Petroleum Hydrocarbon in Seawater and Some Sediments of the South China Sea, Area I: Gulf of Thailand and East Coast of Peninsular Malaysia

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ABSTRACT

Petroleum hydrocarbon in water samples and sediments collected during the Pre-Southwest Monsoon Cruise in the Gulf of Thailand and Eastern Peninsular Malaysia in April-May 1996 point out that land-based and sea-based sources were both important. High concentration (> 0.5 mg/l) found in coastal water of the northern part and western part near Songkhla-Pattani could be derived from land-based sources. Elevated concentration of petroleum hydrocarbons in seawater and residuals in sediments of the central area of the Gulf could be originated from offshore activities. However physical oceanography of the Gulf could also play very important roles in redistribution, dispersion and accumulation of petroleum hydrocarbon in the water.

Introduction

Petroleum hydrocarbon in seawater and sediments are derived from 2 sources, natural seepage and anthroupogenic sources. Because the Gulf of Thailand and offshore water off the eastern Peninsular Malaysia are areas where petroleum is explored and produced, natural seepage is a possibility, even though it is not well documented. Contrary, anthropogenic input of petroleum hydrocarbon into marine environment is more concerned by general puplic due to the potential of large scale catastrophic effects on organisms and ecosystems. However, more realistically, large scale oil spill is rarely occurred. Most petroleum hydrocarbon are released into the sea are from small, widely distributed sources, such as from smalll vessels without proper water treatment systems, discharge of bilge water by tankers coming to the region to load oil and condensates, and petroleum products from coastal sources--domestics, transport and industrial.

Concentration and distribution of petroleum hydrocarbon is a good indicator for the health of the sea. It can indicate the source of the pollutant that deserve special emphasis or needs more control.

Petroleum hydrocarbon in coastal water of the Gulf of Thailand has been measured since early 1970s. Hungspreugs (1979), for example, reported the concentration between 0.37-1.42 μg/l. Subsequent studies revealed the concentration is highly variable, depending on location and season (Intarapanich, 1979; Sompongchaiyakul and Lim, 1983; Watayakorn, 1986, 1987; Petpiroon, 1988; and Suthanarak, 1991). The major components of petroleum hydrocarbon are degraded crude oils, combusted hydrocarbons and normal alkanes (Silpipat and Ehrhardt, 1986).

In the offshore South China Sea, Law and Mahmood (1986) found the concentration in the range of 0-75 ppb crude oil equivalent.

Comparison of hydrocarbon concentration reported by different papers are difficult to compare because of different standard used. In the past, crude oil was used as standard but the problem is there are several types of crude with defferent chemical compositions. The extracting solvents used by different people were also different. It was in 1984 that the Intergovernmental Oceanographic Commision had established a standard method for determination of hydrocarbon in seawater by

using hexane as the extractant and chrysene as standard. Concentration reported by this method, however will not be the absolute concentration of total hydrocarbon in seawater. Rather it represent the relative concentration of hydrocarbon that can be compared among locations and times.

Methods

Sampling and sample preparation

Surface seawater were collected from all 81 stations during the Pre-Southwest Monsoon Cruise in the Gulf of Thailand and Eastern Peninsular Malaysia in April - May 1996. Five liters of seawater was collected from each station using the pre-cleaned amber glass bottles (IOC-UNESCO 1984). At stations 7, 60, 62, 64, 74, 79 and 81 duplicates were collected as a quality assurance. About 75 ml of nanograde hexane was added immediacy after sampling. Samples were stored in a dark cool place until analysis.

Surface sediment samples were collected from stations 1, 3, 12, 20, 24, 40, 44 and 46 using a grab sampler.

Laboratory analysis of samples

Fifty one water samples from the Gulf of Thailand were extracted by nanograde hexane. Residual water in hexane was removed by Na_2SO_4. The final volume of extractant was reduced to 5 ml using a rotary evaporator. The extracted petroleum hydrocarbon was quantified using a spectrofluorometer and using chrysene as the standard.

Sediment samples were extracted by dichloromethane. Internal standards were added to sample prior extraction. Aliphatic and aromatic hydrocarbon fractions were separated using silica gel. Both fractions were analyzed by a Varian 3700 gas chromatograph. Seven species of polycyclic aromatic hydrocarbons (PAHs) were measured: naphthalene, biphenyl, phenanthrene, pyrene, chrysene, perylene and benzo (ghi) perylene.

