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Geochemical study on Impact of Tarball on Chendering Beach Kuala Terengganu, Malaysia

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Abstract. Oil pollution is considered one of the main contributors to marine pollution. The threat that oil pollution poses to the marine environment is extremely dangerous to its ecosystem. The South China Sea is an important route for various activities, including fishing, recreational and marine activities, and oil and gas exploration. Tarballs are a common byproduct of oil spills, which arise when the sun, wind, and water break down the oil. Tarballs are clumps or blobs of oil and hydrocarbon that have been weathered and displaced from the main body of oil by ocean currents can be found along the shorelines of the Eastern, South China Sea, and Western, Selat Malacca coasts.. The beaches at Chendering in Kuala Terengganu, which face the South China Sea, are also affected by tarball pollution. The geochemical study of tar balls and surface sediments of Chendering area is located at Chendering beach coastal plain area, 103° 11’ 09” E, 5° 16’ 09” N. In this study, The Inductive Couple Plasma-Optimal Emission Spectroscopy (ICP-OES) was used to analyse 12 soil samples (contaminated with tarballs) for heavy metal components. The ICP-OES result shows that average concentrations of heavy metal of beach sediments display the following ascending pattern Cu < Pb < Ni < Cr < Zn < Mn with the value of range 0.100, 0.331, 0.633, 0.905 and 3.226 ppm respectively.

1. Introduction

In the maritime environment, hydrocarbons are relatively stable and frequently build in biological communities and ecosystems, posing a health risk to humans [1]. According to [2], anthropogenic pollutants accounted for more than three-quarters of all maritime contamination. River pollution (44 %), land and coastal pollution (33 %), ship violation and oil spills (12 %), direct waste discharge to the sea (10 %), and offshore oil and gas exploitation (10 %) are the most polluting sources (1 %). Human activities are thought to have a significant effect on hydrocarbons in marine sediments, particularly in coastal areas. Oil transportation and spills, shipping, and industrial, storm water, and household discharge are among these operations [3].

Weathered tar balls that stranded on the coastal beach is the fragments of oil weathered to a semi-solid or solid are sticky, and difficult to remove from contaminated surfaces. Due to the weathering process, the slick was split into smaller pieces and dispersed across a large region, resulting in tar balls. Various physical, chemical, and biological processes alter the look of oil, resulting in the formation of tar balls. As the stickiness level of tar balls is changed by air and water temperature, the tar balls become more fluid, resulting in the production of sticky-similar asphaltenes. In addition, the amount of particles and sediments present along the shorelines might cause tar balls to stick together. In this research, Chendering Beach is located in Kuala Terengganu facing towards the South China Sea where the areas of exploration of hydrocarbon is active. Oils spilled from these hydrocarbon activities may be transported to the east coast of Peninsular Malaysia [4]. Aside from that, oil carried across the South China Sea has the potential to produce an oil spill, which has resulted in tarballs stranded on the beach.

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Heavy metals are non-biodegradable, non-metabolisable substances that do not degrade into a harmless form. Heavy metals take a long time to exit biological systems. In terms of ecotoxicology, elements like mercury, cadmium, copper, and zinc are the most hazardous [5]. Heavy metal pollution related with petroleum hydrocarbons, such as Ni, V, and S, is likely to be found in sediments along Malaysia's east coast. Pb, Ni,V, Zn, and Cd, were most commonly discovered heavy metals in oil spill-related studies, and they produced a variety of health impacts, including cancer [6].

