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Trace metals and rare earth elements in Rock Oyster *Saccostrea cucullata* along the east coast of Peninsular Malaysia

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Trace metals and rare earth elements (REEs) in the soft tissue of rocky shore Rock Oyster, Saccostrea cucullata*, along the east coast of Peninsular Malaysia were determined. Significant inter-spatial variations (*$p < 0.05$*) in trace metals and REEs were recorded. Significant positive correlations (*$p < 0.01$*) were found among REEs concentrations. A few significant correlations were found for trace metals and REEs. Average distribution of metals indicated that Johor State had the highest concentrations compared with Pahang and Terengganu for all metals, except for Pb and Cu. This could most likely be attributed to the highly urbanized and industrialized activities such as sewage discharge.*

The metal accumulation patterns in the oyster indicated enrichment of essential metals. Sites with relatively high concentrations of the contaminant metals Hg, Cu, Pb and Zn were related to their close proximity to industrial and urban sites or to boating and aquaculture activities. Relative enrichment of Cu, Pb and Zn in oysters in the whole study even from relatively pristine areas is thought to be derived from natural sources as these metals are significantly correlated to REEs distribution. The distribution of REEs show close similarity between all sampling sites, suggesting that they are of similar origins. In all sites, typical saw-tooth chondrite-normalized patterns were observed, which strongly suggested the REEs bioaccumulated in oyster tissues is derived from geogenic sources. Typical deviations from this pattern were found for Ce and Eu and could be explained by their redox chemistry. Results of light to heavy REEs (LREE/HREE) ratios suggested REEs fractionation in coastline marine environment produced more light REEs and less heavy REEs absorbed in the soft tissue of S. cucullata*. The ratio of La/Yb in the oyster of 27.3 was remarkably similar to Terengganu River basin soil of 33.0 and to Terengganu River sediment of 27.6. Comparison of metal concentration with maximum permissible limits of toxic metals in food established in different countries, as well as Malaysian Food Act 1983 and Food Regulations 1985 Fourteen Schedule, indicated values were well within safety levels, except for Cu and Zn. Along with its wide distribution on rocky shore areas along the east coast, the present results of trace metals and REEs recorded in soft tissue of* S. cucullata *collected from 14 sites along the east coast of Peninsular Malaysia served as baseline data for future reference.*

Keywords: heavy metals, food safety level

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Introduction

Heavy metals may transform into persistent metallic compounds with high toxicity, which can be bioaccumulated by organisms, magnify in the food chain and threaten human health (Zhou et al., 2008). All aquatic invertebrates can accumulate trace metals in their tissues whether or not these metals are essential to metabolism. Biomonitoring is a technique for assessing environment response including human exposures to natural and synthetic chemicals, based on analysis of an individual organism's tissues.

Oysters have become widely used for monitoring contamination in coastal and estuarine ecosystems as in the "Mussel Watch" programs (UNEP, 1993). Mussels are ideal organisms for environmental monitoring of trace elements due to their wide geographical distribution, abundance, sedentary habit, tolerance to high concentrations of most environmental contaminants and their high bioconcentration factors for pollutants (Amin et al., 2006; Zhou et al., 2008). The use of bivalve and gastropods bioindicators to study pollution in the Malaysian environment has received much attention (Amin et al., 2006; Shazili et al., 2006; Yap et al., 2009). Several studies on *S. cucullata* related to biomonitoring aquatic pollution has been carried out in Malaysia (Sivalingam, 1979; Shazili et al., 1995; Yap et al., 2010), yet little or no information exists on REEs distribution and behavior in *S. cucullata*.

According to Shazili et al. (2006), information on the levels of heavy metals pollution on the east coast of Peninsular Malaysia is scarce and limited to a small number of studies. Most of the coastal resources, agriculture, economic activities and human population are concentrated on the west coast of Peninsular Malaysia; thus most of the studies on heavy metals have been focused in this area (Abdullah et al., 1999).

REEs is a group of elements whose chemical properties change systematically and have been proven as a tool for investigating paleoclimatic environment, provenance, erosion processes, environmental regulation and soil-water interactions (Milliman and Meade, 1983; Bau et al., 1997; Yang et al., 2007). The intensive use of REEs in the recent technological industry resulted in substantially higher amounts disposed in the environment (Costas et al., 2010). REEs have been proven to being accumulated by biota and have toxic effects similar to heavy metals (Riondato et al., 2001). As a result, there is risk of REEs entering the food chain which lead to the need for the monitoring of REEs in Malaysian coastal waters with regards to human health.

The objectives of this study are to investigate the bioavailabilty and degree of exposure of heavy metal and REEs in soft tissue of *S. cucullata* at different rocky shore locations along the east coast of Peninsular Malaysia and provide baseline data especially for the REEs for the east coast region of Malaysia.

