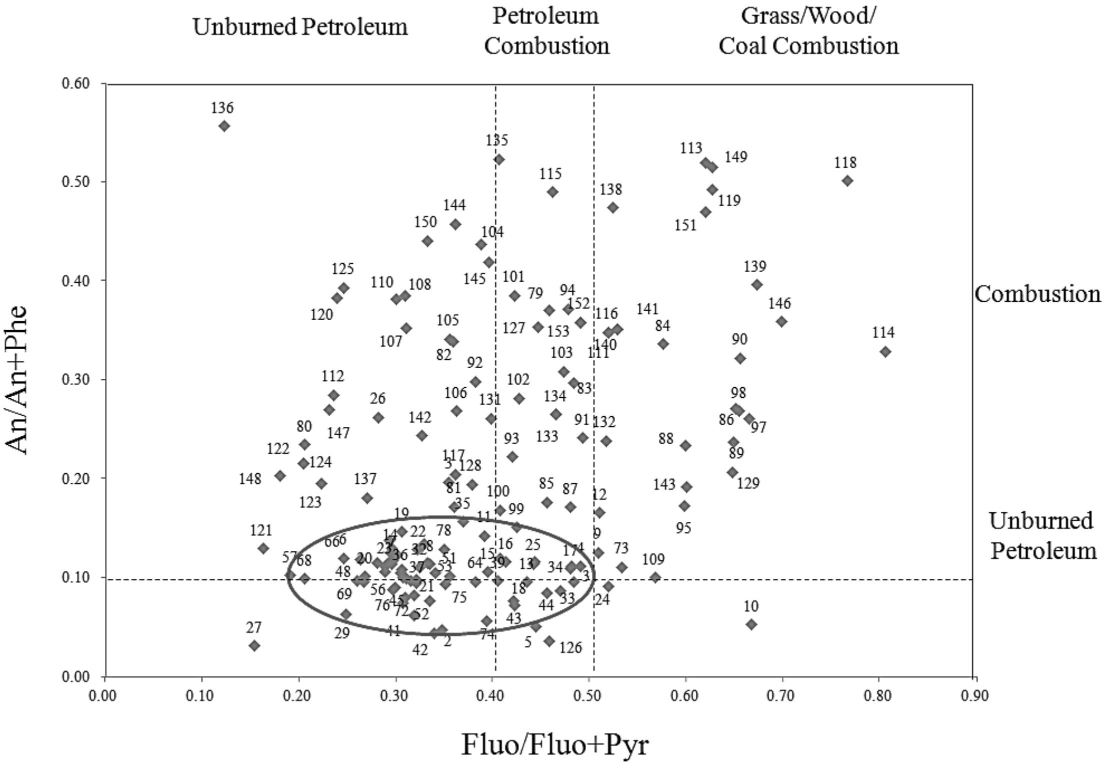


Figure 4.9 Cross-plot between ratios An/An+Phe and Fluo/Fluo+Pyr of Phang Nga coastal sediment.

The distinct discrimination among the sampling stations in front of Khao Lak area (circle in Figure 4.9 and 4.10) and background marine sediment (Koh Phra Thong) were obviously seen in Figure 4.9 and 4.10. For the sampling stations in front of Khao Lak area, the binary cross plot indicated that they originated from both of petrogenic and pyrolysis. In the other hand, the sampling stations at Koh Phra Thong originated from the grass/wood combustion, mixed sources and petroleum combustion.

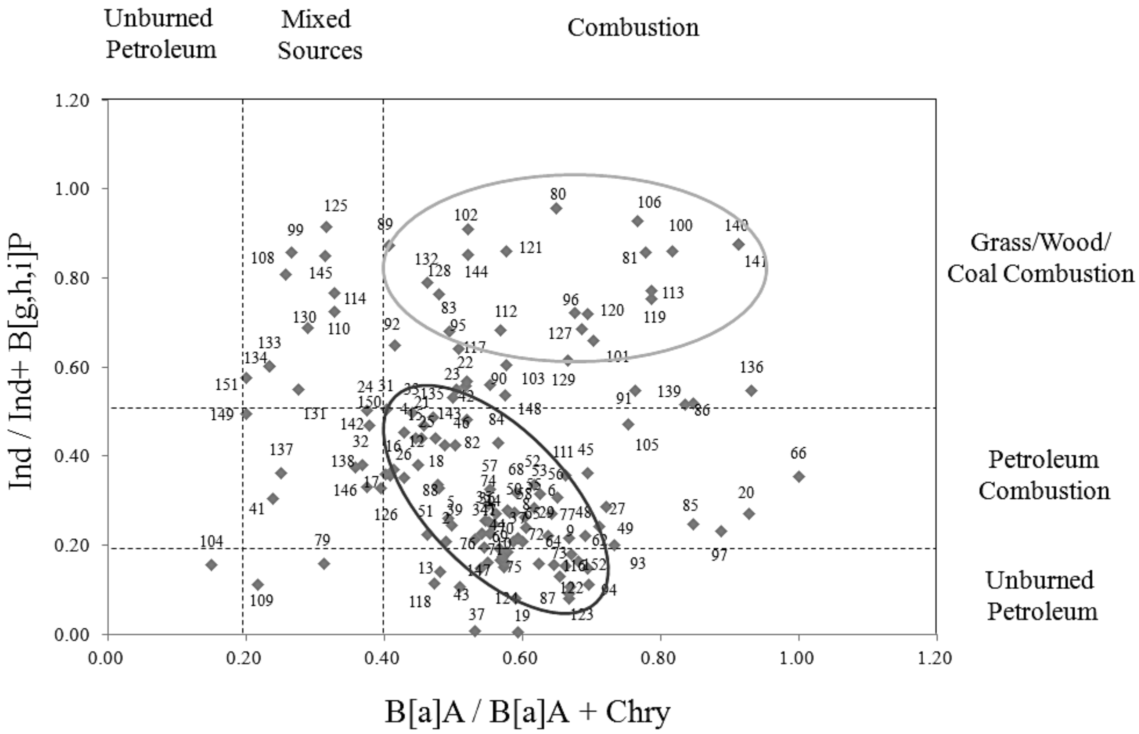


Figure 4.10 Cross-plot between ratios Ind / Ind+ B[g,h,i]P and B[a]A / B[a]A+Chry of Phang Nga coastal sediment.

From the background of human activities in the study area (Section 3.1) and diagnostic PAHs ratios interpretation indicated that the promising PAH sources might be originated from the traffic-related sources such as petroleum combustion, street dust, road paving asphalt, tire and leaking of petroleum used by shipping activities.

Arens and Depree, (2010) reported that PAHs originating from asphalt pavements shift the ratios towards pyrolytic regions which obviously clarify in Figure 4.10 (the spread of dark circle), especially the sampling station in front of Pakarang Cape. Moreover, in the pristine area such as the sampling station in Koh Phra Thong, the binary ratios indicate that they are originated from the grass/wood combustion and also fuel combustion. This result is in good agreement with the promising sources in the rural area which might be originated from the open burning for agriculture or the migration of traffic-related PAHs by atmospheric fall-out mechanism.

For petrogenic source, the potential source should be founded in the Nam Khem and Thup Lamu ports because of the intensive shipping activities in these areas. However, the binary plot ratios did not indicated those expected sampling stations in the unburned petroleum source. As a consequence, more supporting information such as PAHs source fingerprints is needed to apportion the various sources of PAHs in the next Section.

4.2.2 PAHs source fingerprints in Phang Nga coastal sediments

The distribution of PAHs in the environment typically exhibits large variations among different sites. Thus, the chemical composition (source fingerprints) of the major sources of anthropogenic PAHs in Phang Nga coastal sediments were intensively investigated to discriminate the source fingerprint of the major sources of anthropogenic PAHs in the study area.

From Section 4.2.1, the results indicated that the promising PAH sources might be originated from the traffic-related sources such as petroleum combustion, street dust, road paving asphalt, tire and leaking of petroleum used by shipping activities. Thus, in this section, the source fingerprints that derived from the previous studies in Malaysia and Thailand were used to apportion the predominant sources in the study area. The modified source fingerprint is shown in Figure 4.11.

By investigating the source fingerprint of the 145 of coastal sediment sampling stations, the results concluded that the promising sources are consist of street run-off, asphalt, tire, biomass burning and petrogenic source. The specific PAHs source fingerprints for Phang Nga coastal sediments are shown in Figure 4.12.

Comparison was also made among the street dust samples from the previous works, the result showed that the Phang Nga street dust are similar to that of Malaysia street dust. This might be due to the similar environmental conditions among the investigated areas. PAHs from most of the sampling stations (> 50 %) originated from the street dust source.

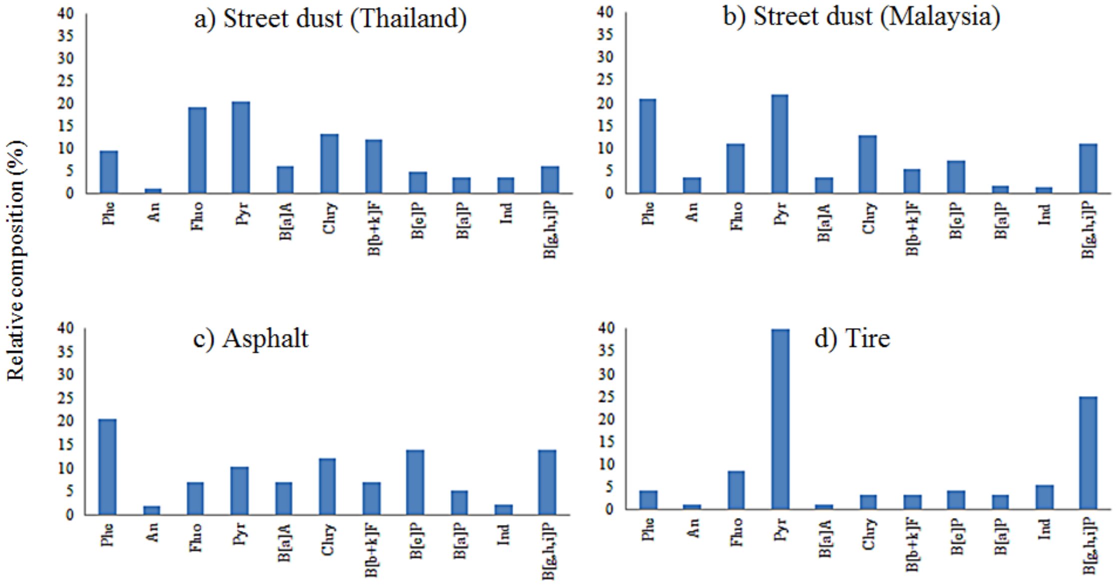


Figure 4.11 PAH profiles of the potential source materials:

a) Street dust (Thailand) b) Street dust (Malaysia) c) Asphalt d) Tire

modified from Boonyatumanond et al., 2006 and Zakaria et al., 2002.

For asphalt source, it was found in the sampling stations where located in front of Pakarang Cape (20, 24, 25, 31, 32, 33, 35, 36, 37, 40, 41, 115 and 143). It is reasonable to conclude that the road paving asphalts were eroded during the tsunami 2004 and then transported into seabed far from the Pakarang Cape. Moreover, the tire source was found in the sampling stations 21, 46 and 66. This result also indicated the land to sea transportation of terrestrial materials into the seabed.

For terrestrial material source, it was found in stations 22, 34, 90, 93, 95, 110, 113, 114, 118, 139, 140, 141, 152 and 153. All of these sampling stations located in front of Pakarang Cape and Nam Khem village which were heavily destroyed by Tsunami 2004. The high loading of high molecular weight PAH (Ind, D[a,h]A and B[g,h,i]P) are shown in this source fingerprint. This source might be originated from the strong coastal erosion during the Tsunami 2004.

For leakage of petroleum product source, it was found in stations 7, 8, 9, 10, 14, 49, 51, 53, 56, 58, 61, 62, 65 and 66. All of these sampling stations located in front of Nam Khem river mouth and Thup Lamu port which have intensive shipping activity. The high loading of Phe, Fluo and Pyr are shown in this source fingerprint.

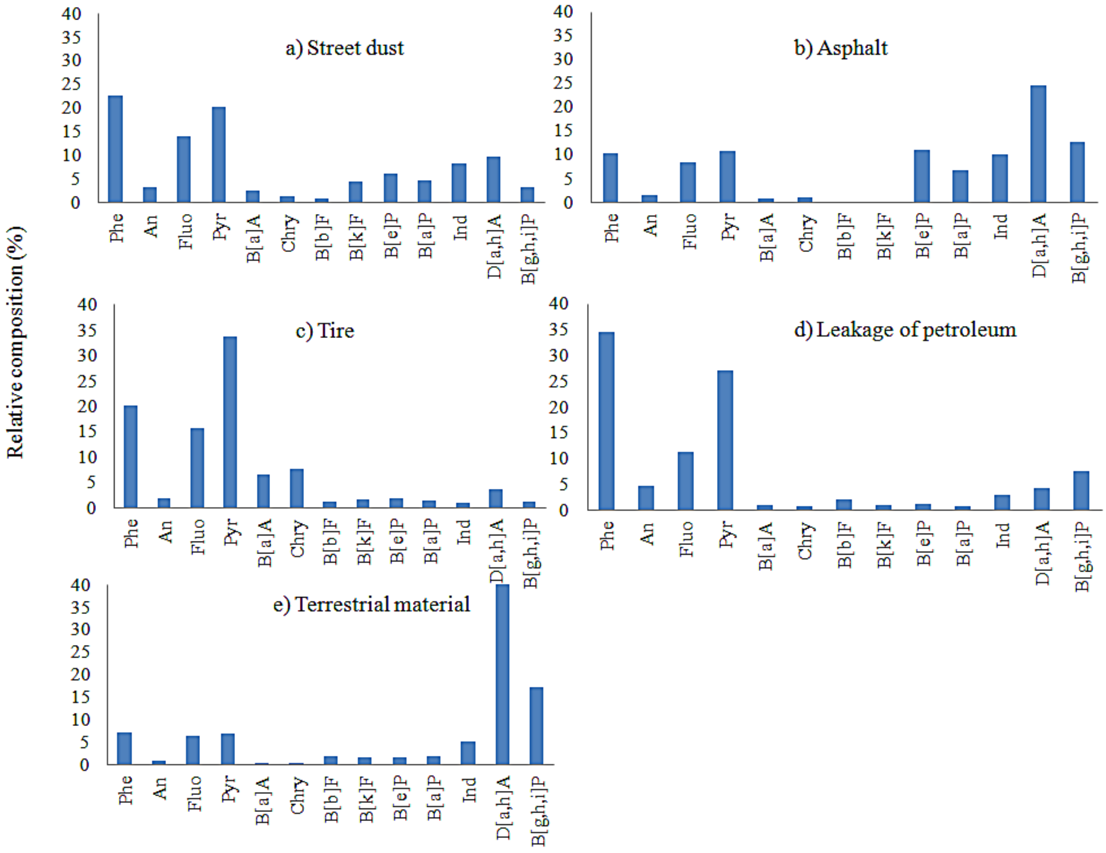


Figure 4.12 Specific PAH profiles of the Phang Nga coastal sediment

a) Street dust b) Asphalt c) Tire d) Leakage of petroleum

e) Terrestrail material

The source apportionment of Phang Nga coastal sediment was identified by the PAHs source fingerprints. The promising source of PAHs in the study area was also implicated, the results indicated that the promising PAH sources might be originated from the traffic-related sources such as petroleum combustion, street dust, road paving asphalt, tire and leaking of petroleum used by shipping activities.

4.2.3 Source identification by HCA

HCA was performed to identify the homogeneous groups of individual PAHs in the Phang Nga coastal sediment. The hierarchical dendogram is shown in Figure 4.13. The results reveal that two major groups of the 13 individual PAHs are clearly distinguished.

The first group contains Phe, An, Pyr and Fluo which are 3-4 ring PAHs. Khalili et al. (1995) reported that the high loading of 3-4 ring PAHs is usually originated from wood combustion. Thus, this group may be originated from grass/wood combustion.

The second group consists of 2 subgroups. The first subgroup is dominant with B[a]A, Chry and B[b]F. Motor vehicle emissions have been previously identified as original sources of this group (Dahle et al., 2003). The second subgroup consists of B[k]F, B[e]P, 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. The 5–6 rings PAH appears to be road dust collected from the Shanghai urban area (Liu et al., 2009) and vehicular (gasoline and diesel) in nature (Larsen and Baker, 2003). B[g,h,i]P has been identified as a tracer of auto emissions because it was found to be enriched in a traffic tunnel along with B[a]P (Larsen and Baker, 2003 Boonyatumanond et al., 2007). The higher level of B[k]F relative to other PAHs is suggested to indicate diesel vehicles (Larsen and Baker, 2003). Ind has also been found in both diesel and gas engine emissions (Larsen and Baker, 2003) and gasoline vehicle soot (Boonyatumanond et al., 2007). Therefore, this factor is selected to represent the traffic-related source of PAHs.

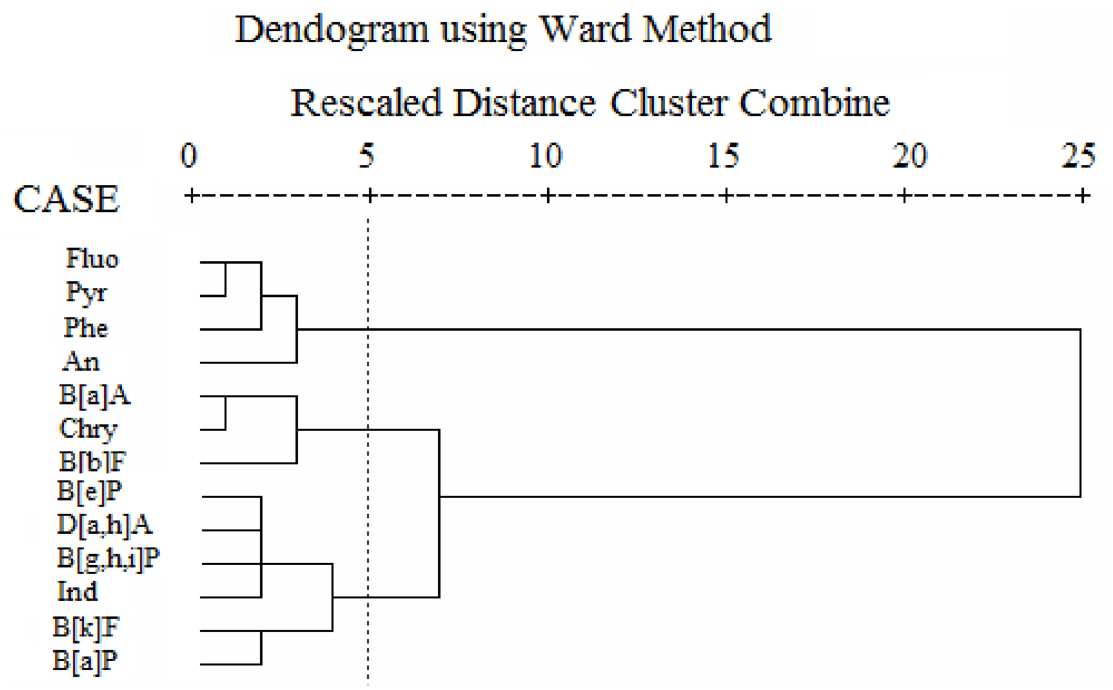


Figure 4.13 Dendrographic classification of 13 individual PAHs in Phang Nga coastal sediment.

