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## Trace Metals in Surface Sediment of the South China Sea, Area II: Sarawak, Sabah and Brunei

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### ABSTRACT

The trace metals composition of surface sediment of the South China Sea off Sarawak, Sabah and Brunei were measured. Total metal concentrations in the 63  $\mu\text{m}$  fraction are reported in this study. For the pre-monsoon cruise, the metal concentrations ranged between 1.01 – 13.0  $\mu\text{g g}^{-1}$  Pb, 8.28 – 99.8  $\mu\text{g g}^{-1}$  Cu, 27.8 – 137.0  $\mu\text{g g}^{-1}$  Zn, 10.1 – 75.7  $\mu\text{g g}^{-1}$  Cr, 175 – 1166  $\mu\text{g g}^{-1}$  Mn, 0.83 – 4.57% and Fe 0.16 – 2.25%. The range of metal concentrations measured in the post-monsoon cruise varied between 1.63 – 18.9  $\mu\text{g g}^{-1}$  Pb, 7.52 – 38.0  $\mu\text{g g}^{-1}$  Cu, 14.4 – 105  $\mu\text{g g}^{-1}$  Zn, 19.6 – 87.6  $\mu\text{g g}^{-1}$  Cr, 157 – 1890  $\mu\text{g g}^{-1}$  Mn, 1.37 – 9.83 % Al and 0.51 – 4.47 % Fe.

The distribution of metals in the sediment showed different patterns between the pre-monsoon and the post-monsoon periods. The Rajang River seems to be one of the major factors affecting the distribution of metals in the seabed off Sarawak.

**KEY WORDS:** South China Sea, Borneo, surface sediments, metals.

### Introduction

Malaysia is a maritime nation and surrounded by the Strait of Malacca, South China Sea and the Sulu Sea off Sabah yet few studies on the metal contents of sediments off the Borneo mainland have ever been carried out. In a study on the geochemistry of the surficial sediments of the South China Sea off Sabah and in the Sulu Sea, the distribution of some metals were related to depth of the water column (Calvert et al., 1993) as well as sediment mineralogy.

Similar studies conducted in 1997 (Shazili et al., 1997) in the Gulf of Thailand and the South China Sea off the east coast of Peninsular Malaysia found that Pb:Al ratios exceeded world average continental crust values. Cu:Al ratios were generally higher in the Upper Gulf of Thailand region compared with values for east coast areas of Peninsular Malaysia.

This study, off Borneo, is a continuation of the measurements of metal contents and their distribution in surface sediment of the South China Sea as the sea off Borneo is much deeper and the sedimentary regime may be different. The influence of large rivers flowing into the sea from the Borneo mainland may have effects on the seabed extending far beyond the coast.

### Methodology

The methodology for sample collection, preparation and metal analyses adopted in the present study was similar to that used during the previous work in the South China Sea (Shazili et al., 1997) and that of Wood et al. (1997). The method involves the conduct of the following activities:-