Methodology

The east coast of Peninsular Malaysia is 957 km and stretching from Kota Bharu in the north to Johor Bharu in the south (Rezaee et al., 2009). Fourteen sites included pristine and recreational sites as well as sites in the proximity of industrial and urbanized areas (Figure 1) were selected so as to provide a wider range of information on bioaccumulation patterns in relation to environmental status. Only sites having abundant Rock Oyster population on natural rocky structures were sampled. Sampling on all sites were done within a period of 10 days in order to avoid possible seasonal changes in metal content in the oysters.

About 10–15 individuals of Rock Oyster with relatively similar size were hand collected during low tide in May and June 2009. All samples were placed in plastic bags, sealed, labelled and stored on ice for transportation to the laboratory. At the laboratory, the samples were rinsed with running Milli-Q water (18.2 Ω) to remove sediment and salt particles. Samples were stored frozen at −20°C until further analysis. After thawing at room temperature, samples were extracted from their shells. In order to evaluate the water content and conversion factor, wet weight of samples were recorded. Extracted soft tissues were freeze dried at −48°C for 3 days before being weighed again for dry weight calculation. Freeze-dried samples were pulverized to a homogenous powder using porcelain mortar and pestle. Powder sample was stored in a dessicator at room temperature until required for analysis.

The analytical procedure used to measure the metals concentration in oysters was based on Azlisham et al. (2009) with little modification. Analysis of heavy metals and REEs were carried out using an Inductive Coupled Plasma Mass Spectrometer (ICPMS) Perkin ELMER ELAN 9000. The concentration of metals in samples was blank corrected

No	Sampling Sites	Coordinates
1	Sungai Rengit	N 01° 21' E 104° 13'
2	Batu Layar	N 01° 27' E 104° 16'
3	Tanjung Balau	N 01° 37' E 104° 18'
4	Sedili Kechil	N 01° 51' E 104° 09'
5	Mersing	N 02° 26' E 103 °51'
6	Kampung Tanjung Batu	N 03° 12' E 103° 27'
7	Teluk Cempedak	N 03° 49' E 103° 22'
8	Tanjung Gelang	N 03° 58' E 103° 25'
9	Cherating	N 04° 08' E 103° 24'
10	Kijal	N 04° 19' E 103° 29'
11	Kemasik	N 04° 25' E 103° 27'
12	Tanjung Jara	N 04° 48' E 103° 25'
13	Chendering	N 05° 16' E 103° 10'
14	Bari Kecil	N 05° 34' E 102° 51'

Figure 1. Map showing 14 sampling sites along the east coast of Peninsular Malaysia.

and expressed as μg g^{-1} dry weight. Mercury content was analyzed by direct analysis of the freeze-dried samples using MA-2 Mercury Analyzer. All the glassware and equipment used were immersed in 10% nitric acid (HNO_3) solution for at least 24 h prior to sampling and laboratory analysis. The quality of method used was checked and confirmed in a separate comparative study of metals in a standard reference material, Lobster Hepatopancreas TORT-2, National Research Council of Canada. Recoveries were as follows: 92.30% for Hg, 113.57% for Pb, 97.31% for Cd, 85.56% for Cu, 86.54% for Zn, 81.80% for Mn, 94.30% for Fe, 96.53% for Co, 88.59% for Se and 82.60% for Sr.

SPSS (Version 17.0, SPSS Inc., Chicago, IL, USA) was used for determining statistical data including descriptive statistics (mean and standard deviation), one-way analysis of variance (ANOVA) and Pearson's correlation coefficient. ANOVA and Duncan's post hoc test was employed for assessment of variation and significant differences observed between metals and REEs concentration in different sites. The strength and direction of the relationship between elements in *S. cucullata* was elucidated using Pearson's correlation. All comparisons were made at least at the 95% ($p < 0.05$) and 99% ($p < 0.01$) level of significance.

Results

Concentrations, expressed on a dry weight basis (μg g^{-1}), for Hg, Pb, Cd, Cu, Zn, Mn, Fe, Co, Se, Sr, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, together with the total contents of REEs (ΣREE), light REEs (ΣLREE) and heavy REEs (ΣHREE) are presented in Table 1. Figure 2 shows chondrite-normalized plots for the REEs in the soft tissue of *S. cucullata* from 14 sampling sites along the east coast of Peninsular Malaysia. There are significant differences between concentration of Hg, Pb, Cd, Cu, Zn, Mn, Co and Se among sampling sites ($p < 0.05$). Table 1 indicated that soft tissue of *S. cucullata* from Tanjung Balau contained the highest concentration of Hg, Cu, Zn, Co and Se

Table 1A. Concentration of metals REEs ($\mu g/g^{-1}$ dry weight) in soft tissue of Rock Oyster, *S. cucullata* (mean and standard deviation) from 14 sampling sites along the east coast of Peninsular Malaysia.

