IMPLICATIONS FOR INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA) TO STUDY THE BHAIRAB RIVER SEDIMENTS USING RESEARCH REACTOR BASED GAMMA SPECTROMETRY

M. Sc. Thesis

SHEIKH MD. ANOWAR HOSSAIN
ROLL NO: 1655554
SESSION: JULY-2016

DEPARTMENT OF PHYSICS
KHULNA UNIVERSITY OF ENGINEERING & TECHNOLOGY
KHULNA-9203, BANGLADESH
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**A THESIS SUBMITTED TO THE DEPARTMENT OF PHYSICS,
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**DEPARTMENT OF PHYSICS
KHULNA UNIVERSITY OF ENGINEERING & TECHNOLOGY
KHULNA-9203, BANGLADESH**
APRIL-2018

DECLARATION

This is to certify that the thesis work entitled "Implications for Instrumental Neutron Activation Analysis (INAA) to Study Bhairab River Sediments using Research Reactor Based Gamma Spectrometry" has been carried out by Sheikh Md. Anowar Hossain in the department of Physics, Khulna University of Engineering & Technology, Khulna, Bangladesh. The above thesis work or any part of this work has not been submitted anywhere for the award of any degree or diploma.

Signature of Supervisor

….....

(Professor Dr. Jolly Sultana)

Signature of Candidate

……..……...

(Sheikh Md. Anowar Hossain)

Approval

This is to certify that the thesis work submitted by Sheikh Md. Anowar Hossain entitled "Implications for Instrumental Neutron Activation Analysis (INAA) to Study Bhairab River Sediments using Research Reactor Based Gamma Spectrometry" has been approved by the board of examiners for the partial fulfillment of the requirements for the degree of M. Sc. in the Department of Physics, Khulna University of Engineering & Technology, Khulna, Bangladesh in April 2018.

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MY BELOVED PARENTS

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Author

ABSTRACT

Pollutions are increasingly becoming great concerns for human beings. The present study investigates the distribution and contamination of trace elements in the sediment samples of the Bhairab River, passing through the Khulna city, Bangladesh. Instrumental Neutron Activation Analysis (INAA) method has been used for analyzing the sediment samples collected from Bhairab River during September-october'2016. Quality control of the analysis has also been performed by analyzing certified reference materials IAEA-Soil-7. The irradiation of the samples and standards have been performed using 3 MW TRIGA Mark-II Research Reactor and the gamma-ray spectrometry has been performed by High Purity Germanium (HPGe) detector system. Total element of 28 like Na, Mg, Al, K, Ca, Sc, Cr, Mn, Fe, Co, Zn, Ga, As, Br, Sb, Cs, Ba, Ce, Nd, Eu, Tb, Dy, Ho, Tm, Yb, Lu, Ta, and W has been determined from ten sediment samples collected from different areas of the Bhairab River. In this experiment, NIST-1633b (coal fly ash) has been used as the standard and the analytical accuracy and precisions have been ensured by the repeated (n = 4) analysis of IAEA-Soil-7. Both geochemical and anthropogenic origins of heavy metals (HMs) are considered during the evaluation of compositional trends by the environmental indices such as contamination factor (CF), pollution load index (PLI), geo-accumulation index (Igeo) and enrichment factors (EF). Experimental evidence as pollution level of pollutants evaluated by different pollution indices suggests that Bhairab river sediments are less contaminated. The calculated pollution load index values also suggest the corrosion of the sediment quality and to be helpful to set a picture of metal contamination of the Bhairab River and will be able to find out the elemental abundances of the sediments.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
AERE	Atomic Energy Research Establishment
AS	Analytical Signal
CEC	Cation Exchange Capacity
CEPT	Common Effluent treatment Plant
CHNX	Carbon, Hydrogen, Nitrogen and Heteroatoms
CV-AAS	Cold Vapor Atomic Absorption Spectroscopy
ED-XRF	Energy Dispersive X-Ray Fluorescence
EF	Enrichment Factor
ENAA	Epithermal Neutron Activation Analysis
F-AAS	Flame Atomic Absorption Spectroscopy
GF-AAS	Graphite Flame Atomic Absorption Spectroscopy
GI	Gastrointestinal
GIS	Geographic Information System
HPGe	High Purity Germanium
IAEA	International Atomic Energy Agency
ICP	Inductively Coupled Plasma
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
Igeo	Geo-accumulation Index
INAA	Instrumental Neutron Activation Analysis
IPI	Integrated Pollution Index
IPI	Integrated Pollution Index
LAFS	Laser Atomic Fluorescence Spectroscopy
LIBS	Laser Induced Breakdown Spectroscopy
LTE	Local Thermodynamic Equilibrium
MPC	Mounted Pelican Controller
NAA	Neutron Activation Analysis
NDNAA	Non-Destructive Neutron Activation Analysis

PCA	Principal Component Analysis
PIXE	Proton Induced X-Ray Emission
PLI	Population Loaded Index
PXRF	Portable X-Ray Fluorescence
RBS	Rutherford Back Scattering
REE	Rare Earth Elements
RK	Rock Samples
SEM	Scanning Electron Microscope
SRM	Standard Reference Material
TS	Top Soil
TXRF	Total Reflection X-Ray Fluorescence
WHO	World Health Organization
XPS	X-ray Photoelectron Spectrometry
XRD	X-Ray Diffraction
XRF	X-ray Fluorescence

CHAPTER 1

Introduction

1.1: General Introduction

Environmental Pollutions are increasingly becoming great concerns for human beings. Nature is the place where human being and all other creature conduct their life. But if the environment is polluted then man and other creature can't conduct their life successfully. Men are polluting the environment in various ways. So man should be aware to protect their life. For conducting life in environment it is necessary to keep it free from radioactive pollution. Various elements are responsible to pollute the environment such as heavy metal, various chemicals, toxic element etc. But the most dangerous reason of environment pollution is radiation.

To assess the radiation of the selected area near the Sundarban the largest mangrove forest of the world which is situated in the southernmost part of Bangladesh. It is acting as a natural shield for the coastal region from the cyclones and other natural disasters. Lot of rivers and tributaries are flowing through Bangladesh and marched with the Bay of Bengal after crossing the Sundarban. Most of the rivers are moderately to severely contaminated by heavy metals and metalloids originated from growing industrialization and (/or) urbanization. Bhairab Rivers are the important rivers those contain heavy metals from the Mongla export processing zone as well as from other industrial and urban sources. As these rivers are crossing the Sundarban, the sediments of Bhairab River should be monitored and checked for the potential presence of heavy metals. In the present work sediment samples has been collected from Bhairab to find the radiation level and contamination by using instrumental neutron activation analysis (INAA).

Instrumental Neutron Activation Analysis (INAA) use the neutrons produced by research reactor and it is the most prominent nuclear technique. INAA is a nondestructive nuclear analytical technique that utilizes nuclear research reactor and high purity Germanium (HPGe) detector to determine multi-elements simultaneously in samples with different matrices. High Purity Germanium (HPGe), nuclear research reactors, detectors are playing

a vital role in the applied and theoretical field of physics. But its maintenance cost is so high and HPGe gamma detector requires a huge funding (Rudnick, 2014). Bangladesh Atomic Energy Commission (BAEC) possesses the country's only nuclear research reactors at Savar Research reactors produce neutrons by the fission of ^{235}U and these neutrons are used for the theoretical and applied researches.

Over several analytical techniques, INAA is considered as the referee method. In INAA, samples (e.g., Cosmochemical, geochemical, biological etc) with known mass are irradiated by neutron in research reactor which activates the elements of that sample by the capture of thermal neutron. Each of the activated (radioactive) elements emits gamma ray of specific energy and these gamma rays are then analyzed by the HPGe gamma detector. Presence of any elements is ensured by the gamma peak of specific energy (qualitative analysis). In the relative method of INAA, relevant standards are simultaneously irradiated by neutrons with those of the unknown samples. Then from the decay corrected specific activities of the samples and standard are compared to determine the accurate and precise concentrations of any elements (quantitative analysis) in the unknown samples. In our countries prospects, INAA can be used to study the environmental geochemistry, public health & nutrition, urban & industrial contamination and so on. By choosing the proper neutron irradiation (i.e., with different reactor power) and gamma counting schemes (gamma counting after specific decay time), practically 25-35 elements can be accurately measured in single sample specimen by INAA. In present study, an initiative is taken to prepare a baseline data for the elemental abundances of Bhairab River to monitor this area in future for a potential contamination.

1.2: Sources of River Contamination

There are various ways to categories and examine the inputs of pollution into our ecosystems. Generally, there are three main types of inputs of pollution: direct discharge of waste into the ocean, runoff into the water into the rain, and pollutants that are released from the atmosphere. They are discussed below with some other types of origin of contamination:

Pollutant enters rivers and the sea directly from urban sewerage and industrial waste discharge, sometimes in the form of hazardous and toxic wastes. Inland mining for copper,

Gold etc., is another source of marine pollution (Bashar Bhuiyan, 2013). Most of the pollution is simple soil, which end up in rivers flowing to the sea. However, some minerals discharged in the course of the mining can cause problems, such as copper, a common industrial pollution, which can interfere with the life history and development of coral polyps. Mining has a poor environmental protection agency, mining has contaminated portion of the hand wastes of over 40% of watersheds in the western continental US. Much of this population finishes up in the sea. Surface runoff from farming, as well as urban runoff from the construction of roads, building, ports, channels, and harbors, can carry soil and particles laden with carbon, nitrogen, phosphorus, and minerals. This nutrient-rich water can cause fleshy algae and phytoplankton to thrive in coastal areas, known as algal blooms, which have the potential to create hypoxic condition by using all available oxygen. Polluted runoff from roads and highways can be significant source of water pollution in coastal area (Rushlan, 2007).

Ships can pollute waterways and oceans in various ways. Oil spills can have devastating effects. While being toxic to marine life, polycyclic aromatic hydrocarbons (PAHs), the components in crude oil, are very difficult to clean up, and last for years in the sediment and marine environment. Discharge of cargo residues from bulk carriers can pollute ports, waterways and oceans. In many instances vessels intentionally discharge illegal wastes despite foreign and domestic regulation prohibiting such year (usually during storms).

The invasive freshwater zebra mussels, native to the black, Caspian and Azov seas, were probably transported to the Great Lakes via ballast water from transoceanic vessel. Meinesz believes that one of the worst cases of a single invasive species causing harm to an ecosystem can be attributed to a seemingly harmless jellyfish. *Mnemiopsisleidyi*, a species of comb jellyfish that spread and so it now inhabits estuaries in many parts of the world. It was the first introduced in 1982, and thought to have been transported to the Black sea in a ship's ballast water. The population of the jellyfish shot up exponentially and, by 1988, it was wreaking havoc upon the local fishing industry. Now that the jellyfish have exhausted the zooplankton, including fish larvae, their numbers have fallen dramatically, yet they continue to maintain stranglehold on the ecosystem.

Another pathway of pollution occurs through the atmosphere. Wind-blown dust and debris, including plastic bags, are blown seaward from landfills and other areas. Dust from the Sahara moving around the southern periphery of the subtropical ridge moves into the Caribbean and Florida during the warm season as the ridge builds and moves northward through the subtropical Atlantic the USGS links dust events to a decline in the health of coral reefs across the Caribbean and Florida, primarily since the 1970s. Climate change is raising ocean temperature and raising levels of carbon dioxide in the atmosphere (Peavy, 1985). These rising levels of carbon dioxide are acidifying the oceans. This, in turn, is altering aquatic ecosystems of fisheries and the livelihoods of the communities that depend on them. Healthy ocean ecosystems are important for the mitigation of climate change.

The oceans are normally a natural carbon sink, absorbing carbon dioxide from the atmosphere. Because the of atmosphere carbon dioxide are increasing, the oceans are becoming more acidic. The potential consequences of oceans acidification are not fully understood, but there are oceans structures made of calcium carbonate may become vulnerable dissolution, affecting corals and the ability of selfish to form shells. Oceans and costal ecosystem play an important role in the global carbon cycle and have removed about 25% of the carbon dioxide emitted by human activities between 2000 and 2007 and about half the anthropogenic CO_2 released since the start of the industrial revolution. Rising ocean temperatures ocean acidification means that capacity of the ocean carbon sink will gradually get weaker, giving rise to global concerns expressed in the Monaco Declarations.

Marine debris is mainly discarded human rubbish which floats on, or is suspended in the ocean. Eighty percent of marine debris is plastic – a component that has been rapidly accumulating since the end of the World War two**.** The mass of plastic in the oceans may be as high as one hundred million metric tons. Toxic additives used in the manufacture of the plastic materials can leach out their surroundings when exposed to water. Waterborne hydrophobic pollutants collect and magnify on the surface of plastic debris, thus making plastic far more deadly in the ocean than it would be on land.

Apart from plastics, there are particular problems with other toxins that do not disintegrate rapidly in the marine environment. Examples of persistent toxins are PCBs, DDT, pesticides, furans, dioxins, phenols and radioactive waste. Heavy metals are metallic

chemical element that have a relatively high density and are toxic or poisonous at low concentrations. Examples are mercury, lead, nickel, arsenic and cadmium. Such toxins can accumulate in the tissue of many species of aquatic life in a process called bioaccumulation.

Marine pollution causes to accelerate the environmental pollution greatly. So it gets priority to most of the countries which share ocean or bay. Most of these governments conduct regular and extensive studies on marine pollution. In USA, for example, researches have been conducted to provide a reliable database on contamination of marine pollution. Similarly, Australia, Spain, UK, China, Japan, Netherlands, India, etc. have their own researches on the issue. Unfortunately, in Bangladesh, there is no reliable database available for marine pollution.

1.3: Theory of Neutron Activation Analysis

Neutron activation analysis (NAA) was discovered in 1936 when Hevesy and Levi (Laul, 1979) found that samples containing certain rare earth elements became highly radioactive after exposure to a source of neutrons. From this observation, they quickly recognized the potential of employing nuclear reaction on samples followed by measurement of the induced radioactivity to facilities both qualitative and quantitative identification of the elements present in the samples. NAA is now one of the most sensitive and accurate techniques used for qualitative and quantitative analysis of major, minor, and trace elements in samples from almost every conceivable field of scientific or technical interest. For many elements, NAA offers sensitivities that are superior to those possible by any other technique.

The principle involved in NAA consists of first irradiating a sample with neutrons in a nuclear reactor to produce specific radionuclides. As the sequence of events occurring during the most common type of nuclear reaction used for NAA, namely the neutron capture or (n,γ) reaction (Glascock, 2004), is illustrated in Figure 1.7, when a neutron interacts with a target nucleus via an inelastic collision a compound nucleus forms in an excited sate. The excitation energy of the compound nucleus is gained due to the addition of binding energy of the neutron with the nucleus. The compound nucleus will almost instantaneously de-excite into a more stable configuration through emission of one or more

characteristic prompt gamma rays. In many cases, this new configuration yields a radioactive nucleus which also de-excites (or decays) by emission of one or more characteristic delayed gamma rays, but at a much slower rate according to the unique half-of the radioactive nucleus. Depending upon the particular radioactive species, half-lives can range from fractions of second to several years.

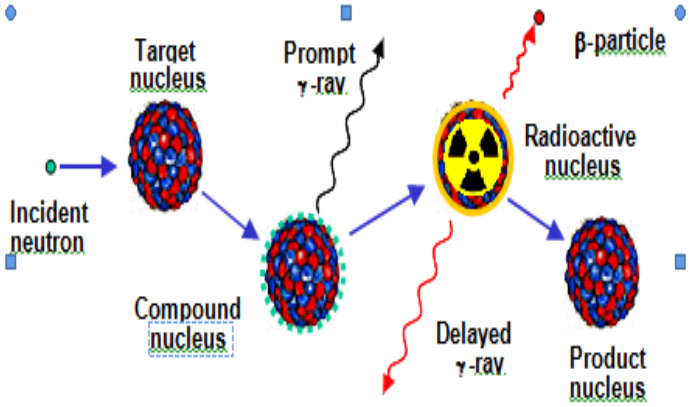

Figure 1.1: Diagram illustrating the process of neutron capture by target nucleus followed by the emission of gamma rays.

When a neutron interacts with a target nucleus, a compound nucleus is formed. The compound nucleus has certain finite lifetime (10^{-13}-10^{-15}sec) during which it remains highly excited state due to high binding energy and kinetic energy of the incident neutron in the nucleus. De-excitation of the compound nucleus is formed. Each of these processes (shown in Figure 1.8) has a certain probability, depending on the nuclear cross-section of each mode, which is related to the excitation of the compound nucleus (Laul, 1979). As stated earlier, radioactive capture reaction is used in NAA.

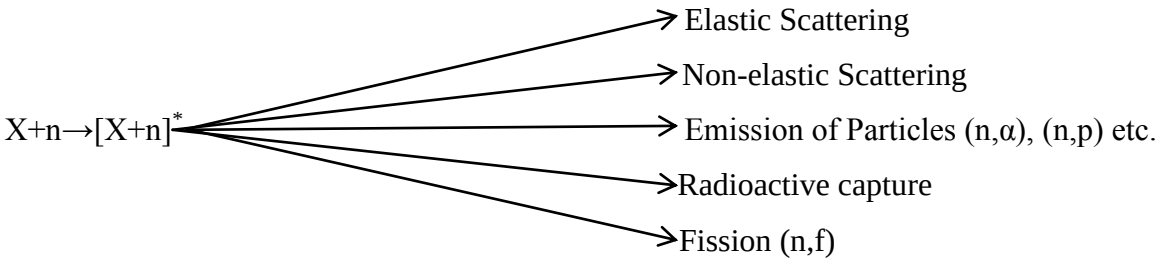

Figure 1.2: Probability of occurring nuclear reaction.

Neutron activation is a method of determining the elemental composition of a sample. Being a nuclear technique, its results refer only to the number of atoms of various elements present, not there chemical state .Thus, no information about compounds or types of chemical bonding is provided by NAA. The sample to be activated is placed into a concentrated beam of neutrons, which is usually provided by a nuclear reactor. The neutron produced by a fission reaction interacts with the nucleus- in an excited state. The activity of the targeted elements depends on the following factors (Avino, 2007)

1) The number of the inactive target nuclei (the higher their number, the more intense is their activity);
2) The collision cross section;
3) The intensity of the neutron flux;
4) The duration of the irradiation; and lastly;
5) The radioactive decay coefficient (a parameter which is a characteristic of the newly-formed nuclear specials);

The sample may be counted immediately, for elements with short half-lives. The reason for the delay for isotopes with longer half-lives is to allow the isotopes with a short half-life to decay away, thereby preventing interference and allowing the isotopes with longer half-lives to be more easily measured .After the sample decays, it is counted using high purity Germanium (HPGe) gamma ray detectors. Gamma rays are very penetrating, so the gamma rays emitted from the center of the simple easily reach the detector. The position of each peak determines the energy of the gamma ray (identifying responsible element), and the area under the peak is proportional to its concentrations. Final results are obtained after correcting for detector efficiency, decay time, size of the sample, and counting and irradiation times. The comparator standard approach is normally employed with this method. A standard is irradiated and counted along with the sample. Although matrix problems are not usual, standards are usually selected to be similar to the sample.

Classification of Neutron Activation Analysis

- **Instrumental neutron activation analysis (INAA)**

NAA with the use of automated sample handling gamma-ray measurement with solid-state detectors, and computerized data processing is generally possible to simultaneously measure more than thirty elements in most sample types without chemical processing. The application of purely instrumental procedures is commonly called instrumental neutron active analysis (INAA) and is one of NAA's most advantages over other analytical techniques (Glascock, 2004). INAA is often referred to as non-destructive NAA or NAA without post-irradiation radiochemical separation.

- **Radiochemical neutron activation analysis (RNAA)**

NAA in which chemical separation are done to sample after irradiation to remove interferences or to concentrate the radioisotope of interest, the technique is called radiochemical neutron active analysis (RNNA) (Glascock, 2004). This technique referred as destructive NAA and is performed infrequently due to its high labor cost. The NAA technique can also be categorized according to whether gamma rays are measured during neutron irradiation or at some time after the end of the irradiation as-

- **Prompt gamma- ray neutron activation analysis (PGNAA)**

The PGNAA technique is generally performed by using a beam of neutron extracted through a reactor beam port. Fluxes on samples irradiated in beams are on the order of one million times lower (Glascock, 2004) than on samples inside a reactor but detectors can be placed very close to the sample compensating for much of the loss in sensitivity due to flux. The PGNAA technique is most commonly used for determination of lighter elements (H, B, Si etc.) and elements with extremely high neutron capture cross-sections (B, Cd, Sm, and Gd); elements which decay too rapidly to be measured by delayed gamma-ray neutron active analysis (DGNAA).

- **Delayed gamma ray neutron activation analysis (DGNAA)**

DGNAA is useful for the vast majority of elements that produce radioactive nuclides. The technique is flexible with respect to time such that the sensitivity for a long-lived

radionuclide that suffers from interference by a shorter-lived radionuclide can be improved by waiting for the short-lived radionuclide to decay. This selectivity is a key advantage of DGNAA over other analytical methods.

- **Epithermal neutron activation analysis (ENAA)**

ENAA is useful when the nuclides of interest have much higher nuclear cross-section (n, ϒ) by resonance capture of epithermal neutron than the thermal neutron, while the interfering elements have not, or have lower reaction cross-sections, the activity by epithermal neutrons can considerably increase the sensitivity of the detection for an element.

- **Fast neutron activation analysis (FNAA)**

When the measurement of elements (lighter elements as C, N, O, F and S) by thermal neutron is not favorable because of the very low (n, ϒ) cross-section, the first neutron (14Mev) can be used to produce reaction of type (n, 2n), (n, α), (n, p) and (n, n). The advantage of 14 MeV NAA are that it is fast and non-destructive, can be used on a routine basis, is ideal for short irradiations, and is particularly sensitive for detection of lighter elements.

Characteristics of NAA

The development of analytical techniques has led to the expansion of new methods (ICP-AAS, ICP-NS, etc), which can also be widely applied in analytical chemistry (Cristache et al, 2008) NAA is still competitive in many areas. There are many situations in which INAA has theoretically better analytical characteristics than other methods of elemental analysis such as atomic absorption spectroscopy (AAS), inductively coupled plasma spectroscopy (ICPS) and total reflection X-ray fluorescence (TR-XRE). So it is important to remain realistic in evaluating the roll of INAA. Therefore, the most typical analytical characteristics of INAA are given as follows:

- The method is of a multi element character, i.e. it enables the simultaneous determination of many elements without chemical separation.

- In the case of instrumental determination, the preparation of samples involves only the preparation of representative samples and this reduces the danger of contamination to a minimum and accelerates the whole analytical process.
- Relative freedom from matrix and interference effects.
- Sensitivity and applicability for minor and trace elements in a wide range of matrices.
- An inherent potential for accuracy compared to other analytical technique. Since the theoretical basis of NAA is well understood, a complete uncertainty budge can be made.
- The totally independent nature of the method as a nuclear-based property in contrast to the electronic nature of most other analytical techniques.
- INAA performs non-destructive analysis of the samples.
- The capability of INAA for multi-element determination, often allowing 30 to 40 elements to be determined in many matrices.

Application of NAA

- Archaeology.
- Study the redistribution of uranium and thorium due to processing.
- Selenium distribution in aquatic species in selenium-contaminated fresh water impoundments.
- In-situ radiotracers for dosage-form testing.
- Nutritional epidemiology –nutritional and biochemical/genetic markers of cancer.
- Nutritional epidemiology –a cohort study of the relationship between diet, molecular, markers, and cancer risk.
- Nutritional epidemiology –thyroid cancer study, non-melanoma skin cancer study, molecular epidemiology of prostate cancer.
- Geological science.
- Cosmo chemical samples.
- Semiconductor materials and other high-purity materials.
- Soil science.

1.4: Instrumental Neutron Activation Analysis

Instrumental Neutron Activation Analysis (INAA) is one type of Neutron Activation Analysis. It is used to determine the concentration of trace and major elements in a variety of matrices. A sample is subjected to a neutron flux and radioactive nuclides are produced. As these radioactive nuclides decay, they emit gamma rays whose energies are characteristic for each nuclide. Comparison of the intensity of these gamma rays with those emitted by a standard permit a quantitative measure of the concentrations of the various nuclides.

Importance of INAA

We have seen that elemental analysis is a technique where inorganic or organic compounds were used to determine elements present in different samples such as soil, vegetables, human body parts (e.g. hair, nail, skin etc.). From ancient time to present, men are trying to invent techniques which are more accurate, precise, sensitive, reliable etc. Due to their hard and soul try they have invented various techniques to determine elements in samples. Now a day we have various techniques to determine elements. Through these techniques we have understood that how much the elements we have examined are polluted or safe. We have taken proper steps if any problem arises. It is easy to treat any disease in its initial stage. But proper steps need to take to diagnose such disease. We can know the place where we live are safe or polluted by testing various elemental analyses. If it is polluted we can take proper steps to live there. Among different types of elemental analysis neutron activation analysis is more perfect and useable. Neutron activation analysis has various types such as Instrumental neutron activation analysis, Radiochemical neutron activation analysis, Prompt gamma neutron activation analysis, Epithermal neutron activation analysis, Fast neutron activation analysis etc. Among these types of neutron activation analysis we have chosen instrumental neutron activation analysis.

Instrumental Neutron Activation Analysis (INAA) has become very important due to its various advantages such as:

a) Number of elements -Sixty-seven common and rare earth elements become radioactive when exposed to the neutron flux in a reactor. Of these 67 elements, over 50 can be

identified and measured quite readily. No other methods can determine such number of elements at a time.

b) Multi-element - By using different combinations of irradiation and decay times, it is possible to measure a large number of elements from isotopes of different activities and half-lives. A standard analysis package can routinely analyze for 32 elements in a single sample. INAA is the only procedure that can simultaneously measure so many elements.

c) Highly sensitive - The method permits measurement of all detectable elements with great sensitivity; many elemental concentrations are measurable in parts per million (ppm) or parts per billion (ppb).

d) Elemental analysis-Determines element regardless of their chemical form (ferric vs. ferrous). This can be either an advantage or a disadvantage.

e) Non-destructive -Unlike other techniques, the sample is not destroyed by the analysis, and can be re-analyzed if necessary.

