Use of Radioisotopes in Assessment of Ecological Risk due to Sedimentation and Heavy and Trace Element Pollution in Aquatic Streams

Rakesh Kumar Singhal* and Hirakendu Basu
Analytical Chemistry Division
Bhabha Atomic Research Centre
Mumbai-400085, India

*Email: rsinghal@barc.gov.in

Abstract

Pollution of water bodies by heavy and trace elements is an environmental issue world-wide. Natural and anthropogenic sources are responsible for increase in concentration of trace and heavy element in aquatic medium. Evaluating the likelihood of the environment or atmosphere to be impacted due to the exposure to environmental stressors such as trace or heavy element pollution is called ecological risk assessment. In order to know the chronology of heavy metal deposition, it is important to know sedimentation rate in water bodies. Rate of sedimentation can be directly correlated with heavy metal deposition over the years. Rate of sedimentation can be easily evaluated by either measuring the concentration of ^{210}Pb which is a natural radioisotope or by measuring the concentration of ^{137}Cs which is manmade radioisotope. It is widely dispersed in terrestrial environment due to atmospheric testing of Nuclear weapons until 1961 thereafter Chernobyl (1986) nuclear plant accident added enough inventory of ^{137}Cs in the terrestrial environment. There is also a minor contribution due to Fukushima Daiichi nuclear disaster (2012). Aim of the book chapter is to understand methodology for evaluation of rate of sedimentation using ^{210}Pb or ^{137}Cs radioisotopes and correlate with the chronology of heavy and trace element profiling in sediment and assess associated ecological risk.

Keywords: *Sedimentation rate; ^{210}Pb, ^{137}Cs, Mumbai Harbour Bay*

1. Introduction

To understand distribution and migration behaviors of the trace and heavy element is an important objective of environmental scientists. Elements entering aquatic streams can get accumulated and subsequently incorporated in sediments through series of geological processes, hence finally depositing in sediment [1-7]. As a result, the quantification of heavy and trace element in sediment can be an indicator of pollution level in that waterbody. Over the years layer by layer fresh sediment gets deposited with varying concentration of trace and heavy elements. In order to evaluate ecological risk to aquatic organisms it's necessary to know depth profiling of the heavy metals along with the sedimentation rate.

One most important use of radioisotopes in ecological risk assessment is in the evaluation of sedimentation rate and sediment dating. Radionuclides such as ^{137}Cs and ^{210}Pb are normally preferred for dating and sedimentation rate analysis for lakes, sea, estuaries, river and other coastal systems. The natural radionuclides distribution in the bottom sediment of water bodies can work as tracer for study of accumulation and dispersal mechanism. This plays a role in sedimentological composition study in waterbodies. Natural radionuclides are present everywhere in earth's environment which includes soil, water, air, sediments, flora and fauna. Many natural radionuclides in environments arise from the decay series of thorium and uranium. Some of these are in practice to evaluate the sedimentation rate. Among them the most favorable isotopes in practice for evaluating the sedimentation rate are ^{210}Pb and ^{137}Cs [1,8-9].

2. Dating of sediment with ^{210}Pb

Most widely used and most discussed sediment dating technique is the ^{210}Pb method, which results from ^{238}U series and occurs naturally. This technique is not dependent on any anthropogenic radioactivity inputs in the waterbodies. The technique is accurate, well defined, especially in stable environment with consistent sediment input. This technique also yields reasonably accurate results for non-uniform sediment inputs (in-consistent sedimentation rate). In this technique, two simple models, namely Constant Initial Concentration (CIC) and Constant Rate of Supply (CSR) models are usually applied [10,11]. ^{226}Ra is parent isotope for ^{210}Pb in the radon series. Disequilibrium between these two radio isotopes arises through diffusion or escape of intermediate radioisotope ^{222}Rn which is gaseous in nature. Fraction of ^{222}Rn atoms produced from ^{226}Ra in sediment, may escape into atmosphere and then decay to ^{210}Pb through a series of short-lived radionuclide in-between. Thus produced ^{210}Pb is removed from atmosphere by precipitation. It may fall on land surface or in the waterbodies. The ^{210}Pb falling into the waterbodies gets transported by the stream of water then subsequently deposited at bottom surface and mix with the sediment. The ^{210}Pb therefore has two origins of inputs (both natural) into the sediment. One is ^{210}Pb, originally formed in atmosphere from ^{222}Rn decay which is termed as "unsupported ^{210}Pb". Other one, termed as "supported ^{210}Pb" is originated from ^{222}Rn produced due to natural ^{226}Ra present in sediments. Pictorial presentation of same is shown in the Figure-1 along with a core showing various section of the core [8-9]. To give better insight for the evaluation of excess ^{210}Pb at a given depth in given core is shown in Figure 1, where x=0 is taken as water-sediment interface, x is given depth of the core and x $=\infty$, is the depth of the core where it is assumed that there is no physical disturbance to the sediment. At x= ∞, the concentration of ^{210}Pb is taken as supported ^{210}Pb. In order to evaluate the excess ^{210}Pb value a X_t, concentration of ^{210}Pb at x point minus the concentration of ^{210}Pb at point ∞.