	Sungai Rengit	Batu Layar	Tanjung Balau	Sedili Kechil	Mersing	Kampung Tanjung Batu	Teluk Cempedak
Hg	$0.11 \pm 0.03^{a,b}$	$0.18 \pm 0.05^{c,d}$	0.53 ± 0.05^{f}	0.26 ± 0.04^{e}	$0.14 \pm 0.02^{a,b,c}$	$0.14 \pm 0.03^{a,b,c}$	$0.14 \pm 0.00^{a,b,c}$
Pb	1.19 ± 0.17^{a}	0.98 ± 1.31^{a}	0.85 ± 0.38^{a}	0.35 ± 0.19^{a}	1.02 ± 0.22^{a}	3.47 ± 3.03^{b}	0.24 ± 0.1^{a}
Cd	$1.79 \pm 0.26^{a,b,c,d}$	$2.49 \pm 0.36^{c,d,e}$	$2.24 \pm 0.13^{b,c,d,e}$	4.37 ± 0.71^{f}	2.84 ± 0.39^{e}	2.78 ± 0.52^{e}	1.15 ± 0.15^{a}
Cu	$211.46 \pm 35.27^{d,e,f}$	$226.18 \pm 47.70^{d,e,f}$	256.38 ± 12.7^{f}	$212.44 \pm 29.3^{d,e,f}$	$166.12 \pm 54.5^{b,c,d,e}$	$188.59 \pm 42.3^{c,d,e,f}$	$94.75 \pm 15.7^{a,b}$
Zn	$2253.09 \pm 459.6^{c,d}$	$1114.67 \pm 247.0^{a,b,c}$	5277.3 ± 843.3^{e}	5190.6 ± 1510.0^{e}	$810.3 \pm 245.1^{a,b}$	$1076.7 \pm 357.3^{a,b}$	339.4 ± 20.4^{a}
Mn	10.92 ± 7.17^{c}	$4.39 \pm 2.79^{a,b}$	$4.03 \pm 1.58^{a,b}$	$5.30 \pm 2.54^{a,b}$	$5.12 \pm 2.31^{a,b}$	3.15 ± 1.10^{a}	$8.47 \pm 0.36^{b,c}$
Fe	1788.04 ± 2240	1206.78 ± 1695	630.3 ± 91.2	517.5 ± 144.9	402.5 ± 132.9	448.7 ± 57.5	274.9 ± 111.5
Co	$0.23 \pm 0.08^{d,e}$	0.08 ± 0.02^{a}	0.42 ± 0.05^{f}	0.29 ± 0.05^{e}	$0.20 \pm 0.05^{c,d}$	$0.13 \pm 0.03^{a,b,c}$	$0.09 \pm 0.02^{a,b}$
Se	$3.05 \pm 0.30^{a,b,c}$	3.85 ± 0.95^{c}	6.83 ± 1.20^{e}	$6.46 \pm 0.20^{d,e}$	$3.08 \pm 0.17^{a,b,c}$	5.80 ± 0.03^{d}	$3.40 \pm 0.40^{b,c}$
Sr	89.37 ± 86.40	49.02 ± 11.35	45.9 ± 1.13	168.7 ± 161.4	80.7 ± 38.0	36.8 ± 20.6	60.2 ± 51.9
La	7.41 ± 7.77^{b}	0.63 ± 0.59^{a}	2.06 ± 0.99^{a}	1.61 ± 1.08^{a}	7.36 ± 0.42^{b}	7.23 ± 5.63^{b}	0.11 ± 0.03^{a}
Ce	21.96 ± 20.74^{c}	$1.88 \pm 1.72^{a,b}$	$7.48 \pm 3.56^{a,b}$	$4.93 \pm 3.43^{a,b}$	24.0 ± 1.64^{c}	$14.05 \pm 7.04^{b,c}$	0.35 ± 0.13^{a}
Pr	2.29 ± 2.12^{b}	0.19 ± 0.18^{a}	0.77 ± 0.34^{a}	0.53 ± 0.37^{a}	2.63 ± 0.28^{b}	2.14 ± 1.53^{b}	0.04 ± 0.01^{a}
Nd	12.53 ± 11.57^{c}	0.98 ± 0.91^{a}	$4.31 \pm 1.78^{a,b}$	2.80 ± 1.87^{a}	14.04 ± 1.53^{c}	$11.10 \pm 8.06^{b,c}$	0.19 ± 0.06^{a}
Sm	2.61 ± 2.12^{b}	0.18 ± 0.18^{a}	1.02 ± 0.35^{a}	0.70 ± 0.45^{a}	2.99 ± 0.44^{b}	2.39 ± 1.78^{b}	0.05 ± 0.02^{a}
Eu	0.38 ± 0.29^{c}	0.02 ± 0.02^{a}	$0.16 \pm 0.05^{a,b}$	$0.10 \pm 0.07^{a,b}$	0.39 ± 0.06^{c}	$0.29 \pm 0.24^{b,c}$	0.00 ± 0.01^{a}
Gd	2.71 ± 2.21^{b}	0.18 ± 0.17^{a}	1.03 ± 0.34^{a}	0.75 ± 0.50^{a}	2.88 ± 0.38^{b}	2.44 ± 1.94^{b}	0.05 ± 0.01^{a}
Tb	0.30 ± 0.21^{c}	0.02 ± 0.02^{a}	$0.11 \pm 0.03^{a,b}$	0.10 ± 0.07^{a}	0.32 ± 0.05^{c}	$0.25 \pm 0.18^{b,c}$	0.01 ± 0.01^{a}
Dy	1.51 ± 0.92^{c}	0.12 ± 0.11^{a}	$0.60 \pm 0.19^{a,b}$	$0.61 \pm 0.42^{a,b}$	1.62 ± 0.30^{c}	$1.27 \pm 0.88^{b,c}$	0.07 ± 0.03^{a}
Ho	0.21 ± 0.12^{c}	0.02 ± 0.02^{a}	0.09 ± 0.02^{a}	$0.10 \pm 0.07^{a,b}$	0.22 ± 0.04^{c}	$0.18 \pm 0.11^{b,c}$	0.01 ± 0.01^{a}
Er	$0.48 \pm 0.25^{c,d}$	$0.05 \pm 0.05^{a,b}$	$0.21 \pm 0.06^{a,b}$	$0.28 \pm 0.19^{b,c}$	0.52 ± 0.10^{d}	$0.44 \pm 0.27^{c,d}$	$0.04 \pm 0.02^{a,b}$
Tm	0.03 ± 0.02	0.00 ± 0.01	0.01 ± 0.01	0.03 ± 0.02	0.04 ± 0.01	0.04 ± 0.02	0.00 ± 0.01
Yb	0.20 ± 0.06^{b}	0.03 ± 0.02^{a}	0.09 ± 0.03^{a}	0.20 ± 0.10^{b}	0.21 ± 0.06^{b}	0.22 ± 0.12^{b}	0.03 ± 0.01^{a}
Lu	0.02 ± 0.01	0.00 ± 0.00	0.01 ± 0.00	0.02 ± 0.02	0.02 ± 0.01	0.02 ± 0.02	0.00 ± 0.00
ΣREE	52.63 ± 6.31	4.31 ± 0.53	17.96 ± 2.13	12.76 ± 1.39	57.23 ± 6.91	42.08 ± 4.51	0.97 ± 0.10
ΣLREE	46.80 ± 8.18	3.86 ± 0.70	15.64 ± 2.81	10.57 ± 1.82	51.03 ± 8.98	36.92 ± 5.26	0.75 ± 0.13
ΣHREE	5.83 ± 0.89	0.45 ± 0.06	2.32 ± 0.34	2.19 ± 0.26	6.20 ± 0.95	5.16 ± 0.80	0.22 ± 0.03

