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SURFACE SEDIMENT ANALYSIS ON PETROLEUM HYDROCARBON AND TOTAL ORGANIC CARBON FROM COASTAL AREA OF PAPAR TO TUARAN, SABAH

(Analisis Sedimen Permukaan Terhadap Petroleum Hidrokarbon dan Jumlah Karbon Organik daripada Pesisiran Pantai Papar ke Tuaran, Sabah)

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Abstract

Total petroleum hydrocarbons (TPH) and total organic carbon (TOC) were investigated in surface sediments along coastal area of Papar to Tuaran, Sabah. Surface sediment samples were collected in 24 different stations in each area by using Ponar grab sampler. Samples were extracted for TPH using standard method sediment/sludge APHA 5520E and analyzed using UV/VIS spectrophotometer while for TOC method analysis using United Nations Environment Programme (UNEP)/MAP Athens (2006). The range of TPH concentrations in surface sediments were recorded at 0.24 – 20.65 mg/kg dw Miri crude oil equivalents, meanwhile the TOC percentage ranged from 0.03 – 4.02%. In the mean time, the statistical analysis by Pearson correlation showed a positive correlation with coefficient, r = 0.790 which showing the TPH concentrations significantly have influence on the TOC accumulations in the surface sediment.

Keywords: total petroleum hydrocarbon, surface sediment, total organic carbon

Abstrak

Jumlah petroleum hidrokarbon (TPH) dan jumlah karbon organik (TOC) telah dikaji dalam sedimen permukaan di sepanjang kawasan persisiran pantai Papar ke Tuaran, Sabah. Sampel sedimen permukaan dikumpul di 24 stesen yang berbeza di setiap kawasan dengan menggunakan *Ponar grab sampler*. Sampel telah diekstrak bagi TPH menggunakan kaedah piawai sedimen /enapcemar APHA 5520E dan dianalisis menggunakan UV/VIS spektrofotometer manakala bagi kaedah analisis TOC pula menggunakan United Nations Environment Programme (UNEP)/MAP Athens (2006). Julat kepekatan TPH dalam sedimen permukaan direkodkan pada 0.24 – 20.65 mg / kg bk setara dengan minyak mentah Miri, sementara peratusan TOC adalah di antara 0.03 – 4.02%. Sementara itu, analisis statistik dengan korelasi Pearson menunjukkan korelasi positif dengan pekali, r = 0.790 yang menunjukkan kepekatan TPH ketara mempunyai pengaruh ke atas pengumpulan TOC dalam sedimen permukaan.

Kata kunci: jumlah petroleum hidrokarbon, sedimen permukaan, jumlah karbon organik

Introduction

Petroleum pollution has become a serious environmental concern because of its extensive use as energy source which has led to its widespread distribution in the biosphere [1]. An increase of petroleum hydrocarbons concentration in the marine environments has negative impact not only on aquatic life but also may affect human health [2]. Petroleum hydrocarbons are complex mixtures in both composition and molecular structure, mostly

originated from crude oil, and contain a wide range of chemical products such as kerosene, gasoline, fuel oil, jet oil, heavy oil and lubrication oil [3]. The composition and distribution of these hydrocarbons often serve as means for distinguishing their different sources [4]. These hydrocarbons in the marine environment have several sources which can be classified either as anthropogenic or biogenic. The anthropogenic pollution occurs into the environment mainly through accidents, marine operations or land based discharges [5, 6]. Biogenic hydrocarbons are generated either by biological processes or in the early stages of diagenesis in recent marine sediments including land plants, phytoplankton, animals, bacteria, macroalgae and microalgae [7].

The subject of this study is surface sediment because sediment and sand serve as excellent sink or an ultimate reservoir for marine pollutants such as hydrocarbons or organic pollutants [8, 9, 10]. Moreover, sediments are composite materials, which consist of inorganic components, mineral particulates and organic matter in various stages of decomposition, which it can be a good indicator for chemical analysis in environmental pollution [11, 12, 13].

The pollutants in sediment can be released back to water phase by the process which is known as re-suspension. It makes the compound or pollutant trapped in the sediment to be remobilized [14]. Investigation on the composition of hydrocarbon compounds in different marine sediments can provide much information about their sources and diagenetic processes and reflect the extent of anthropogenic pressures on the environment [13, 15]. The sedimentary hydrocarbon has received special attention because it is readily adsorbed onto particulate matter and bottom sediments ultimately act as a reservoir of possible contaminants [13, 16].

