16 Case Study: Oil Spills in the Strait of Malacca, Malaysia

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16.1 Strait of Malacca, Malaysia: Introduction

The Strait of Malacca is located between the east coast of Sumatra and the west coast of Peninsular Malaysia (Figure 16-1). The Strait of Malacca is an important sea route for local and international trade and shipping traffic. It is also a major shipping route for oil tankers transporting crude oil from the Middle East countries to the northeast Asian countries.

Strategically located and rich in coastal resources, the Strait of Malacca through the centuries has been a center of international trade and civilization. More than 500 years ago, merchants from the State of Gujerat, India, and Arab Islamic missionaries flocked to the area and turned Malacca into an important trading center. Eventually, the Europeans established a spice trade in the whole of the Malay Archipelago, transforming the Strait of Malacca into a busy trade route. Today, the southeast Asian economy remains closely linked with maritime trade and activities such as shipping, fisheries, and eco-tourism.

The Strait of Malacca has valuable and vulnerable marine and coastal resources. The Strait has been constantly exposed to a variety of sea-based and land-based pollutants (Abdullah et al., 1999). With increased maritime transportation in the area, it is expected that the impact of oil pollution will increase. The importance and contributions of the coastal and marine environmental resources of the Strait are being increasingly recognized. With extensive mangrove and forest resources, coral reefs, and sea grass along the path of a major migratory bird route from Siberia to Australasia, the area contains a number of ecosystems values for their biodiversity and cultural significance by the surrounding littoral states.

16.1.1 Hydro-Oceanographic Condition of the Strait

The length of the Strait of Malacca is approximately 600 nautical miles, while its width ranges between 8 nautical miles near Riau Archipelago to 220 nautical miles at the northwest entrance. The northern part of the Strait is deeper but becomes shallower southwards. In the southern part are many sandbars that are elongated in shape, following the shape of the Strait itself, and hence they imperil navigation. The water in the middle of the Strait is deeper but shoals closer to shore.

The oceanographic characteristics of the Strait of Malacca are strongly affected by the adjacent oceans. Surface currents in the Strait are generated as a result of interactions

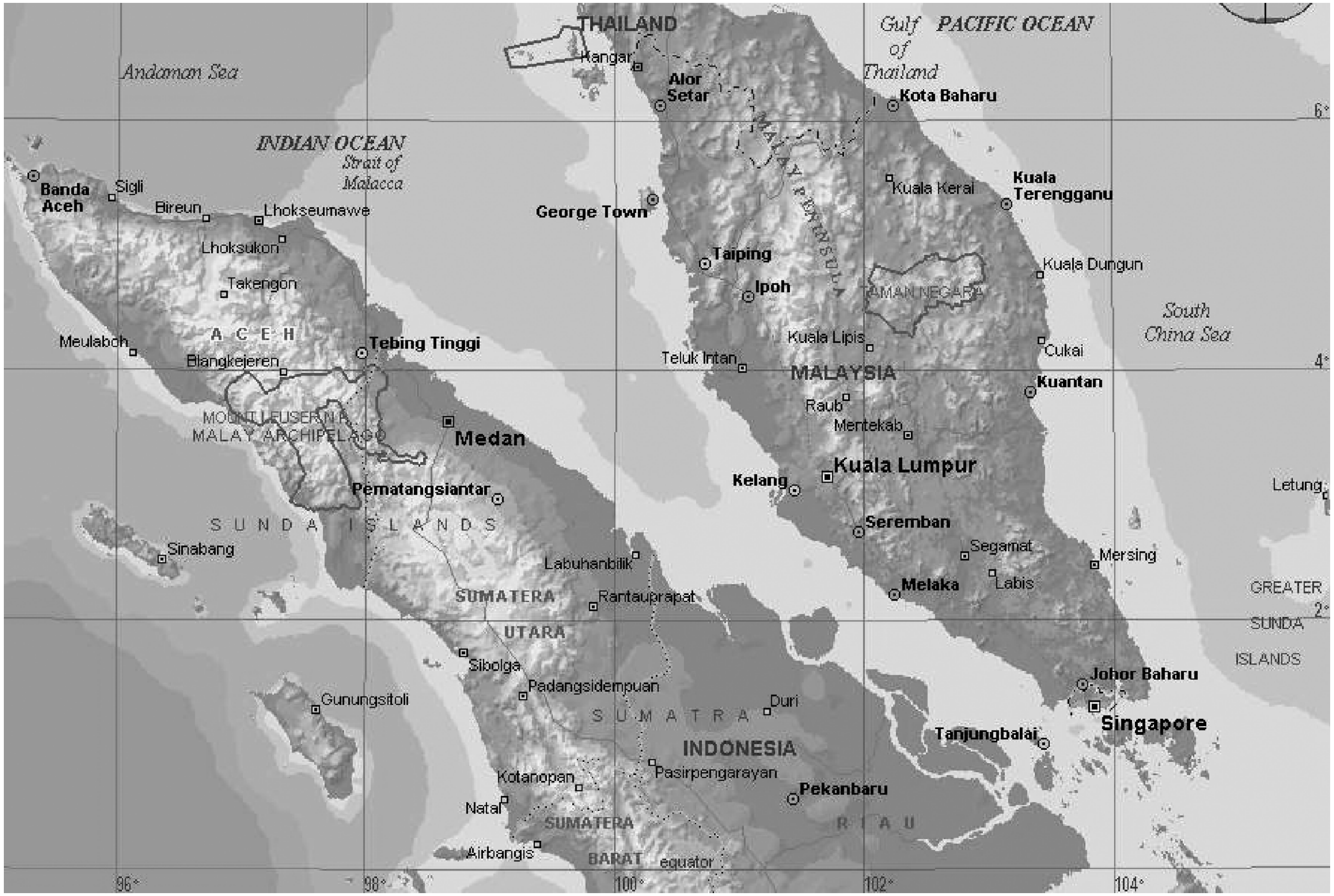

Figure 16-1 Map of Peninsular Malaysia showing the Strait of Malacca.

between oceanic currents and weather conditions in the Indian Ocean and the South China Sea. The current flows mainly in two directions for both monsoon seasons and depends on the sea-level differences between the southeast and northwest entrances (Wyrtki, 1961). The dominant direction is northwestward from the southeast entrance (Andaman Sea). Another surface current enters the Strait of Malacca from the northwest entrance (Andaman Sea) with a southeasterly flow, but reverses to the northwest direction near the northern tip of the Peninsular Malaysia.