#### 3.1 Sample Collection

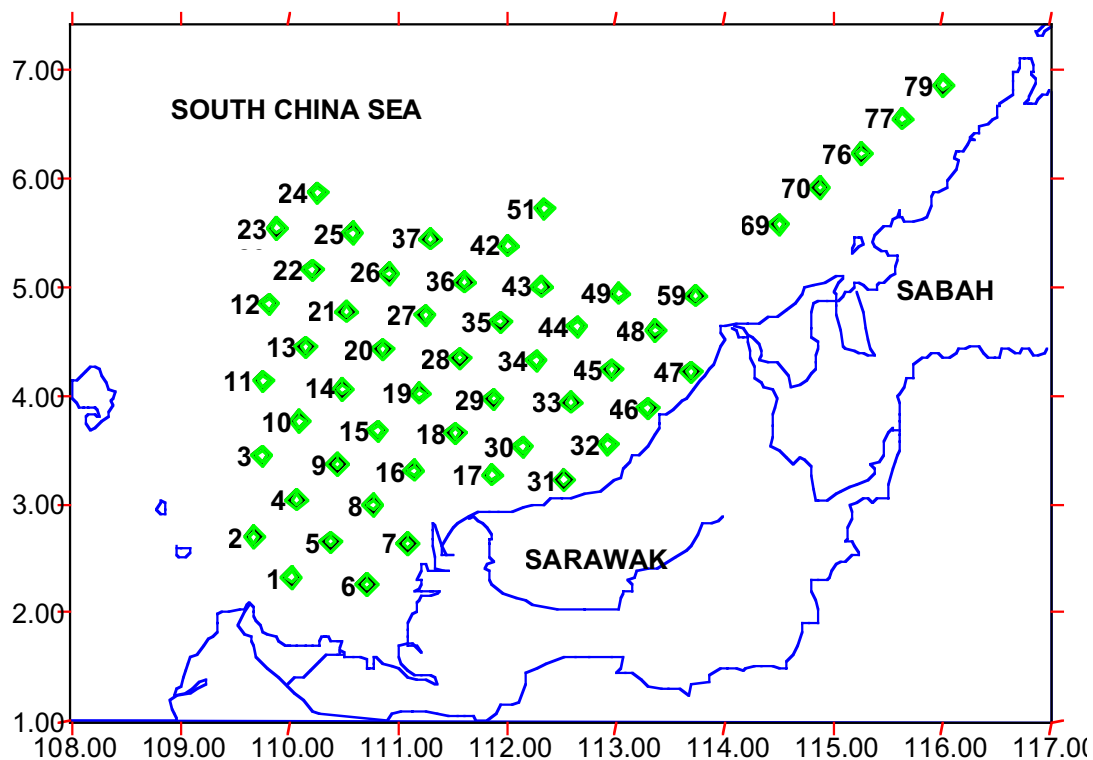


Fig. 1. Location of sampling stations off Sarawak, Sabah and Brunei Darussalam.

Surface sediment samples were collected using a Smith McIntyre grab from 52 sampling locations (Fig. 1). The top 3cm of sediment were carefully collected with a clean plastic spatula, kept in acid-cleaned glass bottles and preserved at  $-20^{\circ}\text{C}$  until ready for analysis.

### 3.2 Sample Preparation

The sediment samples were dried at  $95^{\circ}\text{C}$  then lightly ground to break up the particles. The sediment was sieved through a  $63\mu\text{m}$  mesh and about 1g aliquots of this silt and clay fraction was then totally digested in a mixture of nitric, perchloric, hydrofluoric and hydrochloric acids in open PTFE beakers. The digest was then made up to 50ml with Milli-Q water.

For quality assurance, a standard reference material (1646a Estuarine Sediment) from the National Institute of Standards and Technology was digested as above and analysed for metals.

### 3.3 Metal Analysis

Metals were analysed using a flame atomic absorption spectrophotometer equipped with Deuterium corrector. Analyses of NBS 1646a Estuarine Sediment (National Bureau of Standards) indicated good recoveries of all metals (Table 1).

## **Results and Discussion**

The total metal contents in surface sediment for the pre-monsoon period and post-monsoon period cruises are shown in Tables 2 and 3 respectively. The measured values for the pre-monsoon cruise ranged between  $1.01 - 13.0\mu\text{g}\text{g}^{-1}$  for Pb,  $8.28 - 99.8\mu\text{g}\text{g}^{-1}$  for Cu,  $27.8 - 137.0\mu\text{g}\text{g}^{-1}$  for Zn,  $10.1 - 75.7\mu\text{g}\text{g}^{-1}$  for Cr,  $175 - 1166\mu\text{g}\text{g}^{-1}$  for Mn,  $0.83 - 4.57\%$  for Al and  $0.16 - 2.25\%$  for Fe. The range of metal concentrations measured in the post-monsoon cruise varied between  $1.63 - 18.9\mu\text{g}\text{g}^{-1}$

Table 1. Analysis of certified reference materials (NBS 1646a Estuarine Sediment)

	Certified value		Measured value		% Mean Recovery
	$(\mu\text{g g}^{-1})$		$(\mu\text{g g}^{-1})$		
Aluminium (%)	2.297	0.018	2.356	0.95 %	104.7
Iron (%)	2.008	0.039	2.048	0.12 %	102
Copper	10.01	0.34	10.28	0.64	102.6
Chromium	40.9	1.9	38.7	1.03	94.7
Lead	11.7	1.2	10.6	0.63	90.5
Zinc	48.9	1.6	48.1	1.2	98
Manganese	234.5	2.8	227.5	4.0	97

Table 2. Concentrations of elements surface sediments in  $\text{mg g}^{-1}$  dry wt. for the pre-monsoon period

