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Distribution of Heavy Metals in Seawater and Surface Sediment in Coastal Area of Tuaran, Sabah

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Abstract

Heavy metal concentrations (Cd, Cr, Cu, Pb and Zn) were analyzed in seawater and surface sediment samples in coastal area of Tuaran, Sabah, Malaysia. Metal concentrations of these samples were analyzed using Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES). The mean concentration of heavy metals Zn, Cu, Cr, Pb and Cd in surface sediment were 22.03, 6.49, 3.81, 2.63, and 0.40 mg/kg, respectively. The corresponding mean concentration values in seawater were 5.56×10^{-3}, 8.22×10^{-4}, 7.70×10^{-4}, 3.37×10^{-4} mg/L and below detection limit (BDL) for Pb, Zn, Cu, Cd and Cr, respectively. The correlation test ($p<0.01$) showed that there was a strong correlation among the concentrations of heavy metals in sediment ($r=0.936$-0.770). While in different compartment, significant correlation ($p<0.01$) was showed only between Pb in seawater with Cr ($r=0.828$), Cu ($r=0.756$), Pb ($r=.739$) and Zn ($r=0.696$) in sediment. According to the Malaysia Marine Water Quality Criteria and Standard (IMWQS) and Interim Sediment Quality guidelines (ISQGs), these heavy metals concentrations are in the range of acceptance limit, except Pb in seawater was considered slightly polluted.

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Introduction

Coastal area interfaced between sea and land. The boundaries of coastal areas are unambiguously delineated due to the shape, dynamic and function is diverse. In Malaysia, besides as residential centers, coastal areas also become the potential areas of strong development pressure, particularly in connection with the development of tourism, agriculture and industry (Siry, 2006). The rapid developments increase the urbanization process which will contribute to the pollutants such as heavy metals in aquatic environment (Afiza & Mohamed, 2012). Thus, it is very important to know the current status of heavy metal concentrations that may be increased above the normal range in the marine environment and effects on marine organisms.

Heavy metals intruded in the coastal areas through naturally occurring substances (biogenic) and several human activities (anthropogenic) such as domestic wastes, agricultural activities and industrial practices (Rout *et al.*, 2013). The change of heavy metals levels in seawater influences the quality of the environment and ecosystem of the coastal area due to they are not removed from water body as a result of self-purification, but they can accumulate in reservoirs and then enter the food chain (Loska and Wiechuła, 2003). Heavy metals in seawater have the tendency to be incorporated in the bottom sediments. Sediments are the final destination of heavy metals accumulation after several processes such as adsorption, precipitation, diffusion processes, chemical reactions or biological activity (Turki, 2007). In seawater, the sediment could act as a source of metal whenever there is a change in environmental and geochemical conditions in sediment-seawater interface. Therefore, sediment is a suitable environmental indicator to trace contamination and monitor contaminants (Yousry *et al*., 2013).

The present study attempts to analyze the distribution of heavy metals (Cd, Cr, Cu, Pb and Zn) concentrations in seawater and sediment in coastal area of Tuaran, Sabah. The study focused on this area due to the location of the coastal area that is surrounded by nearby villages, industries and other development activities. These potential areas discharged effluents, sewage, wastes and pollutants directly to coastal or from the river to coastal which will increase the existing concentration of particular heavy metal. Aquatic organisms living in seawater and sediment can accumulate heavy metals. Meanwhile, villagers' living nearby are depending on this coastal area for food and daily consumption. Polluted heavy metals in seawater and sediment can be directly affect villagers' health through food chain. Therefore, attention on investigation of this area was important due to no practical information on its environmental study. Hence, the collected data were then compared with the metals concentration with Malaysia Marine Water Quality Criteria and Standard (IMWQS) (BOBLME, 2011) and Interim Sediment Quality guidelines (ISQGs) (CCME, 1999) to determine the degree of metal contamination or pollution status in this area.

