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Elemental Concentrations in the Surface Sediments Collected from the Straits of Malacca: 2004 Sampling Cruise

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ABSTRACT

In this study, surface sediments from four geographical sampling sites in the Straits of Malacca (three near the northern part and one near the central part) were collected between February and March 2004 and they were analyzed for 35 elements by using an Inductively Coupled Plasma Mass Spectrometry (7 elements) and an Instrumental Neutron Activation Analysis (28 elements). It was found that one site at the northern part had highest levels of 23 elements out of 35. This indicated that the sampling site located at the northern part had received anthropogenic inputs due to shipping activities. However, illegal dumpings and other unidentified sources could not be rule out. In general, As, Cd, Cr, Cu, Pb and Zn have low potential to cause adverse effects on biota except for Ni that a biological effect could affect some benthic species occasionally, as compared to the Interim Sediment Quality Values. Therefore, this study provided an evidence that high elemental concentrations is plausibly due to shipping activities since the Straits of Malacca is the busiest shipping lane in this region.

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1. INTRODUCTION

The Straits of Malacca is the busiest shipping lane in this region. Studies of metals in the sediments from the Straits of Malaysia are mainly focused on heavy metals such as Cd, Cu, Pb and Zn [5]. The information on the other metallic elements is limited or scarce in the literature.

In this paper, 35 element total concentrations in four surface sediment samples, collected from the Straits of Malacca, were determined by using Instrumental Neutron Activation Analysis (INAA) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). INAA is a non-destructive multi-element nuclear technique and its high sensitivity permits the simultaneous determination, without any chemical separation, of a large number of elements in the periodic table. ICP-MS is a very rapid, multi-element and accurate analytical technique with very low detection limits for most elements [2].

Since there is no recent data regarding the metallic concentrations in the Straits of Malacca surface sediments, and thus the objective of this paper is to provide a baseline of 35 elemental metallic concentrations in the Straits of Malacca. In addition, some commonly heavy metals were compared against those of Malaysian reports as well as against to average shale and Interim Sediment Quality Values (ISQVs).

2. MATERIAL AND METHOD

The surface sediments (0-5cm) samples were collected from 4 sampling sites in the Straits of Malacca (Table 1, Figure 1) by using standard ponar grab sampler (8.2 LV^{-1}). This type of grab sampler was useful for the most of sediment types in the marine environment. The samples were collected between February and March 2004. The wet sediment samples were stored in polyethylene bottles and the samples refrigerated at -5ºC immediately when returned to the laboratory.

Table 1. Geographical coordinates, distance from the offshore and water depth of the core marine sediment samples for four sampling sites in the Straits of Malacca

	WC01	WC02	WC03	WC04
Longitude	098°58.30'E	099°29.80'E	099°19.00'E	100°22.97'E
Latitude	06°06.60'N	05°56.70'N	05°28.35'N	03°21.73'N
Water depth (m)	83.0	50.0	77.5	66.3
Distance from offshore (km	88.9.	94.45	92.6	89.3

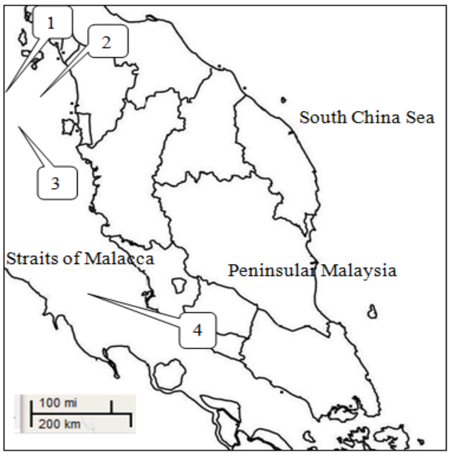

Figure 1. The sampling sites for sediments in the northern part of the Straits of Malacca. (1= WC1; 2= WC2; 3= WC3; 4= WC4)

The sediment samples were dried in an oven at 65ºC for period of time (5-10 days) until constant dry weights. Then the dried samples were grinded by using an electronic agate homogenizer to obtain homogeneous powder (2mm mesh size) to ensure the elements of each sample were uniformly distributed. Then the samples were stored in polyethylene bottles for future analysis.