Stn	Fe (%)	Al (%)	Cu	Cr	Pb	Zn	Mn
2	1.17	2.75	28.6	47	7.5	75	-
3	0.67	1.48	45.7	40	9	68.1	501
4	0.67	1.38	39	31	6.01	39.1	250
11	0.71	0.78	66	21	3	45.1	250
12	0.67	0.83	99.8	32	2	55.1	301
13	0.8	0.75	60.1	36.1	4.51	75.6	275
14	0.69	1.33	16.5	21.5	9.52	42.1	351
16	0.89	0.88	98.8	29.1	8.03	34.1	477
19	0.67	0.83	55.1	27	4.56	49.1	576
21	1.8	3.63	-	39.5	5.01	92.5	725
22	2	3.85	24.6	42.5	4.5	83.1	801
25	1.42	1.68	-	37.6	13	67.1	551
26	1.98	3.48	36.4	53	4	80.5	850
27	1.39	2.53	30.3	43.6	2	78.2	701
28	2.04	4.23	27.6	42.5	4.5	66	625
31	1.37	2.96	20.4	42.6	8.03	64.7	853
32	1.95	4.56	8.28	72.7	8.53	77.3	778
33	1.63	3.43	28.3	55	3.03	75.2	833
34	1.87	3.53	33.3	53.5	2.02	62.6	581
35	2.25	4.36	35.8	67.1	8.52	113.7	601
36	1.84	4.42	32	59.2	2.01	74.3	878
37	2.17	3.5	43.9	66.8	9.33	97.9	1166
44	0.7	0.53	56.2	28	9.01	50.6	551
45	2.03	4.18	45.1	75.7	10	78.7	952
48	0.81	1.4	38.4	39.1	7.51	61.6	551
49	1.49	1.43	26.4	35.1	9.01	74.1	425
53	1.27	2.37	49.6	76	4	137	175
60	1.8	3.86	56.8	53.6	4.01	109	401
70	1.82	4.57	21.6	65.8	4.52	120	628
77	0.16	1.37	42	10.1	1.01	27.8	329

Table 3. Concentrations of elements surface sediments in mgg-1 dry wt. for the post-monsoon period.

<b>Stn</b>	<b>Fe (%)</b>	<b>Al (%)</b>	<b>Cu</b>	<b>Cr</b>	<b>Pb</b>	<b>Zn</b>	<b>Mn</b>
1	2.66	3.16	14.96	35.74	9.14	30.76	490
2	2.78	5.19	15.52	53.72	5.37	44.77	334
3	3.18	6.4	17.92	67.84	9.6	66.56	538
4	2.74	6.23	16.32	60.73	13.14	59.83	557
5	4.47	7.33	16.09	77.67	18.89	64.37	623
6	2.67	5.89	15.4	64.53	15.4	49.13	279
7	4.07	9.83	18.3	87.62	9.46	69.31	301
8	3.19	1.37	10.42	32.2	13.26	25.57	294
9	2.75	5.53	16.21	54.01	12.15	46.59	358
10	3.31	6.02	18.54	64.55	13.05	57.68	570
11	3.31	6.55	18.01	63.38	11.34	66.05	560
12	2.9	6.27	38.03	59.94	11.6	52.2	432
13	3.08	6.35	18.08	59.05	18.68	59.65	578
14	3.15	6.72	16.13	62.05	17.34	60.81	441
15	2.79	5.59	14.16	57.37	9.92	48.16	354
16	2.75	6.8	14.11	63.84	12.89	46.65	203
17	2.45	3.98	12.44	47.01	9.68	38.03	249
18	2.33	4.51	13.53	46.3	7.84	42.03	235
19	2.46	5.35	12.37	56.43	12.75	51.4	344
20	3.01	6.2	15.85	61.56	6.7	62.16	408
21	2.78	6.21	17.89	57.62	11.92	83.44	550
22	2.63	5.49	16.45	53.15	12.66	83.52	487
23	2.64	4.9	17.96	48.93	10.53	87.34	458
24	3.71	7.51	26.5	74.83	17.89	104.66	364
25	2.54	5.36	15.76	52.73	6.67	66.67	442
26	2.68	5.82	16.13	54.11	10.41	61.4	479
27	2.7	5.02	15.29	53.53	9.56	61.18	465
28	2.9	5.65	17.53	61.36	9.93	68.96	543
29	2.82	6.38	16.07	57.14	12.5	66.67	411
30	1.73	3.07	16.58	33.16	4.88	76.07	244
31	2.78	5.94	15.78	61.87	13.26	77.02	347
32	3.29	8.31	19.83	76.41	12.25	88.66	420
33	2.38	5.37	15.85	51.82	6.71	74.37	329
34	3.09	6.55	18.8	65.52	9.69	85.46	473
35	3.26	6.83	18.39	58.71	7.78	90.54	516
36	2.77	6.01	17.66	52.34	17.03	76.3	498
37	3.41	6.94	24.58	66.81	14.5	93.91	1891
42	2.67	5.26	17.94	53.82	5.52	72.45	462
43	2.74	6.28	17.13	61.08	8.56	70.78	525
44	2.99	6.51	17.25	65.07	7.23	77.91	506
45	3.51	7.85	18.65	75.93	16.65	69.27	440
46	2.28	4.83	21.01	47.67	8.89	41.21	242
47	3.54	8.08	17.96	77.16	8.65	69.18	412
48	3.38	7.27	21.9	73.98	11.25	68.06	426
49	2.07	4.27	15.21	42.31	10.46	46.59	347
51	2.53	5.03	10.81	48.66	6.08	56.1	406
59	2.34	4.54	13.43	41.04	9.7	43.28	261
69	3.33	7.48	11.8	63.97	14.9	69.56	323
70	2.57	5.48	10.72	50.74	14.29	51.45	307
76	2.57	5.01	13.05	44.96	18.85	45.69	703
77	1.94	4.84	12.87	49.22	3.92	42.51	302
79	0.51	1.85	7.52	19.61	1.63	14.38	157