Methodology

Study area

The study area is located in Tuaran's coastal within the area of latitude 06°06'10.7"N to 06°13'56.0"N and longitude 116°07'53.2" E to E 116°12'49.1"E. Tuaran consist of 180 villages with various ethnic and cultures. The annual rainfall for Tuaran reaches 2500 mm to 3500 mm. The southwest monsoon is the main cause for the heavy rain which occurs from May to August. However, the heaviest rainfall occurs in September and November. This is due to the landform of Tuaran where Crocker Range is the dominant landform with height of 1200 to 2500 m from the sea level. Tuaran landform has approximately 65% hill while the flat land available only at the coastal area and hillsides from Tamparuli to estuary of Tuaran River. Tuaran famous for their tourism industry beach resort such as Shangrila's Rasa Ria Resort, Mimpian Jadi Resort and Sabandar Resort. Besides that, Tuaran also famous for its reserved mangrove swamps in Teluk Mengkabong which is also the famous site for mangrove swamps' researchers. In addition, there were some villages that also become one of Tuaran tourist attraction which are the Mengkabong water village and Penandawan water village with stilt house built by Bajaus over the shore.

Sampling and analysis methodology

This study was conducted in end of October 2012. Samples were collected from eight stations along the coastal area of Tuaran (Figure 1). All samples were triplicates in each station. The exact position and coordinate for each sampling stations are shown in Table 1. Seawater samples (~1 meter depth from the sea water surface) were collected using Van Dorn sampler. Seawater samples were filtered and preserve the dissolved form with nitric acid until pH below 2 then stored in 2L polyethylene bottle. Whereas, surface sediment samples (0-1 cm) were also collected using Ponar grab sampler (5 to 7 meter depth of the sea) and put in a plastic bag and stored in ice box. Perkin Elmer Optima 5300DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) were used to analyze the heavy metals concentration in both seawater and sediment samples. Quality Control Standard 21 (Perkin Elmer Pure) was used as standard reference material (SRM) for instrument recovery.

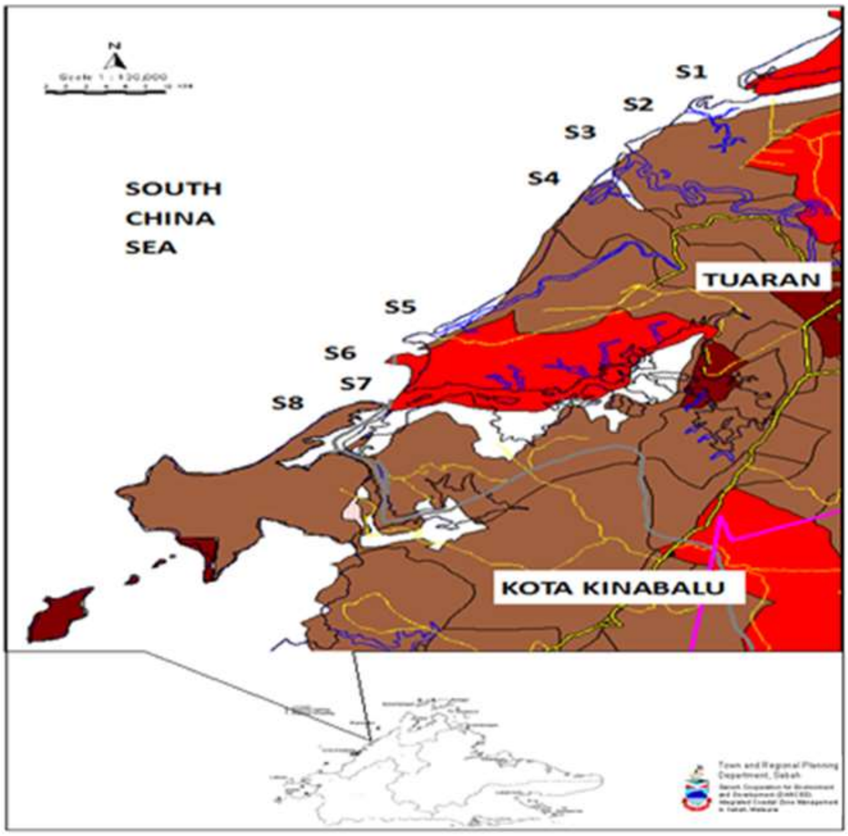

Figure 1. Location of the sampling sites

Table 1. The coordinate of sampling stations

Stations	Latitude	Longitude
1	N 06°14’38.4”	E 116°12’49.1”
2	N 06°06’10.7”	E 116°09’54.3”
3	N 06°13’56.0”	E 116°10’45.4”
4	N 06°11’52.1”	E 116°10’07.2”
5	N 06°09’52.9”	E 116°08’37.6”
6	N 06°08’29.1”	E 116°08’55.4”
7	N 06°07’52.6”	E 116°07’53.2”
8	N 06°08’16.4”	E 116°08’14.0”

