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Distribution of Oil and Grease and Petroleum Hydrocarbons in the Straits of Johor, Peninsular Malaysia

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The Straits of Johor is a narrow stretch of water separating Peninsular Malaysia from Singapore. The two land masses bordering the Straits of Johor are characterised by a wide range of landscapes and activities. On the Malaysian side, which constitutes the state of Johor, lies the state capital as well as a rapidly developing international seaport, in the vicinity of a major industrial area. The eastern portion of the state bordering the straits is relatively undeveloped, comprising of wetland forests. On the Singapore side, apart from a power-generating facility, much of northern Singapore which borders the straits is undeveloped. The Straits of Johor and nearby-waters also represent an important area for fishing and aquaculture activities. Fish traps are a common sight along the length of the straits.

Oil pollution has been identified as the major contribution to the deterioration of the marine water quality in the Straits of Johor (DOE,1994). Shipping activities involving tankers and other vessels plying the Straits of Malacca, have been recognised as a source of petroleum hydrocarbons in these waters. Land-based industrial and urban sources also contribute to the overall oil pollution load in these waters.

In recognising the need for baseline data in assessing environmental pollution, the Department of Environment has been conducting pollution monitoring programmes since 1976, at numerous sampling stations situated in the major river systems of the nation, as well as coastal areas, including the Straits of Johor. However, as far as oil pollution is concerned, these programs have been restricted to measuring oil and grease. The present study was undertaken to determine petroleum hydrocarbons, as well as oil and grease in water and sediments along the near-coastal areas of the Straits of Johor and near-by waters.

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MATERIALS AND METHODS

The location of the sampling stations are shown in Figure 1. The sampling stations were selected to represent a wide range of anthropogenic sources of oil pollution. The majority of stations were located in the vicinities of shipping lanes, industrial and urban zones. Stations 29-31 were expected to reflect background levels of contamination since they correspond to relatively pristine areas. Sampling took place in March 1995.

Water samples were collected from a depth of 1 metre using a van Dorn water sampler. The partition-gravimetric method using 1,1,2-trichloro-1,2,2-trifluoroethane as the extracting solvent was adopted to indicate the levels of oil and grease in water (APHA, 1989). Artificial seawater spiked with 100 mg of Seligi crude oil, a light crude gave recoveries in excess of 92 % and a standard deviation of 9 %. The analysis of petrogenic hydrocarbons in water was determined according to the fluorospectrometric method of Parsons et al. (1984). Briefly, multiple extractions of the water sample with dichloromethane was followed by drying with anhydrous sodium sulphate and removal of polar materials with silica gel (60-120 mesh).

Samples of surface sediments were collected by means of a van Veen grab sampler. The samples were wrapped with hexane-cleaned aluminium foil and stored at -20 °C until analysis. The extraction and subsequent clean-up procedure for sediment samples were in accordance with established procedures (Hilpert et al. 1978). Thus, freeze-dried samples were soxhlet-extracted with a toluene:methanol (3:2) mixture, saponified with methanolic KOH, followed by hexane extraction and column chromatography on silica.

Petrogenic hydrocarbons in water and sediments were determined on a Shimadzu UV Spectrophotometer RF 5000. The fluorescence of the samples were measured at 310nm excitation and at 374nm emission wavelength respectively. Chrysene and Seligi crude oil were used as standards. Solvent blanks were run with each batch of samples and one or more standard solutions of chrysene and Seligi crude measured on each working day to verify the calibration program prior to the analysis of samples. Recoveries from fortified samples were not less than 88 % and 85 % from water and sediment samples respectively. The relative standard deviations ranged between 8-13 % and 11-16 % of the mean for water and sediment samples respectively.

Fractionation of the extracts from water and sediments were carried out by passing through chromatographic columns containing 5 % water-deactivated silica gel. Aliphatic hydrocarbons were eluted with hexane followed by elution with 25 % toluene in hexane to yield polynuclear aromatic hydrocarbons.