Moreover, the results based on the cluster analysis by the 145 individual sampling stations revealed two major groups as shown in Figure 4.14 The HCA revealed the presence of two main clusters with three different sub-clusters. The first major cluster consists of 3, 5, 7, 8, 10, 11, 13, 14, 17, 27, 43, 45, 47, 48, 49, 51, 52, 53, 56, 58, 64, 65, 74, 75, 77 and 83. As previous discussion, all of samples are located at Thub Lamu port and Nam Khem village. They may be originated from the petrogenic sources caused by the shipping activities at the daily mail port and fishery vessel.

The second major cluster is divided into two sub-clusters which may be responsible for pyrogenic sources. The first sub-cluster contains the Tsunami-affected sediment sampling station. When taken their location into consideration, they are located in the tsunami-affected route. All of samples are located in front of Pakarang cape. Therefore, this sub-cluster may be representative to the Tsunami-affected group**.**

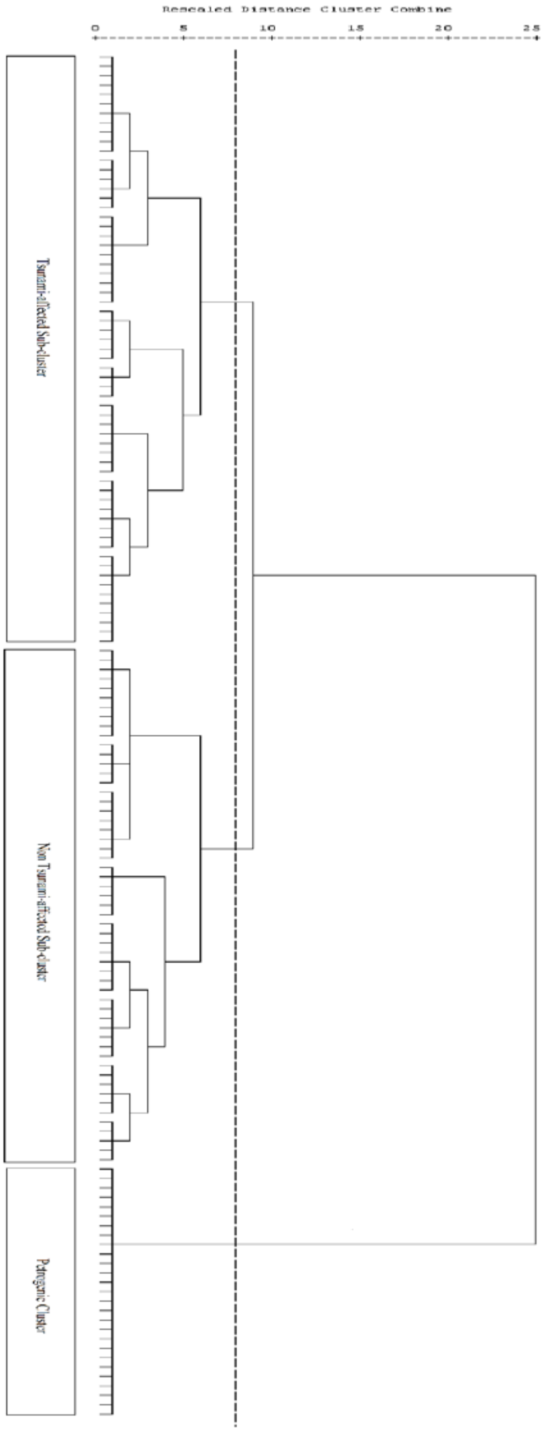


Figure 4.14 Dendrographic classification of 145 Phang Nga coastal sediment.

Tsunami-affected sub cluster: *2, 6, 15, 16, 19, 20, 22, 23, 24, 25, 29, 31, 32, 34, 35, 36, 37, 40, 41, 42, 44, 50, 55, 57, 61, 62, 63, 68, 69, 70, 71, 72, 73, 76, 78, 87, 88, 90, 93, 95, 109, 112, 113, 115, 118, 119, 122, 123, 124, 125, 129, 130, 133, 134, 137, 139, 140, 141, 147, 152, 153*

Non Tsunami-affected sub cluster:*4, 12, 18, 21, 26, 39, 46, 79, 80, 81, 82, 84, 86, 89, 91, 92, 94, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 110, 111, 114, 116, 117, 120, 121, 126, 127, 128, 131, 135, 136, 138, 142, 143, 144, 145, 146, 148, 149, 150, 151*

Petrogenic cluster: *3, 5, 7, 8, 10, 11, 13, 14, 17, 27, 43, 45, 47, 48, 49, 51, 53, 56, 58, 62, 64, 65, 66, 74, 75, 77, 83*

The second sub-cluster contains all of sampling stations at Koh Phra Thong which have less anthropogenic in this area. Thus, this sub-cluster is the representative of control site for the human activities impact to Phang Nga coastal zone. The dendogram are illustrated the sampling stations from Koh Phra Thong to the river mouth of Nam Khem into this sub-cluster. Therefore, this sub-cluster may be the representative of non-Tsunami-affected group.

4.2.4 Source identification by PCA

In order to specify source apportionment, 145 samples of sediment samples as subjects were selected and 13 PAHs concentrations were used as active variables in PCA treatment. The results indicate the majority of the variance (66.2 %) of the scaled data was explained by three eigenvectors–principal components. The PC1, PC2, and PC3 can explain 34.6, 18.3 and 13.3 % of the total variance, respectively. The estimated sources are shown in the Table 4.4.

The PC1 is heavily weighted on B[k]F, B[e]P, Ind, D[a,h]A and B[g,h,i]P, which are the high molecular weight PAHs with 5–6 rings. The literature reports that 5-6-ring PAHs are abundant in the road dust in urban area (Zakaria et al., 2002). Moreover, B[g,h,i]P and Ind have been used by several researchers as a source identifier for aerosols from automobiles (Greenberg et al., 1981; Harkov et al., 1984). This group usually originates from road paving asphalt, crude oil, bitumen and road dust. Therefore, the PC1 is a representative of the road dust sources of PAHs.

The second factor accounts for 17.0 % of the total variance. This factor is predominately composed of Fluo and Pyr. The high loading of 3-4 ring PAHs usually originates from wood combustion (Khalili et al., 1995). In combination with diagnostic PAHs ratios and HCA, this group may be originated from grass/wood combustion.

The last factor is predominately composed of B[a]A and Chry which originate~~d~~ from pyrolysis of fuel and oil burning (Fang et al., 2006). Thus, this factor should contribute to the fuel combustion.

Table 4.4 Rotated component matrix of 13 PAHs from Phang Nga coastal sediments.

PAH composition	Principle component (PC)		
	PC1	PC 2	PC 3
Phe	-0.10	**0.81**	-0.22
An	0.03	0.15	0.22
Fluo	0.13	**0.85**	0.10
Pyr	-0.02	**0.89**	0.00
B[a]A	0.11	-0.04	**0.84**
Chry	0.14	-0.01	**0.88**
B[b]F	0.44	-0.28	0.38
B[k]F	**0.76**	-0.16	0.22
B[e]P	**0.85**	0.19	0.11
B[a]P	0.60	-0.11	0.44
Ind	**0.71**	-0.12	0.23
D[a,h]A	**0.78**	0.07	0.07
B[g,h,i]P	**0.81**	0.05	-0.11
Percentage	**34.6**	**18.3**	**13.3**
Estimated sources	**Street dust**	**Grass/wood combustion**	**Vehicle combustion**

[a] *Rotation Method: Varimax with Kaiser Normalization*

[b] *Bold loading > 0.70*

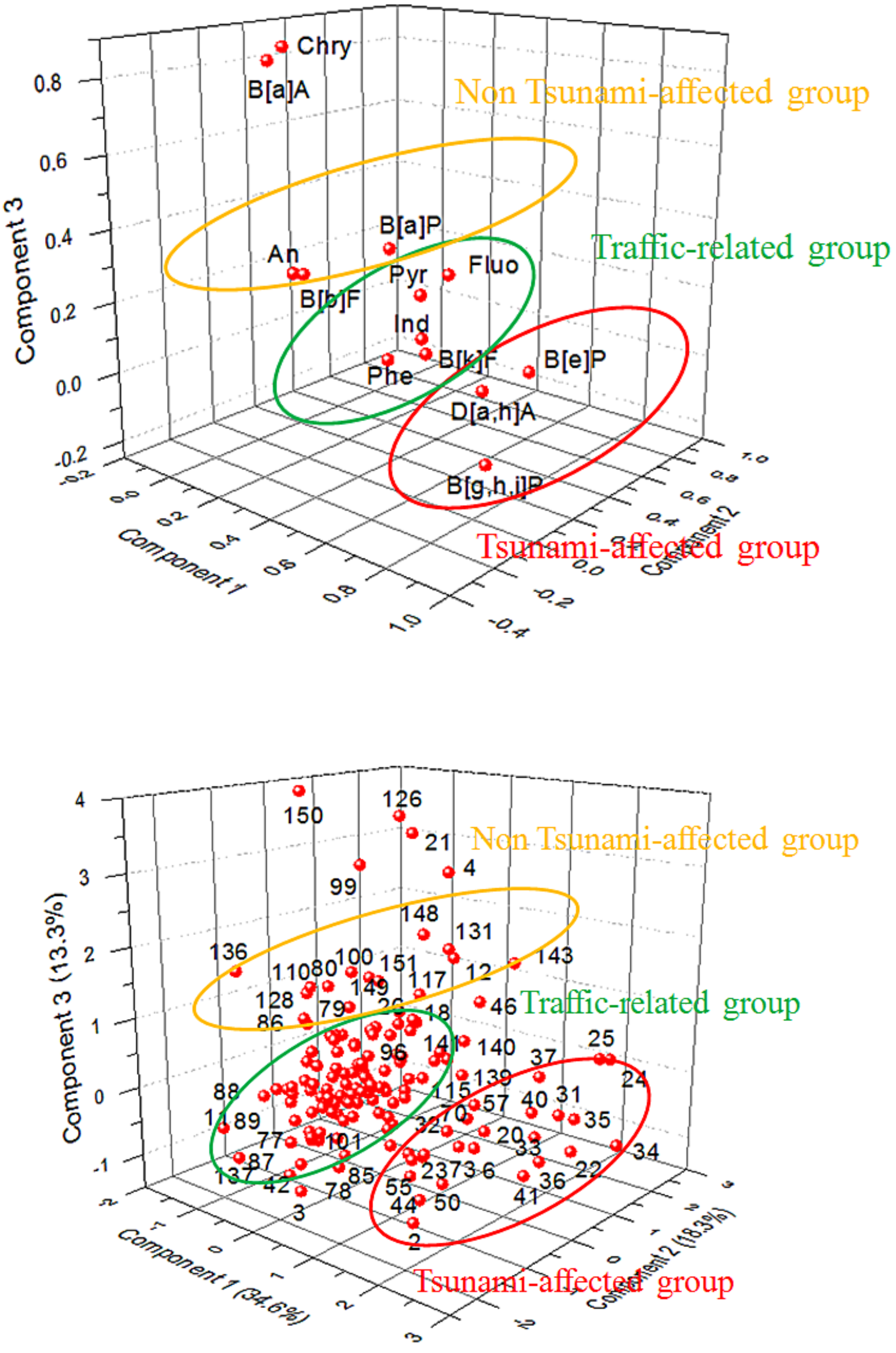


Figure 4.15 The loading and score plot of PCA of Phang Nga coastal sediment.

The loading and score plot of PCA of anthropogenic PAHs from Phang Nga coastal sediments are shown in Figure 4.15. The score plot discriminates the samples into 3 groups; Tsunami-affected group, non Tsunami-affected group and traffic-related group. The 3 dimensional visualization plot provides clearly distinguish in between groups. The PCA results are in good agreement with HCA in the Section 4.2.3.

The projection of Tsunami-affected group is distinct out of the other group due to the different individual composition from the road paving material eroded by Tsunami wave. The traffic-related group is the indicator for evaluate the anthropogenic impact in the study area. Finally, the non Tsunami-affected consist of both of pyrogenic (grass/wood combustion) and petrogenic (shipping activities).

In summary, the source apportionment of Phang Nga coastal sediments was identified by the spatial distribution, diagnostic PAHs ratios, source fingerprints, HCA and PCA. The promising source of PAHs in the study area was also implicated, the result contributed to 3 possible sources which consist of road dust, vehicle combustion and grass/wood combustion. These promising sources indicated that the potentially high adverse anthropogenic impacts to the coastal ecological system can be expected in this study area. Their ability to identify the dominant sources of PAH contamination is useful to manage the risk of PAHs to environmental and human health. It meets the objective of this study to identify the dominant sources of sedimentary PAHs in order to improve and design effective management and remediation strategies for improving the degraded coastal ecosystems

4.3 Transport and distribution of PAHs in Phang Nga coastal sediments

On the basis of the analysis of the $\sum$PAHs in coastal sediment, soil and aerosol samples in the Section 4.1, the results provide that the 2004 Tsunami plays an important role in bringing the terrestrial-derived PAHs from land and dredging into the near-shore seabed in front of the Pakarang Cape. To further clarify the overview of transport and distribution of PAHs in coastal sediments, the compositions of PAHs in coastal sediment, coastal soil and aerosol samples were analyzed in combination with application of diagnostic PAHs ratios and the multivariate descriptive statistical techniques to evaluate the land to sea transportation. In addition, the ship-board aerosol samples were used as the local background of atmospheric PAHs (pyrogenic origin) that input into the study area.

In this section, the distribution of PAHs in each of aerosol, soil and sediment samples was investigated to clearly examine the potential sources of PAHs especially~~,~~ to prove the transport of contaminant~~s~~ PAHs from land to seabed. Once produced, PAHs can be widely dispersed into the atmospheric phase and then fallen out and distributed in both of soil and sediment phase. Thus, the phase distribution provides supported evidence on more patterns of the predominant emission sources.

The 115 of coastal sediment samples (both of Tsunami-affected sediments and marine background sediments), 18 of coastal soil samples and 11 of aerosol samples were analyzed. The results found that $\sum$PAHs in coastal sediments, coastal soil samples and aerosol samples ranged from 11.9 to 272.0 ng g^{-1} dry weight, (mean ± SD; 61.0 ± 38.6 ng g^{-1} dry weight) , 22.0 to 2083.8 ng g^{-1} dry weight,(mean ± SD; 139.1 ± 416.4 ng g^{-1} dry weight wt.), and 174 to 376 pg/m^{3}, (mean ± SD; 267 ± 75 pg/m^{3}), respectively. The spatial distribution of $\sum$PAHs in coastal sediment and soil samples is shown in figure 4.16.

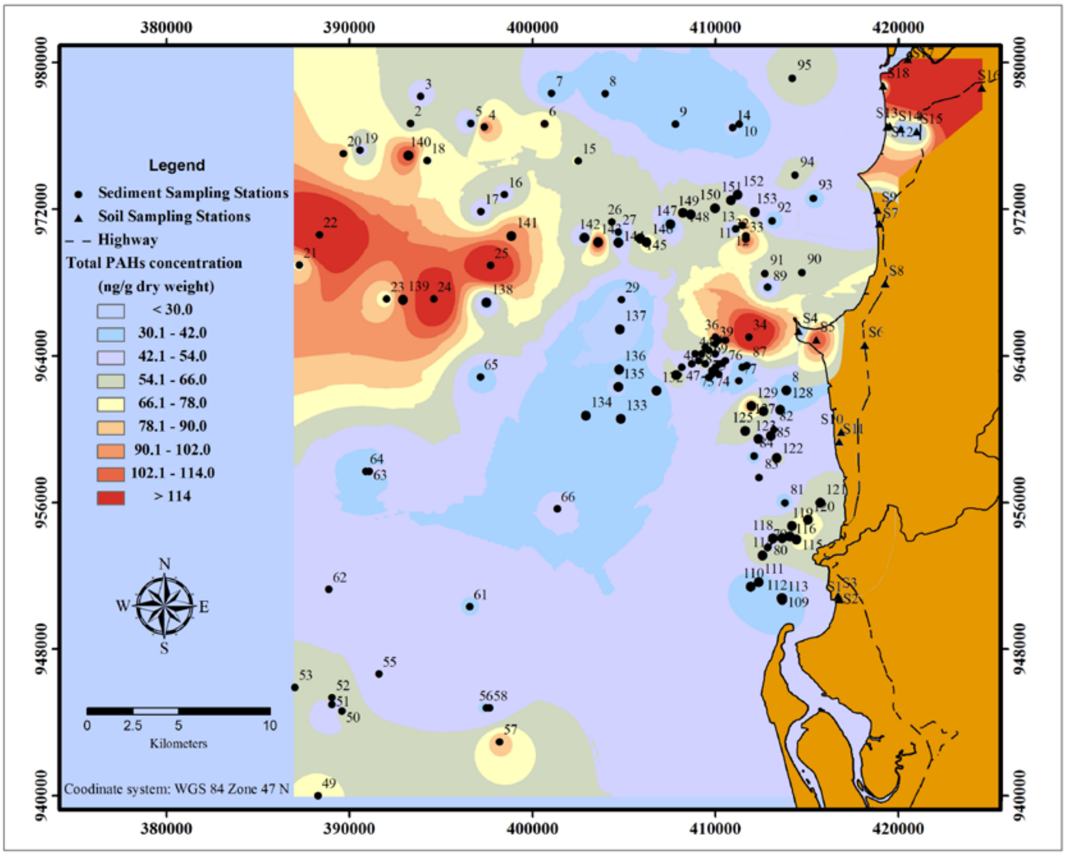


Figure 4.16 The evidence of land to sea transportation using the PAHs spatial distribution in the Khao Lak coastal area.

(Note that numbers indicating sampling stations and the contour scale representing total PAHs concentrations as labeled in the legends)

4.3.1 Spatial distribution of land to sea transportation

The coastal soil sampling stations, which were affected by the 2004 Tsunami, were investigated to prove the land to sea transportation of anthropogenic PAHs in the Khao Lak seabed. The coastal soil sampling stations were selected by choosing the consistent location in the transect line of the coastal sediment sampling stations.

Figure 4.16 shows the spatial distributions of PAHs contamination in coastal soil and sediment in the Khao Lak coastal area. From the figure, the prominent feature of sediments exported from the Pakarang Cape can be observed, as mentioned in the Section 4.1 and 4.2. For coastal soil samples, the high levels of PAHs contaminations were found at the Pakarang Cape and Nam Khem village. The potential sources of anthropogenic PAHs in coastal soil samples may originate from the intensive human activities in the urban/tourist areas especially the traffic-related sources.

When comparison the positions of PAHs hot spots among the coastal soil and sediment samples (Figure 4.16), the high PAHs concentration profile can track back to the potential sources on land, especially at the Pakarang Cape. This evidence confirmed that the land to sea transportation of anthropogenic PAHs occurred in here. Moreover, Di Geronimo et al. (2004) reported that, on the Pakarang northern side, a sandy coast is generally affected by Tsunami that ran up the opened small river mouths and tidal channels with widened cut banks. This evidence confirmed the heavy erosion which introduced a huge of terrestrial derived material into seabed.

Based on this evidence, it is reasonable to say that the potential sources of terrestrial-derived PAHs originated on land and then transported into the seabed by both of the normal transporting mechanisms such as high precipitation in rainy season and the Tsunami 2004 events which contributed high impact on sediment loading into the coastal zone. However, the comparison between the source identification in soil and sediment samples are additionally needed for supporting the above-mention notation.

4.3.2 Diagnostic PAH isomer ratios of coastal soil and sediment

Binary cross plots between the ratios of B[a]A/B[a]A+Chry and Ind/Ind+B[g,h,i]P and the ratios of Fluo/Fluo+Pyr and Ind/Ind+B[g,h,i]P were applied to identify the potential sources of PAHs contamination in coastal sediment and soil in the study area. Each of binary PAHs ratios provides the difference in possible pollution sources as shown in Figure 4.17and 4.18. PAH diagnostic ratios may be an efficient supporting tool in studying the mechanisms of PAH transport to the soil and subsequently to the coastal sediment and assessing the range of influence of particular emission sources on the surrounding areas.

