CHANGING OF MANGANESE AND TOTAL ORGANIC CARBON IN MARINE SEDIMENT CORE AS A SIGNAL FOR MARINE PRODUCTIVITY

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ABSTRACT

^{210}Pb dating, Mn and total organic carbon have been used in this study to determine the sedimentation rate and the productivity in coastal of Kelantan. Four sediment cores which are SF1, SF3, SF5 and SF7 were taken using the gravity corer on June 2008. The 125 µm dry sediment with particle mesh was used to determine the concentration of ^{210}Pb, Mn and total organic carbon. Activity level of ^{210}Pb was determined using the Tennelec XLB-5 Gross Alpha-Beta Counter, Canberra, after the ingrowth of ^{210}Pb by the outgrowth of ^{210}Bi. While the content of Mn was measured using the Perkin Elmer SCIEX Inductively Coupled Plasma Mass Spectrometry ELAN 9000 technique and the organic carbon content was estimated using combustion method. The analysed result showed the ^{210}Pb activity for all samples were decreasing from top to the bottom sediment. While the vertical profile of Mn concentration had scattered distribution throughout the core sediments. However, Mn concentrations in the samples were lower than the Mn concentration in the earth crust that is 770.00 mg/kg. Values of the total organic carbon (TOC) content are higher in sites that are closer with land and lower in offshore sites. The value of sedimentation rate was 0.59 cm yr^{-1}, 0.47 cm yr^{-1}, 0.36 cm yr^{-1} and 0.46 cm yr^{-1} for SF1, SF3, SF5 and SF7, respectively. This indicates various sediment age ranges and year of accumulation of sediments. It shows that the organic carbon contents produced Mn^{2+} during anaerobic decomposition process in the sediment.

ABSTRAK

Teknik penyurihan ^{210}Pb, Mn dan total organik telah digunakan dalam kajian ini untuk menentukan kadar pemendapan dan produktiviti di pantai Kelantan. Empat teras sedimen yang SF1, SF3, SF5 dan SF7 diambil menggunakan corer graviti pada bulan Jun 2008. Sedimen kering 125 µm dengan mesh zarah digunakan untuk menentukan kepekatan 210Pb, Mn dan jumlah karbon organik. Tahap aktiviti 210Pb ditentukan dengan menggunakan Tennelec XLB-5 Kaunter Alpha-Beta Kasar, Canberra, selepas penanaman 210Pb dengan hasil 210Bi. Walaupun kandungan Mn diukur menggunakan teknik Spekrometri Massal Plasma Perkin Elmer SCIEX yang Digabungkan ELAN 9000 dan kandungan karbon organik dianggarkan menggunakan kaedah pembakaran. Hasil analisa menunjukkan aktiviti 210Pb untuk semua sampel telah menurun dari sedimen bawah ke bahagian bawah. Sedangkan profil menegak kepekatan Mn telah menyebarkan pengedaran sepanjang sedimen teras. Walau bagaimanapun, kepekatan Mn dalam sampel adalah lebih rendah daripada kepekatan Mn dalam kerak bumi iaitu 770.00 mg / kg. Nilai kandungan karbon total (TOC) adalah lebih tinggi di tapak yang lebih dekat dengan tanah dan lebih rendah di tapak luar pesisir. Nilai kadar pemendapan ialah 0.59 cm yr-1, 0.47 cm yr-1, 0.36 cm yr-1 dan 0.46 cm yr-1 untuk SF1, SF3, SF5 dan SF7. Ini menunjukkan pelbagai rentang umur sedimen dan tahun pengumpulan sedimen. Ia menunjukkan bahawa kandungan karbon organik menghasilkan Mn2 + semasa proses penguraian anaerobik dalam sedimen.

Keywords: Total organic carbon, ^{210}Pb dating, productivity, core sediment, accumulation

INTRODUCTION

Organic matter incorporated with two types of cycles that exist in the ocean which is the biological and geological cycle [1]. The organic compounds that incorporated with biological cycle started with photosynthesis of organic matter by using carbon dioxide or bicarbonate in the ocean surface. While geological cycle involve with oil and gas, fossil sediments, coal and metamorphic sediment such as graphite. Geological cycle is a larger depot for organic carbon (6.4 x 10^{15} ton of C) than in biological cycle (3.10 x 10^{12} ton of C) [2]. It may be reoxidized to carbon dioxide after erosion of sedimentary rocks or by combustion of fossil fuels that exist in the ocean. It will then used for photosynthesis that will produce another organic compound. This process is called as marine productivity. The productivity changes in marine environment affected the chemical composition [3] which gives the highest possibility to study the chemical evolution in the sediments.

It is estimated that 30 to 50 x 10^9 ton of C has been produced by phytoplankton for marine productivity in the modern world ocean [4 & 5]. Most of the C is produced in the photic zone where photosynthesis takes place while only a small portion of C will sink to the seafloor and be buried in the sediment and it will be oxidative degraded. However, paleoproductivity still can be estimated to get background idea of the past productivity that occurs in a particular place although only 1 to 0.01% of the primary productivity is buried deeply in marine sediment [2].

Paleoproductivity estimation can be determine using several chemical tracers such as (1) trace elements [6]; (2) the carbon composition of marine organic matter [7]; (3) the carbonate of pelagic and benthic fossils [8] and (4) the flux rate of biogenic silica [9]. The organic carbon (OC) is one of the biogenic elements that have been produced by degradation and the decomposition of carbon compound in the dead organisms in marine environment [10]. The use of natural radionuclide ^{210}Pb to determine the marine sedimentation rate is an established method [11; 12; 13]. Hence, this study was conducted to observe the past marine productivity using the changing of manganese (Mn) and total organic carbon (TOC). ^{210}Pb is used as ^{210}Pb dating for the sedimentation rate and the aging of the marine core sediments. It is important as these sampling sites were located facing the open ocean of the South China Sea as well as the paleoproductivity of coastal of Kelantan, Peninsula Malaysia.

METHODOLOGY

Core sediment samples were taken from Kelantan's coast which located in the eastern coast of Peninsular Malaysia as shown in Figure 1. Sampling was held in June 2008 with the collaboration of Ministry of Science, Technology and Innovation (MOSTI). Four core sediments were brought back to Chemical Oceanography laboratory, National University of Malaysia (UKM) to pre-weigh before dried the wet sample in an oven with 60°C for 24 hours. Samples were cooled in room temperature as to measure the post-weight. Samples were then homogenized using mortar and pestle and sieved with mesh size 125µm and weighed. The dry samples were kept for ^{210}Pb, Mn and total organic carbon analysis.

^{210}Pb analysis

^{210}Pb activity was determined by using ^{210}Bi method which allowed the outgrowth of ^{210}Bi and the ingrowth of ^{210}Pb. 1 g of samples was spiked with Pb carrier (20 mg/ml) with known volume as yield carrier. Then, it was digested with 30 ml of concentrated HCl for 3 hours and about 80°C. The samples were then evaporated near dryness after the sediment was filtered and centrifuged after dissolved with 30 ml of 1M HNO_3. Samples were added with Fe carrier and concentrated NH_4. Precipitate formed was centrifuged with 4000 rpm in 5 minute. Precipitates were dissolved with 30 ml of 1M HNO_3 before electrodeposited with platinum bucket as anode while platinum wire as cathode. ^{210}Pb that deposited on the bucket surface were rinsed with the H_2O_2 and HNO_3 mixture solution. The samples were then evaporated to dryness and diluted with 30 ml of 1M HNO_3 and 3 ml of concentrated H_2SO_4 before it was filtered and counted using Gross Alpha-Beta Spectrometry.