Seven elements namely Sr, Ti, Ni, Cu, Cd, Pb and Mo were analyzed by using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Liquid form needed for the ICP-MS analysis. Thus, the samples were digested by a proper chemical method so that we can measure the non-measureable element by NAA with acceptable accuracy and precision. A duplicate sample of approximately 200-300 mg was transferred to valve Teflon beaker. 3ml of concentrated hydrofluoric acid (HF) and 10 ml of concentrated nitric acid (HNO_3) added to the weight sample and the valve beaker was closed and digested inside a commercial microwave oven 440-W for 15 minutes. Then, the heated samples cooled to room temperature and reheated inside a commercial microwave oven 600-W for 20 minutes. After that, the samples were cooled to room temperature and the valve Teflon beakers were opened carefully in fume hood. The digested samples was transferred to 100ml polyethylene bottle and diluted to about 50 ml by double distilled water. 1 ml of diluted solution was transfer to test tube and diluted by a factor of 10 by adding 9ml of double distilled water. Certified reference material (CRM) IAEA-SOIL-7 was prepared and used as quality control with each batch. The blank sample was also prepared. The recoveries of the 7 elements were acceptable as being between 65-133% (Table 2).

Table 2. Comparison of concentrations (µg/g dry weight) determined between the certified reference material (IAEA-SOIL-7) and measured values by using ICP-MS

Elements	Certified values	Measured values (N=5)	Recovery (%)
Sr	108.00±5.40	83.43±2.00	77
Ti	3000±550	3201±124	106
Ni	26.0±8.0	34.66±1.25	133
Cu	11.00±1.98	14.44±0.39	131
Cd	1.30±0.80	0.84±0.01	65
Pb	60.0±7.8	68.73±0.63	114
Mo	2.50±2.10	1.73±0.03	69

Table 3. Comparison of concentrations (µg/g dry weight) determined between the certified reference material (IAEA-SOIL-7) and measured values by using INAA

Element	Certified values	Measured values (N= 6)	Recovery (%)
Al	47000±3500	41925±4519	89
As	13.40±0.80	13.63±0.56	102
Br	7.0±3.5	7.93±0.78	113
Ca	163000±8500	150449±11584	92
Ce	61.00±6.71	77.33±4.83	127
Co	8.90±0.89	9.27±0.73	104
Cr	60.0±12.6	69.00±7.33	115
Cs	5.40±0.76	5.72±0.81	106
Eu	1.0±0.2	1.05±0.23	105
Fe	25700±550	26100±1745	102
Hf	5.10±0.36	4.85±0.23	95
K	12100±7010	11898±199	98
La	28.00±1.12	19.46±3.22	70
Lu	0.30±0.15	0.27±0.03	90
Mg	11300±400	10364±858	92
Mn	631±25	605±24	96
Na	2400±100	2419±20	101
Rb	51.00±4.59	47.87±4.18	94
Sb	1.7±0.2	1.72±0.14	101
Sc	8.30±1.08	8.47±0.66	102
Sm	5.10±0.36	5.84±0.51	114
Ta	0.80±0.20	0.83±0.21	104
Tb	0.60±0.19	0.53±0.11	88
Th	8.20±1.07	8.02±0.53	98
U	2.60±0.55	3.15±0.29	121
V	66.00±7.26	64.10±1.85	97
Yb	2.40±0.36	2.74±0.55	114
Zn	104.00±6.24	110.08±13.47	106

The other 28 elements namely Al, As, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Mg, Mn, Na, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, V, Yb and Zn were analyzed by using Instrumental Neutron Activation Analysis (INAA). A duplicate weight ranging from 0.05 to 0.1 g was prepared for short radiation while 0.15-0.20 g was prepared for long radiation into a polyethylene vial and heat sealed. Certified reference material (CRM) IAEA-SOIL-7 was prepared and used as quality control with each patch of short-lived and long-lived isotopes. The recoveries of the 28 elements were acceptable as being between 70-127% (Table 3).

The irradiations were performed in the TRIGA MARK II research reactor at the Agensi Nuklear Malaysia (NUKLEAR MALAYSIA) reactor. A pneumatic transfer system (PTS) was used for short irradiation for immediate counting of short- lived isotopes such as Al, Ti, V, Mn, Mg, Na, K and Ca. Long irradiation with neutron flux of 4-5 x 10^{12} n/cm^2 was used for long lived isotopes such as As, Ba, Ce, Co, Cr, Fe, Hf, La, Lu, Sb, Sc, Sm, Tb, U and Zn.

After irradiation by thermal neutron flux by TRIGA MARK II, the radioactivity measurement of sediment samples will be carried out after proper cooling time by using various close-end coaxial high purity germanium detectors (Model GC3018 CANBERRA Inc and Model GMX 20180, EG4G ORTEC Nuclear Instrument) and their associated electronics.

In the case of the short irradiation, each sample will be irradiated for a period of 30-60 second on the same position by using pneumatic transfer system (PTS) and cooling time varies from 5-20 minutes for 1^{st} gamma-ray counting for determination of the following elements Al, Ca, K, Mg, Mn, Na, Ti and V while 2^{nd} ray counting will be performed after 24 hours for determination of K and Na. The live time for the 1^{st} counting short-lived radioisotopes was 300 seconds while the live time for 2^{nd} counting was 1200 seconds.

