^{234}U and ^{238}U Isotopes in the Marine Sediment of Kuala Selangor, Selangor, Malaysia

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ABSTRACT

Vertical profiles of uranium in sediments at river, estuary and near-shore along Sungai Selangor have been studied, where ^{238}U and ^{234}U activities were fluctuated from surface to the deeper layers. Activity ratio of ^{234}U/^{238}U was also fluctuated with value less than 1.14, except surface layers of river and estuary stations. The fluctuated vertical profiles of ^{238}U, ^{234}U and ^{234}U/^{238}U were correlated slightly significant with the contents of organic carbon ($r^2 > 0.1$). The changing value of ^{234}U/^{238}U more than 1.14 in the sediment core was more related to the sediment characteristics. In the estuary sediment, the activity ratios of ^{234}U/^{238}U decreased with depth after 21 cm and vary widely. It was the highest disequilibrium between activities of ^{234}U and ^{238}U isotopes in the near shore sediment. The accumulation of U in the oxic zone was more affected by Fe^{2+} and organic carbon in the anoxic zone. But bacteria also played an important role in an anoxic zone, especially in the estuarine sediment.

ABSTRAK

Profil menegak kandungan uranium dalam sedimen pada sungai, estuari dan berdekatan pantai sepanjang Sungai Selangor telah dikaji, di mana ^{238}*U and* ^{234}*U mempunyai aktiviti berubah-ubah daripada permukaan sehingga lapisan dalam sedimen. Nisbah aktiviti juga berubah-ubah dengan nilai yang kurang daripada 1.14, kecuali lapisan permukaan sedimen daripada sungai dan estuari. Perubahan profil menegak* ^{238}*U,* ^{234}*U and* ^{234}*U/*^{238}*U juga mempunyai korelasi yang agak signifikan dengan kandungan organik karbon (*$r^2 > 0.1$*). Perubahan nilai* ^{234}*U/*^{238}*U yang lebih daripada 1.14 di dalam teras sedimen mempunyai kaitan yang lebih rapat dengan sifatnya. Dalam sedimen estuari, nisbah aktiviti* ^{234}*U/*^{238}*U menurun dengan kedalaman selepas 21 cm dan perbezaan variasi yang agak besar. Ia merupakan ketidak-seimbangan yang paling tinggi di antara aktiviti isotop*

^{234}U dan ^{238}U berdekatan dengan sedimen pantai. Pengumpulan U di zon oksik lebih dipengaruhi oleh Fe^{2+} dan organik karbon di zon anoksik. Tetapi bakteria juga memainkan peranan yang penting di kawasan zon anoksik, terutamanya di sedimen estuari.

Keywords: Uranium; ^{234}U/^{234}U activity ratio; river; estuary; near shore

Introduction

The source of uranium in the marine environment is the atmospheric precipitation as well as terrigenous materials (Skwarzec 1995). In the oxidized seawater, natural U(VI) exists predominantly in the dissolved form of U carbonate anions (Langmuir 1978). Meanwhile, in the reduction areas, the reduction process from U(VI) to U(IV) as well as removal of non- dissolved authogenic U(IV) from water column to sediment (Bonatti et al. 1971).

The evidence of uranium removal in organic-rich marine sediments that accumulating below an anoxic water column have been reported extensively by previous researchers such as Anderson (1985). Such sediments often show a positive correlation between U concentration and organic matter content (Baturin & Kochenov 1973) yet it remains unclear whether this correlation arises through complexation of U(VI) by organic matter or through reduction to U(IV). Anderson (1985) has shown that solid phase U increases with depth below the sediment water interface in Cariaco Trench sediments, and such pattern is consistent with the diffusion of U into sediment, reduction and removal from solution. Other anoxic basins such as the Orca Basin fail to show a similar pattern, possibly due to extensive turbidity deposition and strong density gradient which inhibits U supply by diffusion (Weber & Sackett 1981).

Sediments accumulating below an oxic water column also may show solid phase of U enrichments if the sediments become reduced with depth. Estuarine sediments commonly become reduced near the sediment-water interface and U enrichments in such sediments have been noted in Long Island Sound (Aller & Cochran 1976) and Puget Sound (Carpenter et al. 1984).

