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Distribution of trace elements and total organic carbon in surface sediments of the Sulu and Sulawesi Seas

(Taburan Unsur Surih dan Organik Karbon di permukaan sedimen di Laut Sulu dan Sulawesi)

[1]Asamuddin, A.H., [2]Mohamed, C.A.R

[1]School of Environmental Sciences and Natural Resources
Faculty of Science and Technology
Universiti Kebangsaan Malaysia,
43600 Bangi, Selangor, Malaysia

[2]Marine Ecosystem Research Centre (EKOMAR)
Faculty of Science and Technology
Universiti Kebangsaan Malaysia,
43600 Bangi, Selangor, Malaysia

ABSTRACT

The concentrations of TOC, Al, Fe, Mn, Pb, Cu, Ni, Co and Cr in 27 surface sediments have been determined from the Sulu and Sulawesi Sesa during the 'Saintifik Perdana 2009' expedition cruise from 18 June to 1 August 2009. Sampling was conducted to elucidate concentrations and spatial distributions throughout the study area. The samples were digested using a total digestion technique and the concentrations were determined using the ICP-MS. The distribution of trace elements fluctuated with stations and water depth, but showed high metal concentrations in some locations such as Marudu Bay, Sandakan and Darvel Bay. The concentrations of trace elements were mostly lower than the earth's mean crust and the world's mean sediments with the exception of a few trace elements in certain stations. The Geoaccumulation Index (I_{geo}) was calculated and the results showed that Ni are in class 1 (unpolluted to moderately polluted) while other trace elements are considered unpolluted. It can therefore be concluded that the Sulu and Sulawesi Seas are unpolluted and pristine.

Keywords: surface sediment, metals, earths crust, I_{geo}

ABSTRAK

Kepekatan TOC, Al, Fe, Mn, Pb, Cu, Ni, Co dan Cr di 27 permukaan sedimen dari Laut Sulu dan Sulawesi telah ditentukan semasa 'Ekspedisi Pelayaran Saintifik Perdana 2009' dari 18 Jun hingga 1 Ogos 2009. Persampelan telah dijalankan bagi menentukan kandungan dan taburan di kawasan kajian. Sampel telah dicerna dengan menggunakan teknik penghadaman penuh dan kandungannya telah ditentukan dengan menggunakan ICP-MS. Taburan unsur surih dan berubah-ubah mengikut stesen dan kedalaman air, tetapi menunjukkan kandungan unsur surih yang agak tinggi di beberapa lokasi seperti Teluk Marudu, Sandakan, dan Teluk Darvel. Kandungan unsur surih kebanyakannya adalah lebih rendah daripada kerak bumi dan sedimen di dunia kecuali bagi unsur tertentu di stesen-stesen tertentu. Geoakumulasi Indeks (Igeo) telah dikira dan keputusan menunjukkan Ni adalah di dalam kelas 1 (dari tidak tercemar ke sederhana tercemar) manakala unsur lain adalah tidak tercemar. Maka, dapat disimpulkan bahawa Laut Sulu dan Sulawesi dikategorikan sebagai kawasan yang tidak tercemar dan masih terpelihara dengan baik.

