STUDY ON MONGLA AND RUPSHA RIVER SEDIMENTS FOR POTENTIAL HEAVY ELEMENTAL CONTAMINATION BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

M. Sc. Thesis

MD. NOMAN HOSSAIN
ROLL NO: 1655553
SESSION: JULY-2016

DEPARTMENT OF PHYSICS
KHULNA UNIVERSITY OF ENGINEERING & TECHNOLOGY
KHULNA-9203, BANGLADESH
APRIL - 2018

STUDY ON MONGLA AND RUPSHA RIVER SEDIMENTS FOR POTENTIAL HEAVY ELEMENTAL CONTAMINATION BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

M. Sc. Thesis

MD. NOMAN HOSSAIN
ROLL NO: 1655553
SESSION: JULY-2016

A THESIS SUBMITTED TO THE DEPARTMENT OF PHYSICS,
KHULNA UNIVERSITY OF ENGINEERING & TECHNOLOGY,
IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE
DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF PHYSICS
KHULNA UNIVERSITY OF ENGINEERING & TECHNOLOGY
KHULNA-9203, BANGLADESH
APRIL - 2018

Declaration

This is to certify that the thesis work entitled **"Study on Mongla and Rupsha River Sediments for Potential Heavy Elemental Contamination by Instrumental Neutron Activation Analysis"** has been carried out by Md. Noman 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.

1. Signature of Supervisor	Signature of Candidate
....	.....…………………....
(Professor Dr. Jolly Sultana)	Md. Noman Hossain

2. Signature of Co-Supervisor

....

(Dr. Rahat Khan)

Approval

This is to certify that the thesis work submitted by Md. Noman Hossain entitled “Study on Mongla and Rupsha River Sediments for Potential Heavy Elemental Contamination by Instrumental Neutron Activation Analysis” 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.

BOARD OF EXAMINERS

Sl. No.	**Name, Designation & Address**	
1.	Prof. Dr. Jolly Sultana Department of Physics Khulna University of Engineering & Technology	……………… Chairman (Supervisor)
2.	Dr. Rahat Khan Senior Scientific Officer, Room#148 Institute of Nuclear Science & Technology (INST) Bangladesh Atomic Energy Commission, Ashulia, Ganakbari, DEPZ, Savar, Dhaka-1349	……………….. Co- Supervisor
3.	Head Department of Physics Khulna University of Engineering & Technology	………………. Member
4.	Prof. Dr. MD. Abdullah Elias Akhter Department of Physics Khulna University of Engineering & Technology	…………….... Member
5.	Dr. Debasish Paul Chief Scientific Officer and Head Health Physics & Radioactive Waste Management Unit, Inst, AERE, Bangladesh Atomic Energy Commission (BAEC), Ganakbari, Savar, Dhaka.	……………… Member

DEDICATED

TO

MY BELOVED PARENTS

ACKNOWLEDGEMENTS

At first I express my entire admiration, devotion, greatest and deepest attitude to the almighty, the supreme of the universe, to whom all praise go for enabling me to complete the thesis work.

I would like to express my gratitude, appreciation, deepest sense and indebtedness to my honorable teacher and respective supervisor **Prof. Dr. Jolly Sultana**, Department of Physics, KUET, Khulna and co-supervisor **Dr. Rahat Khan**, SSO, Reactor & Neutron Physics Division (RNPD), Institute of Nuclear Science & Technology (INST), Atomic Energy Research Establishment (AERE), Savar, Dhaka for their enthusiastic guidance and instruction, constructive suggestion and consultant encouragement through this research work.

I am grateful to **Prof. Dr. Sibendra Shekhar Sikdar**, Head, Department of Physics, KUET, Khulna to permit me to carry on this research work. I am extremely grateful to **Dr. Imtiaz Kamal**, Director, INST and **Mr. Tapash Kumar Datta**, PSO & Head, RNDP, INST for kindly allowing me to use all the laboratory facilities that I required for research work.

I would like to convey my gratitude to all of my teachers, Department of Physics, KUET, Khulna. Without their continuous help and direction it is impossible to complete my thesis work. I am also grateful to **Dr. Kamrun Naher** (PSO), INST, AERE, Savar, Dhaka. I would like to express my gratitude to **Dr. Md. Amirul Islam** (SSO), **Mr. Sopan Das** (SO) and **Ms. Umma Tamim** (SO) for their constant support and help in conducting the experiment. I would like to acknowledge **Md. Ahad Ali**, **Md. Ali Azam** and **Ibrahim Khalil** for their kind help to perform the experiment.

Now I want to express my gratitude to my parents. During this thesis period they were always with me. Finally, I want to dedicate the essence of my purest love to those two persons who have made my existence possible. The greatest pleasure to me is to think about them.

Author

ABSTRACT

This study has been carried out on the concentrations of constituent major, minor and trace like elements present in sediment samples collected from different parts of Mongla River and Rupsha River during the month of September to October, 2016. The objective of this study is to provide the base-line data for the elemental contents of sediments for environmental monitoring. In carrying out the analysis, TRIGA Mark-II research reactor based Instrumental Neutron Activation Analysis (INAA) was adopted due to its versatile applicability and non-destructive nature. A total of 28 elements, i.e., 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 from eleven sediment samples collected from Mongla and Rupsha Rivers. In this experiment, NIST-1633b (coal fly ash) has 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). Along with the environmental characterization, experimental data are also compared to those of coal fly ash (NIST-1633b), which will be one of the major by product of the coal based power plant in Bangladesh. The data reveals that elemental contents in the coal-fly-ash are almost double (reflected by the *NIST-1633b/mean soil abundances*) than those of the elemental abundances in sediments of this study. The industrial effluents and municipal waste discharging into the Mongla and Rupsha Rivers are the main possible sources of the elemental pollution of the river. The results of this study suggest for future monitoring of the elemental pollution as well as possible threat to the biota of the river. Moreover, this study will be helpful to set a picture of contamination of the Mongla and Rupsha Rivers and the nearby Sundarban Mangrove forest area.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

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
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

Natural environment plays a great role in the existence of life on earth and it helps human beings, animals and other living things to grow and develop naturally. Contamination is the mixing of some harmful or poisonous materials into the natural resources available on the earth. It affects the ordinary living of the living things on this planet by disturbing the natural life cycle. Thousand years ago our planate was more fresh and harmless. Due to increasing population and various industries, nature contaminated with various heavy metals and radioactive elements. Human activities essentially lead to elevated level of air, soil, and water pollution. Air pollution and water pollution can have inimical effect to soil thereby altering its elemental composition. In addition, soils may become contaminated by the accumulation of heavy metals and metalloids through emissions from the rapidly expanding industrial areas, mine tailings, disposal of high metal wastes, leaded gasoline and paints, land application of fertilizers, animal manures, sewage sludge, pesticides, wastewater irrigation, coal combustion residues, spillage of petrochemicals, and atmospheric deposition. Heavy metals constitute an ill-defined group of inorganic chemical hazard, and those most commonly found at contaminated sites are Lead (Pb), Chromium (Cr), Arsenic (As), Zinc (Zn), Cadmium (Cd), Copper (Cu), Mercury (Hg), and Nickel (Ni). Soils are the major sinks for heavy metals released into the environment by aforementioned anthropogenic activities and unlike organic contaminants which are oxidized to carbon (IV) oxide by microbial action, most metals do not undergo microbial or chemical degradation, and their total concentration in soils persists for a long time after their introduction. Changes in their chemical forms (speciation) and bioavailability are, however, possible. The presence of toxic metals in soil can severely inhibit the biodegradation of organic contaminants. Heavy metal contamination of soil may pose risks and hazards to humans and the ecosystem through: direct ingestion or contact with contaminated soil, the food chain (soil-plant-human or soil-plant-animal-human), drinking of contaminated ground water, reduction in food quality (safety and marketability), reduction in land usability for agricultural production causing food insecurity, and land tenure problems. Thus soil is the mother of the universe, and must be give a first treatment.

For increasing heavy metals and radioactive element various disease specially skin disease are occurred frequently. So to prevent such fatal disease and live happily, man should look forward such an environment which is free from such pollution. Different kinds of 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.

Among the various kinds of elemental analysis, Instrumental Neutron Activation Analysis (INAA) possesses very importance of this field. It is a technique in which samples are irradiated by neutron in research reactor which activates the elements of that sample by the capture of thermal neutron. The activated elements emit gamma ray of specific energy and these gamma rays are then analyzed by the HPGe gamma detector. The irradiation and gamma counting are held for about 25-30 samples. The data obtained in this study will be useful a base line data for elemental abundances of Rupsha and Mongla River to monitor this river in future.

1.1 Origin of River Contamination

Contamination is often classed as point source or non-point source contamination. Point source contamination occurs when there is a single, identifiable, and localized source of pollution and example is directly discharging sewage and industrial waste into the river or ocean (Tamim, 2016). Pollution such as this occurs particularly in developing nation. Non-point source pollution occurs when the solution comes from ill-defined and diffuse source. These can be difficult to regulate. Agricultural runoff and wind- blown debris are prime example. 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:

Direct discharge of water into Ocean: 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.

Land runoff: 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).

Transshipment pollution: 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.

Atmospheric pollution: 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 (United states Geological Survey) 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 H. S, 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.

Acidification: 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.

Plastic debris: 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.

Toxins: Apart from plastics, there are particular problems with other toxins that do not disintegrate rapidly in the marine environment. Examples of persistent toxins are 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.

World status: 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.

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.

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 (Carbon, Hydrogen, Nitrogen and Heteroatoms) 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.

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:

1. Quantitative Elemental Analysis.
2. Qualitative Elemental Analysis.

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. Thermogravimetryis 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.

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:

Chemical 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 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 18th and at the beginning of the 19th 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 20th century the other schemes, such as acid-base, ammoniac-phosphate, were also proposed.

Chemical 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.

Chemical 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

$$5I^- + IO_3^- + 6H^+ = 3H_2O + 3I_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.1)$$

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 molybdate solution, forming yellow crystals of ammonia molybdenum phosphate. Arsenic 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.

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.

The main merit of another spectroscopic method – the method of Laser Atomic Fluorescence Spectroscopy (LAFS), is its high selectivity, which is conditioned by an exceptional simplicity of atomic fluorescent spectrum, and hence, by an absence of a superposition of spectrum lines of different elements. Methods of X-ray Emission Spectroscopy (XES) and X-ray Fluorescence (XRF) are also used for qualitative elemental analysis. XRF method can't be used at all for detecting elements lighter than sodium and can be partially applied for the detection of elements, which are situated in the Periodic System before calcium.

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. The luminescent detection of metals is usually based on their reactions with organic reagents, which result in forming luminescent compounds. 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.

1.2 Instrumental Neutron Activation Analysis (INNA)

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.

1.3 Importance of INAA

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 there are 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 instrumental neutron activation analysis have chosen in the present study.

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 which have analyzed do not losses any of its property. So sample can re-use it in several times. If any confusion is occurred then sample can re-analyze.

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 (Tamim, 2016). 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). Aim of this study is to use INAA for the chemical characterization of Mongla and Rupsha River sediments.

1.4 Motivation of This Study

Bangladesh, the land of river, contains thousands of rivers and these rivers play an important role to our day to day life. The Rivers as well as river water have an impact to our environment. The sediments samples in the river contain various elements. Balance presence of elements in the sediments is healthy, but imbalance presence of elements in the sediments is harmful. It can disrupt ecosystems. Excess elements or radioactive elements can cause damage to human, fish gills, habitats. In addition, Sediments are a natural part of a stream, lake, or river, and the type and amount found in streams are influenced by the geology of the surrounding area. Natural processes that add to sediments in waterways include in stream scouring of the river bed and banks and erosion of sediments from the surrounding catchment from natural slips and any exposed soils. Sediments can enter streams from alongside a reach or from upstream via the myriad smaller interconnecting streams that form a river network within a catchment area.

While sediment movement is a natural part of a functioning freshwater ecosystem, human activities around a waterway (such as dam or road construction or land use change from native forest to pasture) can greatly increase the amount of sediment that enters the system. This can have considerable effects on water quality and the plants and animals that live there. The addition of sediment to rivers and streams above normal levels is a serious issue. Sediments are absolutely necessary for aquatic plant and animal life. Managed properly, sediments are a resource; improper sediment management results in the destruction of aquatic habitat that would have otherwise depended on their presence.

Sundarban is the largest mangrove forest in the world which is situated on the southern part of Bangladesh. This mangrove forest has long been acted as a natural shield during the natural disasters originating from the Bay-of-Bengal. Nevertheless, from the point of biodiversity and economic prospect, Sundarban possesses a huge importance. Most of the rivers are moderately to severely contaminated by heavy metals and metalloids originated from growing industrialization and (/or) urbanization. Rupsha and Mongla rivers are the two important rivers those contain heavy metals from the Mongla export processing zone as well as from other industrial and urban sources. Additionally, these rivers which are washing away most of the urban and industrial wastes of Khulna district and marched with the Bay of Bengal after passing through the largest mangrove forest of the world, Sundarbans. So, heavy-metal pollution is suspected, if the management is not properly managed. Aim of this Study is to prepare a baseline data for the elemental abundances of Mongla and Rupsha rivers sediments to monitor this area in future for a potential contamination.

CHAPTER 2

Literature Review

Being concern about the danger of the environmental pollution numerous works are being done to determine the pollution level and its remedy. Bangladeshi urban rivers are under threat of metal pollution due to direct discharge of untreated industrial wastage and municipal garbage into the rivers. There are various methods to determine the toxic elements of sediment samples like Neutron Activation Analysis (NAA), Atomic Absorption Spectroscopy (AAS), Flame Atomic Absorption Spectroscopy (FAAS), X-ray Fluorescence (XRF), X-ray Diffraction (XRD), Energy Dispersive X-ray Fluorescence (EDXRF), Inductively Coupled plasma Mass Spectroscopy (ICP-MS), Inductively Coupled plasma Atomic Emission Spectrometer (ICP-AAS), Inductively Coupled plasma Atomic Emission Spectrometer (ICP-AES) etc. The present research work has been done to investigate the amount of heavy metals in sediment sample near Mongla and Rupsha River. Now from the literature data it has been known the limit of pollution 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.

Tamim et al., (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.

Bettinelli et al., (2000) presented on determination of heavy metals in soils and sediments by microwave-assisted digestion and inductively coupled plasma optical emission spectrometry analysis. In their performance the determination of the total content and the leachable aliquot by aqua regia dissolution of eight heavy metals (Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn) in soils and sediments was developed by microwave digestion technique combined with inductively coupled plasma atomic emission spectrometry (ICP-AES). The tests carried out provide evidence that the extraction of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn from soils by microwave-assisted aqua regia solubilisation is a viable alternative to the traditional reflux systems. Contamination is minimized, sample preparation times are significantly shorter and the extraction efficiency is guaranteed. The results obtained with CRM 141R, CRM 142 and CRM 143 are in good agreement with BCR certified values. Recoveries range from 89 to 110%, except for Pb (82–89%). The recoveries obtained with five certified reference materials were good (83–108%). The relevant precision values (r and R%) were greater than the ones found with aqua regia digestions. A nested design statistical analysis was carried out for both procedures and showed that the major source of variability in the analysis was due to ICP-OES measurements rather than microwave-assisted dissolution.

Khan et al., (2015) present chemical characteristic of R chondrites in the light of P, REEs, Thand 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 acquireddata. 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.

Kogo et al., (2009) performed on neutron activation analysis of soil samples from different parts of Abuja Metropolis. Their study was carried out on the concentrations of constituent (major, minor and trace) elements present in soil samples. In carrying out the analysis, the best and most convenient method being the Instrumental Neutron Activation Analysis (INAA) otherwise known as Non-Destructive Neutron Activation Analysis (NDNAA) was adopted. Soil/ Rock Samples were obtained, crushed to powdery form and samples prepared for INAA. Analyzing samples following elements were identified: Al, Ti, Ca, Mg, K, Na, V, Mn, Dy, Sc, Zn, La, Sm, Co, Th, Rb, Ce, Hf, Fe, Yb, As, Eu, Lu and U. There have been higher concentrations found in the Airport Road soil than in the other soils as seen in Fe from the following results: Airport Soil (0.4212±0.014), Airport Road Soil (1.31±0.20), Also Radio Soil (0.6641±0.017) and Karu soil (0.528±0.013); indicating that soil in that region might favor the growth of particular plants compared with soils from other region; however there was relative distribution in the overall outcome of trace and major elements. The results and technique compared with that of Oladipos who had a total of 22 elements from 7 different clay samples indeed showed that NAA is effective method of elemental analysis.

Reguigui et al., (2002) performed on determination of trace elements in Tunisian soil, desert and beach sand using instrumental neutron activation analysis. Due to huge advantages Instrumental Neutron Activation Analysis (INAA) has been used and several samples of environmental concern were analyzed. The samples included two clay soils and three sands from two beaches from the north and south of Tunisia, respectively, and the Sahara desert. The results indicate a close relationship between the clay soil and the beach sand from the region of Tunis in terms of trace element concentrations. Similarly, there is a close relationship between the trace element content in both samples from the south (the beach and Sahara sand). However, there is a difference about twofold in concentration of trace elements between the samples from the north and the samples from the south. Overall, concentrations of trace elements are higher in the soil of Sidi Thabet than in the other samples of sand. Except for Hf, the concentrations in trace metallic elements are similar in both samples of the south, i.e., the Metouia beach and the Sahara. Arsenic concentration is much higher in the samples of the north (sand and soil) compared to samples of the south. It is evident that the heavily frequented Raoued beach contains much more arsenic than the Metouia beach in the south and the Sahara.

Hailu et al., (2012) studied on application of Instrumental Neutron Activation Analysis (INAA) of various rocks from areas around Debre birhan city, Ethiopia. In their study they have used high resolution γ-ray spectrometry to determine the elemental concentrations in rocks. For establishing the provenance (same or different origin) of the rock samples, Mn to Er concentration ratio as well as statistical cluster analysis was used using SPSS.20 statistical program. For the cluster analysis, concentration values of selected nine elements namely Mn, Na, Cd, Dy, Er, Ge, In, Se, and Sm were used. From these analyses, it was observed that the rock samples studied belong to three different groups. The largest constituent of the rock minerals in the area are found to be manganese, sodium gallium and germanium. Gadolinium and Indium is also found in samples DBTR1 and DBTR2 as major elements. Copper is found only in DBTR4 and DBTR5, Dysprosium in DBTR1 and DBTR5, Titanium in DBTR2 and DBTR4 and Gadolinium in rocks DBTR1 & DBTR4. On the other hand the element Yttrium is found only in sample DBTR2. Concerning the provenance of the rocks, as confirmed by this work, the rocks in the studied area fall into three groups. Although the number of samples considered in the study is limited.

Najam and Younis (2015) present assessment of natural radioactivity level in soil samples for selected regions in Nineveh Province (IRAQ). The radioactivity of 19 soil samples was determined by gamma spectrometry using NaI (Tl) detector. The activity of radionuclide's, ^{238}U, ^{232}Th, ^{226}Ra and ^{40}K ranged from 21.25 to 58.13Bq/kg , 11.22 to 31.63Bq/kg, 17.02 to 40.98 Bq/kg and from 206.51 to 509.56 Bq/kg respectively. The activity concentrations for these radionuclides were compared with world average activity in soil. It has been found that the average of activity concentrations of ^{238}U and ^{226}Ra are higher than world average value while the activities of ^{232}Th and ^{40}K are found to be lower. In order to evaluate the radiological hazard of the natural radioactivity, the radium equivalent activity, the absorbed dose rate, the annual effective dose rate, internal and external hazard indices and finally, gamma index have been calculated. The average activity concentrations (^{238}U and ^{226}Ra) for 19 soil samples collected from 11 districts from Nineveh province were higher than the permissible maximum values reported by world average ,but the average activity concentrations of (^{232}Th and ^{40}K) were lower than the permissible maximum values reported by world average. The study provides background radioactivity concentrations in Nineveh Province.

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.

Mohammed et al., (2012) present analysis of Cr in dumpsite soil samples using AAS and ED-XRF Techniques. In their presentation, speciation analysis of dumpsite soils from Kurmin Mashi (KM), Narayi (NY) and Tudun Wada (TW) of Kaduna metropolis, Nigeria was carried out. A modified Tessier extraction procedure was employed for the analysis. The concentration of Cr in the samples was determined using atomic absorption spectrometry (AAS) and Energy Dispersive X-Ray Fluorescence (ED-XRF) techniques. The results revealed that KM dumpsite had the highest amount of Cr. From the ANOVA ($P= 0.000 < 0.05$), it was established that there is a significant difference in the total chromium content across the three locations. The results also showed that the metal was distributed between oxides, carbonate and carbonate/organically bound fractions and that acetic acid extracted the highest amount of Cr across the dumpsites. Similarly, the ANOVA ($P =0.020 < 0.05$) indicated a significant difference in the Cr extracted using the three extraction media.

Ulmanu et al., (2011) present rapid determination of some heavy metals in soil using an X-Ray Fluorescence Portable Instrument. Contaminated soils present a major global health problem especially in urban areas with dense population. The new generation of portable XRF instruments is equipped with miniatures X-ray tubes in order to reduce the regulatory demands encountered with radioactive isotopes. Soil samples were collected from an old metallurgical industrial area, situated in Romania. The X-ray tube based sources offer a faster analytical time because the X-ray flux can be higher than most isotope based sources. The collected samples were XRF measured, then dried in air, XRF measured, sieved through the 2 mm sieve to remove non-soil particles and XRF measured again. The samples were homogenized and passed through the 200 microns sieve and XRF measured. After XRF determination, these fine samples were laboratory analyzed. The XRF results are presented comparatively with laboratory analysis data. From these results it is evident that the soil particle size have no important influence upon the XRF data, an important factor appears to be the metal concentration in soil. The results confirm the influence of metal concentration in soil upon the XRF data, smaller is metal concentration in soil sample, higher are the difference between XRF and laboratory analysis results. In all samples laboratory results are many times smaller than XRF data, in chromium and cobalt determination. Best correlation was obtained in lead and manganese determination.

Liang et al.; (2011) Performed on assessment of heavy metal pollution in soil and plants from Dunhua sewage irrigation area. 270 samples in different depth (0-120 cm) and 23 plant samples were collected at five different sites. Physical and chemical properties of the long-term sewage irrigation soil were analyzed, including soil texture, bulk density, pH, caution exchange capacity (CEC), organic matter; the heavy metal total concentrations were measured using Atomic Absorption Spectrometry (AAS) and Atomic Emission Spectrometry (AES). The average value of soil pH was 8.01, the soil was alkaline; the soil CEC changes from 59.35 mmol to 118.95 mmol, average value was 80.96 mmol; content of organic matter in surface soil maintained 1.27% to 2.18%; the bulk density of soil ranges from 0.94 to 1.57 g/cm3; average concentrations of heavy metals in surface samples were: Cr, 28.249 mg/kg; Cd, 1.247 mg /kg; Pb, 37.468 mg/kg; heavy metal concentration in the three different crops of different portions was: root>stem>leaf>grain; the vertical distribution and migration the concentration of 0-20 cm soil was significantly higher than other soil layers, showing the characteristic of enrichment at surface, relatively stable in deep. Heavy metals pollution degree was Cd (2.069)>Cr (0.113)>Pb (0.107), pollution risk degree of different sample point's range was EC>MF>Xg>WD>XG. Irrigation by wastewater has increased the heavy metal concentrations in soil and plants of receiving area.

Parth et al., (2011) performed on assessment of heavy metal contamination in soil around hazardous waste disposal sites in Hyderabad city (India): natural and anthropogenic implications. Geo-environmental evaluation of heavy metals was carried out to define the degree of contamination of soil environment. In the present study, heavy metals (As, Cr, Cu, Ni, Pb, Zn) in soil samples were analyzed by X-ray fluorescence spectrometer to quantify their concentrations. Natural background values were used to delineate their derivation as geogenic or anthropogenic. The average concentrations of As, Cr, Pb was found to exceed the threshold and natural background values, whereas the upmost concentrations of Cu, Ni and Zn exceeded the prescribed threshold limit. Soil pH varies from 5.7 to 8.9 and is acidic to near neutral and alkaline in nature. Soil pH significantly affects the solubility and mobility of these metals, as most of the metals are soluble in acid soils than in neutral or slightly basic soils. The methodology used has proved to be a useful tool to separate geological and anthropogenic causes of variation in soil heavy metal content and to identify common pollution sources.

Opaluwa et al., (2012) performed on heavy metal concentrations in soils, plant leaves and crops grown around dump sites in Lafia Metropolis, Nasarawa State, Nigeria. According to their study the level of heavy metals were determined using digestion and Atomic Absorption Spectrophotometer methods (AAS). Soil and plant samples were collected from farms around the dump sites (sites A and B) and other samples from an area where there were no dump sites, which served as control. The concentration of metals in soil samples in mg/kg from site 'A' determined were As(0.66), Cd(0.48), Co(0.58), Cu(0.91), Fe(0.63), Ni(0.31), Pb(0.49), and Zn(0.38) while that of site 'B' were As(0.55), Cd(0.84), Co(0.63), Cu(0.82), Fe(0.64), Ni(0.42), Pb (0.53), and Zn(0.40). The metal concentrations in plant leaves and crops showed high level of Co(0.33) and Fe(0.32) in roselle leaves; Cu (0.71) and As(0.37) in groundnut; Cu(0.48) and As(0.28) in maize grains; As(0.36) and Co (0.32) in spinach leaves; and Cu(0.36) and Co(0.32) mg/kg in okro. The values of all the metals analyzed for samples from dumpsites were higher than those from the control site suggesting possible mobility of metals from dumpsites to farmlands through leaching and runoffs, but were below values recommended by the World Health Organization (WHO). However lead was found to be above the WHO standard maxima of 0.01mg/kg though is still safe i.e. the values are below the tolerable levels of 90-300mg/kg recommended by EC, 1986, but in very high concentrations plants may pose danger to consumers of plants around these areas.

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.