16.1.2 Ship Traffic in the Strait of Malacca: Historical and Present

The Strait of Malacca are recognized as one of the busiest shipping lanes in the world. Historically, the importance of the Strait was heightened by the opening of the Suez Canal in 1869, which had the effect of diverting ships away from the southern route around the Cape of Good Hope and chanelling ships through Colombo and the Strait. Naidu (1997) noted that the estimated traffic through the Strait was 43,633 vessels in 1982 and 84,414 in 1991. In 1997, the vessel traffic increased to 131,003 vessels, which amounts to about 358 vessels per day. The total number of ships that passed through the Strait in 2003 was 62,334. The Marine Department of Malaysia estimated that about 34% of these vessels in 2003 were oil tankers.

16.2 Chronic and Acute Oil Spill Events in the Strait

The threat of oil spills as a result of accidents has been recognized over the years, as can be seen in Figure 16-2. Therefore, we can deduce that there was an increasing number of oil spill incidents in the Strait. The impacts of oil spills on marine habitats in the Strait, such as the mangroves, coral reefs, and seagrass beds, are major concerns. Coral reefs in the Straits have been largely affected by years of spills, and their recovery has been very slow (Dow, 1997).

There were several major oil spill incidents involving oil tankers in the Strait of Malacca from 1976 to 1997. Examples of such spills are *Diego Silang* (1976), *Asian* (1977), *M. T. Ocean Treasure* (1981), *Mv. Pantas* (1986), *Nagasaki Spirit* (1992), *An Tai* (1997), and *Sun Vista* (1999).

16.2.1 Contribution of Oil Pollution Sources in Malaysia

Although Malaysia has a relatively short history of industrialization and modernization as compared to the more established and developed countries, several factors may contribute to petroleum. First, the Malacca Strait is a major international tanker route transporting crude oil from the Middle East to northeast Asia. Oil spills and tanker accidents are frequent in the Strait. Second, a major

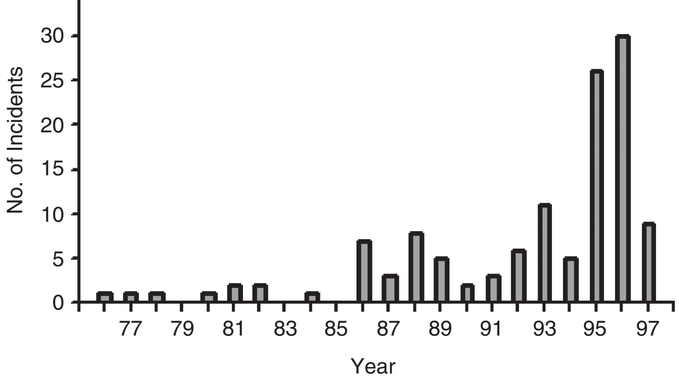

Figure 16-2 Oil spill incidents in the Strait of Malacca (Malaysian Marine Department, 2004).

oil field was discovered along the eastern seaboard of Peninsular Malaysia that produces and exports crude oil to other countries. Third, Malaysia is undergoing rapid industrialization, and petroleum is the most important source of energy for this process. The demand for petroleum has increased very rapidly in the past few decades with increasing population and urbanization. Motor-vehicle ownership has also quadrupled in recent years. Furthermore, current lax enforcement of environmental laws and regulations, especially in the dumping of used oil products, can lead to serious oil pollution problems in Malaysia. Industrial activities may also be important sources. Routine car maintenance, petrol stations, and motor-vehicle workshops are other important contributors; contributions from ports, harbors, marinas, and tanker accidents are also becoming more important in Malaysian coastal environments.

16.3 Methodology

16.3.1 Sample Collection

Figure 16-3 shows sampling locations for tar balls, while Figure 16-4 shows sampling locations for sediment on the west coast of Peninsular Malaysia.

16.3.2 Source Petroleum

Crude oil samples including three Middle East oils (Marban, Arabian Light, and Ummu Shaif) and four southeast Asian oils (Tapis, Labuan, Miri, and Sumatra) were kindly supplied by the Maritime Agency of Japan.

16.3.3 Tar-Ball Samples

Twenty tar-ball samples were collected by hand using clean plastic gloves in the tidal zones from 19 locations of the west and east coasts of Peninsular Malaysia (Figure 16-3). Two samples, MYKETR-T1 and MYKETR-T2, were taken from the same location but on two different dates. The samples were wrapped with aluminum foil, stored in clean plastic Zippered-lock bags, kept in a cooler box, transported to the laboratory, and stored at −18°C until analysis.

16.3.4 Sediment Samples

Twelve sediment samples were collected from 10 rivers on the west coast of Peninsular Malaysia in 1998 and 1999 (Figure 16-4). The locations were selected as such to cover the whole west coast including both rural (e.g., Teluk Intan, Nibong Tebal) and urban (e.g., Pinang Estuary, Port Klang, Malacca city, Johor Bahru) areas. Five estuarine sediments (St.A, St.C, St.E, St.G, and St.H) were collected along the Klang Estuary in both 2000 and 1998. Four inshore sediment samples (St.2, St.9, St.11, and St.15) were collected off the Klang Estuary. Eight offshore sediment samples (St.2, St.8, St.14, St.17, St.18, St.21, St.22, and St.23) were collected in the Strait of Malacca. The sampling locations cover a broad range of the narrow Strait. River and estuarine sediments were collected using an Eckman Dredge. The collected sample of the sediments was placed on a stainless steel pan, and the top 0–5 cm of sediments were taken using a precleaned stainless steel scoop. Because of both active input of terrestrial material to the rivers and estuaries and strong flushing of the bottom sediments caused by the frequent and strong rain in the tropical area, the top 5-cm layers of the sediments are thought to represent modern input. The coastal samples were collected using a Smith-McIntyre sampler. Immediately after the sampler was raised onto the boat, the top 0–2-cm layers were taken using a precleaned stainless steel scoop. Considering sediment accumulation rate in the coastal area, the coastal sediments are also expected to represent accumulated modern pollution input (e.g., during the last 10–20 years). For example, the sediment accumulation rate for the coastal area off the Klang Estuary was reported to be ~2 mm/year (Ibrahim, 1988), indicating that the 0–2-cm layers of the inshore sediment samples correspond to input of the last 10 years. However, the effects of bioturbation of the sediment samples were not accounted. The samples were placed in tight-sealed, solvent-