A Shimadzu GC 17A gas chromatograph interfaced to a QP-5000 mass spectrometer

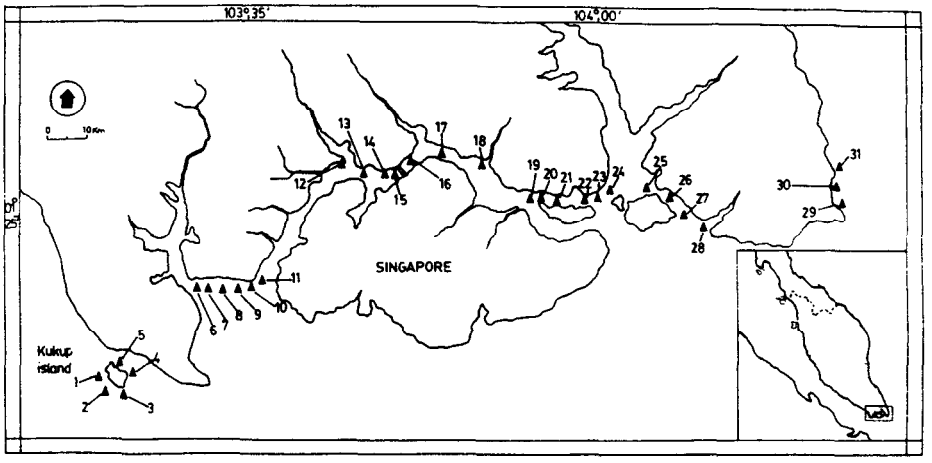

Figure 1. Sampling location in the Straits of Johor

was used for the analysis of the aliphatic hydrocarbon fractions. A HiCap OV 1701 fused silica capillary column (25m x 0.2 mm i.d.) was programmed from 60°C to 280°C at 8°C/min and held at 280°C for 35 min. The ion source and analyzer were maintained at 290°C. Helium was used as the carrier gas at a flow rate of 40 cm^3/min. Injection volume was 2 µL and the splitless mode was used. The ionization potential was 70 eV. Identification of component peaks was based on comparison with the GC retention times and mass fragmentation patterns of standard materials and with the aid of the National Institute of Standards and Technology (NIST) standard library incorporated in the data system of the QP-5000.

RESULTS AND DISCUSSION

Oil and grease comprises a diverse group of compounds with the common characteristic of solubility in the extracting solvent, trichlorotrifluoroethane. Hence, in addition to hydrocarbons from petrogenic sources, other organic compounds such as fatty acids and their derivatives are also included in the measurement of oil and grease. The relatively simple technique of fluorescence spectroscopy is a widely accepted procedure for the estimation of petroleum hydrocarbons (Parsons et al. 1984). The concentration of polynuclear aromatic hydrocarbons (PAH) as measured by fluorescence spectroscopy is indicative of the concentrations of crude oils and oil products in seawater and sediments. It should be noted that the limitation in accuracy of this technique arises from the possibility that the aromatic composition of the samples and the chosen standard were not likely to be the same. The samples collected in this study probably contained hydrocarbons from a variety of sources.

The results of the water and sediment analysis, reported as the average of at least duplicate determinations, are given in Tables 1 and 2 respectively. Oil and grease

and petroleum hydrocarbons were present at all the stations sampled. The range of oil and grease in water were 0.270 to 3.534 mg/L. The corresponding concentrations of petroleum hydrocarbons ranged between 0.001-0.135 mg/L and 0.025-2.795 mg/L, expressed as equivalent concentrations of chrysene and Seligi crude oil, respectively. Petroleum hydrocarbons in sediment samples ranged from 0.71l-36.695 mg/kg and 14.259-361.371 mg/kg, expressed as equivalent concentrations of chrysene and Seligi crude oil respectively.

The highest concentrations of oil and grease (3.534 mg/L) and petroleum hydrocarbons (0.135 mg/L chrysene equivalent or 2.795 mg/L Seligi crude oil equivalent) in water were recorded in samples taken from the vicinity of the island of Kukup (stations l-5) located near the main shipping lane in the south end of the Straits of Malacca. All the stations sampled in this area exhibited high levels of oil and grease and petroleum hydrocarbons. The levels of petroleum hydrocarbons measured in Seligi crude equivalent were also noted to approach the concentrations of oil and grease in these waters, indicating that a substantial proportion of the oil and grease measured were from petroleum hydrocarbons. These elevated levels of petroleum hydrocarbons are attributed to marine-based sources, in particular those due to shipping activities. In recent years, the Department of Environment has begun to document illegal desludging activities in these waters from vessels in transit to Singapore (DOE, 1995), although it is widely considered that such activities have been going on for some time. Both the island and the mainland bordering these sampling stations are relatively undeveloped and hence land-based sources contributing to the observed levels are minimal.

The concentrations of oil and grease in water from other sampling stations, although not as high as those found near the island of Kukup, were all in excess of 100 µg/L. Furthermore, with very few exceptions, the proportion of petroleum hydrocarbons in water, relative to the oil and grease content were indicative of the relatively high contribution of non-petrogenic pollutants in these waters as compared to the samples taken from the island of Kukup.

