LEVELS OF FLUORIDE ION AND SELECTED HEAVY METALS AND THEIR IMPACT ON RIVER KIMWARER ENVIRONMENT IN KERIO VALLEY- KENYA

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A thesis submitted to the Graduate School in partial fulfilment for the requirements of Master of Science degree in Chemistry of Egerton University.

EGERTON UNIVERSITY

OCTOBER, 2009

DECLARATION AND RECOMMENDATION

DECLARATION

I hereby declare that this is my original work and has not been submitted for the award of a degree in any other university.

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DEDICATION

This work is dedicated to my late brother, Andrew for his sacrifice in providing for my education.

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ABSTRACT

The levels of selected heavy metals in water, plant, soil and sediment samples collected around the Fluorspar Mining and Processing Plant in Kerio Valley were determined using AAS and EDXRFS. Digested soil 7 reference material (IAEA) was used as the standard for analysis of the soil and sediment samples. The results obtained from AAS were compared with those obtained using EDXRFS. The concentration of fluoride in the water, soil and sediment samples was determined using fluoride selective electrode. The mean concentrations in mg/Kg of the elements in the water samples ranged from 0.480 – 54.97 for Fe, 0.138 – 0.319 for Zn, 0.030 –1.280 for Mn, 0.026 – 0.117 for Cu, 0.015 – 0.275 for Pb, 0.000 – 0.102 for Cr and 0.600 – 40.08 for F^-. The concentration of the heavy metals and fluoride in the soil and sediment samples though higher than those of the water samples followed a similar trend with the downstream and effluent stream samples having higher concentration than the upstream and lower downstream samples. There was a gradual decrease in concentration of these elements on descending the river lower downstream implying that the factory effluents were responsible for the increased levels of the selected metals and fluoride observed downstream. The roots of *Eicchornia crassipes* (water hyacinth) had the highest concentration of heavy metals and fluoride followed by the stems while the leaves had the lowest concentration of these elements. Adsorption studies of heavy metals using *Eicchornia crassipes* showed that the roots of the plant were the most effective in adsorbing the heavy metals and fluoride from artificially prepared solutions of the heavy metals with the mean % adsorption ranging from 75.71 – 85.44, the stems had moderate adsorption ranging from 40.39 – 63.45 while the leaves were the least effective with the mean % adsorption ranging from 23.33 – 37.56. Statistical analysis showed that there was significant difference between the upstream samples and downstream and effluent samples implying that the Fluorspar mining and processing plant was responsible for the increased concentration of heavy metals and fluoride downstream of river Kimwarer. Suitable control measures of reducing the concentration of the hazardous chemical effluents such as periodic excavation of the sedimentation ponds and phytoremediation were proposed.

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LIST OF ABBREVIATIONS

APHA – America Public Health Association

ASAL – Arid and Semi Arid Lands

ATSDR – Agency for Toxic Substances and Disease Registry

D – Downstream

DHHS – Department of Health and Human Services

EPA – Environment Protection Agency

EDXRFS – Energy Dispersive X-ray Fluorescence Spectrometer

E. farm – Effluent Farm

Eff. Str. – Effluent stream

EFSS – Effluent farm sub-soil

EFTS – Effluent farm topsoil

ESS – Effluent soil sample

FAAS – Flame Atomic Absorption Spectrometer

IAEA – International Atomic Energy Agency

IARC – International agency for Research on Cancer

KSD – Kimwarer soil downstream

KSLD – Kimwarer soil lower downstream

KSU – Kimwarer soil upstream

KWD – Kimwarer water downstream

KWLD – Kerio water lower downstream

KWU – Kimwarer water upstream

NaDDC – Sodium diethyldithiocarbamate

ND – Not Detected

NEMA – National Environmental Management Authority

RTI – Research Triangle Institute

TISAB – Total Ionic Strength Adjustment Buffer

U – Upstream

WHO – World Health Organisation

XRFS – X-ray Fluorescence Spectrophotometer

CHAPTER ONE

INTRODUCTION

1.1. Background information

Mining activities can cause a variety of soil contamination problems including the deposition of sediments having high concentrations of heavy metals on alluvial soils (Pierzynsky & Schwab, 1993). The pollution of soil environment with toxic materials from mining has increased dramatically since the onset of the industrial revolution (Khan, 2004). Due to increasing mining activities worldwide, heavy metal pollution of land and water is becoming a globally important environmental health, economic and planning problem. The increase in world population and unpleasant disposal of industrial and mineral processing effluents especially in the third world countries can result in extensive air, soil and water pollution. Utilization of the contaminated lands and water sources requires a safe and efficient decontamination process (Channey & Oliver, 1998). Various strategies including bioremediation and phytoremediation are normally employed to remove the heavy metals from such soils and water sources hence making them suitable for agricultural and domestic purposes as well as urban developments (Khan, 2004).

Fluorspar is the rock containing the mineral fluorite (CaF_2), a purple product used in the glazing industry, making of fibreglass, manufacturing of toothpaste, aluminium, steel, uranium fuel, refrigerants and insulating foams. It is also used as a window material for both infrared and ultraviolet radiation, since it is transparent in these regions. Natural fluorspar is commonly associated with other minerals such as quartz, barite, calcite, galena, siderite, celestite, chalcopyrite and phosphates. It occurs as well-formed isometric crystals in massive and earthy forms and as crusts or globular aggregates with radial fibrous texture. In crystalline form, it can be colourless or may exhibit a wide range of colours, including yellow, blue, purple, green, rose, red, bluish, purplish black and brown (Miller, 1993).

The main fluorite deposits in Kerio Valley, which are located in Kimwarer, Choff, Tiati hills and Kamnaon, were first discovered in 1967 in the southern part of the valley by Mohammed Alamin, a prospector who was searching for semi-precious stones (Aljabri, 1990). At first, the unprocessed ore was ferried away for export by the prospector, who discovered the mineral. Later, the government intervened and this resulted in the injection of much larger sums of money for the purpose of processing the ore on site (Jones, 1982). The acid grade fluorspar (>97% CaF_2) is processed at a froth floatation concentrator plant located at Kimwarer, with a maximum capacity of 1,000 tonnes acid-spar per month (Aljabri, 1990).

The Fluorspar Mining and Processing Plant is one of the largest capital investments that have been made in the Kerio valley. The mining activities resulted in the introduction of new communication network and electrical energy into the valley. The Eldoret–Nyaru road was quickly constructed and power supply was connected from the Lessos junction. The main problem however, has been the brushing aside of the traditional land tenure rules by the Company. Since the land on which the mines are located had not been adjudicated, it did not legally belong to any individual but to the county council, which held it in trust for the community. The company however did not compensate the members of the community (Kipkorir, 1981).

The nature of the base rock history and geology shows that the area is rich in diverse types of minerals although their distribution and concentration have yet to be accurately established to facilitate economic exploitation. Comprehensive and exhaustive geological surveys are therefore necessary. At present fluorspar is mainly mined at Kimwarer at the southern end of the Kerio valley, though other substantial deposits have been located at Kolloa and Kapedo in the north. Limestone deposits also exist in the area. Alluvial gold is collected along river Muruny in west Pokot. The hill and mountain blocks are predominantly of Precambrian metamorphic complexes and rift volcanic pyroclastics and sediments while the plains are of sub–miocene sediments. The precambrian metamorphic complexes are highly mineralised in base and precious metals such as gold, silver, platinoids, chrome and copper while the rift volcanoes are rich in radioactive and industrial minerals such as pitchblende and fluorite (Were, 1981).

The Kerio Valley is predominately arid and falls within the arid and semi arid land (ASAL) classification. This is characterized by harsh conditions of extremes; high temperatures and drought during the dry season, heavy rainfall, flash floods and serious gully and surface erosion during the rainy season. The harsh climatic conditions coupled with remoteness of this area from the major urban centres calls for direct and deliberate government attention if socio-economic development in the area is to be raised to the level in other parts of the country. The area is very sensitive to both natural and man-made conditions. During the dry season, the hardy stunted and thorny acacia stands alone in parched dry and exposed ground, while during the rainy season, the underground is rich with quick growing grasses and other leafy shrubs. The highest disturbance by man through cultivation of hill side and river valley, intensified livestock grazing and bush clearing for charcoal burning or extension of farmland has lead to very heavy losses of surface soil with the consequent danger of desertification. This has drastically reduced the area's agricultural potential (Were, 1981).

In the lowlands and parts of the escarpments in Kerio Valley, furrow irrigation is widely practised. There are a number of operational irrigation schemes within these areas. Their socio-economic impact on these predominantly nomadic pastoralists has been very impressive. This is particularly so in terms of food and crop production and creation of productive employment opportunities (Were, 1981).

1.2. Mining and processing of fluorspar

The mining of fluorspar in Kerio Valley is carried out by open cast method. Overburden is removed by ripping and dozing waste rock on the hanging wall down the slope of the hillside. Once exposed, the ore is blasted and loaded into dump trucks which transport it to the factory. The ore is stock piled prior to primary crushing because the mine haulage capacity is far in excess of the crusher throughput and to allow a certain amount of blending to take place when the wheel loader feeds the crushing section. The blending is done to maintain a constant feed grade to the beneficiation plant. The crushed ore is then ground in a conventional rod and ball mill circuit (Jones, 1982).

Three principal grades of fluorspar are processed commercially: acid, ceramic and metallurgical. The acid grade contains an excess of 97% CaF_2, the ceramic grade contains 85-96% CaF_2 while the metallurgical grade contains a minimum of 60% CaF_2 (Miller, 1993). The Kerio fluorspar mines produce the acid grade fluorspar. The ground fluorite ore is concentrated in beneficiation plants by a combination of gravity and froth floatation processes using agitated chemical solutions such as oleic, hydrochloric, vinyl sulfonic, allyl sulphonic or trifluoroacetic acid in a floatation circuit and soda ash to modify the pH. The grains of fluorite preferentially stick to bubbles rising through the tank and overflow the rims as froth (British Geological Survey, 2003). The concentrates are cleaned using liberal quantities of clean water in a total of 48 Denver cells, each giving a maximum of 5 stages of counter- current cleaning. The number of cells in the last cleaner stage, producing the final concentrate can be increased or decreased depending on the CaF_2 grade. The final concentrates are dewatered in a 15 metre diameter thickener then in rotary drum vacuum filters. The thickener overflow water is returned to the milling circuit (Jones, 1982).

1.3. Statement of the problem

Many questions regarding environmental defacing and pollution, especially of Kerio River have been raised and not altogether satisfactorily dealt with. The mining wastes that are deposited in the nearby farms, streams and river are characterised by potentially toxic elements that are not only harmful to human beings but also to animals and plants, hence increasing the poverty levels in the area. Residents have complained about the abrupt deaths of their livestock, which they believe are caused by the emission of chemical wastes from the factory into the rivers. Many residents also complain of chest problems, objectionable taste of the river water downstream and diarrhoea, which they attribute to the pollution of the river water by the factory. Trees around the river have dried up due to what the residents say are the effects of the toxic waste deposited in the river. The residents also complain of migration/death of fish in river Kimwarer.

1.4. Research hypotheses

i) The levels of selected heavy metals and fluoride discharged from the Fluorspar mining and processing plant are not significantly different from the natural levels in the water and soil samples.

ii) Water hyacinth does not adsorb appreciable amounts of fluoride and heavy metals from water.

1.5. Objectives of the study

The general objectives of the study were to determine the variation of some physico–chemical parameters of water, soil and sediment samples taken at different points along river Kimwarer and effluent samples from Fluorspar Mining Plant during dry and rainy seasons and to determine any relationship between the chemical effluents from the Fluorspar Mining Plant and the environmental problems experienced in the area.

The specific objectives of the study were:

i) To determine and compare the levels of fluoride and heavy metals in water, dust, soil and sediment samples taken at different points along river Kimwarer and in effluents from the Fluorspar processing plant.

ii) To determine and compare the conductivity, turbidity and pH of various water, soil and sediment samples.

iii) Investigate the levels of the selected heavy metals in different parts of *Eicchornia crassipes* (water hyacinth) and assess its ability to adsorb the heavy metals from water samples.

iv) To propose some mitigation measures to combat the environmental problems identified in the area.

1.6. Justification of the study

During the mining and processing of fluorspar, both solid and liquid wastes from the factory are released into the river Kimwarer, dispersed on to the surrounding farms and air pollutants released to the environment. These activities pose a great danger to the lives of people and animals using the water downstream. Animals grazing in the surrounding farms are exposed to greater danger since they drink water directly from the factory discharge. The processing wastes are released into river Kimwarer, a tributary of river Kerio, which is used by the neighbouring community for irrigation and domestic purposes. River Kerio is clear upstream but changes brown downstream due to the effects of fluorspar processing wastes. The residents of the area have complained that the deterioration of the river water quality has led to decreased fish catch, loss of aquatic biodiversity, miscarriage of livestock and health problems. The company however downplays the effects of pollution caused by the mining activity saying that the impact of what they produce is minimal.

This study investigated any possible relationship between the levels of selected heavy metals and fluoride in the chemical effluents emitted from the Plant and the various environmental and health problems experienced by the members of the community living around the plant.

1.7. Scope and limitations of study

The study was carried out in Kerio Valley around the Fluorspar Mining and Processing Factory at Kimwarer shopping centre. The concentrations of fluoride ion and selected heavy metals were analyzed in water and soil samples collected along river Kimwarer, effluent streams and from sedimentation ponds. The concentrations of the elements in the upstream river water samples were compared with those in the downstream, lower downstream samples and effluent samples from sedimentation ponds. LSD and t – test values at 95% confidence level were used to determine any significant difference between the concentrations of these elements in the samples. The levels of these elements in water and soil samples were also compared with the NEMA and WHO recommended levels. The possible effects of the high concentrations of these elements on animal, plant and human health were explained based on previous studies.

The levels of fluoride and selected heavy metals in the roots, stem and leaves of water hyacinth collected from one of the sedimentation ponds was determined. The ability of the water hyacinth to adsorb fluoride and heavy metals from an artificially prepared solution was also measured. Due to limited time and finance, it was not possible to analyze the levels of these elements on the various animal and plant tissues and compare them with those from control areas.

CHAPTER TWO

LITERATURE REVIEW

2.1. Aqueous chemistry of heavy trace metals

Heavy metals are the most persistent pollutants found in lake, reservoir and river sediments. Because of this reason, they are useful as markers of environmental change in the aqueous systems (Arnason and Fletcher, 2002). Heavy metals of ecotoxic significance exist in natural waters according to the water type and location. The main pathways of input from natural and anthropogenic sources are dry and wet deposition from the atmosphere and run-off water from land and discharge of wastewater. Wet deposition of ecotoxic heavy metals in rain and snow is the dominant deposition mode in terrestrial ecosystems and contributes, therefore, very significantly to their pollution burden by ecotoxic metals via the atmospheric pathway. In the water column, heavy metals occur in the dissolved phase and are bound to suspended particulate matter including phyto-plankton. The total concentration in the water column and its distribution over the suspended matter and dissolved phase is governed by a number of parameters such as physical mixing, re-suspension and re-dissolution from bottom sediments, uptake and release by phyto-plankton and zoo-plankton and its detritus convection, up welling recycling water bodies, currents and sedimentation of suspended particles to the bottom. The concentration of heavy metals in water systems sometimes depends on the depth of water. Thus lead concentration will be extremely high in deep-sea water but Cd, Cu, and Ni are much more elevated in surface water (West and Nurnberg, 1988).

Heavy metals in surface water may create either acute or chronic poisoning in fish and other aquatic animals. It is usually the ionic forms, which produce the fish kills while complexed metal compounds tend to act by accumulation in the body tissue over a considerably longer period (Welch, 1980). The sources of heavy metals in water may be diverse but are commonly considered being generally associated with industrial discharges (Agg and Zabel, 1987). The effects of various toxicants depends not only on their concentration in the water or on the form which they take (ionic, complexed or organic) or even on the species of organisms affected, but also on the condition and quality of the water and the number, type and concentration of other toxicants present. The effect of two or more toxicants can be additive, antagonistic or synergistic. Thus the presence of Ca is antagonistic to the effect of Pb, Zn and Al. Copper behaves synergistically with Cl, Zn, Cd and Hg but antagonistically with cyanide. The effects of Cu and the synthetic detergent sodium lauryl benzene sulphonate are synergistic (Mason, 1981).

One of the major problems that trace heavy metals cause with their effects on aquatic organisms is their long biological half-life (Muohi, et. al, 2002). The toxicity of various compounds in a stream will be strongly affected by the quality of water, especially by such factors as dissolved O_2 concentration, water hardness, temperature and pH. Toxicity normally increase with decrease in dissolved O_2 and pH while it declines with increasing hardness. The toxicities of Zn, Cu and Cd are all increased by decreasing water hardness and by reduced levels of dissolved O_2. The toxicity of Cd also increases with temperature (Allabaster and Lloyd, 1980).

2.2. Methods of analysis for heavy metals and fluoride

The determination of heavy metals and other toxic elements in soils and water may be carried out for many reasons. These include the measurement of the total elementary content, which provides base-line knowledge of soil and water components with respect to which changes produced by elution, pollution, plant uptake or agricultural manipulation can be assessed. Analysis may also be designed to assess the availability of elements to agricultural crops and hence the likelihood of their entry into the food chain of animals and man. Soil and water analysis, therefore, provides vital information in the prediction of plant uptake and in the prediction and diagnosis of deficiency related diseases in crops and farm animals as well as in the assessment of agricultural and environmental toxicity problems (Ure, 1997).

Accurate analytical procedures, which combine high reliability and sensitivity with good precision, reasonable determination rate and convenience of operation are, therefore, of crucial significance for monitoring tasks in environmental protection of natural soils and waters and the control of their input into terrestrial ecosystems such as forests and agricultural land as well as for providing a reliable data base for research on the behaviour, transfer and fate of ecotoxic heavy metals in rivers, ponds, lakes, estuaries and sea. Special monitoring requirements arise with respect to drinking water since a majority of the population is immediately affected by heavy metal doses taken up with food and drinking water (West & Nurnberg, 1988). In this study, the concentration of heavy metals was determined by Atomic Absorption Spectroscopy while the concentration of fluoride was determined by fluoride-ion selective electrode meter. A multi-elemental analysis of the heavy metals and other toxic elements was done using an Energy Dispersive X – Ray Fluorescence Spectrometer. The results obtained using this method were compared with those obtained using the atomic absorption spectrometer and the fluoride-ion selective electrode meter.

2.2.1. Atomic absorption spectrometer

Atomic absorption spectrometer (AAS) is very suitable for the analysis of trace elements, particularly metals in water samples. It may handle liquid samples directly with little or no chemical pre-treatment so that contamination is minimised. AAS can be used for the determination of major, minor and trace elements using the same basic equipment with the alteration of only instrumental or procedural settings such as analytical line, absorption path length and dilution. Because of its versatility and simplicity of operation, AAS is the most extensively used method for the determination of metals in water (West & Nurnberg, 1988).

AAS may be applied basically with three different ways of atomisation: flame atomisation, electrothermal atomisation and atomisation with preceding chemical generation of a volatile analyte species of hydride. The last technique, though applicable to only rather limited number of elements, attains the lowest limit of detection. Due to its power of detection, AAS allows the determination of most trace elements of interest at their normal concentrations in unpolluted natural waters. In few cases where the limits of detection are not sufficient, a simple concentration step may be included such as precipitation, liquid-liquid extraction, ion exchange, electro deposition, sorption or co-precipitation (West & Nurnberg, 1988).

AAS is based on the absorption of radiation at a particular wavelength by neutral excited atoms of the analyte. The narrow bandwidth at which this occurs ensures a high degree of selectivity of determination. In flame atomic absorption spectrometer (FAAS), the analytical sample is nebulized into a chemical flame, which serves as atomizer and atom reservoir. In graphite AAS, a definite volume of water sample is introduced into a graphite tube placed in the optical axis of the monochromator. By passing a low voltage, high intensity current through the tube, this is gradually or rapidly step wise heated to increasing temperature according to the pre-selected programme, the sample is thus successively dried, thermally decomposed and atomised. The atomic absorption measured during the atomisation is then proportional to the amount of analyte in the graphite tube (West & Nurnberg, 1988).

2.2.2. Fluoride-ion Selective electrode

Lanthanum fluoride is the substance used for the preparation of membrane electrode for the determination of fluoride ion concentration. Fluorides of neodymium and praseodymium have also been used for the same purpose. Although these fluorides are natural conductors, their doping with europium fluoride, EuF_2, can enhance conductivities. Membranes are prepared by cutting disks from a single crystal of the doped compound (Skoog, 1985).

The mechanism of the development of a fluoride sensitive potential across a LaF_3 electrode is quite analogous to that for glass pH sensitive membranes. At the two interfaces, ionisation creates a charge on the membrane surface,

$$LaF_3 \rightleftharpoons LaF_2^+ + F^-$$

The magnitude of the charge is dependent upon the fluoride ion concentration of the solution. Thus, the side of the membrane encountering the lower fluoride concentration becomes positive with respect to the other surface. It is this charge difference that provides a measure of the difference in fluoride concentration of the two solutions. The potential of a cell containing a LaF_3 electrode is given by the equation:

$$pF = \frac{L - Ev}{0.0591}$$

The response of the fluoride electrode is linear down to 10^{-6} M (0.02 mg/Kg), where the solubility of LaF_3 begins to contribute to the concentration of fluoride in the analyte solution. The only ion that interferes directly with fluoride measurement is OH^-. This interference becomes detrimental at a pH greater than 8. At a pH less than 5, H^+ ions also interfere in total F-determination; here undissociated HF forms to which the electrode is not responsive. In most respects, the fluoride electrode approaches the ideal for selective electrodes (Skoog, 1985). These interferences can be minimised by using total ionic strength adjustment buffer (TISAB).

2.2.3. X – Ray Fluorescence Spectrometry (XRFS)

X – Rays are generated when high-speed particles such as electrons, protons or x–ray photons collide with a solid target. When an atom is bombarded in this manner, an electron is ejected from one of the inner shells. This vacancy is immediately filled by an electron from a higher-energy shell, creating a vacancy in that shell which is, in turn filled by an electron from yet another higher shell. Thus by a series of transitions, $L \longrightarrow K$, $M \longrightarrow L$, $N \longrightarrow M$, each new vacancy is filled until the excited atom returns to its ground state. Each electronic transition results in the emission of characteristic x-ray spectral line whose energy, hυ, is equal to the binding energies of the two electrons involved in the transition (Christian and O’Reilly, 1986).

It is possible to identify the emission peaks that are characteristic of the element contained in the target. The wavelengths of the peaks can be related to the atomic number of the elements producing them, so that they may provide a means of identifying the elements present in the target sample. Under controlled conditions the intensity of the peaks can be used for quantitative analysis. XRFS is widely employed in metallurgical research, examination of geological samples and determining metallic elements in biological materials (Vogel, 1989).

XRFS is a non-destructive instrumental method of qualitative and quantitative analysis for chemical elements based on the measurements of the wavelengths and intensities of the X–ray spectral lines emitted by secondary excitation. The primary beam from an X–ray tube irradiates the specimen (sample or standard), exciting each chemical element to emit secondary spectral lines having wavelengths characteristic of that element and intensities related to its concentration. The specimen can have practically any form including solid, powder, briquet, fusion product, film, liquid, slurry and fabricated forms (Christian and O’Reilly, 1986).

XRFS was used to evaluate the accuracy of AAS and to identify any other hazardous element, which was not detected using AAS. Evaluation of precision, reproducibility and repeatability was performed by replicate analyses of selected samples.

2.3. Trace and toxic elements in soil

Fertile soils supply plants with all the trace elements essential for the growth, which include Fe, Mn, Zn, B, Cu, Mo and Cl. These elements are called micronutrients due to the small quantities needed by plants but not necessarily the concentrations found in soil. Deficiencies of these elements can occur in soils which contain extremely low concentrations of these elements or because the elements are present in insoluble form. Many trace elements including all the micronutrients can reach concentrations in soil that are toxic to the plants and microorganism. Some of the toxic trace elements are Pb, Cd, Cu, Ni and Co. The first two are particularly toxic to higher animals. The last three are more toxic to plants than animals and are termed "phytotoxic" (McBride, 1994).

Sediments usually act as a sink for aquatic pollutants. Consequently, sediment associated contaminants can influence the concentrations of trace metals in both water and the biota if they are desorbed or become available to benthic organisms (Muohi, et. al, 2002). Pollution from human activity such as mining and smelting and accumulation from natural biogeochemical processes can result in elevated concentrations of the micronutrients and trace toxic elements which are greatly in excess of those expected for a particular soil or water. Whether an element is present naturally in the soil or has been introduced by pollution, the most useful measure is an estimation of "availability" or "lability" of the element since this property is related to the mobility and uptake by plants and extractability by the chemical treatments. The concentration of the element at any one time in the soil solution often seems a better measurement of availability (McBride, 1994).

2.4. Effects of fluoride and heavy metals associated with fluorspar mining

Toxic heavy metals constitute one of the most formidable groups of environmental pollutants known because they are non-degradable. It is therefore very important to monitor the concentration levels of these elements, especially in the areas around chemical factories or mineral processing plants (Omoga and Kagwanja, 1999). Heavy metal pollution can affect all environments but its effects are most long lasting in soils because of the relatively strong adsorption of many metals onto the humic and clay colloids in soils. Unlike organic pollutants, which will ultimately be decomposed, metals will remain as metal atoms, although their speciation may change with time as the organic molecules binding them decompose or soil conditions change. The extent to which the metal ions are adsorbed by cation exchange depends on the properties of the metal concerned, the pH, redox conditions, the nature of the adsorbent, the concentrations and properties of other metals present, and the presence of soluble ligands in the surrounding fluids (Alloway and Aryes, 1997). The heavy metals posses bioaccumulation property, and the possibility of reaching a critical value and threatening human and animal health increases the need to monitor their levels (Sezgin et al., 2003).