Ene et al., (2008) present XRF-AAS analysis of heavy metals in soils around of a ferrous metallurgical plant in eastern part of Romania. They used Energy Dispersive X-Ray Fluorescence (ED-XRF) technique and Atomic Absorption Spectrometry (AAS) to determine the concentration of heavy metals. The concentrations of heavy elements decrease with the distance from the metallurgical works and they are greater than the ones detected in the control soil sample collected from a zone situated far from traffic and industrial activity. For the majority of metals, pronounced maximum concentrations for all depths were detected in the locations near the South gate of the integrated works, in the prevailing wind direction. The soils located in influence zones of industrial objectives with ferrous processing activities recorded heavy metals loading (contamination) or pollution. The soil heavy metal concentrations were compared with the maximum values admitted by the Romanian guideline.

Louhi et al., (2012) present determination of some heavy metal pollutants in sediments of the Seybouse River 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 cation exchange in acid and alkali chemo sorption. 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.

Carr et al., (2008) performed on identification and mapping of heavy metal pollution in soils of a sports ground in Galway City, Ireland, using a portable XRF analyzer and GIS. Since heavy metals in urban soils have long-term effects on human health. So it is necessary to measure the amount heavy metal in urban soil. During a previous investigation of urban soils in Galway city, Ireland, a pollution hotspot of Pb, Cu, Zn and as was identified in the sports ground of South Park in the Claddagh. The sports ground was formerly a rubbish dumping site for both municipal and industrial wastes. In this study, a portable X-ray fluorescence (PXRF) analyzer was used to obtain rapid in-situ elemental analyses of topsoil (about 5 - 10 cm depth) at 200 locations on a 20 × 20 m grid in South Park. Extremely high values of the pollutants were found with the maximum values of Pb 10297 mg/kg, Zn 24716 mg/kg, Cu 2224 mg/kg and As 744 mg/kg. High values occur particularly where the topsoil cover is thin whereas lower values were found in areas where imported topsoil covers the polluted substrate. GIS techniques were applied to the dataset to create elemental spatial distribution maps, 3D images and interpretive hazard maps of the pollutants in the study area. Immediate action to remediate the contaminated topsoil is recommended to safeguard the health of children who play at the sports ground.

Ololade (2014) present an assessment of heavy metal contamination in soils within auto-mechanic workshops using enrichment and contamination factors with geo-accumulation indexes. Samples were collected in different layers (0 - 15 cm; 15 - 30 cm and 30 - 45 cm depth). The soils showed remarkably high levels of all the metals above background concentrations with most (Ni, Cu, Fe, Cr and Cd) decreasing with soil depth. The distribution pattern were in the following order Fe > Cu > Zn > Pb > Cr > Ni > Cd. Across all the sampling locations and profiles, Fe and Cd showed the highest (476.4 $\mu g \cdot g^{-1}$) and least (37.5 $\mu g \cdot g^{-1}$) mean concentrations respectively. Pollution load index (PLI) and index of geo-accumulation (Igeo) revealed overall high and moderate contamination respectively but the enrichment factors (EFs) for Pb Ni and Cd are severe. The inter-element relationship revealed the identical source of elements in the soils of the studied area. The mechanic waste dumps represent potential sources of heavy metal pollution to environment. The elevated levels of heavy metals in these soil profiles constitute a serious threat to both surface and groundwater.

Addo et al., (2012) performed on evaluation of heavy metals contamination of soil and vegetation in the vicinity of a cement factory in the Volta region, Ghana. In this work, 34 soil samples and 29 Tephrosiaelegans plants collected in the vicinity of the Diamond Cement Factory, Aflao, Ghana were analyzed for As, Co, Cr, Cu, Mn, Ni, Pb and Zn using energy dispersive XRF. The results of the metal analysis indicated that some metallic levels were in excess of natural background and critical limits for the soil and plants respectively. The results further revealed that the metal distribution were in a fluctuating manner considering various distances and directions from the cement facility. However, it was observed that the mean metal concentrations of the soil and plants decrease as distance from the cement facility increased for most metals. This indicated that the facility which is the only industrial source in the area is the major cause of the pollutants contamination in its vicinity. In an attempt to understand the pattern of metal contamination in the area, useful tools including enrichment factor, geo-accumulation index and pollution load index were employed to indicate the sources of soil contamination were anthropogenic in character. Recommendations for the need for other studies on environmental and human health around the cement and similar facilities to protect human life and the environment are suggested.

Dhawal et al., (2013) present terrestrial background radiation studies in South Konkan, Maharashtra, India. These radionuclides are mostly gamma ray emitting radionuclides which contribute to the radiation dose in long term behavior of radionuclides in soil. Health hazards associated with natural radioactivity are of great concern and it is necessary to assess risk due to them. The most common radionuclides found are ^{238}U, ^{232}Th and ^{40}K. The activity concentration of natural radionuclides in the soil samples were analyzed using HPGe based gamma spectrometry. The activity concentrations from the selected villages are found to be ranging from 24.78 ± 0.14 to 76.38 ± 0.31Bq kg^{-1} for ^{238}U, 30.08 ± 0.14 to 96.18 ± 31Bq kg^{-1} for ^{232}Th and 105.34 ± 0.24Bq kg^{-1} to 432.51 ± 0.48Bq kg^{-1} for ^{40}K. The average absorbed dose rate in air was calculated as 66.89nGyh^{-1}.The annual effective dose rates were varied from 0.27mSvy^{-1} to 0.85mSvy^{-1} with an average of 0.49mSvy^{-1}. The mean radium equivalent activity value for soil samples was 144.84 Bq kg^{-1} which is lower than 370 Bqkg^{-1} of world average. It is observed that the study area is free from hazards of Radium and its progeny nuclides like Radon. The external hazard index for all soil samples was lower than unity denoting that the villages from this study area are safe for human health.

Yu et al., (2002) present determination of multi-element profiles of soil using energy dispersive X-ray fluorescence (ED-XRF). The source profile for soil in Hong Kong is important both for determination of the main air pollutant source in Hong Kong and for assessment of the impact of Asian dust storms on Hong Kong. Soil associated with different rock types have been sampled, and the concentrations of 19 chemical elements, Na, Al, Si, Ti, V, Cr, Mn, Fe, Co, K, Ca, Ni, Cu, Zn, Pb, Rb, Sr, Y and Zr, have been determined using energy dispersive X-ray fluorescence. A profile for the average soil for Hong Kong has been determined by taking average values for the different soil categories. The values for the Hong Kong soil are commensurate with values for rural soil derived by other workers, except that Hong Kong soil has much lower Fe and Ca concentrations. The abundance of Al, Ca and Fe in the average Hong Kong soil is 9.23%, 0.11% and 0.85%. It concludes that Ca provides a good marker element for identifying dust episodes in Hong. Kong while Al does not.

Lee et al., (1995) present evaluation of metal and radionuclide data from neutron activation and acid-digestion-based spectrometry analyses of Background Soils. In this project, a total of 120 soil samples were collected from uncontaminated areas. The samples were taken at three 'different depths and from three different geologic groups to establish background concentrations of metals and radionuclides. The advantages and disadvantages were evaluated from Al, Sb, As, Cr, Co, Fe, Mg, Mn, Hg, K, Ag, ^{232}Th, ^{235}U, ^{238}U, V, and Zn data. The ADS methods used for this project were inductively coupled plasma (ICP), ICP-mass spectrometry (ICP-MS), and alpha spectrometry. The scatter plots showed that the NAA results for As, Co, Fe, Mn, ^{232}Th, and W is reasonably correlated with the results from the other analytical methods. Compared to NAA, however, the ADS methods underestimated Al, Cr, Mg, K, V, and Zn. Because of the high detection limits of the spectrometric methods, the NAA results and the ADS results for some elements, including Sb, Hg, and Ag, did not show a definite relationship. The NAA results were highly correlated with the alpha spectrometry results for ^{232}Th and W but poorly correlated for ^{235}U, probably because of a larger counting error associated with the lower activity of the isotope. The NAA methods, including the delayed neutron counting method, were far superior techniques for quantifying background levels of radionuclides (^{232}Th, ^{235}U, and ^{238}U) and metals (Al, Cr, Mg, K, V, and Zn) in soils.

CHAPTER 3

Methodology

3.1 Introduction

Neutron Activation Analysis (NAA) is a highly sensitive method for the accurate determination of elemental concentrations in a material. Sensitivities are sufficient to measure certain elements at the nano gram level. Neutron activation analysis was discovered in 1936 when Hevesy and Levi (Laul, 1979) found that samples containing certain rare earth elements become highly radioactive after exposure to a source of neutron.

The NAA method is based on the detection and measurement of characteristic gamma rays emitted from radioactive isotopes produced in the sample upon irradiation with neutrons. In reactor- based NAA, samples with unknown elemental concentrations are irradiated with thermal neutrons in a nuclear reactor together with standard reference materials of known elemental concentrations. Neutrons are absorbed in the nuclei of constituent atoms, and later these nuclei emit radiation with energy and quality characteristic of the particular element. This emitted radiation is a ‘fingerprint’ of the element and the amount of radiation given off at certain energy is indicative of the element present in the sample. A comparison between specific activities induced in the standards and unknown provides the basis for computation of elemental abundances. From this analysis, a report is issued giving elemental concentrations in the unknown sample. Figure 3.1 and Figure 3.2 shows fission process and diagram illustrating the process of neutron capture by target nucleus followed by the emission of gamma rays respectively.

In this diagram of the NAA process, a nucleus absorbs a neutron from the top left. The nucleus becomes excited and immediately releases a gamma ray and decays to a lower energy level, although it still is an excited state. Then after a period of time (dependent on the nucleus) the excited nucleus emits a beta particle and a gamma ray, at which time the gamma ray is detected by a detector (not shown). Analysis of the spectrum of gamma rays emitted allows determination of the elemental composition of the sample.

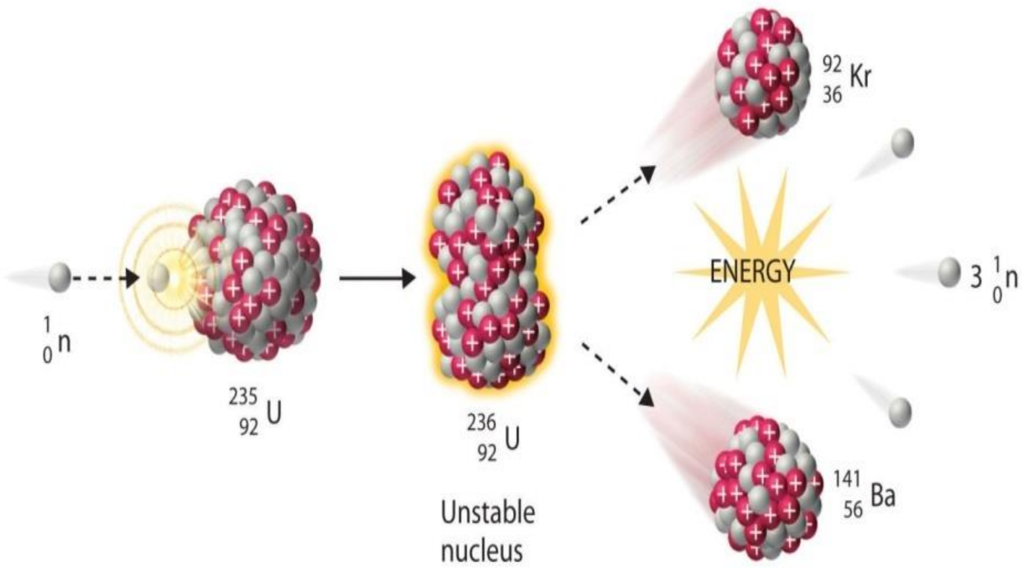


Figure 3.1: Fission process.

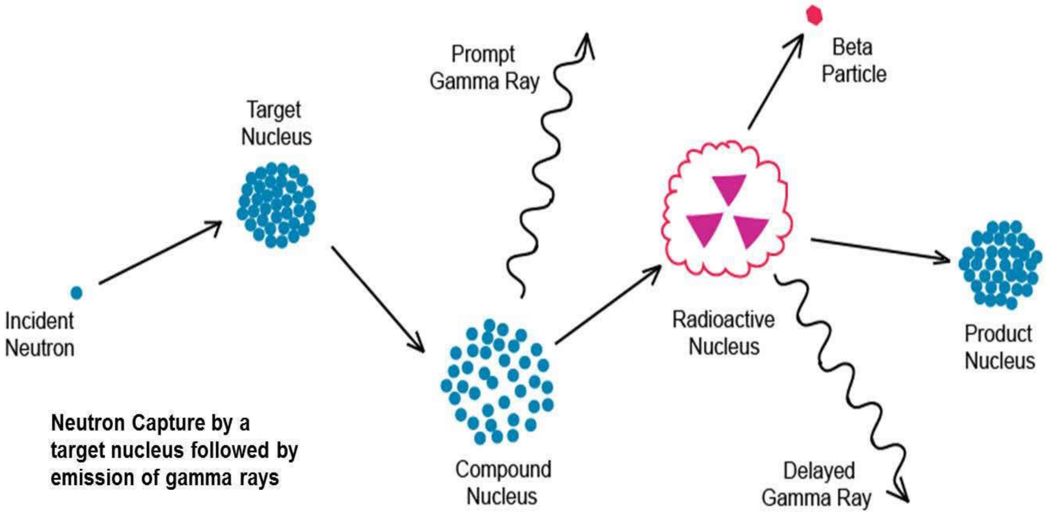


Figure 3.2: Diagram illustrating the process of neutron capture by target nucleus followed by the emission of gamma rays.

In the existing facility, sample is activated with neutrons using the 3MW TRIGA Mark-II research reactor at Atomic Energy Research Establishment (AERE), Savar. A high resolution high-purity germanium (HPGe) gamma ray spectrometer is used to detect the delayed gamma rays emitted from the radioactive samples for both qualitative and quantitative analysis.

Samples containing certain rare earth elements become highly radioactive after exposure to a source of neutrons. They determine the content of Dy and Eu in a rare earth mixture. Since then the use of NAA has increased with the increase knowledge of nuclear properties of the elements and with the advantages in nuclear reactors and radiation detectors.

3.2 Theory of Instrumental Neutron Activation Analysis

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 their chemical state. Thus, no information about compounds or types of chemical bonding is provided by NAA. The name “neutron activation” is ambiguous. It does not mean that neutrons are activated, but rather than neutrons do the activating. The sample to be activated is placed into concentrated beam of neutrons, which is usually provided by a nuclear reactor, where the fissioning of U (235) to lighter elements produces excess neutrons that move rapidly about until they are absorbed by nucleus of a nearby atom. The heavier nuclei produced by this neutron-capture process are frequently unstable, and proceed to decay with characteristic half-live and radiation. The radiation is some combination of alpha-particles (nuclei of helium), beta –particles (electrons), and gamma-rays (high-energy photons with no rest mass). The gamma rays are best for measurement purposes because they have sharply defined energies that are not reduced by passing through matter and can be measured accurately by modern detectors. In contrast, the energies of alpha particles and beta particles are varying greatly because their electrical charges make them interact more with matter and so lose large and variable amounts of energy.

After the sample has been irradiated, it removed from the reactor, repackaged, and taken to a counting room where it is placed near a semiconductor detector. Modern gamma-ray detectors are large single crystals of pure germanium (Ge). The radioactive sample is counted until a suitable gamma-ray spectrum is obtained. A gamma-ray spectrum is just a plot of the relative number of gamma counts versus the energy of the gamma rays. A typical spectrum is a series of sharp photo peaks superimposed on a broad sloping background. Each photo peak represents the decay of a specific radioisotope, although most radioisotopes have more than one photo peak. A computer program calculates the number of counts above background in each peak, compares it with standard mixtures of elements irradiated and counted similarly, and calculates the masses of each element detected in the sample. Because useful half-lives of elements range from seconds to decades, a full analysis consists of two or more irradiations of lengths ranging from minutes to days, followed by several counts at decay times ranging from minutes to months.

Neutron activation is a nuclear reaction phenomenon. 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 in a highly excited state due to high binding energy and kinetic energy of the incident neutron in the nucleus. De-excitation of the compound nucleus can occur in different ways that are independent of the way the compound nucleus is formed. Each of the processes has a certain probability, depending on the nuclear cross-section of each mode, which is related to the excitation of the compound nucleus. Figure 3.3 shows probability of occurring nuclear reaction.

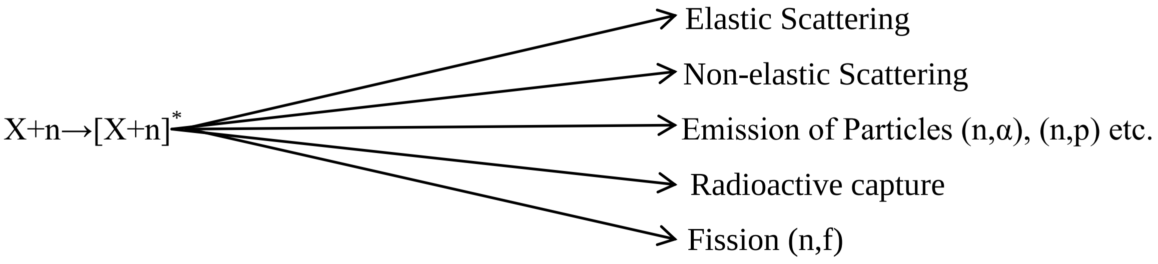


Figure 3.3: Probability of occurring nuclear reaction.

Elastic scattering: In this case ejected particle y (say) is the same as the projectile (x). It comes out with the same energy and angular momentum as x, so that the residual nucleus Y is the same as the target nucleus X and is left in the same state (ground state) as the latter. It can represent the process as X (x, x) X. Basically particles kinetic energy is constant in center of mass system but not constant in laboratory reference frame system. It can be mind that the kinetic energy of a particle is conserved in the center of mass frame, but its direction of propagation is modified by interaction with other particles and/or potentials.

Inelastic Scattering: In this case y is the same as x. but it has different energy and angular momentum, so that the residual nucleus Y (=X) is left in the excited state. The process can be written as X (x, y) X^*. In this process the energy is not conserved.

Radioactive Capture: In this case the projectile x is absorbed by the target nucleus X to form the excited compound nucleus (c^*) which subsequently goes down to the ground state by emission of one or more γ-ray quanta. This can be written by the process as X (x, y) Y^*. Radioactive capture is the most favorable and important nuclear reaction in NAA.

Fission: Nuclear fission is a special type of nuclear reaction in which an excited compound nucleus breaks up into two fragments of comparable mass number and atomic number. It also called a radioactive decay process. The fission process often produces free neutrons and gamma photons, and releases a very large amount of energy even by the energetic standards of radioactive decay. Fission usually occurs amongst the isotopes of heaviest elements known as Uranium, Thorium etc.

3.3 Classification of NAA Method

There are various forms of neutron activation analysis, which are as follows:

- Instrumental Neutron Activation Analysis (INAA)
- Radiochemical Neutron Activation Analysis (RNAA)
- Thermal Neutron Activation Analysis (TNAA)
- Epithermal Neutron Activation Analysis (ENAA)
- Prompt Gamma-ray Neutron Activation Analysis (PGNAA)

- Fast Neutron Activation Analysis (FNAA)
- Delayed Gamma-ray Neutron Activation Analysis (DGNAA)
- Molecular Neutron Activation Analysis (MNAA)
- Cyclic Neutron Activation Analysis (CNAA)

In the present study INAA method is used for this present analysis.

3.4 Fundamental Equations for INAA Method

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

- Absolute INAA method
- Comparative INAA method

3.4.1 Absolute INAA Method

In a neutron-induced reaction, the growth of the product is dependent on the size of neutron flux. The larger the neutron, the greater the rates at which interaction occurs:

Activation rate ∞ Neutron flux (φ)

$A_0= (MN_A)/ W \sigma \varphi \{1-e^{\wedge(-\lambda)}\}$…………………………………………………..(3.1)

Where,

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

M is the mass of the element

$N_A= 6.673\times10^{23}$, is the Avogadro's number

σ is the cross-section, in barn

φ is the neutron flux, in neutrons $m^{-2}s^{-1}$

θ is the isotopic abundance

W is the atomic weight

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

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

Where, Decay factor, $F_d= \exp(-\lambda_{td})$ and

Counting factor, $F_c= (1-\exp(-\lambda_{tc})$

So, the basic equation for INAA calculation in absolute method becomes,

$A_0 = (MN\_A)/w\ \sigma\varphi/\{1\text{-exp}(-\lambda_{ti})\}\{\text{ex}(-\lambda_{td})\}\{1\text{-exp}(-\lambda_{tc})\}\{\lambda_{tc}\}$……………..(3.2)

Hence,

$M= (A_0W)/(N\_A\ \sigma\theta\sigma)\{1\text{-exp}(-\lambda_{ti})\}\times F_c \times F_c)$………………………………...(3.3)

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 sample the basic equation used for INAA calculation in absolute method is,

$A_0= WN_A\ \varphi\ \sigma\ \theta\ \{1\text{-exp}\ (-\lambda_t)/A\}$……………………………………………...(3.4)

Where, $A_0= N\ \{1\text{-exp}\ (-\lambda_t)\}$, is the activity or the disintegration rate at the end of irradiation time t.

W 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 neutrons $m^{-2}s^{-1}$

θ is the isotopic abundance

A is the atomic weight

$$\text{So, } W = \frac{A_0 A}{N_A\varphi\sigma\theta\{1-exp(-\lambda t)\}}\text{…………………………(3.5)}$$

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

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

The difficulty of accuracy measurement of σ leads to the difficulty of measuring neutron flux density φ and also have the value of φ changes depending 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,

$$A = R/I_{\gamma}\varepsilon \quad \text{........ ....(3.6)}$$

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

3.4.2 Comparative INAA Method

In the comparative INAA method, an element of “X” in a sample and 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 σ, φ, γ 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.

$$\frac{Weight\ of\ element\ \text{"X"}\ in\ sample}{Weight\ of\ element\ \text{"X" in standard}} = \frac{Ax*\ in\ sample \times\ e^{\lambda t}\ sample}{Ax*\ in\ sample\ \times e^{\lambda t}\ standard}$$

Knowing the activities of X^* in sample and standard, the sample and standard decay times and the weight of “X” in the standard, the weight of element “X” in the sample is then calculated (Perry, 1991)

3.5 Characteristics of INAA Method

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 Spectroscopy (TR-XRE). So it is important to remain realistic in evaluating the role of INAA. Therefore, the most typical analytical characteristics of INAA are given as follows:

- Relative freedom from matrix and interference effects.
- Virtual absence of an analytical blank.
- Sensitivity and applicability for mirror and trace elements in a wide range of matrices.

- An inherent potential for accuracy compared to other analytical technique. Since the theoretical basis of INAA is well understood, a complete uncertainty budget can be made.
- The totally independent of nature of the method as a nuclear-based property in contrast to the electronic nature of most other analytical techniques.
- The possibility of performing non-destructive analysis using instrumental neutron activation analysis.
- High specificity based on the individual characteristics of the induced radionuclides.
- The capability of INAA for multi-element determination, often allowing 30 to 40 elements to be determined in many matrices.
- In case where the induced radionuclides of trace elements are marked by matrix activity, radiochemical separation provides interference free detection limits close to theoretical ones. Thus, in the radiochemical mode of INAA (RNAA) the technique has other advantages feature.

3.6 Application of INAA Method

INAA can be applied to virtually all sample types without any pre-treatment of the sample. This includes:

- Archaeology such as pottery, obsidian, chert, basalt and limestone.
- Study the Redistribution of Uranium and Thorium due to Ore processing.
- The use of radiotracers to study the fte of Hazardous elements in Waste Materials/ Coal-Char admixtures under gasification- an emerging waste management technology.
- Selenium distribution in aquatic species in Selenium-contaminated fresh water impoundments.
- In-situ radiotracers for dosage form testing.
- Nutrition Epidemiology – Nutritional and Biochemical/Genetic marks of cancer.
- Nutrition Epidemiology – A cohort study of the relationship between Diet, Molecular Markers, and Cancer risk.
- Nutrition Epidemiology – thyroid cancer study.
- Nutrition Epidemiology – Non-Melanoma skin cancer study.
- Nutrition Epidemiology – Molecular Epidemiology of prostate cancer.

- Knock-out Gene mouse model for cystic fibrosis.
- Calcium metabolism study.
- Geological science.
- Semiconductor materials and other high-purity materials.
- Soil Science.

3.7 Neutron Sources

A range of different sources can be used:

- A nuclear reactor
- An actinide such as californium which emits neutrons through spontaneous fission
- An alpha source such as radium or americium, mixed with beryllium; this generates neutrons by a (α, C+n) reaction
- A D-T fusion reaction in a gas discharge tube

3.7.1 Reactor

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.

3.7.2 Isotope Sources

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.

3.7.3 Gas Discharge Tubes

These 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.

3.8 Nuclear Reactor

The term nuclear reactor refers to devices 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, there by inducing a chain of fission events.

3.8.1 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. In this experiment 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. A partial view of the 3 MW TRIGA MARK – II research reactor is shown in Figure 3.4 and Figure 3.5 respectively.

3.8.2 Components of TRIGA Mark-II Research Reactor

Brief description about the components of TRIGA Mark-II research reactor is given below:

- Reactor Tank
- Reactor Core
- Fuel
- Control Road
- Moderators
- Reflector
- Coolants
- Reactor Shield
- Reactor Poisoning

Figure 3.4: TRIGA Mark – II research reactor at Savar, Dhaka.