These levels of contamination might be expected for stations 12-24 which were located in the vicinity of urban, port and industrial areas. However, samples from stations 6-11, 25-28 and particularly 29-31 were taken from areas where there were no obvious sources of oil pollution. Hence, the observed levels of oil and grease in these stations, as well as the corresponding levels of petroleum hydrocarbons were thought to be due to the transport of these pollutants from their points of origins by tidal currents, in addition to the shipping activities within the straits itself, involving fishing vessels as well as traffic to and from the seaport located in the vicinity of station 21. The observed levels of contamination at stations 29-31, originally considered to represent relatively pristine waters, may be attributed to the residual effects of recent illegal desludging activities in the South China Sea (DOE, 1995). The discharge of oily waste from shipping activities in the south end of the Straits

of Malacca may also be transported by tidal currents to waters in stations 6-l1 especially during the south west monsoon season.

Table 1. Oil and grease and petroleum hydrocarbons in seawater

Sampling station	Concentration (mg/L)		
	Oil and grease	Petroleum hydrocarbons	
		Chrysene equivalent	Seligi crude oil equivalent
1	3.534	0.114	2.362
2	3.478	0.103	2.099
3	2.141	0.096	1.999
4	2.941	0.135	2.795
5	2.130	0.100	2.086
6	0.457	0.003	0.044
7	1.029	0.002	0.032
8	0.750	0.005	0.078
9	1.097	0.006	0.105
10	1.071	0.006	0.101
11	0.436	0.010	0.174
12	0.667	0.018	0.358
13	0.943	0.009	0.183
14	0.367	0.012	0.241
15	0.297	0.007	0.118
16	0.577	0.005	0.111
17	1.446	0.010	0.192
18	0.893	0.002	0.064
19	0.573	0.006	0.102
20	0.524	0.006	0.097
21	0.636	0.005	0.083
22	0.425	0.002	0.028
23	0.394	0.001	0.025
24	0.449	0.001	0.026
25	0.719	0.003	0.057
26	0.824	0.003	0.061
27	1.067	0.003	0.055
28	1.400	0.004	0.099
29	0.545	0.001	0.100
30	1.020	0.007	0.133
31	0.270	0.004	0.085

The lowest concentrations of petroleum hydrocarbons in sediments were found in stations 29-31. This finding is not consistent with the relatively high levels in sea water collected from the same site. Levels of hydrocarbons in seawater tend to fluctuate throughout the year, and are subjected to seasonal variations such as the monsoon season which effects tidal currents. Hydrocarbon content in the sediment

is probably a better measure of oil pollution, and hence the observed low levels of petroleum hydrocarbons in sediment from these sampling stations provide justification for their choice as background levels in the present study.

Table 2. Petroleum hydrocarbons in surficial sediments

Sampling station	Concentration (mg/kg)	
	Chrysene equivalent	Seligi crude oil equivalent
3	11.810	159.460
4	4.645	91.756
5	8.889	174.714
6	8.108	150.360
7	7.680	135.700
11	8.721	179.651
12	35.408	361.371
13	26.001	290.679
15	5.086	103.750
16	14.248	141.710
17	9.143	182.815
18	8.288	164.966
23	3.190	103.540
24	1.453	58.907
25	9.608	175.761
27	36.695	75.744
29	1.065	21.358
30	0.711	14.259
31	1.280	25.484

The majority of sediment samples contained petroleum hydrocarbons exceeding 100 mg/kg dry weight Seligi crude oil equivalent. All samples in the present study contained varying proportions of mud and fine sand. Sediments containing fine particles tend to be good accumulators of organic pollutants presumably because of their greater effective surface area (Law 1981; Burns et al. 1982). Consistent with the corresponding high levels of petroleum hydrocarbons in water, it is probable that the Straits of Johor has been subjected to a variety of hydrocarbon inputs for sometime.

The chromatograms of the aliphatic hydrocarbon fractions clearly indicated that the anthropogenic contribution of hydrocarbons in the straits to be prodominantly petrogenic in origin. The majority of samples exhibited a complex series of resolved peaks overlying an unresolved mixture of hydrocarbons (UCM), as examplified by the gas chromatogram of a water extract taken from station 2 (Figure 2). The unresolved complex mixtures of alkanes with carbon number preferences approaching unity, in addition to the presence of the isoprenoid hydrocarbons