Among all properties, non-destructiveness is most efficient property. Due to this property the samples we have analyzed do not losses any of its property. So we can re-use it in several times. If any confusion is occurred then we can re-analyze it. Among all techniques and all properties if INAA this is a referee method.

Various types of analytical tools have been implemented for studying the chemical composition of environmental geochemical samples, such as atomic absorption spectroscopy (Soto-Jiménez 2001), inductively coupled plasma mass spectrometry (Khan 2015a; Barnard 2013), inductively coupled plasma atomic emission spectrometry (Schramel and Xu, 1991), inductively coupled plasma optical emission spectrometry etc. Unlike the above mentioned analytical methods, instrumental neutron activation analysis (INAA) is free from chemical digestion and is nondestructive as well as independent of chemical form (Tamim2016). INAA is considered to be a primary method of measurement (Greenberg, 2011) and possesses a versatile applicability (Noli and Tsamos, 2016; Rakib

2013; Kong and Ebihara, 1997). So in this study we have used INAA for the chemical characterization of Bhairab River.

Fundamental Equation for INAA Method

There are two ways in which INAA can be treated mathematically such as:

- Absolute INAA method
- Comparative INAA method

Absolute INAA Method

The basic equation used for INAA calculation in absolute method is,

$$A_0 = \frac{MN_A\theta}{W}\sigma\varphi\{1 - e^{-\gamma t_i}\} \quad \ldots\ldots\ldots\ldots\ldots\ldots(1.1)$$

Where, A_0 is the activity or the disintegration rate at the end of irradiation time t_i.

M is the mass of the element, $N_A = 6.673 \times 10^{23}$, is the Avogadro's number, σ is the cross-section in barn, φ is the neutron flux, in neutron m^{-2} s^{-1}, θ is the isotopic abundance, W is the atomic number.

Usually, in neutron activation analysis, the activity of the radionuclide is measured experimentally in a sample to deduce the unknown mass (M) of the element by the above equation.

Correction must be made for the decay period t_d and counting period t_c

Where,

Decay factor, $F_d = e^{-\gamma t_d}$ and

Counting Factor, $F_c = \frac{1-e^{-\gamma t_c}}{\gamma t_c}$

So, the basic equation for INAA in absolute methods becomes,

$$A_0 = \frac{MN_A\theta}{W}\sigma\varphi\{1 - e^{-\gamma t_i}\}\{e^{-\gamma t_d}\}\{\frac{1-e^{-\gamma t_c}}{\gamma t_c}\} \ldots\ldots\ldots(1.2)$$

Hence

$$M = \frac{A_0 W}{N_A\theta\sigma\varphi\{1-e^{-\lambda t}\}\times F_d \times F_c} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1.3)$$

All the factors on the right side of the above equation are, in principle, known or can be measured. Thus, it can be possible to calculate the mass of the element in a simple. The

difficulty of accurate measurement of σ leads to the difficulty of measuring neutron flux density φ and also the value of φ changes defending on time and the location in most powerful neutron sources like nuclear reactors, sample and its container cause perturbation of neutron flux density (flux depletion and self-shielding of neutrons), which is very difficult to evaluate precisely.

The activity A can be obtained from the following relationship.

$$A = \frac{R}{\varepsilon I_\gamma} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.4)$$

Where, R is the counting rate to full energy peak caused by the gamma rays used for the activity measurement, ε is the absolute counting efficiency of the gamma rays, and I_γ is the intensity of gamma rays.

Comparative INAA method

In the comparative INAA method, an element "X" in a sample and a known amount of the same element "X" as a standard are irradiated together and both sample and standard are counted under exactly the same conditions by the same radiation detector. This procedure eliminates any uncertainty in the parameter and in the decay scheme and detection efficiency. The INAA equation by the comparative method is thus reduced to a simple form, as shown below

$$\frac{Mass\ of\ element\ \text{X} in\ sample}{Mass\ of\ element\ \text{"X" in standard}} = \frac{A_X In\ sample \times \left(e^{\gamma t_d}\right) sam}{A_{X\ in\ standard} \times \left(e^{\gamma t_d}\right) std}$$

Knowing the activities of X^* in sample and standard, the sample and standard decay times and the mass of the element "X" in the standard, the mass of the element "X" in the sample is then calculated.

In a multi element determination of 30 to 40 elements in the comparative method requires the use of several synthetic individual or mixed solutions, or certified reference material, whereas the absolute method requires only one standard (Laul, 1979).

1.5: Motivation

Human, animal, plants, earth and environment are indirectly connected to each other and necessary for the existence of healthy life. A healthy environment depends on the good habits of human beings and the circumstances they create. Men are polluting the environment in various ways. So man should be aware to protect their life. For conducting life in environment it is necessary to keep it free from pollution. Various elements are responsible to pollute the environment such as heavy metal, various chemicals, toxic element etc. But the most dangerous reason of environment pollution is radiation. Contamination of the natural environment gives birth to the lots of diseases which make human beings weak mentally and physically. Air pollution, water pollution and soil pollution are the most dangerous forms of pollution causing direct heath disorders to the human beings. This widely spreading pollution need to be taken under control for the healthy survival of life on the planet in future. Various experiments were taken for knowing the situation of pollution. Elemental analysis of soil particles has become important, because the particles have effects on the environment and health.

Khulna, a district city of Bangladesh, is called an industrial city. It is the third largest economic centre in Bangladesh. It is situated north of the Port of Mongla and has various heavy and light industries. The major sectors are jute, chemicals, fish and seafood packaging, food processing, sugar mills, power generation and shipbuilding.

Khulna is an old river port which is an important hub of Bangladeshi industry and hosts many national companies. It is served by Port of Mongla, the second largest seaport in the country. It is also one of the two principal naval command centres of the Bangladesh Navy. Navy base BNS Titumir is located in the city. It is regarded as the gateway to the Sundarbans, the world's largest tidal forest and home of the Bengal tiger. Khulna is also situated north of the Historic Mosque City of Bagerhat, a UNESCO World Heritage Site. There are several mills. Some of them are Cable Factory, Sonali Jute Mill, Mohasin Jute Mill, Anser Flour Mill, Jute Press, Senhati Re-rolling Mill, Star Jute Mill etc. This economically important city is situated by the river of Bhairab. The River is getting polluted by the heavy metals and other radioactive metals due to the rapid urbanization. That is so much hazardous for public health. But very little initiative has taken of measuring this. Aim of the present study is to assess the radiation of the selected area near

the Sundarban. The objectives of this study are multi-elements determination in the ten sediment samples collected from the different places of Bhairab River by INAA, identification and quantification of heavy elemental contaminants, Study of heavy element's provenance and the potential ecological risk assessment for the heavy elemental contamination.

CHAPTER 2

Literature Review

The present research work has been done to investigate the amount of heavy metals in sediments at Bhairab River. Not only man but also other creature lived on soil. So it is necessary to free from pollution. Now a day's most of soil in every country is polluted. But the limits of pollution are different at different countries. To know the limit of pollution and to know the amount substances that are responsible for soil pollution various experiment has been taken. So from the literature data the limit of pollution can be known at different countries. Thus, a review work on this regards was carried out by searching the most recent edition of some journals which are given below with the relevant information.

Vasconcelos et al., (2009) present determination of Uranium and Thorium activity concentrations using activation analysis in beach sands from extreme south Bahia, Brazil. Since levels of natural radioactivity are the major cause of external exposure to gamma radiation. So the determination of activity concentration of primordial radionuclides, such as ^{238}U and ^{232}Th, in soils, sand and rock is of basic importance to estimate the radiation levels to which man is directly or indirectly exposed. In their study beaches sands samples were collected from eight different locations in order to process of specific activity of ^{238}U and ^{232}Th. The samples have been analyzed by instrumental neutron activation analyses and for determination of thorium concentrations and delayed neutrons analysis for determination of uranium. The mean specific activity for ^{238}U and ^{232}Th was higher in Cumuruxatiba than in others locations studied. Alcobaça and Caraíva also presented high values. The concentrations of these radionuclides were compared with typical world values and Cumuruxatiba have specific activity higher than the others locations, 2,984 Bq/kg maximum value for ^{238}U and 1,8450 Bq/kg maximum value for ^{232}Th and activity concentrations in Cumuruxatiba are higher in black sand than in no black sand, suggesting presence of monazite.

Gowd et al., (2010) presented heavy metal contamination in soils. They were collected fifty three samples from Jajmau and Unnao industrial areas India, from top 15 cm layer of

the soil and were analyzed for heavy metals by using Philips Magi X PRO-PW 2440 X-ray fluorescence spectrometer. The data reveals that the soil in the area is significantly contaminated with heavy metals. Table 2.1 shows the average concentrations of various elements.

Table 2.1: Concentrations of various elements

Element	Experimental Data (mg kg^{-1})	Average (mg kg^{-1})
Cr	161.8 - 6227.8	2652.3
Ba	44.1 - 780.9	295.7
Cu	1.7 - 126.1	42.9
Pb	10.1 - 67.8	38.3
Sr	46.6 - 150.6	105.3
V	1.3 - 208.6	54.4
Zn	43.5 - 687.6	159.9

Soil contamination was assessed on the basis of geo-accumulation index (I_{geo}), enrichment factor (EF), contamination factor (CF) and degree of contamination. Indiscriminate dumping of hazardous waste in the study area could be the main cause of the soil contamination, spreading by rainwater and wind. So the results of the study show the impact of anthropogenic agents on abundances of heavy metals in soils of the study area and it is extremely contaminated due to many years of random dumping of hazardous waste and free discharge of effluents by number of industries like cotton and wool textile mills, tanning and leather manufacturing industries, large fertilizer factories and several arms factories. The detected levels of total metal contamination in many of samples were found to exceed international threshold values.

Etim and Adie (2012) performed on assessment of toxic heavy metal loading in topsoil samples. Samples that were loaded Pb, Cd, Cr, Cu, Co, Mn, Ni, Zn, and Fe in topsoil samples (TS) collected from the vicinity of limestone quarry in South Western Nigeria was investigated. Thirty TS were sampled within ½ km radius from exploration area and 5 background samples from undeveloped area 10 km away from the study area. Limestone rock samples (RK) were also analyzed for metals' content. All samples were pretreated and leached with appropriate acid solutions for some properties. All leachates were analyzed

with Atomic Absorption Spectrophotometry (AAS) technique. Table 2.2 shows pH range of various elements.

Table 2.2: pH range of various elements

Element	pH Range	Average
Soil	6.65 to 8.23%	7.44%
Sand	55.8 to 75.0%	65.4%
Silt	16.6 to 34.6%	25.6%
Clay	8.43 to 13.6%	11.015%

These properties compared with those of background samples. Rock samples (RK) showed high Fe and Mn enrichment. Metals levels (mg/kg) in TS with background levels in parenthesis ranged as follows: 11.5 to 27.7 (10.5) Pb, 0.28 to 3.18 (0.55) Cd, 12.1 to 17.4 (5.50) Cr, 80.6 to 55.8 (3.81) Cu, 8.93 to 23.5 (11.1) Co, 262 to 710 (637) Mn, 6.34 to 17.4 (6.10) Ni, 36.0 to 620 (24.4) Zn, and 6585 to 13440 (4563) Fe. The elevated enrichment suggests influence from exploration activities. Residual phase showed highest enrichment for all metals possibly, because of high sand content. Positive correlations were shown between all metals, except Mn and Cd that were negative. Geo-accumulation index rating showed <0 for Mn denoting un-contamination, while others ranged from 1 to 2 indicating moderate contamination.

Bhuiyan et al., (2010) performed on heavy metal pollution of coal mine-affected agricultural soils in the northern part of Bangladesh due to coal mine-affected agricultural soils. From their analysis soil pollution assessment was carried out using enrichment factor (EF), geo-accumulation index (Igeo) and pollution load index (PLI). The soils show significant enrichment with Ti, Mn, Zn, Pb, As, Fe, Sr and Nb, indicating inputs from mining activities. The Igeo values have revealed that Mn (1.24±0.38), Zn (1.49±0.58) and Pb (1.63±0.38) are significantly accumulated in the study area. The PLIs derived from contamination factors indicate that the distal part of the coal mine-affected area is the most polluted (PLI of 4.02). Multivariate statistical analyses, principal component and cluster analyses, suggest that Mn, Zn, Pb and Ti are derived from anthropogenic sources, particularly coal mining activities, and the extreme proximal and distal parts are heavily contaminated with maximum heavy metals.

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Shahabuddin et al., (2010) performed on soil contamination in nuclear reactor surrounding areas in Savar, Bangladesh. The contamination level of fourteen elements (Al, Ca, Mg, V, Ti, Na, Mn, As, Br, La, Sm, Sc, U, Yb) from different soil samples of the nuclear reactor surrounding areas in Savar, Bangladesh was investigated with Instrumental Neutron Activation Analysis (INAA) method. The soil contamination level of all heavy metals and trace elements was compared to the range, mean, and median values of the world soil as well as with other studies. The concentration of K (1.65%), U (3.17 mg kg^{-1}), Sm (6.10 $mgkg^{-1}$) and Sc (10.53 mg kg^{-1}) is relatively higher than that of the world mean value. Furthermore, compared to world range value for soil revealed that the high concentration range is also observed for Al (3.87-9.39%), Na (0.37-0.76%) and Yb (0.11-5.36 mg kg^{-1}). However, contamination level of all elements was not evenly distributed in the studied areas. For instance, the pollution levels of U, Yb, Mn, and V were unevenly higher in the areas near to the overhead tank, decay tank, in the vicinity of the underground tank, cooling tower and reactor building area. Interestingly, the contamination level of potassium is high everywhere near the nuclear reactor installations.

Kassem et al., (2004) determine the trace elements in soil and plants in the Orontes basin of Syria. Instrumental Neutron Activation Analysis (INAA) have been used for the determination of some major, minor and trace elements (As, Cr, Co, Ni, Zn, Sb, Sc, Ce, Ti, Fe, Mn and V) in various plant leaves together with their soil. The obtained accurate and reliable data of some trace elements on microgram level for plants and soil will serve as baseline values and will be helpful to monitor the changes in the trace element content of soil and plant leaves. Table 2.3 shows concentrations of various elements with worldwide range.

Table 2.3: Concentrations of various elements with worldwide range

Element	Experimental Data mg/kg	Worldwide Range mg kg^{-1}
As	1.35 - 23	8.7
Ce	6.36 - 91	30
Co	2 - 57	1 - 40
Cr	9 - 346	65

Similarly the concentrations of different element are varying in different plants. The concentration of arsenic is varied from (0.05±0.01) to (0.85±0.07) in different plants such as olive, eggplant, alfalfa, cabbage etc. The concentration of Cerium is varied from (0.11±0.03) to (0.66±0.05), concentration of Cobalt is varied from (0.10±0.01) to (0.69±0.01), concentration of Chromium is varied from (0.32±0.02) to (1.42±0.05), Ni is from (0.59±1.02) to (2.34±0.53), Zinc is varied from (6.9±0.5) to (37.6±3.0), Sb is from (0.008±0.001) to (0.026±0.004), Scandium is from (0.021±0.001) to (0.55±0.01) and the concentration of Vanadium is varied from (0.35±0.07) to (6.14±0.32). Observing overall result it has been seen that in most cases the concentration of element has crossed the international range. This is due to the addition of high amount of sewage sludge and phosphate fertilizer. In case of plants where irrigation is from polluted water such as water polluted by industrial waste or sewage sludge. Where irrigation is from fresh water the concentration of element is lowest there.

Bounouira et al., (2008) present multi-element analytical procedure coupling INAA, ICP-MS and ICP-AES. They determine major and trace elements in sediment samples of the Bouregreg River (Morocco). Through these three techniques they have analyzed different elements. Major and minor elements in solutions, Si, Al, Fe, Mn, Mg, Ca, Na, K, P, and Ti were determined by ICP-AES, while the measurements of As, Ba, Be, Bi, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, In, La, Lu, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sm, Sn, Sr, Ta, Tb, Th, U, V, W, Y, Yb, Zn, and Zr were achieved by ICP-MS. Results obtained in this work show that LPs results for INAA showed no significant bias with respect to recommended values for IAEA Soil-7; as except ICPa showed a significant negative bias for elements that may be present in acid-insoluble compounds. Results for sediments obtained by ICPf are negatively biased in comparison with INAA, but deviations are on the average less than 10%. However, results obtained by ICPa are consistently positively biased in comparison to ICPf. A general good agreement was found between INAA and ICPf techniques, while, the ICPa technique has been revealed useful only for a few elements. Thus, when only INAA and ICPa techniques are available, like at LPS, it was possible to determine concentrations for the 33 following elements: Na, Al, K, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Nb, Mo, Sb, Cs, Ba, La, Ce, Sm, Eu, Tb, Dy, Yb, Lu, Ta, W, Pb, Th and U. Also A principal component analysis has been used for analyzing the variability of concentrations, and defining what are the most influent sites with respect to

the general variation trends. In this case different group elements are linked with concentration variations with different elements. Through the concentration variability studies in sediments, revealed by the PCA, it appears that the Bouregreg river basin is geochemically homogeneous.

Tamim (2016) carried out experiments on elemental distribution of metals in urban river sediments near an industrial effluent source. In their study they have analyzed river (Buriganga, Bangladesh) sediments by instrumental neutron activation analysis (INAA) and energy dispersive X-ray fluorescence (EDXRF). In nine sediment samples 27 elements were determined where Na, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Zn, As, Rb, Cs, La, Ce, Sm, Dy, Hf, Th and U were determined by INAA and Cu, Sr, Ba, Hg and Pb were determined by EDXRF. Pollution level and the origin of pollutants were evaluated by the aid of geo-accumulation index (Igeo), enrichment factor (EF), pollution load index (PLI) and the inter-element correlation analysis. Among the heavy metals, Cr is the dominant pollutant, though the pollution level varies systematically with the sampling depth and the distance from the contamination source. Positive linear correlation between Cr and Zn (0.94) ensures the similar anthropogenic source(s) for these two metals, but the sediments of this study respond differently depending upon their geochemical behavior. Rare earth elements (here La, Ce, Sm and Dy), Th and U seem to have crustal origin and the Th/U ratio varies from 2.58 to 4.96.

Kucˇera et al., (2009) present preparation and characterization of a new set of IAEA reference air filters. In their study a new set of reference air filters were prepared for proficiency testing of laboratories involved in air pollution. The set consists of one filter, loaded with airborne particulate matter (APM) and one blank filter. Target values and their standard deviations were established using instrumental neutron activation analysis (INAA) and proton induced X-ray emission (PIXE) with proven accuracy. Rutherford back scattering (RBS) was used to help in deriving the necessary corrections in PIXE. The wet deposition procedure employed in this work proved useful and yielded a good reproducibility of the APM mass deposited onto the filters with the relative standard deviation of 2.9%. Element heterogeneities determined by both whole-filter and partial-filter assays using INAA and PIXE, respectively, were in the range of 5 to 6%. The corrections for the effective deposit area and deposit thickness in PIXE were found very

important for arriving at accurate results. For their evaluation, the simultaneous employment of PIXE and RBS appeared very useful. In total, target values and information target values for 15 and 23 elements, respectively, were established using INAA and PIXE for APM loaded filters. For blank filters, information target values were established for 10 elements and for 27 elements upper limit values were evaluated. The set of filters is intended for testing of analytical techniques that analyze the whole filter, such as INAA and various destructive techniques, or only a part of the filter, such as ion beam techniques. The loss of water soluble components in the APM deposition procedure employed amounted to 30% of the original APM mass and yielded depletion of several elements up to one order of magnitude. This should be considered the most serious drawback of this approach to APM loaded filter preparation. Nevertheless, the resulting composition of APM on the filters is still quite close to that of real APM samples.

Shakhila and Mohan (2014) performed on study of heavy metal contamination on soil and water in major vegetable tracks of Pathanamthitta District, Kerala, India. According to their study heavy metal contamination on soil and water causes a serious environmental problem because it does not biodegrade. It accumulates in different levels of the food chain. The concentrations of heavy metals namely Zinc, Iron, Lead, Chromium, Copper and Cadmium were determined by Atomic Absorption Spectroscopy. The concentration of heavy metals in soil from the study sites are given below in Table 2.4. Water samples showed low values of BOD, COD and slightly acidic pH.

Table 2.4: Concentrations of various elements

Element	Experimental Data	Average
Zn	0.07-0.2mg/kg	0.135 mg/kg
Fe	0.2-1.4 mg/kg	0.8 mg/kg
Pb	0-0.5mg/kg	0.25 mg/kg
Cu	0.1-1.0 mg/kg	0.55 mg/kg

Capitelli et al., (2002) performed on determination of heavy metals in soils by Laser Induced Breakdown Spectroscopy (LIBS). In order to validate the technique, LIBS data were compared with data obtained on the same soil samples by application of conventional Inductively Coupled Plasma (ICP) spectroscopy. Results obtained in this work show that

the LIBS technique applied to the determination of several heavy metals in soils is successful for the qualitative recognition of metal species but is still to be considered semi quantitative when the metal concentration values have to be measured. With this regard, at the moment LIBS can be considered a “young” and innovative analytical technique with respect to the ICP technique that is a “mature” and consolidated one. Many theoretical and experimental problems need to be solved before the LIBS technique can become competitive with other analytical techniques for metal analysis, such as ICP and AAS. These include the adequate control of plasma temperature, plasma plume behavior caused by laser ablation, laser– sample and laser–plasma interactions, and matrix effects. Despite its drawbacks, LIBS can be considered a promising analytical technique for its intrinsic advantages. The technique is relatively simple allowing the elimination of sample preparation and of its solubilisation prior to analysis, as required by other current techniques.

Coskun et al., (2006) presented heavy metal pollution of surface soil in the trace region, Turkey. They collected 73 sites in the thrace region and use epithermal neutron activation analysis (ENAA) and atomic absorption spectrometry (AAS) to determine 35 elements in the soil samples. Concentrations of As, Cd, Co, Cu, Mn, Ni, Pb and Zn were determined using AAS and GF AAS, and ENAA was used for the remaining 27 elements. The results show that concentrations of most elements were little affected by the industrial and other anthropogenic activities performed in region. Except for distinctly higher levels of Pb, Cu, Cd and Zn in Istanbul district than the median values for the Thrace region, the observed distributions seem to be mainly associated with lithogenic variations. Analyzing the result of various samples we have seen that present maximum values of all elements except Pb, Cd and Cu are below than the maximum value of normal range values of natural soils cited by the EEA report. However, the same values of As, Cd, Cr, Cu, Ni, Pb and Zn exceed the Dutch standard values (normal level in good soil) for these elements. On the other hand, median values of all these elements are below than the Dutch standard values for good soil but the maximum values of Cr, Cu, Ni and Pb are high than the maximum allowable levels of Dutch standard values. The results obtained in this work are also compared with similar data for Izmit Gulf surface soil. The two sets of data show good agreement for rural soil. Where it shows a close relationship between the concentrations of different elements. So some affected areas are polluted with heavy metals.

Charlesworth et al., (2003) studied heavy metal concentration and distribution in deposited street dusts in Birmingham and Coventry, West Midlands, UK. Their studied results are presented from a study of the distribution of heavy metals in street dusts of two cities in Midland England. The first (Birmingham) is a large urban area (population of 2.3 million), the second, Coventry, a small one (population of 0.3 million). Several trends were identified from Birmingham: higher concentrations were located near industrial areas in the northwest of the city and within the ring road. However, lower concentrations were found to the southwest in areas of mainly residential properties and parks. High values were also identified in association with junctions controlled by traffic lights where vehicles were likely to stop regularly. This last trend was further investigated in Coventry, where it was found that concentrations of heavy metals at junctions controlled by traffic signals and by pedestrian-controlled pelican lights (Mounted Pelican Controller, MPCs) were lower than those found in Birmingham, apart from Ni. It also has been seen that the concentrations of heavy metal with the greatest variations exhibited by Zn and Cu e.g. Zn in Birmingham street dusts varied from 81.3 to over 3000 mg kg^{-1} and Cu varied from 16.4 to over 6600 mg/kg.

Khan et al., (2015) present chemical characteristic of R chondrites in the light of P, REEs, Th and U abundances. Rare earth elements (REEs), Th, U and P were determined in 15 Rumuruti (R)-type chondrites and the Allende CV chondrite. Repeated analyses of Allende for REEs, Th and U by ICP-MS and P by ICP-AES, and comparisons of these data with literature values ensure high reproducibility (precision) and reliability (accuracy) of acquired data. A mean Th/U ratio of R chondrites is 3.81 ±0.13 (1σ), which is 5.1% higher than the CI ratio. Probably, the Th–U fractionation was inherited from the nebula from which the R chondrite parent body formed. Besides the Th–U fractionation, REEs and Th–U are heterogeneously fractionated in R chondrites, for which parent body processing is assumed to be the cause. A mean P content of R chondrites (1254μg/g) is higher than for any ordinary chondrite and is close to the EL mean. There appears to be a negative correlation between P and REEs contents in R chondrites.

Saini et al., (2002) performed on estimation of trace element in soils using group analysis scheme of ED-XRF. The present study shows the performance of an ED-XRF system in

analyzing 15 important trace elements (V, Cr, Co, Ni, Cu, Zn, Ga, Pb, Th, Rb, U, Sr, Y, Zr, and Nb) in soils and sediment samples. These elements were divided into two groups and were analyzed at different operating conditions suitably optimized for each group. The medium-Z elements (V, Cr, Co, Ni, Cu, Zn, and Ga) were called as group ‘‘A’’ elements, while the rest were taken into group ‘‘B.’’ Well characterized soil and sediment reference samples were used to estimate precision and accuracy of the analysis data produced by ED-XRF. From the experiment it may be concluded that the soil analysis results obtained using ED-XRF and the analytical scheme adapted in the present programmed, satisfy well the quality criteria recommended for several geochemical applications. The present analysis scheme is capable of producing good precision and reliable data. The measured precision for most of the trace elements is better than 5%. The trace group ‘‘A’’ calibration produces even more precise data with less analysis time (600 s against 1000 s for trace group ‘‘B’’ calibration). Pb is however analyzed using trace group ‘‘B’’ calibration. The precision and accuracy observed are satisfactory.