Total organic content in sediments was analyzed by $K_2Cr^2O_7$ wet oxidation method.

Details of sample preparation and quantitative analysis can be found in Wongnapapan(1996).

Results

Seawater

The concentration of petroleum hydrocarbon in surface seawater at each station is shown in Table 1. Duplicate samples indicated that the precision of these results was better than 18%. The arithmetic mean concentration was 0.564 μg/l and the geometric mean was 0.252 μg/l. The highest concentration of 4.128 μg/l was found at station 46, which is an offshore station.

Sediments

Porosity (percent water content) and total organic carbon in sediments are given in Table 2.

Aliphatic hydrocarbons

Concentration of n-alkane in sediments is ranged from non-detectable to 232.5 ng/g dry weight. The total identified aliphatic hydrocarbons were between 0.04-1.36 μg/g (average 0.27 μg/g dry weight). The result is shown in Table 3.

Aromatic hydrocarbons

Seven polycyclic aromatic hydrocarbons (PAHs)-- naphthalene, biphenyl, phenanthrene, chrysene, pyrene, perylene and benzo (ghi) perylene--existent and concentration in sediments are given in Table 4.

Discussion

Table 1. Concentration of petroleum hydrocarbon at each station (in mg/l chrysene equivalent)

Station	Concentration
1	1.74
2	0.38
3	1.14
4	0.66
5	0.13
6	0.15
7	0.42
8	2.08
9	0.16
10	0.08
11	0.14
12	0.49
13	0.26
14	3.64
15	0.14
16	NA
17	0.69
18	0.47
19	1.09
20	0.20
21	0.07
22	0.14
23	0.25
24	0.09
25	0.39
26	0.11
27	1.48
28	NA
29	0.18
30	0.11
31	0.82
32	0.09
33	0.12
34	0.27
35	0.29
36	0.11
37	0.19
38	0.19
39	0.18
40	2.31
41	0.14

Station	Concentration
42	2.75
43	0.11
44	0.08
45	0.44
46	3.61
47	4.13
48	0.31
49	0.63
50	0.08
51	0.05
52	0.214
53	0.124
54	0.107
55	0.086
56	0.108
57	0.149
58	0.084
59	NA
60	0.125
61	0.162
62	0.130
63	0.144
64	0.159
65	0.092
66	0.101
67	0.133
68	0.359
69	0.305
70	0.786
71	0.191
72	0.135
73	NA
74	0.116
75	0.097
76	0.176
77	0.130
78	0.161
79	3.928
80	0.089
81	0.157

NA = Data not available

Generally the order of magnitude of petroleum hydrocarbon concentration in seawater found in this study is not different from that reported by Hungspreugs (1979) for the same general locations. This can be interpreted either as the sources were not increased much during the last 15 years or the natural processes (physical and chemical) in the Gulf that control and remove petroleum hydrocarbon in seawater were still fast relative to the input.

Elevated concentration of petroleum hydrocarbon in seawater (>0.5 μg/l) were found at four distinct areas (Fig. 1). Firstly, the area near the mouth of the upper Gulf and extended eastward to Rayong Province. This is quite understandable because the Upper Gulf of Thailand and Rayong are considered the most busiest sea routes in the Gulf, for large cargo vessels and tankers as well as small crafts. There are also several large cities and industrial eatates in this area. The second area is the coastal water off the city of Songkhla and Pattani Provinces. This area also consists of deep-sea ports and several fish-landing piers which can be the significant distribution sources of petroleum hydrocarbons. Cities, towns and industries along the coast culd contribute additional land-based source of hydrocarbons to the coastal waters.