2.4.1. Zinc

Zinc is an essential trace element to all organisms and is present in many enzymes. It is found in dehydrogenase, functioning as a catalyst in hydride transfer in co-enzymes such as flavin co-enzymes. The metal is non cumulative and the amount absorbed is believed to be inversely proportional to the amount ingested. Zinc deficiency causes lesions of the skin, abnormalities of the skeleton and defects in the reproductive organs especially testicular development in the male (Goyer, and Myron, 1977).

Zinc is moderately toxic, causing metal fume fever and pulmonary disorders, which have been observed in industrial workers exposed to the fumes. Casual ingestion of $ZnSO_4$ causes drowsiness, lethargy and increased serum lipase and amylase levels. Acute toxicity of zinc has been observed in patients with renal failure following haemodialysis. Vomiting, fever and severe anaemia have also been observed in acute toxicity (Alala, 1981).

The two Zn enzymes which have received much attention are carboxypeptidase which catalyses the hydrolysis of the terminal peptide bond in proteins during digestion process and carbonic anhydrase which catalyses the equilibrium reaction:

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

In mammalian erythrocytes, the forward reaction (hydration) occurs during the uptake of CO_2 by blood in tissues, while the backward reaction (dehydration) takes place when CO_2 is subsequently released in the lungs. The enzyme increases the rates of these reactions by a factor of about one million (Greenwood and Earnshaw, 2001).

Zinc tends to be found only in trace amounts in unpolluted surface and ground waters. However, it is often found in domestic supplies at consumers' taps as a result of corrosion of galvanised iron piping or tanks and dezincification of brass fittings. Zinc has a threshold taste at approximately 5 gm/L and can also cause opalescence above this value (Twort et al., 1994).

2.4.2. Copper

The element is essential to all organisms and is a constituent of redox enzymes and O_2-transport pigments. It occurs in metalloproteins such as hemocyanin (an oxygen carrier in molluscs and anthropoids), cytochrom oxidases and plastocyanin (Hughes, 1975). The element is essential in the maintenance of vascular and skeletal integrity and central nervous system. The cupric ion is the one, which serves as an oxidative catalyst, for example in the oxidation of ascorbic acid by molecular O_2 to form dehydroascorbic acid. Copper deficiency causes anaemia, neonatal ataxia, lack of pigmentation, connective tissue defects including bone disorders and cardiovascular failure (O'Dell and Campell, 1971).

Copper is very toxic to most plants, highly toxic to invertebrates and moderately so to mammals in high concentrations. In trace amounts copper is beneficial and essential for the nutrition in aquatic environment. Increased levels of copper in receiving waters may have profound, detrimental impact on the resident biota. Copper naturally enters water from soils and mineral deposits by erosional action of water. The main anthropogenic sources of copper are power plants, municipal wastewater discharge, industrial processes and agricultural activities. Copper is toxic to human in large quantities, resulting to Wilson's disease. This is a hereditary metabolic disorder, which results in accumulation of copper in some organs of the body, mainly brain and liver being the most sensitive. The disease is transmitted as an automatic recessive trait. Sheep can also be affected with copper toxicosis under practical husbandry (Goyer and Myron, 1977).

2.4.3. Lead

Lead occurs naturally as the sulphide mineral galena, carbonate cerussite and as the sulphate anglesite. It is nearly always present in soil although in small amounts. The solubility of lead in soil increases with acidity and in acid soil, plants accumulate it. Food plants may acquire toxic amounts of lead to the consumer (Hesse, 1972). Lead is neither essential nor beneficial for plants and animals. It is well known for being poisonous to mammals and there are fears that human body burdens below that at which clinical symptoms of Pb toxicity appear may cause mental impairment in young children. Soil and dust are important sources of lead for young children and lead in blood can be related directly to Pb in soil or water (Alloway and Aryes, 1997).

Soil is a sink for anthropogenic lead and there are several well-recognised major sources, namely, mining and smelting activities, manures and sewage sludge usage in agriculture and contamination from vehicle exhausts (Frank et. al., 1976). Lead is a general protoplasmic poison that is cumulative, slow acting and subtle (Oyaro et. al, 2006). The toxicity of the metal is based on the fact that it is a potential enzyme inhibitor because it binds to the SH groups on the enzymes. It also inhibits heme synthesis and utilization of Fe in the body. The pathological effects of lead are observed in three organ systems: the nervous system, kidney and haematopoietic system. Other effects that may occur are endocrine and reproductive abnormalities. Children with overt lead poisoning have central nervous disorders ranging from ataxia to stupor, coma and convulsions. Adults may have lead encephalopathy. Lead produces a variety of symptoms such as anaemia, mental retardations and bone malfunctioning due to the shortened erythrocyte life span and impairment of the heme synthesis (Alala, 1981, Oyaro et. al, 2006).

2.4.4. Cadmium

Cadmium is a highly toxic non-essential metal, which accumulates in the kidneys of mammals and can cause kidney dysfunction and skeletal damage (osteoporosis). In mammals, kidney damage diagnosed by the presence of microglobulin proteins in the urine is the main toxic effect resulting from chronic exposure to the metal. Cadmium becomes very volatile at temperatures above 400^{o}C and hence is likely to be dispersed as an aerosol when mixtures of metals containing cadmium are heated or cast. Cadmium tends to be less strongly adsorbed than many other divalent metals and is, therefore, more labile in soils and sediments and more bioavailable. There is more danger from this metal moving through the food chain from contaminated soils than most other metals. Serious cases of cadmium poisoning have been observed where Pb-Zn mining and smelting have caused widespread Zn and Cd contamination of alluvial soils which are used for paddy rice production. Cd toxicity is exacerbated by a low protein and vitamin D diet and the birth of several children (Alloway and Ayres, 1997).

Pollutant Cd in water may arise from industrial discharges and mining wastes. Since Cd is very chemically similar to Zn, these two metals normally undergo geochemical processes together and both metals are found in water in the +2 oxidation state. The effects of acute Cd poisoning in human are very serious, among them are high blood pressure, kidney damage, destruction of testicular tissue and red blood cells. Much of the physiological action is probably due to the similarity of Cd to Zn, thus Cd may replace Zn in some enzymes thereby altering the stereostructure and impairing the catalytic activity. Symptoms of diseases ultimately result (Manahan, 1993).

Other effects of cadmium exposure are disturbances in calcium metabolism, hypercalciuria and formation of renal stones. The International Agency for Research on Cancer (IARC) classifies Cadmium as class I human carcinogen (IARC, 1993b). Cd is toxic to a wide range of microorganisms. The main effect is on growth and replication. The most affected soil microorganisms are fungi, some species being eliminated after exposure to Cd in soil. Aquatic organisms readily absorb Cd in the free ionic form from water as Cd^{2+} (AMAP, 1998).

2.4.5. Chromium

Chromium in the form of Cr^{3+} is essential to human and animals. The most widespread human effect is chromium allergy caused by exposure to Cr (VI) compounds in the working environment. Chromium is necessary for the metabolism of insulin. It is also essential for animals, whereas it is not known whether it is an essential nutrient for plants although plants contain the element (WHO, 1988). Effects in humans occupationally exposed to high levels of Cr especially by Cr (VI) inhalation may include respiratory and possible circulatory effects, effects on stomach and blood, liver and kidney effects and increased risk of death from lung cancer (RTI, 2000). Evidence from experimental studies on animals has shown that Cr (VI), especially those of low solubility can induce lung cancer. Cr (III) is not considered carcinogenic (IARC, 1990).

Chromium (VI) is more toxic to organisms in the environment than Cr (III). Chromium (VI) is relatively stable in air and pure water but it is reduced to Cr (III) when it comes into contact with organic matter in biota, soil and water. Chromium in high concentration can be toxic to plants. The main feature of Cr intoxication is chlorosis, which is similar to iron deficiency (RTI, 2000).

2.4.6. Nickel

Exposure to dust containing nickel compounds can cause serious harmful health effects such as chronic bronchitis, reduced lung function, and cancer of the lung and nasal sinus. Lung and nasal sinus cancers have been observed in workers who were exposed to more than 10 mg nickel/m^3 as nickel compounds that were difficult to dissolve, such as nickel subsulfide. Exposure to high levels of nickel compounds that dissolve easily in water may also result in cancer when nickel compounds that are less soluble are present, or when other chemicals that can cause cancer are present. The concentrations of soluble and less-soluble nickel compounds that have been found to cause cancers are 100,000 to 1 million times greater than the normal level of nickel in the air in the United States. The U.S. Department of Health and Human Services (DHHS) has determined that nickel metal may reasonably be anticipated to be a carcinogen and nickel compounds are known human carcinogens. The International Agency for Research on Cancer (IARC) has determined that some nickel compounds are carcinogenic to humans and that metallic nickel may possibly be carcinogenic to humans. The Environment Protection Agency (EPA) has determined that nickel refinery dust and nickel subsulfide are human carcinogens (ATSDR, 2003).

Lung inflammation and damage to the nasal cavity have been observed in animals exposed to nickel compounds. At high concentrations, the lung damage is severe enough to affect lung function. Long-term exposure to lower levels of a nickel compound that dissolve easily in water does not cause cancer in animals. Lung cancer developed in rats exposed for a long time to nickel compounds that do not dissolve easily in water. Eating or drinking levels of nickel much greater than the levels normally found in food and water have been reported to cause lung disease in dogs and rats and to affect the stomach, blood, liver, kidneys, and immune system in rats and mice, as well as their reproduction and development (ATSDR, 2003).

2.4.7. Manganese

Manganese, whose compounds are very common on earth, is a toxic essential trace element. The uptake of manganese by humans mainly takes place through food, such as vegetables, tea, grains, rice, olive oil, eggs, and nuts. Shortages of manganese in human diet can cause health effects such as fatness, glucose intolerance, blood clotting, skin problems, lowered cholesterol levels, skeleton disorders, birth defects, changes of hair colour and neurological symptoms (Holding, 2004).

Manganese is necessary for the production of manganese superoxide dismitase, one of the key antioxidants in the body. Enzymes involved in cholesterol synthesis are manganese dependent hence deficiency can decrease sex drive. Manganese is required for normal thyroid and adrenal gland activity and is essential for the formation of thyroxine that is necessary for vitamin K production. Mn deficiency can cause dizziness and deafness. Mn helps treat myasthemia gravis and is important in the treatment of multiple sclerosis and diabetes (Eder et al, 1996).

Toxic effects of manganese occur mainly in the respiratory tract and in the brain. Common symptoms of manganese poisoning include hallucinations, forgetfulness and nerve damage. Manganese can also cause Parkinson disease, lung embolism and bronchitis. When men are exposed to manganese for a longer period of time they may become impotent. A syndrome that is caused by manganese has symptoms such as schizophrenia, dullness, weak muscles, headaches and insomnia. Chronic Manganese poisoning may result from prolonged inhalation of dust and fume. The central nervous system is the chief site of damage from the disease, which may result in permanent disability. Symptoms include languor, sleepiness, weakness, emotional disturbances, spastic gait, recurring leg cramps, and paralysis. A high incidence of pneumonia and other upper respiratory infections has been found in workers exposed to dust or fume of Manganese compounds (Holding, 2004).

Manganese uptake through the skin can cause tremors and coordination failures. In plants manganese ions are transported to the leaves after uptake from soils. When too little manganese can be absorbed from the soil, disturbances in plant mechanisms such as the decomposition of water into hydrogen and oxygen, in which manganese plays an important part occurs. Manganese can cause both toxicity and deficiency symptoms in plants. When the pH of the soil is low manganese deficiencies are more common. Highly toxic concentrations of manganese in soils can cause swelling of cell walls, withering of leafs and brown spots on leaves. Deficiencies can also cause these effects. The concentration of manganese required for optimal plant growth can be detected between toxic concentrations and concentrations that cause deficiencies (Holding, 2004).

2.4.9. Fluoride

Fluoride occurs naturally in high concentrations in water and soil in some parts of the world. In some cases fluoride is added to public water supply to a level of 1mg/L because it is safe and effective in reducing dental caries. The greatest reduction of dental decay occurs if fluoridated water is drunk in childhood during the period of tooth formation. Fluoride levels have to be closely controlled as excessive amounts can lead to fluorosis with resultant mottling of the teeth. The optimum fluoride concentration has to be related to climatic conditions and the amount of water likely to be consumed (Twort et. al., 1994). Fluorine commonly finds its way into soil from phosphate rocks and during volcanic eruptions where it is deposited into the atmosphere via rain. In soils fluorine is found from minute trace amounts up to about 0.1%. Fertilizers such as super phosphates and limestone can avertedly increase the fluorine content of soil, probably in form of fluoroapetite, $Ca_5F(PO_4)_3$. The element does not appear to be essential in any way for the plant growth (Hesse, 1972).

Fluoride is the most phytotoxic of the common air pollutants and accumulates in plants (Weinstsin and Alscher-Herman, 1982). Fluoride damage to vegetation has been observed in areas around aluminium smelters. Fluoride pollution can result in fluorosis in livestock and wild animals due to ingestion of contaminated plant material. Elevated levels of fluoride have been observed in bones of wild animals living in the vicinity of Al smelters in Norway (Vikoren and Stuve, 1994). Most of the fluoride in plants in F polluted areas is taken up through the stomata in the leaves. Good correlations have been found between the fluoride concentrations in air and content in leaves in the vicinity of Al smelters (Vike and Habjorg, 1995, Arnesen, 1997). Fluoride pollution can lead to increased solubility and hence uptake of Al by plants (Polomski et al., 1982). Aluminium in certain forms is toxic to roots, but the availability and toxicity depends on speciation and plant species (Cameron et al., 1986).

2.5. Water hyacinth (*Eicchornia Crassipes)*

Water hyacinth is an aquatic plant which can grow and reproduce freely on the surface of fresh waters or can be anchored in mud. The plant is a perennial aquatic herb which belongs to the family Pontedericeae, closely related to the Liliaceae (lily family). The plant originated in the Amazon basin and was introduced into many parts of the world as an ornamental garden pond plant due to its beauty. It has proliferated in many areas and can now be found on all continents apart from Europe. The vegetation reproduction is asexual and takes place at a rapid rate under tropical and sub tropical climates (Herfjord et al., 1994). Water hyacinth is one of the worst weeds in the world. Its floating mats can weigh up to 200 tons per acre. It is a floating plant with thick glossy, round leaves, inflated leaf stems and lavender flowers. Although the plant is one of the worst fresh water weeds, several control methods involving the use of mechanical harvesters and chopping machines and weevils have been introduced to help in its management (Holm et al. 1977).

Water hyacinth is seen in many countries as a weed and is responsible for many problems such as clogging of intakes for irrigation and water supply systems, blockage of canals and rivers leading to flooding, micro-habitat for a variety of disease vectors, reduction of biodiversity, increased evapotranspiration and reduced access to fishing sites. However, many individuals, groups and institutions have been able to turn the problem around and find useful applications for the plant. Although the plant is composed of more than 95% water, it has a fibrous tissue, high energy and protein content. Some of the possible uses of the plant include paper, biogas and fibre board production, charcoal briquetting, animal fodder and water purification (Gopal, 1987 and Eden, 1994).

The ability of water hyacinth to absorb and adsorb heavy metals from water has been reported in various studies. Orata (2003) showed that the ground roots, stem and leaves of the plant were all effective in adsorbing the heavy metals from artificially prepared solutions. He showed that the roots were the most effective followed by the stems and leaves respectively.

2.6. Previous studies

The contamination of water and soil samples by acidic factory discharges laced with hazardous heavy metals and fluoride in Kerio Valley has been reported in previous studies. Nguta (2004) showed that acidic factory effluents laced with high concentrations of heavy metals and fluoride were discharged directly into river Kimwarer and the neighbouring farms. He also noted very high levels of the heavy metals in animal tissues obtained from the area compared to those obtained from control areas such as Nakuru, Kenya. He recommended that regular analysis by independent organizations such as NEMA and research organizations should be done to determine any change in the levels of the metals, fluoride and acidity of the chemical effluents.

The contamination of agricultural land with lead, zinc and fluoride has been reported by Geeson et. al (1997) in the old Fluorspar mining areas of Derbyshire, UK. He showed that the mining process resulted in an extensive fluorine and metal enrichment of soils and pasture herbage in the area and that there was a direct relationship between the levels of fluorine in the soils and plants to those of the heavy metals. He reported that if livestock are permitted to graze in the proximity of these areas, toxicity problems may be expected due to the high levels of heavy metals and fluoride in the soil and herbage.

Lagerwerff and Brower (1974) showed that persons living downwind of an old smelter site in the Tri – State region (near Galena, KS) could ingest at least 50% more Pb and Cd by consuming some of their home produced vegetables, meat, and milk than comparable food items purchased in a control area. Chlorosis reported by Bradley and Cox (1986) and observed in the Tri – State region limits crop productivity. Nguta (2004) showed that milk, honey and animal tissues collected around the Kerio Fluorspar mining and processing plant had relatively higher concentrations of the heavy metals and fluoride compared to Nakuru. These results show that the mining of fluorspar can lead to increased levels of the heavy metals in the surrounding areas and animal tissues, especially if the effluents are not properly treated.

The use of plants such as *Eicchornia Crassipes* and *Vetiveria zizanioides* in adsorption of heavy metals and fluoride from contaminated water samples has been reported in various studies. Orata (2003) showed that *Eicchornia Crassipes* are very effective in adsorbing heavy metals from polluted water. The use of the ecofriendly vetiver grass [*Vetiveria zizanioides* L (Nash.)] in phytoremediation of sites contaminated with heavy metals has been reported by Greenfield (1988). The grass which is both a xerophyte and hydrophyte is not affected by droughts and floods once established. It is highly tolerant to frost, heat, extreme soil pH, sodicity, salinity, Al and Mn toxicity. It is also highly tolerant to a range of trace elements such as As, Cd, Cu, Cr, and Ni (Truong & Claridge, 1996). The grass has been successfully used to stabilize mining overburden and highly saline, sodic and magnesic and alkaline or acidic tailings of coal and gold mines (Truong, 1999). These findings show that certain plants are very effective in removing heavy metals from polluted water and soil systems and can therefore be employed in phytoremedial measures.

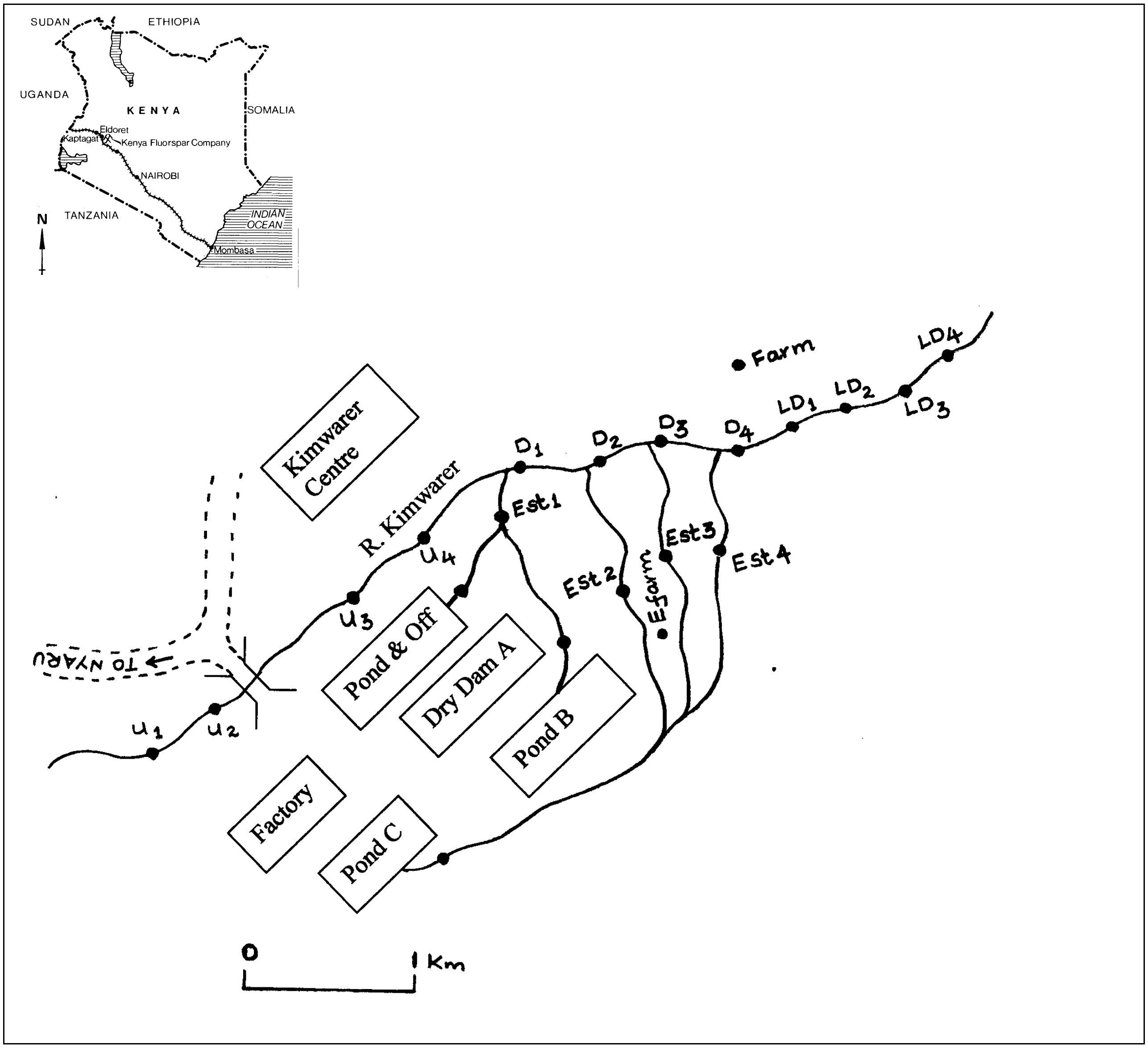
Pierzynski and Schwab (1993) showed that the addition of limestone and cattle manure greatly reduce the bioavailability of Zn, Cd, and Pb to soybean grown in a metal-contaminated alluvial soil while at the same time increasing the yield. This is due to the reduction in labile metal ion-soil fractions.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Area

Figure 1 shows the location of Kerio Fluorspar mining and processing plant (K.F.C) and the sampling points along river Kimwarer.



Key

- Sampling points

Figure 1: Map showing the location of Kenya Fluorspar Company and sampling points.

3.2. Reagents

Standard stock analytical solutions of Cd, Pb, Zn, Fe, Ni, Cr, Co and Cu, (1000 mg/Kg or 100 mg/Kg) manufactured by Kanto Chemical Co. Inc. Japan, concentrated nitric and hydrochloric acids, de-ionised water, TISAB-buffer, hydrochloric acid, sodium hydroxide, APDC, NaDDC, standard NaF solution, F–electrode filling solution, starch were used. All chemicals were of analytical grade purchased from established suppliers.

3.3. Equipments and apparatus

Beakers (250, 100 and 50 ml) Volumetric flasks 100 ml, Sample bottles, Pipettes (various sizes), conical flasks (100ml and 50ml), Petri dishes, Poly ports, pH meter, Atomic Absorption Spectrometer (Thermo–Jarrell S11) using air acetylene flame, Hollow cathode lamps, Digestion tubes, digestion block, Hot plate, Fluoride ion selective electrode meter (Model 94-09), Oven, Whattman filter papers No. 40, EDXRFS with ^{109}Cd X-ray source (Canberra detector model SL80175), 0.45µm filter papers, Analytical balance (Mettler Toledo), Pestle and mortar, Filter funnels, 0.45µm filter papers, mylar paper, Soil auger.

3.4. Sampling of water

One litre water samples were collected at selected points shown in figure 1 using polypropylene bottles, upstream and downstream of river Kimwarer from the Fluorspar mining plant. Four samples were collected upstream and eight samples downstream. The downstream sampling points were taken from the various effluent streams and subsequent points after the effluent streams had joined the river. The sampling was continued two kilometres lower downstream after the last effluent stream from the factory sedimentation ponds at intervals of about half a kilometre. Water samples were also collected from the dams and the main factory effluent. Measurement of the pH, conductivity and turbidity were done at the field and were used to identify the most polluted points and the points where the river was less polluted. The water samples were then preserved at the field by adding 5 ml of concentrated HNO_3/L to each sample. The samples were then transported and stored in a refrigerator at 4^0C to prevent any change in volume due to evaporation (APHA, 1989).

3.5. Soil and dust sampling and processing

Topsoil (0–5 cm) and sediments samples from the riverbed and riverbank were collected using a soil auger upstream and downstream along river Kimwarer around the Fluorspar mining and processing plant and on the neighbouring farms. Sampling was started approximately 2 Km upstream and continued up to 2 Kilometres downstream from the last Fluorspar plant waste discharge point. Subsoil (5 – 10 cm) samples were also collected from the farms where the factory effluents were normally discharged during the dry season. A total of forty-eight soil samples weighing about 500 g each were collected.

The samples were dried in an oven at 70^{o}C for 24 hours and ground in a porcelain mortar with a pestle (Kashem and Singh, 1998). The sediment material which passed through <63 µm sieve were collected for further analysis.

Dust samples were collected by placing pre–weighed filter papers under selected open roofs near and away from the roads and next to the factory. The papers were collected after two weeks and re–weighed on an analytical balance. The mean weight of dust deposited on the filter papers was then determined.

3.6. Plant sampling and processing

Samples of *Eicchornia Crassipes* (Mart.) were randomly collected from pond B within the factory area. The samples were identified at University of Nairobi, Department of Botany herbarium. The samples were thoroughly washed with tap water then rinsed with distilled water to remove any heavy metal on their surface. The plant samples were dried to constant weight in an oven at 60^{0}C. The samples were then divided into roots, stems and leaves, which were then separately ground using a pestle and mortar. The ground samples that passed through a 150 µm sieve were kept in polythene bags for further analysis (Orata, 2003).