Duncan post hoc test comparisons of elements levels between sampling sites; means with different letters are significantly different, $p < 0.05$.

Table 1B. Concentration of metals REEs ($\mu g/g^{-1}$ dry weight) in soft tissue of Rock Oyster, *S. cucullata* (mean and standard deviation) from 14 sampling sites along the east coast of Peninsular Malaysia.

	Tanjung Gelang	Cherating	Kijal	Kemasik	Tanjung Jara	Chendering	Bari Kechil
Hg	0.08 ± 0.01^{a}	$0.15 \pm 0.06^{b,c}$	$0.14 \pm 0.05^{a,b,c}$	$0.14 \pm 0.05^{a,b,c}$	$0.23 \pm 0.06^{d,e}$	$0.18 \pm 0.01^{c,d}$	$0.10 \pm 0.03^{a,b}$
Pb	4.38 ± 0.96^{b}	0.70 ± 0.09^{a}	0.65 ± 0.03^{a}	0.64 ± 0.25^{a}	0.84 ± 0.46^{a}	0.82 ± 0.18^{a}	0.74 ± 0.05^{a}
Cd	0.99 ± 0.11^{a}	$1.69 \pm 0.67^{a,b,c}$	$1.42 \pm 0.41^{a,b}$	1.21 ± 0.47^{a}	$2.45 \pm 0.65^{c,d,e}$	$1.79 \pm 0.38^{a,b,c,d}$	$2.64 \pm 0.62^{d,e}$
Cu	$107.75 \pm 22.2^{a,b}$	84.12 ± 42.2^{a}	$156.54 \pm 32.5^{b,c,d}$	$119.32 \pm 80.0^{a,b,c}$	$194.78 \pm 36.4^{d,e,f}$	$238.15 \pm 11.7^{e,f}$	$167.00 \pm 7.41^{b,c,d,e}$
Zn	$1648.9 \pm 350.0^{b,c}$	$796.4 \pm 599.1^{a,b}$	$1395.3 \pm 742.4^{a,b,c}$	$747.5 \pm 326.9^{a,b}$	$1128.8 \pm 491.8^{a,b,c}$	2758.1 ± 687.7^{d}	$675.0 \pm 295.6^{a,b}$
Mn	2.84 ± 1.62^{a}	$5.36 \pm 1.16^{a,b}$	2.88 ± 1.00^{a}	$3.95 \pm 2.94^{a,b}$	1.02 ± 0.06^{a}	2.88 ± 0.35^{a}	$4.23 \pm 2.64^{a,b}$
Fe	203.2 ± 22.6	368.6 ± 27.8	296.6 ± 42.2	397.7 ± 163.5	136.2 ± 14.4	390.4 ± 86.0	202.9 ± 24.9
Co	$0.16 \pm 0.02^{b,c}$	$0.11 \pm 0.01^{a,b}$	0.09 ± 0.01^{a}	$0.13 \pm 0.01^{a,b}$	$0.10 \pm 0.02^{a,b}$	$0.14 \pm 0.03^{a,b,c}$	$0.10 \pm 0.01^{a,b}$
Se	$3.11 \pm 0.37^{a,b,c}$	$2.97 \pm 0.06^{a,b,c}$	2.41 ± 0.56^{a}	$2.61 \pm 0.17^{a,b}$	$3.43 \pm 0.17^{b,c}$	$2.76 \pm 0.28^{a,b}$	$2.67 \pm 0.56^{a,b}$
Sr	35.5 ± 19.2	74.4 ± 36.2	72.3 ± 18.4	105.0 ± 92.3	25.7 ± 2.24	50.5 ± 12.7	30.9 ± 6.95
La	1.54 ± 0.34^{a}	0.42 ± 0.27^{a}	0.25 ± 0.12^{a}	1.09 ± 1.56^{a}	1.42 ± 1.50^{a}	2.06 ± 2.03^{a}	1.28 ± 1.09^{a}
