2011 3rd International Conference on Chemical, Biological and Environmental Engineering
IPCBEE vol.20 (2011) © (2011) IACSIT Press, Singapore

Anthropogenic Heavy Metals, U-238 and Th-232 Profiles in Sediments from an Abandoned Tin Mining Lake in Malaysia

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Abstract. Many abandoned areas around and within tin mining lakes system in Malaysia in recent years have been converted into more economically important areas with activities such as agriculture, recreational and residential. The sediment profiles at locations in the lakes are expected to be impacted by the discharge of these near shores and on lakes activities. The studied lake at Kampung Gajah, Malaysia was abandoned for nearly 40 years, and the intensified anthropogenic activities began about a decade ago. The present study explored the heavy metals profiles of sediment at five locations in the lake impacted by such activities. Instrumental neutron activation analysis (INAA) was employed for the determination of metals concentration. Generally synchronous higher concentrations were observed in the younger section of the cores. This coincides with the period of the intensification of anthropogenic activities in the area. Mean metal concentrations for all cores for As, Cr, Mn, Zn, U-238 and Th-232 were 48.9 ppm, 41.1 ppm, 407.9 ppm, 199.1 ppm, 30.6 ppm and 85.7 ppm respectively. These results are twice as high compared to results of a control location on undisturbed land. Discharges from such activities containing heavy metals get their way into the lake through surface deposition by rain water, and remobilized from the depositional areas to the sediment coring sites. U-238 and Th-232 may be attributed to the minerals contained in the tin tailings left in the area.

Keywords: Mining lake sediment, radionuclides, neutron activation analysis.

1. Introduction

Malaysia was once the chief producer and exporter of tin, through her many open cast mining areas that was then known as the "Tin Belt" of Kinta valley at the central Peninsular Malaysia. Due to depletion in deposits, fall in world demands and drop on market value of tin, many of these tin mining operators ceased their operation about 30 to 40 years ago. The ceased mining activities had disturbed the land structure and form, and "wounded and scared" with no-economical value interconnecting man-made lakes. To add salt to the wounds discharges from the activities pollutes the lakes with heavy and toxic metals. Recently, to add values to the abandoned areas, many were converted into agriculture farm, recreational sites and residential areas. However, not much study was carried out on the impact of the presence of pollution, especially heavy metals and radionuclides, in the area to such land conversions.

Heavy metals are released into the environment via airborne contaminants, rural land use activities, sewage sludge, mine waste, industrial waste, wastewater, pesticides and fertilizers applications Thus, in general industrialization and human activities clearly the main contributors to heavy metals discharged into our ecosystem, such as rivers, lakes, estuaries and marines [1, 2, 3]. These metals subsequently enter into the human food chain either directly or indirectly. Some heavy metals are potentially harmful (Cd, Hg, Pb) but some are essentially important to human health (Fe, Ca, Mg), however high concentration could affect human health.

Profiles of sediments could facilitate us to acquire information on contamination of lakes such as heavy metal discharge, atmospheric deposition, past drainage basin or land-use history [4, 5]. Sediments composed

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of fine sand and silt, and due to its stable condition metals to be more easily entrapped in the sediment. Moreover, the fine-grained sediment will acted as effective carrier of heavy metals [1]. The present study explored the vertical profile distributions of heavy metals and radionuclides of anthropogenic origin in sediments of a representative fresh water former tin mining lake, to evaluate the extent of pollution contributed by these metals and radionuclides.

2. Method

2.1. Study Area

The studied former tin mine fresh water lake is about five hectares in area, located on central Peninsular Malaysia, centre at around N 04° 14.954", E 101° 3.023". It is representing one of the many interconnecting lakes system in the vicinity. The deepest point is about 9 m, located near the middle of the lake. During sampling in September 2007 the water volume is estimated to be around 10^8 m^3.

The lake is located about 50 m from a main road. Within the lakes water system there are fish and ducks rearing activities. There are water buffalos and cattle farms, as well as recent settlements on land areas within the lakes system. On the studied lake there are two small islands located near the centre.

