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Natural Uranium and Thorium Isotopes in Sediment Cores Off Malaysian Ports

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Abstract – Sediment cores collected from three Malaysian marine ports, namely, Kota Kinabalu, Labuan and Klang were analyzed to determine the radioactivities of ^{234}U, ^{238}U, ^{230}Th, ^{232}Th and total organic carbon (TOC) content. The objectives of this study were to determine the factors that control the activity of uranium isotopes and identify the possible origin of uranium and thorium in these areas. The activities of ^{234}U and ^{238}U show high positive correlation with TOC at the middle of sediment core from Kota Kinabalu port. This result suggests that activity of uranium at Kota Kinabalu port was influenced by organic carbon. The ^{234}U/^{238}U value at the upper layer of Kota Kinabalu port was ≥1.14 while the ratio value at Labuan and Klang port was ≤ 1.14. These results suggest a reduction process occurred at Kota Kinabalu port where mobile U(VI) was converted to immobile U(IV) by organic carbon. Therefore, it can be concluded that the major input of uranium at Kota Kinabalu port is by sorptive uptake of authigenic uranium from the water column whereas the major inputs of uranium to Labuan and Klang port are of detrital origin. The ratio of ^{230}Th/^{232}Th was used to estimate the origin of thorium. Low ratio value (< 1.5) at Labuan and Klang ports support the suggestion that thorium from both areas were come from detrital input while the high ratio (> 1.5) of ^{230}Th/^{232}Th at Kota Kinabalu port suggest the anthropogenic input of ^{230}Th to this area. The source of ^{230}Th is probably from phosphate fertilizers used in the oil-palm cultivation in Kota Kinabalu that is adjacent to the Kota Kinabalu port.

Key words – uranium, thorium, sediment core, Kota Kinabalu port, total organic carbon (TOC), detrital

1. Introduction

Natural uranium and thorium isotopes have been used commonly as radiotracers for studies of marine sediment including their sources, transport and also sedimentation rates (Dawood 2010; Handerson and Anderson 2003; San Miguel et al. 2004; Porcelli et al. 1995). Uranium has three naturally occurring isotopes, ^{234}U (progeny of ^{238}U, half-life 2.45×10^5 years), ^{235}U (half-life 7.04×10^8 years) and ^{238}U (half-life 4.47×10^9 years). Thorium occurs in nature in four isotopic forms, ^{228}Th, ^{230}Th, ^{232}Th and ^{234}Th. Of these, ^{228}Th is the decay product of the naturally occurring ^{232}Th, and both ^{234}Th and ^{230}Th are decay products of natural ^{238}U. The ^{230}Th with half-life: 75.69 ± 0.23 kyr is a member of the ^{238}U decay series whose parents is ^{234}U (Cheng et al. 2000).

The geochemical behaviors of uranium and thorium have been extensively studied due to the importance of uranium as a geochronology indicator and its application in environmental monitoring. In an anoxic sediment, the major input of uranium to sediment is by sorptive uptake of authigenic uranium whereas in an oxic sediment, the major input of uranium is by lithogenic origin (Chase 2008; Zheng et al. 2002). Chen and Chung (1990) reported that the activity of uranium in sediment at the western Philippine sea is in the range of 0.9 - 1.5 dpm/g, while very low activity was recorded at the Ryuku trench (0.6 dpm/g) due to an oxic environment. There is correlation between particulate uranium and the organic carbon settling flux in a variety of oceanographic regimes (Anderson et al. 1998; McManus et al. 2006). Organic carbons contain the functional groups which can form complexes with radionuclides such as uranium, thus affecting the physical and chemical properties of the uranium (Zeng et al. 2002). In marine environments, once uranium forms complexes with organics compounds, the uranyl ion U(VI)

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may be subsequently reduced to the uranous state U(IV) because of the decrease in oxidation potential (Eh) associated with organic matter burial (Bednar et al. 2007; Zeng et al. 2002; Gascoyne 1982).

Thorium commonly exists in +4 oxidation state and unlike uranium, thorium is highly insoluble in seawater, thus thorium is promptly removed from the water column by adsorption on settling particles called particle scavenging (Bacon and Anderson 1982). The ^{230}Th introduced into marine environments is mostly by in situ decay of dissolved ^{234}U. The long-lived ^{232}Th isotopes (half-life = 1.4×10^{10} years) enter the marine ecosystem in continental detritus (Robinson et al. 2008) and hence enriched the activity of ^{232}Th in area adjacent to the continental margin and in high dust flux zones (Anderson et al. 1995).

Under equilibrium conditions, the activities of any two radionuclides are equal to 1. However disequilibrium between ratios of ^{234}U/^{238}U in sea water is common phenomenon. The approximate ratio of ^{234}U/^{238}U in conservative mixing of river water with sea water is 1.14 while the activity ratio in river sediment is 0.94 (Scott 1982). Chung and Chang (1996) reported that the ratio of ^{234}U/^{238}U in sediment from Northeastern Taiwan was in the range of 0.9 to 1.5 which suggests the enrichment activity of ^{234}U compared to ^{238}U due to the domination of authigenic sources from the water column. However, Cole et al. (1986) and Anderson et al. (1989) have argued that the enrichment activity of ^{234}U compared to ^{238}U in sediment is due to a diffusion process where ^{234}U can be diffused out through the pore water and hence decrease the activity of ^{234}U in sediment. High activity of ^{238}U at lower depth of core sediment is due to a diagenesis process (Srisukawad et al. 1997).

Thorium isotopic activity ratio has been widely used to determine the geochemistry of thorium in marine environments. The ratios of thorium isotopes may provide clues of their origin as well as their pathways to the marine environment. The inputs of ^{232}Th to sediments were used to estimate the detrital input at any location (Robinson et al. 2008; Chung and Chang 1996). Thus, the ratio of ^{230}Th/^{232}Th can be used to estimate the major input of thorium either by detrital or authigenic origin. The ratio of ^{230}Th/^{232}Th can be used to estimate the contamination of ^{230}Th. The contamination might have occurred either as a result of being directly discharged from fertilizer factories (San Miguel et al. 2004) or because of the high usage rates of fertilizer in the plantation area (Dawood 2010; Yii et al. 2009). Normal values of ^{230}Th/^{232}Th in sediment range between 0.8 and 1.5, and a value of more than 1.5 indicates that the area has received additional input of ^{230}Th, which might be the result of high scavenging process or because of contamination that has occurred in the studied area (San Miguel et al. 2004).