<sup>1</sup> for Pb, 7.52 – 38.0  $\mu\text{gg}^{-1}$  for Cu, 14.4 – 105  $\mu\text{gg}^{-1}$  for Zn, 19.6 – 87.6  $\mu\text{gg}^{-1}$  for Cr, 157 – 1890  $\mu\text{gg}^{-1}$  for Mn, 1.37 – 9.83 % for Al and 0.51 – 4.47 % for Fe.

#### 4.1 Metal Distribution in the Pre-monsoon period

The distribution of metals in the surface sediments for the pre-monsoon period are shown in Figure 2. The highest levels of Al, Fe, Cr and Pb seems to be located in the region off Bintulu and extending northwest while Zn levels were generally highest in the region above 4°N. These metals are generally lowest in concentration off the Rajang River Basin. The concentration of Mn generally showed a pattern of increasing concentration with distance towards offshore. Cu concentrations however showed a different distribution pattern, with the highest levels being found directly off the Rajang River Basin and in another region further offshore.

#### 4.2 Metal Distribution in the Post-monsoon period

The results for the post-monsoon period are shown in Figure 3. Concentrations of Al, Fe, Cr, Zn and to a lesser extent Pb were lowest at stations directly off the Rajang River Basin extending northwestward to the deeper stations. Mn showed a clear increase in concentration with depth of water while Zn was highest at the deeper stations and in the region off Bintulu extending northwestward. Copper concentrations (7.52 – 38.03  $\mu\text{gg}^{-1}$ ) in sediments are lower than the established standard value of 55  $\mu\text{gg}^{-1}$  for the Earth crust.

#### 4.3 Normalisation of Metals to Al and Comparison with normal Earth crust values

As some variability was found in the distribution of Zn, Mn, Fe the metal concentrations were normalised against Al (Windom et al., 1984; Windom et al., 1988) in order to elucidate real differences in their distribution patterns for both the pre-monsoon (figure 4) and post-monsoon (figure 5) periods.

Concentrations of Cu normalised to Al gave ratios of between 2 and 8  $\times 10^{-4}$  with most of samples taken within the study area having ratios of 2 – 4. These values are lower than the standard Cu:Al values of 7.12  $\times 10^{-4}$  for shale and 8.14  $\times 10^{-4}$  for continental sands and silts (Hanson et al., 1986). Concentrations of Pb measured in this study are within the average concentration for the Earth's crust (13  $\mu\text{gg}^{-1}$ ). However most of the samples from the study area have a Pb:Al ratio of <2.0 which is lower than the standard value of 2.91  $\times 10^{-4}$  in continental shelf sands and silts but is similar to average shale (1.52  $\times 10^{-4}$ ).

Zinc concentrations were between 14.3 and 114  $\mu\text{gg}^{-1}$  and Zn:Al ratios between 8 – 20  $\times 10^{-4}$ . These ratios are higher than the standard value of 8.6 – 9.15  $\times 10^{-4}$  for the Earth's crust.

Input of sediment and particulates from the very large Rajang River probably influences the sedimentary characteristics of the seabed which may change between the pre-monsoon and the post-monsoon periods. In the pre-monsoon period, the distribution pattern of all metals (Fig. 4) were somewhat similar, showing highest ratios at 3 locations off Bintulu and the Rajang River Basin. However for the post-monsoon period (Fig. 5), the highest ratios for Fe, Cr and Pb to Al were located just west off the Rajang River Basin, while Mn:Al ratios were highest off the Rajang River as well as at the deep water regions. Zn:Al was highest off the Rajang river and in a wide region extending off Bintulu northwestwards towards the deepwater stations. For the post-monsoon period the Fe:Al values for almost all of the study area, is much lower than the pre-monsoon period, with very little variation between stations above 3°N as the ratios.