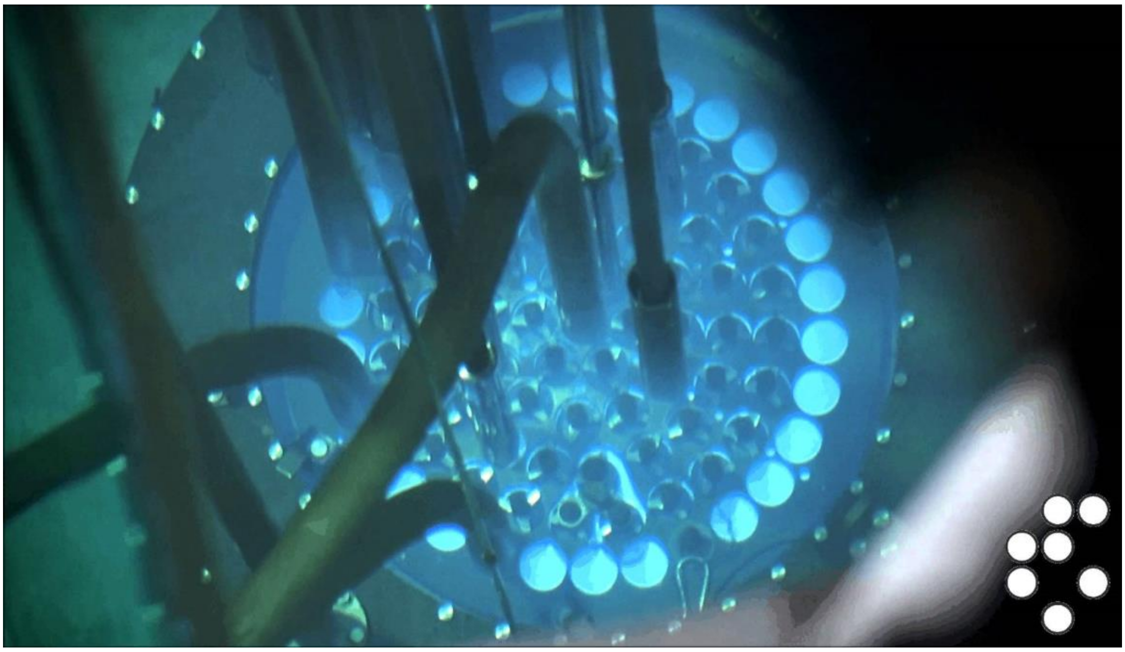


Figure 3.5: Inner view of TRIGA mark – II research reactor at Savar, Dhaka.

3.8.3 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. Table 3.1 shows that irradiation condition used for the experiment. 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)

Table 3.1: Irradiation condition used for the experiment

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

3.8.4 Pneumatic Transfer Systems

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 shows that values of neutron at TRIGA MARK – II research reactor.

Table 3.2: Values of Neutron flux 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}

3.9 Interaction of Gamma Rays with Matter

Gamma rays are the electromagnetic radiations consists of sharp lines of discrete wavelengths. The emissions of gamma rays are regarded simply as a means by which a nucleus can pass from an excited state to a less excited state. For many radioactive elements the emission of α or β particle from a nucleus is immediately followed by emission of a γ ray. Due to very short wavelength (even less than ordinary x-rays) γ-rays are highly energetic and hence possess a very high penetrating property (OyesKurni, 2011).

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:

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. Figure 3.6 shows photoelectric emission. 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 3.7 shows the production of auger electrons.

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. 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. Figure 3.8 shows Compton scattering of gamma radiation.

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 1.02 Mev 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 3.9 shows pair production and Figure 3.10 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. 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.

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.

$$e^{+} + e^{-} \rightarrow \gamma + \gamma \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3.7)$$

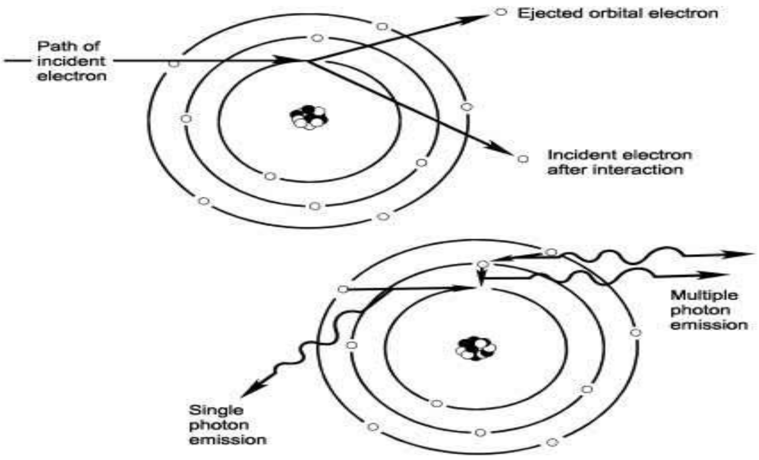


Figure 3.6: Photoelectric emission.

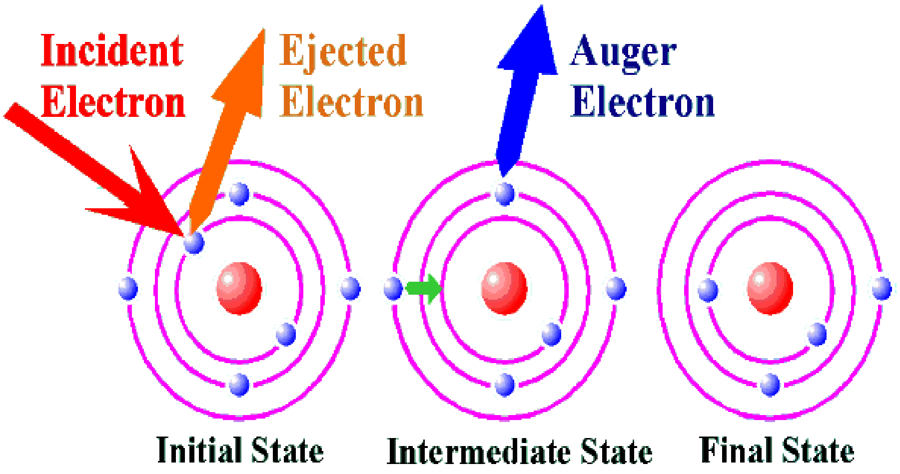


Figure 3.7: Auger electrons.

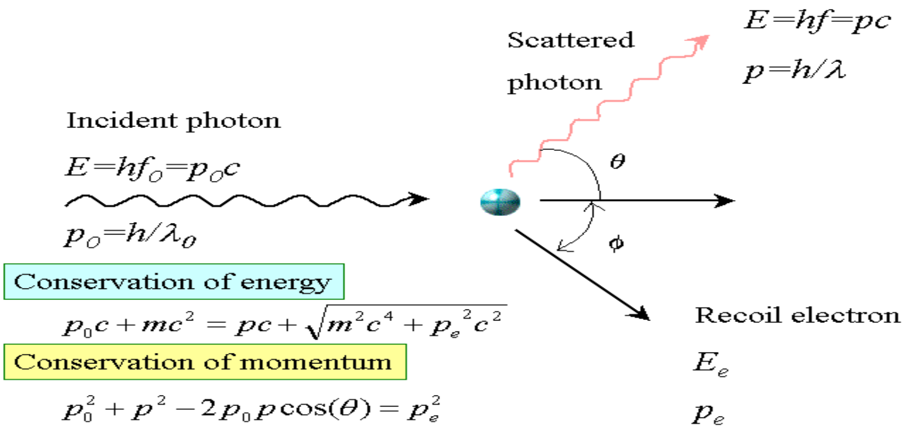


Figure 3.8: Compton scattering of gamma radiation.

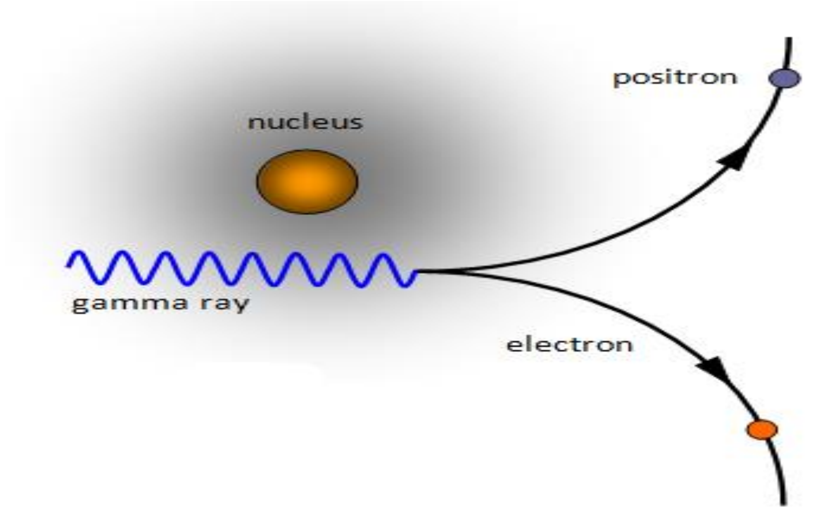


Figure 3.9: Pair Production.

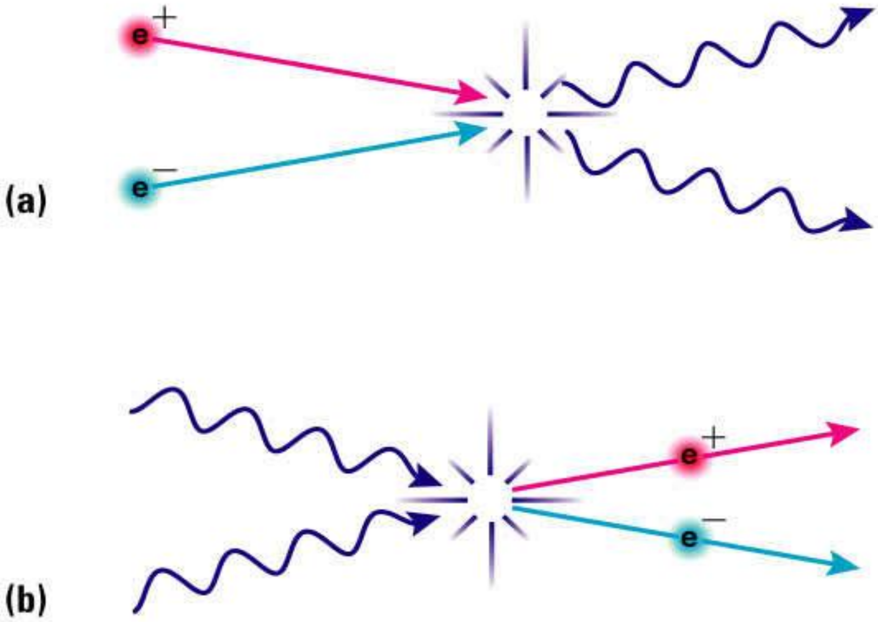


Figure 3.10: Pair Production and Positron Annihilation process.

3.10 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 3.11 shows that block diagram of gamma ray detection arrangement.

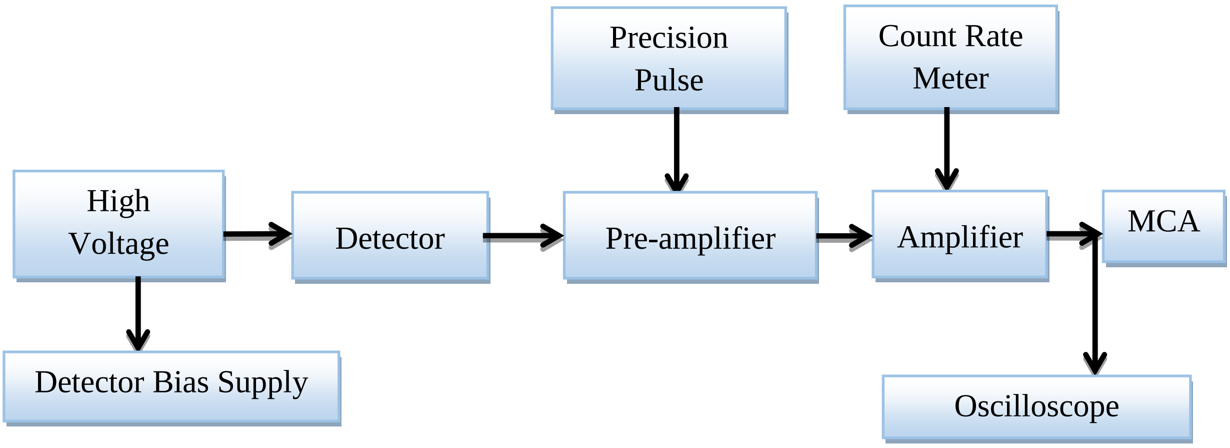


Figure 3.11: Block diagram of gamma ray detection arrangement.

3.11 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 3.12 shows cross - sectional view of HPGe detector.

It 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 3.13 and Figure 3.14 shows HPGe detector system available at BAEC Savar, Dhaka and the component of digital gamma ray spectrometry system respectively.

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 detector and the Dewar vessel are placed inside the shielding. During the upgrading a steel horizontal plate was placed into the existing shielding between the detector and the preamplifier. Additional lead and copper shielding have been arranged on this plate. A door-equipped copper box which used as a further shield of the detector inside the original shielding. The weight of the additional shielding was almost 500 kg and reduced the free volume around the detector to 30 dm^3, which still allowed measurement of 3L volume Marinelli beakers. Output of gaseous nitrogen vaporizing from the Dewar vessel which attached to the copper box. Due to the supply of nitrogen a slight overpressure has expected in the copper box to reduce air input from outside of the shielding.

3.12 Materials Need for Experiment

In present study the amount of radioactive materials in sediments near Rupsha and Mongla River is determined by Instrumental Neutron Activation Analysis. In this method the element present in sediment is activated by high energetic neutron. After that excited atom wants to stable by emitting radioactive ray. Measuring the energy of radioactive ray we can calculate what type of atom is present in those samples.
Instrument needs for this research can be classified into two groups;

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

Figure 3.15 and Figure 3.16 shows that instrument needed during collecting sample and instrument needed during experiment.

3.13 Justification of Sample Site Selection

Among all elements in nature soil and water 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 Rupsha and Mongla River respectively and to compare it to future, in the present study eleven sediments samples have been collected from eleven different places near Rupsha and Mongla River respectively.

3.14 Location of the Study Area

Rupsha is an upazila of Khulna District in the Divison of Khulna and Mongla is an upazila of Bagerhat District which is bounded by Rampal Upazila on the North and Bay of Bengal on the South. Rupsha River is a river in Southwestern and a distributary of the Ganges. It flows by the side of Khulna, and connects to the Posur River at Mongla channel. Near Chalna, it changes its name to Mongla River and flows into the Bay of Bengal after crossing the Sundarbans. Figure 3.17 shows the study area where the samples have been collected.

3.15 Sample Collection and Sample preparation

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 was made at upper layer of soil. Then the pipe has inserted through the soil by screwing at around 25 cm depth. After that the upper opening of the pipe has 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 was 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. Table 3.3 represents symbol and full name of elements and the details of the sample information are tabulated in Table 3.4. Collected samples have been then allowed to dry in an electric oven at 85°C until having constant weight. The dried sediment samples 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 ground with an agate mortar and pestle. The weight of each of the 10 cm long cylindrical sample volume was 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. Table 3.5 indicates weight of the sample and poly bag.

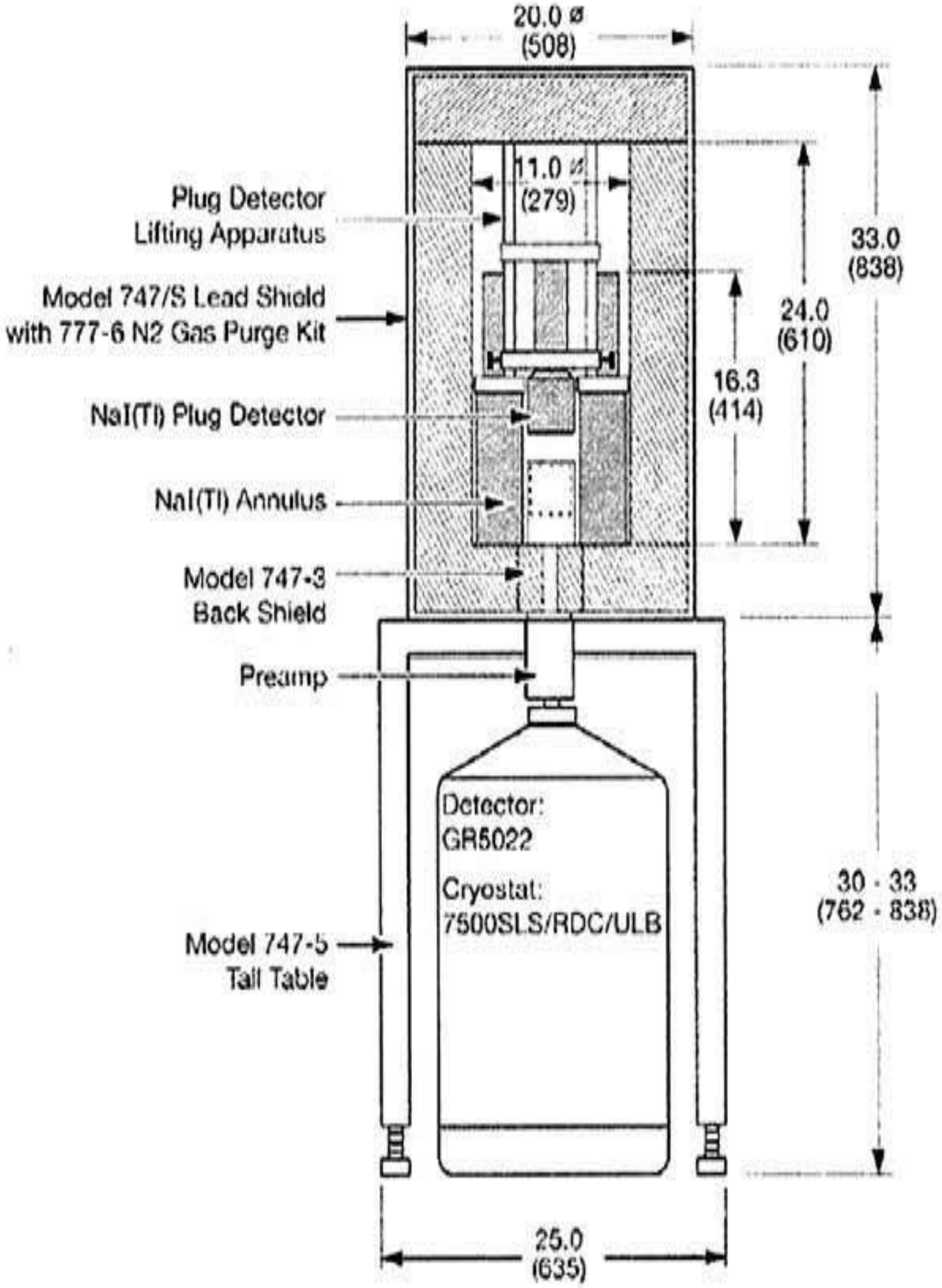


Figure 3.12: Cross - sectional view of HPGe detector.

Figure 3.13: HPGe detector system at BAEC Savar, Dhaka.

Figure 3.14: The component of digital gamma ray spectrometry system.

GPS System

GPI pipe

Zip-lock pack

Hand spade

Collected sample in pack

Hand glove

Ball pen & note book

Marker pen

Figure 3.15: 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 3.16: Instruments needed during experiment.

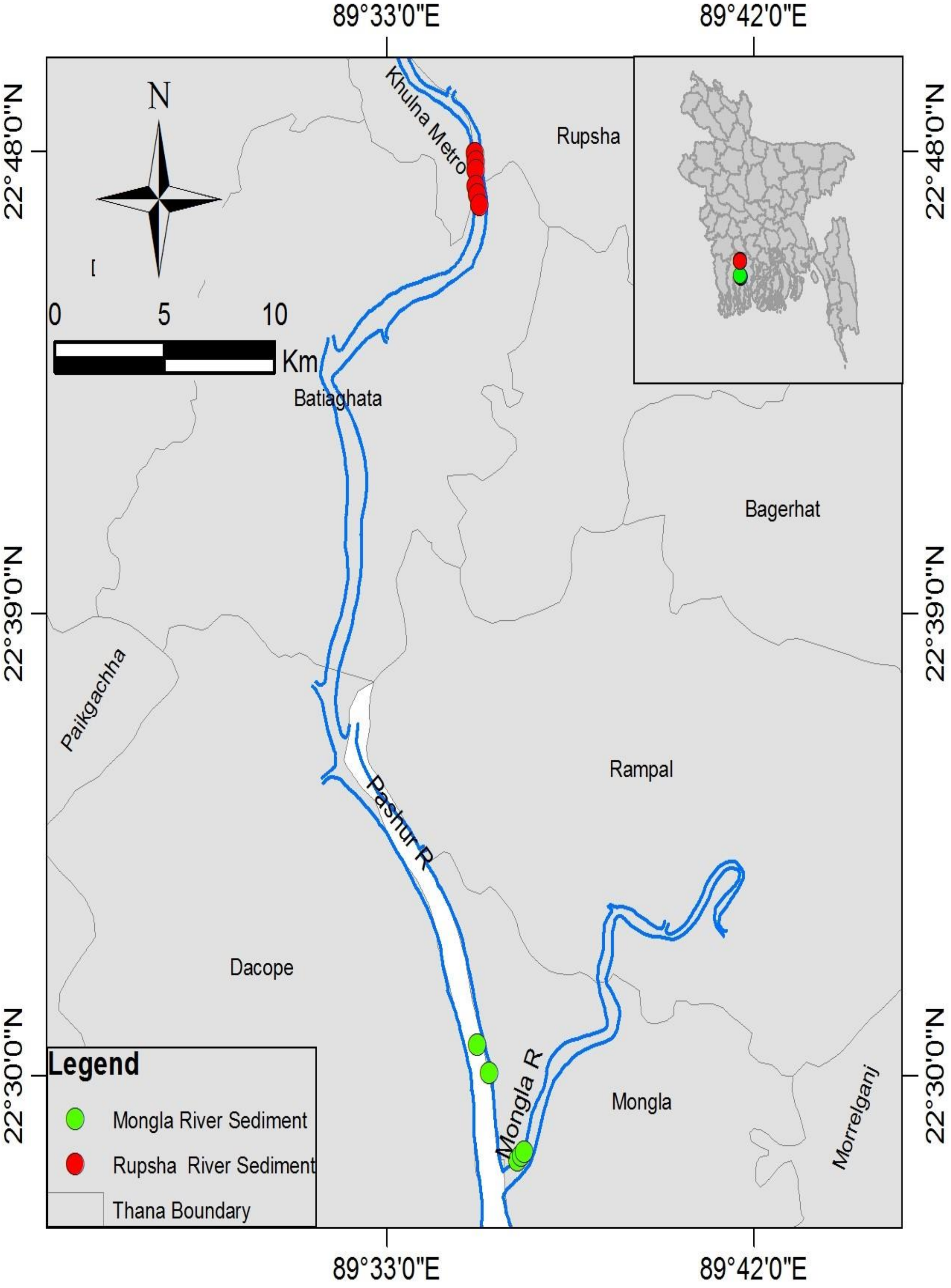


Figure 3.17: Study area

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	Co-ordinates	
			Longitude	Latitude
1	Mongla River (M-1)	Near an urban market	89º 36.189' E	22º 28.348' N
2	Mongla River (M-2)	Near a large educational institution	89º 36.294' E	22º 28.435' N
3	Mongla River (M-3)	Near an urban area	89º 36.367' E	22º 28.522' N
4	Mongla River (M-4)	Starting from an Export processing zone	89º 35.234' E	22º 30.534' N
5	Mongla River (M-5)	Middle point of Export processing zone	89º 35.221' E	22º 30.580' N
6	Rupsha River (R-1)	At Rupsha Ferry Ghat	89º 34.871' E	22º 47.909' N
7	Rupsha River (R-2)	In front of Khulna Shipyard	89º 34.866' E	22º 47.743' N
8	Rupsha River (R-3)	Between Shipyard and cement Factory	89º 34.881' E	22º 47.619' N
9	Rupsha River (R-4)	Middle point of Seven ring Cement Factory	89º 34.925' E	22º 47.251' N
10	Rupsha River (R-5)	Near about another cement Factory	89º 34.932' E	22º 47.136' N
11	Rupsha River (R-6)	Near at Rupsha Bridge	89º 34.928' E	22º 46.947' N

Steps of Sample Preparation

For Instrumental Neutron Activation Analysis various steps are taken. 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 3.18 shows flow-chart illustrating the pre-treatment of sediment samples.

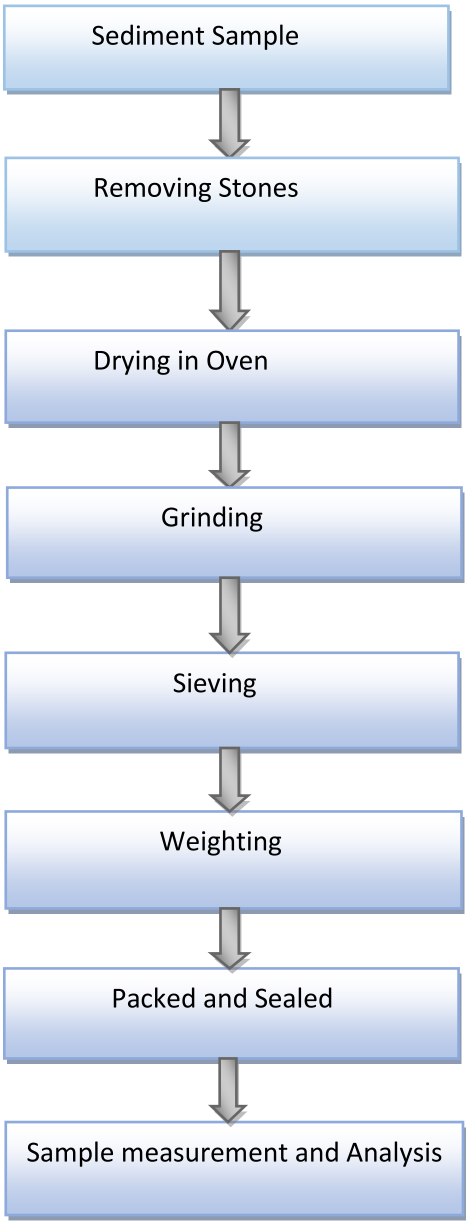


Figure 3.18: Flow-chart illustrating the pre-treatment of sediment samples.

Drying: Eleven 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. Then the Petri dish containing sediment samples and allowed to dry in an electric oven at 85°C until having constant weight (Parry, 1991). The time required varies with the water content of the sample. Figure 3.19 shows that drying samples at microven.

Sieving: It is a simple and convenient technique of separating particles of different sizes. A small sieve such as that used for sifting flour has very small holes which allow only very fine flour particles to pass through. The coarse particles are retained in the sieve or are broken up by grinding against the screen windows. Depending upon the types of particles to be separated, sieves with different types of holes are used. After some days when the samples were dried up .The dried samples were sieved with a mesh having a hole diameter of 0.25 mm in order to remove organic materials, stones and lamps. Figure 3.20 shows that sieving the sediment sample.

