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Distribution Of Trace Metals In Pore Water Along Terengganu Beach

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Abstract: The aim of this paper was to analyze some trace metal concentrations (Cd, Cu, Al, Pb and Zn) in pore water along Terengganu beach. The samples were extracted by using the APDC-MIBK solvent extraction technique and analyzed by ICP-MS. The results showed that the range of trace metal concentration in pore water for Cd, Cu, Al, Pb and Zn were 0.01 μg L^{-1}, -0.26 μg L^{-1}, 0.65 μg L^{-1}, 5.01 μg L^{-1}, 1.70 μg L^{-1}, -28.9 μg L^{-1}, 0.37 μg L^{-1}, -10.5 μg L^{-1}, 7.66 μg L^{-1}, -271 μg L^{-1}, respectively. In overall, trace metal concentration in pore water does not reaching the limit of Department of Environment (DOE) and it is still under safety level where there are no anthropogenic effects.

Key words: Trace Metal, Pore Water, ICP-MS, APDC-MIBK.

INTRODUCTION

Water quality can be affected either by natural factors such as weather, watershed characteristics (topography, vegetation, wild animals etc), geology, microbiological condition or anthropogenic factors such as agricultural activities, wastewater discharges, mining, recreational activities, and urbanization. Rapid developments of land use activities and other human activities have exerted great effects to the water quality. Pore water contains naturally dissolved gases from atmosphere and dissolved minerals and gases from the soil and rock through which it passes. Pore water also contains hydrogen and oxygen atom from the water. The soil filters the water, absorbs and removes many contaminants though some will pass through unconstrained. But if the soil layer is thin, has high permeability, or if the water table is close to the land surface, then the soil is less likely to sufficiently treat contamination. The excess contaminants may pass through the zone of aeration and enter the pore water. Because the top of the sand is also the land surface, it is highly susceptible to human-induced and naturally occurring pollutants. Pore waters had essentially the same concentration, within 10% as the deep water for calcium, magnesium, manganese, sodium, silicon and zinc. It is approximately four times higher in ferrous concentration in the pore water of the upper sediment layers, than in the deep water.Principal feature of pore water bodies that differ from surface water bodies was due to relatively slow movement of water through the ground by means of residence times in pore water are generally orders of magnitude longer than in surface waters. Once polluted, a pore water body could remain so for decades, or even for hundreds of years, because the natural processes of through-flushing are so slow. Furthermore, there is a considerable degree of physico-chemical and chemical interdependence between the water and the containing material. Pore water and surface water are fundamentally interconnected. This makes pore water useful for assessing contaminant level as pore water more static than surface water. Trace metals are metals in extremely small quantities, in which they are almost at the molecular level that resides in or is present in animal and plant cells and tissue. Trace metals include iron, magnesium, zinc, copper, chromium, molybdenum, and selenium. Trace metals are depleted through the expenditure of energy by living organism. They are replenished in animals by eating plants, and replenished in plants through the uptake of nutrients from the soil in which the plant grows. Trace metal carried in surface water and accumulate in pore water by wave action in the swash zone. This study would provide information to public health authorities for making decisions about beach associated risks. This is including whether or not pathogens can accumulate or multiply to potentially hazardous levels if they migrate to the sand surface or to the water column where human exposure may occur.

The objectives of this study are to determine the concentration of cadmium (Cd), copper (Cu), aluminium (Al), lead (Pb) and zinc (Zn) in pore water along Terengganu beach and the sources of metal pollution. The result obtained from this study will provide baseline data on trace metals in pore waters along Terengganu beach and compared with the water quality of Terengganu beaches regarding to the metals data based on the Interim National Water Quality Standard (INWQS) in Malaysia.

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Methodology

Sampling station	Location
D1	Seberang Takir
D2	Chendering
D3	Pantai UiTM
D4	Rantau Abang
D5	Tanjung Jara
D6	Paka
D7	Kerteh
D8	Kuala Kemaman

Sampling:

Pore water samples were collected from eight stations, D1 to D8 that located along Terengganu beach (Fig. 1). Station and location descriptions are given in the Table 1. Established collection, preservation and storage methodologies were used to ensure that each sample was representative of pore water quality. All sampling apparatus were cleaned by detergent (metal fee non-ionic detergent) and soaked in 10% nitric acid for one week and rinsed with deionized water. Polyethylene bottles were kept in plastics bag to prevent contamination. At each sampling sites, the polyethylene bottles were rinsed several times before they were filled up. Plastic scoop was used to dig an approximately 30cm hole at transect near seaside and water was collected within the hole. The bottles were kept in a plastic bag and stored in ice-packed cooler immediately. Few in situ measurements were collected including salinity (ppt), dissolved oxygen (DO), pH, temperature and turbidity.