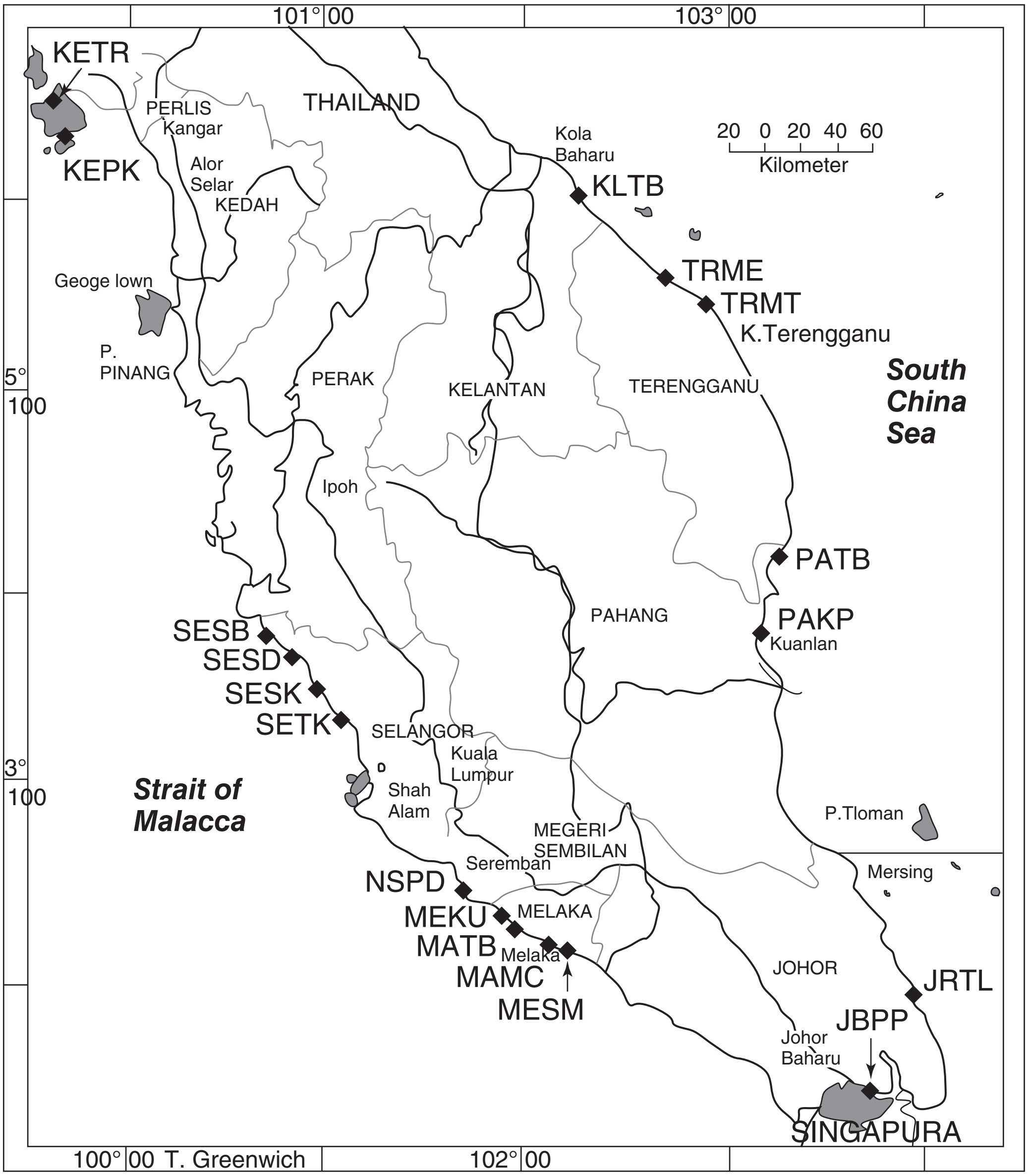

Figure 16-3 Sampling stations for tar ball samples (solid diamond) in Peninsular Malaysia.

rinsed stainless steel containers and transported on ice to the laboratory. The samples were then stored at −35°C until further analysis.

16.3.5 Street Dust Samples

Three street dust samples (KL-1, KL-2, KL-3) were collected from three heavy-trafficked streets in Kuala Lumpur in 1998. The samples were collected using a clean straw brush and stored in solvent-rinsed, tight-sealed vials with a Teflon-lined cap. The samples was transported to the laboratory and stored at −18°C until further analysis.