3.7. Preliminary preparation

All glassware were thoroughly cleaned with detergent, tap water then rinsed three times with deionised water to remove any traces of metal. They were then left to dry in a clean tray. A series of working standards of the metals to be analysed were then prepared from the standard solutions by diluting the appropriate volume with distilled water using the formula: $C_1V_1 = C_2V_2$. Where:

- C_1 = initial concentration of the standard solutions
- C_2 = final concentration to be prepared
- V_1 = volume of standard solution used
- V_2 = volume of working solution to be prepared

3.8. Water analysis

The water samples were thoroughly mixed and 100 ml transferred into a 250 ml beaker. 5 ml of concentrated HNO_3 and few boiling chips were added to the sample. The mixture was brought to a slow boiling and evaporation on a hot plate while checking to make sure that no precipitation occurred. The heating and addition of concentrated HNO_3 was continued until a light coloured clear solution was formed. This showed that digestion is complete. The digested solution was transferred into 100 ml volumetric flask. The beaker was rinsed twice with about 10 ml of distilled water and the rinsing also transferred into a 100 ml volumetric flask. The solution was then diluted to the mark with distilled water and mixed thoroughly. The same procedure was repeated for reagent blank containing distilled water. Portions of the resulting solutions were separately taken and used for the determination of the concentrations of the heavy metals (APHA, 1989).

A series of calibration standards for each metal were prepared within the linear ranges as outlined in the AAS operation manual. The reagent blank was used as the solution with a concentration of zero for all the heavy metals analysed.

A hollow cathode lamp for the metal to be determined was fitted and the AAS operated at the optimum settings for each metal as outlined in the AAS manufacturer's manual as shown in table 3.1.

Table 3.1: Optimum setting for Thermo-Jarrel AAS for analysis of metal concentration in digested soil, plant and water samples.

Parameter	Fe	Zn	Mn	Cu	Pb	Cd	Cr	Ni
Wavelength (nm)	248.3	213.9	279.5	324.7	217	228.8	357.9	232
Lamp current (mA)	8.0	3.0	5.0	5.0	5.0	3.0	6.0	10
Band pass (nm)	0.3	1.0	0.5	1.0	1.0	1.0	0.5	0.15
Burner Height (mm)	20	22	22	24	20	24	22	24
Fuel and oxidizer flow rate (cm^3/min)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0

The concentration of the metals in the samples were determined by running a series of the calibration standard solutions for each element within the linear range, followed by the digested sample solutions in triplicates and the mean absorbance value recorded. A graph of the mean absorbance against concentration of the working standard solutions was drawn for each metal using the access computer program. The graphs were used to determine the concentration of the unknown samples.

The concentration of fluoride in the water and soil samples was determined by fluoride ion (F^-) specific electrode. The water and soil samples were mixed with TISAB III buffer to dissociate F^- complexes and stabilize pH before measurement.

3.9. Analysis of *E. Crassipes* and adsorption studies

The *E. Crassipes* were digested by adding 5 ml of concentrated HNO_3 to 0.5 grams of the sieved plant parts in a digestion tube and allowing the mixture to stand overnight before heating in a block digestor at 100^0C until approximately half of the acid had boiled off. The samples were diluted with distilled water to 50 ml and filtered into polypropylene bottles. The concentrations of the heavy metals in the plant samples were determined in triplicates using AAS in air – acetylene flame and the mean concentration recorded (Orata, 2003).

Synthetic solutions containing 100 mg/L of fluoride and the heavy metals under investigation were prepared. 100 ml of each solution was added to 2 grams of the ground plant parts in separate polypropylene bottles. The bottles were shaken at 300 revolutions per minute for 3 hours and the resulting mixtures filtered through a 125 mm Whatmann filter paper no. 41. The solution obtained was transferred into 100 ml polypropylene bottles and the levels of the heavy metals analysed using AAS (Orata, 2003).

3.10. Soil analysis

The soil pH was measured in a 1: 2.5 soil to water ratio by weight. The suspension was allowed to stand overnight prior to pH determination. Electrical conductivity was measured in saturation extracts of soils using EC meter (Kashem and Singh, 1998). Exactly 1.00 gram triplicate sieved soil samples were weighed into digestion tubes. The samples were digested in 20 ml concentrated hydrochloric acid for three hours at 100 ^{0}C in an aluminium heating block. The digestion mixture was cooled to room temperature and 1 ml of hydrogen peroxide carefully added. The digestion tubes were heated for a further 30 minutes. The mixture was allowed to cool and quantitatively transferred into 50 ml volumetric flasks and made up to the mark using distilled water. The mixture was finally transferred into polypropylene bottles ready for analysis. Reagent blanks were prepared in a similar manner using distilled water to cater for matrix effects (Muohi, 2002). Thermo-Jarel S11 Atomic Absorption Spectrophotometer was used to determine the concentration of the heavy metals. All the analyses were carried out using air-acetylene flame at optimum instrument operating conditions recommended by the manufacturer.

Water-soluble F^- was measured by shaking 10 g soil with 74 mm distilled water for 16 hours followed by filtration through a filter paper (Adriano and Doner, 1982). The amounts of F^- in the supernatants were determined by F^--specific ion electrode. The solutions were mixed with TISAB III buffer to dissociate F^- complexes and stabilize pH before measurement.

3.11. Elemental analysis using EDXRFS

The values obtained from atomic absorption spectrophotometer were evaluated by analysing selected samples using EDXRFS. The soil/sediment samples were mixed with about 20% starch to act as a binder. About 0.6 grams of the mixture was weighed and compressed to form a pellet. The weights of the pellets were accurately determined using a mettler tolledo analytical balance and recorded. The nature and concentration of the selected heavy metals in the soil/sediment samples were determined from the spectrum obtained from EDXRFS with ^{109}Cd X–ray source in 3000 seconds.

Exactly 100 ml of the digested water samples was placed in clean 250 ml beakers and the pH adjusted to between 5-6 using analyitcal grade ammonia solution. 10 ml of 2% freshly prepared sodium diethyl dithiocarbamate (NaDDC) was added to the water samples to precipitate the heavy metals. The metallic precipitates formed by various water samples were allowed to stand for 15 minutes and then filtered through a Millipore of porosity 0.45μm using an extraction pump. The filter papers were air dried and then analyzed x – ray fluorescence. (Orata, 2003). The nature and concentration of the selected heavy metals deposited on the filter papers were determined by analysis of the spectrum obtained from EDXRFS with a new ^{109}Cd X-ray source for 1500 seconds.

Evaluation of precision, reproducibility and repeatability was performed by triplicate analysis of the selected samples. EDXRFS analyses (Canberra detector model SL80175) were done using pellet preparation method as described in the manual. Evaluation of the accuracy of the EDXRFS was done using SOIL – 7 Reference Material from IAEA (Muohi, et al., 2003).

3.12. Statistical analysis

The results obtained during both the dry and rainy seasons were analysed using Genstat-statistical software. Anova, t-tests and range were used to determine whether there were any significant differences between the concentrations of the selected heavy metals and fluoride in the soil, sediment and water samples collected downstream and upstream of the river Kimwarer from the Fluorspar mining and processing plant as well as the factory effluent samples.

The triplicate values for each analysed sample were analysed using the Genstat ststistical package and the output for the t-test and least significant difference (LSD) values obtained. The t-test and LSD values were tabulated. The results for the t-test and the LSD values were used to explain any significant difference between the various samples studied. The results for t-tests and LSD are presented and discussed in chapter 4. The mean values of concentration, turbidity and conductivity were calculated using the Microsoft excel spreadsheet. The mean values were used to draw the graphs for the variation of these parameters in the water and soil samples along the river and around the factory. The graphs obtained for the various physicochemical parameters are also presented and discussed in chapter 4.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1. Calibration curves for AAS and analysis using EDXRFS

The concentrations of the heavy metals were determined using the AAS by first preparing working standard solutions within the linear range of the metal to be analysed as stated in the manufacturer's manual and a calibration graph of absorbance against concentration plotted using Microsoft excel program. The equations of the graphs were used to determine the concentration of the unknown sample solutions. The calibration graphs used in determination of the concentration of the unknown solutions are shown in appendices 12 to 18. All the calibration graphs gave straight lines with very high R-square values. Table 4.1 shows the concentrations of the calibration standards used and the corresponding absorbance values obtained.

Table 4.1: Calibration standards and absorbance values.

Element	Parameters					
Fe	Conc (ppm)	0.000	1.000	2.000	3.000	4.000
	Absorbance	0.000	0.038	0.098	0.159	0.205
Zn	Conc (ppm)	0.000	0.100	0.200	0.300	0.400
	Absorbance	0.000	0.032	0.064	0.090	0.128
Mn	Conc (ppm)	0.000	0.500	1.000	1.500	2.000
	Absorbance	0.000	0.048	0.100	0.152	0.202
Cu	Conc (ppm)	0.000	1.000	2.000	3.000	4.000
	Absorbance	0.000	0.099	0.196	0.295	0.386
Cr	Conc (ppm)	0.000	1.000	2.000	4.000	5.000
	Absorbance	0.000	0.012	0.024	0.048	0.059
Pb	Conc (ppm)	0.000	2.000	4.000	6.000	8.000
	Absorbance	0.000	0.076	0.151	0.213	0.280
Ni	Conc (ppm)	0.000	1.000	2.000	3.000	4.000
	Absorbance	0.000	0.036	0.071	0.102	0.132
Cd	Conc (ppm)	0.000	0.500	1.000	1.500	2.000
	Absorbance	0.000	0.170	0.332	0.470	0.626

The concentrations of the heavy metals were also determined using EDXRFS by analysis of their X–ray spectral lines using Canberra S–100 program and the values tabulated.

4.2. Accuracy, precision and reliability of instruments

The accuracy and precision of the EDXRFS was determined by comparing the concentration of the heavy metals determined using the instrument in soil 7 (IAEA) standard material with the certified values from the IAEA. All the concentrations obtained using the EDXRFS were within the range of values tabulated by the IAEA. The results showed a good agreement between the levels of the heavy metals obtained from EDXRFS and those tabulated by the IAEA in the standard soil 7 reference material implying that all the values obtained using the instrument were within acceptable limits of accuracy and precision. Table 4.2 shows the concentrations of the heavy metals analysed using the EDXRFS and those tabulated by the IAEA.

Table 4.2: Accuracy and precision: Soil 7 (IAEA) analyses by EDXRFS.

Element	XRFS values (mg/Kg)	Certified values (IAEA) mg/Kg (significance level 0.05)
Zn	96.06 ± 6.63	101 - 113
Mn	643 ± 10.07	604 - 650
Cu	12.57 ± 3.34	9 - 13
Cr	63.83 ± 2.83	49 - 74
Pb	62.67 ± 2.00	55 - 71
Rb	52.97 ± 2.15	47 - 56

The reliability of the EDXRFS and AAS were tested by comparing the concentrations of the heavy metals in various soil and water samples obtained using the two instruments. The concentrations of the heavy metals in the samples were measured in triplicates and the mean concentration and standard deviation determined. A good agreement was obtained between the AAS and EDXRFS values. Using the values of AAS as the standard, the mean percentage deviation ranged from 0.503 – 7.81 for Fe, 3.44 – 13.57 for Zn, 2.90 – 10.34 for Mn. The small % deviation implies that the results obtained using the two instruments were reliable. Table 4.3

shows the corresponding mean values of concentration and standard deviation obtained for some of the samples using the two instruments and the % deviations for Fe.

Table 4.3: Comparison of AAS and XRFS concentration of heavy metals in mg/Kg, dry weight unless otherwise stated for selected samples.

Sample		Fe (%)	% dev (Fe)	Zn	Mn	Cu	Cr	Pb	Ni
KWU2(D)	AAS	0.521± 0.004		0.140± 0.002	0.029± 0.001	0.024± 0.002	0.000± 0.000	0.000± 0.000	0.000± 0.000
	XRFS	0.511± 0.098	1.92	0.121± 0.021	0.032± 0.009	0.032± 0.007	0.024± 0.006	0.015± 0.006	0.000± 0.000
KSU4w(R)	AAS	3.861%± 0.033		59.32± 0.163	732.0 ±2.646	56.22± 0.110	43.42± 0.075	6.103± 0.045	22.23± 0.046
	XRFS	4.163%± 1.385	7.81	59.32± 2.567	753.2± 17.85	63.66± 8.928	50.37± 6.749	6.273± 2.893	24.61± 2.594
KSD3d(D)	AAS	5.841%± 0.072		75.64± 0.059	1174± 8.718	64.32± 0.202	54.48± 0.143	8.037± 0.081	25.65± 0.155
	XRFS	5.623%± 1.176	3.73	76.38± 4.738	1086± 11.46	67.84± 4.286	56.12± 7.346	7.631± 1.193	26.13± 3.168
ESS1w(D)	AAS	8.697%± 0.018		127.9± 0.306	1875± 10.24	112.0± 4.244	89.83± 1.252	18.32± 0.568	40.42± 1.990
	XRFS	8.644%± 2.361	0.61	123.5± 6.832	1809± 21.83	102.7± 8.923	84.25± 7.591	20.19± 3.281	46.32± 6.469
EFTS 1(D)	AAS	7.591%± 0.103		122.4± 3.485	1740± 12.21	97.20± 1.822	67.20± 1.114	15.64± 0.227	30.95± 2.711
	XRFS	7.553%± 1.733	0.50	128.0± 7.873	1820± 24.64	83.13± 7.493	62.16± 4.396	14.45± 2.547	32.35± 3.765

4.3. Variation in concentration of heavy metals and fluoride in water samples

The mean and standard deviation of the concentration of heavy metals and fluoride in various water samples collected during the dry and rainy seasons around the Fluorspar factory are presented in Appendices 1 and 2 respectively. The concentrations of the heavy metal and fluoride in the factory effluent streams and ponds were far above the natural background levels in the upstream water samples. The mean concentration of Fe in the effluent stream ranged from 48.64 to 54.90 mg/L, which was about 90 times higher than the mean concentration of Fe in the upstream water samples of 0.515 to 0.634 mg/L. The mean concentration of F^- in the effluent stream ranged from 29.07 to 32.77 mg/L, which was about 50 times higher than the mean concentration of F^- in the upstream water samples of 0.591 to 0.621 mg/L. There was also a wide variation in the total metal and fluoride content of the upstream, downstream, effluent stream, and pond water samples. The upstream water samples had the lowest concentrations of the heavy metals and fluoride. The wide difference in the concentration of heavy metals between the upstream and downstream water samples showed substantial contamination of the downstream river water samples due to the factory processes.

The sedimentation pond B in which *E. crassipes* was growing had the lowest concentration of the heavy metals compared to the other sedimentation ponds and the effluent streams. The mean concentration of Fe in pond B water samples ranged from 1.245 to 1.313 mg/L. The concentration in pond C ranged from 59.04 to 96.34 mg/L while that of the effluent streams ranged from 37.86 to 96.34 mg/L. The concentration of the other heavy metals and fluoride followed a similar trend. This was due to the ability of the plant to absorb the heavy metals and fluoride. The relatively higher levels of the selected heavy metals and fluoride in the downstream river water, soil and sediment samples compared to the upstream samples can be attributed to the very high levels of these elements in the effluent water samples.

The mean concentration of fluoride in the downstream river samples ranged from 5.870 to 6.307 mg/L while those of the effluent water samples ranged from 29.07 to 32.77 mg/L. The levels of fluoride in the downstream water samples are about five times higher while that in the effluent streams is about 20 times higher than the recommended level of 1.5 mg/L by WHO for domestic water. The mean concentrations of Fe in the downstream river samples ranged from 3.831 to 5.412 mg/L while those of the effluent water samples ranged from 48.64 to 64.19 mg/L. The levels of Fe in the downstream water samples are about 20 times higher while that in the effluent streams is about 160 to 200 times higher than the recommended level of 0.5 mg/L by WHO for domestic water. The mean concentrations of Mn in the downstream river samples ranged from 0.071 to 0.122 mg/L while those of the effluent water samples ranged from 0.967 to 1.772 mg/L. The levels of Mn in the downstream water samples were within the WHO recommended standards while that in the effluent streams is about 10 times higher than the recommended level of 1.0 mg/L by WHO for domestic water. The mean concentrations of Cr in the downstream river samples ranged from 0.073 to 0.083 mg/L while those of the effluent water samples ranged from 0.091 to 0.120 mg/L. The levels of Cr in the downstream water samples were nearly within the WHO recommended limits while that in the effluent streams is about 2 times higher than the recommended level of 0.05 mg/L by WHO for domestic water. The mean concentrations of Pb in the downstream river samples ranged from 0.067 to 0.091 mg/L while those of the effluent water samples ranged from 0.181 to 0.254 mg/L. The levels of Pb in the downstream water samples were about $1^1/_2$ times higher while that in the effluent streams were about 4 times higher than the WHO recommended level of 0.05 mg/L for domestic water.

The mean concentrations of Zn and Cu in the downstream river and effluent water samples which ranged from 0.163 to 0.379 and 0.052 to 0.307 mg/L respectively were below the WHO limits for domestic water of 5.0 and 1.0 mg/L respectively. However, these levels were about 8 times higher than the levels obtained for the upstream water samples. The WHO and the NEMA recommended levels are shown in appendices 9, 10 and 11. Increases in the concentrations of heavy metals have also been reported in Villa de la Paz - Matehuala semi-arid mining area in Mexico by Israel et al (2003). Long term ingestion of elevated levels of these elements in the downstream and effluent water samples can result in serious environmental and health problems.
The concentration of the elements in the water samples during the rainy season followed a similar trend as that of the dry season, except that the values were slightly lower. The lower values during the rainy season can be attributed to the dilution of the water samples by the relatively large volume of water during the rainy season. The highest concentrations of the

elements were recorded in the factory followed by the pond effluents, effluent streams and immediately downstream in the water, soil and sediment samples respectively.

There is a steep rise in the concentrations of the heavy metals and fluoride in the river water samples on moving from upstream to downstream after the effluent streams had mixed with the river water during both the dry and rainy seasons. The concentration of these elements however decreases steadily lower downstream. This observation together with the fact that the factory effluents have relatively high concentrations of the heavy metals and fluoride shows that the factory effluents are responsible for the increased concentration of these elements in the downstream river water.

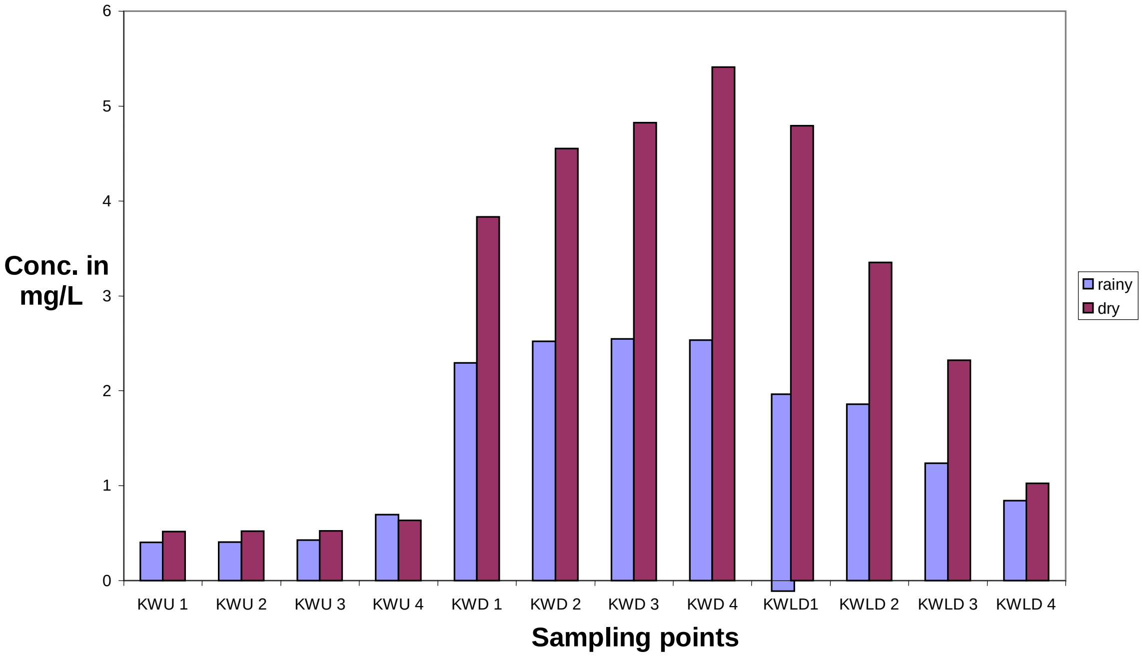


Figure 4.1: Variation in concentration of Fe in water samples along river Kimwarer.

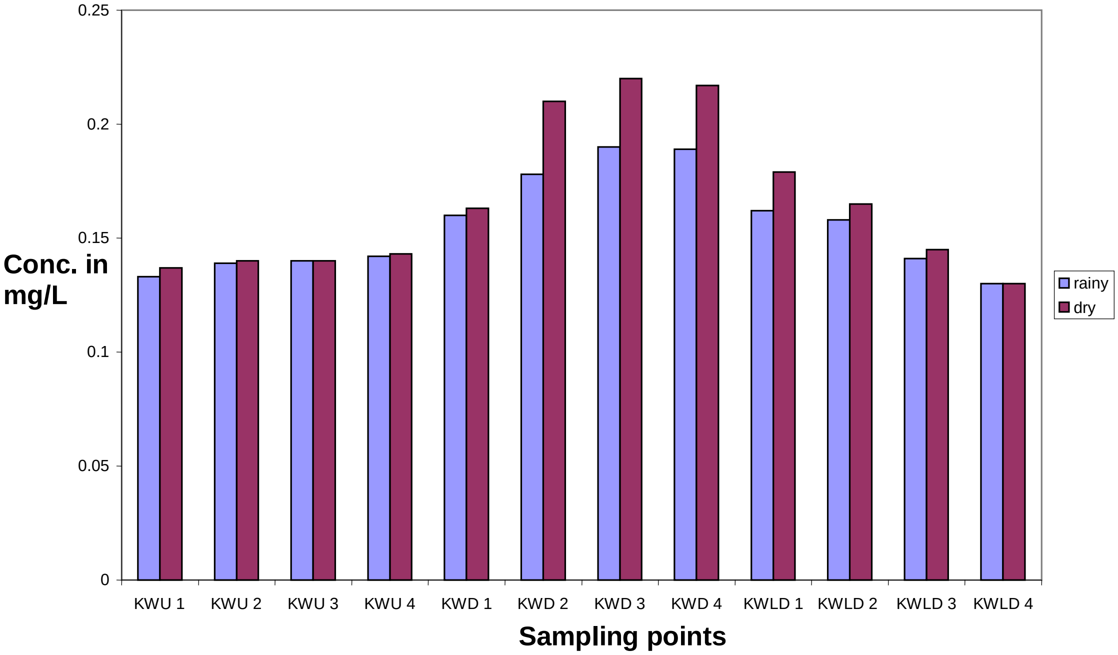


Figure 4.2: Variation in concentration of Zn in water samples along river Kimwarer.

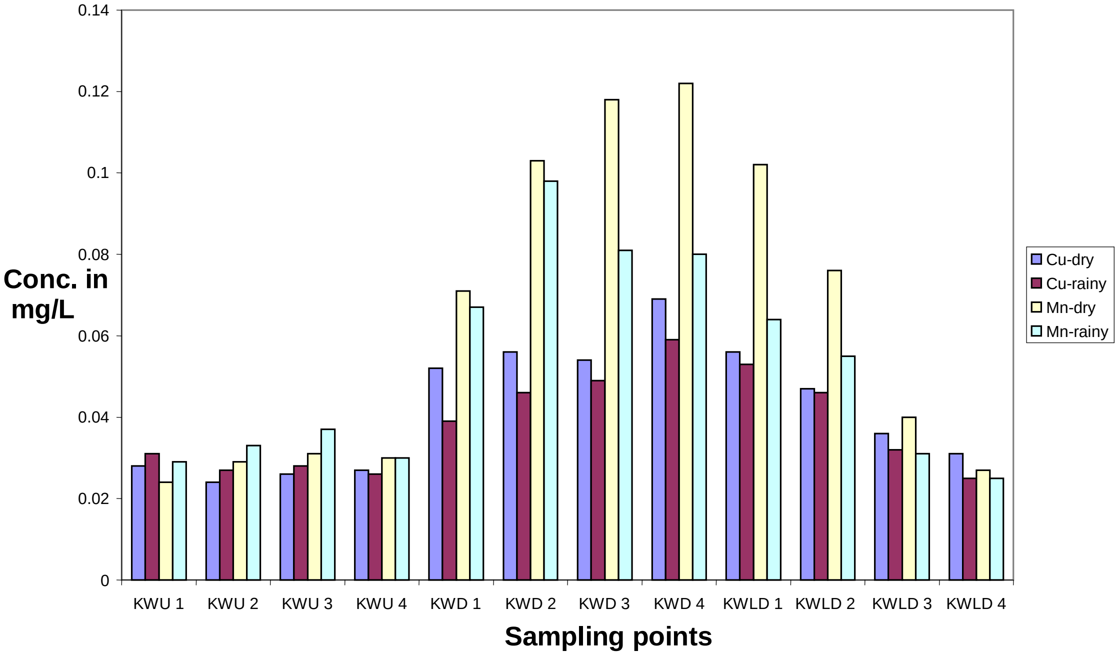


Figure 4.3: Variation in concentration of Cu and Mn in water samples along river Kimwarer.