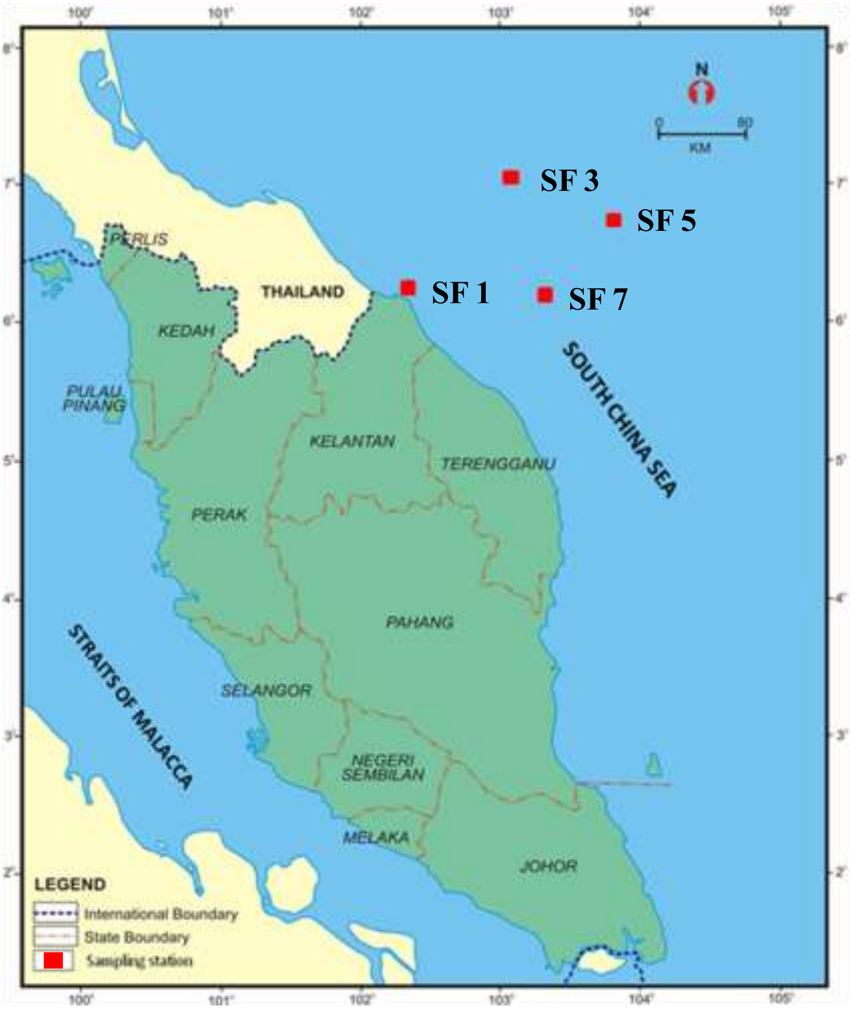

Figure 1 Sampling sites of core sediments in coast of Kelantan

Chemical analysis

Mn content in the sample detected using Perkin Elmer SCIEX Inductively Coupled Plasma Mass Spectrometer (ICP-MS) ELAN 9000. 1g of samples digested using 30 ml of concentrated HCl with temperature about 80°C for 3 hours. The samples were then filtered using Advanced Glass Fibre Filter Paper 25 mm and the residue evaporated until near dryness. Brown paste left dissolved with 30 ml of 1M HNO_3 and diluted with double distilled water before Mn content detected.

Total organic carbon

Total organic carbon content was determining using combustion and it was calculated using weight loss / loss on ignition (LOI) or organic matter (OM) content loss during the combustion. 2 to 3 g of dry sediments were weighed and placed in 20 ml crucible. They were dried in oven with 105°C and the samples were combusted in Carbolite furnace for 4 hours and 500°C. After that, they were cooled in desicator and weighed. Organic carbon content can be calculated using formula (1) [14].

$$LOI_{OM} = \{[(W_s - W_c) - (W_A - W_c)] \,/\, (W_s - W_c)\} \,.\, 100\% \qquad \text{-----------------} \qquad (1)$$

where:

W_s : mass of sediments after dried with 105°C (g)

W_c : mass of crucibles after dried with 105°C (g)

W_A : mass of sediments after combusted in furnace with 500°C (g)

Since organic carbon content (%) only 58 percent from the overall organic matter in the sediment, it will be calculated as in formula (2) [15].

$$OC(\%) = (58/100) \, . \, LOI_{OM} = (1/1.724) \, . \, LOI_{OM} \qquad \text{-----------------} \quad (2)$$

Sedimentation rates

The slope of the least square fit for ln (^{210}Pb) excess values plotted versus depth assuming that the deposition of ^{210}Pb is steady state was used to determine the sedimentation rates [16; 17]. The age of every layer of the sediments was also determined based on the method of the constant initial concentration [16; 18] with the Eq. (2).

$$T_i = 1/\lambda \ln (A_o / A_i) \qquad \text{-----------------} \quad (3)$$

where:

A_o: unsupported ^{210}Pb activity at sediment surface in mBq g^{-1} dry sediment

A_i: unsupported ^{210}Pb activity at depth i in mBq g^{-1} dry sediment

λ : decay constant of ^{210}Pb (0.0311 year)

T_i : difference in age of surface sediment and sediment at depth i in years

RESULT AND DISCUSSION

Sedimentation rate using ^{210}Pb dating

Sedimentation rate is determined using ^{210}Pb dating which is a reliable method for sediment dating in last 100 years. It was measured via its daughter ^{210}Bi. It is the most drastic changes period that was produced in the environment by human activities [19]. These four core sediments showed different sedimentation rate which are 0.59 cm yr^{-1}, 0.47 cm yr^{-1}, 0.36 cm yr^{-1} and 0.46 cm yr^{-1} for SF1, SF3, SF5 and SF7, respectively. SF1 had the highest sedimentation rate followed by SF3, SF7 and the lowest is SF5. This is due to the distance between sampling site and land. SF1 is much closer with the land (coordinate 06°13'06.07"N 102°14'11.04"E) which is only 4.83 nautical miles or 8.95 km as shown in Table 1. The furthest distance is SF5 with only 110 nautical miles or 203 km from the land. Hence, it has the lowest sedimentation rate of 0.36 cm yr^{-1}.

Because of the distance, the sampling sites received domestic and river input from the land. SF1 which is the closest site to the land received more river input which are Pengkalan Chepa River, Badang River and Raja Dali River that come from Kelantan River. This site also received land and domestic input from Semut Api village, Badang village as well as Padang Jambu village. While, SF7 is a bit far from SF1 and only received river input from Pengkalan Datu River.

From the stated sedimentation rate, SF1 has been calculated to have 1.69 yr as the youngest sediment in the surface and accumulated since 1881 to 2007. While the oldest sediment was in layer 74 to 77 cm with age 127.97 yr. SF7 also has been calculated to have 6.52 yr as the youngest sediment and accumulated since 1877 until Its oldest sediment was in layer 59 to 62 cm with age 131.52 yr. Although Table 2 and 5 (for both core, respectively) stated that the deepest core sediment is 111 to 118 cm for SF1 and 68 to 71 cm for SF7, but the sediment age from depth 77 to 80 cm and 62 to 65 cm until the deepest sediment were not valid. It is because ^{210}Pb was decayed completely in 6 times of its half-life that took about 133 years. Hence, ^{210}Pb dating was not reliable for deeper core sediment research that may age hundreds to thousands years ago. However, SF3 and SF5 have aging until 122.34 yr and 102.78 yr, respectively. Both sediment cores have accumulated from 1887 in sediment layer 56 to 59 cm and 1906 in sediment layer 36 to 38 cm until 2006 in the surface sediment.

