Radioactivity Level of Radium Isotopes in the Surface Sediment of Southern South China Sea and Malacca

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ABSTRACT

Surface sediment samples were collected from 31 stations at the southern South China Sea (SSCS) and The Straits of Malacca on August 2003 and February 2004, respectively. Activity concentrations of ^{228}Ra and ^{226}Ra in the surface sediment varied with location. The range of activities of ^{228}Ra and ^{226}Ra at the east coast of Peninsular Malaysia were from 64. 96 to 144.58 $Bqkg^{-1}$ dry and 22.67 to 123.73 $Bqkg^{-1}$ dry, respectively. In the west coast, activities ranged from 35.12 to 64.97 $Bqkg^{-1}$ for ^{228}Ra and 22.96 to 35.62 $Bqkg^{-1}$ for ^{226}Ra respectively. The activity of those radionuclides in the surface sediment varied depending on the sampling locations and the differences were significant with $p <$ 0.001 for ^{228}Ra and ^{226}Ra at both study locations of SSCS and The Straits of Malacca. The distribution activity ratios of $^{228}Ra/^{226}Ra$ were uniform at all sampling stations in the SSCS and The Straits of Malacca with an average of 1.8 slightly corresponding to their parents (^{232}Th and ^{238}U).

Keyword: ^{228}Ra; ^{226}Ra; activity ratio; distribution; surface sediment

Introduction

The two naturally occurring radium isotopes; ^{226}Ra ($t_{1/2}$ = 1602 years) and ^{228}Ra ($t_{1/2}$ = 5.75 years) are radioactive members of the ^{238}U and ^{232}Th decay series, respectively (Cochran, 1979). Both radionuclides are important tracers in oceanographic matters on time-scales from months to years. Additionally, ^{226}Ra, with a deep-sea source has been suggested to act as a tracer for ocean – mixing processes.

High concentrations of radium have been found at the water-sediment interface, where the porewater acts as a medium to transfer radium into the sediment (Cochran, 1979). The same condition is also found in sediment at the coastal area (Key et al., 1985). The distribution of radium is related to the physical, chemical and geochemical properties of sediments at sampling study sites (Khatir et al., 1998). Furthermore, ^{228}Ra and ^{226}Ra are not strongly particle reactive and not scavenged from the sea water, indicating their supply in the surface sediment does not dependent on water column depth but releases from bottom or coastal sediments (Schmidt et al., 1998). Additionally, both radionuclides were released into water column from sediment through decay of thorium isotopes, but due to differences in parent nuclide distribution and half-life, ^{226}Ra was liberated from deep-sea sediments, while ^{228}Ra accumulated to higher activities in shallow water regions. Meanwhile, the ^{228}Ra/^{226}Ra ratio may vary greatly because of a large difference in their half-lives. Furthermore, Moore (1997) suggested that this was due to high regeneration of ^{228}Ra by thorium at bottom sediments.

Studies on ^{228}Ra and ^{226}Ra as geochemical tracers in marine environments are poorly known in Malaysia. Thus, the aim of this study was to provide an improved understanding of the sources, distribution and behaviour of the naturally occurring radionuclides ^{226}Ra and ^{228}Ra and the activity ratio of ^{228}Ra/^{226}Ra in the surface sediment at the southern South China Sea and The Straits of Malacca.

Materials and Methods

Sampling

Surface sediments were collected using a ponar grab sampler at the southern South China Sea (SSCS) and The Straits of Malacca on August 2003 and February 2004, respectively (Table 1, Figure 1). The sediments were kept in sample containers for further analyses. All the sediment samples were dried in an oven at 60 ^{o}C until a constant weight was achieved, and ground properly to homogeneity.

Analytical technique

About 300 to 350 g of homogenous dried sediment were transferred into a 350 ml polyethylene container, sealed and kept for four weeks to reach secular equilibrium between radium and their progenies. The specific activities of gamma emitting radionuclides (^{228}Ra and ^{226}Ra) were measured using the calibrated E & G ORTEC, high-purity, vertical germanium detectors (HpGe) of gamma spectrometry for 15 hours. The HpGe detector energy and efficiency were calibrated using several sources of nuclides, such as ^{60}Co and ^{137}Cs; and a mixed standard of gamma radionuclides, respectively. Meanwhile, QA/QC was confirmed using IAEA standard reference material (Soil 6) on the same geometry with measured samples. A relative efficiency for gamma counting about 25% and energy ranges were used at 1.95 keV to 1332 keV (El Memoney & Khater, 2004; Brunskill et al., 2004; Dukat & Kuehl, 1995). Natural background was used as a blank. Measurements were taken over several days and sediment activities were corrected for self-adsorption.

