Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) Found in Water Along the Northern Straits of Malacca

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ABSTRACT   Marine water samples were collected during the SESMA I expedition along the northern Straits of Malacca. The route encompassed the Klang islands, the estuaries of the Selangor, Bernam and Perak rivers, Pulau Sembilan, Pulau Jarak, the estuaries of the Dinding, Matang and Gula rivers, southern Penang and Pulau Perak. Samples were collected from the surface to 1.5-2.0 m depth from a total of 18 stations located along the straits. The samples were analyzed for concentrations of a range of persistent organic polycyclic aromatics hydrocarbons (PAHs) namely: naphthalene, fluorene, anthracene, fluoranthene and pyrene. The total of these five PAHs concentrations were found to vary between 0.58 to 79.26 μgL^{-1}.

ABSTRAK   Sampel air laut telah diambil semasa ekspedisi SESMA I di sepanjang Selat Melaka. Laluan termasuklah pulau-pulau di Klang, kuala sungai Selangor, Sungai Bernam dan Sungai Perak, Pulau Sembilan, Pulau Jarak, kuala Sungai Dinding, Sungai Matang, Sungai Gula, selatan Pulau Pinang dan Pulau Perak. Kutipan sample dilakukan di bahagian permukaan air sehingga ke kedalaman 1.5 – 2.0m di kesemua 18 stesyen di sepanjang selat. Analisis telah dijalankan ke atas sampel-sampel untuk mengetahui kepekatan hidrokarbon aromatic polisiklik (HAP), iaitu naftalena, florena, antrasena, fluorantena dan pirena. Jumlah kepekatan bagi kelima-lima PAH ini adalah di antara 0.58 ke 79.26 mgL^{-1}.

(polycyclic aromatics hydrocarbons, estuaries, Straits of Malacca)

INTRODUCTION

Background

The Straits of Malacca is located between the east coast of Sumatra Island in Indonesia and the west coast of Peninsular Malaysia. It is bordered by four littoral States, namely Thailand, Indonesia, Malaysia and Singapore. Its length about 600 nautical miles (nm) with the widest section (220 nm) near the north-west entrance, narrowing gradually to about 8 nm at its southeast entrance near the Riau Archipelago. The Straits has long been an important trade route linking the Indian Ocean to the South China Sea and Pacific Ocean. With a total of 62,334 ships passing through in 2003 it is indeed, one of the most important international shipping routes in the world. With its wealth of resources such as productive coastal ecosystems, extensive and intensive aquaculture, coastal tourism, mining and natural gas reserves, it provides a life support system to the millions of people that inhabit the towns and villages that dot the coastline from Langkawi to Tanjung Piai. Decades of human activities have however taken a serious toll on the natural environment especially the fragile coastal and marine ecosystems. Consequently, the coastal areas and water fronts are under constant threat from the various sources of pollutants which include discharges from agricultural activities, human settlements, industries and shipping [1]. In this paper, we report results of the analysis of 18 water samples for polycyclic aromatic hydrocarbon (PAHs).

Sources of PAHs

The major source of PAHs is from hydrocarbon oil. Sources of oil input to the marine environment are often divided into natural, land-based and sea-based sources. Marine oil pollution in near-coastal water is generally attributed to land-based activities such as the utilization of petroleum related products, the direct discharge of untreated municipal and industrial wastes containing refined and partly weathered oils to sewers and rivers, and the discharge of effluents from refineries and other similar sources [1].

Figure 1. Designated collection stations along the northern Straits of Malacca.

Generally in most cases encountered, the latter source accounts for a large part of the total annual input of oil to the marine environment. The major contributing factors are accidental oil spills from tankers caused by collision or grounding and operational discharges of oil from all kinds of commercial vessels such as deballasting, oil tank and cargo cleaning. Another important contributing source is from atmospheric pollution leading to the deposition of PAHs mainly from the incomplete combustion of hydrocarbons. Amongst organic pollutants, PAHs are a major group of the marine environmental contaminants. It comprises the largest class of chemical compounds known to be cancer-causing agents. PAHs are included in the European Union and United States Environmental Protection Agency (EPA) priority pollutant list due to their mutagenic and carcinogenic properties [2]. Thus it is imperative to determine the levels of PAHs particularly in areas where there are intense anthropologic activities such as the Straits of Malacca.

MATERIALS AND METHOD

Samples and sampling locations
Water samples were collected from eighteen different sampling stations in the Straits of Malacca. The collection points began from Port Klang (PJ1) along the coastline off Tanjung Piandang (PJ2-PJ6) and then crossing the Straits to Pulau Perak (PJ7-PJ12). The transverse journey back from Pulau Perak to Pulau Pangkor (PJ13-PJ18) covered mainly the middle of the Straits (Figure 1).