Tu¨rkdog˘an et al., (2002) studied on heavy metals in soil, vegetables and fruits in the endemic upper gastrointestinal cancer region of Turkey. In their study the environmental exposure to heavy metals is a well-known risk factor for cancer. They investigated levels of seven different heavy metals, (Co, Cd, Pb, Zn, Mn, Ni and Cu) in soil, fruit and vegetable samples of Van region in Eastern Turkey where upper gastrointestinal (GI) cancers are endemic. Heavy metal contents of the samples were determined by flame atomic absorption spectrometer. Four heavy metals (Cd, Pb, Cu and Co) were present in 2- to 50-fold higher concentrations whereas zinc levels were present in 40-fold lower concentrations in soil. The fruit and vegetable samples were found to contain 3.5- to 340-fold higher amounts of the six heavy metals (Co, Cd, Pb, Mn, Ni and Cu) tested. The volcanic soil, fruit and vegetable samples contain potentially carcinogenic heavy metals in such a high levels that these elements could be related to the high prevalence of upper GI cancer rates in Van region.

Ene et al., (2011) present ED-XRF and INAA analysis of soils in the vicinity of a metallurgical plant. In their work they have used ED-XRF and INAA techniques to determine the soil composition and its pollution with heavy metals and trace elements in the vicinity of Iron and Steel Works at Galati, Romania. The following elements were

determined: Ag, As, Au, Ba, Br, Ca, Cd, Co, Cr, Cs, Fe, Hf, Hg, K, Mo, Na, Ni, Rb, Sb, Sc, Se, Sr, Ta, Th, U, W, Zn, Zr, and rare-earth elements (Ce, Eu, Gd, La, Lu, Nd, Sm, Tb, and Yb) by long-lived activity INAA; Al, K, Mg, Mn, Na, Sr, Ti, and V by short-lived activity INAA; Ag, As, Ca, Cd, Cr, Cu, Fe, Hg, K, Mn, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, V, and Zn by ED-XRF. Anthropogenic releases due to metallurgical industry at Galati give rise to higher concentrations of some heavy metals (Ni, Cr, and As) in all the investigated samples (3-2 times), relative to the normal levels admitted by Romanian norms. Moreover, at some of the sites elemental concentrations exceed the alert levels for Hg, Cd, and Se, as well as the intervention threshold for Hg in soil. Compared with European and world median levels in topsoil, similar or slightly higher values were obtained for most elements in the investigated soils. Much higher Cd and Hg contents (by 1-2 orders of magnitude, respectively), and, to a less extent higher As, Ca, Cr, Ce, Co, Hf, Nd, Ni, Sc, Sm, U, Yb, Zn and Zr contents (by 1.9-1.2 times) were also determined in soils from Galati.

Wei and Yang (2010) present a review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils in China. The results indicate that nearly all the concentrations of Cr, Ni, Cu, Pb, Zn, As, Hg and Cd are higher than their background values of soil in China. The geo-accumulation index shows that the contamination of Cr, Ni, Cu, Pb, Zn and Cd is widespread in urban soils and urban road dusts of the cities. Generally, the contamination levels of Cu, Pb, Zn and Cd are higher than that of Ni and Cr. Agricultural soils are also significantly influenced by Cd, Hg and Pb derived from anthropogenic activities. The integrated pollution index (IPI) indicates that the urban soils and urban road dusts of the developed cities and the industrial cities have higher contamination levels of the heavy metals. The comparison of the IPIs of heavy metals in urban soils and urban road dusts of Shanghai, Hangzhou, Guangzhou and Hong Kong reveals that the contamination levels of the metals in urban road dusts are higher than that in urban soils in the cities. Moreover, the main sources of the metals in urban soils, urban road dusts and agricultural soils are also different. According to the IPI, approximately 65% of all the cities have high or extremely high contamination levels of heavy metals in urban soils and urban road dusts. This indicates that the urban soils and urban road dusts in the cities have been significantly impacted by heavy metals derived from anthropogenic activities.

Louhi et al., (2012) present determination of some heavy metal pollutants in sediments of the Seybouseriver in Annaba, Algeria. For this study, they used two protocols of digestion of sediments, the first, using a mixture of hydrofluoric acid and perchloric acid, and the second, using aqua regia. They used atomic absorption spectrometry (AAS) to measure these heavy metals. The functional groups characteristic of organic matter and particularly clays were identified by infrared spectroscopy. The average concentrations of metals exceeded acceptable standards for sediment pollution with heavy metals. Maximum concentrations in mg/kg respectively of the elements studied (Fe, Zn, Mn, Sn, Ni, Cr, Pb and Cu) were, respectively, 2460.20 ± 74.8; 1140.65 ± 38.2; 3.60 ± 1.2; 1.20 ± 0.5; 16.80 ± 2.6; 9.50 ± 3.2; 476.31 ± 21.6 and 145.15 ± 35.2. Elements tend to accumulate in sediments containing (8.60%) organic matter and pH = 7.80. Organic matter and pH of the medium can cause heavy metal mobility. Sediment collected at points S2 and S3 have a pH greater than 6, which can promote the complication of metals. On the other hand, a pH greater than 5 and an organic matter content of less than 5%, favor the accumulation of lead. In sediments analyzed, the predominant form was chromium VI. Metals can absorb in sediment according to mechanisms of caution exchange in acid and alkali chemisorption. However, the metals studied tend to contaminate the broad agricultural plain region of Annaba because of pollution by agrochemicals, industrial effluents and domestic sewage. These results clearly show that the sediments deposited by the Seybouse River are heavily polluted.

Segarra et al., (2007) performed on chemical forms and distribution of heavy metals in core sediments from the Gdańsk basin, Baltic Sea. Short sediment cores (30 cm length) were taken along a transect of the Gdańsk basin from the mouth of the Vistula river out into the Baltic Sea in June 1996. The chemistry and mineralogy of surficial and buried sediments were determined and Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were analyzed in total and in fractions using a sequential extraction procedure. The bulk and clay mineralogy of the sediments were determined by XRD and SEM. The concentrations of some of the trace metals in sediments are above pre-anthropogenic background. In particular, the surficial samples are substantially enriched in Cu, Pb and Zn, suggesting an anthropogenic origin. The concentrations of Cu, Pb and Zn range are from 21-71 $\mu g \cdot g^{-1}$, 56-210 $\mu g \cdot g^{-1}$ and 21-83 $\mu g \cdot g^{-1}$, respectively. Unexpectedly, the concentrations of trace metals increase seawards within the Gdańsk Basin. The forms of binding are different for each metal. Cobalt, Cr and

Fe are mainly associated with the residual mineral fraction of the sediment, although in samples with high Fe concentrations there is a significant correlation with organic compounds. In contrast, Mn, Ni, Pb and Zn are predominantly associated with oxides and the organic fractions, with a significant percentage associated with the carbonate and exchangeable caution fractions, whilst Cu is mainly bound with the organic fraction.

CHAPTER 3

Methodology

3.1: Introduction

For many workers in the field, a reactor is an item which is too expensive; instead it is common to use a neutron source which uses a combination of an alpha emitter and beryllium. These sources tend to be much weaker than reactors. Some reactors are used for the neutron irradiation of samples for radioisotopes production for a range of purpose. The sample can be placed in an irradiation container which is then placed in the reactor; if epithermal neutrons are required for the irradiation then cadmium can be used to filter out the thermal neutrons. Gas Discharge Tubes can be used to create pulses of neutrons. They have been used for some activation work where the decay of the target isotope is very rapid. For instance in oil wells. In the present research work samples are irradiated by 3 MW TRIGA Mark – II research reactor at the Atomic Energy Research Establishment (AERE), Savar, Dhaka is the only nuclear reactor of the country.

3.2: Elemental Analysis

Elemental analysis is the techniques of qualitative detection and quantitative determination of chemical elements (atoms, ions) in a sample. To detect an element, one should fix an appearance of an analytical signal: the formation of precipitate or characteristic crystals, color change, an isolation of gaseous products, an appearance of a definite line in spectrum, luminescence, etc. To determine elements quantity, it is necessary to measure a value of an analytical signal: a precipitate mass, intensity of a current, solution absorption, spectrum line, luminescence or radioactivity, a reaction rate and so on. The content of an element is calculated on the basis of functional dependence of the analytical signal value (AS) on a mass or concentration of this element which is established by calculations or experiments. To obtain the analytical signal, chemical reactions of different types (acid-base, oxidation-reduction, complex formation), various processes (e.g., precipitation) as well as different chemical, physical, biological properties of elements themselves or products of their reactions, are used. Methods for the detection and determination of elements are divided to chemical, physical and biological. The most important

characteristics of those methods are the detection limit, sensitivity, selectivity, precision, rapidity and analysis cost.

One can also define it is an experiment that determines the amount (typically a weight percent) of an element in a compound. Just as there are many different elements, there are many different experimental methods for determining elemental composition. The most common type of elemental analysis is for carbon, hydrogen, and nitrogen (CHN analysis). This type of analysis is especially useful for organic compounds (compounds containing carbon-carbon bonds).
A highly-skilled approach to elemental analysis is required that combines appropriate instrumentation with sample preparation and methodology that are most relevant to both the sample matrix and the aim of the study. To meet various industry challenges, the ability to work to relevant standards is essential. For organic chemists, elemental analysis or "EA" almost always refers to CHNX analysis—the determination of the mass fractions of carbon, hydrogen, nitrogen, and heteroatoms (X) (halogens, sulfur) of a sample. This information is important to help determine the structure of an unknown compound, as well as to help ascertain the structure and purity of a synthesized compound.

Antoine Lavoisier is regarded as the inventor of elemental analysis as a quantitative, experimental tool to assess the chemical composition of a compound. At the time elemental analysis was based on gravimetric determination of specific adsorbent materials before and after selective adsorption of the combustion gases. Today fully automated systems based on thermal conductivity or infrared spectroscopy detection of the combustion gases, or other spectroscopic methods are used.

Though elemental analysis has discovered very early age but it was difficult to analyses different elements in various samples. Different methods were discovered to determine elements in samples. These methods had also restriction to determine elements in different samples because it was unable to activate samples properly and counting radiation. Many years after the invention of elemental analysis nuclear reactor has been invented. Chicago Pile-1 (CP-1) was the world's first nuclear reactor to achieve criticality. Its construction was part of the Manhattan Project, the Allied effort to create atomic bombs during World

War II. It was built by the Manhattan Project's Metallurgical Laboratory at the University of Chicago, under the west viewing stands of the original Stagg Field.

The reactor was assembled in November 1942at 3:25 PM, by a team that included Fermi, Leo Szilard, discoverer of the chain reaction, and Herbert L. Anderson, Walter Zinn, Martin D. Whitaker, and George Weil. It contained 45,000 graphite blocks weighing 400 short tons (360 t) used as neutron moderators, and was fueled by 6 short tons (5.4 t) of uranium metal and 50 short tons (45 t) of uranium oxide. In 1943, CP-1 was moved to Red Gate Woods, and reconfigured to become Chicago Pile-2 (CP-2). At first the energy range, performance, accuracy was low but day by day its performance and all other activities are increasing. Now a day we have used very powerful and controlled nuclear reactor.

3.3: Types of Elemental Analysis

The most common form of elemental analysis, CHN analysis, is accomplished by combustion analysis. In this technique, a sample is burned in an excess of oxygen and various traps, collecting the combustion products: carbon dioxide, water, and nitric oxide. The masses of these combustion products can be used to calculate the composition of the unknown sample. Modern elemental analyzers are also capable of simultaneous determination of sulfur along with CHN in the same measurement run. Two main types of elemental analysis are: Quantitative and Qualitative.

3.3.1: Quantitative Elemental Analysis

Quantitative analysis is the determination of the mass of each element or compound present. Different quantitative methods include:

Gravimetry: Where the sample is dissolved and then the element of interest is precipitated and its mass measured or the element of interest is volatilized and the mass loss is measured. This method is extremely accurate, owing to the fact that it is possible to weigh substances to great accuracy with analytical balances; it is common practice to determine a weight to 5 digits. For the first time gravimetry was described in details by C.R Fresinius in his hand-book (1846). The main field of gravimetry application is a precise determination of large and middle amounts of elements with an error not more than 0.1-0.2 percent. Thermo gravimetry is applied for the direct determination of elements

without their separation; for instance, the content of calcium and barium can be determined without their separation, using a derivatogram of their oxalates.

Titrimetry: Titrimetric method of analysis was developed in the middle of the 18th century. The essence of this method is in a measuring a volume or mass of a reagent solution, which is spent to interact completely with a component to be determined. The endpoint of a reaction is detected as a change of a solution color or any other parameters. It is worth mentioning that J.L. Gay-Lussac (1778-1850) has made a valuable contribution to titrimetry development. Owing to his investigations, the rapid, handy, rather precise titrimetric method became widely practiced in scientific and industrial laboratories. But a real revolution in the theory, instruments, procedure of titrimetric analysis has been connected with C.F. Mohr (1806-1879). There are a lot of various reactions used in titrimetry: acid-base, redox, complex formation.

Inductively coupled plasma atomic emission spectroscopy: This is a type of quantitative analysis, which probe the outer electronic structure of atoms.

Optical atomic spectroscopy: Flame atomic absorption, graphite furnace atomic absorption etc. are such types of elemental analysis.

Neutron activation analysis: This involves the activation of a sample matrix through the process of neutron capture.

3.3.2: Qualitative Elemental Analysis

Quantitative elemental analysis is a type of elemental analysis which determines the elements quantitatively present in a sample. Several methods are used for this type of analysis. The methods are:

3.3.2.1: Qualitative elemental analysis

Chemical elemental qualitative analysis arose from time immemorial. Ancient Roman historian plying has described an application of a papyrus impregnated with a tannic-galls extract for distinguishing copper from iron: the papyrus became black in a solution of iron sulfate. There are some evidence that at the beginning of 18th century Russian Tsar Peter the First has made himself not very complicated chemical analysis for distinguishing sulfur

and arsenic containing ores. R. Boyle was the first to use hydrogen sulfide as a chemical reagent for lead and tin determination; T. Bergman has shown an important role of hydrogen sulfide in chemical analysis using it for the precipitation of many metals sulfides. At the close of the 18^{th} and at the beginning of the 19^{th} centuries the majority of reagents for elemental qualitative analysis were known already. In 1829 G. Rose was the first to describe not only reactions for individual elements detection, but the first scheme for the systematic analysis of elements mixtures in his "Handbook on analytical chemistry". Modern hydrogen sulfide scheme for qualitative analysis has been firstly formulated by C.R. Fresinius. Later, in the 20^{th} century the other schemes, such as acid-base, ammoniac-phosphate, were also proposed.

In chemical methods of detection, the appearance of an analytical signal in the result of a chemical reaction is fixed visually, as a rule. Modern elemental qualitative analysis have available numerous selective reactions with low limits of elements detection. To lower limits of detection, one can use different approaches, such as extraction, flotation, drop reactions on filter paper, micro crystalline, catalytic, luminescent reactions, etc.

3.3.2.2: Qualitative Inorganic Analysis

The detection of individual elements in a mixture with other accompanying elements is a rather difficult problem, because all of them can interact with the same reagents with a similar outward effect. Using specific reagents and reactions, makes it possible to detect some elements in mixtures with a fractional method. For instance, starch is a specific reagent for iodine detection (a blue compound is formed), alkali is used for nitrogen detection in ammonia salts. Using different ways to improve selectivity (varying pH values, temperature, masking, changing oxidation degree, etc.) allows us to increase a number of elements, which can be individually detected in mixtures. Application of organic reagents makes easier the fractional detection of elements. A typical example of such reagents is dimethylglyoxime, which can be a specific reagent for the determination of nickel, forming red complex with it under definite conditions (pH, masking interferents). In those cases when elements can't be detected fractionally, it is necessary to separate them preliminarily. Majority of separation methods are based on selective distributing elements of an analyzed sample between two unmixed phases. The detected elements should be transferred completely to one of such phases. Precipitation, extraction, thin-layer

chromatography are often used for elements separation in qualitative analysis. The systematic schemes for analysis of elements mixtures are based on these separation methods. When the precipitation is used for elements separation, the systematic scheme for analysis includes a successive isolation of a small number of elements, their groups, with the help of group reagents with their following fractional detection, sometimes additional separation of elements of the same group is necessary. Inorganic (HCl, H_2SO_4, H_2S, Na_2HPO_4, NaOH, NH_3), and organic (8-hydroxyquinoline, dimethylglyoxime, cuppherone) precipitators are used as group reagents. Chromatographic separation of elements (thin-layer and paper chromatography) is based on transferring components of a mobile phase through a stationary phase with a different rate. In paper and thin-layer chromatography, cellulose fiber of a paper and thin layers of different sorbents (metal oxides, silica gels, cellulose) on plates are used as bearers for stationary phases (water, for instance). Various solvents or their mixtures, organic and inorganic acids, can play the role of a mobile phase.

Components of a mobile phase form separate zones (spots) on plates or paper strips (chromatograms), which position is characterized by Rf-coefficient, or a relative rate of different components transfer through a stationary phase. Colored zones on a chromatogram can appear immediately, or as a result of developing invisible zones by correspondent reagents, forming colored compounds with elements to be detected.

3.3.2.3: Qualitative Organic Analysis

Contrary to qualitative inorganic analysis, the detection of elements in organic analysis serves as a preliminary identification of characteristic functional groups of organic compounds, containing a definite element. For example, if preliminary studying has shown sulfur absence, it is not necessary to carry out reactions for the detection of SH-, SO_3H- or S-C- groups containing compounds. The main way to detect metals and non-metals (excluding hydrogen and oxygen) while analyzing organic substances, is a distraction of analytic molecules to obtain an inorganic compound which can be identified with chemical reactions. For instance, in order to detect carbon in non-volatile compound, the latter should be heated with KIO_3 at 300-4000C for KI formation.

The products of this reaction are dissolved then in acidified water, and KI is detected owing to the reaction

$$5I^- + IO_3^- + 6H^+ = 3H_2O + 3I_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.1)$$

Halogen containing organic compounds, after their mixing with copper oxide and following heating, form copper halogenides, carbon dioxide and water. Copper halogenide can be detected by a typical blue–green flame color. While heating nitrogen, arsenic and phosphorus-containing organic compounds with calcium oxide, ammonia, calcium tertiary arsenate and phosphate, respectively, are formed. Ammonia can be detected with the help of an indicator paper. Calcium phosphate is dissolved in nitric acid and then phosphate-ions are precipitated by ammonia moly date solution, forming yellow crystals of ammonia molybdenum phosphate. Arsenic (V) can be detected using its reaction with potassium iodide, since the product of this reaction – iodine, forms a blue complex with starch. Metals in organic substances are detected in solutions, obtained after burning to ashes, and following dissolution of analyzed compounds in acids; either treatment with a hot concentrated nitric acid (Carious method) or heating with a concentrated sulfuric acid (Kyeldahl method) can be also used for this purpose. Metals identification can be carried out by common methods for inorganic qualitative analysis.

3.3.2.4: Physical Methods of Qualitative Elemental Analysis

At present, elements are mostly detected with the help of physical methods, which are based on physical phenomena or processes, e.g., an interaction of elements with an energetic current. Among such methods, the method of Atomic Emission Spectroscopy (AES), based on a thermal excitation of atoms of free elements and registration of the optic spectrum of excited atoms emission, should be distinguished first of all. This method was developed by K. Kirchgoff and R. Bunsen (the 19thcentury). Since 1861 till 1932, 25 elements of the Periodic System (Cs, Rb, Ti, In, Ga, He, Ar, Ne, Kr, Xe, Hf and 14 rare earth elements) were opened with the help of AES method. In 1932, hydrogen isotope – deuterium was opened. The main advantage of the AES method is the possibility to identify with its help a great number of elements in samples, since it allows us to fix a lot of emission lines, which position in the spectrum is individual for each element. The most intensive, so called “last” lines, which are the last to disappear in the spectrum, when the

element concentration decreases, are used for elements detection. To improve the reliability of elements identification, it is necessary to detect several lines of the same element in the spectrum.

Method of X-ray Photoelectron Spectrometry (XPS) allows carrying out indestructible qualitative elemental analysis of solid samples surface, and it is possible to detect any element from lithium to uranium. The analytical essence of qualitative X-ray photoelectron analysis consists of individual values of electron energy in an atom of each element. Luminescence is also often used for qualitative elemental analysis. Phenomenon of luminescence consists in an emission of atoms, ions, molecules and other more complicated particles, after absorbing energy of the excitation, and this emission is surplus in comparison with a thermal emission of a solid at definite temperature. Not so many metal ions (U, Sm, Eu, Tb, Dy) have their own luminescence in compounds (e.g., minerals). The most interesting practical problem is detection of uranium in rocks and waters, based on the mentioned phenomenon. The luminescent detection of metals is usually based on their reactions with organic reagents, which result in forming luminescent compounds. So, numerous derivatives of oxyazo and oxyazomethine compounds are widely used for the detection of Al, Ga, Mg and other elements which form uncolored complexes.

Mass-spectrometric method is widely practiced for elemental analysis of solid organic compounds and materials. This method is based on the ionization of atoms and molecules of a compound, and following separation of formed ions in space and in time. The identification of elements consists in decoding mass-spectrum and a comparison of a location of lines of an element to be sought for, and lines of a known main component or added inner standard. This method allows detection of about 50 elements – admixtures in different solid samples, using special instrumentation. Radiometric methods, based on measuring radioactivity of natural radionuclides are used for qualitative analysis of geographical samples. Thus, using γ-emission, allows us to find uranium and thorium deposit and to solve other geological problems.

3.4: Interaction of Gamma Rays with Matter

Gamma ray photons are uncharged and create direct ionization or excitation of the material through which they pass. The detection of γ-rays is therefore depending on causing the γ-ray photon to undergo an interaction that transfers all or part of the photon energy to an electron in the absorbing material. Although a large number of possible interaction mechanisms are known for γ-rays in matter, only four major types play an important role in radiation measurements. They are:

a) Photoelectric Effects
b) Compton Scattering
c) Pair production
d) Positron annihilation

All these processes partially or completely transfer gamma ray energy to electrons in the atom of the interacting medium. These processes are strongly on photon energy and the atomic number Z of the interacting material. Thomson scattering and others are much less important and so ignored in detection process. A brief description of the major processes is given below.

3.4.1: The Photoelectric Effect

A photon of relatively low energy (less than 1 MeV) may transfer all its energy to a tightly bound electron in an inner shell, causing the electron to be ejected from the absorber atom The ejected electron, known as a photoelectron will move through the absorber causing secondary ionization and excitation.

For typical photon energies, the most probable origin of the photoelectron is the innermost electron orbit or K shell. The absorber atom is left in an excited state with vacancy in one of its inner shells. The vacancy is quickly filled by the capture of a free electron from the absorber, or by rearrangement of electrons from other shells of the atom. In the latter case, electrons move from a higher energy shell to fill the vacancy; as they do so, energy is released in the form of characteristic x-rays. In a few case, the x-rays produced by the above process will interact with an outer shell electron and cause it to be ejected from the atom. It has a low energy and is known as an auger electron. Note that the photoelectric

effect is most likely to occur in materials with a high atomic number, so a material such as lead (Z=82) makes a useful shielding material for low energy photons. The photoelectric effect is relatively unimportant in low Z materials such as aluminum. Figure 3.1 shows the process of photoelectric effect and Figure 3.2 shows the production of auger electrons.

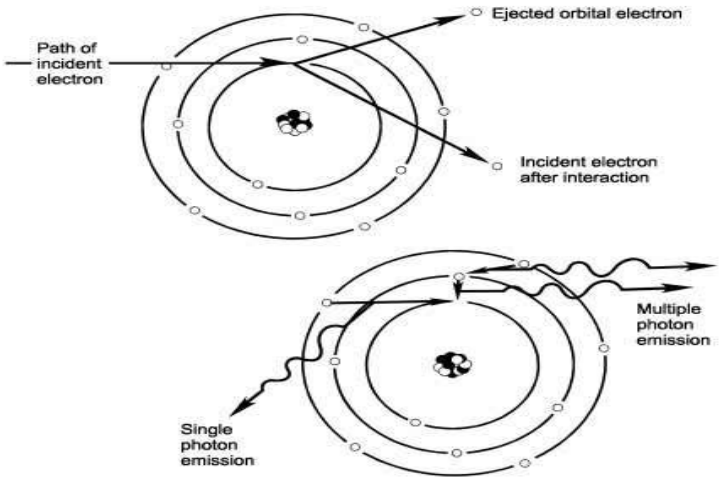


Figure 3.1: Photoelectric emission

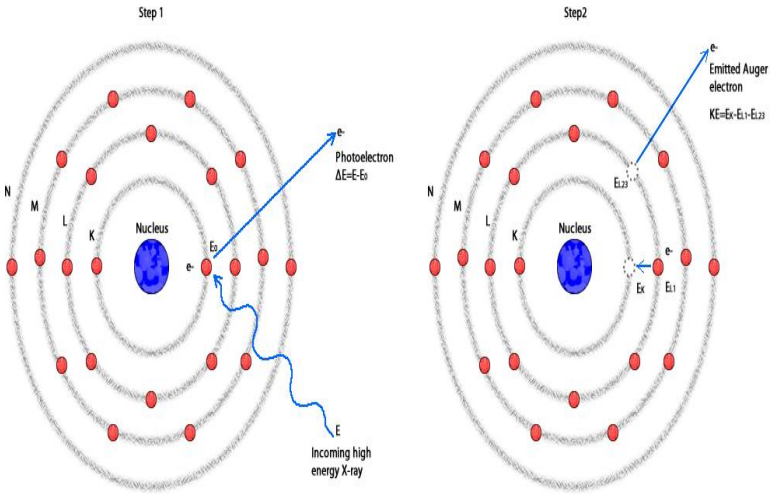


Figure 3.2: Auger electrons.

3.4.2: Compton Scattering

Compton scattering involves a collision between a photon and an outer shell electron in which only part of the photon energy is transferred to the absorber atom. The electron is released from the atom (primary ionization) and will continue moving through the absorber

causing secondary ionization and excitation. The photon is scattered with reduced energy and may also continue to interact with other absorber atoms. Figure 6 shows an incoming photon releasing an outer shell electron and being scattered with a reduced energy. The angle at which the photon is scattered depends on its original energy and the energy transferred to the electron. Low energy photons transfer very little energy to the released electron and scattered through large angles. However, high energy photons (10 to 100 MeV) transfer most of their energy to the released electrons and are not scattered very much. Compton scattering is most important for photon energies between about 0.2 and 5.0 MeV, and predominates in absorbers with higher values of Z.