Katakunci: permukaan sedimen, unsur surih, kerak bumi, I_{geo}

Corresponding email: carmohd@ukm.my

INTRODUCTION

Estuarine systems play an important role in the removal of suspended matter and associated pollutants from the natural water cycle. Their environmental significance has made them the subjects of considerable scientific interest over past decades (BaptistaNeto et al., 2006). Sediment in an estuary is the most important reservoir or sink of metals and other pollutants (Salomon and Forstner, 1984). Trace metals released into the aquatic environment generally bind themselves to particulate matter, which then becomes incorporated into sediments. Physical, chemical and biological characteristics of the sediment and water column and also the chemical partitioning of the metals play an important role in determining the bioavalability of the metals. The enrichment of metals into marine sediments are a combined process of weathering, river runoff, anthropogenic, authigenic, biogenic and cosmogenic sources. Most metals tend to be rich in organic rather than inorganic sediments. Heavy metals in marine sediments have both natural and anthropogenic origins but their distribution and accumulation are influenced by sediment texture, mineralogical composition, reduction status, oxidation state, adsorption and desorption processes as well as physical transport (Buccoleri et al., 2006). Sediment is believed to be a metal repository and only a minor fraction of materials escapes into coastal waters. Bottom sediment is a long term integrator of geochemical processes; therefore, information on heavy metals in the sediments can establish long term behaviors of these metals (Yap et al., 2002).

The Sulu Sea is a large sea in the southwestern area of the Philippines. It is separated from the South China Sea in the northwest by the Palawan Straits and from the Celebes Sea in the southeast by the Sulu Archipelago. The sediments surrounding the Sulu Sea consist of calcareous sand and gravel, derived from coral/algae reefs and benthic macrofauna, and volcanic and other terrigenous detritus depending on local source areas such as islands and rivers (Exon et al., 1981 and Calvert et al., 1993). The Sulawesi Sea (or the Celebes Sea) of the western Pacific Ocean is bordered on the north by the Sulu Archipelago and Sulu Sea and Mindanao Island of the Philippines, on the east by the Sangihe Islands chain, on the south by Sulawesi, and on the west by Kalimantan in Indonesia. Strong ocean currents, deep sea trenches and sea mounts, combined with active volcanic islands in this area result in complex oceanographic features.

No comprehensive studies of heavy metals in sediment from the Sulu Sulawesi Seas have been done before. Therefore it is essential that we investigate the distribution and enrichment of metal concentrations in this area and possibly identify the source of these metals if any.