A previous study done by Mohamed et al. (2006) showed that the uranium in the water column of the river system at Peninsular Malaysia was controlled by Fe-oxides during high tide and released as oxide reduction during low tide. Others studies have mainly focused on the determination of sedimentation rates (e.g. Zaluyun et al. 2011; Mohamed et al. 2008; Choy et al. 2007; Theng and Mohamed 2005). However, there is currently a lack of data on uranium and thorium isotopes at port areas in the Malaysia regions. The radionuclide at the marine port might originate from sea water or, from lithogenic sources such as river and dust or from anthropogenic sources such as waste released to the port. High physical activities such as dredging projects might influence the behavior of uranium and thorium isotopes at the port area. Marine ports in Malaysia are undergoing dredging on the basis of the Malaysian Government's Vision 2020 project. These construction efforts are being carried out to increase the capacity of the marine ports. Therefore, the goals of this paper are to determine the factors that control the activity of uranium and thorium isotopes and identify the possible sources of uranium and thorium at Malaysian marine ports.

2. Materials and Method

Sampling location

Sediment cores were obtained from the ports of Kota Kinabalu, Labuan and Klang, Malaysia. Fig. 1 shows the map of the study area while Table 1 shows the location, coordinates, water depth and length of core sediment obtained from the study area. The coordinates of the exact sampling location were recorded using Geographical Positioning System (GPS). The core sediments were collected using the gravity corer with 130 kg weight, 250 cm length and 7.5 cm diameter.

Analytical techniques

The analytical separation techniques such as extraction, column separation and detection of uranium and thorium isotopes were modified from those procedures published by Mohamed et al. (2006). About 0.25 g of dried sediments was digested with a mixture of concentrated hydrofluoric acid (HF) and nitric acid (HNO_3) (1:2 v/v). About 2 ml of perchloric

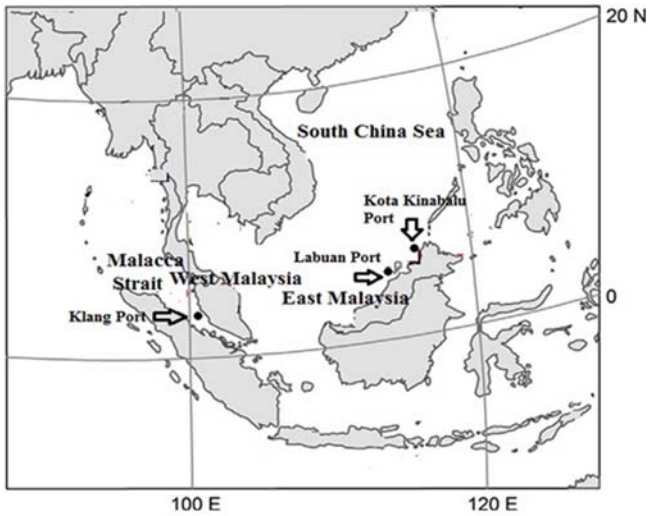

Fig. 1. Map of the study area

acid ($HClO_4$) and 0.5 g of boric acid (H_3BO_3) were added to remove the excess fluoride. The cation column of Bio-Rad AG 50W × 4 (200-400 mesh) was used to fractionate the uranium and thorium isotopes from the solutions.

The uranium fraction was obtained by passing 200 mL of 1M hydrochloric acid (HCl) while the thorium fraction was obtained by passing 200 mL of 2M sulphuric acid (H_2SO_4). Both fractions were then purified with an anion column after precipitated with ammonium hydroxide (NH_3OH). Iron (Fe) in both fractions was removed with 30 mL of 7.5M HNO_3 using an anion column Bio-Rad AG 1 × 8 (50-100 mesh) and then the purified uranium was obtained with 50 mL of 0.5 M HCl while the purified thorium was obtained by using 6 M HCl. The purified uranium and thorium fractions were then electrodeposited onto silver disks for two hours at 200-250 mA with 15 V and then determined using an alpha spectroscopy (CANBERRA's Alpha Analyst) for 48 hours. The accuracy of the methods was validated with triplicate of NIST standard reference material (SRM) 4357 and recovery of ^{234}U and ^{238}U are 84.31 ± 7.68% and 87.02 ± 9.97%, respectively, while for ^{230}Th and ^{232}Th, the recovery is 89.36 ± 9.45 and 79.93 ± 18.03%, respectively.

The organic carbon was estimated based on the loss of ignition (LOI) method described by Heiri et al. (2001). The 0.5 g of dried sample was heated for 4 hours at 550°C. TOC content in the sediment was estimated to be 58% of the total organic matter (Sutherland 2001). The porosity of sediment was determined based on the procedure described by Breitzke (2006).

3. Results and Discussion

Depth profile of uranium and thorium isotopes in sediment core

Activity of ^{234}U and ^{238}U

The activities of ^{234}U and ^{238}U from three Malaysian ports (Kota Kinabalu, Labuan and Klang) were in the range of 0.41 ± 0.09 dpm/g to 6.45 ± 0.66 dpm/g and 0.38 ± 0.09 dpm/g to 5.99 ± 0.63 dpm/g, respectively. The profiles of ^{234}U and ^{238}U in sediment core layers were categorized based on the porosity profile of the sediment core as shown in Fig. 2. Kota Kinabalu port and Labuan port show a similar porosity profile. The porosity of the top layer (< 20) displays erratic trends and is in contrast to the porosity of sediment core at the middle layer, while a decrease in porosity was measured from the bottom layer. Thus, the depth profile of uranium isotopes at Kota Kinabalu port and Labuan port were divided into three parts that are top (0 - 20 cm), middle (24 - 87 cm) and bottom (> 97 cm), while the depth profile of uranium isotopes at Klang port was divided into two parts that are top (0 - 24 cm) and bottom (> 27 cm) because the sediment core was shorter than at Labuan port and Kota Kinabalu port (Fig. 2). The result of ^{234}U and ^{238}U at these ports in sediment core were presented in Fig. 3 (b and c), Fig. 4 (b and c) and Fig. 5 (b and c).

