Assessment of marine contamination by Neutron Activation Analysis in Bangladesh

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Abstract— The sand samples collected from Himchhori sea beach of Cox's Bazar in Bangladesh were analyzed to detect the elements qualitatively and quantitatively by Neutron Activation Analysis (NAA) method. The relative standardization approach was used for the qualification using IAEA certified Reference Materials Soil-7 and SL-1 and the NIST 1633b Coal Fly Ash. Short irradiation and long irradiation were performed by using the pneumatic transfer system with the thermal neutron flux of 2.75×10^{12} n/cm^2/sec and at dry central thimble (DCT) of the reactor with a neutron flux of 1×10^{13} n/cm^2/sec respectively. The gamma spectrometry, the data acquisition and the gamma peak analysis were done by using a pc-based HPGe detector coupled with a digital gamma spectrometry system, the software Genie-2000(Canberra) & MAESTRO-32(ORTEC) and the software Hypermet PC version 5.12 respectively. Quality control of the analysis was completed by analyzing several certified materials as mentioned above. The uncertainty was calculated based on the total uncertainty budget of the NAA method. Based on short irradiation of K, Dy, Mg, Ti, Mn and V, and on long irradiation, Ce, Fe, Cr, Co, Rb and Th were determined quantitatively and qualitatively. The measured concentrations of these elements were compared with the world reference values. Most of the elements are in the normal level whereas some elements like Cr, Co and Ti exceeded the reference values.

Index Terms— BDL, Contamination, Gamma spectrometry, HPGe Detector, NAA, Marine pollution, Trace Element.

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1 Introduction

Marine pollution may cause of direct discharge of industrial, agricultural and residential waste, the spread of invasive organisms into the ocean or runoff hazardous pollutants released from the atmosphere into the waters due to rain. Potential toxic chemicals may adhere to tiny particles which are taken up by plankton and benthos animals, most of which are primary foods for secondary feeders. As a result, toxins are concentrated within ocean food chain and quickly absorbed into marine food webs. In this way, marine toxins can be transferred to land animals, and appear later in meat and dairy products [1]. These can cause a change to tissue matter, biochemistry, behavior, reproduction, and suppress growth in marine life. Land mining for copper, gold, etc., are another sources of marine pollution e.g, according to the United States environmental protection agency (USEPA), more than 40% of watersheds in the western continental US has been contaminated due to mining [2]. Discharge of cargo residues from bulk carriers can pollutes ports, waterways and oceans. Windblown dust and debris, including plastic bags, are blown seaward from landfills and other areas. The global climate change raise the temperature of the ocean and increase the levels of carbon dioxide (CO_2) in the atmosphere which subsequently acidifying the oceans. Consequently, aquatic ecosystems are altering and modifying fish distributions, with impacts on the sustainability of fisheries and the livelihoods of the communities that depend on them. Healthy ocean ecosystems are also important for the mitigation of climate change [3].

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The marine pollution causes a significant health impacts and most of the countries in the world which share ocean or bay conducts regular and extensive studies on marine pollution. USA, Australia, Spain, UK, China, Japan, Netherlands, India etc. have been conducted research work to provide a reliable database on marine contamination. Unfortunately, in Bangladesh, there is no reliable database available for marine pollution [4]. All the inhabitants in Bangladesh may be affected directly or indirectly by marine pollution. For example, marine pollution causes of desertification and the great asset in the country like mangrove forest 'Sundarban' is at under risk. Due to marine pollution, it is very difficult for biota to survive. Concerning the safe and healthy life of mass peoples of Bangladesh, the present study has been conducted on Himchhori sea beach sediments that lie nearly nine (09) km from the Cox's Bazar town. The major (Al, Ca, Fe, K, Ti, Mg, Na) and trace (Ba, Co, Cr, Cu, Ga, Ni, P, V) elements are very important from aspects of both soil and environment quality. Excess or meager levels of these elements can cause toxicities or deficiencies in plants, and thus ultimately, in mammals and human being, which feed upon them. So the presence of these materials is of primary interest for human health, animals, plants, as well as aquatic environment. Nowadays, the presence of potentially toxic trace elements in soil is of intense public concern on both global and regional scale. So this study include the detection of trace elements present in sea beach sand and establish the baseline concentration data of major, minor and trace elements in the coastal area of the Bay of Bengal, taking Himchhori sea beach as an experimental site. Finally this work determined the contamination of marine pollution to understand the health risk of millions of peoples of Bangladesh.

2 Experimental Method

Neutron activation analysis (NAA) is a nuclear analytical technique that can be used for determining the concentrations of elements in a diminutive amount of materials. It can allow the precise identification and quantification of the elements in the samples. In the present study the nuclear reactor based NAA

method is applied due to its sensitivity and capability of performing both elements of qualitatively and quantitatively in the sand samples [5].