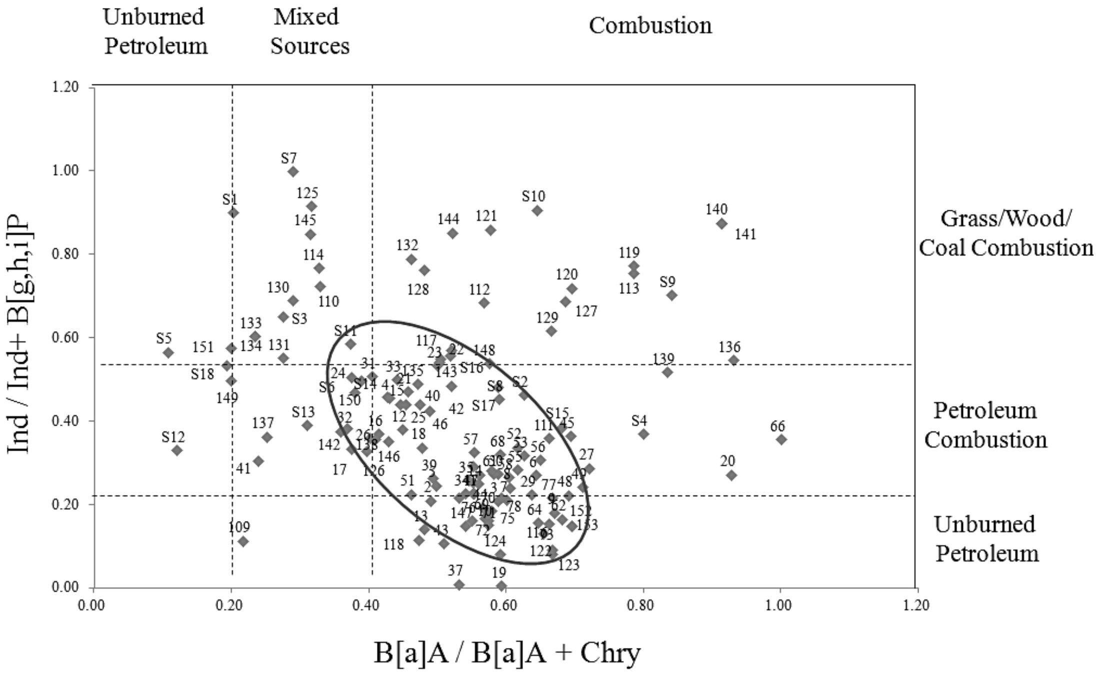


Figure 4.17 Cross-plot between ratios Ind / Ind+ B[g,h,i]P and B[a]A / B[a]A+Chry of sediment and soil samples in Khao Lak area.

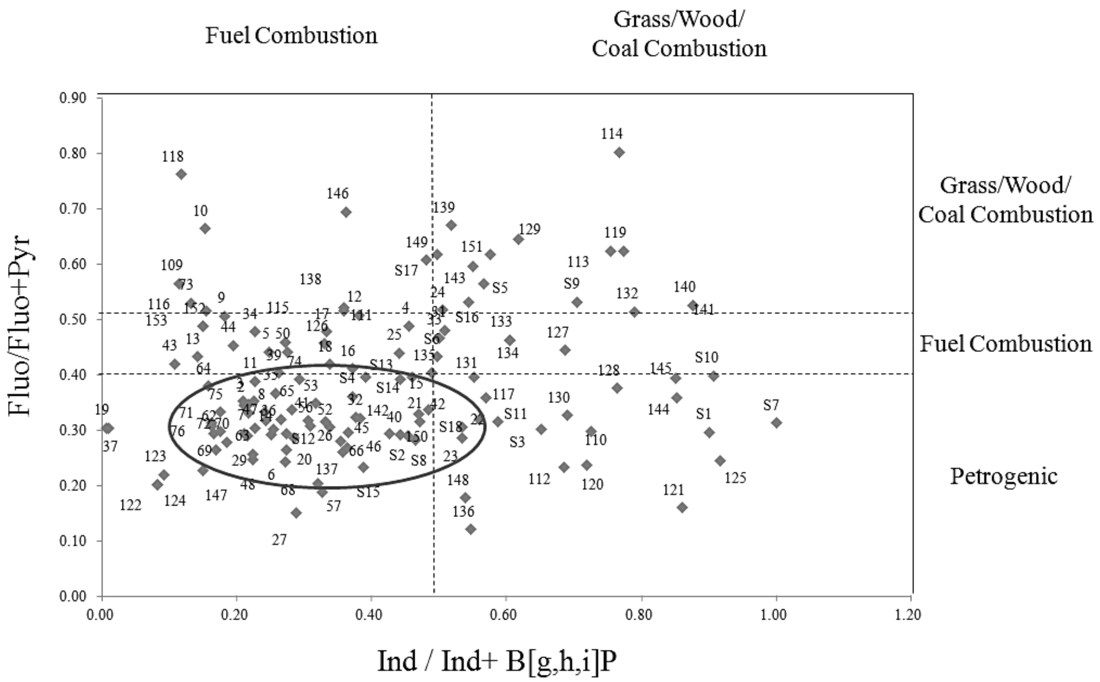


Figure 4.18 Cross-plot between ratios Fluo/Fluo+Pyr and Ind / Ind+ B[g,h,i]P of sediment and soil samples in Khao Lak area.

Only one binary cross plot in Figure 4.17 provides not enough information to indicate the possible pollution sources in the study area. The results do not shows the clearly distinguish between the possible sources of coastal sediment and soil samples. All samples are mainly clustered in the boundary of unburned petroleum and petroleum combustion. It is important to note that isomer pair ratios of the entire dataset are not restricted to the extreme values of only specific source, because there is a chance to misinterpret when the mixtures of heterogeneous PAH sources are analyzed as mention in Section 4.2.2. Moreover, the coal combustion is excluded due to the unavailable source using as fuel in the study area.

Figure 4.17 indicated that most of samples are originated from the combustion (pyrogenic origin) and mixed sources. The percentage of unburned petroleum is less than 15 % of all samples. In addition, Figure 4.18 also indicates that the fuel combustion is the predominant source in the study area.

In summary, the predominant source of PAHs contaminations is the traffic-related sources such as petroleum combustion and road-derived material caused by strong erosion of the Tsunami 2004. The grass/wood combustion is found in station 113, 114, 119, and 129 where located in the near shore of the Khao Lak bay.

From the interpretation of 2 binary cross plots, the results show that the possible sources of PAHs contaminations in soil are the same sources as in the coastal sediment samples, especially in the Tsunami-affected samples as shown in the circle on Figure 4.17 and 4.18. While, the non Tsunami-affected soil also found to related to the near-shore sediment station in their transect line.

By using the correlation between the PAHs diagnostic ratios of soil and coastal sediment samples, the results confirm that the land to sea transportation has occurred during the strong erosion of the Tsunami 2004 especially the hot spot stations in front of the Pakarang Cape. For the near-shore stations, they are also found the land to sea transportation but their mechanisms may be different from the Tsunami-affected group. The possible mechanisms may be by the normal transporting pathways such as those associated with the annual reversals of monsoon and high precipitation in rainy season.

4.3.3 Source identification by HCA

To investigate the possible sources of PAHs contamination in the study area, the aerosol samples were also taken into consideration for using as the representative of local atmospheric fall-out PAHs source around the study area, in additional to soil and coastal sediment.

HCA was performed to identify the homogeneous groups of individual PAHs in 3 phases of samples. The hierarchical dendogram is shown in Figure 4.19. The results reveal that two major groups of the 13 individual PAHs are clearly distinguished. The first group contains Phe, An, Pyr and Fluo which are 3-4 ring PAHs. Khalili et al. (1995) reported that the high loading of 3-4 ring PAHs is usually originated from wood combustion. Moreover, in Section 4.3.2 diagnostic PAHs ratios indicate that the grass/wood combustion is the one of possible source in the study area. Thus, this group may be originated from grass/wood combustion.

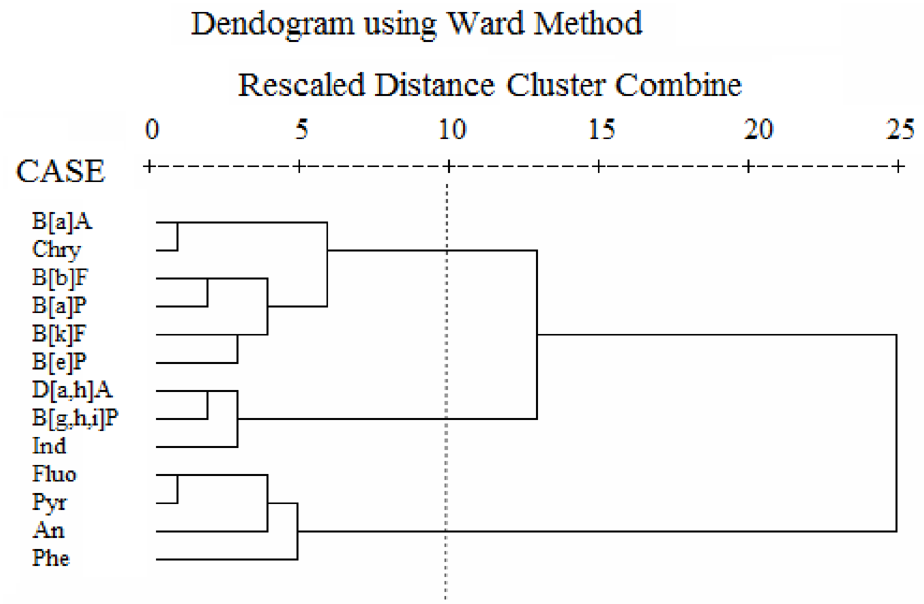


Figure 4.19 Dendrographic classification of 13 individual PAHs in coastal soil, sediment and aerosol in Khao Lak area.

The second group consists of 2 subgroups. The first subgroup is dominant with B[a]A, Chry, B[b]F, B[k]F, B[e]P and B[a]P which are originated from the pyrogenic origin (Fang et al., 2009; Liu et al., 2009). Motor vehicle emissions both of gasoline and diesel emission, leakage of used oil and road dust have been previously identified as original sources of this group (Dahle et al., 2003). According to the literature reports, the 4-5 ring PAHs have been found in the road dust in urban cities as well (Zakaria et al., 2002; Boonyatumanond et al., 2007).

The second subgroup consists of Ind, D[a,h]A and B[g,h,i]P, which are the high molecular weight PAHs with 5–6 rings. This group is usually originated from road paving asphalt, crude oil, bitumen (Ahrens and Depree, 2010) and road dust (Khalili et al., 1995; Larsen and Baker, 2003).

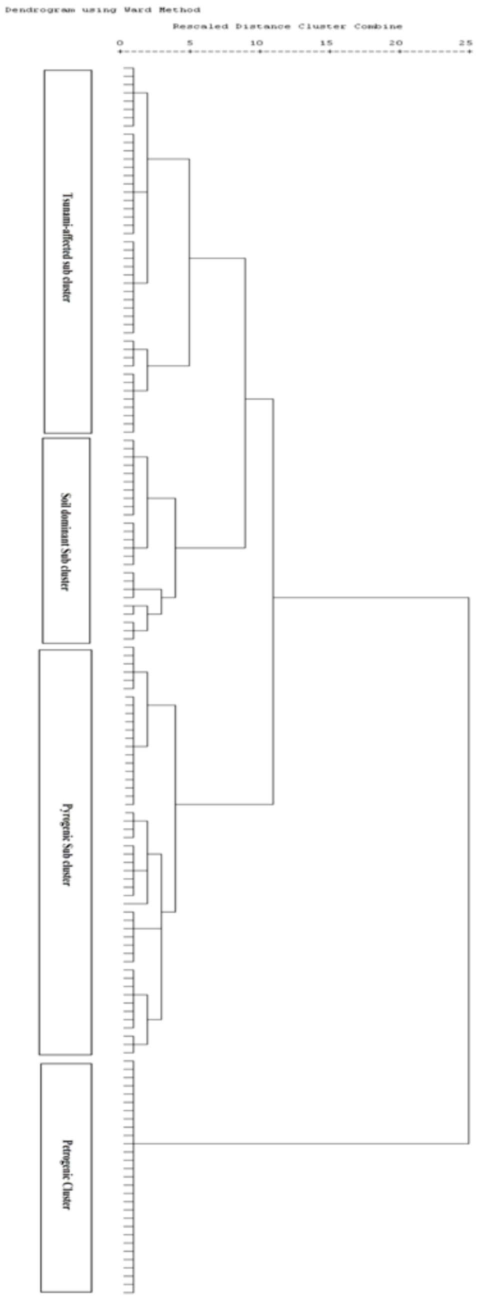


Figure 4.20 Dendrographic classification of 149 of coastal soil, sediment and aerosol in Khao Lak area.

Tsunami-affected sub cluster: *2, 15, 16, 18, 20, 24, 25,26, 29, 31,32, 33, 37, 38, 39, 40, 41, 42, 44, 50, 55, 61, 62, 63, 69, 70, 71, 72, 73, 76, 78, 127, 130, 133, 134, 137, 152, 153, S4, S6, S12*

Soil dominant sub cluster: *4, 21, 46, 57, 68, 112, 126, 150, S2, S3, S4, S7, S9, S10, S14, S15, S16 ,S17, S18, aero8, aero11*

Pyrogenic sub cluster: *6, 12, 22, 23, 34, 109,110, 112, 113, 114, 115,116, 117, 118, 119,120, 121, 122, 123, 124, 125, 127, 128, 129, 131, 135, 138, 139, 140, 141,142, 143, 144, 147, 149, 151, S1, S5, S13, aero1, aero2, aero3, aero4, aero5, aero6, aero7, aero9, aero10*

Petrogenic cluster: *3, 5, 7, 8, 10, 11, 13, 14, 17, 27, 43, 45, 48, 49, 51, 52, 53, 56, 58, 62, 64, 65, 66, 74, 75, 77, S8, S10*

Moreover, the results based on the cluster analysis by the 149 individual sampling stations revealed two major groups as shown in Figure 4.20. The dendogram revealed the presence of two main clusters with three different sub-clusters. The first major cluster consists of 3, 5, 7, 8, 9, 10, 11, 13, 14, 17, 27, 43, 45, 48, 49, 51, 52, 53, 56, 58, 64, 65, 66, 74, 75, 77, S8 and S10. This major cluster contains only sediment and 2 of soil samples. The aerosol do not include in this cluster while in the other sub-cluster found the aerosol involve in those sub-cluster. This may be due to the emission sources in this group did not originate from the combustion sources (pyrogenic origin).

When taken their location into consideration, they are located out of the Tsunami-affected route. All of samples are located at Thub Lamu port and Nam Khem village. They may be originated from the petrogenic sources caused by the shipping activities from the daily mail port and fishery vessels.

The second major cluster is divided into three sub-clusters. The first sub-cluster contains the Tsunami-affected sediment sampling station, similar to those mentioned in Section 4.2.3. The soil samples such as S4, S8, S12 and S13 which are in the Tsunami route are the member of this group. Moreover aerosol samples do not also include in this sub-cluster.

The second sub-cluster consists of 61 % of soil samples (11 out of 18 soil samples) and 2 of aerosol samples (aero 8 and aero 11). The sediment sampling stations in this sub-cluster are 4, 21, 46, 57, 68, 112, 132, 136 and 150. Because of this sub-cluster are in the main cluster with the Tsunami-affected group, so that it is in good agreement for proving the land to sea transportation. Once PAHs are emitted and fall-down to accumulate in soil particles, the Tsunami wave play an important role to brought the terrestrial-derived material into the sea. Thus, HCA provide the reasonable evidence that illustrate the soil dominant group and Tsunami-affected group in the same main cluster.

The third sub-cluster contains 82 % of aerosol samples (9 out of 11 aerosol samples), 3 of soil samples and most of near-shore sediment sampling stations. The distinctly homogeneous into this sub-cluster illustrated that the aero 7 and aero 9 as the representative of local atmospheric PAHs around the study area are in the same group as the near-shore sediment such as 110, 114, 118, 123, 3-15, 125, 145, 146 and 147. This sub-cluster may be the representative of the influence of atmospheric PAHs fall down.

4.3.4 Source identification by PCA

In this study, concentrations of 13 PAHs as active variables and 149 of 3 different phases of samples as subjects were selected. The majority of the variance (70.9 %) of the scaled data was explained by three eigenvectors–principal components. The first principal component (PC1) can explain 43.3 % of the total variance, and the second (PC2) and the third (PC3) explained 17.0 % and 10.6 % of the total variance, respectively as in Table 4.5.

The PC1 is heavily weighted on B[k]F, Ind, D[a,h]A and B[g,h,i]P, which are the high molecular weight PAHs with 5–6 rings. The literature reports that 5-6-ring PAHs are abundant in the road dust in urban area (Zakaria et al., 2002). This group usually originates from road paving asphalt, crude oil, bitumen and road dust. Therefore, the PC1 is a representative of the road dust sources of PAHs.

The second factor accounts for 17.0 % of the total variance. This factor is predominately composed of B[a]A and Chry which originate~~d~~ from pyrolysis of fuel and oil burning (Fang et al., 2006). Thus, this factor should contribute to the fuel combustion.

The last factor is predominately composed of Phe, Fluo and Pyr. The high loading of 3-4 ring PAHs usually originates from wood combustion (Khalili et al., 1995). In combination with diagnostic PAHs ratios and HCA, this group may be originated from grass/wood combustion.

Table 4.5 Rotated component matrix of 13 PAHs from soil, sediments and aerosol samples in Khao Lak area.