3.4.3: Pair Production

Pair production takes place when a photon with energy greater than 1.02 MeV interacts with the strong electric field close to the heavy nucleus of an absorber atom and produces two particles, an electron and a positron. The energy value of 1.02Mev is the energy equivalent of the total mass of positron-electron pair and any photon energy in excess of this value provides kinetic energy to the electron and positron and may also cause the nucleus of the target atom or recoil. The electron and positron then move off and lose kinetic energy through secondary ionization. A positron cannot exist without kinetic energy so when it has lost all its energy it will combine with an absorber atom electron in a process called annihilation. In this process, the two particles destroy each other and are converted into two annihilation photons, each of 0.51 MeV. These photons are emitted in opposite directions from each other. Figure 3.3 shows the Compton scattering of gamma radiation and Figure 3.4 shows the pair production. Fig 3.5 shows the whole process of pair production and annihilation in the electric around the nucleus of a lead atom. For photons with energies above the threshold, the probability that pair production will take place increase with atomic number of the absorber.

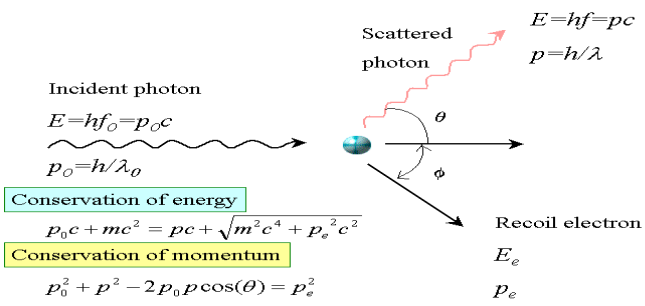


Figure 3.3: Compton scattering of gamma radiation.

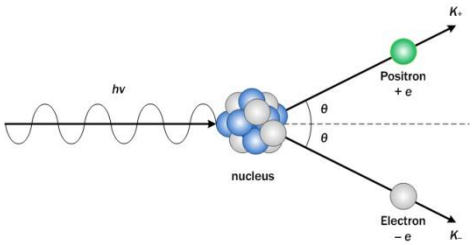


Figure 3.4: Pair Production.

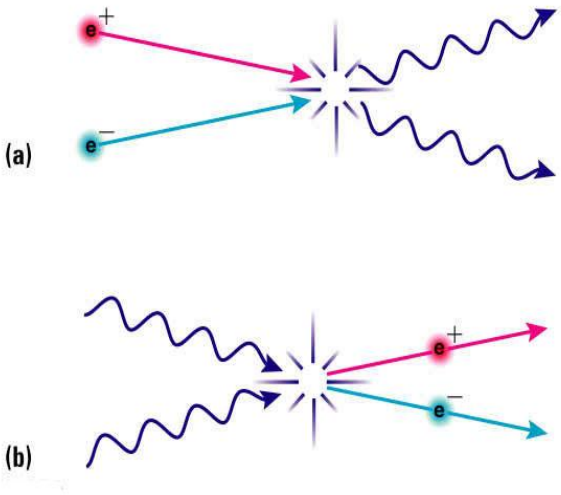


Figure 3.5: Pair Production and Positron Annihilation process.

The effect also increases with photon energy, slowly from 1.02 to 5 MeV and more rapidly above that. Pair production is the most likely interaction for high energy photons in materials with a high atomic number.

3.4.4: Positron Annihilation

If pair production occurs, the positron slows down in the material by successive collision. When the positron comes to rest, it combines with nearby electron and then annihilates, producing two 0.511 MeV photons emitted in opposite directions due to energy and momentum conservation law.

$$e^{+} + e^{-} \rightarrow \gamma + \gamma \quad \text{.....(3.2)}$$

3.5: Detection of Gamma Rays

After irradiation the samples and standards are placed on the HPGe detector. For the detection of the gamma rays emitted from the experimental samples an experimental arrangement was established that includes a High Purity Germanium (HPGe) detector, a Digital Spectrum Analyzer DSA-1000 with Canberra Detector Interface Module (DIM) containing a high voltage power supply, a pre-amplifier, analog to digital converter (ADC) and PC based Multi-Channel Analyzer (MCA) software-Genie 2000 etc. Figure 3.6 shows block diagram of gamma ray detection arrangement

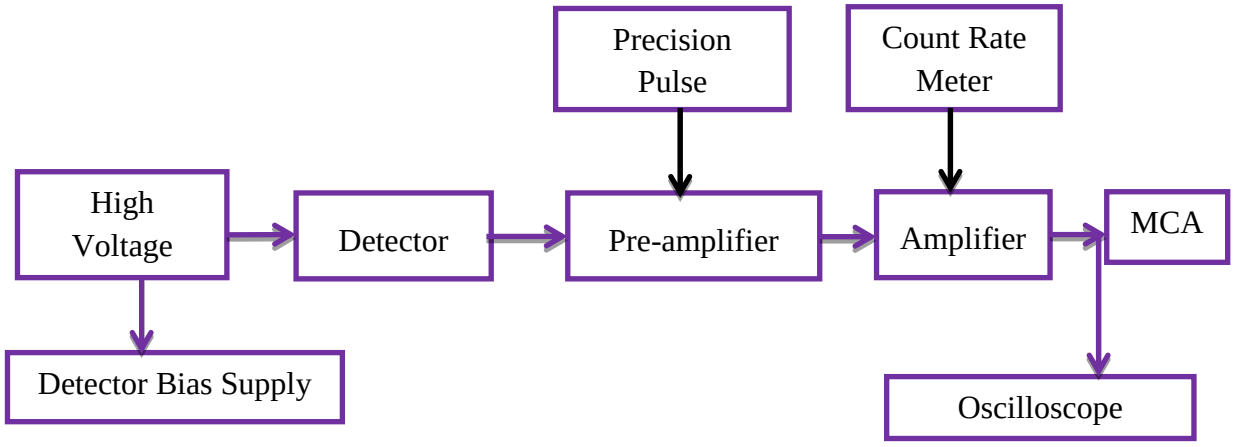


Figure 3.6 shows block diagram of gamma ray detection arrangement

3.6: Nuclear Reactor

The term nuclear reactor refers to device in which controlled nuclear fission chain reactions can be maintained. In such device, neutrons are used to induce nuclear fission reaction in heavy nuclei. This nuclear fission into lighter nuclei (fission products) accompanied by the release of energy (some 200 MeV per event) plus of several additional neutrons. These fission neutrons can then be utilized to induce still further fission reactions, thereby inducing a chain of fission events.

3.6.1: TRIGA Mark-II Research Reactor

It is a tank type research reactor and is used for training, research and isotope production. The reactor has been designed and constructed by General Atomics of USA. The installation of the reactor was started at the end of 1980 under a non-turnkey project. Figure 3.7 represents TRIGA Mark – II research reactor and Figure 3.8 represents inner view of TRIGA Mark – II research reactor at Savar, Dhaka.

Figure 3.7: TRIGA Mark – II research reactor at Savar, Dhaka.

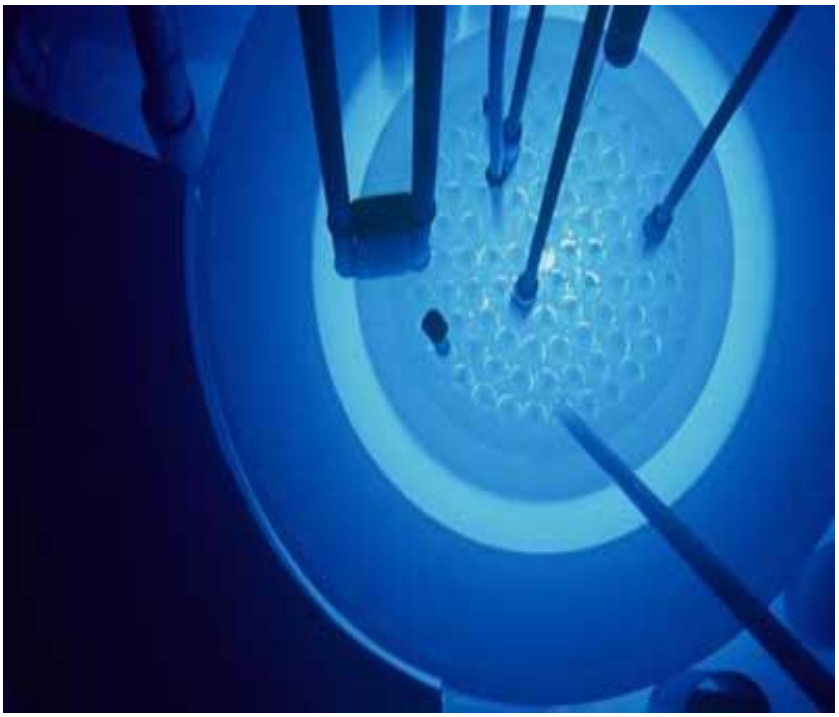


Figure 3.8: Inner view of TRIGA Mark – II research reactor at Savar, Dhaka

3.6.2: Irradiation Facilities of TRIGA Mark-II Reactor

The TRIGA Mark – II research reactor at AERE (Atomic Energy Research Establishment) is designed to provide intense fluxes of ionizing radiation for research, training and isotope production. Experiments with the TRIGA Mark – II research reactor can be carried out using the following facilities:

- Dry central irradiation tube
- Neutrons beam tubes
- Pneumatic transfer system
- Rotary specimen rack (lazy Susan)
- Triangular cut-outs in the core
- Hexagonal cut-out at the center of the core
- Thermal column for future use (presently filled up with heavy concrete blocks). (3 MW TMRR, 2003)

Irradiation condition used for the experiment has been given in Table 3.1

Table 3.1: Irradiation condition used for the experiment

Research reactor	3 MW TRIGA Mark – II
Neutron flux	~ 2.0 $\times 10^{13} n^{-1} cm^{-2} s^{-1}$
Reactor power	3 MW
Irradiation time	7 minutes
Irradiation facility	G ring

3.6.3: Pneumatic Transfer System

The pneumatic transfer system, which has a transfer time of about 4.6 sec, is used to irradiate monitors that produce short-lived radioisotope. Production of very short-lived radioisotope is accomplished by a pneumatic transfer system, which rapidly conveys a specimen to and from reactor core. When the polyethylene specimen capsule on "rabbit" is ejected into the core, it comes to rest in a vertical position approximately at the mid-plane of the core. With automatic control, the specimen capsule is ejected from the after a predetermined length of time. Table 3.2 gives the values of Neutron flux ($n/cm^2/cm$) at TRIGA Mark – II research reactor.

Table 3.2: Values of Neutron flux ($n/cm^2/cm$) at TRIGA Mark – II research reactor, AERE, Savar, Dhaka (Glascock, 2004)

Different position	Epithermal	Thermal
Average flux in rector core	1.1×10^{13}	5.3×10^{13}
Central tube	1.5×10^{13}	5.56×10^{13}
Rotary rack (at the bottom)	0.26×10^{13}	0.75×10^{13}
G- ring (the last circle of fuel center)	1.0×10^{13}	2.0×10^{13}

3.7: High Purity Germanium (HPGe) Detector

The instrumentation used to measure gamma rays from radioactive samples generally consists of a semiconductor detector, associated electronics, and a computer-based multi-channel analyzer. Hyper-pure or intrinsic germanium (HPGe) detectors are commonly used. These detectors operate at liquid nitrogen temperatures by mounting the germanium crystal in a vacuum crystal thermally connected to a copper rod or "cold finger". Figure 3.9 gives the Cross - sectional view of HPGe detector.

High Purity Germanium (HPGe) detector is one type of semiconductor detector. The emitted gamma rays from the product nucleus are detected by the HPGe detector. An HPGe detector is a high quality precision system and is being widely used for gamma spectroscopic measurement because of their superior resolution compared to NI crystal. Semiconductor detectors produce the available free charge carriers which can be used for the detection and measurement of incident radiation. Figure 3.10 represents a HPGe detector system available at BAEC Savar, Dhaka and Figure 3.11 represents the component of digital gamma ray spectrometry system.

HPGe detectors are available in two relatively simple geometrics:

1. The planer detector in which the electric field is fairly uniform and
2. The co-axial configuration in which the electric field varies inversely with the radial distance from the detector axis.

The gamma ray detection efficiency and response function for an HPGe detector are identical to those observed in a Ge (Li) detector of the same size and shape.

The HPGe gamma spectrometry system consists of the following parts:

1. HPGe detector:
    a) Cryostat
    b) Liquid Nitrogen (LN2)
    c) Pre-amplifier
2. Digital Gamma Spectrometer
    a) Amplifier
    b) High Voltage Unit
    c) Analog to Digital Converter (ADC)
3. Shielding arrangement

The last 3 items are integrated in a box. The product of Canberra is called DSA and the product of ORTEC is called DSPEC. (Kabir, 2012)

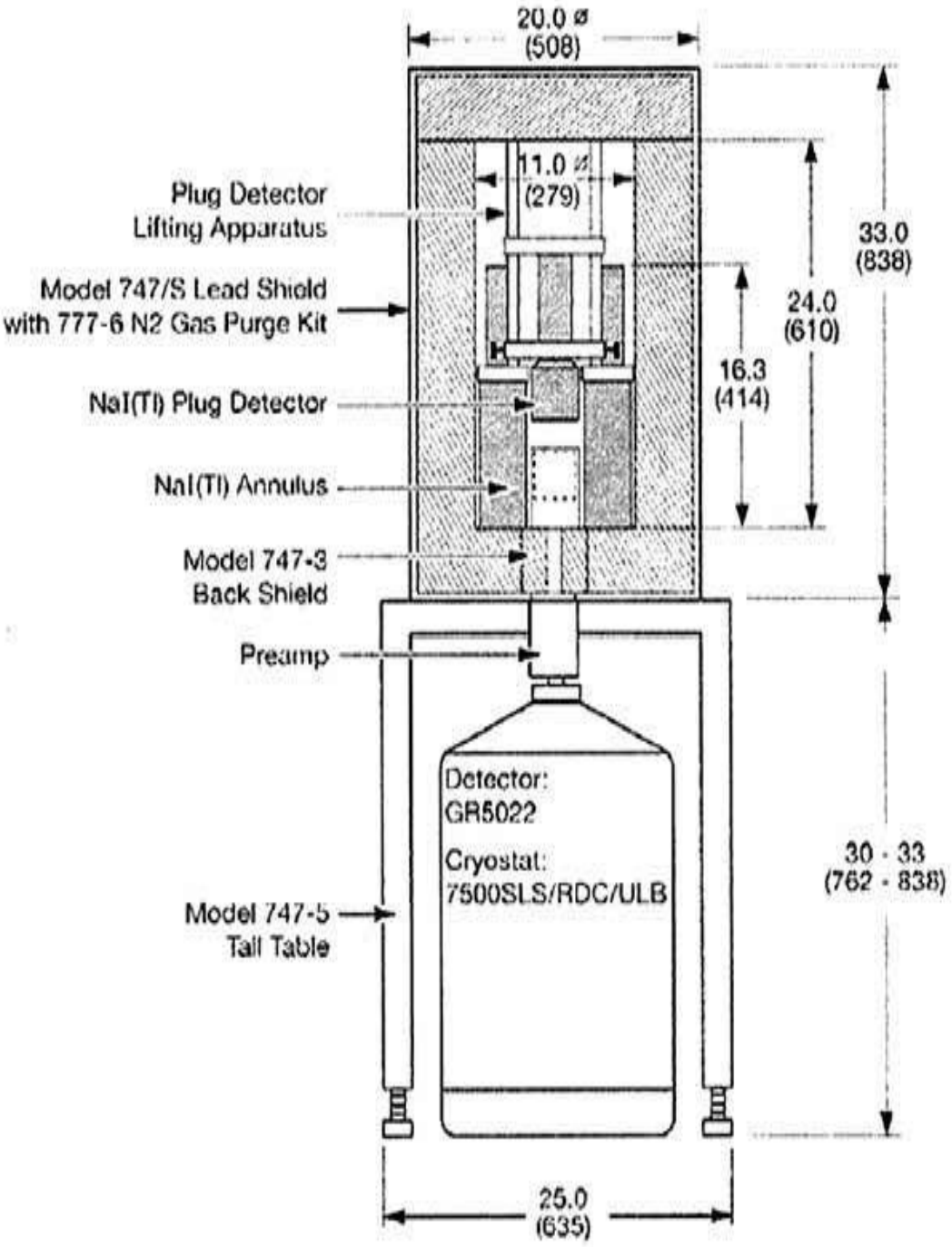


Figure 3.9: Cross - sectional view of HPGe detector.

Figure 3.10: HPGe detector system available at BAEC Savar, Dhaka.

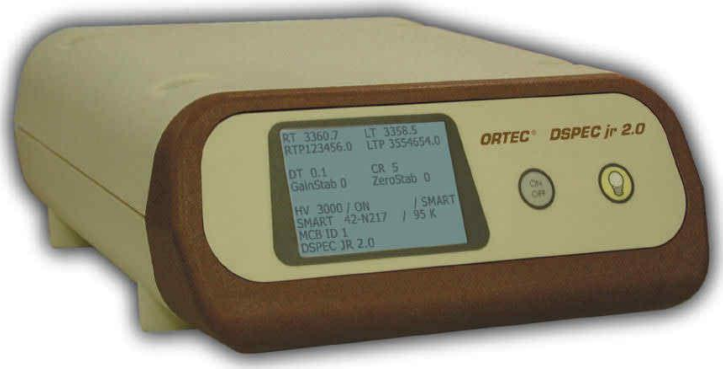


Figure 3.11: The component of digital gamma ray spectrometry system.

3.8: Materials and Methods

In the present study the amount of radioactive materials in sediments near Bhairab River is determined by Instrumental Neutron Activation Analysis. In this method the element

present in sediments is activated by high energetic neutron. After that excited atom wants to stable by emitting radioactive ray. Measuring the energy of radioactive ray what type of atom is present in those samples can be calculated.

3.8.1: Materials used for the Experiment

Instrument needs for this research can be classified into two groups: Figure 3.12 and Figure 3.13 shows the materials needed during collecting sample and experiment

1. Instrument need during collecting sample
2. Instrument need in laboratory.


GPS system


GPI pipe

Zip-lock pack


Hand spade


Collected sample in pack


Hand glove


Ball pen & note book


Marker pen

Figure 3.12: Instrument needed during collecting sample.


Mortar & pestle


Oven


Gamma counter


Mesh


Hot plate


Sieve

Petri dishes

Digital micro balance

Teflon (Plastic)

Impulse sealer

HPGe detector

De-ionized water

Figure 3.13: Instrument used during experiment.

3.8.2: Justification of Sample Site Selection

Among all elements in nature sediments are most polluted by heavy metals which are unstable. Various experiments show that soil near industrial areas is most polluted than non-industrial areas. To know the present situation of sediments near Bhairab River and to compare it to future, 10 sediments sample have been collected from 10 different places near Bhairab River.

3.8.3: Location of the Study Area

Bhairab River is a river in the south western part of Bangladesh. It passes through Khulna, dividing the city into two parts. Bhairab River originates from Tengamari border of Meherpur District. Bhairab River flows through the Khulna city and connects to the Rupsha River and then it connects to the Posur River at Mongla channel near Chalna. From there it flows to the Bay of Bengal after crossing the Sundarbans, as shown in the Figure 3.14

3.8.4: Sample Collection

Samples have been collected by using GPI pipe (diameter 10 cm and height 40 cm) with a rubber stopper and a rubber sample remover. At first the sampling positions have been fixed by a digital (G. P. S) system. Then a hole with 10-15 cm deep has been made at upper layer of soil. The pipe has been then inserted through the soil by screwing at around 25 cm depth. After that the upper opening of the pipe has been blocked with a rubber cork. The pipe has taken out slowly by unscrewing, and kept in horizontal position. After

removing the rubber cork, another rubber remover (which diameter is smaller than the diameter of the pipe) has been used for removing the samples. The samples have been then collected to a zip-lock pack. The samples have been marked separately by giving the identification (ID) number carefully according to their positions. To avoid contamination, separate hand gloves have been used to collect each sample. The details of the sample information are tabulated in Table 3.4 and Table 3.3 gives the symbol and full name of elements.

Collected samples have been then allowed to dry in an electric oven at 85°C until having constant weight. The dried sediment samples have been sieved with a 0.25 mm mesh in order to remove organic materials stones and lumps. For making small grain size and homogeneous mixture, each of the samples has been ground with an agate mortar and pestle. The weight of each of the 10 cm long cylindrical sample volume is around 300-400 gm. For the chemical characterization of a meteorite 0.5 to 0.8 gm sample is considered to be a representative sample (Khan, 2015). In this study the sample ground mass was about 300-400 gm (400-800 times higher than those of meteorite samples). So, it can be assumed that our collected samples will give the representative geochemical history of the respective layer as well as the sampling position having specific distance from the sluice gate.

3.9: Steps of Sample Preparation

For Instrumental Neutron Activation Analysis various steps are taken such as sample collection, sample preparation, sample irradiation by reactor and analysis etc. All of them are important and should be taken extra care. Among them sample preparation takes the following steps.

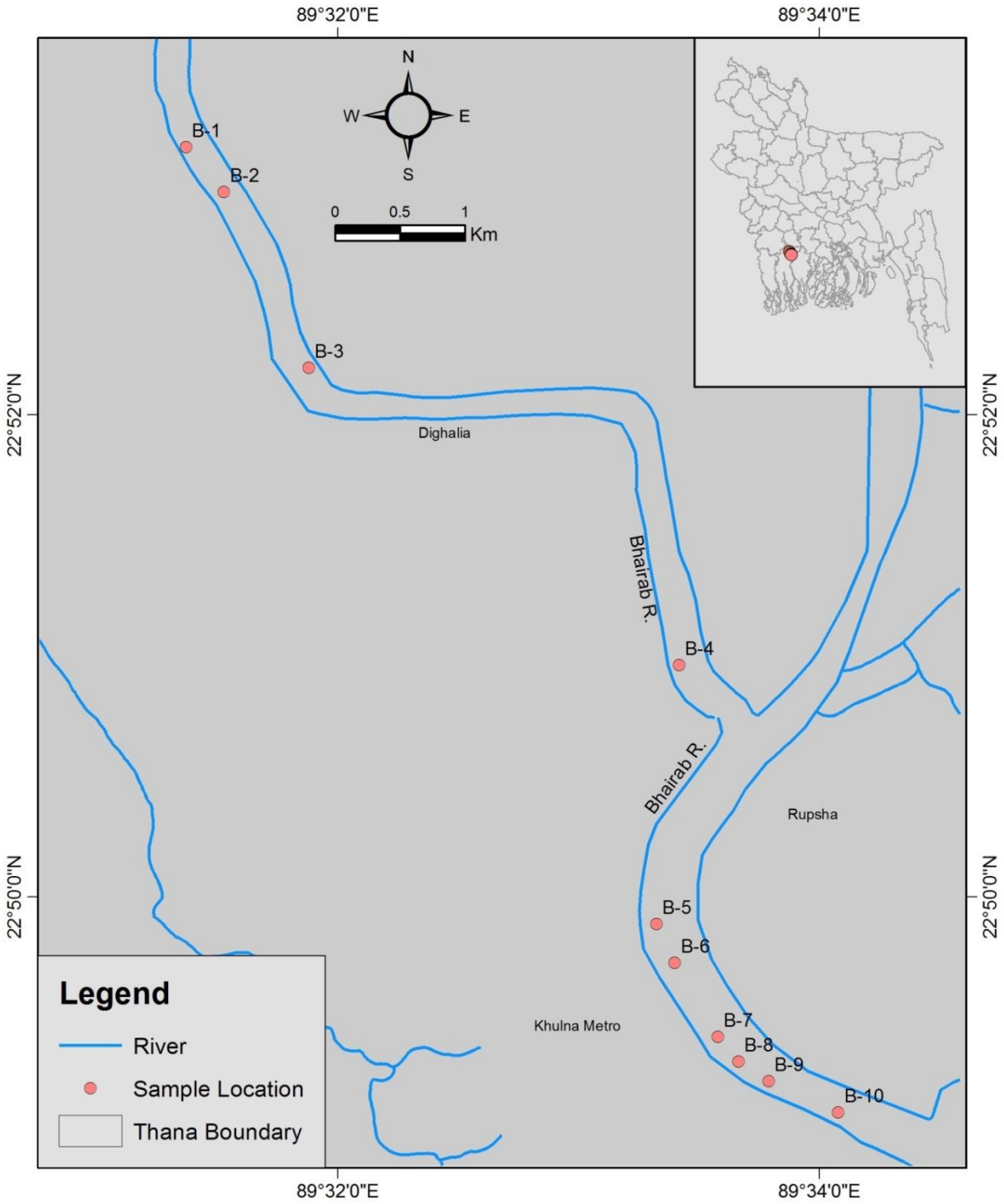


Figure 3.14: Study area

Table 3.3: Symbol and full name of elements

Sl. No.	Symbol	Name of the elements
1	Na	Sodium
2	Mg	Magnesium
3	Al	Aluminum
4	K	Potassium
5	Ca	Calcium
6	Sc	Scandium
7	Cr	Chromium
8	Mn	Manganese
9	Fe	Iron
10	Co	Cobalt
11	Zn	Zinc
12	Ga	Gallium
13	As	Arsenic
14	Br	Bromine
15	Sb	Antimony
16	Cs	Cesium
17	Ba	Barium
18	Ce	Cerium
19	Nd	Neodymium
20	Eu	Europium
21	Tb	Terbium
22	Dy	Dysprosium
23	Ho	Holmium
24	Tm	Thulium
25	Yb	Ytterbium
26	Lu	Lutetium
27	Ta	Tantalum
28	W	Tungsten

Table 3.4: Sample information with ancillary data

SL No	Sample ID	Location	GPS	
			Longitude	Latitude
1	Bhairab River (B-1)	Near about S S Jute Traders	89º 31.368' E	22º 53.104' N
2	Bhairab River (B-2)	Near about Zaman Jute Traders	89º 31.388' E	22º 53.070' N
3	Bhairab River (B-3)	Near about Bangladesh Pat kol Corporation	89º 31.232' E	22º 51.031' N
4	Bhairab River(B-4)	Starting from chorer hat	89º 33.376' E	22º 50.949' N
5	Bhairab River(B-5)	Six Number Ghat at Zora Gate	89º 33.296' E	22º 49.798' N
6	Bhairab River (B-6)	Five Number Ghat at Zora Gate	89º 33.329' E	22º 49.726' N
7	Bhairab River(B-7)	Four Number Ghat at Zora Gate	89º 33.587' E	22º 49.340' N
8	Bhairab River(B-8)	Near at Lunch Ghat	89º 33.618' E	22º 49.308' N
9	Bhairab River(B-9)	Near at Bazar Ghat	89º 33.716' E	22º 49.253' N
10	Bhairab River(B-10)	In front of a Hospital	89º 34.064' E	22º 49.098' N

3.9.1: Drying

Ten petri dishes have been cleaned by de-ionized water and put into the oven to be dried. The identification number (ID) has given on each petri dishes according to the sample ID. Collected samples have been put into the petri dishes corresponding to the given ID. The petri dish containing sediments allowed drying in an electric oven at 85°C until having constant weight (Parry, 1991). The required time will vary with the water content of the sample. Figure 3.15 shows the micro oven used in the lab.