3 Samples Collection and preparation

The sand samples were collected from various depths (0-5 ft.) of several locations of Himchhori to Inani Sea Beach in Cox's Bazar and were coded distinctly. The samples were made air dried under laboratory temperature and relative humidity condition in an oven until having constant weight to remove the moisture and crushed into fine powder with an Agate mortar and pestle. These samples are transferred into ultra-clean polyethylene vial individually with identification number. The bullets are then sealed and preserved carefully for irradiation. To apply relative standardization approach, 3 standards: IAEA-Soil-7, IAEA-SL-1 and NIST 1633b Coal Fly Ash was prepared as the same way as the sample.

4 Irradiation and Gamma ray counting

For short-lived radio-nuclides, individual sample was taken into a larger polyethylene irradiation tube (Rabbit) and irradiated in the 3 MW TRIGA reactor using the pneumatic transfer system with the thermal neutron flux of 2.75×10^{12} n/cm^2/sec at the reactor power 250 kW for only a minute. In case of long-lived radio-nuclides, the total number of samples and standards, along with some Al-0.1% Au foils, were taken into a long polyethylene irradiation tube at a time; then it was kept close tightly and sent for irradiation with the thermal neutron flux of 1×10^{13} n/cm^2/sec at 500 kW. After long irradiation (about 40 minutes to 1 hour), samples turned into highly radioactive and were kept in a shielded place for 3 or 4 days to decay the short lived radio-nuclides. The gamma spectrometry of all the irradiated samples and certified reference materials was performed by using a pc-based HPGe detector coupled with a digital gamma spectrometry system. The data acquisition and the gamma peak analysis were done by using the software Genie-2000(Canberra) & MAESTRO-32(ORTEC) and the software Hypermet PC version 5.12 respectively. For short lived radio nuclides the counting was taken for 3 minutes for the determination of Al, Ti, V, Mg etc and counting duration were 6 minutes for the determination of K, Dy, Mn etc. The counting period for long irradiated samples was set to 1800s and subsequently increased to 2400s and 3000s on 2nd and 3rd day of counting, respectively. For relatively long half-lived elements, a second counting was recorded about a month after the 1st counting being recorded.

5 Standardization and Detection Limit

Quality control of the analysis was assured by considering Soil-7 as a principal standard, the ratios of obtained vs. certified concentrations of different elements for SL-1 and 1633b were calculated and were found to be within 10% deviation from the certified values which certify a good agreement of the experiment. The ability of NAA procedure to determine the minimum amounts of an element reliably is presented by the detection limit (DL). The DL depends on the irradiation, the decay and the counting conditions. It also depends on the interference situation including such things as the ambient background, Compton continuum from higher energy gamma rays, as well as the gamma ray spectrum interference from such factors as the blank from pre-irradiation treatment and from packing materials. The detection limit was calculated using Currie's formula,

$$\text{Detection limit (DL)} = 2.71+4.65\sqrt{B} \qquad (1)$$

Where, B is the background under a γ–ray peak. The detection limit of the elements that we have got, is below the experimental results which indicate the reliability of our study.

6 Results and Discussions

The concentrations of different elements were measured by evaluating the gamma ray peak areas from (n, γ) reaction. The reaction is chosen on the basis of the detector efficiency, the reaction cross-section and the gamma emission probability. However, only the reactions, which lead to the highest yield of gamma rays, were considered. For instance, in the case of Fe, $^{58}Fe(n,\gamma)^{59}Fe$ reaction of 1099.3 keV, energy was chosen as it produces the most intense gamma line [6]. The peak areas were used for the determination of the specific metal concentration by relative standardization using equation given below which was then formulated and therefore, concentrations of elements were calculated. The activation equation for relative NAA is

$$\frac{\text{Weight of element "x" in sample}}{\text{Weight of element "x" in standard}} = \frac{A_x(sample)\times(e^{-\lambda t})_{sample}}{A_x(sample)\times(e^{-\lambda t})_{standard}} \qquad (2)$$

From the equation (2), knowing the activities of A_x in sample and in standard, the sample and standard decay times and the weight of "x" in the standard, the weight of element "x" in the sample can be calculated.

Total Uncertainty Budget

Uncertainty of the measurement was defined as "a parameter associated with the results of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measured". Its quantification was of utmost importance in all types of measurement. Uncertainty of the samples was calculated according to the 1993 ISO Guide and was added to the uncertainty in the measurement.

The elements

The average elemental concentrations are shown in figure-1. Among the twelve elements in the sediment sample, the concentration of four major elements Fe, K, Ti and Mg are found to be 204.5±7, 117.9±5, 48.6±12 and 179.3±3 mg/g, respectively, while the three trace elements Co, Cr and V have the concentrations of 58.9±2.21, 138.03±4.69 and 75.67±2.59 µg/g, respectively. The concentrations of other five elements of Ce, Rb, Th, Mn and Dy are 97.49±3.25, 50.44±3.6, 15.87±0.52, 80.31±2.95, and 6.68±0.23 µg/g , respectively.