PAH composition	Principle component (PC)		
	PC1	PC 2	PC 3
Phe	0.01	-0.07	**0.82**
An	0.32	0.36	0.21
Fluo	0.08	0.27	**0.83**
Pyr	0.06	0.16	**0.90**
B[a]A	0.13	**0.83**	0.15
Chry	0.08	**0.89**	0.11
B[b]F	0.61	0.51	0.11
B[k]F	**0.76**	0.35	0.02
B[e]P	0.61	0.44	0.35
B[a]P	0.60	0.62	0.10
Ind	**0.79**	0.19	-0.01
D[a,h]A	**0.87**	-0.02	0.03
B[g,h,i]P	**0.86**	-0.02	0.07
Percentage	**43.3**	**17.0**	**10.6**
Estimated sources	**Road dust**	**Fuel Combustion**	**Grass/wood combustion**

[a] *Rotation Method: Varimax with Kaiser Normalization*

[b] *Bold loading > 0.70*

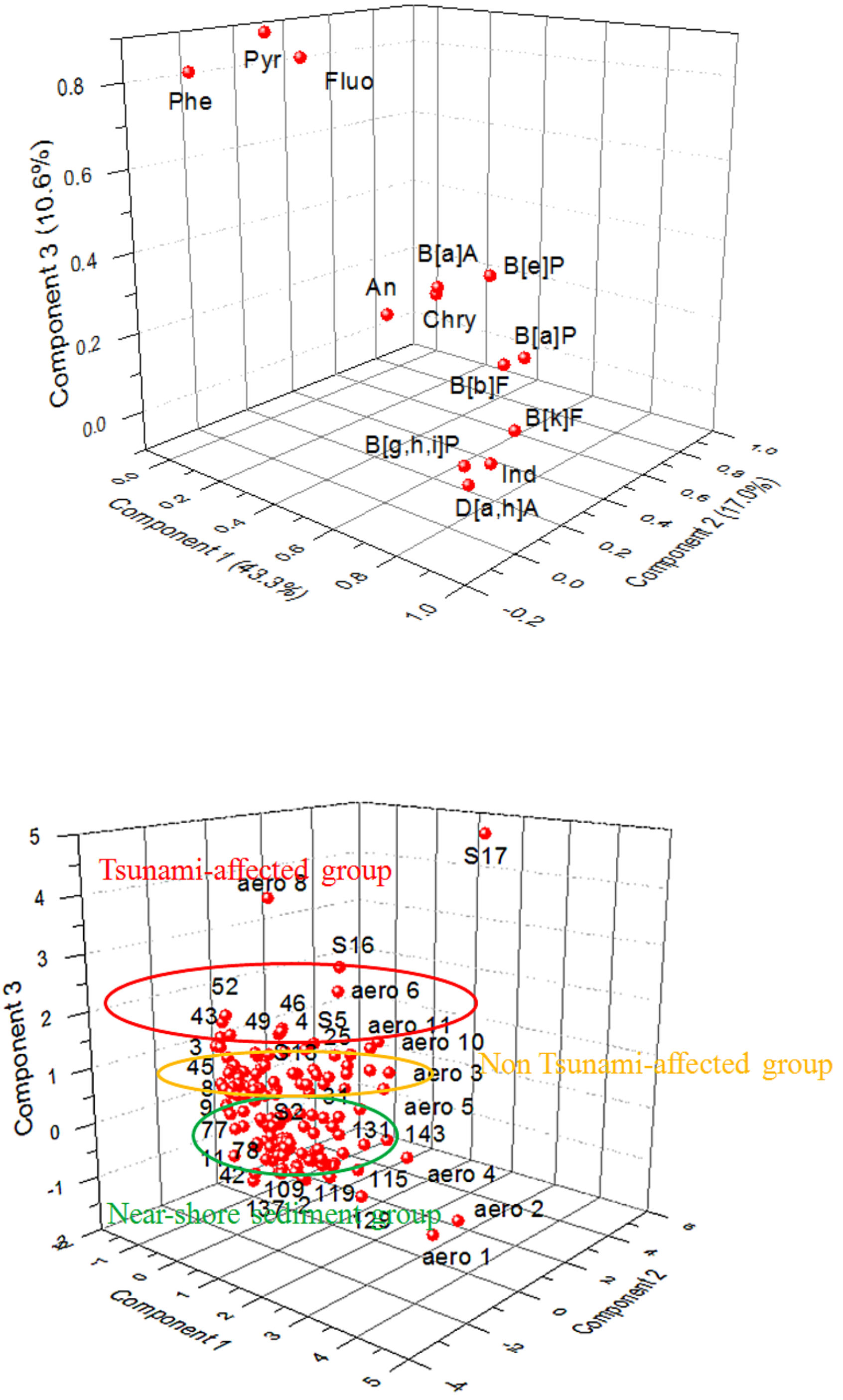


Figure 4.21 The PCA loading and score plot of coastal soil, sediment and aerosol samples in Khao Lak area.

The loading and score plot of PCA of anthropogenic PAHs from aerosol soil and sediment samples in the study area are shown in Figure 4.21. The score plot discriminates the samples into 3 groups; Tsunami-affected group, non Tsunami-affected group and near-shore sediment group. The 3 dimensional visualization plot provides clearly distinguish in between groups. The PCA results are in good agreement with HCA in the Section 4.3.3.

In summary, the land to sea transportation has been proven by the spatial distribution, diagnostic PAHs ratios, HCA and PCA. The dominant mechanism of land to sea transportation is the introduction of the huge sediment into seabed by the 2004 Tsunami. Moreover, for non Tsunami-affected samples, they are also found the land to sea transportation but their possible mechanisms may be by those associated with the annual reversals of monsoon and high precipitation in rainy season.

The PAHs distribution in aerosol, soil and sediment were clarify, it found that the input of anthropogenic PAHs originated from 3 possible pathways consist of atmospheric fall-out, street run-off (including unusual event as Tsunami 2004) and soil erosion due to heavily affect from the strong rain inherent to tropical Asia climate. The promising source of PAHs in the study area was also implicated, the result contributed to 3 possible sources which consist of road dust, fuel combustion and grass/wood combustion. These promising sources indicated that the high adverse anthropogenic impact to the ecological system in the study area.

4.4 Assessment of an occurrence of adverse ecological effects due to the levels of contamination with PAH

By using PAH diagnostic ratios in combination with the multivariate descriptive statistical techniques, the status of PAHs contaminations and their source apportionment were evaluated in the study area. The results showed that the high levels of PAHs contamination in coastal sediment were introduced by the 2004 Tsunami. The tsunami backwash carried the anthropogenic PAHs to the nearby coastal area as far as approximately 25 kilometers from the shoreline. ΣPAHs for 145 samples of the Phang Nga coastal sediments were in range of 11.9 to 272.0 ng g^{-1} dry weight, with an average of 57.1±35.7 ng g^{-1} dry weight. Therefore, the assessment of possibly adverse ecological effects due to the contaminated levels of PAHs is further needed to evaluate the possibility of occurrence of adverse ecological effects to benthic species by using Sediment Quality Guideline (SQGs).

Analysis of sediment pollution has been the basis for the development of different approaches to ecotoxicological risk evaluation (Neff et al., 2005; Wang et al., 2012). As a result, SQGs have been developed biological effects database for sediments (BEDS) which consist of information about the effects of sediment-associated contaminants, including spiked-sediment toxicity test data, matching sediment chemistry and biological effects data from field studies (MacDonald et al., 1996).

Numerical SQG were derived using the information in both data with effects and the data without effects. Statistical calculation led to two SQG values for each PAH. If concentrations with no biological effects were negligible, the effects range low (ERL) and the effects range medium (ERM) values were defined (Long and Morgan, 1990). The ERL was calculated as the 10th percentile and the ERM as the 50th percentile of the effects concentration.

In case of both effects and without effects data were used in calculations, the threshold effects level (TEL) and probable effects level (PEL) values were defined The TEL values were calculated as the geometric mean of the 15^{th} percentile of the effects data and 50^{th} percentile of the without effect dataset, while the PEL values were determined as the geometric mean of the 50^{th} percentile of the effects and 85^{th} percentile of the without effects data.

Basically, the ERL corresponds to TEL, and ERM to the PEL value. Both sets of values, PEL/TEL and ERL/ERM, define three concentration ranges for a chemical, including those that can be found rarely (below ERM or TEL), occasionally (above ERL or TEL but below ERM or PEL), and frequently (above ERM or PEL) associated with adverse effects on benthic species. Exceedances of ERM or PEL values classify the sediment as potentially toxic.

For the screening level concentration (SLC), is an estimate of the highest concentration of a contaminant that can be tolerated by a pre-defined proportion of benthic infaunal species. The SLC was defined as the concentration which the 95 % of the species can tolerate for the contaminant.

To conduct an environmental risk assessment for evaluating the possibility of occurrence of adverse ecological effects to benthic species due to the exposure to PAHs concentrated in the sediments, SLC, TEL, ERL, PEL and ERM effect have been used to assess the marine sediment (Long et al., 1995; Xu et al., 2007). Long et al. (1995) noted that correlation between impacts and chemical concentrations are fairly good for individual PAHs and total PAH, so that ERL and ERM values are useful in addressing sediment quality issues and provide qualitative guidelines on what needs to be done to effectively protect the aquatic environment. The SQGS values are shown in Table 4.6.

The measured concentrations of PAHs both of the average and maximum values were compared with the standard SQGs values. The results showed that the total PAH concentrations at all sites were below the SQGs values. For the individual PAHs, they were found that at all site did not exceed the SQG values (except for the sampling station 34; the highest ΣPAHs in this study). In station 34, the level of D[a,h]A (113.8 ng g^{-1}) is higher than the NOAA TEL and ERL values(62.2 and 63.4 ng g^{-1}, respectively). As a consequence, this station was classified as occasionally associated with adverse effects on benthic species.

Since the hot spot area have higher contribution from the 5-6 ring PAHS in most of stations in front of Pakarang Cape. As a consequence, the levels of high molecular weight (HMW) PAHs concentration were taken into consideration due to their high probably carcinogenic to human. However, the level of HMW PAHs contamination (the sum of Fluo, Pyr, B[a]A, Chry, B[b]F, B[k]F, B[a]P, B[e]P, B[g,h,i]P, D[a,h]A and Ind) for all sampling station did not exceed the lowest SQG values. It was concluded that the level of PAHs at all sampling stations should not exert adverse biological effects to marine environmental in Phang Nga coastal area.

Table 4.6 Assessment of the PAHs contamination by using numerical SQGs (ng g^{-1})

PAHs	NOAA TEL marine	TEL	ERL	SLC	NOAA PEL marine	PEL	ERM	Average	Maximum
Phe	86.68	90	240	270	86.68	540	1500	6.7	37.2
An	46.85	50	90	160	543.53	240	1100	1.6	8.9
LMW PAHs	311.7				1442			8.2	46.1
Fluo	112.82	110	600	640	1493.54	1490	5100	3.6	21.9
Pyr	152.66	150	660	660	1397.6	1400	2600	6.3	37.6
B[a]A	74.83	70	260	260	692.53	690	1600	1.6	9.9
Chry	107.77	110	380	380	845.98	850	2800	2.1	15.3
B[b]F		70	320	320		710	1880	2.6	16.1
B[k]F		60	280	280		610	1620	3.3	18.7
B[e]P								3.6	20.6
B[a]P	88.81	90	430	400	763.22	760	1600	2.2	11.7
Ind								6.6	38.4
D[a,h]A	62.2		63.4		134.61		260	13.7	113.8
B[g,h,i]P								6.4	46.5
HMW PAHs	655.34		1700		6676.14		9600	52.0	350.5
Total PAHs	1684.6	870	3500	4090	16770.4	8040	23580	35.7	272.0

4.5 Using PAHs as a chemical proxy for tracing the 2004 Tsunami

In Section 4.1, when arrange the top 20 highest ΣPAHs contaminated stations in coastal sediments, all of sampling station are located in front of the Pakarang cape. One of this study's hypothesis is "PAHs can be used as a "Proxy" to discriminate the terrestrial deposit from the background sediment for the first time in tsunami-affected coastal areas", as a consequence the intensive study for proving this hypothesis were carried out by investigation the hot spot sampling stations at the heavily affected area by the Tsunami 2004 where focus on the Khao Lak area.

During the research cruises in 3 years (2007,2008 and 2010), seafloor map were constructed using side scan sonar, multi-beam echo sounder and shallow reflection seismic with a boomer system along the study area. The seafloor mapping provides the useful visualization data for choosing the sediment which are the representative of terrestrial-derived PAHs from land during the Tsunami 2004.

The 70 of sampling stations were chosen on the basis of the data acquired from hydroacoustic mapping to investigate the sedimentary deposition on near-shore seabed (Feldens, 2011). Surface sediment samples were collected along the Khao Lak coastal area, in order to analyze the distribution of 13 individual PAHs. The sampling stations are shown in Figure 4.22.

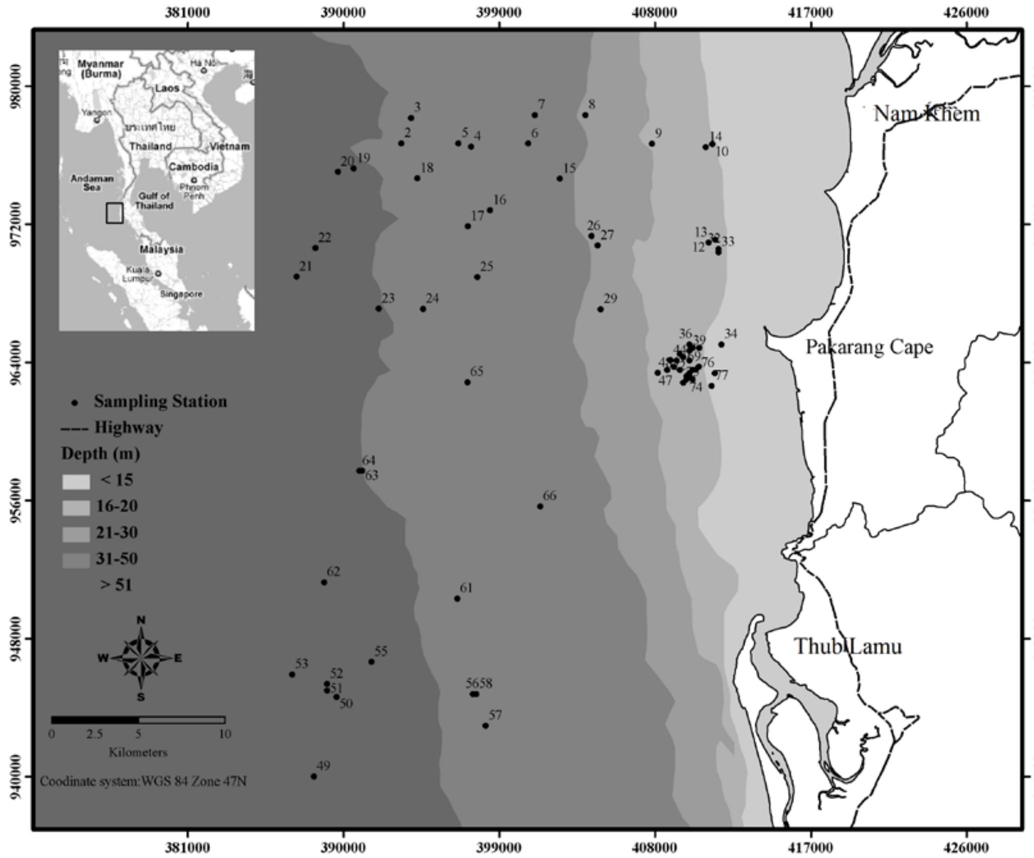


Figure 4.22 Sampling locations at Khao Lak coastal areas, Phang Nga coastal zone.

(The study area is indicated by the black box; Numbers indicate sampling stations;
the color contours represent the water depth)

In 26 December 2004, the Indian Ocean tsunami attacked the Andaman coastal zones in Thailand, especially in the Phang Nga coastal area. The powerful nature of 2004 tsunami resulted in extensive erosion and deposition of sediment throughout near-shore portions of the seabed in the Phang Nga coastal zones. The marine and terrestrial environments along the coastal zones were destroyed and widespread introduction of contaminated materials to the sea (UNEP, 2005; Tang et al., 2006; Zhang et al., 2008; Feldens et al., 2009). Therefore, in the area which was heavily affected by the withdrawal of tsunami wave should contain more terrigenous sediments and thus relatively high proportions of anthropogenic derived sediment-associated contaminants.

A number of approaches have been used to distinguish between marine and terrigenous components in marine sediments, including polycyclic aromatic hydrocarbons (PAHs), hopanes and cholestanes (Takada et al., 1991; Yunker et al., 1995, 2002; Tolosa et al., 2004; Mostafa et al., 2009). However, PAHs are amongst the most promising sediment-associated contaminants that can indicate the sedimentary deposition which has affected by tsunami backwash. This is due to the fact that they are known to enter aquatic environments through petroleum spills, coal and fossil fuels combustion, automobile exhausts, biomass burning and from non-point sources such as street runoff and atmospheric fall-out (Jiang et al., 2009; Tolosa et al, 2009; Ahrens and Depree, 2010).

For decades, PAHs have been used as a “chemical proxy” to distinguish the anthropogenic source and biogenic source in marine sediment (Christensen et al., 1996; Cantwell et al., 2007; Fang et al., 2009; Tobiszewski and Namieśnik, 2012). They can be categorized as anthropogenic combustion sources (i.e. oil spill, automobile exhaust, and street runoff) and as natural combustion sources (i.e. forest fires, volcano eruption) by using PAHs diagnostic ratios (Yunker et al., 2011, 2002; Yunker and Macdonald; 2003). PAHs of molecular mass 178, 202 and 258 are commonly used to distinguish between pyrogenic (combustion-derived) and petrogenic (unburned petroleum-derived) sources. In addition, Phe/Ant (m/z 178), Fluo/Pyr (m/z 202) and B[a]A/Chry (m/z 258) have been previously used by some works (Wang et al., 2006; Khairy et al., 2009; Liu et al., 2009). Because of their usefulness in source identification, the use of PAHs as a chemical proxy may provide better understanding of huge terrigenous sediments caused by the rare events such as the withdrawal of tsunami wave.

Like many newly 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 Khao Lak coastal area. Motor vehicle emissions, leakage of used oil, vehicle tire and asphalt road surfaces, are typically diffuse sources of the anthropogenic PAHs in the coastal areas (Brown and Peake 2006; Kose et al., 2008).

During the tsunami backwash, severe damages occurred including coastal shoreline erosion and destructive infrastructures such as buildings, road network, bridges, fishing vessels, as well as the near-shore environment. As a consequence, the anthropogenic PAHs were believed to be transported from the potential sources on land and deposited into the near-shore seabed. Moreover, their spatial distribution should provide the extinctive patterns (concentration profile from shoreline to off-shore, compositions and concentrations of transporting PAHs) different from the normal transporting mechanisms such as those associated with the annual reversals of monsoon and hydro-meteorological extreme events or high precipitation in rainy season.

In this section attempt to use PAHs spatial distribution for tracing the transport and distribution of land-derived materials which caused by the tsunami backwash to better understand how it may have affected the distribution of sedimentary deposition throughout the seabed in the Khao Lak coastal areas. In addition, the composition of the sedimentary PAHs of the Khao Lak coastal areas was analyzed using PAH diagnostic ratios in combination with the multivariate descriptive statistical techniques to distinguish among different sources of PAHs.

4.5.1 PAHs contamination in Khao Lak coastal area

ΣPAHs in the Khao Lak area, which was heavily destroyed by the tsunami runup, were in range of 12.6 to 272.0 ng g^{-1} dry weight, with an average of 64.5±44.3 ng g^{-1} dry weight. It should be noted that the PAHs concentrations detected in the Khao Lak coastal sediments are comparable with those contaminations found previously in other coastal area in South East Asian region (Table 4.7). However, they were in the similar range with Thai coastal area, and were much lower than other coastal area where has highly influence of human activities such as Jakata Bay.

Table 4.7 Comparisons of $\sum$PAHs in surface sediment collected from different coastal and bays (ng g^{-1} dry weight).

Location	Range	Mean	Reference
Phang Nga Coastal	12.6 - 272.0	64.5	This study
Gulf of Thailand			
Coastal areas	11-1,992	506	
Offshore areas			Wattayakorn, 2005
Upper Gulf	39-95	70	
Eastern Seaboard	11-324	79	
Lower Gulf	14-67	51	
Malaysian riverine and coastal	4-924	139.5	Zakaria et al., 2002
Jakarta coastal sediment, Indonesia	257-1511	-	Rinawati et al., 2012

Figure 4.23 shows the spatial distributions of sedimentary PAHs in the Khao Lak coastal area. The prominent feature of sediments exported from the Pakarang Cape can be observed. This evidence indicates that the tsunami backwash may play an important role in transporting anthropogenic PAHs to the nearby coastal area far from the shoreline up to approximately 25 km. It is also in good agreement with the study of Siripong (2006), who found that the tsunami wave height was over 15m high at Pakarang Cape. Such a giant wave could have a tremendous impact on transporting massive terrigenous sediments far from the shoreline, as evidenced from the distinct spatial patterns of PAHs concentrations.

Feldens et al. (2009) provide the strong evidence which can be confirmed the impact of 2004 Tsunami that carried the anthropogenically derived materials into the sediment in front of Pakarang Cape. They found that the impact was probably most effective during the backwash when stiff mud deposits containing grass, wood fragments and shells were transported by high density backwash flows.