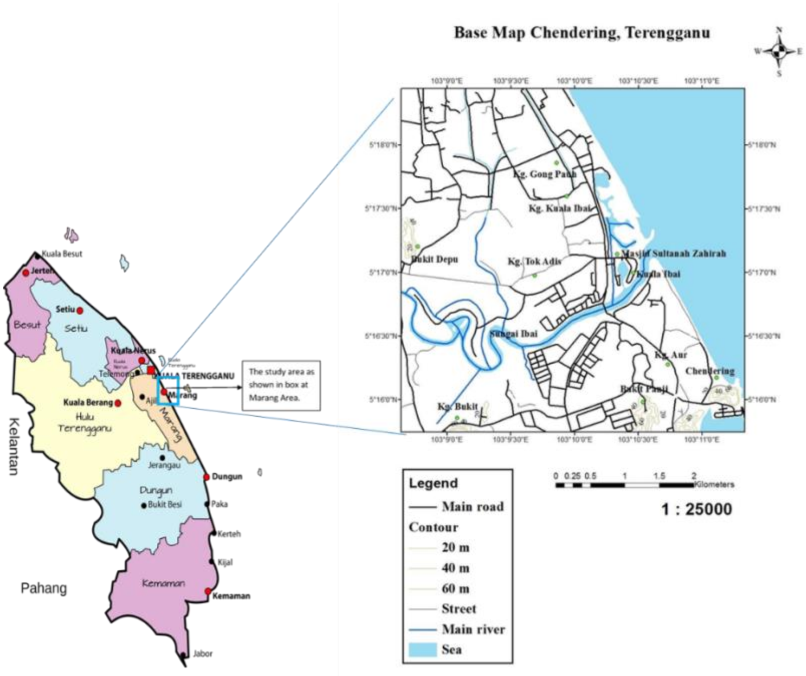

Figure 1. Location map of Chendering Beach, Terengganu

2. Methodology

The identification of the concentration of heavy metal on the surface sediments at Chendering beach was conducted by field sampling and laboratory procedures. The surface sediment was collected using a random sampling method at a depth of 0 to 5 cm, and heavy metal concentrations were determined using an acid digestion method and analysis using Perkein Elmer Optima 2100 DV ICP-OES (Inductive Coupled Plasma- Optical Emission Spectroscopy) equipment at all locations. The relationship between grain size and heavy metal concentration was reviewed, as well as a comparison of heavy metal samples to the background value.

2.1. Sampling location

The sampling location was at 5° 16’ 16” N / 103° 10’ 60” E at Chendering coastal plain location where the tar balls stranded as shown in Figure 2 and Figure 3, was chosen for sediment sampling. By referring to [7], the range 0 to 5 cm depth samples were taken to the north-east of the sample map. As the features of sediment deposited at the top of the coastal plain area exhibit grain sizes ranging from silt to medium sand spread evenly, a depth range of 0 to 5 cm is ideal.

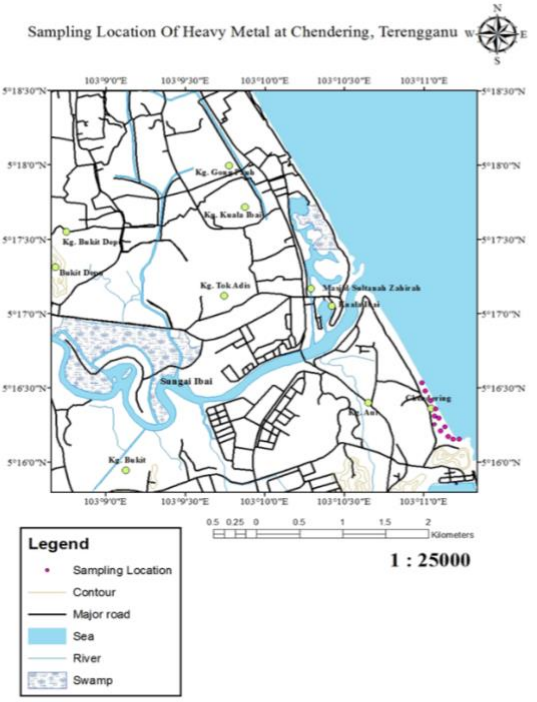

Figure 2(a). Sampling location at Chendering Beach

Figure 2(b). Stranded tar balls along Chendering Beach, Terengganu

2.2. *Sample preparation*

The sediment sample preparation was carried out according to procedure described by [8]. The sample collected transferred to the oven and heated with 60 °C for 24 hours refer to Figure 3. Next step was, the sediment samples were grinned by porcelain mortar to crush the aggregates into finer fraction. Then, the sample were sieved to <63µm. The coarse fraction was discarded and the portion of the sediment passing through sieve was collected for analysis.

Figure 3. Sediment sample after heated 60° C for 24 hours.

2.3. Grain Size Analysis
The grain size analysis of the surface sediment at the study area is conducted with mesh the sediments after dried, 10 g of the samples is weighed and sieved with 63 µm size. The data is compared to Lane's Classification (1947).

2.4. Acid digestion method
For dissolving the metal in solution, an acid digestion procedure is required, which is then analysed using an analytical method Inductively Coupled Plasma Spectroscopy (ICP-OES) to determine the concentration of element present in the sample. Basically, the 10 g of sediment sample were taken and crushed, later it was sieved by using 2.36 mm sieve. It was then weighted and transferred into a beaker.. Acid digestion is the process of adding acid to a metal sample, such as nitric acid, and heating it until the metal solid is entirely dissolved. For this research paper, sediment sample that were not contaminated with tar balls was used to compare the composition of heavy metal.

2.5. Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES).
The solution was analysed for the metals content using ICP-OES model Optima 2100 DV Perkin Elmer by preparing the standards solution of heavy metal to detect the heavy metal values of sample in range limit part per million (ppm). The samples were analysed for Ni, Cu, Pb, Mn, Zn, and Cr. Prior to ICP-OES reading, the value was tabulated for both sediment sample contact with tar ball and not respectively.