$$- \frac{dA}{dt} = \lambda A$$

$$\int_{A_1}^{A_2} - \frac{dA}{A} = \int_{t_1}^{t_2} \lambda dt$$

$$\ln \frac{A_1}{A_2} = \lambda \left(t_2 - t_1 \right)$$
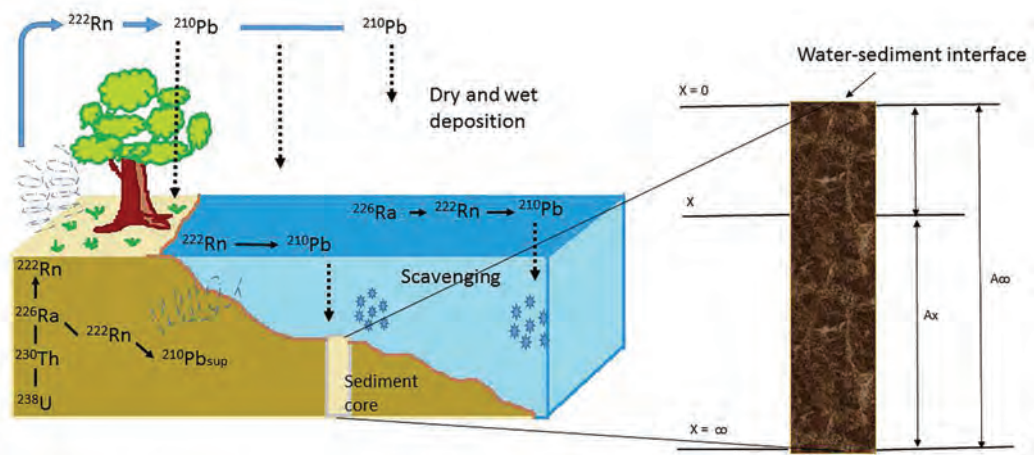
Figure 1: Pictorial presentation of deposition of excess ^{210}Pb in terrestrial environment and how to calculate concentration of excess ^{210}Pb at particular depth in a given sediment core.

Basis of ^{210}Pb dating method is determination of "unsupported [210]Pb" activities at different layers of cores (with depth) in sediments. These excess ^{210}Pb activities are obtained by subtracting "supported [210]Pb" activity from ^{210}Pb activities experimentally determined in each layer. "Supported [210]Pb" is calculated from an undistorted layer at sufficient depth. In this model, namely CIC model the assumption is that inputs of "unsupported [210]Pb" to sediment is done at constant flow and sedimentation rate with time is constant.

To derive mathematical expression to calculate the sedimentation rate in this method radioactive decay equation is used.

$$\ln \frac{A_1}{A_2} = \frac{\lambda \left(z_2 - z_1 \right)}{S}$$

Sedimentation rate can be expressed as $S = (Z_2-Z_1)/(t_2-t_1)$ and (t_2-t_1) can be replaced in the above equation by $(Z_2-Z_1)/S$ where A_1 is activity at time t_1 and depth Z_1 and A_2 is activity at time t_2 and depth Z_2. So the following equation is obtained.

$$S = \frac{\lambda \left(z_2 - z_1 \right)}{\ln \frac{A_1}{A_2}}$$

Slope of ln (excess ^{210}Pb) vs depth plot is $\ln(A_2/A_1)/(Z_2-Z_1)$ which gives

Sedimentation rate (S) = $-\lambda$/-Slope

λ is known theoretically for ^{210}Pb [0.0311 y^{-1} for ln (activity) plot and 0.01352 y^{-1} for log (activity) plot]; Slope is obtained from the ln (excess ^{210}Pb) vs depth plot and sedimentation rate (cm/y) is calculated. Figure 2 is a typical plot of log (^{210}Pb excess) vs core depth showing sedimentation rate of 1.3 cmy^{-1}.