Figure 3.15: Drying samples at micro oven.

3.9.2: Sieving

After some days the samples have been dried up and then the dried samples have been sieved with a mesh having a hole diameter of 0.25 mm in order to remove organic materials, stones and lamps. Figure 3.16: shows sieving the soil sample.

Figure 3.16: Sieving the soil sample.

3.9.3: Grinding

For making small grain size each of the samples have been grind with an agate mortar and pestle. The grain should be as small as possible so that it is easy to weighing and packing for irradiation in reactor. Figure 3.17 shows grinding samples with mortar and pestle

Figure 3.17: Grinding samples with mortar and pestle.

3.9.4: Weighing

In order to get correct result about elements weighing must be accurate. For weighing the sediment samples firstly, the weight of each empty petri dish has been set to zero by a digital electronic micro balance. After that pot (sample container) has been taken. Now sediment samples have been placed into the pot. The weight of the pot and sample then took. In every time reading has been noted into the register book. Now by subtracting the pot weight from pot plus sample weight. In this way the samples actual weight has been taken. The weight of each sample is kept around 100 gm and net weight was recorded in register book also. In INAA lab a digital electro micro balance is used that can measure 0.001- 60/200 gm. Figure 3.18 shows a digital electro micro balance and Table 3.5 shows the weight of the sample and polybag.

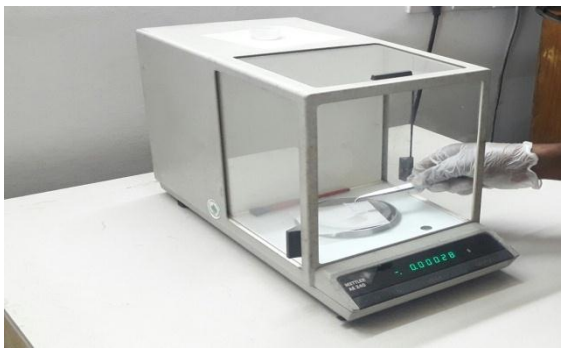


Figure 3.18: Digital electro micro balance.

Table 3.5: Weight of the Sample and Poly Bag

Sl. No	**Sample-ID**	**Poly Bag (gm)**	**Poly Bag with Sample (gm)**	**Sample (gm)**
1	1633b	0.09142	0.13535	0.04393
2	Soil-7	0.11112	0.15298	0.04186
3	B-1	0.07975	0.12124	0.04149
4	B-2	0.06823	0.11168	0.04345
5	B-3	0.06598	0.10981	0.04383
6	B-4	0.06797	0.11242	0.04445
7	B-5	0.07862	0.12513	0.04651
8	B-6	0.06919	0.10936	0.04017
9	B-7	0.06601	0.11460	0.04859
10	B-8	0.07184	0.11737	0.04553
11	B-9	0.06825	0.12002	0.05177
12	B-10	0.06995	0.10801	0.03806
13	Blank	-	0.06616	0.06616

3.10: Sample Preparation for INAA

After weighing, the sediment samples has been made individual packet with individual identification number. The size and shape of packets has been kept approximately same. The packets then preserved carefully for neutron irradiation. For this experiment approximately 50 mg of each dried powder samples has been weighted in polyethylene bag and heat sealed. For relative standardization approach, one Reference Materials: IAEA-Soil-7, and one standard reference material NIST-1633b (Coal Fly Ash) has been used in the present work. Each of the standards has been prepared as the same way as those of samples. Samples and standards have been placed in a vial for irradiation. The samples, one standard and one foil have been packed in a vial for irradiation. NIST-1633b has been used as the standard while IAEA-Soil-7 has used as the control sample. Figure 3.19 shows ready samples for Neutron Irradiation.

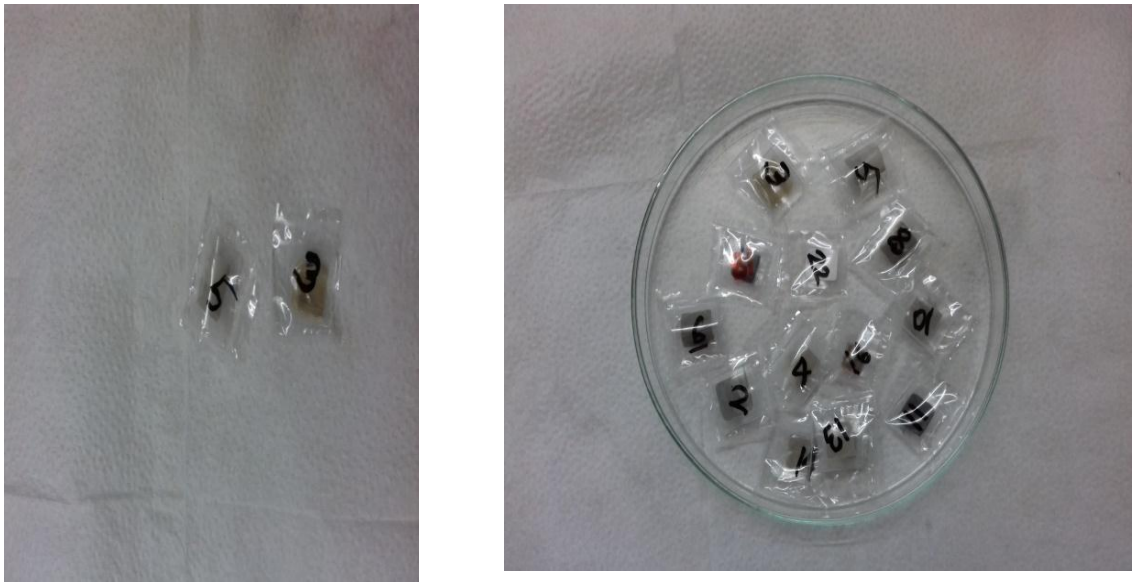


Figure 3.19: Samples for Neutron Irradiation.

3.10.1: Irradiation

Two irradiation schemes were performed using pneumatic transfer (rabbit) system at the 3 MW TRIGA Mark-II research reactor of Bangladesh Atomic Energy Commission, Savar:
(i) Long irradiation was performed simultaneously with all the samples and standards with the thermal neutron flux of 2.11×10^{13} n.cm^{-2}.sec^{-1} for 7 min at 2.4 MW and

(ii) Short irradiation was performed separately for each sample with the thermal neutron flux of 5.28×10^{12} n. cm^{-2} sec^{-1} for 1min at 250 kW.

To determine the neutron flux gradient within the sample stack, three IRMM-530RAAl-0.1% Au (0.1 mm foil) monitor foils were also irradiated by placing them at the bottom, middle and top of the sample stack for the long irradiation scheme. After long irradiation, samples were turned into highly radioactive. For this reason, they usually were not handled immediately. They were in a shielded place for 2 days. (Tsoulfanidis, 1995) Figure 3.20 shows sending and receiving center for sample vial at BAEC at Savar.

Figure 3.20: Sending and receiving center for sample vial at BAEC Savar.

3.10.2: Gamma Ray Counting

After irradiation, gamma-ray counting was performed with a high purity germanium (HPGe) detector (CANBERRA, 25% relative efficiency, 1.8 keV resolution at 1332.5 keV of 60 Co) coupled with a digital gamma spectrometer (ORTEC, DSPEC Jr™).

For short irradiation, first counting was performed for 300 s after a decay time of about 300 s and second counting for 600 s after decay time of 2-3 h. For long irradiated samples, first counting was performed for 3600 sec after a decay time of 2-3 days while the second counting was performed for 7200 sec after a decay time of 7-10 days and third counting

was performed for 8-12 hours after a decay time of 2-3 weeks. The gamma spectrometry of all the irradiated samples and certified reference materials was performed using a PC-based HPGe detector coupled with a digital gamma spectrometry system. The data acquisition was performed using the software Genie-2000 (Canberra) and MAESTRO-32 (ORTEC) and the gamma peak analysis was performed using the software Hypermet PC version 5.21 The gamma peak analysis is shown in Figure 3.21 and Figure 3.22(Wyttenbach, 1971).

Figure 3.21: Gamma peak analysis using Hypermet PC version 5.12

Figure 3.22: Counts the gamma peak area using Hypermet PC version 5.12

3.10.3: Interference Correction

During neutron activation analysis ^{27}Al (n, γ) ^{28}Al and ^{28}Si (n, p) ^{28}Al, both produce same radioactive isotope (^{28}Al) and give gamma signal at 1779.0 keV. So for the accurate determination of Al, correction of the interference of ^{28}Si (n, p) ^{28}Al on ^{27}Al(n, γ)^{28}Al was made by irradiating Al and Si reagents (from Spex, USA) simultaneously.

The experimental gamma spectra for NIST-1633b and IAEA-Soil-7 of our experiments are given below in Figure 3.23 and Figure 3.24

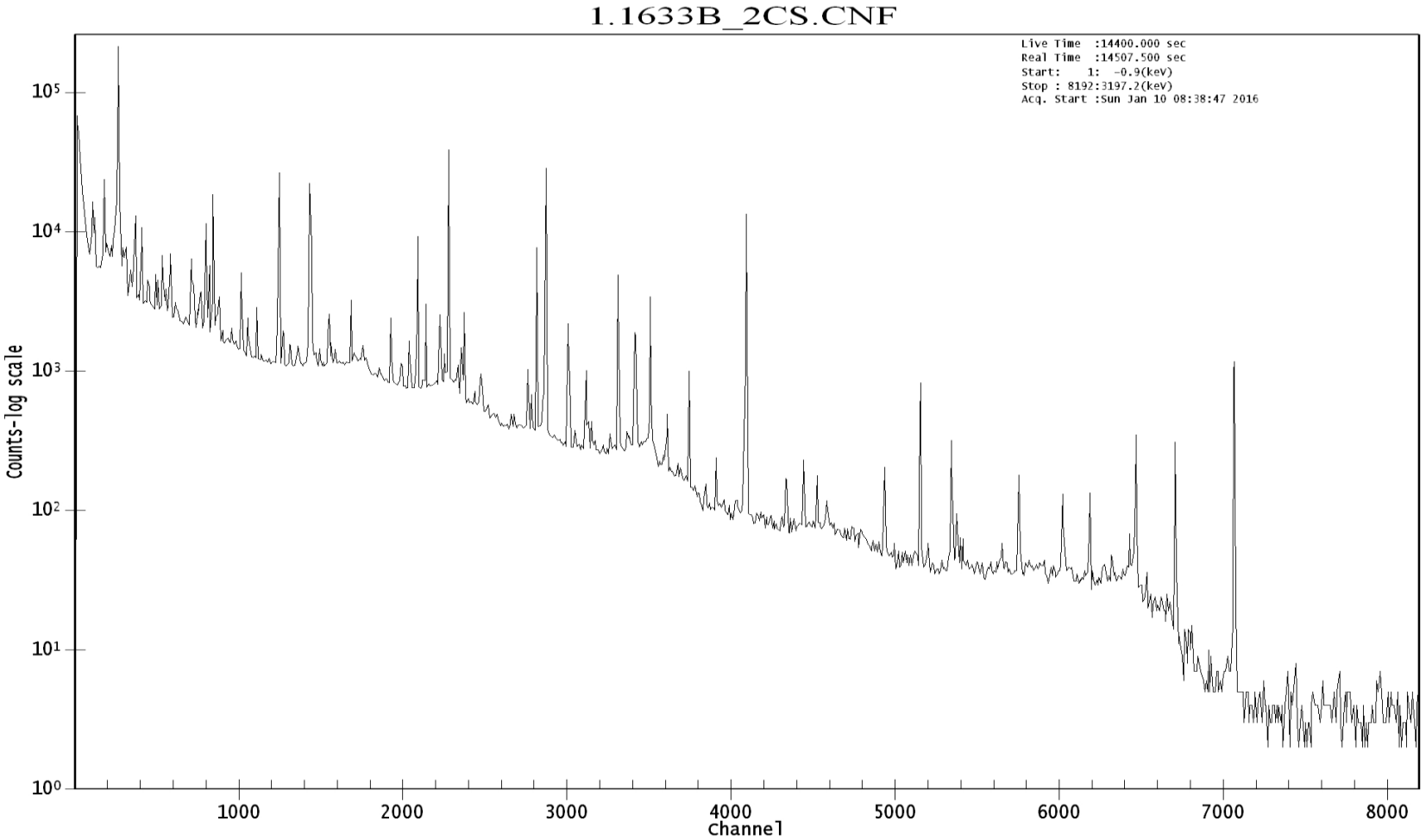


Figure 3.23: Gamma spectra for NIST-1633b.

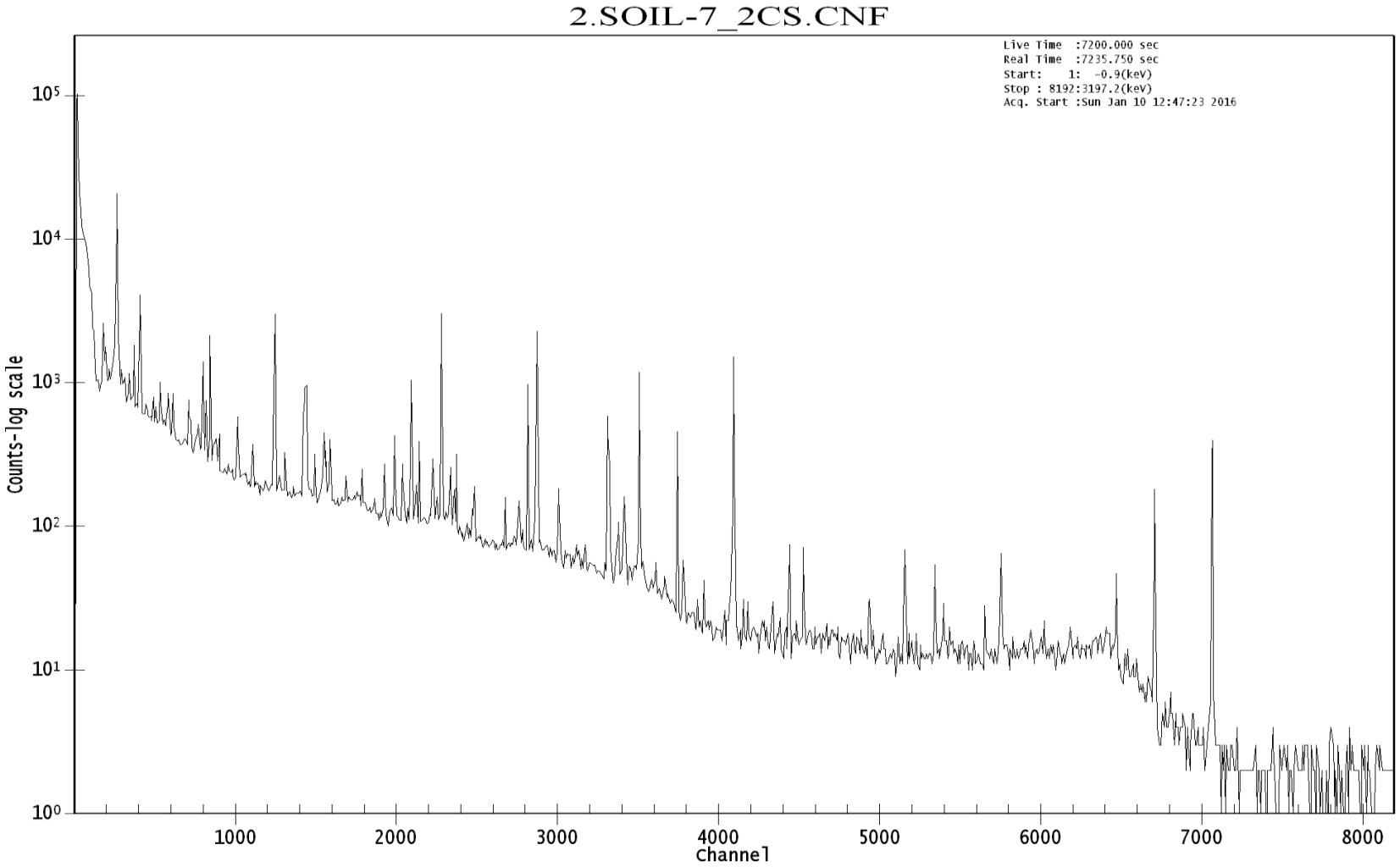


Figure 3.24: Gamma spectra for IAEA-Soil-7

3.10.4: Concentration Calculation

The concentration calculation was performed by the relative standardization method using equation below, which were then formulated in excel sheet and therefore, concentrations of elements were calculated. The activation equation for relative NAA is

$$\frac{weight\ of\ element\ \text{"X"}\ in\ sample}{Weight\ of\ element\ \text{"X" in standard}} = \frac{\mathrm{A}_{x^*}\ \text{in sample}\ \times \left(e^{\lambda t}\right)_{sam}}{A_{x^*}\ in\ sample\ \times (e^{\lambda t})_{std}}$$

Knowing the activities of x^* in sample and in standard, the sample and standard decay times and weight of "x" in the standard, the weight of element "x" in the sample can be calculated.

3.10.5: Accuracy and Precisions

In elemental analysis accuracy and precision are two most important words. In every analysis it is calculated carefully. Due to a small incognizance a great disturbance is occurred which makes inaccuracy and imprecision between data. Precision is a description of random errors, a measure of statistical variability. And in more commonly "Accuracy is a description of systematic errors, a measure of statistical bias". In the fields of science, engineering and statistics; the accuracy of a measurement system is the degree of closeness of measurements of a quantity to that quantity's true value. The precision of a measurement system, related to reproducibility and repeatability, is the degree to which repeated measurements under unchanged conditions show the same results. Figure 3.25 represents graphical presentation of accuracy and precision

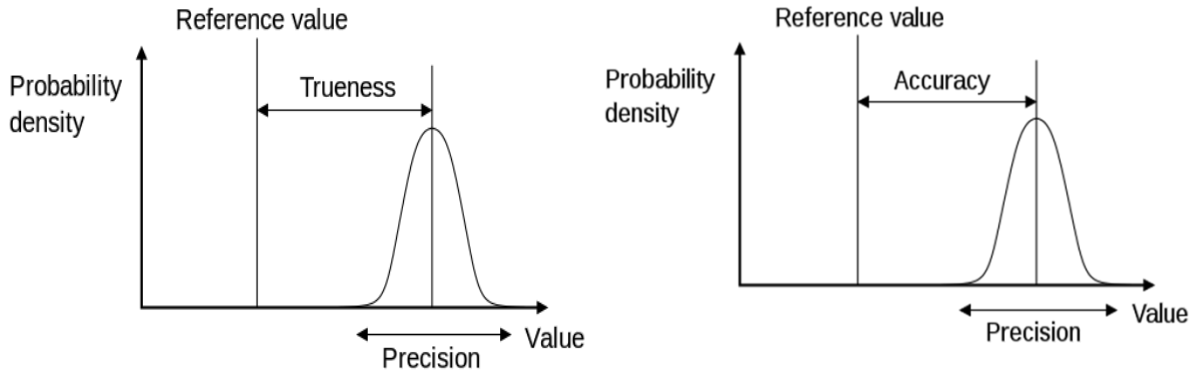


Figure 3.25: Graphical presentation of accuracy and precision.

According to ISO 5725-1, Accuracy consists of Trueness (proximity of measurement results to the true value) and Precision (repeatability or reproducibility of the measurement). Where repeatability is the variation arising when all efforts are made to keep conditions constant by using the same instrument and operator, and repeating during a short time period. And reproducibility is the variation arising using the same measurement process among different instruments and operators, and over longer time periods. Figure 3.26 shows Precision and Accuracy.

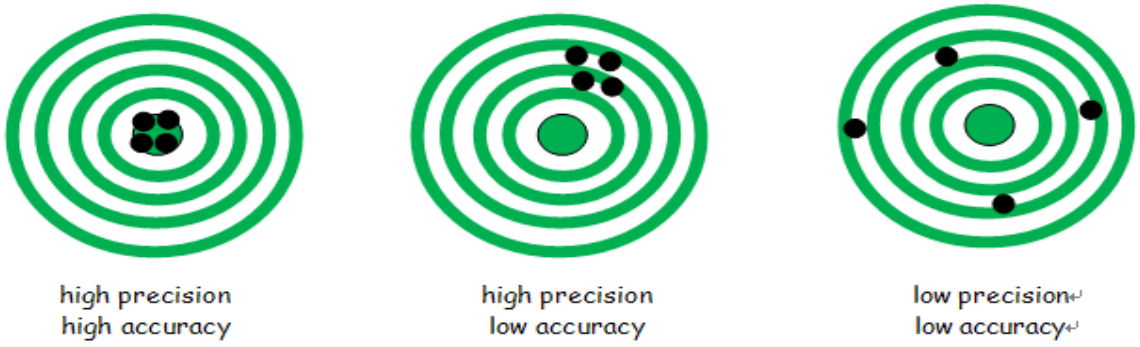


Figure 3.26: Precision and Accuracy

For assessing the data quality we have analyzed the experimental result extensively. Analyses were repeated 4 times. Analytical results were summarized above tables, where average and uncertainty values for n (the number of analyses) = 4 are also included. Uncertainties are given one standard deviations (1σ). Table 3.6 represents elemental abundances in repeated analyses (n = 3) of IAEA-Soil-7 of this study along with the certificate values.

Table 3.6: Elemental abundances in repeated analyses (n = 3) of IAEA-Soil-7 of the present study along with the certificate values.