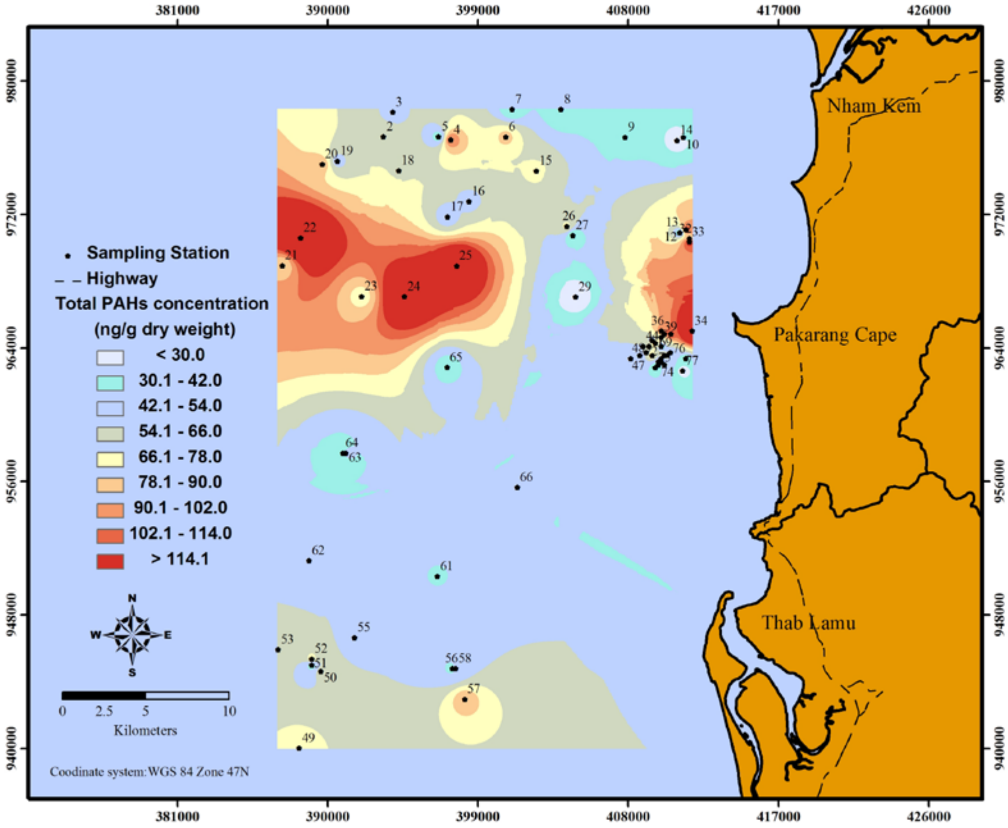


Figure 4.23 The spatial distribution of sedimentary PAHs in the Khao Lak coastal area.

(Numbers indicate sampling stations; the contour scale represents total PAHs concentrations as labeled in the legend)

Generally, PAH concentrations should gradually decrease offshore further along the distance far from the point source that has original concentration (Boonyatumanond et al., 2006). But the PAH concentrations from sediments exported from the Pakarang Cape increased further along the distance up to 25 kilometers. These behaviors are triggered by a rare event such as the Tsunami backwash not originating from normal transporting mechanisms such as those associated with the annual reversals of monsoon and hydro-meteorological extreme events or high precipitation in rainy season.

4.5.2 Source identification by diagnostic PAH isomer ratios

The characteristics of PAH patterns in the coastal sediments are subject to different emission sources. Thus, 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).

The four PAH isomer pairs used in the present study were An/(An+Phe) (m/z 178), Flu/(Flu+ Pyr) (MW 202), B[a]A/(B[a]A+Chry) (m/z 228), and Ind/ (Ind+B[g,h,i]P) (m/z 276). Table 4.8 shows ranges of the 4 diagnostic PAH ratios for petroleum and single-source combustion.

Table 4.8 Characteristic values of selected diagnostic ratios for petroleum and single-source combustion (Modified from Yunker et al., 2002).

Source	An/ (An+Phe)	Flou/ (Flou+Pyr)	B[a]A/ (B[a]A+Chry)	Ind / (Ind+B[g,h,i]P)
Petroleum				
Lubicating oil	-	0.29	0.10	0.12
Asphalt	-	-	0.50	0.52-0.54
Combustion				
Gasoline (n=2)	0.11	0.44	0.33-0.38	0.09-0.22
Road dust	0.18	0.42	0.13	0.51
Used engine oil, gasoline passenger car	0.22	0.30	0.50	0.18
Used engine oil, diesel car, truck and bus	-	0.37	-	0.29

Cross-plots between ratios B[a]A/(B[a]A+Chry) and Ind/(Ind+B[g,h,i]P) were applied to identify the potential sources of sedimentary PAHs in study area. The results indicated that most of sediment samples originated from the mixed pyrogenic sources as results of the incomplete combustion, pyrolysis of fuel, biomass burning and oil burning.

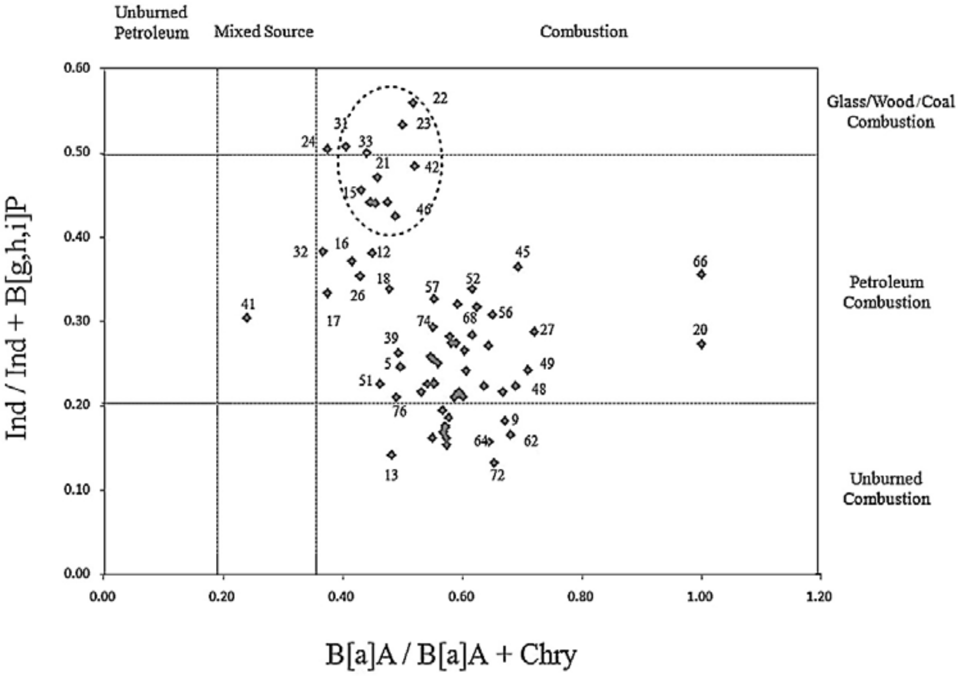


Figure 4.24 Cross-plot between ratios Ind/Ind+B[g,h,i]P and B[a]A / B[a]A+Chry in Khao Lak area.

(Numbers indicate sampling stations; The dashed circle represents the stations which PAHs were originating from road paving asphalt)

On the basis of the results shown in Table 4.7, the B[a]A/(B[a]A+Chry) and Ind/(Ind+B[g,h,i]P) ratios were 0.50 and 0.52–0.54, respectively, indicating the plausible emission source from asphalt pavements. Moreover, Yang et al. (2010) reported that even minimal contamination of sediments with pavement material may lead to a significant input of PAHs to the aquatic environment. This agreed with our results that hot spot stations (22, 25, 31, 33 and 42 in Fig. 4.23) showed the higher concentration of total PAHs. The signature diagnostic PAHs isomer ratios, which indicated to road paving asphalt were observed in the stations 22, 25, 31, 33 and 42 (The dashed circle in Figure 4.24). This result indicated that the promising PAH sources of these stations originated from the road paving asphalt heavily eroded by the tsunami wave in front of Pakarang Cape.

Pomonis et al. (2005) reported that the damage to the road surface was observed in the areas near the Khao Lak coastline. This damage was probably due to increased pore water pressure under the flexible pavement. This evidence was visible on small areas of road surface adjacent to the beach front and especially on grasscrete surfaces (e.g. at Kamala Beach and Pakarang Cape).

From the results derived from the diagnostic PAH isomer ratios, it meets our attempted goal to use PAHs as a chemical proxy to trace the transport of land-derived materials caused by the tsunami backwash. The diagnostic PAH isomer ratios provide clear evidence that the anthropogenic PAHs were transported from the coastal land and deposited into the nearshore seabed during the tsunami backwash.

Nevertheless, it is important to note that isomer pair ratios of the entire dataset were not restricted to the extreme values of only specific source, because there is a chance to misinterpret when the mixtures of heterogeneous PAH sources are analyzed, especially in the case of the powerful and strongly turbulent tsunami wave that can transport the PAH contaminated materials to the sea floor all at once (Tang et al., 2006).

4.5.3 Source estimation from HCA

HCA was performed to identify the homogeneous groups of individual PAHs in the Khao Lak sediment. The hierarchical dendogram is shown in Figure 4.24. What emerged from these results is that three major groups of the 13 individual PAHs were clearly distinguished. The first group contains B[a]A, Chry, B[b]F, B[k]F, B[a]P and An, which originated from the pyrogenic source (Fang et al., 2009; Liu et al., 2009). Motor vehicle emissions both of gasoline and diesel emission, leakage of used oil and road dust have been previously identified as original sources of this group (Dahle et al., 2003).

According to the literature reports, the 3–4 ring PAHs have been found in the road dust in urban cities as well (Zakaria et al., 2002; Boonyatumanond et al., 2007).
The second group consists of B[e]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 originated from road

paving asphalt, crude oil, bitumen (Ahrens and Depree, 2010) and road dust (Larsen and Baker, 2003). The last group comprises Pyr, Fluo and Phe, which are the anthropogenic PAHs from the using of petroleum products (Zhou et al., 1999). It is reasonable to say that three of the potential sources which were identified by HCA could be transported from original sources during the tsunami backwash as we expected.

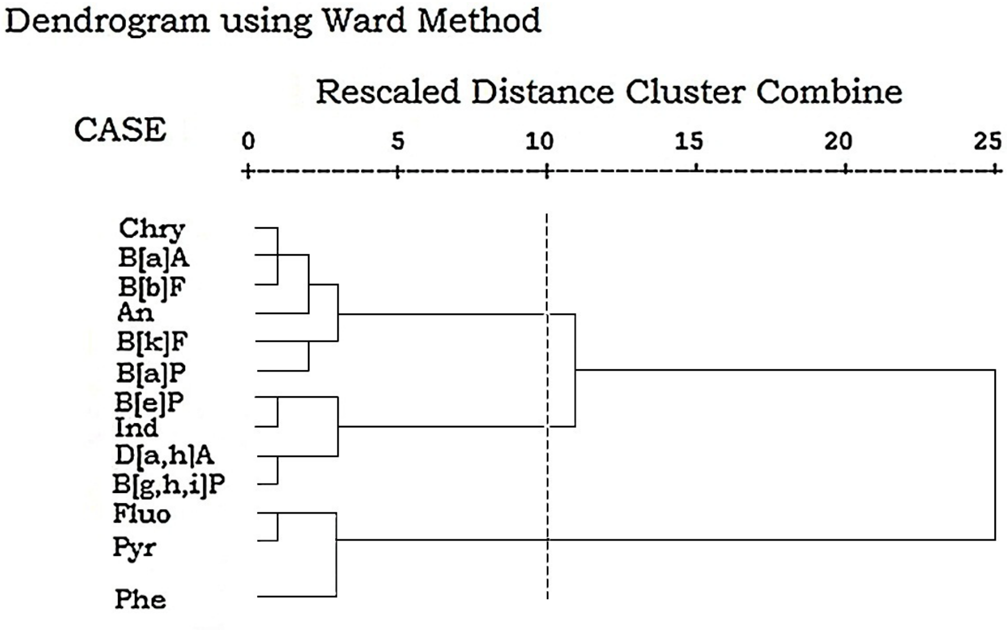


Figure 4.25 The hierarchical dendogram of 13 individual PAHs in Khao Lak sediment.

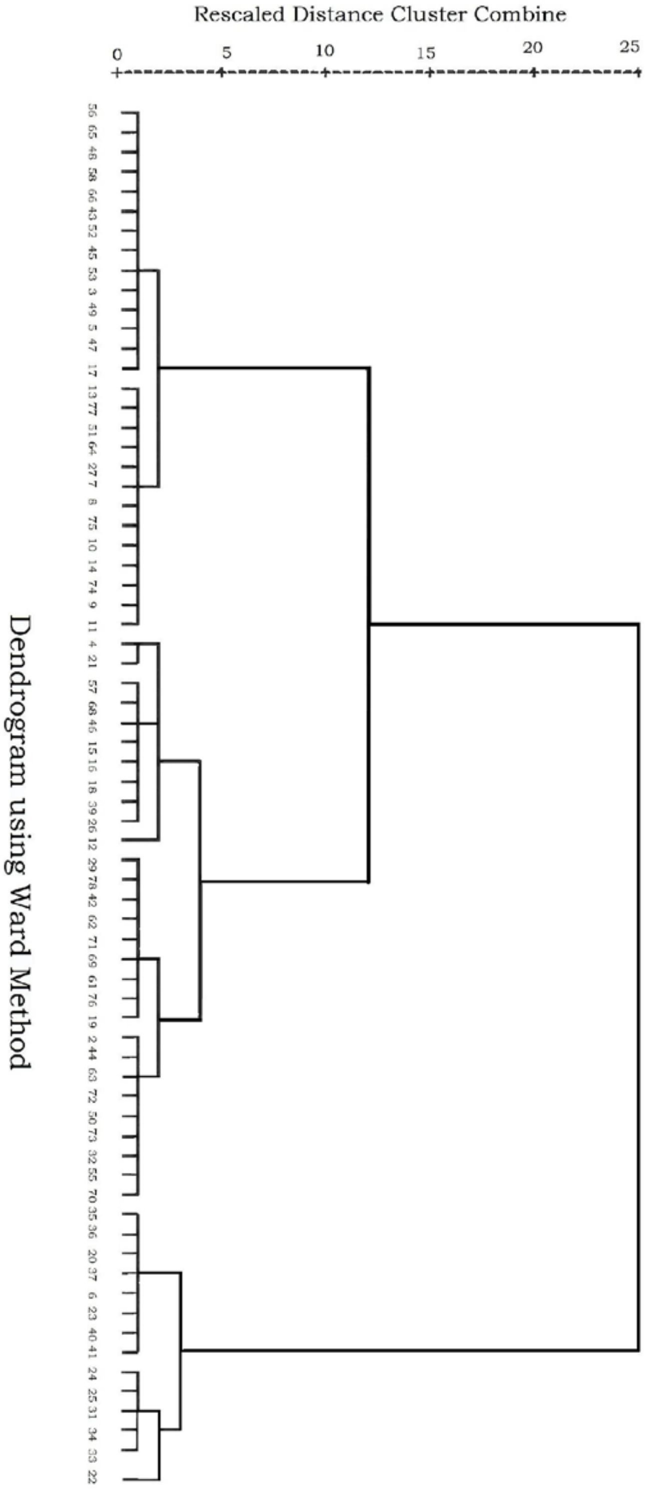


Figure 4.26 The hierarchical dendogram of 70 individual sampling stations in Khao Lak sediment.

Moreover, the results based on the cluster analysis by the 70 individual sampling stations revealed two major groups as shown in Figure 4.26. The first group includes stations 6, 20, 22, 23, 24, 25, 31, 33, 34, 35, 36, 37, 40 and 41. All of these stations have distinct characteristics from other areas, consistent with what is documented in Figure 4.23. Thus, this group should be the representative of the tsunami backwash and so results can provide the approximate direction of the tsunami backwash that was transported from the shoreline at Pakarang Cape back to far further than 25 km into the seabed. In contrast, the second group includes the rest of sampling stations. The nearby group which has less linkage distance between homogeneous groups (more similarity), contains stations 2, 32, 44, 50, 55, 63, 70, 72 and 73, and also indicates the influence of the Tsunami backwash.

4.5.4 Source identification by PCA

In this study, concentrations of 13 PAHs and the 70 samples were selected as active variables and subjects, respectively. The majority of the variance (73.0 %) of the scaled data was explained by two eigenvectors–principal components. The first principal component (PC1) can explain 61.4% of the total variance, and the second (PC2) can explain 11.6% of the total variance, respectively, as shown in Table 4.9.

The PC1 is heavily weighted in B[b]F, B[e]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 road paving asphalt, crude oil, bitumen and road dust. Therefore, the PC1 is a representative of the road dust sources of PAHs. In contrast, the PC2 is predominately composed of Pyr and Fluo. This group usually originates from the use of petroleum product and oil combustion. Fang et al. (2006) reported that high loadings of Pyr and Fluo indicated incomplete combustion, pyrolysis of fuel and oil burning. This factor is believed to be the oil burning source of PAHs.

Table 4.9 Rotated component matrix of 13 PAHs from Khao Lak coastal sediments.[a]

PAH composition	Principle components (PC)	
	PC1	PC 2
Phe	0.02	0.58
An	0.08	0.53
Fluo	0.12	**0.88**
Pyr	0.04	**0.86**
B[a]A	0.15	0.54
Chry	0.24	0.48
B[b]F	0.47	0.22
B[k]F	**0.75**[b]	0.18
B[e]P	**0.89**	0.19
B[a]P	0.60	0.42
Ind	**0.91**	0.03
D[a,h]A	**0.93**	0.17
B[g,h,i]P	**0.92**	-0.10
Variance (%)	**61.4**	**11.6**
Estimated source	**Road dust**	**Oil burning**

[a] *Rotation Method: Varimax with Kaiser Normalization*

[b] *Bold loading > 0.70*

Since a tsunami wave can have tremendous impacts on transporting a large amount of terrigenous sediments to the sea, the mixtures of heterogeneous PAH sources are needed to take into account source identification. Even though the PCA results are similar to those of the HCA, the estimated sources from the PCA can reduce the estimated sources from three (HCA) to two sources. Thus, the PCA makes it easier to interpret the estimated sources. A significant correlation identified by PCA, which indicates 2 estimated sources of the PAHs signatures, clearly supports our hypothesis that PAHs were transported from the potential sources on land and deposited into the near-shore seabed during tsunami backwash.

By analyzing the compositions of sedimentary PAHs in combination with application of the multivariate descriptive statistical techniques, PAHs were proven to be a promising chemical proxy to indicate the tsunami backwash which have affected to near-shore portions of the seabed in the Khao Lak coastal zones.

The PAHs spatial distribution could indicate the distance at which the land-derived materials were transported offshore as a result of the tsunami backwash. The prominent feature of surface sediments exported from the Pakarang Cape could be observed. This evidence indicates that the tsunami backwash plays an important role in transporting anthropogenic PAHs to the nearby coastal area as far as approximately 25 kilometers from the shoreline. In addition, the results from diagnostic PAH isomer ratios suggested that road paving asphalt, originated from heavy erosion by the tsunami wave in front of Pakarang Cape, was among the identified sources of PAHs.

Moreover, PCA results provided 2 estimated land-derived sources of PAHs which were the road dust and oil burning sources. These estimated signature source clearly support our hypothesis that PAHs were transported from the potential sources on land and deposited into the near-shore seabed during tsunami backwash. However, the temporal distribution is needed to validate our innovative study in further work.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study, types and concentrations as well as sources of PAHs were assesses in the Phang Nga costal area to better understand the predominant anthropogenic PAHs sources, the plausible transporting mechanisms and the potentially adverse ecological impacts of PAH contaminants. This obtained knowledge will greatly support to improve the ability to design effective management and remediation strategies for degraded coastal ecosystems induced by various human activities and unprecedentedly extreme event, and to support decision-making processes for relevant management authorities. To the best of my knowledge, this is the first assessment of PAHs contamination in the coastal area where was heavily affected by the 2004 Indian Ocean Tsunami. Based on the results, the Phang Nga coastal sediments can be classified as low to moderate contamination of PAHs with the values in range of 11.9 - 272.0 ng g^{-1} dry weight, whereas soil samples are considered as low to high (22.0 - 2083.8 ng g^{-1} dry weight) contamination with PAHs.