Kuala Selangor is a fishing village at Selangor river estuary. It is known for the fireflies, and associate with certain mangrove species (i.e; *Sonneratia caseoloris*) that grows along the river side. Selangor River is one of the major river systems in Selangor and drains into Malacca Straits. Likewise, investigations on tropical river-estuary systems are particularly important because of the higher fluxes of weathered products entering and leaving the estuary. This study has been designed to study the behavior of U in sediment of three systems such as freshwater, brackish water and seawater.

Materials and Methods

Sediment cores were collected from three stations (river, estuary and near shore) along the Selangor River until the Malacca Straits on 21th September 2002 (Fig.1). Sediment samples were segmented at 3 cm interval and stored in the plastic bags for further analyses.

The pH measurement for each segment was determined for identification of respective zones.

In the laboratory, sediment sample was dried in an oven at 80°C for two days and was then sieved into less than 125 µm. The sediment was digested using 15 mL of 9M HCl (Krishnaswami & Sarin 1976; Sarin 1983). About 1 mL of ^{236}U (20.595 dpm/L) was added into 5 g of sediment as chemical yield into glass beaker on the hotplate for 3 hours. After that filter membrane 0.45 µm was used to collect dissolved liquid sample and follow by adding with 50 mL of 7M HCl for uranium purification using an anion exchange column (DOWEX AG1X8, 200 mesh, Cl$^-$) (Krishnaswami & Sarin 1976). Purified liquid plated onto the stainless steel disc at pH 2 using diluted H_2SO_4 (Amin 1970; Borole 1980) and counted activity of uranium using alpha spectrometry (Borole 1980).

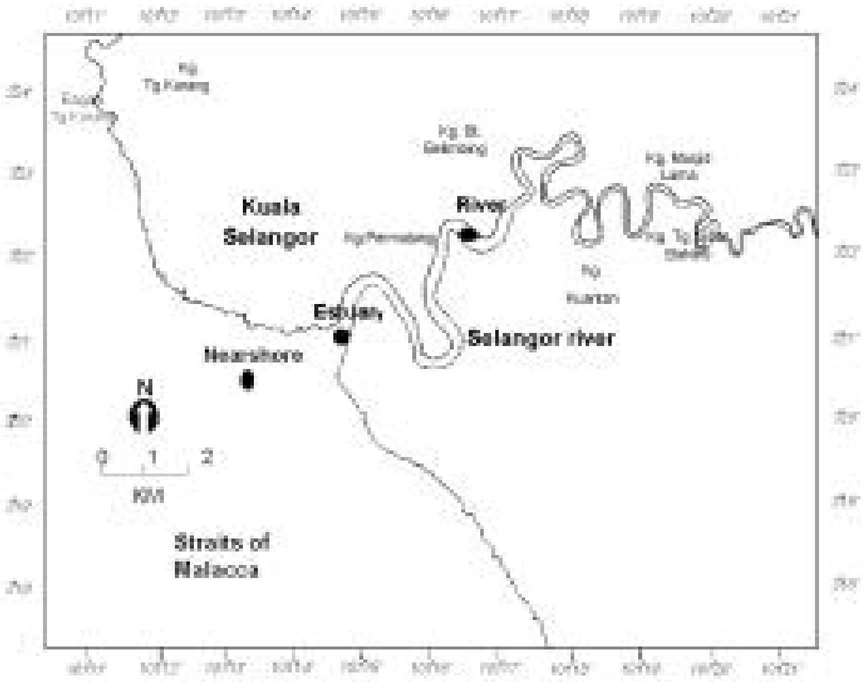

FIGURE 1: Sampling Site in the Kuala Selangor, Selangor

Results and Discussion

Sediment Redox Condition

Manganese, iron and sulfide in pore water were measured to indicate the sediment redox condition and to monitor the utilization of secondary electron acceptors (other than oxygen) in the sediments. The oxic zone is defined as the interval bounded by the sediment/ water interface and the depth at which iron is first detected (i.e. the zone where iron in pore water is oxidized). The suboxic zone is defined as the interval bounded by the base of the oxic zone and the depth at which sulfide is first detected. The remaining core section is defined as anoxic (Shaw et al. 1994).