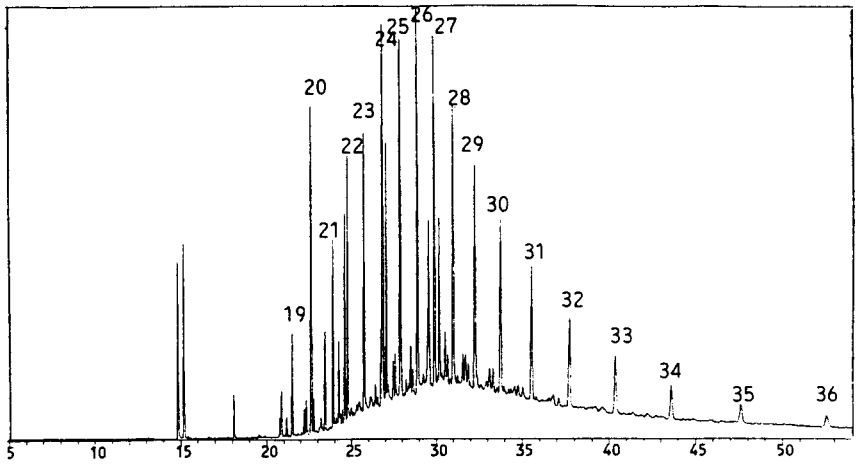

Figure 2. Gas chromatogram of the aliphatic hydrocarbon fraction from a water sample from station 2 (numbers denote n-alkanes, Pr: pristane, Ph: phytane)

pristane and phytane are clear indications of petroleum-derived hydrocarbons (Porte et al. 1990).

In a previous survey, petroleum hydrocarbons were determined in a limited number of sampling stations (approximately corresponding to stations 13-17) in the Straits of Johor (Abdullah et al. 1994). While there was up to 10 fold fluctuation of petroleum hydrocarbon concentrations in water, the concentrations in sediments were in the same order of magnitude as those observed in the present study.

Near-coastal waters generally exhibit higher levels of hydrocarbons than the open sea (Barbier et al. 1973). In the present study, based on the Seligi crude oil standard, the concentrations of petroleum hydrocarbons in water were all in excess of 0.0025 mg/L stipulated by the Food and Agricultural Organisation (FAO 1982), and hence are classified as polluted. Furthermore, with the exceptions of stations 29-31, the petroleum hydrocarbon content in the sediment samples were greater than 100 mg/kg dry weight, an indication of polluted levels (Marchand et al. 1982). On these basis, the levels of oil contamination found in the present study clearly shows that the coastal waters and sediments in the Straits of Johor are polluted.

REFERENCES

Abdullah AR, Mohd. Tahir N, Lee, KW (1994) Hydrocarbons in seawater and sediment from the west coast of Peninsular Malaysia. Bull Environ Contam Toxicol 53: 618-626

American Public Health Association (1989) Standard Methods for the Examination of Water and Wastewater, American Public Health Association, New York, pp496-503

Bat-bier M, Joly D, Sailot A, Tourres D (1973) Hydrocarbons from seawater. Deep Sea Res 20: 305-312

Burns KA, Villanueve JP, Anderlini VC, Fowler SW (1982) Survey of tar, hydrocarbons and metal pollution in the coastal waters of Oman. Mar Pollut Bull 13: 240-247

Department of Environment (1994) Environmental quality report, 1994. Ministry of Science, Technology and the Environment, Malaysia

Department of Environment (1995) A study for the assessment of the sources of marine pollution Ministry of Science, Technology and the Environment, Malaysia

Food and Agricultural organization (FAO) (1982) The review of the health of the oceans. FAO/IMCO/Unesco/WMO/WHO/IAEA/Unep Joint Group of Experts on Scientific Aspects of Marine Pollution (Gesamp) Rep Stud Gesamp 15:108

Hilpert LR, May WE, Wise SA, Chesler SN, Hertz HS (1978) Interlaboratory comparison of determinatons of trace level petroleum hydrocarbons in marine sediments. Anal Chem 50: 458-463

Law RJ (1981) Hydrocarbon concentrations in water and sediments from UK marine waters, determined by fluorescence spectroscopy. Mar Pollut Bull 12: 153-157

Marchand M, Bodennec G, Caprais JC, Pignet P (1982) The AMOCO CADIZ oil spill, distribution and evolution of oil pollution in marine sediments. In: Ecological study of the AMOCO CADIZ oil spill. Report of the NOAA-CNEXO Joint Scientific Commission 143-157

Parsons TR, Maita Y, Lalli CM (1984) A manual of chemical and biological methods for seawater analysis. Pergamon Press, Oxford pp56-59

Porte C, Barcelo, D, Tavares TM, Rocha VC and Albaiges J (1990) The use of the mussel watch and molecular marker concepts in studies of hydrocarbons in a tropical bay (Todos os Santos, Bahia, Brazil). Arch Environ Contam Toxicol 19: 263-274