TABLE 1: Locations, Coordinates and Water Depths of the Surface Sediment Collection in this Study

Region	Location	Station	Latitude, °N	Longitude, °E	Water Depth (m)
Southern SouthChina Sea	Kota Bharu	EC 01	06° 38.67'	103° 36.18'	45.8
	Kuala Terengganu	EC 02	05° 36.14'	103° 24.25'	51.6
	Kuantan	EC 03	03° 58.30'	104° 07.05'	50.1
	Pulau Tioman	EC 04	02° 52.82'	104° 14.05'	44.1
	Desaru	EC 05	02° 08.44'	104° 30.44'	42.0
	Muara Sungai Kelantan	EC 06	06° 16.58'	102° 08.71'	9.2
	Muara Sungai Besut	EC 07	05° 50.61'	102° 36.40'	8.3
	Kuala Terengganu	EC 08	05° 21.65'	103° 09.30'	8.7
	Muara Sungai Dungun	EC 09	04° 47.23'	103° 26.74'	17.3
	Muara Sungai Kemaman	EC 10	04° 13.45'	103° 27.60'	9.5
	Muara Sungai Kuantan	EC 11	03° 47.63'	103° 24.13'	11.9
	Muara Sungai Pahang	EC 12	05° 28.95'	103° 30.39'	11.4
	Muara Sungai Rompin	EC 13	02° 48.55'	103° 32.25'	8.2
	Muara Sungai Sedili Besar	EC 14	01° 52.24'	104° 13.07'	15.1
	Tanjung Datok	EC 15	01° 23.87'	104° 18.36'	13.5
The Straits of Malacca	Kuala Kedah	WC 01	06° 06.60'	099° 58.30'	83.0
	Pulau Pinang	WC 02	05° 56.70'	099° 29.80'	50.0
	Kuala Terung	WC 03	05° 28.35'	099° 19.00'	77.5
	Sabak Bernam	WC 04	03° 21.45'	100° 22.94'	69.9
	Pulau Langkawi	WC 07	06° 09.90'	099° 51.40’	9.8
	Kuala Kedah	WC 08	06° 01.79'	100° 11.52'	7.4
	Sungai Merbok	WC 09	05° 46.88'	100° 10.57'	19.0
	Kuala Terung	WC 10	04° 40.52'	100° 22.78'	12.9
	Kuala Perak	WC 11	03° 55.57'	100° 39.03'	15.2
	Sungai Bernam	WC 12	03° 42.38'	100° 47.59'	20.8
	Kuala Selangor	WC 13	03° 19.43'	101° 08.97'	13.2
	Tanjung Ru	WC 14	02° 40.81'	101° 26.87'	34.2
	Sungai Linggi	WC 15	02° 18.10'	102° 03.00'	7.9
	Sungai Muar	WC 16	01° 58.54'	102° 30.54'	6.4
	Sungai Batu Pahat	WC 17	01° 48.84'	102° 44.85'	14.6
	Sungai Benut	WC 18	01° 36.41'	103° 08.40'	5.2

^{226}Ra activities were determined by measurement of granddaughters photopeak ^{214}Pb at 295.2 and 351.9 keV and ^{214}Bi at 609 keV (Brunskill et al., 2004), while ^{228}Ra activities were determined by its daughter ^{228}Ac at 911 keV (Dukat & Kuehl, 1995).