The profile of ^{234}U and ^{238}U at Labuan port (Fig. 3) and Kota Kinabalu port (Fig. 4) reveal erratic values at the top layer, followed by an increase from 20 cm to 40 cm then decrease

Table 1. Location, water depth and length of core sediment at the study area

Location	Area	Coordinates	Water Depth (m)	Length of core (cm)
Kota Kinabalu Port	East Malaysia	Lat. 06°00'884"N Long 116°04'957"E	19.7	145
Labuan Port	East Malaysia	Lat. 05°16'028"N Long 115°14'779"E	10.2	145
Klang Port	West Malaysia	Lat. 03°55'8"N Long 101°21'12.7"E	2.3	75

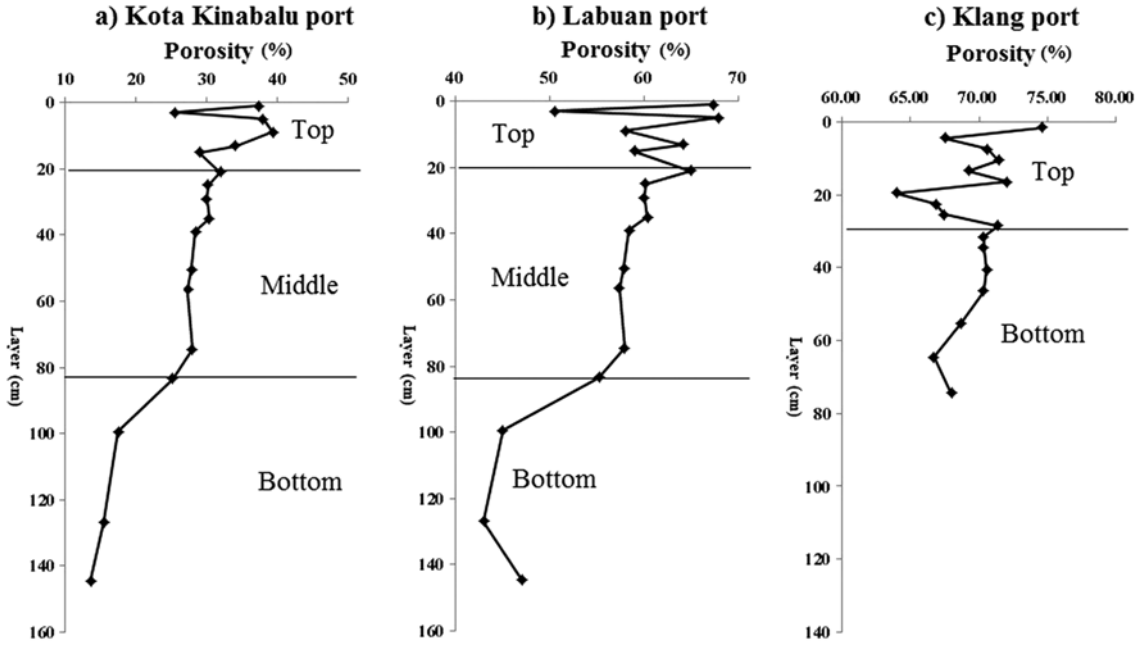

Fig. 2. Porosity profile of a) Kota Kinabalu port, b) Labuan port and c) Klang port

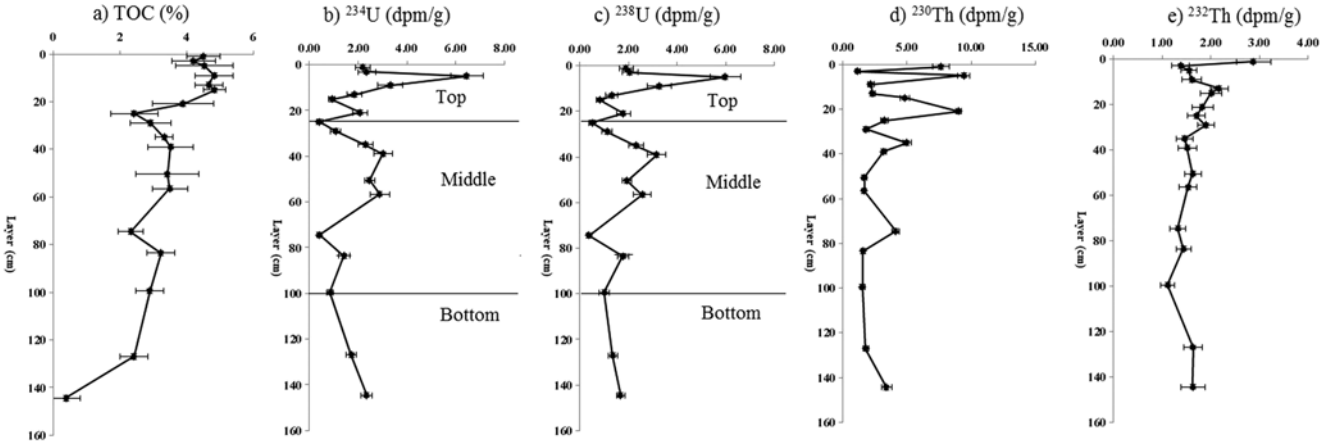

Fig. 3. Vertical profile of a) total organic carbon (TOC), b) ^{234}U, c) ^{238}U, d) ^{230}Th and e) ^{232}Th in sediment core from Kota Kinabalu port

from 40 to 80 cm and an increase at the bottom of sediment core. Uranium isotopes at Klang port show consistent values from surface towards the bottom of sediment core. The erratic values at the top layer might be caused by the bioturbation process that occurs at the top of the sea area studied. Bioturbation refers to particle mixing within unconsolidated sediments through the activities of biological organisms, most commonly at, or close to the water-sediment interface. Bioturbation activity can increase the size of the effective sediment-water interface contributing to enhanced chemical fluxes between the sediment and the water column (Lagauzère et al. 2009; Volkenborn et al. 2007). Coastal sediments support large populations of benthic organism (Volkenborn et al. 2007). Benthic organisms can mix the uranium in sediment and bring it upward to the sediment-water interface, where more oxidizing conditions lead to the remobilization of authigenic uranium and its loss to bottom waters (Zheng et al. 2002). These mixing processes will affect the vertical profile of uranium isotopes at the top layer of sediment core. High and widely varied porosity values at the top layer of sediment core from the study area strengthen the effect of bioturbation on the uranium profile at the top.