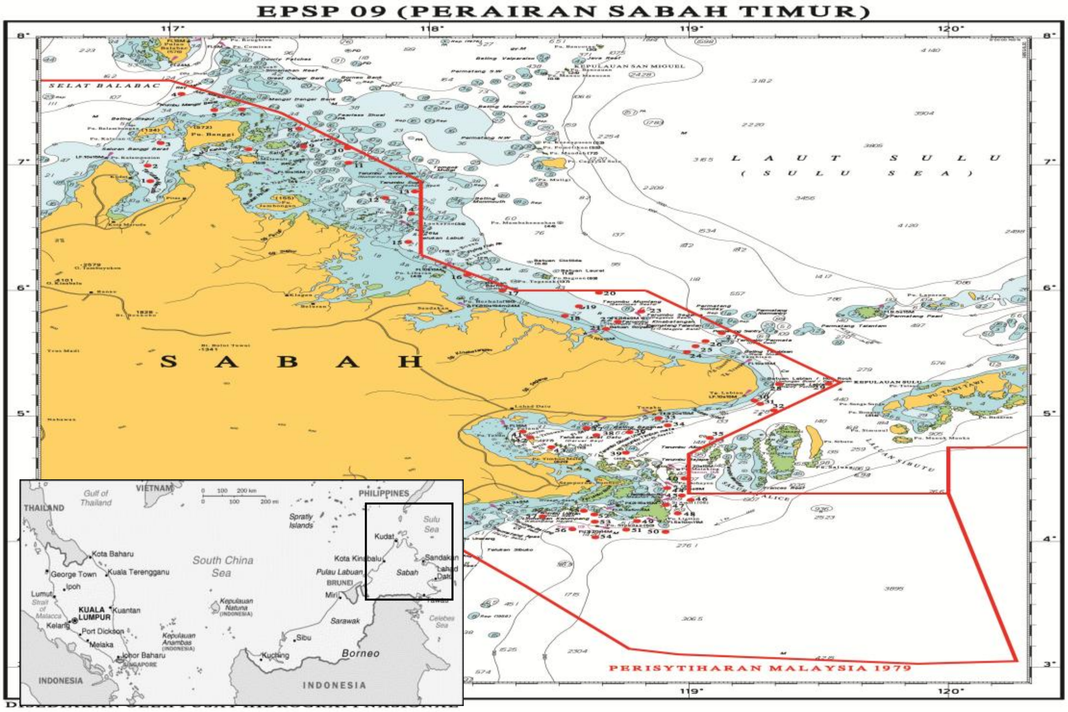
MATERIAL AND METHODS

Sampling

Surface sediments were sampled with a Smith Mc-Intyre grab sampler at 27 stations in the Sulu Sulawesi Seas from July to August 2009 during the 'Ekspedisi Pelayaran Saintifik Perdana 2009' cruise (Fig. 1). Immediately after sampling, samples were frozen and taken to the laboratory for further analysis. In the laboratory, samples were dried at 60ºC in the oven until their weights were constant. Dried bulk sediment was finely powdered using a pastured mortar for further chemical analysis.

Metals analyses

Approximately 100-150 mg of homogenized powdered sediment were weighted into the Teflon beaker together with a mixture of Nitric acid(HNO_3) + Perchloric acid ($HClO_4$)+ Hydroflouric acid (HF) (1:2:1) and applied as the total digestion procedure. About 5 ml of HNO_3 and 10 ml of $HClO_4$ acids were added into the Teflon beaker and heated on the hotplate for 2 hours as a closed digestion technique. Thereafter 5 ml of HF were added to the samples and heated again until dry. About 20 ml of boric acid was immediately spiked into the residue and drying continued. About 50 ml of 2% HNO_3 (Merck) were then added for further analysis using the Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). A NIST standard reference material (SRM 1646a) was used to certify the procedure for this study; most values of the elements of interest were in the 80 -110% range of the certified value.



Courtesy of the National Hydrography Centre

Figure 1. Sampling stations in the Sulu and Sulawesi Seas. Red dots are the sampling locations.

Total Organic Carbon analyses

The total organic carbon (TOC) analysis was conducted using a combustion procedure. About 2 g of each sample was put into a crucible jar and dried at 105°C for 24 hours in the oven. Samples were weighted after being cooled and were then combusted in the furnace at 500°C for 4 hours. The samples were then removed and cooled until it reached a constant weight. The TOC calculation is shown below (Sutherland, 1998):

$$TOC\% = 58\% (.LOI_{OM}) \quad (1)$$

RESULTS AND DISCUSSION

Spatial Distribution of Heavy Metals in Surface Sediments

The concentrations of Al, Fe, Mn, Pb, Zn, Cu, Ni, Co, Cr and total organic carbon (TOC) are presented in Table 1. The range of concentrations for TOC, Al, Fe, Mn, Pb, Zn, Cu, Ni, Co and Cr were 0.96 – 5.27%, 1.12 – 9.44%, 0.63 – 4.62%, 62 – 1597 ug/g, 3.45 – 28.89 ug/g, 34 – 198 ug/g, 6.57 – 101 ug/g, 44 – 125 ug/g, 2.45 – 11.97 ug/g and 7.49 – 125 ug/g respectively. The mean concentrations of TOC, Al, Fe, Mn, Pb, Zn, Cu, Ni, Co and Cr were 2.88%, 4.48%, 2.66%, 305 ug/g, 11 ug/g, 75 ug/g, 23 ug/g, 84 ug/g, 7.35 ug/g, and 50 ug/g respectively. These means were compared to studies done by Bowen (1979) and Calvert et al. (1993) (Table 2). The distribution of these elements varies with water column depth indicating that the concentrations are not dependent on the depth of water in this area.

Table 1: The concentration of trace elements and TOC in surface sediments of the Sulu Sulawesi Seas.

