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Determination of Estuarine Sedimentation Rates using $^{230}Th_{excess}$ and $^{230}Th_{excess}/^{232}Th$ Ratio Methods in the Paka Estuary, Malaysia

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ABSTRACT

The vertical profiles of $^{230}Th_{excess}$ and $^{230}Th_{excess}/^{232}Th$ in a sediment core have been used to determine the sedimentation rates of Terengganu River estuary, Malaysia. Applying the $^{230}Th_{excess}$ and $^{230}Th_{excess}/^{232}Th$ method, U and Th isotopic involved complete dissolution of the samples, followed by separation on anion exchange, average sedimentation rates of 1.02 and 1.01 cm $year^{-1}$ were obtained, respectively. The results of the accretion rate obtained from the both methods are consistent with average sedimentation rates of 1.01 cm $year^{-1}$. Assuming that the accretion rate values are accurate, this may imply that the sediments at the deepest core at 14 cm were deposited during the last 14.2 years ago.

Key words: ^{230}Thexcess, $^{230}Th_{excess}/^{232}Th$, sediment core, isotopic, anion exchange, accretion rate

INTRODUCTION

Recently, much less effort has been focused on estuaries, embayment and coastal waters. It is known that many of these estuaries are heavily or moderately eutrophied (Weckstrom, 2006) but due to the lack of sufficient monitoring data there is no evidence whether the small and shallow estuaries are naturally eutrophic or to the degree they are affected by cultural eutrophication (Vaalgamaa and Conley, 2008). Coastal sediments are important sinks for a wide spectrum of contaminants (Grant and Middleton, 1993; Lee and Cundy, 2001). Human influence has been successfully traced using sediment geochemistry (Cundy *et al*., 1997; Chagué-Goff *et al*., 2000).

Estuarine areas where freshwater encounters seawater are characterized by a lateral variation in salinity and can represent as a transfer box for the sediments between land and the open ocean (Förstner *et al*., 1990; Carvalho, 1995). Estuarine sediments also act as a temporary store of inorganic and organic materials. In high productive system, the decomposition of organic matter consumes oxygen and the sediment becomes anoxic. The reduced conditions cause chemical transformations of metals and important anions in the sediment, as phosphate, ammonium, iron, manganese and bicarbonate could be released to the water and production increases in an amplified positive feedback (Hinga, 1990; Rubio *et al*., 2003; Chau and Jiang, 2004).

Despite the acceptance that the estuary is an important sink for sediments, few studies have addressed sediment accretion using the ^{210}Pb, ^{137}C, ^{230}Th and ^{7}Be (DeMaster, 1981; Andersson *et al*., 1995; Peter *et al*., 2000). One possible way to date sediments is with the $^{230}Th_{excess}$ (non-supported

^{230}Th in sediments) method which can be used to date sediments up to 300 000 years old. The $^{230}Th_{excess}$ method relies on a constant production rate of ^{230}Th from the radioactive decay of dissolved ^{234}U in the water column (Walter *et al*., 2000; Cheng *et al*., 2000). The measurement of ^{230}Th concentrations in sediments provides one method of developing accretion histories. ^{230}Th is valuable tracer of the processes whereby reactive elements are scavenged from seawater (Clulow *et al*., 1998). These isotopes are produced in seawater by the radioactive decay of dissolved uranium, which has a long residence time of about 4×10^5 years and uniform distribution in the oceans (Ku and Broecker, 1965). Thus, ^{230}Th is produced at constant rates throughout the oceans. Following their production in seawater, ^{230}Th is rapidly hydrolyzed and subsequently removed to sediments on a time scale of a few decades in the deep ocean and weeks to months in surface water, transported to some depositional sink. The aim of this study was to determine the accretion rate of sediment which can give detailed estimated information on both the age of the sediments and the paleoceanographic conditions in the study area.

MATERIALS AND METHODS

Description of the study area: The study site area is near to the Paka town, the southern city of Terengganu, Malaysia (Fig. 1). A sediment core sample was collected in the estuary using a piston corer in August 2004. In recent years, the study area especially for the first km along the river has been heavily impacted by discharges from municipal and industrial outflows. This was due to the rapid development of the area via expansion of the industrialization area as well as the increase in population. Steel and petro-chemicals are the main industry in the area and is the catalyst for other supportive industries to develop around the same area. The outfall of Paka River to estuary was usually influenced by the monsoon seasons which prevailed from October to March.