Determination of organic carbon is very important in order to identify the presence of organic substances in sediments and the content depends on geographical locations, pollutants entering rivers and layer depth of tested sediments [17]. These substances either from natural sources, such as humic acids, mineral oils, solvents, pesticides, poly aromatic hydrocarbons or chlorinated organic compounds [2]. It affects biogeochemical processes, nutrient cycling, biological availability, chemical transport and interactions [17]. Organic carbon quantified by the percentage of total organic carbon (TOC), which provides information on all organic substance content in water or sediments [18].

The study focused on this area due to the interest to know whether the areas are polluted or not because many residents are living nearby that depending on it for food resources. The distance along the study area is approximately 84 km. Many points of discharge such as from urban and villages, development activities, industrials and entrance of around 13 rivers are located along the study area. Those potential areas will discharge effluents, sewage, wastes and pollutants directly to coastal or from the river to coastal which will increase the existing petroleum concentration. The information on the distribution of petroleum hydrocarbons in the coastal environment is necessary to determine the extent of oil pollution input into the oceans [3]. Therefore, the aim of this study is to determine the total hydrocarbon concentration (TPH) concentration and total organic carbon (TOC) percentage in the surface sediment along coastal area of Papar to Tuaran, Sabah. Correlations with surface sediment TPH concentration and TOC percentage from sampling stations are also been discussed.

Materials and Methods

Sample Collection

This study was conducted in October 2012. A total of 72 surface sediment samples were collected using Ponar grab sampler from 24 stations (5 to 7 meters above the sea) along coastal area Papar to Tuaran as shown in Figure 1. The coordinate of sampling locations were recorded by Global Positioning System (GPS) device (Table 1). The top layer of sediment sample (0-1 cm) was taken using stainless steel scoop. Sediment samples were wrapped in aluminum foil and placed on ice after sampling, immediately transported to the laboratory and kept in the refrigerator at –20°C for preservation before analysis. The top (1-2 cm) surface layer analysis will provide baseline data for present-day pollution [19, 20].

Table 1. The coordinate of sampling stations

Stations	Latitude	Longitude	Stations	Latitude	Longitude
S1	N $05^0$37.119’	E $115^0$52.412’	S13	N $05^0$57.717’	E $116^0$02.882’
S2	N $05^0$38.737’	E $115^0$52.804’	S14	N $05^0$58.731’	E $116^0$03.742’
S3	N $05^0$39.270’	E $115^0$53.019’	S15	N $06^0$00.061’	E $116^0$05.299’
S4	N $05^0$43.392’	E $115^0$53.232’	S16	N $06^0$00.953’	E $116^0$05.743’
S5	N $05^0$45.234’	E $115^0$53.417’	S17	N $06^0$02.151’	E $116^0$06.263’
S6	N $05^0$46.134’	E $115^0$56.077’	S18	N $06^0$03.880’	E $116^0$06.753’
S7	N $05^0$48.293’	E $115^0$59.281’	S19	N $06^0$07.181’	E $116^0$06.309’
S8	N $05^0$49.689’	E $115^0$59.984’	S20	N $06^0$08.533’	E $116^0$07.964’
S9	N $05^0$52.069’	E $116^0$01.551’	S21	N $06^0$08.274’	E $116^0$08.234’
S10	N $05^0$53.381’	E $116^0$01.755’	S22	N $06^0$11.869’	E $116^0$10.120’
S11	N $05^0$54.471’	E $116^0$01.822’	S23	N $06^0$13.934’	E $116^0$10.756’
S12	N $05^0$56.668’	E $116^0$02.306’	S24	N $06^0$14.641’	E $116^0$12.819’