Therefore, from above definition, the river sediment was found to have three zones, which are oxic zone from surface to 6 cm depth, followed by suboxic zone until 18 cm depth and anoxic zone (Fig. 2). However, estuary and the near shore sediments were characterized by the suboxic and anoxic zones (Fig. 2 & 3). In general, the transition from suboxic to anoxic condition occurs over a much smaller spatial scale in estuary and near shore sediments and has been shown that many estuaries and near shore sediments are dominated by sulfate reduction below a few centimeters in the sediment column (Jorgensen 1982).

Several factors appear to control variations in sediment redox by affecting oxygen availability in the bottom waters and oxygen demand in the sediments. These processes tend to change on a seasonal time scale and include the early fall mixing of oxygen into bottom water and the input and decomposition of biodetritus (Faas 1988).

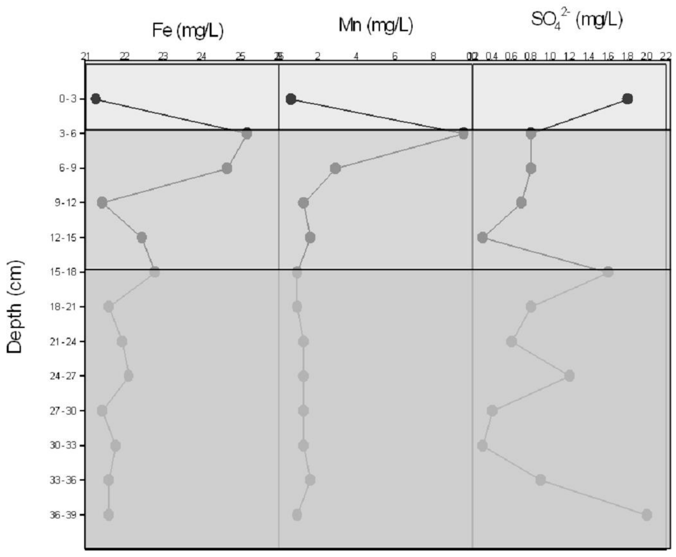

FIGURE 2: Concentration of Manganese, Iron and Sulfide in Pore Water Atb Kuala Selangor River Sediment

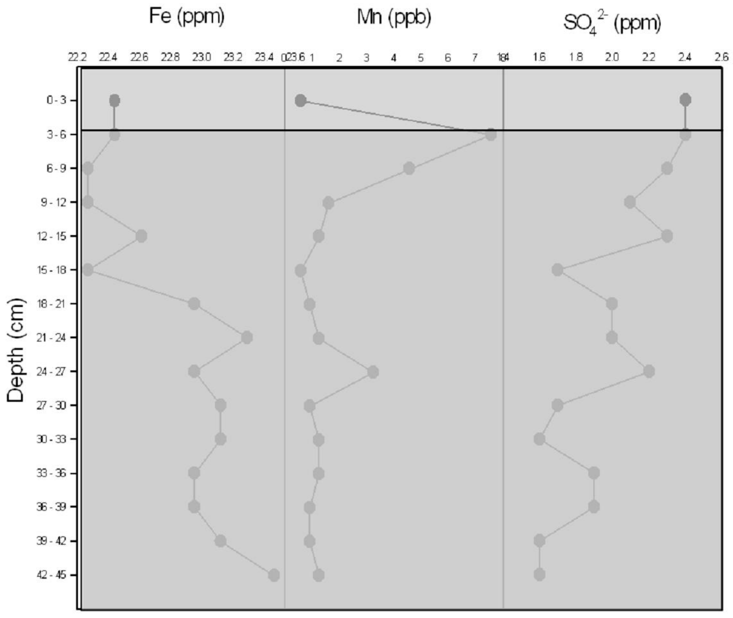

FIGURE 3: Concentration of Manganese, Iron and Sulfide in Pore Water Atb Kuala Selangor Estuary Sediment