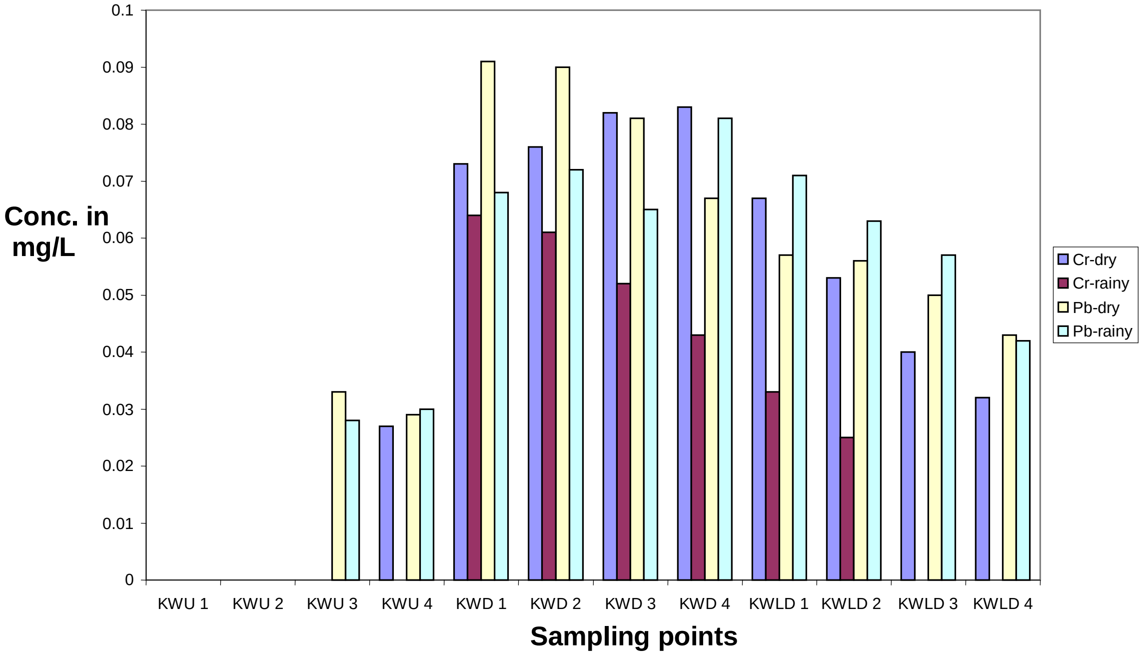


Figure 4.4: Variation in concentration of Cr and Pb in water samples along river Kimwarer.

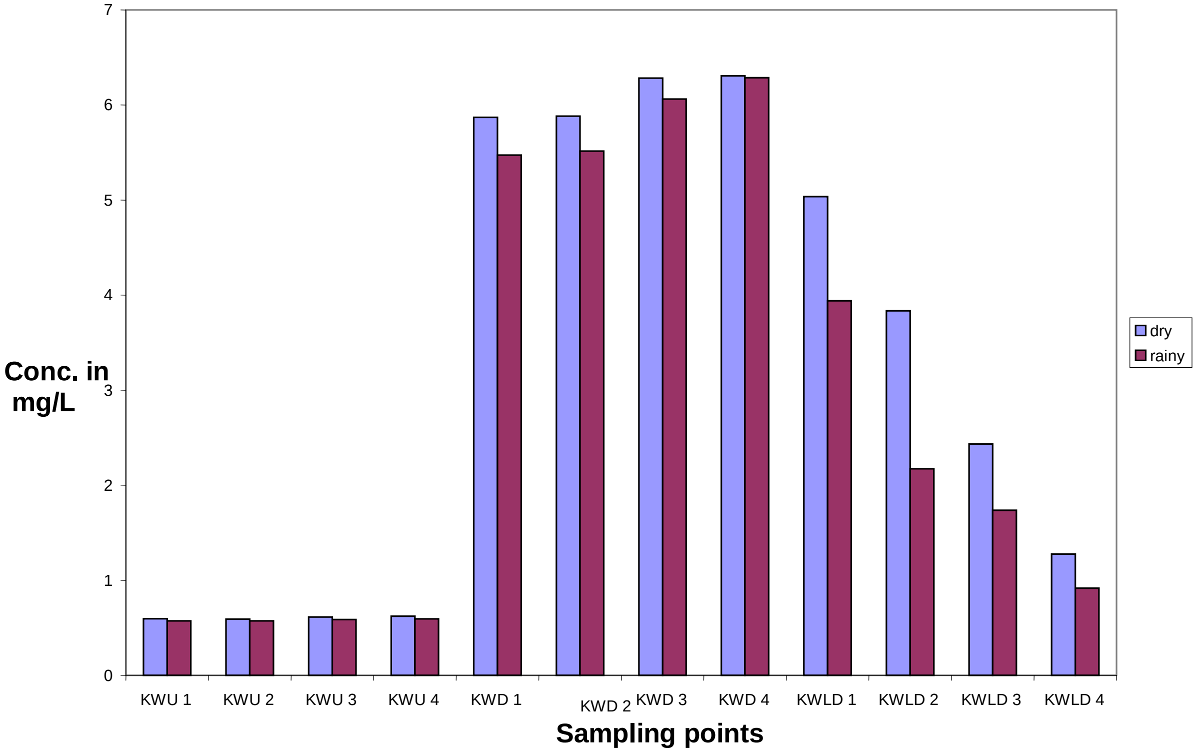


Figure 4.5: Variation in concentration of Fluoride in water samples along river Kimwarer.

Figures 4.1 to 4.5 show the variation of the heavy metals and fluoride along river Kimwarer during the dry and rainy seasons. The figures show that the concentrations of elements in the samples during the dry season are generally higher than those during the rainy season. This observation can be explained by the dilution of the factory effluent samples by the high volume of stream and river water. The decrease in the concentration of the elements lower downstream can be explained by further dilution of the river water as it undergoes self purification.

4.4. Variation in physical properties of water samples

The pH, turbidity and conductivity of river Kimwarer and factory effluent water samples were measured during the dry and rainy season. The pH of the upstream river water samples ranged from 7.24 to 7.32 during the dry season and 7.26 to 7.33 during the rainy season. The pH of the downstream river water samples ranged from 7.88 to 8.15 during the dry season and 7.76 to 8.11 during the rainy season. The pH of the lower downstream river water samples ranged from 7.78 to 8.03 during the dry season and 7.38 to 7.70 during the rainy season. The pH of the factory effluent stream water samples ranged from 8.34 to 8.88 during the dry season and 8.21 to 8.70 during the rainy season. The factory effluent had the lowest pH value of 6.08 during the dry season and 5.96 during the rainy season. The pH of pond B was nearly the same as that of the upstream water samples (7.28 during the dry season and 7.20 during the rainy season). The water samples from the factory office dam showed the highest pH value of 9.32 during the dry season and 9.24 during the rainy season. The pH value of pond C was 8.80 and 8.74 during the dry and rainy seasons respectively. The high pH values of the effluents could be explained by the liming of the factory effluents. Appendices 5 and 6 show the variation of the pH, conductivity and turbidity of the water samples during the dry and rainy seasons respectively.

Although the pH values obtained in this analysis was relatively alkaline, implying extensive liming of the factory effluents, the pH values obtained by Nguta (2004), showed that the factory effluents were quite acidic (pH 3.40 – 5.50). The inconsistency in these results can be explained by the fact that the factory effluents do not undergo constant liming but are probably only limed occasionally when the management is aware that sampling is taking place. This fact can also be supported by the fact that the factory does not readily welcome researchers to collect samples from the area. Hence continuous impromptu sampling and analysis of factory stream effluents should be done by independent organizations such as NEMA to ensure that the factory performs continuous liming of the effluents and also ensure that the levels of hazardous elements are within acceptable limits. Since the metallic ions are more labile in acidic solutions, liming also greatly helps in reducing the concentration of the heavy metals in the effluent water samples since most of the metallic cations are insoluble in alkaline solutions and therefore sink in the sedimentation ponds.

The variation in the values of pH was plotted on a graph as shown in figure 4.6. The factory effluents had the lowest pH values (acidic) while the office pond which is quite close to the factory had the highest pH value. The upstream water samples had lower pH values than the downstream, factory effluent and pond samples. The higher pH values of the effluent stream samples and the ponds can be explained by the liming performed on the factory effluents before they are released into the ponds.

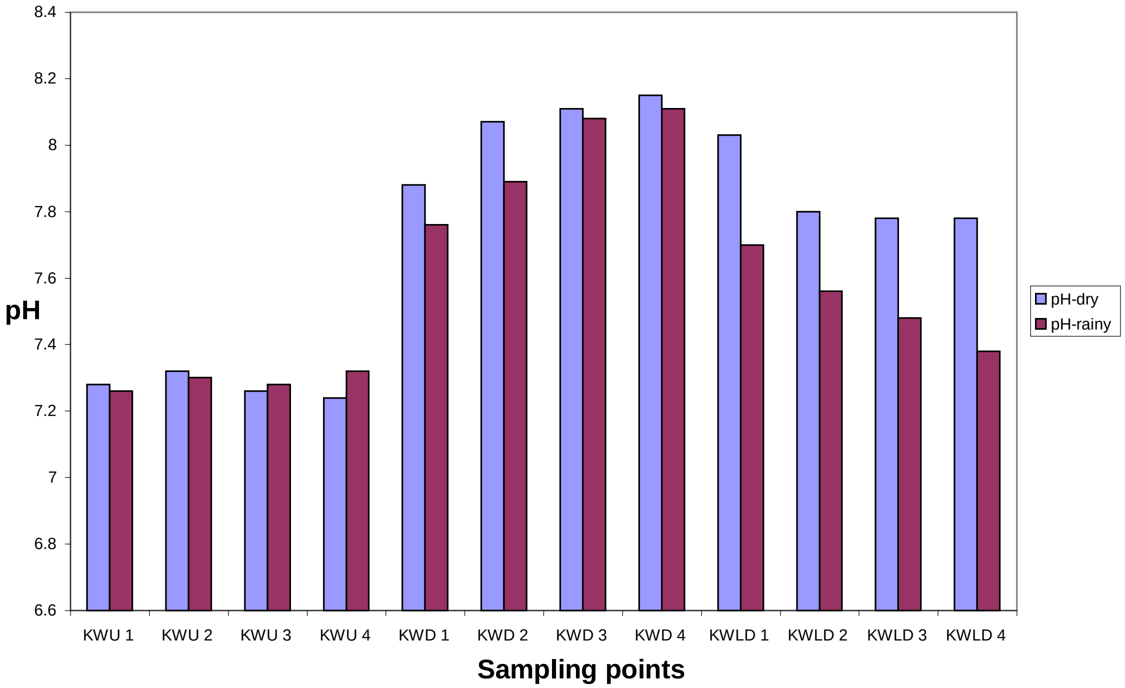


Figure 4.6: Variation in pH of water samples along river Kimwarer (dry and rainy seasons).

The conductivities of the upstream water samples were lower than those of the downstream samples which were also lower than those of the effluent stream and pond samples. Since the conductivity of water samples depends on the amount of ions, this observation shows that the effluent stream and pond water samples had highest concentration of ions while the upstream water samples had the lowest concentration of ions. The fact that the conductivity of the lower downstream water samples gradually decrease also supports the fact that the factory is responsible for the elevated ions in the downstream river water and the factory effluent samples. Figure 4.7 shows variation in conductivity of the river water samples during the dry and rainy seasons. The figure shows similar trends in conductivity during both seasons. The lower conductivity during the rainy seasons can be explained by dilution.

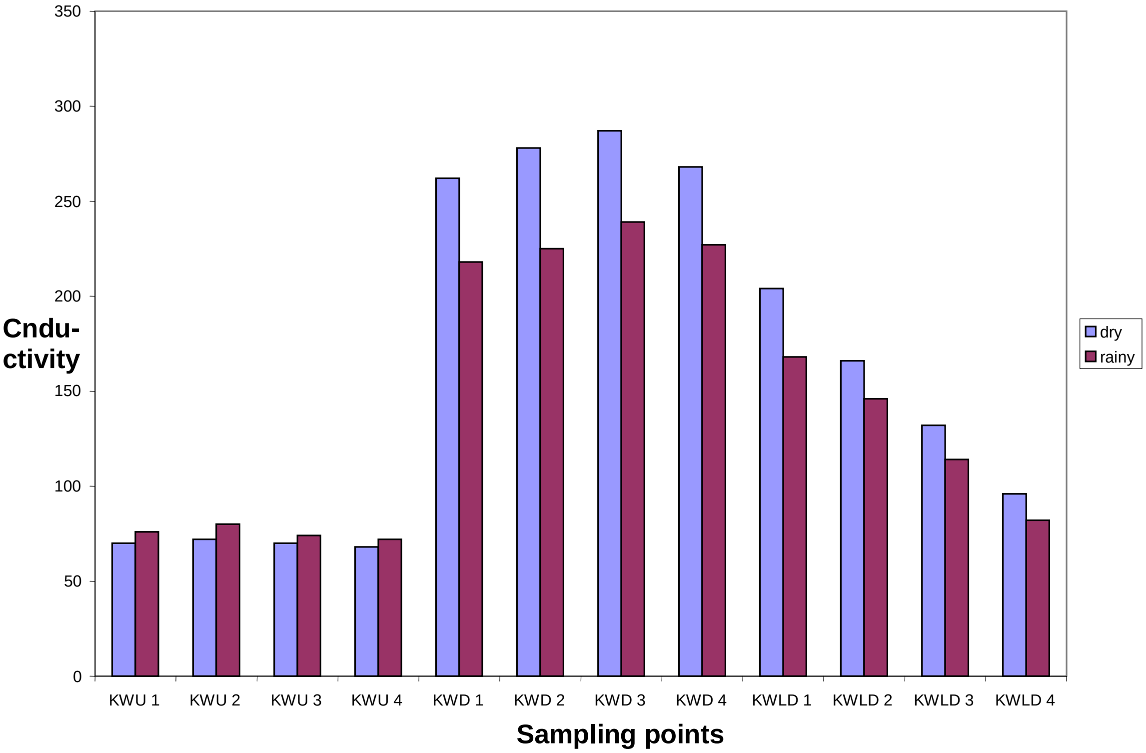


Figure 4.7: Variation in conductivity (μS) of water samples along river Kimwarer.

The upstream water samples were relatively clear as shown by very low turbidity values. The factory effluent had the highest turbidity values and was actually composed of a thick acidic sludge which settled in the sedimentation ponds. The variation in turbidity of the water samples is shown in figure 4.8. Although the effluent stream samples were highly turbid, they were readily diluted upon mixing with the larger volume of river water to produce less turbid water. The turbidity of the river water samples followed a similar trend as the other physical parameters during both the rainy and dry seasons.

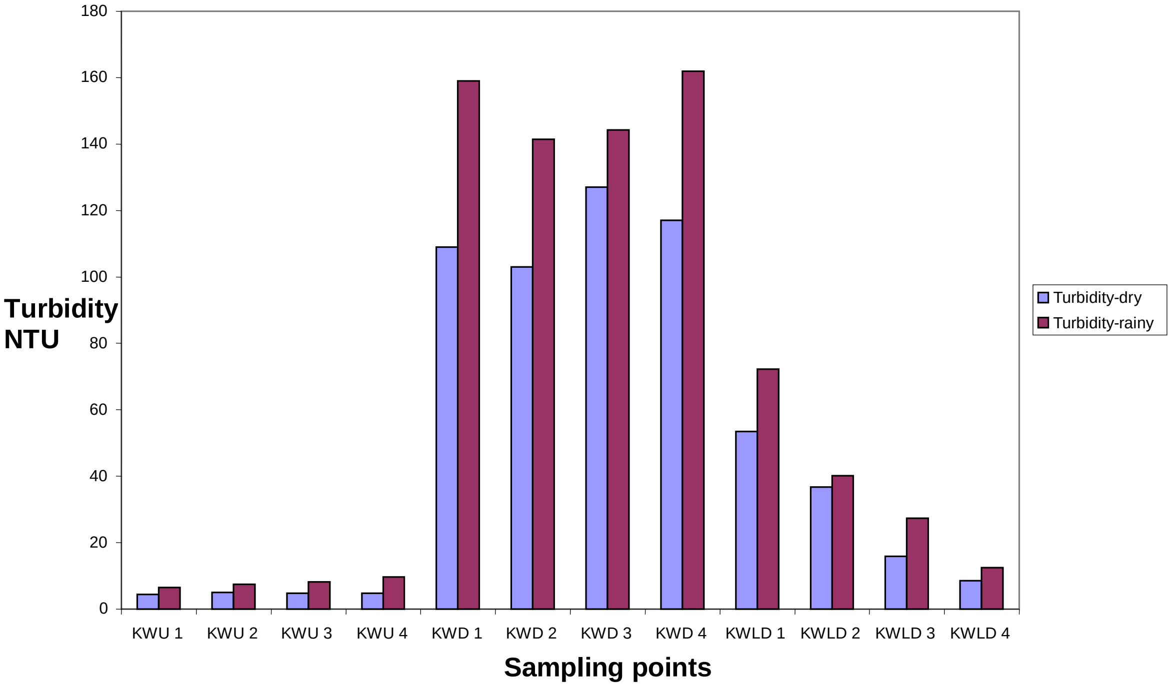


Figure 4.8: Variation in turbidity (NTU) of water samples along river Kimwarer.

4.5 EDXRFS analysis

Soil pellets weighing about 0.5 grams were made and analysed with XRFS using ^{109}Cd X-ray source. Each metal showed characteristic peaks at particular counts, the height of the peaks being directly proportional to the concentration of the metals in the samples. The spectra obtained were analysed in order to obtain the concentration of the heavy metals in the samples. Table 4.4 shows the mean concentrations of the elements in the various soil samples while Figures 4.9 – 4.11 show the spectra for some of the soil samples. The spectra show that the effluent soil samples also had relatively higher values of calcium thus confirming that extensive liming was being done on the factory effluents.

Table 4.4: XRFS Mean concentration of heavy metals in soil samples in mg/Kg unless otherwise stated.

Sample	Fe (%)	Zn	Mn	Cu	Pb	Cr	Ni
KSU 2 (D)	5.072± 1.862	74.03± 5.382	1050± 27.46	56.20± 4.432	8.932± 2.543	41.36± 3.325	22.73± 1.231
KSU 2 (W)	4.577± 0.876	54.57± 3.349	615.7± 11.85	46.92± 4.573	5.238± 3.365	39.53± 1.396	20.17± 2.793
KSU 3w (W)	4.217± 0.697	59.71± 6.370	825± 12.54	35.99± 6.475	4.612± 3.742	50.12± 7.921	32.21± 1.638
KSU4 w (R)	4.163± 1.385	53.62± 2.567	753.2± 17.85	63.66± 8.928	6.270± 2.893	50.37± 6.749	24.61± 2.594
KSD 3 d (D)	5.623± 1.176	76.38± 6.738	1086± 11.46	67.84± 4.286	7.631± 1.193	56.12± 7.346	26.13± 3.168
KSD 2 (W)	6.861± 0.887	109.7± 5.368	1504± 13.36	126.4± 3.372	19.19± 2.235	88.34± 5.548	36.69± 4.326
KSD 3 (W)	6.562± 1.173	93.15± 5.637	1477± 17.36	106.3± 5.597	16.57± 0.864	77.57± 8.732	38.97± 3.321
KSD 4 (W)	7.07± 2.369	103.4± 3.265	1483± 9.679	82.67± 7.139	17.87± 3.598	72.43± 11.82	33.43± 1.634
KSLD 1(D)	5.414± 3.359	70.87± 2.248	1136± 6.843	70.97± 12.48	7.472± 3.76	44.50± 5.492	23.43± 3.460
KSLD 1(W)	6.268± 2.239	93.43± 4.865	1375± 15.69	78.67± 9.954	11.87± 2.250	70.47± 10.69	30.43± 4.832
KSLD 2 (W)	5.641± 0.263	86.47± 6.497	1266± 11.42	73.92± 3.581	8.834± 0.738	67.25± 11.09	28.61± 4.470
ESS 1 (bank)	5.638± 0.638	77.72± 2.257	1190± 16.38	71.05± 2.843	8.731± 2.274	67.47± 8.871	8.253± 2.274
ESS 2 (bank)	5.342± 1.374	73.47± 8.294	1280± 26.16	68.81± 5.387	9.086± 5.046	57.82± 3.728	58.33± 7.849
ESS 3 (D)	5.461± 0.791	66.35± 3.521	1195± 13.03	63.75± 3.175	8.15± 2.391	58.47± 6.663	21.35± 4.387

Table 4.4: Continued.

ESS 1w (D)	8.635± 2.361	123.5± 5.832	1809± 21.83	98.73± 7.923	20.19± 3.281	80.25± 7.591	46.32± 5.469
ESS 2 (W)	8.872± 2.693	118.5± 10.54	1630± 30.28	108.4± 4.850	24.57± 5.930	78.12± 6.498	58.37± 7.294
ESS 3 (W)	9.426± 1.586	122.5± 6.792	1660± 25.36	128.1± 11.37	18.86± 2.931	89.63± 8.934	43.08± 4.972
Pond B (W)	0.949± 0.369	36.42± 2.453	526.7± 16.37	40.20± 4.592	8.96± 3.658	54.63± 5.382	20.52± 2.231
Dry dam A	2.466± 0.632	32.33± 1.765	600± 18.46	39.33± 1.127	12.97± 0.543	36.17± 2.870	23.63± 4.532
Dam C(W)	6.203± 0.932	60.34± 4.954	1025± 15.67	82.35± 9.572	32.30± 2.197	74.45± 3.487	20.60± 3.287
Fact. Off.(W)	6.837± 0.733	115.1± 5.752	1209± 26.39	71.86± 4.568	23.35± 3.873	73.35± 6.684	39.50± 3.367
Fact. Off.(D)	6.53± 2.075	107.4± 8.794	1125± 21.57	68.65± 2.474	19.30± 4.639	69.20± 8.364	24.95± 5.821
EFTS1 (D)	7.553± 1.734	128.0± 5.873	1820± 23.64	83.12± 7.497	14.45± 2.547	62.16± 4.396	32.35± 3.365
KSS2 (D)	7.948± 2.235	120.8± 6.925	1615± 18.36	88.81± 6.793	13.21± 3.193	67.83± 2.157	27.93± 3.934

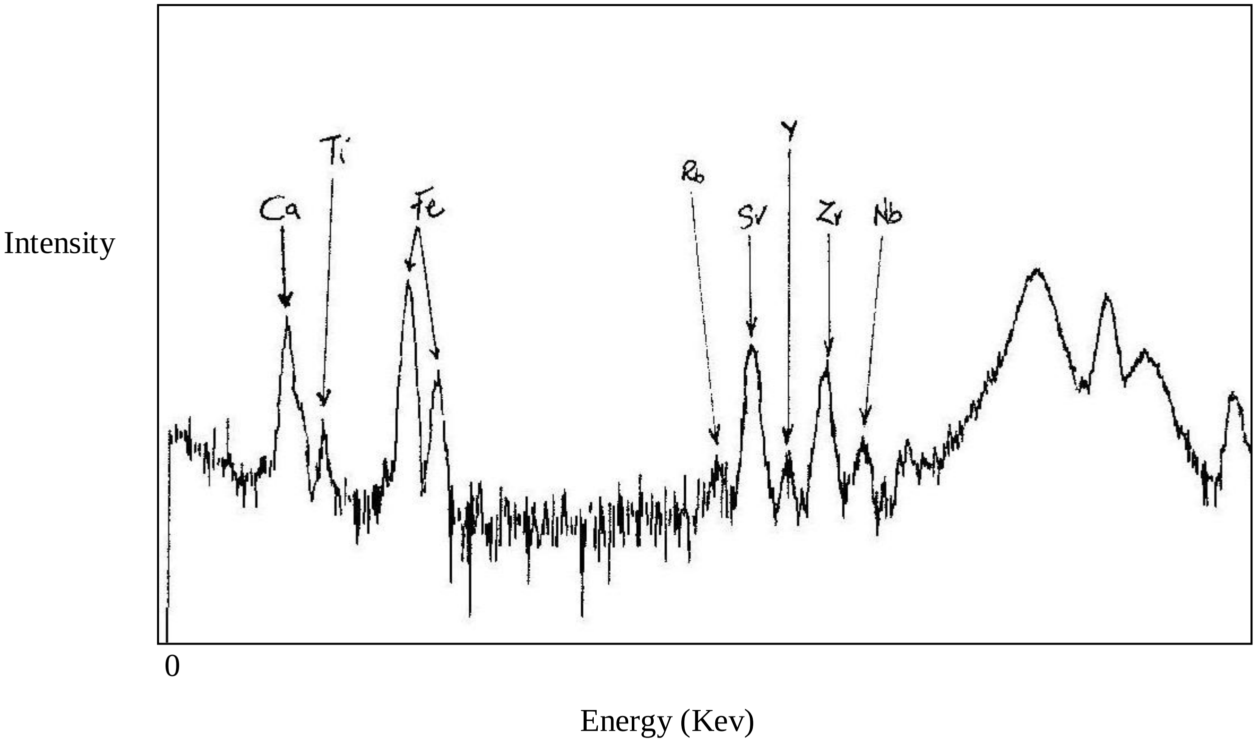


Figure 4.9: XRFS spectrum for effluent soil sample [ESS 3(W)].