3. Results and discussion

3.1. Concentration of Heavy Metals in Surface Sediments.
The concentration of heavy metals in sediment contaminated with tar balls from 12 locations is summarised in Table 2 and Figure 5. As mention in [9] Manganese, Zinc, Lead, Chromium, Nickel, and Copper were all heavy metal contributors to tar ball. From the Table 2, Manganese was the element with the highest concentration on the surface sediments, with levels ranging from 2.721 ppm to 3.792 ppm at location 1 and location 12 respectively. Followed by Zinc which the second highest concentration was discovered to be in the range of 0.347 to 2.106 ppm at location 1 and location 6 respectively. The concentration of Lead, Ni, Cr, and Cu, ranges are distributed below 1 ppm and does not exhibit any significant variances in ppm values. Referring to Figure 5, the average concentration of heavy metals in this study was Mn> Zn>Cr>Ni>Pb>Cu in descending order.

Table 1: Heavy metal concentration of surface sediment values (ppm).

LOCALITY	Zn (ppm)	Pb (ppm)	Ni (ppm)	Mn (ppm)	Cr (ppm)	Cu (ppm)
1	0.347	0.196	0.393	2.721	0.712	0.09
2	0.533	0.211	0.352	3.527	0.706	0.118
3	1.195	0.209	0.25	3.512	0.49	0.098
4	0.726	0.133	0.345	3.638	0.654	0.104
5 (i)	0.627	0.412	0.372	3.199	0.708	0.113
5 (ii)	0.697	0.389	0.354	3.169	0.69	0.104
6	2.106	0.231	0.263	3.092	0.508	0.106
7	0.395	0.184	0.408	2.805	0.751	0.083
8	1.347	0.269	0.297	2.989	0.571	0.114
9	1.752	0.198	0.296	2.845	0.557	0.092
10	1.287	0.184	0.294	3.211	0.575	0.111
11	0.354	0.135	0.335	3.435	0.639	0.085
12	0.393	0.233	0.347	3.792	0.664	0.088
Average	0.905	0.230	0.331	3.226	0.633	0.100

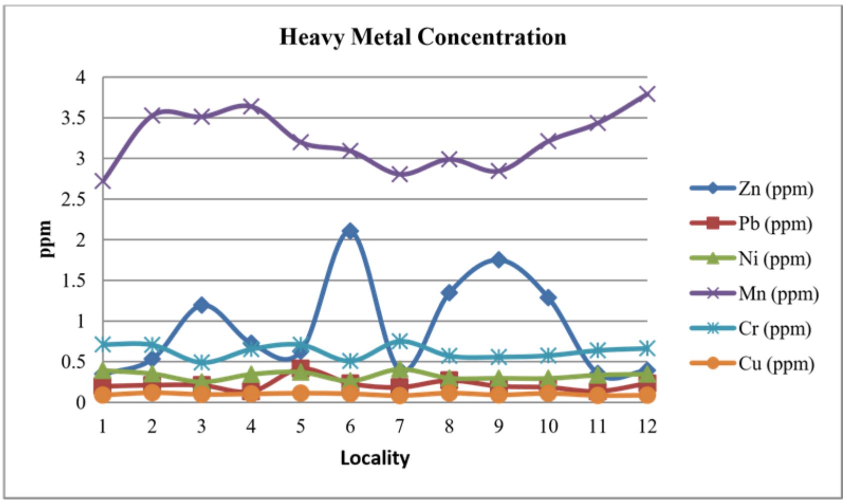

Figure 4. Distribution of heavy metal concentrations at

Table 2: Background concentration standard values of metals in sediments (ppm)

	Elements	Concentrations	References
Sediments (ppm)	Mn	273.42	[10]
	Pb	(20 - 30)	[10]
	Cu	(10 - 30)	[11]
	Zn	<100	[11]
	Cr	<52	[11]
	Ni	< 5.4	[11]

The average results value of the heavy metal concentrations for Pb, Ni, and Zn in the study region are similar in previous research by [9]. The East Coast of Peninsular Malaysia was the location of active petroleum exploration. Pb, Ni, and Zn can also be found in the oil produced by cleaning ship tanks and industrial waste. These heavy metals are previously thought to have come from tar balls because Zn, Pb, and Ni can also come from man-made sources. Lead, for instance, is utilised in cables and pipe systems, and residential industrial waste may be transferred from rivers to coastal areas. Additionally, from the waste disposal region, zinc (Zinc Oxide), which is used in plastic and printing inks, also flowed via the river, passed through to the marine environment and dispersed with sediment at coastal plain area. As the consideration of weathering rate also contribute to the seepage of heavy metal from tar balls to the sediments at the coastal plain of the study area because the viscosity of the oil itself affect the weathering rate. More viscous the hydrocarbon, the longer times taken for the hydrocarbon to become weathered and rate of the seepage of heavy metal from tar balls was slow. During sampling were conducted, the sediment samples were taken below the fresh tar balls, thus it can be assumed that the heavy metal from the tar balls not fully seep into the sediments and influence the low values of these Pb, Zn and Ni concentrations.