The other model namely CRS assumes constant "unsupported ^{210}Pb" accumulation to sediment but variation in sedimentation rate (supply) is permitted [4–6]. As per CRS model (Figure 1):

$$t = \lambda^{-1} \times \ln(A_\infty/A_X)$$

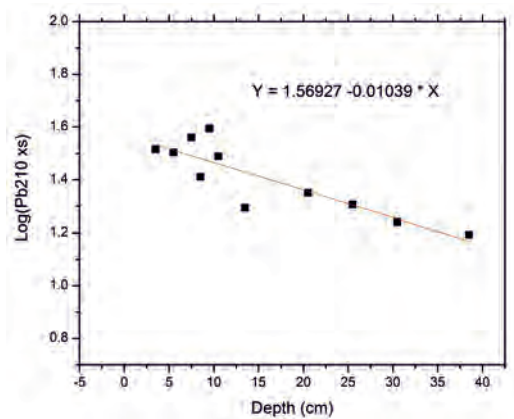where integrated activities of ^{210}Pb are A_∞ : from surface to A_o, and A_x : from x to A_o.

Figure 2: Variation of excess ^{210}Pb with depth in a sediment core

3. Dating of sediment with ^{137}Cs

Another way of dating the bottom sediments of water bodies is by using ^{137}Cs which is artificial radionuclide. Its natural analogue ^{133}Cs (stable) is present in small quantity on earth and Cs is chemically and physiological analogous to potassium. ^{137}Cs is produced by fission of ^{235}U and ^{239}Pu. Its half-life is 30.17 years that decays to ^{137}Ba by beta emission (metastable). ^{137}Ba again decays to ^{137}Ba (stable) by gamma emission. This gamma ray has 661.6 keV energy which is used to characterize ^{137}Cs when studied by gamma ray spectrometry.

At present there are three main inputs of ^{137}Cs in environment namely nuclear weapon tests done between 1953 and 1963, Chernobyl nuclear accident in 1986 and Fukushima Daiichi nuclear disaster in 2011. ^{137}Cs is monovalent cation and strongly fixed by clay minerals in sediments, this help to date the sediment by analyzing ^{137}Cs. High charge density and active organic groups make the clay selective towards metal ions. K$^+$ and Cs$^+$ can penetrate the outer loosely bound layer where they get trapped and attached to the clay. Being gamma active even a trace of ^{137}Cs is detectable in soil or sediment. Studies involving ^{137}Cs adsorption in literature

reveals that sediment and soils can retain fallout originated ^{137}Cs at least in low quantity. [137]Cs found in marine sediments is anthropogenic source due to atmospheric nuclear weapon testing, 90% inputs of which were in the year 1963-1964.

The Use of ^{137}Cs as a tracer for sedimentation process is possible because of its irreversible binding to sediment, sand, clay and silt, and its long half life (30.2 y). [137]Cs is also a marker of major nuclear disasters like Chernobyl accident (1986) and Fukushima disaster (2012). In depth profile of ^{137}Cs activity, will show two peaks, peak close to the surface (0 cm) will corresponds to the year 1986 whereas peak at the bottom corresponds to 1960. Typical plot obtained in case of sediment core sample collected near Mumbai (Mumbai Harbour Bay (MHB)) is given in Figure 3 which can be used for sedimentation rate determination of that site.

4. Pollutant deposition in water bodies and its correlation with sedimentation rate

The concentrations of pollutants like trace metal, heavy metal etc. are sometimes beyond the safe limits in coastal estuaries because of natural, and anthropogenic inputs. Understanding the distribution and migration of these pollutants in the sediment and aquatic system is an important task of the environmental scientists. The pollution is mainly contributed by discharges from industries for metal processing, steel plant (Cd, Cr, Zn from electroplating), dye formulators (Cr, Cd, Cu, Zn), chemical manufacturing plants, smelters (Cu, BP, Ni), refineries (As, BP). Sedimentation rate determination using radionuclides plays an important role here, the sediments can be dated which is utilized for calculating the age of the pollutants (year of inputs) in the aquatic medium [1,2]. It also helps to relate the industrialization or urbanization around the coastal zone.