Grinding: For making small grain size each of the samples were 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 3.21 shows that grinding samples with mortar and pestle.

Weighing: It is an important part in assessment of elemental background in any type of sample in INAA. If any type of mistake is present during weighing then we do not get correct result about elements. For weighing the sediment samples firstly, the weight of each empty Petri dish was set to zero by a digital electronic micro balance. After that pot (sample container) was taken. Now sediment sample has placed into the pot. The weight of the pot and sample then took. In every time reading was noted into the register book. Now subtract the pot weight from pot plus sample weight. In this way get the samples actual weight. The weight of each sample is kept around 100gm and net weight was recorded in register book also. In INAA lab a digital electro micro balance is used that can measure0.001- 60/200 gm. Figure 3.22 shows digital electro micro balance.

Figure 3.19: Drying samples at microven**.**

Figure 3.20: Sieving the sediment sample.

Figure 3.21: Grinding samples with mortar and pestle.

Figure 3.22: Digital electro micro balance.

Sample Preparation for INAA

After weighing, the sediment samples have been made individual packet with individual identification number. The size and shape of packets have been kept approximately same. The packets have been then preserved carefully for neutron irradiation. For this experiment Approximately 50 mg of each dried powder sample has weighted in polyethylene bag and heat sealed. For relative standardization approach, one reference materials (RMs): IAEA-Soil-7 and one standard reference material NIST-1633b (Coal Fly Ash) has been used in this study. Each of the standards has 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 used as the standard while IAEA-Soil-7 have been used as the control sample. Figure 3.23 shows that ready samples for neutron irradiation.

Irradiation

Two irradiation schemes have been 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 at2.4 MW and (ii) Short irradiation has performed separately for each sample with the thermal neutron flux of5.28×10^{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 have been also irradiated by placing them at the bottom, middle and top of the sample stack for the long irradiation scheme. After long irradiation, samples have been turned into highly radioactive. For this reason, they usually were not handled immediately. They were in a shielded place for 2 days. (Tsoulfanidis, 1995) Normally the used irradiation facility is G-ring. Figure 3.24 shows sending and receiving center for sample vial at BAEC Savar.

Table 3.5: Weight of the sample and poly bag

SL. No.	SAMPLE-ID	POLY BAG (gm)	POLY BAG + SAMPLE (gm)	SAMPLE (gm)
1	1633b (1)	0.12401	0.17105	0.04704
2	Soil-7 (1)	0.08852	0.12987	0.04135
3	Mongla River (M-1)	0.10131	0.16122	0.05991
4	Mongla River (M-2)	0.11905	0.16802	0.04897
5	Mongla River (M-3)	0.10376	0.15120	0.04744
6	Mongla River (M-4)	0.11945	0.16782	0.04837
7	Mongla River (M-5)	0.13702	0.18091	0.04389
8	1633b (2)	0.09142	0.13535	0.04393
9	Soil-7 (2)	0.11112	0.15298	0.04186
10	Rupsha River (R-1)	0.13399	0.18507	0.05108
11	Rupsha River (R-2)	0.12787	0.17443	0.04656
12	Rupsha River (R-3)	0.14001	0.18456	0.04455
13	Rupsha River (R-4)	0.12520	0.17300	0.04780
14	Rupsha River (R-5)	0.14141	0.18333	0.04192
15	Rupsha River (R-6)	0.13569	0.18089	0.04520

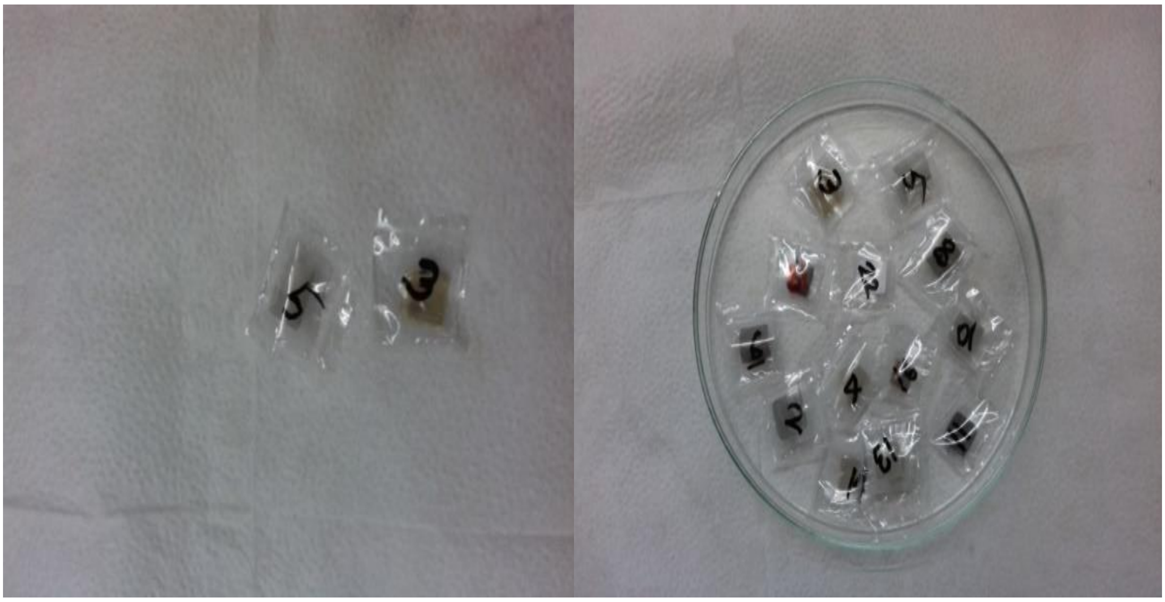


Figure 3.23: Ready Samples for Neutron Irradiation.

Figure 3.24: Sending and receiving center for sample vial at BAEC Savar.

Gamma Ray Counting

After irradiation, gamma-ray counting has 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 has 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 has performed for 3600 sec after a decay time of 2-3 days while the second counting has performed for 7200 sec after a decay time of 7-10 days and third counting has performed for 8-12 hours after a decay time of 2-3 weeks. Short lived and long lived radio-nuclides have been determined from the short and long irradiation separately. The gamma spectrometry of all the irradiated samples and certified reference materials has performed using a PC-based HPGe detector coupled with a digital gamma spectrometry system. The data acquisition has performed using the software Genie-2000 (Canberra) and MAESTRO-32 (ORTEC) and the gamma peak analysis has performed using the software Hypermet PC version 5.12. The gamma peak analysis is shown in Figure 3.25 and Figure 3.26 represent counts the gamma peak area. (Wyttenbach, 1971)

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 has made by irradiating Al and Si reagents (from Spex, USA) simultaneously.

Concentration Calculation

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

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

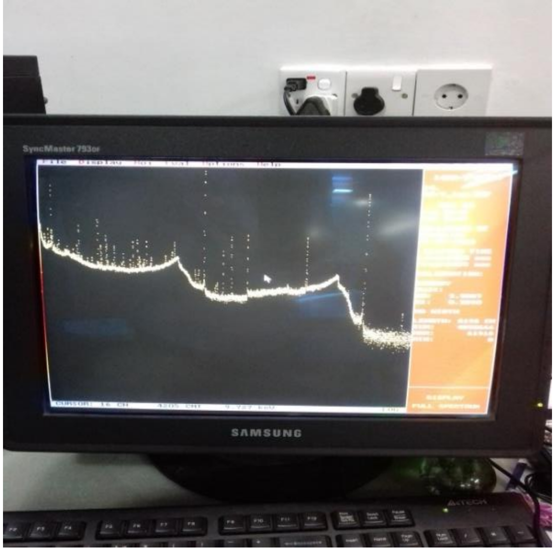
Knowing the activities of x^* in sample and in standard, the sample and standard decay times and weight of “x” in the standard, the weight of element “x” in the sample can be calculated.

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. Here it knows that “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”. It can also define 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 3.27 shows graphical presentations 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 3.28 shows low accuracy, poor precision, good trueness and Figure 3.29 shows low accuracy, good precision, poor trueness.

Table 3.6 represents the elemental abundances in repeated analyses (n = 3) of IAEA-Soil-7 of this study along with the certificate values.

For assessing the data quality it has analyzed the experimental result extensively. Analyses have been repeated 4 times. Analytical results have been 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).



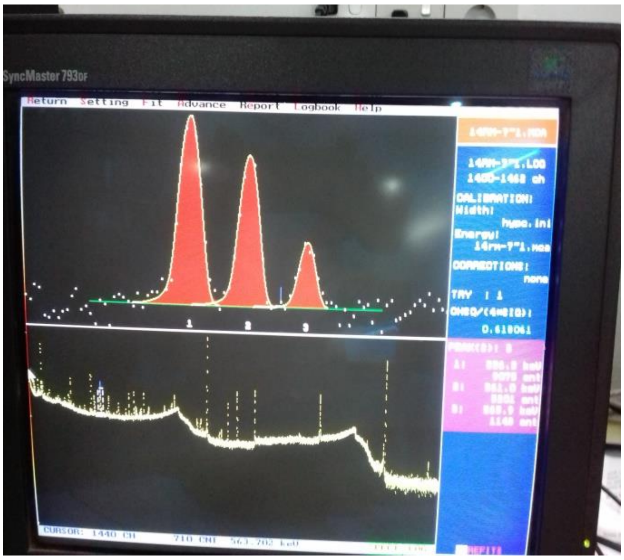


Figure 3.25: Gamma peak analysis using Hypermet PC version 5.12

Figure 3.26: Counts the gamma peak area using Hypermet PC version 5.12

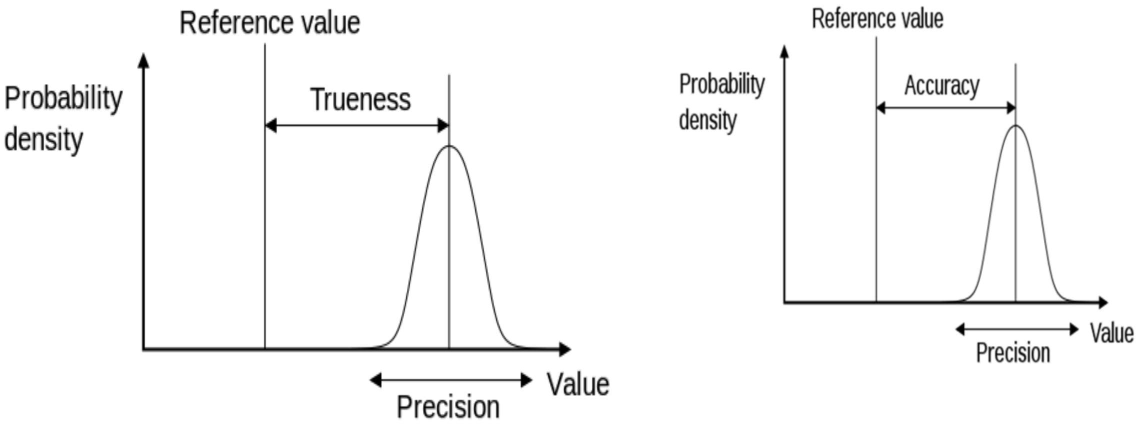


Figure 3.27: Graphical presentation of accuracy and precision.

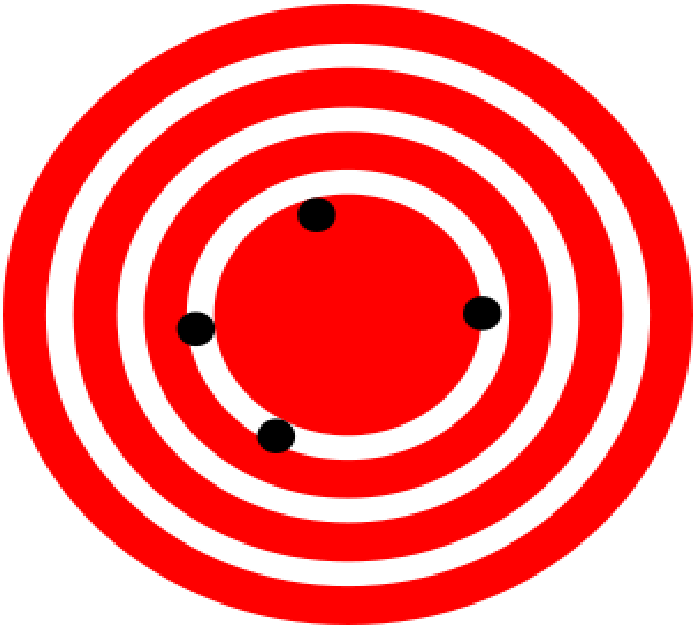


Figure 3.28: Low accuracy, poor precision, good trueness.

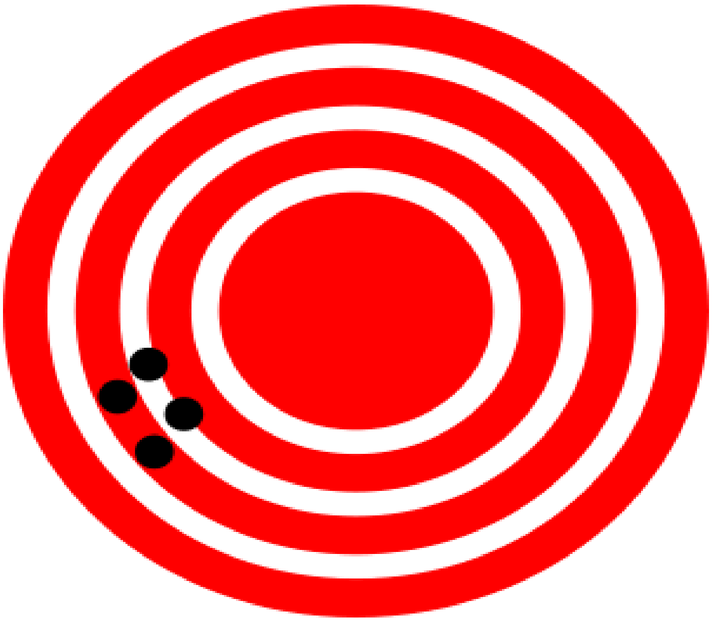


Figure 3.29: Low accuracy, good precision, poor trueness.

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

		This work [n=3]			**Certificate values**		
		Average	**SD**	**RSD [%]**	**Conc.**	**Min.**	**Max.**
Na	[%]	0.230	0.005	2.3	0.240	0.230	0.250
Mg	[%]	1.16	0.08	7.1	1.13	1.10	1.18
Al	[%]	4.95	0.11	2.3	4.7	4.4	5.1
K	[%]	1.23	0.04	3.6	1.21	1.13	1.27
Ca	[%]	17.1	0.9	5.4	16.3	15.7	17.4
Sc	[µg/g]	8.50	0.14	1.6	8.30	6.90	9.00
Cr	[µg/g]	66.1	2.0	3.1	60	49	74
Mn	[µg/g]	637	15	2.3	631	604	650
Fe	[%]	2.53	0.07	2.7	2.57	2.52	26.3
Co	[µg/g]	9.21	0.19	2.1	8.9	8.4	10.1
Zn	[µg/g]	82	19	22.7	104	101	113
Ga	[µg/g]	-	-	-	10	9	13
As	[µg/g]	14.2	1.3	8.9	13.4	12.5	14.2
Br	[µg/g]	8.1	0.8	10.0	7	3	10
Sb	[µg/g]	1.94	0.18	9.1	1.7	1.4	1.8
Cs	[µg/g]	5.86	0.29	4.9	5.4	4.9	6.4
Ba	[µg/g]	159	16	10.3	159	131	196
Ce	[µg/g]	52.9	3.3	6.1	61	50	63
Nd	[µg/g]	23.8	2.8	11.7	30	22	34
Eu	[µg/g]	1.04	0.02	1.6	1.0	0.9	1.3
Tb	[µg/g]	0.66	0.07	10.9	0.6	0.5	0.9
Dy	[µg/g]	4.23	0.10	2.4	3.9	3.2	5.3
Ho	[µg/g]	0.77	0.09	11.7	0.71[a]	-	-
Tm	[µg/g]	1.81	0.39	21.4	1.6[b]	-	-
Yb	[µg/g]	2.18	0.19	8.6	2.4	1.9	2.6
Lu	[µg/g]	0.33	0.03	10.1	0.3	0.1	0.4
Ta	[µg/g]	0.95	0.08	8.8	0.8	0.6	1
W	[µg/g]	2.99	0.55	18.3	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

A total of 11 (eleven) sediment samples, collected from different places around Rupsha River and Mongla River have been analyzed for major, minor and trace elements using Instrumental Neutron Activation Analysis method. Standardization has been performed by the comparative method for the determination of the concentration of the elements. For the standardization, two certified reference materials namely IAEA-Soil-7 and NIST 1633-b 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. (Pollard and Heron, 1996) The decay data of the interested elements has been shown in the appendix.

The concentration of different elements has been measured by evaluating the gamma ray peak areas produced from (n, γ) reaction. (Hevesy and Levi, 1936) The gamma spectrum acquisition for irradiated samples and standards has also 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.

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

Table 4.1: 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 eleven sediment samples are tabulated in Table 4.2 a and Table 4.2 b from Rupsha and Mongla River respectively 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=11), 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 a and Table 4.2 b respectively. Because the ship-yard and cement factories in Rupsha and EPZ in Mongla use coal and generate a huge amount of coal-fly-ash (disregarding the ultramodern technology to control the emission of coal-fly-ash to the open environment). In most of the cases elemental content in the coal-fly-ash is almost double (reflected by the 1633b/mean sediment abundances). Thus, free emission of coal-fly-ash to the environment will increase the heavy elemental abundances of sediment significantly.

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, 2008) used element an abundances of Earth's crust as the base line data. But Rubio et al. (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 mineralogical 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. For this reason the geo-accumulation index (Igeo), Enrichment Factor (EF) and the Pollution Load Index (PLI) of the sediment samples have been calculated. In this study, the elemental abundances of continental crust (Rudnick and Gao, 2014) has been used as the background data. Sediment samples have been used from different places for which continental crust data is suitable.

Table 4.2 a: Elemental abundances in sediment samples of Rupsha River with spatial variation

		R-1	±	R-2	±	R-3	±	R-4	±	R-5	±
Na	[%]	0.924	0.004	1.024	0.005	0.912	0.004	0.938	0.004	0.883	0.005
Mg	[%]	1.49	0.06	1.30	0.05	1.67	0.07	1.72	0.07	1.47	0.06
Al	[%]	6.91	0.05	6.30	0.04	7.90	0.05	7.60	0.05	7.22	0.05
K	[%]	2.46	0.05	2.20	0.04	2.60	0.05	2.45	0.05	2.18	0.06
Ca	[%]	2.27	0.40	2.30	0.41	1.62	0.31	1.66	0.30	2.84	0.50
Sc	[µg/g]	11.8	0.1	10.1	0.1	13.1	0.1	12.6	0.1	10.6	0.1
Cr	[µg/g]	66.4	1.5	57.1	1.5	73.1	1.7	72.4	1.7	59.9	1.6
Mn	[µg/g]	589	9	539	8	719	11	684	10	628	10
Fe	[%]	3.37	0.05	2.93	0.05	3.61	0.06	3.64	0.06	3.42	0.06
Co	[µg/g]	13.6	0.4	11.2	0.4	14.3	0.5	13.7	0.4	12.1	0.4
Zn	[µg/g]	71.3	4.3	62.7	4.1	75.5	4.7	44.5	3.3	38.5	3.2
Ga	[µg/g]	23.5	0.7	18.1	0.6	26.5	0.8	21.5	0.7	42.9	1.5
As	[µg/g]	7.49	0.12	6.37	0.12	8.73	0.14	8.50	0.14	9.25	0.19
Br	[µg/g]	1.76	0.09	1.04	0.06	8.88	0.31	8.79	0.31	1.68	0.10
Sb	[µg/g]	0.801	0.023	0.703	0.023	0.730	0.024	0.778	0.024	0.808	0.028
Cs	[µg/g]	9.44	0.26	8.32	0.24	11.08	0.30	10.16	0.28	8.71	0.26
Ba	[µg/g]	461	21	518	24	538	25	519	24	773	33
Ce	[µg/g]	89.9	1.3	101.3	1.4	84.5	1.3	86.2	1.3	85.2	1.3
Nd	[µg/g]	34.5	1.1	35.0	1.1	35.0	1.2	36.5	1.2	31.8	1.1
Eu	[µg/g]	1.09	0.03	1.27	0.03	1.09	0.03	1.18	0.03	1.02	0.03
Tb	[µg/g]	0.94	0.05	1.05	0.05	0.76	0.05	0.87	0.05	0.87	0.05
Dy	[µg/g]	6.28	0.10	7.02	0.11	6.29	0.11	6.67	0.11	6.45	1.90
Ho	[µg/g]	1.53	0.04	1.51	0.04	1.21	0.04	1.13	0.04	1.09	0.05
Tm	[µg/g]	1.68	0.07	1.76	0.07	2.25	0.09	1.81	0.07	1.77	0.08
Yb	[µg/g]	2.62	0.09	3.59	0.12	2.50	0.09	2.58	0.09	2.60	0.10
Lu	[µg/g]	0.41	0.01	0.56	0.01	0.42	0.01	0.38	0.01	0.06	0.00
Ta	[µg/g]	1.75	0.15	1.72	0.15	1.32	0.13	1.32	0.13	1.61	0.15
W	[µg/g]	3.00	0.13	3.25	0.14	3.18	0.14	3.35	0.14	3.08	0.17

(Continue)

		R-6	±	Mean	SD [n=5]	RSD [%]	Median	Min.	Max.
Na	[%]	0.896	0.005	0.930	0.050	5.4	0.918	0.883	1.024
Mg	[%]	1.24	0.05	1.48	0.19	12.9	1.48	1.24	1.72
Al	[%]	5.94	0.04	6.98	0.75	10.8	7.07	5.94	7.90
K	[%]	1.83	0.06	2.29	0.28	12.0	2.33	1.83	2.60
Ca	[%]	2.64	0.45	2.22	0.50	22.5	2.29	1.62	2.84
Sc	[µg/g]	9.1	0.1	11.2	1.6	13.8	11.2	9.1	13.1
Cr	[µg/g]	48.6	1.3	62.9	9.5	15.1	63.2	48.6	73.1
Mn	[µg/g]	522	8	613	79	12.8	609	522	719
Fe	[%]	2.35	0.04	3.22	0.50	15.5	3.39	2.35	3.64
Co	[µg/g]	8.9	0.3	12.3	2.03	16.5	12.8	8.9	14.3
Zn	[µg/g]	45.3	3.4	56.3	15.6	27.7	54.0	38.5	75.5
Ga	[µg/g]	26.5	1.1	26.5	8.6	32.6	25.0	18.1	42.9
As	[µg/g]	4.94	0.13	7.55	1.64	21.7	7.99	4.94	9.25
Br	[µg/g]	2.26	0.12	4.07	3.71	91.2	2.01	1.04	8.88
Sb	[µg/g]	0.619	0.023	0.740	0.072	9.7	0.754	0.619	0.808
Cs	[µg/g]	6.82	0.21	9.09	1.49	16.4	9.08	6.82	11.08
Ba	[µg/g]	437	22	541	120	22.2	518	437	773
Ce	[µg/g]	96.9	1.4	90.7	6.9	7.7	88.1	84.5	101.3
Nd	[µg/g]	37.8	1.2	35.1	1.999	5.7	35.0	31.8	37.8
Eu	[µg/g]	1.26	0.03	1.15	0.10	8.7	1.14	1.02	1.27
Tb	[µg/g]	0.91	0.05	0.90	0.10	10.6	0.89	0.76	1.05
Dy	[µg/g]	7.68	1.79	6.73	0.54	8.0	6.56	6.28	7.68
Ho	[µg/g]	1.50	0.05	1.33	0.21	15.6	1.35	1.09	1.53
Tm	[µg/g]	1.66	0.07	1.82	0.22	11.9	1.77	1.66	2.25
Yb	[µg/g]	3.48	0.11	2.90	0.50	17.2	2.61	2.50	3.59
Lu	[µg/g]	0.53	0.01	0.39	0.18	45.4	0.42	0.06	0.56
Ta	[µg/g]	1.46	0.14	1.53	0.194	12.7	1.54	1.32	1.75
W	[µg/g]	3.01	0.17	3.14	0.14	4.5	3.13	3.00	3.35

Table 4.2 b: Elemental abundances in sediment samples of Mongla River with spatial variation

		M-1	±	M-2	±	M-3	±	M-4	±
Na	[%]	1.029	0.005	0.957	0.004	0.972	0.004	1.018	0.004
Mg	[%]	1.43	0.05	1.58	0.06	1.46	0.06	1.24	0.06
Al	[%]	6.75	0.04	7.19	0.05	7.24	0.05	5.98	0.05
K	[%]	2.55	0.04	2.32	0.04	2.59	0.05	2.12	0.05
Ca	[%]	2.23	0.58	2.38	0.43	2.05	0.36	2.22	0.42
Sc	[µg/g]	11.9	0.1	10.8	0.1	12	0.1	9.1	0.1
Cr	[µg/g]	65.3	1.4	65.7	1.5	68.5	1.6	47.1	1.7
Mn	[µg/g]	602	9	637	9	632	9	504	9
Fe	[%]	3.51	0.05	3.1	0.05	3.37	0.05	2.5	0.06
Co	[µg/g]	13.8	0.4	11.8	0.4	13.1	0.4	9.7	0.4
Zn	[µg/g]	65	3.8	50.2	3.5	56.6	3.9	47.7	4.1
Ga	[µg/g]	20.1	0.6	23.8	0.7	22	0.7	16.7	0.8
As	[µg/g]	7.64	0.11	7.26	0.12	8.1	0.13	5.21	0.13
Br	[µg/g]	2.93	0.12	3.25	0.13	3.9	0.16	2.21	0.13
Sb	[µg/g]	0.716	0.02	0.719	0.022	0.749	0.023	0.567	0.024
Cs	[µg/g]	9.78	0.25	9.3	0.26	9.84	0.27	7.61	0.28
Ba	[µg/g]	528	21	490	21	548	23	423	24
Ce	[µg/g]	91.9	1.2	80.6	1.2	87.5	1.3	121.4	1.4
Nd	[µg/g]	36.8	1	30.8	1	40	1.2	54.8	1.2
Eu	[µg/g]	1.16	0.03	1.06	0.03	1.19	0.03	1.57	0.03
Tb	[µg/g]	0.9	0.05	0.87	0.05	0.84	0.05	1.4	0.05
Dy	[µg/g]	6.57	0.09	6.67	0.1	5.72	0.09	10.92	0.11
Ho	[µg/g]	1.25	0.04	1.12	0.04	1.14	0.04	2.3	0.04
Tm	[µg/g]	1.69	0.07	1.99	0.08	2.08	0.08	2.13	0.08
Yb	[µg/g]	3.48	0.1	2.82	0.1	2.65	0.09	4.19	0.11
Lu	[µg/g]	0.47	0.01	0.39	0.01	0.41	0.01	0.58	0.01
Ta	[µg/g]	1.5	0.13	1.09	0.11	1.38	0.13	2.31	0.15
W	[µg/g]	3.63	0.14	4.41	0.17	3.56	0.15	3.83	0.14