Results and Discussion

Distribution of ^{228}Ra and ^{226}Ra in the Surface Sediment

The activity concentrations of ^{228}Ra and ^{226}Ra (Bqkg^{-1} dry) in the surface sediments of the southern South China Sea (SSCS) and the Straits of Malacca were from 35 to 145

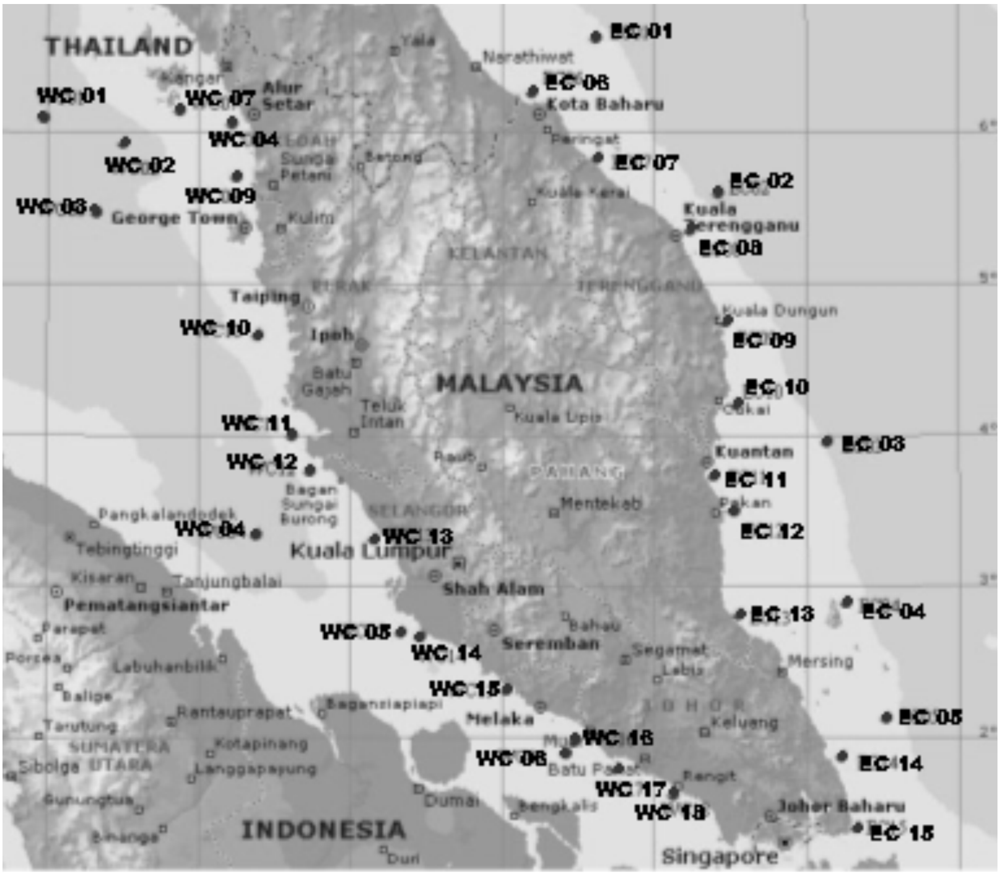

FIGURE 1: Location of Sampling Stations

Bqkg^{-1} dry and 22 to 124 Bqkg^{-1} dry, respectively (Table 2). It was found that the activity concentrations of those radionuclides in the surface sediment varied significantly depending on the sampling location between SSSC and the Straits of Malacca for activities of ^{228}Ra ($F = 74.044$, $df = 1$, $\alpha = 0.05$, $p = 0.000$) and ^{226}Ra ($F = 35.390$, $df = 1$, $\alpha = 0.05$, $p = 0.000$).

In general, the activities of both radionuclides in the SSCS were higher than those in the Straits of Malacca because the former is a semi-closed system, which receives a large input from the neighbouring countries and from the western Pacific as external sources and input from biological remobilisation as internal sources. The Straits of Malacca on the other hand is an enclosed system and received less input from the land (Mohamed et al., 2006).