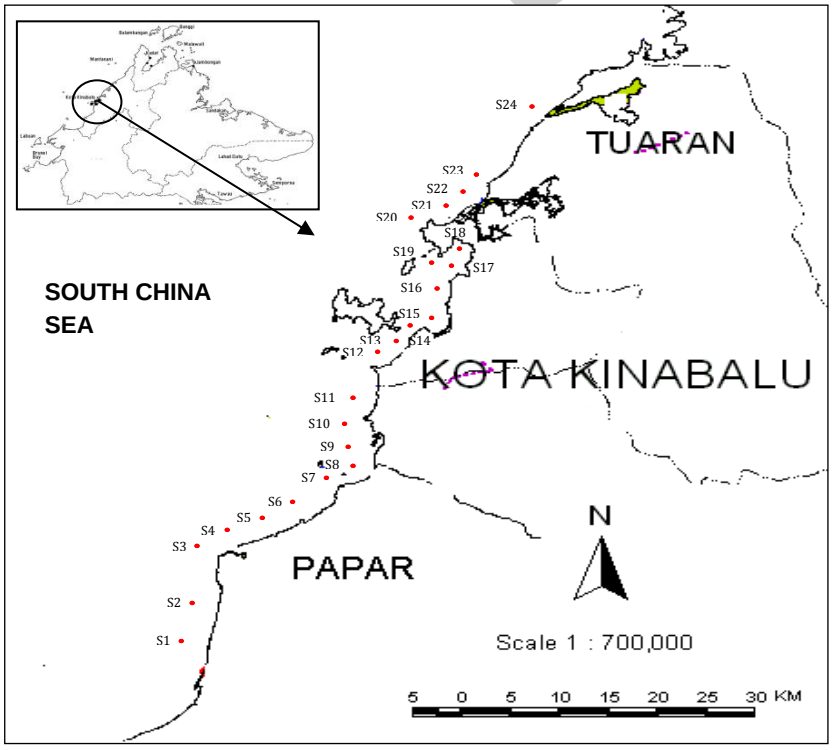

Figure 1. Study area and sampling stations

Petroleum Hydrocarbon Analysis

About 10 g of surface sediments was dried in the oven at 105°C for 2 hours to determine the moisture content analysis. The standard method for the petroleum hydrocarbon content analysis was based on the APHA 5520E [21]. About 10 g of sediment was extracted with saturated hydrochloric acid (HCl) and 15 g magnesium sulphate ($MgSO_4$). After mashing the whole sediment sample with pestle, the sample was extracted with Soxhlet for 4 hours with 250 ml petroleum ether. The extracts were saturated using rotary evaporator and cleaned-up by silica gel columns. The eluate from the columns was concentrated with pure nitrogen and the TPH were analysed by using UV/VIS spectrophotometer Lambda 25 Perkin Elmer (excitation was at 239 nm and emission at 259 nm). A calibration curve was generated using Miri crude oil as arbitrary standard (concentration range between 0 -120 ppm).

Total Organic Carbon Analysis

Sediment sample was put in oven at 60°C for 24 hours. Then approximately 1g of dry sediment was weighted. The sediment was then placed into a furnace at 450°C temperature for 3 hours for ignition. Percentage of TOC was measured based on United Nations Environment Programme (UNEP)/MAP Athens (2006) method [22]. TOC percentage was calculated using formula 1:

$$\text{TOC \%} = \frac{(D_o - D_t)\ g\ /\ 1.724}{D_o} \times 100 \quad (1)$$

where D_o = dry sediment mass before ignition and D_t = dry sediment mass after ignition (in gram).

Results and Discussion

Table 2 shows the concentration of TPH and percentage of TOC in sediment collected along the coastal area of Papar to Tuaran, Sabah. The overall range of the TPH concentrations in all sampling areas were 0.24 – 20.65 mg/kg dw Miri crude oil equivalents, while TOC percentage were recorded at 0.03 – 4.02%. According to [23], sediments containing hydrocarbon levels less than 100 mg/kg dry weight can be classified as not anthropogenically contaminated. Based on the result, it can be stated that the levels of TPH obtained from the study along the Papar to Tuaran coastal areas are still below the alarming pollution level. The overall range percentages for moisture content in surface sediment were 20.2 – 34.7%.

The result shows that the highest TPH concentrations in surface sediment are found at station S19 (20.65 mg/kg) which is in Sepanggar area, where as the lowest concentrations are found at station S8 (0.24 mg/kg) which is Papar area. Meanwhile for TOC, the result shows that the highest level of TOC percentage was recorded at station S18 (4.02%) which is in Sepanggar area, and the lowest level was recorded at station S3 and S7 (0.03%) which both in Papar area. This results show that the equivalent between TOC and TPH concentrations in sediments.