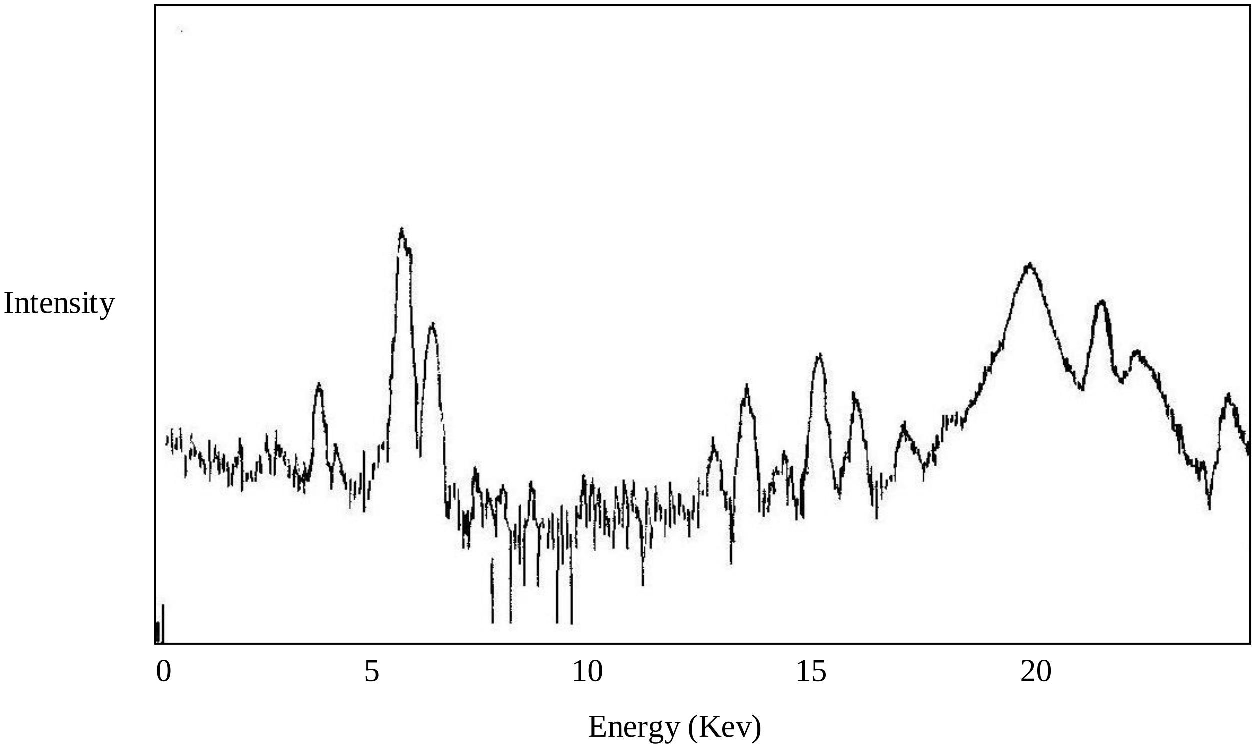


Figure 4.10: XRFS spectrum for downstream soil sample [KSD 1(W)].

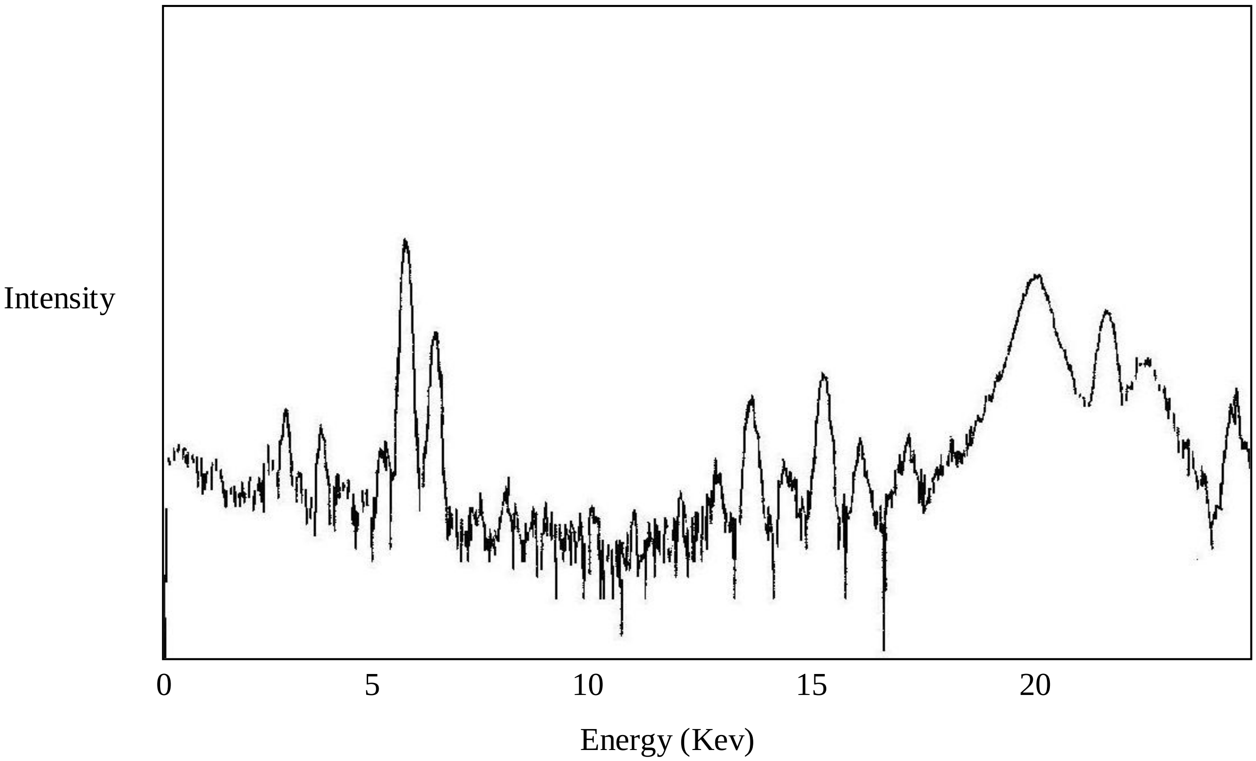


Figure 4.11: XRFS spectrum for downstream soil sample [KSD 2(W)].

The concentrations of the heavy metals in water samples obtained using EDXRFS are shown in table 4.5. The levels of these elements in the effluent water samples are much lower than those in the soil samples. The lower levels of the elements can be explained by the basicity of the water samples which results in lower solubility of the metallic ions including calcium which was used for liming. The values obtained using the Energy Dispersive X – Ray Fluorescence Spectrophotometer are shown in table 4.5. Figures 4.12, 4.13 and 4.14 shows the spectra obtained for some of the water samples.

Table 4.5: XRFS Mean concentration (mg/L) of heavy metals in water samples.

Sample	Fe	Zn	Mn	Cu	Cr	Pb
KWU 1 (D)	0.653± 0.126	0.114± 0.018	0.061± 0.017	0.016± 0.006	0.028± 0.010	0.014± 0.007
KWU 2 (D)	0.511± 0.098	0.121± 0.021	0.032± 0.009	0.031± 0.007	0.024± 0.006	0.015± 0.006
KWU 3 (R)	0.777± 0.354	0.089± 0.025	0.082± 0.014	0.028± 0.009	0.026± 0.007	0.026± 0.005
KWD 1 (R)	3.725± 1.122	0.102± 0.033	0.114± 0.031	0.026± 0.006	0.067± 0.015	0.022± 0.006
KWD 2 (R)	4.144± 1.295	0.090± 0.021	0.212± 0.094	0.047± 0.017	0.041± 0.011	0.019± 0.005
KWD 4	4.488± 0.871	0.086± 0.019	0.182± 0.056	0.026± 0.013	0.066± 0.021	0.019± 0.007
KWLD 1 (R)	3.269± 0.218	0.113± 0.039	0.142± 0.017	0.034± 0.012	0.044± 0.011	0.028± 0.011
KWLD 2 (R)	1.806± 0.169	0.083 0.029	0.071± 0.022	0.036± 0.011	0.029± 0.009	0.014± 0.005
Eff. Stream 1 (D)	36.09± 3.967	0.208± 0.087	1.193± 0.167	0.149± 0.071	0.140± 0.060	0.222± 0.076
Eff. Stream 1 (R)	40.87± 2.147	0.262± 0.078	0.926± 0.217	0.170± 0.035	0.123± 0.024	0.133± 0.037
Eff. Stream 2 (D)	35.23± 3.346	0.191± 0.042	0.850± 0.137	0.060± 0.021	0.080± 0.015	0.136± 0.023
Eff. Stream 2 (R)	49.21± 4.026	0.253± 0.038	1.153± 0.026	0.125± 0.034	0.142± 0.017	0.111± 0.023
Eff. Stream 3 (D)	40.92± 3.895	0.301± 0.093	0.522± 0.152	0.091± 0.027	0.166± 0.039	0.198± 0.044
Eff. Stream 3 (R)	45.74± 3.876	0.234± 0.075	1.130± 0.119	0.114± 0.031	0.811± 0.119	0.193± 0.041

Table 4.5: Continued.

Eff. Stream 4 (R)	60.40±	0.317±	2.499±	0.533±	0.987±	0.179±
	5.213	0.057	1.097	0.113	0.225	0.036
Pond C	84.40±	0.621±	2.702±	0.207±	0.126±	0.232±
	7.326	0.227	0.839	0.053	0.044	0.051
Fact. Off.	199.5±	1.731±	25.17±	0.426±	1.335±	0.888±
	12.11	1.127	4.295	0.115	0.097	0.386
Fact. Eff.	1552±	14.93±	72.78±	2.706±	4.183±	2.020±
	23.70	2.283	7.729	0.162	1.369	1.136
Pond B	1.451±	0.106±	0.307±	0.043±	0.027±	0.063±
	0.553	0.027	0.019	0.024	0.016	0.022

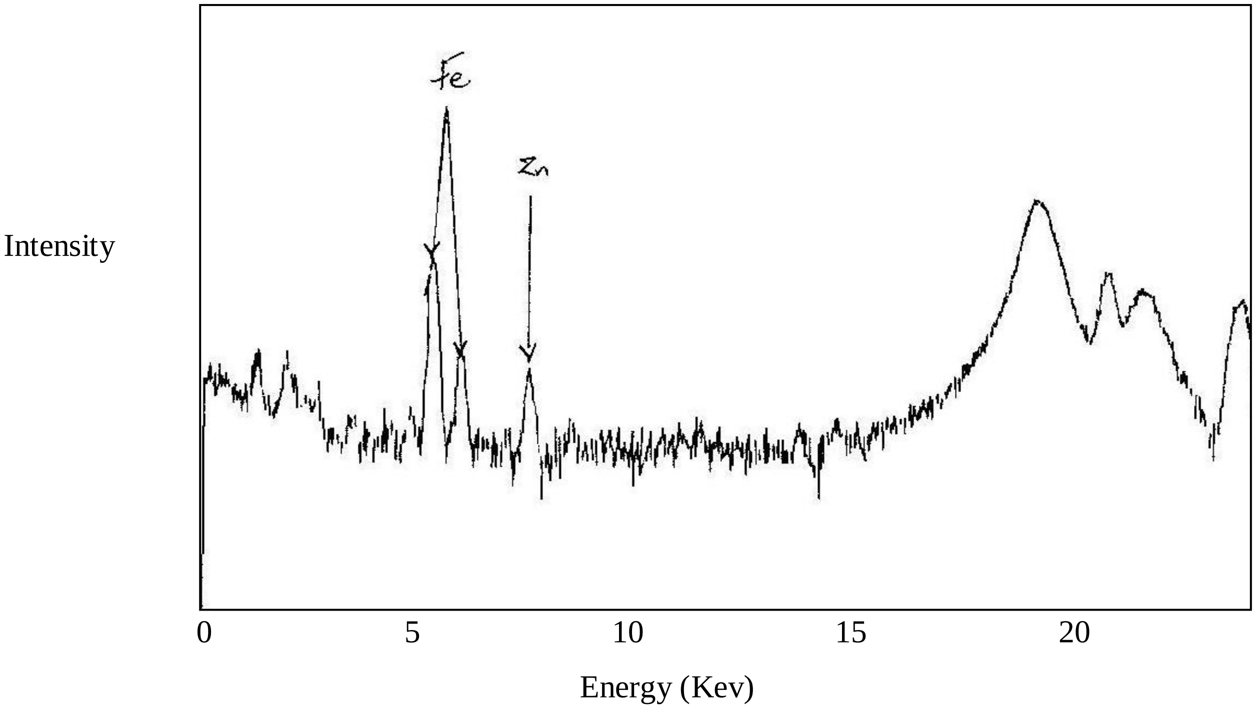


Figure 4.12: XRFS spectrum for upstream water sample [KWU 1(D)].

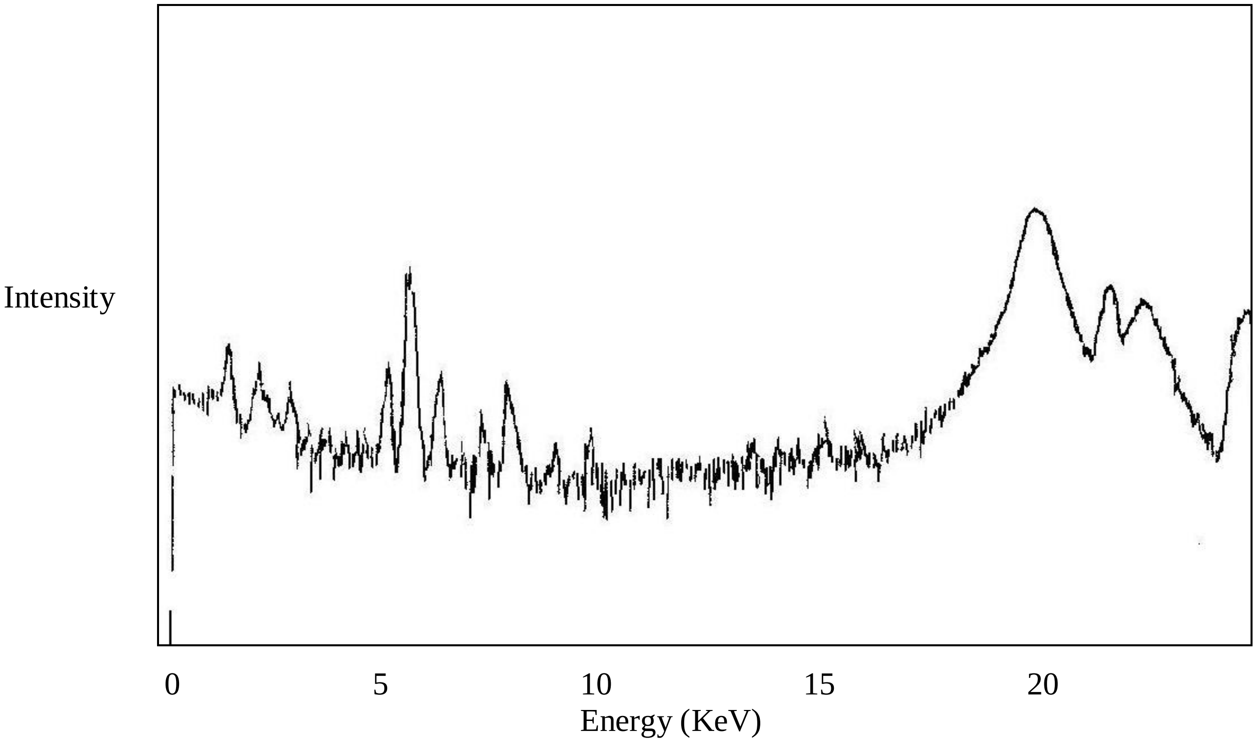


Figure 4.13: XRFS spectrum for effluent stream water sample.

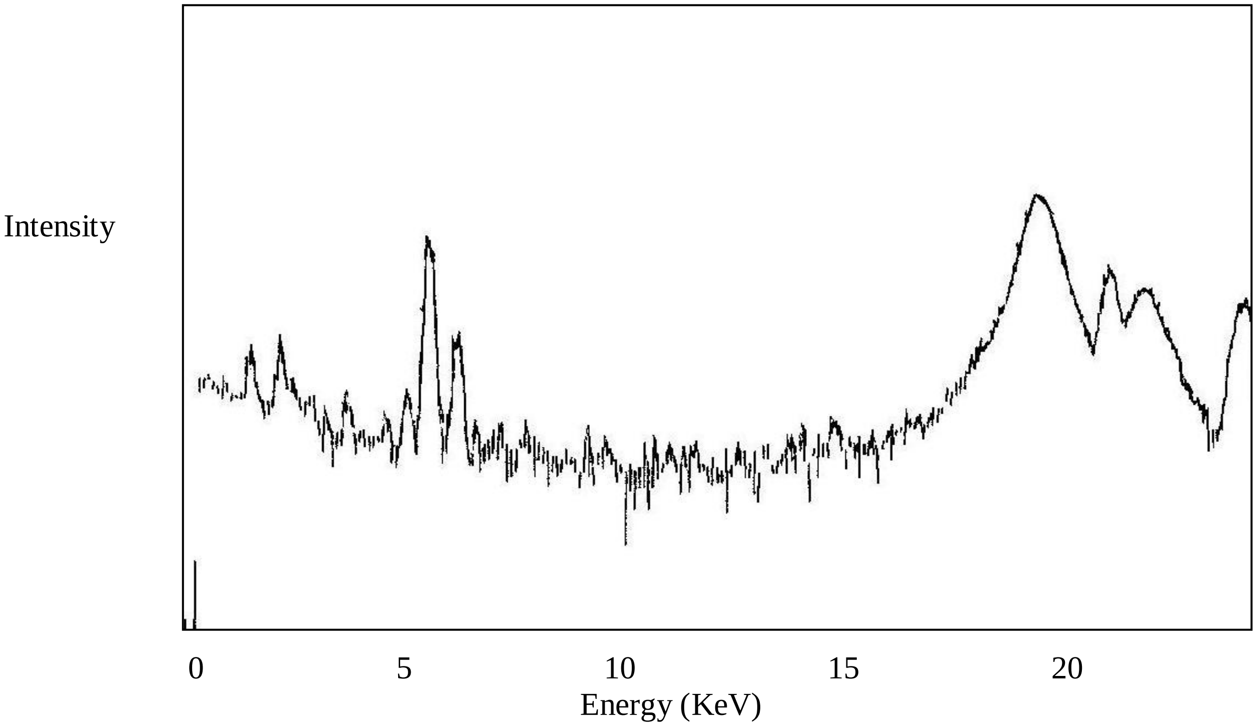


Figure 4.14: XRFS spectrum for downstream water sample [KWD 4 (D)].

4.6. Levels of heavy metals in various parts of *E. crassipes*

The concentration of the selected metals and fluoride in various parts of the *E. crassipes* obtained from the sedimentation pond B, which had the lowest concentration of these elements gave the values shown in Table 4.6. The results show that the roots of *E. crassipes* had the highest concentration of the heavy metals followed by the stem and leaves respectively. The high concentration of the heavy metals and fluoride in the various parts of the plant shows its effectiveness in absorbing the heavy metals and fluoride. Similar results were obtained by Orata (2003). This observation can be used to explain the relatively low levels of these elements in the sedimentation pond B in which the plant was growing. The ability of *E. crassipes* to absorb the heavy metals implies that it can be employed in phytoremediation of highly polluted water ponds.

Although various parts of *E. crassipes* contained elevated levels of the heavy metals, the concentration of these elements in the leaves were lower than toxic levels generally found in plant leaves (appendix 7). It is however possible that not all plants are able to withstand the high levels of these elements in their roots and stems and hence this could be the possible cause of the drying plants on the edges of the ponds.

Table 4.6: Mean concentration of heavy metals and fluoride in mg/Kg in different parts of *E. crassipes.*

Plant part	Fe	Zn	Mn	Cu	Cr	Pb	Ni	F
Roots	587.32	146.01	256.59	60.53	28.97	12.26	24.69	32.45
	±16.39	± 10.23	±15.31	±2.25	±3.68	±2.88	±2.49	±4.36
Stem	363.60	96.43	203.77	37.96	16.44	8.53	11.36	21.22
	±12.58	± 5.11	±11.69	±3.29	±2.76	±1.97	±2.36	±3.02
leaves	139.54	66.21	124.04	15.84	10.43	6.82	4.39	10.39
	±11.33	± 0.04	±10.55	±2.07	±2.17	±2.07	±2.04	±2.71

4.7. Percentage of heavy metal adsorbed by *E. crassipes*

The ability of the roots, stems and leaves of *E. crassipes* samples to adsorb heavy metals was studied by dissolving 2 grams of the ground plant parts in 100 cm^3 of artificially prepared solutions containing 100 mg/Kg of the heavy metals. The results from adsorption studies showed that the roots were the most effective in adsorbing the heavy metals with the mean percentage adsorption ranging from 75.71 to 85.44 followed by the stems which had a mean percentage adsorption ranging from 40.39 to 63.45. The leaves of *E. crassipes* had the lowest mean adsorption of the heavy metals ranging from 23.33 to 37.56. Lead was least adsorbed by the roots while the highest amount of Copper was adsorbed from the solutions. Although lower percentages of the heavy metals were adsorbed by the various parts of *E. crassipes,* the trends in adsorption of the heavy metals were consistent with those obtained by Orata (2003), using plants obtained from Lake Victoria. The lower adsorption of the heavy metals in this study can be attributed to the higher levels of the elements from the sedimentation ponds as compared to the lower levels in Lake Victoria. The levels of the heavy metals in the various parts of the *E. crassipes* obtained from the sedimentation ponds were also higher than those obtained from Lake Victoria. The results from this study show that the ground roots of *E. crassipes* can be employed as effective filters for the heavy metals. Appendix 8 and figure 4.15 shows a summary of the mean percentage amounts of the heavy metals adsorbed from artificially prepared solutions by various parts of *E. crassipes*.

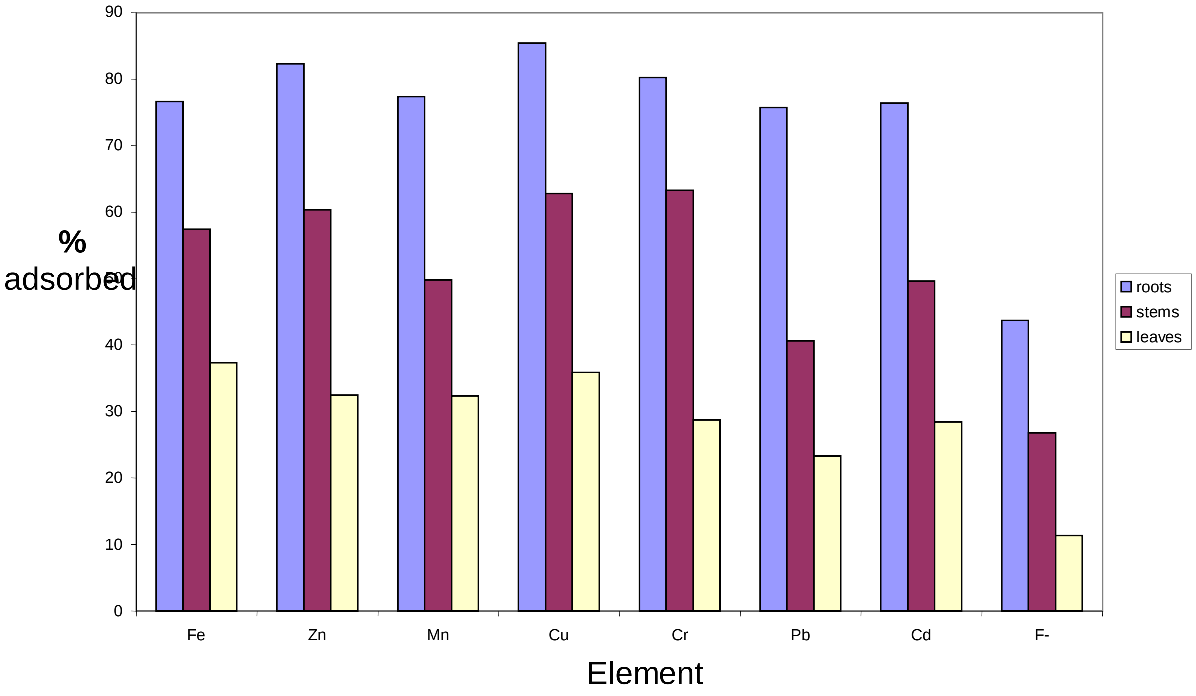


Figure 4.15: Percentage of heavy metals adsorbed by various parts of *E. crassipes.*

4.8 Statistical analysis

In order to determine whether there was any significant difference between the concentration of the heavy metals and fluoride in the upstream and downstream water, soil and sediment samples and hence identify whether the factory was responsible for the contamination of the river water and the surrounding farms, t-test and ANOVA was done on the samples at 95% confidence level. Genstat statistical package was used in this study and the results tabulated.

4.8.1. t- test

A total of 24 samples were tested under each t-test in order to determine whether there was any significant difference between the samples taken from different parts around the fluorspar mining and processing plant. In all the tests performed, $p < 0.05$ implying that there was significant difference between the concentration of the heavy metals and fluoride in the upstream and downstream water samples. The relatively high value of p during the rainy season is possibly due to the dilution of the sample effluent streams by the higher volume of water in the river during the rainy season. In order for the samples tested to have no significant difference under t-test, the value should be $p \geq 0.05$.

The significant difference between the water and soil samples was also tested by comparing the t-tabulated and the t-calculated at 95%. The t-tabulated at 95% confidence level and 22 degrees of freedom was 2.07. Since the value of |t|-tabulated < |t|-calculated, the null hypothesis that, there is no significant difference in the levels of selected heavy metals and fluoride between the upstream and downstream samples was rejected. This is because the t-calculated does not satisfy the equation:

$$-2.06 < |t| \text{-calculated} < 2.06$$

The summarized results for the t-test are shown in tables 4.7 to 4.10.

Table 4.7: t–test on upstream and downstream water samples at 95% confidence level- rainy season.

Element	Degrees of freedom	t(calculated)	P(probability)
Fe	22	3.14	0.005
Zn	22	7.63	<0.001
Mn	22	15.75	<0.001
Cu	22	9.77	<0.001
Cr	22	16.42	<0.001
Pb	22	11.86	<0.001
F^-	22	68.75	<0.001

Table 4.8: t–test on upstream and downstream water samples at 95% confidence level - dry season.