Ce	$6.15 \pm 1.25^{a,b}$	1.11 ± 0.73^{a}	0.75 ± 0.41^{a}	$3.41 \pm 4.92^{a,b}$	$4.92 \pm 5.01^{a,b}$	$6.42 \pm 6.58^{a,b}$	$4.06 \pm 3.26^{a,b}$
Pr	0.64 ± 0.14^{a}	0.11 ± 0.07^{a}	0.06 ± 0.04^{a}	0.31 ± 0.46^{a}	0.51 ± 0.51^{a}	0.70 ± 0.73^{a}	0.47 ± 0.40^{a}
Nd	3.46 ± 0.69^{a}	0.59 ± 0.37^{a}	0.34 ± 0.20^{a}	1.48 ± 2.09^{a}	2.61 ± 2.59^{a}	3.58 ± 3.65^{a}	2.40 ± 2.00^{a}
Sm	0.78 ± 0.10^{a}	0.12 ± 0.08^{a}	0.08 ± 0.04^{a}	0.27 ± 0.36^{a}	0.46 ± 0.44^{a}	0.65 ± 0.68^{a}	0.39 ± 0.31^{a}
Eu	$0.10 \pm 0.01^{a,b}$	0.01 ± 0.01^{a}	0.01 ± 0.01^{a}	0.04 ± 0.04^{a}	$0.06 \pm 0.06^{a,b}$	$0.08 \pm 0.09^{a,b}$	0.05 ± 0.04^{a}
Gd	0.71 ± 0.08^{a}	0.12 ± 0.08^{a}	0.08 ± 0.03^{a}	0.27 ± 0.36^{a}	0.42 ± 0.41^{a}	0.63 ± 0.66^{a}	0.36 ± 0.29^{a}
Tb	0.08 ± 0.01^{a}	0.01 ± 0.01^{a}	0.01 ± 0.01^{a}	0.04 ± 0.04^{a}	0.05 ± 0.04^{a}	0.07 ± 0.07^{a}	0.04 ± 0.03^{a}
Dy	0.40 ± 0.03^{a}	0.11 ± 0.06^{a}	0.06 ± 0.04^{a}	0.15 ± 0.14^{a}	0.23 ± 0.19^{a}	0.38 ± 0.32^{a}	0.22 ± 0.14^{a}
Ho	0.06 ± 0.01^{a}	0.02 ± 0.01^{a}	0.01 ± 0.01^{a}	0.02 ± 0.02^{a}	0.03 ± 0.03^{a}	0.05 ± 0.04^{a}	0.03 ± 0.02^{a}
Er	$0.14 \pm 0.01^{a,b}$	$0.05 \pm 0.03^{a,b}$	0.03 ± 0.03^{a}	$0.06 \pm 0.05^{a,b}$	$0.09 \pm 0.07^{a,b}$	$0.16 \pm 0.11^{a,b}$	$0.09 \pm 0.05^{a,b}$
Tm	0.01 ± 0.00	0.01 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.01	0.01 ± 0.01	0.00 ± 0.01
Yb	0.06 ± 0.00^{a}	0.03 ± 0.03^{a}	0.02 ± 0.02^{a}	0.04 ± 0.03^{a}	0.04 ± 0.03^{a}	0.09 ± 0.03^{a}	0.05 ± 0.02^{a}
Lu	0.01 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.00
ΣREE	14.13 ± 1.75	2.70 ± 0.31	1.70 ± 0.21	7.17 ± 0.94	10.85 ± 1.40	14.89 ± 1.84	9.44 ± 1.18
ΣLREE	12.56 ± 2.32	2.34 ± 0.41	1.48 ± 0.28	6.56 ± 1.28	9.92 ± 1.86	13.41 ± 2.41	8.60 ± 1.54
ΣHREE	1.57 ± 0.23	0.36 ± 0.05	0.22 ± 0.03	0.61 ± 0.09	0.93 ± 0.14	1.48 ± 0.21	0.84 ± 0.12

Duncan post hoc test comparisons of elements levels between sampling sites; means with different letters are significantly different, $p < 0.05$.