In the case of long irradiation, the cooling time for the 1st counting varies 3-6 days depending on the dead time of the samples and 3-4 weeks for second counting. The 1^{st} gamma-rays counting the following elements As, Ba, Br, La, Lu, Sb, Sm and U were determined while 2^{nd} counting the following elements Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sc, Ta, Th, Yb and Zn were determined. The live time for the 1^{st} counting of long-lived radioisotopes was 3600 seconds while 7200 seconds for 2^{nd} counting.

3. RESULTS AND DISCUSSION

The 35 elemental data in the surface sediments analyzed in this study are presented in Table 4. The ranges of all elements investigated in this study were 0.03-0.26 µg/g dw for Cd, 64.17-252.64 µg/g dw for Sr, 13.89-22.75 µg/g dw for Cu, 0.22-0.64 µg/g dw for Mo, 26.11-44.67 µg/g dw for Ni, 18.31-31.47 µg/g dw for Pb, 1.48-2.67 % for Fe, 1.16-1.49 % for K, 0.94-4.04% for Na, 0.98-2.05% for Mg, 3.43-5.91% for Al, 0.20-0.27% for Ti, 26.07-60.8µg/g dw for Cr, 66.07-97.49µg/g dw for Rb, 0.90-1.42µg/g dw for Ta, 71.06-116.88µg/g dw for Ba, 16.25-63.13µg/g dw for V, 2.30-5.07µg/g dw for As, 32.81-276.7µg/g dw for Br, 4.99-9.07µg/g dw for Co, IID-6.45µg/g dw for Ca, 3.50-11.96µg/g dw for Cs, 4.29-8.95µg/g dw for Hf, 0.51-1.09µg/g dw for Sb, 10.22-20.14µg/g dw for Th, 2.05-5.19µg/g dw for U, 37.58-91.16µg/g dw for Zn, 382.39-887µg/g dw for Mn, 3.30-5.56µg/g dw for Sm, 44.70-80.44µg/g dw for Ce, 0.51-1.14µg/g dw for Eu, 20.16-33.26µg/g dw for La, 0.29-0.35 µg/g dw for Lu, 3.36-11.11µg/g dw for Sc and 1.57-3.49 µg/g dw for Yb.

Table 4. Elemental concentrations (All elements are presented in µg/g dw except for those indicated by * which are presented in %) in surface sediments collected from the Straits of Malacca

Sites	Cd (ICPMS)	Sr (ICPMS)	Cu (ICPMS)	Mo (ICPMS)	Ni (ICPMS)	Pb (ICPMS)		
WC01	0.26±0.03	252.64±10.86	22.75±1.21	0.53±0.01	44.67±2.36	31.47±1.34		
WC02	0.08±0.01	232.28±10.88	16.96±0.89	0.64±0.02	26.79±1.31	19.43±1.21		
WC03	0.05±0.01	116.96±6.50	15.73±0.94	0.22±0.01	32.45±1.18	19.28±1.10		
WC04	0.03±0.01	64.17±4.01	13.89±0.87	0.23±0.01	26.11±1.52	18.31±1.05		
Sites	Fe (%)	K (%)	Na (%)	Mg (%)	Al (%)	Ti (%ICPMS)		
WC01	2.67±0.24	1.27±0.22	4.04±0.40	1.59±0.46	5.91±0.66	0.26±0.02		
WC02	1.79±0.21	1.16±0.89	3.94±0.56	2.05±0.44	4.72±0.44	0.27±0.02		
WC03	1.88±0.22	1.49±0.23	1.23±0.16	0.98±0.18	3.82±0.31	0.20±0.01		
WC04	1.48±0.08	1.16±0.19	0.94±0.12	1.30±0.31	3.43±0.29	0.20±0.01		
Sites	Cr	Rb	Ta	Ba	V	As	Br	Co
WC01	60.8±5.22	97.49±13.78	1.42±0.39	73.02±1.41	61.8±15.82	5.07±1.41	276.7±33.44	9.07±0.80
WC02	42.25±4.39	72.69±22.13	1.04±0.23	71.06±0.86	63.13±19.53	3.50±0.78	189.29±45.55	6.29±1.00
WC03	26.98±4.10	82.12±20.84	0.96±0.29	92.42±0.89	22.55±9.88	2.30±0.65	58.48±4.60	6.10±1.01
WC04	26.07±4.33	66.07±19.27	0.90±0.38	116.88±1.20	16.25±8.97	2.50±0.57	32.81±3.12	4.99±1.72
Sites	Ca	Cs	Hf	Sb	Th	U	Zn	Mn
WC01	6.45±0.91	11.96±1.19	6.08±0.46	1.09±0.23	20.14±1.90	5.12±1.92	91.16±14.03	887.00±87.00
WC02	Lld	6.37±0.88	4.29±0.40	1.09±0.35	14.42±1.30	5.19±2.49	65.92±13.11	574.35±72.93
WC03	4.02±0.49	4.27±0.70	8.95±0.64	0.51±0.18	10.22±1.02	2.11±0.72	55.23±12.30	497.75±60.65
WC04	2.38±0.32	3.50±0.85	8.00±0.89	0.51±0.17	11.58±2.33	2.05±0.73	37.58±9.45	382.39±46.74
Sites	Sm	Ce	Eu	La	Lu	Sc	Yb	
WC01	5.56±0.70	80.44±4.97	1.14±0.19	33.26±4.56	0.29±0.10	11.11±0.86	1.74±0.57	
WC02	4.62±0.63	61.24±5.09	0.75±0.09	28.16±4.15	0.35±0.10	6.54±0.72	3.36±1.01	
WC03	3.49±0.44	44.70±4.95	0.60±0.13	20.16±2.74	0.30±0.13	4.30±0.48	3.49±1.07	
WC04	3.30±0.33	50.72±4.69	0.51±0.16	20.64±1.14	0.34±0.27	3.36±0.61	1.57±0.75	