In the surface sediments at stations located in the SSCS such as EC 03, EC 05, EC 06 EC 08 EC 11 and EC 13 (Fig. 2), high activity concentrations of radium found could be due to the enrichment of radium because it was not a strongly particle reactive, and more than 38% of radium was lost from suspended particles and deposited into the sediment (Dukat & Kuehl, 1995). In this case, high activity concentrations of ^{226}Ra at stations EC

TABLE 2: Activity Concentration of ^{226}Ra and ^{228}Ra in the Surface Sediment at Southern South China Sea and the Straits of Malacca

Location	Station	Activity Concentration (Bq/kg dry wt)		^{228}Ra/^{226}Ra Activity Ratio
		^{228}Ra	^{226}Ra	
Southern South China Sea	EC 01	64.96 ± 4.87	22.67 ± 1.59	2.87 ± 1.98
	EC 02	98.82 ± 7.41	41.76 ± 2.92	2.37 ± 2.01
	EC 03	132.07 ± 10.30	62.19 ± 4.18	2.12 ± 1.84
	EC 04	76.81 ± 5.76	30.33 ± 2.12	2.53 ± 1.93
	EC 05	130.86 ± 9.80	97.98 ± 6.86	1.34 ± 1.17
	EC 06	131.15 ± 21.14	57.13 ± 9.20	2.30 ± 1.77
	EC 07	65.39 ± 10.54	50.00 ± 8.06	1.31 ± 1.07
	EC 08	108.83 ± 17.54	81.52 ± 13.13	1.34 ± 1.09
	EC 09	98.87 ± 15.94	82.74 ± 13.33	1.20 ± 1.02
	EC 10	99.98 ± 16.12	65.46 ± 10.55	1.53 ± 1.24
	EC 11	144.58 ± 23.31	123.73± 19.94	1.17 ± 0.95
	EC 12	98.35 ± 15.85	69.24 ± 11.16	1.69 ± 1.27
	EC 13	110.21 ± 17.77	57.29 ± 9.23	1.92 ± 1.56
	EC 14	99.52 ± 16.04	79.44 ± 12.80	1.25 ± 1.01
	EC 15	86.73 ± 13.98	64.20 ± 10.34	1.35 ± 1.09
The Straits of Malacca	WC 01	64.97 ± 4.94	26.40 ± 1.36	2.46 ± 1.99
	WC 02	52.17 ± 6.62	24.67 ± 1.80	2.11 ± 1.71
	WC 03	52.84 ± 3.46	28.02 ± 2.57	1.89 ± 1.53
	WC 04	41.19 ± 4.88	24.85 ± 1.69	1.66 ± 1.34
	WC 07	43.01 ± 6.19	28.62 ± 2.05	1.50 ± 1.22
	WC 08	44.47 ± 3.12	29.01 ± 1.08	1.53 ± 1.24
	WC 09	35.12 ± 5.62	22.96 ± 1.70	1.53 ± 1.24
	WC 10	47.71 ± 5.96	24.79 ± 2.73	1.93 ± 1.56
	WC 11	49.98 ± 6.25	28.96 ± 3.19	1.73 ± 1.40
	WC 12	52.85 ± 5.72	35.62 ± 2.22	1.48 ± 1.20
	WC 13	59.52 ± 7.44	27.19 ± 2.99	2.19 ± 1.75
	WC 14	44.01 ± 5.87	27.06 ± 2.32	1.63 ± 1.32
	WC 15	35.74 ± 4.47	23.04 ± 2.53	1.55 ± 1.26
	WC 16	46.96 ± 5.04	27.99 ± 2.07	1.68 ± 1.36
	WC 17	58.24 ± 7.28	26.72 ± 2.94	2.18 ± 1.77
	WC 18	41.72 ± 3.85	30.36 ± 2.09	1.37 ± 1.11

05, EC 08, EC 09 and EC 11 were related to the enrichment of ^{238}U in the sediment, which was supplied from anthropogenic sources (Love et al., 2003). Low activity concentrations of ^{228}Ra (< 50 Bqkg^{-1}) for stations located in the Straits of Malacca however were due to the small input from the land near the sampling stations (Nozaki & Yamamoto, 2001). Furthermore, the sampling stations far from the mainland of Peninsular Malaysia usually contain less concentration of ^{228}Ra due to the influence of diffusion processes (Hancock & Murray, 1996).