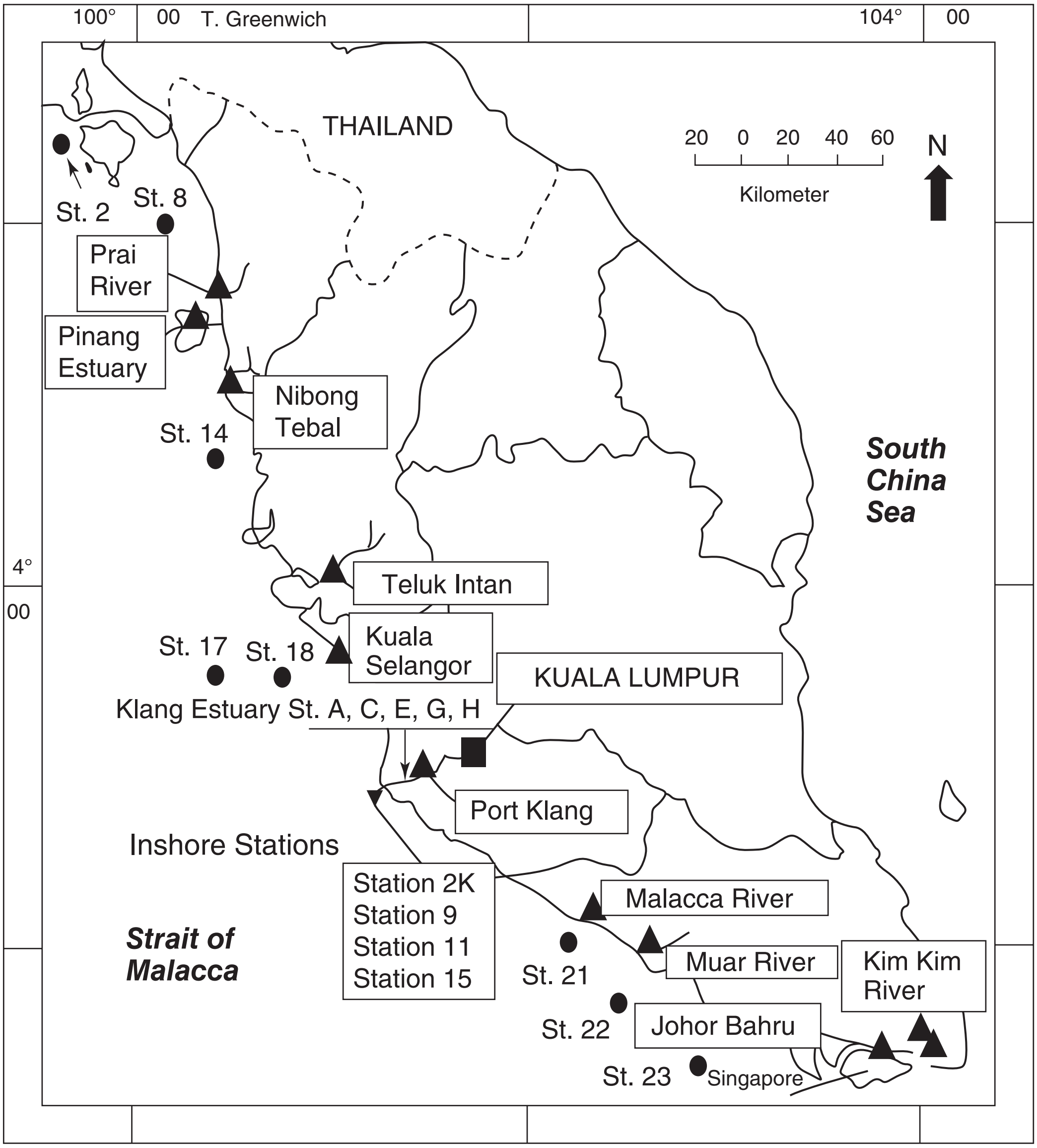

Figure 16-4 Sampling stations for sediment in Peninsular Malaysia. Solid triangles represent river stations and solid circles represents inshore stations.

16.3.6 Asphalt Samples

Fresh asphalt samples (AS-1 and AS-2) were obtained from two pieces of asphalt detached from the surface of an asphalt-paved road near the campus of the Universiti Putra Malaysia, a suburb of Kuala Lumpur. The samples were wrapped with aluminum foil, stored in a clean, plastic Zippered-locked bag, transported to the laboratory, and stored in the freezer until further analysis.

16.3.7 Fresh Crankcase Oil

Two fresh crankcase oil samples (Petronas® and BP®) were randomly purchased from the Malaysian market.

16.3.8 Used Crankcase Oil

Four used crankcase oil samples were taken from storage tanks in a gas station, an automotive workshop, garages, and a motorcycle workshop in Malaysia. The samples were collected using pre-cleaned 10-ml glass pipettes and placed in previously baked 30-ml amber vials. The sample was transported to the laboratory, and stored in the freezer until further analysis.

16.3.9 Automobile Tire Rubber

Tire rubber data and NCBA data were provided by Dr. Hidetoshi Kumata of Tokyo University of Pharmacy and Life Sciences, Hachioji, Tokyo, Japan. Tire particles from four types of used tires were obtained by abrasion of their surfaces with a stainless steel file.

16.3.10 Aerosol Samples

Aerosols data were kindly provided by Dr. Hidetoshi Kumata of Tokyo University of Pharmacy and Life Sciences, Hachioji, Tokyo, Japan. The aerosol samples were collected in Universiti Putra Malaysia (UPM), Petaling Jaya (PJ), Port Dickson (PD), and Langkawi. Aerosol samples from UPM were acquired in both 1997 and 1998, whereas aerosol samples from PJ were acquired in 1998. The aerosol samples were acquired using a high-volume sampler (HVS) (Ecotech, Australia) fitted with a glass fiber filter (Filter #6424596, UPM, exposed during haze in 1997; #6424527, UPM; exposed during haze in 1998; #39472, PJ, exposed during haze in 1997; #40060, PJ, exposed during haze in 1997) (20.3 cm × 25.4 cm, Whatman EPM 2000, England). The HVS was operated at a flow of ~1.0 $\mathrm{m^3\,min^{-1}}$, and ~750 $\mathrm{m^3}$ of air passed through the filter during the 24-hr sampling. Before weighing, all fresh and exposed filters were conditioned for 24 hr in a dry cabinet where the temperature was maintained at 25°C, with relative humidity at 45%. Exposed filters were folded, stored in pre-cleaned aluminum foil, kept in a glass jar, and kept refrigerated until further analysis.

Aerosol samples from PD and Langkawi were acquired in 1998 using a high-volume sampler (Staplex TFIA-2) fitted with quartz fiber filters (Pallflex 2500QAT-UP) (filter #0001, Langkawi, and filter #0003, PD). Approximately 1500 $\mathrm{m^3}$ of air passed through the filter during the 24-hr sampling.

16.4 Analytical Procedure

16.4.1 Chemicals

Authentic standards of n-C_{16}, C_{18}, C_{20}, C_{22}, C_{24}, C_{26}, C_{28}, C_{32}, and C_{36} and deuterated PAHs (acenaphthene-d_8, chrysene-d_{12}, anthracene-d_{10}, p-terphenyl-d_{14}, naphthalene-d_8, benz(a)anthracene-d_{12}, perylene-d_{14}), and PAHs (phenanthrene, anthracene, methylphenanthrenes, fluoranthene, pyrene, benz(a) anthracene, chrysene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno[1,2,3-cd]pyrene, benzo(ghi)perylene, and coronene) were purchased from Wako pure Chemical Ltd. 17β, 21(H)β-hopane, 17α(H)-22,29,30-trisnorhopane (Tm), 17β(H), 21α(H)-norhopane (C_{29} 17β), 17α(H), 21β(H)-hopane (C_{30} 17α), 17bβ(H), 21α(H)-hopane (C_{30} 17α), 18α(H)-oleanane, and 18β(H)-oleanane were purchased from Chiron, Norway. A 100–200-mesh silica gel (F.C.923) from Davison Chemical Corp. was baked at 400°C for ~4 hr, cooled, and then activated at 200°C overnight and deactivated with 5% (w/w) of distilled water. A 60–200-mesh silicic acid (SIL-A-200) from Sigma Chemical Company, USA, was rinsed with methanol and dichloromethane (DCM) using Soxhlet extraction, dried at 50°C, and fully activated at 200°C overnight, and stored in dry n-hexane. Organic solvents were distilled in glass before use. All glassware was washed with detergents and tap water and rinsed successively with methanol, DCM, and distilled hexane. Elemental copper (granular, 0.2–0.9 mm) was purchased from Kishida Chemicals Co. Ltd., Osaka, Japan.

