

DETERMINATION OF TRACE ELEMENTS IN THE KUBANNI RIVER

SEDIMENTS USING ENERGY DISPERSIVE X-RAY FLUORESCENCE

TECHNIQUE

BY

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DEDICATION

**This work is dedicated to my parents, my wife, my two daughters (Aichatou and Asmaou)
and my son Abdoullahi.**

ACKNOWLEDGEMENT

First and foremost, I am indeed grateful to ALLAH who has guided me through this work. I wish to express my sincere gratitude to my father Mallam Hankouraou and my mother Mallama Hadjara for their moral and financial support for my education since childhood.

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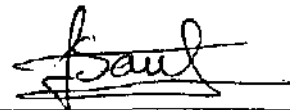
I will end this acknowledgement by thanking *Le Ministere de l'Enseignement Superieur de La Recherche et de la Technologie au Niger*, as well as *Le Gouvernement de la Republique du Niger* for granting me *La Bourse d'Etudiant* for my studies. All my friends from Niger Republic who also gave me both financial and moral assistance in terms of their various contributions to the success of my course are hereby acknowledged.

May ALLAH [S.W.A.] bless us all - Ameen.

DECLARATION

I hereby declare that, the report in this thesis is the result of my original research. This thesis has not been submitted to any other University, Institute, Organization or body for any award other than Ahmadu Bello University, Zaria, Nigeria.

All inclusions from works other than this have been referenced and acknowledged.

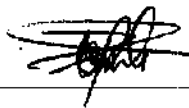


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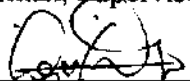
CERTIFICATION

This thesis titled 'DETERMINATION OF TRACE ELEMENTS IN THE KUBANNI RIVER SEDIMENT USING ENERGY DISPERSIVE X-RAY FLUORESCENCE TECHNIQUE' by HANKOURAOU SEYDOU, meets the regulation governing the award of the degree of Master of Science [Physics] of Ahmadu Bello University and is approved for its contribution to knowledge and literary presentation.



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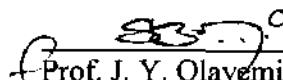
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ABSTRACT

Trace quantities of thirteen elements have been determined from the aquatic sediment, of the Kubanni River a principal waterway at Zaria, Nigeria. Energy Dispersive X-ray Fluorescence (EDXRF) Technique was used in determining Si, Ca, K, Ti, V, Fe, Co, Zn, Rb, Sr, Y, Zr and Nb in the sediment. An AXIL computer programme was used for the spectral analysis. The degree of pollution of the Kubanni River was ascertained and compared with literature toxicity data. Other pollution indices like pH and turbidity were assessed for the sediments and found to be tolerable for portable upper sediment water layer. Significant correlation was found for most of the elements determined while K seemed to show negative correlation with four elements viz. Co, Ti, Fe, and Sr. Geochemical ratios like Clarke values investigated for the elements showed high sediment enrichment for Zr while six of the elements (K, Ca, Ti, Fe, Co and Sr) were depleted in the sediments. The Kubanni river sediments studied showed relatively low state of pollution for the elements determined and the River could still be used as a principal potable water source for Zaria inhabitants .

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CHAPTER ONE

INTRODUCTION

1.1 River Sediments

Naturally occurring trace elements are deposited in aquatic environments either in the soluble or insoluble form and eventually settle as bottom sediments along the course of the river. The presence of these trace elements in aquatic environments is not without significance: for some of them are known to be very toxic and act as contaminants in the sediments. Man's activities have increased the loading of municipal and industrial contaminants to the nation's waterways. One of such waterways is the Kubanni River - our study area in Zaria.

This river runs as a major principal drainage artery dissecting Zaria town. The increased loading of riverbeds with wastes could result in increased concentration of many heavy metal contaminants in sediments adversely affecting water quality and even the survival of aquatic organisms. Contaminants in sediments have a wide range of sources, and could be affected by lotic (running water), lentic (standing water), estuarine or lacustrine conditions; physical properties of sediments, and the chemical state and biological composition of the water involved (Jenett *et al* 1980).

To date, most research in aquatic systems has been concerned with the form of contaminants present, rather than the amount of potential toxic material bound up in the sediments. The low concentration elements are undoubtedly the most difficult to study because background levels are always present in the environment masking their presence, and a small perturbation on an ecosystem could bring about rapid increase in the rates of synthesis of these heavy metals.

The potential impact of trace elements in sediments is determined here strictly with respect to the Kubanni River sediments. The detection of such elements from the Kubanni River requires sensitive and accurate analytical methods. In this work the Energy Dispersive X-Ray Fluorescence (EDXRF) is chosen due to its reliability amongst other merits. This method of analysis offers an easy and sensitive way of determining any trace element in sediments.

Its advantages include:

- (i) Simple sample preparation
- (ii) Non-destructive capability for sample analysis and
- (iii) Ability to determine many elements simultaneously.

Although a number of difficulties still need to be satisfactorily resolved, mainly connected with the preparation of standards and calibration, it is believed that, the method in its present stage of development is already very promising. EDXRF analysis suffers from certain set backs such as high initial investment, rigorous radiation protection, matrix effects, need for well trained personnel; thus limiting its application to few laboratories and research institutes such as the Centre for Energy Research and Training, Ahmadu Bello University, Zaria, where this work was carried out.

1.2 Nature of Kubanni Sediments

The term sediment is used to describe both the suspended and deposited material in aquatic systems. There are always varying amounts of suspended sediments in all natural waters. In aquatic systems, sediments include all particulate material which are washed or blown into a lake or river (allochthonous), or are formed in the water-body itself

(autochthonous). In the Kubanni River, both processes are known to account for the deposition of sediments along the riverbed. Alterations (diagenesis) which occur in the sediments produce new compounds (authigenic). Diagenetic processes also cause changes in the chemical composition of fluids and thus could result in the variation of heavy metals along the Kubanni river basin.

Sediments consist of inorganic and organic compounds, both of which come from sources outside or within the river or lake. The organic matter along the Kubanni river sediments consists of micro-organism (phytoplankton, zooplankton, and bacteria), the remains of macrophytes and other large-sized organisms, together with the detritus derived from decaying material of vegetables and food plants grown along the Kubanni River Basin. The inorganic matter consists of erosion products from fertilizers used by farmers, bed-rock and basement complex detritus of the Kubanni watershed (rock particles and clays, together with compounds such as $\text{Fe}(\text{OH})_3$, SiO_2 and CaCO_3 which may be brought into the water, or formed within it, from soluble products or compounds (UNESCO, 1983). Such compounds account for the increase deposition of heavy metals along the Kubanni River, which became our research focus.

The composition of sediment is largely controlled by the composition of the source rock from which it is derived by erosion and weathering; it is additionally influenced by climatic regime (weathering and hydrological conditions), landform, land use and time in transit (UNESCO, 1983).

Sediments affect and influence water use and availability in many ways. Quantitatively wide variation in the particle size, such as gravel, sand, silt and amount of material, may cause channel instability or excessive erosion or deposition in rivers. The

Kubanni River suffers periodically from such defects during the onset of the early rains where the water volume is not sufficient enough to create an appropriate stream velocity having enough competence to translate the eroded sand and silt along the river course.

1.3 Sediment Transport and Deposition

Streams, ground water and gravity effects are continually at work transporting soils and rock debris away from the zone of weathering. Each may cause marked physical changes in the sediment it carries. The suspension movement of all sediments carried by the winds and water is controlled by the settling velocity of the particles and laws of fluid motion (Mitchell, 1976). Particles like aerosols from the seasonal harmattan winds in Zaria stay in suspension once they have been set in motion as long as the turbulence of the Kubanni stream is greater than the settling velocity. This therefore makes the Kubanni River water appear turbid most of the time. The result will be discussed further in the thesis.

Not all sediments is moved in suspension. The largest particles are carried by traction, which consists of rolling and dragging along the boundary or riverbed between the transporting agent and the ground surface since the gradient of the Kubanni River from the upper watershed to the lower course appears favourable for such translocations. Such sediments are deposited during the heavy rains and are not good markers of the contamination of the riverbed since irrigation farming is not carried out during this period. For sediment to be transported, the eroding agent must pick it up, and greater average stream velocities may be necessary to erode than to transport particles. Particles are

eroded when the drag and lift of the fluid exceeds the gravitational, cohesive and frictional forces acting to hold them in place.

1.4 Stream Velocity

The stream velocity is usually the average velocity to which a stream transport its detritus. Such a velocity required to erode does not decrease indefinitely with decreasing particle size, because small particles remain within the boundary layer adjacent to the stream bed where the actual velocity is much less than average (Mitchell, 1976). Thus, transportation depends mainly on average velocity and boundary layer thickness relative to the projection of the particle. In the case of the Kubanni River, however, due to continuous abrasion of the unconsolidated rock structure of the river basin, splash erosion caused by the impact of rain on unprotected soil surfaces (clay and silt), detachment and removal of thin sheets (sheet erosion) of soil, etc. the stream velocity varies from point to point.

As the stream velocity plays an important role in sediments transportation, there is a need for one to determine it so as to know the differences between sediments deposited at different places along the course of the river. Many methods have been developed. These fall into three general classes depending upon the principles on which they operate:

- (i) Floats
- (ii) Pressure instruments and
- (iii) Current meters.

In this work only the first method (i.e. Floats) was used. Floats, in as much as they move with the same velocity as the transporting medium e.g. water; provide a direct means of measuring the velocity. There are three kinds of floats: Surface, subsurface and

rod. For surface floats which was used in this work, objects that float may be used such as fresh leaves, bottles partly filled with water, drift wood, pieces of paper etc. The surface velocity is found by timing the travel of these 'floats' at various points across the stream through measured distances. In this work fresh leaves were used as floats for determination of the stream velocity along the course of the Kubanni River at different places. Bridges were used, as reference Points Data obtained for stream velocities at different points along the Kubanni River will be discussed later. Not much has been reported on sediment analysis of the Kubanni River; however, other workers have studied sediments extensively.

1.5 Previous Works on Sediments

Many researchers have carried out analysis of sediment samples. Fong and Chatt (1987) used Neutron Activation Analysis (NAA) for determination of thirty-five elements in deep-sea sediments as part of a study on the disposal of highly radioactive waste sub-seabed burial. The elements obtained are: Al, Ca, Cl, T, Mg, Mn, Na, Si, Ti, U, V, As, Br, K, La, Sb, Sm, Yb, Ba, Ce, Co, Cr, Cs, Eu, Fe, Gd, Hf, In, Lu, Nd, Rb, Sc, Se, Sr, Ta, Tb, Th, Tm, Zn and Zr.

An IAEA (1973) report has shown that by the use of NAA, sixteen elements were detected in different Rivers (Rhine; Ems. Chao phya; Amazon) sediments. In the reported work, Ge(Li) Gamma Ray spectroscopy was used for identification of the following elements: Fe, Mn, Zr, Cr, Pb, Cu, As, La, Co, Sc, In, Sb, Tb, Eu, Ta and Ir .