5. A case study for deposition of metal in Mumbai Harbour Bay (MHB)

In order to understand the metal deposition in water bodies, work done by Singhal et al in MHB is considered [1]. The MHB is a land surrounded waterbody connected with Arabian Sea (in south) and Ulhas river (in north) [latitude $19.01°$ to $19.50°$N longitude $72.55°$ to $73.01°$E]. It is locally called Thane Creek covering approximately 200 km^2 during high tide and approximately 150 km^2 during low tide. Maximum depth in the creek is 10.4 m. Concentration of different elements from 50 core sediment samples were analyzed and time of their inputs were evaluated using sedimentation rate determined in MHB using [137]Cs (Figure 3).
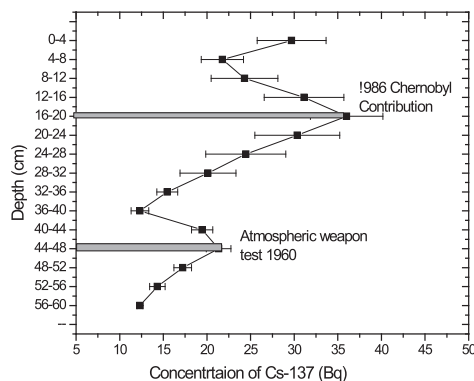
Figure 3: 137Cs depth profiling in core sediment samples collected at sampling station 15 of MHB. (Reprinted with permission from Springer Nature)

5.1 Concentrations of elements in core sediment samples

Concentration of various metal ions observed in case of samples collected from MHB is shown in the Figure 4 and Figure 5. From these Figures, it is clear that metal ions coming under the category of Major elements show no variation within the core. Elemental depth profiling of the sediments in 50 different core samples collected from floating stations show K (potassium), Mn (manganese), Ca (calcium), Fe (iron) and Ti (titanium) concentrations did not have significant variation as longitudinal variation for all 5 elements were within 1–3% suggesting homogenous nature of sediments. These variations may arise due to statistical error. Concentration of Ni, Cu, Zn varied with depth (Figure 5). Maximum values for Cu (copper), Ni (nickel) were 16–20 cm depth core fractions. In case of Zn maximum concentration was at 24–28 cm depth from surface. This indicates that Cu, Ni and Zn intrusions are because of industrial activities towards downstream direction. Similar longitudinal variations were observed for all the sampling locations in both upstream and downstream direction of MHB.
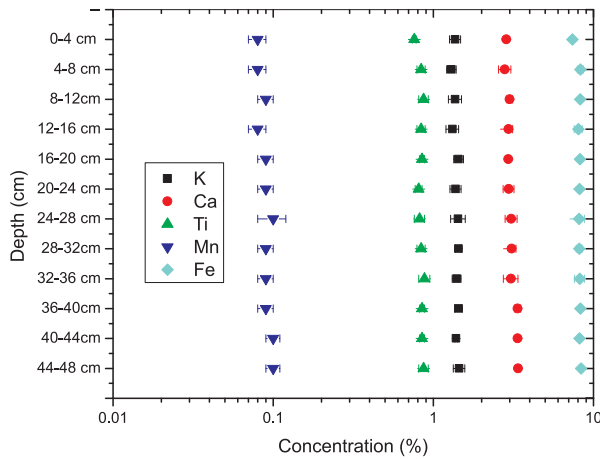

Figure 4: Concentration of Ca, Ti, K, Mn and Fe in core sediment samples from various depths. (Reprinted with permission from Springer Nature)
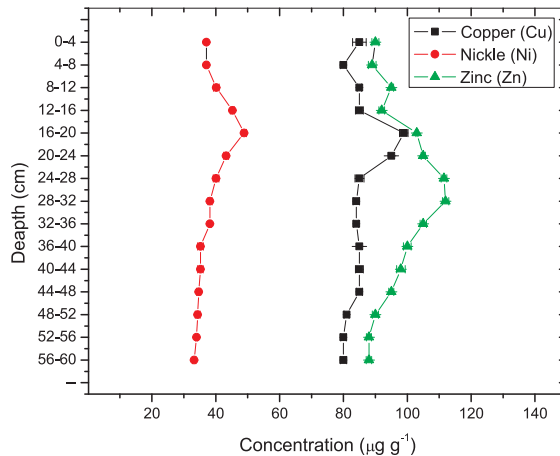

Figure 5: Depth profile of Ni, Cu, Zn for the core sediments. (Reprinted with permission from Springer Nature)