In the meantime, ^{210}Pb activity has been plotted vertically for all cores. ^{210}Pb activity in SF1 as in Figure 2 shows a scattered distribution with a high activity. The highest ^{210}Pb activity is in surface sediment layer, 0 to 2 cm that is 62.01 ± 15.63 mBq/kg and the lowest ^{210}Pb activity is in the deepest sediment which is 71 to 74 cm with 14.17 ± 9.31 mBq/kg as stated in Table 2. SF3 has the obvious ^{210}Pb activity decreasing throughout the core in range of 27.09 ± 15.15 mBq/kg in 2 cm of surface sediment to 8.07 ± 10.67 mBq/kg in sediment layer 44 to 47 cm as shown in Figure 3 and Table 3. Other than that, Figure 4 and Table 4 shows the highest ^{210}Pb for SF5 is 22.85 ± 7.68 mBq/kg in the surface sediment while the lowest ^{210}Pb activity was in sediment layer 20 to 22 cm with 4.48 ± 1.93 mBq/kg. While Figure 5 and Table 5 shows a low ^{210}Pb activity towards the deepest core sediment. It ranges from 15.43 ± 5.24 mBq/kg in layer 12 to 14 cm to 1.70 ± 2.79 mBq/kg in layer 23 to 26 cm.

Table 1 Details of samples and sampling location

Site	Coordinate	Sediment Layers / Thickness (cm)	Date Time	Distance of Sites from Land (n.m./km)	Sediment composition	Tide condition
SF 1	06° 13.99' N 102° 19.00' E	40 (0-118cm)	18 June 2008 7.23 am	4.83 n.m. (8.95 km)	Slightly sandy clay	High
SF 3	07° 05.03' N 103° 04.99' E	23 (0-59cm)	17 June 2008 12.07 pm	72.3 n.m. (134 km)	Sandy clay	Low
SF 5	06° 56.09' N 103° 56.04' E	18 (0-38cm)	16 June 2008 4.11 pm	110 n.m. (203 km)	Sandy clay, shells	Low
SF 7	06° 10.00' N 103° 01.00' E	26 (0-71cm)	16 June 2008 7.30 am	46.6 n.m. (86.3 km)	Silty sand	High

n.m. = nautical miles

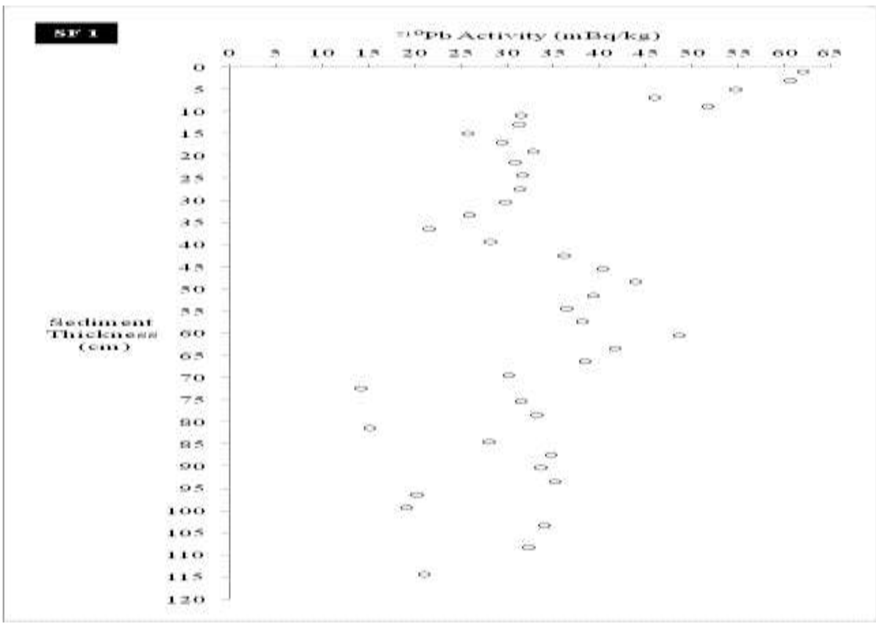

Figure 2 ^{210}Pb vertical distributions for core sediment SF 1

Based on Figure 2, it shows that ^{210}Pb activity is started to decrease in layer 18 to 20 cm of the core sediment. It is also the same with SF3, SF5 and SF7. ^{210}Pb activity in SF3 is started to decreasing in layer 23 to 26 cm which is the most obvious pattern than the other core. ^{210}Pb activity for both SF5 and SF7 are started to decreasing in layer 18 to 20 cm of the core sediment. Generally, it shows that the ^{210}Pb activity decreasing due to decay processes of the radionuclide and having equilibrium with its progeny that is ^{210}Bi. The scattered ^{210}Pb activity distribution in all core sediment (the most obvious in SF1) is due to the bioturbation of diverse marine organisms that lived temporarily in sediment such as worms. This turbation causes spatial rearrangement of the sediment's solid phase. Bioirrigation also could occur which is the living organisms in the sediments actively transport bottom water through their habitats. These processes usually occurred in approximately 50 to 100 cm of the sediment depth [20].

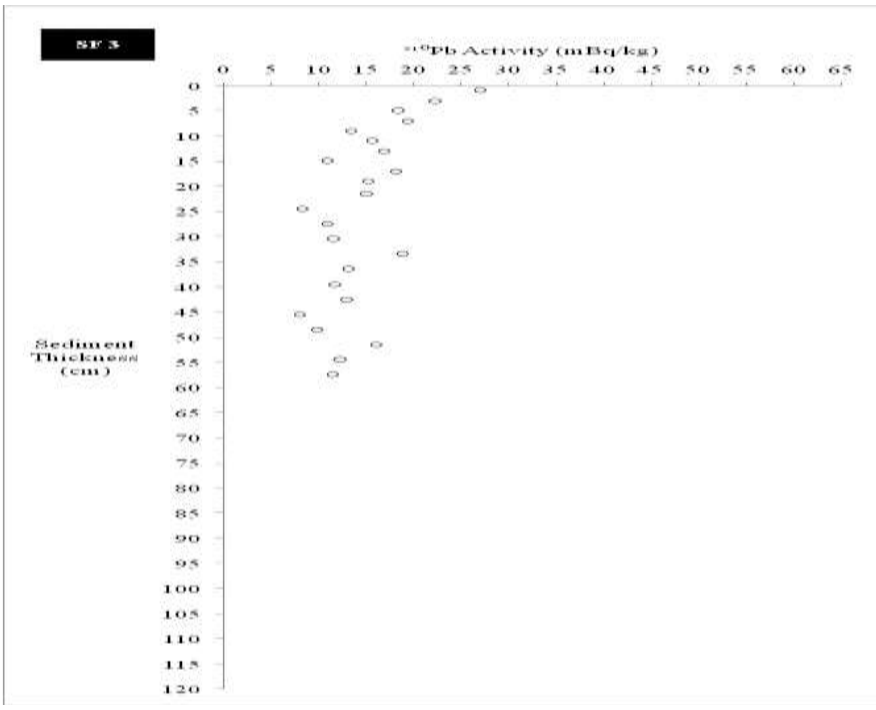

Figure 3 ^{210}Pb vertical distributions for core sediment SF 3

Table 2 ^{210}Pb activity, sediment age and years of sediment accumulation for core sediment SF1

Sediment Thickness (cm)	Moisture content (%)	Sediment age (year)	Year	^{210}Pb activity ± S.D. (mBq/kg)	Mn concentration ± S.D. (mg/kg)	TOC (%)
0-2	103.10	1.69	2007	**62.01 ± 15.63**	483.95 ± 12.29	3.65
2-4	65.17	5.08	2004	60.53 ± 17.01	465.62 ± 8.50	3.67
4-6	58.89	8.47	2001	54.64 ± 16.31	466.87 ± 4.62	3.69
6-8	51.46	11.86	1997	46.02 ± 13.77	466.90 ± 9.88	3.51
8-10	55.04	15.25	1994	51.72 ± 16.83	451.77 ± 12.52	3.52
10-12	51.08	18.64	1990	31.54 ± 9.88	232.55 ± 4.56	3.51
12-14	53.68	22.03	1987	31.22 ± 10.15	452.10 ± 1.61	3.40
14-16	62.04	25.42	1984	25.89 ± 7.63	463.51 ± 3.77	3.31
16-18	66.19	28.81	1980	29.52 ± 9.86	442.46 ± 9.15	3.69
18-20	67.88	32.20	1977	32.93 ± 10.12	448.22 ± 8.48	**6.21**
20-23	68.01	36.44	1973	30.78 ± 8.64	461.25 ± 10.76	3.77
23-26	51.34	41.53	1967	31.73 ± 9.47	385.01 ± 7.67	3.28
26-29	73.52	46.61	1962	31.40 ± 12.35	456.85 ± 5.71	3.23