The distribution pattern of PAHs in the background group can be characterized as pyrogenic in origin due to relatively higher contribution from HMW PAHs with 4~6 rings and sources because of no petrogenic point sources from mainland in that area (Koh Phra Thong). In case of the hot spot group, the result can be indicated the totally different of its distribution pattern. The hot spot area have higher contribution from the 5-6 ring PAHS in most of stations. The highest percentage of 5-6 ring PAHs was found at stations in front of Pakarang Cape, indicating fuel combustion or street run-off as the predominant sources.

The source apportionment of the Phang Nga coastal sediment was identified by the spatial distribution, diagnostic PAHs ratios, source fingerprint, HCA and PCA. The diagnostic PAHs ratios and fingerprints indicated that the promising PAH sources might be originated from the traffic-related sources such as petroleum combustion, street dust, road paving asphalt, tires and leaking of petroleum used by shipping activities. In addition, application of the multivariate descriptive statistical techniques (e.g. HCA and PCA) also identified the three possible sources of PAHs to be road dust, fuel combustion and grass/wood combustion. As a consequence, all of the promising sources implied that this coastal marine have been impacted with high anthropogenic activities. Their ability to identify the dominant sources of PAH contamination is usefulness to manage the risk of PAHs to environmental and human health. It meets the objective of this study to simplify the dominant sources for improved ability to design effective management and remediation strategies for degraded coastal ecosystems.

The land to sea transportation has been proven by the spatial distribution, diagnostic PAHs ratios, HCA and PCA. The dominant mechanism of land to sea transportation is the introduction of the huge sediment into seabed by the 2004 Tsunami. Moreover, for non Tsunami-affected samples, it was also found the land to sea transportation but their possible mechanisms may be by those associated with the annual reversals of monsoon and high precipitation in rainy season.

The distribution of PAHs in aerosol, soil and sediment were additionally clarified, It was found that the input of anthropogenic PAHs originated from 3 possible pathways consists of atmospheric fall-out, street run-off (including the unusual event such as the Tsunami 2004) and soil erosion due to heavy effect from the strong rain associated with the Asia monsoonal climate.

The measured concentrations of PAHs were compared with the SQGs values. Results showed that the total PAH concentrations at all sites were below the ERL value. Moreover, individual PAHs found at all sites did not exceed the ERL value (except station 34, D[a,h]A is higher than the NOAA TEL and ERL values. These findings indicated that no samples may frequently pose biological impairment.

Since the hot spot area have higher contribution from the 5-6 ring PAHS in most of stations in front of Pakarang Cape. As a consequence, the levels of high molecular weight (HMW) PAHs concentration were taken into consideration due to their high probably carcinogenic to human. However, the level of HMW PAHs contamination for all sampling station did not exceed the lowest SQG values. It indicated that the level of PAHs at all sampling stations should not exert adverse biological effects to marine environmental in Phang Nga coastal area.

By analyzing the compositions of sedimentary PAHs in combination with application of the multivariate descriptive statistical techniques, PAHs were proven to be a promising chemical proxy to indicate the tsunami backwash which have affected to near-shore portions of the seabed in the Khao Lak coastal zones. The PAHs spatial distribution could indicate the distance at which the land-derived materials were transported offshore as a result of the tsunami backwash. One of the noteworthy results derived from this analysis is the prominent feature of surface sediments exported from the Pakarang Cape could be observed. This evidence suggests that the tsunami backwash plays an important role in transporting anthropogenic PAHs to the nearby coastal area as far as approximately 25 kilometers from the shoreline. In addition, the results from diagnostic PAH isomer ratios showed that road paving asphalt, originated from heavy erosion by the tsunami wave in front of Pakarang Cape, was among the identified sources of PAHs. On the basis of PCA results, two estimated land-derived sources of PAHs which are the road dust and oil burning were identified. These estimated signature source further support the hypothesis that PAHs were transported from the potential sources on land and deposited into the near-shore seabed during tsunami backwash.

As results, the promising sources of PAHs in the study area are non-point sources pollution which originated from road dust, fuel combustion and grass/wood combustion. Because nonpoint sources of pollution are so diverse, and each individual source may contribute only a small quantity of contaminants to coastal sediments. The identification of the exact sources of non-point sources pollution is evaluated, but the management actions are still needed to help solve the problem of PAHs accumulation in marine environment.

The alternative solutions to manage with the non-point source PAHs in the study have to take into consideration. First, the highly PAHs contamination with the road paving asphalt during the erosion by Tsunami wave should replace to be the free PAHs material such as concrete for shoreline road construction. Second, the buffer zone is needed for preventing the street dust run-off such as the design of sediment trap in waterway construction, the conservative of the peat land/mangrove to be the natural filtration for the coastal sediment and the design of artificial pond for trapping the street dust and then easily remediate. Reducing the amount of private vehicle to entrance to the beach area and encouragement for using the public transportation is significant to prevent the prominent source of PAHs contamination in the beach area. Urban planning is needed to minimize the anthropogenic influence to the ecological system in the study area.

5.2 Recommendations

1) It is important to note that isomer pair ratios of the entire dataset were not restricted to the extreme values of only specific source, because there is a chance to misinterpret when the mixtures of heterogeneous PAH sources are analyzed, especially in the case of the powerful and strongly turbulent tsunami wave that can transport the PAH contaminated materials to the sea floor all at once.
2) The combination between the technology, enforcement and encouragement of the stakeholders are needed for managing with the non-point sources PAHs contamination in the marine environment.

3) Since Thailand national guideline has not yet been established for managing PAHs contaminated sediment, the strategy for management cannot enforce for the violators
4) Frequent and heavy rain inherent to the tropical climate should be investigate to better understand greater erosion of soil materials and, therefore, larger inputs of sediments to rivers and coastal waters.
5) Analysis of PAHs in sediment cores (temporal distribution) may supply information on the historical trends of the activities of PAH pollution sources.
6) To gain a comprehensive understanding of pathways of PAH transport in aquatic environments, the other molecular markers (*e.g* hopane and methyl PAHs) are needed in future research.

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APPENDICES

APPENDIX A

PAHs analysis

A.1 Accuracy test with SRM 1941b

Table A.1 Accuracy test with SRM 1941b

SRM	Abbr	n	Reference Valve ng/g dry weight	Measuring Valve ng/g dry weight	%Accuracy
Phenanthrene	Phe	8	406 ± 44	486 ± 66	120 ± 16
Fluoranthene	Fluo	8	651 ± 50	733 ± 79	113 ± 12
Pyrene	Pyr	8	581 ± 39	551 ± 65	95 ± 11
Benzo[a]anthracene	B[a]A	8	335 ± 25	277 ± 46	83 ± 13
Chrysene	Chry	8	291 ± 31	227 ± 83	78 ± 28
Benzo[b]fluoranthene	B[b]F	8	453 ± 21	396 ± 134	87 ± 29
Benzo[k]fluoranthene	B[k]F	8	225 ± 18	197 ± 86	88 ± 38
Benzo[e]pyrene	B[e]P	8	325 ± 25	409 ± 175	126 ± 53
Indeno[1,2,3-cd]pyrene	Ind	8	341 ± 57	438 ± 92	129 ± 26
Benzo[g,h,i]perylene	B [g,h,i]P	8	307 ± 45	382 ± 84	124 ± 27

Table A.2 Mean percent recoveries of d_{10}-fluorene and d_{12}-perylene.

Compound	Mean Recovery (%)	Range
d_{10}-fluorene	90	35-145
d_{12}-perylene	75	24-150

Table A.3 Instrument detection limit (IDL) of PAHs analysis.

PAH_s	$[M]^+$	RT (Second)	IDL ($pg\ \mu l^{-1}$)
Phe	178	1294	2.63
An	178	1303	2.80
Fluo	202	1507	1.47
Py	202	1546	1.35
B[a]A	228	1764	2.41
Chry	228	1768	2.55
B[b]F	252	1942	48.66
B[k]F	252	1946	43.42
B[a]P	252	1982	45.54
B[e]P	252	1993	70.32
D[a,h]A	276	2175	61.25
Ind	278	2184	50.90
B[g,h,i]P	276	2227	15.52

[M]+: Molecular ion, RT: Retention time

APPENDIX B

Level of PAHs contamination

B.1 Level of each of PAHs and total PAHs (ΣPAHs) contamination in coastal sediment, soil and aerosol.

Table B.1 Level of each of PAHs and total PAHs (ΣPAHs) contamination in sediment samples (ng g^{-1} dry weight).

Stations	Phe	An	Fluo	Pyr	B[a]A	Chry	B[b]F	B[k]F	B[e]P	B[a]P	Ind	D[a,h]A	B[g,h,i]P	∑ PAHs
2	8.7	0.5	1.4	2.6	0.2	0.3	n.d.	6.5	2.6	n.d.	4.9	13.4	18.6	60.1
3	17.6	4.3	8.9	16.3	0.3	0.2	n.d.	n.d.	0.1	0.1	0.1	0.2	0.3	48.5
4	16.3	2.1	21.9	22.8	3.9	5.2	1.3	0.7	1.1	0.7	1.3	12.2	1.5	100.3
5	15.4	0.8	5.5	7.0	0.8	0.8	0.1	0.2	0.1	0.1	0.2	2.1	0.6	34.7
6	12.4	1.7	3.3	10.2	0.5	0.3	1.7	2.8	4.6	3.3	2.9	28.3	7.7	79.9
7	16.0	2.2	3.2	7.7	0.4	0.3	0.1	0.1	0.1	n.d.	n.d.	0.5	0.2	31.1
8	15.4	2.0	4.0	8.0	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.2	0.2	30.7
9	22.3	3.3	2.8	2.7	0.7	0.3	n.d.	n.d.	0.2	n.d.	0.1	0.5	0.6	34.6
10	14.6	0.8	8.3	4.2	0.4	0.3	0.1	0.1	0.2	0.1	0.2	0.5	1.1	31.5
11	7.1	1.2	1.0	1.6	0.3	0.2	n.d.	n.d.	0.1	n.d.	0.1	0.2	0.3	12.6
12	36.7	7.4	6.3	6.1	4.5	5.5	5.1	1.4	4.3	2.7	5.8	6.6	9.4	112.3
13	11.9	1.3	2.1	2.8	0.6	0.7	n.d.	n.d.	0.6	0.1	0.3	0.5	2.1	23.6
14	14.9	2.2	1.7	4.2	0.6	0.5	0.1	0.1	0.1	n.d.	0.1	0.7	0.2	26.2

Stations	Phe	An	Fluo	Pyr	B[a]A	Chry	B[b]F	B[k]F	B[e]P	B[a]P	Ind	D[a,h]A	B[g,h,i]P	∑ PAHs
15	20.6	2.5	5.0	7.7	1.2	1.5	n.d.	n.d.	0.9	0.1	2.2	19.1	2.7	66.3
16	16.7	2.2	2.6	3.7	1.0	1.4	1.6	1.4	1.7	n.d.	2.2	7.8	3.8	48.6
17	20.2	2.5	6.4	7.0	0.5	0.9	n.d.	n.d.	0.6	0.1	0.5	3.0	1.1	44.7
18	27.9	2.4	6.7	9.3	1.5	1.7	n.d.	3.0	1.2	n.d.	1.5	3.7	2.9	64.0
19	4.4	0.8	4.9	11.2	1	0.7	n.d.	n.d.	n.d.	0.1	n.d.	16.7	6.5	47.8
20	23.2	2.7	7.5	20.8	0.5	n.d.	n.d.	4.5	2.9	n.d.	1.5	14.8	4.1	83.6
21	15.1	1.4	11.8	25.5	4.8	5.8	0.8	1.2	1.3	1	0.7	2.7	0.8	75.6
22	21.3	3.2	5	10.5	1.3	1.2	16.1	18.1	12.7	0.1	21.1	72.6	16.6	202.7
23	12.1	1.5	1.8	4.4	0.5	0.5	3.9	4.8	3.7	1.9	4.8	23.9	4.2	69.6
24	21.6	2.2	14.6	13.6	1.0	1.6	n.d.	7.7	11.7	8.6	20.8	21.4	20.4	158.3
25	17.4	2.3	14.2	18.1	1.1	1.4	n.d.	n.d.	18.5	11.2	16.9	41.5	21.5	170.2
26	22.1	7.9	5.8	14.9	1.6	2.1	n.d.	n.d.	1.8	0.9	1.3	3.0	2.5	67.4
27	15.4	0.5	1.8	9.9	0.3	0.1	n.d.	n.d.	0.7	n.d.	0.5	n.d.	1.1	30.8
29	4.3	0.3	1.7	5.2	0.2	0.1	n.d.	n.d.	1.3	0.1	1.0	1.4	3.6	19.8
31	10.6	1.1	11.8	12.7	0.4	0.7	5.8	4.1	11.4	4.7	15.4	11.8	14.9	110.8
32	17.1	2.2	4.3	8.9	0.5	0.9	n.d.	n.d.	5.1	n.d.	8.7	4.5	14.1	67.7
33	15.2	1.5	7.4	8.4	0.9	1.1	n.d.	n.d.	20.6	0.1	22.3	24.7	22.3	128.8
34	19.0	2.4	17.0	18.5	0.6	0.5	4.6	3.8	4.0	5.1	13.6	113.8	46.5	272.0
35	11.2	2.1	10.6	18.2	0.6	0.5	n.d.	6.9	12.4	2.7	5.9	27.4	17.0	117.0
36	16.4	2.0	6.6	15.1	0.4	0.3	n.d.	12.0	8.1	n.d.	4.4	25.2	12.8	104.3
37	16.1	2.0	10.4	23.8	0.5	0.5	n.d.	8.9	7.3	3.1	0.1	24.1	6.2	104.1
39	15.0	1.6	7.1	10.4	0.7	0.7	n.d.	1.4	1.6	0.1	0.6	3.9	1.7	46.2

Stations	Phe	An	Fluo	Pyr	B[a]A	Chry	B[b]F	B[k]F	B[e]P	B[a]P	Ind	D[a,h]A	B[g,h,i]P	∑ PAHs
40	16.1	2.6	5.6	13.6	0.4	0.4	n.d.	9.3	10.7	7.7	3.9	15.7	5.0	92.1
41	23.0	1.6	2.5	5.4	0.2	0.5	n.d.	13.0	6.7	7.2	5.7	25.3	13.0	104.5
42	5.9	0.3	1.3	2.5	0.1	0.1	n.d.	n.d.	0.1	n.d..	3.5	3.6	3.8	21.5
43	16.8	1.3	15.9	21.9	0.3	0.3	n.d.	n.d.	0.8	0.1	n.d.	n.d.	0.3	65.2
44	13.4	1.3	2.2	2.7	0.3	0.2	n.d.	3.8	5.9	n.d.	2.4	8.5	9.8	50.9
45	27.6	2.8	6.1	14.5	0.4	0.2	n.d.	n.d.	0.3	0.1	0.5	0.4	0.8	54.6
46	13.2	1.3	15.7	37.6	1	1	1.5	1.8	2.2	1.1	2.2	4.8	3	87.7
47	12.3	1.4	5.2	11.9	0.9	0.7	0.2	0.2	0.2	n.d.	0.3	1.1	1.2	36.9
48	14.5	1.6	5.5	15.9	0.5	0.2	0.2	n.d.	0.4	0.4	0.3	0.7	1.0	41.7
49	37.2	4.1	7.4	15.9	0.6	0.2	0.6	n.d.	1.0	0.1	0.7	1.4	2.0	71.6
50	11.2	1.5	5.4	6.8	0.2	0.1	1.8	1.7	3.1	n.d.	4.1	9.7	10.9	57.0
51	13.9	1.6	2.8	5.2	0.4	0.5	n.d.	0.3	0.3	0.3	0.8	0.7	2.9	32.8
52	19.4	1.6	14.4	32.6	0.5	0.3	n.d.	n.d.	0.6	0.1	0.5	0.5	1.0	72.6
53	27.9	2.9	8.5	15.8	0.2	0.1	n.d.	0.3	0.5	n.d.	0.3	0.6	0.7	60.9
55	10.6	1.3	2.6	6.4	0.4	0.2	n.d.	n.d.	3.7	0.1	5.4	5.2	13.6	50.1
56	13.5	1.5	5.7	12.7	0.3	0.1	0.0	n.d.	0.7	n.d.	0.4	0.7	0.9	37.0
58	15.6	1.7	5.9	12.4	0.3	0.2	n.d.	0.0	0.9	0.4	0.3	0.6	0.9	48.1
57	25.4	3.0	4.3	18.2	0.8	0.6	2.5	2.4	2.5	1.5	3.9	10.4	8.1	85.5
61	14.3	1.9	4.7	11.2	0.4	0.3	0.8	0.4	0.5	0.3	1.2	1.7	3.1	41.6
62	13.8	2.1	4.7	11.1	0.5	0.2	0.8	0.3	1.0	0.1	1.3	3.2	6.5	46.2
63	12.1	1.6	3.1	7.5	0.4	0.4	0.0	1.1	1.7	n.d.	3.4	4.9	12.4	49.4

Stations	Phe	An	Fluo	Pyr	B[a]A	Chry	B[b]F	B[k]F	B[e]P	B[a]P	Ind	D[a,h]A	B[g,h,i]P	∑ PAHs
64	12.5	1.4	4.1	6.6	0.3	0.2	n.d.	0.6	0.7	0.1	0.3	0.3	1.5	28.9
65	15.4	1.8	5.3	10.4	0.3	0.2	n.d.	n.d.	0.7	n.d.	0.5	0.5	1.2	36.4
66	10.6	1.5	7.5	21.2	0.3	n.d.	n.d.	0.2	0.4	0.1	0.5	0.1	0.8	43.6
69	11	1.2	3.8	10.5	0.3	0.2	n.d.	0.8	1.1	0.1	1.4	1.9	6.9	39.4
70	16.8	2.2	9.2	23.6	0.4	0.3	n.d.	0	2.1	n.d.	3.1	5	13.4	76.4
68	12.6	1.4	4.1	16	0.7	0.5	1.8	1.7	1	0.9	1.6	6	3.3	53.1
71	12.4	1.8	5.6	13.1	0.7	0.5	n.d.	n.d.	1	0.1	1.9	3.2	8.9	50.6
72	9.7	1.1	3.7	8.0	0.3	0.2	0.8	0.6	1.4	0.4	3.0	5.8	15.3	50.9
78	9.4	1.4	1.8	3.4	0.4	0.2	n.d.	n.d.	1.4	n.d.	1.8	3.5	6.4	30.3
73	14.6	1.8	10.7	9.4	0.3	0.2	1.2	1.5	2.0	0.1	2.0	6.7	13.1	63.6
74	14.2	0.9	2.7	4.2	0.3	0.3	n.d.	0.1	0.1	n.d.	0.1	0.2	0.3	23.7
75	12.7	1.1	4.0	8.1	0.2	0.2	n.d.	n.d.	0.1	0.1	0.1	0.2	0.5	27.5
76	11.1	1.0	4.0	9.1	0.2	0.2	1.1	n.d.	0.9	n.d.	0.7	0.6	3.6	32.7
77	11.8	1.6	1.7	3.4	0.2	0.1	n.d.	n.d.	0.4	0.1	0.5	0.6	1.6	22.3
79	15.1	8.9	4.7	5.6	1.9	4.1	2.3	1.1	0.5	0.3	1.0	1.9	5.5	52.9
80	9.3	2.9	2.0	7.7	2.4	1.3	3.9	0.5	0.3	10.2	5.9	5.1	0.3	51.8
81	9.1	1.9	3.8	6.7	0.9	0.3	0.2	3.2	0.4	3.2	0.9	1.5	0.2	32.3
82	11.7	6.0	5.2	9.3	1.6	1.5	0.5	1.7	1.1	1.3	1.7	2.6	2.2	46.4
83	8.4	3.6	4.7	5.1	1.4	1.4	0.6	1.7	2.0	0.4	7.2	6.6	3.4	46.4