The increasing and decreasing trend at the middle of sediment core from Labuan and Kota Kinabalu port might

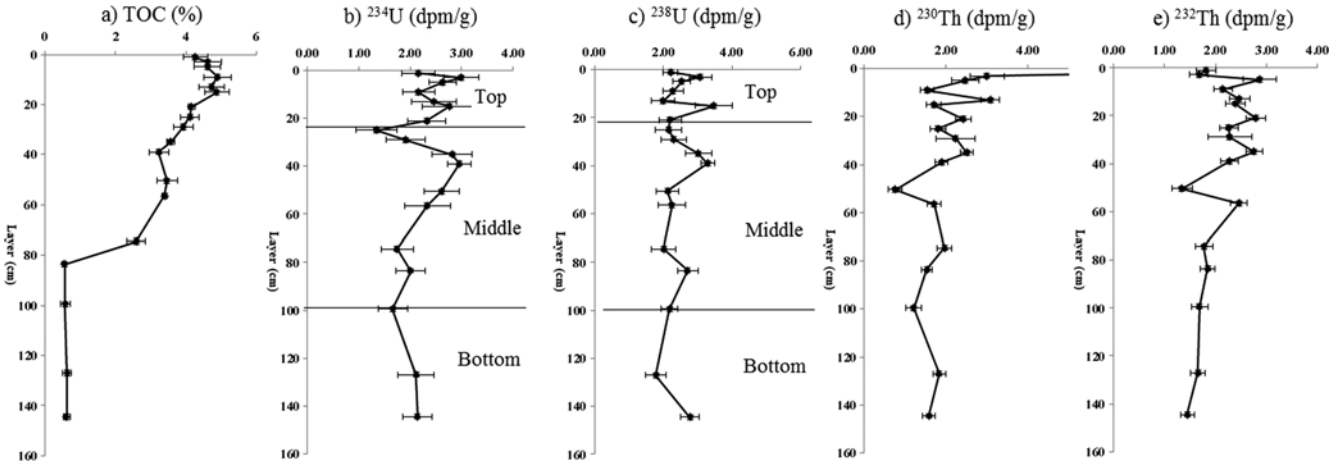

Fig. 4. Vertical profile of a) total organic carbon (TOC), b) ^{234}U, c) ^{238}U, d) ^{230}Th and e) ^{232}Th in sediment core from Labuan port

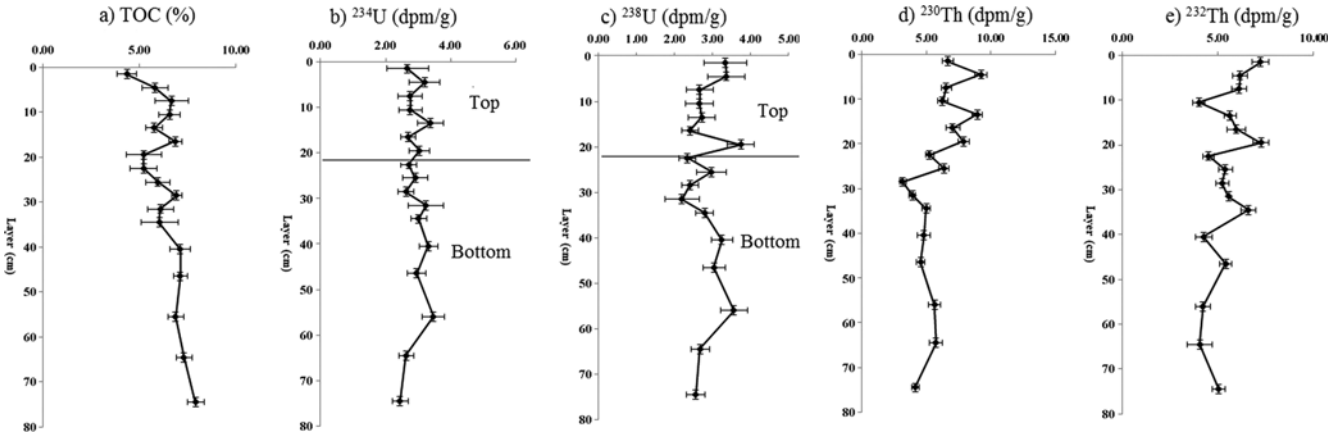

Fig. 5. Vertical profile of a) total organic carbon (TOC), b) ^{234}U, c) ^{238}U, d) ^{230}Th and e) ^{232}Th in sediment core from Klang port

be controlled by a major carrier (discussed in the next section) of uranium in these sediments. Uranium is a relatively mobile element due to the high solubility of U (VI) in aqueous complexes. However, it may be precipitated by reduction to U (IV) by organic carbon or incorporated into minerals of detrital origin such zircon, apatite and monazite (Dawood, 2010). The major carrier of uranium from these ports will be discussed in next section. The activity of ^{234}U and ^{238}U at Kota Kinabalu port and Labuan port increases at the bottom of sediment core > 97 cm, which suggest the occurrence of an earlier diagenesis process (Srisukawad et al. 1997).

Activity of ^{230}Th and ^{232}Th

The activity of ^{230}Th and ^{232}Th ranges from 1.39 ± 0.13 dpm/g to 9.84 ± 0.51 dpm/g and 1.11 ± 0.13 dpm/g to 9.22 ± 0.03 dpm/g, respectively. The activity of the ^{230}Th at Kota Kinabalu port as shown in Fig. 3(d) shows fluctuation at the top layer and consistent values at the bottom layer of sediment core. The activity of the ^{232}Th at Kota Kinabalu port decreases slightly from the surface toward the bottom sediment with the range value 1.11 ± 0.13 dpm/g to 2.88 ± 0.51 dpm/g.

The activity of ^{230}Th at Labuan port displays very high values at the surface with 9.84 ± 0.47 dpm/g which might be due to the high scavenging process that occurred at the study area. ^{230}Th produced from the decay of dissolved ^{234}U is promptly removed from the water column by adsorption on settling particles called particle scavenging (Bacon and Anderson 1982). This process will make the activity of ^{230}Th in seawater is nearly four orders of magnitude lower than the activity of its parent ^{234}U (Handerson and Anderson 2003) and the activity of ^{230}Th will increase in surface sediment layer. The activity of ^{232}Th detected at Labuan Port decreases along the sediment core in the range from 2.87 ± 0.35 dpm/g to 1.31 ± 012 dpm/g. The outlier value at 49 - 52 cm might be

because of physical factors such as dredging activities that occur in this area.