Element	Degrees of freedom	t(calculated)	P(probability)
Fe	22	22.97	<0.001
Zn	22	11.87	<0.001
Mn	22	12.13	<0.001
Cu	22	9.41	<0.001
Cr	22	15.56	<0.001
Pb	22	11.93	<0.001
F^-	22	73.73	<0.001

Table 4.9: t–tests on upstream and downstream sediment samples at 95% confidence level - rainy season.

Element	Degrees of freedom	t(calculated)	P(probability)
Fe	22	53.58	<0.001
Zn	22	29.23	<0.001
Mn	22	62.92	<0.001
Cu	22	30.64	<0.001
Cr	22	39.99	<0.001
Pb	22	44.19	<0.001
Cd	22	30.49	<0.001
Ni	22	47.69	<0.001
F^-	22	46.73	<0.001

Table 4.10: t–test on upstream and downstream sediment samples at 95% confidence level - dry season.

Element	Degrees of freedom	t(calculated)	P(probability)
Fe	22	24.79	<0.001
Zn	22	-24.52	<0.001
Mn	22	-28.13	<0.001
Cu	22	-28.32	<0.001
Cr	22	-26.71	<0.001
Pb	22	-31.64	<0.001
Cd	22	-11.63	<0.001
Ni	22	-38.15	<0.001
F^-	22	-37.24	<0.001

4.8.2 Analysis of variance (ANOVA)

The significant difference between the various water, soil and sediment samples was also tested using ANOVA. The least significant differences at 95% confidence level {LSD (0.05)} were used to determine whether there was any significant difference between the various water and soil samples collected during the dry and rainy seasons. The LSD value showed that there was significant difference between the concentration of Fe in the upstream and downstream water samples since the difference between the mean concentrations (5.11) was greater than the LSD value (3.267). The mean concentration of Fe in the upstream, lower downstream, Pond B and effluent stream water samples during the dry season, (table 4.11), were 0.580, 2.870, 1.310 and 44.97 mg/L respectively implying that there was no significant difference between the upstream, lower downstream and pond B water samples since the difference between their mean concentrations is less than 3.267 (LSD 5%). However, there was significant difference between these water samples and that from the effluent streams since the difference between the mean concentration of Fe in these water samples and that of the effluent stream is greater than 3.267. All the other elements except Zn showed significant difference between the upstream and downstream water samples. These observations reinforce the fact that the factory effluents are responsible for the pollution of the river water downstream and hence the factory should ensure that the effluents are properly treated before they are released into the surrounding farms and river Kimwarer through the open streams. Tables 4.11, 4.12, 4.13 and 4.14 show a summary of the results obtained using the AAS for heavy metals and fluoride meter.

The lower levels of the heavy metals and fluoride in the sedimentation pond B, which had water hyacinth as compared to pond C, which did not have any water hyacinth, can be attributed to the ability of this plant to absorb high quantities of these elements. The LSD values showed that there was a significant difference between the levels of these elements in the pond B and both pond C and the effluent stream sample effluents, hence the null hypothesis that water hyacinth does not absorb appreciable amounts of heavy metal and fluoride was rejected. Similar variations were observed during the rainy season and in the soil samples during both dry and rainy seasons.

Table 4.11 Mean concentration of Fluoride and heavy metals in mg/L and LSD values for water samples - dry season.

Sampling points	Fe	Zn	Mn	Cu	Cr	Pb	F^-
KWU	0.580	0.140	0.032	0.026	ND	0.016	0.612
(Upstream)	±0.242	±0.002	±0.004	±0.001		±0.001	±0.011
Pond B	1.310	0.083	0.045	0.037	ND	0.081	22.94
	±0.027	±0.004	±0.014	±0.004		±0.003	±1.138
KWLD	2.870	0.155	0.060	0.042	0.048	0.052	3.140
(Lower Downstream)	±0.019	±0.016	±0.018	±0.012	±0.008	±0.013	±0.99
KWD	5.660	0.204	0.100	0.068	0.079	0.083	6.040
(Downstream)	±0.350	±0.014	±0.011	±0.010	±0.014	±0.007	±0.186
Effluent Streams	44.97	0.319	1.280	0.177	0.102	0.206	37.75
	±3.620	±0.014	±0.353	±0.009	±0.009	±0.025	±2.625
Pond C	66.34	0.557	2.480	0.173	0.165	0.235	61.48
	±0.226	±0.006	±0.031	±0.006	±0.006	±0.004	±1.626
Factory office pond	273.7	2.232	36.87	0.424	0.810	0.753	273.3
	±14.92	±0.120	±1.513	±0.016	±0.023	±0.024	±5.798
Factory Effluent	1762	15.40	105.4	1.879	3.924	2.029	509.9
	±23.33	±0.948	±4.568	±0.070	±0.148	±0.041	±23.76
LSD (5%)	3.267	0.143	0.508	0.031	0.035	0.038	3.624

The mean concentrations of the elements under study in the water samples during the rainy season though lower, followed a similar trend as those during the dry season. The values of the mean concentrations of all the heavy metals and LSD values showed that there was no significant difference between the upstream, lower downstream and pond B samples. There was however significant difference in the mean concentration of all the elements except Zn and Mn in the upstream and downstream water samples. The mean concentration of all the elements however showed that there was significant difference between the upstream and effluent stream samples.

Table 4.12: Mean concentration of Fluoride and heavy metals in mg/L and LSD values for water samples - rainy season.

Sampling points	Fe	Zn	Mn	Cu	Cr	Pb	F
KWU	0.550	0.130	0.030	0.028	ND	0.015	0.582
(Upstream)	±0.216	±0.002	±0.004	±0.003		±0.023	±0.015
Pond B	1.250	0.075	0.425	0.025	ND	0.079	19.40
	±0.049	±0.001	±0.016	±0.001		±0.003	±1.556
KWLD	2.500	0.148	0.054	0.039	0.045	0.058	1.960
(Lower Downstream)	±1.581	±0.023	±0.03	±0.016	±0.015	±0.007	±0.996
KWD	4.470	0.179	0.072	0.048	0.072	0.071	5.880
(Downstream)	±0.662	±0.008	±0.023	±0.010	±0.005	±0.019	±0.186
Pond C	59.04	0.477	2.246	0.126	0.175	0.260	61.51
	±0.919	±0.021	±0.204	±0.010	±0.004	±0.004	±2.74
Effluent Stream	42.86	0.298	1.085	0.109	0.098	0.225	35.08
	±7.665	±0.046	±0.386	±0.087	±0.013	±0.033	±1.521
Factory office pond	268.5	2.160	24.01	0.416	0.792	0.703	315.4
	±3.677	±0.034	±1.414	±0.011	±0.014	±0.014	±16.19
Factory Effluent	1626	14.01	84.81	1.752	3.396	1.684	487.1
	±50.20	±0.982	±1.202	±0.050	±0.106	±0.031	±6.576
L.S.D (5%)	2.045	0.168	0.350	0.015	0.020	0.021	3.500

The mean concentrations of the heavy metals were much higher in the soil samples than in the water samples. This observation can be attributed to the alkalinity of the factory effluents which results in the insolubility and hence sedimentation of the metallic ions. There was significant difference between the mean concentrations of all the elements under study in the top and subsoil of the farm where the sample effluents were discharged, implying that the effluents were causing a great change in the composition of these elements in the surrounding farms.

Although there was no significant difference in the mean concentration of the heavy metals and fluoride in the upstream and lower downstream water samples, there was significant difference between the upstream and lower downstream soil and sediment samples. This observation can be attributed to the insolubility of the metallic ions under alkaline conditions and resulting in their deposition at the bottom of the river.

Table 4.13: Mean concentration of Fluoride and heavy metals in mg/Kg unless otherwise stated and LSD values for soil and sediment samples – dry season.

Sampling points	Fe (%)	Zn	Mn	Cu	Cr	Pb	Cd	Ni	F
Pond B	3.278	58.24	642.9	49.91	43.14	6.399	0.602	16.700	15.55
(D)	±0.261	±7.477	±29.44	±1.895	±7.183	±1.501	±0.219	±0.322	±1.574
Pond B	3.609	60.85	656.0	50.54	43.51	6.030	0.612	16.01	13.13
(W)	±0.422	±7.314	±22.90	±2.552	±16.13	±1.478	±0.533	±0.847	±2.871
FSS	3.625	58.46	666	53.60	42.01	5.495	0.478	21.23	0.567
	±0.527	±2.259	±6.639	±0.416	±1.264	±0.230	±0.044	±0.993	±0.106
KSU (W)	3.647	59.61	712.3	55.44	43.66	5.794	0.487	16.03	0.590
	±0.174	±2.641	±11.12	±0.375	±1.169	±0.256	±0.048	±1.363	±0.034
FTS	4.601	64.57	1021	60.81	45.85	6.320	0.556	23.82	0.629
	±0.285	±4.253	±16.71	±2.042	±2.435	±0.822	±0.099	±0.321	±0.013
KSU (D)	4.617	68.59	1020	60.51	46.93	6.273	0.551	23.83	0.683
	±0.276	±5.139	±17.04	±1.322	±2.177	±0.503	±0.045	±0.721	±0.027
KSLD (D)	4.923	68.78	1058	60.71	50.85	6.328	0.685	22.25	0.852
	±0.255	±6.408	±43.32	±1.134	±3.183	±0.728	±0.064	±1.956	±0.47

Table 4.13: Continued.

Sampling points	Fe (%)	Zn	Mn	Cu	Cr	Pb	Cd	Ni	F
ESS (D)	5.663 ±0.053	72.77 ±6.306	1219 ±40.52	66.56 ±1.611	54.51 ±0.994	7.530 ±0.366	0.727 ±0.042	26.20 ±0.567	12.21 ±1.656
KSLD (W)	5.178 ±0.349	65.93 ±6.706	1209 ±55.75	62.32 ±5.978	61.17 ±4.414	6.020 ±0.661	0.653 ±0.107	24.23 ±2.799	1.981 ±0.552
KSD (D)	5.741 ±0.062	79.31 ±3.458	1097 ±44.73	63.27 ±0.861	53.47 ±1.688	7.431 ±0.367	0.622 ±0.116	24.40 ±0.684	1.015 ±0.056
EFSS	5.279 ±0.156	55.37 ±3.394	1006 ±51.60	62.46 ±4.453	43.96 ±1.558	6.965 ±0.316	0.739 ±0.062	26.52 ±1.954	2.614 ±0.423
Off. Pond (D)	6.348 ±0.516	115.6 ±4.447	1057 ±17.18	53.79 ±4.636	73.90 ±4.461	21.92 ±0.956	1.072 ±0.021	28.32 ±1.921	180.0 ±33.554
Pond C (D)	6.576 ±0.331	186.1 ±12.99	1861 ±49.15	75.98 ±6.639	70.33 ±5.329	24.21 ±2.031	1.247 ±0.088	29.79 ±2.033	46.08 ±10.227
KSD (W)	6.585 ±0.173	94.92 ±8.359	1564 ±24.44	87.54 ±2.466	72.74 ±6.583	13.26 ±1.777	0.910 ±0.112	32.00 ±1.616	3.231 ±0.028
Off.Pond (W)	6.683 ±0.481	146.2 ±23.42	1173 ±105.4	79.00 ±25.07	94.70 ±13.59	31.37 ±8.702	1.443 ±0.203	39.46 8.687	252.2 ±37.70
EFTS	7.508 ±0.367	132.3 ±8.545	1736 ±143.4	90.48 ±4.227	59.86 ±3.244	14.55 ±1.039	0.886 ±0.041	32.23 ±1.699	2.470 ±0.234
Pond C (W)	7.394 ±0.708	223.9 ±25.9	2021 ±154	96.25 ±7.424	87.88 ±6.876	35.51 ±6.358	2.807 ±1.149	39.93 ±2.017	59.14 ±7.545
ESS (W)	8.398 ±0.098	117.7 ±6.685	1925 ±46.26	101.4 ±4.644	84.34 ±3.678	15.52 ±1.223	1.035 ±0.114	38.81 ±0.733	25.77 ±1.226
LSD(5%)	0.521	3.837	43.47	2.633	3.754	0.539	0.092	1.188	1.057

The top soil (0 – 5 cm) of the farms where the effluents were discharged had a higher mean concentration of the heavy metals and fluoride during the dry season than the rainy season while the subsoil (5 – 10 cm) of these farms had a lower mean concentration of these elements during the dry season than the rainy season. These observations can be explained by leaching of these elements during the rainy season.

Table 4.14: Mean concentration of Fluoride and heavy metals in mg/Kg unless otherwise stated and LSD values for soil and sediment samples– rainy season.

Sampling points	Fe %	Zn	Mn	Cu	Cr	Pb	Cd	Ni	F^-
Pond B (D)	3.220 ±0.423	50.86 ±4.091	637.2 ±79.10	44.35 ±1.883	40.55 ±6.944	6.052 ±1.331	0.592 ±0.278	16.09 ±1.821	14.17 ±1.557
Pond B (W)	3.507 ±0.422	49.24 ±4.096	643.9 ±94.08	46.55 ±1.482	40.70 ±13.81	5.99 ±1.805	0.602 ±0.533	15.98 ±0.969	12.59 ±2.351
FSS	3.476 ±0.442	56.55 ±2.521	648.3 ±5.421	50.98 ±1.883	39.66 ±3.479	6.032 ±1.053	0.447 ±0.075	20.23 ±1.161	0.556 ±0.100
KSU (W)	3.671 ±0.159	57.77 ±5.122	671.3 ±31.70	53.75 ±3.024	41.93 ±1.334	5.516 ±0.293	0.507 ±0.056	21.20 ±0.818	0.588 ±0.013
FTS	4.487 ±0.321	60.92 ±5.664	1010 ±25.22	58.79 ±3.241	44.66 ±2.115	5.862 ±0.557	0.565 ±0.046	23.07 ±1.045	0.603 ±0.055
KSU (D)	4.692 ±0.221	65.05 ±3.914	1024 ±33.05	60.88 ±2.002	46.35 ±1.653	6.284 ±0.318	0.570 ±0.072	24.12 ±1.262	0.642 ±0.043
KSLD (D)	5.313 ±0.286	66.05 ±2.611	1128 ±49.70	60.30 ±1.714	50.18 ±2.106	6.837 ±0.503	0.647 ±0.121	26.42 ±1.728	0.774 ±0.080
ESS (D)	5.650 ±0.101	70.66 ±8.312	1211 ±32.90	66.53 ±1.564	53.78 ±2.548	7.339 ±0.625	0.65 ±0.082	25.67 ±0.897	12.24 ±1.602
KSLD (W)	5.688 ±0.390	77.96 ±6.932	1212 ±183.5	67.05 ±3.244	61.20 ±4.827	8.443 ±1.542	0.757 ±0.165	26.23 ±5.361	1.816 ±0.450
KSD (D)	5.772 ±0.064	79.47 ±5.322	1066 ±22.09	63.38 ±0.755	50.60 ±1.059	6.991 ±0.566	0.641 ±0.063	24.58 ±0.729	1.032 ±0.072
EFSS	5.816 ±0.096	65.62 ±3.352	1245 ±122.0	62.48 ±3.816	43.88 ±1.181	8.249 ±0.373	0.556 ±0.059	22.58 ±0.97	2.643 ±0.377
Off.Pond (D)	6.198 ±0.365	107.4 ±4.556	1020 ±22.74	54.38 ±5.037	65.76 ±3.719	17.73 ±1.044	1.000 ±0.032	23.61 ±1.633	166.9 ±36.27

Table 4.14: Continued.

Sampling points	Fe %	Zn	Mn	Cu	Cr	Pb	Cd	Ni	F-
Pond C (D)	6.054 ±0.292	162.0 ±10.51	1742 ±55.48	70.64 ±7.007	66.05 ±4.822	19.50 ±1.843	1.011 ±0.049	25.32 ±2.014	40.19 ±8.691
KSD (W)	6.933 ±0.162	114.2 ±4.935	1627 ±44.55	91.22 ±3.163	75.83 ±2.169	14.36 ±0.708	1.050 ±0.036	33.26 ±0.327	2.907 ±0.164
Off. Pond (W)	6.577 ±0.127	116.9 ±13.51	1124 ±84.60	73.85 ±10.47	84.45 ±14.64	29.25 ±3.822	1.239 ±0.273	33.99 ±7.979	221.8 ±49.48
EFTS	7.314 ±0.176	112.6 ±11.32	1719 ±77.10	90.75 ±1.56	57.90 ±4.832	13.58 ±0.407	0.873 ±0.104	32.29 ±2.582	2.182 0.268
Pond C (W)	7.047 ±0.552	198.3 ±13.06	1944 ±112.0	81.55 ±7.275	79.83 ±12.73	30.00 ±8.494	2.091 ±1.117	35.03 ±6.473	52.48 ±8.610
ESS (W)	8.414 ±0.058	118.2 ±10.23	1882 ±52.41	101.3 ±4.887	84.38 ±1.129	15.52 ±0.505	1.048 ±0.081	36.71 ±0.677	25.714 ±1.006
LSD(5%)	0.254	3.664	37.56	1.866	3.884	0.724	0.109	1.221	1.003

4.9. Environmental effects of sample effluents

The dispersion of sample effluents with elevated levels of heavy metals and fluoride to the neighbouring farms and the discharge of these sample effluents into the river through open drainage poses a great danger to both the livestock and people living around the area. This is because livestock from the neighbouring area continually drink water directly from the highly polluted downstream river water and factory effluent streams and also feed on the short grass growing on the farms where the sample effluents are discharged during the dry season. The consumption of the high levels of heavy metals and fluoride in the effluents, downstream river water and the surrounding farms can result into accumulation of these elements on the animal tissues (Geeson, 1997). Such accumulation may result to toxicity and can cause health problems such as fluorosis and other diseases that may lead to sudden death of these animals, both of which have been reported by the residents to occur in livestock living around the factory. These effects may also be passed to human who feed on meat and milk from these animals as well as plants grown on the farms using downstream river and effluent water for irrigation (Lagerwerf and Brower, 1974). Nguta (2004) also showed that the animal tissues from this area had relatively higher levels of the heavy metals and fluoride than those from other areas such as Nakuru. Figure 4.16 shows some goats drinking polluted water immediately downstream.

Figure 4.16: Goats drinking polluted water immediately downstream.

The factory sample effluents with relatively high concentration of the heavy metals and fluoride flowed freely from the sedimentation ponds into open streams from where they were dispersed onto the neighbouring farms or flowed into river Kimwarer. This resulted into higher concentration of the heavy metals and fluoride downstream and the farms where the effluents were dispersed. Figure 4.17 shows partially treated factory effluent water flowing freely from sedimentation pond C into an open stream.

Figure 4.17: Water flowing freely from dam C into an open drainage.

The drying and poor health of plants growing around the Fluorspar mining and processing plant can be attributed to both the phytotoxicity of the heavy metals and fluoride and the large amount of dust laced with these elements which are continuously deposited on these plants (Weinstein and Alscher-Herman, 1982). Fluoride pollution can lead to increased solubility and uptake of phytotoxic metals such as Al by plants (Polomski et al., 1982). Thus despite the continuous supply of water, most of the trees and other plants growing around the effluent ponds, streams as well as the farms where the effluents were dispersed were either drying up or displayed signs of unhealthy plants such as brown/yellow leaves while those growing along the river Kimwarer were quite green and healthy. This observation shows that the factory effluents were responsible for the poor health of the plants growing around the dams and the farms where the effluents are discharged. Continuous use of the polluted downstream river water can either result in phytotoxity of the plants or accumulation of the heavy metals and fluoride in the tissues of animals and people who feed on the plants. Figure 4.18 shows a tree at the edge of pond C drying up.

Figure 4.18: A tree drying up at the edge of pond C.

Nearly all the pipes used for transferring the factory effluents from one sedimentation pond to other were leaking thereby emitting the thick sludge composed of high levels of heavy metals and fluoride to open fields. Since these effluents are eventually discharged into river Kimwarer through open streams and along the roads, the leaking pipes also results to an increase in the levels of heavy metals and fluoride in the surrounding farms and the river water. Figure 4.19 shows leaking connecting pipes discharging thick sludge onto an open field.

Figure 4.19: Leaking connecting pipes and taps between the sedimentation ponds.

Analysis of the thick sludge showed that the concentration of the heavy metals and fluoride were similar to those of the factory effluents. Figure 4.20 shows thick red brown sludge flowing along the road.

Figure 4.20: Thick reddish-brown sludge of effluents flowing along a road towards the river.

The rate of dust deposition around the factory and along the roads was found to range between 1–2.5 gm/m^2/day during the dry season and 0.4 – 1.2 gm/m^2/day during the rainy season. The rate was found to be at its peak around the buildings next to the factory and along the road. Analysis of the dust showed relatively high levels of the heavy metals and fluoride especially those collected around the factory. Since the dust contained considerable quantities of fluoride, and heavy metals, exposure and inhalation of large quantities of the polluted dust can result in widespread health problems such as chest problems and other problems associated with breathing difficulties, which many residents in the area were constantly complaining about.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The general increase in concentration of the heavy metals, fluoride, turbidity, pH and conductivity of the downstream river water samples followed by a decrease of these physicochemical parameters lower downstream shows that the highly turbid and alkaline factory effluent samples containing high levels of heavy metals and fluoride are responsible for the variation of these parameters along the river Kimwarer.

The levels of the heavy metals and fluoride in the effluent streams and sedimentation ponds were generally higher during the dry season than the wet season. This observation can be attributed to the dilution of the water samples by the large volumes of water and leaching of these elements in the soil samples during the rainy season. The levels of fluoride and heavy metals in the river water and sediment samples downstream were much higher than those in the upstream samples. The levels of fluoride and heavy metals emitted from the Fluorspar mining plant to the environment as well as those in the samples downstream were also much higher than those recommended by the WHO and NEMA (appendices 9, 10 and 11) for both drinking water and effluent discharge into public rivers respectively. These findings provide strong evidence that the Fluorspar mining plant is responsible for the elevated levels of these elements in the surrounding areas.

Statistical analysis showed that there was significant difference between the levels of fluoride and heavy metals in the upstream water samples and both the downstream and effluent water samples emitted from the sedimentation ponds into the river and surrounding farms. The levels of the heavy metals and fluoride in soil samples collected from the farm where the factory effluents were discharged were also quite high and significantly different from those of other soil samples collected in the area. The higher concentration of these elements in the topsoil than in the subsoil and the general decrease in the levels of these elements lower downstream due to dilution reinforces the idea that the Fluorspar processing operations is the major contributing factor to the elevated levels of these elements in the downstream water and soil/sediment samples. These findings reinforce the fact that the fluorspar mining and processing plant is responsible for the elevated levels of these elements in the downstream river water samples and the surrounding farms where the factory effluent samples are disposed.

The high levels of fluoride in the factory effluent streams and downstream river water can be used to explain the symptoms of fluorosis, which was observed in most animals' teeth. The direct consumption of the factory effluents and downstream river water by the animals may result into accumulation of relatively high quantities of fluoride and the heavy metals in their body tissues and could lead to the sudden death of these animals that the area residents have complained about. The high levels of dust deposition around the factory and along the road can result in diseases such as bronchitis and other health complications leading to breathing difficulties, which many residents in the area complained about.

The low levels of heavy metals and fluoride in pond B which had *E. crassipes* can be attributed to the adsorption of these elements by the plant. Although other plants such as papyrus were growing in all the other sedimentation ponds, the levels of the heavy metals in these ponds were not as low as that in pond B, where the *E. crassipes* were growing implying that these plants were not as effective in absorbing the heavy metals and fluoride as the *E. crassipes.* Adsorption studies also showed that the ground roots of *E. crassipes* were very effective in adsorbing the fluoride and heavy metals. The results from this study show that planting of *E. crassipes* in the sedimentation ponds which can be then dried, ground and eventually used as filters can greatly reduce the levels of the heavy metals emitted from the factory into the environment.

5.2. Recommendations

Since the factory plays a very important role in the economy of both the local area as well as that of the country, it would be very important if the following proposed actions are taken to protect the lives of the people and their animals who depend on the river water and crops grown around the Kimwarer Sugutek area using water from the river for irrigation:

Periodic excavation of the effluent settling ponds and unblocking of the connecting pipes should be performed to prevent direct overflow of the sample effluents into the river and the neighbouring farms.

In order to prevent the dangers of the heavy metals to livestock and people living around the factory and downstream of river Kimwarer, the factory should fence the sedimentation ponds and reduce the levels of the elements in the effluent streams. The leaking pipes connecting the sedimentation ponds should also be sealed.

The factory should perform continuous liming of the factory effluents and the farmers in the surrounding communities should be encouraged to apply cattle manure on their farms since this helps in reducing the bioavailability of the heavy metals and increases the yield of plants grown in polluted soils.

Modern dust reduction facilities should be installed in the factory and periodic spraying of the roads with water, especially during the dry season should be done to reduce the health problems caused by dust laced with heavy metals and fluoride.

Plants such as water hyacinth and vetiver grass [*vetiveria zizanioides* L (Nash.)] should be introduced into the sedimentation ponds, surrounding farms and along effluent streams to adsorb the heavy metals. Finely ground roots of the water hyacinth could be installed at the sample discharge points from the dams into effluent streams to act as heavy metal and fluoride filter and hence reduce the levels of these elements in the sample effluents. The stems and leaves of the water hyacinth can be used as manure, making ropes, paper, biogas and fibre board production.

Extensive periodic internal and external environmental audits should be carried out by both the factory and other organisations such as NEMA and other research institutions to help in preventing any excessive discharge of harmful effluents which has not been treated to the required standards.

Further research should be done to identify the nature of element(s) responsible for the drying of the plants growing around the sedimentation ponds and farms where the factory effluents are discharged. A detailed study should also be done on the filled sedimentation ponds to determine the distribution of the various elements with respect to depth.