Station	TOC (%)	Al (%)	Fe (%)	Mn (ug/g)	Pb (ug/g)	Cd (ug/g)	Zn (ug/g)	Cu (ug/g)	Ni (ug/g)	Co (ug/g)	Cr (ug/g)
1	3.60	9.23	4.12	537	16	2.38	72	39	80	10	65
2	3.62	7.21	3.26	324	12	3.10	104	35	95	8	69
3	3.01	5.26	2.66	301	12	2.25	84	24	118	8	72
7	2.25	1.75	1.41	162	10	2.65	105	14	65	4	26
9	3.44	3.69	1.73	187	8	0.41	72	20	108	6	36
12	1.43	1.14	0.63	73	6	2.75	114	17	71	2	15
14	1.66	1.34	1.01	65	9	0.56	56	7	77	3	22
15	2.57	3.58	1.76	181	13	1.27	87	16	94	5	42
16	3.52	5.77	2.67	290	5	0.80	80	30	94	12	79
17	3.57	9.44	4.45	420	8	0.45	68	33	71	12	75
18	2.69	3.58	2.67	180	6	1.67	72	30	72	11	76
19	3.43	5.36	1.94	187	14	1.77	92	18	89	8	55
20	2.83	2.30	0.78	64	4	1.16	56	13	68	5	26
22	3.92	7.34	3.58	321	29	8.39	91	27	97	9	62
23	2.41	3.46	1.85	149	9	1.08	59	16	64	5	37
24	2.55	3.57	2.80	185	14	0.44	34	21	77	7	39
25	2.69	4.86	3.94	357	6	0.78	53	20	79	9	49
26	1.30	2.66	1.89	166	21	0.52	37	13	44	5	36
30	1.40	1.54	2.04	435	14	0.29	81	45	66	5	99
31	0.96	1.57	4.62	1597	5	0.44	198	101	47	8	247
32	4.69	8.68	4.35	440	18	0.12	105	39	97	11	73
36	2.27	3.27	3.08	206	5	0.06	53	17	84	7	38
37	3.03	5.44	3.68	252	6	0.65	56	23	101	8	47
38	5.27	7.68	3.81	319	18	0.69	45	27	90	10	61
39	2.30	2.88	2.37	240	15	1.86	59	19	92	6	30
43	5.18	7.35	3.80	526	3	0.48	37	29	100	10	67
52	2.16	1.12	0.78	62	15	0.99	40	11	125	4	7

The distribution of the concentration of all the studied elements was not uniform across the locations. However similar element profiles can be seen in some locations such as Marudu Bay, Sandakan and Darvel Bay. The concentrations of TOC, Al, Fe, Mn, Cu, Ni, Co, Cr and Pb in Marudu Bay (St 1 – St 3) showed identical profiles in that the element concentrations were enriched in this area. This may be due to the accumulation of metals and TOC in a bay area which receives input from river discharge and islands surrounding the area. In Sandakan (St 15 and St 23), TOC, Al, Fe, Mn, Zn, Cu, Ni, Cr and Co showed high concentrations. This could possibly be due to the high riverine input from the adjacent Kinabatangan and Segama Rivers as they have large mudflat areas. Upstream activities in the Kinabatangan River such as logging and land clearance (mostly for oil palm plantations) lead to the input of pesticides, fertilizers and sediment from the plantations in addition to sewage from riverside villages. Darvel Bay or Lahad Datu (St 36 – St 43) is a large bay on the east coast of Sabah. It was previously presumed that this area has high particle flux and affected by the river run off and strong currents (Ejria et al. (2007). This could be the reason why concentrations of TOC, Al, Fe, Mn, Pb, Cu, Ni, Cr and Co show a similar profile.

Table 2: Comparison of mean trace metal concentrations obtained in Sulu Sulawesi Seas' sediment.