Samples were collected by the grab method from aboard the MV Reef Challenger at each station along the Straits. Surface samples were collected from a depth of 1.5 m to 2 m to avoid contamination from particulates in the surface micro-layer. Collected samples were contained in cleaned and dried 1 L amber glass sample bottles to prevent degradation of the analytes from UV light. Samples were preserved with 5 ml of hexane and acidified at point of collection with concentrated hydrochloric acid to prevent loss of volatile organic compounds and to render inactive any microorganism that may

Table 1.   Sampling stations with coordinates and physical properties of the water samples.

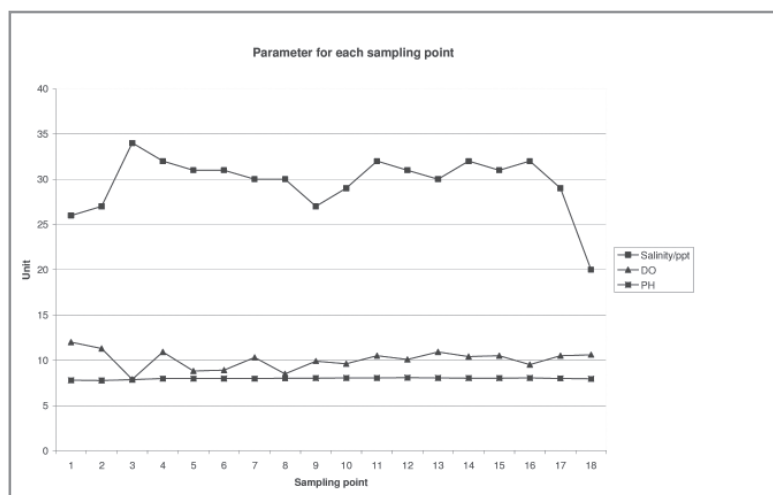| Location	Longitude (N)	Latitude (E)	Salinity/ppt	Temp./^{o}C	DO mg/L	pH
1	03°00'18	101°24'30	26	29.6	12.0	7.78
2	03°22'20	101°07'58	27	31.7	11.3	7.76
3	03°44'25	100°43'59	34	28.5	7.9	7.85
4	04°14'23	100°31'47	32	29.3	10.9	7.97
5	05°29'55	100°05'60	31	29.8	8.8	7.96
6	05°31'60	99°57'01	31	29.8	8.9	7.98
7	05°34'52	99°48'07	30	30.0	10.3	7.97
8	05°31'59	99°40'40	30	30.7	8.5	8.01
9	05°36'17	99°32'53	27	30.9	9.9	8.02
10	05°38'01	99°24'20	29	30.4	9.6	8.05
11	05°39'18	99°16'35	32	30.0	10.5	8.03
12	05°40'49	99°06'23	31	39.6	10.1	8.07
13	05°33'30	99°05'38	30	29.7	10.9	8.05
14	05°26'47	99°15'41	32	29.8	10.4	8.02
15	05°10'39	99°31'17	31	29.8	10.5	8.02
16	04°34'30	99°57'29	32	29.7	9.5	8.03
17	04°23'33	100°07'29	29	30.0	10.5	7.99
18	04°15'49	100°25'11	20	29.7	10.6	7.95

Figure 2. Distribution plot for physical properties of water samples.

cause biodegradation of the samples, respectively. The samples were maintained at ca. 4°C during the entire expedition for 5 days before transporting them to the laboratory where they were stored at a temperature of below 0°C prior to analysis. Table 1 lists the positions of the 18 locations with their GPS readings and some physicals and chemical parameters measured.