The activity of ^{232}Th at Klang port displays consistent values from surface to the bottom sediment with the values ranging from 4.05 ± 0.12 dpm/g to 7.25 ± 0.35 dpm/g. The activity of ^{232}Th at Klang port shows high activity compared to Kota Kinalau and Labuan port. This might be due to the geological differences between Peninsular Malaysia and East Malaysia. Peninsular Malaysia is mainly covered by high thorium-rich and uranium-rich granite rocks, while East Malaysia is underlain by younger tertiary sedimentary rocks (Yii et al. 2009), thus the higher activity of ^{232}Th might be due to the input from granite rock. The origin of uranium and thorium will be explained in the next section.

Origin of uranium and thorium isotopes

Correlation of uranium isotopes and total organic carbon (TOC)

Correlations between uranium and TOC were used to predict the origin of uranium (Table 2). The correlations between uranium isotopes and TOC at top layer did not reveal a strong positive correlation for all sediment cores. This condition might be due to the bioturbation process. This process can influence physical and geochemical properties of the sediment. Mermillod-Blondin et al. (2004) showed that the presence of bioturbating organism in the sediment can decrease approximately 30% of particulate organic matter. The higher anaerobic consumption of particulate organic matter with tubificids worms resulted in a significantly higher loss of sediment organic carbon (Mermillod-Blondin et al. 2004) Bioturbation also inhibit the preservation of authigenic uranium in top sediment because a large fraction of authigenic uranium precipitated within the sediment is periodically remobilized by the action of bioturbating organism (Zheng et al. 2002).

A strong negative correlation was measured between ^{234}U and TOC (r^2 = -0.811, $p < 0.05$) at top layer of sediment core from Klang port. This suggests that, organic carbon may not act as an important carrier for uranium isotopes in this area. Uranium might be incorporated into minerals of detrital origins such as zircon, apatite and monazite. Compared to Labuan port, which is dominated with sedimentary rock, Klang port is surrounded with igneous rock that contain high activity of uranium and thorium isotopes.

The results from Kota Kinabalu core show a significantly strong positive correlation between ^{234}U and TOC (r^2 = 0.949, $p < 0.01$) and ^{238}U and TOC (r^2 = 0.946, $p < 0.01$) from the samples from the middle of sediment core. These suggest that the distribution of uranium isotopes in this area is controlled by organic carbon. In the water column, the organic carbon can act as a carrier to convert U(VI) to U(IV) which subsequently scavenged and settled down. Adsorption of uranium to organic carbon with acidic functional group may occur through ion exchange and complexation processes that result in the formation of stable U(IV) (Borovec et al. 1979). These results suggest that the major contribution of uranium to the sediment of Kota Kinabalu port is by sorptive uptake of authigenic uranium from the water column. The ratio of ^{234}U/^{238}U, which will be discussed later, further support this suggestion.

The weak correlation of ^{234}U and ^{238} U with TOC along sediment core at Labuan port suggests that removing of

Table 2. Pearson's correlation coefficient of total organic carbon (TOC) with ^{234}U and ^{238}U at Kota Kinabalu, Labuan and Klang port

Correlations							
		Kota Kinabalu Port		Labuan Port		Klang Port	
		^{234}U (dpm/g)	^{238}U (dpm/g)	^{234}U (dpm/g)	^{238}U (dpm/g)	^{234}U (dpm/g)	^{238}U (dpm/g)
TOC (%) at the top layer of sediment core	Pearson Correlation	.025	.057	-.095	.173	-.811*	.184
	Sig. (2-tailed)	.957	.904	.839	.710	.027	.693
	N	7	7	7	7	9	9
TOC (%) at the middle of sediment core	Pearson Correlation	.949**	.946**	.045	-.180	n.a	n.a
	Sig. (2-tailed)	.000	.000	.916	.670		
	N	8	8	8	8		
TOC (%) at the bottom of sediment core	Pearson Correlation	-.905	-.940	.517	-.080	-.197	.278
	Sig. (2-tailed)	.279	.222	.654	.949	.585	.437
	N	3	3	3	3	8	8

**: Correlation is significant at the 0.01 level (2-tailed).
*: Correlation is significant at the 0.05 level (2-tailed).
n.a; not available, sediment core from Klang port have divided only into two section (top and bottom).

Table 3. Pearson's correlation coefficient of total organic carbon (TOC) with ^{230}Th and ^{232}Th at Kota Kinabalu, Labuan and Klang port

Correlations										
		Kota Kinabalu Port			Labuan Port			Klang Port		
		TOC (%)	^{230}Th (dpm/g)	^{232}Th (dpm/g)	TOC (%)	^{230}Th (dpm/g)	^{232}Th (dpm/g)	TOC (%)	^{230}Th (dpm/g)	^{232}Th (dpm/g)
TOC (%)	Pearson Correlation	1	.279	.368	1	.325	0.316	1	-.475	-.599*
	Sig. (2-tailed)		.263	.133		.188	.222		.054	.011
	N	18	18	18	18	18	18	17	17	17
^{230}Th	Pearson Correlation	.279	1.000	.396	.325	1	0.722**	-.475	1	.388
	Sig. (2-tailed)	.263		.103	.188		.000	.054		.124
	N	18		18	18	18	18	17	17	17
^{232}Th	Pearson Correlation	.368	.396	1.000	0.316	0.722**	1	-.599*	.388	1
	Sig. (2-tailed)	.133	.103		.222	.000		.011	.124	
	N	18	18		18	18	18	17	17	17

**Correlation is significant at the 0.01 level (2-tailed).
*Correlation is significant at the 0.05 level (2-tailed).

detrital uranium from sea water to sediment is a major part of activity in this area since the activity of the detrital component is inversely proportional to organic input (Ramli 1997). A previous study done by Hasiaha et al. (2013) suggests that Labuan consists of sedimentary rock such as coal and a small fraction of limestone. This strengthens the idea that uranium in Labuan sediment core might originated from coal sedimentary rock which shifted from terrestrial sources into the river and finally was deposited in the marine port. The ratio of ^{234}U/^{238}U, which will be discussed later, further supports this suggestion.