Laure *et al.* (1982) used X-Ray Fluorescence (XRF) for analysis of, 14 soil, 72 sediment cores and 2 sediment samples obtained from the Morro do Ferro basin in Brazil.

The following elements were given by this analysis: Th, U, Ba, La, Ce, Pr, Nd, Sm, Dy, Eu, Gd, Yb, Hf, Fe, Zr, Nb, Mo and Pb.

Not much work has been reported on the Kubanni River Sediments. However, Ewa and Dim (1989) determined major, minor and trace quantities of ten stable elements from the aquatic sediments of the Kubanni River Dam at Zaria, Nigeria, using Instrumental Neutron Activation Analysis (INAA). The elements determined were Na, Al, K, Ti, V, Mn, Ba, Sm, Dy and U.

Ewa, et al. (1998) in their study based on the characterisation of the Kubanni River sediments using Neutron Activation Analysis, identified the following heavy metals (Fe, K, La, Sm, Yb and Lu) along a horizontal strata of the Kubanni River bed: However their sampling was restricted to the University Dam site. This work is more encompassing than the previous work reported. A survey of the literature of the work on Kubanni River so enumerated and their consequent limitations, necessitated the continuation of the work so as to extend the determinations further to meet a more detailed objective in particular.

1.6 Statement of Research Problems and Objectives

The Kubanni River, is one of the most important rivers draining Zaria and its environs. Much consideration and attention has been given to this River because of the numerous farming and irrigation activities that take place seasonally along its course, as well as its economic importance to the inhabitants. A great number of Zaria peasants have farms along the course of the river, from which they obtain their food stock such as rice, maize, beans and vegetables such as tomato, garden egg, carrot, onion etc. Many of the activities are carried out during the dry season by irrigation. This River is also found to be

very important for fishing throughout the year, as large quantities of fish are obtained from the river. The water of the River is made potable through a Dam, near the Ahmadu Bello University. From this Dam, many people around get their drinking water. Unfortunately the river is prone to pollution due to all forms of human activities that take place around the Kubanni River Basin

Environmental pollution is one of the most investigated subjects of research at present time. Most industrial and municipal wastes end up in rivers, lakes and sea. Hence, the idea of having continuous survey of water quality receives wide spread attention. In recent years, because of industrialisation and increasing population, water pollution has become an important problem all over the world (IAEA, 1976). Inorganic materials have proved to be much more persistent than organic matter as sediment pollutants since they are not readily removed by *in situ* oxidation, they too, may render the water unsuitable for irrigation and domestic purposes, and thus it is important to know their concentration in sediment.

Pollution is here considered to have occurred when a substance having deleterious effects on one or more aspects of water quality is at large concentration in water, exceeding a permissible limit.

Substances that cause pollution fall into four main categories (IAEA, 1976):

- (i) Suspended solids
- (ii) Metals and other ions
- (iii) Highly oxidable organic waste and
- (iv) Soluble organic chemicals.

Pollutants determined in the Kubanni watercourse are mostly heavy metals. The activities causing pollution of the Kubanni waterway include:

- (i) Disposal of domestic waste
- (ii) Food processing
- (iii) Industrial Wastes including plastics, pharmaceuticals, metal processing products from Industrial Development Centre (IDC)
- (iv) Pharmaceuticals from Faculty of Medicine Complex
- (v) Paper manufacturing waste from A.B.U Press
- (vi) Horticultural waste from Institute of Agricultural Research(IAR) and
- (vii) Biological wastes from Zango village and the Abattoir

All these wastes are eventually drained into the Kubanni River ending up as metal complexes. There is the need therefore to monitor periodically the Kubanni waterway for heavy metals. This is why this study covered the entire watercourse; beginning from the upper catchment zone of the River at the Kampagi Hills, downstream, to the River confluence with the Galma River.

This thesis is an attempt to resolve the research problems so far discussed by setting out the following objectives to be accomplished:

- (i) Determination of Heavy metals along the Kubanni River Course
- (ii) Determination of Stream Velocities as may affect deposition of sediments along the river bed
- (iii) Discussion on the toxicity and pollution of the elements determined

(iv) **Data Analysis including Correlation, Coefficient of Variation and some geochemical parameters such as Enrichment, Depletion, Clarke Ratio Abundance, of each heavy metal for the Kubanni River.**

CHAPTER TWO

THEORY OF X-RAY FLUORESCENCE TECHNIQUE

2.1 Definition of X-Rays

X-rays may be defined as photons that belong to the family of electromagnetic waves of wave length 10 to 100 Å which can remove the entire photon energy in a single event (absorption) or may alter the direction and energy (scattering). They are produced by deceleration of high-energy electrons and/or by electron transition in the inner orbit atoms (Bertin, 1975). X-rays are emitted on bombardment of matter by sufficiently energetic electrons, protons, deuterons or heavier ions and by irradiation of matter by sufficiently energetic electromagnetic radiation, particularly X- and γ -rays. They are emitted as non-characteristic continuous spectra or as line and band spectra having wavelengths characteristic of the emitting element. They produce characteristic absorption spectra by undergoing differential absorption in matter.

2.2 Interaction of X-Ray with Matter

X-ray or photon can interact with the atomic electrons, nucleons, the electric field surrounding the charged particle and the neutron field surrounding the nucleons. Two broad types of scattering processes occur:

- (i) Elastic or coherent scattering: It is a process in which the internal energy of the interacting systems remains unchanged.
- (ii) Inelastic or incoherent: It is a process in which there is an internal energy change.

The absorption of X-ray by matter may lead to the excitation of secondary characteristic X-rays. Three major processes usually describe X-ray radiation interaction with matter viz.:

Photo electric effect, Compton scattering, and Pair production. Other minor processes include Rayleigh scattering and photonuclear reactions. Interaction of photon with matter is dependent on the material (Z) and the photon energy (E_γ)

2.2.1. The Photoelectric Effect

The photoelectric effect is a collision between a photon and a bound atomic electron. As a result of the interaction, the photon disappears and one of the atomic electrons is ejected as a free electron, called the photoelectron (Fig 2.1a).

The kinetic energy (T) of the electron is given as

$$T = E_\gamma - B.E. \quad 2.2.1$$

Where E_γ = Energy of the photon.

$B.E$ = Binding energy of the electron.

The probability of this interaction occurring is called the photoelectric cross section or photoelectric coefficient, which depends on parameters such as E_γ , Z and A and is denoted as Γ

The equation expressing Γ : (Evans, 1955) may be written as:

$$\Gamma (m^{-1}) = a N (Z^n / E_\gamma^m) [1 - \theta(Z)]$$

Where Γ = Probability for photoelectric effect to occur per unit distance travelled by the photon.

a = Constant, independent of Z and E .

m, n = Constants with a value of 3 to 5 (their value depends on E_γ).

N = Number of atoms/ m^3 for the material through which the particle moves

Z = Atomic number of the material.

The term in parentheses indicates correction terms of the first order in Z .

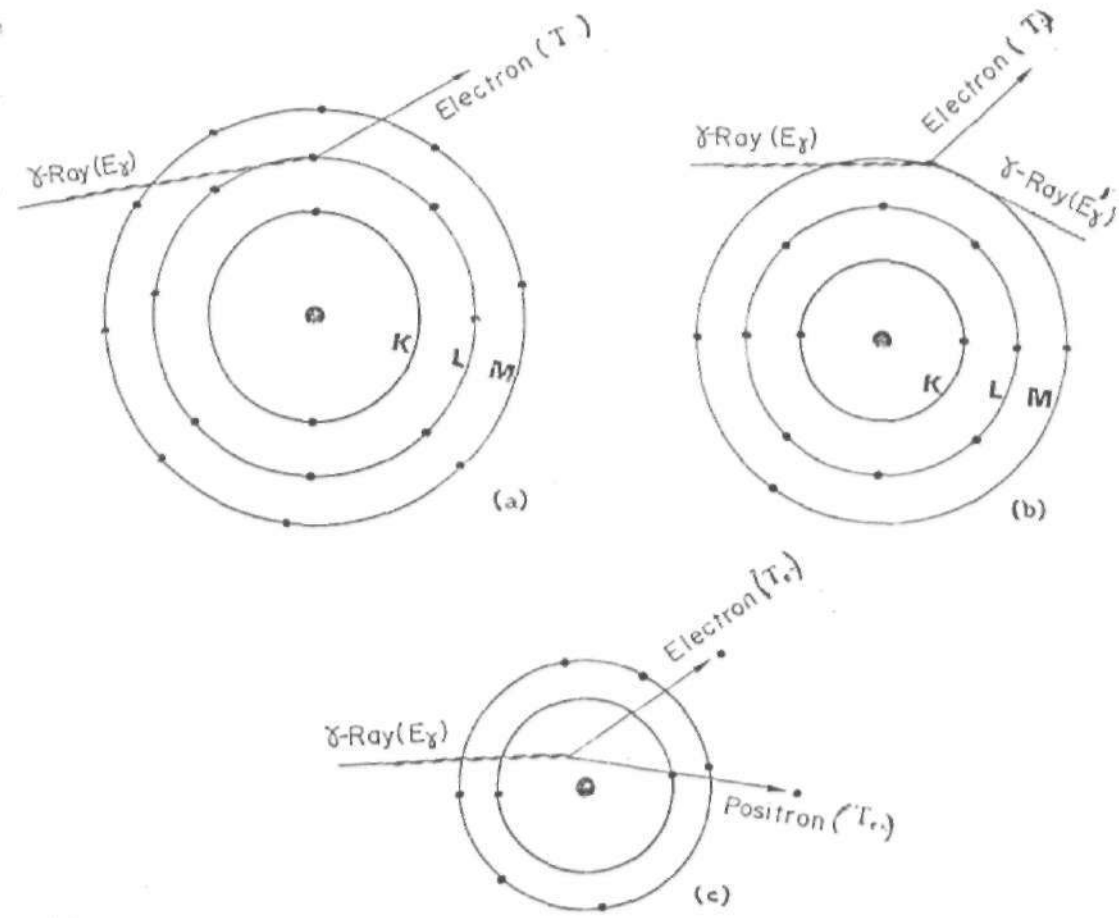


Fig 2.1 PhotoElectric (a) Compton (b) and Pair Production(c) Processes.

2.2.2. Compton Scattering or Compton Effect

The Compton effect is a collision between a photon and a free electron. Fig. 2.1b. illustrates this scattering. The photon does not disappear after a Compton scattering. Only its direction of motion and energy change. The photon energy is reduced by a certain amount that is given to the electron. Assuming the electron is stationary before the collision, the conservation of energy gives:

$$T = E_{\gamma} - E_{\gamma'} \quad 2.2.3$$

Where T = Kinetic energy of the electron.

E_{γ} = Energy of the incident photon.

$E_{\gamma'}$ = Energy of the scattered photon.

The probability that the Compton scattering will occur is called the Compton coefficient or the Compton cross section and it is written in the form:

$$\sigma \text{ (m}^{-1}\text{)} = NZF(E_{\gamma}) \quad 2.2.4$$

Where σ = probability for Compton interaction to occur per unit distance.

$F(E_{\gamma})$ = a function of E_{γ} .