5.2 Evaluation of chronological profile of different element

Uniform distribution of Ti, Ca, K, Fe and Mn at various depths suggests no industrial intrusion for them over the years in MHB and their presence is mainly because of natural origin. Their concentrations in different depth core sediments are also close to world average value [12]. Elevated concentrations of Cu, Ni and Zn at certain depth core sediments suggest industrial inputs of them in year 1991, 1988 and 1982 respectively. These periods were arrived using evaluated sedimentation rate (0.92 ± 0.08 cm y^{-1}) in MHB. The analysis show gradual increase of concentrations of these elements till 1980-1990 which is consistent with industrial development of Thane–Belapur industrial area situated on east side of MHB. The recent decrease in their concentrations may be attributed to effluent release regulations imposed by Govt. The trend suggests the decrease of release were most effective since 1998. Peak depth for Cu, Ni, Zn gradually decreased in sampling stations closer to Thane-Belapur industrial belt validating the observation that intrusion of these elements originated from the effluent of industrial release. Deeper migration of Zn is attributed to its higher K_d (distribution coefficient) value. Identified industries for release of Ni, Cu, Zn are paints, dye, smelter, electroplating, metal associated factories.

5.3 Geochemical indexing for pollution intensity study

Many models are proposed to evaluate ecological risk arising from accumulation of trace and heavy elements in sediment. Work done by Muller is internationally accepted in this regard [13]. The equation introduced by Muller (1979) is as follows:

$$I_{geo} = \log_2 [Me]_{Sed} / 1.5 [Me]_{Reference site}$$

$[I_{geo}]$ is Geo-accumulation Index

$[Me]_{Sed}$ is pollutant concentration at monitoring point;

$[Me]_{Reference}$ is average concentration of same pollutant in sediment of reference site.

Reference site should ideally be an undisturbed area without any industrial activity. In the work on MHB, reference site was chosen a point is an aquatic stream flowing in the Himalayan range of India [$30.34°(N)$ and $79.33°(E)$; altitude 1390 m]. The I_{geo} is a qualitative scale for evaluation of pollution intensity. Using I_{geo} classification, intensity of sediment pollution in MHB was in the order: Ni>Cu>Zn. I_{geo} value was >2 in 20-24 cm depth core sediment for Ni suggesting "Moderately to strongly polluted" by Ni during that time period. For Cu it was "moderately polluted" (I_{geo} = 1.38) and for major elements like K, Ti, Ca, and Mn, I_{geo} was <0 indicating presence of unpolluted sediments with these metals in MHB. I_{geo} value 0.58 for Fe suggest unpolluted to moderately polluted sediment in MHB with respect to Fe. For surface sediments (0-4 cm) I_{geo} for all the elements were either <0 or 0-1 suggesting no pollution or moderate pollution of recent times. Trace metal distribution in the surface and bottom sediment along with geochemical pollution indexing of two different sites namely Sundarban and Pichavaram mangrove ecosystem were carried out details of which were discussed elsewhere [14,3]. Pichavaram is located in Chidambaram region in Tamil Nadu, India. Sundarban mangrove ecosystem is formed on Ganga-Brahmaputra delta spread over hundreds of islands through Bangladesh and India in South East Asia [14,3].

6. Quantification of ecological risk due to metals

Estimate the degree of metals contamination in sediment is generally quantified by enrichment factor (EF).

$$EF = \frac{(C_m/C_{A1})_{sediment}}{(C_m/C_{A1})_{crust}}$$

C_m and C_{Al} are pollutant (metal) and Al content in the area of study (sediment or earth crust), respectively. In general, a metal ion such as Aluminum (Al) with high natural abundance and least effected by anthropogenic activities. Aluminum is used to normalize pollutant concentration in earth crust or sediment. The modified pollution index (MPI) is calculated using given formula [15]:

$$MPI = \sqrt{\frac{(EF_{average})^2 + (EF_{max})^2}{2}}$$

EF_{max} and $EF_{average}$ are max and average value of metal ion enrichment factor, respectively. MPI is combination of EF and Nemerow Pollution Index. Site pollution qualitative assessment can be done with help of MPI [5]. Potential ecological risk index (RI) and the mean effect range median quotient (m-ERM-q) and are used to assess biological effects and ecological risk in earth crust or sediments [16,17]. The RI is given by

$$RI = \sum Er_m$$

$$Er_m = CF \times T_m$$

Er_m: potential ecological risk factor,

CF: contamination factor, $CF = C_m$ (metal concentration in sediment) $/B_m$ (metal background concentration),

T_m: biological toxicity factor.

7. Conclusion

This article describes the use of radioisotopes (^{210}Pb and ^{137}Cs) in the determination of sedimentation rate and its utility in assessment of potential ecological risk due to heavy and trace element pollution in aquatic streams. A case study for deposition of metal in Mumbai Harbour Bay (MHB) was explained as an example to correlate the sediment dating with the inputs of pollutants in the aquatic medium.

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