Correlation of thorium isotopes and total organic carbon (TOC)

Table 3 shows Pearson's correlations matrices for the activities of ^{232}Th, ^{230}Th and TOC in sediment cores from three marine ports in Malaysia. The regression analysis shows that there are varied correlation between thorium isotopes and TOC i.e. medium and weak. The weak correlation was identified at Kota Kinabalu and Labuan ports for both ^{232}Th and ^{230}Th, while medium correlation was identified at Klang port for both ^{232}Th and ^{230}Th (Table 3). These results suggest that, organic carbon may not act as a carrier for thorium isotopes.

Significantly high positive Pearson's correlation between ^{232}Th and ^{230}Th ($r^2 = 0.722$, $p < 0.01$) was obtained from Labuan port. This correlation was obtained after removal of the extreme values caused by high scavenging processes at the surface of sediment. This result suggests that, both radionuclides might originate from the same sources. The weak correlation between thorium isotopes and TOC coupled with high positive correlation between ^{232}Th and ^{230}Th suggest that thorium isotopes in sediment core off Labuan have probably been retained by detrital particles which form the core sediment. This support the value of using uranium isotopes and TOC correlation and suggest that coal rock which are abundant at Labuan island are the main sources of uranium and thorium isotopes at Labuan port.

Ratio of ^{234}U/^{238}U and ^{230}Th/^{232}Th

The results of ^{234}U/^{238}U support previous suggestions about the sources of uranium in the study area. In Fig. 6 (a), the ^{234}U/^{238}U in the upper layer of Kota Kinabalu port shows the same values with the normal ratio of ^{234}U/^{238}U in sea water (1.14 to 1.20) (Scott 1982; Gascoyne 1982). This result supports the earlier suggestion that the reduction process that occurs in this area is where authigenic uranium containing U (VI) is directly converted to U (IV) by organic carbon and it's scavenging into the sediment.

On the other hand, most of the ^{234}U/^{238}U values in the upper layer of Labuan port show < 1.14 as shown in Fig. 6 (b). This result suggests that the reason why this area has more ^{238}U might be because it originate from detrital sources such as coal rock. Furthermore, coal rock contains high ^{238}U activity, which about 20 Bq/kg (UNSCEAR 1993). Thus, high ^{238}U activity in this area might be contributed by the abundance of coal Labuan Island. Most of the ^{234}U/^{238}U ratios at Klang port show < 1.14. High ^{238}U activity might be explained by the abundance of igneous rocks in this area.

The ^{230}Th/^{232}Th activity ratios in Kota Kinabalu port are in the range of 0.84 ± 0.17 to 6.09 ± 0.72 (Fig. 7a). Normal values

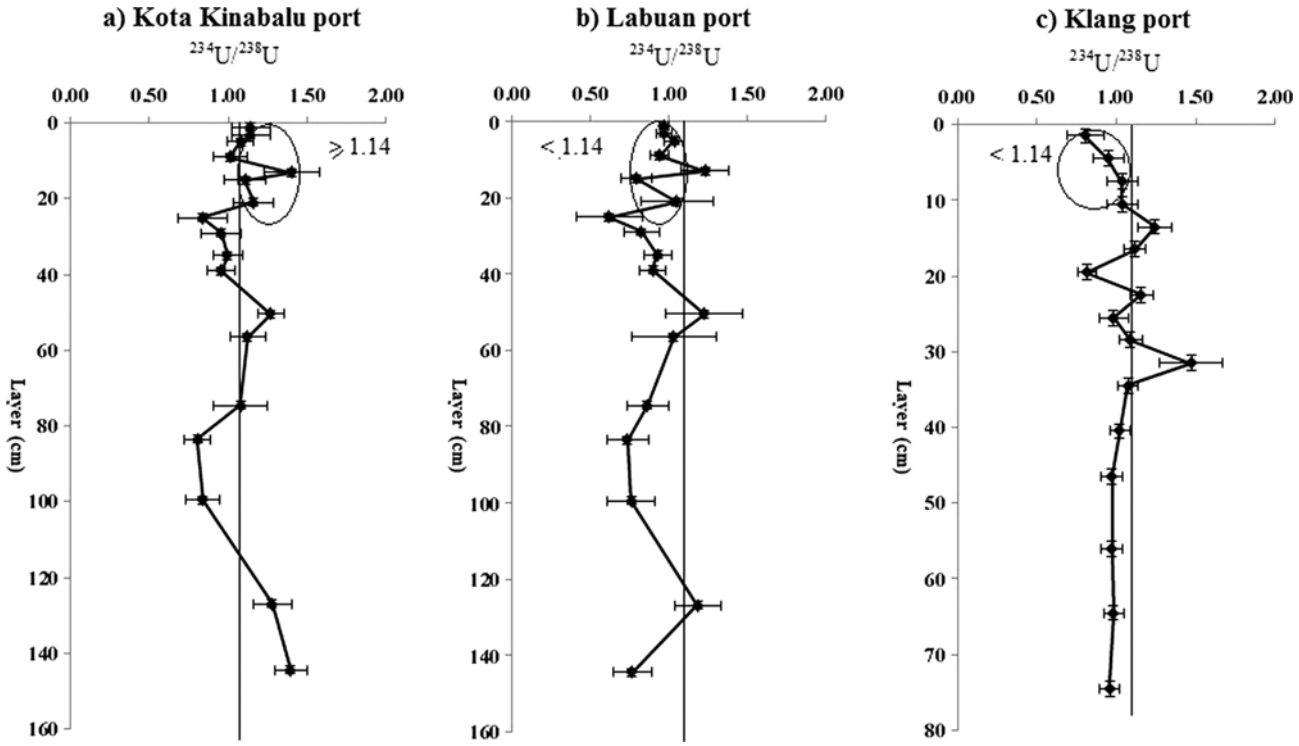

Fig. 6. Activity ratio of $^{234}U/^{238}U$ in core sediments from a) Kota Kinabalu port, b) Labuan port and c) Klang port. The vertical line is the normal ratio of $^{234}U/^{238}U$ in sea water which is 1.14 (Scott 1982; Gascocyne 1982)