Seawater Samples

About 100 mL acidified seawater (acidified with 4N HNO_3) was placed in a separatory funnel. About 1 mL of ammonium pyrrolidine dithiocarbamate (APDC) solution and 10 mL of methyl isobutyl ketone (MIBK: Merck, Germany) were added. The mixture was shaken vigorously for 2 minutes and allowed the content to separate into permanent aqueous and organic phases. The organic layer from this extraction which contained the dissolved metals was transferred into another separatory funnel. About 10 ml of 4N HNO_3 was added in this funnel and shaken for 10 minutes. The extracted metals were then analyzed within 6 hours after extraction.

Sediment Samples

About 1.0g of dried (air dried) surface sediment samples were digested (110°C for 90 min) with 14 ml *aqua-regia* solution (3:1 HNO_3:HCl). After cooled, 14 ml *aqua-regia* solution were added and heated again at 110°C for 30 min. The digested samples were filtered through a 0.45 μm membrane and samples were further analysis by ICP-OES.

Statistical analysis

Data were analyzed using SPSS Statistics version 21. Bivariate Correlation was used to evaluate the relationships among the heavy metals concentrations in seawater and surface sediments.

Result and discussion

Heavy metals in seawater

The heavy metals concentrations in seawater samples from the eight stations of the coastal area of Tuaran are summarized in Table 2. From these results, the distributions of heavy metal Cd was more concentrated at estuary areas. Cd recorded in Station 1 (Estuary of Sulaman River), Station 3 (Estuary of Tuaran River) and Station 7 (Estuary of Salut River) were 2.95×10^{-4}, 2.37×10^{-4} and 4.80×10^{-4} mg/L respectively. According to Pinot *et al.* (2000), anthropogenic sources of Cd are from industrial processes and phosphate fertilizers. Hence, these three stations were the entrance of freshwater to marine water; Cd may be attributed to sewage and wastes discharged from residential (Tambalugu Village and Penambawan water village) and tourism activities (Mimpian Jadi Resort and Golf Club) along the coastal areas.

Table 2. Heavy metal concentrations (mg/L) in sea water

Stations	Metals				
	Cd	**Cr**	**Cu**	**Pb**	**Zn**
1	2.95×10^{-4}	BDL	BDL	4.69×10^{-3}	9.80×10^{-4}
2	BDL	BDL	BDL	7.82×10^{-3}	9.59×10^{-4}
3	2.37×10^{-4}	BDL	7.70×10^{-4}	1.05×10^{-2}	1.17×10^{-3}
4	BDL	BDL	BDL	3.45×10^{-3}	1.03×10^{-3}
5	BDL	BDL	BDL	5.00×10^{-3}	9.30×10^{-4}
6	BDL	BDL	BDL	4.74×10^{-3}	6.76×10^{-4}
7	4.80×10^{-4}	BDL	BDL	4.99×10^{-3}	7.66×10^{-4}
8	BDL	BDL	BDL	3.32×10^{-3}	6.38×10^{-5}
Mean	$\mathbf{3.37 \times 10^{-4}}$	BDL	$\mathbf{7.70 \times 10^{-4}}$	$\mathbf{5.56 \times 10^{-3}}$	$\mathbf{8.22 \times 10^{-4}}$

Note: BDL= Below Detection Limit; BDL Pb & Cr = 1.0×10^{-3}mg/L ; BDL Cu, Zn & Cd = 1.0×10^{-4}mg/L

Cu (7.70×10^{-4} mg/L) only found in Station 3 could be released from the natural constituents of soils which transported into the seawater by natural weathering or anthropogenic soil disturbances. It was estimated 68% of Cu content in soil will be released to the sea during runoff (Georgopoulos *et al*., 2001). In the meantime the highest concentration of Pb (1.05×10^{-2} mg/L) was also found in Station 3, due to highest number of tourist vehicles visited Station 3 (Shangrila's Rasa Ria Resort), causes highest Pb content compared with other stations. Sources of Pb content in seawater could be affected from the flow of tourist vehicles at the tourism beach resorts and then transported to the sea water (Davenport & Davenport, 2006).