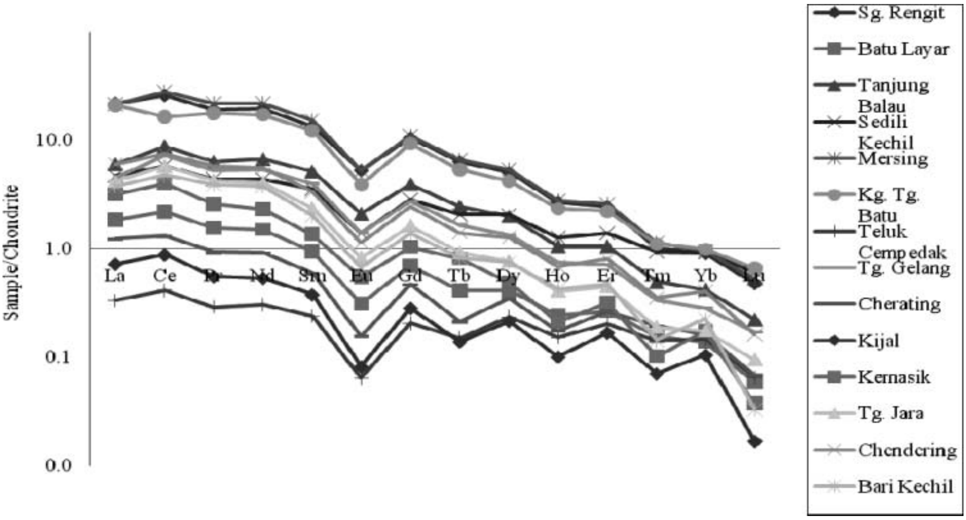

Figure 2. Chondrite-normalized plots for the REEs in the soft tissue of Rock Oyster, *S. cucullata* from 14 sampling sites along the east coast of Peninsular Malaysia.

with 0.53 μg g^{-1}, 256.38 μg g^{-1}, 5277.33 μg g^{-1}, 0.42 μg g^{-1} and 6.83 μg g^{-1}, respectively. Oysters from Sedili Kechil and Sungai Rengit have the highest values of Cd, Sr, Mn and Fe with 4.37 μg g^{-1},168.65 μg g^{-1}, 10.92 μg g^{-1} and 1788.04 μg g^{-1}, respectively. Highest value of Pb in oyster was revealed from Tanjung Gelang populations (4.38 μg g^{-1}).

The pattern of metal occurrence in the oyster tissue decreased in the order of Zn > Fe > Cu > Sr > Mn > Se > Cd > Pb > Hg > Co. From this pattern, it shows that Zn (339.44–5277.33 μg g^{-1}), Fe (136.22–1788 μg g^{-1}) and Cu (84.12–256.38 μg g^{-1}) were the most abundant elements with Cd (0.99–4.37 μg g^{-1}), Pb (0.24–4.38 μg g^{-1}), Hg (0.08–0.53 μg g^{-1}) and Co (0.08–0.42 μg g^{-1}), are the least abundant. Significant positive correlations ($p < 0.01$, $p < 0.05$) from the 14 sampling sites along the east coast of Peninsular Malaysia were found for pairs Hg-Cu, Hg-Zn, Hg-Co, Hg-Se, Cd-Cu, Cd-Zn, Cd-Se, Cu-Hg, Cu-Zn, Cu-Co, Cu-Se, Zn-Co, Zn-Se, Co-Cd, Co-Fe and Co-Se. It has been found that Mn and Fe in studied soft tissue only showed significant positive correlations ($p <$ 0.01) with each other. No negative correlation was discovered.