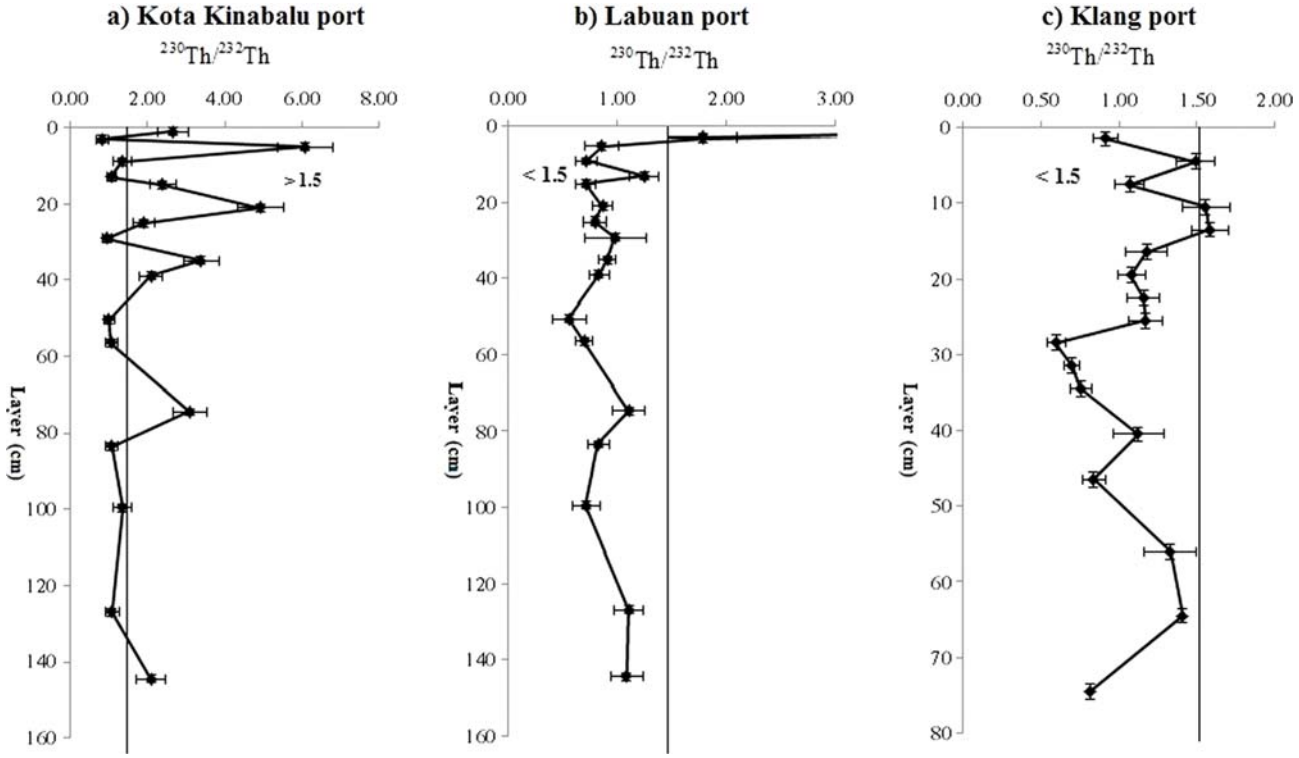

Fig. 7. Activity ratio of $^{230}Th/^{232}Th$ in core sediments from a) Kota Kinabalu port, b) Labuan port and c) Klang port. The vertical line value is 1.5, the ratio over than 1.5 was considered polluted by ^{230}Th as described by San Miguel et al. (2004)

of $^{230}Th/^{232}Th$ range between 0.8-1.5, and values more than 1.5 indicate that contamination had occurred in the study area (San Miguel at al. 2004). High values of $^{230}Th/^{232}Th$ in most layers of the sediment core from Kota Kinabalu port might possibly indicate anthropogenic input of ^{230}Th in recent years. This high activity (6.09 ± 0.72) is within the same order of magnitude with the ratio obtained from contaminated core sediment at Hueleva estuary due to plant fertilizer releases (San Miguel et al. 2004). The continued expansion of oil-palm cultivation in Sabah requires significant amounts of nutrient as fertilizer. Yii et al. (2009) has reported on the high value of ^{40}K detected at the Sabah coastal area which was partly caused by the usage of fertilizers in plantations. The main chemicals in fertilizers are nitrogen, phosphorus, and potassium. Phosphorus is from phosphate rock which contains high ^{230}Th (200-16000 mBq/g). The leakage of phosphorus to Kota Kinabalu port is possible due to the geographical landscape of the plantation area which is closer to the sea. This further confirms the anthropogenic sources of ^{230}Th at Kota Kinabalu port. The low range activity ratio of $^{230}Th/^{232}Th$ at Labuan and Klang port, as shown in Fig. 7(b) and Fig. 7(c), supports the suggestion that the origin of uranium and thorium in Labuan and Klang port might be from detrital origins.

4. Conclusions

The profile activities and origin of uranium and thorium isotopes were successfully determined from sediment cores collected from Kota Kinabalu, Labuan and Klang port. The major inputs of uranium at Kota Kinabalu port is by sorptive uptake of authigenic uranium from the water column, whereas most of the uranium in Labuan and Klang port is of detrital origin. Kota Kinabalu port has received anthropogenic input of ^{230}Th which might be run-off from the fertilizers used in plantations adjacent to the Kota Kinabalu port, whereas the major input of thorium isotopes to Labuan and Klang ports are of detrital origin. These findings support the use of TOC and isotope ratios to determine the origin of uranium and thorium. The ratio of $^{234}U/^{238}U$ proved to be a proxy for the flux of particulate organic carbon to the marine area. Further research, specifically to investigate the relationship between uranium and thorium isotope with other elements such as Calcium (Ca), Barium (Ba) and Zirconium (Zr) in larger sediment core samples is strongly encouraged. This will help to strengthen the evidence concerning the origin of these isotopes and explain how they interact with others elements in marine ecosystems.