16.4.2 Extraction and Fractionation

Crude oil and tar-ball samples (ca. 10 mg) were precisely weighted, dissolved in 1 ml of DCM/hexane (1 : 3, v/v), and transferred onto the top of 5% H_2O deactivated silica gel column (1 cm i.d. × 9 cm). Hydrocarbons ranging from *n*-alkanes to PAHs with 7 rings were eluted with 20 ml of DCM/hexane (1 : 3, v/v). The sample was then reduced in volume to ~5 ml, where approximately 5 g of activated copper were added and allowed to stand overnight to react with elemental sulfur. The solution was passed through a glass funnel plugged with quartz wool, which trapped copper and the copper sulfide on it. The filtrates were roto-evaporated just to dryness and were subsequently dissolved into 0.4 ml of *n*-hexane, and transferred onto the fully activated silica gel column (0.47 cm i.d. × 18 cm). Three fractions were eluted. The first fraction containing aliphatic and alicyclic hydrocarbons was eluted with 4 ml of hexane. Since tar balls do not contain LABs, the second fraction was combined with PAHs fraction and eluted with 18 ml of hexane and 7-ml hexane/DCM (3 : 1, v/v), respectively. This fraction contained the higher-molecular-weight PAHs with 3–7 benzene rings. The first hexane fraction was evaporated and transferred to a 1.5-ml glass ampule. The hexane was evaporated just to dryness under nitrogen and redissolved in 50 µl–1 ml of isooctane for subsequent instrumental analysis. Subsequent treatment of the PAHs fraction is dealt with in the following sections of this chapter.

Sediment samples were freeze-dried and Soxhlet-extracted using DCM over 8 hr. Activated copper was used to remove elemental sulfur. Wet mussel tissue (ca. 10 g) was macerated/extracted with DCM and pre-baked sodium sulfate anhydrous in a glass centrifuge tube by Polytron (RT2000; Kinebatica). The sediment and mussel extracts were purified and fractionated using the same procedure as the oil samples. For the mussel samples, some co-eluting materials such as esters, etc., in the alkane fractions were hydrolyzed with KOH/MeOH prior to alkane and hopane analyses.

16.5 Instrumental Analysis

16.5.1 Analysis of Alkanes and Hopanes

Normal and isoprenoid alkanes were analyzed on Shimadzu 14 B gas chromatograph with flame ionization detector. A J&W Scientific Durabond DB-5, 30-m fused silica capillary column, 0.25-mm i.d., and 0.25-µm film thickness, was used with helium as the carrier gas at 200 kPa. The injection port was maintained at 300°C, and the sample was injected with splitless mode followed by a 1-min purge after the injection. The column temperature was held at 70°C for 1 min, then programmed at 30°C/min to 150°C, 5°C/min to 310°C, and held for 10 min. The detector temperature was held at 310°C. The concentrations of C_{16} to C_{36} normal alkanes, pristane, and phytane were determined. Identification of sample peaks was based on comparison of retention time of the authentic standard run on the same day and confirmed by GC-MS. Quantification was based on peak height, and the response factor was calculated through the standard run. Response factors for compounds with no corresponding standards were estimated by proportional allotment using standards that bracket the target peak on the chromatogram.

After the alkane analysis, the aliphatic and alicyclic hydrocarbon fraction was evaporated to dryness and re-dissolved into an appropriate volume (50–200 µL) of isooctane containing 5 ppm of 17β, 21β(H)-hopane as an internal injection standard for triterpane analysis. Hopane analyses were made using a Hewlett Packard 5972A quadrupole mass spectrometer integrated with an HP5890 gas chromatograph equipped with a J&W Scientific Durabond HP-5MS, 30-m fused silica capillary column, 0.25-mm i.d., and 0.25-µm film thickness, using helium as the carrier gas on a constant-flow rate mode at 1 ml/min. GC-MS operating conditions were 70-eV ionization potential with the source at 200°C and electron multiplier voltage at ~2000 eV. The injection port was maintained at 300°C, and the sample was injected with splitless mode followed by a purge 1 min after the injection. The column temperature was held at 50°C for 2 min, then programmed at 6°C/min to 300°C, and held for 15 min. A selected ion monitoring method was employed after a delay of 4 min, and triterpanes were quantified at *m/z* = 191. Peaks were identified by comparison of their retention times with those for the standards and their mass spectra, which were obtained on a different GC-MS run on Scan mode, with those in the literature (Peters and Moldowan, 1993; Wang et al., 1994). Quantification was made by peak area. The response factor of 18α(H)-22,29,30-trisnorneohopane (Ts) was assumed to be the same as Tm, 17α(H), 21β(H)-30-norhopane (C_{29} 17α) as C_{29} 17β, and homohopanes ranging from C_{31}–C_{35} of carbon number as C_{30} 17β. Because 18α(H)-oleanane and 18β(H)-oleanane cannot be separated on the gas chromatogram, an average of response factors of both isomers obtained from independent runs was applied to the samples. Differences in response factors of both oleanane isomers were within 10% and, therefore, using the averaged factor has not caused significant errors. For another set of stereo isomers (C_{30} 17α and C_{30} 17β), the differences in their response factors were within 20%. These suggest that the expected differences in response factors for the other set of stereoisomers (e.g., Ts and Tm, C_{29} 17α and C_{29} 17β) are within 20%.

Reproducibility of the whole analytical procedure was checked through the triplicate analysis of an oil sample. Relative standard deviations of individual alkanes and triterpane concentrations were less than 11% and 13%, respectively. Recoveries were determined by spiking a mixture of the standards listed above to the oil samples followed by the entire analytical procedure. Recovery of the spiked standards was more than 82% for alkanes and over 87% for triterpanes.

16.5.2 N-*Cyclohexyl-2-Benzothiozolamine (NCBA)*

NCBA data were provided by Dr. Hidetoshi Kumata of Tokyo University of Pharmacy and Life Sciences, Hachioji, Tokyo, Japan. The organic extracts of NCBA were purified by liquid–liquid extraction with sulfuric acid and fractionated with 5% deactivated silica gel column chromatography. The NCBA was quantified by a Hewlett-Packard 5890 Series II gas chromatograph equipped with an HP-35 fused silica capillary column (30 m × 0.25-mm i.d., 0.25-μm film thickness) interphased with a flame photometric detector (FPD).

16.5.3 *Analysis of PAHs*

Polycyclic aromatic hydrocarbon fraction was evaporated to approximately 1 ml, transferred to a 1.5-ml amber ampule, and evaporated to dryness under a gentle stream of nitrogen and re-dissolved into an appropriate volume (50–200 μL) of isooctane containing acenaphthene-d_8 and chrysene-d_{12} as an internal injection standard (IISTD) for PAH analysis. PAHs were analyzed by GC-MS using a 30-m fused silica column (HP-5MS) installed in a gas chromatograph (HP5890) interfaced with a Hewlett-Packard 5972A quadrupole mass selective detector (SIM mode), using helium as the carrier gas on a constant pressure at 60 kg/cm^2. GC-MS operating conditions were 70-eV ionization potential with the source at 200°C and electron multiplier voltage at ~2000 eV. The injection port was maintained at 300°C, and the sample was injected with splitless mode followed by purge 1 min after the injection. The column temperature was held at 70°C for 2 min, then programmed at 30°C/min to 150°C, 4 °C/min to 310 °C, and held for 10 min. A selected ion monitoring method was employed after a delay of 4 min. PAHs were monitored at *m/z* = 178 (phenanthrene, anthracene), *m/z* = 192 (methylphenanthrenes), *m/z* = 202 (fluoranthene, pyrene), *m/z* = 228 (benz(a)anthracene, chrysene), *m/z* = 252 (benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(e) pyrene, benzo(a)pyrene, perylene), *m/z* = 276 (indeno[1,2,3-cd]pyrene, benzo(ghi)perylene), and *m/z* = 300 (coronene).