Overall the concentrations of heavy metals in coastal water of Tuaran found in the following sequence: Pb > Zn > Cd > Cu > Cr. The maximum value of Cu, Pb and Zn were found in Station 3 and Cd in Station 7. Whereas, Cr was not detected in all study stations. It is also found that the levels of heavy metals were lower than the acceptance limit of Malaysia Marine Water Quality Criteria and Standard (IMWQS) (Table 4) except Pb at Station 3 was reported has exceeded the minimum level as recommended (8.5×10^{-3} mg/L).

Heavy metals in sediments

Distributions of heavy metal concentrations (mg/kg) in surface sediments from the eight stations are shown in Table 3. The range of heavy metal concentrations (mg/kg) were: Cd (0.19 – 0.67), Cr (1.97 – 8.60), Cu (0.29 – 18.57), Pb (0.00 – 8.20) and Zn (9.70 – 43.46) respectively. The mean elemental distribution of surface sediments in descending order were Zn (22.03 mg/kg) > Cu (6.49 mg/kg) > Cr (3.81 mg/kg) > Pb (1.32 mg/kg) > Cd (0.40 mg/kg).

In general, the highest values for heavy metals in the coastal area of Tuaran were recorded at Station 3 (Estuary of Tuaran River), while the lowest ones were recorded at Station 8. Anthropogenic contribution was found as the similar factor that affecting the levels of heavy metals in both surface sediments and seawater. The local distribution of heavy metals in surface sediments also gave the similar pattern of higher concentrations with that found in the seawater, which the highest concentrations (mg/kg) are reported as Cr (8.60±0.0023), Cu (18.57±0.0045), Pb (8.20±0.0044) and Zn (43.46±0.0042) in Station 3, whereas Cd (0.67±0.0001) in Station 7. Both results (Table 2 and Table 3) indicated that the accumulations of heavy metals in sediments are predominant than in seawater. This means sediments able to act as sink for contaminants descending from the ecosystem above and remobilized the contaminants to the seawater by re-suspension process (Lick, 2009). Zn was recorded in all study stations either in seawater or surface sediments (the highest level compare with other metals) could due to natural erosion processes such as the weathering and abrasion of rock, soils and sediments by wind and water are continuously being mobilized or transported in the environment (Singh, 2005). The level of Pb in sediments in all stations were low (8.20 – BDL mg/kg), indicate that the sediment was safe from Pb, most probably the source was only through biogenic.

Table 3. Heavy metal concentrations (mg/kg) in surface sediments

Stations	Metals				
	Cd	Cr	Cu	Pb	Zn
1	0.27	4.97	9.78	1.56	34.29
2	0.19	5.31	5.88	0.52	34.64
3	0.28	8.60	18.57	8.20	43.46
4	0.46	2.78	2.48	0.24	16.00
5	0.50	2.17	11.02	BDL	11.60
6	0.43	1.99	1.58	BDL	13.00
7	0.67	1.97	0.29	BDL	13.52
8	0.37	2.70	2.29	BDL	9.70
Mean	**0.40**	**3.81**	**6.49**	**2.63**	**22.03**

Note: BDL= Below Detection Limit; BDL Pb = 1.0×10^{-2} mg/kg

Assessment environmental and geochemical condition of heavy metals in surface sediments by comparison with Interim Sediment Quality Guidelines (ISQGs) showed that the levels of heavy metals in this study area were in the range of the acceptance limit. The levels of Cd at Station 7 (0.67 mg/kg) and Cu at Station 3 (18.57 mg/kg) were very close to 0.7 mg/kg and 18.7 mg/kg, respectively (Table 4). Both stations are estuaries and close to the outfall, may possible to gain the discharge of wastewater in daily usage from residential, tourism and fertilizers from agricultural (Siti Aishah *et al.*, 2014); these will eventually move to seawater and settle down in sediment (Fernandez *et al.*, 2007). Besides that, higher level of Cd and Cu indicates these elements probably have adverse effects on organisms that live in sediment (Tavakoly *et al*., 2011).