29-32	64.55	51.69	1957	29.77 ± 8.63	446.59 ± 2.13	3.21
32-35	53.32	56.78	1952	26.02 ± 7.63	476.57 ± 9.33	3.43
35-38	57.66	61.86	1947	21.51 ± 13.56	488.75 ± 4.80	3.65
38-41	70.11	66.95	1942	28.11 ± 9.80	481.05 ± 1.73	3.41
41-44	77.69	72.03	1937	36.08 ± 10.05	448.53 ± 11.62	4.19
44-47	71.31	77.12	1932	40.39 ± 11.19	441.65 ± 7.28	4.19
47-50	48.36	82.20	1927	43.99 ± 12.18	445.18 ± 7.41	3.57
50-53	64.02	87.29	1922	39.39 ± 10.82	433.59 ± 9.81	3.53
53-56	56.76	92.37	1917	36.37 ± 11.20	484.05 ± 5.83	3.20
56-59	65.10	97.46	1912	38.19 ± 10.42	423.76 ± 3.82	3.44
59-62	64.40	102.54	1906	48.67 ± 12.77	400.77 ± 8.54	4.09
62-65	66.74	107.63	1901	41.74 ± 10.80	470.61 ± 11.93	3.06
65-68	85.96	112.71	1896	38.46 ± 10.69	475.13 ± 2.37	4.39
68-71	66.48	122.88	1891	30.22 ± 7.86	465.30 ± 8.63	3.01
71-74	61.67	122.88	1886	***14.17 ± 9.31***	464.65 ± 9.39	3.56
74-77	63.71	127.97	1881	31.60 ± 9.84	479.77 ± 4.61	3.11
77-80	56.79	133.05	1876	33.14 ± 9.27	506.42 ± 2.84	2.48
80-83	45.88	138.14	1871	15.24 ± 13.36	**538.63 ± 8.98**	2.42
83-86	47.34	143.22	1866	27.96 ± 8.74	496.70 ± 13.34	2.25
86-89	53.42	148.31	1861	34.82 ± 9.04	459.94 ± 4.28	3.05
89-92	62.48	153.39	1856	33.57 ± 9.11	469.86 ± 5.97	3.44
92-95	62.40	158.47	1851	35.30 ± 9.64	463.97 ± 3.59	3.60
95-98	44.82	163.56	1845	20.18 ± 7.83	513.26 ± 16.24	2.82
98-101	75.44	168.64	1840	19.27 ± 10.23	467.91 ± 7.20	1.42
101-106	62.26	175.42	1834	34.13 ± 10.48	489.99 ± 13.03	***1.00***
106-111	53.75	183.90	1825	32.26 ± 10.66	478.00 ± 3.94	1.29
111-118	57.73	194.07	1815	21.09 ± 20.07	***210.59 ± 3.88***	1.39

Table 3 ^{210}**Pb activity, sediment age and years of sediment accumulation for core sediment SF3**

Sediment Thickness (cm)	Moisture content (%)	Sediment age (year)	Year	^{210}Pb activity ± S.D. (mBq/kg)	Mn concentration ± S.D. (mg/kg)	TOC (%)
0-2	54.51	2.13	2007	***27.09 ± 15.15***	555.81 ± 14.01	1.36
2-4	55.50	6.38	2003	22.15 ± 6.92	553.91 ± 9.40	0.97
4-6	72.35	10.64	1998	18.28 ± 5.00	523.51 ± 3.74	0.71
6-8	71.12	14.89	1994	19.49 ± 6.67	541.97 ± 1.20	0.89
8-10	72.46	19.15	1990	13.49 ± 4.09	609.09 ± 8.06	0.59
10-12	65.86	23.40	1986	15.73 ± 5.22	564.01 ± 8.05	***0.48***
12-14	61.90	27.66	1981	16.99 ± 5.34	470.40 ± 2.04	0.81
14-16	71.06	31.91	1977	11.05 ± 5.72	540.35 ± 14.45	0.77
16-18	59.68	36.17	1973	18.19 ± 4.17	**735.99 ± 10.50**	0.74
18-20	54.72	40.43	1969	15.29 ± 4.34	542.21 ± 7.74	0.69
20-23	55.88	45.74	1963	14.96 ± 5.40	586.39 ± 16.77	0.84

23-26	53.29	52.13	1957	8.36 ± 2.37	555.03 ± 4.03	0.56
26-29	53.24	58.51	1950	11.04 ± 4.80	556.05 ± 0.89	0.64
29-32	49.80	64.89	1944	11.48 ± 3.47	529.72 ± 5.56	0.70
32-35	50.42	71.28	1937	18.87 ± 7.42	527.69 ± 5.01	1.37
35-38	48.09	77.66	1931	13.22 ± 3.89	545.71 ± 2.08	1.27
38-41	51.45	84.04	1925	11.62 ± 4.56	450.58 ± 2.65	1.71
41-44	49.79	90.43	1919	12.88 ± 4.65	452.06 ± 3.27	1.56
44-47	50.11	96.81	1912	**8.07 ± 10.67**	437.89 ± 6.07	1.66
47-50	51.42	103.19	1906	9.90 ± 6.48	422.96 ± 10.05	0.79
50-53	52.10	109.57	1899	16.16 ± 5.21	431.50 ± 8.47	1.57
53-56	50.23	115.96	1893	12.19 ± 6.29	455.56 ± 9.23	1.22
56-59	38.49	122.34	1887	11.56 ± 12.45	***395.21 ± 10.41***	**1.99**

Table 4 ^{210}**Pb activity, sediment age and years of sediment accumulation for core sediment SF5**

Sediment Thickness (cm)	**Moisture content (%)**	**Sediment age (year)**	**Year**	**^{210}Pb activity ± S.D. (mBq/kg)**	**Mn concentration ± S.D. (mg/kg)**	**TOC (%)**
0-2	41.31	2.78	2006	**22.85 ± 7.68**	***488.63 ± 6.79***	***1.32***
4-6	45.52	13.89	1995	18.90 ± 6.82	393.47 ± 5.11	1.80
6-8	53.03	19.44	1990	13.06 ± 12.49	***391.15 ± 8.44***	1.75
8-10	42.62	25.00	1984	20.57 ± 6.11	402.23 ± 8.76	1.43
10-12	46.71	30.56	1978	11.84 ± 7.29	473.44 ± 2.18	1.69
12-14	45.23	36.11	1973	19.49 ± 9.50	425.66 ± 4.04	1.68
14-16	50.37	41.67	1967	16.29 ± 9.19	442.44 ± 5.83	1.70
16-18	48.87	47.22	1962	14.68 ± 6.04	408.82 ± 8.85	1.65
18-20	43.99	52.78	1956	9.48 ± 16.81	443.81 ± 2.63	1.82
20-22	50.72	58.33	1951	4.48 ± 1.93	424.43 ± 7.79	**2.75**
22-24	41.84	63.89	1945	6.37 ± 7.61	452.11 ± 9.20	2.55
24-26	45.07	69.44	1940	6.97 ± 5.31	422.23 ± 7.90	2.62
26-28	46.12	75.00	1934	14.69 ± 3.92	408.85 ± 6.23	2.33
28-30	43.37	80.56	1928	11.37 ± 3.39	408.77 ± 8.09	2.70
30-32	43.73	86.11	1923	***4.49 ± 3.15***	407.48 ± 5.94	2.58
32-34	44.47	91.67	1917	9.17 ± 3.01	416.99 ± 9.36	2.48
34-36	41.05	97.22	1912	7.17 ± 3.17	392.71 ± 4.43	2.71
36-38	43.48	102.78	1906	14.99 ± 6.62	439.59 ± 8.38	2.67