2.2. Sampling and Sample Preparation

Sediment cores were collected at five points in the lake by using manual gravity corer with PVC core tube of 50 mm inner diameter. These points represent the different base surface morphology of the lake. Five cores of sediments were sampled at each point. Sediment cores obtained were about 20 to 25 cm in length. The cores were sub-sampled by slicing into 2 cm slices. Samples preparation as described earlier [7] where slices of identical depth of the five cores in each point were mixed to form homogeneous representative aggregate at that depth. The aggregates were oven-dried at 60°C until constant mass, pulverized and sieved through 450 m stainless steel sieves. They were then kept in desiccators for one week to reduce water content. The dried samples were kept in air-tight containers for about six months to ensure secular equilibrium of the uranium and thorium series. Control sample collected approximately 5 km from the study lake and undisturbed by mining activities was prepared in the same manner as the core samples. Table 1 summarizes the sampling locations for samples and control (C2).

Table 1. Sampling locations and water depth

Sampling Points	Latitude	Longitude	Water Depth (m)
S1	N 04° 14.941'	E 101° 03.037'	8.67
S2	N 04° 14.863'	E 101° 03.133'	3.69
S3	N 04° 15.008'	E 101° 03.110'	2.05
S4	N 04° 14.990'	E 101° 02.985'	8.05
S5	N 04° 14.844'	E 101° 03.015'	3.70
C2	N 04° 14.907'	E 101° 02.140'	-

2.3. Measurement of Heavy Metals

The Neutron Activation Analysis (NAA) irradiation and measurement facility at the Malaysian Nuclear Agency was employed to determine heavy metals concentration. Know amount (ca. 0.10 g) of samples and standards were irradiated in the TRIGA MARK II 750 kW research nuclear reactor with thermal neutron flux of 2.0 x 10^{12} $s^{-1}cm^{-2}$. Depending on elements to be determined either short (1 minute) or long (6 hours) irradiation and the corresponding short (20 minutes) or long (3 – 5 days) cooling time procedures were employed. Gamma-ray measurements were carried out using Canberra GEM-series HPGe detector of 1.88

keV resolutions and 25.4% relative efficiency at 1332 keV Co-60 gamma-ray, couple to an MCA. Spectrum analyses were carried out Gamma Vision V6.0 software. Study was done on duplicate samples.

3. Results and Discussion

From Figure 1, generally the results of the present study indicated that all metals concentrations in the sediment cores at all sampling point were more than twice higher than those from the control core, C2. The near uniform trend of metals, uranium and thorium concentrations in the control core profile is an indication of insignificant accumulation of elements over time in the core. However the trend profiles of metals shows synchronously higher concentration in core depth down to about 8 cm. According to previous study on the sediment age of the lake, this correspond to about a decade of sedimentation [6], that coincides with the beginning of anthropogenic activities in and around the lakes system. As for uranium and thorium the same trend is also observable except for cores S4 and S5 (Figure 1(e) and (f)) where higher concentrations were found at older sections of the sediment cores

3.1. Arsenic

The As profile for all cores (Figure 1(a)) showed higher concentration in the younger sediment, near at the surface layers that may be attributed atmospheric deposition from fuel combustion during past mining activities or road traffic and agricultural activities. S2 is located about 50 m from the main road. Previous studies showed atmospheric deposition was mainly linked to high concentration of As, Zn, Co and Pb [7, 8, 9, 10]. It is generally known that As was found in contaminated tin-ore in the form of arsenious oxide and removed by roasting and washing from the ore. The by product, arsenious oxide, might originated from previous mining activities and remobilized into the lake. The similar trend portrayed by As and Mn (Figure 1(c)) could be interpreted as remobilization has taken placed [11]. The overall mean of As concentration in all cores is 48.9 ± 9.6 ppm, which is higher than the Severe Effect Level (SEL) of 33 ppm of the Sediment Quality Guidelines of New York Department of Environmental Conservation (NYDEC), where pronounced disturbance of the sediment dwelling community can be expected [11].