Matrices (local)	Al (%)	Fe (%)	Mn (ug/g)	Pb (ug/g)	Zn (ug/g)	Cu (ug/g)	Ni (ug/g)	Co (ug/g)	Cr (ug/g)
This study	4.5	2.66	305	11	75	23	84	7	50
Earth's crust [a]	8.2	4.17	950	14	75	50	80	20	100
World's sediments [a]	7.2	4.1	770	19	95	33	52	14	72
South Sulu Sea sediment [b]	3.7	1.83	1730	14	42	41	67	21	59

[a]Bowen, 1979
[b]Calvert et al., 1993

Metals originate from authigenic, biogenic or lithogenic sources. The Sulu Sulawesi Seas can be considered pristine as there are no large industries or development in the area. It can therefore be assumed that metal concentrations are naturally enriched here. Zn, Fe and Mn oxyhydroxides play the most important role in metal fractionation and controlled Zn mobility through related sorption processes (Wu et al, 2010). This phenomenon can probably be ascribed to a high stability constant for this Zn – (Fe-Mn) binding form (Ramos et al. 1999; Kelderman and Osman 2007). Co is usually lithogenic (Hansen et al., 1992); however anthropogenic inputs of Co could possibly be derived from industrial and agricultural acitivities. Cr may be incorporated into alumina silicate minerals (Yuan et al., 2004; Wu et al., 2010). Cu was chemisorbed on or incorporated in clay minerals (Pickering, 1986). The preferential Cu binding onto organics could be ascribed to the well-known ease of complexation of Cu with organic materials such as particulate humic and amino acid forms (Perin et al., 1997. Ni is probably derived from natural deposits in laterite soils with high principal nickeliferous limonite ore material (Aleva 1994; Schellmann 1983). Pb incorporated in clay minerals (Pickering, 1986) and associated with the Fe-Mn oxide and form stable complexes with Fe and Mn oxides (Ramos et al., 1994). However a more detailed analysis of trace metals should be done in order to better determine the origin of these metals.

The correlation between TOC, metal concentrations and depth in the surface sediments of the Sulu Sulawesi Seas are shown in Table 3. There is no correlation between depth, metal concentrations and TOC which indicates that the concentration of metals are not dependent on the depth of the water column. However, TOC, Al, Fe, Mn, Cu, Ni, Co, Cr show a good correlation between each other, indicating that there is a strong relationship between the studied elements. This strong relationship shows that these elements come from same source. Since the metal concentrations are lower than the world's mean sediment and the earth's mean crust, it can be said that the metals are from the authigenic and biogenic sources. Furthermore, Pb did not correlate with other metals and TOC which indicates that Pb not only came from the same source as the other elements but also probably come from terrigenous input via wind and atmosphere.

Table 3: Correlations between TOC, metal concentrations and depth in surface sediments of the Sulu Sulawesi Seas.

Element	Depth	TOC	Al	Fe	Mn	Pb	Cu	Ni	Co	Cr
Depth	1									
TOC	-0.206	1								
Al	-0.335	0.934**	1							
Fe	0.151	0.792**	0.850**	1						
Mn	0.173	0.839**	0.864**	0.881**	1					
Pb	0.012	0.478*	0.214	0.194	0.077	1				
Cu	-0.388	0.826**	0.876**	0.776**	0.809**	0.290	1			
Ni	-0.330	0.752**	0.678**	0.540*	0.675**	0.250	0.569*	1		
Co	0.027	0.872**	0.943**	0.965**	0.951**	0.447*	0.900**	0.621**	1	
Cr	-0.349	0.739**	0.840**	0.644**	0.677**	0.383	.845**	0.437	0.911**	1

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

Igeo was calculated for each metal using the following equation:

$I_{geo} = \log_2 Cn / 1.5 \times Bn$ (2)

Table 4

Mu¨ ller's classification for the geoaccumulation index (Müller, 1981)

Igeo value	Class	Quality of sediment
≤0	0	Unpolluted
0–1	1	From unpolluted to moderately polluted
1–2	2	Moderately polluted
2–3	3	From moderately to strongly polluted
3–4	4	Strongly polluted
4–5	5	From strongly to extremely polluted
≥5	6	Extremely polluted

Where I_{geo} = index of geoaccumulation, Cn = measured concentration of the element, Bn = geochemical background value, 1.5 is used because of possible variations in background values given metals in the environment (Muller,1979), as well as very small anthropogenic influences (Buccoleri et al., 2006). Müller's classification for the geoaccumulation index (Müller, 1981) is shown in Table 4. Our Bn value was derived from the world's mean sediment (Bowen 1979). Calculated I_{geo} is shown in Figure 3.