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APPENDICES:

Appendix 1: Mean concentration of heavy metals and fluoride in mg/Kg in water samples– dry season.

Sample	Fe	Zn	Mn	Cu	Cr	Pb	F^-
KWU 1	0.515 ±0.009	0.137 ±0.004	0.024 ±0.002	0.028 ±0.002	0.000 ±0.000	0.000 ±0.000	0.596 ±0.012
KWU 2	0.521 ±0.004	0.140 ±0.002	0.029 ±0.001	0.024 ±0.002	0.000 ±0.000	0.000 ±0.000	0.591 ±0.004
KWU 3	0.525 ±0.005	0.140 ±0.002	0.031 ±0.001	0.026 ±0.002	0.000 ±0.000	0.033 ±0.003	0.613 ±0.012
KWU 4	0.634 ±0.013	0.143 ±0.004	0.030 ±0.002	0.027 ±0.003	0.027 ±0.007	0.030 ±0.012	0.621 ±0.006
KWD 1	4.831 ±0.040	0.163 ±0.005	0.071 ±0.003	0.0520 ±0.002	0.073 ±0.002	0.091 ±0.006	5.870 ±0.020
KWD 2	5.553 ±0.074	0.210 ±0.002	0.103 ±0.005	0.056 ±0.001	0.076 ±0.002	0.090 ±0.002	5.882 ±0.031
KWD 3	5.826 ±0.050	0.220 ±0.003	0.118 ±0.002	0.054 ±0.002	0.082 ±0.002	0.081 ±0.003	6.283 ±0.012
KWD 4	6.412 ±0.034	0.217 ±0.017	0.122 ±0.005	0.069 ±0.001	0.083 ±0.012	0.067 ±0.005	6.307 ±0.025
KWLD 1	4.791 ±0.020	0.179 ±0.004	0.102 ±0.006	0.056 ±0.002	0.067 ±0.002	0.057 ±0.002	5.036 ±0.007
KWLD 2	3.353 ±0.064	0.165 ±0.003	0.076 ±0.005	0.047 ±0.001	0.053 ±0.005	0.056 ±0.004	3.833 ±0.012
KWLD 3	2.321 ±0.042	0.145 ±0.003	0.040 ±0.002	0.036 ±0.001	0.040 ±0.003	0.050 ±0.004	2.433 ±0.110
KWLD 4	1.026 ±0.028	0.129 ±0.003	0.027 ±0.001	0.031 ±0.001	0.032 ±0.001	0.043 ±0.002	1.277 ±0.040
Eff. Stream 1	48.64 ±0.344	0.278 ±0.007	0.967 ±0.022	0.131 ±0.004	0.102 ±0.006	0.254 ±0.016	32.77 ±0.044

Appendix 1: continued.

Eff. Stream 2	52.17	0.335	1.310	0.130	0.120	0.183	31.04
	±0.265	±0.009	±0.020	±0.005	±0.003	±0.007	±0.281
Eff. Stream 3	54.90	0.285	1.073	0.140	0.091	0.207	29.07
	±0.131	±0.005	±0.068	±0.003	±0.004	±0.006	±0.406
Eff. Stream 4	64.19	0.379	1.772	0.307	0.095	0.181	30.13
	±0.263	±0.005	±0.045	±0.006	±0.005	±0.004	±0.311
Pond C	96.35	0.557	2.479	0.173	0.165	0.235	61.48
	±1.016	±0.039	±0.187	±0.010	±0.006	±0.014	±0.697
Fact. Off.	273.7	2.232	21.87	0.424	0.810	0.753	273.3
	±1.297	±0.070	±0.787	±0.014	±0.019	±0.029	±7.288
Fact. Eff	1762	15.40	105.4	1.879	3.924	2.029	509.9
	±13.41	±0.490	±5.186	±0.072	±0117	±0.123	±9.898
Pond B	1.313	0.083	0.448	0.037	0.000	0.081	22.92
	±0.064	±0.004	±0.025	±0.004	±0.000	±0.003	±0.697

Appendix 2: Mean concentration of heavy metals and fluoride in mg/Kg in water samples – rainy season.

Sample	Fe	Zn	Mn	Cu	Cr	Pb	F$^-$
KWU 1	0.403	0.133	0.029	0.031	0.000	0.000	0.573
	±0.021	±0.005	±0.003	±0.005	±0.000	±0.000	±0.035
KWU 2	0.405	0.139	0.033	0.027	0.000	0.000	0.572
	±0.022	±0.003	±0.003	±0.003	±0.000	±0.000	±0.011
KWU 3	0.428	0.140	0.037	0.028	0.000	0.028	0.588
	±0.015	±0.003	±0.001	±0.002	±0.000	±0.002	±0.011
KWU 4	0.694	0.142	0.030	0.026	0.000	0.030	0.593
	±0.008	±0.003	±0.002	±0.002	±0.000	±0.002	±0.014
KWD 1	2.295	0.160	0.067	0.039	0.064	0.068	5.473
	±0.007	±0.003	±0.011	±0.003	±0.002	±0.003	±0.206
KWD 2	2.521	0.178	0.098	0.046	0.061	0.072	5.515
	±0.004	±0.010	±0.002	±0.008	±0.003	±0.002	±0.0432
KWD 3	2.546	0.190	0.081	0.049	0.052	0.065	6.062
	±0.014	±0.002	±0.003	±0.001	±0.0030	±0.007	±0.080
KWD 4	2.533	0.189	0.080	0.059	0.043	0.081	6.287
	±0.011	±0.004	±0.002	±0.001	±0.002	±0.003	±0.032
KWLD 1	2.073	0.162	0.064	0.053	0.033	0.071	3.941
	±0.013	±0.002	±0.011	±0.006	±0.001	±0.002	±0.123
KWLD 2	1.857	0.158	0.055	0.046	0.025	0.063	2.173
	±0.012	±0.003	±0.004	±0.002	±0.001	±0.007	±0.035
KWLD 3	1.237	0.141	0.031	0.032	0.000	0.057	1.737
	±0.005	±0.003	±0.002	±0.002	±0.000	±0.001	±0.051
KWLD 4	0.841	0.129	0.025	0.025	0.000	0.042	0.918
	±0.003	±0.009	±0.002	±0.003	±0.000	±0.006	±0.0192
Eff. Stream 1	38.62	0.313	0.845	0.100	0.090	0.247	36.40
	±0.0200	±0.0030	±0.0132	±0.006	±0.002	±0.004	±0.021

Appendix 2: Continued.

Eff. Stream 2	34.47	0.281	1.320	0.085	0.107	0.259	42.56
	±0.010	±0.003	±0.028	±0.002	±0.003	±0.010	±0.0351
Eff. Stream 3	35.69	0.294	0.934	0.088	0.098	0.309	40.98
	±0.031	±0.002	±0.009	±0.001	±0.005	±0.003	±0.025
Eff. Stream 4	42.65	0.303	1.241	0.121	0.095	0.282	40.40
	±0.023	±0.006	±0.007	±0.003	±0.003	±0.004	±0.029
Pond C	59.038	0.478	2.246	0.126	0.175	0.360	61.51
	±0.920	±0.014	±0.102	±0.006	±0.007	±0.027	±0.196
Fact. Off.	268.5	2.160	44.013	0.416	0.792	0.703	325.4
	±4.682	±0.114	±0.688	±0.026	±0.020	±0.031	±0.088
Fact. Eff.	1625	14.01	84.81	1.752	3.396	1.684	487.1
	±18.07	±0.573	±0.980	±0.039	±0.064	±0.052	±11.07
Pond B	1.245	0.075	0.424	0.025	0.000	0.079	19.40
	±0.061	±0.004	±0.018	±0.002	±0.000	±0.006	±0.891

Appendix 3: Mean concentration of heavy metals and fluoride in soil/sediment samples in mg/Kg unless otherwise stated – dry season.

Sample	Fe %	Zn	Mn	Cu	Cr	Pb	Cd	Ni	F^-
KSU1 (D)	4.509	69.60	1059	60.09	47.77	6.667	0.517	24.32	0.743
	±0.047	±0.320	±21.52	±0.574	±0.230	±0.097	±0.025	±0.320	±0.015
KSU2 (D)	4.549	69.80	1040	61.37	50.07	7.047	0.653	25.53	0.807
	±0.089	±0.131	±6.425	±0.114	±0.031	±0.166	±0.006	±0.252	±0.005
KSU3 (D)	5.016	79.58	1074	63.58	50.06	7.033	0.597	26.23	0.768
	±0.065	±0.581	±7.024	±0.035	±0.412	±0.160	±0.015	±0.044	±0.004
KSU4 (D)	5.023	75.19	1073	62.22	48.49	6.043	0.626	25.06	0.753
	±0.069	±0.282	±6.658	±0.420	±0.121	±0.095	±0.024	±0.123	±0.006
KSU1 (W)	3.223	59.22	726.7	56.67	44.95	5.653	0.440	24.45	0.657
	±0.025	±0.076	±5.033	±0.244	0.104	±0.057	±0.010	±0.030	±0.010
KSU2 (W)	3.365	59.26	732	56.22	42.35	5.703	0.502	21.877	0.446
	±0.015	±0.105	±3.464	±0.108	±0.142	±0.015	±0.007	±0.125	±0.342
KSU3 (W)	3.297	62.45	734	57.05	44.32	6.137	0.53	21.36	0.621
	±0.021	±0.070	±2.000	±0.129	±0.106	±0.091	±0.010	±0.095	±0.003
KSU4 (W)	3.561	59.32	711	56.33	43.42	6.103	0.45	22.23	0.683
	±0.033	±0.163	±2.646	±0.110	±0.075	±0.045	±0.010	±0.064	±0.007
KSD1(D)	5.810	70.37	1145	63.48	51.53	7.560	0.624	24.96	0.868
	±0.028	±0.090	±6.000	±0.120	±0.061	±0.082	±0.008	±0.086	±0.014
KSD2 (D)	5.750	76.60	1108	62.62	53.34	7.087	0.837	24.14	0.957
	±0.010	±0.025	±5.292	±0.071	±0.079	±0.110	±0.017	±0.071	±0.010
KSD3 (D)	5.841	75.64	1174	64.32	54.48	7.037	0.710	25.65	0.977
	±0.072	±0.059	±8.718	±0.202	±0.143	±0.071	±0.017	±0.155	±0.007
KSD4(D)	5.768	69.94	1070	64.56	55.45	7.620	0.660	25.16	1.014
	±0.019	±0.101	±10.60	±0.060	±0.064	±0.052	±0.025	±0.040	±0.024
KSD1(W)	7.053	106.8	1558	86.35	72.96	14.65	0.994	32.47	2.633
	±0.073	±1.266	±16.38	±0.671	±0.732	±0.191	±0.011	±0.516	±0.054

Appendix 3: continued.

KSD2 (W)	6.829	117.2	1595	89.57	77.99	14.31	1.017	33.11	2.858
	±0.062	±0.954	±8.551	±1.050	±0.313	±0.095	±0.035	±0.125	±0.028
KSD3 (W)	6.722	111.5	1644	93.44	77.38	13.21	1.019	33.35	3.017
	±0.037	±0.702	±7.211	±0.271	±0.444	±0.169	±0.032	±0.111	±0.034
KSD4 (W)	6.977	117.5	1663	93.67	73.56	14.61	1.029	33.21	3.025
	±0.085	±0.777	±10.10	±0.110	±0.609	±0.235	±0.047	±0.381	±0.042
KSLD1(D)	5.610	75.18	1215	64.10	53.54	7.330	0.760	28.87	2.277
	±0.071	±0.279	±6.000	±0.206	±0.123	±0.092	±0.020	±0.127	±0.009
KSLD2 (D)	5.507	70.91	1173	62.37	51.40	6.35	0.657	25.89	1.978
	±0.020	±0.512	±8.042	±0.047	±0.150	±0.075	±0.009	±0.121	±0.058
KSLD3 (D)	5.307	64.11	1111	61.43	55.40	7.56	0.701	25.19	1.687
	±0.024	±0.140	±5.568	±0.083	±0.106	±0.108	±0.017	±0.066	±0.035
KSLD4 (D)	5.013	64.55	1150	62.33	47.84	6.670	0.660	24.30	1.238
	±0.028	±0.130	±15.50	±0.104	±0.176	±0.085	±0.020	±0.129	±0.088
KSLD1 (W)	5.68	69.45	1308	68.64	62.86	8.670	0.749	28.62	2.657
	±0.036	±0.070	±10.60	±0.060	±0.140	±0.085	±0.015	±0.183	±0.006
KSLD2 (W)	5.393	65.29	1249	62.66	62.33	7.983	0.657	26.873	2.336
	±0.014	±0.031	±3.512	±0.036	±0.066	±0.055	±0.003	±0.140	±0.010
KSLD3 (W)	5.020	64.42	1183	56.87	58.60	7.543	0.552	24.63	1.825
	±0.060	±0.035	±5.033	±0.114	±0.205	±0.095	±0.007	±0.045	±0.010
KSLD4 (W)	4.866	53.71	1113	55.56	53.39	7.267	0.524	22.28	1.405
	±0.011	±0.070	±6.506	±0.040	±0.027	±0.061	±0.002	±0.035	±0.009
ESS1d	5.685	80.54	1178	68.69	54.62	7.643	0.717	26.26	11.33
	±0.000	±0.020	±6.000	±0.031	±0.020	±0.012	±0.006	±0.036	±0.031
ESS2d	5.713	81.20	1247	70.73	55.51	8.100	0.747	25.21	12.02
	±0.054	±0.040	±8.083	±0.061	±0.023	±0.020	±0.006	±0.031	±0.045
ESS3d	5.785	69.11	1273	68.37	55.55	8.547	0.720	26.23	12.85
	±0.017	±0.042	±4.042	±0.046	±0.042	±0.006	±0.002	±0.015	±0.031

Appendix 3: continued.

ESS4d	5.692	70.90	1220	66.87	53.34	8.113	0.658	25.377	15.19
	±0.009	±0.031	±4.583	±0.030	±0.060	±0.012	±0.002	±0.025	±0.023
ESS1w	8.697	127.9	1875	112.0	88.83	18.32	0.998	40.42	27.74
	±0.018	±0.306	±7.024	±1.644	±0.252	±0.085	±0.007	±0.990	±1.016
ESS2w	8.884	118.7	1927	101.7	87.66	16.98	1.033	39.21	27.25
	±0.019	±0.300	±10.15	±0.306	±0.227	±0.036	±0.015	±0.251	±0.056
ESS3w	8.705	128.9	1988	100.4	88.05	15.91	1.108	38.75	26.66
	±0.009	±0.451	±6.000	±0.777	±0.132	±0.110	±0.013	±0.085	±0.116
ESS4w	8.824	134.1	1944	106.2	84.87	17.33	1.227	39.87	25.29
	±0.008	±0.361	±10.41	±0.557	±0.304	±0.070	±0.042	±0.321	±0.060
PondB(w)	3.278	60.85	656.0	50.54	43.51	6.399	0.612	16.70	14.13
	±0.019	±0.166	±1.183	±0.270	±0.475	±0.292	±0.010	±0.195	±0.141
PondB(d)	3.609	58.24	642.9	49.91	43.14	6.030	0.602	16.01	13.55
	±0.005	±0.298	±1.392	±0.147	±0.389	±0.253	±0.036	±0.235	±0.312
Off.P(w)	6.871	188.6	1275	89.48	96.08	32.99	1.451	41.31	254.2
	±0.018	±1.930	±7.715	±1.119	±0.449	±0.545	±0.017	±0.945	±1.474
Off.P(d)	6.495	108.4	1139	65.86	77.23	26.32	1.157	29.35	191.3
	±0.022	±0.948	±7.872	±0.395	±0.328	±0.232	±0.022	±0.240	±1.645
PodC(w)	7.711	245.2	2063	112.4	92.63	37.49	2.847	42.71	63.38
	±0.014	±1.481	±8.998	±0.931	±0.392	±0.154	±0.087	±0.110	±1.244
PodC(d)	6.698	196.2	1857	101.2	83.40	28.40	1.405	40.09	55.06
	±0.019	±0.877	±9.581	±1.677	±0.525	±0.268	±0.077	±0.183	±0.248
FTS1	4.521	69.91	1047	59.61	47.82	6.653	0.521	24.30	0.728
	±0.044	±0.320	±10.26	±0.928	±0.161	±0.095	±0.027	±0.317	±0.003
FTS2	4.514	69.52	1042	61.27	50.03	6.837	0.637	25.37	0.721
	±0.041	±0.236	±4.163	±0.071	±0.175	±0.076	±0.015	±0.455	±0.014
FTS3	4.571	69.58	1070	63.33	49.70	6.960	0.602	26.23	0.723
	±0.024	±0.602	±3.000	±0.325	±0.433	±0.072	±0.009	±0.042	±0.006

Appendix 3: Continued.

FTS4	4.607	70.58	1066	62.31	48.52	2.451	0.609	25.14	0.709
	±0.020	±1.007	±8.505	±0.407	±0.087	±3.204	±0.011	±0.100	±0.019
FSS1	3.211	59.62	723.7	56.58	45.00	5.703	0.441	24.40	0.657
	±0.035	±0.401	±3.215	±0.164	±0.239	±0.030	±0.010	±0.108	±0.010
FSS2	3.364	59.58	731.3	56.42	43.10	5.637	0.486	21.950	0.455
	±0.018	±0.476	±3.055	±0.155	±0.558	±0.050	±0.023	±0.243	±0.350
FSS3	3.344	61.96	732.3	57.12	44.46	5.950	0.531	21.413	0.627
	±0.047	±0.795	±2.517	±0.225	±0.106	±0.257	±0.009	±0.040	±0.005
FSS4	3.453	60.06	717.7	56.43	43.49	6.130	0.483	21.95	0.665
	±0.080	±1.142	±8.963	±0.127	±0.180	±0.076	±0.044	±0.500	±0.027
EFTS 1	7.591	122.3	1940	97.20	65.20	15.64	0.880	30.95	2.381
	±0.010	±1.210	±7.211	±0.001	±0.223	±0.010	±0.020	±0.087	±0.004
EFTS 2	8.027	142.3	1724	103.1	60.42	14.85	0.837	33.49	2.264
	±0.041	±1.419	±4.000	±0.625	±0.202	±0.020	±0.006	±0.045	±0.005
EFTS 3	7.188	133.1	1635	106.3	59.69	14.827	0.85	35.163	2.707
	±0.010	±0.361	±6.557	±0.557	±0.300	±0.032	±0.027	±0.057	±0.013
EFTS 4	7.815	137.1	1642	99.58	57.85	16.66	0.832	32.52	4.419
	±0.011	±0.265	±4.000	±0.961	±0.061	±0.017	±0.045	±0.035	±0.012
EFSS 1	5.196	52.75	1026	56.25	48.08	6.84	0.459	15.45	2.862
	±0.025	±0.090	±4.002	±0.150	±0.139	±0.060	±0.006	±11.60	±0.005
EFSS 2	5.291	48.36	1053	65.23	45.36	7.083	0.555	19.91	2.47
	±0.010	±0.201	±6.110	±0.121	±0.060	±0.058	±0.000	±0.046	±0.002
EFSS 3	5.136	56.59	999.3	60	45.3	6.567	0.427	22.87	3.16
	±0.013	±0.130	±3.288	±0.200	±0.020	±0.042	±0.006	±0.080	±0.002
EFSS 4	5.490	52.62	945.3	65.32	44.29	7.297	0.463	18.74	3.460
	±0.050	±0.035	±7.024	±0.076	±0.103	±0.055	±0.002	±0.017	±0.003

Appendix 4: Mean concentration of heavy metals and fluoride in mg/Kg (Fe in %) in soil/sediment samples-rainy season.

Sample	Fe %	Zn	Mn	Cu	Cr	Pb	Cd	Ni	F^-
KSU1(D)	4.419	64.42	1037	58.47	45.37	6.110	0.460	22.38	0.638
	±0.030	±0.030	±10.35	±0.306	±0.252	±0.046	±0.020	±0.021	±0.003
KSU2(D)	4.560	60.42	989.2	60.05	47.84	6.110	0.625	25.06	0.662
	±0.079	±0.508	±13.60	±0.397	±0.189	±0.040	±0.006	±0.253	±0.006
KSU3(D)	4.679	69.44	1017	63.07	43.42	6.750	0.567	23.70	0.571
	±0.112	±0.768	±7.444	±0.476	±1.017	±0.120	±0.015	±0.788	±0.023
KSU4(D)	4.812	64.08	1037	60.46	47.09	6.123	0.550	24.19	0.663
	±0.153	±0.487	±9.629	±0.125	±0.282	±0.045	±0.020	±0.172	±0.014
KSU1(W)	3.617	53.56	627.1	56.90	43.24	5.710	0.467	21.96	0.563
	±0.036	±0.125	±1.604	±0.269	±0.326	±0.066	±0.012	±0.244	±0.020
KSU2(W)	3.435	58.98	691.1	49.68	40.84	5.111	0.451	21.403	0.560
	±0.031	±0.171	±2.940	±0.379	±0.227	±0.046	±0.028	±0.125	±0.019
KSU3(W)	3.707	64.23	670.0	52.87	43.09	5.443	0.557	20.603	0.590
	±0.016	±0.249	±2.173	±0.151	±0.128	±0.067	±0.015	±0.150	±0.018
KSU4(W)	3.861	53.66	693.0	54.33	39.46	5.713	0.433	20.17	0.567
	±0.013	±0.140	±4.084	±0.528	±0.946	±0.031	±0.015	±0.279	±0.032
KSD1(D)	5.811	75.34	1083	63.27	50.81	7.325	0.547	24.96	0.971
	±0.022	±0.085	±5.380	±0.030	±0.344	±0.035	±0.020	±0.352	±0.016
KSD2(D)	5.745	75.11	1035	62.28	48.92	7.170	0.694	23.41	0.996
	±0.026	±0.202	±10.47	±0.111	±0.239	±0.076	±0.010	±0.135	±0.037
KSD3 (D)	5.675	80.32	1036	63.99	51.46	6.05	0.627	24.84	1.109
	±0.031	±0.333	±9.822	±0.189	±0.140	±0.040	±0.015	±0.119	±0.023
KSD4(D)	5.734	86.45	1074	63.53	50.69	7.180	0.620	24.39	0.985
	±0.049	±0.110	±6.525	±0.089	±0.311	±0.053	±0.040	±0.194	±0.026
KSD1(W)	6.747	91.92	1535	87.81	73.60	13.31	0.952	32.66	3.039
	±0.065	±0.486	±8.083	±0.107	±0.200	±0.084	±0.009	±0.195	±0.037

Appendix 4: Continued.

KSD2(W)	6.709	91.55	1573	85.17	77.64	15.59	0.998	33.72	3.180
	±0.024	±0.189	±9.539	±0.187	±0.071	±0.061	±0.060	±0.035	±0.019
KSD3(W)	6.531	96.51	1553	86.09	73.43	12.35	0.811	30.30	3.279
	±0.050	±0.177	±8.327	±1.309	±0.061	±0.095	±0.014	±0.137	±0.036
KSD4(W)	6.352	91.68	1593	91.08	66.28	11.80	0.880	31.307	3.428
	±0.080	±0.163	±6.110	±0.180	±0.106	±0.045	±0.005	±0.101	±0.051
KSLD1(D)	5.462	65.03	1186	60.41	50.03	7.020	0.711	27.02	0.857
	±0.095	±0.250	±10.66	±0.471	±0.546	±0.164	±0.022	±0.160	±0.011
KSLD2(D)	5.460	69.49	1106	61.99	50.10	6.047	0.612	27.09	0.766
	±0.070	±0.378	±9.840	±0.354	±0.322	±0.100	±0.029	±0.268	±0.017
KSLD3(D)	5.215	64.20	1105	57.59	52.20	7.130	0.700	27.25	0.679
	±0.062	±0.298	±11.20	±0.810	±0.316	±0.066	±0.020	±0.070	±0.017
KSLD4(D)	4.914	64.38	1073	58.83	47.07	6.717	0.477	23.62	0.705
	±0.020	±0.137	±6.809	±0.524	±0.405	±0.035	±0.035	±0.205	±0.010
KSLD1 (W)	6.130	85.95	1459	70.65	66.59	10.59	0.957	31.30	2.223
	±0.005	±0.070	±4.388	±0.133	±0.031	±0.057	±0.015	±0.050	±0.019
KSLD 2 (W)	5.819	80.59	1221	68.63	63.60	8.297	0.774	30.01	2.015
	±0.018	±0.036	±5.503	±0.070	±0.020	±0.050	±0.009	±0.152	±0.061
KSLD3 (W)	5.530	75.29	1111	65.77	58.79	7.563	0.714	23.17	1.673
	±0.005	±0.042	±7.295	±2.299	±0.023	±0.085	±0.008	±0.111	±0.013
KSLD4 (W)	5.234	69.87	1044	64.23	55.72	7.233	0.606	20.45	1.211
	±0.007	±0.042	±4.678	±0.031	±0.080	±0.031	±0.032	±0.112	±0.018
ESS1(bank)	5.542	77.87	1173	68.71	54.57	7.407	0.630	25.48	10.64
	±0.006	±0.020	±4.149	±0.042	±5.455	±0.023	±0.004	±0.025	±0.056
ESS2(bank)	5.691	75.28	1221	66.55	56.36	6.600	0.758	26.77	11.39
	±0.010	±0.025	±2.506	±0.064	±0.093	±0.020	±0.009	±0.080	±0.070

Appendix 4: Continued.