The probability of Compton to occur depends on the atomic number Z , of the material.

2.2.3. Pair Production:

Pair production is an interaction between a photon and a nucleus as a result of which the photon disappears and an electron positron pair appears (Fig. 2.1c).

The probability for pair production to occur, called the pair production coefficient or cross section, is a complicated function of E_γ and Z (Evans, 1955). It may be written in the form:

$$K \text{ (m}^{-1}\text{)} = N Z^2 F (E_\gamma, Z) \quad 2.2.5$$

Where K is the probability for pair production to occur per unit distance travelled and $F (E_\gamma, Z)$ is a function, which changes slightly with Z and increases with E_γ .

2.3. Combined Effect of X-ray Interactions

Combination of the basic interaction can be used to describe phenomena to which different attributes can be assigned. For example, X-ray attenuation in material is ascribed to photoelectric effect, Compton scattering and Pair production, while diffraction is ascribed to Rayleigh and coherent scattering. In general absorption coefficient is attributed to the three phenomena of photoelectric effect, Compton scattering and pair production, i.e.

$$\mu \text{ (m}^{-1}\text{)} = \Gamma + \sigma + K \quad 2.2.6$$

μ is called the total linear attenuation coefficient. Physically, μ is the probability of interaction per unit distance.

Because of the complex varying dependence of μ on γ - ray energy E_γ and atomic number Z of the material, generally one of these processes becomes a dominant mode of interaction for a given γ - ray energy and atomic number of the material

2.4 Production of Characteristic x-rays

The characteristic X-ray spectral lines of an element arise from electron transitions within the atoms of that element. An atom is the smallest particle of an element that can

undergo, at least in principle, all the chemical actions characteristic of that element. It follows that an understanding of the nature and origin of X-ray spectra requires some knowledge of atomic structure.

Every atom consists of a dense central nucleus, containing Z protons and $(A-Z)$ neutrons, with all Z electrons in orbits around the nucleus. A is the mass number. The orbits are grouped in shells, designated as K, L, M, N..., in order of increasing distance from the nucleus. The closer the shell is to the nucleus the more tightly bound are its electrons. Angular momentum and spin further classify the electron in each shell. Each of the unique parameter of the electron is designated by a quantum number, which has only certain allowed values and no two electrons in an atom can have identical set of quantum number (i.e. Pauli exclusion principle). X-ray line spectrum arises when electrons are expelled from inner orbits and electrons from orbits away fall into the vacancies.

The interaction of X-ray with the electron cloud of an atom creates electron holes, leaving the atom in an excited state. A large number of K and L holes are produced only with high energy X-rays. The lifetime of K and L holes varies between 10^{-9} and 10^{-16} seconds. The holes may be filled by any of the other electrons with higher energy, and the extra is either emitted as a characteristic X-ray or as an Auger electron. An Auger effect (electron) is a competing process in which de-excitation proceeds by emission of an outer shell electron instead of an X-ray photon. This process becomes more likely than X-ray emission for the light elements, where the fraction of vacancies producing x-ray emission may be less than 10% (Wolseth, 1973).

The ratio of the emitted X-ray to the total number of holes is also defined as fluorescence yield for each shell. The different X-ray groups are labelled by capital letters

corresponding to the shells with the electron vacancies, and suffixes for the electrons which drop into the vacancies (K_{α} , K_{β} , L_{α} etc).

The number of these X-ray groups with different energies is very large, corresponding to the various combinations of atomic electron shells and sub-shells. The energy of each of the X-ray lines is characteristic for each of the elements, and increases with increasing atomic number. This is an important feature allowing the identification of the atom from which the specific energy has been emitted.

The study of X-ray produced comprises of methods of dispersion, detection and data storage. The dispersion method could be wavelength or energy dispersive while the detection method could use gas, scintillation or semiconductor detectors. In this work the energy dispersive method and semi-conductor detector Si (Li) were used.

2.5 Principle of Energy Dispersive X-Ray Fluorescence

When an atom is bombarded by high-energy photons or charged particles, an inner orbital electron is ejected (photon electric absorption), creating a vacancy in that inner orbital. Another electron from outer higher orbital fills the vacancy and its excess energy is equal the difference in the binding energies of the electrons in the two orbitals. The ejection photon electron is accompanied by emission of Auger electron and secondary characteristic X-ray. The fluorescence competes with the Auger- electron emission as de-excitation process following the creation of an inner shell hole.

The competition is usually expressed as:

$$n_q = n_A + n_R \quad 2.5.1$$

Where n_q = Number of atoms under a giving transition.

n_A = Number of atoms that omit Auger electrons

n_R = Number of atoms that emit fluorescence

The radiative transition atoms emit discrete lines so n_R can be considered as the sum of the radiative transition atoms ($n_{R1}, n_{R2}, \dots, n_{Rb}$) corresponding to these lines.

$$n_R = n_{R1} + n_{R2} + \dots + n_{Rb} = \sum n_{Ri} \quad 2.5.2$$

The ratio of equation (2.5.1) and (2.5.2) is defined as fluorescent yield (Agarwal, 1979) and denoted by F_y .

$$F_y = \frac{\sum n_{Ri}}{n_A} = \frac{n_R}{n_A + n_R} \quad \dots 2.5.3$$

or in terms of transition probability:

$$F_y = \frac{P_R}{P_R + P_A} \quad \dots 2.5.4$$

The frequency of the characteristics lines from n_R increases systematically as the atomic number Z and its expressed by the Moseley law.

$$[\nu / R_\infty]^{1/2} = (Z / n) - (\sigma_s / n) \quad \dots 2.5.5$$

Where R_∞ = Rydberg constant.

σ_s = Screening constant.

These lines consist of $K_\alpha, K_\beta, L_\alpha, L_\beta$, etc. but the most intense are the K_α and K_β lines.

The emission of the characteristics X-ray by element when bombarded with high enough energy forms the basis for the energy dispersive X-ray fluorescence widely employed in chemical analysis. The analysis is carried out mostly in an energy dispersive X-ray spectrometer.

In the XRF spectrometer, the primary excitation results in the emission of the characteristic X-ray photons of various energies. These photons enter the depletion

volume of the Si (Li) or Ge (Li) detector and loose energies in photoelectric encounters. The resulting photoelectrons ionize the detector material, producing electron-hole pair whose number is proportional to the energy of the absorbed photon (Langheinrich, et. al. 1973). The generated charge, collected by high voltage bias across the detector is converted to voltage pulses and amplified by charge sensitive Field Effect Transistor (FET), a preamplifier and a linear amplifier. The amplitude of each pulse is proportional to the energy of the initial x-ray photon that produces the pulse. The process of generation of the pulse by a photon and collection is accomplished in less than one micro second (Langheinrich et. al. 1973). The repetition of identical events in a measure of a specific radiation relates to the concentration of an element in the sample which can be determined quantitatively.

2.6 Excitation Energies

The excitation energy of elements is what from the basis of choice of excitation sources. In this work only iron source and cadmium sources were. Since the precision of the comparative X-ray Fluorescence Technique depends on the accuracy of the elements identified in the standards, and not all the elements can be excited by any radioisotopes source, there is the need of classifying the elements according to their excitation energies. Elements from Aluminium to Chromium can be excited by the Iron source ($^{25}\text{mCi Fe-}$) whose excitation energy for the K line is 5.9keV. The elements from Manganese to Molybdenum can be excited with the Cadmium source ($^{25}\text{mCi Cd-109}$) where excitation energy for the K-lines is 22.4keV. Americium source whose

excitation energy for the K-lines is 49keV can be used to excite the elements from Molybdenum to Neodymium.

2.7 Radio-Isotope Sources in EDXRF

A Radioisotope source is a specified amount of a specified radioisotope fabricated in a form suitable for a specified application. Usually the radioactive material is encapsulated so as to prevent its dispersion into the open and thereby contaminate the laboratory environment. The shielding; is aimed at the retention of radiation.

Radioisotope sources for x-ray spectrometric application are characterized by four principal properties as follows:

- (1) Radioactive decay process and type of emitted radiation α, β and γ emission, or K, L orbital-electron capture, which results in x-ray spectral-line emission;
- (2) Energy of emitted radiation -(1-150KeV);
- (3) Activity of the source 1mCi to 5 Ci and
- (4) Half-life, the time required for half the atoms of the radioisotope to disintegrate, (for the activity of the source to fall to half its initial value).

The advantages of radioisotopes include the followings:

- (a) Radioisotope source-detector assemblies are very small, light, and inexpensive making them applicable to specimens difficult to present to a tube - excited spectrometer.
- (b) Excitation energies of 100-150 KeV are attainable, so the K lines of the heaviest elements can be excited.

- (c) Excitation conditions during analysis of a series of specimens are, for practical purposes, absolutely stable; this permits use of longer counting times to compensate the lower intensity of radioisotope sources. This low intensity, a disadvantage in some ways, can be advantageous in that it prevents choking of semiconductor detectors and substantially eliminates radiolysis of liquid, organic, and biological specimens and discoloration of glasses, ceramics, arts objects, etc. (Bertin, 1978).
- (d) The low penetration of α and β , rays permit surface analysis and reduces absorption -enhancement effects in bulk specimens.
- (e) Source-target and sources give, practically no continuous background, so that high peak-to-background ratios are realized.
- (f) The high specificity of source-target sources is used to advantage in light, compact, and survey-type instruments for single elements, for example, instruments for environmental surveys for lead in paint.

The principal disadvantages of radioisotope excitation are the following:

- (a) There is some personnel health hazard and possibility of contamination of the laboratory environment.
- (b) The output intensity from a radioisotope source is much lower than that from even low-power x-ray tubes. However, this feature can be compensated by longer counting times made feasible by the low background and high source stability.
- (c) In source-target and orbital-electron capture sources, some of the source X-radiation may scatter coherently and incoherently; from the specimen. The

target must be chosen so that neither type of scattered target line interferes with the analytic line.

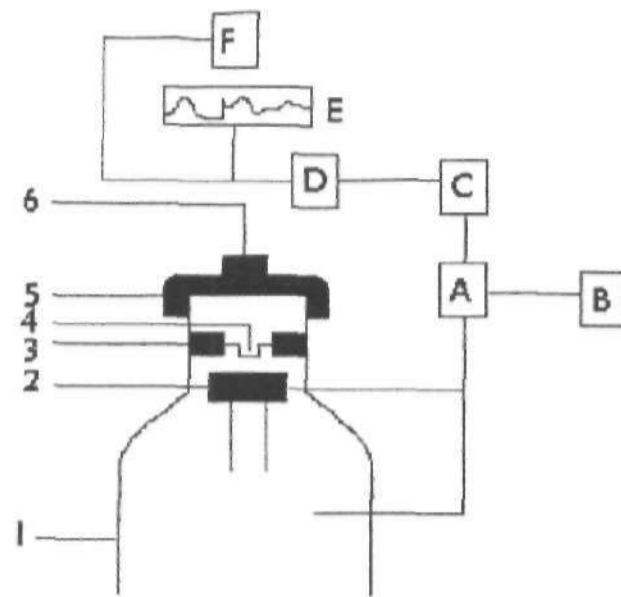
- (d) Long-term radioisotope source intensity gradually decreases with time so that occasional re-calibration is required.