The statistical correlation between radium activity and water depth at SSCS found that weakly positive correlated with r = 0.490 for ^{228}Ra was probably due to high dissolution

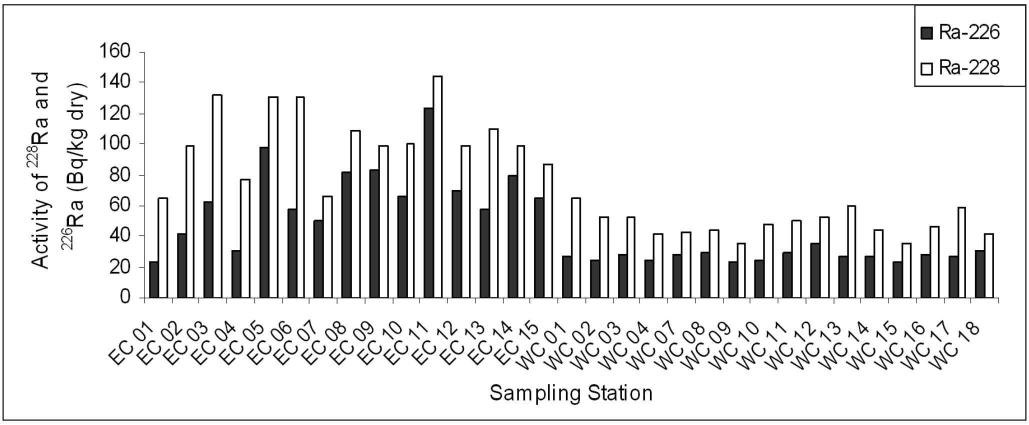

FIGURE 2: Distribution of ^{228}Ra and ^{226}Ra in the southern South China Sea and the Straits of Malacca

or dilution which occurred in seawater because SSCS is an open system. Furthermore, ^{228}Ra was supplied to surface sediment mainly released from bottom or coastal sediments (Schmidt et al., 1998). However, a positive correlation with r = 0.649 for ^{226}Ra was due to low dissolution or dilution, faster mobility and deposit from the water column onto sediment. Meanwhile, at the Straits of Malacca, strong positive correlation with r = 0.725 was shown by ^{228}Ra and negative correlation with r = 0.612 was shown by ^{226}Ra (Figure 3 a-b), due to low dissolution or dilution and active regeneration of ^{228}Ra by its parent, ^{232}Th and more dissolution or dilution of ^{226}Ra in the water column.

The strong positive correlation between ^{228}Ra and ^{226}Ra in the SSCS and the Straits of Malacca with the r values of 0.710 and 0.991 (Fig. 4 a & b), could be due to the same environmental origin, sources and chemical behaviour (Moore, 1997).

$^{228}Ra/^{226}Ra$ Ratio in the Surface Sediment

The activity ratios of ^{228}Ra and ^{226}Ra in the surface sediments of the SSCS and the Straits of Malacca ranged from 1.17 to 2.87 (average of 1.8) (Table 2 & Fig. 5) with a uniform and comparable ratio at both sampling locations ($F = 0.065$, $df = 1$, $\alpha = 0.05$, $p = 0.800$).

In most of the sampling stations high activity ratio of $^{228}Ra/^{226}Ra$, indicating the enrichment of ^{228}Ra was likely due to relatively efficient removal of ^{228}Ra from the water column onto sediment (Fig. 5 & Table 2). The reason was strictly supported by Hancock and Murray (1996), who suggested that the enrichment of this isotope in estuarine and near-shore environments is often much greater than the long-lived ^{226}Ra (half-life 1602 years).

The high activity ratio, which was more than 1.0, indicated that ^{228}Ra half-life (5.75 years) was actively and rapidly regenerated by their parent, ^{232}Th compared to the ^{226}Ra from ^{230}Th. Moore (1997) suggested that this was due to the high regeneration of ^{228}Ra by thorium at the bottom sediments. It might also be due to the addition of more