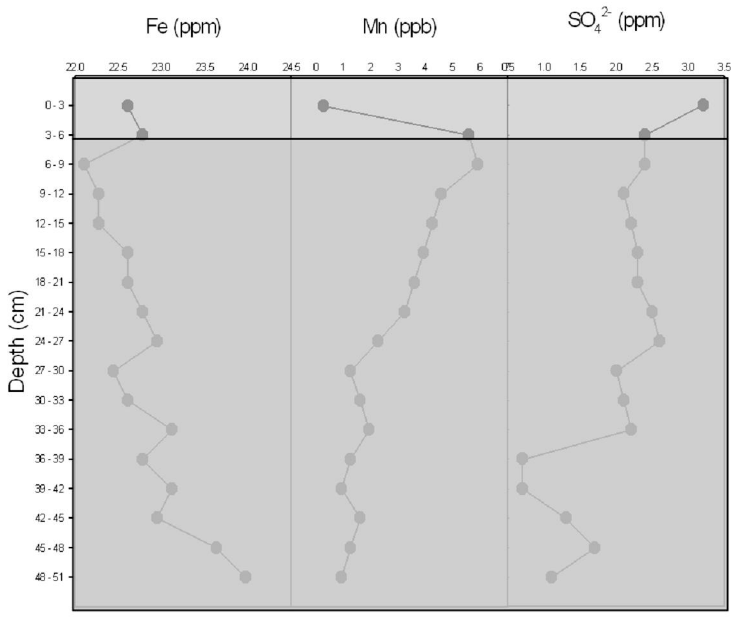

FIGURE 4: Concentration of Manganese, Iron and Sulfide in Pore Water Atb Kuala Selangor Nearshore Sediment

River Sediment

The activities of ^{234}U, ^{238}U and ^{234}U/^{238}U in the Kuala Selangor are given in Table 1. The concentration of ^{238}U from the river sediment lies between 3.03 ± 1.08 dpm/g and 4.78 ± 1.40 dpm/g with an average of 3.88 ± 1.35 dpm/g (Table 1). The activities of ^{234}U are slightly higher, about 3.50 ± 1.13 dpm/g and 6.25 ± 2.08 dpm/g with an average of 4.76 ± 1.63 dpm/g (Table 1). The ^{234}U/^{238}U activity ratio is between 0.73 and 1.60 with a mean of 1.24 (Table 1). The slight enrichment of ^{234}U over ^{238}U in this core shows an additional post-depositional or authigenic supply of U from the water column.

Diffusion of U(VI) from bottom water into sediment, followed by reduction to U(IV), which is precipitated or adsorbed to sediment solid, is regarded as the primary source of U in the sediment. The accumulation of U in sediment reflects not only the input from diffusion and sinking particulate matter, but also the loss caused by U regeneration. In the oxide zone, we assume that U will associate with Fe-oxide affected by oxidation of U(IV) to U(VI) (Hsi & Langmuir 1985; Barnes & Cochran, 1990). When U(IV) is oxidized to U(VI), it is then adsorbed onto newly formed Fe-oxidized. It is also possible that there is an oxidation of U(IV) directly by Fe (and Mn) oxides (Aller and Rude, 1988). On the other hand, Aller et al. (1986) found that the transport of U at upper layer of sediment core from Amazon Rivers was affected by the migration of Fe. High correlation between ^{234}U/^{238}U activity ratio and Fe (R^2 = 0.9555) at 9 cm onwards was found.

But in the suboxic zone the ^{234}U/^{238}U activity ratio increased with depth and the values were more than 1.0. This indicated that, ^{234}U was a main role of U transport along the river sediment core. We also found that the ^{234}U/^{238}U activity ratio wascorrelated strongly with organic carbon (OC), with an r value of 0.9760. As described by Barnes and Cochran (1988), the main transport mechanism of U along the sediment core was a diffusion of dissolve U(VI) to the sediment and followed by chemical reduction process.