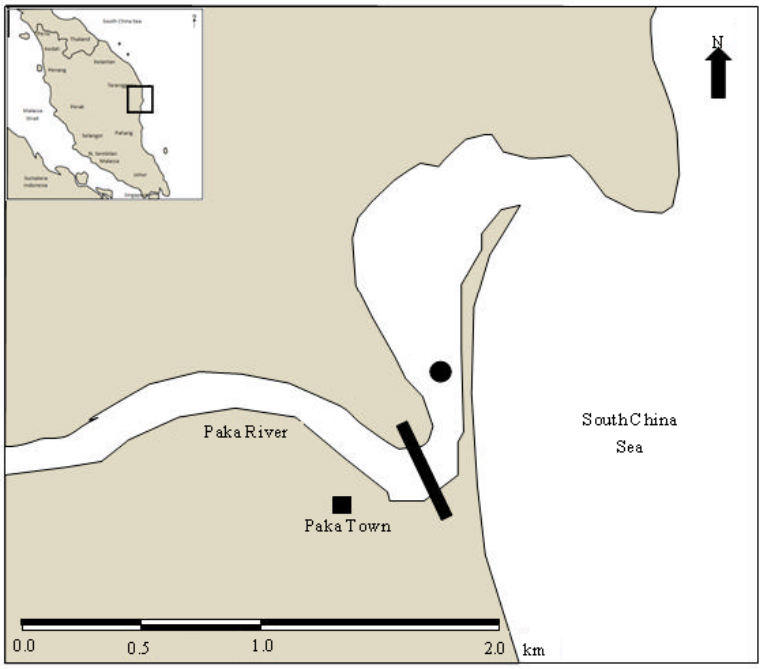

Fig. 1: The location of core (•) in the Terengganu Estuary, Malaysia

Being, a river with smaller discharge rate, the Paka river morphology and hydrological conditions are much influenced by the seawater, even though the maximum tidal range of the area almost exceeds 2 m, thus making the estuary as a microtidal estuary. In this study a 50 cm sediment core was collected with a core sampler in the Paka estuary (Fig. 1). The core was cut into segments of approximately 5 cm interval, labeled and stored until analysis in the laboratory.

Analytical method for ^{232}Th and ^{230}Th.: The analytical method of ^{230}Th and a total Th (^{232}Th) in the sample was carried out according to the published method (Tsunogai *et al.*, 1980; Taguchi *et al.*, 1989; Veeh *et al.*, 2000) with some modifications. An inductively coupled plasma mass spectrometer (ICP-MS) was used, for the quick and precise determination of Th in the digested sediment. The method involved heating 1-2 g of dried sediment and digesting it with a mixture of solution of concentrated HF, HNO_3 and HCl. The solution containing Th was heated to make the solution clear before being treated with anion and cation exchange resins for the separation and purification. The effluent containing Th was then heated to dryness and finally dissolved in 5% HNO_3. The concentration of ^{230}Th was then measured with a fast and sensitive ICP-MS. The precision assessed by the replicate analyses was less than 3%. The accuracy was also examined by analyzing duplicately a Canadian Certified Reference Materials Project standard (DL-1a) and the results coincided with the certified values within a difference of ±3%.

RESULTS

$^{230}Th_{excess}$ was used to determine the accretion rates of the study areas (Suman and Bacon, 1989; Scholten *et al.*, 1994; Thomson *et al.*, 1999). The amounts of $^{230}Th_{excess}$ are calculated using the following equation:

$$^{230}Th_{excess} = {}^{230}Th_{total} - (0.8\times{}^{232}Th_{total}) - {}^{234}U\,(1-\exp\{-\lambda^{230}t\}) \quad (1)$$

where, $^{230}Th_{total}$ and $^{232}Th_{total}$ are the measured concentrations of ^{230}Th and ^{232}Th, respectively and ^{234}U and λ^{230} are the concentration of ^{234}U (of which radioactivity is assumed to be 1.1 times the ^{238}U concentration) and the decay constant of ^{230}Th (9.24×10^{-6} year), respectively. The second term on the right hand side of the equation ($^{232}Th_{total}$) is necessary in order to subtract the lithogenic fraction and the assumed coefficient, 0.8, is a mean activity ratio of ^{230}Th/^{232}Th for the lithogenic fraction as reported by Anderson (1982). The third term (^{234}U (1 - exp {- λ^{230}t}) is for the correction of ^{230}Th produced from ^{234}U in the sediments, which is necessary because ^{230}Th is produced from authigenic U contained in the sediment.