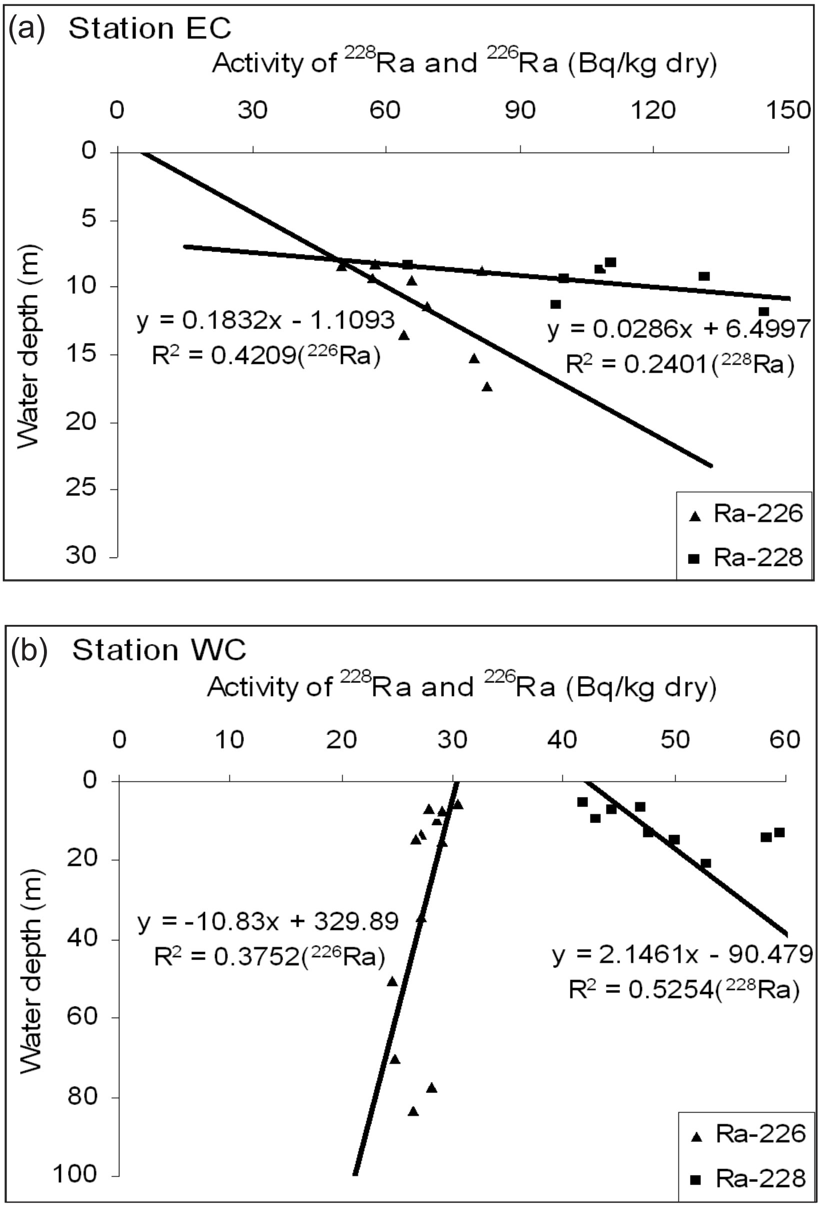

FIGURE 3: Relationship Between Water Depth and Activity Concentration of ^{228}Ra and ^{226}Ra in the Surface Sediment at Southern South China Sea (a) and the Straits of Malacca (b)

biogenic particles containing more ^{232}Th to the sediments nearer to the coastal area (Mohamed et al., 1996).

High value of ^{228}Ra activities could also be due to the presence of black sand at sampling stations as the sand is partly the mineral monazite which usually contain a significant high amount of ^{232}Th (^{228}Ra) (Cowart & Burnett, 1994). Furthermore, continued