Estuarine Sediment

The sediments from the estuary area are characterized by the ^{234}U/^{238}U activity ratio more than 1.0 (1.12) irrespective on depth of sediment layers (Table 1). The concentration of ^{238}U and ^{234}U are between 1.48 ± 0.42 dpm/g to 5.89 ± 1.89 dpm/g with an average of 3.26 ± 1.04 dpm/g and 1.40 ± 0.41 dpm/g to 6.49 ± 1.99 dpm/g with an average 3.69 ± 1.15 dpm/g (Table 1).

The activity ratio of ^{234}U/^{238}U decreased with depth after 21 cm until 0.91 (Fig. 5), the range of activity ratio ^{234}U/^{238}U were also vary widely and itôs difficult to interpret the character of U in the sediment. From the statistical analysis, the activity ratio of ^{234}U/^{238}U did not correlate neither with Fe, Mn nor organic carbon. So we assumed that bacteria played an important role in the U accumulation in the estuarine sediment. Bacteria can remove U from solution and their presence appears to facilitate reduction of U at lower H_2S and U concentration (Mohagheghi et al. 1985). Microbial reduction of U(VI) to U(IV) by Fe-reducing and sulfate-reducing bacteria (microorganisms) has been observed in culture experiments. Sulfate-reducing microorganisms (*Desulfovibrio desulfuricans*) were shown to enzymatically reduce U(VI) in culture experiments, but the mechanism

TABLE 1: The Activity Determination of ^{234}U, ^{238}U and ^{234}U/^{238}U at River, Estuary and Nearshore in Kuala Selangor

Depth (cm)	^{238}U (dpm/g)			^{234}U (dpm/g)		
	River	Estuary	Nearshore	River	Estuary	Nearshore
0 - 3	3.81 ± 1.24	3.81 ± 1.01	3.32 ± 1.00	6.10 ± 1.79	4.70 ± 1.20	3.15 ± 0.99
3 - 6	4.09 ± 1.46	3.78 ± 1.24	4.48 ± 1.22	3.56 ± 1.37	4.44 ± 1.42	3.92 ± 1.12
6 - 9	4.78 ± 1.39	3.70 ± 0.74	1.84 ± 0.81	3.50 ± 1.13	3.95 ± 0.78	1.74 ± 0.80
9 - 12	3.53 ± 1.02	3.39 ± 1.06	3.89 ± 1.95	3.95 ± 1.12	4.08 ± 1.22	3.77 ± 1.94
12 - 15	4.02 ± 1.44	2.84 ± 0.87	1.34 ± 0.59	5.93 ± 1.95	3.32 ± 0.98	1.25 ± 0.59
15 - 18	3.78 ± 1.58	1.90 ± 0.57	1.28 ± 0.52	4.93 ± 1.96	2.25 ± 0.65	1.22 ± 0.52
18 - 21	3.03 ± 1.08	4.94 ± 1.60	1.31 ± 0.54	3.88 ± 1.31	6.49 ± 1.99	1.27 ± 0.54
21 - 24	3.99 ± 1.46	2.78 ± 0.85	1.54 ± 0.52	6.25 ± 2.08	3.51 ± 1.01	1.44 ± 0.51
24 - 27		2.57 ± 0.73	3.57 ± 0.68		2.73 ± 0.77	3.35 ± 0.66
27 - 30		3.20 ± 1.17	2.37 ± 0.89		2.93 ± 1.18	2.33 ± 0.89
30 - 33		5.89 ± 1.89	3.36 ± 1.01		6.41 ± 2.04	4.33 ± 1.23
33 - 36		2.94 ± 0.88	5.00 ± 1.05		3.12 ± 0.94	6.28 ± 1.27
36 - 39		2.74 ± 0.89	5.24 ± 1.96		3.51 ± 1.08	4.75 ± 1.94
39 - 42		1.48 ± 0.42	3.34 ± 0.63		1.40 ± 0.41	3.35 ± 0.64
42 - 45		1.79 ± 0.55	6.48 ± 1.75		1.69 ± 0.54	5.33 ± 1.55
45 - 48		2.33 ± 0.74	3.58 ± 0.85		2.68 ± 0.82	3.25 ± 0.81
48 - 51		5.41 ± 1.25	7.09 ± 2.09		5.58 ± 1.29	6.59 ± 2.01
51 -54			4.27 ± 1.11			4.78 ± 1.22
54 - 57			5.92 ± 1.60			5.93 ± 1.62
57 - 60			2.66 ± 0.65			2.99 ± 0.71
60 - 63			2.96 ± 0.76			2.77 ± 0.74
63 - 66			10.00 ± 2.53			9.94 ± 2.54
66 - 69			4.51 ± 1.53			4.49 ± 1.55
69 - 72			3.24 ± 1.07			4.08 ± 1.28
Mean	3.88 ± 1.35	3.26 ± 1.04	3.86 ± 1.28	4.76 ± 1.63	3.69 ± 1.15	3.85 ± 1.28