Table 5 **^{210}Pb activity, sediment age and years of sediment accumulation for core sediment SF7**

Sediment Thickness (cm)	Moisture content (%)	Sediment age (year)	Year	^{210}Pb activity ± S.D. (mBq/kg)	Mn concentration ± S.D. (mg/kg)	TOC (%)
2-4	67.49	6.52	2002	8.27 ± 8.00	507.20 ± 5.84	3.44
4-6	59.19	10.87	1998	13.23 ± 5.72	475.18 ± 5.39	3.17
6-8	57.26	15.22	1994	12.53 ± 4.99	509.45 ± 10.69	3.18
8-10	57.72	19.57	1989	13.13 ± 6.35	500.54 ± 5.60	3.45
10-12	57.24	23.91	1985	2.09 ± 2.21	500.21 ± 13.28	3.28
12-14	56.76	28.26	1981	**15.43 ± 5.24**	510.61 ± 9.77	**4.11**
14-16	60.47	32.61	1976	10.32 ± 6.22	***386.06 ± 3.19***	3.21
16-18	61.84	36.96	1972	12.15 ± 6.71	510.36 ± 11.20	***2.81***
18-20	58.69	41.30	1968	4.69 ± 4.42	536.58 ± 7.95	3.01
20-23	59.87	46.74	1962	3.86 ± 1.06	450.04 ± 1.22	3.49
23-26	61.53	53.26	1956	***1.70 ± 2.79***	497.87 ± 12.01	3.17
26-29	57.20	59.78	1949	8.51 ± 3.42	454.45 ± 6.80	2.97
29-32	59.54	66.30	1943	b.d.l.	508.86 ± 6.71	3.13
32-35	58.93	72.83	1936	7.70 ± 3.41	480.70 ± 21.10	3.01
35-38	62.42	79.35	1930	5.73 ± 2.78	536.61 ± 13.34	3.20
38-41	57.45	85.87	1923	11.05 ± 4.09	462.39 ± 8.28	3.09
41-44	59.03	92.39	1917	6.29 ± 2.76	465.49 ± 1.59	2.91
44-47	61.81	98.91	1910	11.44 ± 12.45	485.72 ± 8.98	2.75
47-50	58.87	105.43	1904	6.27 ± 1.67	558.58 ± 10.76	2.90
50-53	62.01	111.96	1897	11.54 ± 9.79	499.98 ± 5.82	3.04
53-56	61.38	118.48	1891	7.60 ± 5.64	460.53 ± 15.70	3.11
56-59	62.37	125.00	1884	11.32 ± 2.48	453.26 ± 9.53	2.94
59-62	60.35	131.52	1877	4.75 ± 7.18	444.68 ± 12.41	3.20
62-65	60.28	138.04	1871	3.81 ± 4.09	**617.57 ± 19.13**	3.07
65-68	57.73	144.57	1864	7.49 ± 5.51	443.42 ± 9.33	2.90
68-71	61.81	151.09	1858	7.51 ± 2.83	401.74 ± 0.84	3.21

Table 4 ^{210}**Pb activity, sediment age and years of sediment accumulation for core sediment SF5**

Sediment Thickness (cm)	Moisture content (%)	Sediment age (year)	Year	^{210}Pb activity ± S.D. (mBq/kg)	Mn concentration ± S.D. (mg/kg)	TOC (%)
0-2	41.31	2.78	2006	**22.85 ± 7.68**	**488.63 ± 6.79**	***1.32***
4-6	45.52	13.89	1995	18.90 ± 6.82	393.47 ± 5.11	1.80
6-8	53.03	19.44	1990	13.06 ± 12.49	***391.15 ± 8.44***	1.75
8-10	42.62	25.00	1984	20.57 ± 6.11	402.23 ± 8.76	1.43
10-12	46.71	30.56	1978	11.84 ± 7.29	473.44 ± 2.18	1.69
12-14	45.23	36.11	1973	19.49 ± 9.50	425.66 ± 4.04	1.68
14-16	50.37	41.67	1967	16.29 ± 9.19	442.44 ± 5.83	1.70
16-18	48.87	47.22	1962	14.68 ± 6.04	408.82 ± 8.85	1.65
18-20	43.99	52.78	1956	9.48 ± 16.81	443.81 ± 2.63	1.82
20-22	50.72	58.33	1951	4.48 ± 1.93	424.43 ± 7.79	**2.75**
22-24	41.84	63.89	1945	6.37 ± 7.61	452.11 ± 9.20	2.55
24-26	45.07	69.44	1940	6.97 ± 5.31	422.23 ± 7.90	2.62
26-28	46.12	75.00	1934	14.69 ± 3.92	408.85 ± 6.23	2.33
28-30	43.37	80.56	1928	11.37 ± 3.39	408.77 ± 8.09	2.70
30-32	43.73	86.11	1923	***4.49 ± 3.15***	407.48 ± 5.94	2.58
32-34	44.47	91.67	1917	9.17 ± 3.01	416.99 ± 9.36	2.48
34-36	41.05	97.22	1912	7.17 ± 3.17	392.71 ± 4.43	2.71
36-38	43.48	102.78	1906	14.99 ± 6.62	439.59 ± 8.38	2.67