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References

Anderson RF, Kumar N, Mortlock RA, Froelich PN, Kubik P, Dittrich-Hannen B, Suter M (1998) Late-Quaternary changes in productivity of the Southern Ocean. J Marine Syst **17**(1-4):497-514

Anderson PS, Wasserbug GJ, Chen JH, Papanastassiou DA, Ingri J (1995) ^{238}U, ^{234}U and ^{232}Th-^{230}Th in the Baltic Sea and in river water. Earth Planet Sci Lett **130**(1-4):217-234

Bacon MP, Anderson RF (1982) Distribution of thorium isotopes between dissolved and particulate forms in the deep ocean. J Geophys Res **87**(3):2045-2056

Bednar AJ, Medina VF, Ulmer-Scholle DS, Frey BA, Johnson BL, Brostoff WN, Larson SL (2007) Effects of organic matter on the distribution of uranium in soil and plant matrices. Chemosphere **70**(2):237-247

Borovec Z, Kribek B, Tolar V (1979) Sorption of Uranyl by Humic Acids. Chem Geol **27**:39-46

Breitzke M (2006) Physical properties of marine sediments. In: Schulz H (ed.) Marine geochemistry. 2nd edn. Springer-Verlag, Berlin, pp 28-69

Cheng H, Edwards RL, Hoff J, Gallup CD, Richards DA, Asmerom Y (2000) The half-lives of uranium-234 and thorium-230. Chem Geol **169**:17-33

Choy CC, Ahmad Z, Mohamed CAR (2007) Vertical profile of ^{210}Pb in the sediment core of Kuala Selangor, Malaysia. Malaysian J Anal Sci **11**(1):274-279

Dawood YH (2010) Factors controlling uranium and thorium isotopic composition of the streambed sediments of the River Nile, Egypt. JAKU: Earth Sc **21**(2):77-103

Gascoyne M (1982) Geochemistry of the actinides and their daughters. In: Ivanovich M, Harmon RS (eds) Uranium series disequilibrium: applications to environmental problems. Oxford University Press, New York, pp 35-41

Handerson GM, Anderson RF (2003) The U-series toolbox for paleoceanography. Rev Mineral Geochem **52**:493-531

Hasiaha W, Lee CP, Gou P, Shuib MK, Nga TF, Albaghdady AA, Mislana MF, Mustapha KA (2013) Coal bearing strata of Labuan: mode of occurences, organic petrographic characteristics and

stratigraphic associations. J Asian Earth Sci **76**:334-345

Heiri O, Lettter AF, Lemcke G (2001) Loss an ignition as a method for estimating organic and and carbonate content in sediment: reproducibility and comparability of result. J Paleolimnol **25**:101-110

Lagauzère S, Boyer P, Stora G, Bonzom J (2009) Effects of uranium-contaminated sediments on the bioturbation activity of Chironomus riparius larvae (Insecta, Diptera) and Tubifex tubifex worms (Annelida, Tubificidae). Chemosphere **76**:324-334

McManus J, Berelson WM, Severmann S, Poulson RL, Hammond DE, Klinkhammer GP, Holm C (2006) Molybdenum and uranium geochemistry in continental margin sediments: Paleoproxy potential. Geochim Cosmochim Acta **70**(18):4643-4662

Mermillod-Blondin F, Jean-paul G, Gerino M, Gaston D, Jacques J, Michel CDCT (2004) Relative influence of bioturbation and predation on organic matter processing in river sediments: a microcosm experiment. Freshwater Biol **49**:895-912

Mohamed CAR, Ramli KNM, Ahmad Z (2006) Distribution of ^{234}U and ^{238}U in Sungai Selangor, Peninsular of Malaysia. J Appl Sci **6**:562-566

Mohamed CAR, Mahmood ZW, Ahmad Z (2008) Recent sedimentation of sediments in the coastal waters of Peninsular Malaysia. Int J Pollut Res **27**(1): 27-36

Porcelli D, Anderson PS, Wasserburg GJ, Ingri J, Baskaran M (1997) The importance of colloids and mires for the transport of uranium isotopes through the Kalix River watershed and Baltic Sea. Geochem Cosmichim Acta **61**(19):4095-4113

Ramli AT (1997) Environmental terrestrial gamma radiation dose and its relationship with soil type and underlying geological formations in Pontian district, Malaysia. Appl Radiat Isotopes **48**:407-412

Robinson L, Noble T, Mcmanus J (2008) Measurement of adsorbed and total ^{232}Th/^{230}Th ratios from marine sediments. Chem Geol **252**(3-4):169-179

San Miguel EG, Boliver JP, Garcia-Tenorio R (2004) Vertical distribution of Th-isotope ratios, ^{210}Pb, ^{226}Ra and ^{137}Cs in sediment cores from an estuary affected by anthropogenic releases. Sci Total Environ **318**:143-157

Scott MR (1982) The chemistry of U- and Th-series nuclide in the rivers. In: Ivanovich M (ed) Uranium series disequilibrium: applications to environmental problems. Oxford University Press, New York, pp 181-201

Srisukawad K, Porntepkasemsan B, Nouchpramool S, Yamkate P, Carpenter R, Peterson M, Hamilton T (1997) Radionuclide activities, geochemistry, and accumulation rates of sediments in the Gulf of Thailand. Cont Shelf Res **17**(8):925-965

Sutherland RA (1998) Loss on ignition estimates of organic matter and relationships to organic carbon in fluvial bed sediments. Hydrobiologia **389**:153-167

Theng TL, Mohamed CAR (2005) Activities of ^{210}Po and ^{210}Pb in the water column at Kuala Selangor, Malaysia. J Environ Radioactiv **80**:273-286

United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) (1993) Sources and effects of ionizing radiation: Report the general assembly, with annexes. UNSCEAR, New York

Volkenborn N, Hedtkamp SIC, Beusekom JEE, Van Reise K (2007) Effects of bioturbation and bioirrigation by lugworms (Arenicola marina) on physical and chemical sediment properties and implications for intertidal habitat succession. Estuar Coast Shelf Sci **74**:331-343

Yii MW, Zaharudin A, Abdul-Kadir I (2009) Distribution of naturally occurring radionuclides activity concentration in East Malaysian marine sediment. Appl Radiat Isotopes **67**:630-635

Zal'Uyun WM, Mohamed CAR, Ahmad Z, Ishak AK (2011) Intercomparison of techniques for estimation of sedimentation rate in the Sabah and Sarawak coastal waters. J Radioanal Nucl Chem **287**:255-260

Zheng Y, Anderson RF, Geen AV, Fleisheri QM (2002) Remobilization of authigenic uranium in marine sediments by bioturbation. Geochem Cosmochim Acta **66**(10):1759-1772