Stations S18 and S19 which located near to Sepanggar Bay and Kampung Baru Karambunai have the highest concentration of TPH. High TPH concentrations near to Sepanggar Bay may be because the samples were collected near the coastal villages and surrounds by many industrial areas such as Sepanggar Bay Oil Terminal, Major Naval Base for the Royal Malaysian Navy, Kota Kinabalu Industrial Park (KKIP) and main university campus such as UMS, UiTM and Polytechnic Kota Kinabalu. The human and industrial wastes discharge may increase the availability of TPH in the seawater and sediment itself [24]. The sources of TPH at the Sepanggar Bay and Kampung Baru Karambunai could be also related with the leaded petrol/diesel from vehicles and specially boats activity near to Sepanggar Bay. The present of petroleum hydrocarbon concentrations are compared in Table 3 with the previous studies that have been reported for coastal areas in Malaysia.

Table 2. TPH concentrations and TOC percentage in surface sediment along coastal areas of Papar to Tuaran, Sabah

Area	Station	TPH concentration (mg/kg)	TOC (%)
Papar	S1	0.77	0.14
	S2	0.74	0.05
	S3	0.65	**0.03**
	S4	0.27	0.07
	S5	0.68	0.05
	S6	0.28	0.08
	S7	0.50	**0.03**
	S8	**0.24**	0.07
Putatan	S9	5.11	1.52
	S10	0.38	1.03
	S11	2.54	0.85
Kota Kinabalu	S12	1.45	0.94
	S13	4.73	1.00
	S14	13.11	2.36
	S15	11.80	1.76
	S16	8.34	1.85
	S17	6.97	2.79
Sepanggar	S18	15.36	**4.02**
	S19	**20.65**	2.25
	S20	9.02	2.32
Tuaran	S21	4.50	2.32
	S22	2.95	2.29
	S23	9.71	2.44
	S24	8.64	2.44
	Mean	**5.39**	**1.36**

Table 3. Comparison of petroleum hydrocarbon (mg/kg) in sediment of present study with coastal regions of selected sites in Malaysia

Location	Petroleum Hydrocarbon in Sediment (mg/kg dw)	References
Port Dickson	21.73 – 74.50	[27]
Straits of Johor	14.30 – 183.00	[28]
East coast Peninsular Malaysia	0.80 – 20.00	[29]
Pulau Langkawi, Pulau Ketam,Tanjung Piai, Pulau Tioman and Kemaman	18.20 – 847.40	[30]
Straits of Malacca	52.00 – 128.00	[24]
Papar and Putatan, Sabah	0.26 - 4.59	[30]
Bako Bay, Kuching, Sarawak	35.6 – 1466.1	[26]
Papar to Tuaran, Sabah	0.24 – 20.65	Present study

The results reveal that the range concentrations of the petroleum hydrocarbon in this study is comparatively lower than concentration of petroleum hydrocarbon from those previous studies. High petroleum hydrocarbon concentration in Peninsular Malaysia and South China Sea off Kuching division are mainly contribute from shipping activities, illegal discharge of oil waste from vessels and routine handling of crude oil at the refineries terminals that is polluting and not environmental friendly [24, 25, 26].

The source and transportation of sedimentary organic matter composition can be used as physical indicator to the hydrocarbon concentration or organic pollution [32]. Therefore, statistical T-test was done in this study in order to know the effect of sampling stations with the concentrations of the total petroleum hydrocarbon (TPH) and total organic carbon (TOC) in the surface sediment. From the analysis, it was found that there are highly significance differences for the TPH and TOC concentrations in the surface sediment with $p = 0.002$ ($p < 0.01$) in each sampling stations. It means that the level of TPH observed in the sediments along coastlines of Papar to Tuaran is highly correlate significantly with TOC content in various stations. In addition, correlation Pearson test was conducted in this study to determine the influence of TPH concentrations towards the TOC accumulations, which have shown positive correlation with coefficient, $r = 0.790$. Therefore, this clearly shown that the TPH concentrations significantly have influence on the TOC accumulations in the surface sediment.

Conclusion

Total petroleum hydrocarbons and total organic carbon concentrations in surface sediment along coastal area of Papar to Tuaran, Sabah was quantified and compared. The mean TPH and TOC concentrations in surface sediment in this study are recorded with 5.39 mg/kg dw Miri crude oil equivalents and 1.36% respectively. The sediment samples can be concluded as non-polluted by petroleum hydrocarbon. In addition, the TPH concentrations also found significantly have influence on the TOC accumulations in the surface sediment.

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