(Continue)

		M-5	±	Mean	SD [n=5]	RSD [%]	Median	Min.	Max.
Na	[%]	0.918	0.004	0.979	0.046	4.7	0.972	0.918	1.029
Mg	[%]	1.35	0.06	1.41	0.12	8.8	1.43	1.24	1.58
Al	[%]	7.06	0.05	6.84	0.52	7.6	7.06	5.98	7.24
K	[%]	2.51	0.05	2.42	0.20	8.2	2.51	2.12	2.59
Ca	[%]	2.29	0.42	2.23	0.12	5.4	2.23	2.05	2.38
Sc	[µg/g]	12.2	0.1	11.2	1.3	11.7	11.9	9.1	12.2
Cr	[µg/g]	73.0	1.7	63.9	9.9	15.5	65.7	47.1	73.0
Mn	[µg/g]	630	9	601	56	9.3	630	504	637
Fe	[%]	3.33	0.06	3.16	0.40	12.6	3.33	2.50	3.51
Co	[µg/g]	13.9	0.4	12.5	1.7	13.9	13.1	9.7	13.9
Zn	[µg/g]	59.5	4.1	55.8	7.0	12.6	56.6	47.7	65.0
Ga	[µg/g]	25.6	0.8	21.6	3.4	15.8	22.0	16.7	25.6
As	[µg/g]	8.22	0.13	7.29	1.22	16.8	7.64	5.21	8.22
Br	[µg/g]	2.94	0.13	3.05	0.61	20.0	2.94	2.21	3.90
Sb	[µg/g]	0.767	0.024	0.704	0.079	11.3	0.719	0.567	0.767
Cs	[µg/g]	10.03	0.28	9.31	0.99	10.6	9.78	7.61	10.03
Ba	[µg/g]	544	24	507	52	10.3	528	423	548
Ce	[µg/g]	94.2	1.4	95.1	15.6	16.4	91.9	80.6	121.4
Nd	[µg/g]	37.4	1.2	40.0	9.0	22.4	37.4	30.8	54.8
Eu	[µg/g]	1.21	0.03	1.24	0.20	15.8	1.19	1.06	1.57
Tb	[µg/g]	0.82	0.05	0.97	0.25	25.4	0.87	0.82	1.40
Dy	[µg/g]	6.47	0.11	7.27	2.07	28.5	6.57	5.72	10.92
Ho	[µg/g]	1.27	0.04	1.42	0.50	35.1	1.25	1.12	2.30
Tm	[µg/g]	1.84	0.08	1.95	0.18	9.4	1.99	1.69	2.13
Yb	[µg/g]	3.05	0.11	3.24	0.61	19.0	3.05	2.65	4.19
Lu	[µg/g]	0.45	0.01	0.46	0.07	16.3	0.45	0.39	0.58
Ta	[µg/g]	1.57	0.15	1.57	0.45	28.8	1.50	1.09	2.31
W	[µg/g]	3.10	0.14	3.71	0.47	12.8	3.63	3.10	4.41

4.3.2 Geo-accumulation Index (Igeo)

Geochemical index (Igeo) originally stated by Muller (1969) in order to determine and define metal contamination in sediments by comparing current concentrations with preindustrial levels. To characterize the pollution levels of sediments, geo-accumulation index (Igeo) is an effective tool which can be defined by the following equation (Abrahim and Parker, 2008):

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

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

Class 0 (practically uncontaminated) : $Igeo \leq 0$
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 in Rupsha River where sample ID,

R-1 is moderately contaminated with As, Cs, Dy, Ho, Tm, W and Ta.

R-2 is moderately contaminated with Ce, Tb, Dy, Ho, Tm, W and Ta.

R-3 is moderately contaminated with Ga, As, Br, Cs, Dy, Tm and W.

R-4 is moderately contaminated with As, Br, Cs, Dy, Tm and W.

R-5 is moderately contaminated with Ga, As, Cs, Dy, Tm, W and Ta.

R-6 is moderately contaminated with Ga, Ce, Dy, Ho,Tm, W and Ta.

Only sample ID R-2 is heavily contaminated with Yb and the rest of the samples are practically uncontaminated.

Table 4.4 a indicates that from the sample location in Mongla River where sample ID,

M-1 is moderately contaminated with As, Br, Cs, Dy, Ho, Tm, Ty, Ta And W.

M-2 is moderately contaminated with As, Br, Cs, Dy, Tm, Yb And W.

M-3 is moderately contaminated with As, Br, Cs, Tm, Yb, Ta And W.

M-4 is moderately contaminated with Cs, Ce, Nd, Eu, Tb, Dy, Ho,Tm, Yb, Ta, and W.

M-5 is moderately contaminated with As, Br, Cs, Ce, Dy, Ho, Tm, Yb, Ta And W.

Only sample ID M-4 is heavily contaminated with Yb and the rest of the samples are practically uncontaminated.

Table 4.3 b and Table 4.4 b represents highest and lowest value of Igeo for Rupsha and Mongla sediment samples respectively.

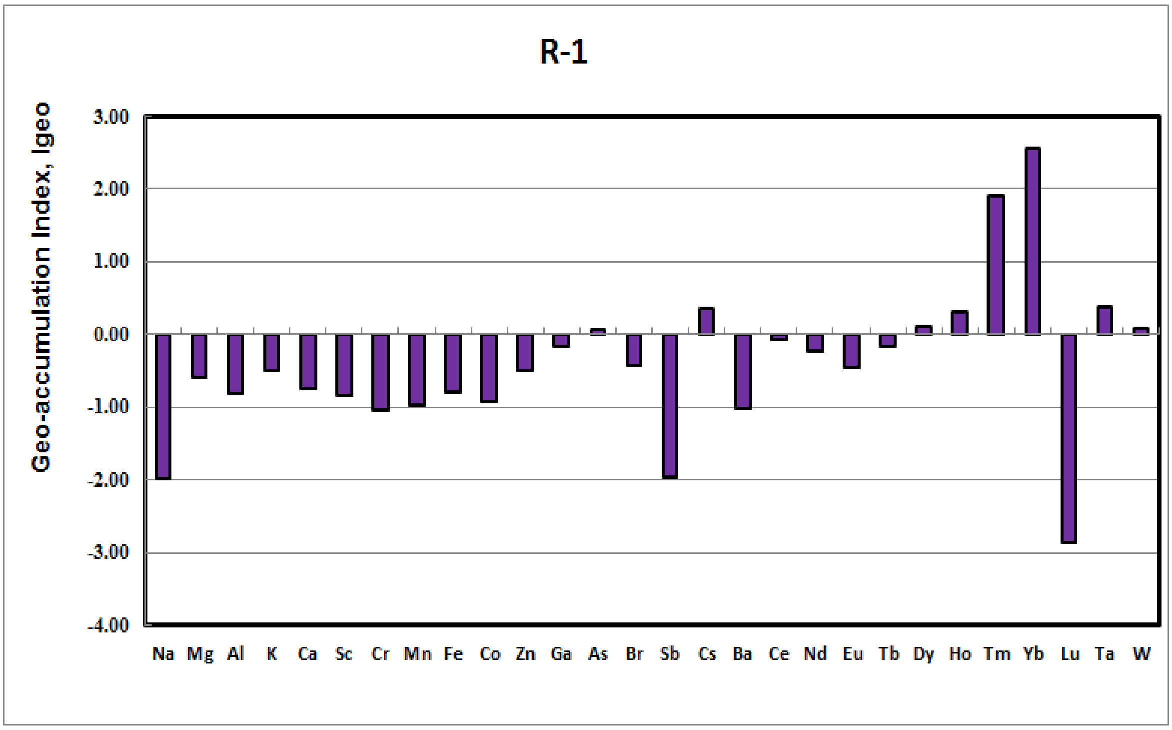
Using Table 4.3a we have got graphical representation of Geo-accumulation index (I_{geo}) for Rupsha River which is shown in Figure 4.1, Figure 4.2 and Figure 4.3
Similarly for Mongla River using Table 4.4a we have got graphical representation of Geo-accumulation index (I_{geo}) which is shown in Figure 4.4 and Figure 4.5

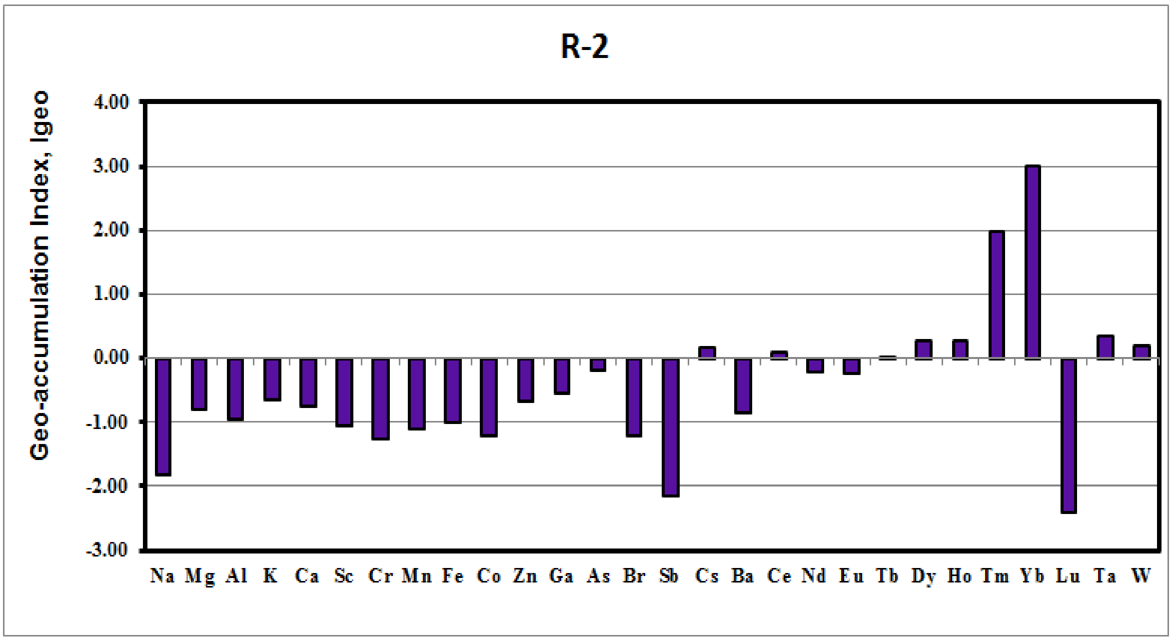
Table 4.3 a: Geo-accumulation index of elements in Rupsha River sediment samples

SL. No.		R-1	R-2	R-3	R-4	R-5	R-6
1	Na	-1.98	**-1.83**	-2.00	-1.96	**-2.045**	-2.02
2	Mg	-0.59	-0.79	-0.43	**-0.39**	-0.614	**-0.86**
3	Al	-0.82	-0.96	**-0.63**	-0.69	-0.760	**-1.04**
4	K	-0.50	-0.66	**-0.42**	-0.51	-0.672	**-0.92**
5	Ca	-0.76	-0.75	**-1.25**	-1.22	**-0.442**	-0.54
6	Sc	-0.83	-1.05	**-0.68**	-0.74	-0.992	**-1.21**
7	Cr	-1.05	-1.27	**-0.92**	-0.93	-1.203	**-1.50**
8	Mn	-0.98	-1.11	**-0.69**	-0.76	-0.889	**-1.16**
9	Fe	-0.80	-1.01	-0.70	**-0.69**	-0.783	**-1.32**
10	Co	-0.93	-1.21	**-0.86**	-0.92	-1.101	**-1.54**
11	Zn	-0.50	-0.68	**-0.41**	-1.18	**-1.384**	-1.15
12	Ga	-0.16	**-0.54**	0.01	-0.29	**0.708**	0.01
13	As	0.06	-0.18	0.28	0.24	**0.362**	**-0.54**
14	Br	-0.45	**-1.20**	**1.89**	1.87	-0.517	-0.08
15	Sb	-1.98	-2.16	-2.11	-2.02	**-1.964**	**-2.35**
16	Cs	0.36	0.18	**0.59**	0.47	0.245	**-0.11**
17	Ba	-1.02	-0.85	**-0.80**	-0.85	**-0.276**	-1.10
18	Ce	-0.07	**0.10**	-0.16	-0.13	**-0.150**	0.04
19	Nd	-0.23	-0.21	-0.21	-0.15	**-0.347**	**-0.10**
20	Eu	-0.46	**-0.24**	-0.45	-0.34	**-0.554**	-0.25
21	Tb	-0.16	**0.01**	**-0.46**	-0.27	-0.271	-0.20
22	Dy	**0.10**	0.26	0.11	0.19	0.141	**0.39**
23	Ho	**0.29**	0.28	-0.04	-0.14	**-0.196**	0.27
24	Tm	1.90	1.97	**2.32**	2.01	1.979	**1.88**
25	Yb	2.54	**3.00**	**2.47**	2.52	2.531	2.95
26	Lu	-2.86	**-2.42**	-2.84	-2.99	**-5.660**	-2.51
27	Ta	**0.38**	0.35	-0.04	**-0.03**	0.258	0.11
28	W	**0.07**	0.19	0.16	**0.23**	0.110	0.08

Table 4.3 b: Highest and lowest value of Igeo for Rupsha sediment Samples

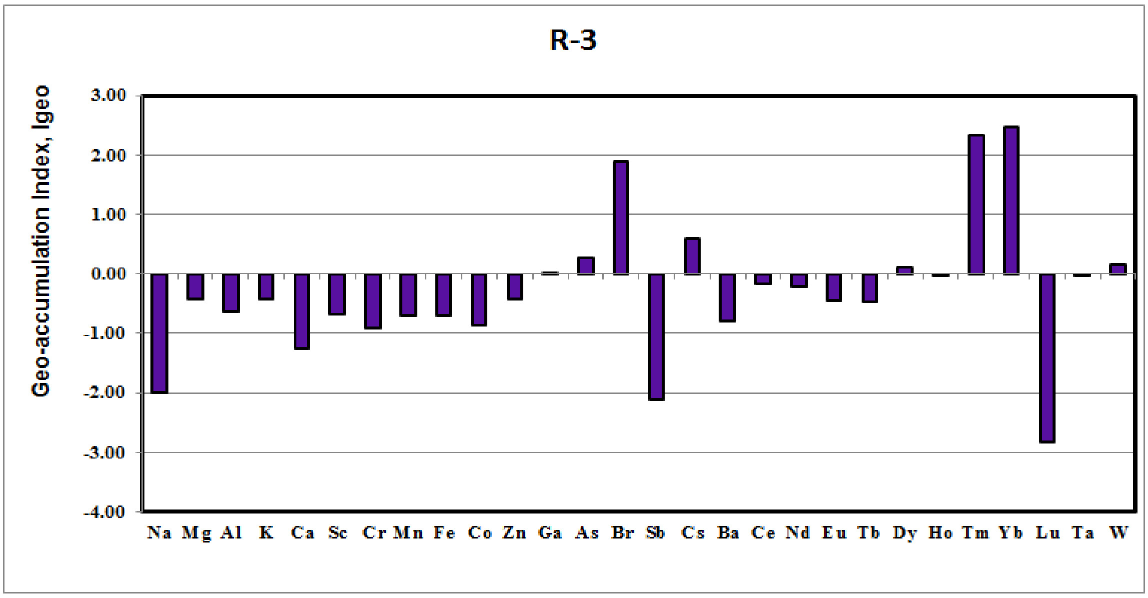
Elements	**Highest value**		**Lowest value**	
	Igeo	**Sample ID**	**Igeo**	**Sample ID**
Na	-1.83	R-2	-2.045	R-5
Mg	-0.39	R-4	-0.86	R-6
Al	-0.63	R-3	-1.04	R-6
K	-0.42	R-3	-0.92	R-6
Ca	-0.442	R-5	-1.25	R-3
Sc	-0.68	R-3	-1.21	R-6
Cr	-0.92	R-3	-1.50	R-6
Mn	-0.69	R-3	-1.16	R-6
Fe	-0.69	R-4	-1.32	R-6
Co	-0.86	R-3	-1.54	R-6
Zn	-0.41	R-3	-1.384	R-5
Ga	0.708	R-5	-0.54	R-2
As	0.362	R-5	-0.54	R-6
Br	1.89	R-3	-1.20	R-2
Sb	-1.964	R-5	-2.35	R-6
Cs	0.59	R-3	-0.11	R-6
Ba	-0.276	R-5	-0.80	R-3
Ce	0.10	R-2	-0.150	R-5
Nd	-0.10	R-6	-0.347	R-5
Eu	-0.24	R-2	-0.554	R-5
Tb	0.01	R-2	-0.46	R-3
Dy	0.39	R-6	0.10	R-1
Ho	0.29	R-1	0.29	R-5
Tm	2.32	R-3	1.88	R-6
Yb	3.00	R-2	2.47	R-3
Lu	-2.42	R-2	-5.660	R-5
Ta	0.38	R-1	-0.03	R-4
W	0.23	R-4	0.07	R-1

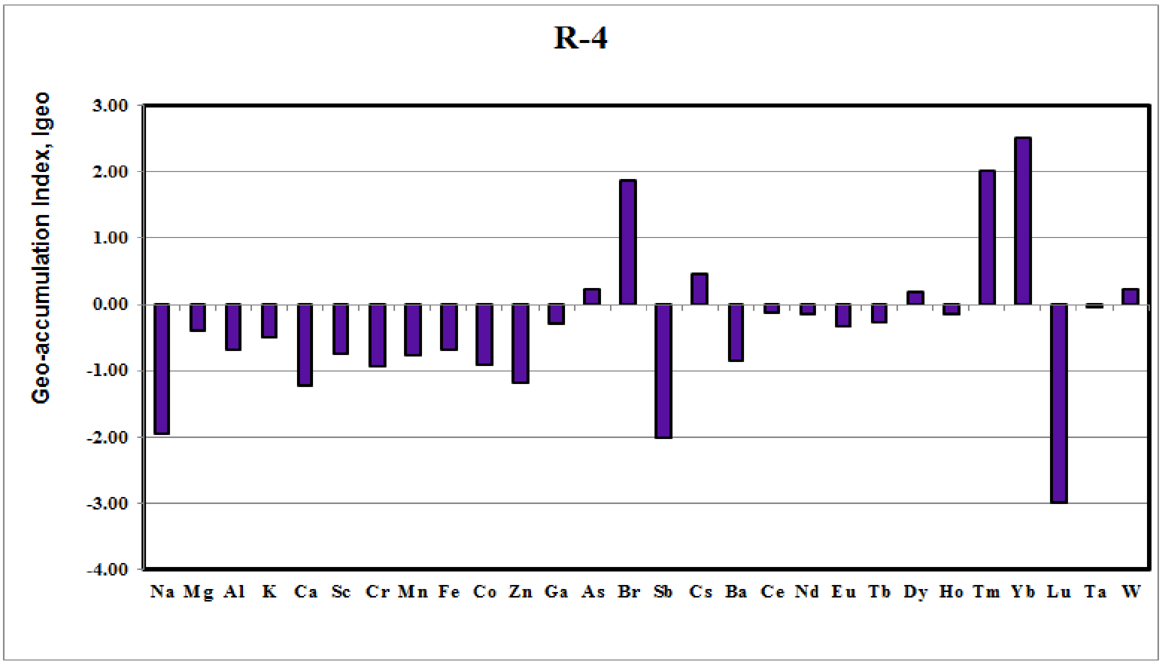




(Continue)

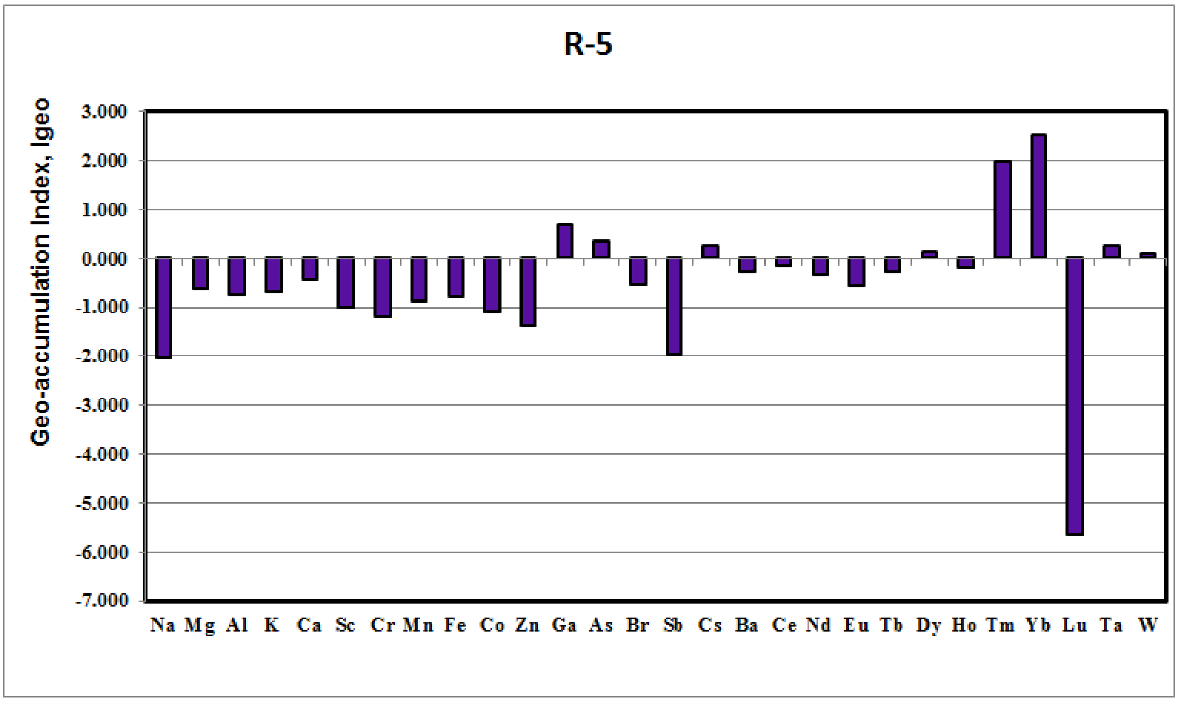
Figure 4.1: Geo-accumulation index (I_{geo}) for Sample No.1 (R-1) and Sample No.2 (R-2) sediments in Rupsha River.





(Continue)

Figure 4.2: Geo-accumulation index (I_{geo}) for Sample no.3 (R-3) and Sample no.4 (R-4) sediments in Rupsha River.



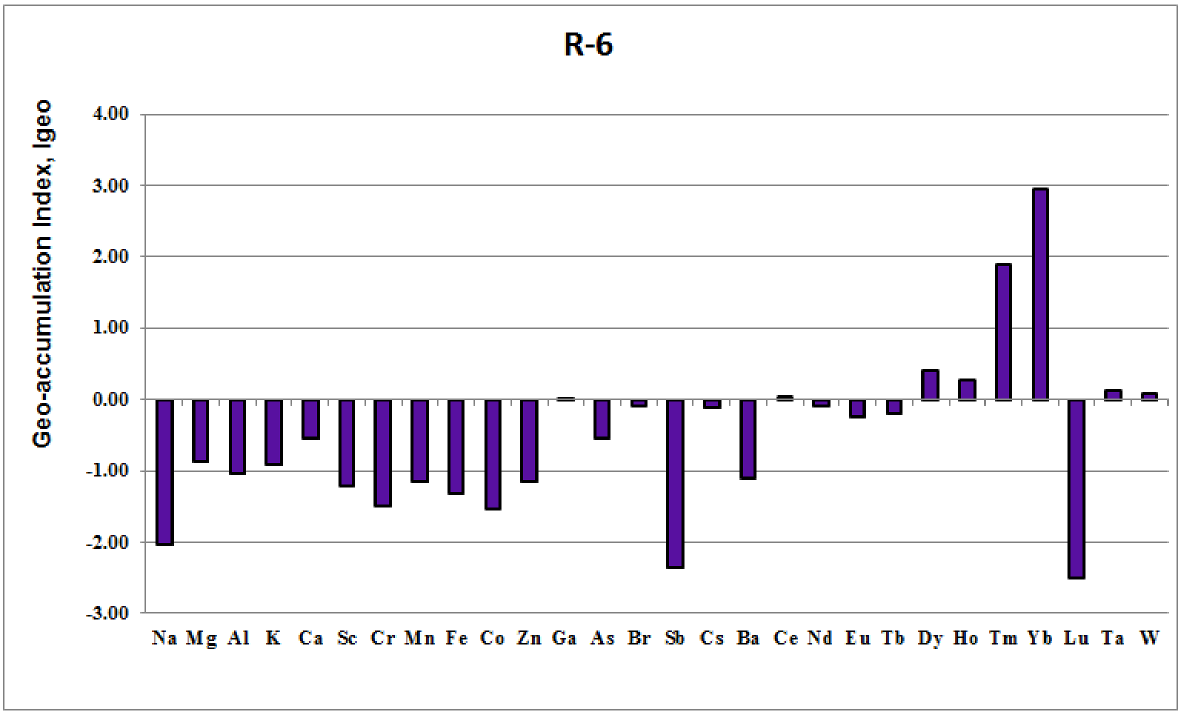


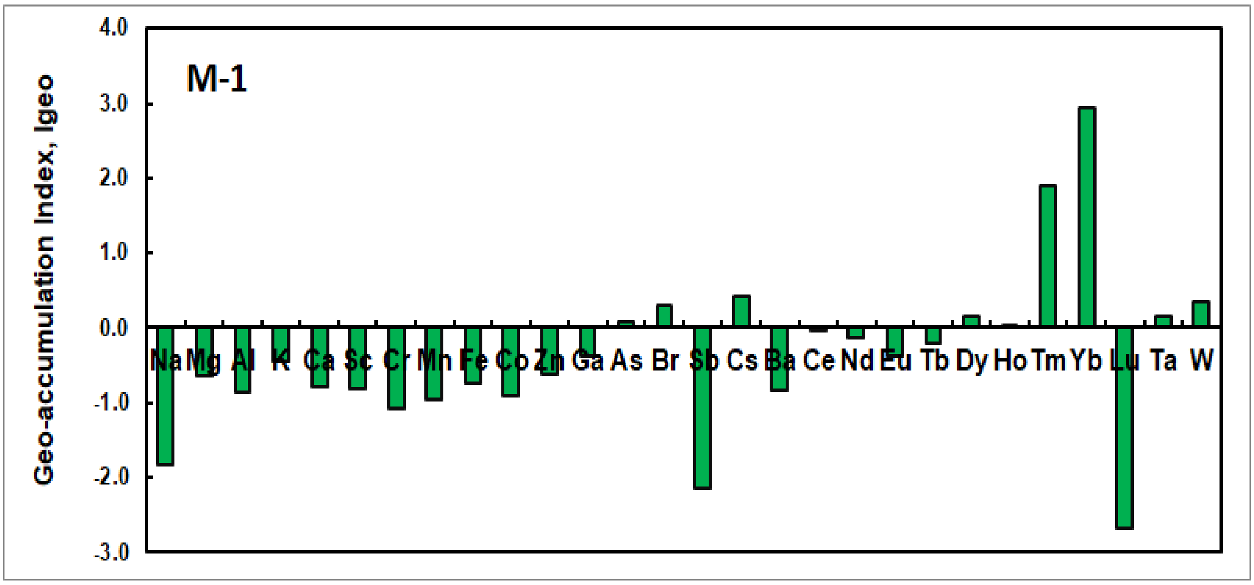
Figure 4.3: Geo-accumulation index (I_{geo}) for Sample No.5 (R-5) and Sample No.6 (R-6) sediments in Rupsha River.