### Conclusions

The concentrations of Fe and Pb in this region are similar to natural values (Table 4) for conti-

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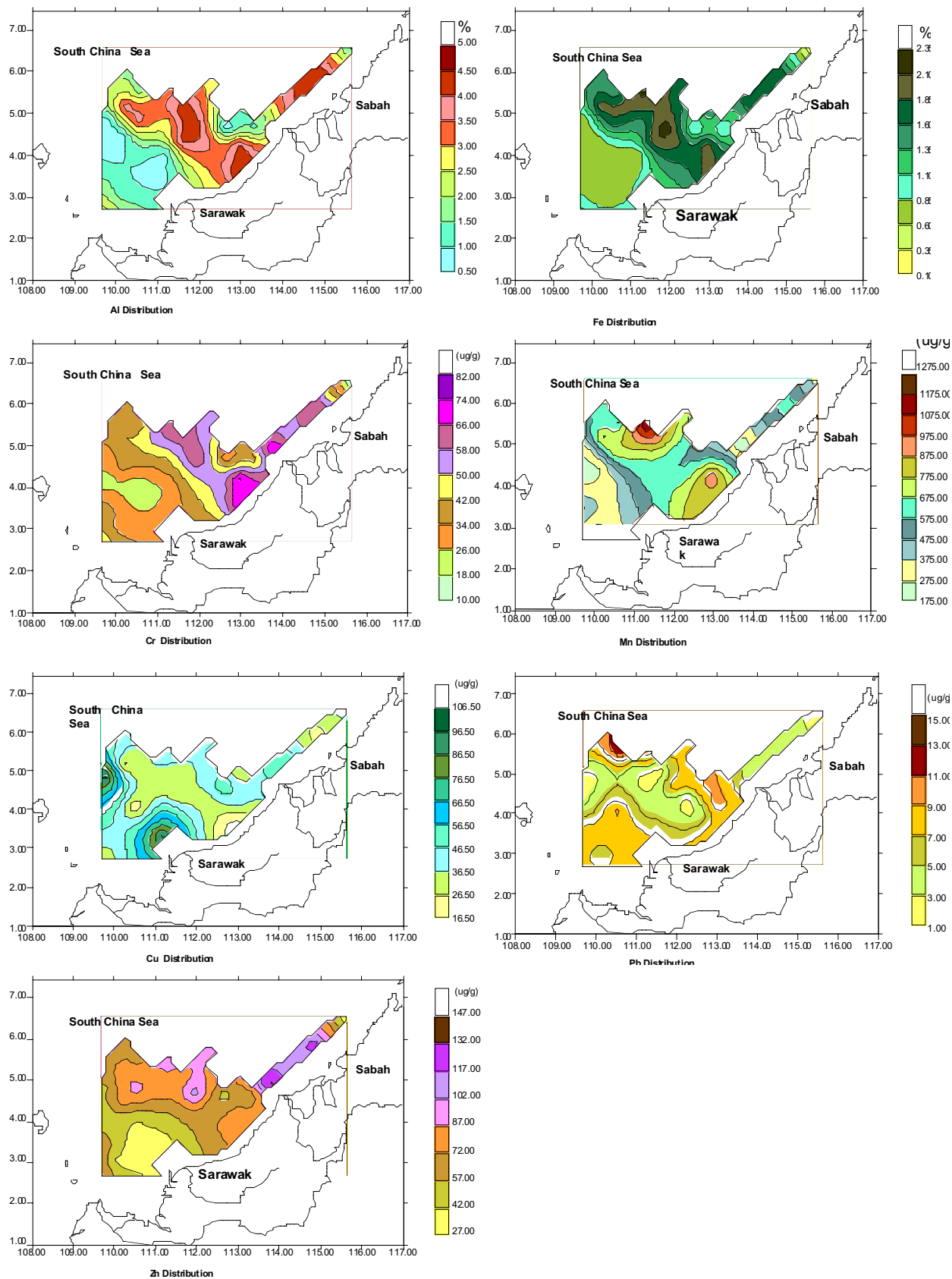


Fig. 2. The pattern of metal distribution in sediment in the pre-monsoon period.