The determination of average sedimentation rate is based on the assumption that the $^{230}Th_{excess}$ is incorporated into the sediments with a constant rate (Osmond, 1979; Ku *et al.*, 1968). For the estimation of the sedimentation rate, both concentrations of $^{230}Th_{excess}$ and the $^{230}Th_{excess}$ /^{232}Th ratio were used. The later method was used in order to minimize the limitation associated with the $^{230}Th_{excess}$ that were produced by the decay of the uranium. Assuming, if the value of $^{230}Th_{excess}$ derived from Eq. 1 is correct, the radioactivity of $^{230}Th_{excess}$ in sediment core which decrease exponentially with depth and the sedimentation rates can be calculated from the following equation:

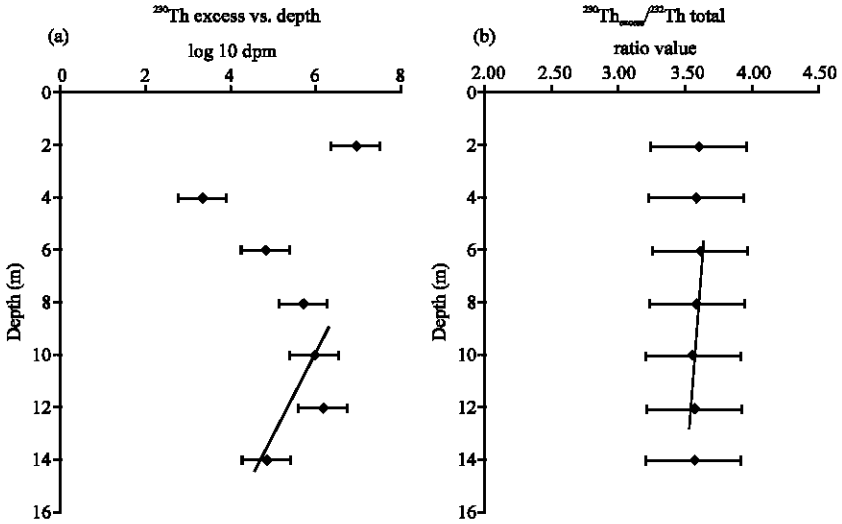

Fig. 2: (a) The concentration of $^{230}Th_{excess}$ and (b) ratio $^{230}Th_{excess}/^{232}Th$ versus depth

$$S=-\lambda^{230}/b \quad (2)$$

where, b is a gradient of the 'best-fit' curve in the plot of log concentrations of $^{230}Th_{excess}$ against depth (cm). In this study the concentrations of $^{230}Th_{excess}$ and the ratio value were plotted linearly with some points displayed anonymous values. As shown in Fig. 2a and b, the calculated sedimentation rates for $^{230}Th_{excess}$ and $^{230}Th_{excess}/^{232}Th$ were 1.01 and 1.02 cm year^{-1}, respectively.

DISCUSSION

By the estuary definition, estuaries are influenced by the marine and freshwater systems. Within any one estuary, the importance of marine versus freshwater influence varies both spatially and temporally. In Paka River, natural variations in freshwater flow play a significant role in influencing suspended sediment levels, siltation rates, bed composition and the position of estuary channel. However, marine influences are also important in supplying sediment to the estuary and suspending sediments through tidally generated currents and wave disturbance.

The results of the study give us a better understanding of the controls on deltaic sedimentation in the study area, which will be useful for evaluating recent deltaic morphological changes, accumulation and erosion budgets in relation to environmental modification at human and catchment dimension (Goodbred and Kuehl, 1998; Syvitski *et al*., 2005). The sedimentation rate recorded in this study was generally comparable to the values reported by other scientist at the Huelva Estuary, Spain (San Miguel *et al*., 2004), Yangtze Estuary (Chen *et al*., 2004) and in Palmones River (Rubio *et al*., 2003). However, the sedimentation rate obtained was relatively much higher when compared with other estuaries such as Rother River and Culm River (Zwoliñski, 1992). Our higher value can be explained by the geographical position of our study area, which is located close to the mouth of the estuary where the 2 main rivers meet, allowing more fine sediment to be deposited. The tides also play a significant role in transporting sediments offshore into the estuary, thus the offshore materials consisting of mostly fine sediments would also be transported into the estuary but only little would reach further upstream due to the opposing river currents. Assuming the sedimentation rate values for the both methods were accurate, the age of sediment at the deepest core at 14 cm were estimated to be 101 and 102 years, respectively.

CONCLUSION

The application of $^{230}Th_{excess}$ and $^{230}Th_{excess}$ / ^{232}Th in river shows the similar trend of radionuclide decay behavior although there was some anonymous existence in the graph. This anonymous somehow assisting in determining the mixing layer of the core sample. The variations in $^{230}Th_{excess}$ activities could be caused by bioturbation in the core as well the sedimentation rates. In this future study, the application geochronology method of ^{210}Pb could be reference in establishing the method of $^{230}Th_{excess}$ and $^{230}Th_{excess}/^{232}Th$ to estimate the sedimentation rates in the river and estuary.

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