Stations	Phe	An	Fluo	Pyr	B[a]A	Chry	B[b]F	B[k]F	B[e]P	B[a]P	Ind	D[a,h]A	B[g,h,i]P	∑ PAHs
84	6.2	3.2	3.3	2.4	1.3	1.0	2.9	1.3	0.7	0.8	3.7	4.3	4.9	36.1
85	6.8	1.5	2.9	3.5	0.5	0.1	0.6	1.2	1.6	0.3	2.3	0.8	7.0	29.2
86	4.2	1.6	5.5	3.0	3.0	0.6	2.6	1.2	0.8	1.0	1.2	1.8	1.1	27.7
87	5.7	1.2	1.5	1.7	0.5	0.2	1.3	1.1	0.6	1.4	1.2	1.0	9.6	26.8
88	6.6	2.0	1.5	1.0	1.0	1.0	1.1	0.4	0.6	0.5	0.7	4.2	1.5	22.3
89	4.2	1.3	2.8	1.5	0.5	0.8	3.6	1.4	0.7	0.8	12.6	1.8	1.8	33.8
90	2.5	1.2	3.1	1.6	1.1	0.9	9.3	2.6	2.6	3.9	3.4	22.1	2.7	57.1
91	8.6	2.8	6.0	6.3	3.3	1.0	9.4	0.8	0.7	0.5	4.6	10.4	3.7	58.2
92	3.5	1.5	2.0	3.2	0.6	0.8	0.4	3.0	1.0	1.9	6.3	1.8	3.4	29.2
93	5.5	1.6	3.5	4.9	1.7	0.6	0.3	0.8	0.3	0.7	3.2	1.8	12.7	37.7
94	9.5	5.7	8.8	9.6	1.9	0.8	2.4	3.1	3.5	1.7	1.4	1.8	11.0	61.3
95	8.3	1.7	7.2	4.9	2.0	2.0	0.9	1.2	0.7	0.7	6.4	24.5	3.6	64.2
96	9.3	1.3	5.7	8.3	1.0	0.5	0.3	1.8	2.5	1.9	3.4	4.0	1.3	41.2
97	8.4	3.0	4.8	2.4	3.3	0.4	1.8	1.0	0.7	0.4	0.8	1.4	2.6	31.2
98	7.7	2.8	5.1	2.7	2.0	1.2	0.6	0.3	1.1	0.3	0.2	2.4	1.0	27.6
99	13.0	2.4	3.7	5.1	4.0	11.2	0.4	2.8	1.6	0.9	8.8	2.4	1.5	57.8
100	20.0	4.1	3.8	5.6	6.0	1.4	1.1	1.2	1.1	1.3	7.0	1.1	1.1	54.8
101	5.1	3.2	3.7	5.1	0.4	0.2	0.6	1.0	1.2	0.9	3.6	2.0	1.8	28.7
102	14.3	5.7	4.9	6.6	1.5	1.3	1.9	1.4	0.5	1.1	10.2	1.4	1.0	51.7

Stations	Phe	An	Fluo	Pyr	B[a]A	Chry	B[b]F	B[k]F	B[e]P	B[a]P	Ind	D[a,h]A	B[g,h,i]P	∑ PAHs
103	8.9	4.0	5.8	6.5	1.5	1.1	0.4	2.2	1.1	2.0	1.3	6.9	0.9	42.5
104	7.5	5.8	4.3	6.9	0.4	2.3	1.2	0.1	6.5	1.0	0.4	1.8	2.3	40.6
105	6.3	3.3	3.4	6.1	1.9	0.6	1.3	2.0	0.5	0.8	3.1	3.9	3.5	36.6
106	18.7	6.9	5.5	9.7	0.9	0.3	4.9	0.6	0.7	4.4	12.1	1.8	0.9	67.5
107	7.7	4.2	2.6	5.9	1.6	1.4	2.4	1.5	0.6	2.8	0.7	2.4	3.0	36.9
108	6.0	3.8	2.1	4.7	0.4	1.2	2.3	1.4	1.0	1.1	8.5	3.6	2.0	38.1
109	7.0	0.8	1.2	0.9	n.d.	n.d.	1.4	0.6	2.5	2.4	0.4	2.0	2.9	22.1
110	1.3	0.8	2.4	5.7	0.8	1.6	0.4	3.9	1.6	11.7	2.5	0.3	0.9	33.9
111	6.6	3.6	3.5	3.3	1.5	0.7	2.6	0.6	0.8	0.9	1.9	4.3	3.5	33.9
112	4.7	1.9	2.0	6.4	0.2	0.2	1.4	1.1	0.8	0.6	2.5	3.7	1.1	26.5
113	4.2	4.5	3.4	2.0	2.8	0.8	3.2	1.9	2.8	3.9	9.0	29.1	2.9	70.7
114	7.1	3.5	4.9	1.2	0.6	1.2	5.2	6.7	4.2	1.6	21.9	1.2	6.6	66.0
115	5.3	5.1	2.2	2.5	2.4	1.9	7.2	9.2	9.8	4.5	2.9	24.3	7.9	85.2
116	6.2	3.3	3.3	3.1	1.4	0.7	2.1	0.5	0.7	0.8	1.6	5.8	8.9	38.3
117	4.0	1.0	3.8	6.8	2.6	2.4	2.6	8.5	1.6	4.6	12.5	7.0	9.5	66.9
118	4.2	4.3	4.6	1.4	1.1	1.2	1.0	2.0	1.3	1.1	2.3	1.9	17.1	43.4
119	3.9	3.8	3.4	2.0	2.8	0.8	3.2	1.9	2.8	3.9	9.9	30.3	2.9	71.7
120	10.2	6.4	5.2	16.9	2.8	1.2	5.2	0.2	3.9	3.4	16.9	n.d.	6.6	78.9
121	8.6	1.3	0.9	4.9	2.2	1.6	3.9	1.8	0.6	2.3	20.3	3.4	3.3	55.2

Stations	Phe	An	Fluo	Pyr	B[a]A	Chry	B[b]F	B[k]F	B[e]P	B[a]P	Ind	D[a,h]A	B[g,h,i]P	∑ PAHs
122	6.6	1.8	1.3	4.9	1.5	0.7	3.4	7.9	2.4	2.4	1.8	2.9	20.0	57.7
123	6.1	1.5	1.3	4.4	1.5	0.7	3.4	7.9	2.1	2.4	1.8	2.9	17.7	53.8
124	7.3	2.0	1.4	5.4	1.6	1.1	2.9	6.6	2.0	2.0	1.5	2.4	16.7	53.0
125	5.7	3.7	1.4	4.4	1.4	3.1	4.7	0.5	n.d.	n.d.	23.3	17.1	2.1	67.5
126	11.4	0.4	8.7	10.3	5.7	8.7	10.0	1.2	3.6	1.3	1.6	0.8	3.3	67.1
127	5.3	2.9	4.0	5.0	1.0	0.5	0.8	1.5	1.2	1.2	6.6	3.7	3.0	36.6
128	6.8	1.6	2.6	4.3	2.5	2.7	1.8	0.3	0.7	0.3	6.6	2.1	2.1	34.3
129	5.9	1.5	1.7	0.9	1.7	0.8	7.7	10.1	11.4	2.4	9.5	37.2	5.9	96.9
130	6.8	1.1	3.1	6.5	0.9	2.2	2.2	1.6	0.3	n.d.	4.2	18.1	1.9	48.9
131	3.6	1.3	3.9	5.9	2.1	5.7	5.0	5.3	10.5	7.5	12.9	3.8	10.5	78.1
132	5.1	1.6	4.1	3.9	0.4	0.4	1.7	0.6	0.5	0.3	3.5	2.2	0.9	25.3
133	4.3	1.6	2.0	2.4	0.2	0.7	0.5	3.7	0.7	0.3	1.6	10.8	1.0	29.8
134	4.7	1.7	2.2	2.6	0.2	0.7	0.5	3.9	0.7	0.3	1.7	11.4	1.1	32.0
135	3.8	4.2	3.0	4.4	0.4	0.5	2.1	1.7	0.4	0.9	2.2	2.7	2.3	28.5
136	2.5	3.1	0.8	6.1	9.9	0.7	0.4	0.4	0.1	0.2	1.5	3.1	1.2	30.1
137	3.3	0.7	0.8	2.3	0.1	0.2	0.3	0.2	0.2	0.2	0.9	1.2	1.5	11.9
138	4.3	3.9	4.4	4.0	0.9	1.2	2.6	2.6	0.9	0.3	2.7	3.2	4.8	35.8
139	6.7	4.4	10.8	5.3	3.0	0.6	6.3	4.6	1.2	5.2	10.5	37.9	9.8	106.3
140	7.5	4.1	8.6	7.7	6.1	0.6	10.7	0.7	6.2	2.6	38.4	22.3	5.4	121.0

Stations	Phe	An	Fluo	Pyr	B[a]A	Chry	B[b]F	B[k]F	B[e]P	B[a]P	Ind	D[a,h]A	B[g,h,i]P	∑ PAHs
141	6.4	3.5	7.4	6.6	5.2	0.5	9.0	0.6	5.2	2.2	32.3	18.8	4.6	102.3
142	5.5	1.8	2.4	4.9	0.7	1.3	0.3	0.7	0.8	2.9	3.0	1.8	5.0	31.0
143	10.4	2.5	5.1	3.4	5.1	5.0	9.8	18.7	13.2	5.4	17.9	20.0	14.6	131.0
144	3.5	2.9	2.3	4	1.4	1.2	1	5.4	1	0.6	5.9	4.7	1	34.9
145	3.3	2.4	2.7	4.2	0.6	1.3	2.7	6.2	6.1	3.3	20.4	2.3	3.6	59.1
146	8.6	4.8	11.7	5.1	1.3	2	4.5	4.3	1.4	3.4	10.7	3	18.9	79.8
147	3.6	1.3	0.7	2.5	1.2	1	3.3	1.5	1.8	3.1	1	1.7	5.9	28.6
148	7.4	1.9	2.1	9.8	4.9	3.6	1	6.4	2.1	6.3	8.1	12.5	6.9	73
149	3.9	4.2	3.2	1.9	2	8	1	3.4	5.1	2.1	8.3	4.1	8.4	55.8
150	5.3	4.2	2.1	4.2	9.3	15.3	1.3	1.6	1.8	1.9	1	6.2	1.2	55.6
151	4.8	4.2	3.2	1.9	2	8	1	4	5.1	2.1	11.4	4.1	8.4	60.3
152	4	2.3	3.7	3.8	1.4	0.6	0.1	1.4	0.5	0.6	1.3	11.4	7.2	38.3
153	4.7	2.6	4.2	4.4	1.6	0.7	0.2	1.5	0.6	0.6	1.4	12.5	7.9	42.9
Average	11.1	2.5	4.9	8.0	1.4	1.3	2.4	2.8	2.5	1.9	4.9	8.4	5.7	57.1
SD	6.7	1.6	3.6	6.3	1.6	2.1	2.6	3.3	3.6	2.3	6.6	13.7	6.4	35.7

Table B.2 Level of each of PAHs and total PAHs (ΣPAHs) contamination in soil samples (ng g^{-1} dry weight).

Station	Phe	An	Fluo	Pyr	B[a]A	Chry	B[b]F	B[k]F	B[e]P	B[a]P	Ind	D[a,h]A	B[g,h,i]P	Total PAHs
S1	7	5.2	2.3	5.4	0.2	0.9	3.6	1	1.4	2.7	14.3	15.4	1.6	60.9
S2	4.4	0.4	4.6	11.7	1	0.6	5.2	1.1	0.5	2.1	0.4	5.8	0.5	38.4
S3	5.3	0.7	2.7	6.2	1.7	4.4	1.9	2.1	3.1	1.6	3.3	0.6	1.8	35.3
S4	7.6	2	3.8	6.7	1.2	0.3	0.2	1.5	0.5	0.2	2.7	2.3	4.6	33.6
S5	15.9	4.3	26.5	20.3	0.5	4.4	17.5	1	0.8	8.5	9.2	2.2	7	118.1
S6	3.7	0.9	2.9	3.7	0.3	0.5	n.d.	0.5	0.2	0.4	2.8	3.9	2.9	22.7
S7	4.8	2.6	2.4	5.2	0.9	2.3	n.d.	n.d.	1.6	1.9	0.4	n.d.	n.d.	22
S8	9.3	1.1	4.9	11.8	1.1	0.7	0.4	0.8	0.1	0.2	0.1	1.5	0.1	32.2
S9.1	6.7	0.1	5.7	10	0.6	3.1	1.1	0.5	0.5	0.4	2	1	0.2	31.9
S9.2	5	0.1	13.5	11.8	2.8	0.5	9.7	1.3	2.2	5.5	0.1	0.6	n.d.	53.2
S10	4.3	0.6	5.3	8	0.9	0.5	2.3	0.4	1.2	0.2	4.3	2.2	0.4	30.6
S11	14.3	1.9	5.7	12.4	0.5	0.8	0.2	1.6	0.5	0.1	1	n.d.	0.7	39.7
S12.1	7.6	0.3	3.7	7.9	0.6	4.6	0.8	0.3	2.6	2.8	4.5	1.3	9.2	46.2
S12.2	7.1	0.9	3.5	7.1	n.d.	0.5	0.7	0.1	0.3	0.7	4.8	7.8	7	40.6
S12.3	4.9	2.9	2.4	7.6	2.7	4.2	0.6	2.2	1.5	n.d.	1.4	0.7	1	32.3
S13.1	21.6	2.5	10.2	15.5	1.8	3.9	n.d.	n.d.	2.5	2.1	3.8	11.9	5.9	81.4
S13.2	4.2	0.8	2.3	5.8	1.4	2	1	7.1	3.5	0.2	2.3	18.5	11.8	60.7
S13.3	5.1	0.7	4.4	6.5	2	3.1	0.8	0.6	0.8	0.5	3.3	1.8	0.5	30.1

Station	Phe	An	Fluo	Pyr	B[a]A	Chry	B[b]F	B[k]F	B[e]P	B[a]P	Ind	D[a,h]A	B[g,h,i]P	Total PAHs
S14	5.1	0.8	3.9	6	0.6	0.8	1.9	0.2	0.4	0.9	1	3.4	1.1	26.1
S15	6.7	0.5	2.8	9	0.6	0.3	1	2	1.2	0.5	1	5.3	1.5	32.4
S16	20.3	0.3	57.1	50.2	11.9	11.8	21.9	3.1	10.1	10.7	0.4	1.9	0.4	200.1
S17	194.1	28.4	545.1	350.4	148.8	104.7	212.5	62	120.7	160.1	67.8	16.1	73.1	2083.8
S18	12.8	2.1	6.1	13.8	1.2	5	1	0.8	0.5	0.1	1.6	n.d.	1.4	46.4
Average	16.4	2.6	31.4	25.8	8.3	7	14.2	4.3	6.8	9.2	5.8	5.2	6.3	139.1
SD	38.2	5.6	110.2	69.8	30.7	21	45.9	13	24.4	33	13.6	5.5	15.3	416.4

Table B.3 Level of each of PAHs and total PAHs (ΣPAHs) contamination in aerosol samples (pg m^{-3})

Station	Phe	An	Fluo	Pyr	B[a]A	Chry	B[b]F	B[k]F	B[e]P	B[a]P	Ind	D[a,h]A	B[g,h,i]P	ΣPAHs
aero 1	5	17	1	6	10	2	25	27	n.d.	41	455	121	115	832
aero 2	8	1	n.d.	12	1	n.d.	35	35	11	48	55	460	122	789
aero 3	27	17	24	79	n.d.	n.d.	185	98	n.d.	n.d.	231	267	242	1217
aero 4	12	4	7	2	1	16	6	6	6	40	27	122	47	299
aero 5	15	3	11	14	n.d.	n.d.	31	14	23	14	9	59	13	236
aero 6	28	18	28	49	2	6	10	5	23	3	7	16	4	208
aero 7	21	2	6	28	1	13	11	47	16	17	3	4	1	174
aero 8	110	1	50	135	4	n.d.	1	n.d.	10	2	15	3	2	376
aero 9	n.d.	29	76	39	2	4	5	20	16	7	1	4	32	265
aero 10	53	52	5	25	11	7	12	1	37	35	71	42	5	368
aero 11	30	30	2	23	17	20	4	24	17	4	n.d.	5	8	208
Average	28	16	19	37	4	6	30	25	15	19	79	100	54	452
SD	31	16	24	39	6	7	53	28	11	18	141	144	77	340

n.d.: Not detected

APPENDIX C

Diagnostic PAHs ratios

C.1 Diagnostic ratios of Khao Lak sediments

Table C.1 Five of Diagnostic ratios of Khao Lak sediments.