2.8. Instrumentation

The detection system as shown in (Fig. 2.2) consists of a high-purity semiconductor detector (Si(Li) system (including a preamplifier and high voltage filter), a high voltage bias supply and an amplifier.

The Si(Li) detector and its associated electronics are coupled to a series of MCA of Canberra industries. The Si(Li) detector is an ORTEC GEM series (Canberra Model 2008) Si(Li) detector. The detector operates at near liquid nitrogen temperature (77K) in order to reduce the leakage current and hence the noise of the system, and may be cycled to room temperature without its performance being damaged when not in use.

The high intrinsic resolution (170 eV at 5.9 KeV) and excellent stability of a semiconductor detector Si(Li) permit a direct measurement of the intensity of characteristics x-ray of the element of interest with very little interference from other excited or scattered radiation (Papez and Cameron, 1973).



1. Dewar
 2. Si(Li) Detector
 3. Annular Source
 4. Be Detector Window
 5. Sample Holder
 6. Sample
-
- A. Pre-Amplifier
 - B. High Voltage Supply
 - C. Amplifier
 - D. MultiChannel Analyzer
 - E. Computer
 - F. Printer

Fig. 2.2 Detection System for the EDXRF Technique used

CHAPTER THREE

METHODOLOGY OF RESEARCH

3.1 Study Area

The Kubanni River course is the aquatic environment of interest in Zaria (Fig. 3.1). Located within the plains of the Northern Nigeria Savannah region, this study area, where our sediments were obtained lies approximately, between latitude $11^{\circ} 8' N$ and $11^{\circ} 10' N$ as well as longitude $7^{\circ} 41' E$ and $7^{\circ} 42' E$ on the Zaria Sheet No. 102 SW of the Nigerian Ordinance Survey Map. The Kubanni River watershed with its dendritic pattern drains these area, flowing at gentle gradients southerly, carrying along its course alluvial sands, silts, eroded trace elements and organic matter which constitute the debris-load obtained from the water catchment zones. Sites least disturbed by continuous turbulence of the mid-stream current of the river, but yet rich in overlain sediment, were chosen as fairly suitable enough for the collection of samples.

3.2 Sampling and Sample Preparation

In order to study the distribution of trace elements in sediments, along the Kubanni River, eleven sediment samples were collected at seven different locations as shown in Fig. 3.1. The samples were collected in polyethylene containers. Care was taken during sample collection to minimise contamination. Stream velocities were measured before the samples were collected at each site. The distances separating each sampling point is approximately a kilometre.

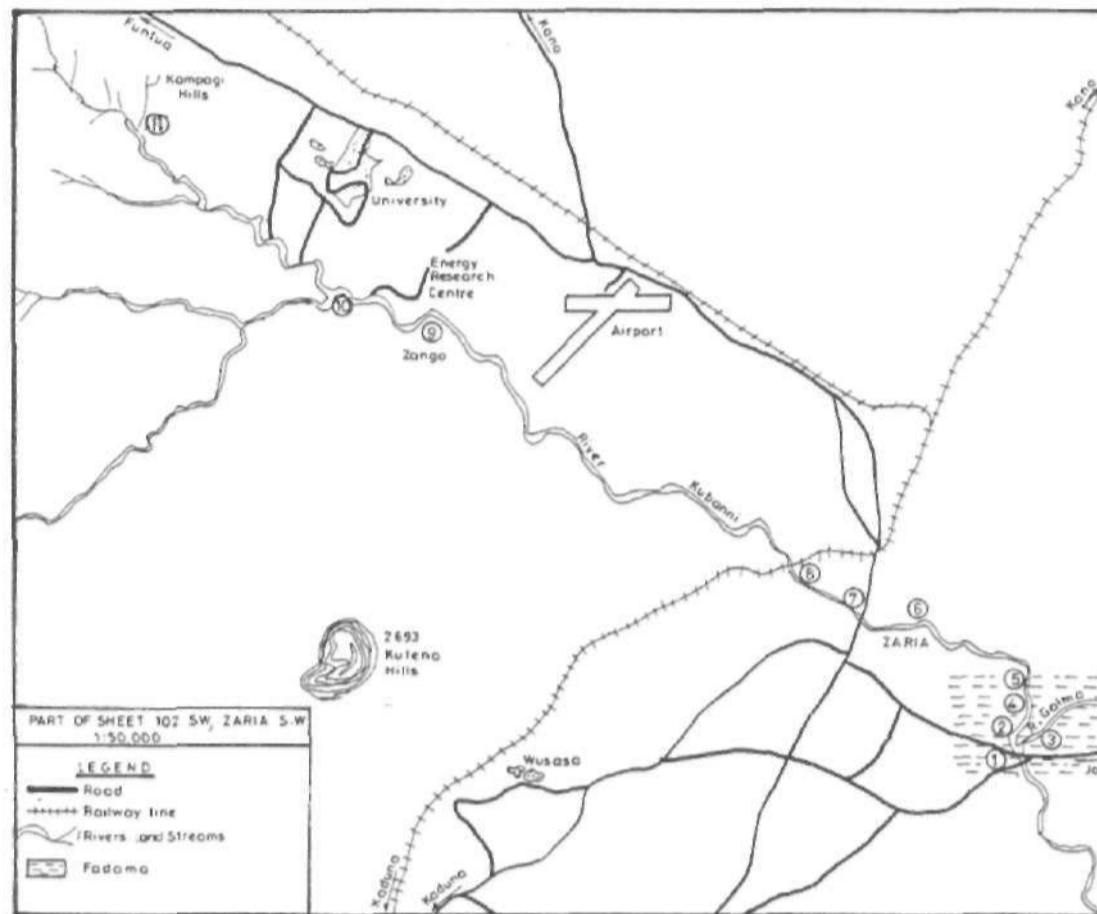


Fig. 3.1 Study Site and Sampling Locations along the Kubanni River

The first five samples (KFP1, KFP2, KFP3, KFP4 and KFP5) were obtained from a 'Fadama' within a wide basin of the river Kubanni along Jos Road. At this point the Kubanni River and the Galma River meet at a confluence. The second sampling point was the Maje Road Bridge where the sample KFP6 was obtained. After this point, the next point was the Tudun Wada Bridge where the sample KFP7 was obtained. The sample KFP8 was obtained at the Kano - Kaduna Bye-Pass Bridge. After Kano-Kaduna Bye-Pass Bridge, the next point taken into consideration was the Zango Bridge where sample KFP9 was obtained. Another sample was obtained at the Ahmadu Bello University (A.B.U.) Dam (KFP10). The last point where the sample KFP11 was obtained is at the Kampangi Hills.

These sediments were allowed to dry in an oven at 50°C for three days and were then homogenized, by manual grinding in an agate mortar. The powder obtained after grinding was used for the preparation of pellets used for the analysis. A Mettler 100CA digital balance was used for weighing the powdered samples, with only 2.0-g of each sample required for the making of the pellets. A cellulose binder Polyvinyl Chloride (PVC) was added to each 2.0 g of the sediments (powder) sample. The mixture was re-homogenized in an agate mortar. The samples were then pelletized (using the *Specac Hydraulic Press*) by applying constantly a pressure of about 11.5 tones per cm². Pellets of 20 mm diameter and constant thickness of 5 mm were obtained from the samples.

3.3 Experimental

The absorption of X-ray by matter may lead to the excitation of secondary characteristic X-rays that is applied in Spectro-chemical Analysis and Fluorescence

Spectrometry. X-ray emission spectrometry is a group of non-destructive instrumental methods used in chemical analysis. The emission of characteristic x-rays following atomic excitation has long been used for elemental analysis (Bertin, 1978). Chemical elements can be analysed quantitatively by measuring the intensities of their characteristic photo-peaks or energy. These measurements can be performed in two ways.

(a) Wavelength Dispersive XRF (WDXRF) Technique

The use of the various wavelengths of the emitted X-rays could be used in analysis in a method termed the wavelength dispersive technique. In this method the several X-ray lines emitted by the specimen are dispersed specially by crystal diffraction, prior to detection, on the basis of their wavelengths. This method was not used in this work.

(b) Energy Dispersive XRF (EDXRF) Technique

The separation of the characteristic X-ray lines according to their energies could be achieved with the use high resolution Si(Li) detectors. This capability leads to another form of XRF known as Energy Dispersive XRF (EDXRF). Useful in qualitative and quantitative elemental analysis of solid or liquid materials. Although it is similar WDXRF spectrometry in principle, there are some important differences in its application. The basic of operation of an EDXRF spectrometer includes the collection and display of information about several elements (from Sodium to Uranium) in a sample. Johnson and King, (1987) attributes the versatility of the technique to its rapid, real-time multi-elemental detection capability for various samples. This can be accomplished by adjusting the energy of the excitation radiation just above the absorption edge of the element of interest leading to high sensitivity and selectivity in the analysis. This can be accomplished by using excitation sources such as secondary X-rays, X-ray tube or radioisotope sources.

Generally, the energy dispersive spectrometer consists of an excitation source (radioisotope or x-ray generator), a detector, and a counting unit, which consists of a high voltage power supply, preamplifier, amplifier, single or multi-channel analyser. The characteristic peaks are resolved from the spectrum by tube height analysis. The present work was performed at the Centre for Energy Research and Training, Ahmadu Bello University, Zaria, where the following radio-isotope sources:- 25mCi Fe-55, 25mCi Cd-109 and 30mCi Am-241 are available although in this work only two radioactive sources, 25mCi Fe-55 and 25mCi Cd-109 were used for excitation of the characteristic K-lines of light and medium elements. Light elements up to Chromium, $Z = 24$ can be detected by use of Fe-55. Medium elements from Germanium, $Z = 32$, to Molybdenum $Z = 42$, can be effectively excited by Cd-109 source.

The quantitative analysis with EDXRF requires optimisation of the sample preparation technique for the problem at hand and then determination of an adequate method of correction for absorption and enhancement (Johnson and King, 1987). The analysis of energy dispersive spectra is based on quantitative analysis, determination of line intensities and quantification of results based on different models for correcting intensities for matrix effects. Since X-ray spectra contains only few lines per element, qualitative X-ray spectrometric analysis which consists in excitation and recording of the X-ray spectrum of the sample, identification of the peaks, and perhaps classification of each element as a major, minor, or trace constituent on the basis of the intensities of its peaks. In this work a non-linear least square fitting programme developed by IAEA and called AXIL is used for the determination of line intensities. In routine analysis of many samples, the situation frequently occurs where all the samples have very similar

composition; the concentrations of the elements to be analysed do not vary much from sample to sample, and the matrix remains almost identical. By using good standards, a direct comparison of the spectra can yield accurate quantitative results. This simple method is useful for thin targets and also for thick targets if the matrix of the standard and the unknown sample is identical.

The comparative analysis programme takes the results from the AXIL fitting for the standard and for the analysed samples. By knowing the composition of the standard with good accuracy and precision, the unknown spectrum results can be directly compared, and the resulting concentrations of the elements in the sample can be determined.