Table 1: Sampling points and locations

Sampling station	Location
D1	Seberang Takir
D2	Chendering
D3	Pantai UiTM
D4	Rantau Abang
D5	Tanjung Jara
D6	Paka
D7	Kerteh
D8	Kuala Kemaman

Sample preparation:

In the laboratory, all samples were filtered through 0.45 μm cellulose acetate membrane filters, acidified with nitric acid to pH less than 2 and stored in polyethylene samples tube at 4 ^{0}C in order to distinct the dissolved metals or suspended metals. Ammonium Pyrrolidinedithiocarbamate (APDC) and Methyl Isobutyl Ketone (MIBK) solutions were prepared for solvent extraction. APDC solution was prepared by dissolving 1g APDC in 100 mL deionized water. Nitric acid 2M was prepared by diluted 13.9 mL concentrated nitric acid in 100 mL deionized water. Sodium hydroxide solution was used to determine the optimum pH value before MIBK solution was added.

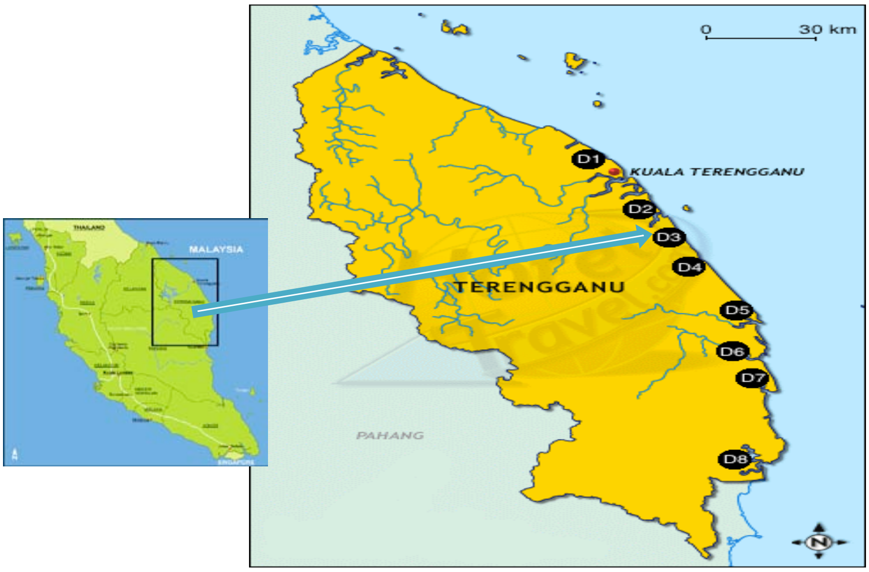

Fig. 1: Map of Terengganu showing the sampling stations

Sample Analysis:

Due to the low concentrations of trace metals in most seawater, solvent extraction method, APDC-MIBK was used to preconcentration prior to ICP-MS determination. Standard stock solution (Merck) was prepared by using deionized water and acidified with 1 mL concentrated nitric acid (HNO_3) and kept in refrigerator. Standard calibration curves were prepared by dilution with deionized water according to sample concentrations from the stock solution with a series of concentration range from 0 μg L -^{1}, 5 μg L -^{1}, 10 μg L -^{1} , 25 μg L -^{1}, 50 μg L -^{1}, 100 μg L -^{1}. Intensity readings for metal concentration were obtained by ICP-MS. 100 mL of water sample and 2.5 mL APDC 1 % were inserted in 250 mL Teflon separatory funnel. For chelate extraction, pH water sample was adjusted until the optimum extraction efficiency was obtained. 3 mL MIBK was added and shook vigorously for 30 seconds until the contents were separated into aqueous and organic layers. Lower portion (aqueous layers) was drained into another Teflon separatory funnel and another 2 mL of MIBK was added and shook vigorously. The first and second funnel that contains the top portion (organic layers) were combined and mixed with 2.5 mL HNO_3 2 M and transferred to polyethylene tubes for ICP-MS analysis. The quality of the method used was checked and confirmed in a separate comparative study of metals using metal solutions of 5 μg L-^{1} and 10 μg L-^{1}. Recoveries were as follows: 87.40% and 88.53% for Cd, 96.28% and 94.30 % for Cu, 90.22% and 95.01% for Al, 86.50% and 88.53% for Pb and 96.34% and 92.73% for Zn, for 5 μg L-^{1} and 10 μg L-^{1}, respectively. SPSS was used for determining statistical data including descriptive analysis and one-way analysis of variance (ANOVA). All comparisons were made at least at the 95% ($p<0.05$) and 99% ($p<0.01$) level of significance.