3.2. Chromium

Figure 1(b) showed increasing trend in less deep sediment for Cr concentration in sediments at coring points. However, the profile of S5 sediment core showed an almost constant trend from the upper layer to the bottom of sediment. The presence of Cr in the sediment lake might be due to industrial emission, lithogenic origin (mine extraction), naturally origin or atmospheric deposition [8]. One notable observation here is that the overall mean concentration of 41.1 ± 3.6 ppm is lower than the SEL of 110 ppm, however higher than the NYDEC Lower Effect Limit (LEL) of 26 ppm. This can cause toxicity to some aquatic species in the vicinity [10].

3.3. Manganese

Mn showed an almost identical profile trend as As (Figure 1(c)). Generally, concentration of Mn showed decreasing trend to the upper layer and high at about 10 cm depth. Only S2 and S5 showed significantly high concentration of Mn observed in the upper layer of sediment. Mn could also be attributed to remobalization from into the lake from former ore processing activities. The overall average of Mn in all cores is 407.9 ± 68.3 ppm. This is lower than the LEL concentration of 460 ppm [12].

3.4. Zinc

Smelting operation, usage of fertilizer and pesticides in agriculture, soil erosion due to human activities, fossil fuel and land development could contribute to high concentration of Zn in sediment lake [7, 8, 9]. The studied lake is located near to duck farming activity and main road. This factor as well as the other factors mentioned earlier seems to be consistent in contributing to increasing concentration of Zn in lake sediment, especially the younger sediments (Figure 1(d)). The overall mean of Zn concentration in all cores is 199.1 ± 17.6 ppm, which is higher than LEL of 120 ppm but lower than SEL of 270 ppm of the Sediment Quality Guidelines of New York NYDEC [12].

3.5. Uranium and Thorium

Two contrasting patterns of profile were observed for U and Th (Figures 1(e) and 1(f)). One at locations S1, S2 and S3 that showed almost similar pattern to other metals, while S4 and S5 showed an opposite pattern. The U and Th concentration at the surface layers of the sediment may be due to anthropogenic input from fertilizer used in agriculture. The overall mean of U and Th concentration in all cores are 30.6 ± 6.1 ppm and 85.7 ± 10.0 ppm respectively, which is much higher than the average earth crust composition of 3.5 ppm and 11.0 ppm [13] is expected, due to the high concentration of U and Th in monazite and ilmenite minerals that are abundance in former tin mining areas. Over the years, weathering and erosion remobalized the minerals into the lake [13]. This may explained the observation that higher concentration in older layer of sediments in S4 and S5. The concentration of Th is always higher than U in the lake sediment due to the fact that Th that occurs naturally is among the least soluble and immobile trace element in natural water. Relatively U is more soluble than Th thus has greater mobility in water. A study on the ratio of Th/U of the five cores showed the average values ranged between 2.20 – 4.21. These agreed well to the world average ratio of Th/U of approximately 3.5 – 4.0.