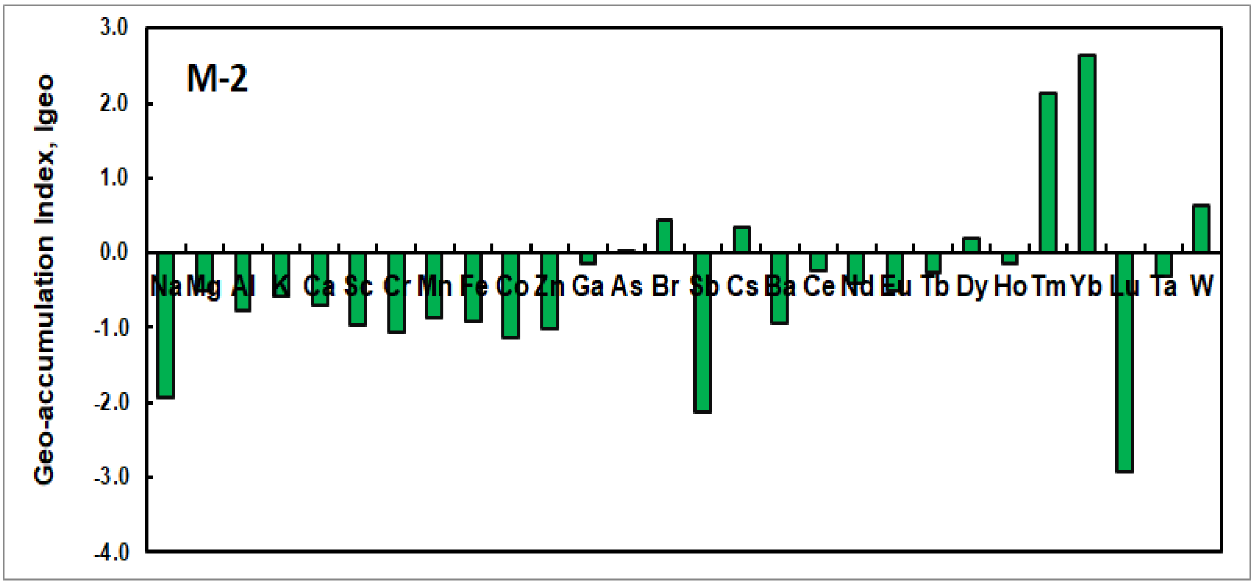
Table 4.4 a: Geo-accumulation index of elements in Mongla River sediment samples

Sl. No		M-1	M-2	M-3	M-4	M-5
1	Na	**-1.82**	-1.93	-1.91	-1.84	**-1.99**
2	Mg	-0.65	**-0.51**	-0.63	-0.86	**-0.73**
3	Al	-0.86	-0.77	**-0.76**	**-1.03**	-0.79
4	K	-0.45	-0.59	**-0.43**	**-0.72**	-0.47
5	Ca	-0.79	**-0.70**	**-0.91**	-0.80	-0.75
6	Sc	-0.82	-0.96	-0.81	**-1.21**	**-0.79**
7	Cr	-1.08	-1.07	-1.01	**-1.55**	**-0.92**
8	Mn	-0.95	**-0.87**	-0.88	**-1.21**	-0.88
9	Fe	**-0.74**	-0.93	-0.80	**-1.23**	-0.82
10	Co	-0.92	-1.13	-0.99	**-1.41**	**-0.90**
11	Zn	**-0.63**	-1.00	-0.83	**-1.08**	-0.76
12	Ga	**-0.38**	-0.14	-0.25	-0.65	**-0.04**
13	As	0.09	0.01	0.17	**-0.47**	**0.19**
14	Br	0.29	0.44	**0.70**	**-0.12**	0.29
15	Sb	-2.14	-2.13	-2.07	**-2.47**	**-2.04**
16	Cs	0.41	0.34	0.42	**0.05**	**0.45**
17	Ba	-0.83	-0.93	-0.77	**-1.15**	**-0.78**
18	Ce	**-0.04**	-0.23	-0.11	**0.36**	**0.00**
19	Nd	-0.14	**-0.40**	-0.02	**0.44**	-0.12
20	Eu	-0.37	-0.50	-0.33	**0.07**	**-0.30**
21	Tb	**-0.22**	-0.27	-0.32	**0.42**	-0.36
22	Dy	0.17	0.19	**-0.03**	**0.90**	0.14
23	Ho	0.01	**-0.15**	-0.12	**0.89**	0.03
24	Tm	**1.90**	2.15	2.21	**2.25**	2.03
25	Yb	2.95	2.65	**2.56**	**3.22**	2.76
26	Lu	-2.67	**-2.93**	-2.88	**-2.36**	-2.74
27	Ta	0.15	**-0.31**	0.03	**0.77**	0.22
28	W	0.35	**0.63**	0.32	0.43	**0.12**

Table 4.4 b: Highest and lowest value of Igeo for Mongla sediments Samples

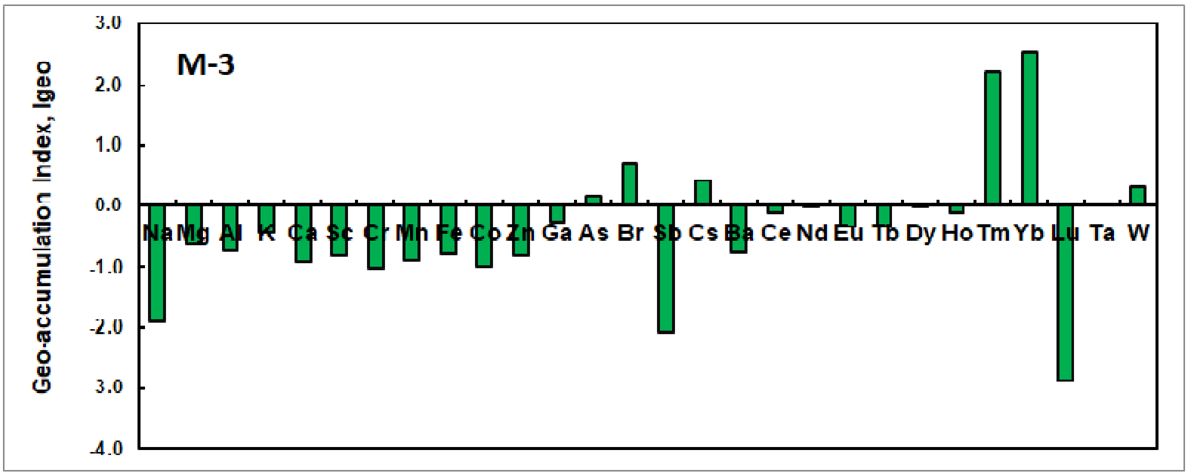
Elements	**Highest value**		**Lowest value**	
	Igeo	**Sample ID**	**Igeo**	**Sample ID**
Na	-1.82	M-1	-1.99	M-5
Mg	-0.51	M-2	-0.73	M-5
Al	-0.76	M-3	-1.03	M-4
K	-0.43	M-3	-0.72	M-4
Ca	-0.70	M-2	-0.91	M-3
Sc	-0.79	M-5	-1.21	M-4
Cr	-0.92	M-5	-1.55	M-4
Mn	-0.87	M-2	-1.21	M-4
Fe	-0.74	M-1	-1.23	M-4
Co	-0.90	M-5	-1.41	M-4
Zn	-0.63	M-1	-1.08	M-4
Ga	-0.04	M-5	-0.38	M-1
As	0.19	M-5	-0.47	M-4
Br	0.70	M-3	-0.12	M-4
Sb	-2.04	M-5	-2.47	M-4
Cs	0.45	M-5	0.05	M-4
Ba	-0.78	M-5	-1.15	M-4
Ce	0.36	M-4	-0.04	M-1
Nd	0.44	M-4	-0.40	M-2
Eu	0.07	M-4	-0.30	M-5
Tb	0.42	M-4	-0.22	M-1
Dy	0.90	M-4	-0.03	M-3
Ho	0.89	M-4	-0.15	M-2
Tm	2.25	M-4	1.90	M-1
Yb	3.22	M-4	2.56	M-3
Lu	-2.36	M-4	-2.93	M-2
Ta	0.77	M-4	-0.31	M-2
W	0.63	M-2	0.12	M-5

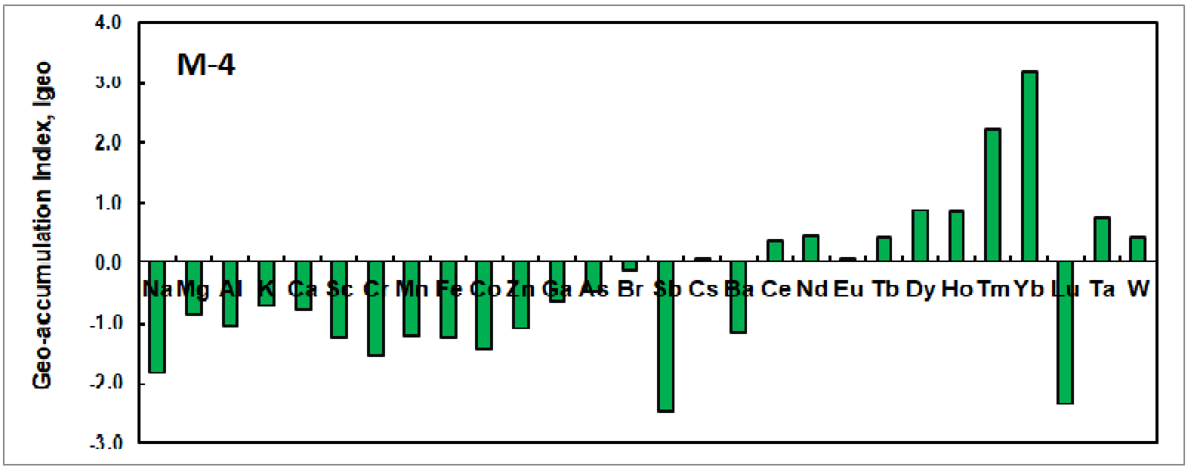




(Continue)

Figure 4.4: Geo-accumulation index (I_{geo}) for Sample No.1 (M-1) and Sample No.2 (M-2) sediments in Mongla River.





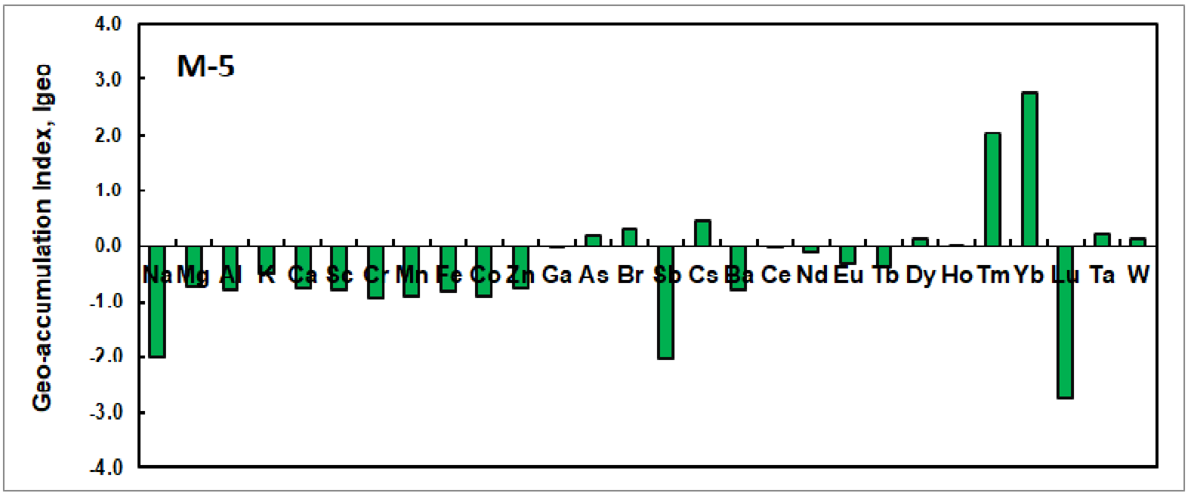


Figure 4.5: Geo-accumulation index (I_{geo}) for Sample No.3 (M-3), Sample No.4 (M-4) and Sample No.5 (M-5) sediments in Mongla River.

4.3.3 Enrichment Factor (EF)

A common approach to estimate the anthropogenic impact on soil 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:

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

In this study, iron (Fe) has been 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 EF values close to unity indicate crusted origin, those less than 1.0 suggest a possible mobilization or depletion of metals (Zsefer, 1996), whereas EF >1.0 indicates that the element is of anthropogenic origin. EF values 1.5-3, 3-5, 5-10 and >10 are the evidence of minor, moderate, severe and very severe modification respectively (Brich and Olmos, 2008).

Enrichment Factor (EF) for the Rupsha and Mongla river sediments are given below in the Table 4.5a and Table 4.5b respectively.

From Table 4.5a it shows that Br, Tm, Yb are the evidence of minor and rest of the elements are from possible mobilization or depletion of metals.

Similarly, Table 4.5b represents that Tm is the evidence of minor where Yb is the evidence of both minor and moderate and rest of the elements are from possible mobilization or depletion of metals.

Using Table 4.5a and Table 4.5b we have got the graphical representation of Enrichment Factor for Rupsha River and Mongla River respectively which shown in Figure 4.6 and Figure 4.7 respectively.

Table 4.5 a: Enrichment Factor of elements in Rupsha sediment samples

SL. No		R-1	R-2	R-3	R-4	R-5	R-6
1	Na	0.443	0.565	0.407	0.416	0.417	0.616
2	Mg	1.157	1.161	1.205	1.235	1.125	1.378
3	Al	0.987	1.036	1.051	1.004	1.017	1.218
4	K	1.236	1.271	1.216	1.138	1.081	1.321
5	Ca	1.030	1.198	0.682	0.696	1.267	1.718
6	Sc	0.982	0.971	1.017	0.970	0.866	1.084
7	Cr	0.841	0.831	0.862	0.847	0.747	0.883
8	Mn	0.885	0.932	1.006	0.951	0.929	1.124
9	Fe	1.000	1.000	1.000	1.000	1.000	1.000
10	Co	0.915	0.866	0.899	0.852	0.802	0.860
11	Zn	1.238	1.254	1.223	0.715	0.659	1.129
12	Ga	1.560	1.382	1.642	1.324	2.811	2.530
13	As	1.817	1.777	1.973	1.906	2.212	1.718
14	Br	1.280	0.874	6.017	5.917	1.203	2.362
15	Sb	0.444	0.448	0.377	0.399	0.441	0.492
16	Cs	2.243	2.273	2.452	2.233	2.040	2.324
17	Ba	0.860	1.111	0.935	0.895	1.422	1.170
18	Ce	1.661	2.154	1.454	1.474	1.551	2.568
19	Nd	1.489	1.734	1.407	1.454	1.354	2.337
20	Eu	1.273	1.703	1.187	1.275	1.172	2.102
21	Tb	1.561	2.017	1.183	1.339	1.426	2.174
22	Dy	1.876	2.409	1.750	1.842	1.898	3.289
23	Ho	2.141	2.442	1.583	1.467	1.503	3.016
24	Tm	6.507	7.867	8.137	6.502	6.784	9.247
25	Yb	10.169	16.039	9.038	9.275	9.947	19.380
26	Lu	0.241	0.375	0.228	0.203	0.034	0.440
27	Ta	2.267	2.559	1.588	1.577	2.058	2.711
28	W	1.835	2.290	1.816	1.899	1.858	2.647

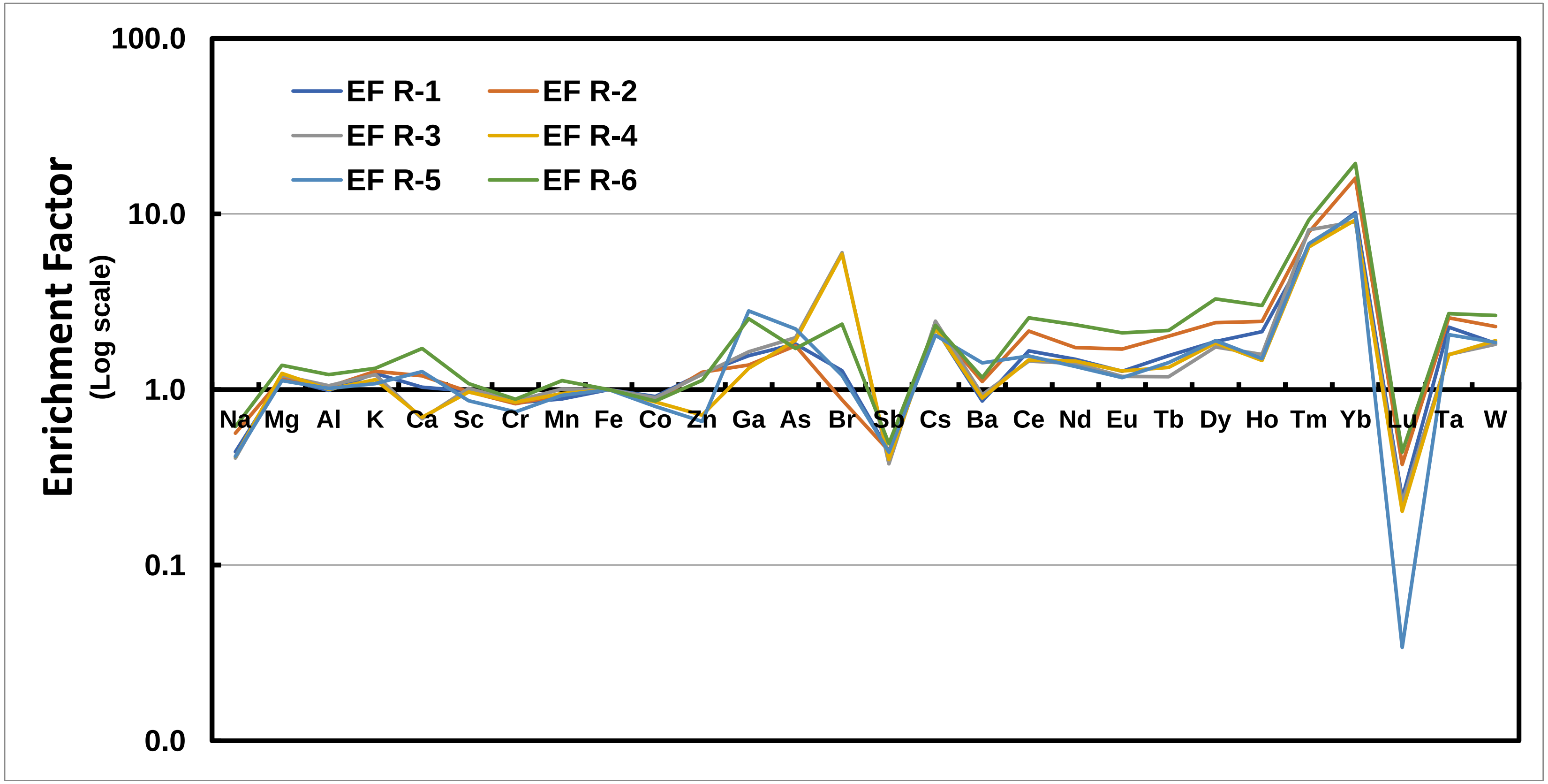


Figure 4.6: Enrichment factor (EF) for sediment samples in Rupsha.

Table 4.5 b: Enrichment Factor of elements in Mongla sediment samples

SL. No.		M-1	M-2	M-3	M-4	M-5
1	Na	0.472	0.499	0.465	0.657	0.445
2	Mg	1.064	1.334	1.129	1.299	1.062
3	Al	0.924	1.117	1.033	1.150	1.020
4	K	1.226	1.265	1.296	1.430	1.274
5	Ca	0.969	1.173	0.927	1.353	1.048
6	Sc	0.950	0.975	0.996	1.015	1.025
7	C	0.792	0.904	0.865	0.802	0.935
8	Mn	0.867	1.041	0.948	1.019	0.958
9	Fe	1.000	1.000	1.000	1.000	1.000
10	Co	0.887	0.866	0.878	0.883	0.950
11	Zn	1.082	0.948	0.983	1.115	1.046
12	Ga	1.283	1.725	1.461	1.496	1.721
13	As	1.776	1.916	1.962	1.701	2.017
14	Br	2.046	2.574	2.833	2.166	2.163
15	Sb	0.380	0.433	0.415	0.423	0.430
16	Cs	2.227	2.404	2.335	2.435	2.412
17	Ba	0.944	0.994	1.021	1.062	1.027
18	Ce	1.627	1.621	1.614	3.020	1.762
19	Nd	1.522	1.443	1.723	3.179	1.631
20	Eu	1.298	1.340	1.387	2.468	1.431
21	Tb	1.438	1.576	1.393	3.140	1.380
22	Dy	1.880	2.166	1.705	4.387	1.954
23	Ho	1.686	1.709	1.600	4.346	1.809
24	Tm	6.266	8.407	8.064	11.145	7.231
25	Yb	12.921	11.923	10.266	21.876	11.977
26	Lu	0.263	0.250	0.237	0.457	0.265
27	Ta	1.855	1.537	1.783	4.022	2.053
28	W	2.130	2.939	2.177	3.159	1.924

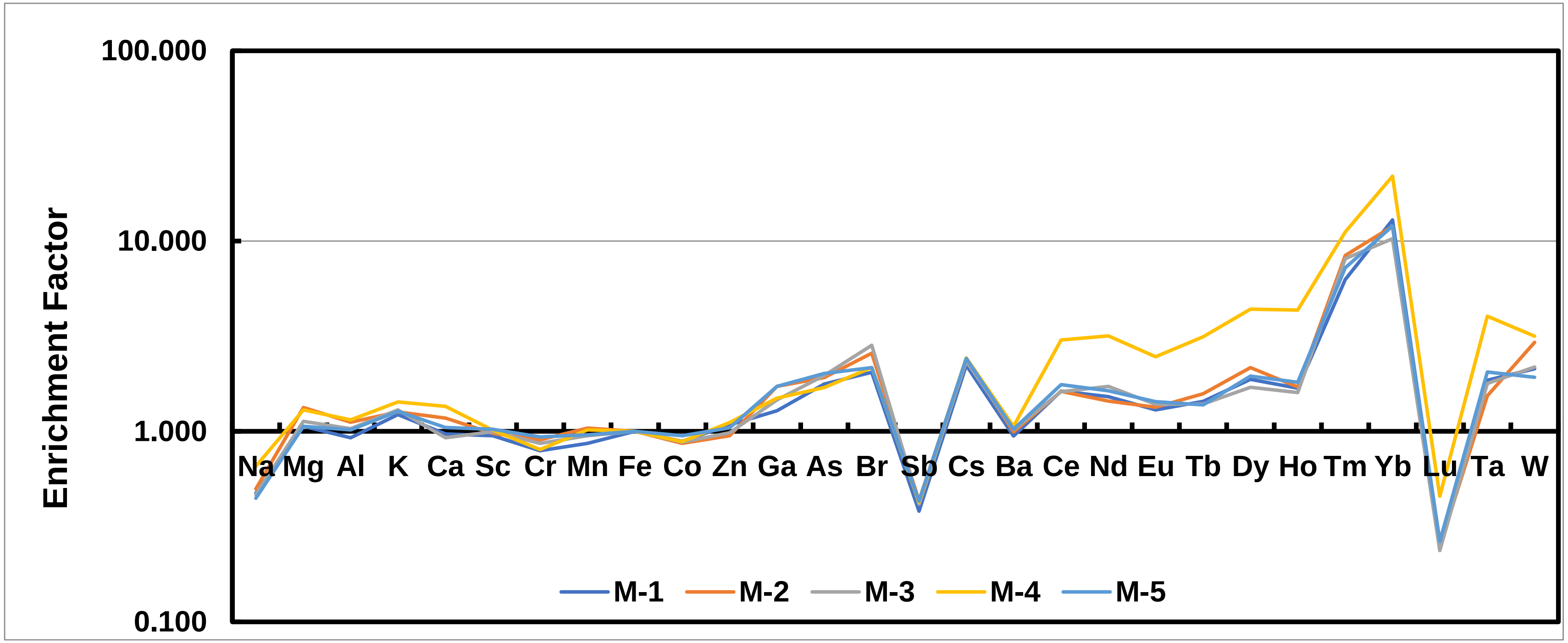


Figure 4.7: Enrichment factor of the individual elements (relative to the upper continental crust and Fe) are plotted for the Mongla River sediments

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):

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

Then, according to Tomlinson et al., (1980) PLI is represented by the following equation:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots\ldots\ldots\ldots \times CF_n)^{1/n} \ldots\ldots\ldots\ldots(4.3)$$

Where, CF = Contamination Factors, n = the total number of contamination factors, C metal = metal concentration in polluted elements and C background value = background value of that metal. It has been considered five highest CFs for calculating the pollution load index (Tomlinson, 1980). PLI value 1 (one) indicates the presence of only baseline levels of pollutants while values above 1 (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 Rupsha and Mongla rivers sediment sample are given below in the Table 4.6 a and 4.6 b respectively. For Rupsha River Sediments Mg, K Ca, Zn, Ga, As, Br, Cs, Ce, Nd, Eu, Tb, Dy, Ho, Tm, Yb, Ta and W are the highly polluted elements, where the other elements are not polluted. In the same way for Mongla River Sediments Mg, K, Zn, Ga, As, Br, Cs, Ce, Nd, Eu, Tb, Dy, Ho, Tn, Yb, Ta and W are the highly polluted elements, where the other elements are not polluted. Using Table 4.6a we have got the graphical representation of Pollution Load Index for Rupsha River which is shown in Figure 4.8 and here we can see the mean value is 1.119 which is above 1 that means Rupsha River is polluted. Similarly, Using Table 4.6b we have got the graphical representation of Pollution Load Index for Mongla River which is shown in Figure 4.9 and here the mean value is 1.154 which is also above 1 that means Mongla River is also polluted.