Table 4. Malaysia Marine Water Quality Criteria and Standard (IMWQS) and Interim marine sediment quality guidelines (ISQGs) (BOBLME, 2011; CCME, 1999).

Heavy metals	Malaysia Marine Water Quality Criteria (IMWQS), μg/L	Interim marine sediment quality guidelines (ISQGs), mg/kg
Cd	2.0	0.7
Cr	10	52.3
Cu	2.9	18.7
Pb	8.5	30.2
Zn	50	124.0

Statistical analysis

Results of simultaneous bivariate correlation analysis in Table 5 showed high significant relationships ($p<0.01$) which are relatively self-evident, e.g., relationships among the concentrations of heavy metals Cu, Cr, Pb and Zn in sediment with their respective correlation coefficient (r); Cu_{sed}- Cr_{sed} (0.936), Pb_{sed}-Cu_{sed} (0.902), Pb_{sed}-Cr_{sed} (0.896), Zn_{sed}-Cr_{sed} (0.848) and Zn_{sed}-Cr_{sed} (0.770). Moderate significant correlation also demonstrated between Zn and Pb (r=0.655) in sediment and Cd and Zn (r=0.527) in seawater. These relationships are possible with heavy metals that share the same chemical environment or probably they are from the same source(s). On the other hand, this might be due to similar uptake and release mechanisms by organisms living in or overlying the sediments (Abolfazl & Tooraj, 2015).

Table 5. Correlation between elements of heavy metals in seawater and surface sediment

	Cd_{sed}	Cr_{sed}	Cu_{sed}	Pb_{sed}	Zn_{sed}	Cd_{wat}	Cu_{wat}	Pb_{wat}	Zn_{wat}
Cd_{sed}	1								
Cr_{sed}	-.014	1							
Cu_{sed}	-.052	.936**	1						
Pb_{sed}	-.093	.896**	.902**	1					
Zn_{sed}	.371	.848**	.770**	.655**	1				
Cd_{wat}	-.061	.322	.345	.268	.373	1			
Cu_{wat}	-.062	.225	.312	.089	.152	.381	1		
Pb_{wat}	-.135	.828**	.756**	.739**	.696**	.379	-.070	1	
Zn_{wat}	.204	.166	.100	.022	.290	.570**	.292	.199	1

**. - Correlation is highly significant at the 0.01 level (2-tailed).
Sed. - sediment
Wat. - water

In different compartment, significant negative correlation ($p<0.01$) was found between Cd_{sed}-Cd_{wat} (r=-0.61); weak correlation between Cu_{sed}-Cu_{wat} (0.312) and Zn_{sed}- Zn_{wat} (0.290). These indicated that interchange or exchange process occurred between the heavy metals in seawater and sediment (Chakraborty *et al.*, 2009). Most probably heavy metals were released from sediment to seawater in

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this case, due to higher heavy metal concentrations in sediment. Whereas significant positive correlation ($p<0.01$) was showed only between Pb_{sed}-Pb_{wat} with correlation coefficient (r) 0.739. This positive correlation found between Pb in seawater and in sediment proves that the contamination of Pb in seawater mainly came from the anthropogenic sources than natural origin.

Conclusion

The results of this study can be used as basic data for current state of heavy metal concentrations in seawater and sediments in coastal area of Tuaran, Sabah, Malaysia. The level of heavy metals in seawater and sediment was different at each station with the sequence: Pb > Zn > Cd > Cu > Cr and Zn > Cu > Cr > Pb > Cd respectively. Naturally occurring substances, urbanization areas and anthropogenic effluent were the sources that contributed to the local distribution of heavy metals in this coastal area. The levels of heavy metals in coastal area of Tuaran were found in the range of acceptance limit of IMWQS and ISQGs except for Pb in seawater was considered slightly polluted.

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