Reagents
All chemicals and reagents were of analytical grade and of highest purity possible. HPLC-grade
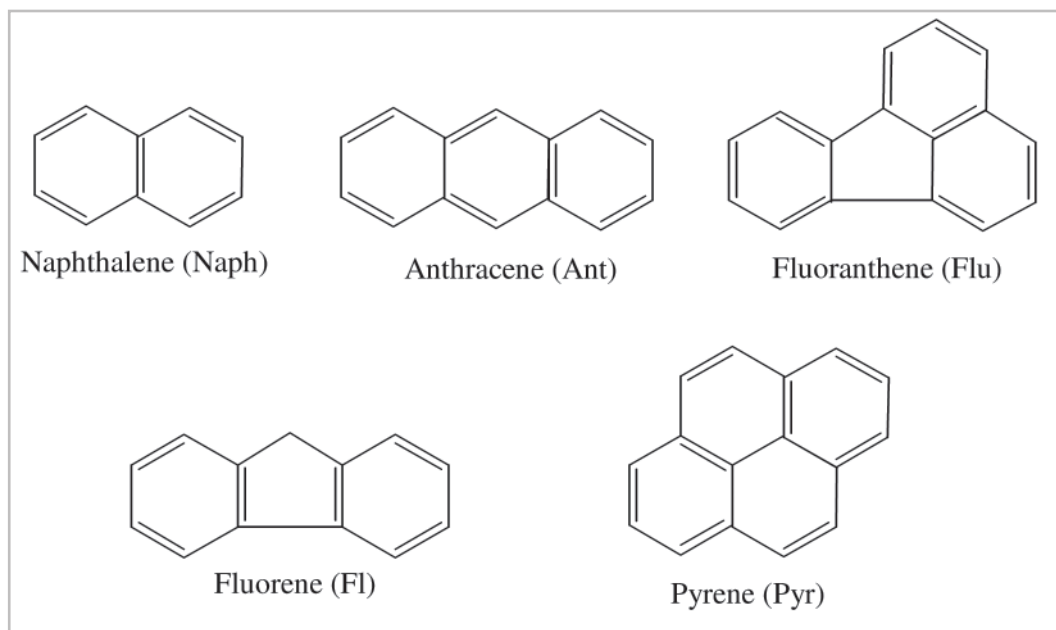
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Figure 3. The 5 types of PAHs determined in this study.

n-hexane, dichloromethane, diethyl ether and petroleum ether (40-60º) used for extractions were obtained from Merck (Germany). Purified water was obtained from a Milli-Q-system (Millipore, Milford, MA, USA). Florisil (60-100 mesh size) used in clean-up was obtained from BDH. AR grade anhydrous sodium sulfate was supplied by Merck. A sixteen-compound PAH standard stock solution (i.e. 10 μgmL^{-1} of each analyte) is purchased from Supelco (Bellefonte, PA, U.S.A.) and containing naphthalene, fluorene, anthracene, fluoranthene, and pyrene was used.

PAHs extraction procedure

The method used for PAH extraction was performed by liquid-liquid extraction. Five types of PAHs were analyzed namely: naphthalene, fluorene, anthracene, fluoranthene and pyrene (Figure 3). The apparatus consisted of a 500 mL volume separating funnel mounted on a retort stand. The separating funnel was thoroughly washed and dried overnight in an oven at 120ºC. Prior to use the funnel was rinsed vigorously with dichloromethane for several minutes. This was removed and allowed to drain and dry completely in a fume cupboard. 100 mL of water sample to be extracted was transferred to the separating funnel and to this was added 100 mL of dichloromethane. This was shaken vigorously for 2 min and allowed to separate and settle. After 10 min the organic layer was removed and the process repeated with the aqueous layer twice. The three portions of the organic phase were combined and anhydrous sodium sulfate was then added to the organic layer to remove trace amounts of water. Extracts were pre-concentrated in a rotary evaporator to a total solvent volume of *ca*. 20 mL, and then transfer quantitatively into a 50 mL round bottom flask for clean up procedures. The subsequent clean-up of the concentrated extracts was performed using a florisil column (20 x 1 cm i.d.) prepared in *n*-hexane. The extracts were loaded into the column and the fractions eluted out using a mixture of *n*-hexane-petroleum ether mixture. Each fraction was reduced to *ca.* 1 mL by evaporation using nitrogen gas.

Analysis by GC

Chromatographic analyses were performed using a Shimadzu GC–17A (Tokyo, Japan) gas chromatograph fitted with an ECD detector at 300°C. Nitrogen was used as carrier gas and column head pressure was maintained at 75kPa to give an approximate flow rate of 3 mL/min. All sample volumes in 1 µL were injected into the GC in splitless mode and it was held isothermally at 260ºC. Analytes were separated using a non-polar fused silica capillary column from Supelco BPX-5 (0.25 mm ID x 30 m length) with a film thickness of 0.25 mm. The column temperature was initially set

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Table 2.   Chromatographic characteristics of the target compounds.