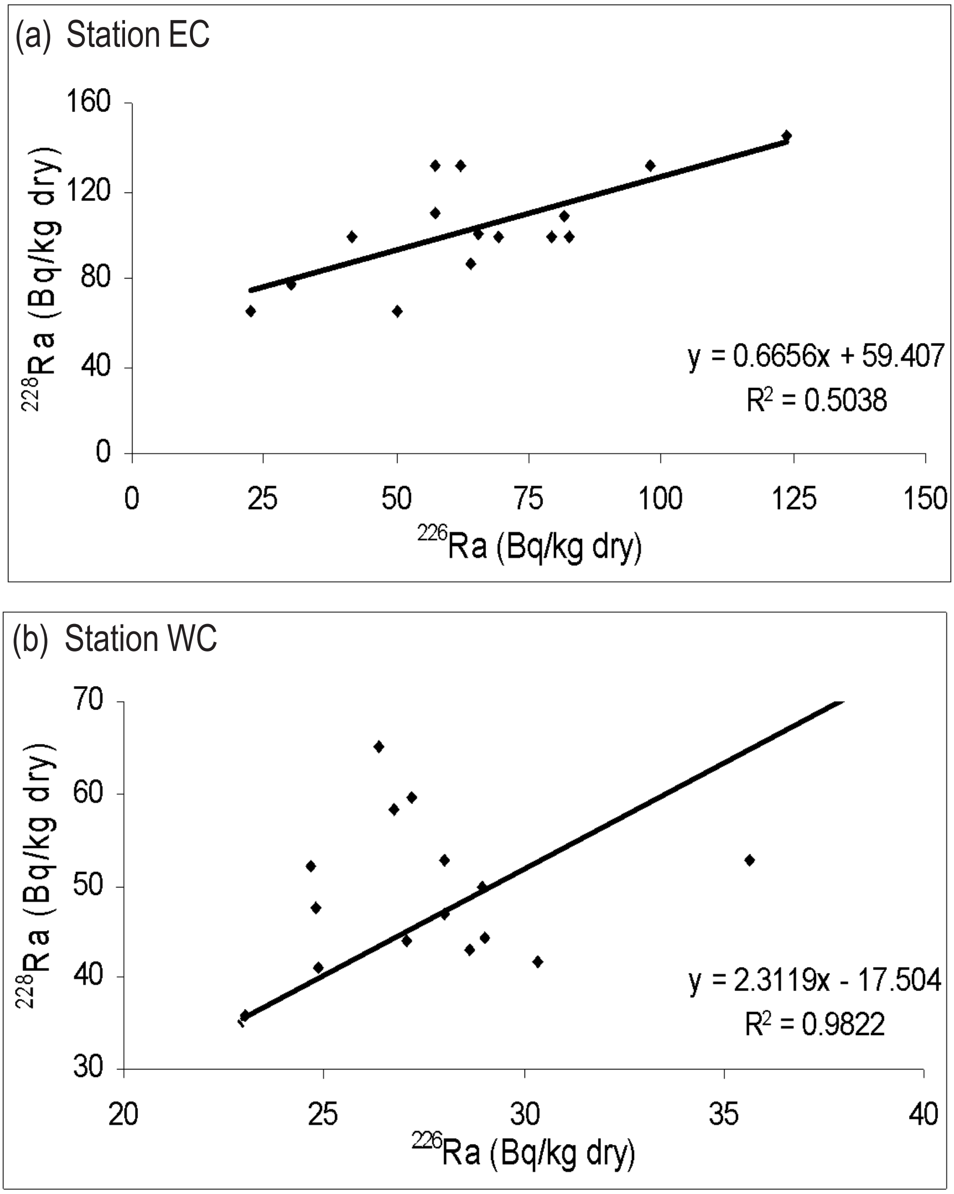

FIGURE 4: ^{228}Ra Concentration as a Function of ^{226}Ra in the Surface Sediment at Southern South China Sea (a) and the Straits of Malacca (b)

production and release of ^{228}Ra from the freshly deposited sediments are responsible for the enhancement of ^{228}Ra at the studied stations (IAEA, 1990). They also suggested that the original or bottom sediments contribute a little addition of ^{226}Ra, but may desorb ^{228}Ra produced by the ^{232}Th decay. The differences in the geochemical behaviour of uranium and thorium could explain the wide variation in their daughter's activity ratios of

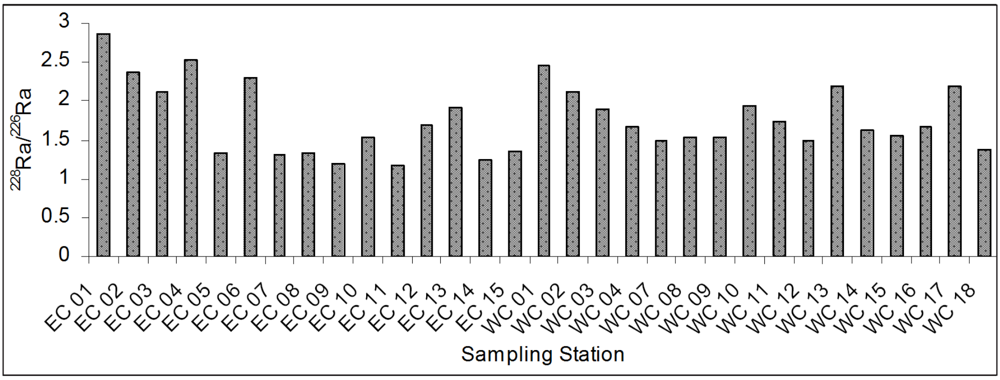

FIGURE 5: Distribution of $^{228}Ra/^{226}Ra$ Activity Ratio Obtained in this Study