Individual PAHs were quantified by comparing the integrated peak area of the selected ion with the peak area of the IISTD. Acenaphthene-d_8 and chrysene-d_{12} were used as IISTD for the quantification of PAHs ranging from phenanthrene to 1-methylphenanthrene and for PAHs from fluoranthene to coronene, respectively. Corrections for relative response at the corresponding mass/charge ratio were made by analyzing a PAH standard (phenanthrene, anthracene, 1-methylphenanthrene, fluoranthene, pyrene, chrysene, benzo[b]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, benzo[ghi]perylene, coronene) under the same instrumental conditions as the sample analyses. No 2-, 3-, or 9-methylphenanthrene standards were available; therefore, an estimated response factor for these compounds was based on a response for 1-methylphenanthrene. Similarly, benz[a]anthracene, benzo[j]fluoranthene + benzo[k]fluoranthene, and indeno[1,2,3-cd]pyrene concentrations were based on the chrysene/triphenylene, benzo[b]fluoranthene, and benzo[ghi]perylene response, respectively. Since naphthalenes were difficult to quantify due to their high volatility, the present study focused on PAHs with three or more benzene rings (i.e., phenanthrene-benzo[ghi]perylene). PAHs concentrations were recovery-corrected using the spiked surrogates, and recoveries were in the range of 64–83%. The precision of the method was determined through four replicated analyses of the heavy residual oil sample. The relative standard deviation (RSD; $n = 4$) of individual PAHs identified in sample extracts was <10%.

16.6 Establishment and Application of Biomarker Analysis for Source Identification of Oil Pollution Sources in the Strait of Malacca

Identification of oil pollution sources is an important task in order to assess environmental damage, and to understand the fate and behavior of spilled oils on the environment. Since spilled oils may cause extensive damage to marine and terrestrial organisms including human health, identification of the exact source of oil pollution can provide quite an accurate prediction of the long-term impact of spilled oil on the environment. Recently, Wang and Fingas (2003) reviewed development of chemical analysis methodologies that are most frequently used in oil spill characterization and identification studies and environmental forensic investigations.

In the Strait of Malacca, Zakaria et al. (2000) investigated oil pollution where various samples including Malaysian oil, Middle East crude oils (MECO), southeast Asia crude oils (SEACO), tar balls, sediments, and mussels were collected and analyzed. Case Study I is introduced explaining the development of the analytical method for oil pollution source identification using biomarkers in the Straits of Malacca. The major finding from Case Study I was that approximately 30% of the sea-based petroleum hydrocarbon pollution was derived from MECO, while the rest is of domestic source. Therefore, the remaining 70% of the domestic source of either sea- or land-based petroleum hydrocarbon pollution can be very significant and important (see Section 16.8).

The above scenario was examined in Case Study II, where a major finding was that very serious petroleum hydrocarbon pollution is occurring in Peninsular Malaysia. Polycyclic aromatic hydrocarbons (PAHs) of petrogenic origin are widely distributed in Malaysian riverine and coastal sediments, and used crankcase oil and street dust appear to be the major contributors of the pollution. It has been proposed that rapid transfer of land-based pollution into the aquatic environments was due to intense rainfall and runoff waters. If PAHs of terrestrial origin could be transferred rapidly to aquatic environments, this would bring a serious threat to Malaysia. A brief summary of Case Studies I and II follows. Case Study I is based on studies conducted by Zakaria et al. (1999), (2000), and (2001), while Case Study II is based on studies conducted by Zakaria et al. (2002).

16.7 Case Study 1: Development of the Analytical Method for Oil Pollution Source Identification Using Biomarkers in the Strait of Malacca

Crude oil samples typical of petroleum sources included four southeast Asian crode oils

(SEACO), three Middle East (MECO) crude oils, and two Malaysian fresh crankcase oils, which were analyzed for alkanes and hopanes. SEACO were characterized by lower C_{29}/C_{30}-hopane and ΣC_{31}–C_{35}/C_{30} hopane ratios, and the reverse was true for MECO. The C_{29}/C_{30} and ΣC_{31}–C_{35}/C_{30} hopane ratios were thus potential source identifiers to distinguish between SEACO and MECO. In addition, PAHs were also used as additional source identifiers to get information on weathering of tar balls.

16.7.1 Weathering of Tar Balls

PAHs and alkane compositions were utilized to evaluate the weathering of the tar ball samples. Table 16-1 lists concentrations of PAHs and alkanes and the compositional indices for the tar balls collected from the west and east coasts of Malaysia together with data on crude oils.

PAHs in the tar-ball samples were more abundant in higher-molecular-weight compounds (more depleted in lower-molecular-weight compounds) as compared to the crude oil. Evaporation, dissolution, and biodegradation enhance losses of low-molecular-weight PAHs (Heitkamp and Cerniglia, 1987). The difference in molecular-weight distributions is parameterized as the L/H-PAH ratio, as defined in Table 16-1. L/H-PAH ratios ranged from 7.5–44 in crude oil, compared with 0.23–8.57 in the tar-ball samples. The lower ratios indicate that the tar-ball samples had undergone variable weathering, from slightly to severely. Tar-ball samples SESB, SESK, MEKU, MESM, JBPP, MAMC-T2, JRTL, and SESD showed much lower L/H-PAH ratios (0.23–1.48) than those for crude oil samples (8–44). This is consistent with low PAH contents in the eight tar-ball samples (10–343 μg/g) compared with those in the crude oil samples (193–3069 μg/g). Alkane data are consistent with the PAH compositions. The above eight tar-ball samples were extremely depleted in lower-molecular-weight alkanes, and their L/H-alkane ratios (0.00–1.11) were lower than those for the crude oil samples (1.62–4.60). Furthermore, the unresolved complex mixture (UCM), an indicator of weathering of petroleum (Volkman et al., 1997), was observed for three of the eight samples (i.e., SESB, SESK, and MEKU). However, the other five tar-ball samples (i.e., MESM, SESD, MAMC-T2, JBPP, and JRTL) showed no UCM. This means that lower-molecular-weight components of PAHs and *n*-alkanes might have been depleted due to some other processes than weathering. One of the possible causes is tank washing and discharges from oil tankers. This possibility will be discussed in the following subsection. Other molecular ratios of PAHs such as fluoranthene/pyrene, benzo[a]pyrene/benzo[e]-pyrene, and benz[a]anthracene/chrysene had also been examined as weathering indicators for the tar balls. However, those ratios did not show clear trends due to variation among crude oils.