RESULTS AND DISCUSSION

The physical parameters determined for the seawater are reported in Table 2. Water samples analyzed are near neutral to slightly basic (pH of 5.94 - 7.93). DO ranges from 0.96 to 7.17 mgL^{-1}with temperature varied from 20.4 to 33.9 °C. The range of salinity is from 1.3 to 32.7 ppt and turbidity ranges from 3.0 to 443.0 NTU. Overall results show in Table 3 and Fig. 2, the variation of concentrations level of the trace elements with the sampling station and sampling period. It can be seen that all the elements show relatively the same trend of disparity with the sampling station with the exception of Zn. Besides, the concentrations were varied between the two sampling sessions.

Table 2: Physical parameters in water from the sampling station

Station	Sampling	pH	DO (mgL^{-1})	Temperature (°C)	Salinity (ppt)	Turbidity (NTU)
D1	S1	7.07	6.60	28.8	32.7	281.0
	S2	5.97	4.44	30.1	18.6	253.0
D2	S1	7.08	3.72	30.7	29.6	25.0
	S2	7.32	6.58	28.0	26.5	62.4
D3	S1	7.71	5.07	30.6	11.2	15.0
	S2	6.35	6.39	33.9	23.9	90.5
D4	S1	7.07	0.96	31.6	1.3	3.0
	S2	7.82	7.17	28.4	28.9	53.2
D5	S1	7.41	1.68	20.4	26.9	179.0
	S2	7.51	4.63	27.8	18.5	160.0
D6	S1	7.82	5.07	30.5	22.3	15.0
	S2	6.23	6.99	28.0	3.8	54.4
D7	S1	7.87	6.69	30.1	32.1	10.0
	S2	5.94	6.48	30.8	27.6	39.3
D8	S1	7.93	6.63	32.4	23.1	443.0
	S2	6.06	6.18	29.6	3.1	39.9

Table 3: Mean concentration (μg L $^{-1}$) and classification of trace elements according to INWQS

Sampling Station		Cd	Cu	Al	Pb	Zn
D1		0.15	3.14	15.6	4.73	145
D2		0.11	2.83	11.9	5.2	91.7
D3		0.07	1.35	6.15	1.71	31.8
D4		0.17	1.63	6.36	1.64	90.8
D5		0.07	2.83	15.6	4.24	72.7
D6		0.08	1.68	8.87	5.52	29.6
D7		0.1	2.22	7.38	2.83	58
D8		0.14	1.64	14.1	1.76	19.4
Class	I	N.L	N.L	N.L	N.L	N.L
	IIA	0.01	0.02	-	0.05	5
Classes	IIB	0.01	0.02	-	0.05	5
	III#	0.01*(0.001)	-	-0.06	0.02*(0.01)	0.4*
	IV	0.01	0.2	0.5	5	2
	V	+	+	+	+	+

Zn concentration significantly differed from other metals that varied between 7.66 µg L $^{-1}$and 271 µg L $^{-1}$ throughout the sampling period. The highest average value of Zn was found at station D1 with 145 µg L $^{-1}$(Table 3), (R.T. Ramessur, 2000) stated that Zn and Cd associated with diesel and fuel products presented the broadest ranges in an industrial area. Zn can enter the aquatic environment from a number of sources including industrial discharges, sewage effluent and runoff (R. Alagarsamy, 2006). First sampling recorded highest Zn concentration with 108 µg L $^{-1}$ whereas second sampling was recorded with 26.8 µg L $^{-1}$as shown in Fig. 2.

Cd concentrations in pore water along Terengganu beaches are all within natural levels. Table 1shows the highest average level of Cdconcentration was found at station D4 with 0.17 µg L $^{-1}$ and station D1 with 0.15µg L $^{-1}$. Station D4 highest Cd concentration might be due to nearby with recreation place while station D1 nearby the bus station in which the exhaust gasoline may contain Cd (X.T. Wang Sato, et al., 2004) where the combustion of motor fuels (petrol) in cars and busses and particles from tire wear result in emission to water.The concentration of Cd during the second sampling is highest than the first sampling at 0.16 µg L $^{-1}$and 0.06 µg L $^{-1}$, respectively. There were significant differences ($p < 0.05$) between the two samplings whilst there were no significant differences ($p > 0.05$) between the eight sampling station.

The concentration of Cd during the second sampling (monsoon season) increased at all station except for station D5 compared to the first sampling as shown in Figure 2, which is could be one of the main factor due to the quantity of rain water increase and dissolve into the ground hence weathering of Cd based minerals in pore water.