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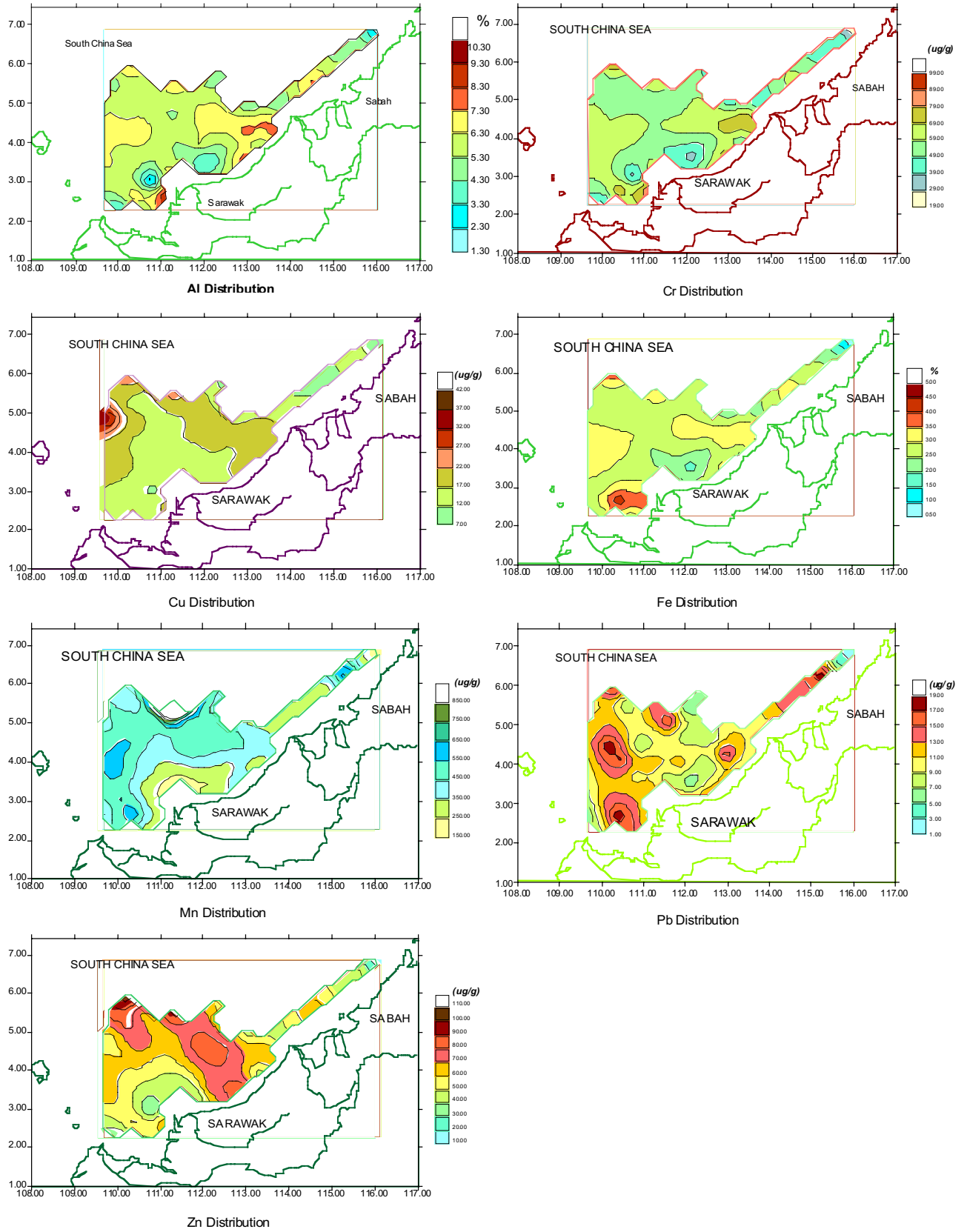


Fig. 3. The distribution pattern of trace metals in sediment in the post-monsoon period