Table 4.7 a and Table 4.7 b represents inter-element correlation matrix for the sediment samples collected from Rupsha River Mongla River respectively.

Table 4.6 a: Pollution loaded index in Rupsha River sediment samples

SL. No		R-1	R-2	R-3	R-4	R-5	R-6	Mean	SD
1	Na	0.380	0.422	0.375	0.386	0.363	0.369		
2	Mg	0.994	0.867	1.111	1.147	0.980	0.825		
3	Al	0.848	0.773	0.969	0.932	0.886	0.729		
4	K	1.061	0.949	1.121	1.057	0.942	0.791		
5	Ca	0.885	0.894	0.629	0.646	1.104	1.029		
6	Sc	0.843	0.725	0.938	0.900	0.754	0.649		
7	Cr	0.722	0.620	0.795	0.786	0.651	0.529		
8	Mn	0.760	0.696	0.928	0.883	0.810	0.673		
9	Fe	0.859	0.747	0.922	0.929	0.871	0.599		
10	Co	0.786	0.647	0.829	0.791	0.699	0.515		
11	Zn	1.064	0.936	1.127	0.664	0.575	0.676		
12	Ga	1.340	1.032	1.514	1.229	2.450	1.515		
13	As	1.561	1.327	1.819	1.770	1.928	1.029		
14	Br	1.100	0.653	5.547	5.494	1.049	1.414		
15	Sb	0.382	0.335	0.348	0.371	0.385	0.295		
16	Cs	1.927	1.697	2.261	2.073	1.778	1.391		
17	Ba	0.739	0.829	0.862	0.831	1.239	0.701		
18	Ce	1.427	1.608	1.341	1.369	1.352	1.538		
19	Nd	1.279	1.295	1.297	1.350	1.180	1.399		
20	Eu	1.094	1.272	1.095	1.184	1.021	1.259		
21	Tb	1.341	1.506	1.091	1.243	1.243	1.302		
22	Dy	1.611	1.799	1.613	1.711	1.654	1.969		
23	Ho	1.840	1.823	1.459	1.362	1.309	1.806		
24	Tm	5.590	5.874	7.502	6.037	5.912	5.537		
25	Yb	8.736	11.975	8.332	8.612	8.669	11.605		
26	Lu	0.207	0.280	0.210	0.188	0.030	0.264		
27	Ta	1.948	1.911	1.464	1.464	1.793	1.623		
28	W	1.576	1.710	1.674	1.763	1.619	1.585		
	PLI	1.130	1.093	1.222	1.181	1.048	1.040	1.119	0.073

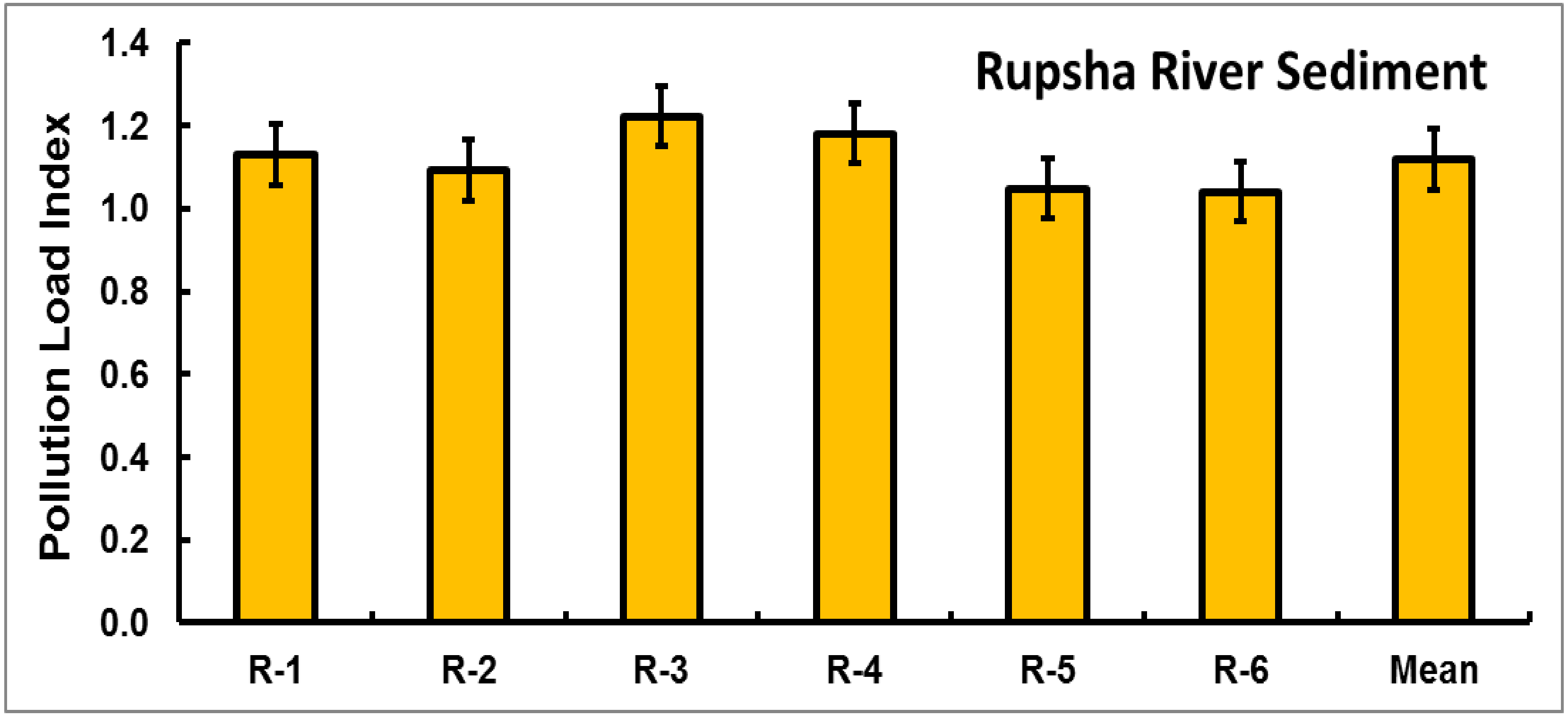


Figure 4.8: Pollution Loaded Index (PLI) for sediment samples in Rupsha River

Table 4.6 b: Pollution loaded index in Mongla River sediment samples

SL. No.		M-1	M-2	M-3	M-4	M-5	Mean	SD
1	Na	0.423	0.394	0.400	0.419	0.378		
2	Mg	0.954	1.053	0.971	0.829	0.902		
3	Al	0.829	0.882	0.889	0.734	0.866		
4	K	1.099	0.999	1.115	0.912	1.081		
5	Ca	0.869	0.926	0.797	0.864	0.890		
6	Sc	0.851	0.770	0.857	0.647	0.870		
7	Cr	0.710	0.714	0.744	0.512	0.794		
8	Mn	0.777	0.822	0.815	0.651	0.813		
9	Fe	0.896	0.790	0.860	0.638	0.849		
10	Co	0.795	0.684	0.755	0.564	0.806		
11	Zn	0.970	0.749	0.845	0.711	0.887		
12	Ga	1.150	1.362	1.257	0.955	1.460		
13	As	1.592	1.513	1.688	1.085	1.712		
14	Br	1.834	2.033	2.437	1.382	1.836		
15	Sb	0.341	0.342	0.357	0.270	0.365		
16	Cs	1.996	1.898	2.009	1.554	2.047		
17	Ba	0.846	0.785	0.878	0.678	0.872		
18	Ce	1.458	1.280	1.389	1.927	1.495		
19	Nd	1.364	1.140	1.483	2.029	1.385		
20	Eu	1.164	1.058	1.193	1.575	1.215		
21	Tb	1.289	1.244	1.199	2.004	1.171		
22	Dy	1.685	1.711	1.467	2.799	1.658		
23	Ho	1.511	1.350	1.376	2.773	1.536		
24	Tm	5.617	6.639	6.938	7.112	6.138		
25	Yb	11.583	9.416	8.832	13.960	10.166		
26	Lu	0.235	0.197	0.204	0.292	0.225		
27	Ta	1.663	1.214	1.534	2.567	1.743		
28	W	1.909	2.321	1.873	2.016	1.633		
	PLI	1.166	1.114	1.158	1.161	1.173	1.154	0.0S23

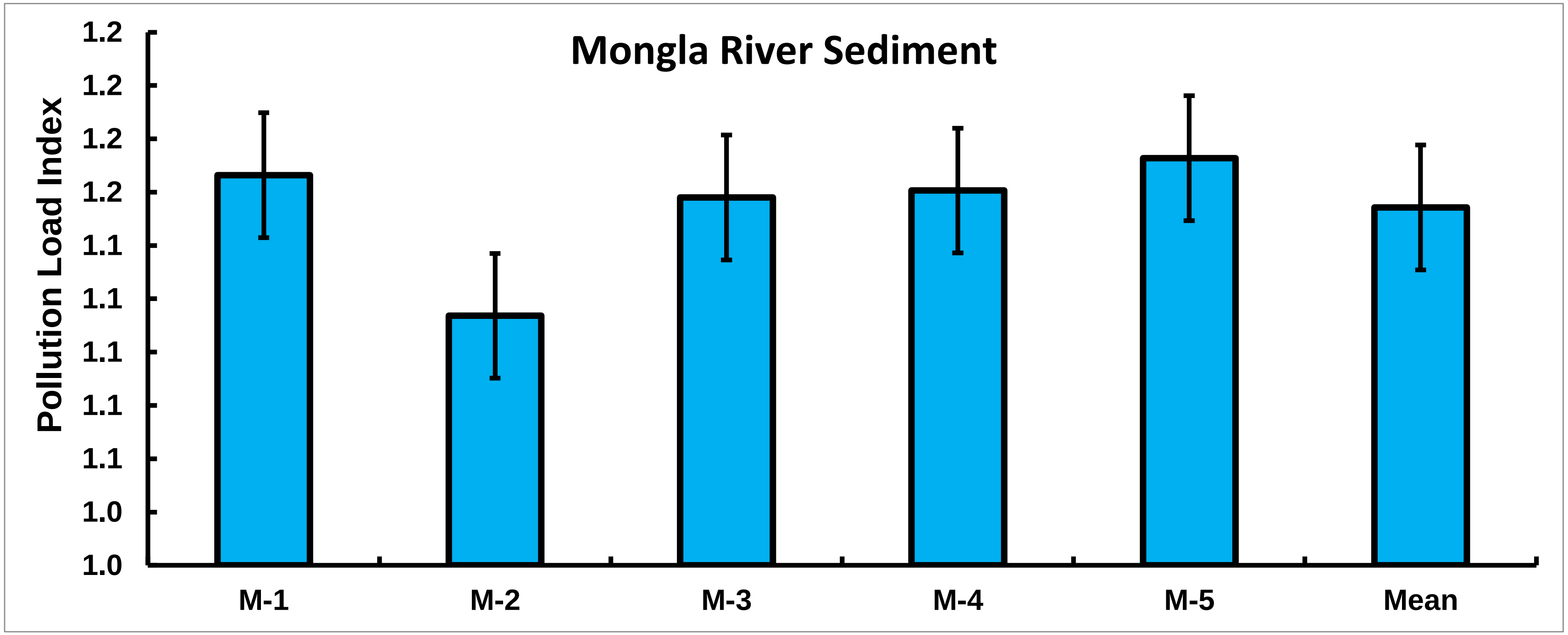


Figure 4.9: Pollution Loaded Index (PLI) for sediment samples in Mongla River.

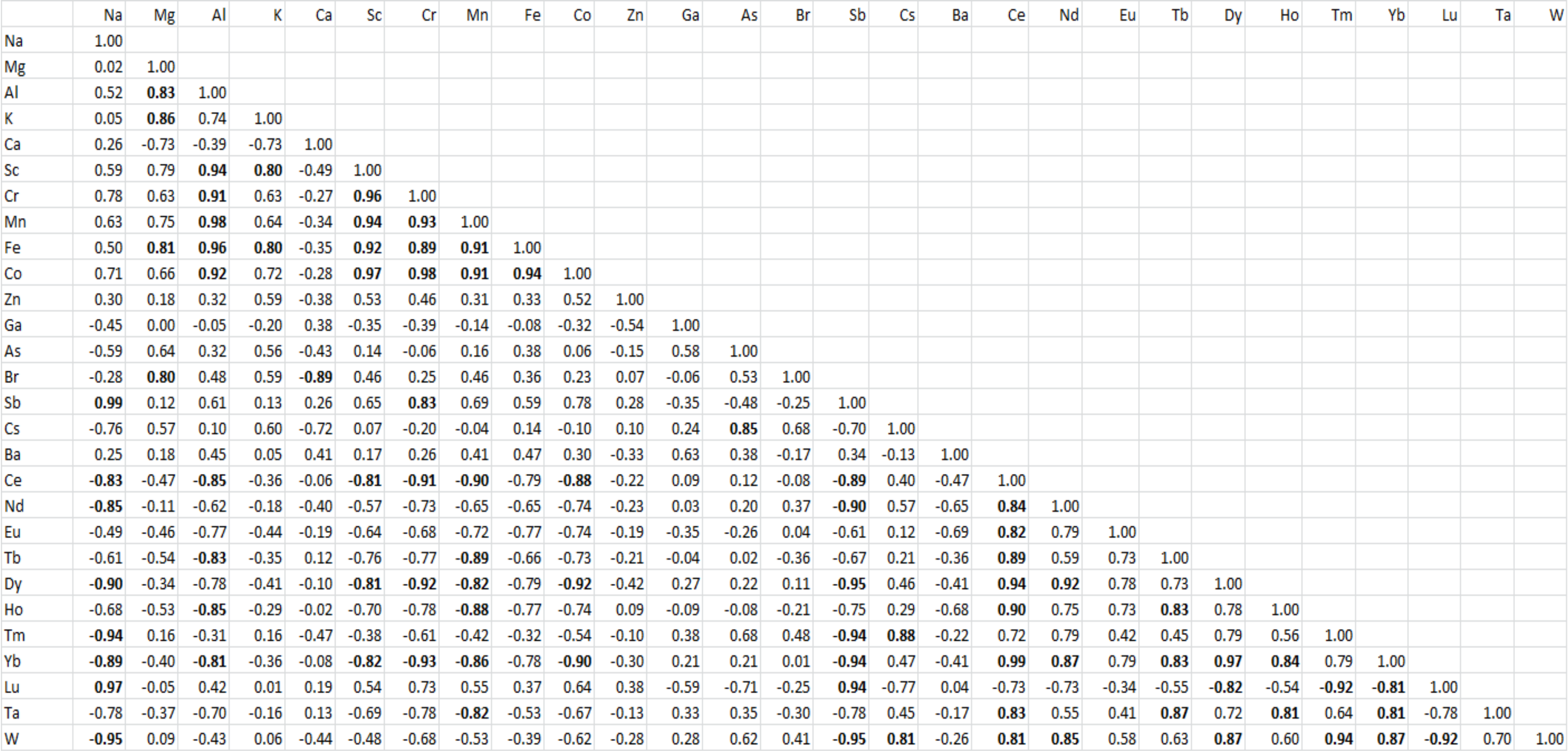
4.3.5 Inter-element Correlation and the Sediment Responses towards the Contaminants

For establishing a relationship among elements, determine the common source (and/or carrier substances) of metals (Datta and Subramanian, 1998) and to discuss the sediments response towards the anthropogenic contaminants in Rupsha, a correlation (r - value) matrix was calculated for the elements in the sediments (Table 4.7 a). Some elements 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) have poor correlation. Majority of elements show very poor correlation with Ca, K, Zn and As. that indicate the presence of carbonate and organic fraction and K-Zn oxy-hydroxides have an insignificant influence on accumulation of heavy metals (Datta and Subramanian, 1998). However Sc (r = 0.94), Cr (r = 0.91), Mn (r = 0.98), Fe (r = 0.96), Co (r = 0.92), Ce (r = -o.85), Tb (r = -0.83), Ho (r = -0.85) and Yb (r = -0.81). Our sampling site is very minutely modified by the Zn contamination. Thus, Zn, Al, K, Sc, Cr, Co, As, Sb and Cs seem to have similar mineralogical and (or) anthropogenic source(s) of origin. Sodium shows almost no or anti-correlation with most of the elements (in correlation table). Cr shows a good correlation with Mn (r = 0.93), Fe (r = 0.89), Co (r =0.98), Sb (r =0.83), Ce (r = -0.91), Dy (r = 0.92) and Yb (r = -0.93).

Similarly, the sediments response towards the anthropogenic contaminants in Mongla, a correlation (r - value) matrix was calculated for the elements in the sediments (Table 4.7 b). Poor correlations of some elements 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). In Table 4.7 b, a majority of elements show very poor correlation with Ca, K and Zn, that indicate the presence of carbonate and organic fraction and K-Zn oxy-hydroxides have an insignificant influence on accumulation of heavy metals (Datta and Subramanian, 1998). However Sc (r = .90), Cr (r =.96), Mn (r = .99), Fe (r = .87), Co (r = 0.44), Zn (r = 0.64), Sb (r = 0.82), Ba (r = 0.92), Ce (r = -0.97), Nd (r = -0.89), Eu (r = -0.89), Tb (r = - 0.90), Dy (r = -0.95), Ho (r = -0.91), Yb (r = -0.96), Ta (r = -0.93) show good correlation with Al suggesting their accumulation in association with clays. The environmental contamination, urban sludge and industrial waste (e.g., Tamim, 2016) are considered to be the major source of Cr and Zn. Zinc has negative correlation with Tm (-0.74), w (-0.75), Dy (-0.74), Tb (-0.71), Ce (-0.64) and Ba (0.86). Fe has a correlation with Co (r = 0.96), Zn (r = 0.92), Ba (r = 0.97), Ce (r = -0.96), Nd (r = -0.83), Eu (r = -0.85), Tb (r = - 0.91), Dy (r = -0.95), Ho (r = -.90), Yb (r = -0.81) and Ta (r = -0.82).

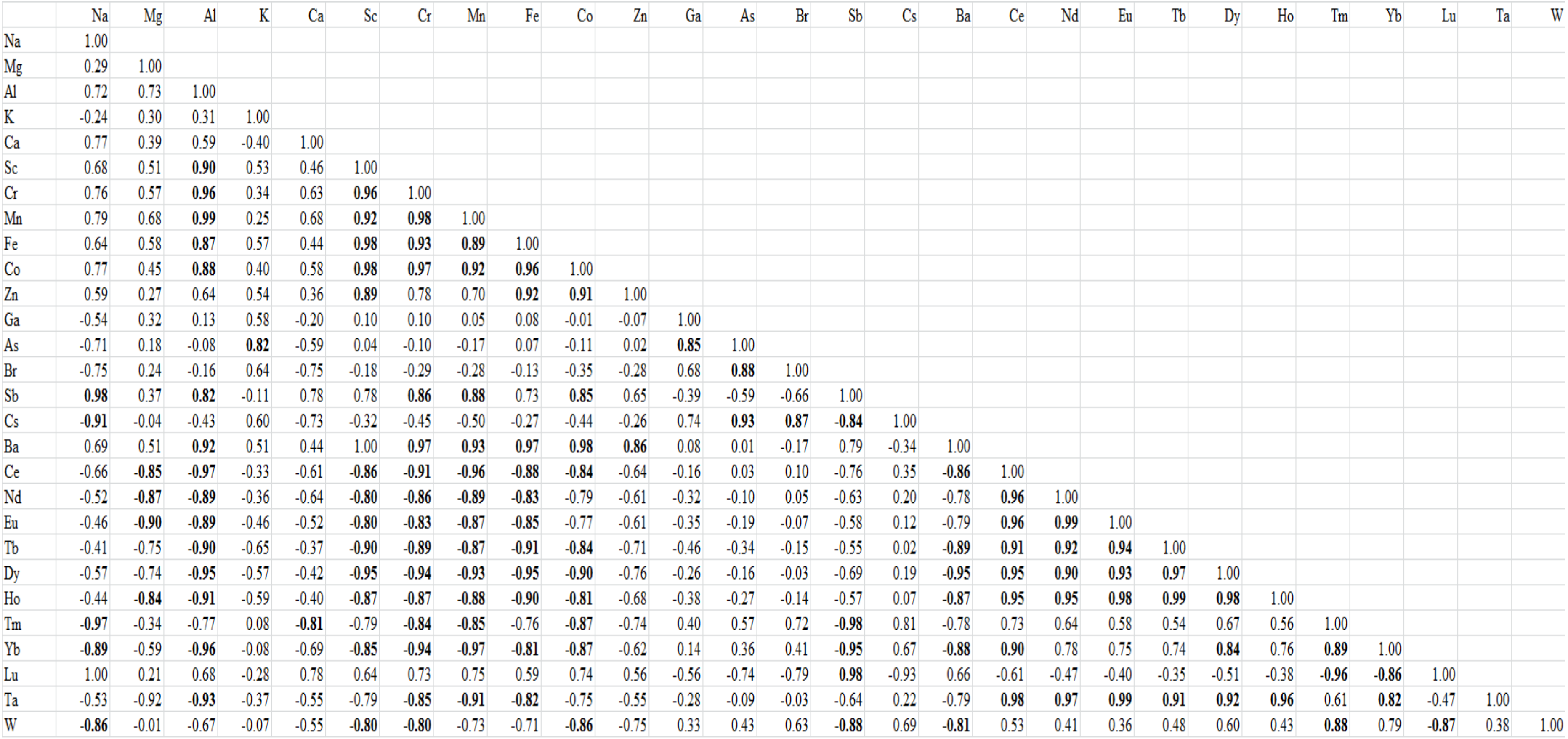
Regarding the environmental contamination, urban sludge and industrial waste (e.g., Tamim, 2016) are considered to be the major source of Cr and Zn. Our sampling site is very minutely modified by the Zn contamination. Thus, Zn, Al, K, Sc, Cr, Co, As, Sb and Cs seem to have similar mineralogical and (or) anthropogenic source(s) of origin. Sodium shows almost no or anti-correlation with most of the elements (in correlation table).