The ΣREEs concentrations in soft tissue of *S. cucullata* varied from 0.97–57.23 μg g^{-1}. Ce was the most abundant with 7.24 μg g^{-1} while Lu was the least abundant (0.01 μg g^{-1}). Highest ΣREEs concentration was recorded in oyster populations from Sungai Rengit, Mersing and Kampung Tanjung Batu with 52.63 μg g^{-1}, 57.23 μg g^{-1} and 42.08 μg g^{-1}, respectively. The lowest ΣREEs were measured from Teluk Cempedak (0.97 μg g^{-1}). Significant differences were found between concentration of all REEs among sampling sites ($p < 0.05$). REEs may be divided into two groups; the incompatible light REEs (LREE; La–Sm) and the selectively compatible heavy REEs (HREE; Eu–Lu) (Rezaee et al., 2009). In general, the abundance follow the order of Ce > Nd > La > Sm > Pr for the LREEs and Gd > Dy > Er > Eu > Tb > Yb > Ho > Tm > Lu for the HREEs. The mean values of ΣLREEs and ΣHREEs were 15.74 and 2.03 μg g^{-1}, respectively, indicating LREEs enrichment over HREEs. All REEs were found to yield strong positive correlation among each other. The chondrite-normalized REEs pattern in soft tissue of *S. cucullata* (Figure 2) indicated patterns that are generally having higher LREEs concentrations, smooth downward pattern and depletion in HREEs concentrations. In LREEs, negative Ce anomaly was only observed at Kampung Tanjung Batu. Negative Eu anomaly in all sites was clearly noted. The saw-tooth chondrite-normalized pattern in each sample was similar to one another although the concentrations of REEs in each station were different.

Discussion

The accumulated concentrations in a biomonitor are a direct reflection of the bioavailability and contamination of the sampling sites because they bioaccumulate metals in their tissues in proportion to the degree of environmental contamination from water, suspended particle matters, sediments and through food chains (Blackmore and Morton, 2001). Sampling of *S. cucullata* in different locations but within the same period characterizes the spatial variations in the samples. Specimens inhabiting Tanjung Balau that was characterized by the greatest concentrations of Hg, Cu, Zn, Co and Se may be due to anthropogenic factors influenced by human activities instead of natural origins of the metals. This area is adjacent to a resort vacation area and fishing landing jetty with heavy fishing boat traffic. The use of Zn block in fishing vessels and Cu leachate from the antifouling paints of boat with semi-enclosed topography of Tanjung Balau would have resulted in enhanced metal concentrations in coastal waters. Also, the release of scrap metals and paint residues from boats are sources for Zn and Cu (Goldberg, 1976) while anthropogenic sources of Se are oil combustion and sewage effluent (Maher and Batley, 1990; Kirby et al., 2001).

It is evident that Pb concentration in soft tissue from Kampung Tanjung Batu and Tanjung Gelang specimens was higher by approximately one order of magnitude compared with those from other sites. High values related to Tanjung Gelang can be understood as it is located in the vicinity of industrial complexes. Effluents from the nearby domestic and industrial inputs flow through this area through large drains discharging directly to the sea. Kampung Tanjung Batu site may be considered a pristine area, however pollution at this area are probably derived from the organic wastes discharged from a massive shrimp culture complex nearby. Heavy metal such as Pb contamination has been found to originate from aquaculture activities (Yap et al., 2002) and organic wastes discharged from fish farms were found to have impacts on the water quality around fish culture zones (Wu et al., 1994; Yap et al., 2003).

Generally, the average distribution of metals indicated that sampling sites in the state of Johor showed higher concentration than Pahang and Terengganu. This is probably due to the higher urbanization and industrialization in Johor. High concentration can often be attributed to anthropogenic activities because they are found at locations where human population is high. However, there are many instances showing areas where metals were at high concentrations for purely natural reasons and were not evidence of contamination (Jeng et al., 2000). This also explains the discovery of unexpectedly high metal levels in chosen pristine areas in this study.

The inter-spatial variation has been reported for *S. cucullata* taken from sampling sites similar to the previous study along the east coast of Peninsular Malaysia (Shazili et al., 1995) and from other countries around the globe (Burdon-Jones and Klumpp, 1979; Phillips, 1979; Denton and Breck, 1981; Fowler, 1988; Chu et al., 1990; Fowler et al., 1993; Denton et al., 1999; Blackmore, 2001; Mora et al., 2004; Cheung and Wang, 2008). The concentration data obtained for soft tissue in Pb, Cd, Cu and Zn were comparable with those collected in the similar sampling sites by Shazili et al. (1995) but the present Pb and Zn data showed increasing values from the previous measurements. Comparison with other countries indicated that Co concentration were within the same range. High concentrations of Hg, Pb and Zn were found in this study with Zn having comparable concentration with *S. cucullata* from Hong Kong waters and Apra Harbor, Guam. Cd and Cu concentration in this study is considered low in comparison with other studies. This observation led to the conclusion that sampling sites within this study were not polluted.

The pattern of trace metals accumulation (Zn > Fe > Cu > Sr > Mn > Se > Cd > Pb > Hg > Co) revealed enrichment of the essential metals Fe, Zn and Cu in soft tissue compared with the other metals. Fe, Zn and Cu are well-known essential elements for filter-feeder organisms including oyster. Ferritin, the most important Fe storage and detoxification protein, has been isolated from *S. cucullata* in a study by Webb et al. (1985). Oysters accumulated high concentration of Zn in detoxified granules while mussels excreted high accumulated Zn in granules from the kidney, making oysters strong accumulators of Zn (Amiard et al., 2008). Furthermore, high Zn concentration in *S. cucullata* was derived from its efficient dietary assimilation and its exceedingly low rate of Zn efflux (Ke and Wang, 2001; Wang et al., 1999). This explains the high Zn concentration determined in the study (1800 $\mu g\ g^{-1}$). High metal body concentrations in *S. cucullata* are in conjunction with their feeding behaviour of passing a large amount of water over gills and the organisms ingesting potentially metal rich particles.