3.4 Standards

The quantitative determination of trace elements of sediments in this work was achieved by the use of simple comparative X-Ray Fluorescence Analysis (XRFA). The method consists of comparing the fluorescence parameters of a 'Sample' to a second material designated as the 'Standard'. Such standards have accurately predetermined concentration of the appropriate trace element(s) of interest.

Sediment standards are usually those of identical matrices or materials as close as possible to the composition of the sediment. The aim of this is to avoid complicated calculation as in the fundamental parameter methods. Standards are usually referred to as 'Certified' or simply Standard Reference Materials (SRMs). SRMs from the following sources namely:

- (a) National Institute of Standards and Technology (NIST). Office of Standard Reference Materials, Washington, D.C.20234, USA and

(b) The United State Geological Survey (USGS)

Were used for the sediment analysis. Four SRMs were used in the comparative analysis of Kubanni River sediment. They are:

- (i) NIST - 278 (Obsidian Rock).
- (ii) NIST - 688 (Basalt Rock).
- (iii) USGS - AG V-1 (Analyzed Andasite) and
- (iv) USGS - G.2 (Granite)

Were prepared in the same manner as the samples in readiness for the EDXRF analysis. Care was taken during sample preparation in order to minimise the contamination of the samples and standards due to excessive direct contact, adding too much binder or by applying excessive pressure as these could give rise to errors in the measured concentrations of trace elements in the samples and standards.

The standards were prepared in identical manners with the samples. This is necessary in order to reduce matrix effect, as well as ensuring uniform X-ray attenuation and absorption.

3.5 Quality Control

In XRF, the validation of sample comparative technique could be achieved by using standard reference materials (SRMs) of similar matrix as a control for the sample under investigation. The essence of this validation is to check the accuracy of the entire system since the unknown or literature values of the SRM is re-investigated by the analyst. The bias of the system could be deduced from the imprecision of the results. The accuracy of the entire system could be established by observing the variation in the precision

between differences with the literature value and the experimental values. Four SRMs (NIST 278, NIST 688, USGS-G-2 and USGS AGV-1) were used as quality control in this work. Pellets of these SRMs were irradiated by Fe-55 and Cd-109 sources and their characteristic X-rays analysed in the same way as the samples. The concentration of each element determined from this work was compared with the literature values. The results are shown on Table 3.1a, b, c and d.

Table 3.1a. Determination of Elemental Content of NIST - 278 SRM

(Values in ppm otherwise, as specified)

| Elements | Literature Values | This Work |
|----------|-------------------|-----------|
| Si% | 34.0 | 33.15 |
| K % | 3.44 | 3.49 |
| Ca % | 0.70 | 0.82 |
| Ti % | 0.15 | < 0.17 |
| V | 15.0 | ND- |
| Fe% | 1.05 | 1.06 |
| Co | 1.50 | 12.6 |
| Zn | 55.0 | < 73.4 |
| Rb | 127 | 127.4 |
| Sr | 63.5 | 63.8 |
| Y | 41.0 | 41.3 |
| Zr | 295 | 295 |
| Nb | ND- | 16.8 |

Table 3.1b. Determination of Trace Element in NIST-688 SRM.

(Values in ppm otherwise, as specified)

| Elements | Literature Value | This Work |
|----------|------------------|-----------|
| Si% | 22.5 | 26.5 |
| K% | 0.16 | 0.05 |
| Ca% | 8.68 | 8.35 |
| Ti% | 0.70 | 0.67 |
| V | 250 | 223 |
| Fe% | 5.93 | 2.23 |
| Co | 49.7 | 49.7 |
| Zn | 58.0 | < 79.6 |
| Rb | 1.91 | ND- |
| Sr | 169 | 162.5 |
| Y | 17.0 | 15.4 |
| Zr | 60.6 | 60.6 |
| Nb | ND - | < 13.0 |

Table 3.1c Determination of Elemental Content of USGS- G-2 SRM
(Values in ppm otherwise, as specified)

| Elements | Literature Value | This Work |
|----------|------------------|-----------|
| Si% | 32.2 | 32.0 |
| K% | 3.71 | 3.58 |
| Ca% | 1.40 | 1.28 |
| Ti% | 0.28 | 0.20 |
| V | 36.0 | 36.5 |
| Fe% | 1.60 | 1.11 |
| Co | 4.60 | < 10.7 |
| Zn | 86.0 | 86.0 |
| Rb | 170 | 170 |
| Sr | 478 | 495 |
| Y | 11.0 | 12.2 |
| Zr | 309 | 309 |
| Nb | 12.0 | 12.0 |

Table 3.1d. Determination of Elemental Content of USGS- AGV I SRM,
(Values in ppm otherwise, as specified)

| Elements | Literature Values | This Work |
|----------|-------------------|-----------|
| Si% | 27.4 | 25.1 |
| K% | 2.41 | 2.50 |
| Ca% | 3.53 | 3.71 |
| Ti% | 0.63 | 0.68 |
| V | 121 | 140 |
| Fe% | 1.60 | 1.60 |
| Co | 15.3 | < 22.0 |
| Zn | 88.0 | < 86.7 |
| Kb | 67.3 | 51.1 |
| Sr | 662 | 651 |
| Y | 20.0 | 15.4 |
| Zr | 227 | 227 |
| Nb | 15.0 | < 25.5 |

The quality assurance results show that the determinations are better than 5% for most of the elements. The worst data was the value for the determination of Co in NIST 278 (Obsidian Rock.) This could not be explained. However, all other elements determined showed that the quality control for the experiment justified the accuracy of the results of the analysis since most of the elements determined were in good agreement with literature values.

3.6 Data Evaluation Methods

After determining the concentrations for elements in sediments for different sites along the Kubanni River, the data so obtained were subjected to various statistical analysis in order to study the trend and distribution of the elements. Different geochemical (Enrichment Factors, Clarke Ratios) and statistical methods were used to for the interpretation of the data. The following is a discussion of the data evaluation methods used.

3.6.1 Enrichment Factors

The determination of the Enrichment Factors (EFs) is the *a priori* prediction of the variation of the concentration of an element determined with respect to its concentration in the earth crust. The knowledge on the enrichment factors could assist in establishing the reference data as desirable for Kubanni River monitoring. Enrichment factor in sediment studies is defined as the ratio of an element concentration in sediment to some reference element within the same matrix. The enrichment factor of an element in the sediment relative to its abundance in the earth's crust is termed Crustal Enrichment; usually known as Clarke Enrichment (Gluskoter, et. al., 1977). Crustal enrichment tends to throw some light on the modification of elemental concentrations in sediment depositions. The enrichment ratios of trace elements determined for each of the deposits studied along the course of the Kubanni River, were calculated relative to the concentration of silicon in the samples, since silicon is always present in the earth's crust as alumino-silicates.

Enrichment factor as defined in this work is thus:

$$EF_{(Crustal)} = \frac{[X]_s / [Si]_s}{[X]_c / [Si]_c} \dots \quad 3.1$$

Where EF denotes the Enrichment Factor:

- $[X]_s$ = Concentration of the element X in the sample.
- $[Si]_c$ = Concentration of the Silicon in the earth's crust.
- $[X]_c$ = Concentration of the element X in the earth's crust.
- $[Si]_s$ = Concentration of Silicon in the sample.

Other normalising elements like Fe, Sc has been discussed by Pardue, et. al. (1988), Adetunji and Ong (1989) respectively, but with some limitations for sediments in the case of iron. EFs were determined for all the sediment analysed and the interpretation will follow later.

3.6.2 Clarke Ratio

Clarke ratio is defined as the ratio of concentration of element in the sample to the mean global concentration of the same element in the earth's crust. Clarke Ratio tends to throw some light on the modification of elemental concentrations in sediment depositions. It shows the magnitude of the variation of an element in a given location with respect to a geochemically accepted and globally fixed value called the 'Clarke Value'.

Clarke Ratio as defined in this work is thus:

$$R = [X_s / X_c] 100 \dots \quad 3.2$$

X_s = Concentration of element in sample

X_c = Clarke Value for the given element.

The Clarke ratios were determined for all elements and the discussion will follow later.

3.6.3 Coefficient of Variation (CV)

The Coefficient of Variation is the ratio of the standard deviation of the concentration of a given element in the sample at a given site with respect to the average concentration of the element in the river sediments for all the sites determined, expressed as a percentage.

Coefficient of variation as defined in this work is:

$$CV = [S.D / X]. 100\% \quad \dots \quad 3.3$$

Where S.D. = Standard deviation of the element concentration in the sample for different sites.

X = Mean concentration of the element determined for a given site along the river course.

This evaluation for each element gives an assessment of how each element varies along the river course. The variation could be either due to depletion or enrichment that could arise due to various physico-chemical or geochemical factors. It could also be used to assess pollution along the riverbeds if all the factors responsible for pollution are rightly assessed.

3.6.4 Correlation Analysis

The measure of similarity between paired data is termed correlation analysis. The degree of inter-relation between variables can be estimated with the help of correlation

coefficients (r) without any influence by measurement units. Correlation is the ratio of covariance (joint variation of two variables about their common mean) of two variables to the product of the standard deviation (Davis, 1973).

Correlation Coefficient being a ratio is a dimensionless number and covariance may equal but can never exceed the product of the standard deviation of its variables. Correlation ranges from +1 to -1. A correlation of +1 is an indication of a perfect direct relationship between two variables. While that of -1 indicates that one variable changes inversely in relation to the other. A spectrum of less than perfect relationships lies between the two extremes including zero which indicates the lack of any linear relationship.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Elements determined from Kubanni River Sediments

X-ray fluorescence Analysis has been successfully used in determining the elements present in the Kubanni River Sediments. The different sites from which sediments were obtained are coded as shown in Table 4.1.

Table 4.1 Location and Sample codes

| Location | Sample Codes |
|-----------------------------------|---------------------------|
| Around Galma/Kubanni River | KFP1, KFP 2, KFP 3, KFP4, |
| Confluence (<i>Fadama</i> areas) | and KFP5 |
| Maje road | KFP6 |
| Tudun Wada Bridge | KFP7 |
| Kano/Kaduna Bridge | KFP8 |
| Zango Bridge | KFP9 |
| University Dam | KFP10 |
| Kampagi Hill | KFP11 |

Table 4.2 gives the report of the abundance of the elements determined. This table gives a list of the concentrations for all the trace elements detected from the Kubanni River sediments in this work. Some of the concentrations are reported as 'less than' values because they are below the limit of quantitative accuracy but above zero (Gluskoter, *et. al.*, 1977). Several workers fore example Ruch *et. al.* (1974) and Valkovic, (1983) reported that less than values do not alter much the statistics of the population notably where the total population is not in size with the total number of such data sets.

Table 4.2 Trace Elements in Kubanni River Sediments as Determined in This Work.