Two offshore areas where high concentrations of petroleum hydrocarbon were found were the area near the mouth of the Gulf that opens to the South China Sea and extends inward to the center of the Gulf, and the offshore area off the coast of the State of Johor. This result was quite controver-

Table 2. Water content (%) and total organic carbon (%) in sediments

Station	% water	% organic carbon
1	26.56	0.2
3	38.66	0.55
12	51.75	0.24
20	34.13	0.67
24	45.19	1.13
40	31.94	0.69
44	36.93	0.27
46	47.48	0.57

Table 3. Petroleum hydrocarbons in sediments (ug/g dry weigth)

Station	Total identified n-alkanes	Total identidied PAHs	Total HC
1	0.12	0.06	0.18
3	0.05	0.28	0.33
12	0.04	0.02	0.06
20	1.36	0.04	1.40
24	0.10	0.04	0.14
40	0.12	0.01	0.13
44	0.05	0.10	0.15
46	0.34	0.08	0.42
range	0.04-1.36	0.01-0.28	0.06-1.40
mean	0.27	0.08	0.35
S.D.	0.45	0.09	0.44

Table 4. Polycyclic aromatic hydrocarbons (PAHs) in the Gulf of Thailand sediments (ng/g dry weight).

Chemical	Station							
	1	3	12	20	24	40	44	46
Naphthalene	16.40	49.26	2.32	4.07	22.93	12.68	39.07	20.06
Biphenyl	12.15	41.54	ND	11.25	4.98	ND	10.92	10.65
Phenanthrene	ND	40.47	5.63	12.97	9.90	ND	10.31	11.08
Chrysene	ND	19.95	ND	12.73	ND	ND	ND	30.15
Pyrene	ND	ND	ND	ND	ND	ND	ND	7.33
Perylene	ND	88.02	ND	ND	ND	ND	37.71	ND
Benzo(ghi)perylene	30.18	43.29	13.26	ND	ND	ND	ND	ND
Total	58.73	282.5	21.21	41.02	37.81	12.68	98.01	79.27

ND = not detectable

sial at the bigining since we expected the offshore area to be less "polluted" than the coastal area. However, this finding supports a previous study by Wattayakorn (1986) that concentration of petroleum hydrocarbons in offshore water in the
Gulf was higher than in coastal waters.

In addition to those in seawater, petroleum hydrocarbon in offshore sediments (Stations 12, 20, 44, and 46) were also higher than that at coastal staions (Stations 1, 3, 24 and 40). From the results of seawater and sediments of this study, we suspect that offshore activities, such as navigation in the South China Sea sea-routes and offshore oil exploration and production, might leave some measurable impacts on water and sediments. However, we can not rule out the highly probable hypothesis that the circulation pattern of the Gulf could cause petroleum hydrocarbon to be redistributed accumulated in the central region surface water. As chemical degradation proceeds, petroleum hydrocarbons in the water could be assimilated into the particulate phases and eventually deposited in sediments.

Conclusions

1) Concentration of petroleum hydrocarbons in seawater found in this study was not sinificantly different than that reported for 15 years ago for the same general locations.
2) Land and harbor based sources could be important for coastal areas near the Upper Gulf of Thailand, and Rayong, Songkhla and Pattani Provinces.
3) Concentration of petroleum hydrocarbons in water and sediments at some offshore stations in the Gulf of Thailand and the South China Sea appeared to be higher than at most coastal stations. Offshore sources as well as physical oceanography of the area might be attributed to this observation.

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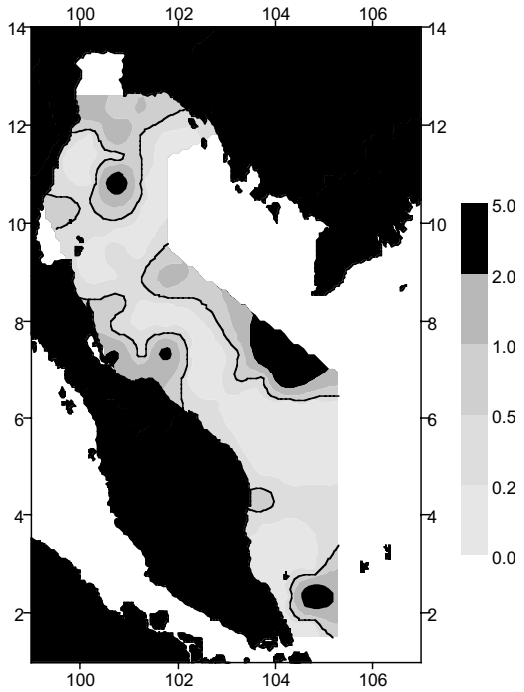

Fig. 1. Distribution of petroleum hydrocarbon in seawater in the Gulf of Thailand (contoured by Krigging). The 0.5 mg/l in chrysene equivalent contour lines are shown.

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