ESS3(bank)	5.717	59.60	1220	65.50	55.50	7.207	0.631	25.56	12.42
	±0.008	±0.476	±5.519	±0.087	±0.035	±0.031	±0.003	±0.085	±0.040
ESS4(bank)	5.701	70.31	1221	65.47	51.61	8.107	0.570	24.57	14.39
	±0.037	±0.020	±4.518	±0.061	±0.031	±0.023	±0.002	±0.101	±0.036
ESS 1(bed)	8.392	111.7	1862	104.0	82.74	14.84	1.026	37.37	26.71
	±0.010	±0.577	±5.303	±0.306	±0.078	±0.012	±0.027	±0.119	±0.147
ESS 2(bed)	8.478	117.9	1822	97.74	85.10	15.90	1.023	36.87	25.35
	±0.013	±0.361	±3.863	±0.550	±0.138	±0.020	±0.031	±0.137	±0.121
ESS 3 (bed)	8.398	109.1	1948	97.83	85.28	15.42	0.934	36.06	24.58
	±0.010	±0.416	±8.996	±0.651	±0.075	±0.035	±0.011	±0.453	±0.040
ESS 4 (bed)	8.324	132.1	1876	106.2	84.23	15.91	1.157	36.96	26.44
	±0.007	±0.361	±6.490	±0.561	±0.061	±0.012	±0.038	±0.200	±0.090
Pond B (W)	3.609	50.86	636.0	44.54	40.51	6.030	0.592	16.01	14.13
	±0.193	±3.056	±17.53	±1.095	±17.48	±1.374	±0.383	±0.692	±1.705
Pond B (D)	3.278	49.24	642.9	46.91	40.15	5.993	0.602	15.96	12.56
	±0.012	±0.144	±0.904	±0.174	±0.357	±0.061	±0.015	±0.066	±0.188
Off.Pond (W)	6.684	126.2	1173	79.00	94.70	31.37	1.443	39.457	252.2
	±0.029	±1.634	±11.56	±1.161	±0.244	±0.510	±0.017	±0.182	±2.982
Off.Pond (D)	6.348	115.6	1057	53.79	73.90	21.93	1.072	28.32	180.0
	±0.078	±1.311	±7.518	±0.128	±0.231	±0.293	±0.059	±0.207	±3.809
Pond C (W)	7.394	203.9	2021	86.25	87.88	35.51	2.807	38.93	57.14
	±0.041	±2.177	±7.196	±0.676	±0.916	±0.298	±0.083	±0.643	±1.117
Pond C (D)	6.576	186.1	1861	75.98	70.33	24.22	1.247	29.79	46.08
	±0.129	±1.407	±7.826	±0.426	±0.333	±0.114	±0.007	±0.637	±0.264
FTS 1	4.410	64.08	1043	58.54	45.57	6.170	0.459	22.38	0.639
	±0.021	±0.609	±5.538	±0.308	±0.162	±0.063	±0.020	±0.027	±0.002
FTS 2	4.607	60.40	994.4	60.24	47.84	6.157	0.626	25.20	0.659
	±0.018	±0.506	±14.93	±0.414	±0.190	±0.050	±0.004	±0.286	±0.010

Appendix 4: Continued.

FTS 3	4.657	69.44	1015	63.07	43.42	6.750	0.567	23.70	0.571
	±0.084	±0.768	±5.033	±0.476	±1.017	±0.120	±0.015	±0.788	±0.023
FTS 4	4.727	64.34	1030	61.41	46.58	6.203	0.574	24.01	0.648
	±0.117	±0.894	±5.462	±1.767	±0.621	±0.104	±0.058	±0.241	±0.014
FSS 1	3.570	53.56	629.4	56.90	43.24	5.710	0.467	21.96	0.563
	±0.017	±0.125	±4.400	±0.269	±0.326	±0.066	±0.012	±0.244	±0.020
FSS 2	3.485	57.40	669.5	51.92	41.56	5.304	0.446	21.59	0.556
	±0.117	±2.624	±34.73	±4.253	±1.470	±0.370	±0.021	±0.339	±0.013
FSS 3	3.622	62.45	678.4	51.97	42.54	5.360	0.527	21.10	0.579
	±0.133	±2.891	±13.98	±1.623	±0.856	±0.190	±0.042	±0.469	±0.007
FSS 4	3.822	60.43	684.6	53.63	40.69	5.607	0.473	20.29	0.571
	±0.004	±5.932	±13.90	±0.738	±2.181	±0.182	±0.084	±0.457	±0.039
EFTS 1	7.188	101.9	1811	89.16	63.78	13.63	0.994	33.223	2.087
	±0.010	±0.306	±3.055	±0.268	±0.111	±0.040	±0.023	±0.247	±0.009
EFTS 2	7.369	125.0	1642	91.51	59.33	13.32	0.892	31.04	1.820
	±0.028	±0.702	±4.041	±0.829	±0.070	±0.058	±0.026	±0.075	±0.036
EFTS 3	7.173	104.0	1744	91.79	55.52	13.21	0.738	35.20	2.389
	±0.007	±0.436	±6.028	±0.560	±0.047	±0.042	±0.004	±0.050	±0.012
EFTS 4	7.504	118.2	1665	89.47	52.80	14.03	0.918	29.46	2.384
	±0.023	±0.100	±4.726	±0.082	±0.040	±0.065	±0.016	±0.060	±0.005
EFSS 1	5.745	66.81	1356	57.26	45.64	7.943	0.547	22.80	2.437
	±0.021	±0.930	±8.000	±0.268	±0.937	±0.070	±0.025	±0.133	±0.076
EFSS 2	5.917	68.83	1169	64.46	44.40	8.393	0.507	22.20	2.152
	±0.028	±0.031	±4.163	±0.125	±0.020	±0.031	±0.025	±0.031	±0.005
EFSS 3	5.707	64.41	1332	66.01	42.92	7.960	0.483	23.66	2.842
	±0.050	±0.042	±4.000	±0.031	±0.040	±0.046	±0.025	±0.082	±0.005
EFSS 4	5.824	61.43	1117	62.10	42.90	8.763	0.620	21.42	3.024
	±0.023	±0.090	±3.06	±0.116	±0.035	±0.042	±0.020	±0.036	±0.003

Appendix 5: Physical properties of river Kimwarer and factory effluent water samples – dry season.

Sample	pH	Conductivity, μS	Turbidity (NTU)
KWU 1	7.28	70	4.40
KWU 2	7.32	72	5.00
KWU 3	7.26	70	4.70
KWU 4	7.24	68	4.80
KWD 1	7.88	262	109
KWD 2	8.07	278	103
KWD 3	8.11	287	127
KWD 4	8.15	268	117
KWLD 1	8.03	204	53.4
KWLD 2	7.80	166	36.7
KWLD 3	7.78	132	15.9
KWLD 4	7.78	96	8.50
Eff. Stream 1	8.34	781	809
Eff. Stream 2	8.76	734	796
Eff. Stream 3	8.79	768	784
Eff. Stream 4	8.88	795	823
Pond C Eff.	8.80	765	840
Fact. Off.	9.32	736	826
Fact. Eff.	6.08	886	9820
Pond B	7.28	146	12.3

Appendix 6: Physical properties of river Kimwarer and factory effluent water samples– rainy season.

Sample	pH	Conductivity, μS	Turbidity, NTU
KWU 1	7.26	76	6.50
KWU 2	7.30	80	7.40
KWU 3	7.28	74	8.20
KWU 4	7.33	72	9.60
KWD 1	7.76	218	159
KWD 2	7.89	225	141.4
KWD 3	8.08	239	144.2
KWD 4	8.11	227	162
KWLD 1	7.70	168	72.3
KWLD 2	7.56	146	40.2
KWLD 3	7.48	114	27.3
KWLD 4	7.38	82	12.4
Eff. Stream 1	8.21	853	396
Eff. Stream 2	8.28	781	863
Eff. Stream 3	8.60	795	774
Eff. Stream 4	8.70	832	927
Pond C Eff.	8.74	735	96.4
Fact. Off.	9.24	724	796
Fact. Eff.	6.16	806	9845
Pond B	7.20	130	13.2

Appendix 7: Normal and phytotoxic metal concentrations (mg/Kg) generally found in plant leaves (Alloway, 1995).

Element	Concentration in leaves	
	Normal range	Toxicity
Zn	1 – 400	100 – 400
Cu	5 – 20	20 – 100
Ni	0.02 – 5	10 – 100
Pb	5 – 10	30 – 300
Cr	0.03 – 14	5 – 30
Cd	0.1 – 2.4	5 – 30

Appendix 8: Percentage metals adsorbed from 100 cm^3 of 100 mg/Kg solutions by various parts of *E. crassipes.*

Element	roots	stems	leaves
Fe	76.65 ± 5.43	57.43 ± 4.66	37.36 ± 3.07
Zn	82.32 ± 4.04	60.32 ± 3.39	32.49 ± 2.29
Mn	77.35 ± 3.78	49.82 ± 2.74	32.33 ± 2.48
Cu	85.44 ± 4.27	62.76 ± 3.85	35.88 ± 2.69
Cr	80.21 ± 5.33	63.29 ± 4.61	28.75 ± 3.17
Pb	75.71 ± 5.45	40.66 ± 3.66	23.33 ± 3.07
Cd	76.40 ± 3.16	49.58 ± 2.58	28.46 ± 2.22
F^-	43.66 ± 2.65	26.76 ± 3.08	11.34 ± 1.77

Appendix 9: WHO Guidelines for Drinking Water Quality.

Characteristic	Action level
Chromium	0.05 mg/L
Lead	0.05 mg/L
Nickel	0.1 mg/L
Iron	0.3 mg/L
Copper	1.0 mg/L
Zinc	5.0 mg/L
Manganese	0.1 mg/ L
Fluoride	1.5 mg/L
Turbidity	5 NTU
pH	6.5 to 8.5
Total dissolved solids	1000 mg/L

Source: Guidelines for Drinking Water Quality, World Health Organisation (WHO), Geneva, 1984.

Appendix 10: Guidelines for Effluent Discharge Standards into Public Sewers.

Parameter	Maximum levels permissible
Chromium (total)	2 mg/L
Lead	1.0 mg/L
Nickel	3.0 mg/L
Iron	-
Copper	1.0 mg/L
Zinc	4.0 mg/L
Manganese	-
Fluoride	-
PH	6-9
Total dissolved solids	2000 mg/L

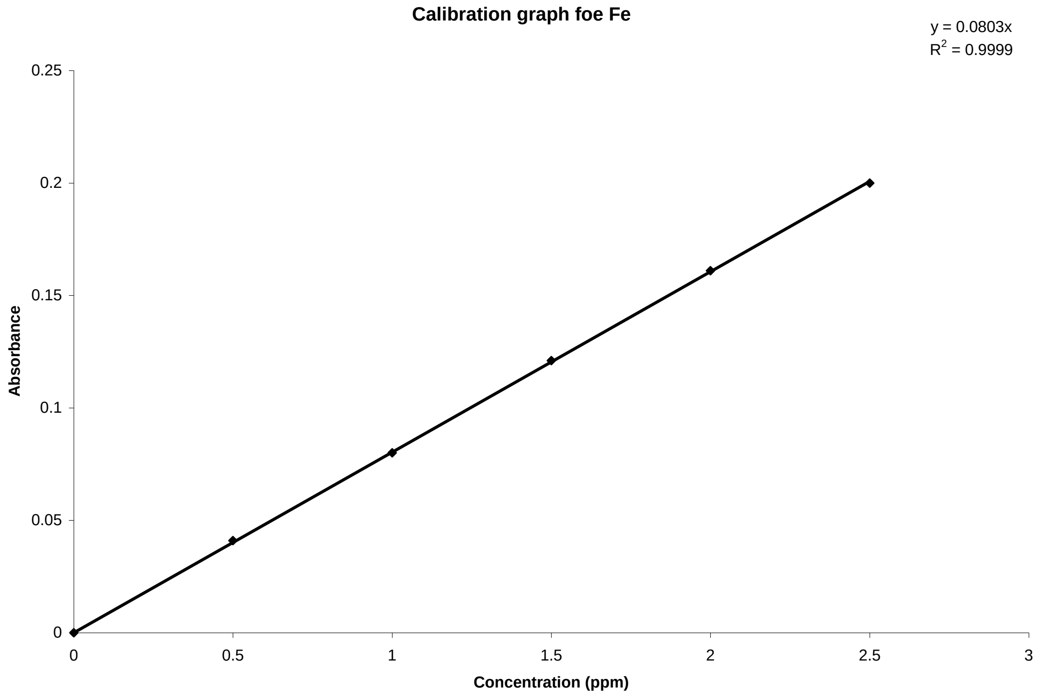
Source: Guidelines for Effluent Discharge Standards into Public Sewers. National Environmental Management Authority, Kenya (NEMA).

Appendix 11: Guidelines for Effluent Discharge Standards into the Environment.

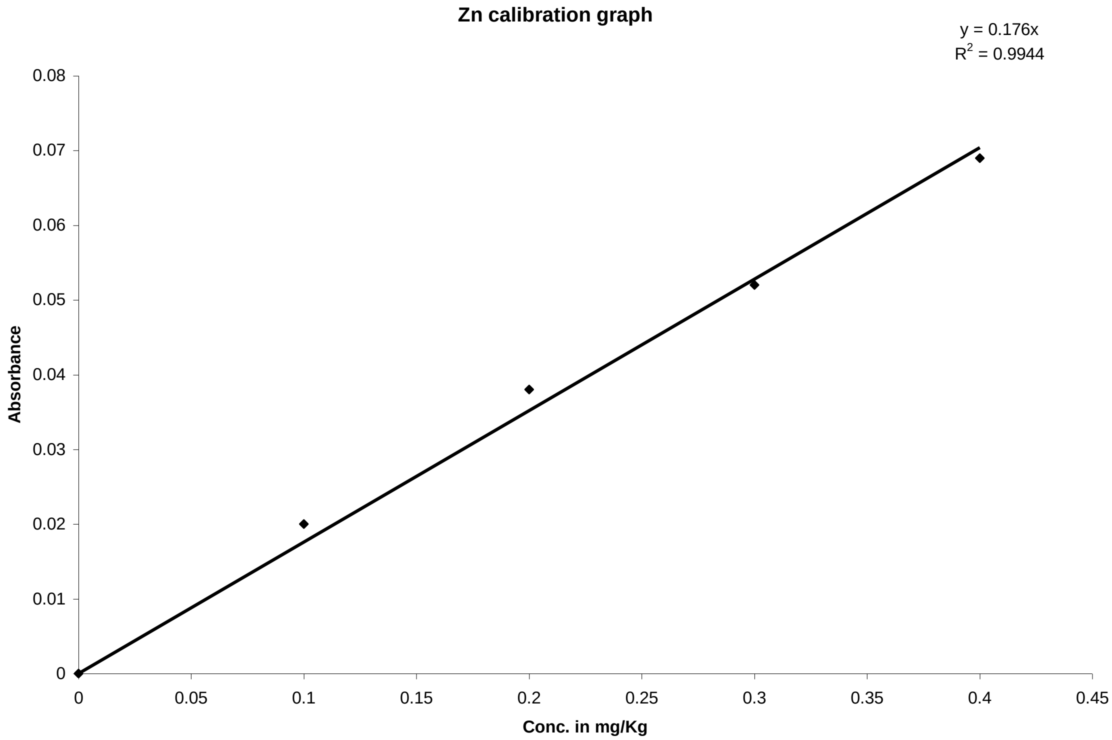
Parameter	Maximum levels permissible
Chromium (total)	2 mg/L
Lead	0.01 mg/L
Nickel	-
Iron	-
Copper	1.0 mg/L
Zinc	0.5 mg/L
Manganese	-
Fluoride	8 mg/L
Colour	15 Hazen units
PH	6.5-8.5

Source: Guidelines for Effluent Discharge Standards into Public Sewers. National Environmental Management Authority, Kenya (NEMA).

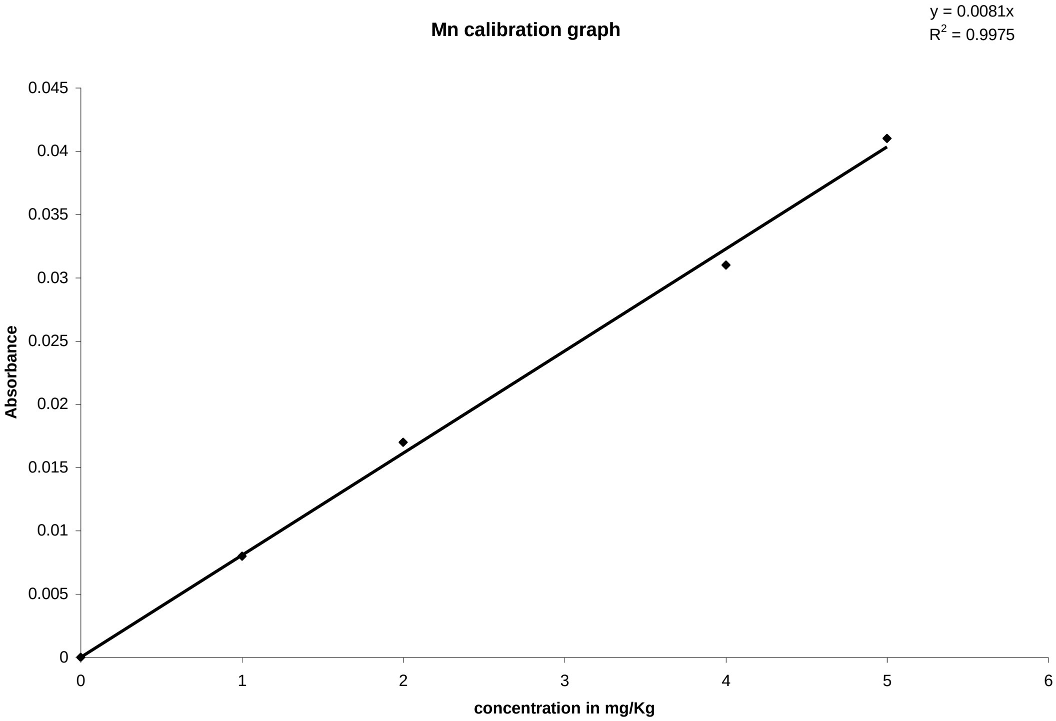
Appendix 12: Calibration graph for Fe.



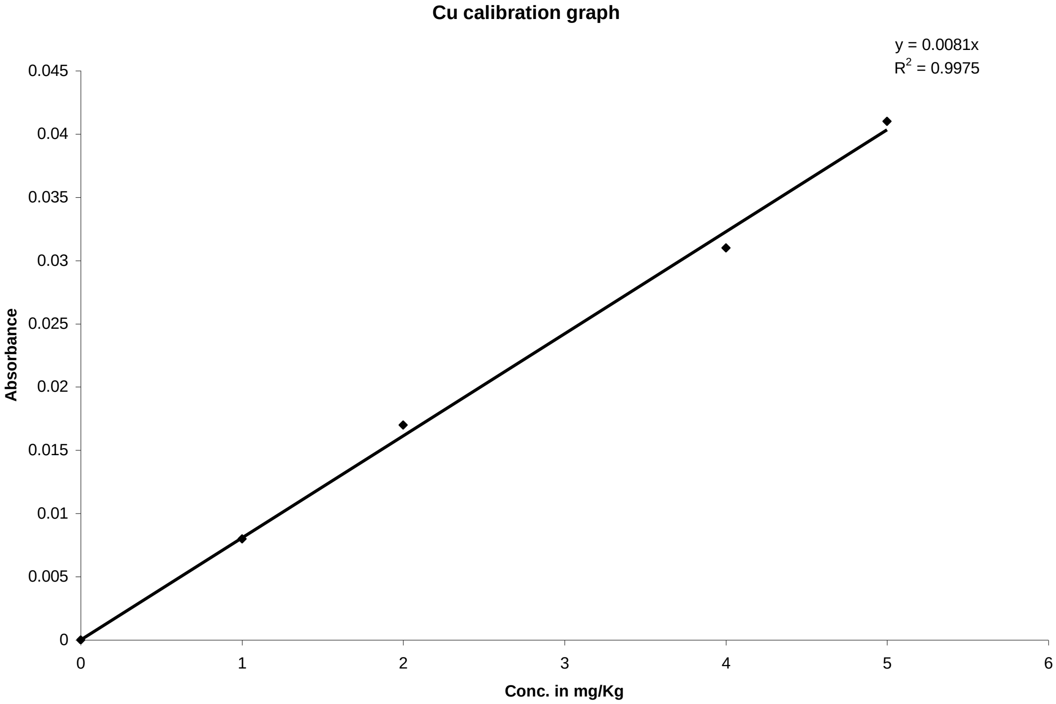
Appendix 13: Calibration graph for Zn.



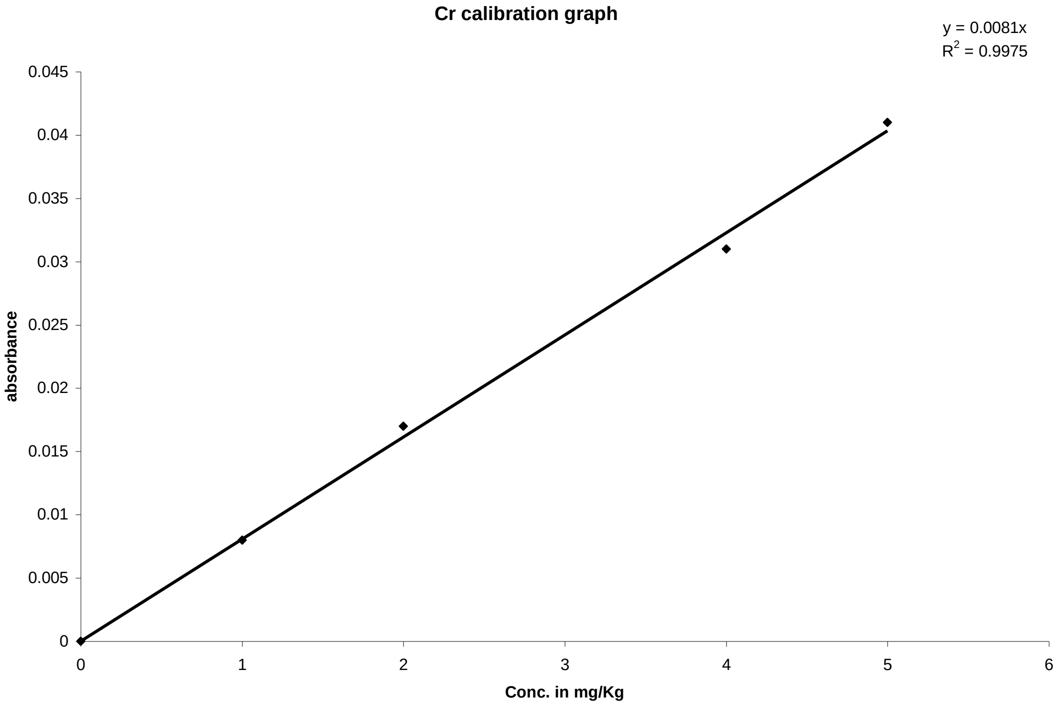
Appendix 14: Calibration graph for Mn.



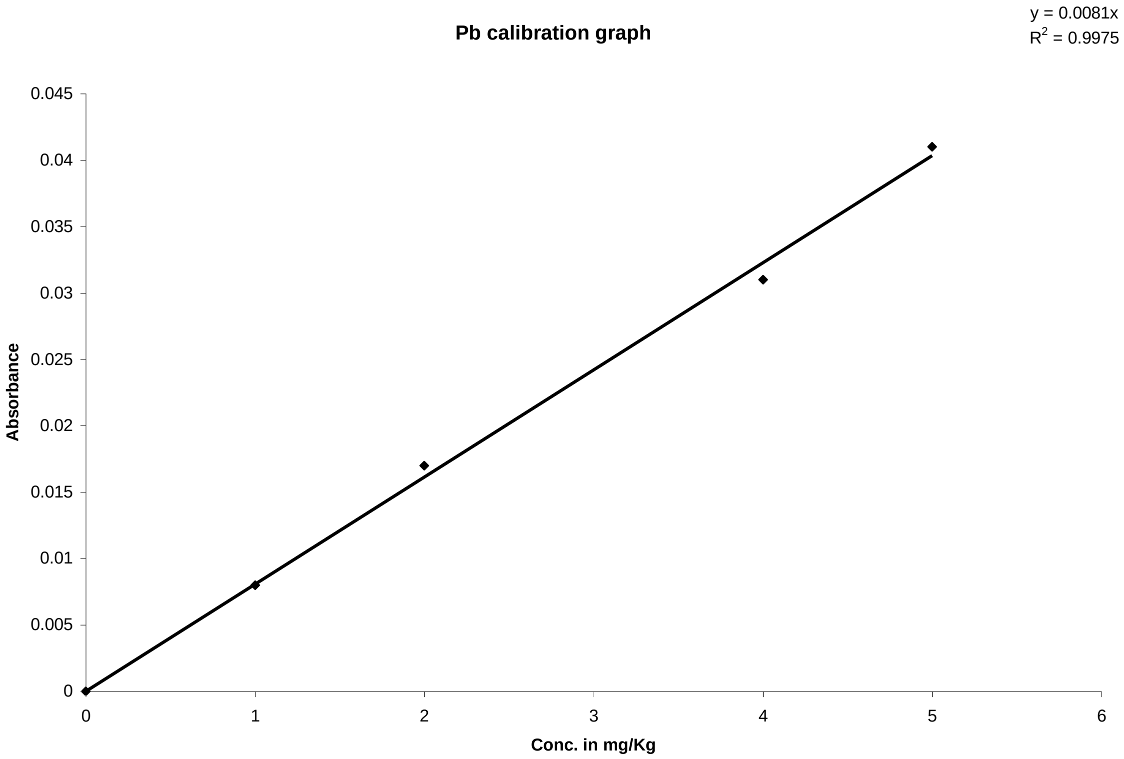
Appendix 15: Calibration graph for Cu.



Appendix 16: Calibration graph for Cr.



Appendix 17: Calibration graph for Pb.



Appendix 18: Calibration graph for Ni.