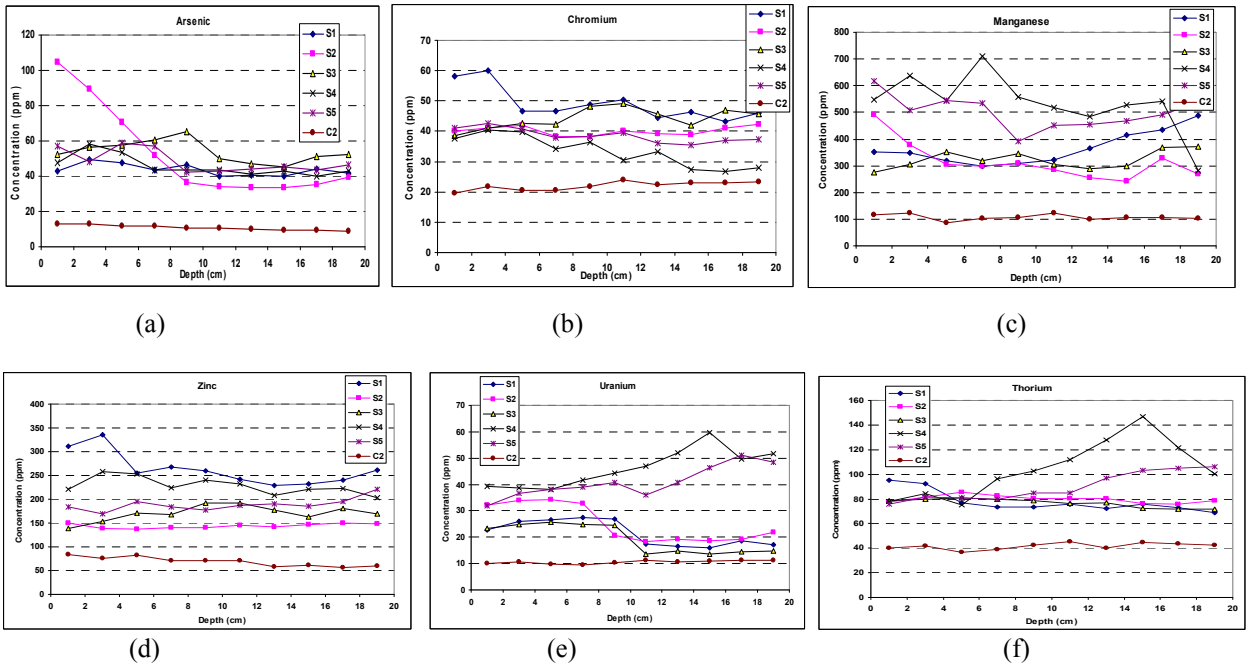

Fig. 1: Depth profiles of As, Cr, Mn, Zn, U and Th in sediment cores and control site.

3.6. Enrichment Factor (EF)

In this study EF was calculated with respect to Aluminum as reference element due to the fact that Al is the one of the most abundance elements on the earth. The mean EF values can be utilized to indicate the degree of anthropogenic pollution within the lake sediment. Range of EF value for As, Co, Cr, Fe, Mn and Zn, Th and U is 14.46 – 16.53 with mean value 15.82, 0.41 – 0.62 (0.51), 0.27 – 0.39 (0.32), 0.27 – 0.41 (0.33), 0.25 – 0.46 (0.33), 1.31 – 2.43 (1.84), 3.23 – 8.99 (4.37) and 2.03 - 11.48 (4.94) respectively. The mean EF values for Co, Mn, Fe and Cr of less than one indicated these metals presence as natural origin or close to background value. While As, U and Th and Zn the mean EF values are all greater than one. This value indicated the lake sediment lake is highly contaminated by As, U, Th and fairly enriched by Zn. The contaminants might be earlier anthropogenic origin because As, U and Th are the characteristics of mining origin or possibly input by the recent human activities [13].

A note worth mentioning here is that although the five cores were collected from different water depths (Table 1) the study was found that no obvious migration of most metals (except Zn) taking place from less

deep to deeper location of the lake. In the case of Zn, the deeper locations (S1 and S4) consistently showed higher concentration in all core layers.

4. Conclusion

The study has found that most of the anthropogenic metals showed an almost regular pattern of depth profile concentrations. Higher concentrations were observed at relatively younger layers (about 10 years old) that that may be attributed to the impact of recent intensification of anthropogenic activities in the area. However natural weathering and erosion may also contributed to the recent accumulation. The sediments were found to be highly enriched with As, U, Th and Zn.

5. Acknowledgements

The authors would like to thank the MOHE Malaysia and RMI UiTM for the approved FRGS Grant No. 600-IRDC/ST/FRGS 5/3/1333 to carry out the study, and the Malaysian Nuclear Agency for the permission to use their gamma-spectrometry and NAA facilities.

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