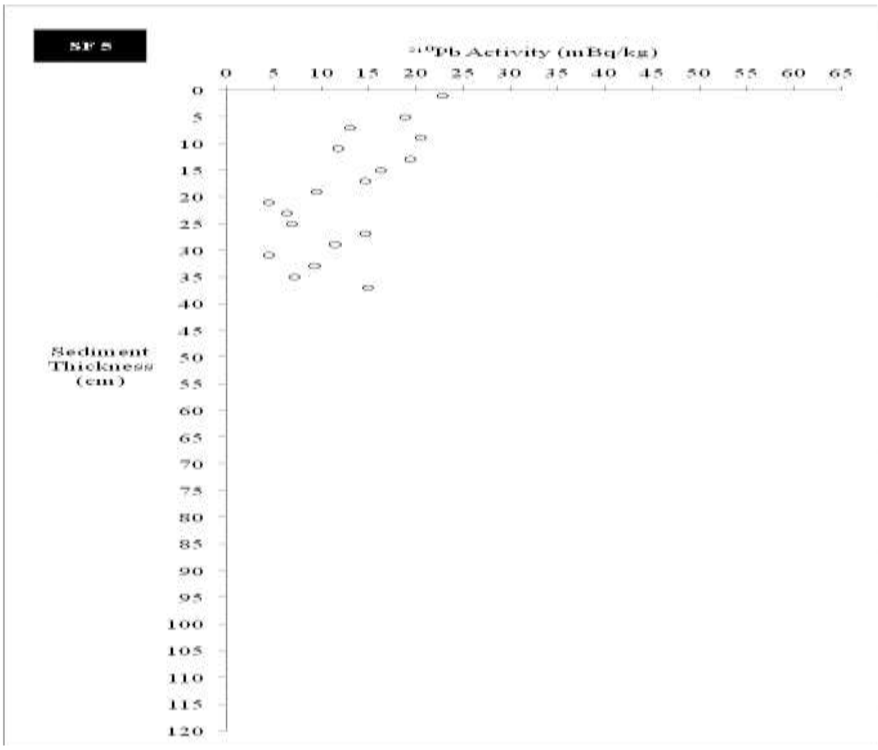

Figure 4 ^{210}Pb vertical distributions for core sediment SF 5

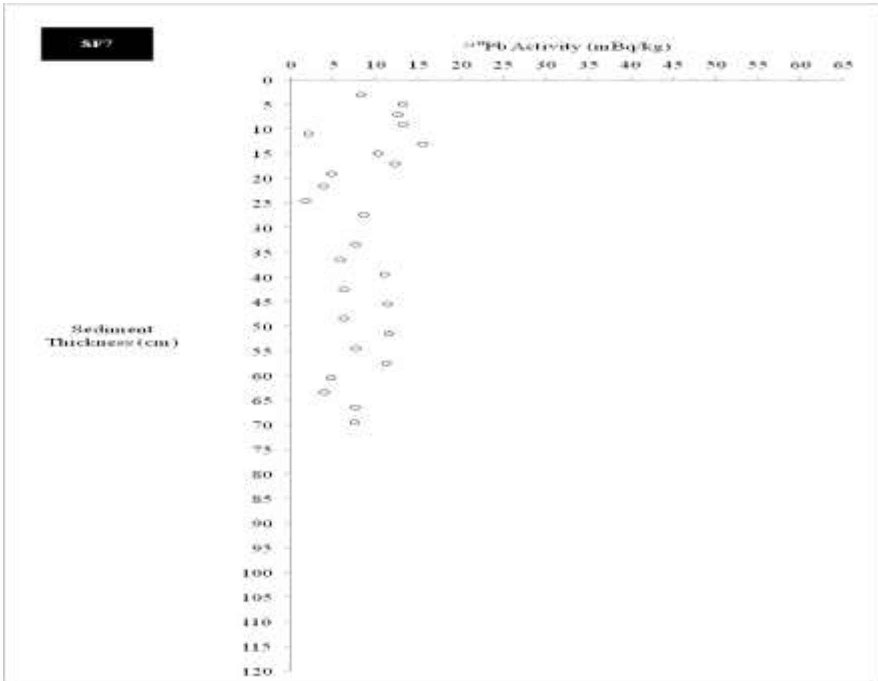

Figure 5 ^{210}Pb vertical distributions for core sediment SF 7

Manganese concentration and vertical profile

At a glance, it can be seen that all Mn concentration vertical profile distribution for SF1, SF3, SF5 and SF7 have the same pattern as shown in Figures 6, 7, 8 and 9, respectively. However, there some differences in Mn concentration in different core. SF1 shows the higher concentration in layer 80 to 83 cm with 538.63 ± 8.98 mg/kg while the lowest Mn concentration is 210.59 ± 3.88 mg/kg in the deepest core sediment that is 111 to 118 cm. Mn concentration in SF3 shows the highest concentration in layer 16 to 18 cm with 735.99 ± 10.50 mg/kg and the lowest concentration is 395.21 ± 10.41 mg/kg in the bottom core sediment that is 56 to 59 cm.

Mn concentration in SF5 is ranging from 488.63 ± 6.79 mg/kg in the surface sediment to 391.15 ± 8.44 mg/kg in 6 to 8 cm of sediment thickness. While Mn distributed in SF7 with the highest concentration 617.57 ± 19.13 mg/kg in the layer of 62 to 65 cm and the lowest of Mn concentration is 386.06 ± 3.19 mg/kg in sediment layer 14 to 16 cm depth.