Compound	Retention time (mins)	Coefficient of determination, R²	LOD (µg/L)	Recovery (%)	RSD (%)
Naphthalene	11.8	0.985	0.03	67.31	4.35
Fluorene	16.6	0.987	0.02	75.53	5.21
Anthracene	18.9	0.986	0.02	78.45	4.36
Fluoranthene	22.4	0.988	0.03	91.08	2.52
Pyrene	23.3	0.989	0.04	89.32	3.73

at 60°C, held for 3 min, ramped to 280°C at a rate of 5°C/min, and maintained for 5 min. Extraction recoveries of each analyte are listed in Table 2. A strict quality control procedure was followed that included the analysis of spiked and real seawater samples with each set of field samples analyzed. Method detection limits were calculated by subtracting the background noise with the lowest extraction concentrations, and these values varied between 0.1 µgL⁻¹ to 1.5 µgL⁻¹. Identification of the compounds was based on the retention time match against standard solutions. Quantitation was performed by the method of internal standardization. Calibration curves were obtained using a series of varying concentrations of a multi-component standard containing each of the 5 PAHs. The curves were obtained by plotting target analyte/internal standard peak area against concentration.

RESULTS AND DISCUSSION

A linear fit (R^2=0.985 to 0.989) between initial spike concentration and chromatogram area was observed. The average percent recoveries of common PAHs were consistent and standard deviations were relatively low. Other analytical parameters for chromatographic method such as retention times, coefficients of determination, relative standard deviations (RSD) and limits of detection (LOD) are presented in Table 2. The total distribution levels of all the 5 species of PAHs are summarized in Table 3. The total PAHs concentration varied from 0.58–79.26 µgL⁻¹ with the highest concentration of total PAHs detected at station PJ1 and lowest at station PJ12. Not all the five PAHs were detected in every water samples. All five species of PAHs were detected from stations PJ1-9 and PJ16-18. The highest total PAH

Table 3.   Distribution levels of PAHs from sampling stations located along the Straits of Malacca.

Sampling Location	Naphthalene /µgL⁻¹	Fluorene /µgL⁻¹	Anthracene /µgL⁻¹	Fluoranthene /µgL⁻¹	Pyrene /µgL⁻¹	Total PAHs /µgL⁻¹
PJ1	10.13	8.31	35.33	12.15	13.34	79.26
PJ2	11.65	6.23	31.31	7.19	12.35	68.73
PJ3	15.14	7.25	25.05	9.10	9.23	65.77
PJ4	12.65	9.35	20.51	9.37	8.20	60.08
PJ5	8.13	7.35	28.53	5.05	10.01	59.07
PJ6	13.21	8.67	33.53	4.12	12.05	71.58
PJ7	8.32	3.15	13.21	3.08	7.55	35.31
PJ8	8.67	2.56	10.32	2.11	3.08	26.74
PJ9	2.15	1.09	6.37	3.22	2.25	15.08
PJ10	2.32	nd	2.67	1.53	2.08	8.60
PJ11	1.35	nd	0.91	nd	nd	2.26
PJ12	0.58	nd	nd	nd	nd	0.58
PJ13	nd	nd	nd	nd	1.03	1.03
PJ14	nd	nd	nd	0.88	nd	0.88
PJ15	1.05	1.35	2.55	nd	1.38	6.33
PJ16	8.13	1.67	10.57	1.03	1.57	22.97
PJ17	9.45	1.92	13.12	1.05	5.67	31.21
PJ18	10.37	2.03	15.37	2.35	3.13	33.25

*nd – not detected.

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concentrations were found in PJ1 (79.26 μgL^{-1}) followed by PJ6 (71.58 μgL^{-1}) which were located in the vicinity of Port Klang and Tanjung Piandang respectively. These locations have operations in shipyards and industrial activities. The distribution of PAHs levels found in the middle of the Straits (i.e. PJ11 to PJ14) was much lower as compared to the elevated concentrations observed along the coastal areas. The differences probably indicate a higher degree of pollution attributed mainly by land-based sources. This distribution pattern of PAHs shares similar trends to earlier findings in local water [3] and including neighboring countries like Gulf of Thailand [4] and Singapore [5]. The levels of PAHs between 150-300 μgL^{-1} [6] and 1-135 μgL^{-1} [7] as detected in the Straits are agreeable with our finding.

CONCLUSION

The marine environment in the Straits is subjected to a great variety of environmental stresses and is threatened by PAHs pollution evidently from land-based and sea-based sources. Hydrocarbon inputs from shipping activities, oily wastes from industrial discharges and atmospheric pollution are some of the important contributing sources. Marine pollution in the Straits is a common problem encountered by similar water channels in many parts of the world. Although the level of PAHs contamination in the Straits has not reached a chronic stage yet, there is an urgent need to respond and take preemptive measure againts it. To maintain and ensure a clean environment in the Straits, it is imperative that all stakeholders of the littoral states co-operate. Marine pollution prevention and management policies must be addressed and implemented. As such, the development of a Strategic Environment Management Plan (SEMP) for the Straits to guide future development in the area over the long term should be seriously considered [8].

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