TABLE 1: *Continued*.

Depth (cm)	[^{234}U/^{238}U]		
	River	Estuary	Nearshore
0 - 3	1.60	1.23	0.95
3 - 6	0.87	1.17	0.88
6 - 9	0.73	1.07	0.95
9 - 12	1.12	1.20	0.97
12 - 15	1.47	1.17	0.93
15 - 18	1.30	1.18	0.95
18 - 21	1.28	1.31	0.97
21 - 24	1.57	1.26	0.93
24 - 27		1.06	0.94
27 - 30		0.91	0.98
30 - 33		1.09	1.29
33 - 36		1.06	1.25
36 - 39		1.28	0.91
39 - 42		0.95	1.00
42 - 45		0.94	0.82
45 - 48		1.15	0.91
48 - 51		1.03	0.93
51 -54			1.12
54 - 57			1.00
57 - 60			1.12
60 - 63			0.93
63 - 66			0.99
66 - 69			1.00
69 - 72			1.26
Mean	1.24	1.12	1.00

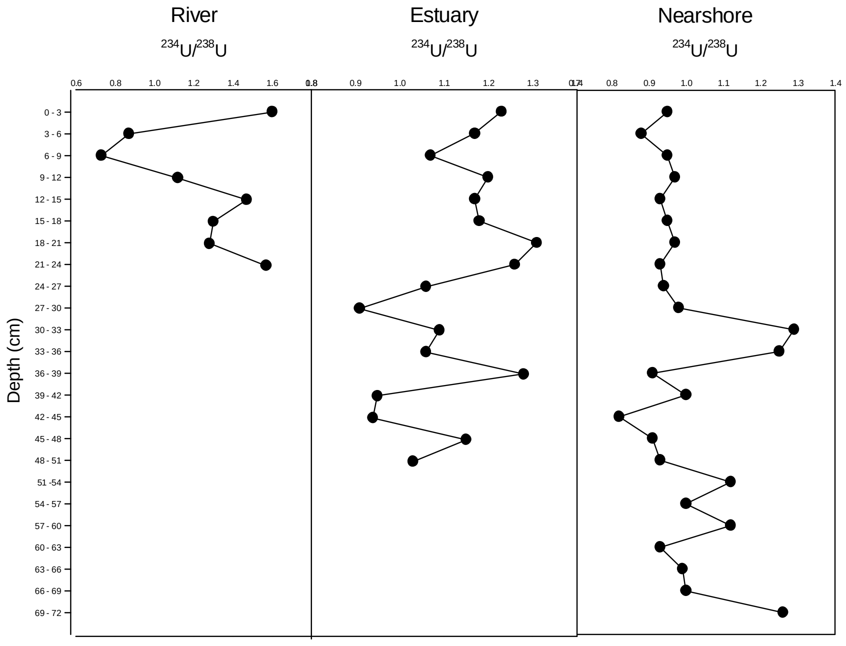

FIGURE 5: The Activity Ratio $^{234}U/^{238}U$ in the Sediment at Kuala Selangor

of the reduction has not yet been elucidated (Lovley & Phillips 1992). In similar culture experiments *D. desulfuricans* enzymatically reduced U(VI) and sulfate simultaneously, which is consistent with the removal of U from solution coincident with sulfate reduction (Lovley & Phillips 1992). However, the important of microbially mediated U reduction mechanisms is difficult to demonstrate in nature.