Table 4.7 a: Inter-element correlation matrix for the sediment samples collected from Rupsha 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	0.02	1.00																										
Al	0.52	**0.83**	1.00																									
K	0.05	**0.86**	0.74	1.00																								
Ca	0.26	-0.73	-0.39	-0.73	1.00																							
Sc	0.59	0.79	**0.94**	**0.80**	-0.49	1.00																						
Cr	0.78	0.63	**0.91**	0.63	-0.27	**0.96**	1.00																					
Mn	0.63	0.75	**0.98**	0.64	-0.34	**0.94**	**0.93**	1.00																				
Fe	0.50	**0.81**	**0.96**	**0.80**	-0.35	**0.92**	**0.89**	**0.91**	1.00																			
Co	0.71	0.66	**0.92**	0.72	-0.28	**0.97**	**0.98**	**0.91**	**0.94**	1.00																		
Zn	0.30	0.18	0.32	0.59	-0.38	0.53	0.46	0.31	0.33	0.52	1.00																	
Ga	-0.45	0.00	-0.05	-0.20	0.38	-0.35	-0.39	-0.14	-0.08	-0.32	-0.54	1.00																
As	-0.59	0.64	0.32	0.56	-0.43	0.14	-0.06	0.16	0.38	0.06	-0.15	0.58	1.00															
Br	-0.28	**0.80**	0.48	0.59	**-0.89**	0.46	0.25	0.46	0.36	0.23	0.07	-0.06	0.53	1.00														
Sb	**0.99**	0.12	0.61	0.13	0.26	0.65	**0.83**	0.69	0.59	0.78	0.28	-0.35	-0.48	-0.25	1.00													
Cs	-0.76	0.57	0.10	0.60	-0.72	0.07	-0.20	-0.04	0.14	-0.10	0.10	0.24	**0.85**	0.68	-0.70	1.00												
Ba	0.25	0.18	0.45	0.05	0.41	0.17	0.26	0.41	0.47	0.30	-0.33	0.63	0.38	-0.17	0.34	-0.13	1.00											
Ce	**-0.83**	-0.47	**-0.85**	-0.36	-0.06	**-0.81**	**-0.91**	**-0.90**	-0.79	**-0.88**	-0.22	0.09	0.12	-0.08	**-0.89**	0.40	-0.47	1.00										
Nd	**-0.85**	-0.11	-0.62	-0.18	-0.40	-0.57	-0.73	-0.65	-0.65	-0.74	-0.23	0.03	0.20	0.37	**-0.90**	0.57	-0.65	**0.84**	1.00									
Eu	-0.49	-0.46	-0.77	-0.44	-0.19	-0.64	-0.68	-0.72	-0.77	-0.74	-0.19	-0.35	-0.26	0.04	-0.61	0.12	-0.69	**0.82**	0.79	1.00								
Tb	-0.61	-0.54	**-0.83**	-0.35	0.12	-0.76	-0.77	**-0.89**	-0.66	-0.73	-0.21	-0.04	0.02	-0.36	-0.67	0.21	-0.36	**0.89**	0.59	0.73	1.00							
Dy	**-0.90**	-0.34	-0.78	-0.41	-0.10	**-0.81**	**-0.92**	**-0.82**	-0.79	**-0.92**	-0.42	0.27	0.22	0.11	**-0.95**	0.46	-0.41	**0.94**	**0.92**	0.78	0.73	1.00						
Ho	-0.68	-0.53	**-0.85**	-0.29	-0.02	-0.70	-0.78	**-0.88**	-0.77	-0.74	0.09	-0.09	-0.08	-0.21	-0.75	0.29	-0.68	**0.90**	0.75	0.73	**0.83**	0.78	1.00					
Tm	**-0.94**	0.16	-0.31	0.16	-0.47	-0.38	-0.61	-0.42	-0.32	-0.54	-0.10	0.38	0.68	0.48	**-0.94**	**0.88**	-0.22	0.72	0.79	0.42	0.45	0.79	0.56	1.00				
Yb	**-0.89**	-0.40	**-0.81**	-0.36	-0.08	**-0.82**	**-0.93**	**-0.86**	-0.78	**-0.90**	-0.30	0.21	0.21	0.01	**-0.94**	0.47	-0.41	**0.99**	**0.87**	0.79	**0.83**	**0.97**	**0.84**	0.79	1.00			
Lu	**0.97**	-0.05	0.42	0.01	0.19	0.54	0.73	0.55	0.37	0.64	0.38	-0.59	-0.71	-0.25	**0.94**	-0.77	0.04	-0.73	-0.73	-0.34	-0.55	**-0.82**	-0.54	**-0.92**	**-0.81**	1.00		
Ta	-0.78	-0.37	-0.70	-0.16	0.13	-0.69	-0.78	**-0.82**	-0.53	-0.67	-0.13	0.33	0.35	-0.30	-0.78	0.45	-0.17	**0.83**	0.55	0.41	**0.87**	0.72	**0.81**	0.64	**0.81**	-0.78	1.00	
W	**-0.95**	0.09	-0.43	0.06	-0.44	-0.48	-0.68	-0.53	-0.39	-0.62	-0.28	0.28	0.62	0.41	**-0.95**	**0.81**	-0.26	**0.81**	**0.85**	0.58	0.63	**0.87**	0.60	**0.94**	**0.87**	**-0.92**	0.70	1.00

Table 4.7 b: Inter-element correlation matrix for the sediment samples collected from Mongla 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	0.29	1.00																										
Al	0.72	0.73	1.00																									
K	-0.24	0.30	0.31	1.00																								
Ca	0.77	0.39	0.59	-0.40	1.00																							
Sc	0.68	0.51	**0.90**	0.53	0.46	1.00																						
Cr	0.76	0.57	**0.96**	0.34	0.63	**0.96**	1.00																					
Mn	0.79	0.68	**0.99**	0.25	0.68	**0.92**	**0.98**	1.00																				
Fe	0.64	0.58	**0.87**	0.57	0.44	**0.98**	**0.93**	**0.89**	1.00																			
Co	0.77	0.45	**0.88**	0.40	0.58	**0.98**	**0.97**	**0.92**	**0.96**	1.00																		
Zn	0.59	0.27	0.64	0.54	0.36	**0.89**	0.78	0.70	**0.92**	**0.91**	1.00																	
Ga	-0.54	0.32	0.13	0.58	-0.20	0.10	0.10	0.05	0.08	-0.01	-0.07	1.00																
As	-0.71	0.18	-0.08	**0.82**	-0.59	0.04	-0.10	-0.17	0.07	-0.11	0.02	**0.85**	1.00															
Br	-0.75	0.24	-0.16	0.64	-0.75	-0.18	-0.29	-0.28	-0.13	-0.35	-0.28	0.68	**0.88**	1.00														
Sb	**0.98**	0.37	**0.82**	-0.11	0.78	0.78	**0.86**	**0.88**	0.73	**0.85**	0.65	-0.39	-0.59	-0.66	1.00													
Cs	**-0.91**	-0.04	-0.43	0.60	-0.73	-0.32	-0.45	-0.50	-0.27	-0.44	-0.26	0.74	**0.93**	**0.87**	**-0.84**	1.00												
Ba	0.69	0.51	**0.92**	0.51	0.44	1.00	**0.97**	**0.93**	**0.97**	**0.98**	**0.86**	0.08	0.01	-0.17	0.79	-0.34	1.00											
Ce	-0.66	**-0.85**	**-0.97**	-0.33	-0.61	**-0.86**	**-0.91**	**-0.96**	**-0.88**	**-0.84**	-0.64	-0.16	0.03	0.10	-0.76	0.35	**-0.86**	1.00										
Nd	-0.52	**-0.87**	**-0.89**	-0.36	-0.64	**-0.80**	**-0.86**	**-0.89**	**-0.83**	-0.79	-0.61	-0.32	-0.10	0.05	-0.63	0.20	-0.78	**0.96**	1.00									
Eu	-0.46	**-0.90**	**-0.89**	-0.46	-0.52	**-0.80**	**-0.83**	**-0.87**	**-0.85**	-0.77	-0.61	-0.35	-0.19	-0.07	-0.58	0.12	-0.79	**0.96**	**0.99**	1.00								
Tb	-0.41	-0.75	**-0.90**	-0.65	-0.37	**-0.90**	**-0.89**	**-0.87**	**-0.91**	**-0.84**	-0.71	-0.46	-0.34	-0.15	-0.55	0.02	**-0.89**	**0.91**	**0.92**	**0.94**	1.00							
Dy	-0.57	-0.74	**-0.95**	-0.57	-0.42	**-0.95**	**-0.94**	**-0.93**	**-0.95**	**-0.90**	-0.76	-0.26	-0.16	-0.03	-0.69	0.19	**-0.95**	**0.95**	**0.90**	**0.93**	**0.97**	1.00						
Ho	-0.44	**-0.84**	**-0.91**	-0.59	-0.40	**-0.87**	**-0.87**	**-0.88**	**-0.90**	**-0.81**	-0.68	-0.38	-0.27	-0.14	-0.57	0.07	**-0.87**	**0.95**	**0.95**	**0.98**	**0.99**	**0.98**	1.00					
Tm	**-0.97**	-0.34	-0.77	0.08	**-0.81**	-0.79	**-0.84**	**-0.85**	-0.76	**-0.87**	-0.74	0.40	0.57	0.72	**-0.98**	0.81	-0.78	0.73	0.64	0.58	0.54	0.67	0.56	1.00				
Yb	**-0.89**	-0.59	**-0.96**	-0.08	-0.69	**-0.85**	**-0.94**	**-0.97**	**-0.81**	**-0.87**	-0.62	0.14	0.36	0.41	**-0.95**	0.67	**-0.88**	**0.90**	0.78	0.75	0.74	**0.84**	0.76	**0.89**	1.00			
Lu	1.00	0.21	0.68	-0.28	0.78	0.64	0.73	0.75	0.59	0.74	0.56	-0.56	-0.74	-0.79	**0.98**	-0.93	0.66	-0.61	-0.47	-0.40	-0.35	-0.51	-0.38	**-0.96**	**-0.86**	1.00		
Ta	-0.53	-0.92	**-0.93**	-0.37	-0.55	-0.79	**-0.85**	**-0.91**	**-0.82**	-0.75	-0.55	-0.28	-0.09	-0.03	-0.64	0.22	-0.79	**0.98**	**0.97**	**0.99**	**0.91**	**0.92**	**0.96**	0.61	**0.82**	-0.47	1.00	
W	**-0.86**	-0.01	-0.67	-0.07	-0.55	**-0.80**	**-0.80**	-0.73	-0.71	**-0.86**	-0.75	0.33	0.43	0.63	**-0.88**	0.69	**-0.81**	0.53	0.41	0.36	0.48	0.60	0.43	**0.88**	0.79	**-0.87**	0.38	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 Rupsha River and Mongla River respectively. The investigations of the elements have been performed by means of the Instrumental Neutron Activation Analysis (INAA). 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. 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. 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 has been 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. The findings of this study and future works can be summarized as follows:

1. Sediments from Rupsha and Mongla are seemed to have heavy metal contaminants.
2. For Rupsha River Mg, K ,Ca, Zn, Ga, As, Br, Cs, Ce, Nd, Eu, Tb, Dy, Ho, Tm, Yb, Ta and W are the highly polluted elements. Where the other elements are not polluted.
3. For Mongla River Mg, K, Zn, Ga, As, Br, Cs, Ce, Nd, Eu, Tb, Dy, Ho, Tm, Yb, Ta and W are the highly polluted elements. Where the other elements are not polluted.
4. Spatial differences of sampling locations are giving some information regarding to the aquatic transportation of heavy metals.

5. Theoretical calculations indicate the contamination level and the potential ecological risk.
6. After comparing the elemental abundances of Rupsha and Mongla River sediments with those of coal-fly-ash (NIST-1633b), it reveals that ytterbium (Yb) will be the potential candidate for the future elemental contaminants.
7. Physics and Chemistry has been utilized to explain the environmental geochemistry.
8. This study will be helpful for further monitoring of the elemental pollution of the Sundarban as well as possible threat to the biota of the Sundarban.

References

Abrahim, G. M. S. and Parker, R. J., 2008, “Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand”, Environ. Monit. Assess. Vol. 136, p 227-238.

Abugassa, I.O., Khrbish, Y. S., Abugassa, S. O., Faid, N. B., Bashir, A. T. and Sarmani, S., 2007, “Installation of Kayzero-INAA standardization in the TNRC and its applications for trace elements determination in different materials”, Journal of Radioanalytical and Nuclear Chemistry, Vol. 271 (1), p 27–30.

Addo, M. A., Darko, E. O., Gordon, C., Nyarko, B. J. B., Gbadago, J. K., Nyarko, E., Affum, H. A. and Botwe, B. O., 2012, “Evaluation of Heavy Metals Contamination of Soil and Vegetation in the Vicinity of a Cement Factory in the Volta Region, Ghana”, International Journal of Science and Technology, Vol, 2, No, 1.

Barnard, P. L., Foxgrover, A. C., Elias, E. P. L., Erikson, L. H., Hein, J. R., McGann, M., Mizell, K., Rosenbauer, R. J., Swarzenski, P. W., Takesue, R. K., Wong, F. L. and Woodrow, D. L., 2013, “Integration of bed characteristics, geochemical tracers, current measurements, and numerical modeling for assessing the provenance of beach sand in the San Francisco Bay Coastal System”, ELSEVIER, Marine Geology 345, p 181–206.

Bashar Bhuiyan, A., Mokhtar, M. B., Toriman, M. E., Gasim, M. B., Ta, G. C., Elfithri, R., & Razman, M. R., 2013, “The environmental risk and water pollution: A review from the river basins around the world”, American-Eurasian Journal of Sustainable Agriculture, 7(2), 126-136.American-Eurasian Journal of Sustainable Agriculture, 7(2): p 126-136

Bettinelli, A., Beone, G. M., Spezia, S. and Baffi, C., 2000, “Determination of heavy metals in soils and sediments by microwave assisted digestion and inductively coupled plasma optical emission spectrometry analysis”, Analytica Chimica Acta 424, p 289–296.

Boszke, L., Sobczynski, T., and Kowalski, A., 2004, “Distribution of Mercury and Other Heavy Metals in Bottom Sediments of the Middle Odra river (Germany/Poland), Polish”. Journal of Environmental Studies, Vol. 13, No.5, p 495-502.

Brich, G. F. and Olmos, M. A., 2008, “Sediment-bound heavy metals as indicators of human influence and biological risk in coastal water bodies”, ICES, J. Mar. Sci. 65, p 1407–1413.

Carr, R., Zhang, C., Moles, N. and Harder, M., 2008, “Identification and mapping of heavy metal pollution in soils of a sports ground in Galway City, Ireland, using a portable XRF analyser and GIS”.

Daskalakis, K. D., O'Connor T. P., 1995, "Normalization and elemental sediment contamination in the coastal states". Environ Sci. Technol, 29, p 470-477.

Datta, D. K. and Subramanian, V., 1998, "Distribution and fractionation of heavy metals in the surface sediments of the Ganges-Brahmaputra-Meghna river system in the Bengal basin", Environ. Geol. 36, p 93-101.

Dhawal, S. J., Kulkarni, G. J. and Pawar, S. H., 2013, "Terrestrial background radiation studies in South Konkan, Maharashtra, India". International Journal of Radiation Research, Volume 11, No 4, 11(4): p 263-270.

Dickinson, W. W., Dunbar, G. B. and McLeod, H., 1996, "Heavy metal history from cores in Wellington Harbour, New Zealand", Environ. Geol. 27, p 59 - 69.

Dragovic, S., Mihailovic, N. and Gajic, B., 2008, "Heavy metals in soils: distribution, relationship with soil characteristics and radionuclides and multivariate assessment of contamination sources". Chemosphere 72, p 491-495.

Ene, A., Pantelică, A., Freitas, C. and Boşneagă, A., 2011, "EDXRF and INAA analysis of soils in the vicinity of a metallurgical plant", Romanian Journal of Physics, Vol, 56, Nos, 7–8, P 993–1000.

Ene, A., Stihi, C., Popescu, I. V., Bosneaga A. 1, Radulescu, C. and Gheboianu, A., 2008, "XRF-AAS Analysis of Heavy Metals in Soils around of a Ferrous Metallurgical Plant in Eastern Part of Romania", Project SOP HRD - SIMBAD 6853, 1.5/S/15 – 01, p 10.

Glascock, M. D., 2004, "An overview of neutron activation analysis, Research Reactor". University of Missouri, Colombia. http://archaeometry.missouri.edu/naa_overview.html

Greenberg, R. R., Bode, P. and Fernandes, E. A. D. N., 2011, "Neutron activation analysis: A primary method of measurement". ELSEVIER, Spectrochimica Acta Part B 66, p 193–241.

Hailu, A. T., Chaubey, A. K., Mamo, D. A. and Hibstie, A. Y., 2012, "Application of Instrumental Neutron Activation Analysis for the elemental analysis of various rocks from areas around Debrebirhan city Ethiopia" , IJRRAS, Vol. 12, Issue-1.

Hakanson, L., 1980, "An ecological risk index for aquatic pollution control", a sedimentological approach, Water Res. 14, p 975 – 1001.

Hevesy, G. and Levi, H., 1936, Math, fys. Med., 145, p 34.

Harikumar, P. S., Nasir, U. P., Mujeebu Rahman, M. P., 2009, "Distribution of heavy metals in the core sediments of a tropical wetland system", Int. J. Environ. Sci. Tech., 6 (2), p 225-232.

Hornung, H., Krom, M. D., and Cohen, Y., 1989, "Trace metal Distribution in sediments and Benthic Fauna of Haifa Bay, Israel", Estuarine, Coastal and Shelf Science, 29, p 43-56.

Kabir, S., 2012, "Application of Nuclear Reactor Based Neutron Activation Analysis for determination of Toxic elements in soil due to ship breaking activities at Sitakunda in Chittagong", M. Sc. Thesis, Department of Physics, University of Chittagong.

Kafala, S. I. and MacMahon, T. D., 2007, "Comparison of neutron activation analysis methods", Journal of Radioanalytical and Nuclear Chemistry, Vol. 271, No. 2, p 507–516.

Khan, R., Shirai, N. and Ebihara, M., 2015^a, "Chemical characteristic of R chondrites in the light of P, REEs, Th and U abundances", ELSEVIER , Earth and Planetary Science Letters, 422, p 18–27.

Khan, R., Yokozuka, Y., Terai, S., Shirai, N. and Ebihara, M., 2015^b, "Accurate determination of Zn in geological and cosmochemical rock samples by isotope dilution inductively coupled plasma mass spectrometry". The Royal Society of Chemistry, J. Anal.At.Spectrom, 30, p 506–514.

Kogo, B. E., Gajere, E. N., Ogunmola, J. K. and Ogbole, J. O., 2009, "Neutron Activation Analysis of Soil Samples from Different Parts of Abuja Metropolis". Middle-East Journal of Scientific Research 4 (4): p 254-262.

Kong, P. and Ebihara, M., 1997, "The origin and nebular history of the metal phase of ordinary chondrites", ELSEVIER,Geochimicaet Cosmochimica Acta, Vol. 61, No. 11, p 2317-2329.

Laul, J. C., 1979, "Neutron activation analysis of geological materials". Atomic Energy Rev. 17, p 603-695.

Lee, S. Y., Watkins, D. R., Jackson, B. L., Schmoyer, R. L., Lietzke, D. A., Burgoa, B. B., Branson, J. T. and Ammons, J. T., 1995, " Evaluation of Metal and Radionuclide Data from Neutron Activation and Acid-Digestion-Based Spectrometry Analyses of Background Soils: Significance in Environmental Restoration", Oak Ridge National Laboratory, Oak Ridge, Tennessee, 3783 1 USA.

Liang, J., Chen, C., Song, X., Han, Y. and Liang, Z., 2011, "Assessment of Heavy Metal Pollution in Soil and Plants from Dunhua Sewage Irrigation Area", Int. J. Electrochem, Sci, 6, p 5314 – 5324.

Louhi, A., Hammadi, A. and Achouri, M., 2012, "Determination of Some Heavy Metal Pollutants in Sediments of the Seybouse River in Annaba, Algeria", Air, Soil and Water Research: 5, p 91–101.

Ma, X., Zuo, H., Tian, M., Zhang, L., Meng, J., Zhou, X., Min, N., Chang, X. and Liu, Y., 2016, "Assessment of heavy metals contamination in sediments from three adjacent regions of the Yellow River using metal chemical fractions and multivariate analysis techniques". Chemosphere 144, p 264 - 272.

Mohammed, S. S., Batu, M. A. and Mohammed, M. B., 2012, “Analysis of Cr in dumpsite soil samples using AAS and EDXRF techniques”, Research Journal of Chemical Sciences, Vol. 2(12), p 65-68.

Mohiuddin, K. H., Y. Ogawa., Zakir, H. M., Otomo, K., Shikazono, N., 2011, “Heavy metals contamination in water and sediments of an urban river in a developing country”. International Journal on Environmental Science & Technology, Volume-8, p 723-736.

Muller, G., 1969, “Index of Geo-accumulation in Sediments of the Rhine River”. Geology Journal, Vol.2, p 109–118.

Najam, L. A. and Younis, S. A., 2015, “Assessment of Natural Radioactivity Level in Soil Samples for Selected Regions in Nineveh Province (IRAQ)”. International Journal of Novel Research in Physics Chemistry & Mathematics, Vol. 2, Issue 2, p 1-9.

Noli, R. and Tsamos, P., 2016, “Concentration of heavy metals and trace elements in soils, waters and vegetables and assessment of health risk in the vicinity of a lignite-fired power plant”. ELSEVIER, Science of the Total Environment 563–564, p 377–385.

Ololade, I. A., 2014, “An Assessment of Heavy-Metal Contamination in Soils within Auto-Mechanic Workshops Using Enrichment and Contamination Factors with Geo-accumulation Indexes”. Journal of Environmental Protection, 5, p 970-982.

Opaluwa, O. D., Aremu, M. O., Ogbo, L. O., Abiola, K. A., Odiba, I. E., Abubakar, M. M. and Nweze, N.O., 2012, “Heavy metal concentrations in soils, plant leaves and crops grown around dump sites in Lafia Metropolis, Nasarawa State, Nigeria”. Advances in Applied Science Research, 3 (2): p 780-784.

Oyeskurni, M. 2011. “Elemental Status of Bangladesh tea using instrumental neutron activation analysis method”, M.Sc. Thesis, Department of Physics, Shahjalal University of Science & Technology, Sylhet.

Parry, S. J. 1991, “Activation Spectrometry in Chemical Analysis”. Vol.119. John Wiley & Sons, New York.

Parth, V., Murthy, N. N. and Saxena, P. R., 2011, “Assessment of heavy metal contamination in soil around hazardous waste disposal sites in Hyderabad city (India): natural and anthropogenic implications”, E3 Journal of Environmental Research and Management Vol. 2(2). p. 027-034.

Peavy, H. S., Rowe, D. R., and Tchobanoglous, G., 1985, “Environmental Engineering, McGraw Hill, Inc, New York, p 56-70.

Pollard A.M., Heron and C., 1996, “Archeological Chemistry, Cambidge”, Royal Society of Chemistry.

Rabee, A. M., Al-Fatlawy, Y. F., NajimAbd, A. A. H. and Nameer, M., 2011,“Using Pollution Load Index (PLI) and Geo-accumulation Index (I-Geo) for the Hssessment of Heavy Metals Pollution in Tigris River Sediment in Baghdad Region”, Journal of Al-Nahrain University, Vol. 14 (4), p 108 – 114.

Rakib, M. A., Huda, M. E., Hossain, S. M., Naher, K., Khan, R., Sultana, M. S., Akter, M. S., Bhuiyan, M. A. H. and Patwary, M. A., 2013, “Arsenic Content in Inactive Tissue: Human Hair and Nail”, Journal of Scientific Research & Reports 2(2): p 522-535.

Reguigui, N., Kucera, J. Kraiema, and H. B., 2002, “Determination of trace elements in Tunisian soil, desert and beach sand using instrumental Neutron Activation Analysis”, Proceedings of International Symposium on Environmental Pollution Control and Waste Management 7-10, Tunis (EPCOWM’), p 70-82.

Rubio, B., Nombela, M.A. and Vilas, F.’ 2000, “Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): an assessment of metal pollution”, Mar. Pollut. Bull. 40, p 968-980.

Rudnick, R. L. and Gao, S., 2014, “Composition of the Continental Crust, Treatise on Geochemistry”, second ed., p 64.

Schramel, P. and Xu, L. Q., 1991, “Determination of arsenic, antimony, bismuth, selenium and tin in biological and environmental samples by continuous flow hydride generation ICP-AES without gas-liquid separator”, Fresenius J Anal Chem, 340: p 41 – 47.

Soto-Jimenez, M. F., Paez-Osuna, F., Scelfo, G., Hibdon, S., Franks, R., Aggarawl, J., 2008, “Lead pollution in subtropical ecosystems on the SE gulf of California Coast: a study of Concentrations and composition”, Mar Environ Res. 66, p 451-458.

Tamim, U., Khan, R., Jolly, Y. N., Fatema, K., Das, S., Naher, K., Islam, M. A. and Hossain, S, M. 2016, “Elemental distribution of metals in urban river sediments near an industrial effluent source” ELSEVIER, Chemosphere, 155, p 509-518.

Tomlinson, L., Wilson, G., Harris, R., Jeffrey, and D.W., 1980, “Problems in the assessments of heavy-metal levels in estuaries and formation of a pollution index”, Helgol Meeresunters, 33, p 566-575.

Tsoulfanidis, N., 1995, “Measurement and Detection of Radiation, Second Ed, Taylor & Francis” Washington DC, p 177-235.

Ulmanu, M., Anger, I., Gamenţ, E., Mihalache, M., Plopeanu, G. and Ilie, L., 2011, “Rapid Determination of some Heavy metals in soil using an X-Ray Fluorescence Portable Instrument”, Research Journal of Agricultural Science, 43, (3).

Wan, I., Ruslan, and Timah Tasoh., 2007, “Environmental Management of a Reservoir within an Agriculture Scenario”, Lake and Reservoir Colloquium, p 81-97.

Wasim, M., Zafar, W. A., Tufail, M., Arif, M., Daud, M. and Ahmad, A., 2011, "Elemental analysis of topaz from northern areas of Pakistan and assessment of induced radioactivity level after neutron irradiation for color induction", JRNC, 287: p 821–826.

Wayttenbach, A., 1971, "Coincidence losses in activation analysis", JRNC, 8: p 335.

Wei, B. and Yang, L., 2010, "A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China" ELSEVIER, Microchemical Journal 94, p 99–107.

Yu, K. N., Yeung, Z. L. L., Lee, L. Y., L., Stokes, M. J. and Kwok, R.C.W., 2002, "Determination of multi-element profiles of soil using energy dispersive X-ray fluorescence (EDXRF)", ELSEVIER, Applied Radiation and Isotopes 57, p 279–284.

Zsefer, P., Glasby, G.P., Sefer, K., Pempkowiak, J. and Kaliszan, R., 1996, "Heavy-metal pollution in superficial sediments from the southern Baltic Sea off Poland", J. Environ, Sci. Health A 31, p 2723 - 2754.

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, γ) ^{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, γ) ^{141}Ce	88.45	0.5704	0.3446	32.508 d	145.5	48.29
^{152}Eu	^{151}Eu(n, γ)^{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, γ)^{153}Sm	26.75	205.9	2978	1.94 d	103.2	29.25
^{160}Tb	^{159}Tb(n, γ) ^{160}Tb	100	23.13	409.1	72.3 d	298.6, 879.4, 1177.9	26.13
^{175}Yb	^{174}Yb(n, γ) ^{175}Yb	31.83	63.21	25.48	4.19 d	282.5, 396	13.15
^{177}Lu	^{176}Lu(n, γ) Lu^{177}	2.59	×	×	6.71 d	208	10.36
^{181}Hf	^{180}Hf(n, γ) ^{181}Hf	35.08	12.92	29.34	42.39 d	132.9, 482	80.5
^{182}Ta	^{181}Ta(n, γ) ^{182}Ta	99.988	20.68	660	114.74 d	1189, 1221.4	27.23
^{233}Pa	^{232}Th(n, γ, β^-) ^{239}Np	99.27	2.683	275.6	2.356 d	106, 228	26.3, 11.1
^{238}U	^{237}Np(n, γ, β^-)P	99.274	16.83	994.5	4.468 $\times 10^9$ y	106.1, 228.2, 277	×

PUBLICATION RELATED TO THE PRESENT WORK

Conference Paper

(1) “Study on Mongla and Rupsha River Sediments for Potential Heavy Elemental Contamination by Instrumental Neutron Activation Analysis (INAA)”
(International Conference on Physics, March- 2018)