Alkane and hopane data were very powerful molecular markers for source identification of oil pollution in the Strait of Malacca. However, integration of alkane and hopanes with PAHs could facilitate for more specific source identification and may provide further information on weathering.

The analytical results from the present study have established and successfully applied biomarkers as a molecular tool in tracing and determining the sources of oil pollution (MECO vs. SEACO) in the Strait of Malacca. This study has shown that C_{29}/C_{30} and ΣC_{31}–C_{35}/C_{30} ratios are not only powerful but reliable source identifiers of oil pollution. This study has also shown that high-oleanane concentration in tar balls indicates domestic petroleum origin (i.e., SEACO). However, low concentrations of oleanane in tar balls could not be identified as SEACO or MECO because both crude oils contain low concentrations of oleanane. This is probably due to the variability in oleanane contents in SEACOs. The results imply that low concentration of oleanane does not always indicate Middle East petroleum contribution although at high concentration oleanane can still be useful biomarker for Southeast Asian oil sources. Also,

Table 16-1 PAHs and Alkanes Compositions for Crude Oils and Malaysian tar-ball

	PAHs			*Alkanes*			
	Total PAHs (ug/g)[a]	*MP/P ratio*[b]	*L/H-PAH*[c]	*Total Alkanes*[d] *(mg/g)*	*Pr/Ph*[e]	*L/H-Alkane*[f]	*UCM*[g]
Crude oils							
MECO (Middle East Crude Oil)							
Arabianligh	193	3.39	12.13	25	0.64	4.60	x
Umushyfu	700	4.34	20.35	38	0.97	3.35	x
Marban	341	3.88	15.68	49	0.94	3.92	x
SEACO (South East Asian Crude Oil)							
LABUAN	3069	2.43	44.46	99	4.01	2.43	x
MIRI	495	2.45	12.43	52	4.03	2.45	x
TAPIS	952	3.17	21.52	128	3.66	4.52	x
Sumatra	702	2.24	7.50	109	2.91	1.62	x
Tar-ball							
West Coast							
KETR-T2	469	6.83	6.95	101	2.36	1.24	x
KETR-T1	463	8.91	3.96	11	1.60	1.59	x
KEPK	60	3.05	2.48	51	1.38	0.32	x
SESB	18	1.40	0.36	0.4	n.c.[b]	0.09	o
SESD	31	0.16	1.48	106	n.c.[h]	0.46	x
SESK	73	2.68	0.23	1	n.c.[h]	0.07	o
SETK	112	1.70	2.34	4	0.42	1.72	x
NSPD	189	6.24	5.61	128	3.85	0.83	x
METB	557	3.63	8.57	175	4.14	1.07	x
MEKU	180	6.75	0.43	1	n.c.[h]	0.00	o
MESM	75	8.56	0.27	192	3.05	0.62	x
MAMC-T2	343	3.99	0.97	54	1.14	0.21	x
JBPP	41	12.09	0.75	8	0.83	1.11	x
East Coast							
JRTL	10	9.00	0.72	16	1.70	0.75	x
PAKP	248	8.47	2.79	33	0.69	1.29	x
PATB	195	8.03	3.13	37	1.46	1.19	x
TRMT	95	5.56	4.77	108	2.10	1.31	x
TRMT-T2	57	12.86	3.07	103	1.80	1.21	x
TRME	42	5.16	7.20	20	2.19	0.97	x
KLTB	476	8.86	4.57	62	0.84	0.80	x

[a] Total PAHs = sum of concentrations of phenanthrene + anthracene + 3-methylphenanthrene + 2-methylphenanthrene + 9-methylphenanthrene + 1-methylphenanthrene + fluoranthene + pyrene + benza(a)anthracene + chrysene + benzofluo thenes + benzo(e)pyrene + benzo(a)pyrene + perylene + indeno(1,2,3-cd)pyrene. [b] MP/P ratio = a ratio of sum of 3-methylphenanthrene + 2-methylphenanthrene + 9-methylphenanthrene + 1-methylphenanthrene relative to phenanthrene concentrations. [c] L/H = sum of concentrations of phenanthrene to pyrene relative to sum of concentrations of benz(a)anthracene to benzo(ghi)perylene in a. [d] Σ(C16–C36) = sum of n-C16 alkane to n-C36 alkane. ealkane/(pr + py) = sum of alkane relative to sum of pristane and phytane. [f] L/H = sum of n-C16 alkane relative to sum of n-C27–n-C36 alkane. [g] UCM = unresolved complex mixture. X = not present, o = present

Source: Zakaria, M. P., T. Okuda, and H, Takada. "Polycyclic Aromatic Hydrocarbon (PAHs) and Hopanes in Stranded Tarballs on the Coast of Peninsular Malaysia: Applications of Biomarkers for Identifying Sources of Oil Pollution. Marine Pollution Bulletin, 2001, **42**(12), 1357–1366.

the homohopane index was shown to be useful as a source identifier in this study since it clearly distinguishes MECO from SEACO. This study, however, did not find that the Tm/Ts ratio is a useful source identifier of the oil spill in the Strait of Malacca since the ratio is inconsistent between MECO tar balls and SEACO tar balls.

This study has also shown that PAHs provide useful additional information on source identification of petroleum pollution, and their molecular distributions are useful as an index of weathering. Thus, the combination of biomarkers of triterpanes, alkanes, and PAHs has become an extremely powerful tool for source identification of petroleum pollution.

16.8 The Application of Molecular Markers for Source Identification of Tar-Ball Pollution in Malaysia

Using the source identifiers, the C_{29}/C_{30} and $\Sigma C_{31}–C_{35}/C_{30}$ ratios, the origins of 20 tar-ball samples collected from 18 locations in the coastal beaches of Peninsular Malaysia were determined (Figure 16-5).

PAH profiles were also utilized to obtain information on weathering of tar balls, and the absence of PAHs was found to be a good indicator of weathering. Using the molecular marker approach, we demostrated that approximately 30% of tar-ball samples collected from the west coast of Peninsular Malaysia originated from the Middle East crude oil (MECO). This suggests that a tanker-derived source has significantly contributed to the petroleum pollution in the Strait of Malacca.