		This work								Certificate values		
		Soil-7 (1)	±	Soil-7 (2)	±	Soil-7 (3)	±	Average	SD	Conc.	Min.	Max.
Mass	[g]	0.04135		0.04186		0.04008						
Na	[%]	0.235	0.002	0.225	0.003	0.229	0.004	0.230	0.005	0.240	0.230	0.250
Mg	[%]	1.13	0.10	1.26	0.10	1.10	0.09	1.16	0.08	1.13	1.10	1.18
Al	[%]	5.08	0.05	4.85	0.04	4.92	0.04	4.95	0.11	4.7	4.4	5.1
K	[%]	1.20	0.03	1.21	0.03	1.28	0.03	1.23	0.04	1.21	1.13	1.27
Ca	[%]	18.1	2.8	16.3	2.5	16.9	2.6	17.1	0.9	16.3	15.7	17.4
Sc	[µg/g]	8.52	0.07	8.64	0.08	8.36	0.08	8.50	0.14	8.30	6.90	9.00
Cr	[µg/g]	65.9	1.6	64.2	1.6	68.2	1.8	66.1	2.0	60	49	74
Mn	[µg/g]	626	3	631	3	654	3	637	15	631	604	650
Fe	[%]	2.56	0.04	2.58	0.04	2.45	0.04	2.53	0.07	2.57	2.52	26.3
Co	[µg/g]	9.27	0.36	9.37	0.37	9.00	0.37	9.21	0.19	8.9	8.4	10.1
Zn	[µg/g]	64	4	80	5	101	6	82	19	104	101	113
Ga	[µg/g]	9.50	0.86	-	-	-	-	-	-	10	9	13
As	[µg/g]	15.5	0.2	14.1	0.2	13.0	0.2	14.2	1.3	13.4	12.5	14.2
Br	[µg/g]	9.0	0.4	8.0	0.4	7.4	0.3	8.1	0.8	7	3	10
Sb	[µg/g]	2.03	0.04	2.05	0.05	1.73	0.04	1.94	0.18	1.7	1.4	1.8
Cs	[µg/g]	5.82	0.20	6.17	0.21	5.59	0.20	5.86	0.29	5.4	4.9	6.4
Ba	[µg/g]	161	7	174	8	141	8	159	16	159	131	196
Ce	[µg/g]	49.9	0.9	56.4	1.1	52.5	1.1	52.9	3.3	61	50	63
Nd	[µg/g]	27.0	1.0	22.6	1.0	21.8	1.0	23.8	2.8	30	22	34
Eu	[µg/g]	1.02	0.02	1.04	0.03	1.05	0.03	1.04	0.02	1.0	0.9	1.3
Tb	[µg/g]	0.70	0.07	0.71	0.07	0.58	0.06	0.66	0.07	0.6	0.5	0.9
Dy	[µg/g]	4.12	0.08	4.30	0.09	4.28	0.10	4.23	0.10	3.9	3.2	5.3
Ho	[µg/g]	0.85	0.03	0.67	0.04	0.79	0.04	0.77	0.09	0.71[a]		
Tm	[µg/g]	2.26	0.09	1.62	0.07	1.56	0.06	1.81	0.39	1.6[b]		
Yb	[µg/g]	2.00	0.12	2.16	0.14	2.37	0.15	2.18	0.19	2.4	1.9	2.6
Lu	[µg/g]	0.35	0.01	0.34	0.01	0.29	0.01	0.33	0.03	0.3	0.1	0.4
Ta	[µg/g]	1.02	0.10	0.98	0.10	0.86	0.09	0.95	0.08	0.8	0.6	1
W	[µg/g]	2.40	0.13	3.11	0.14	3.48	0.16	2.99	0.55	1.57[c]		

[a]Kafala(2007)JRNC,271,505-516;

[b]Abugassa(2007)JRNC,271,27-30;

[c]Wasim(2011)JRNC,287,821-826

CHAPTER 4

Results and Discussion

In this study, research reactor-based Neutron Activation Analysis (NAA) technique has been applied to determine elemental concentrations in sediment samples of the river Bhairab, Khulna city, Khulna. It has been done by Instrumental Neutron Activation Analysis (INAA) technique. A total of 10 (ten) sediment samples have been collected from different places of the study area. The collected sediments have been analyzed by Instrumental Neutron Activation Analysis (INAA) method. To determine elemental concentrations in sediments of the river by comparative NAA method, two standards-International Atomic Energy Agency (IAEA) Certified Reference Materials namely IAEA-Soil-7 and NIST-1633b Coal Fly Ash have been used for long irradiation method. The gamma ray counting of all irradiated samples and standards have been performed using the HPGe detector coupled with a digital gamma spectrometer. Gamma spectrometry was performed several times depending on the half-lives of the product radionuclides of the interested elements. The decay data of the interested elements have been shown in the appendix (Pollard and Heron, 1996).The concentration of different elements has been measured by evaluating the gamma ray peak areas produced from (n, γ) reaction. The gamma spectrum acquisition for irradiated samples and standards has been performed using software MAESTRO-32 (ORTEC) and the gamma ray peak has been analyzed by using the software Hyper Mate PC version 5.2 (Hevesy and Levi, 1936)

4.1 Detection limits of NAA

The ability of a given procedure to determine the minimum amounts of an element reliably is presented by the detection limit. The detection limit depends on the amount of material to be irradiated and to be counted, neutron flux, irradiation time, decay time and the counting condition. 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 rays spectrum interference from such factors as the blank from pre-irradiation treatment and from packing materials. The detection limits of the studied elements for samples under the present experimental conditions are given in Table 4.1

Table4.1: Detection limits (3σ) calculated from the procedure blank within this experimental condition (Tamim, 2016)

		Detection Limit
Na	[%]	0.0006
Al	[%]	0.003
K	[%]	0.009
Ca	[%]	0.042
Sc	[µg/g]	0.039
Ti	[%]	0.005
V	[µg/g]	0.11
Cr	[µg/g]	1.26
Mn	[µg/g]	0.03
Fe	[%]	0.011
Co	[µg/g]	0.20
Zn	[µg/g]	3.65
Ga	[µg/g]	1.56
As	[µg/g]	0.04
Br	[µg/g]	0.16
Rb	[µg/g]	2.54
Sb	[µg/g]	1.15
Cs	[µg/g]	0.11
Ba	[µg/g]	39.85
La	[µg/g]	0.017
Ce	[µg/g]	1.48
Nd	[µg/g]	4.26
Sm	[µg/g]	0.072
Eu	[µg/g]	0.06
Tb	[µg/g]	0.037
Dy	[µg/g]	0.005
Ho	[µg/g]	0.09
Tm	[µg/g]	2.23
Yb	[µg/g]	0.52
Lu	[µg/g]	0.005
Hf	[µg/g]	0.35
Ta	[µg/g]	0.08
W	[µg/g]	0.11
Th	[µg/g]	0.08
U	[µg/g]	0.04

4.2 Elemental Abundances in the Sediment Samples

A total of ten sediment samples are tabulated in Table 4.2 with associated uncertainties (1σ). Na, Mg, Al, K, Ca, Sc, Cr, Mn, Fe, Co, Zn, Ga, As, Br, Sb, Cs, Ba, Ce, Nd, Eu, Tb, Dy, Ho, Tm, Yb, Lu, Ta, and W have been determined by INAA. All the calculations have been done in the Excel Worksheet.

Mean abundances (n= 10), Standard Deviations (SD), Relative Standard Deviations (RSD), Median value, Minimum value and the Maximum values as well as the literature data for the coal fly ash (NIST-1633b) for the respective elements are also given in Table 4.2

4.3: Quantification of Sediment Pollution

4. 3. 1: Base-line Data for Elemental Abundances

In elemental analysis base-line data is important for quantifying the level of pollution for sediments and soils. Dragovic (Dragovic, 2008) used element abundances of Earth's crust as the base line data. But Rubio (Rubio, 2000) recommended the use of regional background values. Similarly, in previous works (Hornung, 1989) the approach of establishing reference values is to compare the target metal concentrations in contaminated and uncontaminated sediments that are miner logically and texturally similar or identical.

But the regional difference of sample collecting place between the contaminated and uncontaminated sediments may cause the significant difference in elemental compositions. So it has been calculated the Geo-accumulation Index (Igeo), Enrichment Factor (EF) and the Pollution Load Index (PLI) of the sediments. In the study, it has been used the elemental abundances of continental crust (Rudnick and Gao, 2014) as the background data. It has been used sediments from different place for which continental crust data is suitable.

Table 4.2: Elemental abundances in sediment samples of the Bhairab River with spatial Variation

		B-1	±	B-2	±	B-3	±	B-4	±	B-5	±
Na	[%]	0.926	0.005	0.958	0.005	0.978	0.006	0.973	0.006	0.717	0.005
Mg	[%]	1.48	0.06	1.33	0.05	1.30	0.05	1.46	0.06	1.50	0.06
Al	[%]	7.04	0.05	6.63	0.04	6.45	0.04	6.77	0.05	7.33	0.05
K	[%]	2.47	0.09	2.56	0.10	2.23	0.12	2.58	0.13	2.10	0.11
Ca	[%]	2.29	0.42	2.60	0.45	2.08	0.38	2.81	0.50	2.48	0.44
Sc	[µg/g]	13.1	0.1	12.3	0.1	11.6	0.1	12.8	0.1	11.2	0.1
Cr	[µg/g]	76.5	1.9	72.6	1.8	74.1	1.9	70.2	1.8	61.8	1.6
Mn	[µg/g]	636	10	583	9	579	9	571	9	645	10
Fe	[%]	3.76	0.06	3.57	0.06	3.27	0.06	3.51	0.06	3.12	0.06
Co	[µg/g]	15.2	0.5	14.6	0.5	13.0	0.4	14.2	0.5	12.5	0.4
Zn	[µg/g]	75.3	5.2	69.8	4.9	105.9	6.4	77.4	5.2	57.7	4.3
Ga	[µg/g]	49.1	1.7	48.6	1.7	86.7	3.4	94.0	3.6	88.6	3.5
As	[µg/g]	9.00	0.19	7.98	0.18	8.04	0.22	7.55	0.21	5.86	0.19
Br	[µg/g]	2.54	0.17	4.82	0.28	4.31	0.27	4.01	0.26	2.63	0.19
Sb	[µg/g]	0.861	0.030	0.790	0.028	0.793	0.030	0.846	0.031	0.763	0.029
Cs	[µg/g]	11.94	0.34	10.79	0.31	10.29	0.30	10.66	0.31	10.00	0.29
Ba	[µg/g]	432	23	444	24	507	26	499	26	532	27
Ce	[µg/g]	97.7	1.5	85.7	1.3	85.6	1.3	95.8	1.4	72.9	1.2
Nd	[µg/g]	32.9	1.2	28.9	1.1	40.2	1.3	36.1	1.2	32.8	1.1
Eu	[µg/g]	1.23	0.03	1.14	0.03	1.11	0.03	1.25	0.03	1.01	0.03
Tb	[µg/g]	1.09	0.06	0.81	0.05	0.86	0.05	0.99	0.05	0.57	0.04
Dy	[µg/g]	6.49	0.12	5.41	0.10	6.48	0.12	6.41	0.12	6.52	0.12
Ho	[µg/g]	1.27	0.05	1.42	0.05	2.07	0.08	1.54	0.07	1.28	0.06
Tm	[µg/g]	1.96	0.08	1.90	0.08	2.18	0.09	1.78	0.07	1.77	0.07
Yb	[µg/g]	3.09	0.11	2.52	0.10	3.50	0.12	2.77	0.10	2.28	0.09
Lu	[µg/g]	0.47	0.01	0.43	0.01	0.55	0.01	0.42	0.01	0.35	0.01
Ta	[µg/g]	1.82	0.16	1.86	0.17	1.66	0.15	1.53	0.14	1.45	0.14
W	[µg/g]	3.33	0.18	3.32	0.18	3.80	0.23	3.52	0.22	2.85	0.20

Continue

		B-6	±	B-7	±	B-8	±	B-9	±	B-10	±
Na	[%]	0.904	0.006	0.914	0.006	0.845	0.006	0.793	0.006	0.918	0.007
Mg	[%]	1.23	0.05	1.44	0.06	1.13	0.05	0.82	0.04	1.33	0.06
Al	[%]	6.45	0.04	6.79	0.05	5.76	0.04	3.75	0.03	6.56	0.04
K	[%]	2.39	0.13	2.34	0.12	1.87	0.11	1.69	0.10	2.12	0.14
Ca	[%]	2.66	0.47	2.58	0.45	2.94	0.50	1.49	0.28	2.48	0.44
Sc	[µg/g]	11.3	0.1	11.6	0.1	9.9	0.1	8.4	0.1	11.2	0.1
Cr	[µg/g]	63.7	1.8	66.9	1.7	62.7	1.7	46.8	1.3	64.8	1.8
Mn	[µg/g]	589	9	570	9	547	9	322	5	565	9
Fe	[%]	3.32	0.06	3.25	0.06	2.74	0.05	2.42	0.05	3.03	0.06
Co	[µg/g]	12.5	0.4	13.4	0.4	11.0	0.4	9.0	0.3	11.9	0.4
Zn	[µg/g]	49.3	4.1	53.6	4.0	95.7	5.9	57.2	4.1	57.6	4.6
Ga	[µg/g]	110.7	4.3	116.9	4.1	91.6	3.8	81.8	3.5	115.6	4.9
As	[µg/g]	7.67	0.23	7.40	0.21	8.15	0.23	5.24	0.18	6.57	0.23
Br	[µg/g]	2.80	0.21	3.84	0.25	2.74	0.20	2.76	0.19	3.54	0.26
Sb	[µg/g]	1.045	0.037	0.686	0.027	1.191	0.038	0.542	0.023	0.843	0.034
Cs	[µg/g]	9.07	0.28	10.49	0.30	7.40	0.24	7.70	0.23	8.80	0.28
Ba	[µg/g]	353	23	499	26	417	25	315	20	584	30
Ce	[µg/g]	89.4	1.4	87.6	1.3	89.7	1.3	68.9	1.1	101.1	1.6
Nd	[µg/g]	32.3	1.2	29.8	1.1	34.5	1.2	27.6	1.0	32.9	1.3
Eu	[µg/g]	0.96	0.03	1.16	0.03	1.20	0.03	0.91	0.02	1.26	0.03
Tb	[µg/g]	1.15	0.06	0.92	0.05	0.90	0.05	0.68	0.04	0.97	0.06
Dy	[µg/g]	8.41	0.15	6.21	0.11	5.80	0.11	3.83	0.08	7.36	0.13
Ho	[µg/g]	1.75	0.08	1.09	0.05	1.47	0.07	1.03	0.05	1.55	0.08
Tm	[µg/g]	2.34	0.09	1.94	0.08	1.89	0.08	1.55	0.07	2.27	0.09
Yb	[µg/g]	4.57	0.14	2.57	0.09	2.65	0.10	2.17	0.08	2.88	0.11
Lu	[µg/g]	0.64	0.02	0.39	0.01	0.36	0.01	0.34	0.01	0.41	0.01
Ta	[µg/g]	1.52	0.15	1.26	0.12	1.43	0.14	1.01	0.10	1.26	0.13
W	[µg/g]	2.28	0.19	3.69	0.23	1.79	0.16	2.51	0.18	3.31	0.25

Continue

		Mean	SD [n=5]	RSD [%]	Median	Min.	Max.
Na	[%]	0.893	0.084	9.4	0.918	0.717	0.978
Mg	[%]	1.30	0.21	15.8	1.33	0.82	1.50
Al	[%]	6.35	1.00	15.8	6.56	3.75	7.33
K	[%]	2.23	0.29	13.2	2.34	1.69	2.58
Ca	[%]	2.44	0.41	16.9	2.48	1.49	2.94
Sc	[µg/g]	11.3	1.4	12.1	11.3	8.4	13.1
Cr	[µg/g]	66.0	8.4	12.8	64.8	46.8	76.5
Mn	[µg/g]	561	89	15.9	571	322	645
Fe	[%]	3.20	0.40	12.4	3.25	2.42	3.76
Co	[µg/g]	12.7	1.8	14.4	12.5	9.0	15.2
Zn	[µg/g]	69.9	18.8	26.9	69.8	49.3	105.9
Ga	[µg/g]	88.4	24.2	27.4	91.6	48.6	116.9
As	[µg/g]	7.35	1.14	15.5	7.67	5.24	9.00
Br	[µg/g]	3.40	0.82	24.0	3.54	2.54	4.82
Sb	[µg/g]	0.836	0.179	21.4	0.843	0.542	1.191
Cs	[µg/g]	9.71	1.44	14.8	10.00	7.40	11.94
Ba	[µg/g]	458	82	18.0	499	315	584
Ce	[µg/g]	87.4	10.2	11.7	87.6	68.9	101.1
Nd	[µg/g]	32.8	3.7	11.1	32.8	27.6	40.2
Eu	[µg/g]	1.12	0.12	11.1	1.14	0.91	1.26
Tb	[µg/g]	0.89	0.18	19.8	0.92	0.57	1.15
Dy	[µg/g]	6.29	1.20	19.0	6.41	3.83	8.41
Ho	[µg/g]	1.45	0.31	21.4	1.47	1.03	2.07
Tm	[µg/g]	1.96	0.24	12.4	1.90	1.55	2.34
Yb	[µg/g]	2.90	0.70	24.2	2.65	2.17	4.57
Lu	[µg/g]	0.44	0.10	21.9	0.41	0.34	0.64
Ta	[µg/g]	1.48	0.26	17.8	1.52	1.01	1.86
W	[µg/g]	3.04	0.66	21.8	3.32	1.79	3.80

4.3.2 Geo-accumulation Index (Igeo)

To characterize the pollution levels of soils, geo-accumulation index (Igeo) is an effective tool which can be defined by the following equation (Abrahim and Parker, 2008):
Geo-accumulation Index

$$(I_{geo}) = \mathrm{Log}_2\left(\frac{c_n}{1.5\times B_n}\right) \quad \text{.....(4.1)}$$

Where, C_n is the measured concentration of the metal n,
B_n is the geochemical background concentration of metal n.
Factor 1.5 is the background matrix correction factor due to lithospheric effects.
The geo-accumulation index consists of seven grades or classes (Bhuiyan 2010; Ma 2016).

Class 0 (practically uncontaminated)	: Igeo≤0
Class 1 (uncontaminated to moderately contaminated)	: 0 <Igeo< 1
Class 2 (moderately contaminated)	: 1 <Igeo< 2
Class 3 (moderately to heavily contaminated)	: 2 <Igeo< 3
Class 4 (heavily contaminated)	: 3 <Igeo< 4
Class 5 (heavily to extremely contaminated)	: 4 <Igeo< 5
Class 6(extremely contaminated)	: 5 <Igeo.

Class 6 is an open class and comprises all values of the index higher than Class 5.
The elemental concentrations in Class 6 may be hundredfold greater than the geochemical background value (Bhuiyan, 2010, Boszke, 2004, Muller, 1969, Rabee 2011).

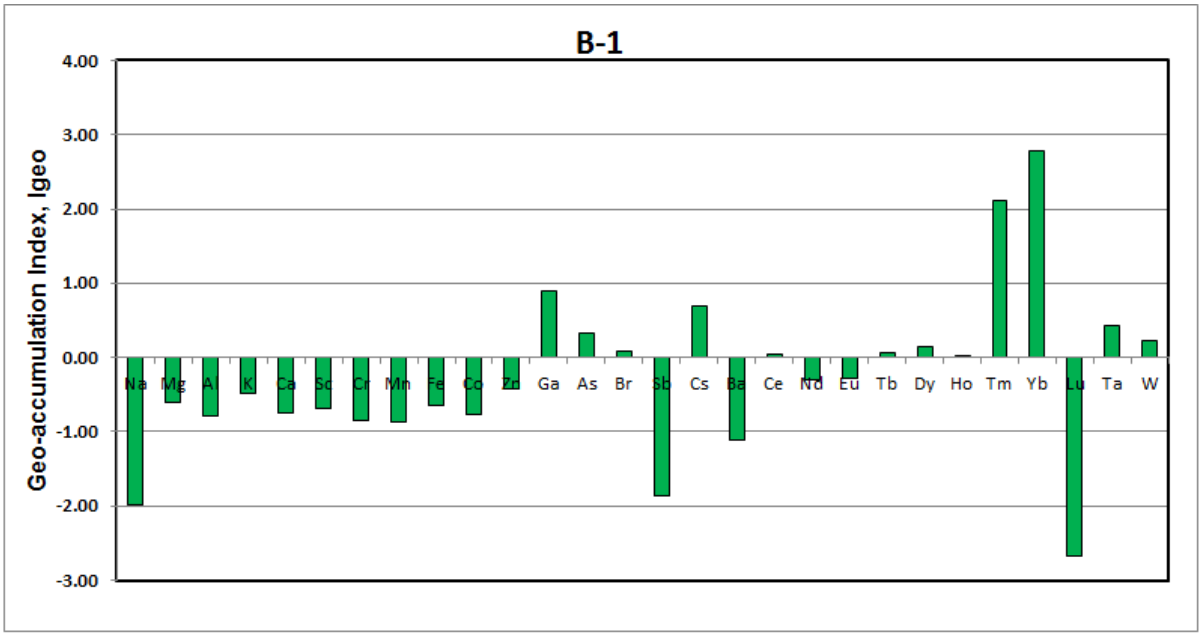
Table 4.3 (a) indicates that from the sample location B-1, B-2, B-3, B-4, B-5 and B-6 the areas which are moderate to heavily contaminate for Yttrium (Yb) and Thulium (Th). And the sample ID B-7 shows that the area which is moderate to heavily contaminated. From the Igeo value (equation no.1) it shows that rests of the samples are practically uncontaminated.

Table 4.3: Geo-accumulation index of elements in Bhairab river sediment samples

Sl. No		B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9	B-10
1	Na	-1.98	-1.93	-1.90	-1.90	-2.35	-2.01	-2.00	-2.11	-2.20	-1.99
2	Mg	-0.61	-0.75	-0.79	-0.63	-0.58	-0.87	-0.65	-1.00	-1.45	-0.76
3	Al	-0.80	-0.88	-0.92	-0.85	-0.74	-0.92	-0.85	-1.08	-1.70	-0.90
4	K	-0.49	-0.45	-0.64	-0.43	-0.73	-0.54	-0.57	-0.90	-1.05	-0.72
5	Ca	-0.75	-0.57	-0.89	-0.45	-0.64	-0.53	-0.58	-0.39	-1.37	-0.64
6	Sc	-0.69	-0.78	-0.85	-0.71	-0.91	-0.90	-0.86	-1.08	-1.32	-0.91
7	Cr	-0.85	-0.93	-0.90	-0.98	-1.16	-1.11	-1.05	-1.14	-1.56	-1.09
8	Mn	-0.87	-1.00	-1.00	-1.02	-0.85	-0.98	-1.03	-1.09	-1.85	-1.04
9	Fe	-0.65	-0.72	-0.85	-0.74	-0.91	-0.82	-0.86	-1.10	-1.28	-0.96
10	Co	-0.77	-0.83	-1.00	-0.87	-1.05	-1.06	-0.96	-1.24	-1.52	-1.12
11	Zn	-0.42	-0.53	0.08	-0.38	-0.80	-1.03	-0.91	-0.07	-0.81	-0.80
12	Ga	0.90	0.89	1.72	1.84	1.76	2.08	2.16	1.80	1.64	2.14
13	As	0.32	0.15	0.16	0.07	-0.30	0.09	0.04	0.18	-0.46	-0.13
14	Br	0.08	1.01	0.84	0.74	0.13	0.22	0.68	0.19	0.20	0.56
15	Sb	-1.87	-2.00	-1.99	-1.90	-2.05	-1.59	-2.20	-1.40	-2.54	-1.90
16	Cs	0.70	0.55	0.49	0.54	0.44	0.30	0.51	0.01	0.07	0.26
17	Ba	-1.12	-1.08	-0.88	-0.91	-0.82	-1.41	-0.91	-1.17	-1.57	-0.68
18	Ce	0.05	-0.14	-0.14	0.02	-0.37	-0.08	-0.11	-0.07	-0.46	0.10
19	Nd	-0.30	-0.48	-0.01	-0.17	-0.30	-0.33	-0.44	-0.23	-0.55	-0.30
20	Eu	-0.28	-0.40	-0.44	-0.27	-0.58	-0.64	-0.37	-0.33	-0.72	-0.26
21	Tb	0.06	-0.38	-0.28	-0.09	-0.89	0.13	-0.19	-0.21	-0.62	-0.12
22	Dy	0.15	-0.11	0.15	0.13	0.16	0.52	0.09	-0.01	-0.61	0.33
23	Ho	0.03	0.19	0.73	0.31	0.04	0.49	-0.19	0.24	-0.28	0.31
24	Tm	2.12	2.08	2.28	1.98	1.97	2.38	2.11	2.07	1.79	2.33
25	Yb	2.78	2.49	2.96	2.62	2.34	3.34	2.52	2.56	2.27	2.68
26	Lu	-2.67	-2.80	-2.44	-2.83	-3.12	-2.23	-2.94	-3.07	-3.13	-2.87
27	Ta	0.43	0.47	0.30	0.18	0.10	0.17	-0.10	0.08	-0.42	-0.10
28	W	0.22	0.22	0.42	0.30	0.00	-0.32	0.37	-0.67	-0.18	0.22

Table 4.4: Highest and lowest value of Igeo

Elements	Highest value		Lowest value	
	Igeo	Location	Igeo	Location
Na	-1.90	B-4	-2.35	B-5
Mg	-0.58	B-5	-1.45	B-9
Al	-0.74	B-5	-1.70	B-9
K	-0.43	B-4	-1.05	B-9
Ca	-0.39	B-9	-1.37	B-9
Sc	-0.69	B-1	-1.32	B-9
Cr	-0.85	B-1	-1.56	B-9
Mn	-0.85	B-5	-1.85	B-9
Fe	-0.65	B-1	-1.28	B-9
Co	-0.77	B-1	-1.52	B-9
Zn	0.08	B-3	-1.03	B-6
Ga	2.16	B-7	0.89	B-2
As	-0.46	B-9	0.32	B-1
Br	1.01	B-1	1.01	B-2
Sb	-1.40	B-8	-2.54	B-9
Cs	0.01	B-7	0.70	B-1
Ba	-0.68	B-10	-1.57	B-9
Ce	-0.37	B-5	0.10	B-10
Nd	-0.01	B-3	-0.55	B-9
Eu	-0.26	B-10	-0.72	B-9
Tb	0.13	B-6	-0.89	B-5
Dy	0.52	B-6	-0.61	B-9
Ho	0.73	B-3	-0.28	B-9
Tm	2.38	B-6	1.79	B-9
Yb	3.34	B-6	2.27	B-9
Lu	-2.23	B-6	-3.13	B-9
Ta	0.47	B-2	-0.42	B-9
W	0.42	B-3	-0.67	B-8



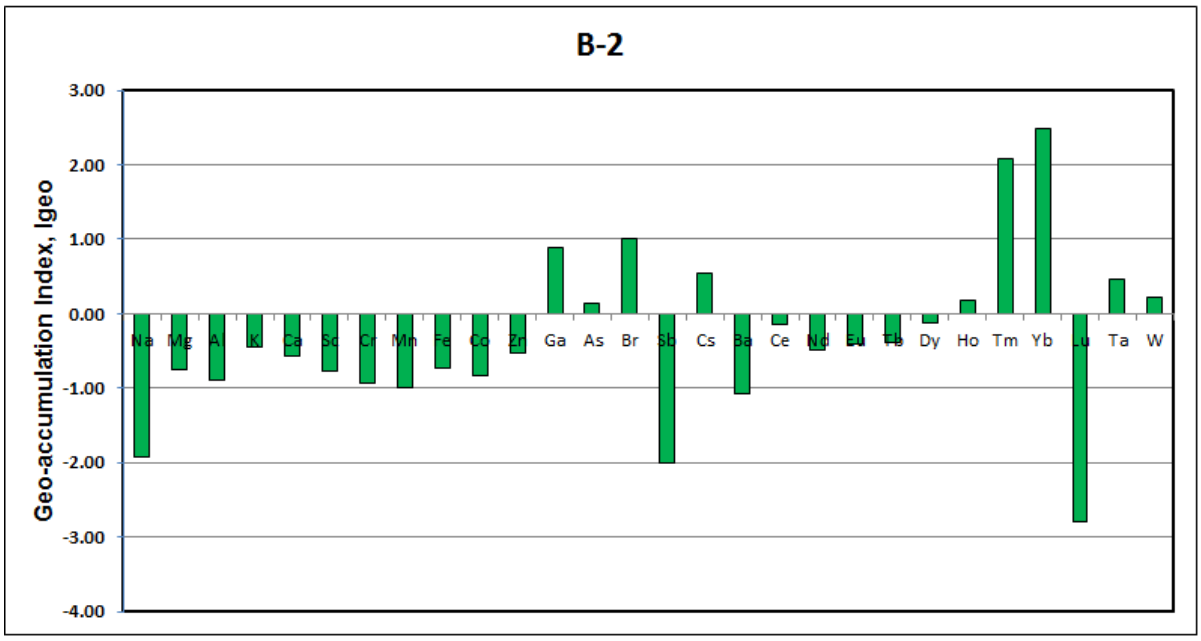
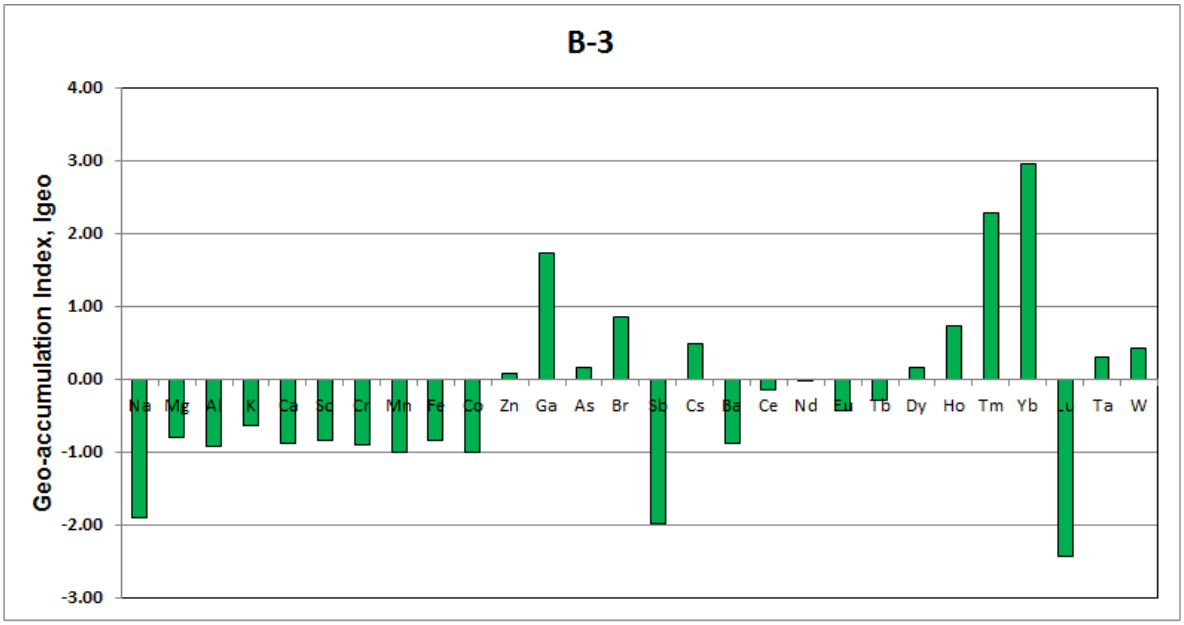