3.2. Grain Size Analysis

Table 2 shows that the sediment grain size distribution in the research region ranged from silt to extremely fine sand, fine sand, and medium sand. As mention in Lane's Classification (1947), the sediment range from depth 0 to 18 cm are fine sand to medium sand, thus imply to the surface sediment sample obtained at the study area. Grain size of sediments can reflect spatial inhomogeneity, as the sediment varies in depth, revealing a diverse size range of grain size, affecting heavy metal adsorption and desorption. [7] The distributions of silt to extremely fine sand size can be seen uniformly at the sampling area.

Table 3: Distribution of surface sediment grain size at the study area

Sample No.	Grain Size **Silt < 0.064 mm**	**Extremely Fine Sand 0.064-0.125 mm**	**Fine Sand 0.125-0.25 mm**	**Medium Sand 0.25-0.50 mm**
1			■	■
2				■
3	■	■		
4				■
5		■		
6		■		
7	■	■		
8			■	
9		■		
10	■	■		
11		■		
12	■	■		

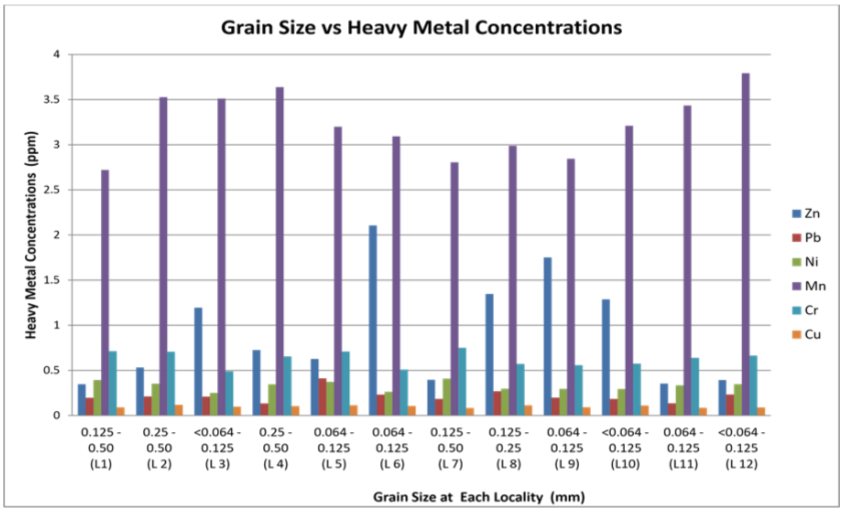

Figure 5. Grain size surface area versus heavy metal concentration at all localities.

The composition of the surface sediments' grain sizes reveals that they were all smaller than 1 mm in size for every locality with most of the grain sizes were between 0.064 and 0.50 mm. [13] stated that, heavy metal concentrations in sediments were most definitely significantly impacted by the distribution of sediment grain sizes. Higher metal content levels in sediments are associated with finer particle sizes, and vice versa. The other parameters, such as increased clay mineral and organic matter contents, which also impact the concentration value of heavy metals in sediments, need to be taken into consideration together with grain size.

Based to this study's findings (Figure 5), the maximum manganese content was found at location 12 in the grain size range of 0.064 to 0.50 mm. Noting that the grain size range included silt and extremely fine silt, the surface area of the grain sizes rises, adsorbing heavy metals at a greater rate than in other sampling locations. In addition to grain size, the sediment of Chendering's coastal plain contains silt-sandy sediment, colloidal materials, and both iron oxide and manganese oxide in association, according to the geochemistry of the rock, which can contribute to the deposition of metal. However, these materials were typically surface active and contain both iron oxide and manganese oxide in association. The sources for manganese may derived from it and dispersed over the research region.

4. Conclusion

Sediments functions as a natural reservoir for metals, the source of pollution. Once metal concentrations surpass certain threshold in sediments, they may cause serious environmental problems due to their toxicity, non-biodegradable properties and widespread distribution. In this study, Manganese shows the highest value out of all the elements, despite having a high concentration, when compare to the standard concentration of heavy metal permissible limit, it shows that the manganese value in Chendering is below background levels at 3.226 ppm. In term of environmental aspects, the area is safe for human activities, tourism and free from heavy metal contamination. The anthropogenic sources as mention earlier, do affects the environment and human health, therefore constantly monitoring these anthropogenic sources and oil spills at the East Coast of Terengganu can maintain the permissible limit of heavy metal to sustain and promote sustainable environment.

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