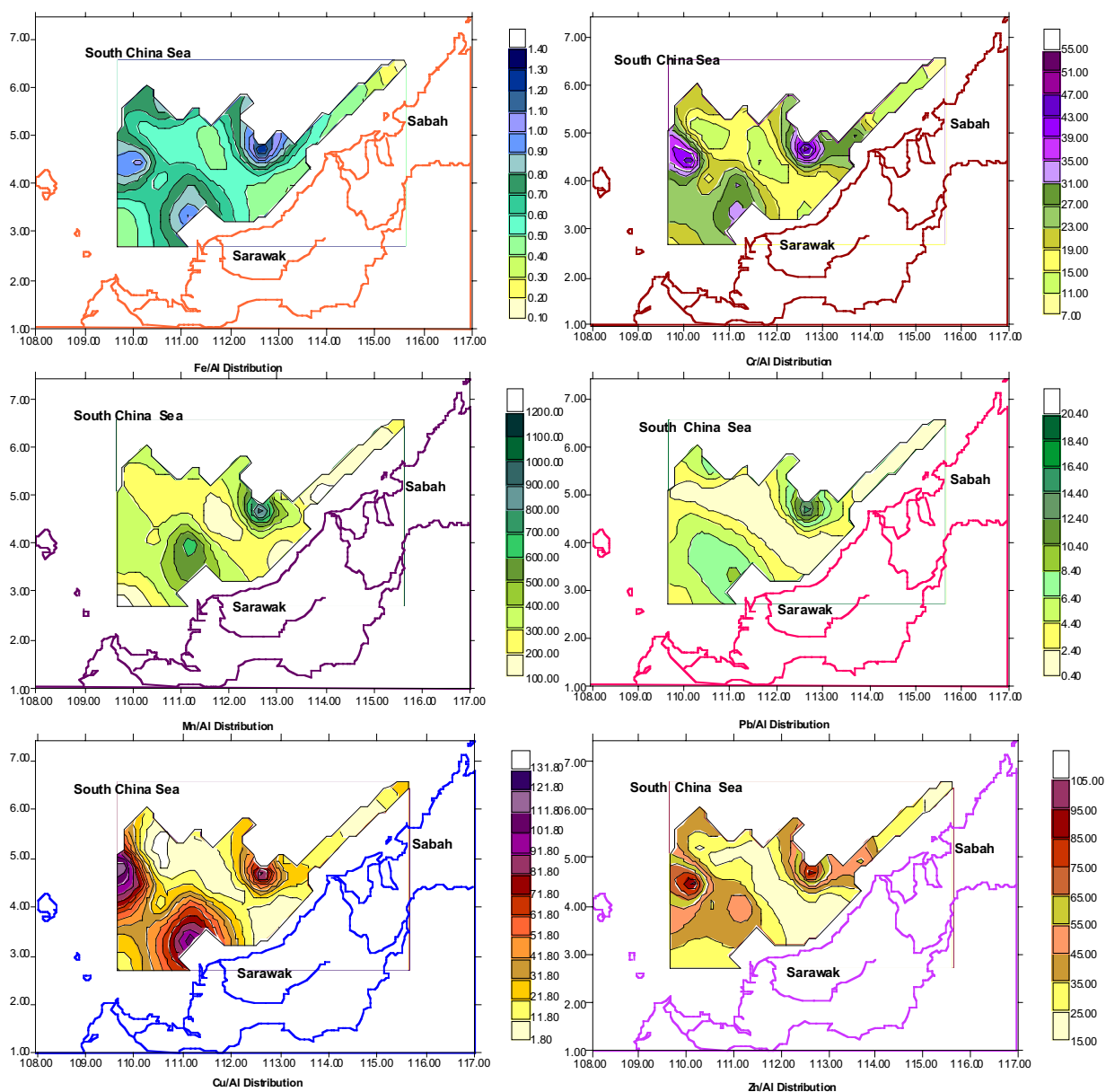


Fig. 4 The pattern of metal:Al ratios in sediment in the pre-monsoon period.