Figure 4.1: Geo-accumulation index (I_{geo}) for Sample no.1 (B-1) and Sample no.2 (B-2)



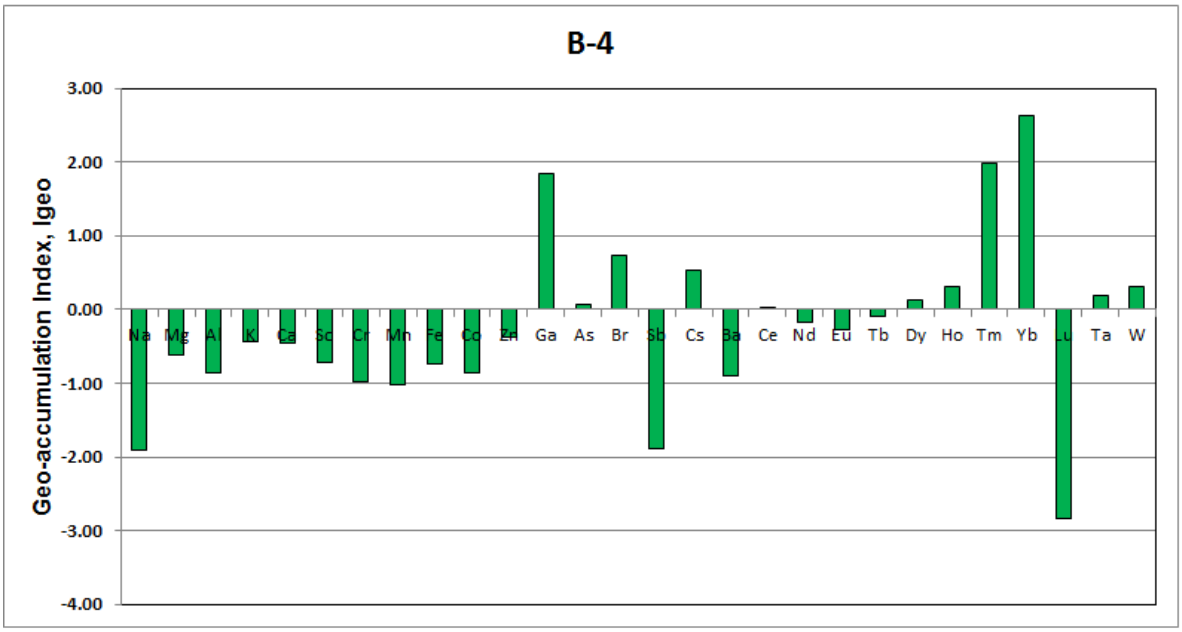
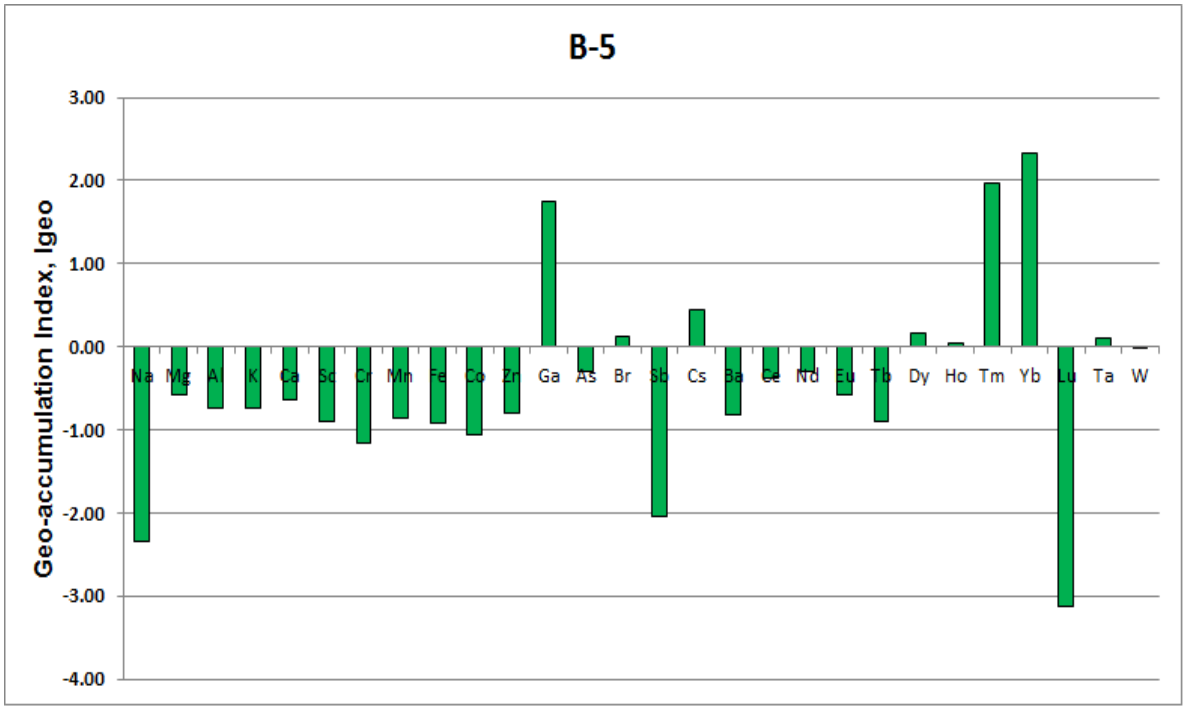


Figure 4.2: Geo-accumulation index (I_{geo}) for Sample no.3 (B-3) and Sample no. 4 (B-4)



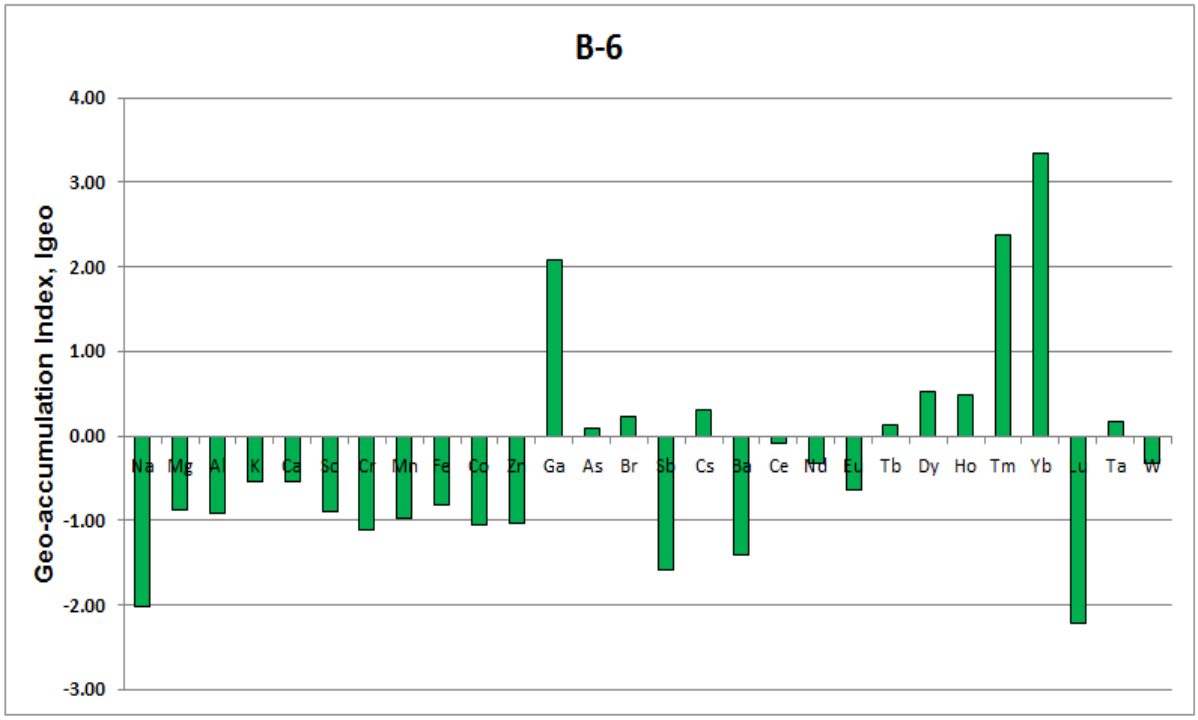
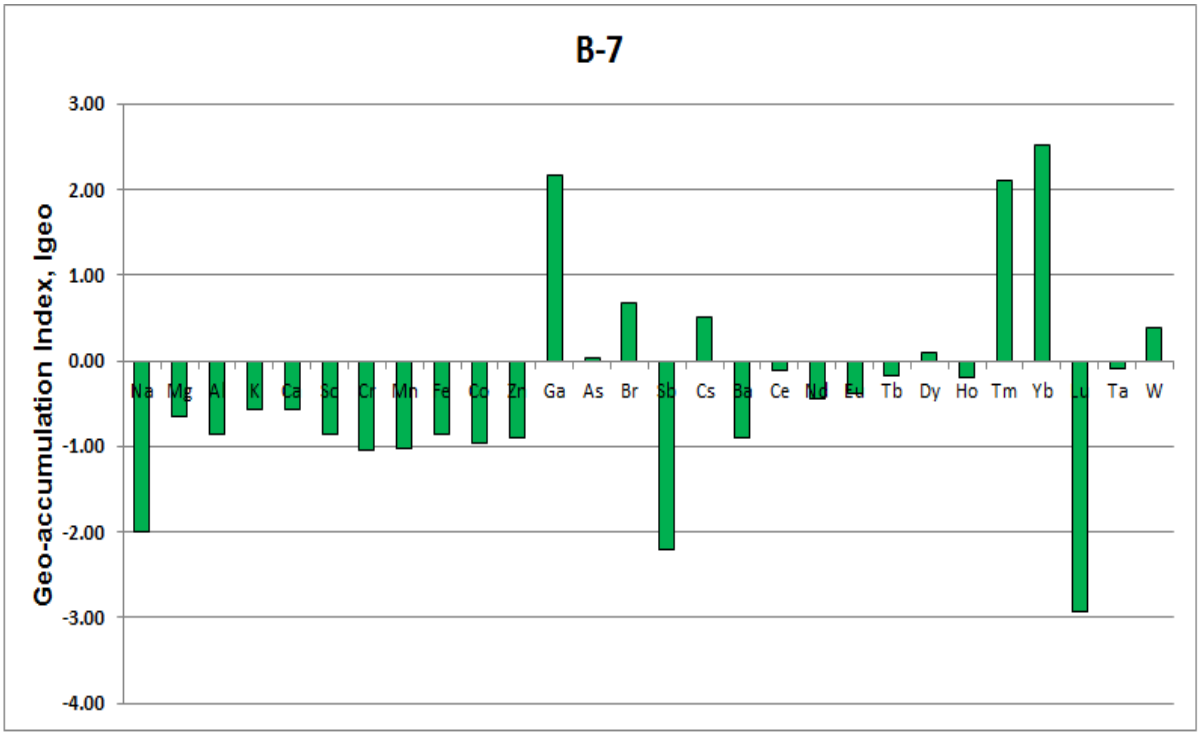


Figure 4.3: Geo-accumulation index (I_{geo}) for Sample no.5 (B-5) and Sample no.6 (B-6)



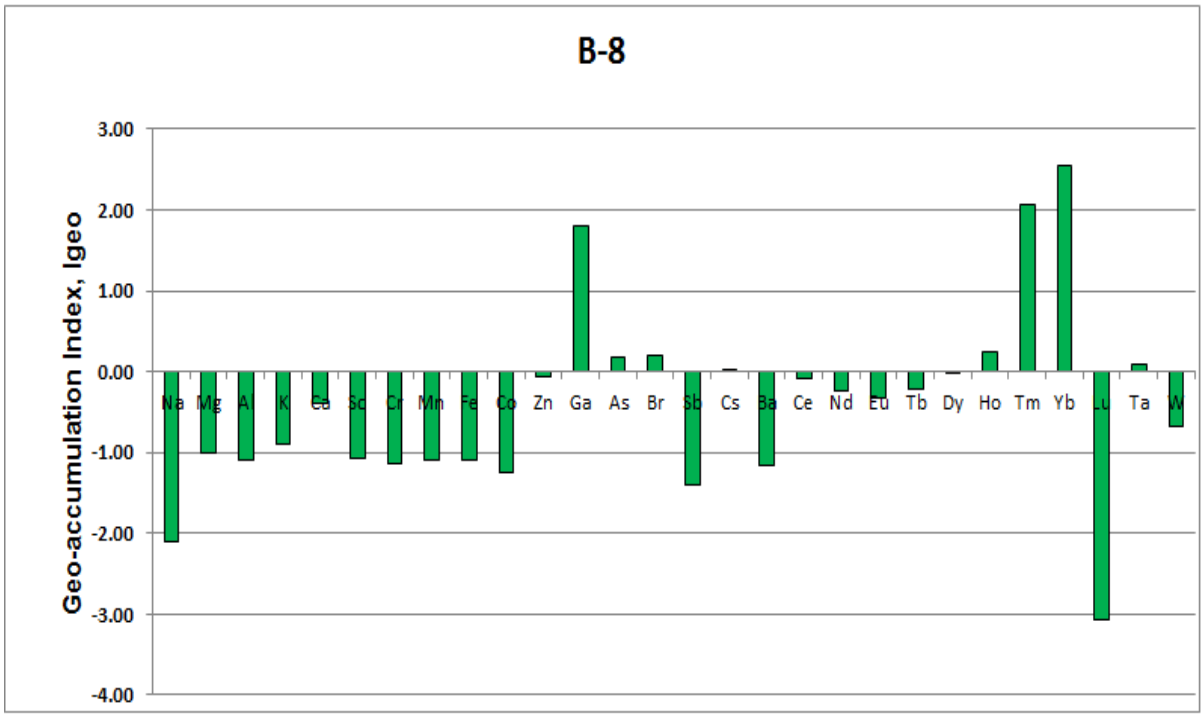
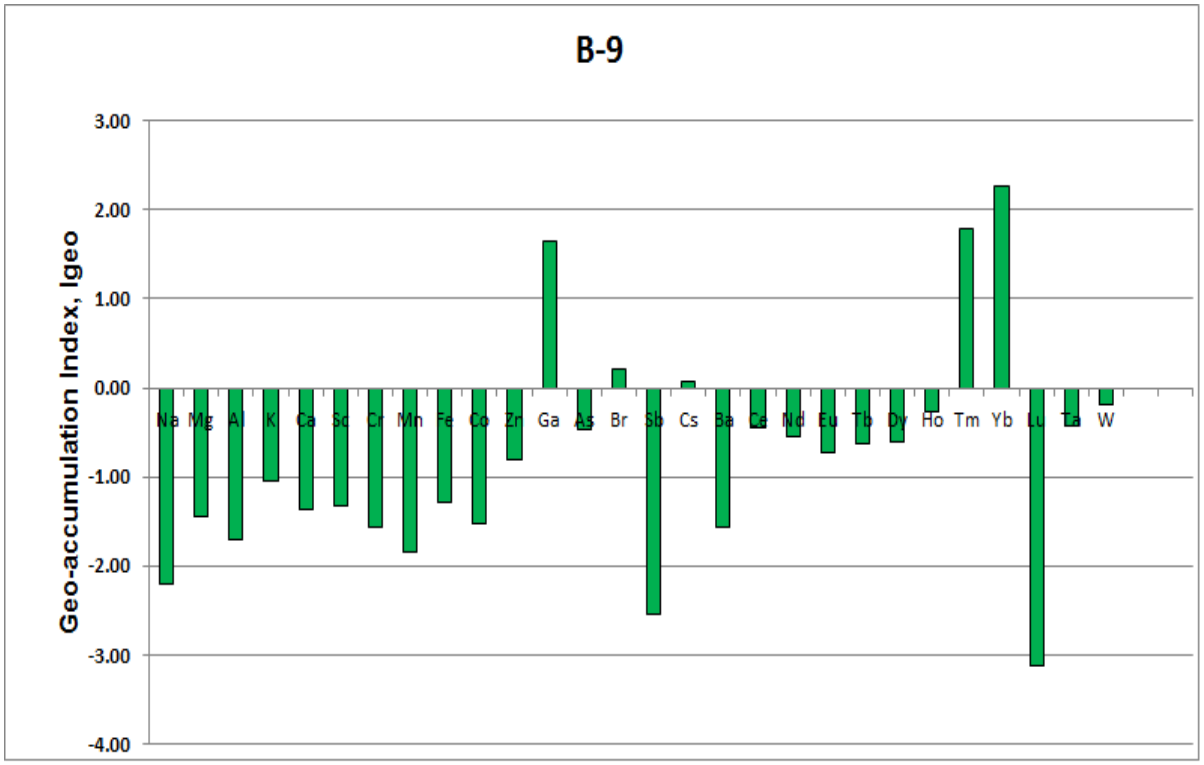


Figure 4.4: Geo-accumulation index (I_{geo}) for Sample no.7 (B-7) and Sample no.8 (B-8)



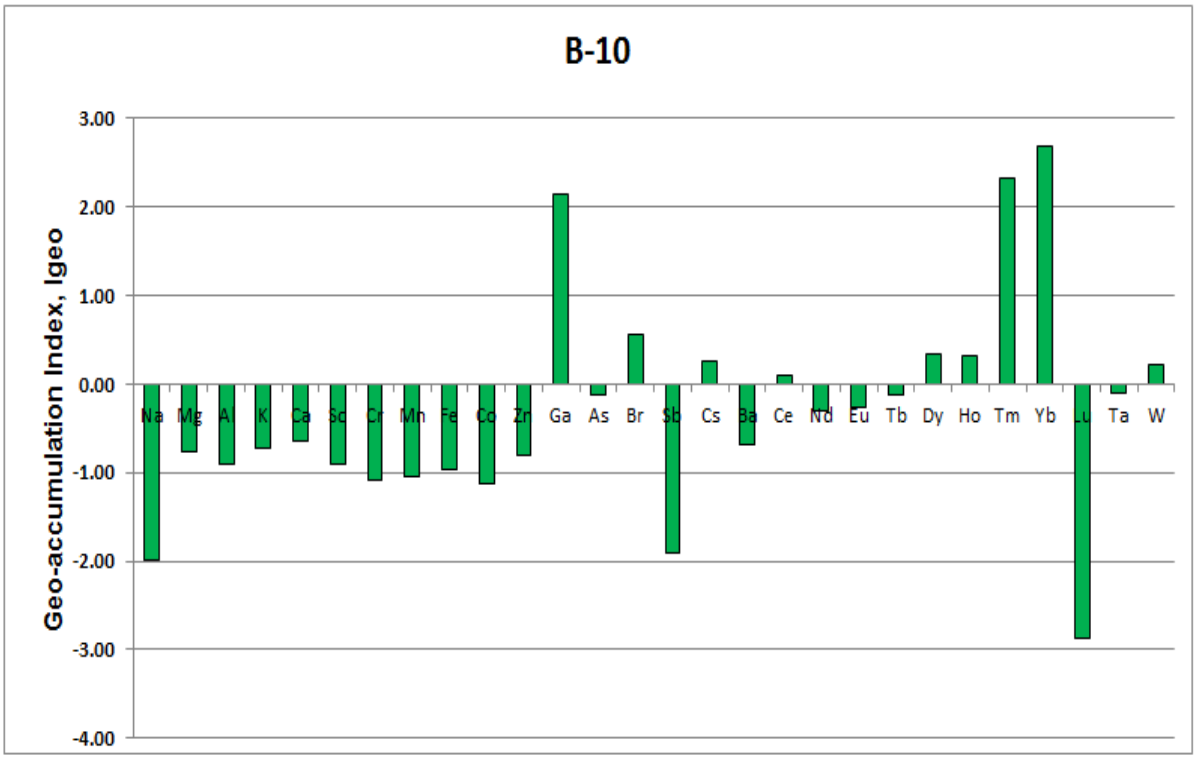


Figure 4.5: Geo-accumulation index (I_{geo}) for Sample no.-9 (B-9) and Sampleno.10(B-10)

4.3.3 Enrichment Factor (EF)

A common approach to estimate the anthropogenic impact on sediments is to calculate a normalized enrichment factor (EF) for metal concentrations above uncontaminated background levels (Hornung 1989; Dickinson 1996; Abrahim and Parker, 2008; Bhuiyan 2010). Thus EF can be calculated by using the following equation:

$$\text{Enrichment Factor (EF)} = \frac{\left(\frac{Metal}{Fe}\right)_{Sample}}{\left(\frac{Metal}{Fe}\right)_{Background}} \text{----------(4.2)}$$

In this study, iron (Fe) was used as the reference element for geochemical normalization because of the following reasons:

- Fe is associated with fine solid surfaces.
- Its geochemistry is similar to that of many trace metals.
- Its natural concentration tends to be uniform (Bhuiyan 2010).

The Enrichment Factor (EF) consists of six grades or classes (Brich and Olmos, 2008)

Class 0 (Crusted origin)	: EF=1
Class 1 (A possible mobilization or depletion of metals)	: EF<1
Class 2 (Anthropogenic origin)	: EF>1
Class 3 (Evidence of minor)	: EF=1.5-3
Class 4 (Evidence of moderate)	: EF=3-5
Class 5 (Evidence of severe)	: EF=5-10
Class 6 (Evidence of very severe)	: EF>10

Enrichment Factor for the Bhairab River sediments are given below in the Table 4.4.
Table 4.4 shows that Na, Al, Ca, Sc, Cr, Mn, Co, Sb, Ba and Lu elements are originated from anthropogenic origin. Fe is from crusted origin. The other elements are the evidence of minor, moderate, severe and very severe modification, respectively. Using the values of table 4.4 we have got the graphical representation which is shown in the figure 4.7

Table 4.5: Enrichment Factor (EF) of elements in the Bhairab River sediments.