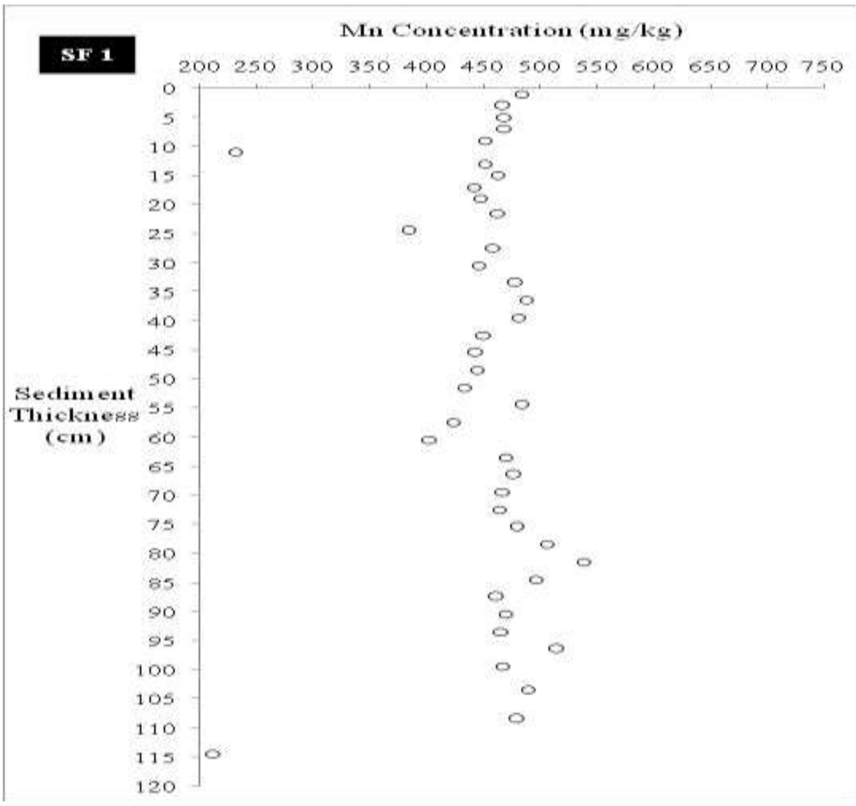

Figure 6 Mn vertical distributions for core sediment SF 1

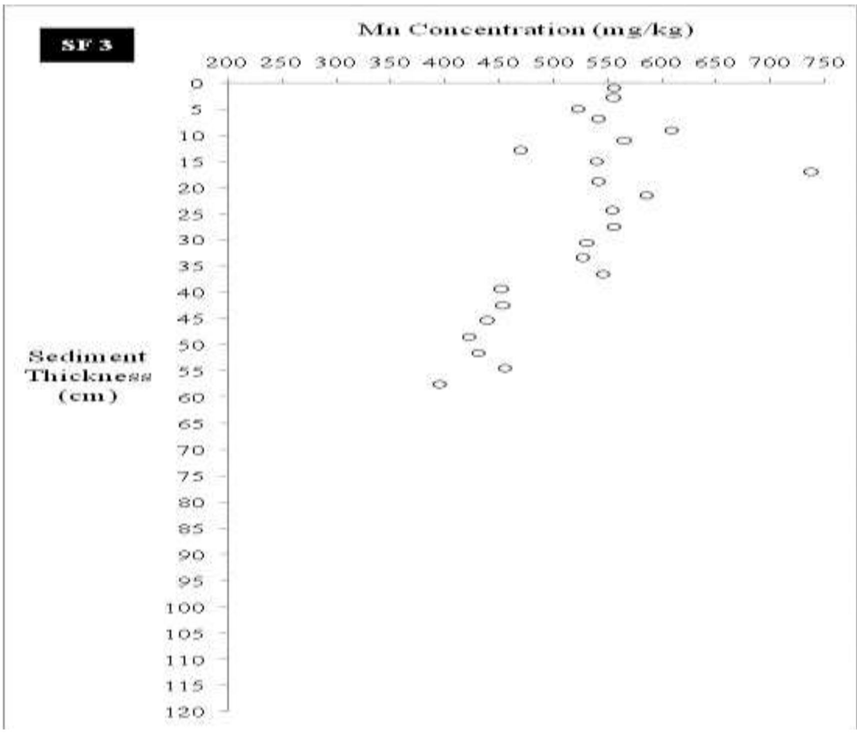

Figure 7 Mn vertical distributions for core sediment SF 3

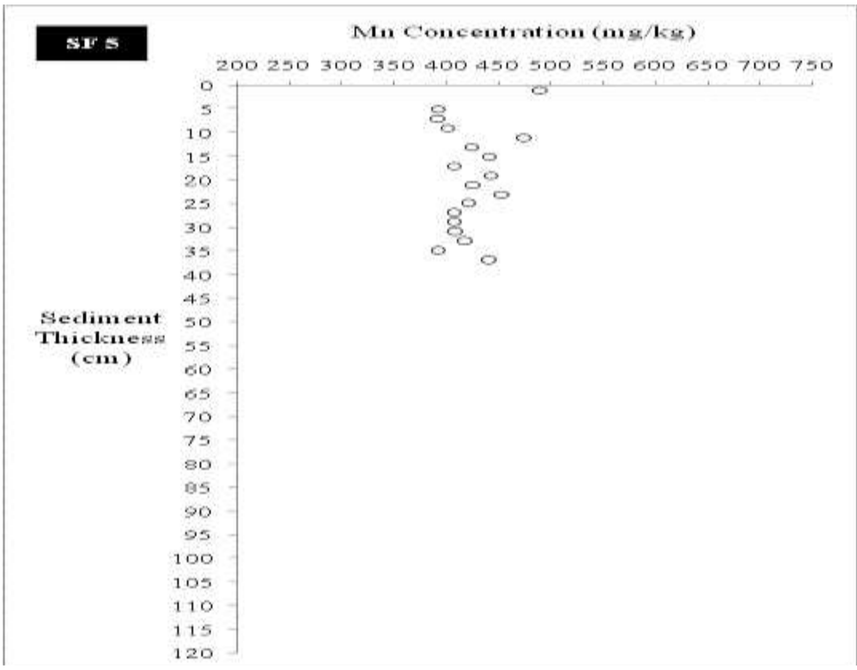

Figure 8 Mn vertical distributions for core sediment SF 5

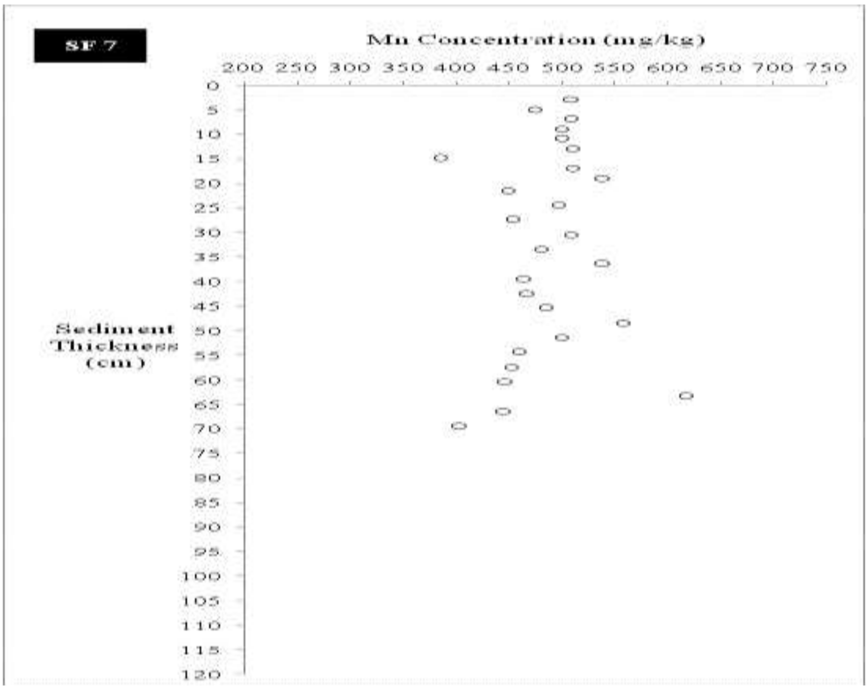

Figure 9 Mn vertical distributions for core sediment SF 7

Li, Y.H stated that the Mn concentration in the earth crust is 770.00 mg/kg [21]. It is clearly shown that Mn concentration in all cores is below the Mn concentration in earth crust. So, there is no antropogenic input of Mn in the samoling sites. The ups and downs of the Mn distribution in all cores are due to the Mn early diagenesis which is a bit complex than any other biogenic elements [20]. This process might include microbiological redox reaction, abiotic reactions of dissolution and precipitation in the core sediment. All of these processes are reflected to the pore water composition in the sediments. Hence, all of the chemical reaction occurred in the aquatic (pore water) phase in the sediments.

In the surface sediment (0 to 10 cm) for all cores, Mn concentration has only a little changes (Table 2, 3, 4 and 5) before the concentration was slightly increase from the surface sediment concentration. This increment shows the dissolved oxygen (DO) from seawater penetrates into the sediment. It will then reoxidize and precipitate Mn content in the sediment to MnO. Mn concentration continued to have a slight decreasing towards the bottom sediment. This is due to the MnO function as an electron acceptor that reacts with organic matter in this depth which is about 40 cm in SF1, SF3 and SF7 and 25 cm depth in SF5. Basically, MnO in this region is chemically reduced or divalent Mn dissolved. Then after a several depth, Mn concentration started to have flat gradient as it precipitates as $MnCO_3$ or MnS.

Total organic carbon content in sediment core

TOC content is slightly higher in SF1 and SF7 while a bit lower in SF3 and SF5 as shown in Figures 10, 11, 12 and 13. TOC content in the surface sediment for SF1, SF3, SF5 and SF5 is 3.65%, 1.36%, 1.32% and 3.44%, respectively. TOC content in SF1 is the highest in layer 18 to 20 cm with 6.21% and the lowest is in layer 101 to 106 with 1.00%. TOC content of SF3 is ranging from 1.99% in the bottom sediment (56 to 59 cm) to 0.48% in layer 10 to 12 cm. While, SF5 has the lowest TOC content in the sediment surface which is 1.32% and the highest is in layer 20 to 22 cm with 2.75%. SF7 has TOC content that range from 4.11% to 2.81% which is in layer 12 to 14 cm and 16 to 18 cm, respectively. It is expected to have a higher TOC content in SF1 and SF7 as it is closer to the land rather than SF3 and SF5.

Usually, sediments within the oxygen-minimum zone of upwelling areas contain TOC content exceeding 10% [2] where upwelling is very intense. But, OC content will be decreasing towards the increasing depth because of the microbiology remineralization and also an oxidation occur during diagenesis in the sediment. Diagenesis process includes the organic carbon as the electron donor and many other electron acceptors such as Mn. Whenever the oxidative process destroying or altering the OC, a reaction partner (in this case is Mn) has to be reduced. Because of this reaction, organic carbon contents in the sediments produced Mn^{2+} during anaerobic decomposition process in the sediment. This is the reason of the decreasing TOC content downward the bottom sediment. The pattern of organic carbon accumulation was found to closely to the historic changes of P loading into the sediment; hence, it is reliable to trace the changing of nutrient input in the ocean or lake [22; 23].