(Concentrations are in ppm or as stated otherwise. ND -Not determined).

| Elements | KFP1 | KFP2 | KFP3 | KFP4 |
|----------|---------|----------|---------|---------|
| Si(%) | 28.730 | 36.740 | 32.450 | 33.030 |
| K(%) | 2.100 | 2.540 | 2.460 | 2.110 |
| Ca(%) | 0.520 | 0.290 | 0.320 | 0.450 |
| Ti(%) | 0.477 | 0.385 | 0.440 | 0.518 |
| V | ND | ND | ND | 10.769 |
| Fe(%) | 1.239 | 1.133 | 1.143 | 1.246 |
| Co | 13.486 | < 12.612 | <10.730 | 19.461 |
| Zn | 138.944 | 57.511 | 57.360 | 201.824 |
| Rb | 113.667 | 97.415 | 132.694 | 112.924 |
| Sr | 75.02 | 63.053 | 54.893 | 76.383 |
| Y | 47.133 | 32.726 | 47.388 | 48.876 |
| Zr | 878.000 | 640.463 | 821.681 | 995.108 |
| Nb | 32.416 | 15.441 | 26.048 | 34.321 |

Table 4.2 *Continued*

| Elements | KFP5 | KFP6 | KFP7 | KFP8 |
|----------|---------|---------|---------|----------|
| Si(%) | 37.740 | 31.280 | 28.520 | 37.070 |
| K(%) | 2.620 | 2.660 | 1.920 | 2.470 |
| Ca(%) | 0.350 | 0.770 | 0.840 | 0.250 |
| Ti(%) | 0.447 | 0.460 | 0.442 | 0.395 |
| V | 124.943 | ND | 470.388 | 514.895 |
| Fe(%) | 1.033 | 1.142 | 1.196 | 1.137 |
| Co | < 8.207 | <10.450 | <19.138 | <18.429 |
| Zn | 80.239 | 141.268 | 664.534 | 65.054 |
| Rb | 129.160 | 105.665 | 114.514 | 126.064 |
| Sr | 61.315 | 70.318 | 78.575 | 59.365 |
| Y | 85.600 | 38.219 | 42.281 | 42.923 |
| Zr | 227.931 | 984.163 | 882.901 | 1018.030 |
| Nb | 32.562 | 25.784 | 29.648 | 66.920 |

Table 4.2 *continued*

| Elements | KFP9 | KFP10 | KFP11 |
|----------|---------|---------|---------|
| Si(%) | 21.220 | 27.930 | 31.890 |
| K(%) | 1.260 | 1.440 | 1.670 |
| Ca(%) | 0.440 | 0.270 | 0.250 |
| Ti(%) | 0.600 | 0.631 | 0.680 |
| V | 310.899 | ND | 35.390 |
| Fe(%) | 1.529 | 1.186 | 1.180 |
| Co | 22.699 | 22.715 | 22.320 |
| Zn | 56.225 | 108.155 | 57.150 |
| Rb | 147.189 | 97.415 | 123.220 |
| Sr | 78.361 | 63.053 | 79.430 |
| Y | 44.935 | 32.726 | 94.370 |
| Zr | 464.237 | 640.463 | 2171.0 |
| Nb | 44.580 | 15.441 | 41.180 |

Most of the elements determined could be affected by the deposition rates, which is directly influenced by the stream velocities, however the values obtained could not properly reflect stream velocity rates, since other factors could account for the variation. Stream velocities were determined for various sampling sites and the data given in Table 4.3

Table 4.3 Stream velocities at Different Points along the WaterCourse of the Kubanni River

| Location | Average Velocity (ms^{-1}) |
|-------------------------|---------------------------------------|
| Kaduna/Bye Pass Bridge. | 0.643 |
| Zango Bridge | 0.091 |
| Kampangi Hill | 0.063 |

Apart from the Kaduna Bye-Pass Bridge, other sites showed a slow moving velocity for the Kubanni River and consequently there will be enhanced deposition of sediments at Zango Bridge and Kampangi Hill. Other sites showed complete drought, as there was stagnant water during the time of sampling. This period was chosen so as to obtain the actual status of the riverbed in terms of its bio-accumulation of bed debris as serious leaching and drainage of the waterway could have affected sampling during the rains. More-over in terms of environmental measurements, the dry-season irrigation of the Kubanni River calls for intensive usage of the slowly moving debris-load of the water that happens to be collected during irrigation. These factors determined the concentration of the elements and could either lead to enrichment or depletion of the elements determined.

The data obtained in this work will therefore be discussed in terms of Enrichment Factors (EFs), Clarke Ratios, Coefficient of Variations and Correlation Coefficient as defined earlier.

Enrichment Factors (EFs) of each element were determined for all the sediment deposits investigated along the course of the river (Table 4.4). The values of $[X]_c$ and $[Si]_c$ are shown in Appendix A

Table 4.4 Crustal Enrichment Factors (CEFs) of Trace Elements in Kubanni River Sediments

| Elements | KFP1 | KFP2 | KFP3 | KFP4 |
|----------|-------|-------|-------|-------|
| K | 1.084 | 1.033 | 1.124 | 0.947 |
| Ca | 0.106 | 0.046 | 0.057 | 0.076 |
| Ti | 0.717 | 0.452 | 0.585 | 0.677 |
| V | ND- | ND | ND | 0.065 |
| Fe | 0.189 | 0.135 | 0.154 | 0.165 |
| Co | 0.441 | 0.723 | 0.311 | 0.554 |
| Zn | 1.737 | 0.562 | 0.634 | 2.194 |
| Rb | 1.384 | 0.928 | 1.430 | 1.196 |
| Sr | 0.185 | 0.122 | 0.120 | 0.164 |
| Y | 1.444 | 0.784 | 1.286 | 1.303 |
| Zr | 5.149 | 2.937 | 4.267 | 5.077 |
| Nb | 1.540 | 0.573 | 1.095 | 1.418 |

Table 4.4 *continued*

| Elements | KFP5 | KFP6 | KFP7 | KFP8 |
|----------|-------|-------|-------|-------|
| K | 1.030 | 1.071 | 0.998 | 0.988 |
| Ca | 0.540 | 0.144 | 0.172 | 0.039 |
| Ti | 0.511 | 0.635 | 0.669 | 0.460 |
| V | 0.664 | ND | 3.310 | 2.788 |
| Fe | 0.120 | 0.160 | 0.184 | 0.134 |
| Co | 0.204 | 0.314 | 0.631 | 0.467 |
| Zn | 0.763 | 1.622 | 8.369 | 0.630 |
| Rb | 1.197 | 1.182 | 1.405 | 1.190 |
| Sr | 0.115 | 0.159 | 0.195 | 0.113 |
| Y | 1.997 | 1.076 | 1.305 | 1.019 |
| Zr | 5.483 | 5.302 | 5.216 | 4.627 |
| Nb | 1.177 | 1.125 | 1.418 | 2.464 |

Table 4.4 *continued*

| Elements | KFP9 | KFP10 | KFP11 |
|-----------|-------|-------|--------|
| K | 0.880 | 0.764 | 0.776 |
| Ca | 0.121 | 0.056 | 0.045 |
| Ti | 1.220 | 0.975 | 0.918 |
| V | 2.941 | ND | 0.222 |
| Fe | 0.316 | 0.186 | 0.163 |
| Co | 1.006 | 0.765 | 0.659 |
| Zn | 0.951 | 1.390 | 0.643 |
| Rb | 2.427 | 1.220 | 1.352 |
| Sr | 0.262 | 0.160 | 0.177 |
| Y | 1.864 | 1.031 | 2.605 |
| Zr | 3.686 | 3.864 | 11.482 |
| Nb | 2.869 | 0.754 | 2.059 |

The EF is usually compared to the Clarke values of the element in the earth's crust. Clarke values as proposed by Fortescue(1992) were used in determining the EFs in Kubanni River sediments. Mean values of Crustal EFs for Kubanni River sediments as determined in this work are shown in Table 4.5

It could be seen that K, Ca, Ti, Fe, Co and Sr were depleted with respect to their normalized Clarke Values of Fortescue (1992). Also Si, V, Zn, Rb, Y, Zr and Nb were enriched with factors ranging between 1 to 6. The depleted elements could either suggest absence of periodic contamination or dilution of the metal complexes in which they exist. Crustal Enrichment Factors also gives a comparison of geochemical changes between river sediment and sedimentary rock in the earth's crust.

Table 4.5 Mean Values of Enrichment Factors for elements determined at all the sites.

| Elements | Mean \pm SD |
|----------|-------------------|
| K | 0.972 \pm 0.120 |
| Ca | 0.127 \pm 0.147 |
| Ti | 0.710 \pm 0.237 |
| V | 1.665 \pm 1.499 |
| Fe | 0.173 \pm 0.052 |
| Co | 0.552 \pm 0.235 |
| Zn | 1.780 \pm 2.251 |
| Rb | 1.355 \pm 0.382 |
| Sr | 0.161 \pm 0.044 |
| Y | 1.291 \pm 0.596 |
| Zr | 5.190 \pm 2.235 |
| Nb | 1.499 \pm 0.703 |

A summary of Clarke Enrichment is given in Table 4.6.

Table 4.6. Summary of Clarke Enrichment Factors for the Kubanni River Sediments

| CEF Ranges | Elements |
|------------|---------------------------|
| < 1 | K, Ca, Ti, Fe, Co, Sr. |
| 1- 6 | Si, V, Zn, Rb, Y, Zr, Nb. |

The most enriched element is Zirconium. This element is reported to be toxic.

A dose of 250 - 700 mg per day is found to be lethal to rats (Bowen, 1979). Its level in

all the sediment showed very highly Enrichment Factors relative to their Clarke values. Most CEFs ranged from 2.235 to a high value of 11.482 for the upper water -catchment area of the Kubanni River at Kampagi Hills as shown earlier for site KPF11 in Table 4.4. Elements like Si, V, Zn, Rb, Y, Zr and Nb with enrichment factors between 1 and 6 are known to be toxic to some extent (Bowen, 1979), even though useful in some cases. Among the depleted elements (K, Ca, Ti, Fe, Co and Sr) some are toxic while others are relatively harmless to all organisms. Calcium and Titanium are known to be harmless to all organisms (Bowen, 1979).

Table 4.7 shows the toxicity of all the elements detected in the Kubanni River sediments with comments on their toxicity as reported by Bowen (1979).

Bowen (1979) had shown that Ca, Co, Fe, K and Zn are probably essential to all plants. This could be of use to the seasonal crops grown at the Kubanni basin. Elements like Si are essential to some groups, not necessarily for all. Rb, K, Sr and Ca are known to have a very high toxicity, which only arises when a large proportion of the essential ion has been replaced. Elements like Co are known to be very toxic to seed plants. Fe, V and Zn are moderately toxic while Ca, K, Rb and Sr are only toxic to very high concentrations.

Zinc is the element most frequently concerned with plant damage from industrial emissions, e.g. on mine wastes, near smelters, sewage sludges, river dredgings, near galvanised steel buildings and where rubber tyres are burnt (Patterson, 1971; Barrow and Webber 1972). Excess of it inactivates soil enzymes (Tyler, 1974, 1976) and reduces the bacterial population (Griffiths, *et al.* 1975), but does not have marked effects on the fauna. The Kubanni river levels of zinc was found to in the range 56.22 to 664.53 ppm as shown in Table 4.8 which was less than 900 ppm - an upper toxic limit for animals as given by (Jenett *et al.* 1980) .