	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9	B-10
Na	0.398	0.434	0.482	0.447	0.371	0.439	0.453	0.497	0.528	0.489
Mg	1.026	0.978	1.037	1.085	1.259	0.966	1.155	1.073	0.890	1.147
Al	0.901	0.894	0.948	0.927	1.131	0.933	1.005	1.010	0.746	1.042
K	1.111	1.211	1.154	1.239	1.137	1.217	1.215	1.149	1.177	1.181
Ca	0.928	1.110	0.970	1.221	1.213	1.223	1.212	1.633	0.942	1.248
Sc	0.973	0.962	0.997	1.022	1.005	0.950	0.998	1.013	0.970	1.037
Cr	0.867	0.868	0.966	0.851	0.844	0.817	0.877	0.974	0.823	0.912
Mn	0.856	0.827	0.896	0.822	1.046	0.896	0.886	1.009	0.672	0.944
Fe	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Co	0.918	0.930	0.898	0.916	0.911	0.849	0.933	0.905	0.846	0.890
Zn	1.172	1.145	1.895	1.289	1.082	0.868	0.965	2.039	1.383	1.113
Ga	2.927	3.050	5.939	5.990	6.365	7.465	8.059	7.474	7.572	8.550
As	1.955	1.827	2.008	1.753	1.535	1.884	1.859	2.426	1.768	1.773
Br	1.654	3.315	3.230	2.796	2.063	2.064	2.899	2.445	2.798	2.861
Sb	0.427	0.413	0.453	0.449	0.457	0.587	0.394	0.810	0.418	0.520
Cs	2.541	2.421	2.518	2.426	2.565	2.184	2.583	2.158	2.546	2.325
Ba	0.722	0.782	0.974	0.891	1.072	0.667	0.964	0.955	0.818	1.211
Ce	1.618	1.495	1.629	1.696	1.454	1.674	1.677	2.034	1.771	2.078
Nd	1.273	1.179	1.786	1.492	1.528	1.409	1.330	1.824	1.656	1.579
Eu	1.286	1.253	1.327	1.391	1.266	1.133	1.397	1.709	1.471	1.625
Tb	1.626	1.268	1.478	1.570	1.015	1.942	1.591	1.846	1.577	1.785
Dy	1.737	1.524	1.991	1.834	2.103	2.544	1.920	2.123	1.591	2.445
Ho	1.595	1.876	2.988	2.075	1.937	2.486	1.589	2.528	2.004	2.415
Tm	6.800	6.961	8.717	6.600	7.409	9.197	7.786	8.984	8.388	9.775
Yb	10.750	9.234	13.996	10.293	9.539	17.964	10.343	12.636	11.699	12.412
Lu	0.245	0.237	0.330	0.235	0.218	0.378	0.236	0.255	0.278	0.265
Ta	2.104	2.278	2.211	1.897	2.024	1.993	1.686	2.271	1.813	1.813
W	1.826	1.923	2.398	2.065	1.885	1.417	2.346	1.342	2.137	2.259

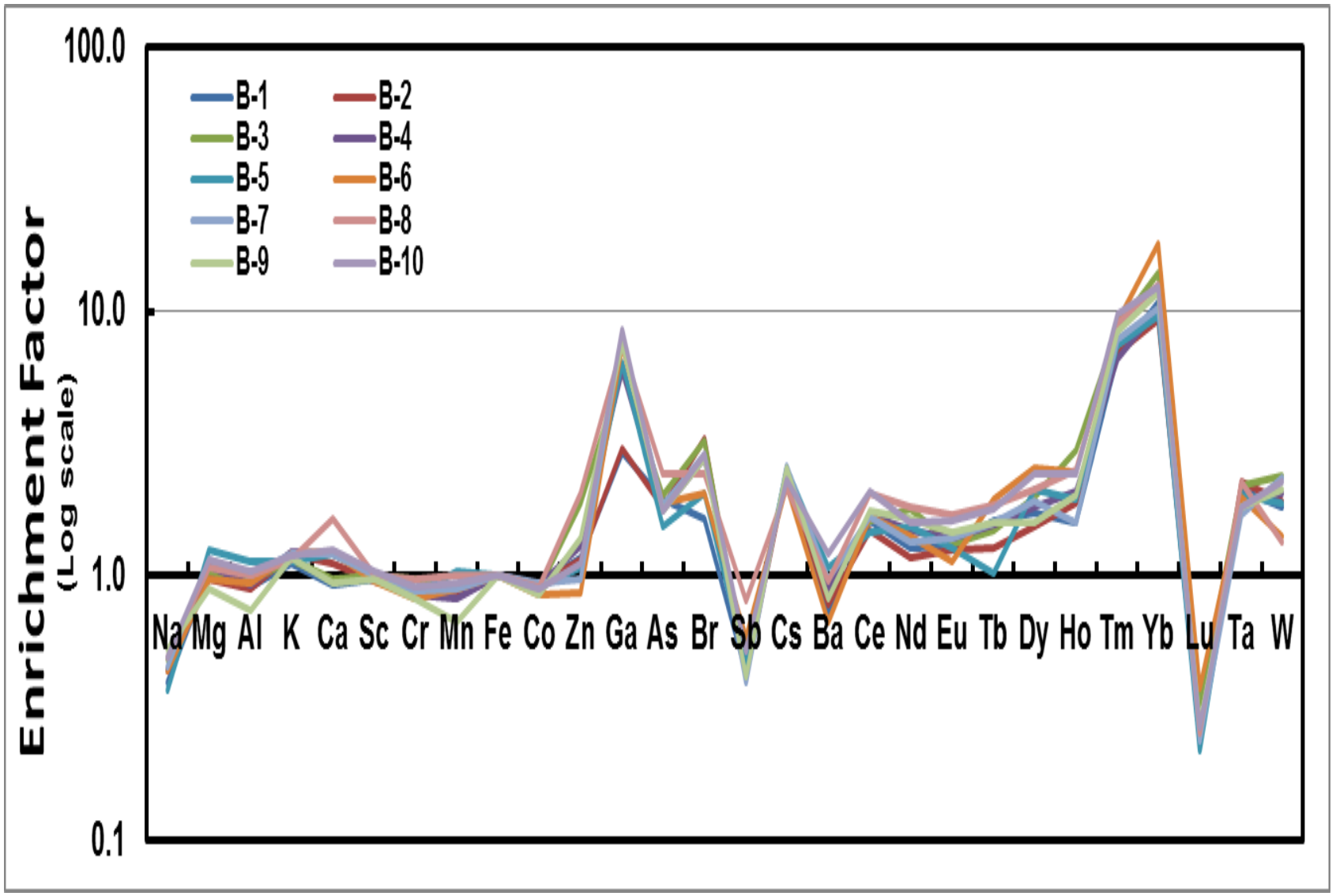


Figure 4.6**:** Enrichment Factor

4.3.4 Pollution Load Index (PLI)

This empirical index provides a simple, comparative means for assessing the level of heavy metal pollution. Pollution load index (PLI) is calculated from the Contamination Factors (CF) of the specific heavy metals for a specific sampling site, which can be defined as follows (Hakanson, 1980):

$$CF = \frac{(Metal\ concentration)_{Sample}}{(Metal\ concentration)_{Background}} = \frac{C\ metal}{C\ background\ Value} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.3)$$

Then, according to Tomlinson (Tomlinson,1980) PLI is represented bythe following equation:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots\ldots\ldots\ldots\ldots\ldots\ldots \times CF_n)^{1/n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.4)$$

Where,

CF= Contamination Factors

n = The total number of contamination factors

C metal= metal concentration in polluted elements

C background value = background value of that metal

Following Tomlinson (1980) we considered five highest CFs for calculating the pollution load index. PLI value 01 (one) indicates the presence of only baseline levels of pollutants while values above 01 (one) would indicate progressive deterioration of the sediments (Mohiuddin, 2011, Rabee, 2011). The PLI value of > 1 is polluted, whereas <1 indicates no pollution (Harikuma, 2009).

Pollution loaded index in the Bhairab River sediments has been given below in the Table 4.5. From the table it has been observed that K, Zn, As, Ga, Br, Cs, Ce, Nd, Eu, Tb, Dy, Tm, Yb, Ta and W are the highly polluted elements, where the other elements are not polluted. Figure 4.7 shows the graphical representation of PLI value and here the average PLI value is 1.182 that indicates that Bhairab River is slightly polluted.

Table 4.6: Pollution load index in the Bhairab river sediments

	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9	B-10	Mean	SD
Na	0.381	0.394	0.402	0.401	0.295	0.372	0.376	0.348	0.326	0.378		
Mg	0.984	0.889	0.865	0.972	1.001	0.819	0.958	0.751	0.550	0.886		
Al	0.864	0.813	0.791	0.831	0.900	0.791	0.833	0.707	0.460	0.805		
K	1.065	1.102	0.962	1.110	0.905	1.032	1.008	0.804	0.727	0.912		
Ca	0.889	1.010	0.809	1.094	0.965	1.037	1.004	1.143	0.582	0.964		
Sc	0.933	0.875	0.831	0.916	0.800	0.805	0.827	0.709	0.599	0.801		
Cr	0.831	0.790	0.806	0.763	0.672	0.693	0.727	0.682	0.508	0.705		
Mn	0.821	0.752	0.748	0.737	0.832	0.760	0.735	0.706	0.415	0.729		
Fe	0.959	0.910	0.834	0.897	0.796	0.848	0.829	0.700	0.617	0.772		
Co	0.880	0.846	0.749	0.821	0.725	0.720	0.773	0.634	0.522	0.688		
Zn	1.124	1.042	1.581	1.156	0.861	0.736	0.800	1.428	0.854	0.860		
Ga	2.806	2.774	4.954	5.371	5.064	6.328	6.681	5.233	4.675	6.604		
As	1.874	1.662	1.675	1.572	1.222	1.597	1.541	1.699	1.092	1.370		
Br	1.586	3.015	2.694	2.507	1.641	1.750	2.403	1.712	1.727	2.210		
Sb	0.410	0.376	0.377	0.403	0.363	0.497	0.327	0.567	0.258	0.401		
Cs	2.436	2.202	2.100	2.175	2.041	1.852	2.141	1.511	1.572	1.796		
Ba	0.692	0.711	0.813	0.799	0.852	0.565	0.799	0.669	0.505	0.936		
Ce	1.551	1.360	1.359	1.521	1.157	1.420	1.390	1.424	1.093	1.605		
Nd	1.220	1.072	1.490	1.337	1.216	1.195	1.103	1.277	1.022	1.220		
Eu	1.233	1.139	1.107	1.247	1.007	0.961	1.158	1.197	0.908	1.255		
Tb	1.560	1.154	1.233	1.407	0.808	1.646	1.319	1.293	0.973	1.379		
Dy	1.665	1.386	1.661	1.644	1.673	2.157	1.592	1.486	0.982	1.888		
Ho	1.530	1.706	2.492	1.861	1.541	2.107	1.318	1.770	1.237	1.865		
Tm	6.520	6.331	7.271	5.917	5.895	7.797	6.454	6.290	5.178	7.550		
Yb	10.308	8.399	11.64	9.229	7.589	15.29	8.574	8.847	7.223	9.587		
Lu	0.235	0.216	0.276	0.211	0.173	0.321	0.196	0.178	0.172	0.205		
Ta	2.017	2.072	1.844	1.700	1.610	1.690	1.398	1.590	1.119	1.400		
W	1.751	1.749	2.001	1.852	1.500	1.201	1.945	0.940	1.320	1.745		
PLI	1.253	1.209	1.299	1.280	1.109	1.241	1.192	1.136	0.876	1.220	1.182	0.122

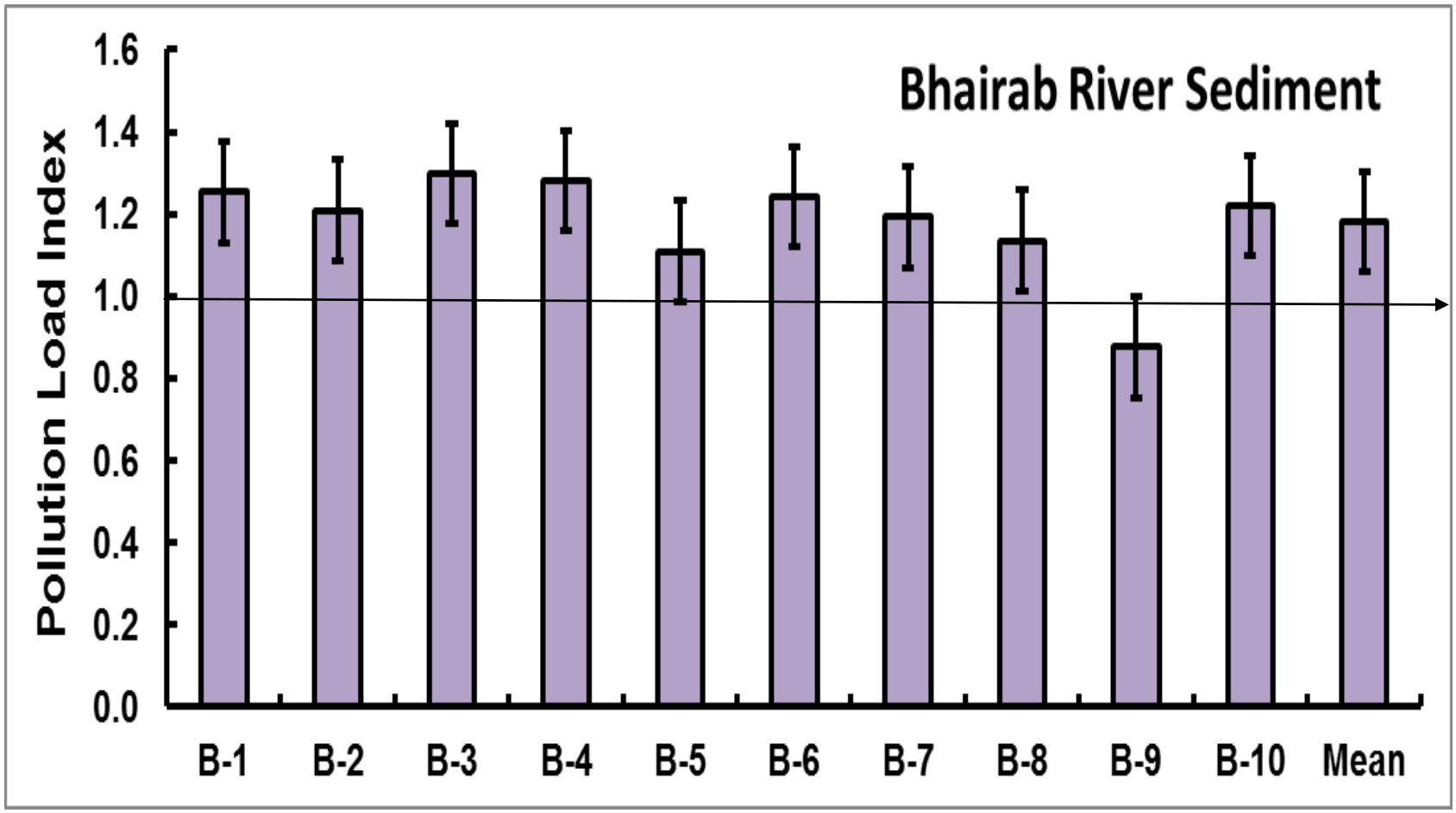


Figure 4.7: Pollution loaded index (PLI) for sediments in the Bhairab River

4.3.5 Inter-element Correlation and the Sediment Responses towards the Contaminants

In order to establish relationships among elements, determine the common source (and/or carrier substances) of metals (Datta and Subramanian, 1998) and to discuss the sediment responses towards the anthropogenic contaminants in the Bhairab River, a correlation (r - value) matrix was calculated for the elements in the sediments (Table 4.6). Some elements show very poor correlations with either Al and/or Fe are due to association of those elements with organic detritus (e.g., Hanson, 1993; Daskalakis and O'Connor, 1995).

Ca, Fe and Co show very poor correlation with major of the elements, which indicate that the presence of carbonate and organic fraction and Fe-Mn oxy-hydroxides have an insignificant influence on accumulation of heavy metals (Datta and Subramanian, 1998).

However, K (r = 0.68), Sc (r = 0.89), Mn (0.97), Ca (0.60), Mg (0.95), Fe (0.84), Cr (r = 0.83), Co (r = 0.86), and Ba (r = 0.76) show good correlation with Al suggesting their accumulation in association with clays.

Regarding the environmental contamination, urban sludge and industrial waste (Tamim, 2016) are considered to be the major source of Cr and Zn. The average EF values for Cr and Zn are 0.847 and 1.30, respectively which indicate that Cr contamination is not occurred but our sampling site is very minutely modified by the Zn contamination.

Zinc has very little positive correlation with other elements. Sodium shows almost correlation or anti-correlation with most of the elements Cr (0.78), Sc (0.61), Mn (0.63), Co (0.69), Ga (0.68), Cs (0.66), Sb (0.91), Tm (-0.86) and Lu (0.99) in correlation table, where Tm shows negative correlation. Cs shows significant positive correlation with Lu (r = 0.68), Ce (r = 0.61), Ta 90.68) and tm (r = 0.69).

Table 4.6: Inter-element correlation matrix for the sediments collected from the Bhairab River

	Na	Mg	Al	K	Ca	Sc	Cr	Mn	Fe	Co	Zn	Ga	As	Br	Sb	Cs	Ba	Ce	Nd	Eu	Tb	Dy	Ho	Tm	Yb	Lu	Ta	W
Na	1.00																											
Mg	0.34	1.00																										
Al	0.53	**0.95**	1.00																									
K	0.21	0.73	0.68	1.00																								
Ca	0.14	0.55	0.60	0.48	1.00																							
Sc	0.61	**0.87**	**0.89**	**0.84**	0.45	1.00																						
Cr	0.78	0.72	**0.83**	0.64	0.39	**0.92**	1.00																					
Mn	0.63	**0.86**	**0.97**	0.58	0.58	**0.86**	**0.87**	1.00																				
Fe	0.58	**0.81**	**0.84**	0.87	0.40	**0.98**	**0.90**	**0.83**	1.00																			
Co	0.69	**0.81**	**0.86**	0.79	0.40	**0.98**	**0.94**	**0.86**	**0.98**	1.00																		
Zn	0.01	-0.01	0.00	-0.02	0.08	0.09	**0.28**	0.08	0.05	0.07	1.00																	
Ga	-0.68	-0.23	-0.34	-0.23	0.10	-0.52	-0.65	-0.45	-0.57	-0.65	-0.20	1.00																
As	-0.48	0.15	0.05	0.45	0.34	0.15	0.08	0.02	0.20	0.08	0.46	0.19	1.00															
Br	-0.47	0.02	-0.13	0.36	0.06	-0.02	-0.12	-0.27	**-0.02**	-0.09	0.24	0.34	0.49	1.00														
Sb	**0.91**	0.31	0.55	0.13	0.39	0.53	0.72	0.70	0.50	0.60	0.10	-0.59	-0.34	-0.60	1.00													
Cs	-0.66	0.31	0.06	0.50	0.01	0.14	-0.12	-0.10	0.18	0.05	0.08	0.28	0.70	0.63	-0.73	1.00												
Ba	0.56	0.73	0.76	0.28	0.34	0.63	0.66	0.71	0.49	0.59	0.08	-0.20	-0.30	-0.05	0.47	-0.19	1.00											
Ce	-0.50	0.18	0.04	0.38	0.38	0.11	-0.05	-0.05	0.08	-0.04	0.17	0.48	0.78	0.47	-0.39	0.61	-0.06	1.00										
Nd	-0.39	0.15	0.07	0.12	0.16	0.03	0.01	0.04	-0.03	-0.12	0.69	0.39	0.56	0.38	-0.27	0.43	0.08	0.53	1.00									
Eu	-0.20	0.41	0.27	0.38	0.48	0.34	0.25	0.18	0.24	0.23	0.38	0.16	0.62	0.43	-0.15	0.46	0.33	**0.82**	0.44	1.00								
Tb	-0.22	0.09	0.06	0.46	0.34	0.21	0.09	0.03	0.24	0.09	0.05	0.33	0.72	0.18	-0.10	0.39	-0.26	**0.81**	0.34	0.49	1.00							
Dy	-0.49	0.28	0.23	0.35	0.40	0.08	-0.11	0.15	0.08	-0.08	-0.10	0.64	0.55	0.26	-0.31	0.52	-0.03	0.72	0.56	0.33	0.67	1.00						
Ho	-0.45	-0.05	-0.06	0.18	0.14	-0.07	-0.09	-0.08	-0.07	-0.21	0.48	0.46	0.59	0.55	-0.33	0.42	-0.13	0.56	**0.85**	0.26	0.46	0.69	1.00					
Tm	**-0.86**	-0.17	-0.30	0.05	0.04	-0.36	-0.50	-0.39	-0.33	-0.49	0.06	0.73	0.67	0.57	-0.75	0.69	-0.39	0.75	0.56	0.35	0.55	0.78	0.74	1.00				
Yb	-0.70	-0.18	-0.25	0.17	0.05	-0.25	-0.38	-0.29	-0.18	-0.37	0.06	0.63	0.68	0.41	-0.56	0.59	-0.51	0.67	0.57	0.16	0.70	**0.83**	0.79	**0.91**	1.00			
Lu	**0.99**	0.31	0.53	0.18	0.11	0.58	0.74	0.64	0.57	0.66	-0.03	-0.66	-0.49	-0.54	**0.92**	-0.68	0.50	-0.54	-0.38	-0.32	-0.21	-0.42	-0.41	**-0.83**	-0.63	1.00		
Ta	-0.50	0.26	0.16	0.54	0.24	0.24	0.10	0.11	0.30	0.17	0.38	0.00	**0.86**	0.56	-0.41	**0.81**	-0.23	0.59	0.52	0.45	0.43	0.51	0.61	0.62	0.61	-0.49	1.00	
W				0.46	-0.15	0.23	0.04	-0.08	0.20	0.13	0.11	0.27	0.41	0.75	-0.63	**0.80**	0.19	0.49	0.41	0.49	0.20	0.31	0.36	0.48	0.32	-0.45	0.48	1.00

CHAPTER 5

Conclusion

In present study, the essential major, minor and trace element have been assessed in sediment samples collected from different places of the Bhairab River. The investigations of the elements have been performed by means of the Instrumental Neutron Activation Analysis (INAA).

1) Twenty eight elements have been found e. g. Na, Mg, Al, K, Ca, Sc, Cr, Mn, Fe, Co, Zn, Ga, As, Br, Sb, Cs, Ba, Ce, Nd, Eu, Tb, Dy, Ho, Tm, Yb, Lu, Ta, and W in different sediment samples from instrumental neutron activation analysis method.

2) The used analytical method was allowed to measure a large number of elements both qualitatively and quantitatively. Quality control of each of the analytical approach was performed using different types of Certified/Reference materials e.g., IAEA-Soil-7, NIST-1633b (Coal Fly Ash) etc. The Quality Control (QC) data quoted in the results and discussion ensure the quality of each of the experimental conditions.

3) In most of the cases the deviation of measured elemental concentration is below 20% compared to the certified values. In this study, uncertainty associated with the concentration values are due to counting statistics. Since counting statistics mainly control the total uncertainty in INAA, it was reported with concentration values. However, there was commonly 3% more uncertainty, estimated in our analysis, was also associated with the reported values which included sample and standard preparation, irradiation, positioning in the detector, pulse-pileup losses and peak integration.

4) The potential site for Bhairab River is chemically characterized by evaluating several environmental indices (e.g., pollution load index, enrichment factor, geo-accumulation index etc.). Along with this, elemental background of Bhairab River's

sediments has been compared with those of NIST-1633b (coal fly ash) to assess the effect of coal fly ash which will be the major byproduct of coal based power plant.

5) Na, Al, Ca, Sc, Cr, Mn, Co, Sb, Ba and Lu elements are originated from anthropogenic origin. Fe from crusted origin. The other elements are the evidence of minor, moderate, severe and very severe modification, respectively.

6) K, Zn, As, Ga, Br, Cs, Ce, Nd, Eu, Tb, Dy, Tm, Yb, Ta and W are the highly polluted elements. Where the other elements are not polluted.

7) After comparing the elemental abundances of Bhairab River sediments with those of coal-fly-ash (NIST-1633b), it reveals that ytterbium will be the potential candidate for the future elemental contaminants.

8) From the overall observations, it can be said that the study area is not heavily polluted.

9) Seasonal variations of the trace elements in sediments of the river will be assessed in future. The ecological risk assessment of the toxic elements on biota of the river can also be studied in future.

10) The results of this study will be helpful for future monitoring of the elemental pollution of the Bhairab River as well as possible threat to the biota of the Bhairab River.

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APPENDIX

Nuclear data for the produced radionuclide in the samples

Radio nuclide	Nuclear reaction	Target abundance %	Cross-section (b)		Half-life	γ-ray Energy (keV)	Intensity (%)
			Thermal	Resonance integral			
^{24}Na	^{23}Na(n, γ) ^{24}Na	100	0.5314	0.3117	15 h	1368.8, 2754	99.86
^{46}Sc	^{45}Sc(n, γ) ^{46}Sc	100	27.14	11.84	83.79 d	889, 1120.5	99.98
^{47}Ca	^{46}Ca(n, γ) ^{47}Ca	0.004	0.7402	0.3649	4.536 d	1297	67.0
^{51}Cr	^{50}Cr(n, γ) ^{51}Cr	4.345	15.38	7.228	27.7 d	320	9.91
^{59}Fe	^{58}Fe(n, γ) ^{59}Fe	0,282	1.300	1.358	44.49 d	1099, 1291.6	56.5
^{60}Co	^{59}Co(n, γ) ^{60}Co	100	37.21	75.85	5.27 y	1173, 1332.5	99.85
^{65}Zn	^{64}Zn(n, γ) ^{65}Zn	48.63	0.7875	1.423	243.93 d	1115.5	50.04
^{72}Ga	^{71}Ga(n, γ) ^{72}Ga	39.892	3.710	32.18	14.1 h	629.9, 834	95.45
^{76}As	^{75}As(n, γ) ^{76}As	100	4.153	63.74	26.24 h	559.1	45
^{86}Rb	^{85}Rb(n, γ) ^{86}Rb	72.17	0.4802	8.752	18.64 d	1076.7	8.64
^{124}Sb	^{123}Sb(n, γ) ^{124}Sb	42.79	4.188	122.4	2.75 d	564.2	57.57
^{131}Ba	^{130}Ba(n, γ) ^{131}Ba	0.106	8.701	176.3	11.50 d	373.2, 496	48.00
^{134}Cs	^{133}Cs(n, γ) ^{134}Cs	100	28.90	446.2	2.065 y	604.7, 795.8	85.46

(Continue)

Radio nuclide	Nuclear reaction	Target abundance %	Cross-section (b)		Half-life	γ-ray Energy (keV)	Intensity (%)
			Thermal	Resonance integral			
^{140}La	$^{139}La(n, \gamma)\ ^{140}La$	99.91	8.940	11.60	1.68 d	328.8, 487, 815.8,1596	45.5, 95.4
^{141}Ce	$^{140}Ce(n, \gamma)\ ^{141}Ce$	88.45	0.5704	0.3446	32.508 d	145.5	48.29
^{152}Eu	$^{151}Eu(n, \gamma)^{152}Eu$	47.81	9169	3143	13.33 y	121.8, 841.6, 963.5, 1408	39.8, 29.9
^{153}Sm	$^{152}Sm(n, \gamma)^{153}Sm$	26.75	205.9	2978	1.94 d	103.2	29.25
^{160}Tb	$^{159}Tb(n, \gamma)\ ^{160}Tb$	100	23.13	409.1	72.3 d	298.6, 879.4, 1177.9	26.13
^{175}Yb	$^{174}Yb(n, \gamma)\ ^{175}Yb$	31.83	63.21	25.48	4.19 d	282.5, 396	13.15
^{177}Lu	$^{176}Lu(n, \gamma)\ Lu^{177}$	2.59	×	×	6.71 d	208	10.36
^{181}Hf	$^{180}Hf(n, \gamma)\ ^{181}Hf$	35.08	12.92	29.34	42.39 d	132.9, 482	80.5
^{182}Ta	$^{181}Ta(n, \gamma)\ ^{182}Ta$	99.988	20.68	660	114.74 d	1189, 1221.4	27.23
^{233}Pa	$^{232}Th(n, \gamma, \beta^-)\ ^{239}Np$	99.27	2.683	275.6	2.356 d	106, 228	26.3, 11.1
^{238}U	$^{237}Np(\ n, \gamma, \beta^-)\ P$	99.274	16.83	994.5	4.468 $\times 10^9$ y	106.1, 228.2, 277	×