Strong positive correlation ($p < 0.01$) among REEs is considerably natural as REEs are very similar in their chemical and physical properties and they are expected to be similar as well in their distribution in biological tissue. The contaminant metals Cd, Pb and Zn are significantly correlated ($p <$ 0.05 and $p < 0.01$) with REEs and thus suggests that these metals are probably non-anthropogenic in origin. The relationship found between some of the metal pairs might derive from a competition or an additional effect on the metal binders at the cellular level (Wright, 1995).

In comparison with the permissible limits set by the Malaysian Food Regulations 1985 Fourteen Schedule for Cd (1.00 μg g^{-1} wet weight), Cu (30.0 μg g^{-1} wet weight), Pb (2.00 μg g^{-1} wet weight) and Zn (100 μg g^{-1} wet weight), Cu and Zn were found to exceed the limits. They also exceeded the recommended guidelines for Cu and Zn set by the Commission Europe (CE, 2006), the Hong Kong Environmental Protection Department (HKEPD, 1997), the Food Standards Australia New Zealand Authority (FSANZ, 1996), the Australian Government (2006), the Food & Drug Administration of the United States (USFDA, 1990), the Brazilian Ministry of Health (ABIA, 1991) and the limits established by the Ministry of Public Health of Thailand (MPHT, 1986). However, Cd and Pb from all populations were lower than the limits.

Chondrite-normalized values display a saw-tooth pattern which strongly suggests that the REEs accumulated by the studied oyster is geogenic in origin. However, some anomalies in the REEs distribution in the oysters are further discussed with respect to possible contamination from human activities. Chondrite has been used for normalization of REEs because bulk composition of the earth is assumed to be close to that of chondrite meteorites which represent the primordial earth (Ohde and Mataragio, 1999). There are variations in REEs abundance among sites but they show similarities in their REEs enrichment pattern, which suggests they are of similar origins. Significant variation between sites may be attributed to biological variation within the oysters and differences in lanthanide availability between sites. Different uptake sources are not taken into account as *S. cucullata* takes up lanthanides from surface water by filter-feeding behavior. Although REEs are proven to be taken up by oysters, they have no established biological function and are considered non-essential metals.

Positive Ce anomaly and negative Eu anomaly observed in chondritic plots can be explained. Ce and Eu act differently where Ce^{3+} under oxidizing conditions becomes insoluble Ce^{4+}, while Eu^{3+} under reducing condition becomes Eu^{2+}. There is tendency that a positive Ce anomaly and a negative Eu anomaly within soft tissue of *S. cucullata* are derived from particulate matter of muddy sediment. Another reason for positive Ce anomaly is possible contamination as a result of discharge of organic materials and contaminations from industrial and agricultural wastes and municipal effluents from the surrounding area. The distribution patterns of LREEs and HREEs in the sample have a similar trend that shows small variation in fractionations between sites. The enrichment of LREEs over HREEs is apparent in the increase of the ratio of LREE/HREE, which is consistent with the ratio of La/Yb. Higher ratio of La/Yb of 37.18 observed at Sungai Rengit is probably due to the relative enrichment derived from the Rengit river.

The chondrite-normalized REEs plots (Figure 2) from various sampling sites are remarkably similar to values from the Terengganu River sediment and granitic rocks of the Terengganu River basin which represents the only published record of REEs measurements in riverine sediments in Malaysia (Sultan and Shazili, 2009). Granite is the dominant rock of the east coast of peninsular Malaysia and thus the main source of metals and REEs supplying the South China Sea. The ratio of light to heavy REEs, La/Yb in the oyster of 27.3 is also remarkably similar to Terengganu River basin soil of 33 and of Terengganu River sediment of 27.6.

Conclusions

Average distribution of metals indicated that the state of Johor has the highest concentration compared with Pahang and Terengganu for all metals except for Cu and Pb. Zn and Cu in the oysters of east coast Peninsular Malaysia are exceeding the permissible limit set by Malaysian Food Regulations 1985 Fourteen Schedule, as well as the limits set by other countries, and thus are not considered safe to be eaten. Chondrite-normalized patterns suggested that light REEs and heavy REEs fractionation in coastline marine environment produces more light REEs and less heavy REEs accumulated in the soft tissue of *S. cucullata.* Along with its wide distribution on rocky shore area along the east coast of peninsula, the present results of trace metals and REEs recorded in soft tissue of *S. cucullata* collected from

14 sites along the east coast of Peninsular Malaysia serve as baseline data for future reference.

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