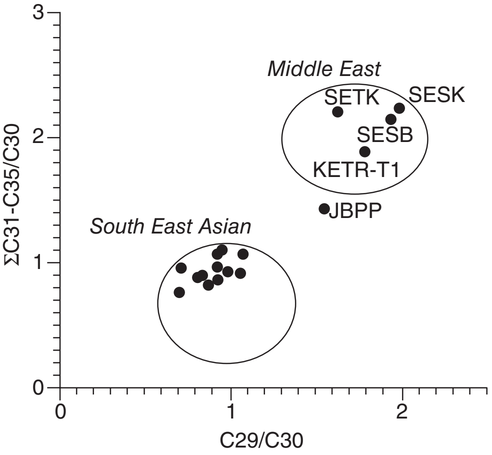

Figure 16-5 Cross-plots for source identification of oils. The circles indicating both categories were established through the analysis of crude oils in Zakaria et al. (2000).

On the other hand, about 70% of the petroleum hydrocarbon input was actually domestically derived. Hence, determination of the distribution and sources of compound-specific petroleum hydrocarbons in Malaysian rivers, coastal sediments, and the Strait of Malacca sediments is necessary. Therefore, the next goal was to identify the distribution and sources of PAH pollution in Malaysia.

The present study clearly demonstrated a substantial contribution of MECO spilled from tankers passing through the Strait to the tar balls (e.g., SETK, SESB, SESK, KETR-T1). Some international action is therefore necessary to reduce the petroleum pollution from the tankers. In addition, domestic sources have been identified as major contributors, and identification of the specific sources and regulations of these sources are even more important. It was thought that oil spills from the petroleum platform off the east coast have largely contributed to the tar-ball pollution on the east coast (e.g., PAKP, PATB, TRMT, TRMT-T2, TRME, KLTB) and perhaps even to some extent on the west coast (e.g., MEKU). More stringent controls and regulations on the offshore platforms to prevent unnecessary spillages could reduce the tar-ball pollution on the Malaysian coasts. Contributions from tank washing and ballasting discharges from the tankers transporting the SEACO could also have contributed significantly to the overall tar-ball pollution along the Strait of Malacca (e.g., SESD, MESM, MAMC-T2). Appropriate treatment of the tank washings and ballast water from the tankers should be enforced. Oil pollution from other domestic sources such as leakage from oil refineries on the west coast and the Sumatran oil fields has been suggested, although their contributions have not specifically been identified. To identify such domestic sources, more efforts are required, and the molecular marker approach proposed in the present study could be a powerful tool.

16.9 Case Study 2: Distribution and Sources of Polycyclic Aromatic Hydrocarbons (PAHs) in Rivers and Estuaries in Malaysia

In order to determine the distribution and sources of PAHs in Malaysia, sediment samples collected in rivers, estuaries, and the Strait of Malacca were analyzed for PAHs. For source discrimination of petroleum-related sources, triterpanes (petroleum biomarker) together with PAHs were measured. Prospective sources, including fresh and used crankcase oil, street dust, and asphalt were also analyzed. To examine the contribution from automobile-related sources, a molecular marker, *n*-cyclohexyl-2-benzothiozolamine (NCBA; Kumata et al., 2000), was utilized in polluted sediment samples and street dust.

Parent PAHs (3 to 7 rings) were analyzed by gas chromatography mass spectrometry (GC-MS). Total PAH concentrations in the sediment ranged from 4 to 924 ng/g, and alkylated homologues were abundant for most of the sediment samples. The ratio of the sum of methylphenanthrenes to phenanthrene (MP/P), an index of petrogenic PAH contributions, was more than unity for 26 of 29 sediment samples and more than 3 of 7 samples for urban rivers covering a broad range of locations.

The MP/P ratio showed a strong correlation with total PAH concentrations with an r^2 of 0.74. This ratio and all other compositional features indicated that Malaysian urban sediments are heavily impacted by petrogenic PAHs. The finding is unique in comparison to other studies reported in many industrialized countries where PAHs are mostly of pyrogenic origin. The MP/P ratio was also significantly correlated with higher-molecular-weight PAHs such as benzo[a]pyrene, suggesting a unique PAH source in Malaysia that contains both petrogenic PAHs and pyrogenic PAHs. PAH and hopane fingerprints indicated that used crankcase oil is one of the major contributors of the sedimentary PAHs. Two major routes of inputs were identified to aquatic environments: (1) spillage and dumping of waste crankcase oil; (2) leakage of crankcase oils from vehicles onto road surfaces with subsequent washout by street runoff. Input from street dust was confirmed by detection of *N*-cyclohexyl-2-benzothiazolamine (NCBA) in polluted sediment samples.

Oil pollution in coastal environments continues to be a major issue. The Strait of Malacca is no exception. The present study expands our limited understanding of possible sources of oil pollution to the fragile ecosystems in the Strait. The Strait have always been a source of valuable living and nonliving resources. Given the region's growing dependence upon Middle Eastern oil-producing nations and increasing trade and transport of fossil fuels, the Strait of Malacca has become a major conduit of world trade. Proper management such as preventive and remedial measures as well as conservation of the Strait will greatly contribute to the benefit of Malaysia and various other countries for years to come.

16.10 Conclusions and Future Scenario

This study has shown that C_{29}/C_{30} and $\Sigma C_{31}–C_{35}/C_{30}$ ratios are not only powerful but reliable source identifiers of the oil pollution. This study has also shown that high oleanane concentration in tar balls indicates domestic petroleum origin (i.e., SEACO). However, low concentrations of oleanane in tar balls could not be identified as SEACO or MECO because both crude oils contain low concentrations of oleanane. This is probably due to the variability in oleanane contents in SEACOs. The results imply that low concentration of oleanane does not always indicate Middle East petroleum contribution although at high concentration oleanane can still be useful biomarker for Southeast Asian oil sources. Also, the homohopane index was shown to be useful as a source identifier in this study since it clearly distinguishes MECO from SEACO. This study, however, did not find that the Tm/Ts ratio is a useful source identifier of the oil spill in the Strait of Malacca since the ratio is inconsistent between MECO tar balls and SEACO tar balls.

The MP/P ratio showed a strong correlation with total PAH concentrations with an r^2 of 0.74. This ratio and all other compositional features indicated that Malaysian urban sediments are heavily impacted by petrogenic PAHs. The finding is unique in comparison to other studies reported in many industrialized countries where PAHs are mostly of pyrogenic origin. The MP/P ratio was also significantly correlated with higher-molecular-weight PAHs such as benzo[a]pyrene, suggesting a unique PAH source in Malaysia that contains both petrogenic PAHs and pyrogenic PAHs. PAH and hopane fingerprints indicated that used crankcase oil is one of the major contributors of the sedimentary PAHs. Two major routes of inputs were identified to aquatic environments: (1) spillage and dumping of waste crankcase oil; (2) leakage of crankcase oils from vehicles onto road surfaces with subsequent washout by street runoff. Input from street dust was confirmed by detection of *N*-cyclohexyl-2-benzothiazolamine (NCBA) in polluted sediment samples.

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