Table 4.7. Toxicity of All the Elements Detected in Kubanni River Sediments

| Elements | Mean Value of the concentration in ppm) | Reported toxicity by Bowen (1979) | Remark on toxicity in Kubanni River Sediment |
|----------|---|-----------------------------------|--|
| Si(%) | 30.269 | Scarcely toxic | Scarcely toxic |
| K(%) | 1.985 | Scarcely toxic | Scarcely toxic |
| Ca(%) | 0.425 | Relatively harmless | Relatively harmless |
| Ti(%) | 0.494 | Relatively harmless | Relatively harmless |
| V | 241.807 | 10 - 40ppm toxic to plants | Expected to be highly toxic |
| Fe(%) | 1.197 | 10 - 200ppm toxic to plants | Not expected to be toxic |
| Co | <16.386 | 0.1 to 3ppm toxic to plants | Expected to be toxic |
| Zn | 148.842 | 60-400ppm toxic to plants | Expected to be toxic |
| Rb | 118.175 | Scarcely toxic to plants | Scarcely toxic |
| Sr | 69.069 | Scarcely toxic to plants | Scarcely toxic |
| Y | 50.652 | Low | Low |
| Zr | 884.179 | 250 - 700 mg/day lethal to rats. | Toxic |
| Nb | 33.122 | Moderately toxic to mammals. | Moderately toxic. |

Most toxicity problems encountered with zinc are due to Cadmium associated with zinc. As Cadmium appears to be highly toxic to aquatic organism in the 0.02 - 2.0 ppm range, where a dose of 4 ppm in the diet of humans is normally considered toxic (Jenett *et al.* 1980). Some specified values have been accepted as the tolerated level in rivers. For example in Missouri the maximum allowed value as given by Jenett *et al.* (1980) was 150 ppm, while the Kubanni River mean value of zinc was obtained to be 148.84 ppm almost peaking up with the quoted value.

Among the elements reported to be enriched in lower layers of soil are Fe, Ti, V and Zr (Bowen, 1979). In this work only Ti, V and Zr were found to be enriched, while Fe is depleted. Zr is highly enriched in the Kubanni River sediments while Ca, K, and Sr are slightly depleted as should for soils (Bowen 1979). Heavy metals are enriched in upper layers of soils (Bowen, 1979). In this work the heavy elements enriched in upper layers of Kubanni River sediments are Si, V, Zn, Rb, Y, Zr, while Nb, Co, Ca, Ti, Fe, K and S are depleted.

A four class grouping of trace elements in sediment according to their toxicity was reported by Wood (1975) in the following order:

- (i) Class A (very toxic and relatively accessible)
- (ii) Class B (Toxic but very insoluble or very rare)
- (iii) Class C (moderate) and
- (iv) Class D (non-critical)

Based on this classification, the EFs of the elements determined from the Kubanni river sediments were plotted to show the extent of sediment enrichments by class groupings (Fig. 4.1).

Table 4.8. Ranges and Average Concentration of Elements Down-Stream Kubanni River with their Coefficient of Variations.(Concentration in ppm or as indicated)

| Elements | Ranges | Mean \pm SD | CV(%) |
|----------|------------------|-----------------------|---------|
| Si(%) | 21.220 - 37.740 | 31.509 \pm 4.856 | 15.410 |
| K(%) | 1.260 - 2.620 | 2.113 \pm 0.489 | 23.142 |
| Ca(%) | 0.250 - 0.840 | 0.431 \pm 0.205 | 47.563 |
| Ti(%) | 0.385 - 0.678 | 0.494 \pm 0.098 | 19.935 |
| V | 10.769 - 514.895 | 244.547 \pm 219.635 | 89.813 |
| Fe(%) | 1.033 - 1.529 | 1.197 \pm 0.124 | 10.405 |
| Co | 8.207 - 22.715 | 16.386 \pm 5.414 | 33.042 |
| Zn | 56.225 - 664.534 | 148.842 \pm 78.048 | 119.622 |
| Rb | 97.415 - 147.189 | 118.175 \pm 5.299 | 12.946 |
| Sr | 54.893 - 79.430 | 69.069 \pm 8.956 | 12.967 |
| Y | 32.726 - 94.368 | 50.652 \pm 20.293 | 40.065 |
| Zr | 464.237-2173.001 | 884.179 \pm 493.055 | 55.764 |
| Nb | 15.441 - 66.920 | 33.122 \pm 14.429 | 43.563 |

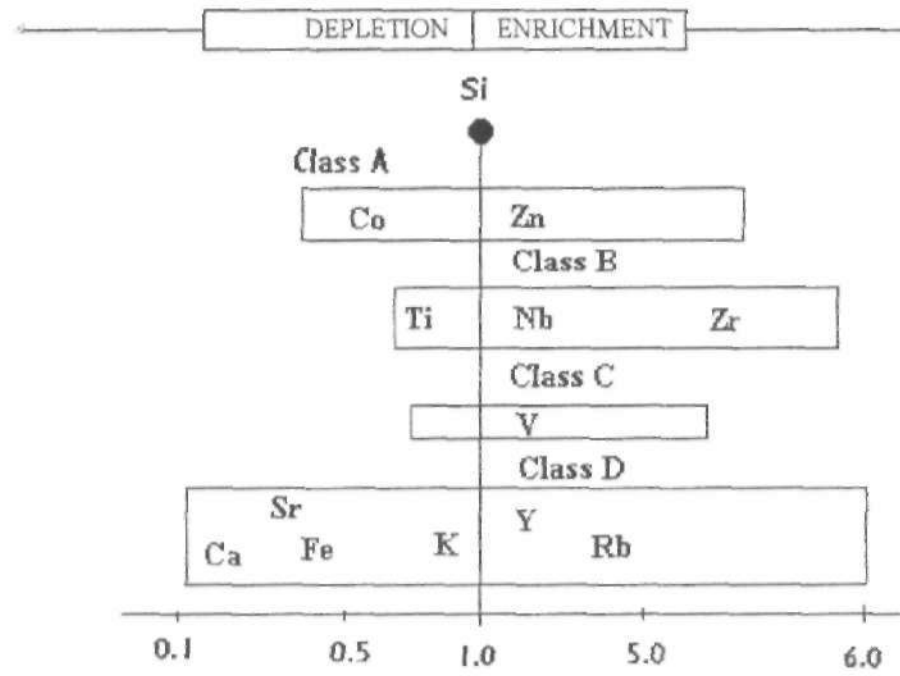


Fig. 4.1 A schematic representation of the Kubannu River Sediment Enrichments

Table 4.9. Clarke Ratio for Trace Elements in Kubanni River Sediments

| Element | FP1 | KFP2 | FP3 | FP4 |
|---------|---------|---------|---------|---------|
| Si | 105.238 | 134.578 | 118.864 | 120.989 |
| K | 114.130 | 138.043 | 133.695 | 114.673 |
| Ca | 11.158 | 6.223 | 6.866 | 9.656 |
| Ti | 75.474 | 60.917 | 69.620 | 81.962 |
| V | ND | ND | ND | 7.918 |
| Fe | 19.919 | 18.215 | 18.376 | 20.032 |
| Co | 46.503 | 43.489 | 37.0 | 67.106 |
| Zn | 182.821 | 75.672 | 75.473 | 265.557 |
| Rb | 145.726 | 124.891 | 170.120 | 144.774 |
| Sr | 19.536 | 16.419 | 14.295 | 19.891 |
| Y | 152.041 | 105.567 | 152.864 | 157.664 |
| Zr | 541.975 | 395.347 | 507.210 | 614.264 |
| Nb | 162.080 | 77.205 | 130.240 | 171.605 |

Table 4.9 *Continued*

| Elements | KFP5 | KFP6 | KFP7 | KFP8 |
|----------|---------|---------|---------|----------|
| Si | 138.241 | 114.578 | 104.468 | 135.787 |
| K | 142.391 | 122.826 | 104.347 | 134.239 |
| Ca | 7.510 | 16.523 | 18.025 | 5.364 |
| Ti | 70.727 | 72.784 | 69.936 | 62.500 |
| V | 91.869 | ND | 345.873 | 378.599 |
| Fe | 16.607 | 18.360 | 19.228 | 18.279 |
| Co | 28.300 | 36.034 | 65.993 | 63.548 |
| Zn | 105.577 | 185.878 | 874.386 | 85.597 |
| Rb | 165.589 | 135.467 | 146.812 | 161.6270 |
| Sr | 15.967 | 18.311 | 20.462 | 15.459 |
| Y | 276.129 | 123.287 | 136.390 | 136.461 |
| Zr | 757.982 | 607.508 | 545.0 | 628.413 |
| Nb | 162.810 | 128.920 | 148.240 | 334.600 |

Table 4.9. *Continued.*

| Elements | KFP9 | KFP10 | KFP11 |
|----------|---------|---------|----------|
| Si | 77.728 | 102.307 | 116.813 |
| K | 68.478 | 78.260 | 90.760 |
| Ca | 9.442 | 5.793 | 5.364 |
| Ti | 94.936 | 99.841 | 107.270 |
| V | 228.602 | ND | 26.022 |
| Fe | 24.581 | 19.067 | 19.051 |
| Co | 78.272 | 78.327 | 76.986 |
| Zn | 73.980 | 142.309 | 75.196 |
| Rb | 188.703 | 124.891 | 157.980 |
| Sr | 20.406 | 16.420 | 20.684 |
| Y | 144.951 | 105.567 | 304.412 |
| Zr | 286.561 | 395.347 | 1341.358 |
| Nb | 222.900 | 77.205 | 205.915 |

Table 4.10 Summary of the Clarke Ratio for the Kubanni River Sediments

| Clarke Ratio Ranges | Elements |
|---------------------|---------------------------------|
| R < 10 | Ca. |
| 10 < R < 100 | Sr, Fe, Co, Ti. |
| 100 < R < 1500 | K, Si, Rb, Y, Nb, V, Zn and Zr. |

The Clarke ratio (Table 4.10) also shows that the following elements Ca, Sr, Fe, Co, and Ti were depleted as we have seen in the case of Enrichment Factors, while K, Si, Rb, Y, Nb, V, and Zn are enriched. From the Clarke ratio one can conclude that Silicon is a good normalizing element, as the enrichment factor results are in good agreement with the Clarke ratio results. Apart from the use of geochemical factors as discussed above for the data evaluation, use was also made of statistical methods to test the relation between the variation of an element with respect to their respective sites

Coefficient of Variation as defined in Chapter 3.5.3 was calculated and the results were shown earlier in Table 4.8. The CV of trace elements in Kubanni River was found within the range 10 to 120. Three elements Fe, Rb and Sr showed low C.V (<20), this could be probably due to low deposition, high washout or that the elements exist in highly soluble forms. The other elements had high CV ranging from 20 to 120, this could be due to high sedimentation and low wash out. The high CV suggests that elements might have come from external sources, therefore polluting the river. This sources could be fertilizers from farm lands, foundry wastes, burnt rubber tyres, sewage

sledges or any other ways suspected of causing pollution.