Station	An / An + Phe	Flou/ Flou + Pyr	B [a]A / B[a]A + Chry	B [a]P / B[a]P + B[e]P	Ind / Ind + B[g,h,i]P
2	0.25	0.35	0.49	-	0.21
3	0.33	0.35	0.59	0.38	0.21
4	0.09	0.49	0.43	0.39	0.46
5	0.13	0.44	0.50	0.33	0.25
6	0.34	0.24	0.64	0.42	0.27
7	0.40	0.30	0.60	-	0.21
8	0.33	0.33	0.61	0.50	0.24
9	0.54	0.51	0.67	-	0.18
10	0.09	0.67	0.57	0.28	0.15
11	0.53	0.39	0.55	-	0.23
12	0.54	0.51	0.45	0.38	0.38
13	0.38	0.43	0.48	0.08	0.14
14	0.56	0.29	0.56	-	0.25
15	0.33	0.39	0.45	0.06	0.44
16	0.46	0.41	0.41	-	0.37
17	0.28	0.48	0.37	0.08	0.33
18	0.26	0.42	0.48	-	0.34
19	0.14	0.31	0.59	1.00	-
20	0.26	0.27	1.00	-	0.27
21	0.10	0.32	0.46	0.45	0.47
22	0.39	0.32	0.52	-	0.56
23	0.47	0.29	0.50	0.34	0.53
24	0.13	0.52	0.37	0.42	0.50
25	0.14	0.44	0.45	0.38	0.44
26	0.58	0.28	0.43	0.34	0.35
27	0.23	0.15	0.72	-	0.29
29	0.15	0.25	0.64	0.04	0.22
31	0.09	0.48	0.40	0.29	0.51
32	0.33	0.32	0.37	-	0.38
33	0.16	0.47	0.44	-	0.50
34	0.12	0.48	0.54	0.56	0.23
35	0.17	0.37	0.55	0.18	0.26
36	0.23	0.30	0.55	-	0.25
37	0.16	0.30	0.53	0.30	0.01
39	0.19	0.40	0.49	0.03	0.26

Station	An / An + Phe	Flou/ Flou + Pyr	B [a]A / B[a]A + Chry	B [a]P / B[a]P + B[e]P	Ind / Ind + B[g,h,i]P
40	0.32	0.29	0.47	0.42	0.44
41	0.38	0.32	0.24	0.52	0.3
42	0.18	0.34	0.52	-	0.48
43	0.08	0.42	0.51	0.06	-
44	0.36	0.45	0.57	-	0.19
45	0.31	0.3	0.69	0.13	0.36
46	0.08	0.3	0.49	0.34	0.43
47	0.21	0.31	0.55	-	0.23
48	0.22	0.26	0.69	0.49	0.22
49	0.36	0.32	0.71	0.05	0.24
50	0.21	0.44	0.59	-	0.27
51	0.36	0.35	0.46	0.5	0.23
52	0.1	0.31	0.62	0.08	0.34
53	0.26	0.35	0.63	-	0.32
55	0.33	0.29	0.62	0.01	0.28
56	0.21	0.31	0.65	-	0.31
58	0.22	0.32	0.6	0.34	0.27
57	0.41	0.19	0.55	0.38	0.33
61	0.29	0.29	0.58	0.38	0.27
62	0.31	0.29	0.68	0.05	0.17
63	0.34	0.29	0.53	-	0.22
64	0.25	0.38	0.65	0.07	0.16
65	0.26	0.34	0.58	-	0.28
66	0.16	0.26	1	0.21	0.36
68	0.26	0.2	0.59	0.47	0.32
69	0.24	0.27	0.57	0.05	0.17
70	0.2	0.28	0.58	-	0.19
71	0.24	0.3	0.57	0.05	0.18
72	0.23	0.31	0.57	0.23	0.16
73	0.15	0.53	0.65	0.02	0.13
74	0.24	0.39	0.55	-	0.29
75	0.21	0.33	0.57	0.42	0.17
76	0.2	0.31	0.55	-	0.16
77	0.48	0.33	0.67	0.1	0.22
78	0.44	0.35	0.59	-	0.22
79	0.37	0.46	0.31	0.34	0.16
80	0.24	0.2	0.65	0.97	0.96
81	0.17	0.36	0.78	0.89	0.86
82	0.34	0.36	0.5	0.54	0.43
83	0.3	0.48	0.49	0.16	0.68
84	0.34	0.57	0.56	0.52	0.43

Station	An / An + Phe	Flou/ Flou + Pyr	B [a]A / B[a]A + Chry	B [a]P / B[a]P + B[e]P	Ind / Ind + B[g,h,i]P
85	0.18	0.45	0.85	0.17	0.25
86	0.27	0.65	0.85	0.57	0.52
87	0.17	0.48	0.67	0.7	0.11
88	0.23	0.6	0.48	0.46	0.33
89	0.24	0.65	0.41	0.55	0.88
90	0.32	0.65	0.55	0.6	0.56
91	0.24	0.49	0.76	0.45	0.55
92	0.3	0.38	0.41	0.66	0.65
93	0.22	0.42	0.73	0.72	0.2
94	0.37	0.48	0.7	0.33	0.11
95	0.17	0.6	0.51	0.49	0.64
96	0.12	0.41	0.67	0.44	0.72
97	0.26	0.66	0.89	0.38	0.23
98	0.27	0.65	0.62	0.23	0.16
99	0.15	0.42	0.27	0.37	0.86
100	0.17	0.41	0.82	0.53	0.86
101	0.39	0.42	0.7	0.42	0.66
102	0.28	0.43	0.52	0.7	0.91
103	0.31	0.47	0.58	0.65	0.61
104	0.44	0.39	0.15	0.14	0.16
105	0.34	0.35	0.75	0.64	0.47
106	0.27	0.36	0.77	0.87	0.93
107	0.35	0.31	0.54	0.83	0.2
108	0.39	0.31	0.26	0.53	0.81
109	0.1	0.57	-	0.49	0.11
110	0.38	0.3	0.33	0.88	0.72
111	0.35	0.52	0.66	0.54	0.36
112	0.29	0.23	0.57	0.43	0.69
113	0.52	0.62	0.79	0.58	0.76
114	0.33	0.8	0.33	0.28	0.77
115	0.49	0.46	0.56	0.32	0.27
116	0.35	0.52	0.66	0.54	0.15
117	0.21	0.36	0.52	0.75	0.57
118	0.5	0.76	0.47	0.47	0.12
119	0.49	0.62	0.79	0.58	0.77
120	0.38	0.24	0.69	0.47	0.72
121	0.13	0.16	0.58	0.78	0.86
122	0.22	0.2	0.67	0.5	0.08

Station	An / An + Phe	Flou/ Flou + Pyr	B [a]A / B[a]A + Chry	B [a]P / B[a]P + B[e]P	Ind / Ind + B[g,h,i]P
123	0.2	0.22	0.67	0.54	0.09
124	0.22	0.2	0.59	0.5	0.08
125	0.4	0.25	0.32	-	0.92
126	0.04	0.46	0.4	0.26	0.33
127	0.36	0.45	0.69	0.51	0.69
128	0.2	0.38	0.48	0.28	0.76
129	0.21	0.65	0.67	0.17	0.62
130	0.14	0.33	0.29	-	0.69
131	0.26	0.4	0.28	0.42	0.55
132	0.24	0.52	0.46	0.4	0.79
133	0.27	0.46	0.23	0.33	0.6
134	0.27	0.46	0.23	0.33	0.6
135	0.52	0.4	0.47	0.71	0.49
136	0.56	0.12	0.93	0.71	0.55
137	0.18	0.27	0.25	0.49	0.36
138	0.48	0.52	0.41	0.26	0.36
139	0.4	0.67	0.83	0.81	0.52
140	0.35	0.53	0.91	0.3	0.88
141	0.35	0.53	0.91	0.3	0.88
142	0.24	0.33	0.36	0.79	0.38
143	0.19	0.6	0.5	0.29	0.55
144	0.46	0.36	0.52	0.37	0.85
145	0.42	0.4	0.31	0.35	0.85
146	0.36	0.7	0.4	0.71	0.36
147	0.27	0.23	0.54	0.64	0.15
148	0.21	0.18	0.57	0.75	0.54
149	0.52	0.62	0.2	0.29	0.5
150	0.44	0.33	0.38	0.52	0.47
151	0.47	0.62	0.2	0.29	0.58
152	0.36	0.49	0.69	0.53	0.15
153	0.36	0.49	0.69	0.53	0.15

C.2 Diagnostic ratios of soil samples

Table C.2 Five of Diagnostic ratios of soil samples.

Station	An / An + Phe	Flou/ Flou + Pyr	B [a]A / B[a]A + Chry	B [a]P / B[a]P + B[e]P	Ind / Ind + B[g,h,i]P
S1	0.43	0.3	0.2	0.65	0.9
S2	0.08	0.28	0.63	0.8	0.46
S3	0.12	0.3	0.27	0.34	0.65
S4	0.21	0.36	0.8	0.31	0.37
S5	0.21	0.57	0.11	0.92	0.57
S6	0.19	0.43	0.39	0.7	0.5
S7	0.35	0.31	0.29	0.55	1
S8	0.11	0.29	0.59	0.65	0.45
S9	0.01	0.53	0.84	0.72	0.7
S10	0.12	0.4	0.64	0.16	0.91
S11	0.12	0.32	0.37	0.15	0.59
S12	0.04	0.32	0.12	0.51	0.33
S13	0.1	0.4	0.31	0.45	0.39
S14	0.14	0.4	0.43	0.68	0.46
S15	0.07	0.23	0.68	0.31	0.39
S16	0.01	0.53	0.5	0.52	0.54
S17	0.13	0.61	0.59	0.57	0.48
S18	0.14	0.31	0.19	0.19	0.53

APPENDIX D

Sediment Description

Table D.1 Description of sediment samples.

Station	Date	Water depth (m)	Sediment description
2	1/12/2007	53.20	muddy fine sand, poorly sorted
3	1/12/2007	52.40	muddy medium sand, poorly sorted
4	1/12/2007	49.20	muddy medium sand, poorly sorted
5	1/12/2007	49.20	muddy medium sand, poorly sorted
6	1/12/2007	39.70	muddy coarse sand, poorly sorted
7	1/12/2007	38.85	muddy coarse sand, poorly sorted
8	1/12/2007	31.30	coarse sand (shell debris), poorly sorted
9	1/12/2007	22.50	coarse sand, poorly sorted
10	1/12/2007	18.00	coarse sand, moderately sorted
11	2/12/2007	20.10	coarse brown sand, moderately sorted (with small amount in lower part of mud)
12	2/12/2007	20.10	on surface 3 cm of coarse brown sand, moderately sorted; below dark grey mud with pieces of wood, some big shells, grass presumably tsunami deposits
13	2/12/2007	19.80	moderately sorted; below dark grey mud with pieces of wood, some big shells, grass presumably tsunami deposits
14	2/12/2007	18.70	coarse sand, moderately sorted
15	2/12/2007	21.60	coarse sand moderately to poorly sorted, below 5 cm muddy medium sand
16	2/12/2007	44.70	fine to medium sand, moderately sorted
17	2/12/2007	44.40	muddy coarse sand, poorly sorted
18	2/12/2007	52.10	coarse silt / fine sand, well sorted
19	2/12/2007	56.90	coarse silt, well sorted
20	2/12/2007	57.80	coarse silt, moderately sorted
21	3/12/2007	63.40	coarse silt/fine sand, moderately sorted
22	3/12/2007	61.80	fine sand, moderately sorted
23	3/12/2007	56.50	muddy medium sand, poorly sorted
24	3/12/2007	52.30	muddy fine sand, poorly sorted; in lower part well sorted medium sand
25	3/12/2007	44.10	muddy medium sand, poorly sorted
26	3/12/2007	33.60	medium sand, well sorted
27	3/12/2007	26.50	very coarse sand with pieces of coral debris

Station	**Date**	**Water depth (m)**	**Sediment description**
29	3/12/2007	25.10	very coarse sand with pieces of coral debris
31	5/12/2007	15.80	very coarse poorly sorted sand
32	5/12/2007	14.80	very coarse poorly sorted sand over muddy coarse sand
33	5/12/2007	17.00	very coarse sand , well sorted
34	5/12/2007	16.70	coarse sand, well sorted
35	5/12/2007	15.20	coarse sand, moderately well sorted
36	5/12/2007	17.30	very coarse sand, well sorted
37	5/12/2007	17.00	muddy very fine sand
39	5/12/2007	17.50	medium sand, very well sorted
40	5/12/2007	17.80	coarse sand, well sorted
41	5/12/2007	16.80	medium sand, well sorted
42	5/12/2007	15.70	coarse sand, well sorted
43	5/12/2007	17.70	medium / coarse sand, well sorted
44	5/12/2007	18.20	coarse sand, well sorted
45	5/12/2007	17.50	medium sand, very well sorted
46	5/12/2007	16.90	coarse sand, moderately well sorted
47	5/12/2007	18.30	medium / coarse sand, well sorted
48	5/12/2007	17.80	coarse sand, well sorted
49	7/12/2007	62.00	muddy fine sand, poorly sorted
50	7/12/2007	57.90	muddy medium sand, poorly sorted
51	7/12/2007	58.60	muddy medium sand, poorly sorted
52	7/12/2007	59.80	muddy fine/medium sand, poorly sorted
53	7/12/2007	59.80	medium sand, moderately sorted
55	7/12/2007	57.10	muddy medium sand, poorly sorted
56	7/12/2007	42.90	muddy coarse sand, poorly sorted
58	7/12/2007	42.90	muddy coarse sand, poorly sorted
57	7/12/2007	40.70	muddy coarse sand, poorly sorted
61	7/12/2007	45.60	muddy medium sand, poorly sorted
62	7/12/2007	57.50	muddy medium sand, poorly sorted
63	7/12/2007	50.70	muddy medium sand, poorly sorted
64	7/12/2007	49.50	silty coarse sand, poorly sorted
65	7/12/2007	40.40	muddy fine sand, poorly sorted
66	7/12/2007	35.80	muddy medium sand, poorly sorted
68	8/12/2007	15.10	coarse sand, moderately sorted
69	8/12/2007	14.20	coarse sand, moderately sorted
70	8/12/2007	15.00	coarse sand, moderately sorted

Station	Date	Water depth (m)	Sediment description
71	8/12/2007	15.80	coarse sand, moderately sorted
72	8/12/2007	16.10	coarse sand, moderately sorted on surface and gray muddy sand below
73	8/12/2007	14.40	coarse sand, well sorted
74	8/12/2007	16.50	medium sand, well sorted
75	8/12/2007	16.80	coarse sand, well sorted
76	8/12/2007	12.70	mud
77	8/12/2007	13.90	silty coarse sand, poorly sorted
78	8/12/2007	16.30	coarse sand, moderately sorted
79	6/12/2008	12.20	Sand
80	6/12/2008	12.25	Coarse sand, red
81	6/12/2008	10.00	Fine silt, brown, red/ox-horizon: 1 – 2 mm, below: grey
82	6/12/2008	13.25	Gravel, carbonate fragments
83	6/12/2008	13.00	Fine silt, shell fragments
84	6/12/2008	13.35	Gravel, carbonate fragments
85	6/12/2008	12.40	Surface: Coarse silt; thickness: 1 – 2 mm; below: fine silt, red/ox: 1 -2 mm, some clay content and some gravel
86	6/12/2008	9.70	Fine sand, silty, brown, no organisms
87	6/12/2008	14.90	Silt, brown, red/ox 2 – 3 mm, below silt, grey, clasts of coarse material up to gravel inside, partly Laterite fragments
88	6/12/2008	19.40	Coarse sand
89	6/12/2008	12.60	Coarse sand, some gravel, shell fragments, each rock-fragments?
90	6/12/2008	9.50	Surface: silt, brown, below: silt, some clay content, grey, stiff, no bioturbation
91	6/12/2008	14.00	Surface, silt, brown, red/ox. 2 mm, sediment below: silt, some clay content, stiff, no bioturbation
92	6/12/2008	15.40	Medium – fine sand, brown, small amount of shell fragments
93	6/12/2008	9.70	Surface, silt, brown, red/ox. 3 -4 mm, sediment below: silt – fine sand, grey, no bioturbation

Station	Date	Water depth (m)	Sediment description
94	6/12/2008	13.00	Sample consists of sediment from fine gravel to silt, some shell fragments
95	6/12/2008	12.00	Surface, silt, brown, red/ox. 2 mm, sediment below: silt, some clay content, increasing to the bottom, grey
96	10/12/2008	6.60	Well sorted fine sand, brown, no shell fragments, no red/ox horizon
97	10/12/2008	11.30	Silt, some clay content, surface brown, red/ox 3 – 4 mm, below surface grey, no bioturbation, no shell fragments
98	10/12/2008	20.50	Coarse to medium sand, brown, a lot of shell fragments and smaller (ø 1 cm) complete shells
99	10/12/2008	26.70	Well sorted fine sand, grey, shell fragments, bioturbation
100	10/12/2008	25.40	Coarse to medium sand, brown, shell fragments
101	10/12/2008	27.80	Coarse sand, brown, high suspension load, a lot of shell fragments and complete shells
102	10/12/2008	22.90	Coarse sand, brown, a lot of shell fragments and complete shells, high suspension load
103	10/12/2008	29.30	Fine sand, grey, some shell fragments, suspension load in the water
104	10/12/2008	24.90	Coarse sand, brown, shell fragments, high suspension load, clasts of fine sediment
105	10/12/2008	19.60	Medium to coarse sand, brown, shell fragments, suspension load
106	10/12/2008	18.90	Fine sand, brown, shell fragments, some suspension load
107	10/12/2008	18.30	Very heterogeneous sediment, fine to coarse sand, big clasts of soft, slightly cohesive grey silt are included, small amount of shell fragments
108	10/12/2008	20.20	Fine sand, grey, Upper layer fine brown silt, only small amount of shell fragments
109	3/3/2010	8.20	silty fine sand
110	3/3/2010	14.50	coarse sand with coral fragment

Station	Date	Water depth (m)	Sediment description
111	3/3/2010	14.00	muddy coarse sand, first top mm of layer cover by org. material, 3 cm below is layer of coarser sand then the last 5 cm is mixture of muddy and coarse sand, very poorly sorted
112	3/3/2010	11.50	muddy coarse sand, top few mm is yellowish layer, below is grayish layer which has dark spot (org. material) inside, poorly sorted
113	3/3/2010	9.00	muddy sand, top few mm is yellowish layer, below is grayish layer which has fine sand clast and muddy clast
114	3/3/2010	8.60	muddy sand, top few mm is yellowish layer, below is grayish layer
115	3/3/2010	9.00	muddy sand, top few mm is yellowish layer, below is grayish layer which has stiff clast of finer materials
116	3/3/2010	9.70	muddy sand, heterogeneous sediment (two layers), stiff muddy clast in bottom layer
117	3/3/2010	10.50	two layers with coarser grain (more offshore), worm tubes have been found, top layer is sand, bottom layer is clayey material which has layer of sand in between
118	3/3/2010	11.50	coarse sand
119	3/3/2010	8.70	pieces of stone
120	3/3/2010	8.30	fine silt, first few mm is yellowish, below is coarser grain in muddy silt layer, also found sandy clast in between, sampling sand layer (A II)
121	3/3/2010	7.20	medium sand, moderately sorted
122	3/3/2010	11.70	fine sand to silt, moderately sorted, has stiff muddy silt clast, at the bottom has two layer (A II)
123	3/3/2010	14.80	sample like 14, worm tubes have been found, stiff clast of clay - silt
124	3/3/2010	13.30	lots of living organism hole, has stiff muddy clast but no layer
125	3/3/2010	17.20	fine layer in between and stiff clast

Station	**Date**	**Water depth (m)**	**Sediment description**
126	3/3/2010	14.20	two layer: first few layer is yellowish, sandy clast in between, more coarse grain and few of worm tube
127	3/3/2010	11.90	stiff material at the base, no worm or shell have been found and not so clearly layer has been found
128	3/3/2010	10.40	very fine sand to silt, thin-fine layer at the top
129	3/3/2010	15.20	coarse sand, lots of coral pieces
130	3/3/2010	14.50	pieces of stone
131	4/3/2010	21.00	coarse sand
132	4/3/2010	24.50	fine material with some silt, some clasts of organic sand are visible
133	4/3/2010	29.10	coarse sand to silt, poorly sorted, lots of worm tubes, olive-grey color of sand
134	4/3/2010	32.00	medium to coarse sand, worm tubes
135	4/3/2010	26.20	well sorted sand, lots of large coral debris
136	4/3/2010	27.00	suspension in water, worm tube, grey sand films
137	4/3/2010	25.00	sand and coral debris
138	4/3/2010	43.00	olive-green silty sand, coarser grain toward base
139	4/3/2010	49.50	olive-green silty sand
140	4/3/2010	49.00	coarser grain toward base
141	4/3/2010	38.60	sample is getting more coarse towards base
142	4/3/2010	31.40	poorly sorted silt to sand,
143	5/3/2010	28.60	fine sediment floating out, olive grey film+ silt, no visible layering in grab sample, worm tubes have been found
144	5/3/2010	23.60	medium sand, well sorted
145	5/3/2010	20.40	coarse sand, well sorted
146	5/3/2010	19.00	coarse sand with coral debris, no suspension in water, more grey sand toward base
147	5/3/2010	15.70	olive green sand
148	5/3/2010	19.00	medium / coarse sand, few mm of organic sand on top, grayish sand below

Station	Date	Water depth (m)	Sediment description
149	5/3/2010	17.20	fine sand, well sorted
150	5/3/2010	15.60	yellow organic sand on top (~1 cm)
151	5/3/2010	15.00	yellow organic sand down to the base, no suspension in water, some muddy clasts with organic material
152	5/3/2010	14.90	coarse sand , no suspension in water
153	5/3/2010	14.80	sand with stones

BIOGRAPHY

Mr.Danai Tipmanee was born on September 15th, 1974 in Suratthani province, Thailand. He obtained his B.Sc. in Chemistry from the Faculty of Science, Prince of Songkla University in 1996. He graduated with a Master's degree in Analytical Chemistry from the Faculty of Science, Prince of Songkla University in 2000.

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Training

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