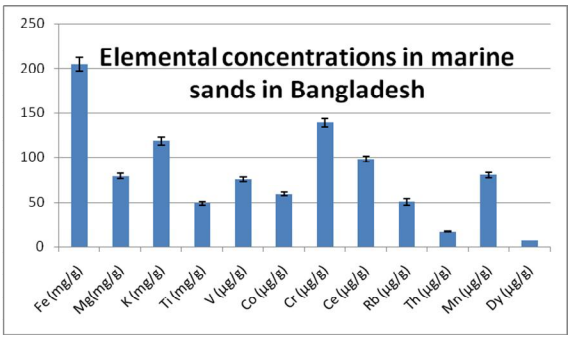

Figure-1: Average elemental concentration in sediment samples

Comparison with earlier studies

The experimental results were compared with earlier studies throughout the world like WA (World's average) [7], WSR(World's surface rock) [7], WAS (World's average soils) [8], Average shale [9], Crustal average [10] and Indian coastal values (East coast and west coast) [11], to estimate whether marine pollution has occurred or not as well as having ability to judge our overall condition. The reason for this comparison is to evaluate the causes of the concentrations that we observed and better understand the possible sources of discrepancies. At the same time, the corresponding values were also compared with US standards [12], Coastal Sediments–Brazilian Antarctic Station [13], Peru margin [14], Namibian mud lens [14] and Gulf of California [14]. The comparison is shown in figure 2(a) and 2(b), the horizontal line indicates the concentration of elements from Himchhori, Bangladesh which is compared with others throughout the world.

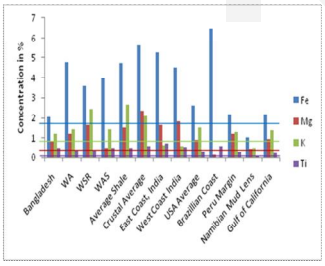

Figure-2(a): Concentration of major element's throughout the world.

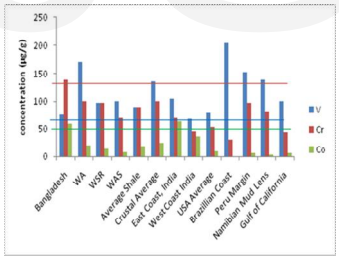

Figure-2(b): Concentration of trace element's throughout the world.

Major Elements (Fe, Mg, K and Ti)

In Figure-2(a) the major elements ***Fe, Mg, K and Ti*** concentrations are compared with earlier studies [7-14]. Here the **Fe** concentration in Bangladesh is well below among all except Namibian mud lens. So it may be concluded from this point that ***Fe*** level may be safe now. The Mg concentration is below from the nine earlier studies and is above from WAS, Brazilian coast Namibian mud lens. Perhaps this does not pose a threat to human beings but it must be noteworthy to point this out. The ***Mg*** concentration shows a significant deviation (around 50%) from that of west and east coast of India but this is very near to US average value. So it seems that ***Mg*** condition is not so bad in the context of contamination. The concentration of ***K*** is in a good consistent compared to earlier studies but it deviates significantly (87% and 103%) from east and west coast of India. It deviates the most from Namibian mud lens but Peru margin, Gulf of California and US values showed a satisfactory unison with it. This needs to study further why this concentration deviates significantly. The concentration of ***Ti*** exceeds a little (16%, 27% and 3%) from three (03) of five (05) earlier studies WA, WSR, Average Shale but exceeds significantly (67%, 94%, 386%, 111%) from US average, Peru margin, Namibian mud lens and Gulf of California. Since its value is below east, west coast of India and Crustal Average, further study is required to reach a conclusion with ***Ti*** contamination.

Trace element (Co, Cr and V)

The concentration of trace elements (**Co, Cr** and **V**) are is shown in the Figure-2(b) which included our finding and earlier studies. This comparison indicates that the concentration of toxic metal ***Cr*** in Bangladesh beach is maximum. It is beyond doubt that the sand of Bangladesh beach is highly contaminated with *Cr*. The comparison of experimental value of **Co** concentration with the earlier studies indicates high concentration. Therefore, our beach is highly contaminated with ***Co*** element. With respect to earlier studies and the values for other part of the world figure-2(b), it can be concluded that the concentration of ***V*** is very good condition in Bangladesh beach.

Conclusions

In summary, it can be concluded that the Sea beach in Bangladesh are highly contaminated with Cr and Co both of which are trace element and highly toxic. In case of ***Ti***, it can be said that the beach is little bit polluted by this element. On the other hand the concentration of ***Fe***, ***K*** and ***V*** are found almost similar or lower than the other parts of the world. These results can be used as base line data and further study is required to find out the reasons and origin of this contamination.

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