The Correlation matrix represents the whole set of sediments. Table 4.11 shows significant correlation for the following pairs of elements determined from the Kubanni River sediments - Ca-Zn (0.753) and Ti - Co (0.702).

Significant positive correlation also exists between Rb - Nb (0.619), Fe - Co (0.604), Fe - Sr (0.588), Sr - Co (0.521), Ti - Sr (0.498), and Ca - Sr (0.488). On the other hand, significant negative correlation exists between K - Co (-0.867); K - Ti (-0.83), K - Fe (-0.740), Si - Fe (-0.514), Si - Sr (-0.520) K - Sr (-0.560). The implication of these results shows that the complexes of other elements within the sediment strata could influence the presence of any given element.

Also another prominent feature of sediments is the effect of the composition of the upper layers of the aqueous environment which is basically determined in terms of the turbidity of the surface layers of the sediment. Where the aqueous layers are less affected by the gravitational settling forces of the sediments the water layers appear highly turbid. This could be used to ascertain the degree of pollution of the water level above the sediments. As a result of this, the Kubanni River was investigated for its turbidity at various sites

Table 4.11 Correlation Coefficients of Elements Determined from the Kubanni River Sediments

| | Si | K | Ca | Ti | Fe | Co | Zn | Rb | Sr | Y | Zr | Nb |
|----|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Si | 1 | 0.374 | -0.187 | -0.330 | -0.514 | -0.429 | -0.191 | -0.009 | -0.520 | 0.145 | -0.047 | 0.007 |
| K | 0.374 | 1 | 0.081 | -0.830 | -0.740 | -0.867 | -0.106 | -0.194 | -0.560 | -0.014 | -0.167 | -0.042 |
| Ca | -0.187 | 0.081 | 1 | 0.226 | 0.124 | -0.150 | 0.753 | -0.145 | 0.448 | -0.278 | 0.091 | -0.177 |
| Ti | -0.330 | -0.830 | -0.226 | 1 | 0.472 | 0.702 | -0.178 | 0.128 | 0.498 | 0.359 | 0.428 | -0.018 |
| Fe | -0.514 | -0.740 | 0.124 | 0.472 | 1 | 0.604 | 0 | 0.436 | 0.588 | -0.226 | -0.055 | 0.217 |
| Co | -0.429 | -0.867 | -0.150 | 0.702 | 0.604 | 1 | 0.158 | 0.079 | 0.521 | -0.045 | 0.380 | 0.292 |
| Zn | -0.191 | -0.106 | 0.753 | -0.178 | 0 | 0.158 | 1 | -0.190 | 0.430 | -0.190 | -0.003 | -0.128 |
| Rb | -0.009 | -0.194 | -0.145 | 0.128 | 0.436 | 0.079 | -0.190 | 1 | 0.064 | 0.414 | -0.058 | 0.619 |
| Sr | -0.520 | -0.560 | 0.488 | 0.498 | 0.588 | 0.521 | 0.430 | 0.064 | 1 | 0.185 | 0.406 | 0.109 |
| Y | 0.145 | -0.014 | -0.278 | 0.359 | -0.226 | -0.045 | -0.190 | 0.414 | 0.185 | 1 | 0.423 | 0.267 |
| Zr | -0.047 | -0.167 | -0.091 | 0.428 | -0.055 | 0.380 | -0.003 | -0.058 | 0.406 | 0.423 | 1 | 0.266 |
| Nb | 0.007 | -0.042 | -0.177 | -0.018 | 0.217 | 0.292 | -0.128 | 0.619 | 0.109 | 0.267 | 0.266 | 1 |

Table 4.12 gives the result of turbidity measurements made for five sites.

Table 4.12 Turbidity Measurements for the Kubanni River

| Site | Turbidity Levels (FTU) | pH Values |
|------|------------------------|-----------|
| KFP1 | 25 | 7.5 |
| KFP2 | 31 | 7.0 |
| KFP3 | 23 | 6.8 |
| KFP4 | 43 | 7.0 |
| KFP5 | 44 | 6.8 |

Turbidity is a good measure of sedimentation, filtration and storage efficiency, particularly if supplemented by the total microscopic and particle count. It is due to suspended material such as clay, silt organic and inorganic materials. Turbidity can interfere with proper disinfecting of water microorganisms, taste and odor. Turbidity measurements were made with the help of turbidity meter. The turbidity-meter used in this work was the Al 1000 Aqualytic Model used at the Zaria Water Board Laboratory.

The results shown in Table 4.12 show that the Kubanni River have a very high turbidity when compared with the limit set by the drinking water regulations. The drinking water regulations require the maximum contaminant level turbidity not exceeding one turbidity unit (Salvato, 1992). The high turbidity might be the cause of the bad odour of the water, showing the presence of some contaminants along the riverbed. These high turbidity values are also indications that the Kubanni River water is not potable, therefore it has to be treated before domestic usage. Closely associated with turbidity levels is the pH value of the sediment superficial waters. This was also determined for the Kubanni river water. It was not clear how the turbidity levels could influence the pH values. However from Table 4.12 the pH was not constant for all the sites although it fell within the ranges of (6.5 to 9.2) as limits tolerated by World Health

Organization (WHO, 1971) for drinking water.

As reported by Salvato (1992), the pH of natural water ranges from 5.0 to 8.5 and these values are acceptable except when viewed from the standpoint of corrosion.

Corrosion is associated with pH levels below 6.5 to 7.0 (Salvato 1992). However the results of this analysis show that the Kubanni River water might not pose any hazards and are quite suitable for treating for drinking purposes if well treated.

4.2 Comparison With Other Works

The mean of the elemental concentrations in Kubanni river sediment is being compared with those of sediments given by Wedepohl (1968) and Deep sea sediment reported by Fong and Chatt (1987). The results are shown in table 4.13

It was found that Si, K, Ti, Co, Rb and Y had concentration in agreement with the observation of Wedepohl (1968), that these elements occur in larger quantities in the earth's crust. The element Ti is usually found in high concentration in the earth crust. Ti was detected as an average of 0.49%, which falls within the range of granitic, rocks (Aubert, *et al.*, 1977).

Concentration of Ca, Fe and Sr was found to be very low compared with those of major and Deep-sea sediments. The Major sediments (Wedpohl, 1968) being rock sediments are expected to have higher concentration of Iron than the Kubanni river sediment, as Iron is not expected to be leached during weathering. The low values of Ca and Sr in this work might be due to the fact that these elements were lost from rocks during weathering and then transported to the river.

The elements Zn, Zr and Nb were found to be enriched in Kubanni river sediment than in the major sediment. The reason for high values determined for Zn could be due to contamination from industrial activities and burning of coal for

domestic usage around the water catchment areas.

Table 4.13 Comparison of elements determined from Kubanni River Sediment with other works for sediments (Results in ppm unless as stated otherwise).

| Elements | Other Sediments (Wedepohl, 1968) | Deep sea sediment (Chatt, 1987) | Kubanni River Sediments (1998) |
|----------|-------------------------------------|------------------------------------|-----------------------------------|
| Si (%) | 24.5 | 12.2 | 30.2 ± 6.28 |
| K (%) | 2.0 | 1.03 | 1.98 ± 0.54 |
| Ca (%) | 6.6 | 19.9 | 0.42 ± 0.19 |
| Ti (%) | 0.38 | 0.22 | 0.49 ± 0.1 |
| V | 105 | 60.7 | 242 ± 200 |
| Fe (%) | 4.10 | 2.27 | 1.20 ± 0.12 |
| Co | 14.0 | 7.57 | <16.4 |
| Zn | 95.0 | <220 | 149 ± 178 |
| Rb | 135 | 4.10 | 118 ± 15.0 |
| Sr | 320 | 905 | 69.0 ± 8.95 |
| Y | 40.0 | ND | 50.6 ± 20.3 |
| Zr | 150 | 391 | 884 ± 493 |
| Nb | 13.0 | ND | 33.1 ± 14.4 |

ND = Not Detected

Vanadium is found to be high in Kubanni river sediment, this could be from contamination for certain types of fuel oil (Bowen, 1979).

The differences between Deep sea and Kubanni river sediments might be due to dilution. Elements such as Si, Ti, K, V, Co, Rb and Zr were found to be less concentrated in the Deep-Sea sediments than in the Kubanni river sediments. The summary of the findings of this work is given in the next chapter.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

The application of EDXRF technique in this work has been successful in the determination of elements from the Kubanni River sediments. Most of the elements identified were heavy metals of environmental concern. The elements determined are: Si, K, Ca, Ti, V, Fe, Co, Zn, Rb, Sr, Y, Zr and Nb. Among these elements, the following: K, Ca, Ti, Fe, Co, and Sr showed depletion while the remaining others were enriched. The depletion shown by certain elements could be due to dilution if the elements had existed in highly soluble form, while the enrichment could be attributed to high sedimentation rates of the derivative complexes of the elements in solution. The enrichment as well as high coefficient of variation could be as a result of the following: contamination from external sources of pollutants such as: fertilizers from farmlands within the vicinity, foundering wastes, burnt rubber tyres as was the case at most of the sites studied; sewage sludge or any other wastes capable of polluting the river. The high turbidity of the raw water is also an indication of sediment contamination, although the pH values obtained were within the tolerable limits set by WHO (1971) for potable water.

Significant positive correlation exists between the following paired data: Ca-Zn, Ti-Co, Rb-Nb, Fe-Co, Fe-Sr, Sr-Co, Ti-Sr, and Ca-Sr while K-Co, K-Ti, K-Fe, Si-Fe, Si-Sr and K-Sr showed negative correlation.

More studies have to be undertaken by periodically sampling all the points outlined in this work in order to establish a very reliable reference data for the identified trace elements. In this work elements with lower atomic number ($Z \leq 13$) could not be identified with Fe-55 and Cd-109 sources. In order to measure K-spectra of elements

down to atomic number 4, the use of ultra-long X-ray Fluorescence Spectrometers and Electron Probe is therefore suggested.

There is need also to use Am-241 and other sources for X-ray spectrometric excitation in order to obtain the concentrations of elements with higher atomic numbers. Also use of other techniques such as Neutron Activation Analysis is recommended in order to fill up the missing gaps for the elements of interest.

A complete reference data for the river will be established if the composition of the trace elements in the raw water and treated water could be determined. This will be considered in future work. In conclusion therefore, EDXRF has been used for the determination of elements from the Kubanni River sediments though with some limitations.

APPENDIX A

Clarke Values for Crustal Elements (Fortescue, 1992)

| Elements | Clarke Values |
|----------|--|
| | (Concentration in ppm or as indicated) |
| Si(%) | 27.300 |
| K(%) | 1.840 |
| Ca(%) | 4.660 |
| Ti(%) | 0.632 |
| V | 136.0 |
| Fe(%) | 6.220 |
| Co | 29.0 |
| Zn | 76.0 |
| Rb | 78.0 |
| Sr | 384.0 |
| Y | 31.0 |
| Zr | 162.0 |
| Nb | 20.0 |

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