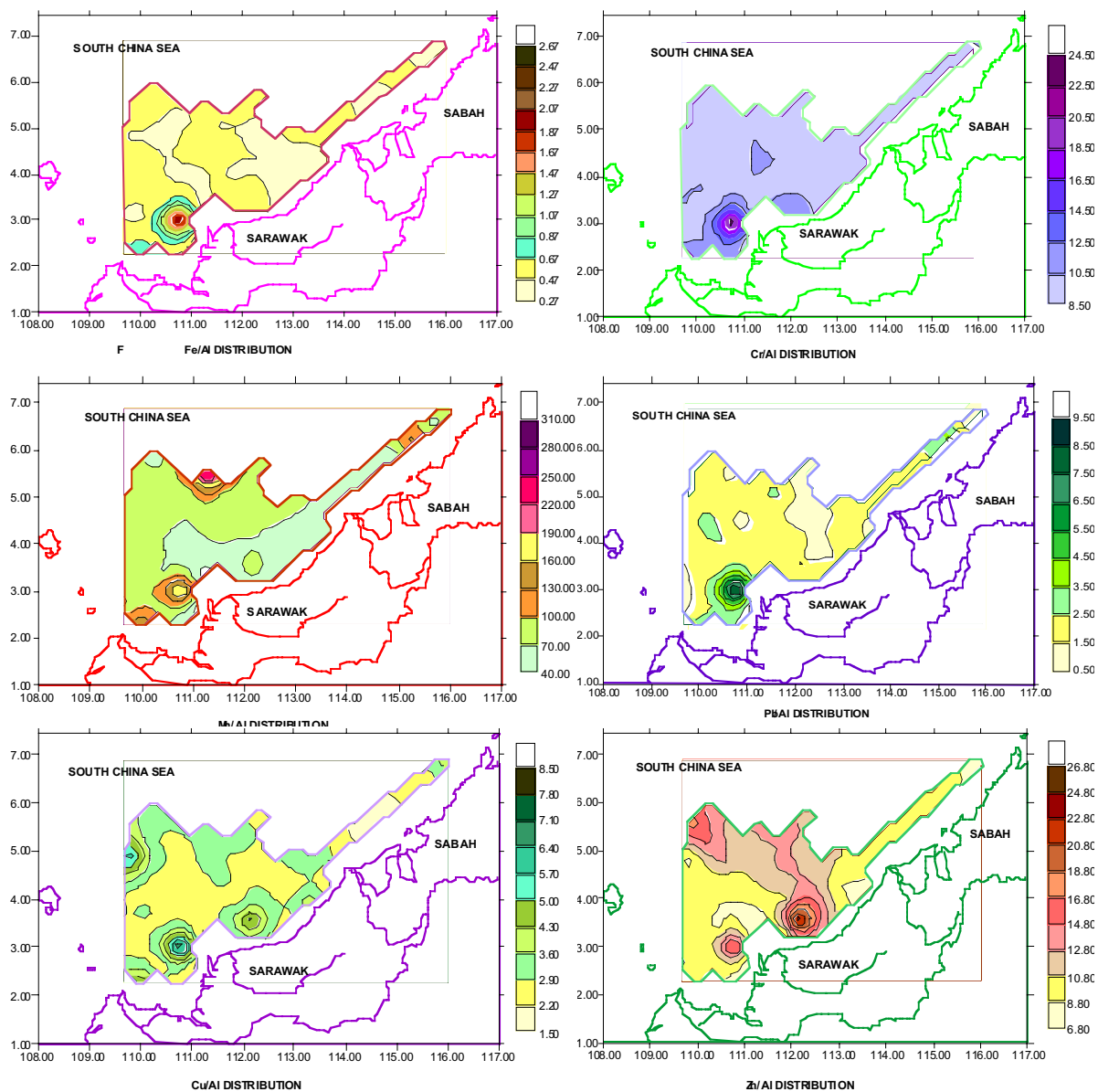


Fig.5. The pattern of metal:Al ratios in sediment in the post-monsoon period

Table 4 Comparisons of normalised data (element:Al ratios) to natural values.

	Element:Al $\times 10^{-4}$	Continental shelf values Element:Al $\times 10^{-4}$ (Hanson et al,1986)	Nearshore sand and mud values Element:Al $\times 10^{-4}$ (Hanson et al,1986)
Cu			
Johor Strait (Khalik Wood et al, 1997)	3.7		9.78
This study (Borneo)		8.14	
Cr		55	17.9
Johor Strait (Khalik Wood et al, 1997)	5.5		
This study (Borneo)		2.91	
Pb			13.6
Johor Strait (Khalik Wood et al, 1997)	5.1		
This study (Borneo)	1.1 - 3	117	
Zn		9.15 mean earth crust value (from Bowen, 1979)	
Johor Strait (Khalik Wood et al, 1997)	16 - 22.6		
This study (Borneo)	7 - 25		
Mn			
This study (Borneo)	30 - 272		
Sulu Sea (Calvert et al., 1993)	100 - 6000		

mental shelf sands and silts and for Earth crust materials, as indicated by similar element:Al ratios (Hanson et al., 1986; Bowen, 1979). The ratios of Pb, Cu, Cr, Ni and to a lesser extent Mn, to Al, however indicate that values in this region are lower than natural values (Table 4) by up to two times.

The ratios of Zn:Al for much of the study area are different from all the other metals, as the values are higher than the value of  $8.6 - 9.15 \times 10^{-4}$  for mean Earth crust materials (Mason and Moore, 1982 and Bowen, 1979). Differences in sediment particle size, organic content and mineralogy may account for this difference.

The Zn:Al ratios found in this study is similar to that found for sediments in the Johor Strait (Wood et al., 1997) and the deep areas of the South China and Sulu Seas of Sabah (Calvert et al., 1993).

## Rereferences

- Bowen, H.J.M. (1979). *Environmental Chemistry of Elements*. Academic Press, London, 333p.
- Calvert, S.E., Pedersen, T.F. and Thunell, R.C. (1993). Geochemistry of the surface sediments of the Sulu and South China Seas. *Marine Geology*, 114, 207-231.
- Hanson, P.J., Wells, J.A. and Newman, M.W. (1986). Preliminary results of the 1984-85 National Benthic Surveillance Project: Southeast Atlantic and Gulf of Mexico coasts. *IEEE Oceans '86 Conference Proceedings*, Washington, D.C., 572-577.
- Shazili, N.A.M., Mohamed, C.A.R. and Yaakob, R. (1989). Heavy metals in sediments of the South China Sea. *Proc. 12<sup>th</sup>. Annual Seminar of the Malaysian Society of Marine Sciences*, 99-106.
- Windom, H.L., Silpipat, S., Chanpongsang, A., Smith, R.G. and Hungspreugs, M. (1984). Trace metal composition of and accumulation rates of sediments in the upper Gulf of Thailand. *Estuarine, Coastal and Shelf Science*, 19, 133-142.
- Windom, H.L., Schropp, S.J., Calder, F.D., Ryan, J.D., Smith, R.G., Burney, L.C., Lewis, F.G. and Rawlinson, C.H. (1989). Natural trace metal concentrations in estuarine and coastal marine sediments of the Southeastern United States. *Environmental Science & Technology*, 23, 314-318.