For comparison, the present Cd, Cu, Pb and Zn levels are compared to those reported for the surface sediments in the Straits of Malacca (from northern to southern parts) collected during sampling cruises conducted between 1998-1999 (Yap *et al.* 2002, 2003). The present ranges of Cu (13.89-22.75 µg/g dw), Pb (18.31-31.47 µg/g dw), and Zn (37.58-91.16µg/g dw for Zn) were almost similar (although a bit higher) when compared to those (0.25 to 13.8 µg/g dw for Cu, 3.59 to 25.4 µg/g dw for Pb and 4.00–79.05 µg/g dw) reported by Yap *et al.* (2002, 2003). However, the present Cd ranges (0.03-0.26 µg/g dw) are lower than that (0.10–1.42 µg/g dw) for the Straits of Malacca [6].

One interesting finding is that one site at the northern part of the Straits of Malacca (W01) was found to have the highest levels of 23 elements out of 35. This suggests elemental contamination at the sampling site and this could plausibly due to the particular site located at the northern part had received anthropogenic inputs due to shipping activities. However, illegal dumpings and other unidentified sources could not be rule out. This was further supported by the studies reported [5]-[6] in which levels of Cd, Cu, Pb and Zn were generally higher in the northern part of the Straits.

Table 5. Comparisons of ranges (min–max) of some metal concentrations (µg/g dry weight) in sediments in the Straits of Malacca with established average shale concentrations and the Interim Sediment Quality Values (ISQV)

	As	Cd	Cr	Cu	Ni	Pb	Zn	Reference
The Straits of Malacca	2.30-5.07	0.03-0.26	26.07-60.8	13.89-22.75	26.11-44.67	18.31-31.47	37.58-91.16	This study
Average shale	13	0.3	90	45	68	20	95	Turekian and Wedepohl (1961)
ISQV-Low	8.2	1.5	80	65	40	75	200	Chapman *et al.* (1999)
ISQV-High	70	9.6	370	270	Not set	218	410	Chapman *et al.* (1999)

By comparing with the average shale values by Turekian and Wedepohl (1961) (Table 5), the present ranges of As, Cd, Cr, Cu Ni and Zn are all below the values. Only Pb ranges are higher than the average shale value of Pb. This paper selected the Hong Kong' ISQVs-Low of effect range low (ERL) and ISQVs-High of effect range median (ERM) for marine sediment as proposed [1] for comparison as informal screening tools in environmental assessments in the present study because the metal values are the most appropriate guidelines that meet the prioritization criteria and consistent with international initiatives and regulations [2]. The ranges for As, Cd, Cr, Cu, Pb and Zn are below the ISQV-low [1] (Table 5). Therefore the abovementioned metal concentrations below the ERL are associated to minimal toxic effects or probably have no adverse biological effects. Only the ranges of Ni are slight higher the ISQV-low value but below ISQV-High and this Ni concentrations between ERL and ERM suggest that biological effects could occur occasionally. Other metallic elements are not included for comparison because they are not available.

4. CONCLUSION

In the study, a total 35 elemental concentrations have been determined in 4 geographical sampling sites collected from the Straits of Malacca. In general, As, Cd, Cr, Cu, Pb and Zn have low potential to cause adverse effects on biota since they are below the ISQV-low except for Ni that a biological effect could affect some benthic species occasionally since they are between the ISQV-low and ISQV-high. The present baseline information is the most recent comprehensive report on 35 elements in the surface sediments collected from the Straits of Malacca.

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