$^{228}Ra/^{226}Ra$ in shore sediment samples (El Memoney & Khater, 2004). Water depth was correlated positively with $^{228}Ra/^{226}Ra$ (r = 0.621) at the sampling stations of SSCS while the Straits of Malacca was very strong correlation (r = 0.937) (Figure 6). The former correlation suggested that the flux of ^{228}Ra was not totally supplied by the water column but came from the coastal sediments and thereafter increased the activity ratio of sediment-water interface (Schmidt et al., 1998).

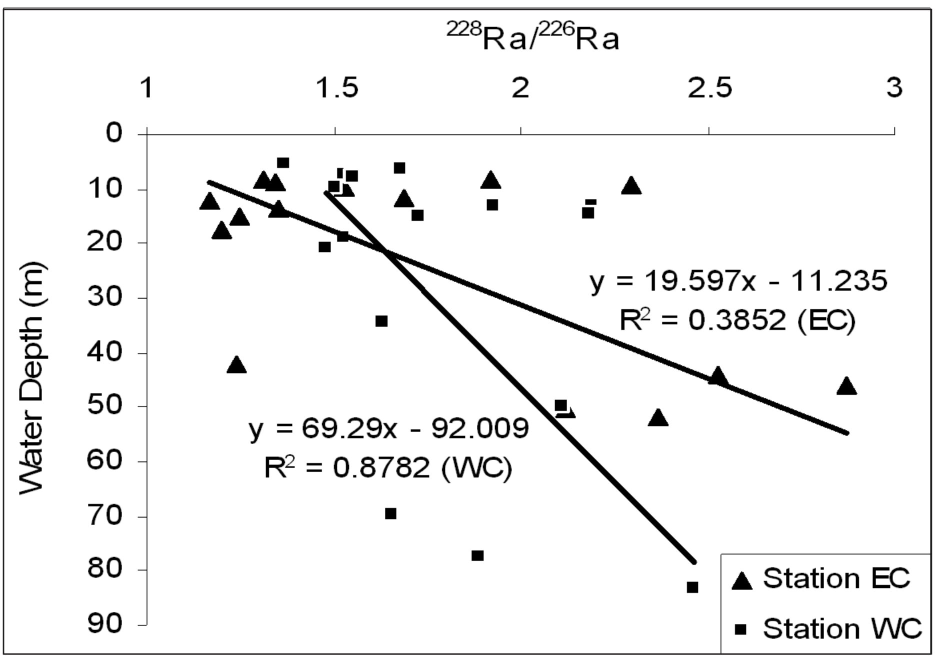

FIGURE 6: Water Depth as a Function of $^{228}Ra/^{226}Ra$ in the Surface Sediment at Southern South China Sea and the Straits of Malacca

Conclusion

The activity concentrations of ^{228}Ra and ^{226}Ra in the surface sediment at southern South China Sea and the Straits of Malacca were wide ranged and varied significantly depending on the sampling location. It was proved by an ANOVA analysis that there was a significant difference at 95% confidence level for activities of ^{228}Ra ($p < 0.001$) and ^{226}Ra ($p < 0.001$) at both study locations. In general, the activity concentrations of both radionuclides in the SSCS were higher than those in the Straits of Malacca. While the distribution of $^{228}Ra/^{226}Ra$ ratios was uniform and comparable at all sampling stations in the southern South China Sea and the Straits of Malacca with an average of 1.8 slightly corresponding to their parents (^{232}Th and ^{238}U).

Acknowledgements

This research is part of the AELB-Nuclear Malaysia project for the study of "Development of Marine Radioactivity Data Base in Malaysian Waters". The authors would like to thank the AELB for providing a fund through the IRPA grant. Thanks also to the MFD, KL PAUS, Malaysian Nuclear Agency and UKM staff members for their help during the sampling and samples analysis and writing of this article.

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