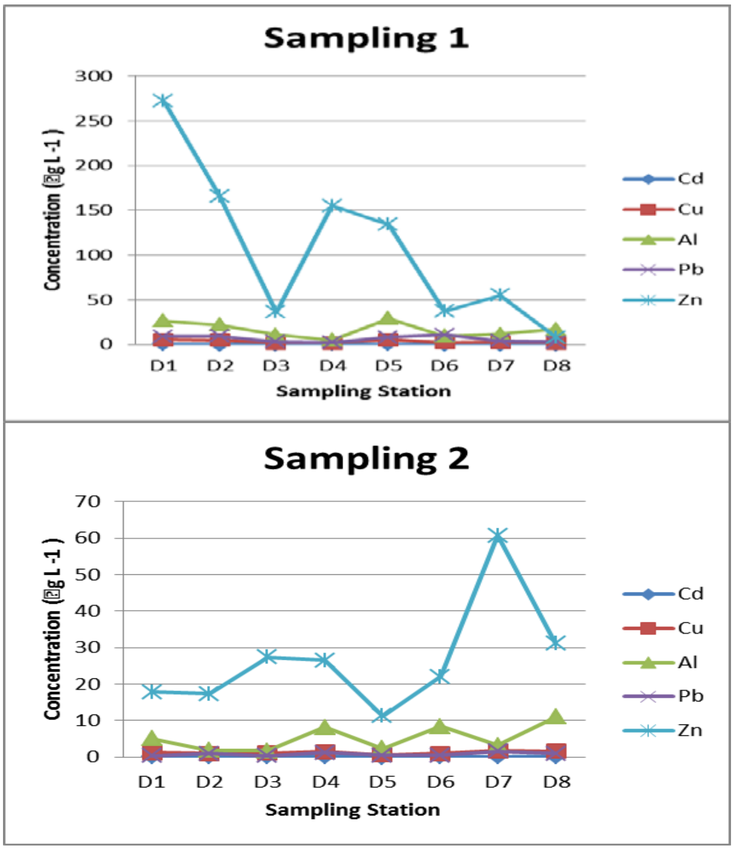

Fig. 2: (a) Variation of trace metal concentrations in pore water during the first sampling.
(b) Variation of trace metal concentrations in pore water during second sampling

The concentration of Cu in the water samples collected from all the eight sampling station were varied from 0.65 µg L $^{-1}$ to 5.01 µg L $^{-1}$. Station D1 recorded the highest average level of Cu concentration with 3.14 µg L $^{-1}$as shown in Table 3. Figure 2 shows first sampling obtained highest average Cu concentration compared to the second one with 3.09 µg L $^{-1}$and 1.24 µg L $^{-1}$ respectively.

The second sampling was carried out during the North East Monsoon that lasts from November to March. The concentration of dissolved metals decrease in monsoon months may due to dilution effect or rainfall and the precipitation or adsorption of dissolved metals onto solids. Besides, other possible factors of decreasing concentration of dissolved metals during monsoon months is because of dilution from tidal flushing or strong dilution of land derived inputs in the coastal ocean (E.H., De Carlo, et al., 2004).

The concentrations of Al in the pore water along Terengganu beach were varied from 1.70 µg L $^{-1}$ to 28.9 µg L $^{-1}$throughout the sampling period (Fig. 2). The highest average level of Al concentration was found at station D1 and D5 with 15.6 µg L $^{-1}$ while the lowest was found at station D3 with 6.15 µg L $^{-1}$as shown in Table 3. The concentration of Al at the first sampling was 16.3 µg L $^{-1}$ is highest than second sampling that was 5.23 µg L $^{-1}$ as shown in Fig. 2. Highest concentration at station D1 might due to near to recreation place, jetty, incomer of boat and bus station while fishery village and boat repair residing are adjacent to the station D5.

Concentration of Pb can be seen clearly in Fig. 2 that ranges from 0.37 µg L $^{-1}$ to 10.5 µg L $^{-1}$. The highest average level of Pb concentration was found at station D6 with 5.52 µg L $^{-1}$followed by station D2 with 5.20 µg L $^{-1}$as shown in Table 3. First sampling recorded highest concentration of Pb compared to second sampling with 6.07 µg L $^{-1}$and 0.83 µg L $^{-1}$, correspondingly. The concentration of Pb has the similar trend with Cu and Al where the metals in second sampling is lower than first sampling. The highest value occurs at station D6 and D2. Both points is close to fishery village, town and jetty Assistance to the Fisheries Development Authority of Malaysia where encircled with automobile exhausts and urban activities as [5] claimed that Pb is used as petrol additives such as Pb tetraethyl and it is lost largely to the atmosphere and enter the water by process of precipitation.

Conclusion:

Cd, Cu, Al, Pb and Zn occurred at considerably variable concentrations in the pore water along Terengganu beach. The observed variation might influence by rainfall and anthropogenic inputs. The concentrations of the five trace metals studiedare classified in Class I according to the INWQS. Results obtained from this study clearly indicate the Zn concentration was the highest among all the metals studied whilst Cd was the lowest.

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