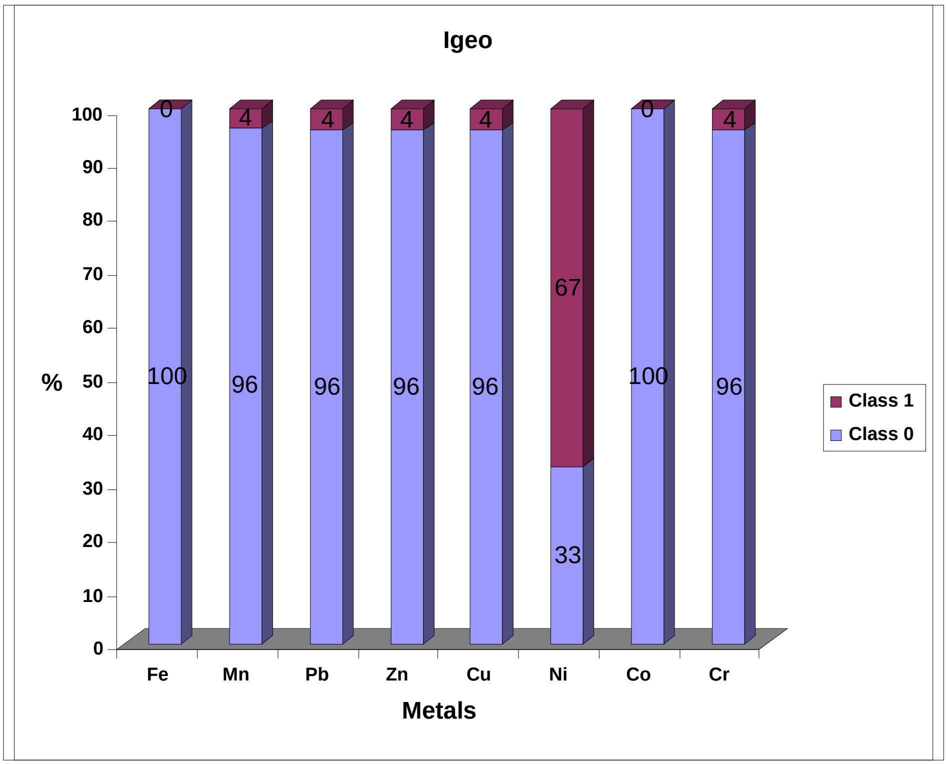


Figure 3. The classification of I_{geo} in studied sediments.

In Figure 3, 100% of Fe and Co fell into class 0 while 96% of Mn, Pb, Zn, Cu, and Cr fell into class 0 while the other 4% were in class 1. On the other hand, only 33% of the Ni concentrations are in class 0 while 67% are in class 1 (Unpolluted to moderately polluted). With the I_{geo} values less than 1 (I_{geo} <1), it can be said that this area can be considered unpolluted by metals with little natural enrichment.

CONCLUSION

The distribution of the concentration of all studied elements fluctuated with the stations and water depth. However similar profiles can be seen in some locations such as in Marudu Bay, Sandakan and Darvel Bay. TOC, Al, Fe, Mn, Cu, Ni, Co, Cr showed strong relationships with each other, not including Pb. Calculated I_{geo} showed that most metals fell into class 0 (unpolluted) except for Ni which showed some enrichment in certain areas (unpolluted to moderately polluted).

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