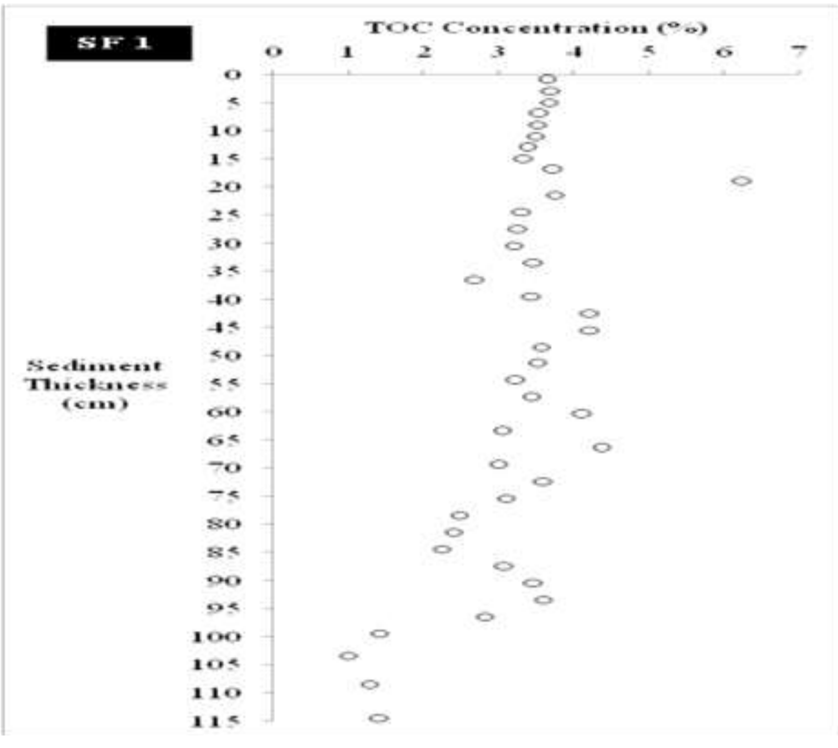

Figure 10 Vertical distributions of TOC percentages in core sediment SF 1

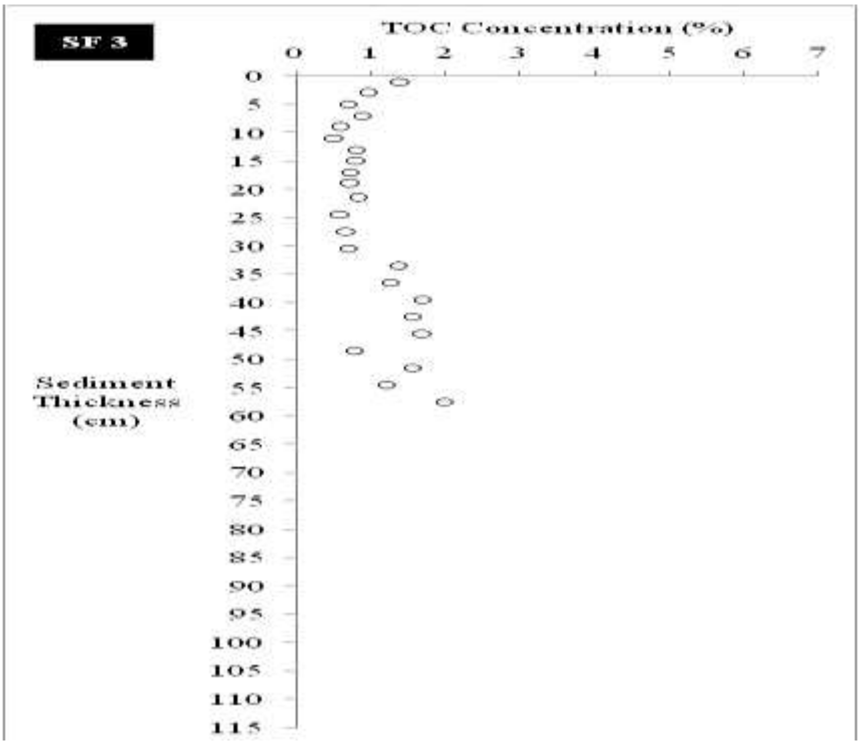

Figure 11 Vertical distributions of TOC percentages in core sediment SF 3

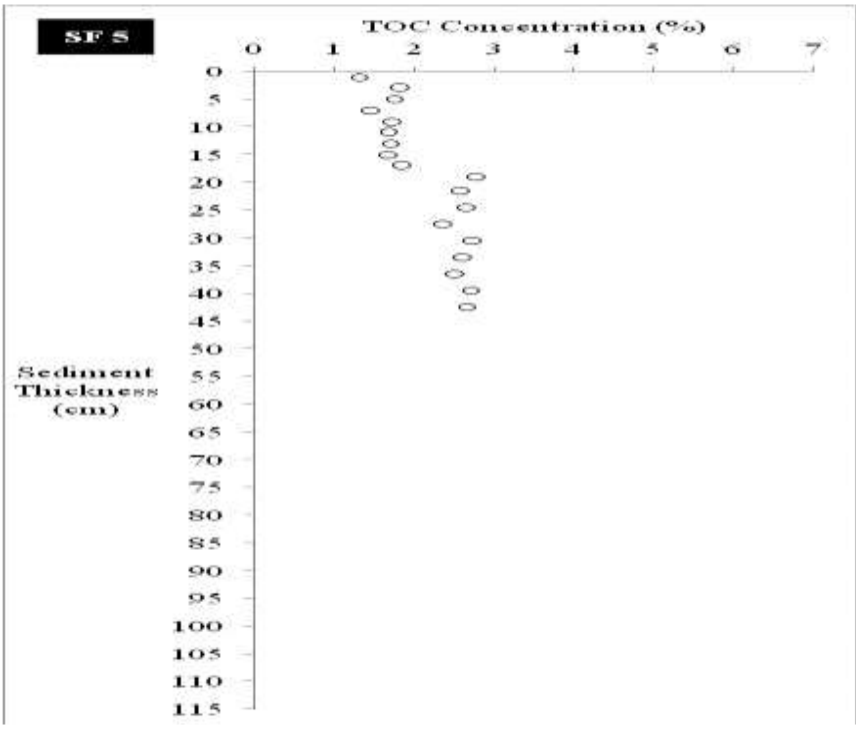

Figure 12 Vertical distributions of TOC percentages in core sediment SF 5

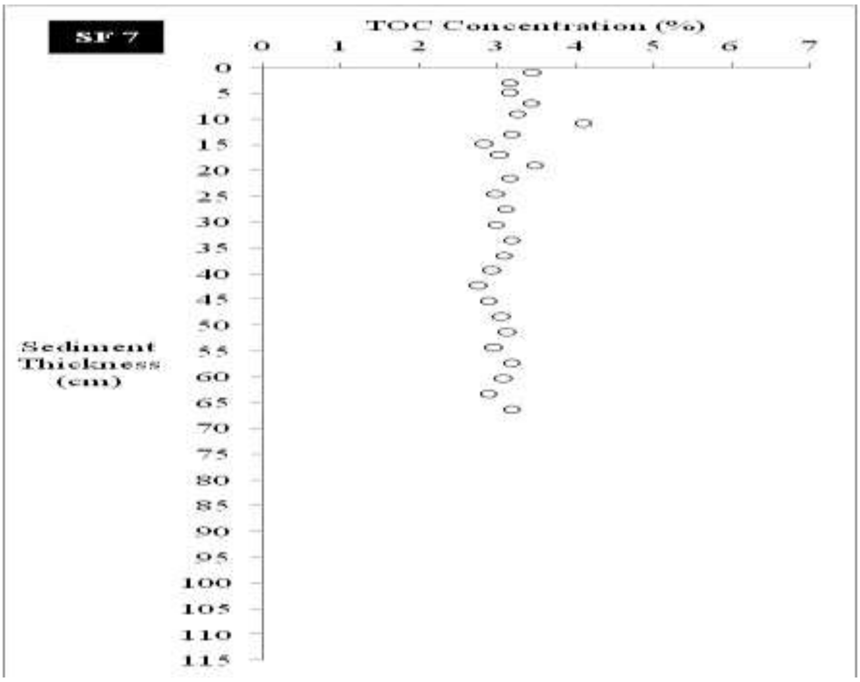

Figure 13 Vertical distributions of TOC percentages in core sediment SF 7

CONCLUSION

Marine core sediment is one the valuable component as it can be used for re-evaluating the past productivity or the environmental condition that occurs in a particular place as well as the aging of the sediment. There are many scientists had used radionuclide ^{210}Pb to observe the age and accumulation years of the sediment. Mn concentration and the total organic carbon content also had been used for the past research to observe the past marine productivity. In modern ocean world, the total annual primary production by phytoplankton is 30 to 50 x 10^9 ton of C. However, total organic carbon content in the sediment is only estimated that only 1 to 0.01% of the primary production is buried deeply in the marine sediments. However, additional work is needed to evaluate the importance of all the processes that occurred in the marine core sediments and its relationship with the past marine productivity.

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