The variability of the diagenetic environment of estuary sediments, reflecting difference in physical, biological and sedimentological parameters, makes it difficult to extrapolate from one system to another with respect to U behavior. In general, however the net effect appears to be one of removal of U to sediments in estuarine environments.

Nearshore Sediment

The wide range concentration of ^{234}U and ^{238}U were observed in sediments from the near shore areas, ranged about 1.28 ± 0.52 dpm/g to 10.00 ± 2.53 dpm/g for ^{238}U and 1.22 ± 0.52 dpm/g to 9.94 ± 2.54 dpm/g for ^{234}U, respectively (Table 1). It was the highest disequilibrium between the activity of ^{234}U and ^{238}U isotopes (average value of the $^{234}U/^{238}U$ activity ratio was 1.0).

The activity ratio $^{234}U/^{238}U$ from the surface to 30 cm depth was close to 1.0 (Fig. 5). It shows that it was the highest disequilibrium between the activity of ^{234}U and ^{238}U isotopes and most of ^{234}U sources were from natural decay of ^{238}U. A slightly high activity of ^{238}U compared to ^{234}U in this layer may be derived from organic matter rich with U (Aoki & Kohyama 1992) or authigenic U once deposited in the anoxic environment.

The range of activity ratio ^{234}U/^{238}U from 36 cm depth downwards varied widely (Fig.5). Rosholt et al. (1996) had shown that the activity ratio ^{234}U/^{238}U more than 1.0, caused by the diffusion of ^{234}U from deep layer of sediment column which was brought up to the upper layer by pore waters. ^{234}U/^{238}U ratios were positively correlated with organic carbon (Fig. 6) which were found at the bottom layer of the near shore sediment (r= 0.7068). It shows that, U is mobilized as organic matter and migrated to more reducing sediment at depth in the deposited area where it is immobilized (Colley & Thomson 1985).

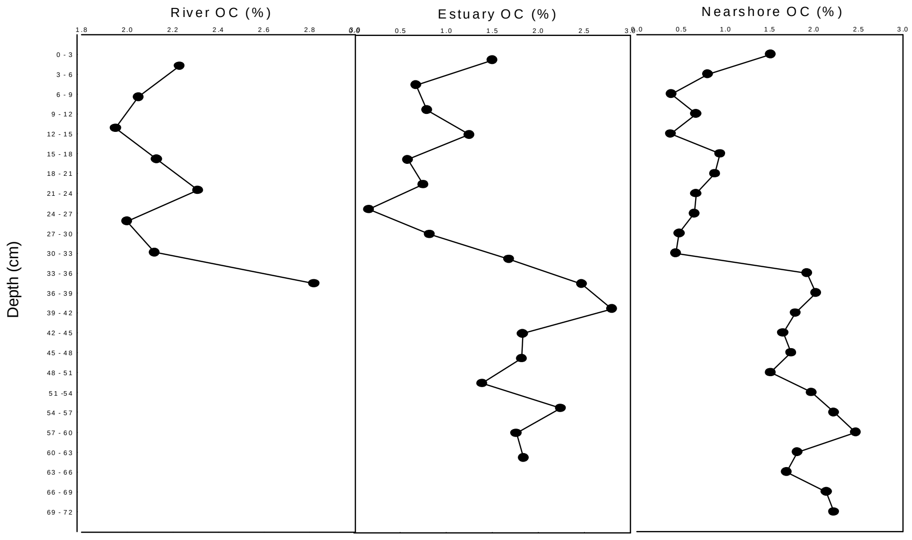

FIGURE 6: The Concentration of Organic Carbon (OC) in the Sediment at Kuala Selangor

Conclusion

The river sediment has been divided by three zones which are oxic, suboxic and anoxic zones. But estuarine and near shore sediments just have the suboxic and anoxic zones. The accumulation of U in the oxic zone was affected by Fe^{2+} and it was affected by organic carbon in the anoxic zone. But the accumulation of U also affected by biology reaction (bacteria reaction) in anoxic zone, especially in estuary sediment.

Acknowledgement

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